1973

Valence isomerization of unsaturated semidiones

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Valence isomerization of unsaturated semidiones

by

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A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1973

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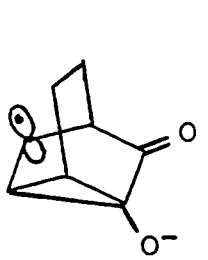
INTRODUCTION

The semidione radical anion has received considerable attention as a useful spin label in the past ten years. This work has been recently reviewed in some depth (1, 2, 3). The research on semidiones has been directed mainly among three broad, interdependent areas, namely: studies of conformation of acyclic and cyclic compounds, studies aimed at the elucidation of structure of naturally occurring ketones via their derived semidiones, and studies concerned with elucidation of the mechanisms of spin propagation. The present work was to have fallen into the last category.

Basically, two mechanisms have been proposed for the transmittal of spin from a radical center to a remote atom. The first of these, hyperconjugative delocalization, is most important for interactions at distances greater than one or two intervening σ bonded atoms. It is important only when the MO to which or through which spin is to be transmitted does not lie in a nodal plane of the HOMO of the spin system. Thus, for bicyclo[2.2.2]octenesemidione spin can be delocalized to C-5 or C-6 by the interaction of ψ_2, the HOMO of the double bond, with ψ_3, the HOMO of the semidione as shown in 1. Similarly, spin can be transmitted to H-7, anti (2) or C-7 (3) by interaction of semidione ψ_3 with the C-H or C-C MO. However, spin cannot be transmitted to H-1 or H-4 by

this mechanism since their MO lie in the nodal plane of the semidione. The hyperconjugative mechanism is stereospecific,



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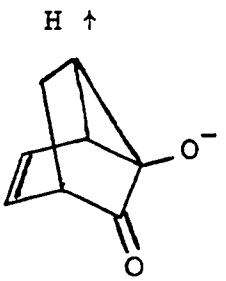

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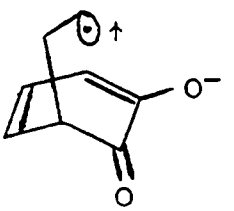

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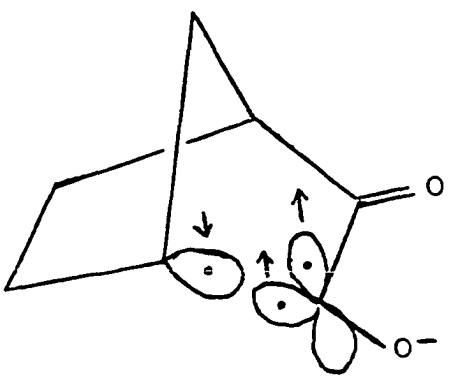
can operate over distances long in terms of number of bonds, and transmits positive spin density.

In the second mechanism, the spin polarization mechanism, spin is transmitted by polarization of spin densities at opposite ends of a MO presumed orthogonal to the radical center. The degree of polarization as measured by the hyperfine splitting constant (hfsc), $\underline{a}^H$, can be expressed simply by an equation due to McConnell (4).

$$\underline{a}^H = Q\rho$$

In this expression ρ is the spin density at the radical center and Q is a constant whose value and sign depend on the type of radical and the hybridization of the radical center. When the radical center is sp^2 hybridized, the value of Q is -20 to -30 gauss; when the radical is sp^3 hybridized, Q is reported to be +15 gauss (5). Thus, the spin density induced at C-1 by the positive spin density on

sp^2 hybridized C-2 (4) is negative while the spin density at H-7, anti (5) induced by positive spin density at the logically sp^3 hybridized C-7 will be positive. The bicyclo-



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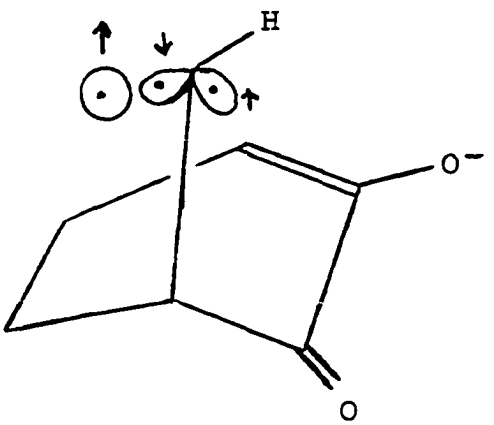

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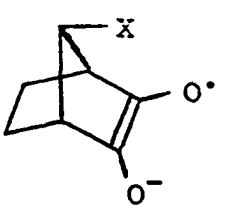
[2.2.1]heptanesemidiones with their rigid geometry and large H-7, anti hfsc seemed an ideal system to sort out the various spin propagation mechanisms. We wished to prepare a series of 7, syn substituted bicyclo[2.2.1]heptanesemidiones (6) since Holland (6) had earlier reported that the hfsc for



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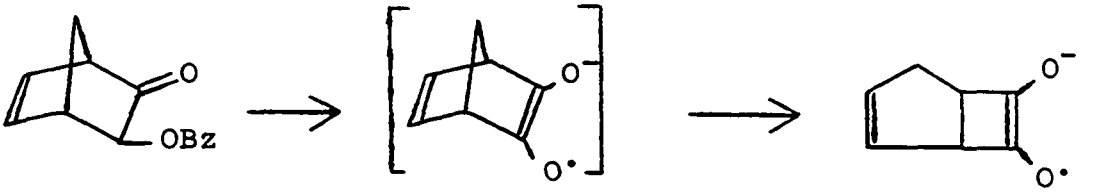
X = halogen
= O-alkyl
= alkyl

H-7, anti fell from 6.48 gauss to 3.11 gauss when X changed from H to CH_3. This was consistent with a steric interference with the hyperconjugative C-2, C-3 to C-7 interaction. This work was, therefore, initially begun on the X = large alkyl compounds.

Shortly after this work was begun, however, Scharpe (7) reported the convenient synthesis of 7, which seemed to be an ideal precursor to the hitherto elusive (6) semidione 8.



7 8 9

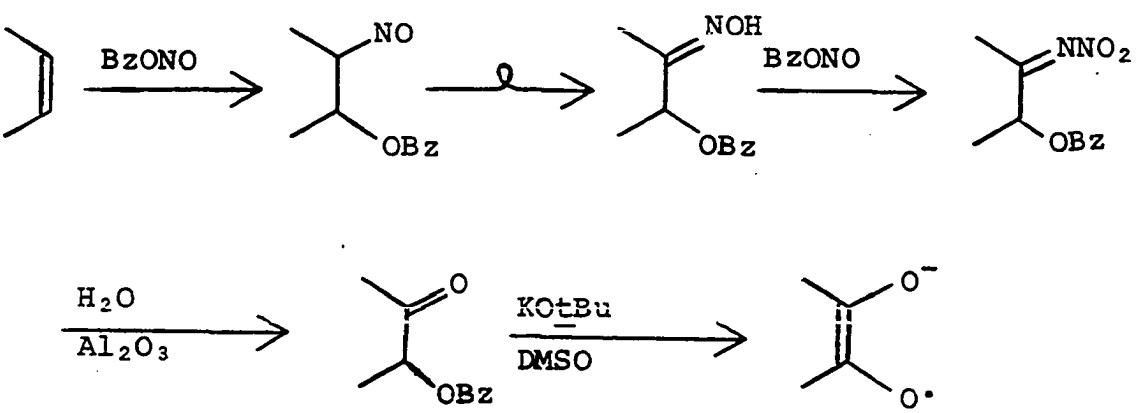
It was decided to devote a small amount of time to 8 since it was of interest to know the relative importance of structures 1, 2, and 3 in the bicyclo[2.2.2]octenesemidione system vis-a-vis the analogous structures in 8. The spectrum expected of radical 8 was not obtained from 7, but instead a spectrum we assigned to radical 9 was seen. The temporary aside turned into a nearly four year project into the proof of structure, mode of formation, and generality of formation of radical 9. It is the results of this project which form the content of this thesis.

DISCUSSION

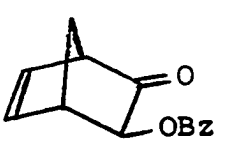
Bicyclo[3.2.0]hept-2-en-6,7-semidione

Scharpe's report (7) that disubstituted olefins formed α-benzoyloxy nitrimines on reaction with 2 equivalents of benzoyl nitrite, which could easily be hydrolyzed to α-benzoyloxy ketones by the method of Boswell (8), led to the production of a number of stable semidiones by Keske (9) (Scheme 1). It was, therefore, felt that benzoyloxy ketone

Scheme 1



7 would be an excellent precursor to semidione 8.



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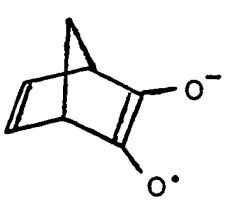
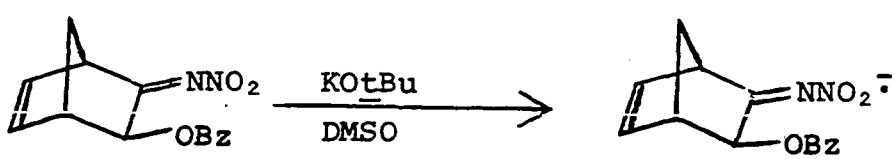


8

Accordingly, norbornadiene was reacted with benzoyl nitrite and the first formed nitrimine hydrolyzed to give a pale green oil (7) whose physical and spectral properties agreed with those given by Scharpe.[1]

Treatment of this oil with potassium-t-butoxide in dimethyl sulfoxide (KOt-Bu/DMSO) under static conditions gave no observable radicals so a solution of the oil was mixed with KOt-Bu/DMSO under flow conditions. A strong signal which seemed to be due to two radicals, each with large splittings for spin = 1 nuclei, was seen. Nitrogen containing impurities were suspected and elemental analysis confirmed the presence of approximately 0.2% nitrogen, although the carbon and hydrogen analyses were correct. It is believed that these radicals may be due to the unknown nitrimine radical anion (10) produced by reduction of the nitrimine 11 by the KOt-Bu/DMSO solution (Scheme 2), a mixture known to have

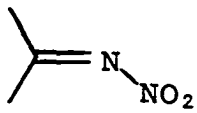
Scheme 2



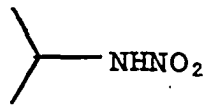
11 10

[1] T. R. Scharpe, Explosives Division, Dupont, Wilmington, Delaware. Private communication (1970).

reducing properties (10). Boswell (8) has observed that $NaBH_4$ reduction of nitrimines to nitramines is a facile process which suggests a low reduction potential. Scharpe[2]

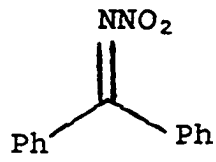


Nitrimine



Nitramine

has observed two geometrical isomers of the nitrimine 11 which may explain why apparently two radicals were seen. Further experiments on compounds more likely to yield stable radicals such as nitrimine 12 need to be carried out to confirm this postulate.



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Careful purification of the oil 7 by chromatography, sublimation, and recrystallization gave a white solid whose elemental analysis showed no nitrogen. Treatment of this

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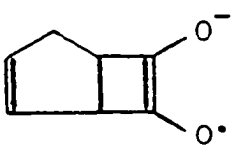
[2] Ibid.

solid (pure 7) with KOt-Bu/DMSO under flow conditions gave a single radical (Figure 1) whose signal was strongest at 3-5 minutes after mixing.[3] The hfsc of this radical, $\underline{a}^H$ = 12.7(1H), 10.2(1H), 2.04(1H), 0.51(2H), 0.10(1H), are clearly not consistent with semidione 8, but are believed more consistent with semidione 9 on the basis of the 10-12 gauss hfsc which are characteristic of α-hydrogens in cyclobutane-semidiones (11, 12).



9

If it is assumed that semidione 9 arises from ketone 7 via semidione 8, then there are ample precedents for both thermal and photochemical processes similar to this in diamagnetic species.

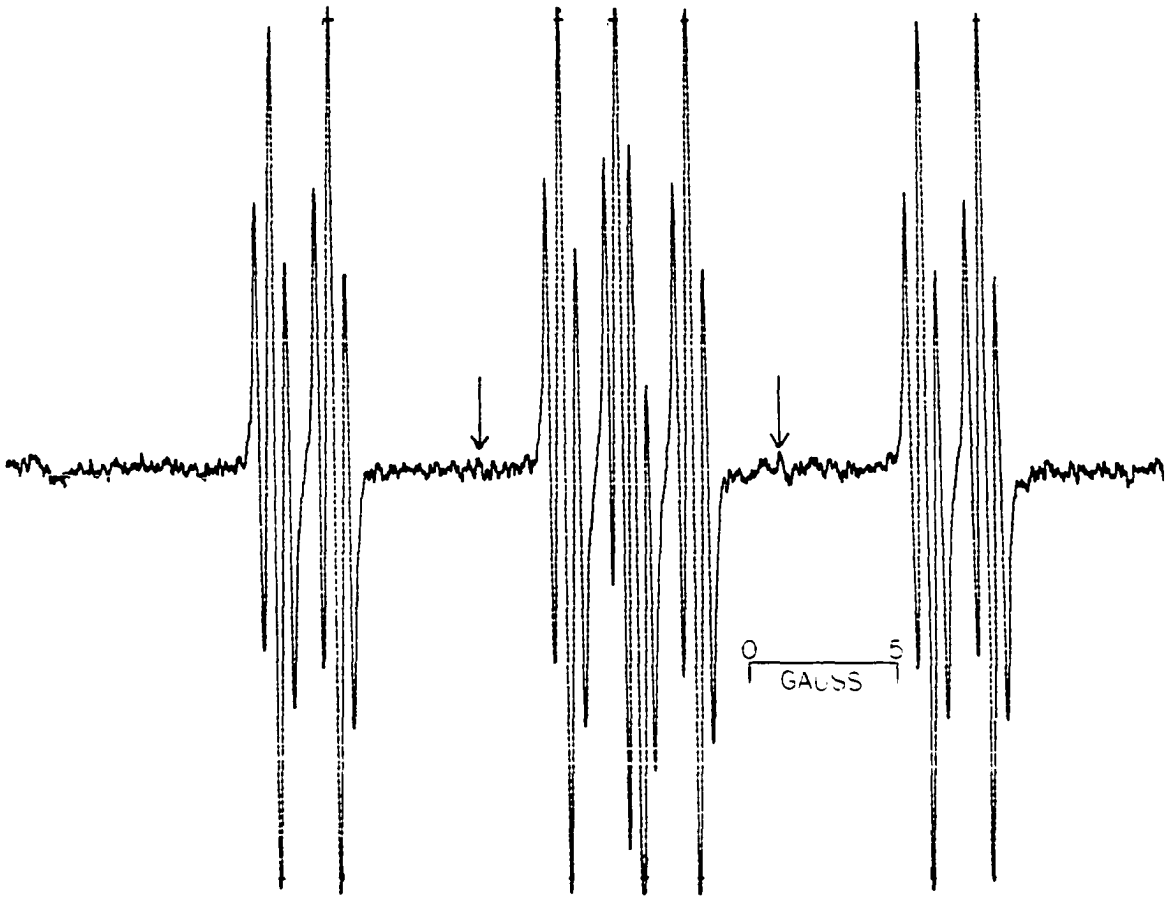
---

[3]All such "minutes after mixing" figures were computed by dividing the lag volume of the flow cell by the total nominal flow rate.

Time = 0.10 ml/flow rate

R. L. Blankespoor, Wisconsin State University-Oshkosh, Oshkosh, Wisconsin. Private communication (1972).

Figure 1. The first derivative esr spectrum of bicyclo[3.2.0]hept-2-en-6,7-semidione (9) (top) in DMSO; calculated spectrum (bottom) for Lorentzian line width 0.21 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.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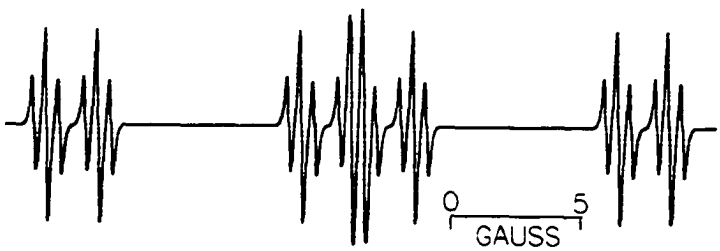
5
GAUSS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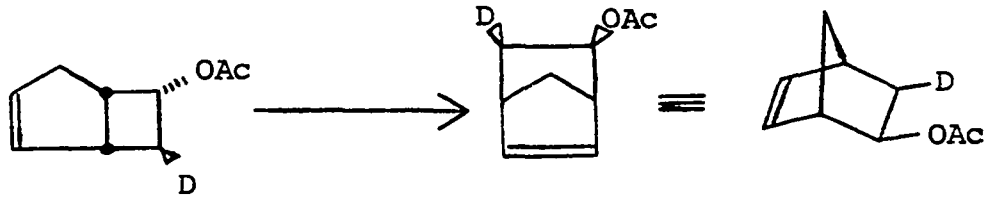
GAUSS

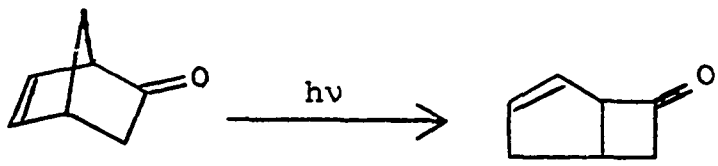
Berson (13) has reported the conversion of acetate 13 to acetate 14 at 300° proceeds via a concerted [1,3] sigmatropic shift of C-7 with inversion of configuration at C-7 (Scheme 3).

Scheme 3



13 14 14

The reverse of this reaction has been reported to proceed photochemically for norbornenone to ketone 15 by Schuster et al. (14).



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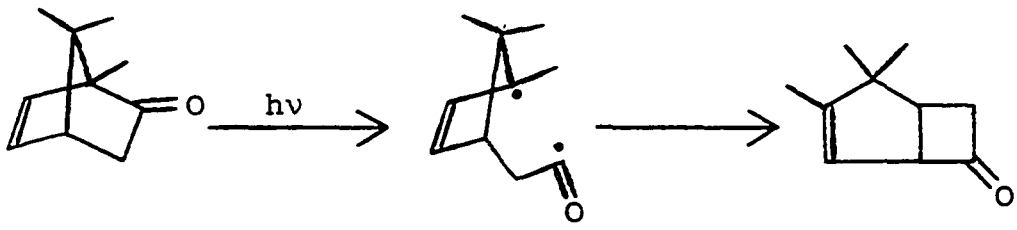
(14). Bays and Cookson have found (15) that the analogous rearrangement for dehydrocamphor (16) to ketone 17 occurs

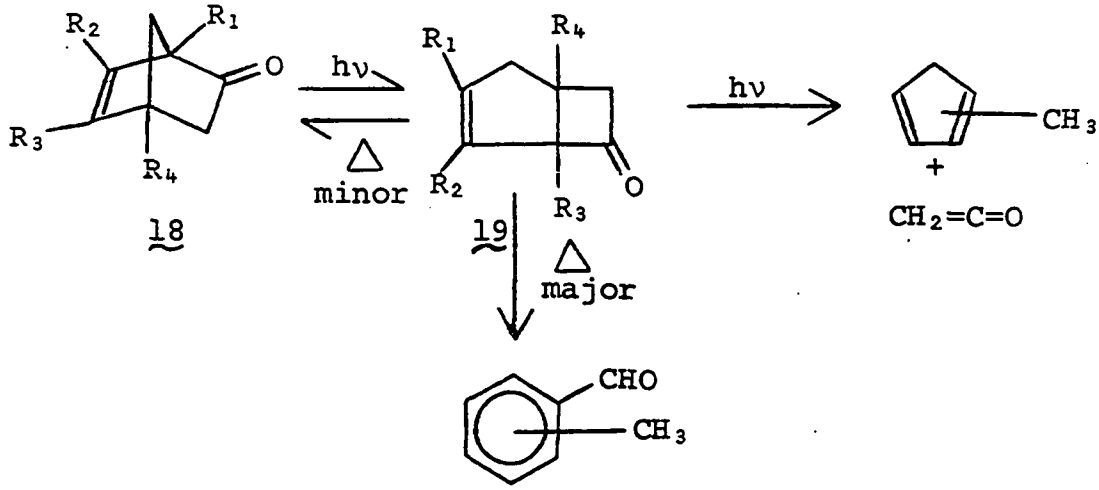


16 17

only upon irradiation at 300-310 nm (the n → π* band) which suggested a diradical intermediate.

Schiess (16) has recently showed that the photochemical transformation of 18a-d to 19a-d (Scheme 4) is at least partially reversible thermally.

Scheme 4



18a $R_1=CH_3$; $R_2=R_3=R_4=H$

18b $R_1=R_3=R_4=H$; $R_2=CH_3$

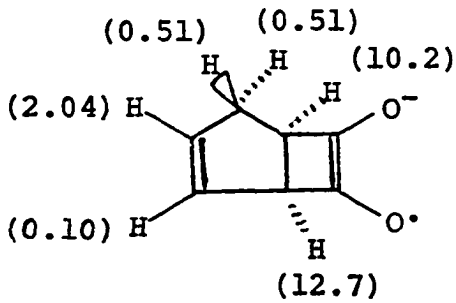
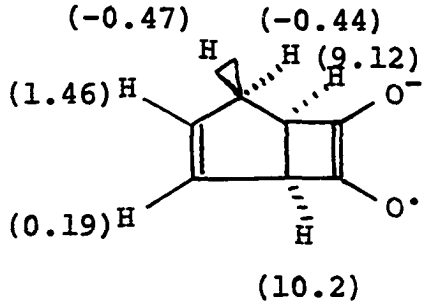
18c $R_1=R_2=R_4=H$; $R_3=CH_3$

18d $R_1=R_2=R_3=H$; $R_4=CH_3$

These analogous reactions, the two cyclobutane type hfsc, and the results of EH-SCF calculations[4] (Table 1) made

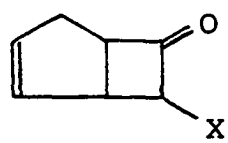
[4]C. Chung, Iowa State University, Ames, Iowa. Private communication (1971).

Table 1. Comparison of experimental and calculated hfsc for semidione 9

Experimental	Calculated
	

structure 9, highly probable. An unequivocal precursor to semidione 9 was, nevertheless, desired.

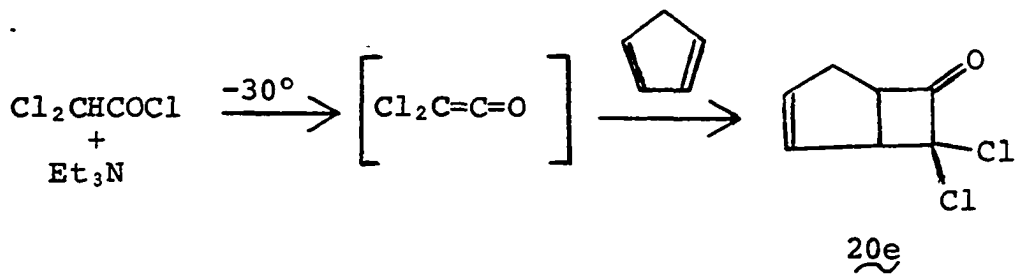
Ketones of general structure 20 seemed ideal. Chloro-



X =		
	=O	20a
	OH	20b
	OAc	20c
	Cl	20d
	Cl_2	20e

ketones 20d and 20e were both readily available from the reaction of cyclopentadiene (Scheme 5) and the corresponding ketene generated in situ (17).

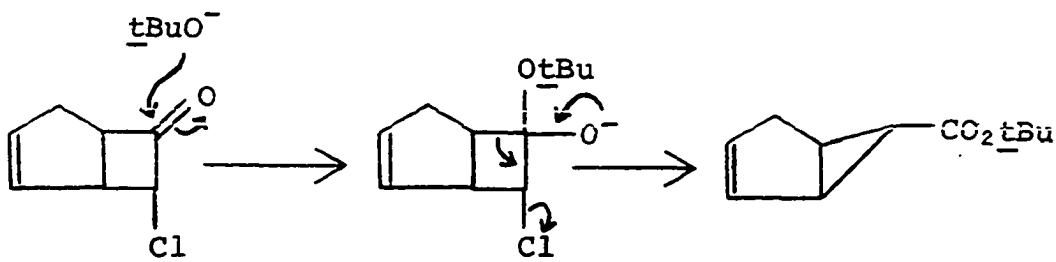
Scheme 5



20e

Mixing chloroketone 20d and KOt-Bu/DMSO under flow conditions produced no detectable radicals. In light of subsequent results (vide infra) it seems probable that all that occurred (Scheme 6) was production of Favorskii ester 21.

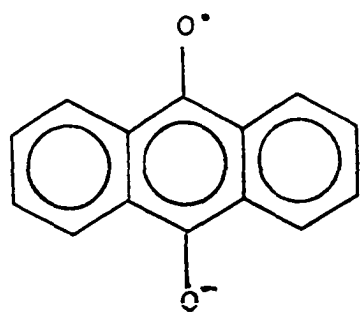
Scheme 6



20d 21

Mixing dichloroketone 20e with KOt-Bu/DMSO under flow conditions did not produce the desired semidione 9, but instead a mixture of two radicals could be observed at 5-8 seconds after mixing. The relative proportions of these radicals could be varied slightly by changing the flow rates.

The hfsc of the radicals (Figure 2) are consistent with: $\underline{a}^{H}_{major}$ = 7.59(1H), 0.97(1H), 0.32(1H); $\underline{a}^{H}_{minor}$ = 6.54(1H), 5.90(1H), 1.94(1H), 0.34(1H). The structures of these radicals are unknown; the fact that they are centered on 3380 gauss suggests they are ketyl or semidione radical anions. After 1-2 minutes these radicals died out and a powerful radical (Figure 3), $\underline{a}^{H}$ = 0.985(4H), 0.293(4H), appeared. The spectrum of this radical (22) was identical in every way to that obtained from anthraquinone (Figure 3).



22

In light of the use of dichloroketone 20e in the synthesis of α-tropolones (18) it is attractive to suggest a mechanism for formation of 22 which invokes initial formation of α-tropolone. Scheme 7 shows one of a number of such more-or-less plausible mechanisms.

Figure 2. The calculated spectrum (top) of minor radical for Lorentzian line width 0.10 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator; first derivative esr spectrum of radicals from 7,7-dichlorobicyclo-[3.2.0]hept-2-en-6-one (20e) under fast flow (middle) in DMSO; calculated spectrum (bottom) of major radical for Lorentzian line width 0.13 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

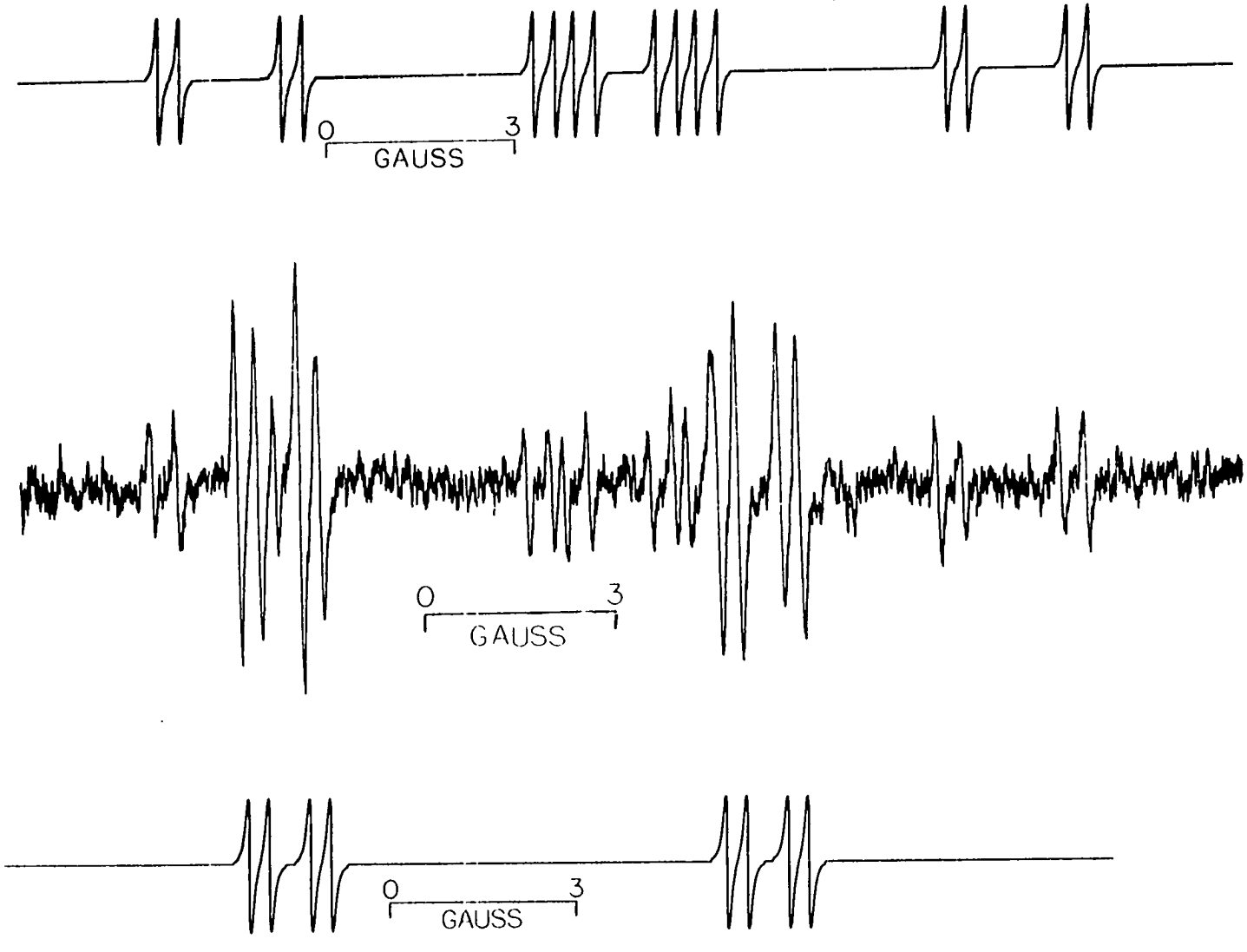
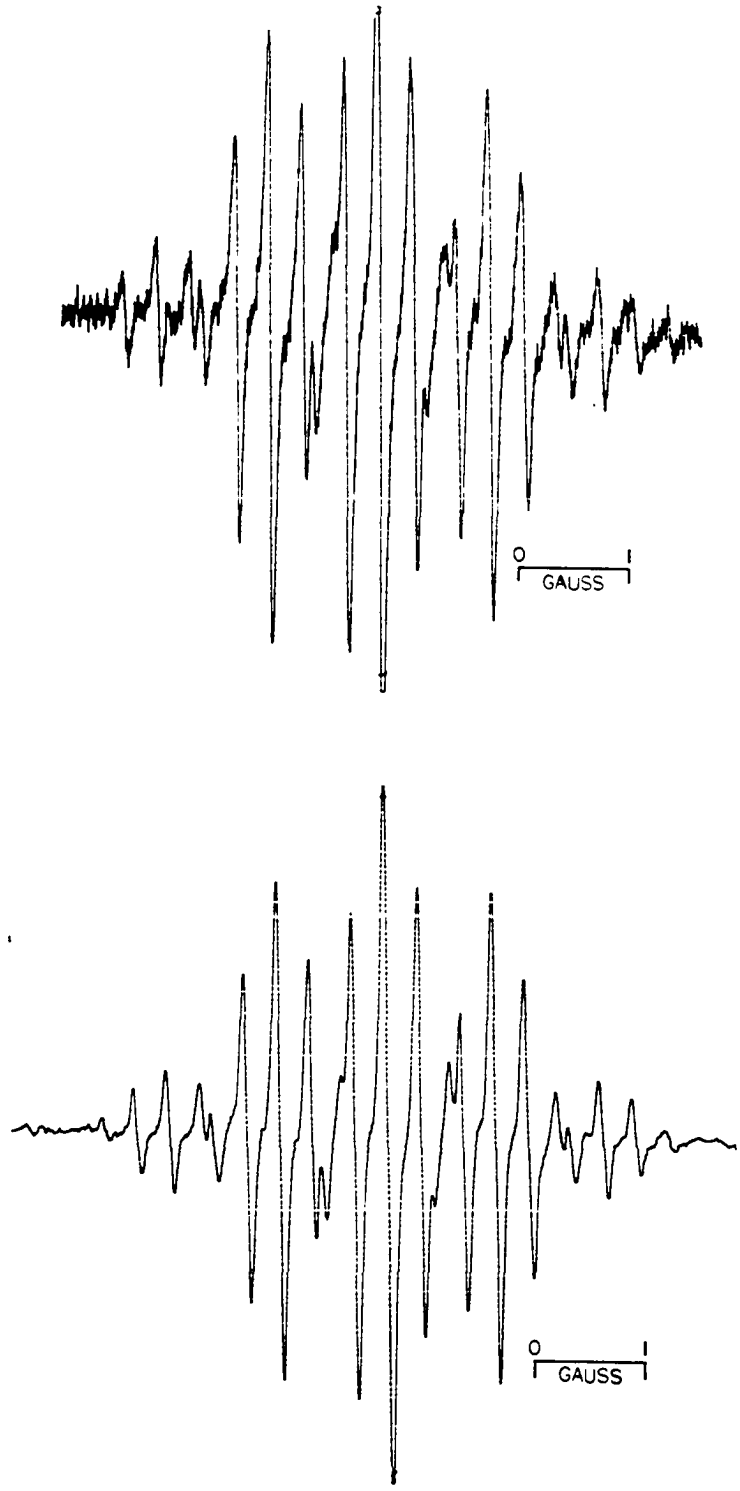
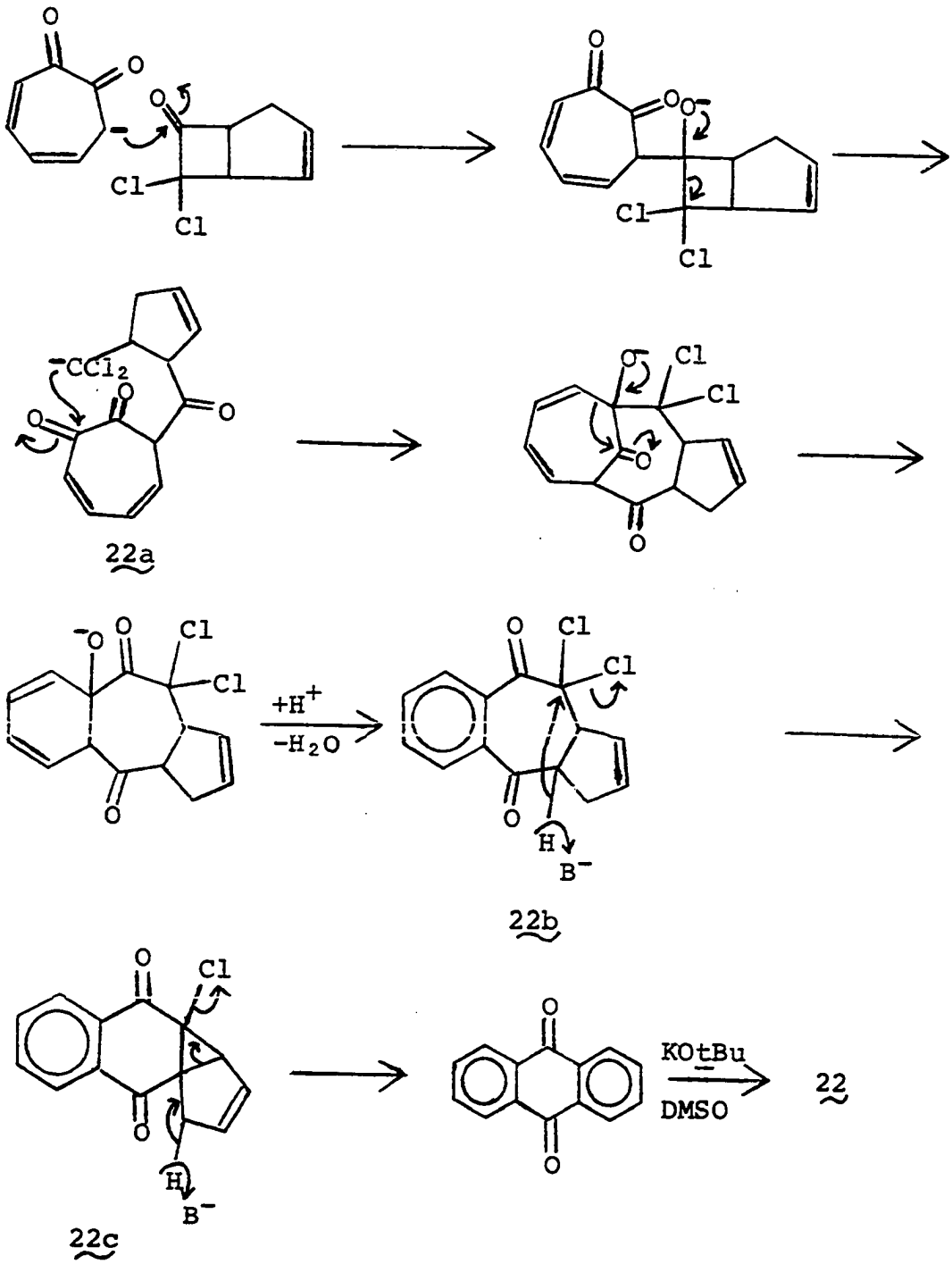

0
3
GAUSS
0
3
GAUSS
0
3
GAUSS

Figure 3. The first derivative esr spectrum of the radical obtained from 7,7-dichlorobicyclo-[3.2.0]hept-2-en-6-one (20e) under static conditions (top) in DMSO; first derivative esr spectrum of anthrasemiquinone (bottom) in DMSO.

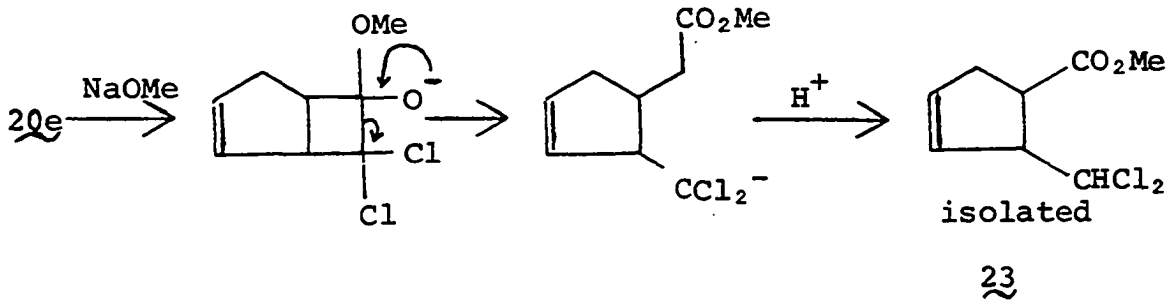

0
GAUSS
0
GAUSS

Scheme 7



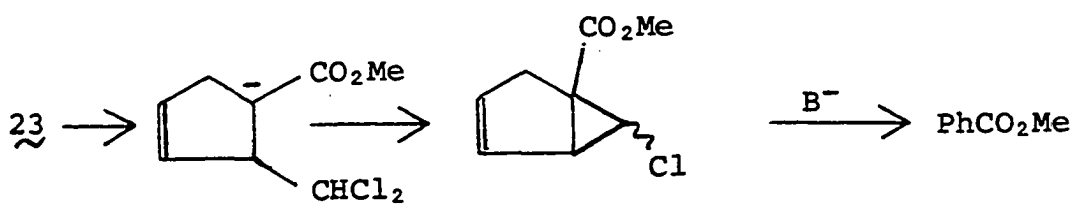
The mode of attack of carbanions on dichlorocyclobutanones has been little studied. The ring opening to 22a is exactly analogous to the reaction described by Brook and Duke (19) for 20e itself (Scheme 8). Formation of the highly strained

Scheme 8



chloride 22c from enolate 22b and its subsequent aromatization is analogous to the formation of methyl benzoate from chloro-ester 23 also observed by Brook and Duke (19) (Scheme 9).

Scheme 9



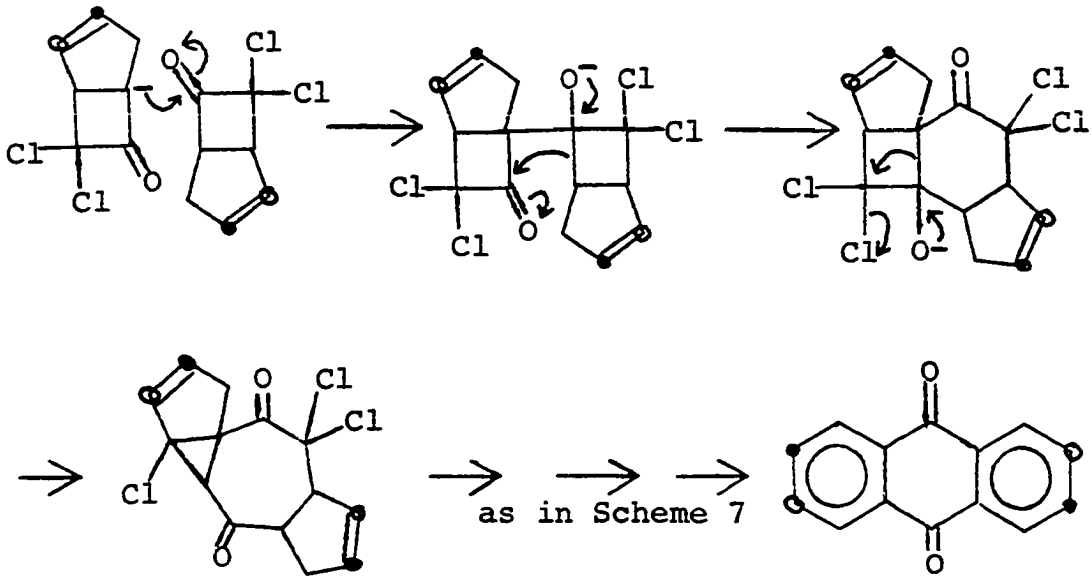
The mechanism of Scheme 7 was tested by addition of α-tropolone to the dichloroketone 20e solution in amounts ranging from 0.005-0.15 = [α-tropolone]/[20e]. No difference in the spectrum was noted in any of these experiments. It was concluded that the mechanism of Scheme 7 was inoperative.

Potassium t-butoxide is a relatively nonnucleophilic base and it is possible that a small amount of the enolate of 20e may react intermolecularly before ring contraction occurs. Semidione 22 could thus be formed without invoking α-tropolone participation as shown in Scheme 10. The aromatization steps are the same as those for the conversion

22b ⟶ 22c ⟶ anthraquinone

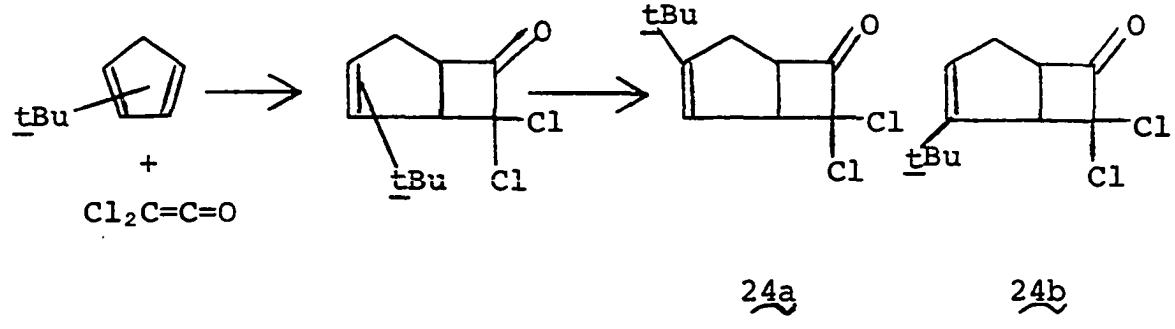
in Scheme 7. The heavy dots, •, and open circles, o, show the position of a label.

Scheme 10



Dichloroketones 24a and 24b (Scheme 11) are currently being synthesized to test Scheme 10. If Scheme 10 is correct, both 24a and 24b should give the same anthrasemiquinone.

Scheme 11

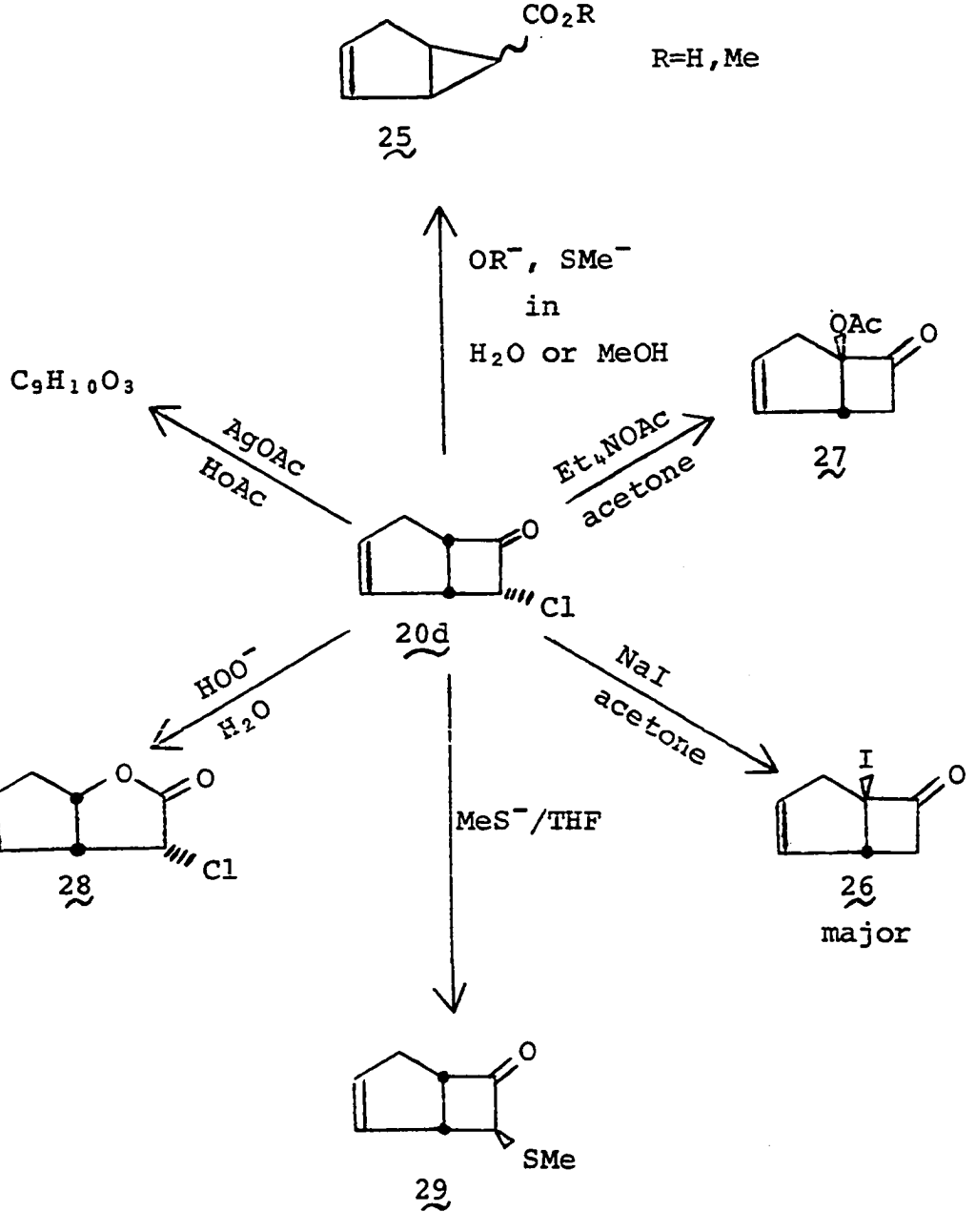


24a 24b

Failure to generate semidione 9 from ketones 20d and 20e prompted a serious attempt to synthesize ketones 20a-c in which the required oxygen is already present. At the time this work was begun, ketone 20d seemed an ideal precursor. The results of this study are shown in Scheme 12.

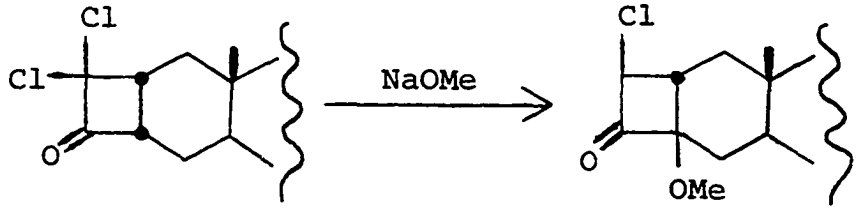
Results exactly like these appeared in the literature either while this work was going on or shortly thereafter. Thus, Brook has reported the formation of acid 25 or its methyl ester when 20d was treated with OH^- or OMe^-, respectively, (20). Cine-substitution, such as formation of iodide 26 or acetate 27, has been reported (21)

Scheme 12


CO2R
R=H,Me
25
OR⁻, SMe⁻
in
H2O or MeOH
OAc
O
27
Et4NOAc
acetone
C9H10O3
AgOAc
HOAc
O
Cl
20d
HOO⁻
H2O
NaI
acetone
MeS⁻/THF
O
O
Cl
28
I
O
26
major
O
SMe
29

for MeO^- attack on 30 (Scheme 13) and for acetate attack on

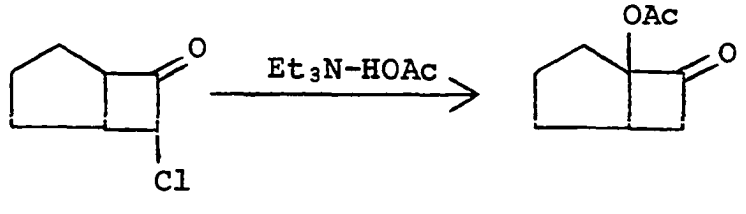
Scheme 13



30

31 (Scheme 14) by Harding, Trotter, and May (22).

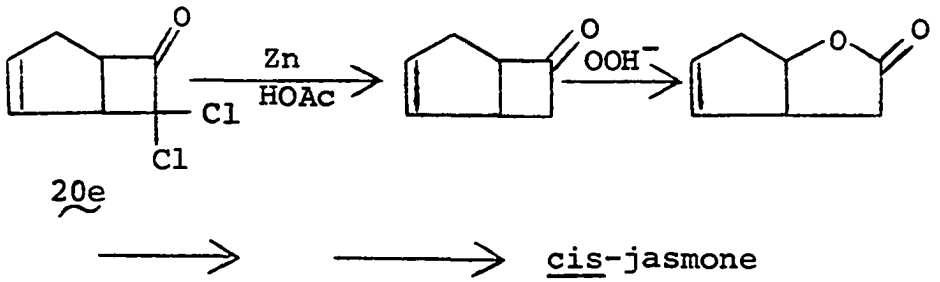
Scheme 14



31

Nucleophilic displacement of chloride in 20d by OOH^-, a good nucleophile, did not take place; the Baeyer-Villager reaction occurred instead to give lactone 28. A similar Baeyer-Villager reaction has been used recently by Grieco (23) in his elegant synthesis of cis-jasmone (Scheme 15).

Scheme 15

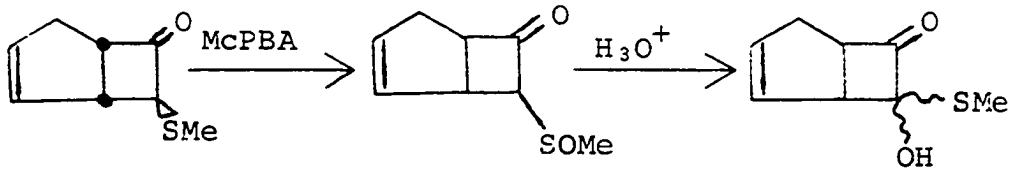


The structure of the product obtained on treatment of 20d with AgOAc/HOAc is unknown. Its combustion analysis and mass spectrum suggest the formula $C_9H_{10}O_3$. Its ir spectrum (1790, 1750 and 1230) suggests an acetate and a strained carbonyl. Although the compound was homogeneous to all gc columns tried, its pmr spectrum suggests it may be a mixture. Rather complex mixtures of products have been observed by Ermann et al. (24) on treatment of fused ring cyclobutanones with acid.

In light of such developments in the literature, it is not surprising that nucleophilic attack on 20d led almost exclusively to cine-substitution or ring expansions or contractions. What is surprising is that the reaction of a heterogeneous mixture of NaSMe and 20d in THF led to a simple nucleophilic displacement of chloride to give sulfide 29.

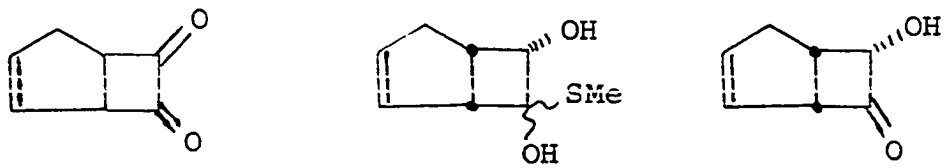
Sulfide 29 was readily oxidized with m-chloroperbenzoic acid (Scheme 16) to the sulfoxide 32 which smoothly underwent

Scheme 16



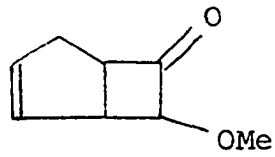
29 32 33

the Pummerer rearrangement to give hemithioketal 33. All attempts to convert hemithioketal 33 to diketone 20a or to convert alcohol 34 (obtained by $NaBH_4$ reduction of 33) to acyloin 35 were unsuccessful. Attempts to generate semidione 9 directly from hemithioketal 33 or alcohol 34 also failed.



20a 34 35

This lack of success in converting the chloride 20d to an oxygen functionality suggested that the oxygen functionality should have been built into the ketene. At about this time Rey et al. (25) reported the low yield addition of methoxyketene generated in situ to cyclopentadiene gave adduct 36.



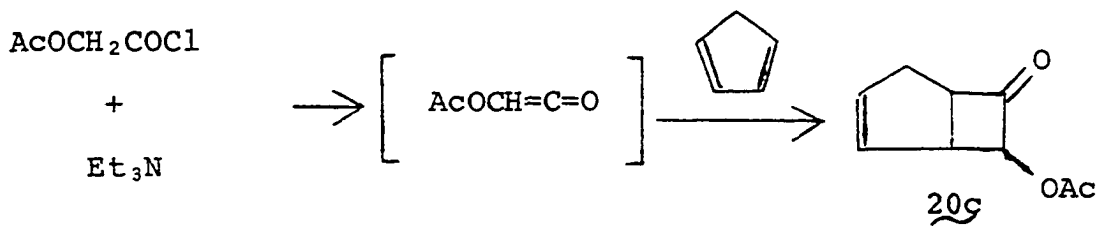
36

Acetoxyketene was unknown but it was felt that it ought to be at least as reactive as methoxyketene since the acetate group is less electron donating and, therefore, ought to be less deactivating than the methoxy group. It was felt that the electronegativity of the substituent would be important because, in general, those ketenes with the most electronegative substituents are the most reactive toward cycloadditions (17).

Acetoxyketene quite satisfactorily added to cyclopentadiene to give the desired acetate 20c (Scheme 17) in a

Scheme 17

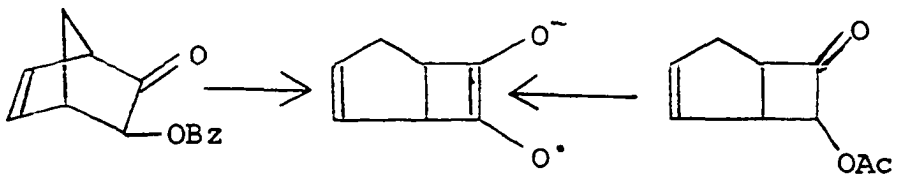
$$HOCH_2CO_2H\,(70\%\text{ in }H_2O) \xrightarrow{AcCl} AcOCH_2CO_2H \xrightarrow{PCl_3} AcOCH_2COCl$$



20c

pleasing 62% yield. Both the exo and endo isomers of 20c were obtained in relative yield 1:50.

Both 20c, exo and 20c, endo behaved in nearly identical fashion when mixed with KOt-Bu/DMSO under flow conditions. Both isomers showed a strong radical, a^H = 12 g(1H), other hfsc unresolved, 5-15 seconds after mixing. At 1-3 minutes after mixing (Figure 4), the exo isomer showed a radical whose spectrum is superimposable on that obtained from benzoate 7. At 3-5 minutes after mixing the endo isomer also showed a radical whose spectrum (Figure 5) is superimposable on that obtained from benzoate 7 or acetate 20c, exo. This difference in kinetic behavior of the endo and exo isomers is attributed to a slower hydrolysis of the endo acetate to the acyloin 20b. These results taken together with the results of EH-SCF calculations (vide supra) firmly established the structure of semidione 9 obtained from benzoate 7.



7 9 20c

exo and endo

Figure 4. The first derivative esr spectrum of the radical obtained from exo, 7-acetoxybicyclo[3.2.0]hept-2-en-6-one (20c) in DMSO.

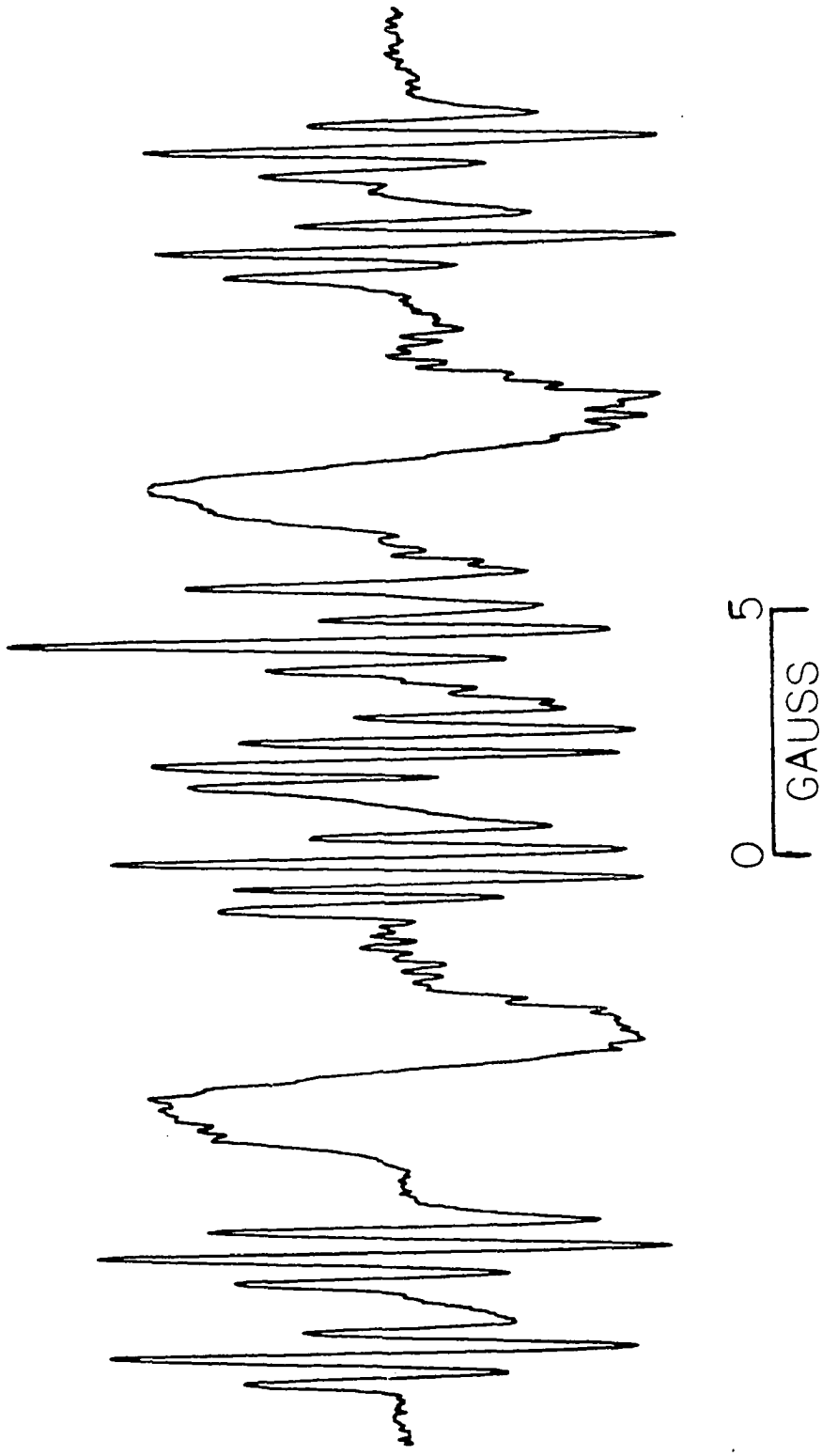
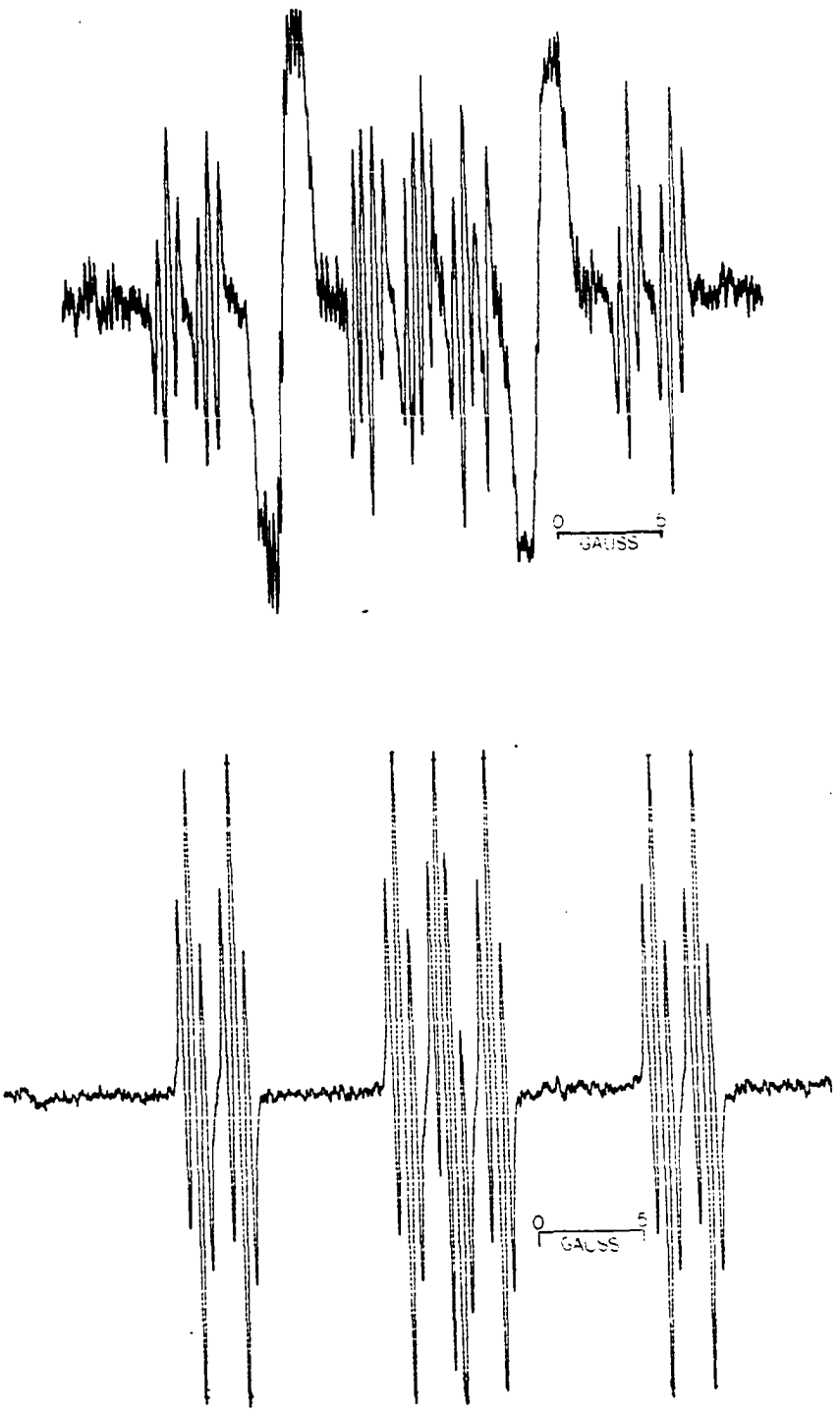

0
5
GAUSS

Figure 5. The first derivative esr spectrum (top) of the radical obtained from endo, 7-acetoxybicyclo-[3.2.0]hept-2-en-6-one (20c) in DMSO; the first derivative esr spectrum (bottom) of the radical obtained from exo, 3-benzoyloxy-bicyclo[2.2.1]hept-5-en-2-one (7) in DMSO.

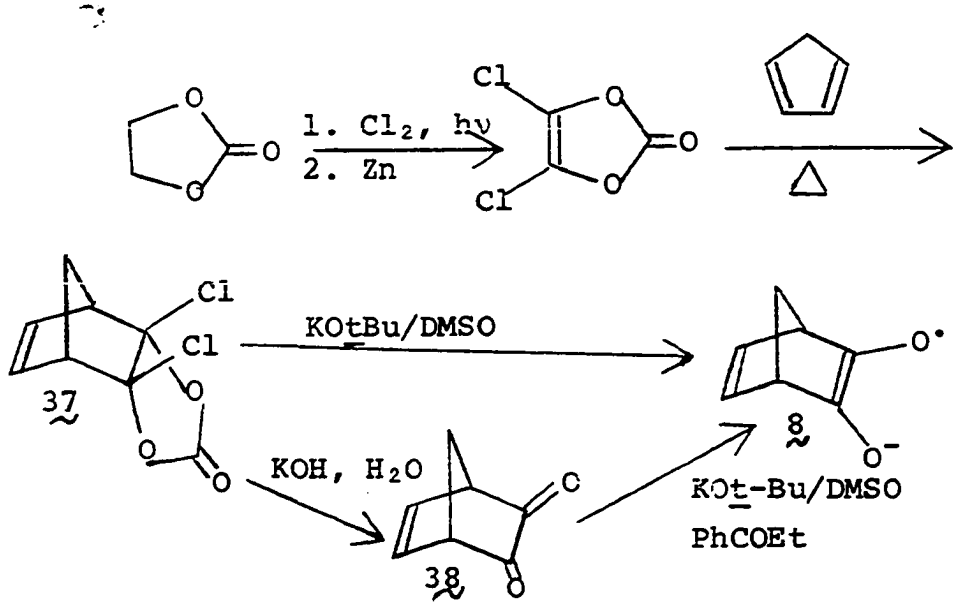

0
5
GAUSS
0
5
GAUSS

The Search for Evidence Implicating the Existence of Bicyclo[2.2.1]hept-5-en-2,3-semidione

It was indeed fortunate that the first experiment in this study was carried out on the exo benzoate 7. If the first experiment had been performed on most of the compounds discussed below, the complexity of the spectra or lack of radicals would probably have caused the project to be abandoned at the outset.

We were led to try to find evidence for the existence of the [2.2.1] semidione 8 as an intermediate in the formation of [3.2.0] semidione 9 by a curious result obtained in trying to repeat some of Holland's work in this area (6). Holland had attempted to generate [2.2.1] semidione 8 by the syntheses due to Scharf et al. (26) (Scheme 18). Holland was able to

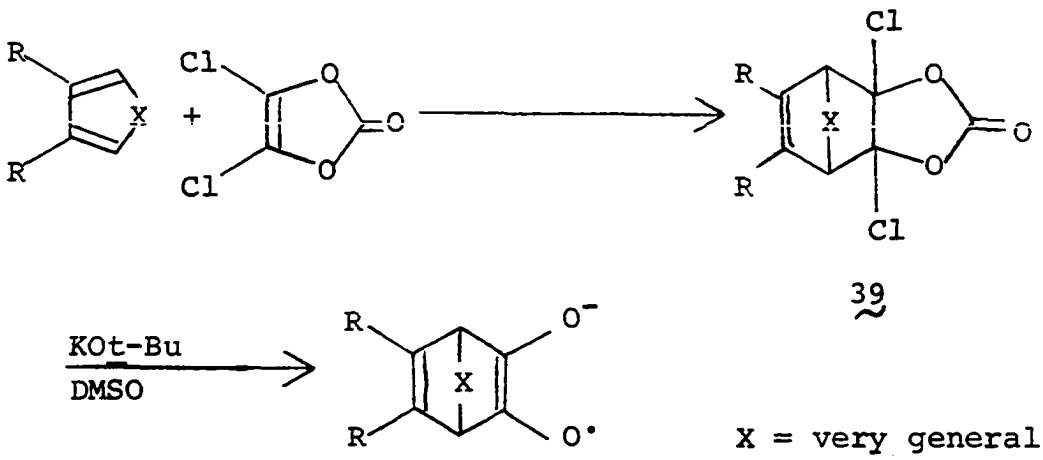
Scheme 18



duplicate the synthesis of Diels-Alder adduct 37 but was unable to produce a material whose pmr spectrum matched that reported by Scharf for the diketone 38. As expected from our later results, neither the *in situ* generation of semidione 8 from adduct 37, nor the reduction of the crude diketone 38 by PhCOEt-KO*t*-Bu/DMSO gave an observable radical under Holland's static conditions. We repeated the synthesis of Scheme 18 and were able to obtain both the Diels-Alder adduct 37 and the diketone 38 with satisfactory spectral properties.

We fully expected diketone 38 to give a spectrum of the rearranged radical 9 but, to our surprise, neither carbonate 37 nor diketone 38 gave observable radicals when the esr experiment was carried out under flow conditions. The failure of the carbonate 37 was especially disappointing since it was hoped that this basic synthetic approach would lead to a very convenient method of generating homoallylically unsaturated semidiones (Scheme 19).

Scheme 19



39

X = very general

Subsequent work by Blankespoor[5] has showed that Diels-Alder adducts 39 are, in fact, not good semidione precursors. The in situ hydrolysis does take place as evidenced by color change and bubbling of the solution, however, the reduction potential of the solvolysis product, the diketone, may be too high to permit formation of the semidione. Furthermore, it has been our experience that the presence of even small amounts of CO_2 (as evidenced by cloudiness of the KOt-Bu/DMSO solution, that is, precipitation of KOC(O)Ot-Bu) was enough to prevent formation of the unstable semidiones in this study.

The implications of the failure to produce a semidione from diketone 38 cannot be passed off so lightly. Numerous attempts to produce a semidione by electrolysis and by varying the propiophenone concentrations were unsuccessful.

One possible explanation (Scheme 20) is that diketone 38 may be attacked very rapidly and destroyed by the strong base present (Haller-Bauer-like cleavage). Since the semidione, diketone, and diketone dianion are in rapid equilibrium (1) in all but the most dilute solutions, immediate chemical destruction of diketone 38 is tantamount to "no formation of semidione 8." Benzoate 7 may then form [3.2.0] semidione

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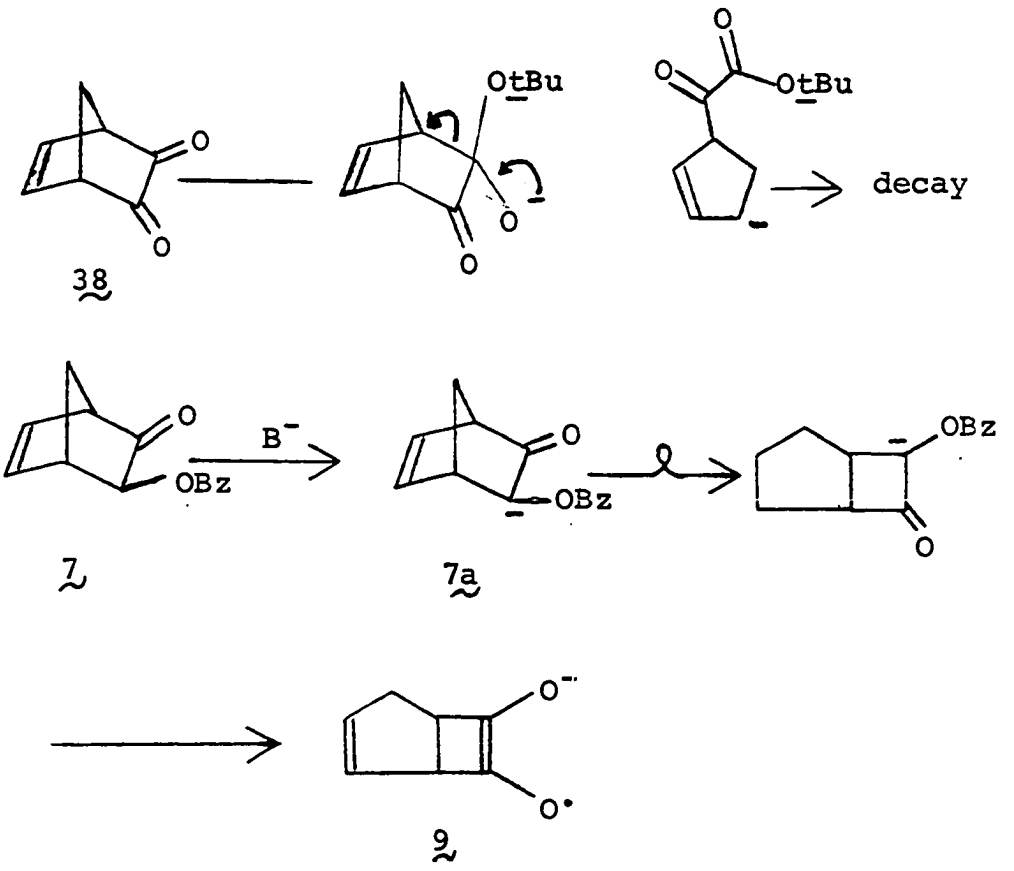
[5]R. L. Blankespoor, Wisconsin State University-Oshkosh, Oshkosh, Wisconsin. Private communication (1972).

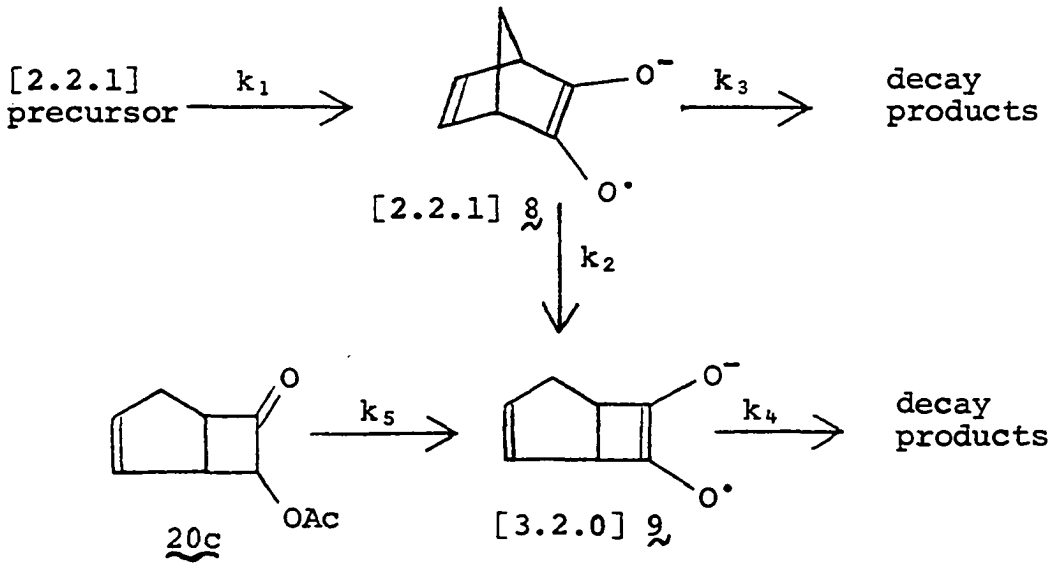
Scheme 20



9 not because it first forms [2.2.1] semidione 8 (in rapid equilibrium with diketone 38) which rearranges to 9, but because it forms an intermediate (perhaps enolate 7a) not possible for 38 which is the intermediate which rearranges to the [3.2.0] system.

A second mechanism may be put forward which does involve the [2.2.1] semidione 8 as an intermediate (Scheme 21). The simple rate constant k_1 can only be a first order rate

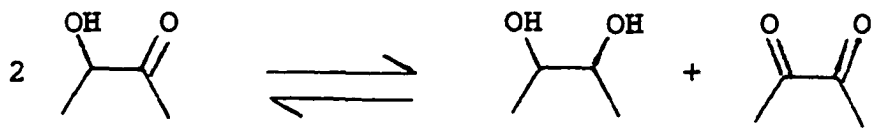
Scheme 21



constant for the diketone 38 where a simple electron transfer represents the process

[2.2.1] precursor ⟶ [2.2.1] 8.

For a precursor such as the exo benzoate 7 hydrolysis to the acyloin followed by disproportionation (1), a second order process, must occur.



If hydrolysis is quite slow compared to disproportionation, the process can be treated as first order. A kinetic expression can be derived for Scheme 21 (27) (not including 20c). Thus, if $R = [9]/[8]$, $a = k_2 + k_3$, and $b = \frac{k_1}{a-k_1}$

$$\text{then } [9] = k_2 b[\text{2.2.1 precursor}] \quad \frac{e^{-k_1 t} - e^{-k_4 t}}{k_4 - k_1} - \frac{e^{-at} - e^{-k_4 t}}{k_4 - a}$$

$$[8] = b[\text{2.2.1 precursor}] \; (e^{-k_1 t} - e^{-at})$$

$$R = k_2 \frac{\left[\frac{e^{-k_1 t} - e^{-k_4 t}}{k_4 - k_1} + \frac{e^{-at} - e^{-k_4 t}}{a - k_4}\right]}{(e^{-k_1 t} - e^{-at})}$$

When k_1-k_4 are all of approximately the same value (order of magnitude) this expression shows interesting properties. If k_2-k_4 are held constant, the ratio R increases as k_1 increases. For values $k_2 \approx k_3 \approx k_4$ the time for maximum [8] and [9] comes sooner as k_1 increases, as certainly would be expected. There are several other interesting implications consistent with the observed results from benzoate 7 and diketone 38. First, if a system has a very rapid rate of formation of semidione 8, the point in time at which the [9] drops below the detection level will come earlier (as for diketone 38). As the rate constant k_1 is made smaller, the maximum [9] observable falls too, but the time at which it occurs comes later so that the time after mixing may fall

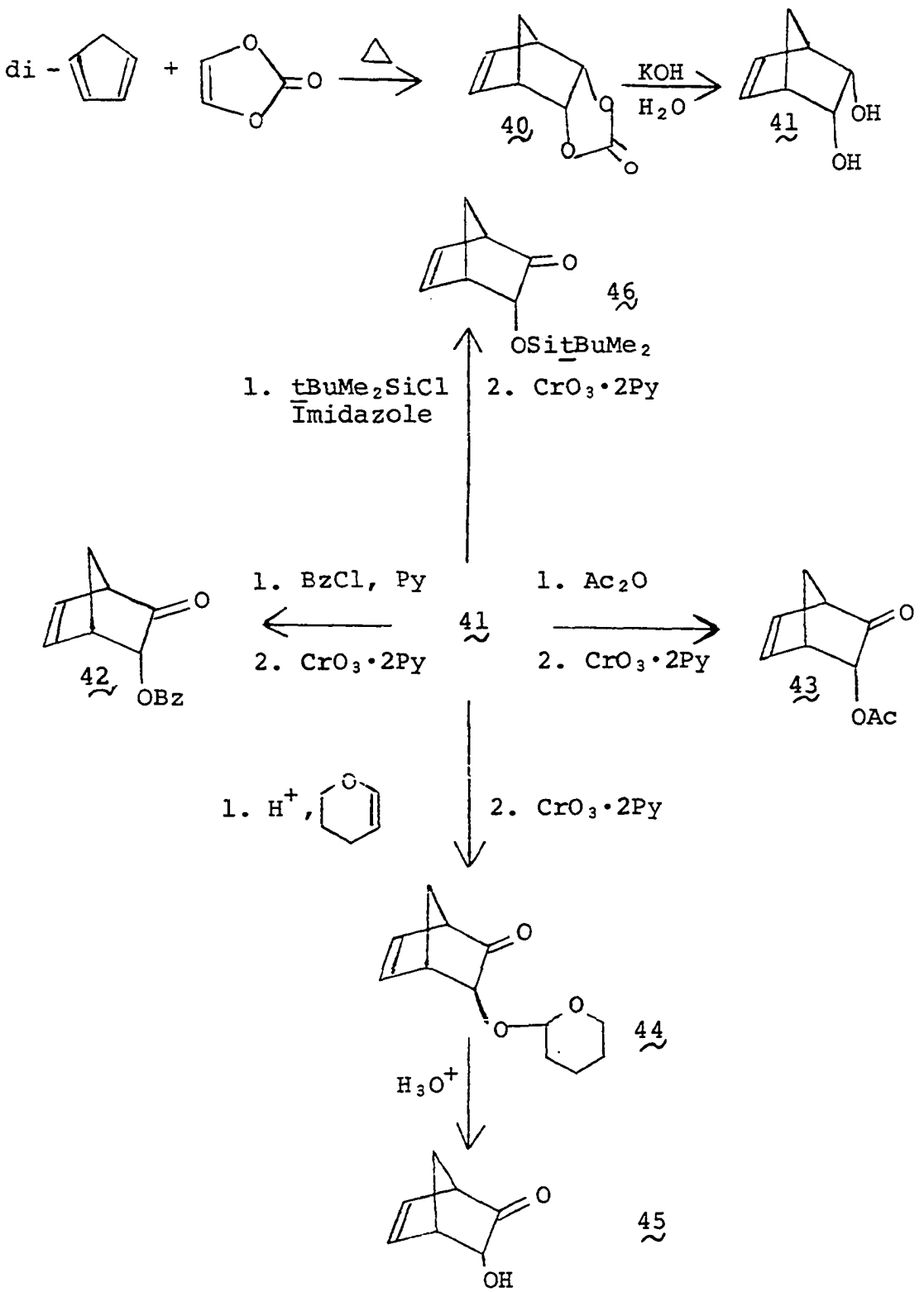
within reasonable limits for flowing the amount of material available. Secondly, the expression predicts that the drop in the maximum [9] will not be as rapid as the drop in R, thus predicting a fighting chance of finding a precursor whose k_1 is low enough to allow a reasonable ratio of [2.2.1] semidione 8/[3.2.0] semidione 9 without allowing the absolute [8] to fall below the detection limit.

Scheme 22 shows the compounds which were synthesized to test the kinetic predictions of Scheme 21 and their method of synthesis.

The syntheses of carbonate 40 and diol 41 are those of Kwart and Vosburgh (28). Vinylene carbonate seems to be about as reactive as dichlorovinylene carbonate if the temperature and duration of heating are any indication. Compared to dichlorovinylene carbonate, which is a powerful lachrymator and not commercially available, vinylene carbonate is a joy to work with.

The basic plan of these syntheses (Scheme 22) was to derivatize one alcohol then oxidize the other to the ketone. Obtaining the monoderivatized diol proved, in general, a simple task because of the extreme ease of separation of the diol, alcohol, and diester (diether) on a silica gel column. Oxidation to the ketone did not prove so simple at first. A fairly long gamut of standard oxidation techniques was run before it was discovered that the $CrO_3 \cdot 2Py$ complex in

Scheme 22

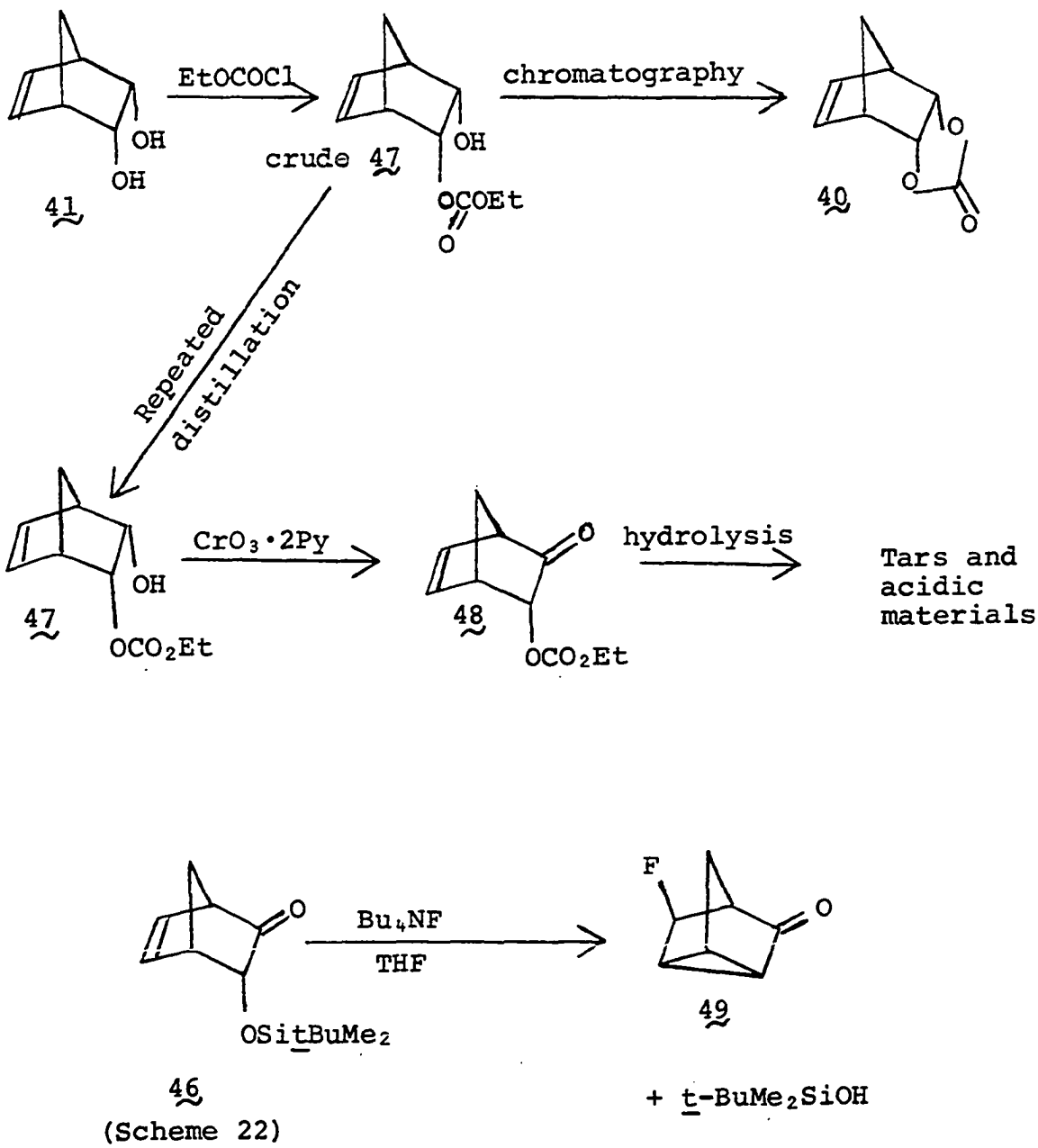

di -
+
KOH
H_2O
40
41
OH
OH
46
OSitBuMe$_2$
1. tBuMe$_2$SiCl
Imidazole
2. CrO_3·2Py
1. BzCl, Py
2. CrO_3·2Py
42
OBz
41
1. Ac_2O
2. CrO_3·2Py
43
OAc
1. H^+,
2. CrO_3·2Py
44
H_3O^+
45
OH

CH_2Cl_2 was ideal. This reagent was subsequently used without a single failure for all alcohol oxidations in this dissertation.

Synthesis of ketones 42, 43 and 46 was routine but obtaining acyloin 45 proved difficult. Acyloin 45 was especially desirable since we felt it unlikely to form an enolate similar to 7a (a dianion enolate for acyloin 45). Observation of [3.2.0] semidione 9 from acyloin 45 would, thus, be powerful evidence against Scheme 20 and for the intermediacy of [2.2.1] semidione 9. The synthesis was, therefore, attempted from various angles along the lines of 41 —> 44 —> 45 (Scheme 22). Scheme 23 shows two of these unsuccessful attempts.

Chromatography of carbonate 47, even with benzene-pyridine eluant on basic alumina, gave transesterification carbonate 40. Repeated Hickmann still distillations gave carbonate 47 pure but, although oxidation proceeded smoothly, the carbonate 48 could not be hydrolyzed to acyloin 45 under conditions mild enough to insure survival of the rest of the molecule. t-Butyldimethylsilyl ether 46 was prepared because of the facile cleavage of such ethers by Bu_4NF reported by Corey and Venkateswarlu (29). Although silyl ether 46 turned out to be extremely useful (vide infra) treatment with Bu_4NF gave nearly 80% t-butyldimethyl silanol (identified by pmr and ir spectra), a volatile white solid which smelled like

Scheme 23


EtOCOCl
chromatography
OH
OH
41
crude 47
OH
OCOEt
O
40
Repeated distillation
CrO3·2Py
OH
47
OCO2Et
48
OCO2Et
hydrolysis
Tars and acidic materials
Bu4NF
THF
OSitBuMe2
46
(Scheme 22)
F
49
+ t-BuMe2SiOH

camphor, and no acyloin 45. The white solid is presumed to be fluoro ketone 49 on the basis of its mass spectrum and mode of formation.

Acyloin 45 was finally obtained (Scheme 22), but both formation and removal of the tetrahydropyranyl (THP) ether moiety (44) were very low yield processes.

The results of esr experiments were exactly in line with the kinetic predictions of Scheme 21. Thus, at 3 minutes after mixing acyloin 45 gave a very weak signal which was barely recognizable as the [3.2.0] semidione 9. At 5 seconds after mixing the spectrum was clearly the [3.2.0] semidione 9, but the small amount of acyloin 45 available precluded obtaining a well resolved spectrum at such a flow rate (1.2 ml/minute).

At 10 seconds after mixing neither benzoate 42 nor acetate 43 showed any [3.2.0] semidione 9 but both showed the same anomalous radical (Figure 6 and Figure 7, respectively). After 3 minutes the first seen radical was nearly gone and a weak, but recognizable spectrum of the [3.2.0] semidione 9 had appeared. The strength of semidione 9 was vastly less from endo benzoate 42 than from exo benzoate 7. Furthermore, the maximum [9] was reached at about 9-11 minutes after mixing for both the benzoate 42 and acetate 43. The spectrum of the benzoate 42 at about 3 minutes after mixing (Figure 8) was still complicated by

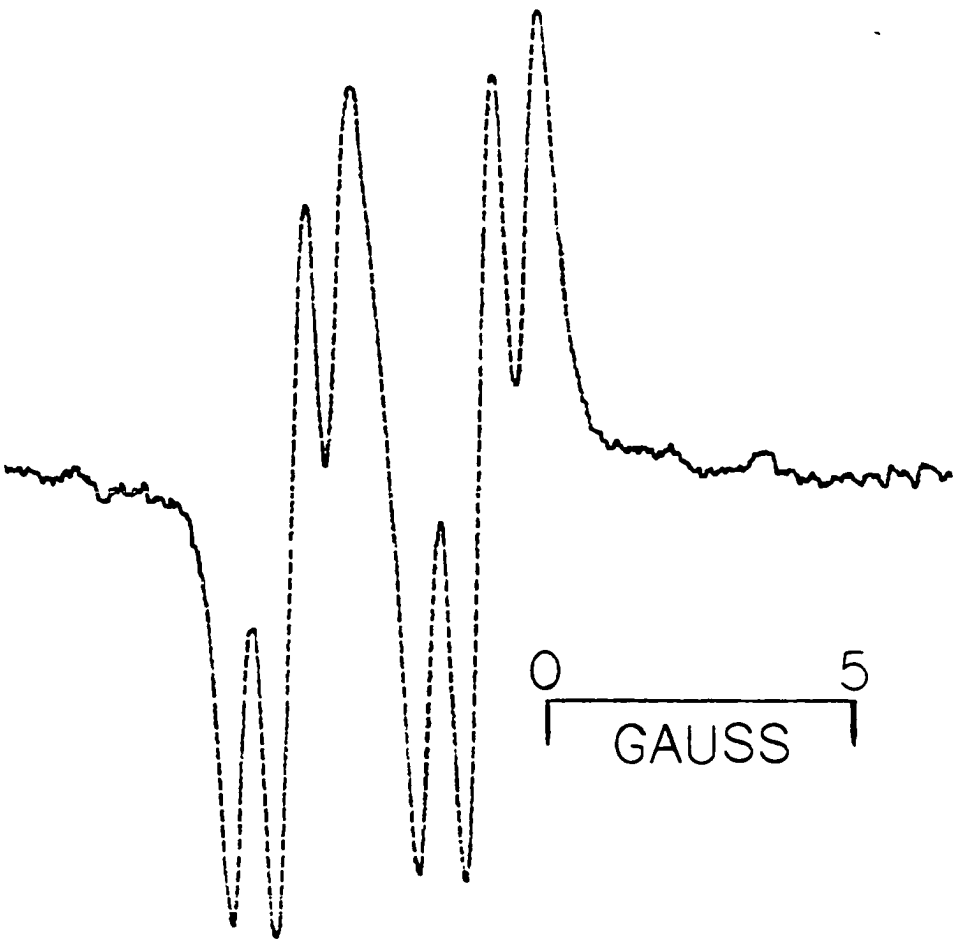
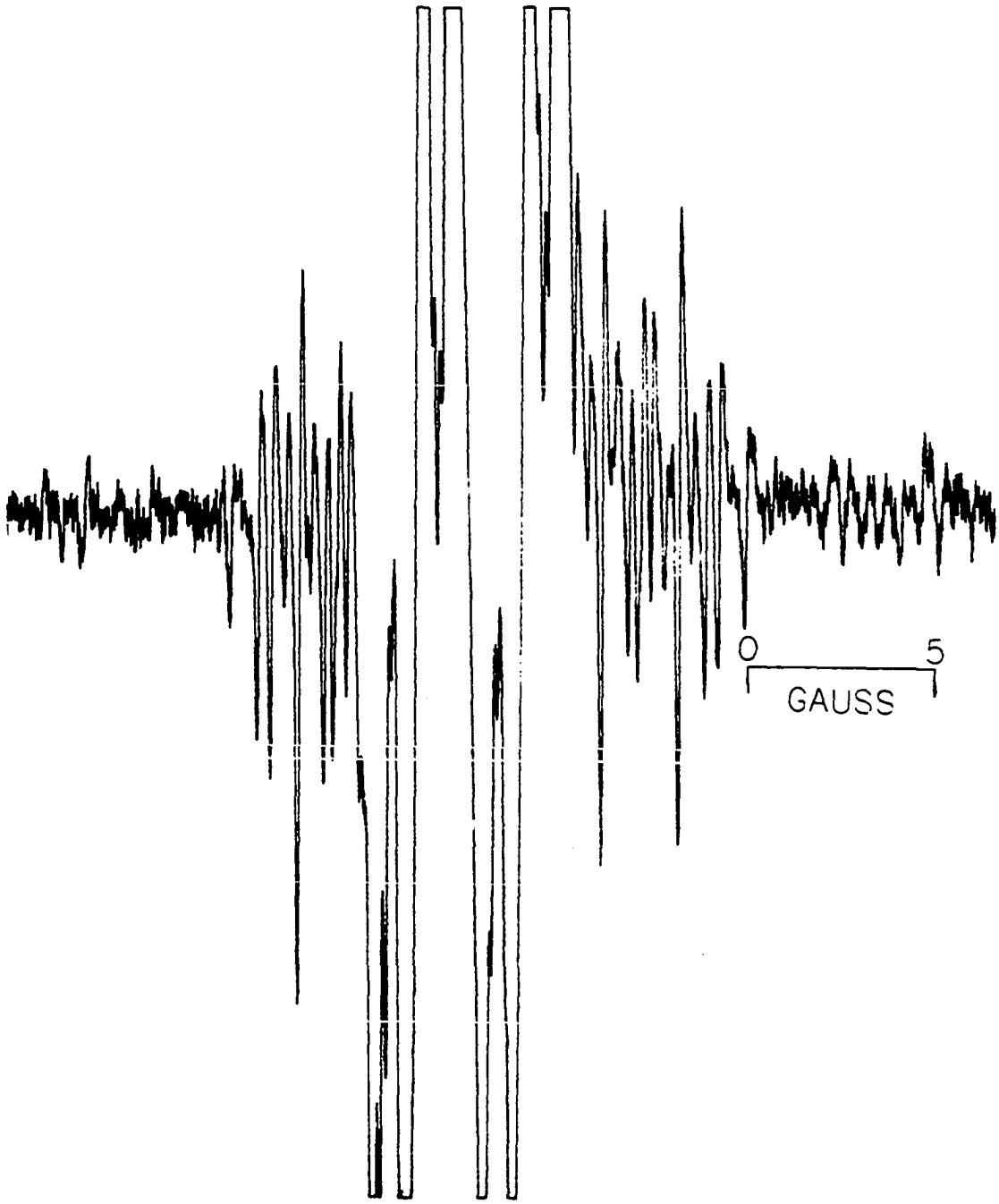


Figure 6. The first derivative esr spectrum of the radical obtained from endo, 3-benzoyloxy-bicyclo[2.2.1]hept-5-en-2-one (42) under fast flow in DMSO.

Figure 7. The first derivative esr spectrum of the radicals obtained from endo, 3-acetoxy-bicyclo[2.2.1]hept-5-en-2-one (43) under fast flow in DMSO.


0
5
GAUSS

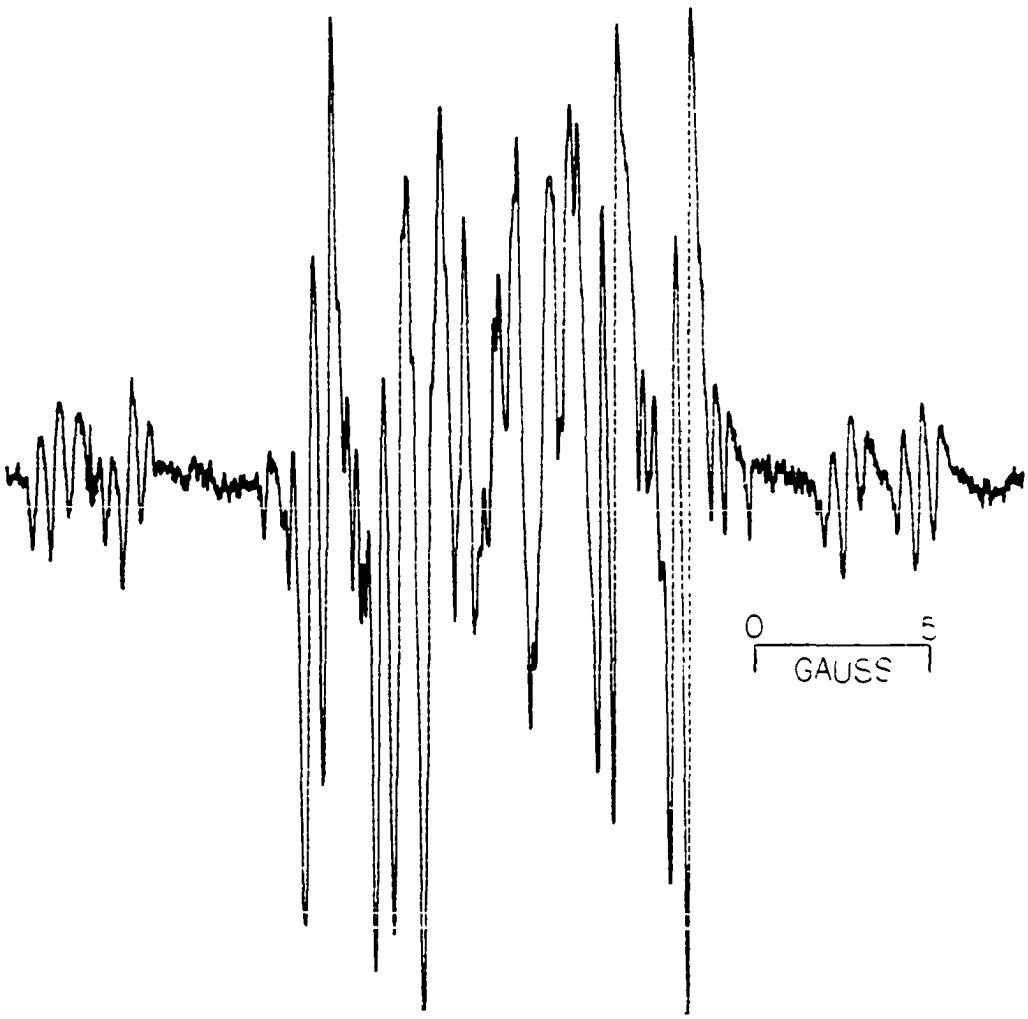


Figure 8. The first derivative esr spectrum of the radicals obtained from endo, 3-benzoyloxy-bicyclo[2.2.1]hept-5-en-2-one (42) under slow flow in DMSO.

undesired radicals, but the spectrum of acetate 43 (Figure 9) at 3 minutes after mixing was much more promising. A weak semidione 9 spectrum was visible, but another radical whose gross features seemed to be a large hfsc of 8 gauss for one proton and a small hfsc of 0.73 gauss for two protons could also be discerned. These two hfsc could be extracted with some certainty from the acetate 43 spectrum (Figure 9) and were entirely consistent with the highly desired [2.2.1] semidione 8. This spurred an effort to obtain a clean spectrum of this radical.

Ethyl carbonate 48 (Scheme 23) failed to give any observable radicals when mixed with KO<u>t</u>-Bu/DMSO under flow conditions. This is consistent with the poor results obtained from <u>in situ</u> hydrolysis of cyclic carbonates mentioned earlier. THP ether 44 (Scheme 22) also failed to give an observable radical, certainly consistent with the known stability of THP ethers to base.

Luckily, the silyl ether 46, obtained in the abortive effort (Scheme 23) to synthesize acyloin 45, was available in large quantities. Silyl ether 46 when mixed with KO<u>t</u>-Bu/DMSO under flow conditions gave a very weak spectrum (Figure 10) of the [3.2.0] semidione 9 after 4 minutes after mixing but, far more important, it showed a weak but very clean spectrum whose hfsc, $\underline{a}^{H}$ = 8.19(1H), 2.10(1H), 1.10(2H), 0.73(2H), were entirely consistent with [2.2.1] semidione 8.

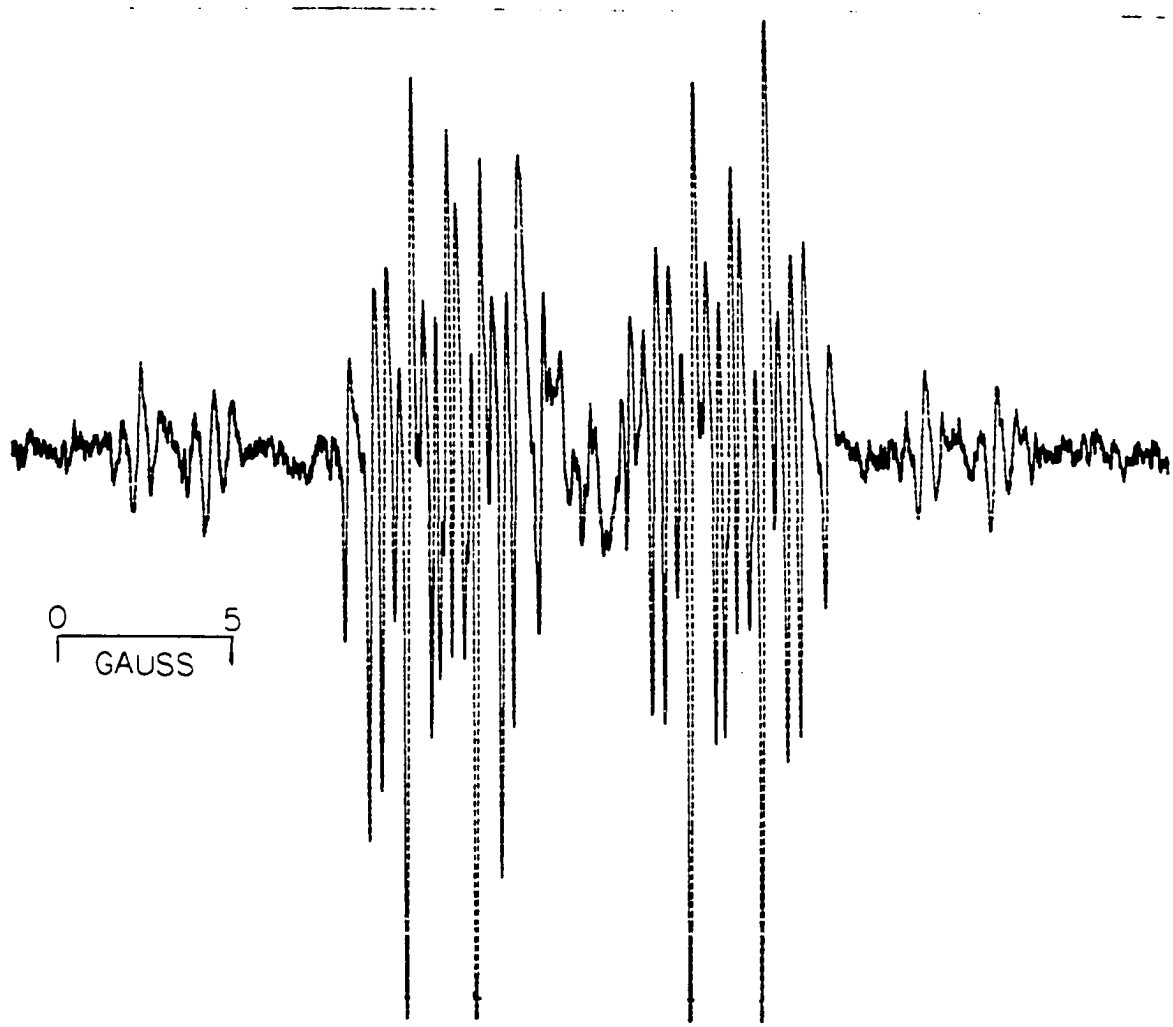
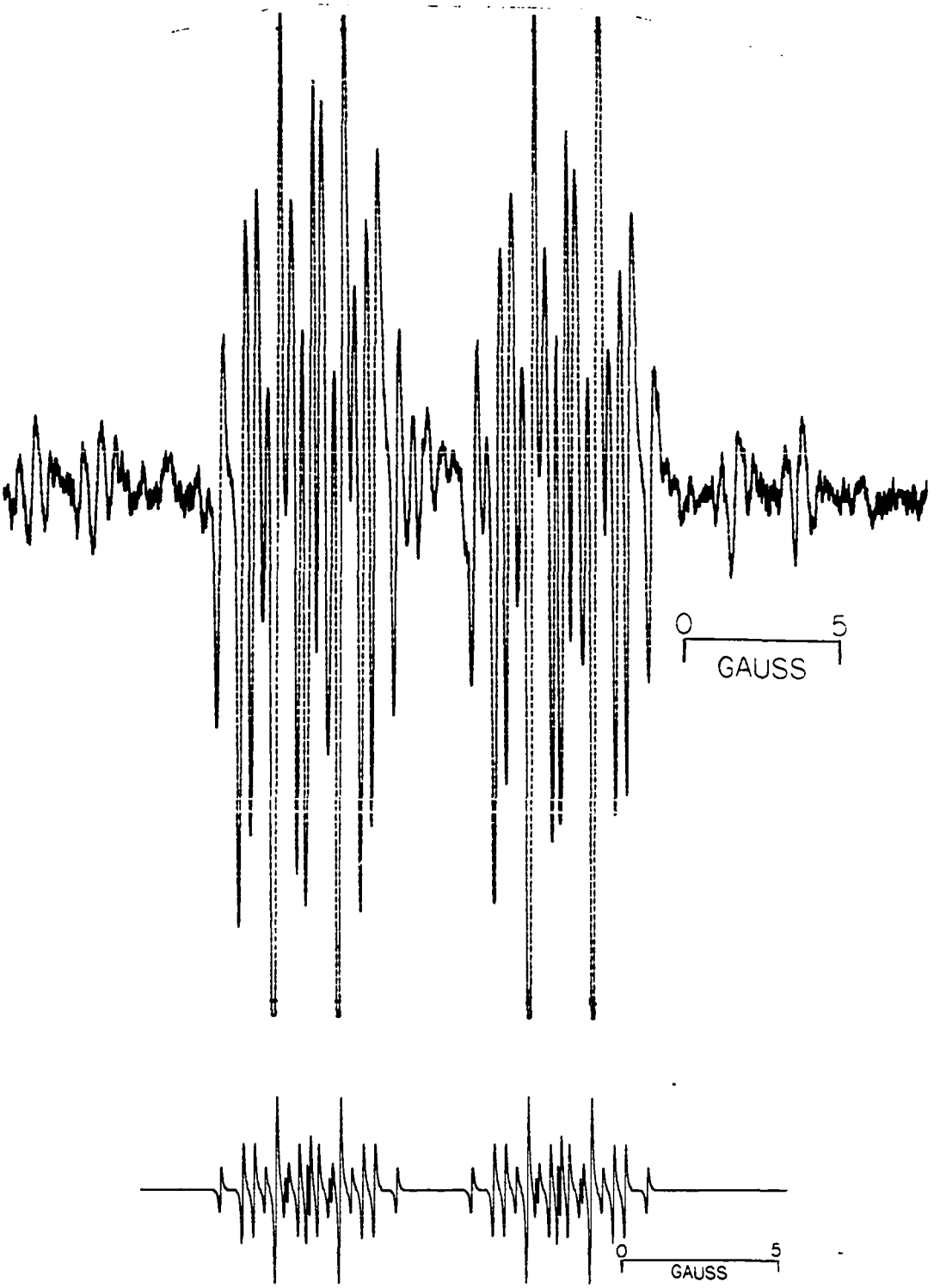
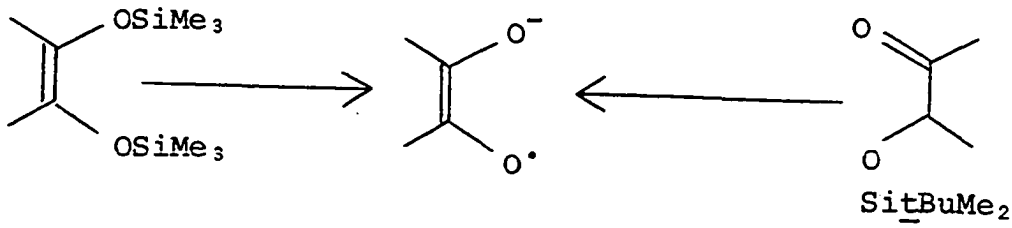


Figure 9. The first derivative esr spectrum of the radicals obtained from endo, 3-acetoxybicyclo[2.2.1]hept-5-en-2-one (43) under slow flow in DMSO.

Figure 10. The first derivative esr spectrum (top) of bicyclo[2.2.1]hept-5-en-2,3-semidione (8) in DMSO; calculated spectrum (bottom) for Lorentzian line width 0.11 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.


0
5
GAUSS
0
5
GAUSS

The generation of semidiones from α-silyl ether ketones is a new mode of generation but is a logical extension of their known, highly useful formation from bis(trimethylsiloxy) alkenes (11,12,30,31).



The detection of [2.2.1] semidione 8 is, of course, the best evidence of all implicating its existence and thus showing it is, or could be, the intermediate forming [3.2.0] semidione 9. The main consequence of Scheme 21 was that it pointed out the direction which led to the detection of [2.2.1] semidione 8, but the results of the other experiments substantiate the kinetic predictions, too. These results are summarized in Table 2.

Bicyclo[2.2.1]hept-5-en-2,3-semidione

Preliminary all valence electron INDO calculations on semidione 8 predict a small negative hfsc for H-7, syn and

Table 2. Comparison of predicted and observed results of mechanistic Scheme 21

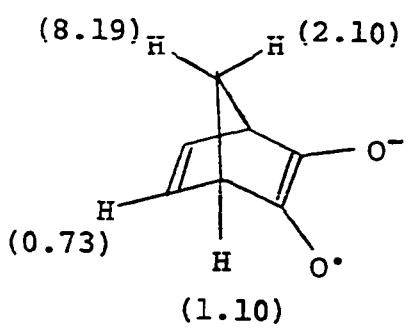
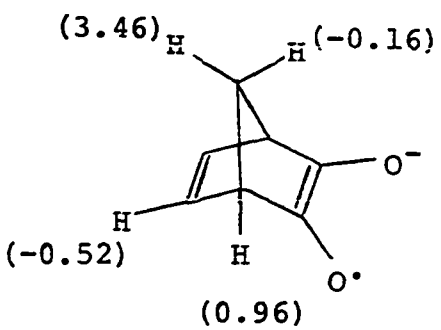
Precursor	Pred. k_1	Pred.[9]/[8][a]	Obsd.[9]/[8][a]	Pred.$[9]^{b}_{max}$	Obsd.$[9]^{b}_{max}$
diketone 38	large	>>1	?	v. early	?<1 sec
acyloin 45			9 only		<10 sec
exo-benzoate 7			>>1		3-5 min
endo-benzoate 42		intermediate	?		9-11 min
endo-acetate 43			≈0.3		9-11 min
endo-silyl ether 46			≈0.15		15 min
	small	<1		late	

[a] [9] = [3.2.0] semidione; [8] = [2.2.1] semidione.

[b] Time after mixing at which [9] is maximum.

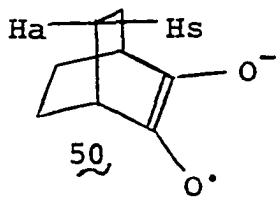
a relatively small positive value for H-7, anti (Table 3).[6] Results of all valence electron INDO calculations based on optimized geometry are not available at this writing but are expected soon after its completion. The discussion in this section will show that the assignment of negative spin density to H-7, syn is wrong and that the actual numerical values for the hfsc of H-7, syn and H-7, anti in semidione 8 could have been predicted from relatively simple considerations of strain energies.

Table 3. Comparison of experimental and calculated hfsc for semidione 8

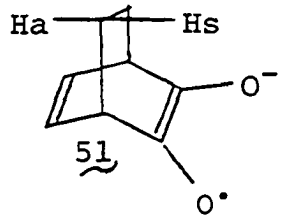
Experimental	Calculated
	

[6] C. Chung, Iowa State University, Ames, Iowa. Private communication (1972).

Russell and Holland (32) have showed that introducing strain into bicyclo[2.2.2]octanesemidione 50 by way of a double bond (51) increases the hfsc of the remaining syn and

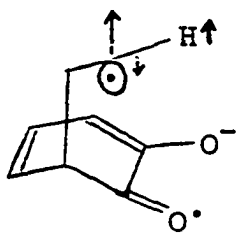


50

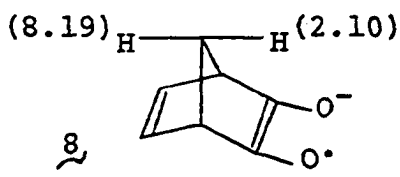


51

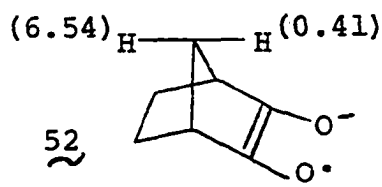
anti protons by the same amount. It was argued that the sign of the H-7, syn and H-7, anti hfsc must be the same based on the mechanism of spin delocalization proposed to explain the increase in hfsc. A homohyperconjugative delocalization was invoked to produce a positive spin density at tetrahedral C-7 which, as was discussed in the Introduction, would impart positive spin density to both H-7, syn and H-7, anti.



An exactly analogous argument can be developed to determine the signs of the H-7, syn and anti hfsc in semidione 8 and 52. Comparing the hfsc of semidiones 8 and 52



8



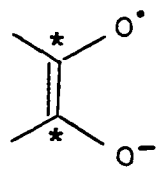
52

shows that the H-7, anti hfsc increases 1.65 gauss in going from semidione 52 to the more strained semidione 8. If this increase is due to the mechanism proposed for the increase in hfsc in semidione 51, that is, an increase in the homohyperconjugative contribution, then the increase in the hfsc of H-7, anti is due to a positive increase in an already positive number. The mechanism demands the change be positive so the increase in magnitude of hfsc of H-7, anti means it was an already positive number in semidione 52.

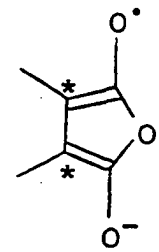
If it is assumed that the H-7, syn hfsc in semidione 8 is -2.10 gauss (the sign indicated by the calculations) subtracting the positive increment 1.65 predicts a hfsc of -3.75 gauss for H-7, syn of semidione 52. The value observed, 0.41 gauss, is not consistent with this assumption. If, on the other hand, it is assumed that the H-7, syn hfsc in semidione 8 is +2.10 gauss, the hfsc of H-7, syn in saturated semidione 52 is 2.10-1.65 = 0.45 gauss, clearly consistent with the 0.41 gauss observed. Thus, the hfsc of H-7, syn in both semidione 8 and 52 is positive.

Correlation of positive spin density at H-7, syn in semidione 8 with positive spin density at H-7, syn of semidione 52 is in agreement with preliminary INDO calculations for semidione 52 (33). Furthermore, the positive spin density assigned to H-7, syn of semidione 52 is also in agreement with the value Mattox (33) found consistent with

his assignment of an 8:1 = a^Hanti/a^Hsyn ratio after contributions for spin polarization and homohyperconjugation had been subtracted from the hfsc. Mattox used algebraic manipulation of hfsc data from 1,2 semidiones and semifuraquinones to sort out these contributions. H-7, anti of



1,2 semidione



semifuraquinone

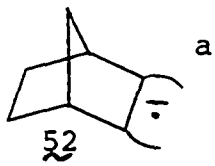
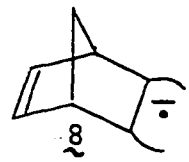
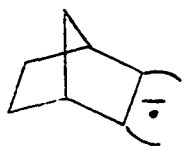
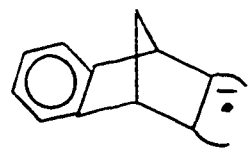
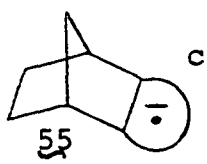
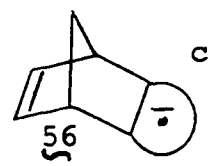
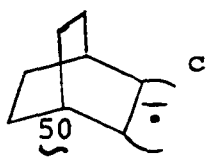
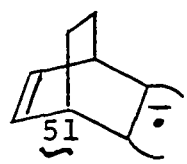
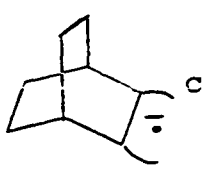
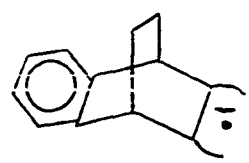
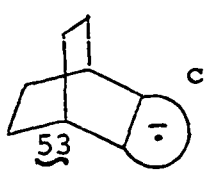
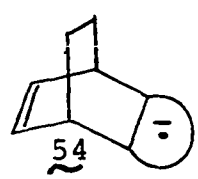
semidione 52 interacts strongly with ψ_3, the HOMO of the 1,2 semidione, but H-7, anti in the corresponding semifuraquinone (55) lies in the nodal plane of the HOMO (ψ_4) and thus does not interact by hyperconjugation. This allowed the direct hyperconjugation contribution to be estimated. The spin density on the starred atoms in the 1,2 semidione and semifuraquinones is the same which implies that the spin polarization contribution to the hfsc in both types of semidiones will also be the same. Consideration of the hfsc of protons in systems where the distance between the spin label and the proton observed implied only direct hyperconjugation led to the 8:1 ratio of a^Hanti/a^Hsyn. Algebraic manipulation of

these facts and empirical hfsc allowed Mattox to predict (or at least agree with the calculations) that the spin density at H-7, syn in semidione 52 is positive.

Semidiones have been used as paramagnetic models for carbon-carbon double bonds and for enolates in studies of conformational mobility and positional reactivity (1,2,3). If introduction of a semidione into a bicyclic molecule is assumed to introduce the same angle strain as a carbon-carbon double bond, surprisingly good results can be obtained by a very naive approach in predicting the increase in hfsc brought about by further straining the molecule.

Table 4 shows values for the increase in hfsc of H-7, syn and H-7, anti brought about by introduction of further unsaturation. The increase is seen to be nearly the same for the syn and anti proton in each case which immediately establishes the sign of the hfsc as positive in all these cases according to the argument used above. The increase in the anti hfsc is a small, but significant (significant at 94% confidence level) (34) amount larger than the syn proton. This may be because C-7 is not perfectly tetrahedral in the homohyperconjugation structure and thus the values of Q in the McConnell equation (4) for the syn and anti hydrogens may be slightly different. This argument implies that C-7 of semidione 8 is nearly perfectly tetrahedral since Δa^{H} syn and Δa^{H} anti are very close.

Table 4. Comparison of Δa^{H}anti and Δa^{H}syn produced by an increase in angle strain

"unstrained"	"strained"	Δa^{H}anti	Δa^{H}syn
 a, 52	 8	1.65	1.69
 a	 a,b	0.52	0.46
 c, 55	 c, 56	0.38	0.32
 c,d, 50	 c,d, 51	0.51	0.41
 c,d	 c,d	0.26	0.20
 c, 53	 c, 54	0.19	0.03

 = semifuraquinone  = semidione

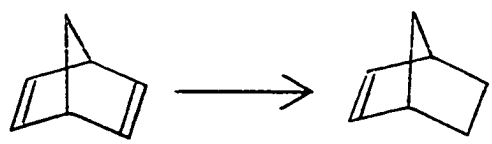
[a] Ref. 6

[b] Treatment of exo,3-benzoyloxybenzobicyclo[2.2.1]hepten-2-one with KOt-Bu/DMSO failed to produce this radical.

[c] Ref. 33

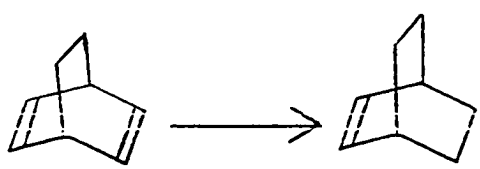
[d] Ref. 32

Schleyer has implied (35) that 25.0 kcal/mole is a good value for the heat of hydrogenation of a no-angle-strain cyclic alkene. If we assume that the presence of a 1,2 or 1,4 semidione is equivalent to a first carbon-carbon double bond, then it is easy to calculate the increase in angle strain for introduction of the "second" carbon-carbon double bond in the bicyclic semidione from the ΔH of hydrogenation (36) of the diene to the alkene. Applying these data to the



ΔH = 35.0 kcal/mole

35.0
-25.0
10.0 kcal/mole increase in angle strain



ΔH = 27.9 kcal/mole

27.9
-25.0
2.9 kcal/mole increase in angle strain

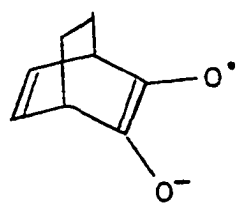
average $\Delta \underline{a}^{H}$ in going from semifuraquinone 53 to 54 we get

$\frac{(0.19+0.03)}{2} \times \frac{10.0}{2.9} = 0.38$ for semifuraquinone 56 (Table 4).

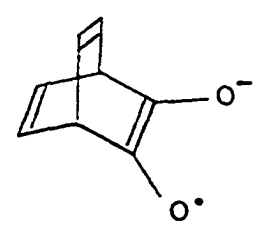
This predicted value, 0.38 gauss, is very close to the

observed average Δa^H, 0.35 gauss, in semifuraquinone 56. Semidione 8 is of much more interest. The average Δa^H in going from semidione 50 to 51 is 0.46 gauss. With this base value we predict the average Δa^H for semidione 8 as 0.46 x 10/2.9 = 1.59 gauss or very close to the observed Δa^H, 1.67 gauss. The necessary ΔH hydrogenation for the benzo derivatives are not known, so Δa^H for these compounds cannot be calculated. Using the simple olefin values for these compounds does not give good results.

Calculations based on two sets of compounds, and rather naive calculations at that, must not be taken too seriously but it is interesting to speculate. Zimmerman and Paufler have shown (37) that there is little delocalization of the π-electrons in barrelene. Indeed, the rather enormous ΔH of hydrogenation (93.8 kcal) (38) indicates very little stabilization by overlap of π-systems. Since ψ_3 (the HOMO) of the 1,2 semidione has ethylene (ψ_1) symmetry, one might predict little change in the overlap, as reflected in the vinylic hfsc, in going from semidione 54 to barrelene

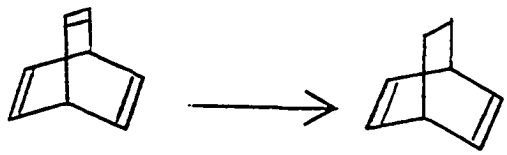


54



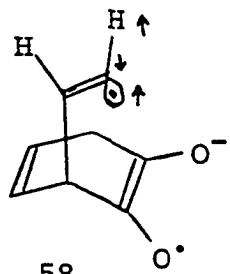
57

semidione (57). The ΔH of hydrogenation, on the other hand, predicts a dramatic increase in the vinylic hfsc due to homohyperconjugation (58) because the calculated increase in strain energy, 12.6 kcal, is quite large.



ΔH = 37.6 kcal/mole

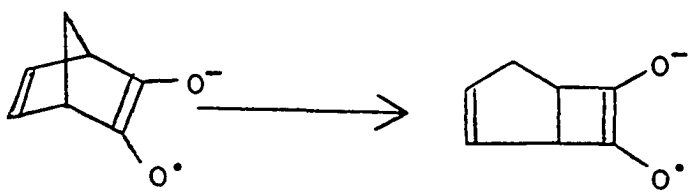
37.6
-25.0
12.6 kcal/mole



58

Methyl Homologues of Bicyclo[3.2.0]hept-2-en-6,7-semidione

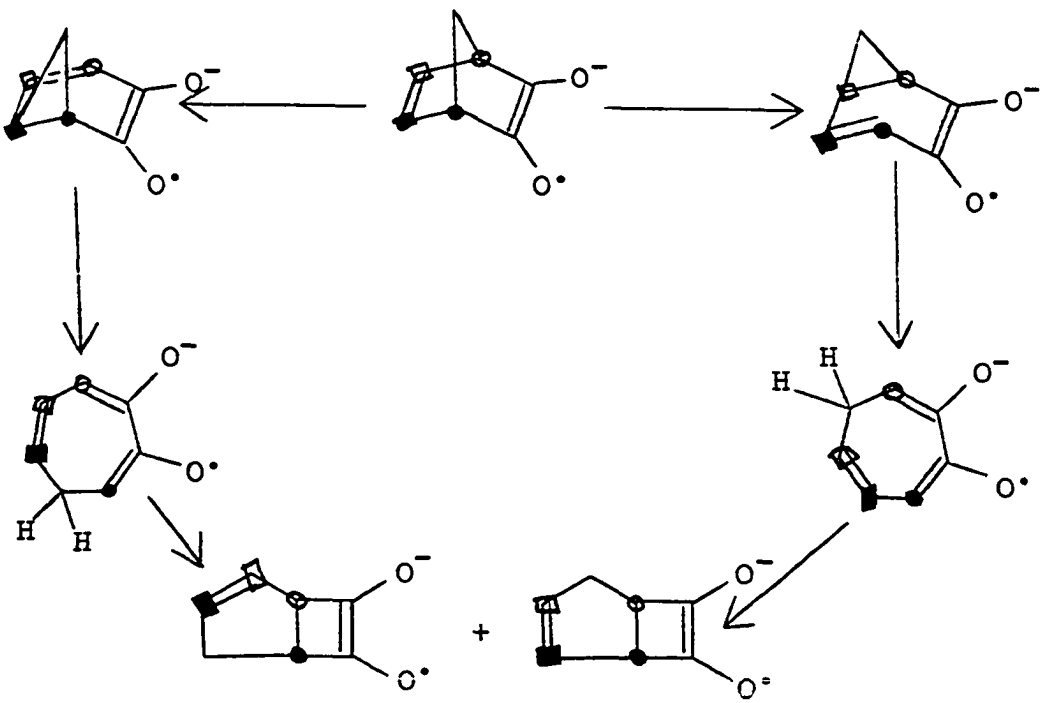
Two conceptual schemes for the conversion of semidione 8 into semidione 9 were considered. These schemes (Scheme 24



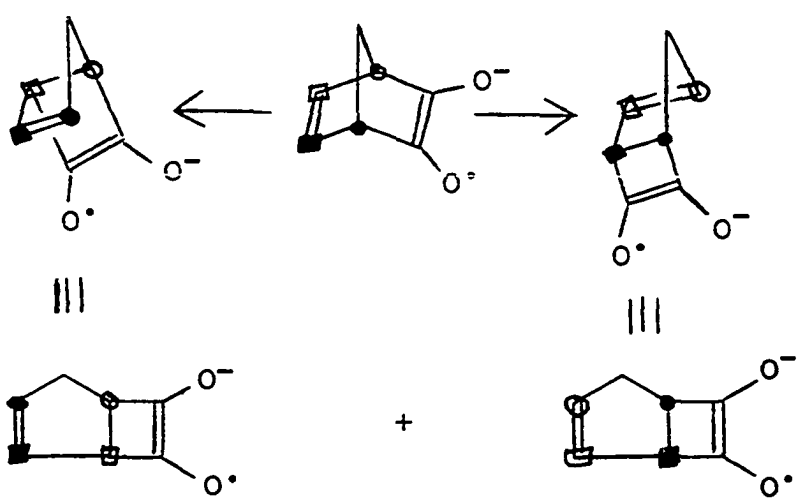
8 9

and Scheme 25) ignore the allowedness or concertedness of individual steps and concentrate on the position of the label in the final [3.2.0] semidione. The labels show that

Scheme 24



Scheme 25

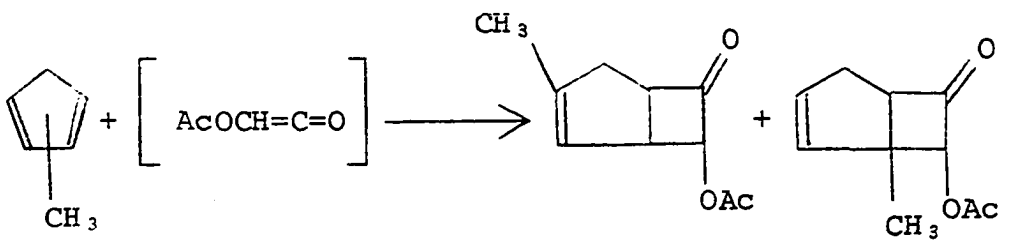


Scheme 24 predicts labels at the bridgehead in the [2.2.1] semidione will wind up only at the bridgehead in the [3.2.0] semidione; labels on the [2.2.1] semidione double bond will appear only on the double bond in the rearranged radical. On the other hand, Scheme 25 predicts a label on the bridgehead can wind up at either C-3 or C-5 (or both); a label on the double bond can find itself at C-1 or C-2 (or both).

The different results predicted by the two schemes allows one to be eliminated by labeling experiments. The logical place to start would be with the [2.2.1] semidione, but chronologically the [3.2.0] semidione precursors were available first.

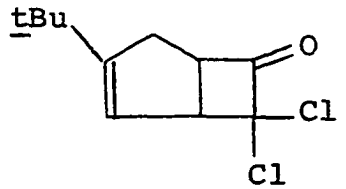
The addition of <u>in situ</u> generated acetoxyketene to a mixture of 1- and 2-methylcyclopentadiene led to a rather surprising result (Scheme 26). The major adduct was the 3-methyl isomer 59, but the minor isomer was the unexpected 1-methyl 60. In light of the transition state projected

Scheme 26

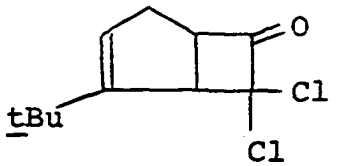


59 60

for the addition of a ketene to the double bond of cyclopentadiene it was believed that the transition state which leads to the 2-methyl adduct would be preferred. Indeed Ando[7] found that addition of dichloroketene to 1- and 2-t-butylcyclopentadiene led to the 3- and 2-t-butyl adducts (24a and 24b) with a selectivity of about 40:1. No 1-t-butyl isomer was observed.



24a



24b

The adducts 59 and 60 could be separated by gas chromatography, but when this work was carried out only a small gc with 1/4" columns was available. The radicals formed from adduct 60 (vide infra) proved stable enough that 40 mg were sufficient for the flow experiment, but a considerably larger quantity of adduct 59 than could be conveniently obtained was required. Later, when a preparative gc with 3/4" columns became available, as much of adducts 59 or 60 as was desired could easily be obtained

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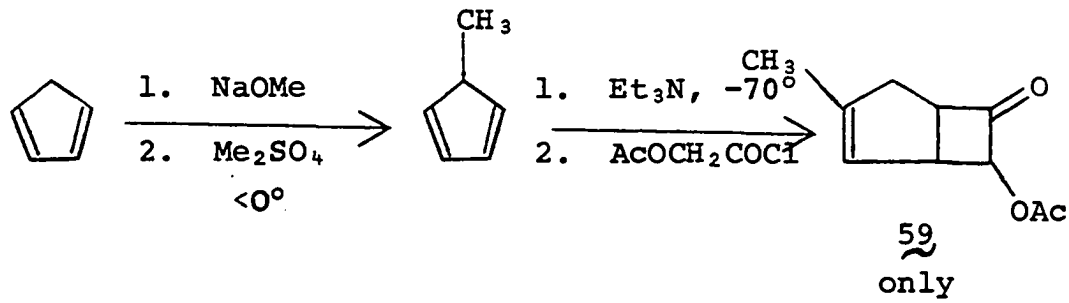
[7] T. Ando, Harvard University, Cambridge, Massachusetts. Private communication (1970).

by Scheme 26 but initially Scheme 27 was resorted to to obtain adduct 59 free of adduct 60. This synthesis (Scheme 27) was prompted by a report by Sih et al. (39) that 1-alkyl

Scheme 27



59
only

cyclopentadienes could be obtained free of the 2-alkyl isomer by addition of the alkylating agent to the cyclopentadienide solution. Presumably, the first formed 5- alkyl cyclopentadiene is isomerized to the 1-alkyl isomer by a base promoted [1,5] proton shift much more rapidly than the shift giving the 2-alkyl isomer (from the 1-alkyl isomer). At any rate, addition of Et_3N to a -70° solution of 5-methylcyclopentadiene in ether followed by addition of acetoxyacetyl chloride gave only the adduct (59) derived from 1-methylcyclopentadiene.

The esr spectral results of mixing adduct 60 and KOt-Bu/DMSO under flow conditions are clear cut. At about 10 minutes after mixing (Figure 11) a single radical, a^H = 12.73(1H), 1.75(1H), 0.51(1H), 0.37(1H), is seen. This radical is clearly semidione 61, the semidione expected from

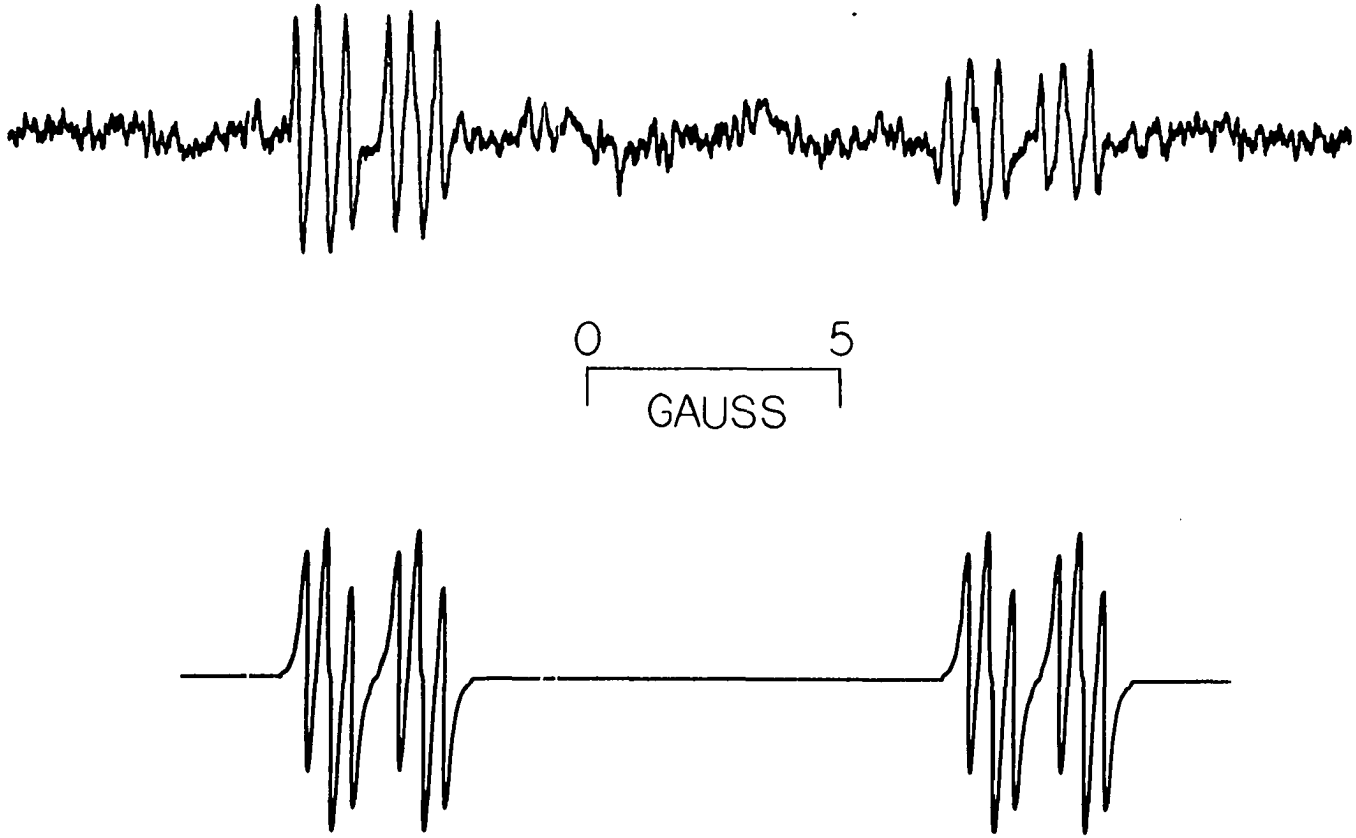
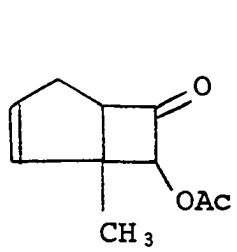
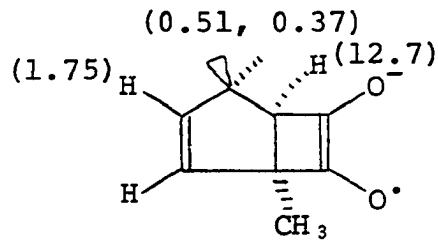


Figure 11. The first derivative esr spectrum (top) of 1-methylbicyclo[3.2.0]-hept-2-en-6,7-semidione (61); calculated spectrum (bottom) for Lorentzian line width 0.26 gauss with splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

adduct 60. At 20 minutes after mixing (Figure 12) the



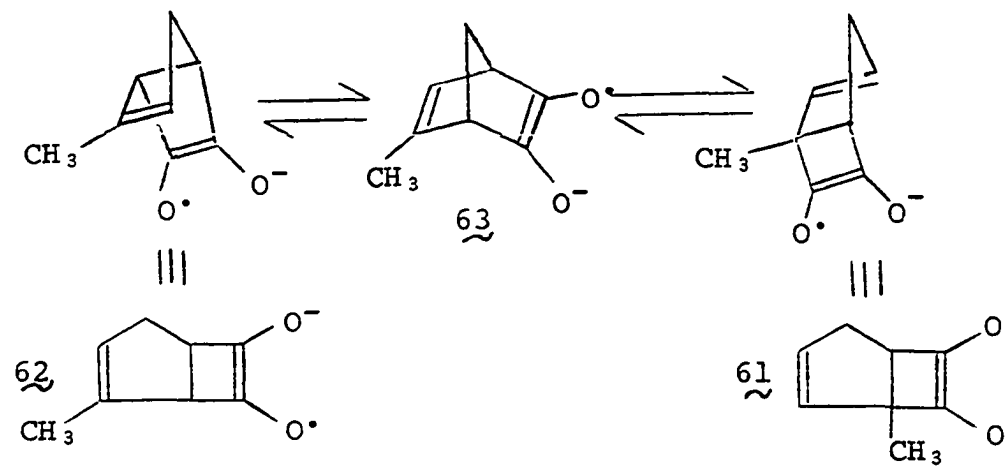
60



61

strength of semidione 61 had diminished considerably and another radical (62), a^H = 12.9(1H), 9.87(1H), 1.94(1H), 0.52(1H), 0.43(1H), 0.187(3H), had appeared. The hfsc of semidione 62 are consistent with a rearrangement of 61 to its [2.2.1] isomer then back to another [3.2.0] isomer. The structure of semidione 62 as deduced from its hfsc, specifically the two large cyclobutane hfsc, is not consistent with the mechanism of Scheme 24 but is predicted by Scheme 25 (Scheme 28).

Scheme 28



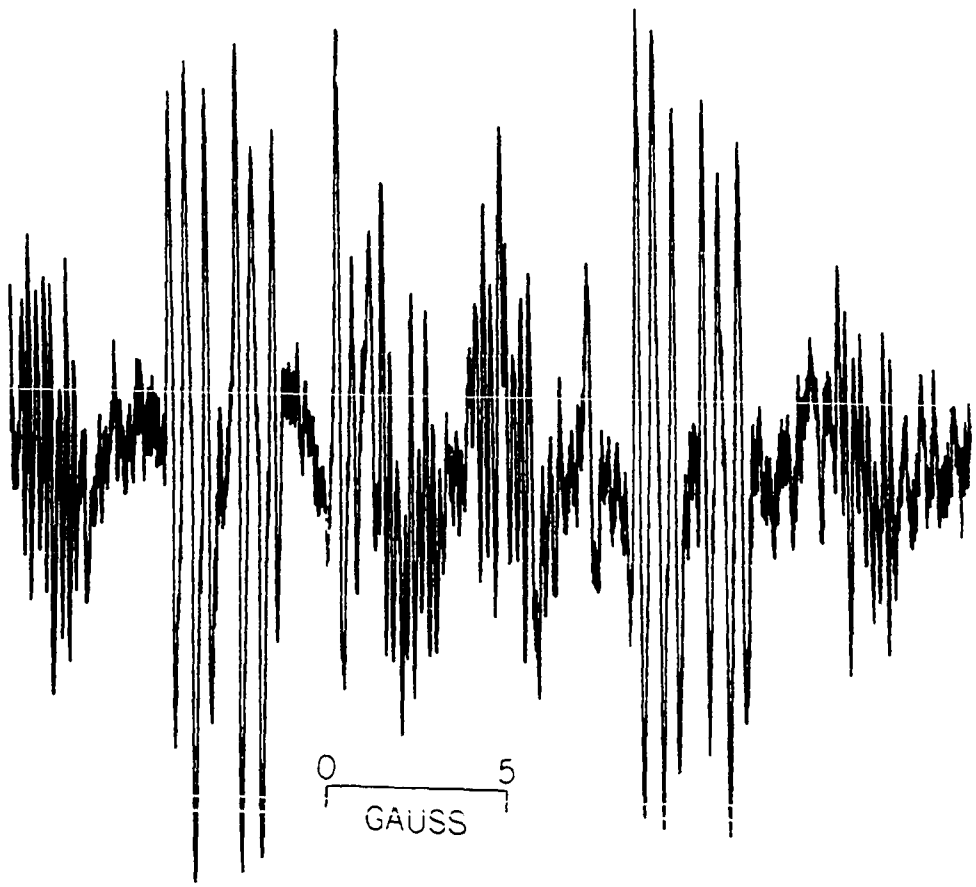
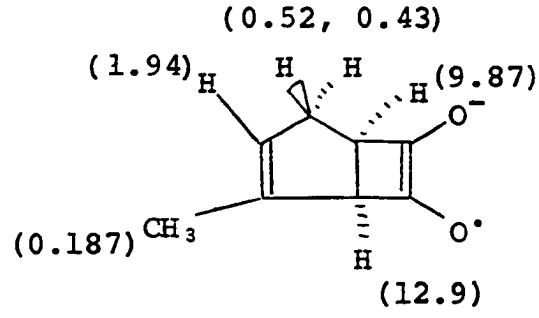


Figure 12. The first derivative esr spectrum of the radicals obtained from endo, 7-acetoxy-1-methylbicyclo-[3.2.0]hept-2-en-6-one (60) under slow flow in DMSO.

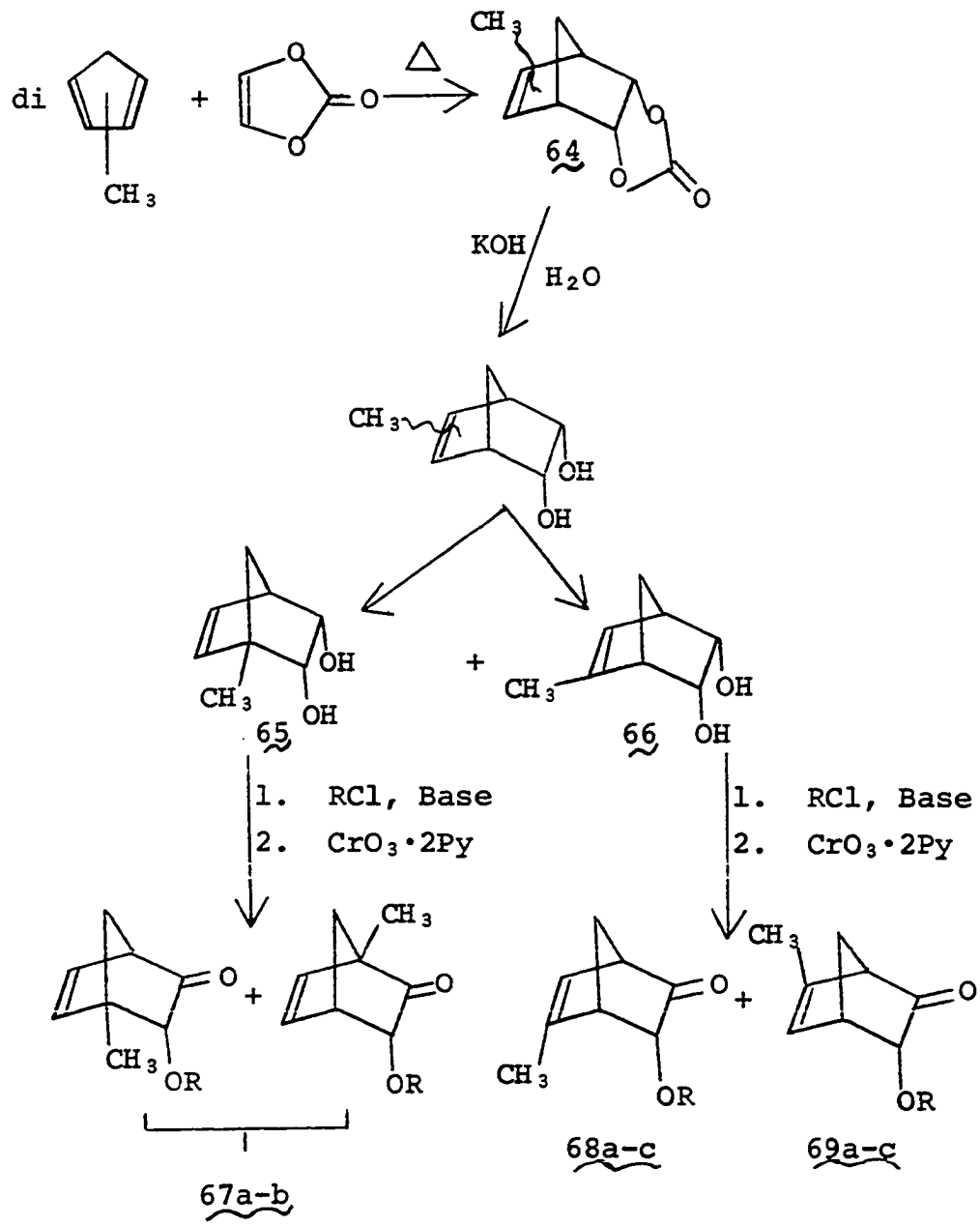


62

The reversibility implied in Scheme 28 was completely unexpected. In order to show that the [2.2.1] semidione 63 was involved we felt it highly desirable to enter Scheme 28 via a suitable norbornenone precursor. A synthetic approach just like that used to obtain [2.2.1] semidione 8 (Scheme 22) was employed (Scheme 29).

Commercially available methyl cyclopentadiene dimer reacted smoothly with vinylene carbonate to give a mixture of carbonate adducts 64 which could not be separated by any technique tried. Hydrolysis of the cyclic carbonates (64) gave a mixture of diols 65 and 66 which were easily separated by gc. Since a large preparative gc was now available, gram quantities of either the major diol 65 or the minor diol 66 could be readily obtained. Treatment of the diol with a small excess of acid chloride (silyl chloride) followed by $CrO_3 \cdot 2Py$ oxidation gave the ketones 67a-b, 68a-c, and 69a-c. Ketones 68a-c and 69a-c were easily separated by gc in every case. However, in every case

Scheme 29



a R = CH_3CO

b R = $tBuMe_2Si$

c R = PhCO

the mixture gave the same esr results as the individual isomers. The bridgehead methylated ketones 67 could not be separated by any technique tried so, necessarily, all esr experiments on them were performed on the mixture.

In order to prepare larger quantities more conveniently silyl ether 68b was prepared by silylating an unseparated mixture of diols, oxidizing, and then carrying out the gc separation. The same process was carried out for acetates 67a, 68a, and 69a although these compounds were also synthesized from the previously separated diols.

Mixing acetates 68a, 69a, 68a + 69a or benzoates 68c + 69c with KO*t*-Bu/DMSO under flow conditions produced exactly the same mixture of radicals (Figure 13 and Figure 14) 20 minutes after mixing as was seen when [3.2.0] ketone 60 was used. Figure 14 shows the spectrum from pure acetate 68a since it gave the cleanest spectrum of the four precursors. These results substantiate the intermediacy of [2.2.1] semidione 63 and supply proof of the structure assigned to semidione 62 (Scheme 30). The fact that either ketone 68a or 69a gave the same results strongly implies that it is the symmetric (with respect to bond moving) semidione 63 or its anion which is the rearranging intermediate.

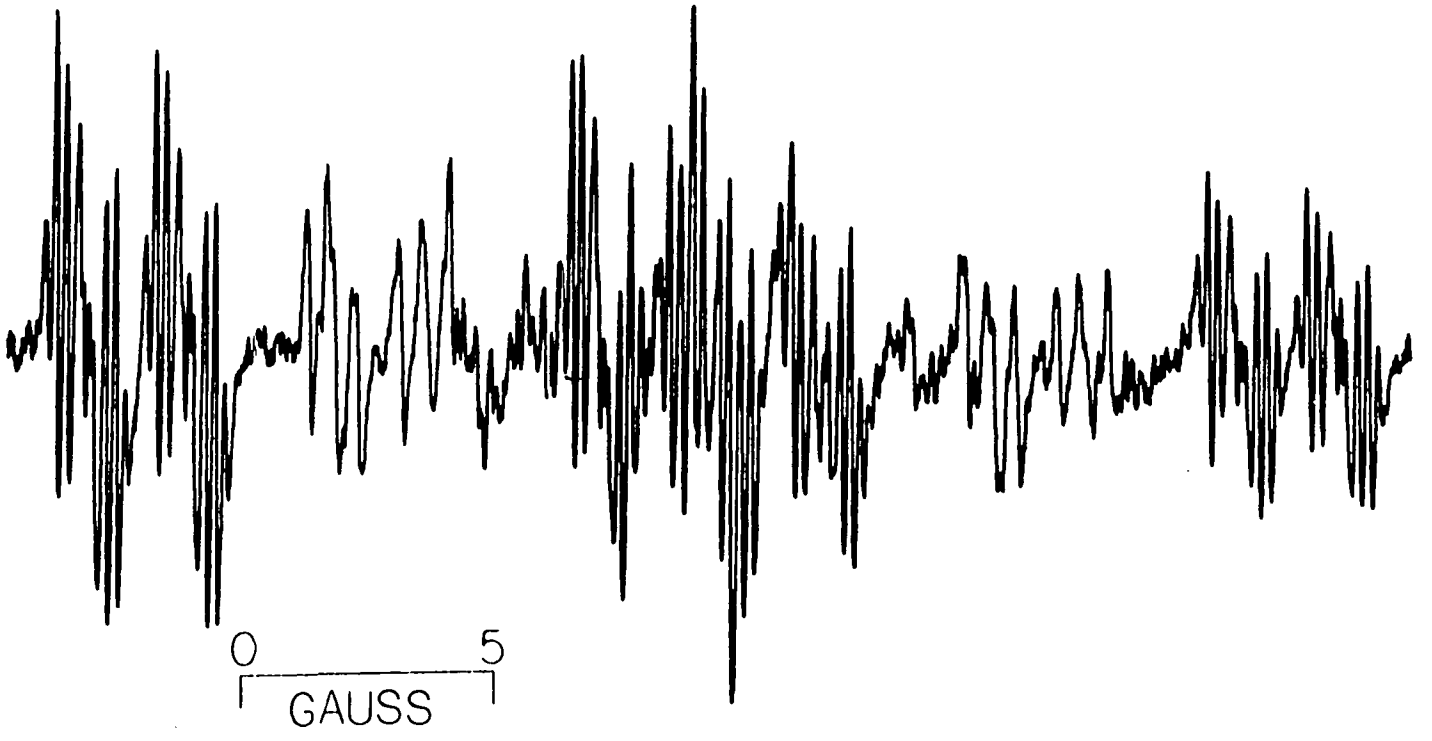


Figure 13. The first derivative esr spectrum of the radicals obtained from endo, 3-acetoxy-5-methylbicyclo[2.2.1]hept-5-en-2-one (68a) under slow flow in DMSO.

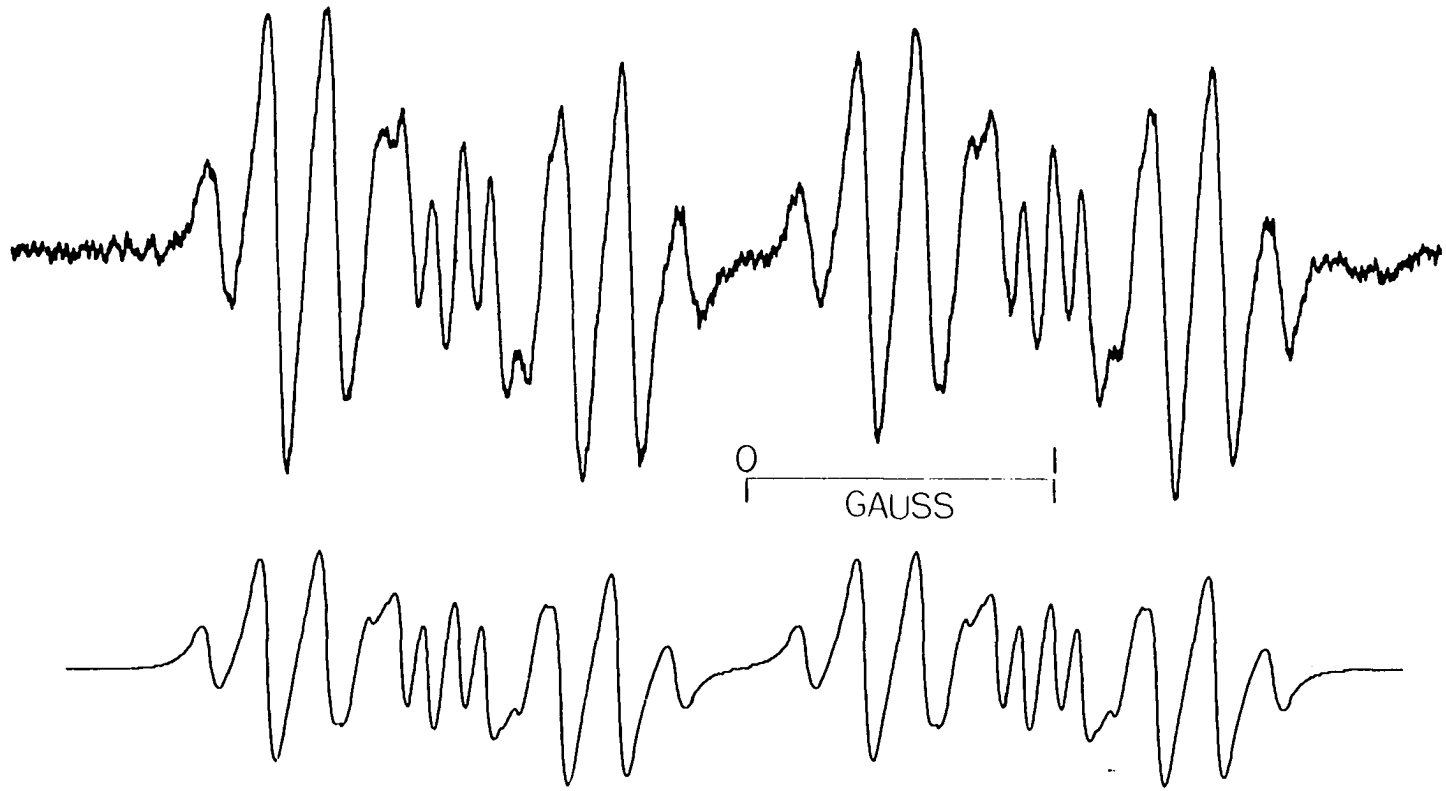
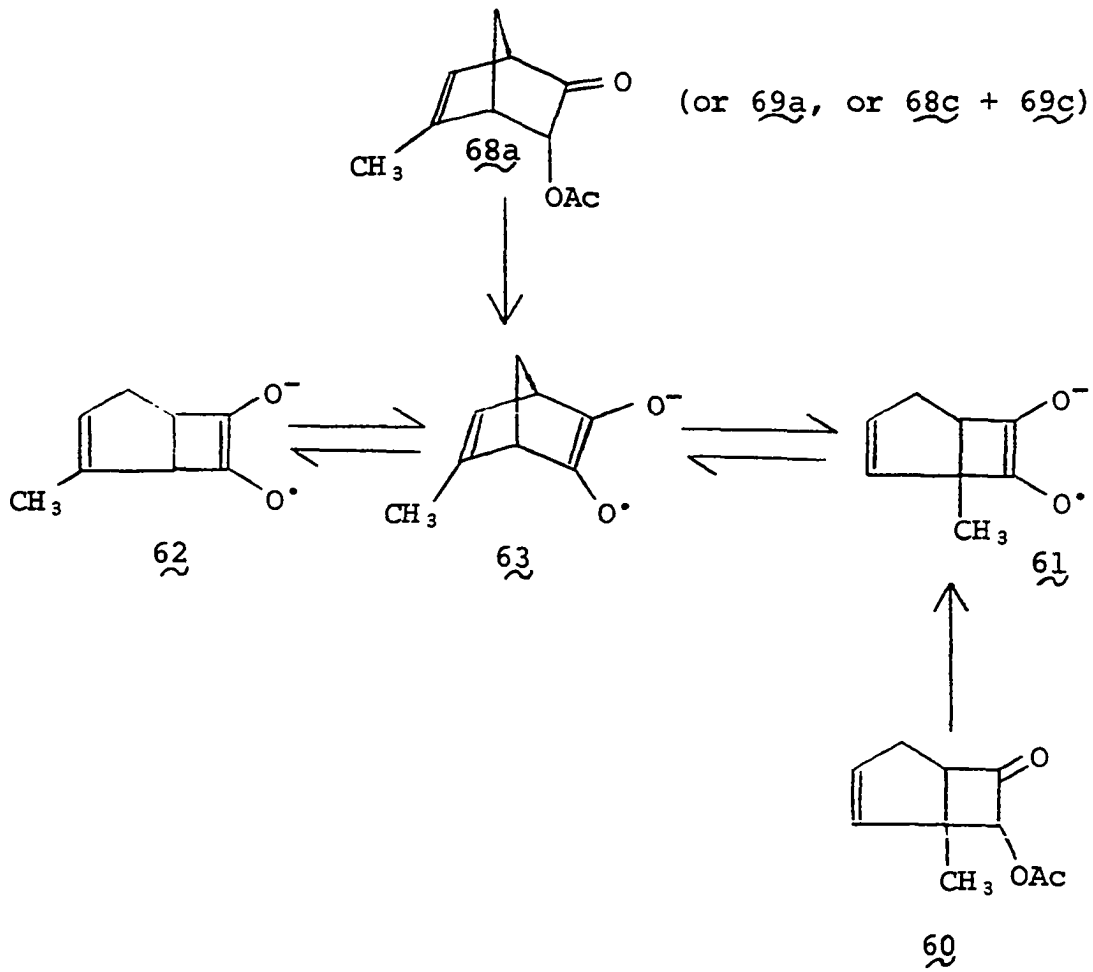


Figure 14. The low field multiplet of the first derivative esr spectrum (top) of 2-methylbicyclo[3.2.0]hept-2-en-6,7-semidione (62); calculated spectrum (bottom) for Lorentzian line width 0.125 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

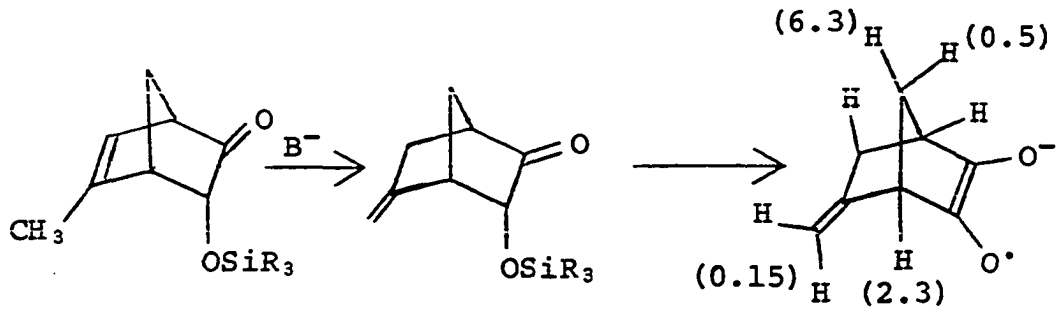
Scheme 30



The hfsc of the bridgehead and olefinic protons in semidione 8 had been assigned on the basis of the calculated values. We hoped that use of silyl ether 68b or 69b would allow us to see the [2.2.1] semidione 63 as the analogous unmethylated silyl ether 46 and allowed us to see semidione 8. However,

at 20 to 70 minutes after mixing silyl ether 68b (or 69b!) with KOt-Bu/DMSO under flow conditions a mixture of radicals was seen (Figure 15) in which one radical predominated. Figure 16 shows a comparison of the wing peaks of Figure 15. It shows that an exact analysis and simulation of the spectrum will be difficult, but it also shows a readily discernible doublet (a^H = 0.51) of triplets (a^H = 0.15). On further examination, splittings of 2.3 gauss and 6.1 gauss seem to be fairly repetitive. This suggests that the silyl ether 68b (or 69b) forms semidione 63 more slowly than it isomerizes to exocyclic ketone 70. Ketone 70 may, then, go on to form the semi-stable semidione 71 (Scheme 31). The

Scheme 31



69a 70 71

width of the spectrum of 71 (Figure 15) is 15.5 gauss which is just wide enough to accommodate the two more 2.6 gauss hfsc needed to justify the bicyclo[2.2.1]heptanesemidione structure drawn for semidione 71 (6,32).

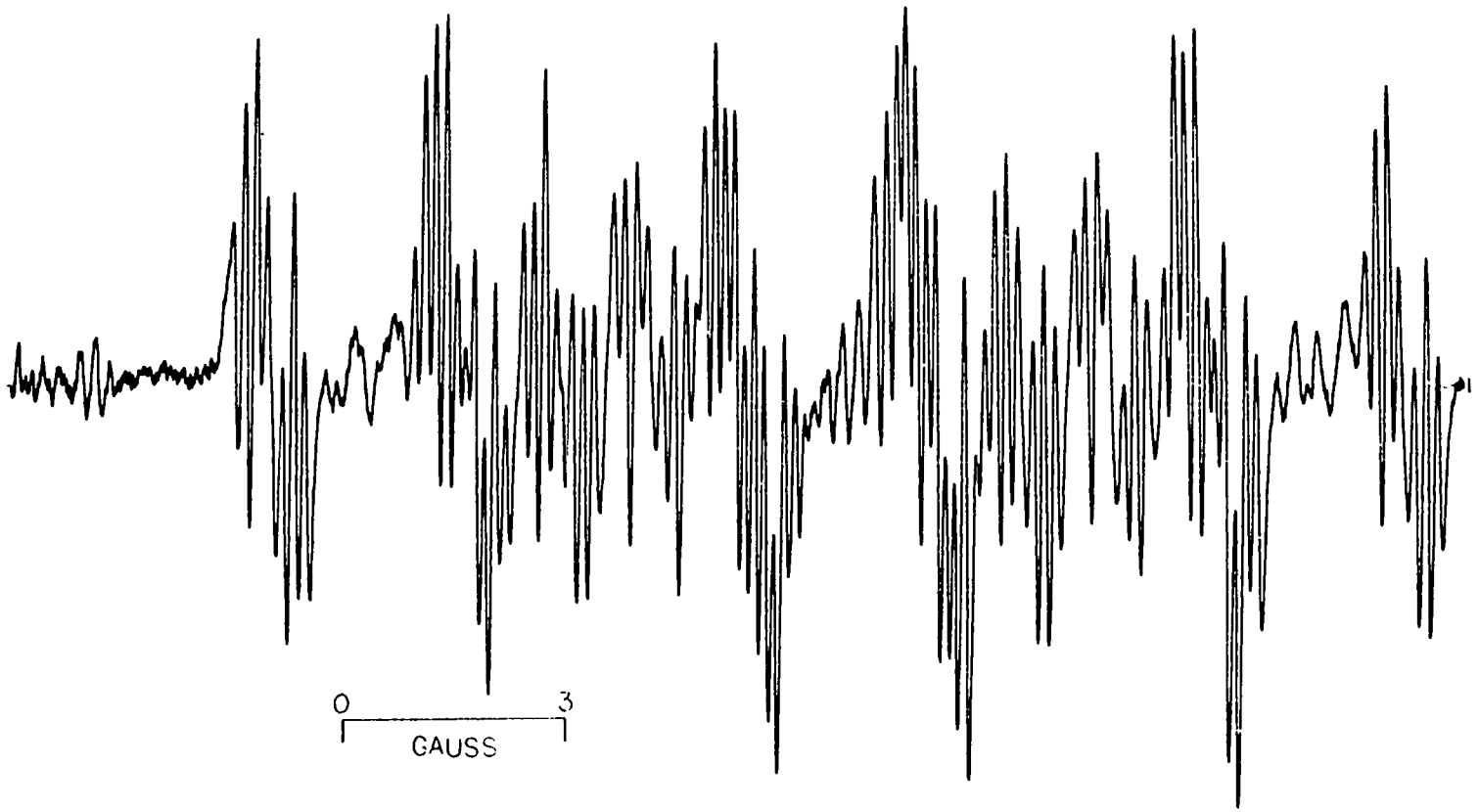
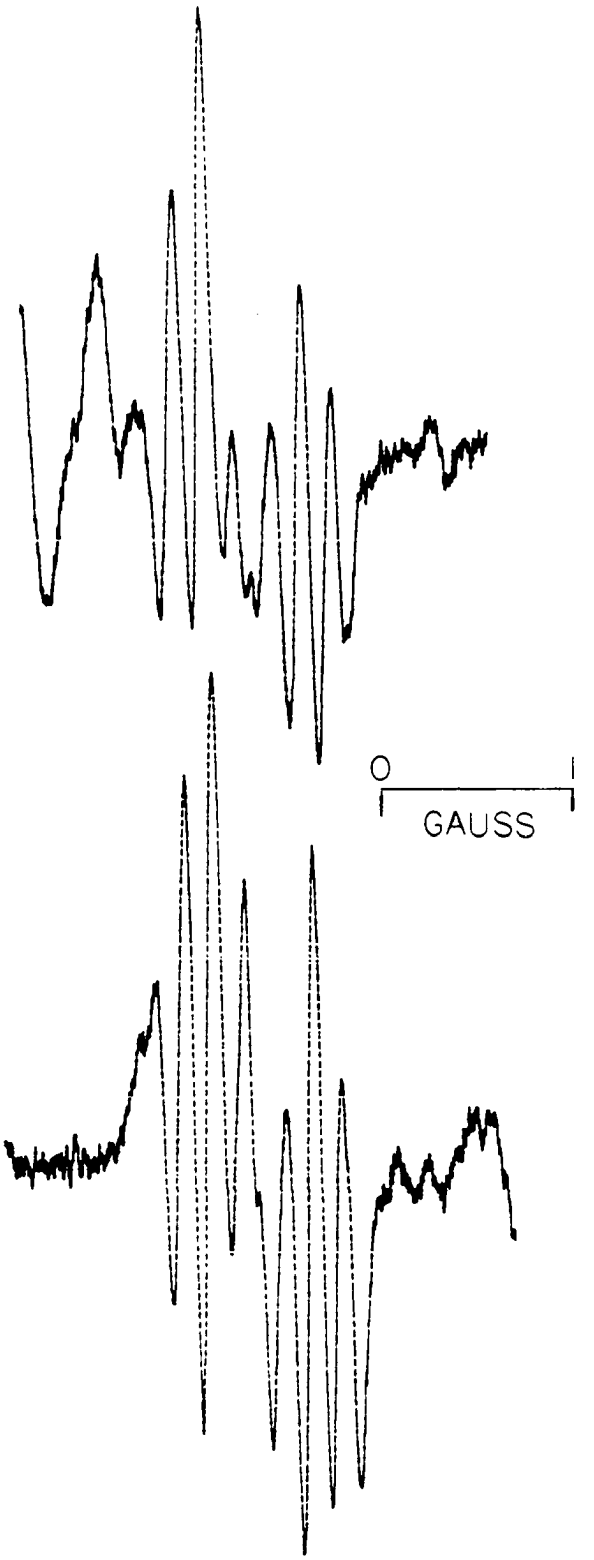
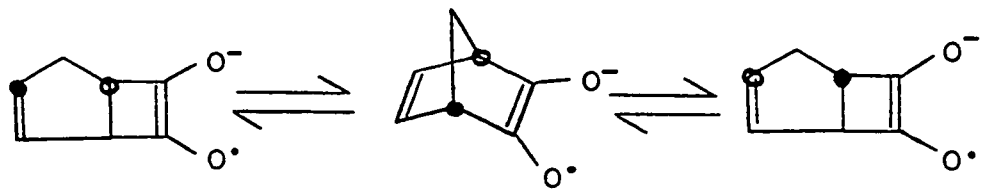


Figure 15. The first derivative esr spectrum of the radical obtained from endo, 3-t-butyldimethylsiloxy-5-methylbicyclo[2.2.1]hept-5-en-2-one (68b) under slow flow in DMSO.

Figure 16. The first derivative esr spectrum of the radical obtained from endo, 3-t-butyldimethylsiloxy-5-methylbicyclo[2.2.1]hept-5-en-2-one (68b) showing the high field (top) and low field (bottom) multiplets at high resolution.

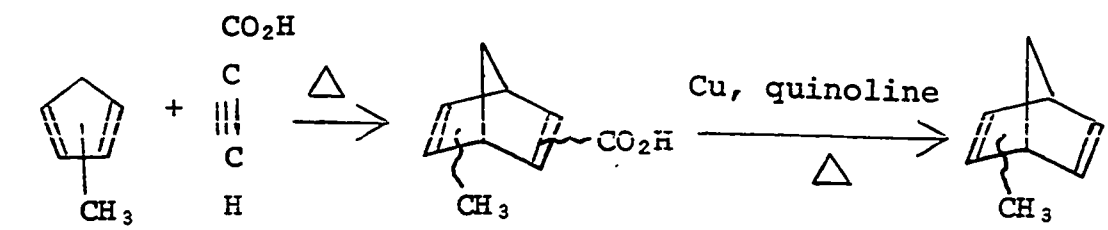

0
1
GAUSS

The results of esr experiments on the other set of isomers in Scheme 25 were not nearly as clean cut as those for the first set.

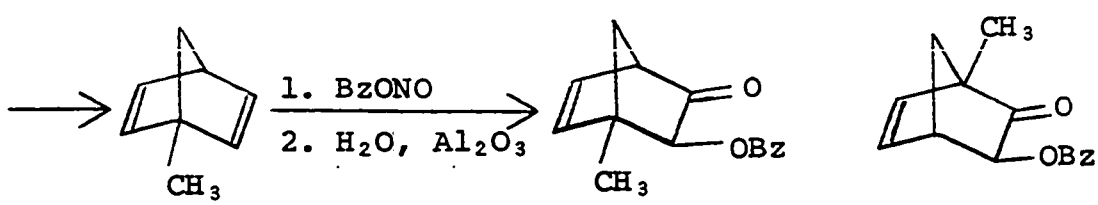


In addition to the ketones 67a-c (Scheme 29) and 59 (Scheme 26 and Scheme 27) already described, synthetic entry into this system was also gained as shown in Scheme 32.

Scheme 32



72



73 74

Diels-Alder addition of propynoic acid to methylcyclopentadiene gave a complex, resinous mixture of adducts 72 which was converted to a mixture of 1- and 2-methylnorbornadiene by decarboxylation. 1-Methylnorbornadiene was converted to benzoates 73 and 74 (separable by column chromatography) by treatment with BzONO followed by hydrolysis.

Mixing exo benzoate 73 (Figure 17), exo benzoate 74 (Figure 18) or [3.2.0] acetate 59 (Figure 19) with KO*t*-Bu/DMSO under flow conditions gave the same ill resolved spectrum. The radical was seen quite strongly 20-90 seconds after mixing, but died out quickly thereafter with no other radicals appearing. Since a rather large quantity of acetate 59 was available the esr experiment was repeated several times using carefully purified acetate 59 and varying the ratio of KO*t*-Bu:59. At about 3:1 = KO*t*-Bu:59 a spectrum was obtained (Figure 20) which was at least partially resolved in the low field multiplet (Figure 20). The high field multiplet (Figure 21) was still unresolved indicating the presence of just enough of another radical with a slightly different chemical shift to interfere with resolution. The computer simulation (Figure 20, bottom) shows an analysis consistent with the following hfsc for semidione 75 (Scheme 33): a^H = 12.5(1H), 0.908(1H), 0.433(1H), 0.163(2H). The results from ketones 73, 74, and 59 are, therefore, consistent with

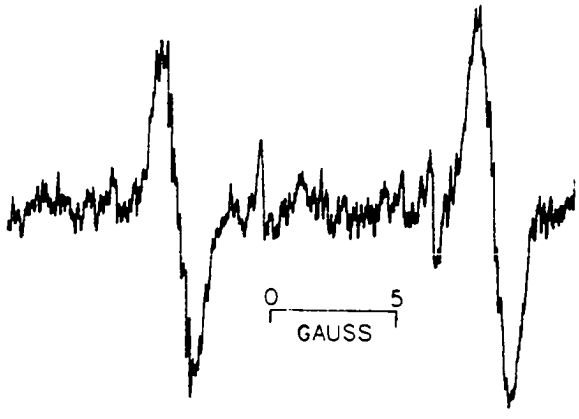


Figure 17. The first derivative esr spectrum of the radical obtained from exo, 3-benzoyloxy-4-methylbicyclo-[2.2.1]hept-5-en-2-one (73) in DMSO.

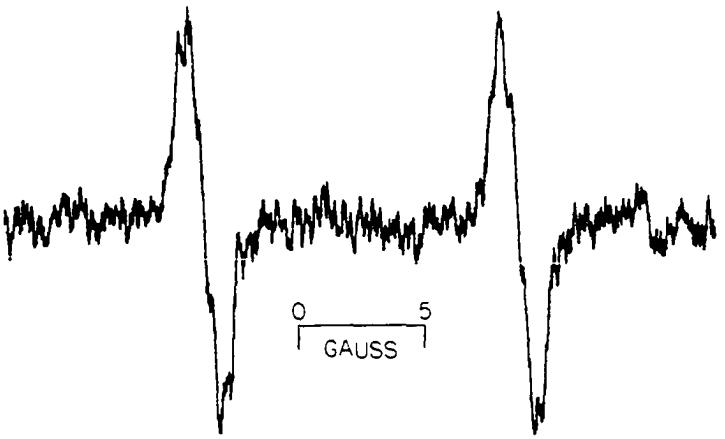


Figure 18. The first derivative esr spectrum of the radical obtained from exo, 3-benzoyloxy-1-methylbicyclo-[2.2.1]hept-5-en-2-one (74) in DMSO.

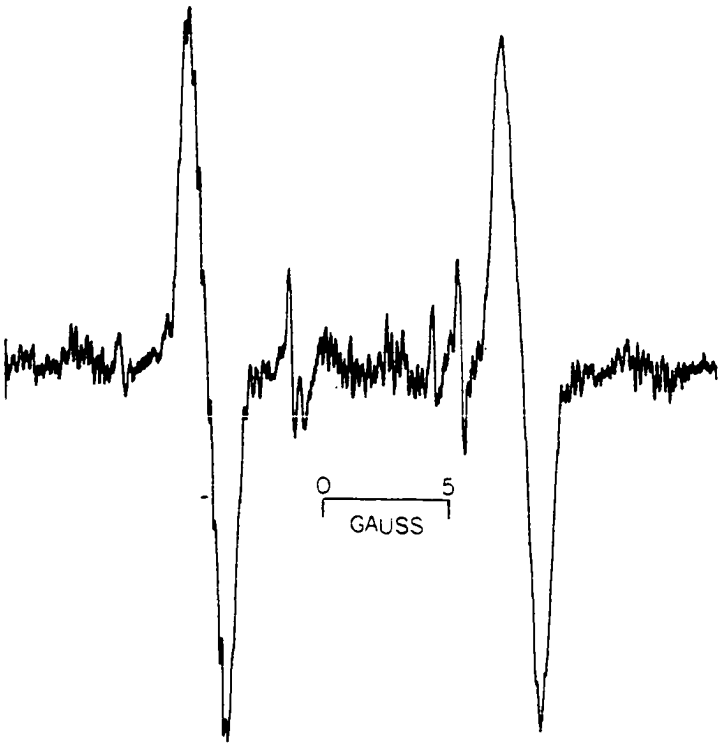


Figure 19. The first derivative esr spectrum of 5-methyl-bicyclo[3.2.0]hept-2-en-6,7-semidione (75) in DMSO.

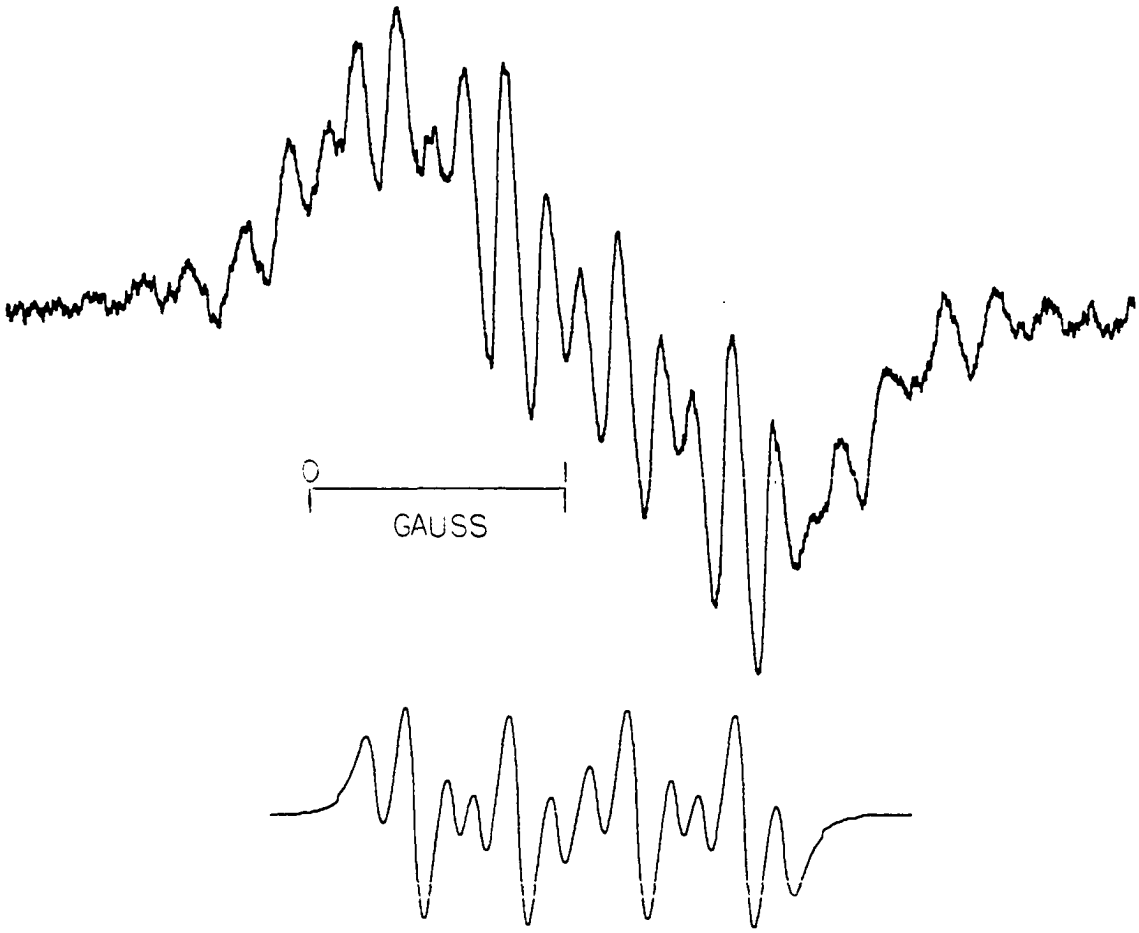


Figure 20. The low field multiplet of the first derivative esr spectrum (top) of 5-methylbicyclo[3.2.0]-hept-2-en-6,7-semidione (75); calculated spectrum (bottom) for Lorentzian line width 0.16 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

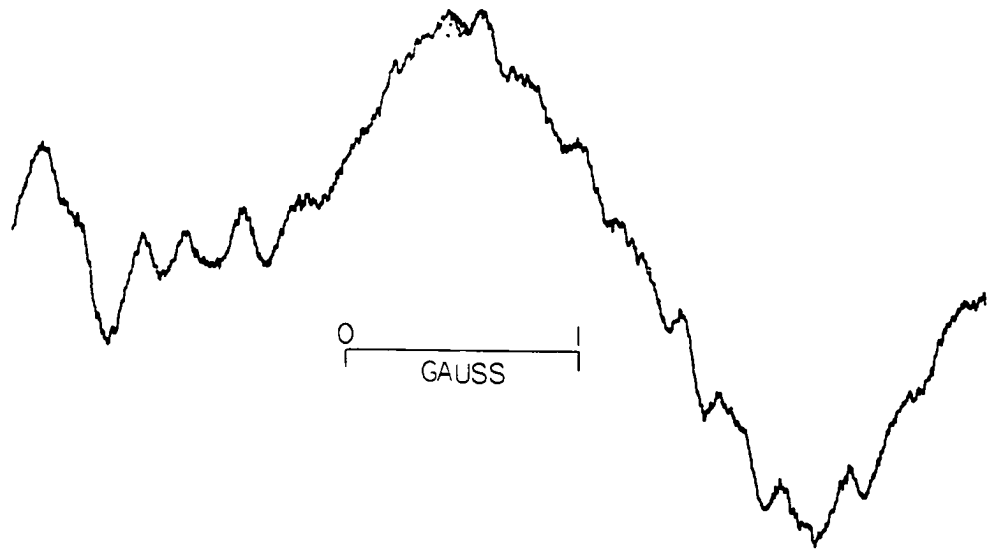
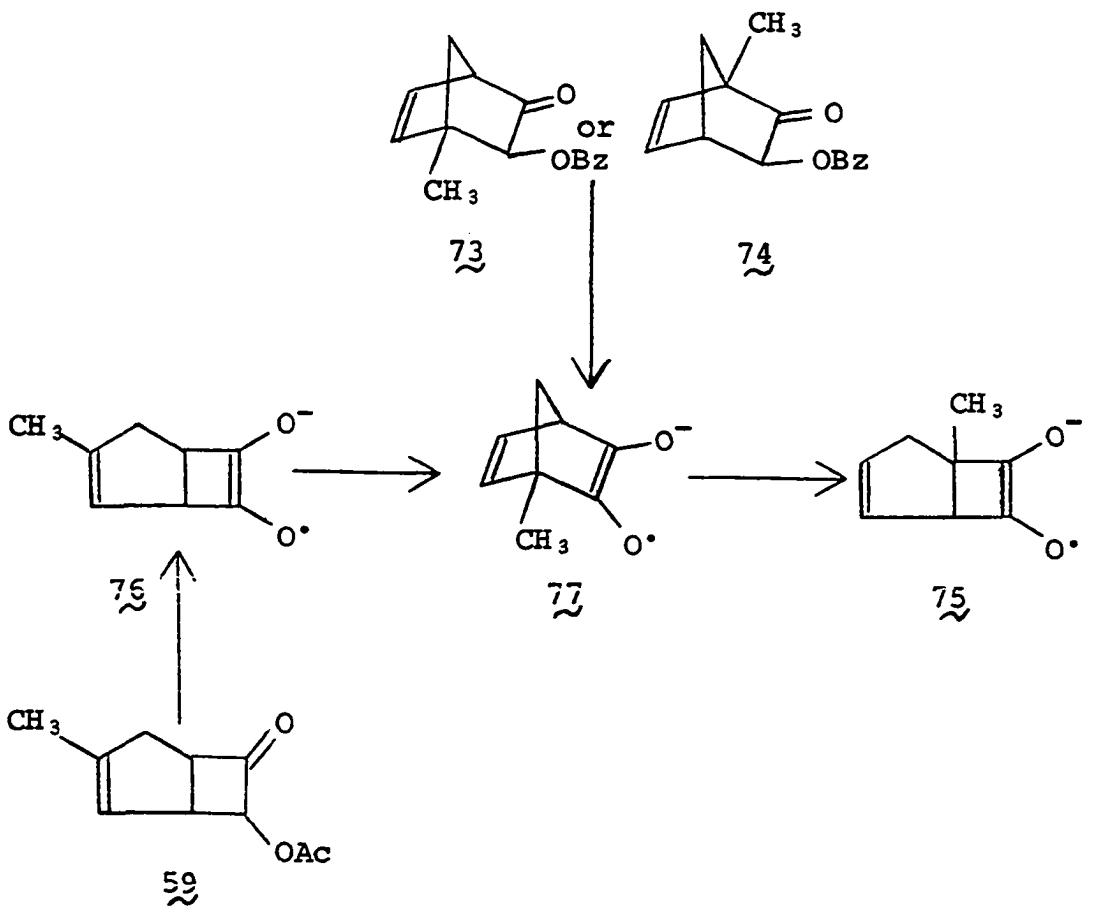


Figure 21. The high field multiplet of the first derivative esr spectrum of 5-methylbicyclo[3.2.0]hept-2-en-6,7-semidione (75) in DMSO.

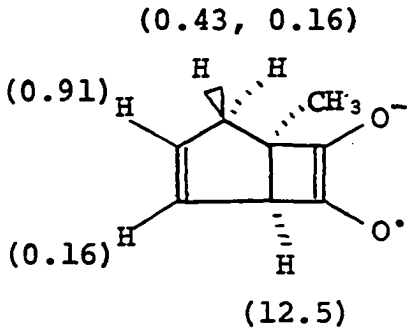
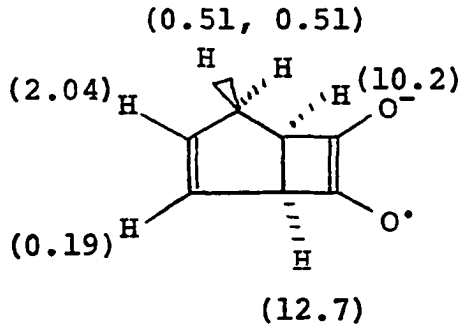
those of the previous set of isomers and with the mechanistic predictions of Scheme 25. Apparently, the rearrangement 76 → 77 → 75 is extremely facile and highly favors the bridgehead substituted semidione 75.

Scheme 33



The hfsc assigned to semidione 75 require that the geometry of semidione 9 be changed slightly to decrease the hfsc of H-3 and either H-4, exo or H-4, endo slightly (Table 5).

Table 5. Comparison of the hfsc of semidiones 75 and 9

75	9
	

The results obtained from esr experiments with the endo substituted ketones 67a-b (Scheme 29) are highly confusing. Mixing endo acetates 67a with KOt-Bu/DMSO gave a mixture of three radicals, one major and two minor which were stable at least 12 hours after mixing (Figure 22). The spectrum appears to be a mixture of two radicals, but a close examination of a pair of multiplets of the minor radical at high resolution (Figure 23) shows the pattern is not repetitive and, thus, is probably due to two very similar radicals with somewhat different chemical shifts. The spectrum of the major radical can be analyzed quite simply as follows: a^H = 10.7(1H), 1.77(1H), 0.533(1H), 0.227(1H), 0.115(3H). When the endo silyl ethers 67b were mixed with

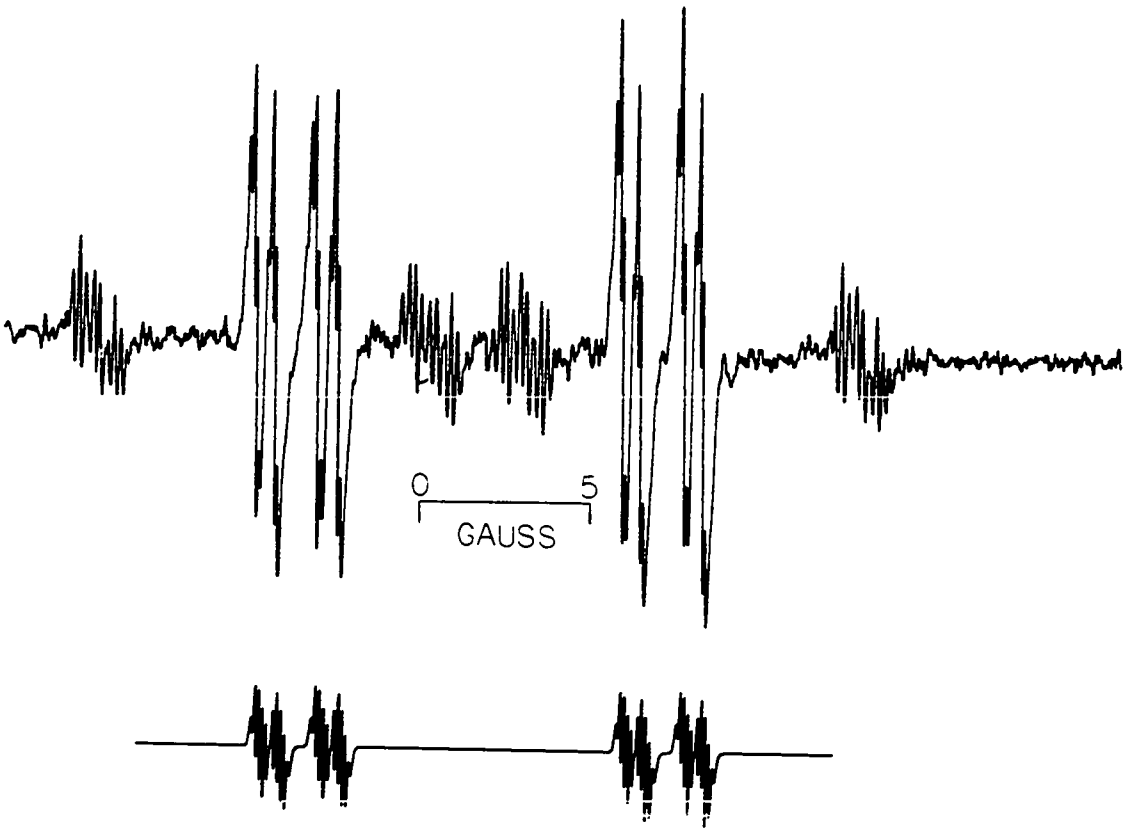


Figure 22. The first derivative esr spectrum (top) of the radicals obtained from a mixture of 1- and 4-methyl-endo,3-acetoxybicyclo[2.2.1]hept-5-en-2-one (67a) in DMSO; calculated spectrum (bottom) for major radical for Lorentzian line width 0.13 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

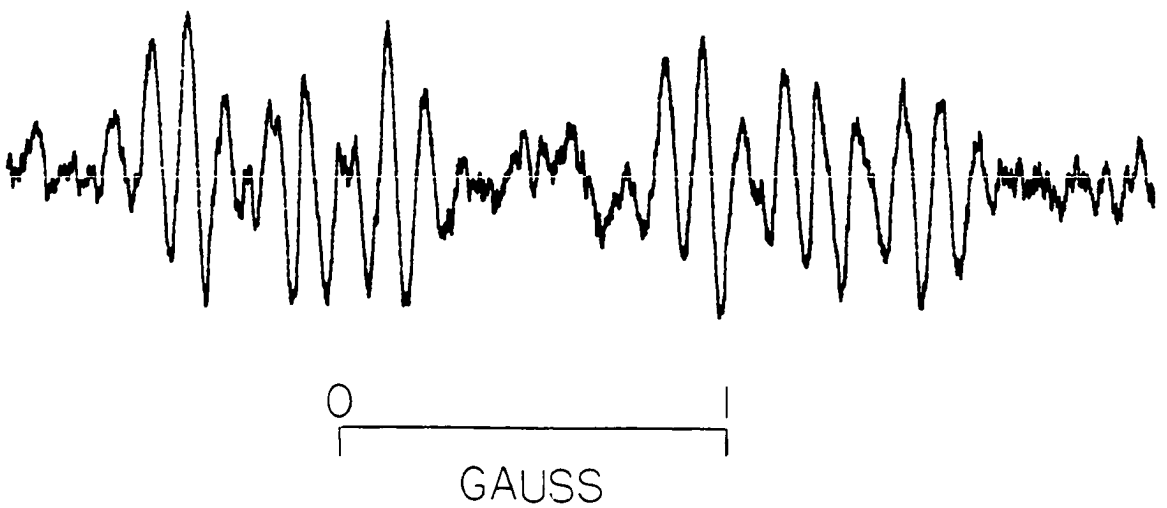
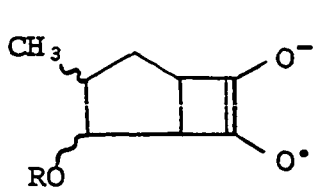


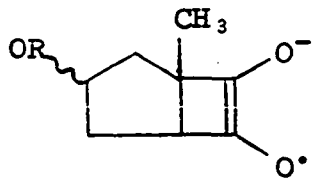
Figure 23. The middle multiplet of the first derivative esr spectrum of the radicals obtained from a mixture of 1- and 4-methyl-endo,3-acetoxybicyclo[2.2.1]-hept-5-en-2-one (67a) in DMSO.

KOt-Bu/DMSO, the major radical (Figure 22) formed from acetates 67a was not seen but the minor radicals (Figure 24), with one apparently predominant, were. Here, again, the radicals were stable for many hours and the spectrum could not be analyzed because of the overlap of two such similar radicals.

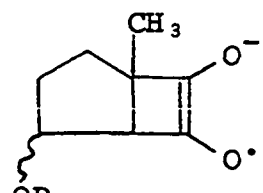
The structures of these radicals are enigmatic. The hfsc from the major radical (Figure 22) fit semidione 75 almost better than the hfsc assigned previously (Table 5), but to assign structure 75 to this stable radical would mean rejecting the self-consistent results of the esr experiments with ketones 59, 73 and 74. It is possible that the anomalous stable radicals have structures like 78a-c and have been formed by addition of acetic acid or t-butyldimethylsilanol to semidiones 75 and 76. It seems highly unlikely, however, that semidiones 78a-c would form from semidiones 75 and 76



78a



78b



78c

generated from the endo substituted [2.2.1] precursors and not from either the exo ketones 73 or 74 or [3.2.0] acetate 59. The explanation may lie in a delicate balance of rate of formation, concentration of various nucleophiles, and rate of destruction.

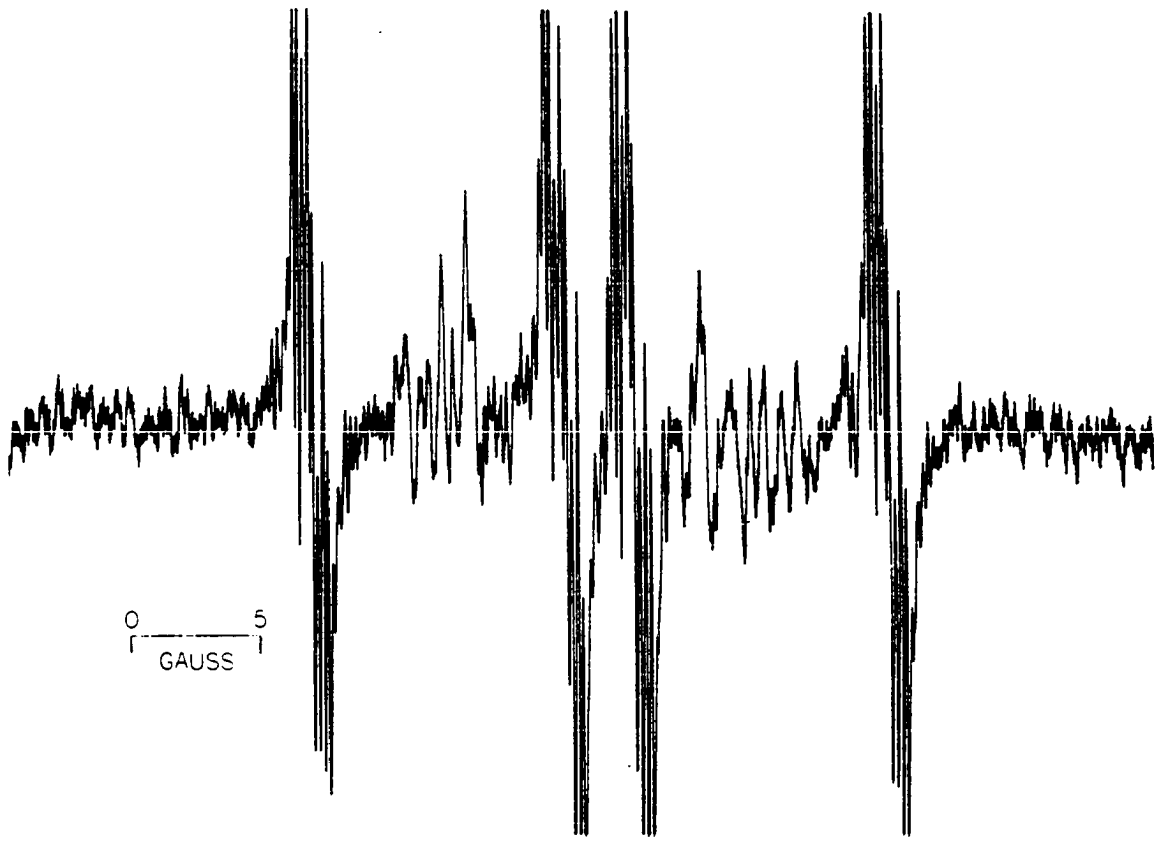
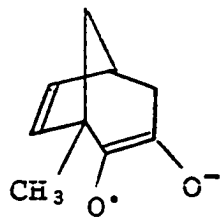
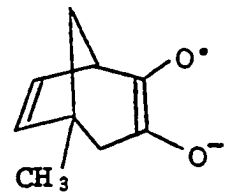


Figure 24. The first derivative esr spectrum of the radicals obtained from a mixture of 1- and 4-methyl-endo, 3-t-butyldimethylsiloxybicyclo[2.2.1]hept-5-en-2-one (67b) in DMSO.

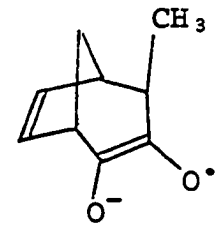
Alternatively, the anomalous stable radicals may not have the bicyclo[3.2.0]heptane framework at all, but may be bicyclo[3.2.1]octenesemidiones (79a-c) resulting from ring expansion by the dimsyl anion. Such methylene insertions are known for monoalkylglyoxals (40). The hfsc listed for



79a

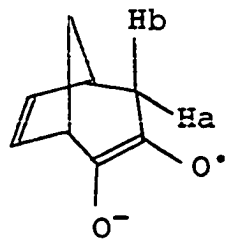


79b



79c

semidione 80 (6,41) are similar to those observed for the anomalous stable radicals.



80

$\underset{\sim}{a}^{H}$ = 8.74(1H) Ha

7.70(1H) Hb

2.66(1H)

1.07(1H)

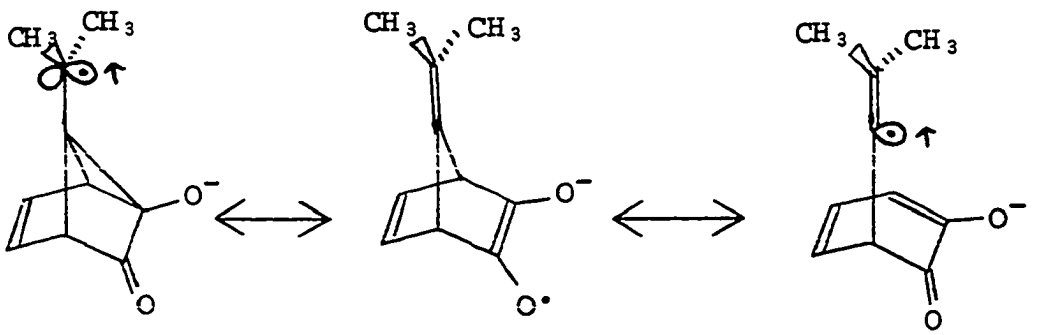
0.70(1H)

0.35(1H)

0.17(1H)

Concerted or Diradical?
Attempts to Sort Out the Mechanism

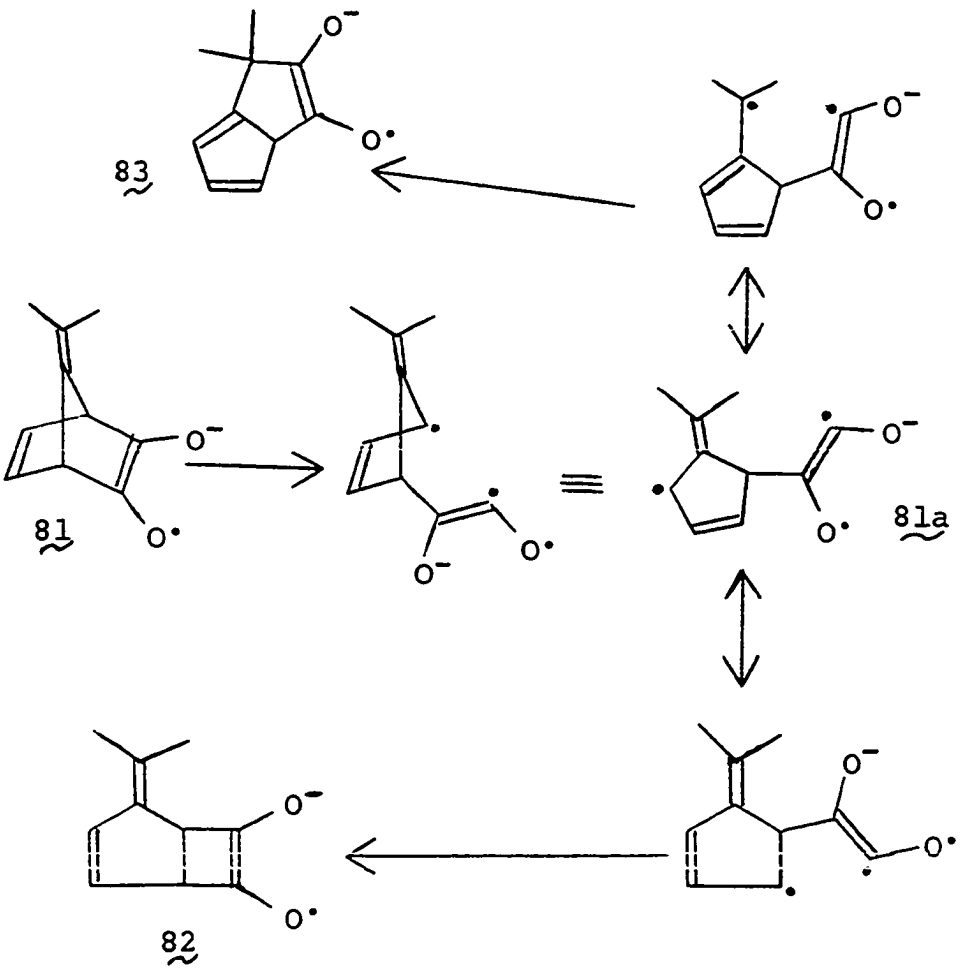
7-Isopropylidenebicyclo[2.2.1]heptenesemidione (81) was of interest for several reasons. The extremely high strain brought about by introduction of another sp^2 hybridized carbon into the norbornadiene framework was expected to generate an even higher spin density at C-7 than in semidione 8 by homohyperconjugation. The symmetry and spatial placement of the isopropylidene MO was expected to result in high spin density at C-7 by hyperconjugation. Both of these factors predicted an unusually large hfsc for the methyl protons.



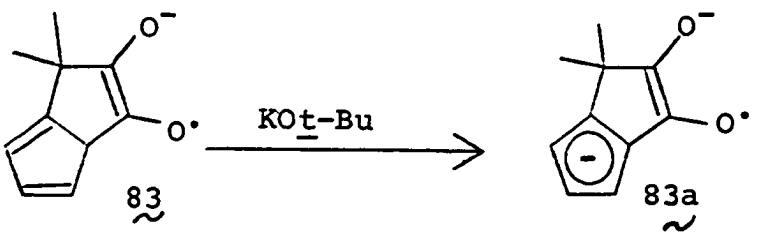
81

In addition, it was felt that semidione 81 might allow us to draw a distinction between a concerted [1,3] shift and a diradical [1,3] shift. Thus, if semidione 81 rearranged to semidione 82 by way of a diradical with a finite lifetime, one would expect two product semidiones (Scheme 34).

Scheme 34



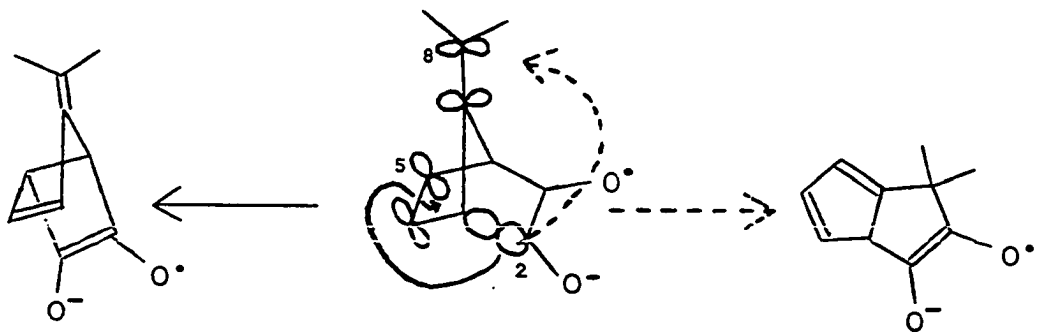
Radical 83 ought to be stable but could be expected to form a more stable anion 83a under the basic conditions



The spin density at the carbon leading to [3.3.0] semidione 83 ought to be greater than that at the carbon leading to [3.2.0] semidione 82 since it is an allylic and tertiary radical while that leading to the [3.2.0] semidione 82 is allylic and secondary. These observations led to the prediction that semidione 83 (and/or 83a) ought to be the predominant radical(s) observed if a diradical mechanism is operative.

A concerted [1,3] shift of C-2 can be envisioned which will produce either semidione 82 or 83 (Scheme 35).

Scheme 35



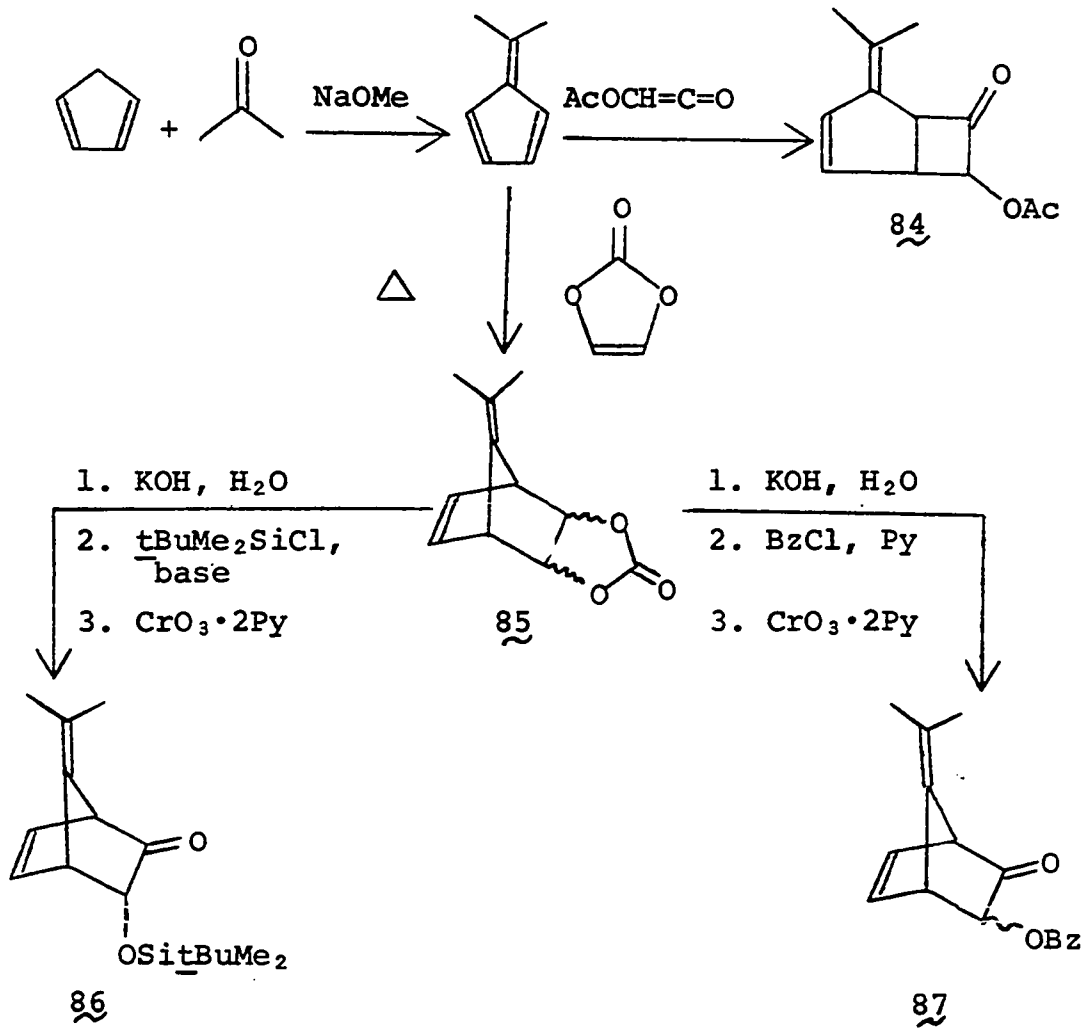
82 81 83

Molecular models show the distance from C-2 to C-5 is only about 2.5Å while the C-2 to C-8 distance is about 3.7Å. Models also show that a simple rotation about the C-3,C-4 bond will bring C-2 into position to bond with C-5 (to form semidione 82). No change in the geometry of the cyclopentene

ring is required to bring C-2 into proximity to C-5. Rotating about the C-3,C-4 bond leads to a transition state at whose "midpoint" C-2 is about 1.8Å from both C-1 and C-5. Contrastingly, a rather massive change (flattening) in the bridge geometry is required to form semidione 83 and the "midpoint" has C-2 about 2.5Å from both C-1 and C-8. Calculations of energy surfaces leading to semidiones 82 or 83 should give a more definite prediction, but a concerted [1,3] shift of C-2 seems to favor the [3.2.0] semidione if the above considerations are important.

The synthesis of the compounds used to study this problem is shown in Scheme 36. Acetoxyketene generated in situ added smoothly to dimethylfulvene to give the authentic precursor to semidione 82 (84). Vinylene carbonate was added to dimethylfulvene under slightly different conditions from those employed by Haq (42) to give approximately double his yield of adducts 85. As part of another study, the endo and the exo isomers of 85 were separated by chromatography (partial resolution) followed by crystallization from CCl_4, but for the purpose of this study the crude mixture of endo and exo 85 was used. Hydrolysis, monoderivatization, and oxidation gave a mixture of endo and exo benzoates 87 and, after gc purification, endo silyl ether 86. These syntheses proceeded very smoothly by the procedures developed earlier.

Scheme 36



Mixing [3.2.0] acetate 84 with KOt-Bu/DMSO gave a mixture of at least two radicals (Figure 25). The major radical had one large hfsc of 12.5(1H) and further unresolved fine structure. It reached its maximum concentration about 25 seconds after mixing. The second most visible radical gave its strongest signal about 8 seconds after mixing but subsided rapidly thereafter. It had gross hfsc: a^H =

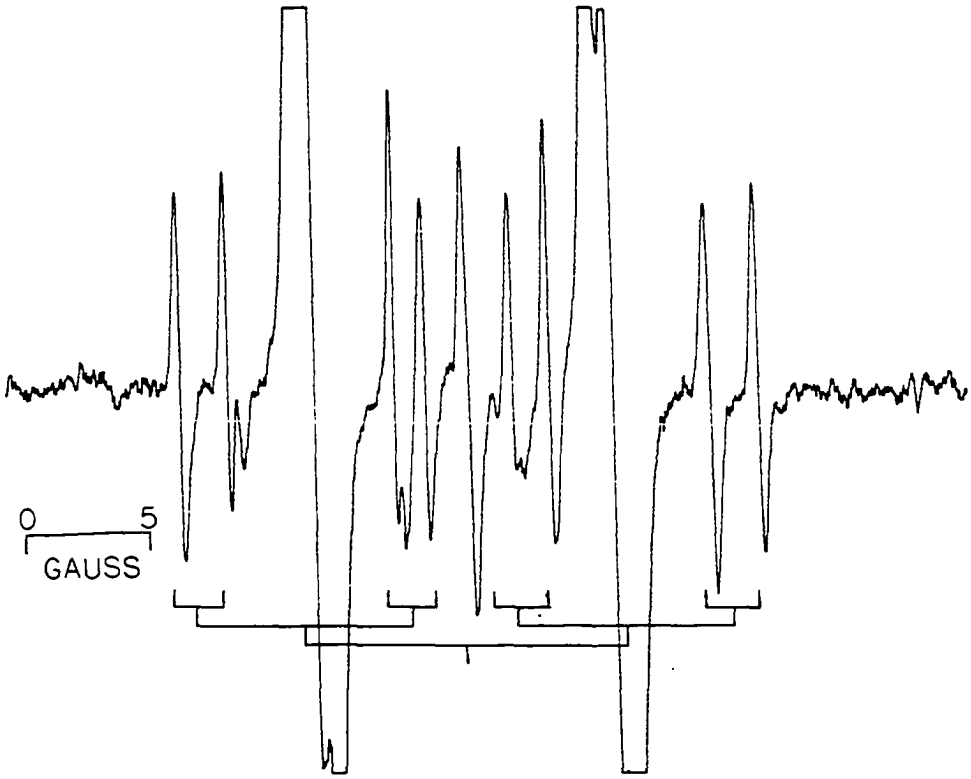
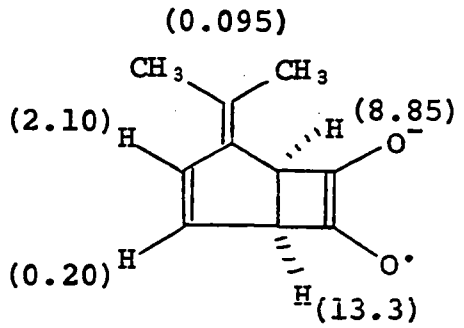


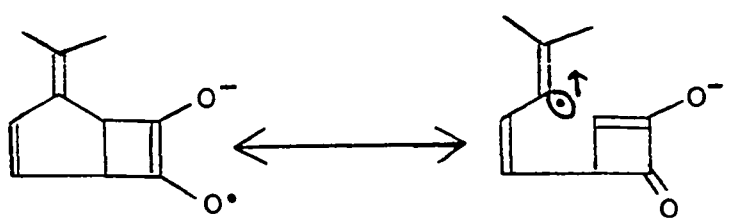
Figure 25. The first derivative esr spectrum of the radicals obtained from endo, 7-acetoxy-4-isopropylidene-bicyclo[3.2.0]hept-2-en-6-one (84) in DMSO.

13.3(1H), 8.85(1H), and 2.10(1H). Examination of the high field doublet (Figure 26) showed further hfsc: $\underline{a}^{H}$ = 0.20(1H), 0.095(6H). This is consistent with semidione 82.



82

The hfsc of the methyl protons in 82 is quite large for protons four carbons removed from the spin center. It is assumed that the strain from the additional sp^2 hybridized carbon increases the importance of homohyperconjugation.



Mixing exo and endo benzoates 87 with KO$\underline{t}$-Bu/DMSO under flow conditions was expected to very rapidly generate [2.2.1] semidione 81 which then would produce the unstable [3.2.0]

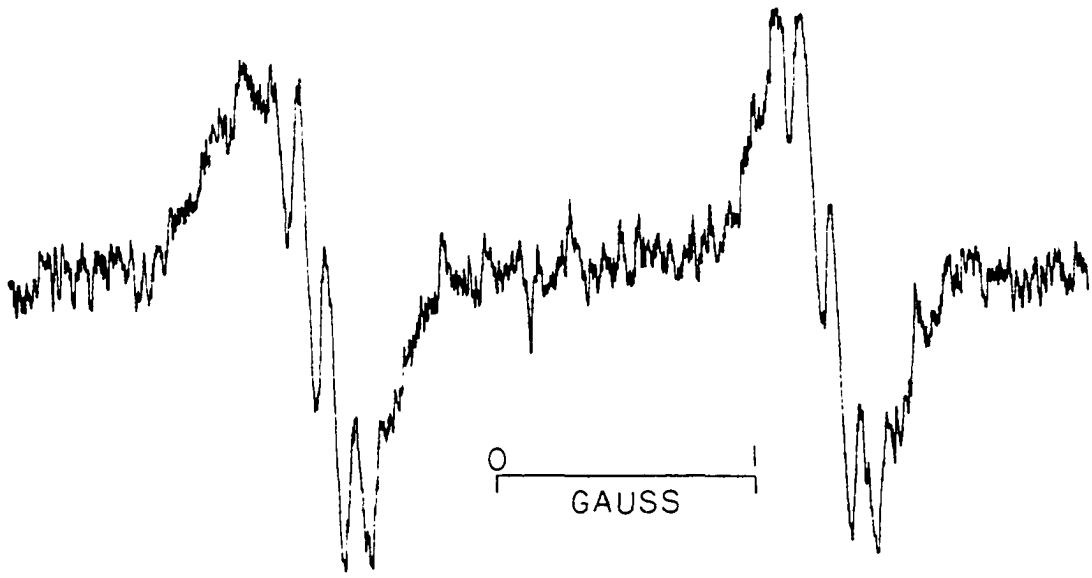
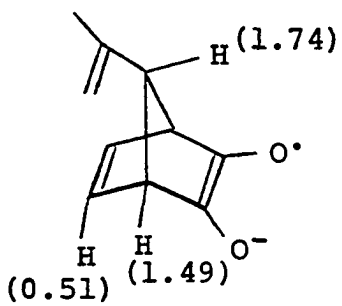
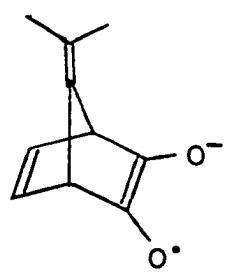


Figure 26. The high field multiplet of the first derivative esr spectrum of the radicals obtained from endo, 7-acetoxy-4-isopropylidenebicyclo[3.2.0]hept-2-en-6-one (84) in DMSO.

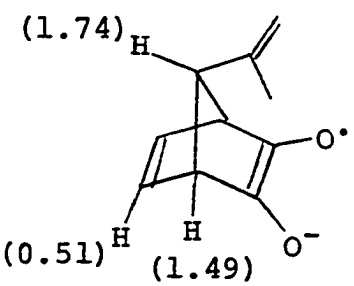
semidione 82 if the shift is concerted or the stable [3.3.0] semidiones 83 and/or 83a if the shift proceeds via a diradical. In fact, the [3.2.0] semidione 82 was seen up until about 15 seconds after mixing (arrows, Figure 27). Another radical (Figure 27), which is easily visible 40-70 seconds after mixing, is seen, but its structure is not that of either of the two [3.3.0] semidiones (83 and 83a). Its hfsc, $\underline{a}^{H}$ = 1.74(1H), 1.49(2H), 0.51(2H) are consistent with a radical formed by a base promoted isomerization of the isopropylidene double bond to an exocyclic position (88 and 89). This



88

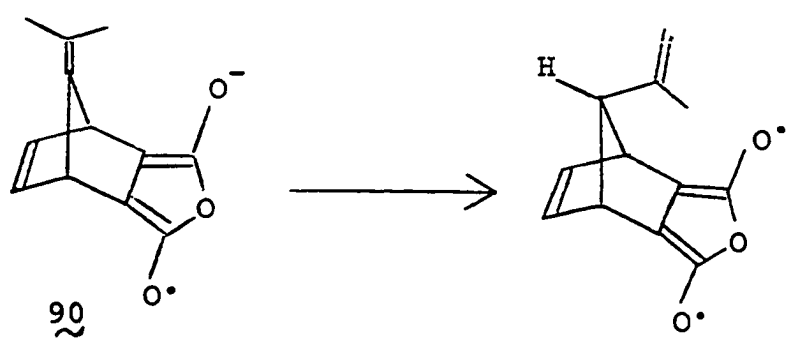


81



89

isomerization is exactly like that proposed by Mattox (33) to arise from semifuraquinone 90. The semidione (88 or 89) is



90

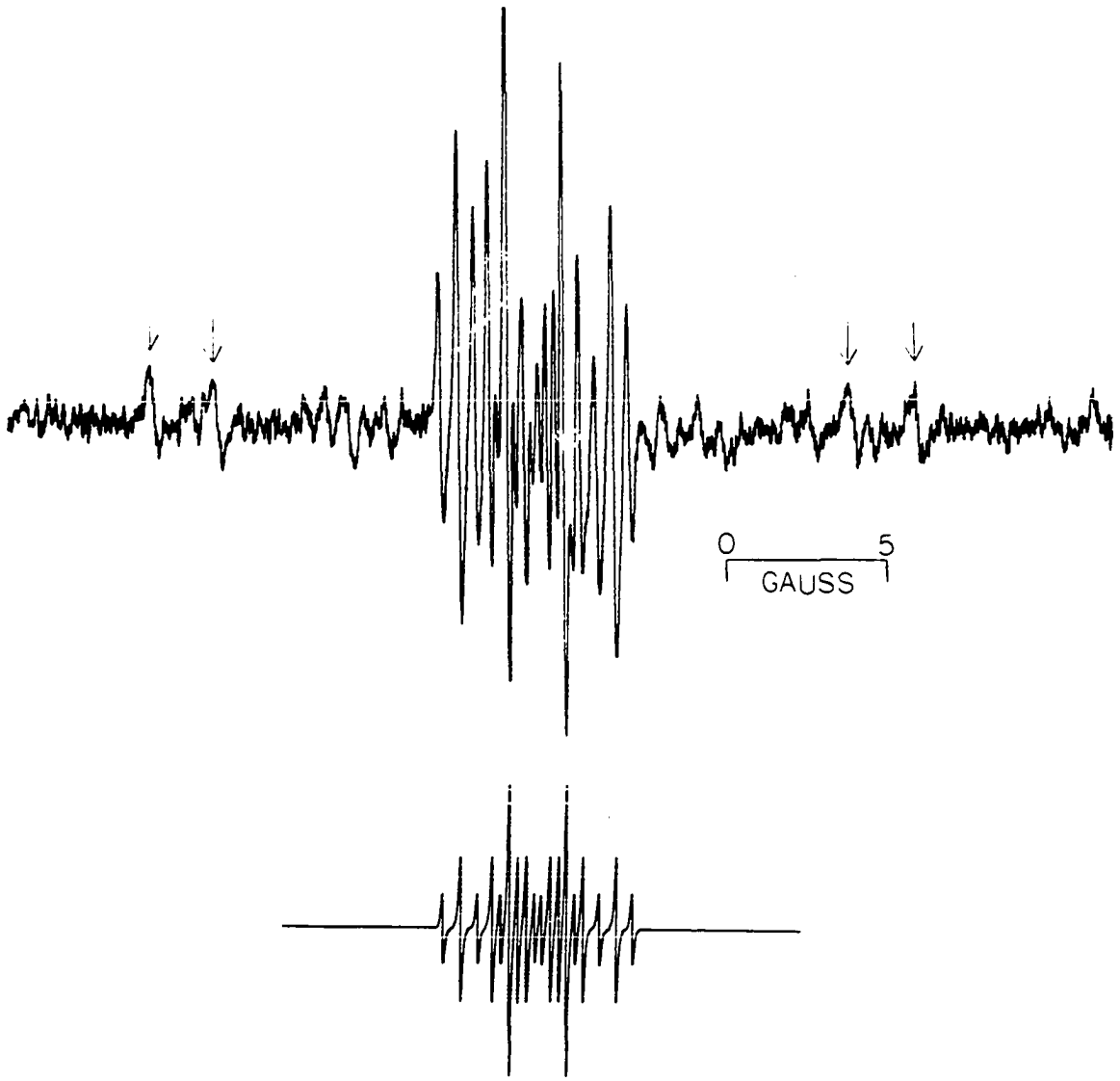
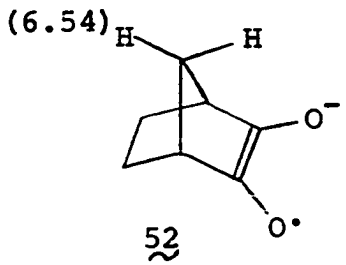


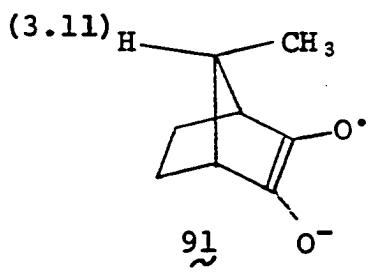
Figure 27. The first derivative esr spectrum (top) of the radical obtained from a mixture of endo and exo, 3-benzoyloxy-7-isopropylidenebicyclo[2.2.1]-hept-5-en-2-one (87) in DMSO; calculated spectrum (bottom) for Lorentzian line width 0.11 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

probably not semidione 88 since (as shown later) semidiones with t-butyl or methyl groups replacing the 2-propenyl group in semidione 88 rearrange rapidly to the quite stable [3.2.0] semidiones.

If the [2.2.1] semidione discussed above has structure 89, the hfsc of H-7, anti must be 1.74 gauss. This is very close to the value of 1.65 gauss assigned above to the homohyperconjugation contribution to the H-7 hfsc in bicyclo[2.2.1]heptenesemidiones. Holland has shown (6) that the H-7, anti hfsc of semidione 52 falls from 6.54 to 3.11 when a methyl group replaces H-7, syn (91). If the 1.74

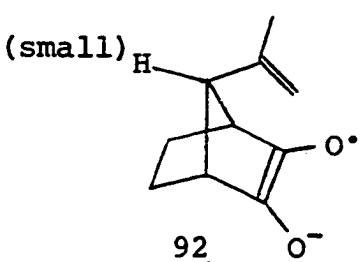


52



91

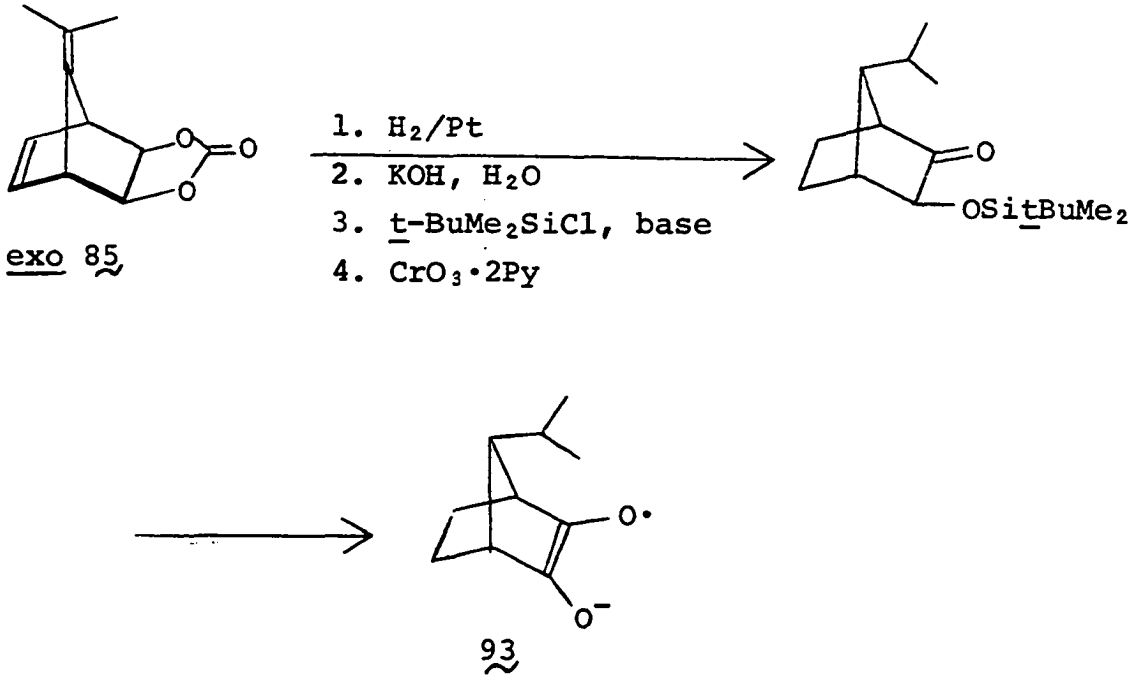
gauss hfsc seen in semidione 89 is due to homohyperconjugation, then this contribution should be absent in semidione 92 and the hfsc of H-7, anti in 92 should be



92

1.74-1.65 = 0.09, or negligible. In order to test this prediction synthetic Scheme 37 is now being carried out to obtain a suitable precursor to semidione 93.

Scheme 37



exo 85

93

Treatment of silyl ether 86 with KOt-Bu/DMSO under flow conditions did not give a spectrum which could be attributed to [2.2.1] semidione 81. Instead, at about 50 seconds after mixing the [3.2.0] semidione 82 (Figure 28) reached a maximum, although low concentration. The rather more leisurely flow rate (0.08 ml/min) allowed a slow, high resolution scanning of the low field doublet (Figure 29). It will be seen that the pattern is identical to that

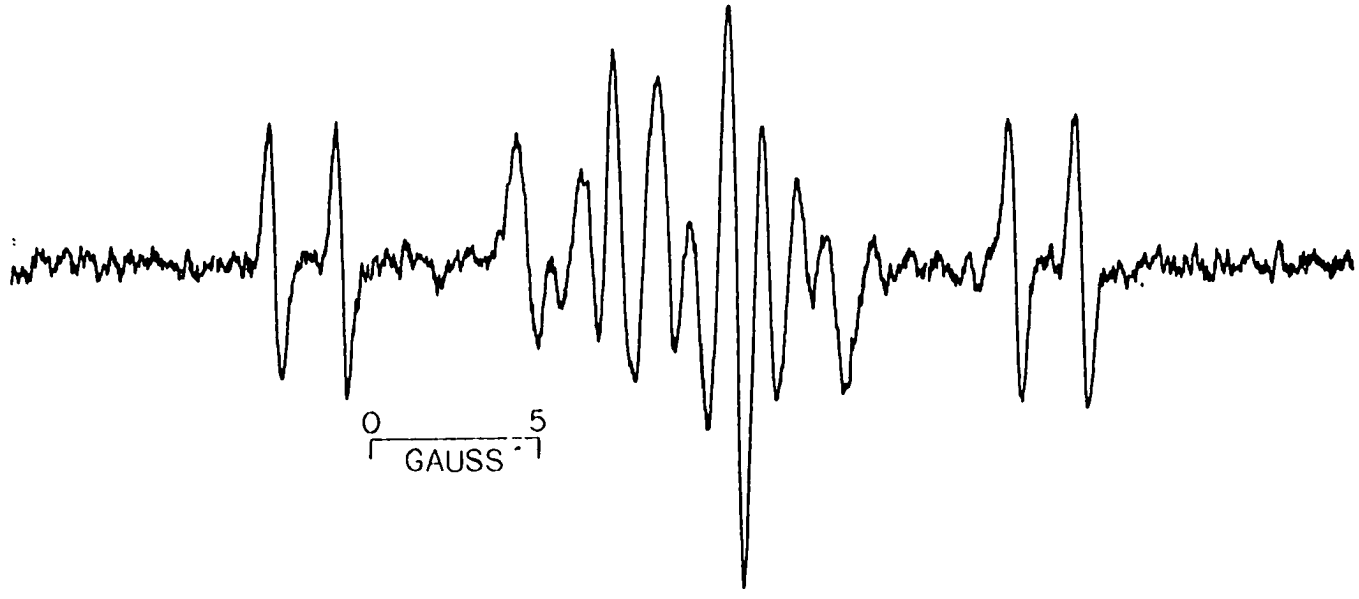


Figure 28. The first derivative esr spectrum of 4-isopropylidene-bicyclo[3.2.0]hept-2-en-6,7-semidione (82) in DMSO.

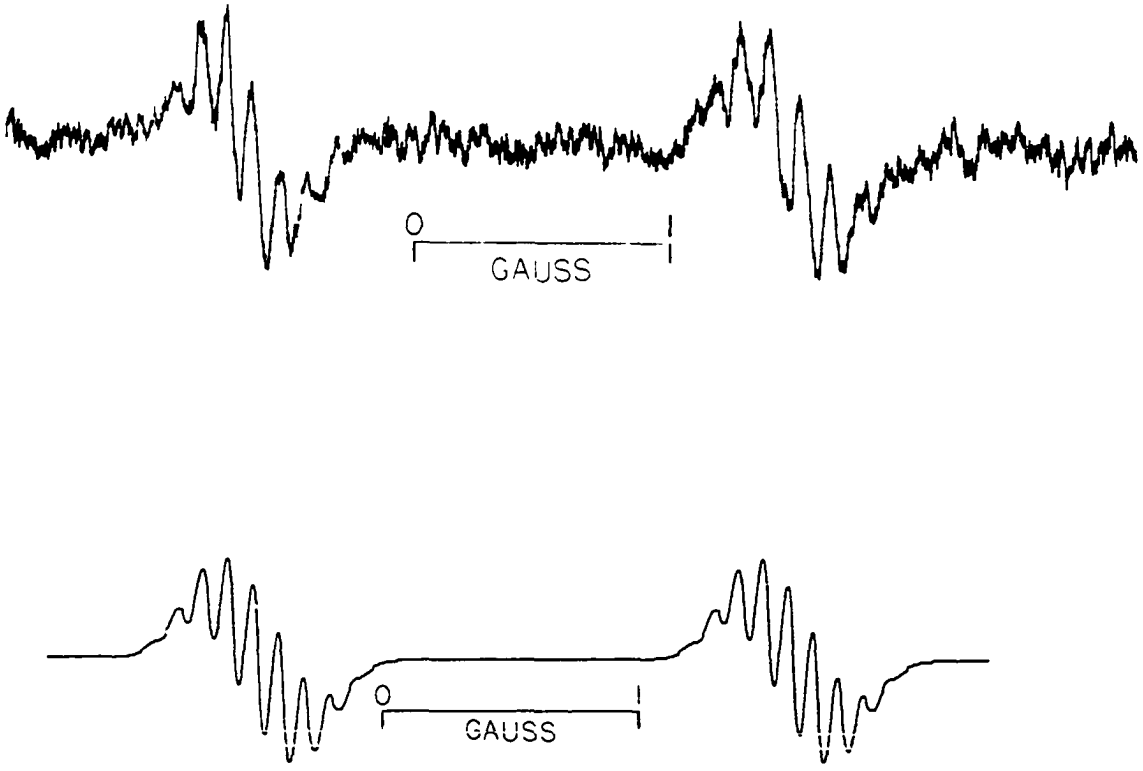


Figure 29. The low field multiplet of the first derivative esr spectrum (top) of 4-isopropylidenebicyclo-[3.2.0]hept-2-en-6,7-semidione (82) in DMSO; calculated spectrum (bottom) for Lorentzian line width 0.13 gauss with splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

obtained from the [3.2.0] acetate 84 and to the computer simulation. Another radical was seen (Figure 28) which confuses the center multiplet, but it was highly unstable and it, as well as [3.2.0] semidione 82 was gone 140 seconds after mixing.

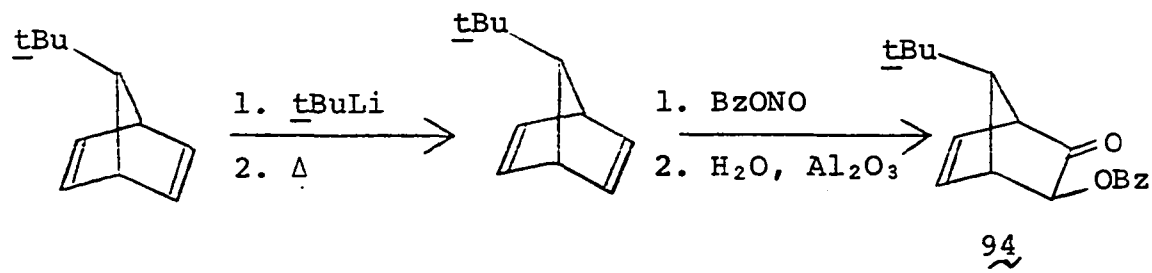
In summary, the highly desirable [2.2.1] semidione 81 could not be observed. Since no stable or unstable radical which could be attributed to a [3.3.0] semidione (83 or 84) was seen, and since both benzoate 87 and silyl ether 86 do give a recognizable [3.2.0] semidione 82, it was concluded that a concerted [1,3] shift is somewhat more probable than a diradical intermediate.

Effect of 4-Alkyl Substituents on the Stability and Rate of Formation of Bicyclo[3.2.0]hept-2-en-6,7-semidione

Comparison of the esr spectra of [3.2.0] semidione 9 (Figure 1) obtained from exo benzoate 7 and [2.2.1] semidione 8 (Figure 10) obtained from endo silyl ether 46 shows that two of the tallest peaks of the [2.2.1] semidione are well separated from the middle multiplet of the [3.2.0] semidione. The arrows on Figure 1 show the location of these two tallest peaks. If the spectrum of [3.2.0] semidione 9 obtained from exo benzoate 7 is examined 0.4-0.9 seconds after mixing, these peaks (which may be noise on

Figure 1) are plainly visible. If such fortuitous spacing would occur in other systems, it might be possible to gain a qualitative impression of the relative rates of rearrangement. The 7-t-butyl benzoate 94 was chosen as a likely precursor for several reasons. It seemed likely that the spectrum of the [3.2.0] semidione derived from 94 (95) would be very simple, thus increasing the chances of fortuitous spacing. Furthermore, the symmetry of the [2.2.1] semidione expected from benzoate 94 is such that a doublet of triplets of triplets is expected. The intensity of the two tallest peaks would be 4 times the wing peak and spaced at the doublet splitting. Finally, an easy synthesis based on known reactions was readily available (Scheme 38).

Scheme 38

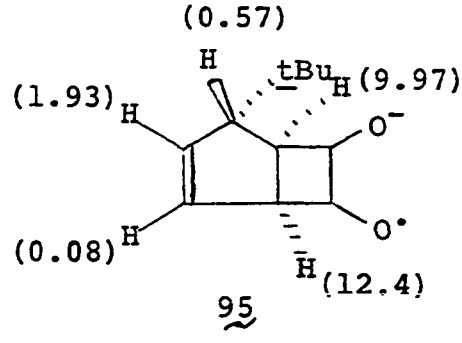


94

The novel conversion of 7-t-butoxynorbornadiene to 7-t-butylnorbornadiene has been shown by Wittig and Otten (43) to proceed by way of decomposition-rearrangement of an intermediate lithiated species. Scharpe (7) has shown

that the addition of benzoyl nitrite to olefins in CCl_4 proceeds through a cyclic transition state. This fact, taken with Brown's observations that 7-alkyl substituents hinder the otherwise preferred exo attack of reagents which proceed through a cyclic transition state (44), predicts the anti configuration shown for benzoate 94. It has been shown (45) that hydroboration, oxymercuration, and diimide reduction of 7-t-butylnorbornadiene all result in the exo, anti adducts, so it is not surprising that addition of benzoyl nitrite also led to the exo, anti adduct 94.

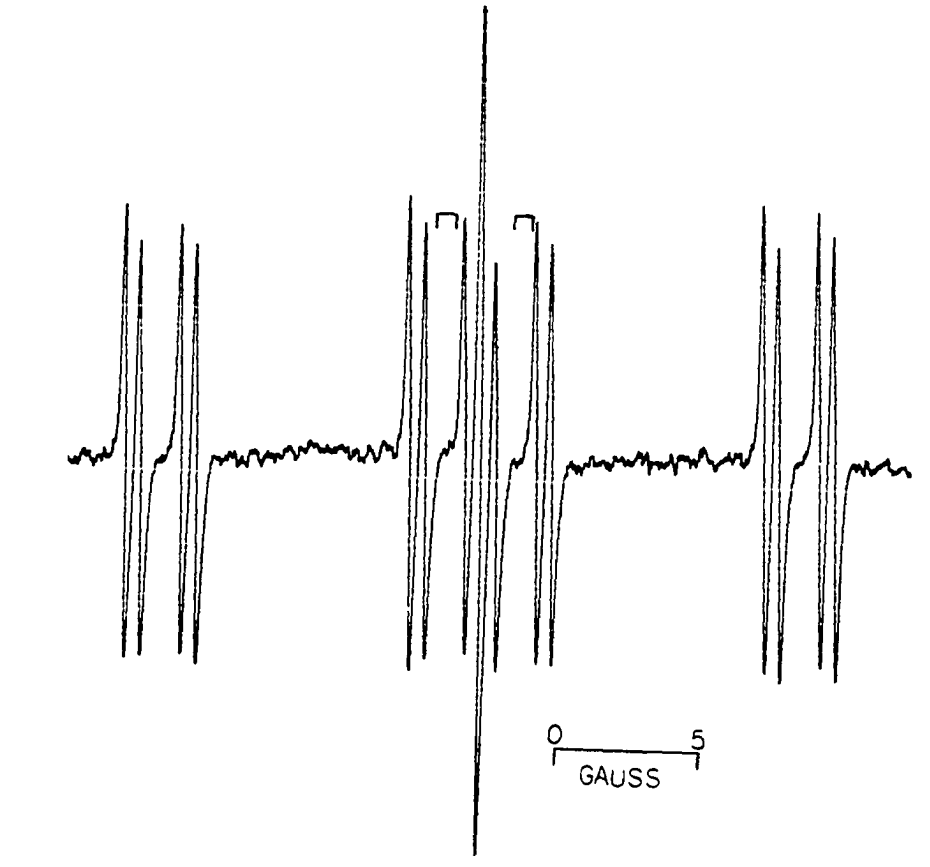
Mixing benzoate 94 with KOt-Bu/DMSO under flow conditions gave [3.2.0] semidione 95 (Figure 30), a^H = 12.4(1H), 9.97(1H), 1.93(1H), 0.57(1H), 0.08(1H), which was visible for about 2 hours after mixing. Examination of the

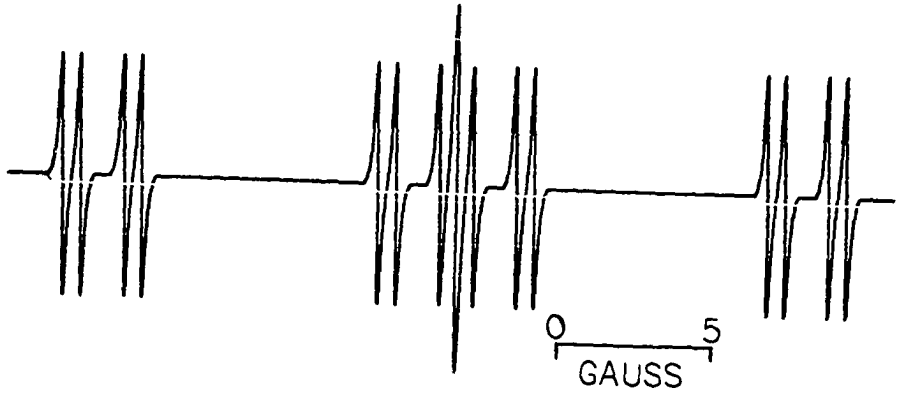


95

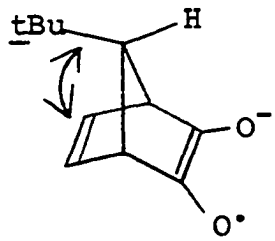
spectrum of 95 showed that the areas of the spectrum in which the tallest peaks of the corresponding [2.2.1] semidione might be expected (brackets on Figure 30, a^H = 1.7-2.10) to appear, were clean. Examination of the spectrum at 0.1 to

Figure 30. The first derivative esr spectrum (top) of exo, 4-t-butylbicyclo[3.2.0]hept-2-en-6,7-semidione (95) in DMSO; calculated spectrum (bottom) for Lorentzian line width 0.18 gauss with splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

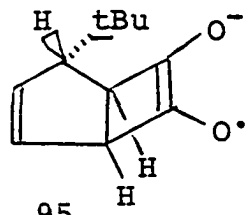

0
5
GAUSS


0
5
GAUSS

0.4 seconds after mixing showed no absorptions. This was taken as evidence that the [2.2.1] semidione 96 rearranges faster than semidione 8. This might have been predicted by consideration of steric factors in semidiones 95 and 96.



96

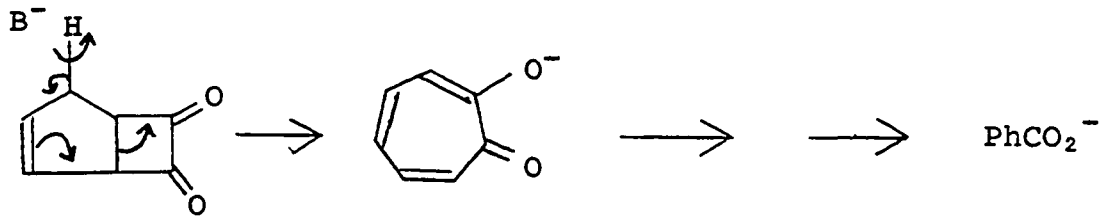


95

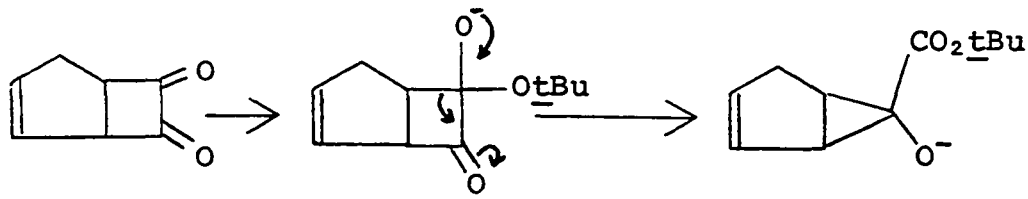
In [2.2.1] semidione 96 the bulky t-butyl group impinges on the 5,6 double bond, but in the [3.2.0] semidione 95 the t-butyl group is in the relatively free exo position. The t-butyl group can be considered to decrease the stability of 96 relative to 95. It also seems reasonable that C-7 should move away from C-5,C-6 in semidione 96 to relieve the strain, thus pushing C-2 closer to C-5 and lowering the distortion of the ground state needed to reach transition state geometry.

The extreme stability of semidione 95 prompted consideration of the factors governing the stability of bicyclo[3.2.0]heptenesemidiones. Unquestionably, the major factor is the chemical reactivity of the cyclobutanedione in equilibrium with the semidione. Scheme 39 and Scheme 40 show possible ways the dione may be degraded to materials

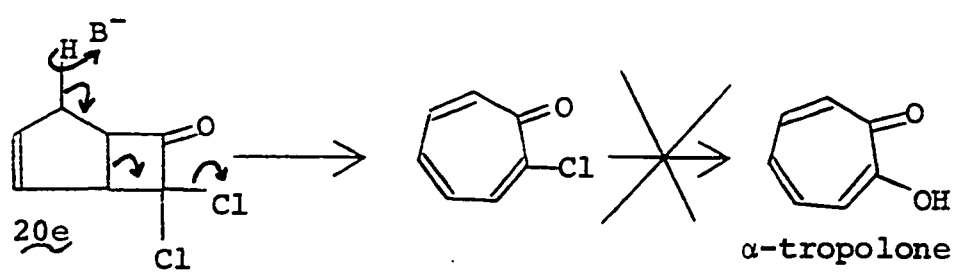
Scheme 39



Scheme 40

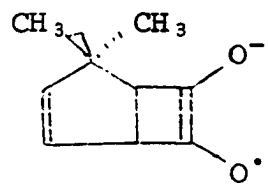


not giving paramagnetic species. A scheme similar to Scheme 39 has been shown to be incorrect for the formation of α-tropolone from dichloroketone 20e (18,46). Attack by a bulky base such as t-butoxide (Scheme 40) must be from the exo side of the cyclobutanedione. Substituents at C-4

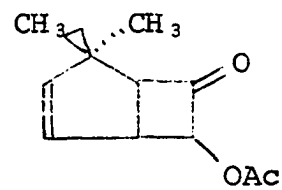


would be expected to have little effect on the ease of attack in Scheme 40. On the other hand substituents at C-4 would have a marked effect on that rate if Scheme 39 were in operation. The exo t-butyl group at C-4 would be expected to reduce both the acidity and accessibility of H-4, endo thus adding greatly to the stability (chemical inertness) of semidione 95.

If attack at the carbonyls or the bridgehead is important in degrading the diketone, little effect can be expected if C-4 is dialkylated. However, if attack by base (Scheme 39) is important, a dialkylated C-4 [3.2.0] semidione (96) could be expected to be very stable.



96

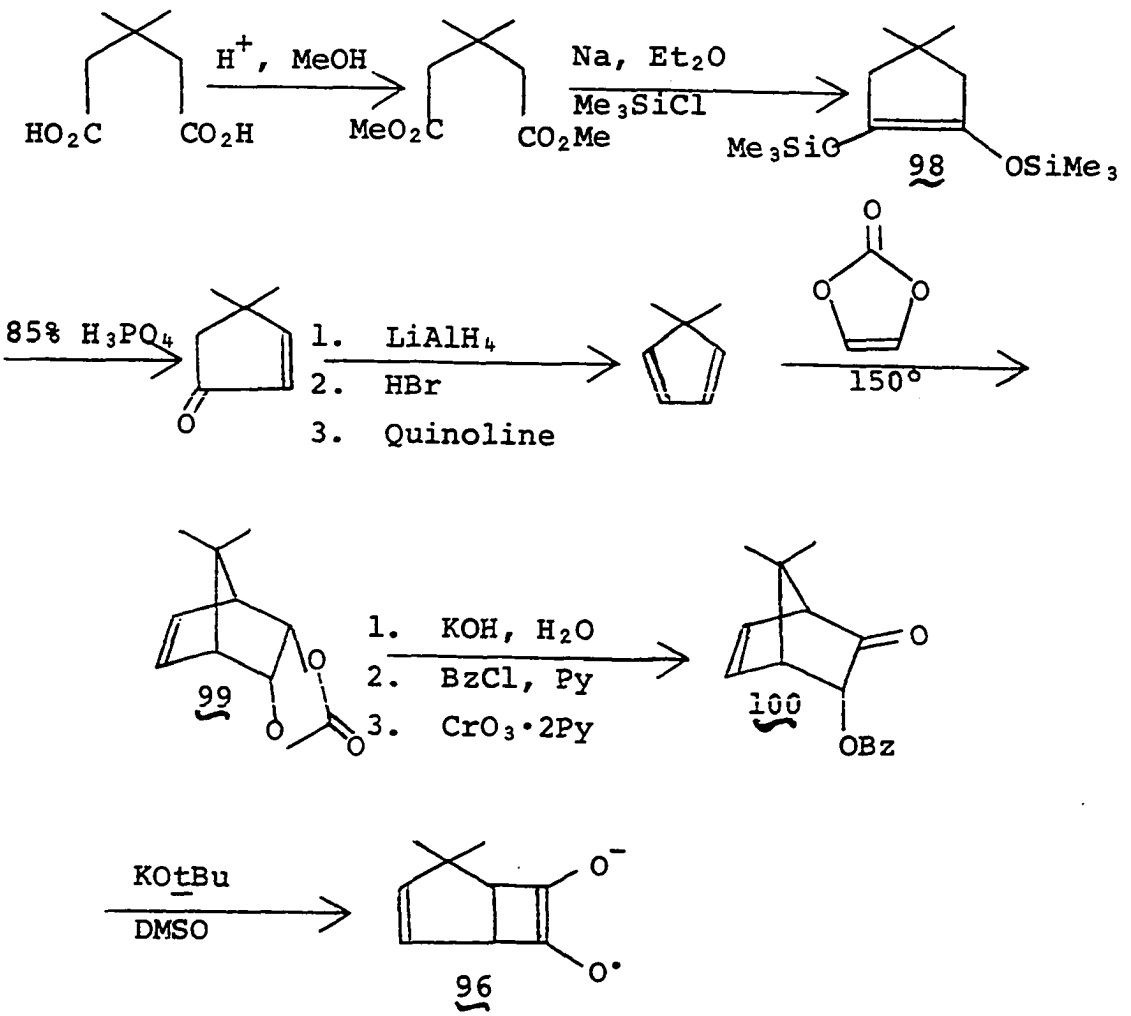


97

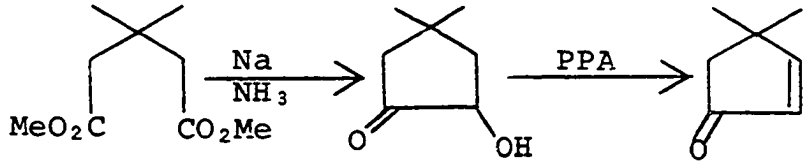
It did not seem likely that acetate 97 could be formed by addition of acetoxyketene to 5,5-dimethylcyclopentadiene because of the severe steric hindrance the methyl groups present to approach by the ketene. This was found to be the case for both acetoxyketene and the much more reactive dichloroketene.

Scheme 41 shows the successful synthetic route to semidione 96. The preparation of 5,5-dimethylcyclopentadiene from β,β-dimethylglutaric acid was essentially that of Rouse and Tyler (47). These authors prepared the acyloin 101 which they dehydrated to dimethylcyclopentenone with polyphosphoric acid (Scheme 42). We have used Rühlmann and Schräpler's technique (48) of trapping the diketone dianion

Scheme 41



Scheme 42



101

with trimethylsilyl chloride. The convenience of reacting 100 g of diester in 1 liter of ether once (our method) instead of 20 g of diester in 3 liters of liquid NH_3 5 times (Rouse and Tyler) cannot be over-emphasized. Similarly, the dehydration of acyloin 101 must be carried out with polyphosphoric acid laboriously prepared to a carefully specified per cent H_3PO_4 with several days reaction time. Our technique requires about 1 hour and uses cheap, off-the-shelf, 85% H_3PO_4. The yields for the two steps are almost exactly the same by both routes.

Hydrolysis, monobenzoylation, and oxidation of Diels-Alder adduct 99 proceeded smoothly to crystalline benzoate 100.

Mixing benzoate 100 with KOt-Bu/DMSO gave a strong radical (Figure 31 and Figure 32) whose hfsc, a^H = 12.15(1H), 9.62(1H), 1.895(1H), 0.266(1H), 0.121(6H), are consistent with semidione 96. Increasing the spectrometer receiver

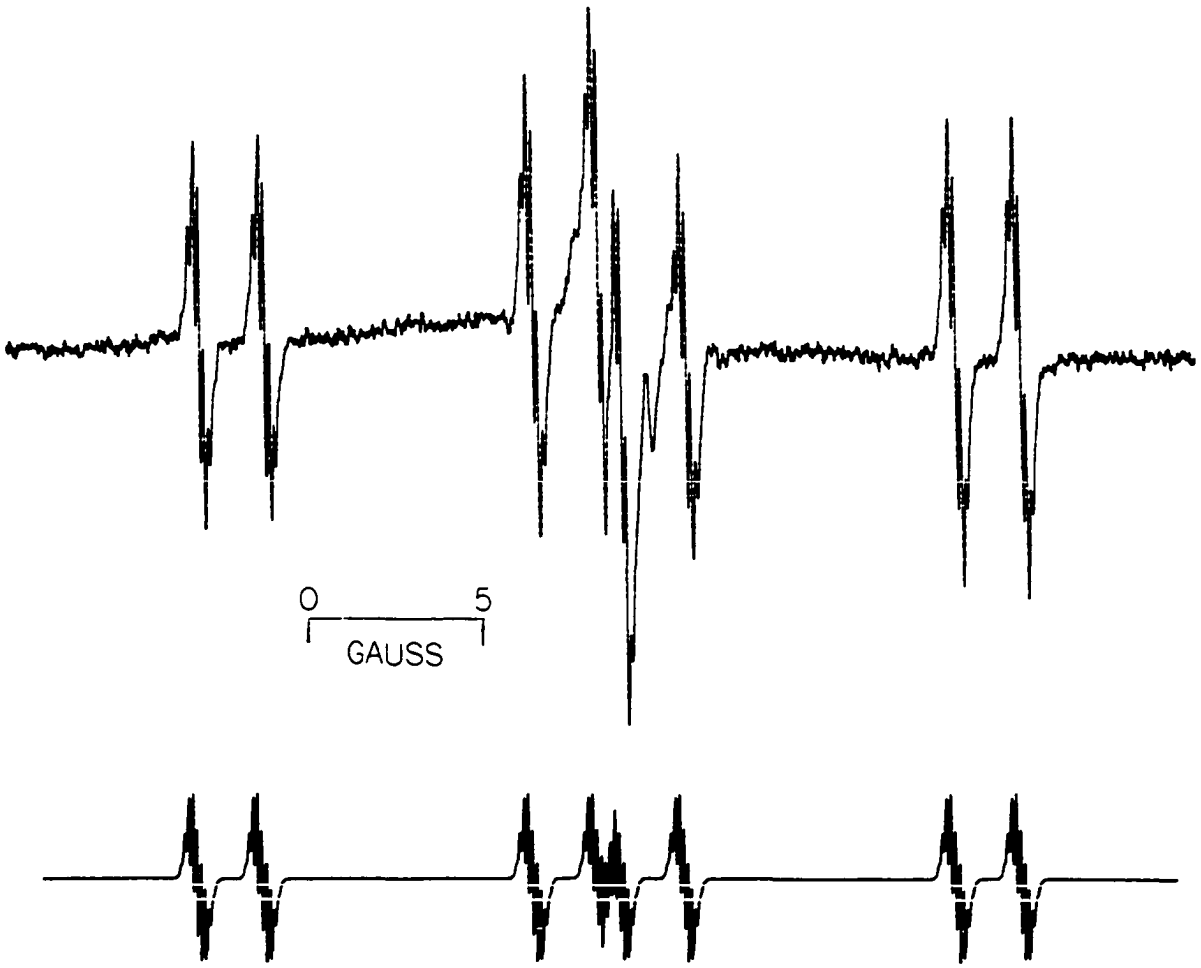


Figure 31. The first derivative esr spectrum (top) of 4,4-dimethylbicyclo[3.2.0]hept-2-en-6,7-semidione (96) in DMSO; calculated spectrum (bottom) for Lorentzian line width 0.14 gauss with splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

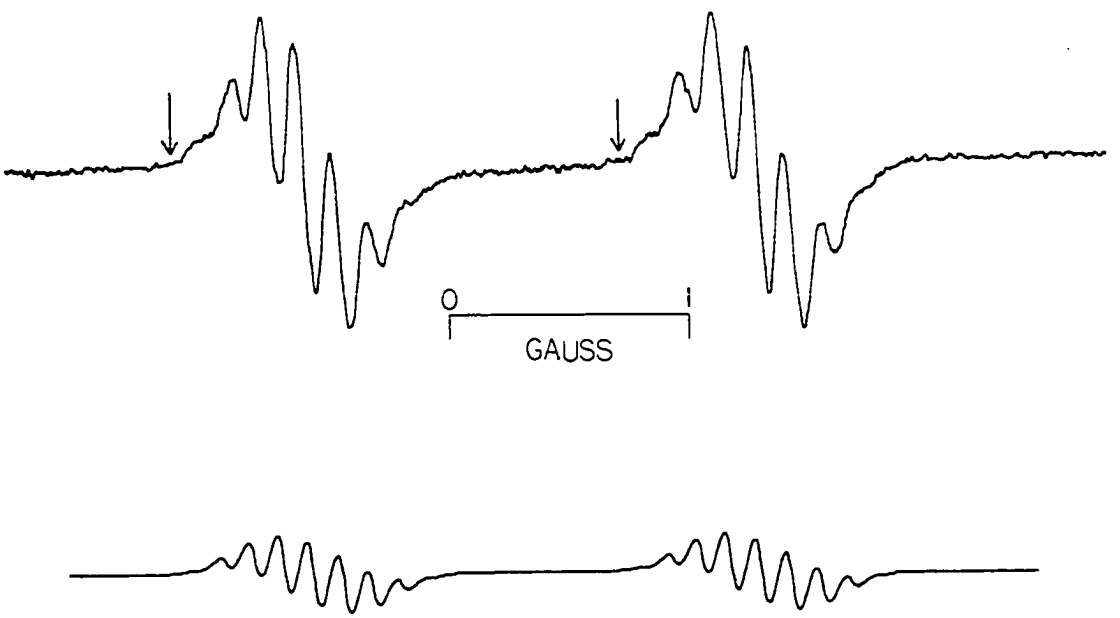
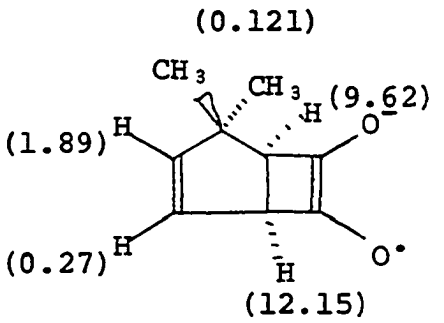


Figure 32. The low field multiplet of the first derivative esr spectrum (top) of 4,4-dimethylbicyclo-[3.2.0]hept-2-en-6,7-semidione (96) in DMSO; calculated spectrum (bottom) for Lorentzian line width 0.14 gauss with splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.



96

gain showed the presence of the intensity one wing peaks (arrows, Figure 32) demanded by this analysis.

The mechanism involving base attack at H-4 (Scheme 39) predicts semidione 96 will be quite stable. In fact, it is the most stable unsaturated [3.2.0] semidione observed in this study. Its intensity was not diminished visibly after 2 days.

EXPERIMENTAL

Reagents

Dimethyl sulfoxide was distilled from CaH_2 at 10-20 mm Hg and used within 1-5 hours of distillation. Potassium t-butoxide was obtained commercially, stored over P_2O_5, and used without purification. Solutions of KOt-Bu in DMSO were considered acceptable if they were perfectly clear or only faintly cloudy. Solvents generally were used as received or stored over 4-A molecular sieves when required dry. Chromium trioxide was stored over P_2O_5.

Preparation of Semidiones

All radicals observed in this study were observed in the apparatus of Figure 33. Dimethyl sulfoxide was distilled into oven dried flasks to a predetermined mark, enough semidione precursor or KOt-Bu was added to make the solution 0.025 M in precursor or 0.05 M in KOt-Bu, the flask was sealed with a septum and N_2 bubbled through for at least 20 minutes. The solution was withdrawn into the syringe and the syringe mounted on a Compact Infusion Pump Model 975 (Harvard Apparatus Co. Inc.). Flow rates were determined by weighing water pumped/time and were found to agree within 2-5% with the values claimed for the pump for 10, 20, and 50 ml syringes. The latex and polyethylene tubing was replaced for each run as were the disposable syringes.

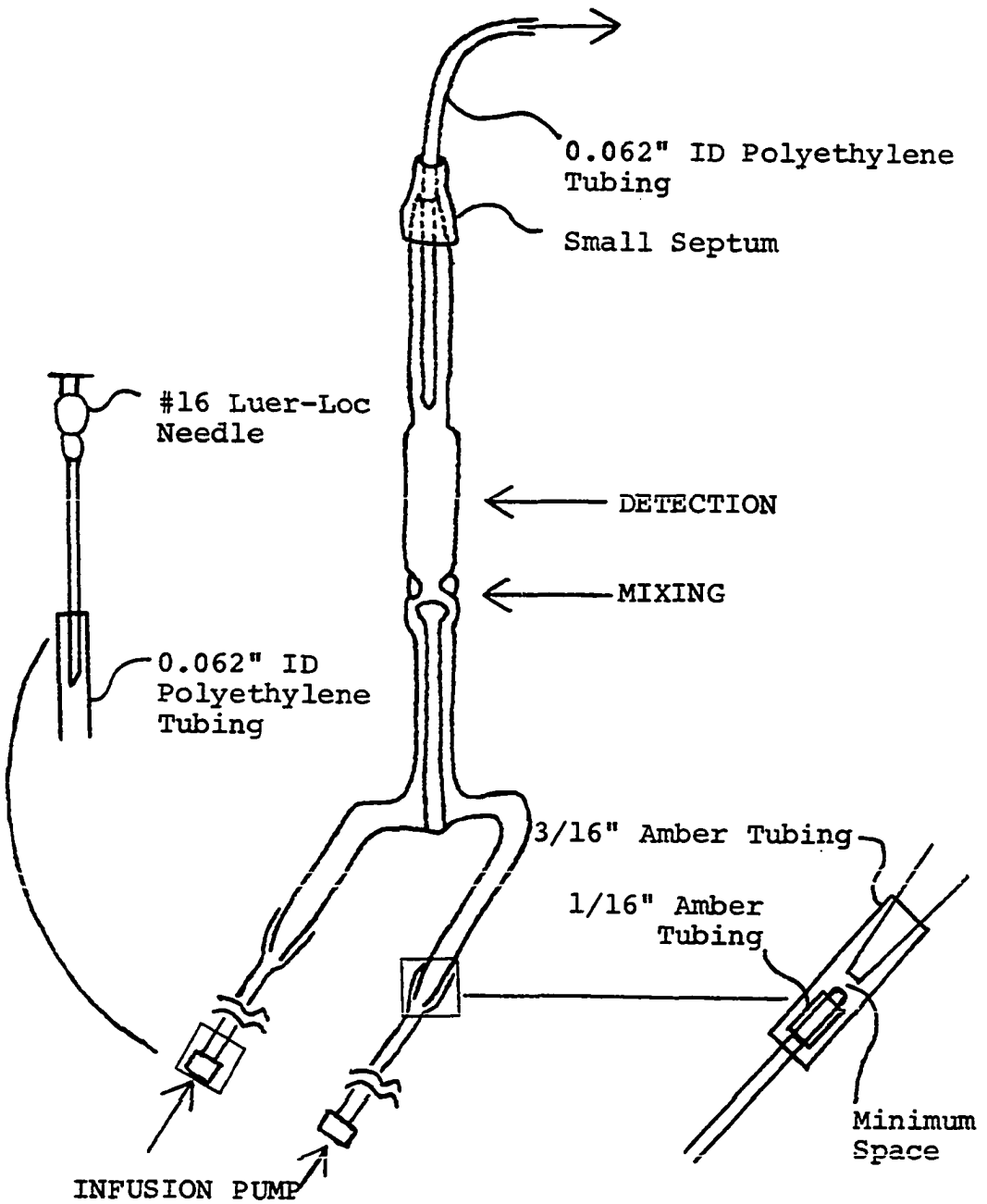


Figure 33. Flow system used for detecting short-lived radicals.

Glass syringes were unusable at very slow flow rates because of erratic leakage past the plunger.

Recording and Simulation of ESR Spectra

The esr spectra were recorded on a Varian E-3 spectrometer (4 inch magnet and 100 KHz field modulation). The esr spectra were simulated on a JNM-RA-1 spectrum accumulator (Japan Electron Optics Company). The program used fit a variable Lorentzian line width to a stick diagram of the spectrum.

Characterization of Compounds

Pmr spectra were recorded on either a Varian A-60 spectrometer or a Perkin Elmer/Hitachi R-20B NMR spectrometer. Chemical shifts were measured in parts per million relative to TMS taken as 0.00 or $CHCl_3$ taken as 7.25. All pmr and ir spectra were obtained in $CDCl_3$ unless noted otherwise. Ir spectra were recorded on a Beckman Model IR-12 Infrared Spectrometer. Mass spectra were obtained on either an Atlas CH4 spectrometer or an AEI-MS-902 spectrometer. Gas chromatographic analysis was performed on either a Beckman GC72-5 or an Aerograph A-90-P chromatograph. Preparative gc was carried out on an F and M Scientific 776 Prepmaster Jr. (Hewlett-Packard). Melting points were uncorrected. Microanalyses were performed by the analyst whose name appears after the analysis.

General Procedures

General procedure for Diels-Alder reactions with vinylene carbonate and dichlorovinylene carbonate

A 125 ml suction flask was sealed at the top and a 4-6 inch piece of heavy walled tubing blown onto the side arm. The flask was charged with diene, vinylene carbonate and 25 g of toluene per 0.10 mole diene. Reactions were carried out on 0.05 mole to 0.10 mole of diene in this apparatus. The side-arm was fitted with a Drierite drying tube, the solution frozen in a Dry Ice-isopropanol bath and the side-arm sealed shut. Rigorous freeze-thaw degassing and drying had no effect on the yield. The flask was then heated in an oil bath for the time and at the temperature specified, cooled to room temperature, the side-arm broken off and the volatile components removed on a rotary evaporator. Further purification was as noted.

General procedure for the preparation of α-benzoyloxy ketones from olefins

The procedure used was similar to that of Scharpe (7). A solution of 0.05 mole of olefin in 40 ml CCl_4 was added dropwise over 20 minutes to a 0° solution of 0.10 mole benzoyl nitrite in 60 ml CCl_4. The mixture was allowed to warm to room temperature, filtered (benzoic acid) and diluted to 300 ml with CCl_4. At this point 50 g of grade III Woelmn

alumina (6% H_2O) were added and the mixture was mechanically stirred and heated at 65-70° until ir showed the disappearance of the $=NNO_2$ band at 1590 cm^{-1}. This generally took 6-15 hours. If the solution was heated at reflux, the hydrolysis took much longer since the H_2O was driven out of the solution and onto the condenser. When all the nitrimine had been hydrolyzed the solution was filtered, the alumina washed with CH_2Cl_2 and the organic solution extracted twice with 60 ml 7% $NaHCO_3$, once with 50 ml saturated NaCl, dried over $MgSO_4$, filtered and the solvent removed in vacuo. Further purification was as noted.

General procedure for the oxidation of alcohols to ketones

The procedure used was essentially that of Ratcliffe and Rodehorst (49) except that the strong acid and strong base extractions used by those authors could not be employed because of the sensitivity of the compounds in this study to acid and base. Thus, 8 mmole of CrO_3 were added to a stirred, Drierite protected solution of 16 mmole dry pyridine in 20 ml dry CH_2Cl_2. After stirring for 20 minutes 1 mmole of the alcohol was added and the solution stirred a further 20 minutes. The solution was decanted, the residue washed with 10 ml CCl_4 and the organic solution washed twice with 10 ml 7% $NaHCO_3$, once with 10 ml H_2O, once with 10 ml sat'd NaCl, dried over $MgSO_4$, filtered, and the solvent

removed *in vacuo*. At this point a solid appeared which was apparently residual chromium salts. The concentrated mixture was dissolved in ether, refiltered, the solvent removed *in vacuo* and the residue immediately purified by column chromatography. If the residue was not purified immediately only intractable tars were obtained from the compounds in this study.

The residue in the reaction flask was conveniently cleaned by dropping in 10-20 NaOH pellets, filling with water and letting stand one hour (in the hood!).

General procedure for the hydrolysis of cyclic carbonates

One gram of the cyclic carbonate was dissolved in 10 ml ether and this solution added to a rapidly stirred solution of one gram KOH in 10 ml water. The two phase system was stirred very rapidly for 1-2 hours at room temperature, the layers separated, and the aqueous layer extracted four times with 10 ml portions of CH_2Cl_2. Drying the organic layers with 10 ml sat'd NaCl, $MgSO_4$, filtering and evaporating the solvent *in vacuo* usually gave a product requiring little further purification.

General procedure for the *in situ* addition of ketenes to cyclopentadienes

The procedure of Brady and Dorsey (50) was used. A solution of 0.09 mole of the acid chloride in 20 ml ether

was added dropwise to a mechanically stirred solution of 1 mole of the cyclopentadiene and 0.095 mole triethylamine (dried over 4A molecular sieves) in 200 ml anhydrous ether at -50° to -60°. The cooling bath was removed, the solution allowed to warm to room temperature and stirred for 3-6 hrs before filtering. Filtration was greatly facilitated by the use of Celite filter aid. Evaporation of the solvent in vacuo followed by distillation gave pure products from chloro or dichloroketene but the adducts from acetoxyketene were always contaminated with an impurity which may have been either acetoxyacetic acid or acetoxyacetic anhydride as evidenced by its pmr absorption at δ 4.6 (s). This impurity as well as the dimerized cyclopentadiene was easily removed by chromatography on silica gel followed by distillation.

Preparation of Compounds

Benzoyl nitrite

By far the major portion of the benzoyl nitrite used in this study was prepared by the method of Pritzkow and Nitzer (51), but since this synthesis involves the tedious and expensive preparation of silver benzoate and the careful use of redistilled nitrosyl chloride a cheaper, easier technique was sought and found. Thus, 48 g (0.33 mole) of USP grade sodium benzoate were placed under 300 ml CCl_4 in

a 500 ml flask equipped with mechanical stirrer, distillation apparatus and N_2 inlet. Approximately 50 ml CCl_4 were distilled off and the flask cooled to -5° (methanol-ice bath). Commercial nitrosyl chloride (Matheson Gas Products) was bubbled directly into the solution through a stainless steel needle until the flask had gained 36 g (1.65 equiv NOCl). The stirred mixture was allowed to warm to 15° over 80 minutes, the contents filtered with suction, the solvent removed in vacuo and the product distilled to give 31.3 g (62%) benzoyl nitrite as a pale yellow solid (receiving flask cooled to Dry Ice temperature to minimize loss): bp 41-42/0.35 mm [Lit. (51). 41-42/0.25 mm]. The yield could probably be greatly improved since no care was taken to eliminate contact with atmospheric water during filtration or transfer.

Warning: Although this author has distilled benzoyl nitrite 9 times without incident, on one occasion when direct sunlight hit the flask a violent explosion occurred.

Exo,3-benzoyloxybicyclo[2.2.1]hept-5-en-2-one (7)

This compound was prepared according to the general procedure for the preparation of α-benzoyloxy ketones from olefins. The crude product from 4.6 g (0.05 mole) norbornadiene was distilled to give 6.0 g (53%) ketone: bp 125-135/0.10 mm [Lit. (7). 85-90/0.07 mm]. After

chromatography on silica gel (4:1 PhH-EtOAc eluant) and recrystallization from 2-propanol-hexane 4.8 g of a pale yellow solid were obtained: mp 72-73 [Lit. (7). Pale green oil]; ir ($CDCl_3$) 1740 and 1275 (benzoate); pmr ($CDCl_3$) δ 7.2-8.3 (m characteristic of benzoates, 5H, $PhCO_2$), 6.6 (d of d, 1H, H-5, J=2Hz, J=4.5Hz), 6.3 (d of d, 1H, H-6, J=4.5Hz, J=2.5Hz), 4.95 (d, 1H, H-3, J=2Hz, irradiating at 2.3 gave s), 3.18 (m, 1H, H-1), 3.08 (m, 1H, H-4), 2.0-2.6 (m, 2H, H-7,syn and anti).

Acetoxyacetic acid

Acetoxyacetic acid was conveniently prepared by adding 480 g acetyl chloride to 200 g of technical glycolic acid (30% H_2O), refluxing for 2 hours and removing the excess acetyl chloride and acetic acid in vacuo. After distillation (through a steam jacketed condenser) there were obtained 110 g (51%) pure white solid: bp 108-112/0.2 mm [Lit. (52). 145/12 mm]; pmr ($CDCl_3$) δ 11.4 (s, 1H, CO_2H), 4.6 (s, 2H, CH_2), 2.18 (s, 3H, CH_3).

Acetoxyacetyl chloride

This compound was prepared by the method of Anschütz and Bertram (52). Thus, 105 g acetoxyacetic acid and 55 g (1.25 equiv.) PCl_3 were heated together at reflux 30 minutes, then the product distilled to give 68.5 g (57%) water white liquid: bp 45-48/9 mm [Lit. (52). 54/14 mm]; pmr ($CDCl_3$) δ 4.7 (s, 2H, CH_2), 2.20 (2, 3H, CH_3).

Exo, and endo,7-acetoxybicyclo[3.2.0]hept-2-en-6-one (20c)

These compounds were obtained by reacting 0.09 mole acetoxyacetyl chloride and one mole freshly cracked cyclopentadiene dimer according to the general procedure. The crude material was chromatographed on 300 g silica gel eluting with benzene then distilled (bp 76-80/0.2 mm) to give 9.3 g (62%) of a pale yellow oil with a pleasantly sweet smell. This oil was easily separated into two components by preparative gc on a 6'x3/4" 7% Carbowax 6000 column at 135°. The minor component [0.32 g (2%) after redistillation] had the shorter retention time (16 minutes) and was the exo isomer as shown by its spectral data: ir ($CDCl_3$) 1796 (cyclobutanone), 1753 and 1228 (acetate), weak 1614 (C=C); pmr ($CDCl_3$) δ 5.8 (s, 2H, CH=CH), 4.82 (t, 1H, H-7, J=3.5Hz), 4.0 (m, 1H, H-5), 3.4 (m, 1H, H-1), 2.6 (m, 2H, CH_2), 2.08 (s, 3H, CH_3); mass spectrum (70 eV) m/e (relative intensity) M^+=166 (not seen), 100(58), 66(100), 65(77), 43(87).

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.05%; H, 6.07%;

Found: C, 65.32%; H, 6.11% (Schwartzkopf).

The major component [6.95 g (46%) after redistillation] had the longer retention time (24 minutes) and was the endo isomer as shown by spectral data: ir ($CDCl_3$) 1791 (cyclobutanone), 1740 and 1230 (acetate), weak 1609 (C=C); pmr ($CDCl_3$) δ 5.5-6.0 (m - d superimposed on m, 3H, H-2,

H-3 and H-7, exo, irradiating at 3.6 gave s from the 5.5Hz d), 3.5-4.0 (m, 2H, H-1 and H-5), 2.55 (m, 2H, CH_2), 2.03 (s, 3H, CH_3); mass spectrum (70 eV) m/e (relative intensity) M^+=166 (not seen), 100(55), 66(100), 65(84), 43(95).

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.05%; H, 6.07%;

Found: C, 65.24%; H, 6.16% (Schwartzkopf).

The pmr spectra show the expected upfield shift of H-7 in going from the endo to the exo acetate and a smaller opposite shift in the acetate methyl.

Endo,7-chlorobicyclo[3.2.0]hept-2-en-6-one (20d)

This compound was prepared in 40% yield from 0.09 mole chloroacetylchloride (Aldrich) and one mole freshly cracked cyclopentadiene as described in the general procedure. It was obtained as a nearly colorless oil: bp 57/0.06 mm [Lit. (50). 57/0.10 mm].

7,7-Dichlorobicyclo[3.2.0]hept-2-en-6-one (20e)

This compound was prepared in 60% yield from 0.09 mole dichloroacetylchloride (Aldrich) and one mole freshly cracked cyclopentadiene as described in the general procedure. It was obtained as a colorless oil: bp 50/1 mm [Lit. (46). 38/0.25 mm].

Tetrachloroethylene carbonate

This compound was prepared by the method of Holland (6) in 86% yield: bp 68/69.5/22 mm [Lit. (26). 40/6 mm].

exo,7-Methylthiobicyclo[3.2.0]hept-2-en-6-one (29)

To 3.0 g (0.043 mole) NaSMe in 100 ml THF at 0° under nitrogen were added 5.0 g (0.035 mole) chloroketone 20d in 10 ml THF. After 2 hours at 0° the magnetically stirred mixture was stored overnight at -20°, allowed to warm to room temperature and four teaspoonfuls of Celite added to the mixture to facilitate filtration of the gummy solid. After filtration and evaporation of solvent in vacuo the product was chromatographed on 175 g silica gel (1:1 PhH-hexane eluant) to give first 0.78 g recovered ketone 20d (after distillation) and 2.96 g (55%) of a foul smelling yellow oil (29): bp 88-94/0.08 mm; ir (neat) 1788 (cyclobutanone), 1437 and 1346 (moderate); pmr (CCl_4) δ 5.8 (s, 2H, H-2 and H-3), 3.4 (m, 3H, H-1, H-4, H-7, endo), 2.6 (m, 2H, CH_2), 2.11 (s, 3H, CH_3S); mass spectrum (16 eV) m/e (relative intensity) M^+ = 154(5), 88(60), 66(100); high resolution mass spectrum,

Calcd. for $C_8H_{10}SO$: 154.045; Found: 154.047

Calcd. for C_5H_6: 66.047; Found: 66.051

Calcd. for C_3H_4SO: 87.998; Found: 88.000.

This compound did not give a satisfactory combustion analysis. Sodium fusion indicated the presence of a considerable amount of halogen containing compound.

exo,7-Methylsulfinylbicyclo[3.2.0]hept-2-en-6-one (32)

To a solution of 7.31 g (0.047 mole) ketone 29 in 200 ml $CHCl_3$ at -60° were added 8.9 g (0.93 equiv) 85%

m-chloroperbenzoic acid (Aldrich) in 100 ml $CHCl_3$ at such a rate that the mechanically stirred solution did not rise above -50° during the addition. After stirring 2 hours at -60° the mixture was warmed to room temperature, filtered, washed three times with 50 ml portions 7% $NaHCO_3$, once with 40 ml sat'd NaCl, dried over $MgSO_4$, filtered, and evaporated *in vacuo* to give 7 g of a pale yellow oil. Recrystallization from hot CCl_4 gave 1.95 g (27%) white crystals (32): mp 79-81; ir (neat) 1783 (cyclobutanone), 1060 (S=O); pmr ($CDCl_3$) δ 5.72 (s, 2H, CH=CH), 3.6-3.9 (m, 3H, H-1, H-4, H-7, *endo*), 2.62 and 2.5-2.69 (s superimposed on m, 5H, CH_3SO and CH_2).

Anal. Calcd. for $C_8H_{10}SO_2$: C, 55.78%; H, 7.02%; S, 18.61%;
Found: C, 55.89%; H, 7.00%; S, 18.43% (Schwartzkopf).

7-Methylthio-7-hydroxybicyclo[3.2.0]hept-2-en-6-one (33)

A solution of 1.00 g (0.0059 mole) sulfoxide 32 in 2 ml DMSO was diluted with 15 ml H_2O and 2 ml concentrated HCl were added dropwise. The mixture was allowed to stand overnight at room temperature. A yellow oil had separated. The DMSO solution was diluted with 5 ml H_2O and extracted 3 times with 15 ml portions Et_2O. The Et_2O extracts were combined, washed with H_2O, dried over $MgSO_4$ and evaporated *in vacuo* to give 0.63 g (63%) of a pale yellow oil which decomposed on attempted vacuum distillation: ir (CCl_4) 1793 (cyclobutanone), 3590 (OH); pmr ($CDCl_3$) δ 5.5-6.0 (m, 2H, CH=CH), 3.4-4.3 (m, 2H, H-1 and H-4), 2.4-2.7 (m, 3H, CH_2, OH, goes to 2H on addition of D_2O), 2.23 and 2.12 (2s, 3H, CH_3S-*exo* and *endo*); mass spectrum (70 eV) *m/e* (relative intensity) M^+ = 170(4), 104(40), 66(100).

Dichlorovinylene carbonate

This compound was prepared in 85% yield by the method of Holland (6): bp 65-70/30 mm [Lit. (26). 65-70/35 mm].

Exo,cis,5,6-dichlorobicyclo[2.2.1]hept-2-en-5,6-diol carbonate (37)

This compound was prepared by heating 6.6 g (0.10 mole) technical dicyclopentadiene (Baker) and 5.0 g (0.032 mole) dichlorovinylene carbonate for 24 hours at 160° as described in the general procedure. The crude product was chromatographed on 200 g silica gel eluting with benzene and the crude product so obtained was sublimed at 50/12 mm to give 2.7 g (28%) of a white solid: mp 145-146 [Lit. (26). 147].

Bicyclo[2.2.1]hept-5-en-2,3-dione (38)

Hydrolysis of 2.7 g (0.012 mole) carbonate 37 by the general procedure followed by continuous ether extraction gave 1.6 g crude α-diketone 38 which could be distilled, bp 45/2 mm, to give an orange oil whose pmr spectrum was as reported by Scharf et al. (26): pmr ($CDCl_3$) δ 6.45 (t, 2H, CH=CH), 3.2 (q, 2H, H-1 and H-4), 2.9 and 2.5 (AB, 2H, H-7, syn and H-7,anti).

Endo,cis-bicyclo[2.2.1]hept-5-en-2,3-diol carbonate (40)

This compound was prepared as described in the general procedure for Diels-Alder reactions with vinylene carbonate.

Thus, 7.0 g (0.053 mole) technical dicyclopentadiene, 8.6 g (0.10 mole) vinylene carbonate (Aldrich) and 34 g toluene were heated 12 hours at 165° to give 9.5 g (63%) of a white solid after recrystallizing from 70 ml ether and 200 ml cyclohexane: mp 113-113.5 [Lit. (28). 113.2-113.5].

Endo,cis-bicyclo[2.2.1]hept-5-en-2,3-diol (41)

This compound was obtained by hydrolysis of carbonate 40 by the general procedure in 70% yield as a white solid after recrystallizing from 300 ml hexane/8 g starting carbonate 40: mp 168-170 [Lit. (28). 201]. Although the melting point was lower than that reported by Kwart and Vosburgh (28) it compared well with the value of 176° given by Pattan (53) and the pmr spectrum of diol 41 was as reported by Thorpe and Coburn (54).

Endo,cis,3-benzoyloxybicyclo[2.2.1]hept-5-en-2-ol

This compound was prepared by heating a mixture of 2.08 g (16.5 mmole) diol 41, 3.48 g (25 mmole) benzoyl chloride and 1.96 g (25 mmole) pyridine in 150 ml benzene at reflux 17 hours. The mixture was filtered, evaporated in vacuo, chromatographed on 150 g silica gel eluting with 4:1 PhH-EtOAc, and distilled to give 2.62 g (69%) of a clear white glass: bp 128-133/0.21 mm; ir ($CDCl_3$) 3590(OH), 1724 and 1280 (benzoate) and 1121 (strong); pmr ($CDCl_3$) δ 7.3-8.1 (m characteristic of benzoates, 5H,

$PhCO_2$), 6.35 (m, 2H, CH=CH), 5.30 (d of d, 1H, CHOBz, J=7Hz, J=3.5Hz), 4.45 (d of d, 1H, CHOH, J=7Hz, J=3.5Hz), 3.2 (m, 2H, H-1 and H-4), 2.2 (s, 1H, OH), 1.6 (d of t, 1H, H-7, syn, J=10Hz, J=2Hz), 1.35 (d of m, 1H, H-7, anti, J=10Hz); mass spectrum (16 eV) m/e (relative intensity) M^+=230(1), 164(35), 108(80), 105(100+), 77(100).

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.02%; H, 6.19%;
Found: C, 72.80%; H, 6.04% (Chemalytics).

Endo,3-benzoyloxybicyclo[2.2.1]hept-5-en-2-one (42)

This compound was prepared in 74% yield by oxidation of 2.4 g of the corresponding alcohol according to the general procedure followed by chromatography on 140 g silica gel (4:1 PhH-EtOAc eluant) and distillation. The product was obtained as a yellow oil which slowly deposited crystals over several days: bp 160-180/0.15 mm; mp 34-36; ir ($CDCl_3$) 1770 (cyclopentanone), 1731 and 1278 (benzoate), 1130 (sharp, strong); pmr ($CDCl_3$) δ 7.2-8.1 (m characteristic of benzoates, 5H, $PhCO_2$), 6.5 (d of d, 1H, H-5, J=5.5Hz, J= 2.5Hz, irradiating at 3.4 gave 5.5Hz d), 6.3 (d of m, 1H, H-6, J=5.5Hz, irradiating at 3.4 gave 5.5 Hz d), 5.3 (d, 1H, CHOBz, J=4Hz, irradiating at 3.4 gave s), 3.3 (pair of m, 2H, H-1 and H-4), 2.3 (d of d of d, 1H, H-7,syn or anti, J=10Hz, irradiating at 3.4 gave 10Hz d), 2.1 (d of m, 1H, H-7,syn or anti, J=10Hz, irradiating at 3.4 gave 10Hz d);

mass spectrum (16 eV) m/e (relative intensity) M^+=228(2), 105(100), 77(46), 51(13).

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.67%; H, 5.31%;
Found: C, 73.69%; H, 5.30% (Chemalytics).

Endo,cis,3-acetoxybicyclo[2.2.1]hept-5-en-2-ol

A solution of 2.65 g (0.021 mole) diol 41 and 2.14 g (0.021 mole) acetic anhydride in 100 ml dry benzene was heated at reflux 10 hours, cooled to room temperature, washed twice with 20 ml portions 7% $NaHCO_3$, once with 15 ml sat'd NaCl, dried over $MgSO_4$, filtered, and evaporated in vacuo. The residue was purified by gc on a 6'x3/4" 7% Carbowax 6000 column at 140° to give 1.52 g (43%) of a water white liquid: ir ($CDCl_3$) 3590(OH), 1737 and 1252 (acetate); pmr ($CDCl_3$) δ 6.3 (t, 2H, HC=CH, J=2Hz), 5.0 (d of d, 1H, CHOAc, J=6Hz, J=4Hz), 4.4 (broadened d of d, 1H, CHOH, J=4Hz, J=6Hz), 3.1 (m, 2H, H-1 and H-4), 2.07 (s, 3H, CH_3CO_2), 1.8 (broad s, 1H, OH), 1.6 (d of t, 1H, H-7, syn, J=10Hz, J=2.5Hz), 1.3 (d of m, 1H, H-7, anti, J=10Hz); mass spectrum (70 eV) m/e (relative intensity) M^+=168 (small), 102(26), 66(25), 43(100).

Anal. Calcd. for $C_9H_{12}O_3$: C, 64.27%; H, 7.19%;
Found: C, 64.13%; H, 7.11% (Chemalytics).

Endo,3-acetoxybicyclo[2.2.1]hept-5-en-2-one (43)

This compound was prepared in 60% yield, after chromatography (150 g silica gel, 4:1 PhH-EtOAc eluant) and distillation, by oxidation of the corresponding alcohol by the general procedure: bp 70-71/0.5 mm; ir ($CDCl_3$) 1765 (cyclopentanone), 1745 and 1250 (acetate), 1077 (strong); pmr ($CDCl_3$) δ 6.5 (d of d, 1H, H-5, J=3Hz, J=5.5Hz, irradiating at 3.22 gave 5.5Hz d), 6.2 (m, 1H, H-6, irradiating at 3.22 gave 5.5Hz d), 5.1 (d, 1H, CHOAc, J=3.5 Hz, irradiating at 3.22 gave s), 3.22 (m, 2H, H-1 and H-4), 2.09 (s, 3H, CH_3CO_2), 1.9-2.4 (m, 2H, H-7 syn and H-7 anti); mass spectrum (70 eV) m/e (relative intensity) M^+=166(3), 124(11), 66(21), 43(100).

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.05%; H, 6.07%;
Found: C, 63.24%; H, 6.04% (Chemalytics).

Endo,cis,2-hydroxy-3-bicyclo[2.2.1]hept-5-enyl α-tetrahydropyranyl ether

This compound could be produced in tolerable yield only by a process involving recycling. Thus, 3.1 g diol 41, 2.1 g dihydropyran (Eastman) and 10 ml dry ether were cooled to -40° and 60 μ l. conc. HCl added. The cooling bath was removed and the solution allowed to warm to 15° whereupon 0.35 g K_2CO_3, 10 ml sat'd NaCl and 60 ml ether were added. The layers were separated and the ether layer dried over $MgSO_4$, filtered, and concentrated in vacuo to give a

semisolid which was recrystallized from 125 ml hexane to give 1.9 g recovered diol 41. The mother liquor was set aside and the diol 41 reacted with more dihydropyran as above. Recrystallizing again gave some (0.7 g) recovered diol 41. The mother liquors were combined and evaporated in vacuo to give an oil which was chromatographed on 150 g silica gel (4:1 PhH:EtOAc eluant) to give 0.61 g diol 41 (after recrystallization) and 1.39 g (33% based on 1.3 g recovered diol) (after distillation) mono THP derivative: bp 100-105/0.09 mm; ir ($CDCl_3$) 3540(OH), 1038 (C-O-C); pmr ($CDCl_3$) peaks are broad and some have nonintegral areas, presumably because the product is a mixture of diastereomers due to the asymmetric carbon in the dihydropyran, δ 6.2 (m, 2H, HC=CH), 4.65 (m, 1H, OCHO), 4.2 (m, 2H, CHOTHP and CHOH), 3-4 (m, about 4H, H-1, H-4, and CH_2O), 1.6 (m, about 7H, OH, $CH_2CH_2CH_2$), 1.2-1.5 (m, about 2H, H-7, syn and H-7, anti); mass spectrum (70 eV) m/e (relative intensity) M^+=208 (weak), 84(100), 66(80), 67(71), 55(65).

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.54%; H, 8.62%;
Found: C, 68.72%; H, 8.55% (Chemalytics).

Endo,3-bicyclo[2.2.1]hept-5-en-2-onyl α-tetrahydropyranyl ether (44)

This compound was obtained in 81% yield by oxidation of 1.39 g of the corresponding alcohol according to the general procedure followed by chromatography on 60 g

silica gel (PhH eluant) and distillation: bp 100/0.10 mm; ir ($CDCl_3$) 1764 (cyclopentanone), 1139, 1082, 1041 (sharp, strong); pmr ($CDCl_3$) δ 6.58 and 6.47 (slightly overlapping pair of d of d, 1H, H-5, irradiating at 3.1 gave a pair of 5.5Hz d), 6.13 (m, 1H, H-6, irradiating at 3.1 gave a pair of 5.5Hz d), 4.8 (m, 1H, OCHO), 3.3-4.3 (pair 3.5Hz d at 4.01 and 4.14 superimposed on broad envelope, 3H, diastereomeric CHOTHP and CH_2O, irradiating at 3.1 gave s at 4.01 and s at 4.14), 3.1 (m, 2H, H-1 and H-4), 2.4 (d of q, 1H, H-7, anti, J=10Hz), 1.4-2.0 (envelope, 8H-should be 7H, $CH_2CH_2CH_2$, H-7, syn); mass spectrum (16 eV) m/e (relative intensity) M^+=224 (not seen), 67(31), 55(39).

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.20%; H, 7.74%.

Found - sample one: C, 66.95%; H, 7.75%;

Found - sample two: C, 69.02%; H, 7.40% (Chemalytics).

Endo,3-hydroxybicyclo[2.2.1]hept-5-en-2-one (45)

This alcohol could not be liberated from its THP derivative (44) by the usual 3:1:1 HOAc:THF:H_2O solution (29) so more drastic conditions were resorted to. Thus, 1.11 g of the THP 44 were dissolved in 40 ml ether and stirred vigorously in contact with 6 ml 5% HCl for 8 minutes at room temperature. The ether was washed once with 10 ml sat'd NaCl, dried over $MgSO_4$, filtered and evaporated in

vacuo to give 400 mg of a tarry residue which was chromatographed on 90 g silica gel (3:1 PhH-EtOAc eluant). The major component was fractionally sublimed (80-90°/0.1 mm) to the cold finger of a Hickmann still to give 75 mg (11%) of a white solid: mp 68-74; ir ($CDCl_3$) 1757 (cyclopentanone), 1072 (prominent); pmr ($CDCl_3$) δ 6.6 (d of d, 1H, H-5, J=3Hz, J=5.5Hz, irradiating at 3.15 gave 5.5Hz d), 6.1 (m, 1H, H-6, irradiating at 3.15 gave 5.5Hz d of m), 4.1 (d, 1H, CHOH, J=4Hz, irradiating at 3.15 gave s), 3.6 (s, 1H, OH), 3.15 (m, 2H, H-1 and H-4), 2.3 (d of t, 1H, H-7,syn or anti, J=10Hz, J=1.5Hz), 2.0 (d of broad s, 1H, H-7,syn or anti, J=10Hz), 1.6 (m, 0.2H, impurity); high resolution mass spectrum, calcd. for $C_7H_8O_2$: 124.052; found: 124.050.

t-Butyldimethylchlorosilane

This compound was prepared by the method of Corey and Venkateswarlu (29) in 61% yield after room temperature, atmospheric pressure sublimation: mp 90-92 [Lit. (29). 92.5].

Endo,cis,2-hydroxy-3-t-butyldimethylsiloxybicyclo[2.2.1]-hept-5-ene

This compound was prepared by Corey's method (29) for preparation of silyl ethers. Thus, 2.86 g (22.6 mmole) diol 41, 4.26 g (27.1 mmole) t-butyldimethylchlorosilane and 3.84 g (56.5 mmole) imidazole were weighed into 25 ml DMF, stirred at room temperature until TLC showed no more

diol (5 hours), and the solution poured into 60 ml H_2O. The water was extracted 3 times with 50 ml portions of CH_2Cl_2 and the CH_2Cl_2 washed with 50 ml H_2O, 50 ml sat'd NaCl, dried over $MgSO_4$, filtered, evaporated *in vacuo*, and the residue chromatographed on 330 g silica gel (5:1 PhH-EtOAc eluant) to give 3.85 g (72%) (after distillation) of a water white liquid: bp 60-69/0.13; ir ($CDCl_3$), 1122 (Si-O-C), 1150 (C-O), 1261, 860, 2940 (prominent), 3510 (medium intensity, bonded OH), 3680 (weak, unbonded OH); pmr ($CDCl_3$) δ 6.1 (nearly collapsed AB, 2H, CH=CH), 4.1 (m, 2H, CHOH and CHOSiMe$_2$tBu), 2.9 (d superimposed on m, 3H, H-1, H-4, and OH, J=6.5Hz, d disappeared on addition of D_2O), 1.4 (d of t, 1H, H-7, *anti*, J=10Hz), 1.1 (d, 1H, H-7, *syn*, J=10Hz), 0.9 (s, 9H, tBu), 0.14 (s, 6H, $(CH_3)_2Si$); mass spectrum (16 eV) m/e (relative intensity) M^+=240 (not seen), 75(100), 117(78).

Anal. Calcd. for $C_{13}H_{24}O_2Si$: C, 64.94%; H, 10.06%, Si, 11.68%; Found: C, 64.72%; H, 10.00%; Si, 11.54% (Spang).

Endo,3-t-butyldimethylsiloxybicyclo[2.2.1]hept-5-en-2-one (46)

Oxidation of 3.40 g of the corresponding alcohol by the general procedure followed by chromatography on 205 g silica gel (PhH eluant) and distillation gave ketone 46 as a water white liquid in 57% yield: ir ($CDCl_3$) 1757

(cyclopentanone), 1133 (Si-O-C); pmr ($CDCl_3$) δ 6.5 (d of d, 1H, H-5, J=5Hz, J=3Hz), 6.1 (m, 1H, H-6), 4.0 (d, 1H, CHOSi, J=4Hz), 3.1 (m, 2H, H-1 and H-4), 2.3 (d of t, 1H, H-7,anti or syn, J=10Hz, J=2Hz), 1.9 (d, 1H, H-7,syn or anti, J=10Hz), 1.0 (s, 9H, t-Bu), 0.2 (s, 6H, $(CH_3)_2Si$); mass spectrum (16 eV) m/e (relative intensity) M^+=238 (not seen), 181(29), 151(64), 75(100), 73(28).

Anal. Calcd. for $C_{13}H_{22}O_2Si$: C, 65.49%; H, 9.30%; Si, 11.78%; Found: C, 65.35%; H, 9.18%; Si, 11.70% (Spang).

Benzonorbornadiene

This compound was prepared from bromofluorobenzene, cyclopentadiene, and magnesium in 61% yield by the method of Wittig and Knauss (55): bp 86-88/14 mm [Lit. (56). 82-83/12 mm].

Exo,3-benzoyloxybenzobicyclo[2.2.1]hepten-2-one

Addition of a solution of benzonorbornadiene in CCl_4 to a solution of benzoyl nitrite in CCl_4 followed by hydrolysis according to the general procedure gave a yellow oil. Chromatography of 8 g of this oil on 300 g silica gel (PhH eluant) followed by crystallization from ether gave a 38% yield of large white transparent crystals: mp 141-142; ir ($CDCl_3$) 1773 (cyclopentanone), 1731 and 1280 (benzoate), 1117 (moderate), pmr ($CDCl_3$) δ 7.9 (m

characteristic of ortho protons of a benzoate, 2H), 7.0-7.5 (m, 7H, aromatic), 4.87 (d, 1H, CHOBz, J=2.5Hz, irradiating at 2.49 gave s), 3.6 and 3.7 (m, 2H, H-1 and H-4), 2.5 (m, 2H, CH_2); mass spectrum (70 eV) m/e (relative intensity M^+=278 (weak), 51(62), 77(100), 115(67), 116(77), 117(74), 128(68), 156(76).

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.68%; H, 5.07%;
Found: C, 77.48%; H, 4.96% (Chemalytics).

Endo, and exo,7-acetoxy-3-methylbicyclo[3.2.0]hept-2-en-6-one (59) and endo,7-acetoxy-1-methylbicyclo[3.2.0]hept-2-en-6-one (60)

These compounds were obtained by reacting 0.09 mole acetoxyacetyl chloride and one mole of freshly cracked methylcyclopentadiene dimer (a mixture of about 1:1 1- and 2-methylcyclopentadiene) according to the general procedure. The crude material was chromatographed on 400 g silica gel (PhH eluant) then distilled (bp 79-84/0.10 mm) to give 13.3 g (82%) of a pale yellow oil which was separated into three components in 53% overall yield (after redistillation) by preparative gc on a 6'x3/4" 7% Carbowax 6000 column at 148°. The fastest component eluted (retention time 12 minutes) was endo acetate 60 of which 0.78 g (5% overall yield) were obtained: ir (neat) 1799 (cyclobutanone), 1755 and 1230 (acetate), 1618 (weak, C=C); pmr ($CDCl_3$) δ 5.7 (m, 2H, olefinic), 5.58 (d, 1H, H-7, exo, J_{57}=3Hz), 3.20 (m, 1H, H-5, J_{57}=3Hz, $J_{5\,4exo}$=6.5Hz,

$J_{5,4\underline{endo}}$=3.0Hz), 2.6 (m, 2H, CH_2), 2.09 (s, 3H, CH_3CO_2), 1.60 (s, 3H, CH_3C).

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65%; H, 6.71%;
Found: C, 66.86%; H, 6.70% (Chemalytics).

The second component eluted (retention time 21 minutes) was exo acetate 59 of which 0.35 g (2% overall yield) were obtained after redistillation: ir (neat) 1787 (cyclobutanone), 1748 and 1225 (acetate), 1648 (weak, C=C); pmr ($CDCl_3$) the multiplets for H-1, H-5, H-7 and CH_2 are superimposable on the respective multiplets of exo acetate 20c, δ 5.4 (m, 1H, H-2), 4.82 (t, 1H, H-7, endo, J=3.5Hz), 3.8-4.2 (m, 1H, H-5), 3.2-3.5 (m, 1H, H-1), 2.5 (m, 2H, CH_2), 2.07 (s, 3H, CH_3CO_2), 1.74 (m, 3H, CH_3); high resolution mass spectrum, calcd. for $C_{10}H_{12}O_3$: 180.078; found: 180.079. The third component eluted (retention time 31 minutes) was endo acetate 59. After redistillation 7.5 g (46% overall yield) were obtained: ir (neat) 1804 (cyclobutanone), 1749 and 1231 (acetate); pmr ($CDCl_3$) δ 5.6 (d of d, 1H, H-7, exo, $J_{7,1}$=7.7Hz, $J_{7,5}$=3.1Hz), 5.1 (m, 1H, H-2), 3.3-2.8 (m, 2H, H-1 and H-5), 2.4 (m, 2H, CH_2), 2.09 (s, 3H, CH_3CO_2), 1.80 (broad s, 3H, CH_2); mass spectrum (70 eV) m/e (relative intensity) M^+=180(3), 80(100), 100(50), 43(90).

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65%; H, 6.71%;
Found: C, 66.43%; H, 6.70% (Chemalytics).

5-Methyl-1,3-cyclopentadiene

This compound was prepared in 62% yield by the method of McLean and Haynes (56), was distilled at 0°/6 mm, and was kept at all times below 0°. Its ir spectrum was identical to that in the literature (56).

Endo, and exo,7-acetoxy-3-methylbicyclo[3.2.0]hept-2-en-6-one (59) free of the 1-methyl isomer 60

A -10° solution of 55 g (0.69 mole) 5-methyl-1,3-cyclopentadiene in 50 ml ether was added to 9.54 g (0.0945 mole) triethylamine in 200 ml ether at -55° then reacted with 12.3 g (0.09 mole) acetoxyacetyl chloride according to the general procedure. After chromatography on 350 g silica gel (PhH eluant) and distillation (bp 84-85/0.30 mm) 9.1 g (56%) of a mixture of endo and exo acetates 59 were obtained in a 96:4 ratio containing no acetate 60 detectable by gc. Acetates 59 were identified by comparison of their ir and pmr spectra and gc retention times with authentic samples prepared above.

Mixture 1- and 5-methyl-endo,cis-bicyclo[2.2.1]hept-5-en-2,3-diol carbonate (64)

Ten grams (0.115 mole) vinylene carbonate and 11 g (0.069 mole) technical methylcyclopentadiene dimer were heated 16 hours at 170° as described in the general procedure. After distillation 17 g (86%) of a pale yellow liquid were obtained: bp 103-106/0.15 mm; ir ($CDCl_3$)

1830 (cyclic carbonate), 1652 (weak, C=C), 1180 and 1110 (C-O). Since no method of separation could be found, this material was used without further characterization to form diols 65 and 66.

1-Methyl-endo,cis-bicyclo[2.2.1]hept-5-en-2,3-diol (65) and 5-methyl-endo,cis-bicyclo[2.2.1]hept-5-en-2,3-diol (66)

The mixture of crude carbonate 64 was hydrolyzed according to the general procedure to give a yellow oil in 91% yield. This oil was easily separated into two components by gc on a 6'x3/4" 7% Carbowax 6000 column at 140°. The first component eluted was 1-methyl diol 65 (retention time 16 minutes). It was obtained in 21% overall yield after recrystallizing from hexane: mp 54.5-55.5; ir ($CDCl_3$) 3590(OH); pmr ($CDCl_3$) δ 6.2 (d of d, 1H, H-5, J=7Hz, J=3Hz), 6.0 (d, 1H, H-6, J=7Hz), 3.7 (m, 1H, H-3, addition of D_2O gave 7.5Hz d), 4.2 (m, 1H, H-2, addition of D_2O gave 7.5Hz and 4.5Hz d of d), 2.9 (m, 1H, H-4), 2.4 (m, 2H, OH), 1.6 (d of m, 1H, H-7, anti, J=10Hz), 1.3 (s, 3H, CH_3C), 1.1 (d of m, 1H, H-7, syn); mass spectrum (70 eV) m/e (relative intensity) M^+=140(8), 80(100), 81(100).

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54%; H, 8.58%;

Found: C, 68.50%; H, 8.37% (Chemalytics).

The second component eluted (retention time 21 minutes) was the 5-methyl diol 66. It was obtained as a yellow oil

in 41% overall yield: ir ($CDCl_3$) 3590(OH); pmr ($CDCl_3$) δ 5.75 (broad s, 1H, CH=C), 4.2 (broad s, 2H, CHOH), 2.35 (s, 2H, OH), 2.8 (m, 2H, H-1 and H-4), 1.5 (d of t, 1H, H-7, anti, J=10Hz, J=1Hz, irradiating at 2.8 gave 10Hz d), 1.11 (d of t, 1H, H-7, syn, J=10Hz, J=2.5Hz, irradiating at 2.8 gave 10Hz d); mass spectrum (16 eV) m/e (relative intensity) M^+=140(5), 80(100), 81(90).

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54%; H, 8.58%;

Found: C, 68.62%; H, 8.61% (Chemalytics).

Mixture of 1- and 4-methyl-endo,3-acetoxybicyclo[2.2.1]-hept-5-en-2-one (67a), pure 5-methyl-endo,3-acetoxy-bicyclo[2.2.1]hept-5-en-2-one (68a), and pure 6-methyl-endo,3-acetoxybicyclo[2.2.1]hept-5-en-2-one (69a)

These compounds were prepared by monoacetylation, oxidation, and gc separation of the mixture of diols 65 and 66 obtained on hydrolysis of carbonates 64. Thus, to 7.5 g of the crude mixture of diols 65 and 66 in 125 ml benzene were added 6.0 g (1.1 equiv) acetic anhydride and the solution heated at reflux 6 hours. After cooling the solution was diluted with ether, washed twice with 50 ml portions of 7% $NaHCO_3$, once with 60 ml sat'd NaCl, dried over $MgSO_4$, filtered, evaporated in vacuo and pumped on at 0.5 mm for 2½ hours (until the odor of Ac_2O was gone). Chromatography on 360 g silica gel (3:1 hexane-EtOAc eluant) followed by distillation (bp 65-72/0.07 mm) gave 2.56 g of a white liquid presumed to be the mixture of

monoesters plus 1.75 g (33%) recovered diols 65 and 66. The presumed mixture of monoesters was oxidized according to the general procedure to give, after chromatography on 150 g silica gel (5:1 hexane-EtOAc eluant) and after distillation (bp 75-85/0.18 mm), 1.89 g of the mixture of ketones 67a, 68a and 69a. No method of separating the bridgehead methyl ketones (67a) from each other was found, but preparative gc on a 9'x3/4" 7% Carbowax 6000 column at 145° easily separated ketones 67a, 68a, and 69a from each other. The first component eluted (retention time 12 minutes) was the mixture of bridgehead methyl ketones 67a. Since gc showed about 5% of the second component present in the first eluate, it was rechromatographed then distilled to give 0.36 g (5% overall from diol) of a water white liquid (67a): bp 75/0.18 mm; ir ($CDCl_3$) 1765 (cyclopentanone and acetate), 1248 (acetate); pmr ($CDCl_3$) δ 5.7-6.4 (m, 2H, CH=CH), 5.0 (s off center in d, 1H, CHOAc), 3.1 (m, 1H, H-1 or H-4), 2.0-2.4 (s superimposed on m, 5H, CH_3CO_2, CH_2, s at 2.07); mass spectrum (70 eV) m/e (relative intensity) M^+=180(4), 80(90), 43(100).

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65%; H, 6.71%;

Found: C, 66.47%; H, 6.82% (Chemalytics).

The second component eluted (retention time 14.9 minutes) was the 6-methyl ketone 69a. After this eluate was rechromatographed and distilled, 0.85 g (11% overall from diol) were obtained: bp 70/0.15 mm; ir ($CDCl_3$)

1765 (cyclopentanone and acetate), 1250 (acetate); pmr ($CDCl_3$) δ 5.80 (m, 1H, H-5), 4.90 (d, 1H, C<u>H</u>OAc, J=4Hz, irradiating at 2.9 gave s), 2.9 (m, 2H, H-1 and H-4), 1.99 (s, 3H, CH_3CO_2), 1.8 (d, 1H, CH_3C=C, J=1.8Hz, irradiating at 5.8 gave s), 1.9-2.3 (m, 2H, CH_2); mass spectrum (70 eV) <u>m/e</u> (relative intensity) M^+=180(4), 80(60), 43(100).

<u>Anal</u>. Calcd. for $C_{10}H_{12}O_3$: C, 66.65%; H, 6.71%;
Found: C, 66.78%; H, 6.78% (Chemalytics).

The third component eluted (retention time 16.6 minutes) was the 5-methyl ketone 68a. It was obtained as 0.41 g (6% overall from diol) of a white solid after sublimation at 60/0.15 mm: mp 60-71. It was contaminated with about 10% of ketone 69a. It gave the following spectral data: ir ($CDCl_3$) 1760 (cyclopentanone and acetate), 1245 (acetate); pmr ($CDCl_3$) δ 5.60 (m, 1H, H-6), 5.0 (d, 1H, C<u>H</u>OAc, J=4Hz, irradiating at 3.00 gave s), 3.00 (m, 2H, H-1 and H-4), 2.06 (s, 3H, CH_3CO_2), 1.8 (d, 3H, CH_3C=C, J=1.8Hz), 1.8-2.1 (m, 2H, CH_2); mass spectrum (70 eV) <u>m/e</u> (relative intensity) M^+=180(5), 80(90), 43(100).

<u>Anal</u>. Calcd. for $C_{10}H_{12}O_3$: C, 66.65%; H, 6.71%
Found: C, 67.00%; H, 6.63% (Chemalytics).

<u>Mixture 1- and 4-methyl-endo,cis,3-t-butyldimethylsiloxy-2-bicyclo[2.2.1]hept-5-ene-2-ol</u>

This mixture was obtained by treatment of 0.63 g (4.5 mmole) gc purified and recrystallized diol 65 with

0.80 g (1.25 equiv) t-butyldimethylchlorosilane, 0.80 g (2.6 equiv) imidazole (Aldrich), and 12 ml DMF for 14 hours at room temperature. The solution was diluted with 20 ml H_2O, extracted 4 times with 40 ml portions of CH_2Cl_2 and the CH_2Cl_2 dried with 25 ml sat'd NaCl then over $MgSO_4$. The mixture was filtered, evaporated in vacuo, chromatographed on 110 g silica gel (15:1 hexane-EtOAc eluant) and distilled to give 0.57 g (50%) of a water white liquid whose analytical data were consistent with an approximately 1:1 mixture of monoethers: bp 58-60/0.12 mm; ir ($CDCl_3$) 3420(OH), 1133 (Si-O-C), 1265, 1223 and 855 (strong); pmr ($CDCl_3$) δ 5.8-6.2 (m, 2H, HC=CH), 3.5-4.4 (m, 2H, CHOSi and CHOH), 2.2-3.0 (m, 2H, H-1, H-4, and OH), 1.35 and 1.40 (2s, 3H, CH_3C), 1.00 (s, 9.8H, t-Bu), 0.24 (s, 6.6H, $(CH_3)_2Si$).

Anal. Calcd. for $C_{14}H_{26}O_2Si$: C, 66.08%; H, 10.30%; Si, 11.04%; Found: C, 65.91%; H, 10.11%; Si, 10.85% (Spang).

Mixture 1- and 4-methyl-endo,3-t-butyldimethylsiloxy-bicyclo[2.2.1]hept-5-en-2-one (67b)

This mixture of ketones was obtained in 67% yield after distillation by oxidation of the corresponding mixture of alcohols according to the general procedure. Not enough material was obtained for both combustion analysis and flow esr. The isomers could not be separated, but the analytical data obtained were consistent with the assigned

structures: bp 58/0.09 mm; ir ($CDCl_3$), 1753 (cyclopentanone), 1263, 850 (strong); pmr ($CDCl_3$) δ 5.7-6.5 (m, 2H, CH=CH), 4.0 (d, 0.4H, H-3, J=3.5Hz), 3.7 (s, 0.6H, H-3), 2.9-3.1 (m, 1H, H-1 and H-4), 1.7-2.3 (m, 2H, CH_2), 1.38 (s, 1.2H, CH_3-1), 1.31 (s, 1.9H, CH_3-4), 1.01 (s, 9H, t-Bu), 0.23 (s, 6H, $(CH_3)_2Si$).

Mixture of 1-, 4-, 5-, and 6-methyl-endo,cis,3-t-butyldimethylsiloxy-2-hydroxybicyclo[2.2.1]hept-5-ene

This mixture was obtained by treatment of 3.21 g (23 mmole) of a mixture of diols 65 and 66 with 3.92 g (25 mmole) t-butyldimethylchlorosilane, 3.40 g (50 mmole) imidazole (Aldrich), and 25 ml DMF at 35° for 6 hours. The DMF solution was diluted with 60 ml H_2O, extracted 3 times with 50 ml portions of CH_2Cl_2 and the CH_2Cl_2 extracts washed once with 50 ml H_2O, once with 50 ml sat'd NaCl, and dried over $MgSO_4$. Chromatography on 350 g silica gel (15:1 hexane:EtOAc eluant) followed by distillation gave 3.72 g (64%) of a colorless white liquid. Pmr clearly showed the presence of all four isomers but, since only two components could be separated by gc, no attempt was made to separate isomers at this stage. The analytical data were consistent with a mixture of monoethers: bp 58/0.12 mm; ir ($CDCl_3$) 3510(OH), 1123 (Si-O-C), 1263 (C-O), 851 (prominent); pmr ($CDCl_3$) peaks at δ 1.20 and 1.24 assigned to CH_3-1 and CH_3-4 and at δ 1.85 and 1.90 to CH_3-5 and CH_3-6.

Anal. Calcd. for $C_{14}H_{26}O_2Si$: C, 66.08%; H, 10.30%; Si, 11.04%; Found: C, 65.98%; H, 10.06%; Si, 10.90% (Spang).

Endo,3-t-butyldimethylsiloxy-5-methylbicyclo[2.2.1]hept-5-en-2-one (68b)

The mixture of four isomeric alcohols obtained above was oxidized according to the general procedure to give 86% of a mixture of the four ketones 67b, 68b and 69b after chromatography on 120 g silica gel (15:1 hexane-EtOAc eluant) and distillation. Gas chromatography was unable to separate ketones 67b and 68b, but ketone 69b was cleanly separated from the others in 22% overall yield (after distillation) on a 9'x3/4" 7% Carbowax 6000 column at 110°. It gave analytical data consistent with its assigned structure: bp 58/0.08 mm; ir ($CDCl_3$) 1765 (cyclopentanone), 1140 (Si-O-C), 860 (strong); pmr ($CDCl_3$) δ 5.7 (m, 1H, CH=C), 4.10 (d, 1H, CHOSi, J=3.5Hz, irradiating at 2.85 gave s), 3.00 (m, 1H, H-1, irradiating at 5.7 sharpened H-1), 2.85 (m, 1H, H-4, irradiating at 5.7 left H-4 unchanged), 2.3 (d of d of d, 1H, H-7, anti, J=10Hz), 2.00 (d of m, 1H, H-7, syn, J=10Hz), 2.03 (d, 3H, CH_3C=C, J=1.8Hz, irradiating at 5.7 gave s), 1.0 (s, 9H, t-Bu), 0.23 (s, 6H, $(CH_3)_2Si$).

Anal. Calcd. for $C_{14}H_{24}O_2Si$: C, 66.61%; H, 9.58%; Si, 11.27%; Found: 66.60%; H, 9.56%; Si, 11.20% (Spang).

Mixture 5- and 6-methyl-endo,cis,3-benzoyloxy-2-hydroxy-bicyclo[2.2.1]hept-5-ene

A solution of 1.84 g (13.1 mmole) gc pure diol 66, 1.30 g (1.25 equiv) pyridine, 2.31 g (1.25 equiv) benzoyl chloride and 100 ml dry benzene was heated at reflux 14 hours. The solution was cooled, filtered, washed once with 50 ml 4% HCl, once with 50 ml 7% $NaHCO_3$, once with 50 ml sat'd NaCl, dried over $MgSO_4$, filtered, evaporated *in vacuo* and pumped on at 50-55°/1 mm until the crude oil no longer smelled of benzoyl chloride. This material was then chromatographed on 200 g silica gel (4:1 PhH-EtOAc eluant) and distilled to give 1.42 g (44%) of a thick pale yellow oil: bp 120-135/0.10 mm; ir ($CDCl_3$) 3590(OH), 1728 and 1280 (benzoate); pmr ($CDCl_3$) δ 7.1-8.1 (m characteristic of benzoates, 5H, $PhCO_2$), 5.75 (broad s, 1H, CH=C), 4.9-5.4 (m, 1H, BzOCH), 4.2-4.5 (m, 1H, CHOH), 2.6-3.1 (envelope, 2H, H-1 and H-4), 2.1 (broad s, 1H, OH), 1.92 (t, 3H, CH_3, 100MHz pmr shows t is pair of 1.8Hz d overlapping at 60MHz to form t), 1.6 (d of m, 1H, H-7, *anti*, J=10Hz), 1.23 (d of broad s, 1H, H-7, *syn*, J=10Hz); mass spectrum (70 eV) m/e (relative intensity) M^+=244 (small), 122(15), 105(100), 80(42), 78(30).

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.75%; H, 6.60%;
Found: C, 73.74%; H, 6.38% (Chemalytics).

Mixture of 5- and 6-methyl-endo,3-benzoyloxybicyclo[2.2.1]-hept-5-en-2-one (68c and 69c)

These compounds were prepared by oxidation of 1.42 g of the corresponding mixture of alcohols according to the general procedure. After chromatography on 100 g silica gel (5:1 PhH-EtOAc eluant) and after distillation there were obtained 0.69 g (49%) of a yellow oil. The two components could be separated on a 6'x3/4" 7% Carbowax 6000 column at 145°, but the long retention times (28 minutes for 69c, 36 minutes for 68c) precluded practical separation. A small amount was separated and the pmr spectra obtained. Structures were assigned on the basis of considerations discussed in the Appendix. Analytical data obtained on the mixture of ketones are as follows: bp 130-145/0.14 mm; ir ($CDCl_3$) 1770 (cyclopentanone), 1738 and 1275 (benzoate); pmr ($CDCl_3$) δ 7.2-8.2 (m characteristic of benzoates, 5H, $PhCO_2$), 5.8 (m, 0.5H, H-5), 5.6 (m, 0.5H, H-6), 5.3 (m, 1H, CHOBz), 3.2 (m, 2H, H-1 and H-4), 2.3 (d of m, 1H, H-7, anti, J=10Hz), 2.1 (d of m, 1H, H-7, syn, J=10Hz), 1.8 (t, 3H, $CH_3C=C$, 100 MHz pmr spectrum showed t at 60 MHz was really a pair of 1.8Hz d); mass spectrum (70 eV) m/e (relative intensity) M^+=242 (small), 120(36), 105 (100).

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.36%; H, 5.82%;
Found: C, 74.08%; H, 6.02% (Chemalytics).

1- and 2-Methylnorbornadiene

The Diels-Alder reaction between methylcyclopentadiene and propynoic acid was conveniently carried out by combining the cracking of the dimeric cyclopentadiene and the Diels-Alder reaction in one flask. The methylcyclopentadiene dimer was cracked by distillation through a 40 cm Vigreux column which was connected to a Friedrich condenser set on a flask containing a gently boiling solution of propynoic acid in ethyl acetate. Thus, methylcyclopentadiene was slowly distilled into a solution of 25.0 g (0.358 mole) propynoic acid (Aldrich, 98%) in 170 ml EtOAc until the receiving flask had gained 32 g (0.400 mole). The solution was boiled overnight then the solvent removed in vacuo. The residue was dissolved in 500 ml H_2O by adding portions of Na_2CO_3, the H_2O was extracted with 150 ml hexane then acidified with conc. HCl to give an oil (72). The oil was separated from the water by extracting with ether, the ether dried with sat'd NaCl and $MgSO_4$, filtered, and evaporated in vacuo to give 49.3 g (91%) of a sticky yellow semi-glass which could be poured at 50-60°: ir (CCl_4) 2800-3300 and 1710 (broad, CO_2H); pmr ($CDCl_3$) δ 11.7 (s, 1H, exchanged with D_2O), 1.3-8 (m).

This crude adduct was converted directly to the mixture of norbornadienes. Thus, a mechanically stirred mixture of 16.5 g acids 72, 30 g quinoline (freshly distilled from

BaO), and 1 g "Copper-chromite catalyst" (57) was heated to 220° with an oil bath over 30 minutes. At about 205° a white liquid began to distill. The temperature of the distillate began at 60°, rose to 155° and fell over 10 minutes to 80°. When the temperature of the vapor again began to rise, the oil bath was removed and distillation discontinued. The distillate was washed with one-half its volume of 5% HCl, dried over $CaCl_2$, and the products of several runs combined and separated using a spinning band distillation apparatus. The first fraction obtained was 1-methylnorbornadiene (8% overall yield from propynoic acid): bp 93 [Lit. (58). 93.5]; pmr ($CDCl_3$) δ 6.7 (d of d, 2H, H-3 and H-5, J=5Hz, J=3Hz), 6.46 (d, 2H, H-2 and H-6, J=5Hz), 3.45 (m, 1H, H-4), 1.9 (broad s, 2H, CH_2), 1.47 (s, 3H, CH_3). The higher boiling fraction was 2-methylnorbornadiene (bp 103 [Lit. (58). 103]) contaminated with a small amount of methylenenorbornene (δ 4.9 absorption in pmr spectrum). It was obtained in 11% overall yield from propynoic acid.

1- and 4-Methyl-exo,3-benzoyloxybicyclo[2.2.1]hept-5-en-2-one (74 and 73)

Benzoates 74 and 73 were obtained in 10% and 18% yields, respectively, by treatment of 1-methylnorbornadiene with BzONO according to the general procedure. Hydrolysis of the first formed nitrimine was carried out at room temperature

for 24 hours. The crude ketones 73 and 74 were chromatographed on 100 g silica gel/1 g crude ketone (4:1 CCl_4-$CHCl_3$ eluant) to give first the 1-methyl (74), then the 4-methyl (73) isomer. Each isomer was obtained contaminated with about 8-12% of the other isomer and various attempts at crystallization failed to produce either crystalline products or further separation. After pumping at 25°/ 0.05 mm for several days, both isomers were obtained as analytically pure yellow foams. Analytical data obtained from the 1-methyl (74) isomer are as follows: ir ($CDCl_3$) 1736 (benzoate and cyclopentanone), 1275 (benzoate), 1610 (C=C); pmr ($CDCl_3$) δ 7.2-8.0 (m characteristic of benzoates, 5H, $PhCO_2$), 6.4 (d of d, 1H, H-5, J=5Hz, J=3Hz), 6.0 (d, 1H, H-6, J=5Hz), 5.1 (d, 1H, H-3, J=2Hz), 3.1 (m, 1H, H-4), 2.3 (d, 1H, H-7, anti, J=9Hz), 2.1 (d of m, 1H, H-7, syn, J=9Hz), 1.28 (s, 3H, CH_3-1); mass spectrum, a satisfactory low resolution mass spectrum could not be obtained; high resolution mass spectrum, calcd. for $C_{15}H_{14}O_3$: 242.094; found: 242.097.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.36%; H, 5.82%;
Found: C, 74.58%; H, 5.81% (Schwartzkopf).

Analytical data obtained for the 4-methyl isomer (73) are as follows: ir (CCl_4) 1740 (cyclopentanone and benzoate), 1275 (benzoate), 1605 (C=C); pmr ($CDCl_3$) δ 7.2-8.0 (m characteristic of benzoates, 5H, $PhCO_2$), 6.1 (d,

1H, H-5, J=5.5Hz), 6.0 (d of d, 1H, H-6, J=5.5Hz, J=3Hz), 4.9 (d, 1H, H-3, J=2Hz), 3.1 (m, 1H, H-1), 2.3 (d, 1H, H-7, anti, J=9Hz), 2.1 (d of m, 1H, H-7, syn, J=9Hz), 1.26 (s, 3H, CH_3-4); mass spectrum, a satisfactory low resolution mass spectrum was not obtained for this compound; high resolution mass spectrum, calcd. for $C_{15}H_{14}O_3$: 242.094; found: 242.100.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.36%; H, 5.82%; Found: C, 74.70%; H, 5.96% (Schwartzkopf).

6,6-Dimethylfulvene

This compound was prepared by the method of Thiele (59) in 65% yield: bp 69-70/40 mm [Lit. (59). 47/11 mm].

Endo,7-acetoxy-4-isopropylidenebicyclo[3.2.0]hept-2-en-6-one (84)

This compound was prepared by the reaction of 53 g (0.50 mole) 6,6-dimethylfulvene with 0.09 mole acetoxyacetyl chloride according to the general procedure for in situ addition of ketenes to dienes. After chromatography on 150 g silica gel (PhH eluant) and distillation, ketone 84 was obtained as 4.6 g (20%) of a yellow oil: bp 106-108/0.15 mm; ir (neat) 1793 (cyclobutanone), 1749 and 1231 (acetate); pmr ($CDCl_3$) δ 6.4 (d, 1H, H-3, J=6Hz, irradiating at 5.7 gave s), δ 5.7 (d accidentally coincident on d of d; d, 1H, H-2, J=6Hz, irradiating at 6.4 gave s at 5.7 and left the rest of the m unchanged; d of d, 1H,

H-7, exo, J=3Hz, J=8Hz), 3.8-4.2 (m, 2H, H-1 and H-5, irradiating at 5.8 gave AB with J_{15}=7Hz), 2.02 (s, 3H, CH_3CO_2), 1.78 (s, 6H, $(CH_3)_2$ C=C). A weak triplet (J=4Hz) at δ 4.93 indicated the presence of a few per cent of the exo acetate 84.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88%; H, 6.84%;
Found: C, 70.35%; H, 6.94% (Chemalytics).

Exo, and endo,7-isopropylidenebicyclo[2.2.1]hept-5-en-2,3-diol carbonate (85)

The "optimum reaction conditions" of Haq (42) (boiling xylene) were considerably improved by the use of the general procedure for Diels-Alder reactions with vinylene carbonate. Thus, 6.4 g (0.075 mole) vinylene carbonate, 5.3 g (0.05 mole) 6,6-dimethylfulvene, and 23 g toluene were heated as described in the general procedure for 5 hours at 150°, cooled, evaporated in vacuo, and pumped on at 35°/1 mm for one hour. This gave 8.6 g of a viscous oil which, after chromatography on 380 g silica gel (PhH eluant), gave 1.2 g (12%) nearly pure endo 85 and 4.2 g of a mixture of endo and exo 85. Crystallization of this mixture from CCl_4 gave 1.3 g (14%) pure exo 85, mp 70-72 [Lit. (42). 74-76], plus 2.9 g (30%) recovered mixture of isomers. The pmr and ir spectra of endo 85 and exo 85 were as reported by Haq (42).

Mixture exo,cis, and endo,cis,3-t-butyldimethylsiloxy-7-isopropylidenebicyclo[2.2.1]hept-5-en-2-ol

A 4.1 g mixture of about 2:1 endo $\underset{\sim}{85}$ to exo $\underset{\sim}{85}$ was hydrolyzed according to the general procedure to give 3.1 g (86%) of a crystalline uncharacterized mixture of the endo and exo diols. The mixture of diols was let stand with 3.4 g (1.1 equiv) t-butyldimethylchlorosilane and 3.0 g (2.5 equiv) imidazole (Aldrich) in 50 ml DMF for 48 hours at room temperature, then diluted with 60 ml H_2O and extracted with two 50 ml portions of CH_2Cl_2. The combined extracts were washed once with 30 ml sat'd NaCl, dried over $MgSO_4$, filtered, evaporated in vacuo, and the residue chromatographed on 225 g silica gel (15:1 hexane-EtOAc eluant). The material so obtained was distilled to give 1.61 g (31%) of a water white liquid: bp 85-97/0.09 mm; ir ($CDCl_3$) 3510(OH), 1150 (Si-O-C); pmr ($CDCl_3$) δ 6.2-6.3 (m, 2H, CH=CH), 2.8-4.3 (m, 5H, H-1, H-2, H-3, H-4 and OH), 1.78 (2s, 3H, $(CH_3)_2$ C=C of exo), 1.69 (s, 3H, $(CH_3)_2$ C=C of endo), 1.07 (s, 9H, t-Bu), 0.30 and 0.26 (2s, 6H, $(CH_3)_2Si$).

Anal. Calcd. for $C_{16}H_{28}O_2Si$: C, 68.51%; H, 10.06%; Si, 10.01%; Found: C, 68.88%; H, 10.01%; Si, 9.90% (Spang).

Endo,3-t-butyldimethylsiloxy-7-isopropylidenebicyclo[2.2.1]-hept-5-en-2-one (86)

This compound was obtained by oxidizing a mixture of the corresponding exo,cis and endo,cis alcohols followed by gc purification. Thus, 1.60 g of the mixture of alcohols obtained above were oxidized with CrO_3 according to the general procedure, the crude product chromatographed on 110 g silica gel (20:1 hexane-EtOAc eluant), and the crude ketone thus obtained purified by preparative gc on a 6'x3/4" 7% Carbowax 6000 column at 140° to give 0.51 g (32%) of the pure endo 86 (after distillation): bp 85-92/ 0.13 mm; ir ($CDCl_3$) 1761 (cyclopentanone), 1123 (Si-O-C), 1221, 1262; pmr ($CDCl_3$) δ 6.6 (d of d, 1H, H-5, J=5.1Hz, J=2.5Hz), 6.3 (m, 1H, H-6), 4.0 (d, 1H, CHOSi, J=3.5Hz), 3.7 (m, 2H, H-1 and H-4), 1.81 and 1.76 (pair of s, 6H, $(CH_3)_2$ C=C), 1.07 (s, 9H, t-Bu), 0.29 (s, 6H, $(CH_3)_2Si$).

Anal. Calcd. for $C_{16}H_{26}O_2Si$: C, 69.01%; H, 9.41%; Si, 10.09%; Found: C, 69.37%; H, 9.30%; Si, 10.00% (Spang).

Mixture endo,cis, and exo,cis,3-benzoyloxy-7-isopropylidene-bicyclo[2.2.1]hept-5-en-2-ol

A 3.6 g mixture of about 1:1 endo 85 to exo 85 was hydrolyzed according to the general procedure to give 2.73 g (88%) of the crude, crystalline diols. This mixture of diols was dissolved in 125 ml PhH containing 3.15 g (1.5 equiv) benzoyl chloride and 2.4 g (1.5 equiv) pyridine

and gently boiled for 18 hours (when TLC showed virtual disappearance of the diols). The solution was cooled; diluted with ether; and extracted; once with 50 ml 3% HCl, once with 50 ml 7% $NaHCO_3$, once with 50 ml H_2O, and once with 60 ml sat'd NaCl; dried over $MgSO_4$; filtered; evaporated in vacuo; and chromatographed on 215 g silica gel (4:1 hexane-EtOAc eluant). The exo and endo isomers were not separated. Pumping on the 2.72 g (61%) of viscous oil 2 days at 30°/0.09 mm gave an analytically pure sample which contained slightly more exo than endo isomer: ir ($CDCl_3$) 3590(OH), 1725 and 1275 (benzoate); pmr ($CDCl_3$) exo isomer δ 7.1-8.0 (m characteristic of benzoates, 5H, $PhCO_2$), 6.18 (t, 2H, CH=CH), 4.8 (d, 1H, CHOBz, J=4.8Hz), 3.9 (d, 1H, CHOH, J=4.8Hz), 3.2-3.7 (m, 2H, H-1 and H-4), 2.8 (broad s, 1H, OH), 1.72 (s, 6H, $(CH_3)_2$ C=C); pmr ($CDCl_3$) endo isomer δ 7.1-7.8 (m characteristic of benzoates, 5H, $PhCO_2$), 6.35 (t, 2H, CH=CH), 5.2 (d of d, 1H, CHOBz, J=7.4Hz, J=4.4Hz), 4.3 (d of d, 1H, CHOH, J=3.6Hz, J=7.4Hz), 3.2-3.7 (m, 2H, H-1 and H-4), 2.8 (broad s, 1H, OH), 1.60 (s, 6H, $(CH_3)_2$ C=C).

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53%; H, 6.71%;
Found: C, 75.30%; H, 6.60% (Chemalytics).

Mixture endo, and exo,3-benzoyloxy-7-isopropylidene-bicyclo[2.2.1]hept-5-en-2-one (87)

Oxidation of 2.72 g of the mixture of alcohols obtained above according to the general procedure followed by

chromatography on 240 g silica gel (4:1 hexane-EtOAc eluant) and distillation gave 0.89 g (33%) of the mixture of endo and exo 87 as a pale yellow, very viscous oil: bp 155-160/0.13 mm; ir ($CDCl_3$) 1763 (cyclopentanone), 1729 and 1269 (benzoate), 1108 (strong); pmr ($CDCl_3$) δ 7.2-8.0 (m characteristic of benzoates, 5H, $PhCO_2$), 6.5 (d of d, 1H, H-5, J=2.8Hz, J=5.2Hz), 6.3(m, 1H, H-6), 5.17 (d, 0.5H, CHOBz, irradiating at 3.92 gave s, endo 87), 4.98 (s, 0.5H, CHOBz, exo 87), 3.6-3.9 (m, 2H, H-1 and H-4), 1.7-1.8 (3s, 6H, $(CH_3)_2$ C=C).

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10%; H, 6.01%;
Found: C, 76.10%; H, 6.08% (Chemalytics).

7-t-Butylnorbornadiene

This compound was prepared as described by Wittig and Klemp (60). Thus, 45 ml of dry heptane were added to a 25 ml solution of 1.25 M t-BuLi (Foote) in pentane and the solution cooled under N_2 to -20°. At this point, 4.7 g 7-t-butoxy-norbornadiene (Frinton) in 10 ml dry heptane were added with a syringe over 10 minutes. An exothermic reaction took place and a white precipitate fell out of the magnetically stirred solution. The solution was then distilled with the addition of a small amount of heptane until an internal temperature of 95° was attained. The mixture was gently boiled at this temperature for 2 hours, cooled, washed with two 20 ml portions of H_2O, once with

20 ml sat'd NaCl, dried over $CaSO_4$, and distilled to give 1.6 g (38%) of a water white liquid: bp 70-73/20 mm [Lit. (60). 64/20 mm]; pmr ($CDCl_3$) δ 6.83 (t, 2H, CH=CH, J=2.5Hz), 6.35 (t, 2H, CH=CH, J=2.5Hz), 3.40 (m, 2H, H-1 and H-4), 2.43 (s, 1H, H-7), 0.82 (s, 9H, t-Bu).

Exo,3-benzoyloxy-syn-7-t-butylbicyclo[2.2.1]hept-5-en-2-one (94)

This compound was prepared by addition of 7-t-butylnorbornadiene to benzoyl nitrite according to the general procedure. However, since the addition did not seem to be exothermic, the cooling bath was foolishly removed immediately upon completion of the addition. After about 3 minutes, the temperature shot to 40° and, although the solution was cooled to 15°, the usual precipitate of benzoic acid never did come down. The high temperature may account for the multiplicity of products as a similarly large number of products was also obtained in another case where the temperature was not properly moderated (one reaction with norbornadiene). Hydrolysis was carried out as noted in the general procedure for 12 hours at 50°. Thin layer chromatography revealed at least 10 components. The crude material was chromatographed on 100 g silica gel/1 g olefin (5:1 PhH-EtOAc eluant) and the three components with the expected retention volume ($r_f \approx 0.70$ on TLC) were collected. Pmr showed three t-butyl components, but by

far the major component appeared to be the desired benzoate 94. The crude contaminated product was obtained in 40% yield as a yellow oil. Various attempts at distillation and crystallization proved futile. Since this yellow oil gave a satisfactory esr spectrum further work to obtain an analytically pure sample was not carried out. Analytical data obtained were as follows: ir ($CDCl_3$) 1765 (cyclopentanone), 1730 and 1280 (benzoate); pmr ($CDCl_3$) δ 7.4-8.0 (m characteristic of benzoates, 5H, $PhCO_2$), 6.25 (d of d, 1H, H-5, J=6Hz, J=3Hz), 6.0 (d of d, 1H, H-6, J=6Hz, J=4Hz), 4.99 (s, 1H, CHOBz), 3.3 (broad s, 1H-estimated, H-1), 3.1 (broad s, 1H-estimated, H-4), 2.7 (s, 1H-estimated, H-7, anti), 0.9 (s, 9H-estimated, t-Bu), plus enough other absorptions to make the baseline look like a field of oats in a light breeze.

Dimethyl β,β-dimethylglutarate

Dimethyl β,β-dimethylglutarate was prepared from β,β-dimethylglutaric acid (Aldrich) by the method of Komppa (61) in 92-93% yield: bp 88-89/6 mm [Lit. (61). 102/15 mm].

Bis(trimethylsiloxy)-4,4-dimethylcyclopentene (98)

The procedure of Rühlmann and Schräpler (48) for improved acyloin condensations was followed. Thus, 52.6 g (2.28 mole) of molten sodium in 1 liter boiling toluene were whipped with a Hershberg stirrer at 1500 RPM (nominal stirrer rating) for 5 minutes, then the solution allowed

to cool gradually with continued stirring until the Na solidified. The Na sand was allowed to settle, the solvent decanted, the sand washed with several small portions of ether and, finally, covered with 1 liter of ether. The stirrer was set in motion and 250 g (2.38 mole) chlorotrimethylsilane added in one portion followed by 107.5 g (0.57 mole) dimethyl β,β-dimethylglutarate. A vigorous reaction set in which kept the uncooled solution at reflux for 4 hours. If the sand was made too fine, however, the reaction had to be moderated with ice water. The reaction mixture was heated at gentle reflux overnight or until the pale purple color had turned to white. The copious precipitate was filtered and the ether removed in vacuo. The product thus obtained was found perfectly suitable for the preparation of 4,4 dimethylcyclopentenone without distillation. Distillation gave 151 g (97%) of a white liquid (98): bp 86-87/5 mm; pmr (CCl_4) δ 2.11 (s, 4H, CH_2), 1.20 (s, 6H, $(CH_3)_2C$), 0.32 (s, 18H, $(CH_3)_3Si$); mass spectrum (70 eV) m/e (relative intensity) calcd. for $C_{13}H_{28}O_2Si_2$: M^+=272(100), 273(24.8), 274(8.1); found: M^+=272(100), 273(24.8), 274(9.0).

4,4-Dimethyl-2-cyclopenten-1-one

This compound was conveniently prepared in 60-70% yield by a one pot hydrolysis and dehydration of bis(trimethylsiloxy)alkene 98. Thus, 203 g (0.75 mole) of alkene 98

were poured into 170 ml 85% H_3PO_4 in a round bottom flask. The flask was immediately attached to a vacuum distillation apparatus, the pressure lowered to 35 mm, and the flask immersed in an oil bath previously heated to 100°. The temperature of the oil bath was raised to 165° over 20 minutes. At first, only H_2O distilled, but when the oil bath temperature reached 150° the enone rapidly distilled into the ice chilled receiver. Heating was discontinued when the temperature of the vapor fell below 60°. The H_2O collected with the enone was saturated with NaCl, the layers separated and the enone distilled to give 56.0 g (68%) of a water white liquid: bp 65-68/35 mm [Lit. (47). 75/45 mm]; pmr ($CDCl_3$) δ 7.3 (d, 1H, C<u>H</u>CO, J=5.5Hz), 5.8 (d, 1H, C<u>H</u>C$(CH_3)_2$, J=5.5Hz), 2.1 (s, 2H, CH_2), 1.24 (s, 6H, $(CH_3)_2C$).

<u>4,4-Dimethyl-2-cyclopenten-1-ol</u>

This compound was prepared by $LiAlH_4$ reduction of the corresponding ketone by the method of Rouse and Tyler (47). It was obtained consistently in 65% yield, never in 90% yield as reported in the literature: bp 48-51/6 mm [Lit. (47). 42/1.5 mm]; pmr ($CDCl_3$) δ 5.5 (s, 2H, CH=CH), 4.7 (m, 1H, C<u>H</u>OH), 4.0 (s, 1H, OH), 1.3-2.2 (m, 2H, CH_2), 1.5 (s, 3H, CH_3), 1.03 (s, 3H, CH_3).

3,3-Dimethyl-5-bromocyclopentene

4,4-Dimethylcyclopentenol was treated with HBr to give the title compound in 70% yield according to the method of Rouse and Tyler (47): bp 65/30 mm [Lit. (47). 76/50 mm].

5,5-Dimethylcyclopentadiene

3,3-Dimethyl-5-bromocyclopentene was heated in quinoline to give the title compound in 69% yield after redistillation according to the method of Rouse and Tyler: bp 65 [Lit. (47). 70]; pmr (CCl_4) δ 6.17 (s, 4H, CH=CH-CH=CH), 1.14 (s, 6H, $(CH_3)_2C$).

Endo,cis,7,7-dimethylbicyclo[2.2.1]hept-5-en-2,3-diol carbonate (99)

This compound was prepared in 51% yield by reacting 4.00 g (41.7 mmole) 5,5-dimethylcyclopentadiene and 7.9 g (97 mmole) vinylene carbonate in 25 ml bromobenzene at 155° for 24 hours according to the general procedure for Diels-Alder reactions with vinylene carbonate. After cooling, the solvent and excess reagent were removed on a rotary evaporator at 55°/1.2 mm to give a pale brown solid which gave 3.1 g (51%) of a white solid after recrystallizing from cyclohexane: mp 74.5-74.8; ir ($CDCl_3$) 1799 (carbonate), 1079 (sharp); pmr ($CDCl_3$) δ 6.1 (t, 2H, CH=CH, J=2Hz, irradiating at 2.9 gave s), 5.2 (d of d, 2H, CHO, J=3Hz, J=1.7Hz, irradiating at 2.9 gave s), 2.9 (m, 2H, H-1 and H-4, irradiating at 6.1 gave t), 1.04 (s, 3H, CH_3),

0.98 (s, 3H, CH_3), mass spectrum (70 eV) m/e (relative intensity) M^+=180 (small), 94(100), 79(65).

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65%; H, 6.66%;
Found: C, 66.49%; H, 6.82% (Chemalytics).

Endo,cis,3-benzoyloxy-7,7-dimethylbicyclo[2.2.1]hept-5-en-2-ol

Hydrolysis of 3.4 g (18.9 mmole) carbonate 99 according to the general procedure afforded 2.7 g (93%) crude, crystalline diol which was not characterized. The crude diol was dissolved in 130 ml dry PhH, 3.10 g (1.25 equiv) benzoyl chloride and 1.74 g (1.25 equiv) pyridine added, and the solution heated at reflux 12 hours. The solution was cooled, filtered, diluted with ether, washed once with 50 ml 3% HCl, once with 50 ml 7% $NaHCO_3$, once with 40 ml sat'd NaCl, dried over $MgSO_4$, filtered, evaporated in vacuo, and pumped on at 40°/0.2 mm until the smell of BzCl had gone. The crude oil so obtained was chromatographed on 300 g silica gel (4:1 hexane-EtOAc eluant) and the major fraction ($r_f \approx 0.6$ on TLC) recrystallized from ether to give 2.2 g (45%) of a white solid: mp 133-134; ir ($CDCl_3$) 3590(OH), 1723 and 1281 (benzoate); pmr ($CDCl_3$) δ 7.1-7.9 (m characteristic of benzoates, 5H, $PhCO_2$), 6.2 (m, 2H, CH=CH), 5.6 (d of d, 1H, CHOBz, J=7Hz, J=3.5Hz, irradiating at low field side of m at 2.7 gave 7Hz d), 4.7 (m, 1H, CHOH), 2.7 (m, 2H, H-1 and H-4), 1.5 (2s, 1H,

OH), 1.08 (s, 3H, CH_3), 1.00 (s, 3H, CH_3).

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.39%; H, 7.02%;
Found: C, 74.41%; H, 7.01% (Chemalytics).

Endo,3-benzoyloxy-7,7-dimethylbicyclo[2.2.1]hept-5-en-2-one (100)

Oxidation of 2.00 g of the corresponding alcohol according to the general procedure gave a brown solid as the crude product. Recrystallization of this solid from 20 ml hot hexane gave 1.48 g (75%) large white crystals (100): mp 95.5-97.0; ir ($CDCl_3$) 1767 (cyclopentanone), 1729 and 1278 (benzoate); pmr ($CDCl_3$) δ 7.2-8.0 (m characteristic of benzoates, 5H, $PhCO_2$), 6.4 (m, 1H, H-5, irradiating at 2.9 gave 5.5Hz d), 6.0 (m, 1H, H-6, irradiating at 2.9 gave 5.5Hz d), 5.5 (d, 1H, H-3, J=3.5Hz, irradiating at 2.9 gave s), 2.9 (m, 2H, H-1 and H-4), 1.26 (s, 3H, CH_3), 1.18 (s, 3H, CH_3).

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98%; H, 6.29%;
Found: C, 74.76%; H, 6.45% (Chemalytics).

1-, 5-, and 6-Methylbicyclo[2.2.1]hepten-2-one (106, 107, 108, respectively)

Ketones 106, 107 and 108 were prepared by the technique used by Freeman et al. (62) in the synthesis of norbornenone. Thus, methylcyclopentadiene was slowly distilled from its dimer through a 40 cm Vigreux column directly into a Friedrich condenser set on a flask containing a gently

boiling solution of 100.5 g (1.15 mole) α-chloroacrylonitrile (Aldrich) in 200 ml PhH. The distillation was continued until 94 g (1.17 mole) methylcyclopentadiene had been added. The contents of the flask were heated at reflux 3/4 hour (total time 3½ hours) then distilled to give 175.8 g (98%) of the crude Diels-Alder adduct (109): bp 50-60/0.07 mm [Lit. (63). bp 60-70/0.4 mm]. One-half (85 g) of this material was dissolved in 470 ml DMSO and a hot solution of 87 g 86% KOH in 29 ml H_2O was added in one portion. The temperature shot to 60°, a white precipitate appeared, and the color became deep red. The solution was allowed to stir 10 hours after the reaction began to cool (40 minutes) then steam distilled until the pungent odor of ketone could no longer be detected in the distillate (about 1300 ml H_2O). The distillate was extracted 4 times with 70 ml portions of ether, the combined ether extracts dried over $CaSO_4$, and the product distilled to give 41.2 g (71%) of a pale yellow liquid (106, 107, and 108): bp 55-62/10 mm [Lit. (63). 48-50/9 mm]. In another, identical preparation which omitted the 10 hours of stirring the yield was 73%. The mixture was easily separated into three components, the 1-methyl (106), 5-methyl (107), and 6-methyl (108) isomers, with retention times 14, 18, and 25 minutes and isolated yields 20, 5, and 16%, respectively, on a 9'x3/4" 7% Carbowax

6000 column at 105°. The structures were assigned by comparison of their pmr spectra with those in the literature (64).

REFERENCES CITED

1. G. A. Russell, "Semidione Radical Anions", in E. Kaiser and L. Kevan, eds., Radical Ions, Interscience Publishers, Inc., New York, N.Y., 1968, chapter 3.

2. G. A. Russell, Science, 161, 423 (1968).

3. G. A. Russell, "Applications of Electron Spin Resonance to Structural Determinations of Diamagnetic Substances; The Generation of Useful Spin Labels in Solution", in A. Weissberger, ed., Techniques of Chemistry, Volume IV, Part I, John Wiley and Sons, Inc., New York, N.Y., 1972, chapter VI.

4. H. M. McConnell, J. Chem. Phys., 24, 632, 764 (1956).

5. R. W. Fessenden, J. Phys. Chem., 71, 74 (1967).

6. G. Holland, "Long range hyperfine splitting in bicyclic semidiones", Ph.D. thesis, Library, Iowa State University, Ames, Iowa, 1969.

7. T. R. Scharpe, "The reaction of acyl nitrites with olefins", Paper for Presentation at Euchem Conference on C-Nitrosocompounds, Sept. 1969.

8. G. A. Boswell, J. Org. Chem., 33, 3699 (1968).

9. R. G. Keske, "The conformations of cycloheptanesemidiones and related systems", Ph.D. thesis, Library, Iowa State University, Ames, Iowa, 1970.

10. G. A. Russell and R. L. Blankespoor, Tetrahedron Lett., 4573 (1971).

11. G. A. Russell and P. R. Whittle, J. Amer. Chem. Soc., 89, 6781 (1967).

12. G. A. Russell, P. R. Whittle, R. G. Keske, G. Holland, and C. Aubuchon, J. Amer. Chem. Soc., 94, 1693 (1972).

13. J. A. Berson, Accounts Chem. Res., 1, 152 (1968).

14. D. I. Schuster, M. Axelrod, and J. Auerbarh, Tetrahedron Lett., 1911 (1963).

15. D. E. Bays and R. C. Cookson, J. Chem. Soc., B, 226 (1967).

16. P. Schiess and P. Fünfschilling, Tetrahedron Lett., 5191 (1972).

17. W. T. Brady, Synthesis, 415 (1971).

18. H. C. Stevens, J. K. Rinehart, J. M. Lavanish, and G. M. Trenta, J. Org. Chem., 36, 2780 (1971).

19. P. R. Brook and A. J. Duke, J. Chem. Soc., C, 1764 (1971).

20. P. R. Brook, J. M. Harrison, and A. J. Duke, Chem. Commun., 589 (1970).

21. V. R. Fletcher and A. Hassner, Tetrahedron Lett., 1071 (1970).

22. K. E. Harding, J. W. Trotter, and L. May, Synthetic Comm., 2, 231 (1972).

23. P. A. Grieco, J. Org. Chem., 37, 2363 (1972).

24. W. F. Ermann, R. S. Treptow, P. Bakuzis, and E. Wenkert, J. Amer. Chem. Soc., 93, 657 (1971).

25. v. M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, Helv. Chim. Acta, 53, 417 (1970).

26. H. D. Scharf, W. Droste, and R. Liebig, Angew. Chem., 7, 215 (1968).

27. A. A. Frost and R. G. Pearson, Kinetics and Mechanism, 2nd ed., John Wiley and Sons, Inc., New York, N.Y. 1965, p 173.

28. H. Kwart and G. Vosburgh, J. Amer. Chem. Soc., 76, 5400 (1954).

29. E. J. Corey and A. Venkateswarlu, J. Amer. Chem. Soc., 94, 6190 (1972).

30. G. A. Russell, J. J. McDonnell, P. R. Whittle, R. S. Givens, and R. G. Keske, J. Amer. Chem. Soc., 93, 1452 (1971).

31. G. A. Russell, P. R. Whittle, and R. G. Keske, J. Amer. Chem. Soc., 93, 1467 (1971).

32. G. A. Russell, G. Holland, and K.-Y. Chang, J. Amer. Chem. Soc., 89, 6629 (1967).

33. J. R. Mattox, "Unsaturated 1,4-semidiones", Ph.D. thesis, Library, Iowa State University, Ames, Iowa, 1973.

34. G. W. Snedecor and W. G. Cochran, Statistical Methods, The Iowa State University Press, Ames, Iowa, 1967, p 92.

35. P. v. R. Schleyer, J. Amer. Chem. Soc., 80, 1700 (1958).

36. R. B. Turner, W. R. Meador, and R. E. Winkler, J. Amer. Chem. Soc., 79, 4116 (1957).

37. H. E. Zimmerman and R. M. Paufler, J. Amer. Chem. Soc., 82, 1514 (1960).

38. R. B. Turner, J. Amer. Chem. Soc., 86, 3586 (1964).

39. C. J. Sih, R. G. Salomon, P. Price, G. Peruzzoti, and R. Sood, Chem. Commun., 240 (1972).

40. G. A. Russell and D. F. Lawson, J. Amer. Chem. Soc., 94, 1699 (1972).

41. K.-Y. Chang, "Radical anions derived from bridged bicyclic α-diketones", Ph.D. thesis, Library, Iowa State University, Ames, Iowa, 1965.

42. M. Z. Haq, J. Org. Chem., 37, 3015 (1972).

43. G. Wittig and J. Otten, Tetrahedron Lett., 601 (1963).

44. H. C. Brown and J. H. Kawakami, J. Amer. Chem. Soc., 92, 1990 (1970).

45. W. C. Baird, Jr. and J. H. Surridge, Symposium on new olefin chemistry, The American Chemical Society, Houston, Texas, Feb. 1970, p E102.

46. H. C. Stevens, D. A. Reich, K. R. Fountain, and E. J. Gaughan, J. Amer. Chem. Soc., 87, 5257 (1965).

47. R. S. Rouse and W. E. Tyler, III, J. Org. Chem., 26, 3525 (1961).

48. U. Schräpler and K. Rühlmann, Berichte, 96, 2780 (1963).

49. R. Ratcliffe and R. Rodehorst, J. Org. Chem., 35, 4000 (1968).

50. W. T. Brady and E. D. Dorsey, J. Org. Chem., 35, 3733 (1970).

51. V. W. Pritzkow and H. Nitzer, J. für Prakt. Chemie, 25, 69 (1964).

52. R. Anschütz and W. Bertram, Berichte, 36, 466 (1903).

53. T. L. Pattan (to Monsanto Chemical Co.), U.S. Pat. 2,857,434, Oct. 21, 1958.

54. M. C. Thorpe and W. C. Coburn, Jr., J. Org. Chem., 34, 2576 (1969).

55. G. Wittig and E. Knauss, Berichte, 91, 895 (1958).

56. S. McLean and P. Haynes, Tetrahedron, 21, 2313 (1965).

57. A. I. Vogel, A Textbook of Practical Organic Chemistry, 3rd ed., John Wiley and Sons, Inc., New York, N.Y., 1966, p 872.

58. J. Hymann, E. Freireich, and R. E. Lidov (to Shell Development Co.), U.S. Pat. 2,875,256, Feb. 24, 1959, Chem. Abstr., 53, 13082e (1960).

59. J. Thiele, Berichte, 33, 666 (1900).

60. G. Wittig and G. Klemp, Tetrahedron Lett., 607 (1963).

61. G. Komppa, Justus Liebigs Ann. Chem., 368, 136 (1909).

62. P. K. Freeman, D. M. Balls, and D. J. Brown, J. Org. Chem., 33, 2211 (1968).

63. S. E. Masar and H. Krieger, Suomen Kemistilehti, B, 41, 217 (1968).

64. S. E. Masar and H. Krieger, Suomen Kemistilehti, B, 42, 1 (1970).

65. J. W. ApSimon, P. V. Demarco, D. W. Mathieson, W. G. Craig, A. Karim, L. Saunders, and W. B. Whalley, Tetrahedron, 26, 119 (1970).

66. J. A. Pople, J. Chem. Phys., 37, 60 (1962).

67. R. M. Silverstein and G. C. Bassler, Spectrometric Identification of Organic Compounds, 2nd ed., John Wiley and Sons, Inc., New York, N.Y., 1967, p 117.

68. W. F. Ermann, J. Amer. Chem. Soc., 89, 3828 (1967).

ACKNOWLEDGEMENT

I would like to thank Dr. Russell for the financial support he has obtained which has allowed me to enjoy a research assistantship for most of my stay at Iowa State and for the wide latitude he has allowed me in my experimental approach.

I thank the members of the Russell group for their almost universal high spirits (and consumption thereof) and those people outside the Russell group who have made my stay in Iowa very pleasant. Dave Lokensgard's running of the 100 MHz NMR is especially appreciated as are the many hours I have spent playing championship ping-pong with him and Mike Engel.

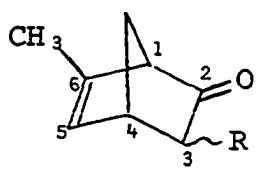
I thank my parents for their continued moral and financial support through my almost never ending formal education, and my wife's parents for many gifts of farm fresh beef, pork, and eggs. My wife, Bonnie, may not be aware of it all the time, but she has been a continual source of joy to me.

Finally, I wish to thank Milwaukee County Local Board #45 for deciding I was unfit for travel abroad with Uncle Sam at a very crucial point in my graduate career.

APPENDIX

Chemical Shifts of H-5 and H-6 in Norbornenones

At one point in this study it was considered important to be able to correctly assign structures to C-3 substituted norbornenones with vinylic methyls (102 and 103). Whether



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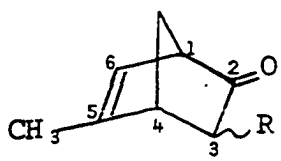

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it is necessary or not, it is much more satisfying to be able to assign a pmr absorption to one specific proton. For these reasons a brief inquiry was made into the relative chemical shifts of H-5 and H-6 in a series of norbornenones.

The pmr spectra in Figure 34 show (upper middle and bottom) what was found to be generally true in this study, that substitution at C-2, C-3, and C-7 does not cause nonequivalence of the vinylic protons. However, Figure 34 (lower middle and top) shows the rather dramatic nonequivalence of the vinylic protons on introduction of a carbonyl. One might hope to use the known anisotropies of various groups at C-3 to get a handle on which absorption goes with

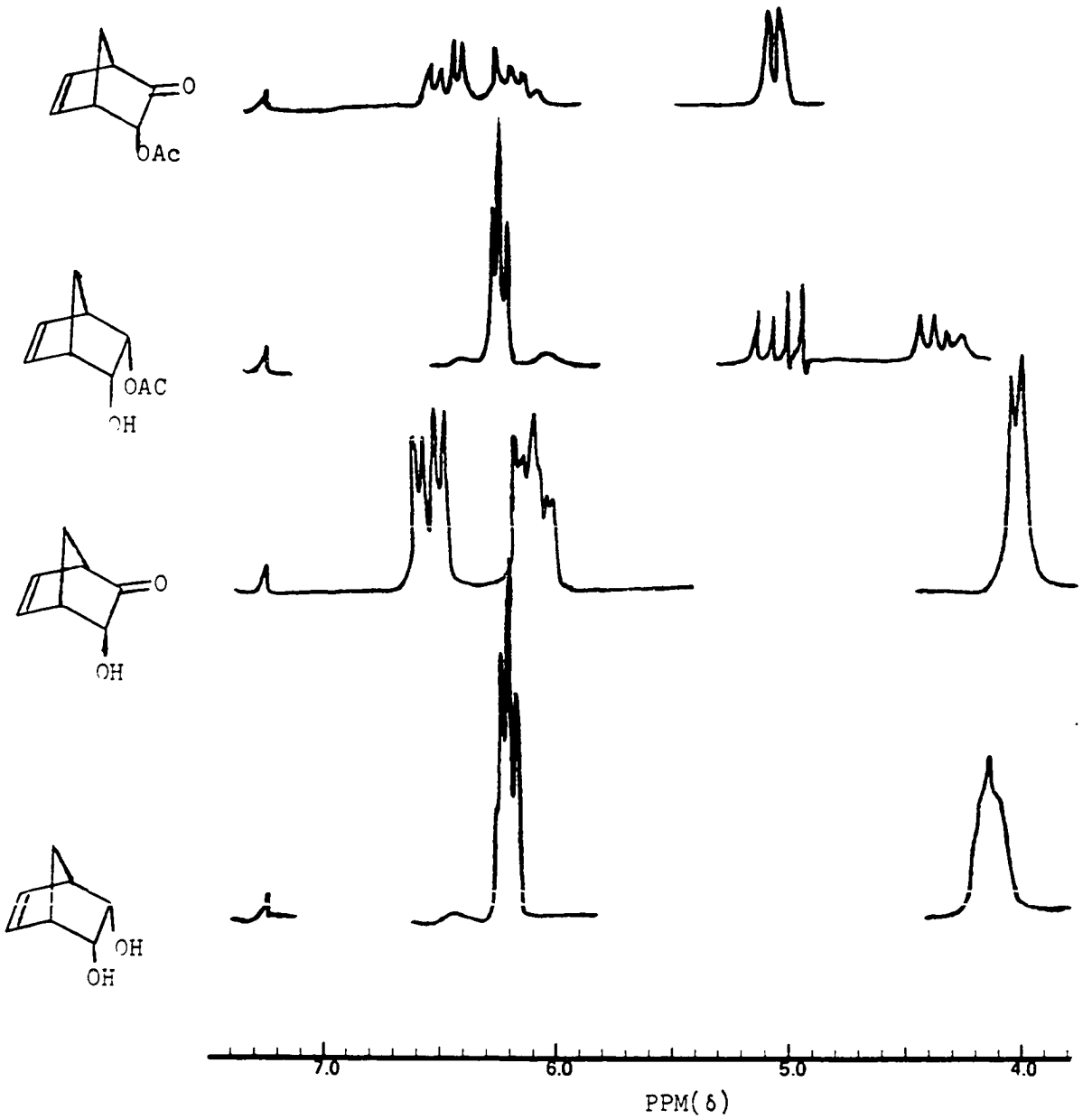
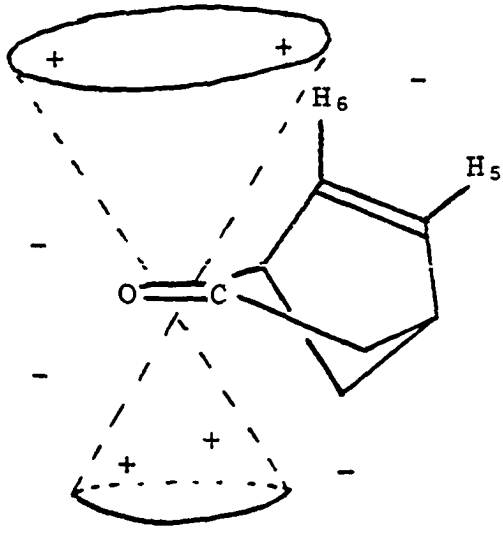


Figure 34. The partial pmr spectra of four norbornenes showing the effect of a carbonyl at C-2 on the vinyl protons.

which proton but, as Figure 35 shows, the anisotropy, stereochemistry, or even existence of a substituent (different from H) at C-3 has little effect on the vinylic protons. Since the bridgehead protons (H-1 and H-4) differ <0.2 ppm in any of these compounds the difference in chemical shift between H-5 and H-6 must be due to a through space effect, not a simple electrostatic effect of the carbonyl.

There are two different descriptions of the shielding and deshielding zones about a carbonyl due to ApSimon et al. (65) and Pople (66). Fortunately, the geometry of norbornenones is such that both models make the same predictions. A simplified version of the shielding and deshielding zones for Pople's model (67) incorporated into a norbornenone framework is shown by structure 104. Molecular models



104

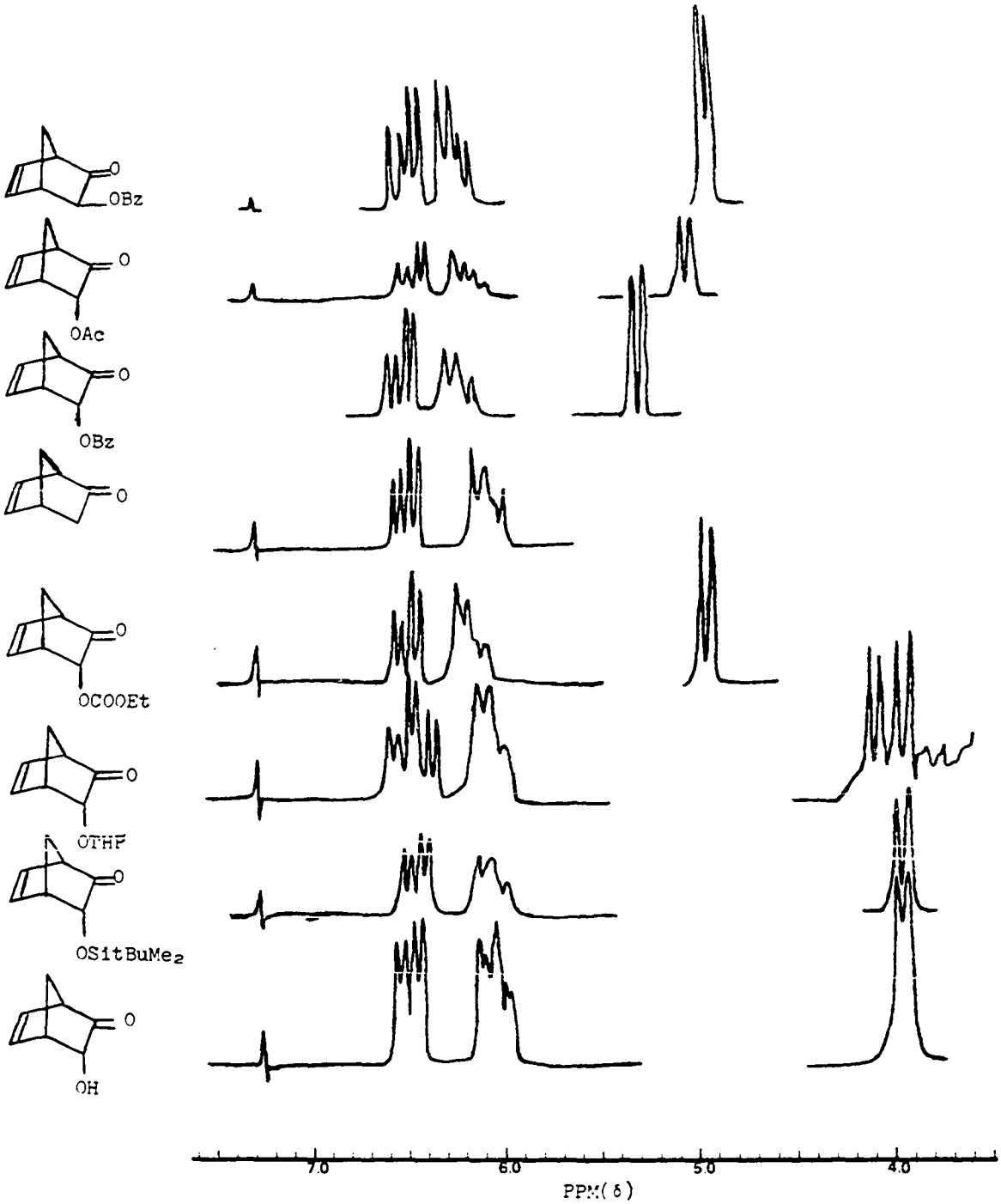


Figure 35. The partial pmr spectra of eight C-3 substituted norbornenones.

quickly show that H-6 lies in the region of little effect, while H-5 ought to be deshielded. On this basis, one could assign the lowest field multiplets in Figure 35 to H-5 and the higher field multiplet to H-6. Similarly, if both norbornenones 102 and 103 were available, the one with the lowest field olefinic protons would be 102 and the other 103.

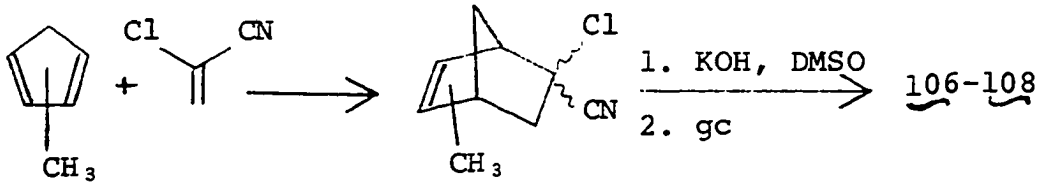
This assignment can be put on somewhat more rigorous grounds by reference to known compounds. Masar and Krieger have synthesized and rigorously established the structures of methylnorborenones 105 - 108 (63) and have published

105 106 107 108

their pmr spectra (64).

For the purposes of comparison and for another project enones 106 - 108 were synthesized (Scheme 43) by a simple

Scheme 43



extension of Freeman's synthesis of norbornenone (62).

In confirmation of the prediction made on the basis of structure 104, the olefinic proton of enone 107 is downfield of that in 108. Figure 36 shows the pmr spectra of enones 107 and 108 and also shows the lack of effect of C-3 substitution on the olefinic protons. It was on the basis of comparisons with enones 107 and 108 that the H-5 and H-6 absorptions of all norbornenones in this study were assigned.

It is interesting to note that in all cases for norbornenones 102 and 103 (R=H, OSi*t*BuMe$_2$, OAc, OBz) the relationship of the carbonyl and the methyl group was the factor determining the relative retention time on the Carbowax 6000 gc column. In every case the CH_3-6 enone (102) eluted faster than the CH_3-5 enone (103).

Endo,7-Acetoxy-1-Methylbicyclo[3.2.0]hept-2-en-6-one

Ketone 60 was one of three products isolated in the reaction between acetoxy ketene and methylcyclopentadiene (Scheme 26). Since, as discussed in the text, ketone 60 was not an expected product and since its structure is not immediately obvious from the spectral data given in the Experimental section, we will discuss in some detail the spectral evidence in favor of structure 60.

The ir spectrum (1799, 1755 and 1230) is consistent with a cyclobutanone and an acetate. The mass spectrum shows a molecular ion of 180 and a base peak of 43, symptomatic of an acetate. The elemental analysis is consistent with the

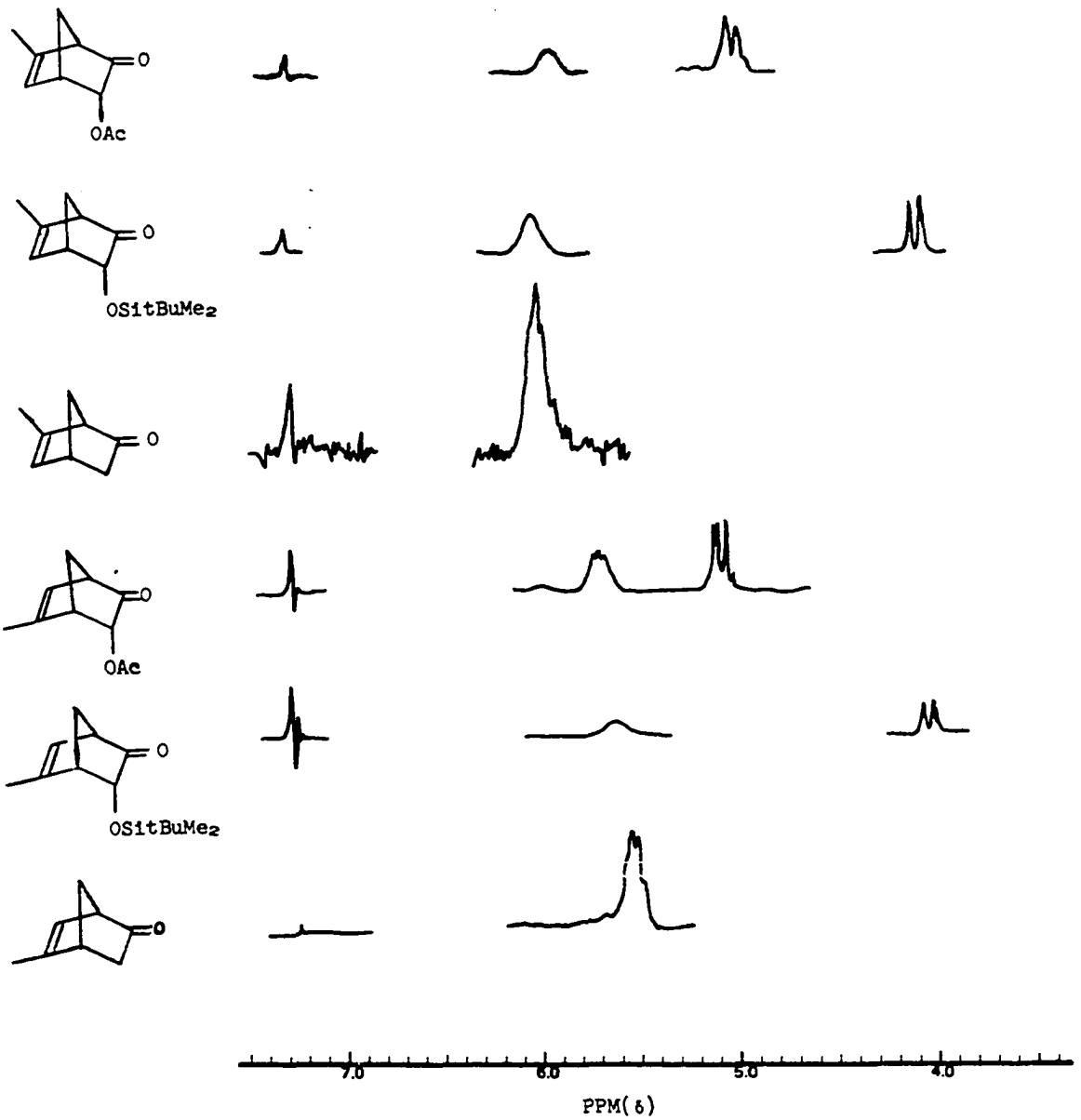
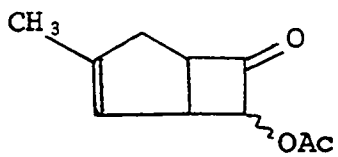
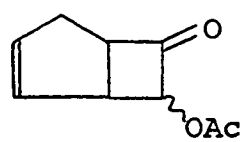


Figure 36. The partial pmr spectra of six C-5 and C-6 methylated norbornenones.

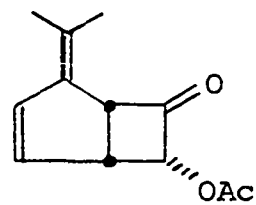
empirical formula $C_{10}H_{12}O_3$ as is the integration of the pmr spectrum. The pmr spectrum (Figure 37) shows two ringing singlets for 3H each at δ 1.60 and 2.09 suggesting a CH_3C and CH_3CO_2. At δ 2.6 there is a 2H multiplet which is virtually superimposable on the 2H multiplet ascribed to H-4, exo and endo in acetates endo and exo 59 and exo and endo 20c. From δ 3 to δ 4, there is a multiplet for 1H; endo and exo 59, endo and exo 20c, and 84 all show two



59

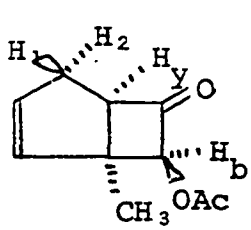


20c

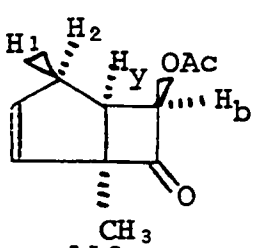


84

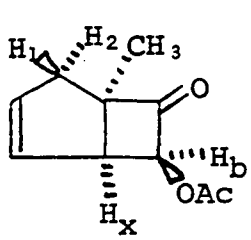
multiplets for 2H assigned to H-1 and H-4 in this area of the spectrum. Finally, there is a multiplet for 3H at δ 5.4-5.9 easily ascribable to CH=CH and -CHOAc-C=O. The olefinic protons in exo 20c are nearly a singlet, while in endo 20c a pattern very similar to that in Figure 37 is seen. Structures 60 and 110-112 are consistent with these data.



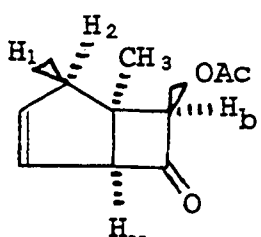
60



110



111



112

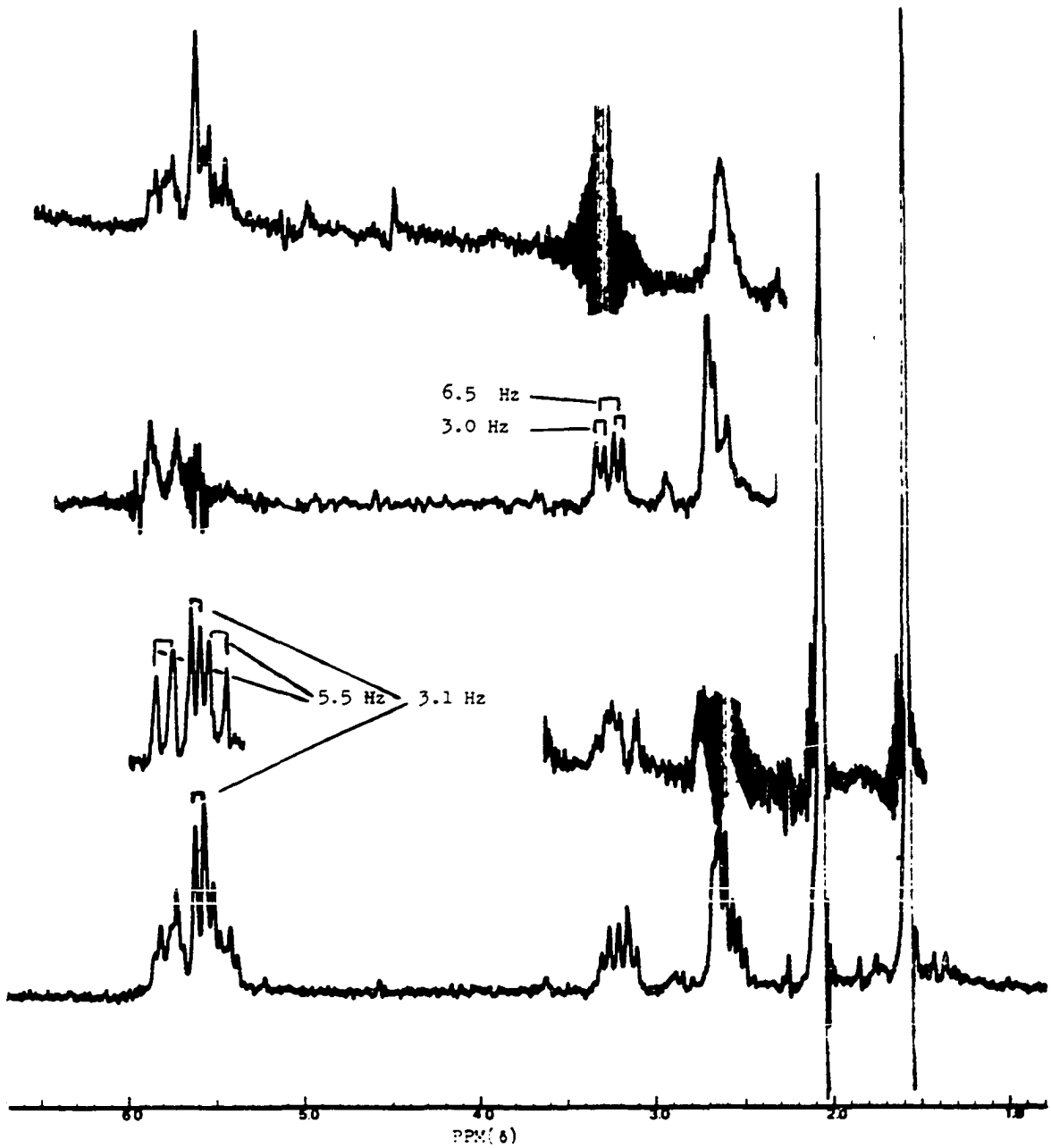
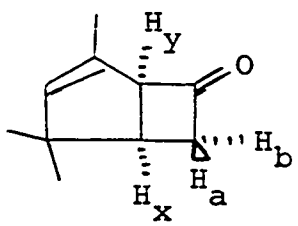


Figure 37. The pmr spectrum (bottom) of endo,7-acetoxy-1-methylbicyclo[3.2.0]hept-2-en-6-one showing the effect (lower middle) of decoupling H-4, endo and exo, the effect (upper middle) of decoupling H-7, and the effect (top) of decoupling H-5.

In all four structures there should be interaction between protons H_1 and H_2 and the olefinic protons. Decoupling (Figure 37, lower middle) H_1 and H_2 reveals the low field multiplet to be two 5.5Hz doublets and a 3.1Hz doublet. A 5.5Hz coupling constant is consistent with cyclopentene olefinic protons. Reference to ketones 113 and 114 studied by Ermann (24,68) allows us to eliminate structures 110-112.



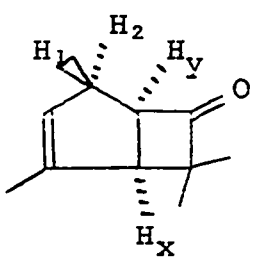
113

J_{ax} = 6.0 Hz

J_{ay} = 2.4Hz

J_{bx} = 8.1Hz

J_{by} = 4.0Hz



114

J_{1y} = 3.0Hz

J_{2y} = 8.0Hz

J_{xy} = 8.0Hz

Decoupling the bridgehead proton (Figure 37, top) leaves the low field multiplet unchanged except for the 3.1Hz doublet which becomes a singlet. This eliminates structures 110 and 111 which ought to have J_{yb} (110) ≈ J_{xb} (111) ≈ J_{bx} (113) ≈ 8.1Hz (and also eliminates the exo

acetate forms of 110 and 111). Decoupling H_b (Figure 37, upper middle) shows the bridgehead multiplet to be a doublet of doublets with J=6.5Hz and J=3.0Hz. This eliminates 112 and is in perfect agreement with 60, that is, J_{1y} (60) = 3.0Hz = J_{1y} (114) and J_{2y} (60) = 6.5Hz ≈ 8.0Hz = J_{2y} (114).