1983

Long-range interactions in bicyclic semidiones and the free radical reactions of unsaturated organostannanes

Lourdes Lucas Herold
Iowa State University

Herold, Lourdes Lucas

LONG-RANGE INTERACTIONS IN BICYCLIC SEMIDIONES AND THE FREE RADICAL REACTIONS OF UNSATURATED ORGANOSTANNANES

Iowa State University PH.D. 1983

Long-range interactions in bicyclic semidiones and the free radical reactions of unsaturated organostannanes

by

Lourdes Lucas Herold

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

1983

TABLE OF CONTENTS

DEDICATION

To

Bob

INTRODUCTION

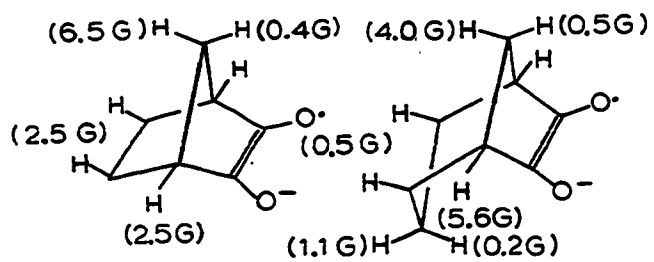
This dissertation has been divided into two main parts, namely: Part I, "Long-Range Interactions in Bicyclic Semidiones" and Part II, "Free Radical Reactions of Unsaturated Organostannanes".

PART I: LONG-RANGE INTERACTIONS IN BICYCLIC SEMIDIONES

I. INTRODUCTION

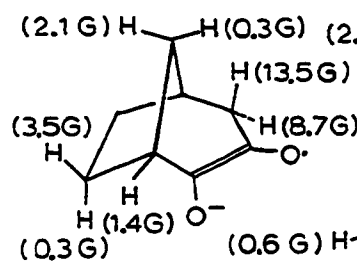
Long-range coupling in bicyclic semidiones has been an extensively studied phenomenon (1-6). However, investigations have centered mostly, if not exclusively, on interactions of hydrogen atoms with the spin probe. Chapter II.A, "Long-Range Interactions in Bicyclic Semidiones Containing Hetero Atoms", in Part I of this dissertation, deals with the interesting possibility of a similar long range interaction occurring between the p-orbital of the spin probe and the hetero atom lone pairs in aza and phospha bicyclic semidiones.

Anti hydrogen atoms in bicyclic semidiones 1-4 reportedly (7-9) exhibit long-range hyperfine splittings. Such

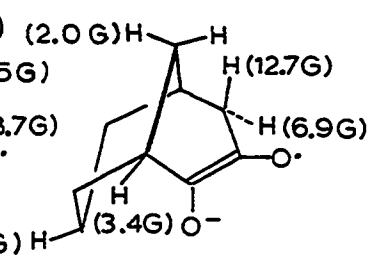


1

2

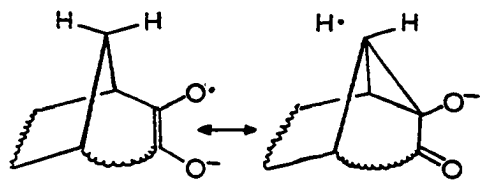


3



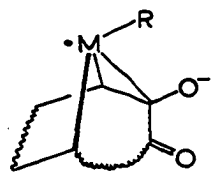
4

behavior can be rationalized by the concept of homohyperconjugation as depicted in 5a↔5b (7-10).



5a 5b

If one replaces the methylene bridge of the semidiones 1-4 with a hetero atom, it is conceivable that the corresponding homoconjugative interaction shown in 6 can occur



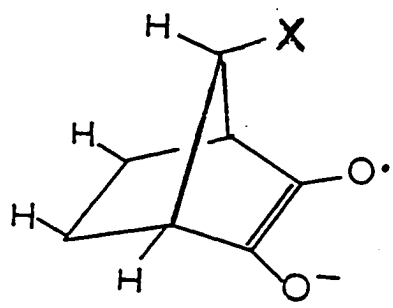
6

between the lone pair of the hetero atom and the p-orbital of the spin probe. This possibility is investigated in Chapter II.A of Part I of this dissertation.

The magnitude of long-range hyperfine splitting constants (hfsc) has been found to be dependent on several factors: (1-6)

1. Extent of contributions from homohyperconjugative and/or spin polarization mechanisms;
2. HOMO symmetry of the molecule; and
3. The rigidity and the compliance to the W-plan arrangement of the molecule.

Though studies on these aspects have been extensive, systematic investigations on charge and/or steric effects brought about by a substituent on the hfsc of atoms in its immediate vicinity have been very meager (7). The second section of Chapter II of Part I of this dissertation, "The Substituent Effects on the Magnitude of $\underline{a}_7^H$-*anti* in Bicyclo-[2.2.1]heptane-2,3-semidiones, attempts to fill this need by studying *7*, a series of 7-*syn* substituted bicyclo[2.2.1]-heptane-2,3-semidiones.



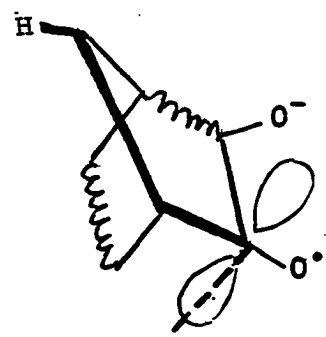
X=halogen, alkyl, alkoxy group

7

II. RESULTS AND DISCUSSION

A. Long-Range Interactions in Bicyclic Semidiones Containing Hetero Atoms

Homohyperconjugative long-range interaction depends, to a large extent, on the geometry of the molecule (9,10). The major hfsc in bicyclic semidiones are usually exhibited by atoms, such as the anti hydrogen in 8, which possess a coplanar zigzag arrangement (W or 2V plan) with the p-orbital of the semidione spin probe (9,10).

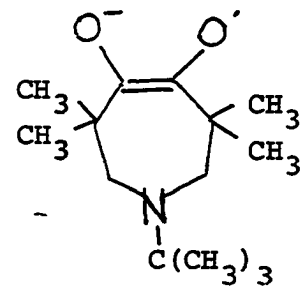


8

In recent years, precursors of semidiones with hetero atoms replacing the methylene bridge of 7 have been reported in the literature (11-18). If the hetero atom alone pair in these semidiones is in the anti position, it should form just like the anti hydrogen in 8, a perfect W or 2V arrangement with the p-orbital of the probe.

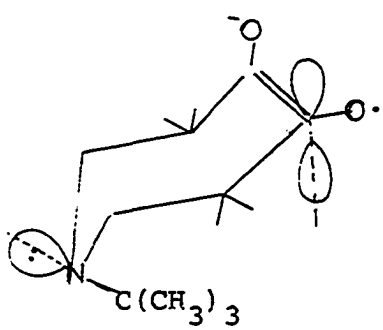
Because of the ease of the preparation of its hydroxy

ketone and diketone precursors (11), semidione 9 was the first to be studied and was designated as the model compound.

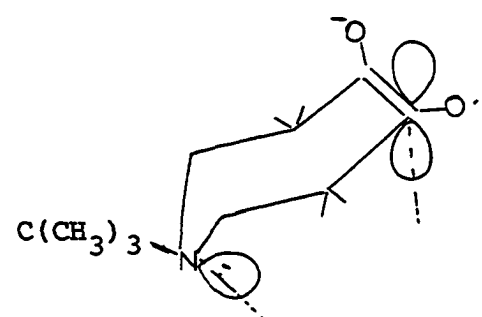


9

Just like its carbocyclic analogue, the cycloheptane semidione (19), 9 is expected to assume the stable chair conformation where the nitrogen lone pair can assume 2 orientations as shown in 10a and 10b. In 10a, the lone



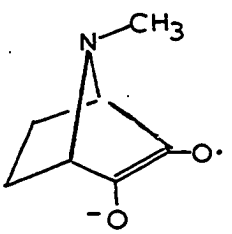
10a



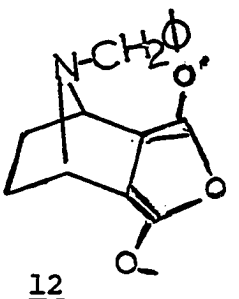
10b

pair forms a 2.5 V arrangement (an extended form of the W or 2V plan), with the p-orbital of the spin probe. The ESR of the semidione derived from the treatment of its monohydroxyketone precursor with Me_3COK indicated no a^N. This observation might be accounted for in part by the fact that 9 must be mostly in the more stable, but unfavorably oriented 10b form.

Semidiones 11 and 12 were desired in order to

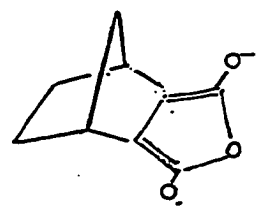


11



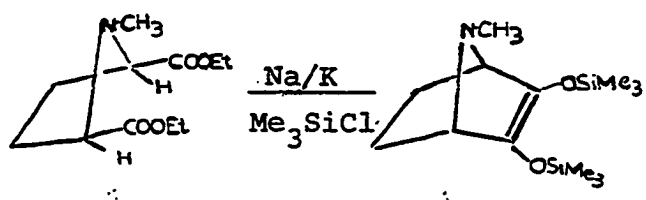
12

illustrate the importance of symmetry in long-range nitrogen coupling (20-22). a^N for 11 is expected to be bigger than for 12 since the HOMO of the semidione moiety of 11 is symmetric with respect to the plane which bisects the spin label and contains the nitrogen lone pair while the HOMO of 12 is antisymmetric. The carbocyclic analogues of 11 and 12 (1 and 13, respectively), gave a marked difference in their anti hydrogen hfsc (6.5G and 1.03G, respectively) (7,23).

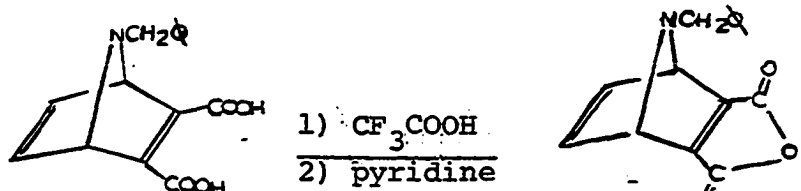


13

Unfortunately, the attempts to synthesize the precursors of 11 and 12 proved to be unsuccessful. A cyclic condensation of 14a (Equation 1) failed to produce 14b, while the attempted closure of 15 to 16 (Equation 2) proved futile.



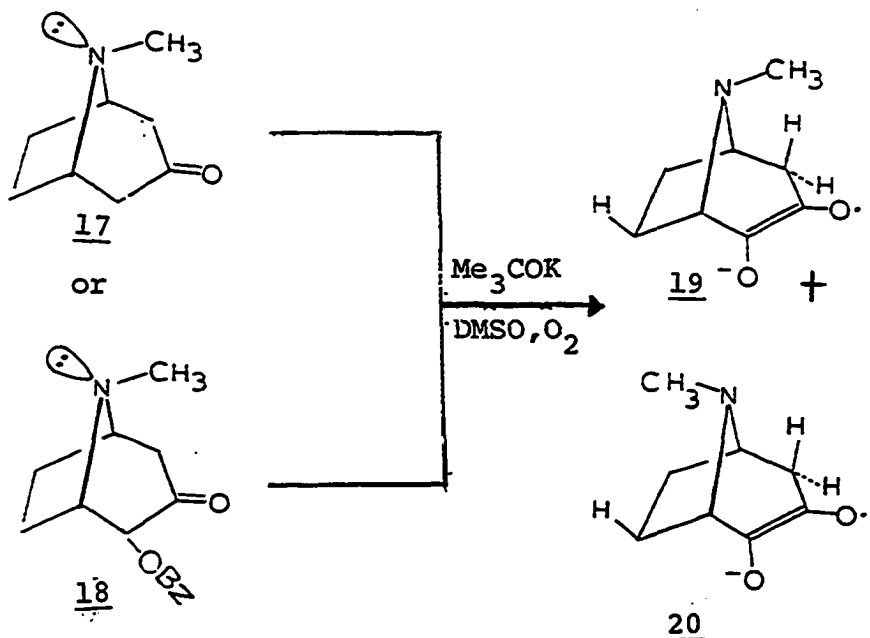
14a 14b (Equation 1)



15 16 (Equation 2)

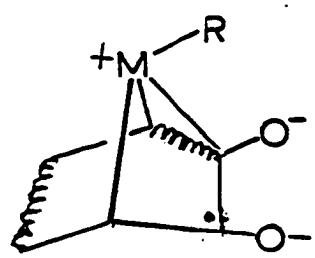
Tropinone 17 and its 2-benzoyloxy derivative 18, when treated with Me_3COK in DMSO (Scheme 1) gave an intriguing ESR spectrum which represents two species. The two sets of splitting constants observed seem to fit the spectra of syn and anti isomers 19 and 20 (a^H = 11, 7.9 and 3.5G and 15, 7.5, 3.5G, respectively), but neither set contained a signal which corresponded to a nitrogen hfs. Variable temperature experiments conducted between -60 and +90°C did not change the relative concentration of the two species.

Scheme 1:



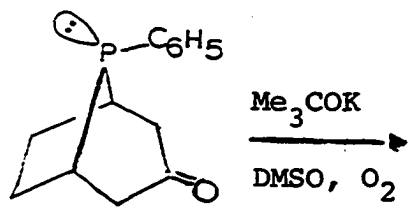
Contributing valence bond structure 6 involves an expansion of the valence shell of M to a pentacoordinated state. This seems to be highly unfavorable for nitrogen since it does not contain a d-orbital. Another contributing

structure 21 can also be considered but it does not place unpaired spin density on the atom M.



21

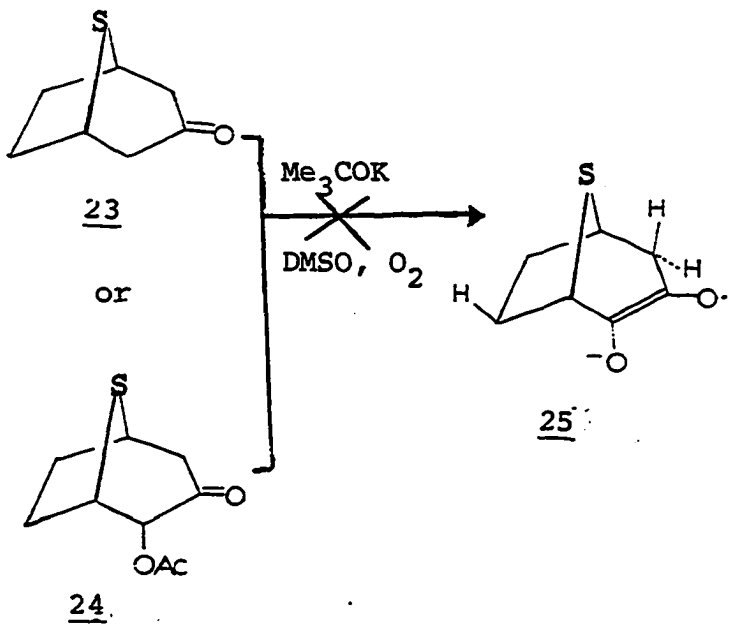
The resonance structure 6 might be more possible when the nitrogen bridge is replaced by a phosphorous atom which can expand its valence shell. The phosphorus analogue of tropinone, 22, was therefore synthesized from the reaction of phenylphosphine with cyclohepta-2,6-dienone (13). Treatment of 22 with Me_3COK in DMSO, however, did not give any ESR signal at all.



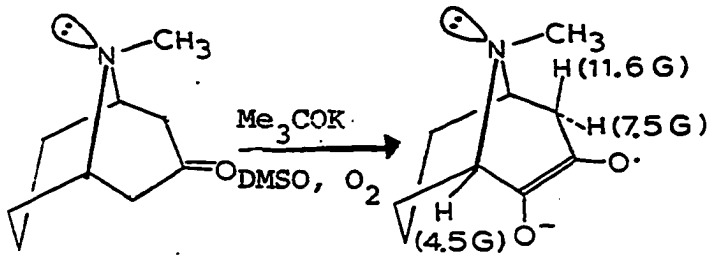
NO SIGNAL

22

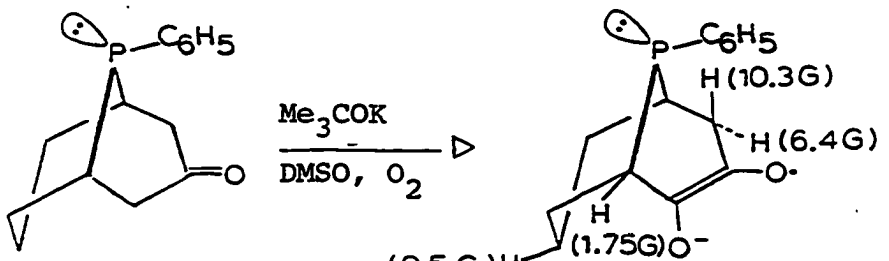
The sulfur analogue of 22 and 17, 9-thiabicyclo[3.2.1] octan-3-one 23 (15), and its 2-acetoxy derivative 24 failed to give the spectrum which would correspond to its semidione 25.



More success was obtained with the [3.3.1] bicyclic ring system. Pseudopelletierine 26a (12) and 9-phenyl-9-phosphabicyclo[3.3.1]nonan-3-one 27a (14) when oxygenated in basic DMSO, gave ESR signals corresponding to semidiones 26b and 27b, respectively.



26a 26b



27a 27b

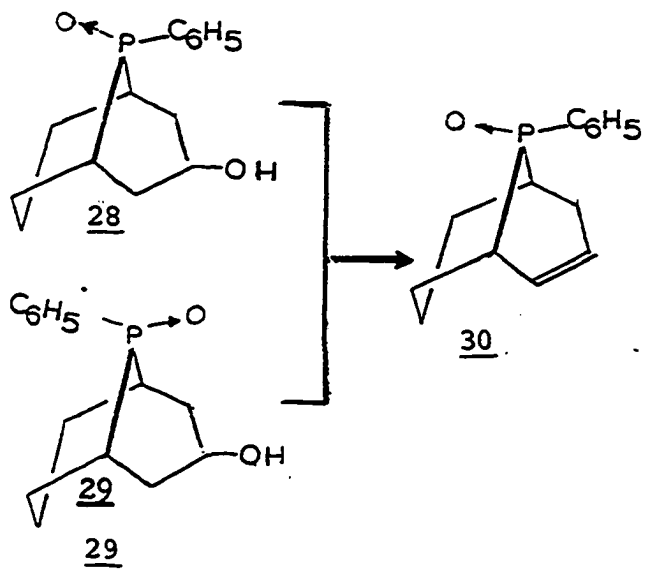
Unlike the spectrum generated from tropinone, the ESR spectra of both 26b and 27b indicated the presence of only a single species. There was, however, no $\underline{a}^{N}$ detected for 26b. In the case of 27b, there was an unassigned doublet splitting of 0.5 gauss which could be

attributed to P^{31} hfs, but this could also be due to the exo-H at C-8 or the endo-hydrogen at C-7.

The lack of hetero atom splitting in the spectra of 26b and 27b may suggest that they do not exist as the syn-alkyl isomers which would contain the correct geometry for homoconjugation to occur. However, precedents in the literature (24,25) show that, because of steric reasons, bicyclic hetero atom systems of this type prefer to exist with their alkyl group in the syn position.

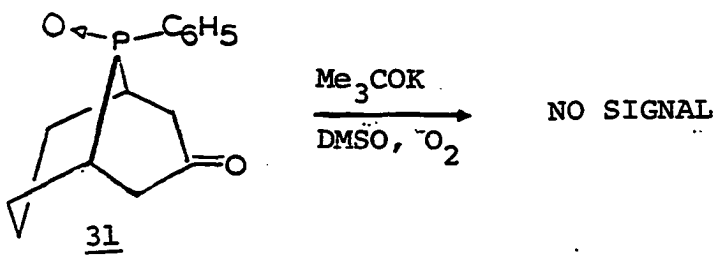
For example, Wiseman and Krabbenhoft reported (24) that dehydration of 28 and 29 (Scheme 2) both gave the syn isomer product 30 only, since steric relief results when a double bond is formed, i.e., the interactions between the ortho

Scheme 2:



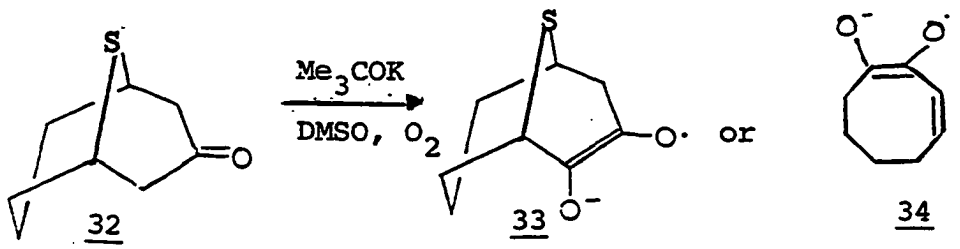
hydrogen of phenyl and axial hydrogen of carbons 6 and 8 in 28 and 29 are diminished. A similar phenomenon must be occurring when the ketone-containing side of the precursors of 26b and 27b is flattened as they are transformed to their respective semidiones.

The possibility that the spectra observed for 26b and 27b could be due to their oxides, generated during their ESR experiment, was eliminated when 9-oxo-9-phenyl-9-phosphabicyclo[3.3.1]nonan-3-one 31 (14) failed to give any signal at all when it was air oxidized in basic DMSO.



31

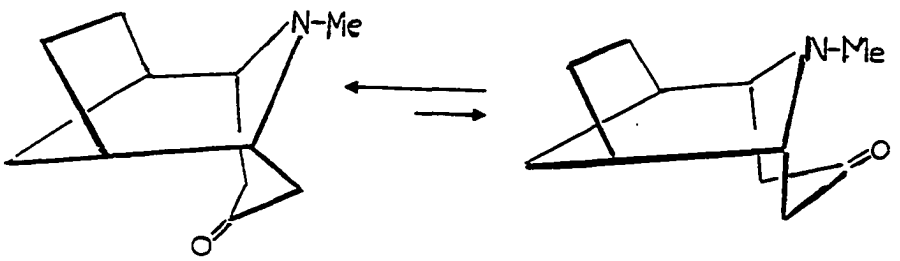
9-Thiabicyclo[3.3.1]nonan-3-one 32 (15), upon oxidation in basic solution, gave species 33, with a^H = 7.9, 5.6, 2.25, 0.63 and 0.06G which may be the sulfur analogue of 26b and 27b. However, the observed hfsc can also be attributed to the product of β-elimination of the thia bridge to give an 8-substituted $\Delta^{3,4}$-cyclooctane-1,2-semidione, 34.



Rigidity has been observed to favor enhanced long-range coupling (6,9,10). For example, among the four carbocyclic semidiones mentioned in the Introduction of Part I, 1, the most rigid of the four, has the biggest anti hydrogen coupling constant. Unfortunately, as previously stated in the first part of this section, the aza bicyclic analogue of 1 was not successfully prepared. There are, however, hetero atom-containing bicyclic compounds which could fill this need.

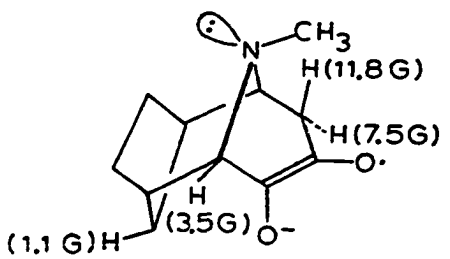
One such molecule is 6,9-endo-methylenehomopseudopelletierine (16). According to Paquette and Heimaster, this tricyclic ketone exists as a mobile equilibrium of conformers 35a and 35b, both of which have their nitrogen

lone pair in the favorable anti position.



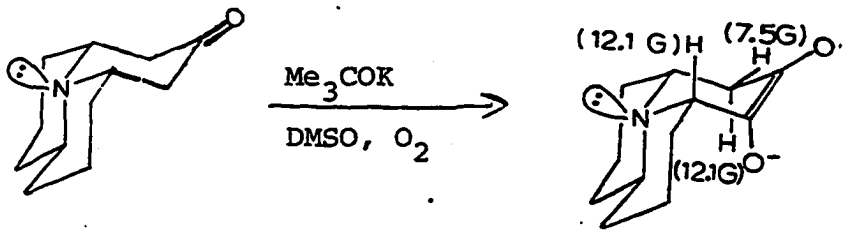
35a 35b

Despite its ideal geometry, this tricyclic ketone, upon oxygenation in basic DMSO, gave a species whose ESR spectrum was consistent with the semidione 36 with no detectable a^N.



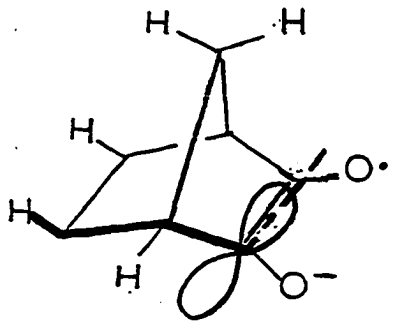
36

The air oxidation of another symmetrical and rigid tricyclic ketone 37a (17-18) gave a species whose ESR spectrum corresponded to its semidione 37b which like 36, failed to give any detectable a^N, despite its perfect geometry.



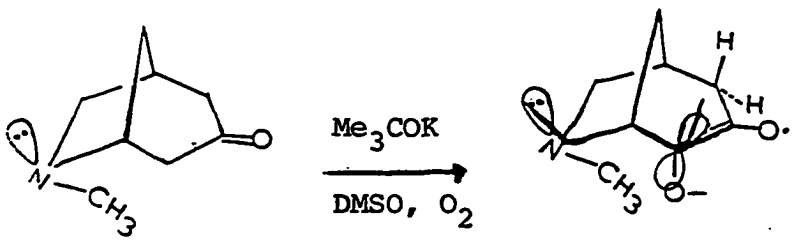
37a 37b

Aside from the anti-hydrogen, the exo-hydrogens in semidiones 1-4 (see Introduction), have also shown sizable hfsc since they also possess a W-arrangement with the p-orbital of the semidione as shown in 38. Compound



38

39a (26) is an ideal precursor to semidione 39b (Equation 3), which as the nitrogen analogue of 3, has its nitrogen lone pair in the correct exo position, similar to the exo-hydrogen on carbon 7 of 3. However, treatment of 39a with base and



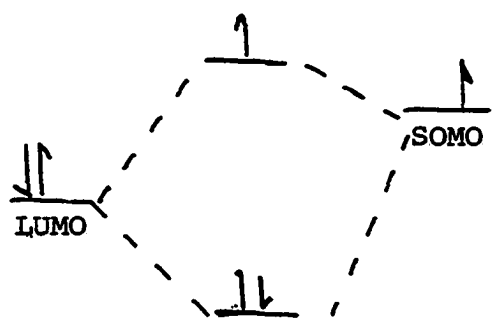
39a 39b

oxygen did not give a spectrum which could be attributed to 39b.

A substituent effect (which is further discussed in the next section and which is exemplified by the decrease in $a^{H}_{7\text{-anti}}$ in bicyclo[2.2.1]heptane-2,3-semidione when its syn H is replaced by methyl) might be a contributing factor for the lack of hetero atom coupling in the aza and phospha bicyclic compounds studied. Due to the difficulty in preparing the precursors of their unsubstituted equivalents, as well as their greater instability under the conditions of

the ESR experiments, the compounds studied were all alkyl substituted. But even so, the total absence of a long-range interaction is very surprising, especially in the case of the phospha derivatives. The lack of coupling to nitrogen might be expected in a way, since it cannot accommodate a valence shell expansion (see p. 10). However, phosphorus with its d-orbital, should not have this problem. Its lack of coupling might be due to the fact that during the homo-conjugative interaction between the p-orbital of the probe and the phosphorus lone pair, only one electron is promoted to the d-orbital. One study (27,28) has suggested that two or more electrons need to be promoted to the d-orbitals for appreciable stabilization to occur.

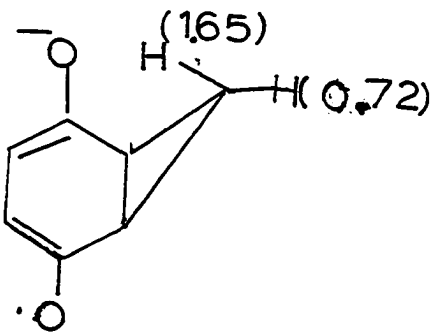
The absence of coupling could also possibly be attributed to a large energy gap between the energy of the LUMO of the hetero atom and the energy of the SOMO of the p-orbital of the semidione. Extended Hückel calculations on



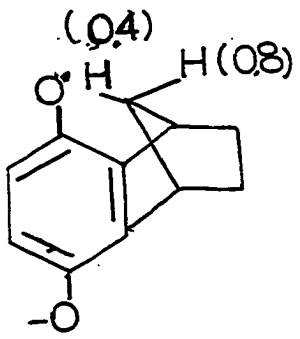
lone pair e⁻s p-orbital e⁻

these semidiones could certainly be helpful in verifying this point. However, at present, parameters necessary to calculate their geometry are not available.

Another point to consider is the important role of spin polarization in observing hetero atom lone pair coupling in the aza and phospha bicyclic semidiones studied. In a further study (29) of the role of the spin polarization mechanism in systems such as 40 and 41 (30), where electron delocalization cannot be a factor because the

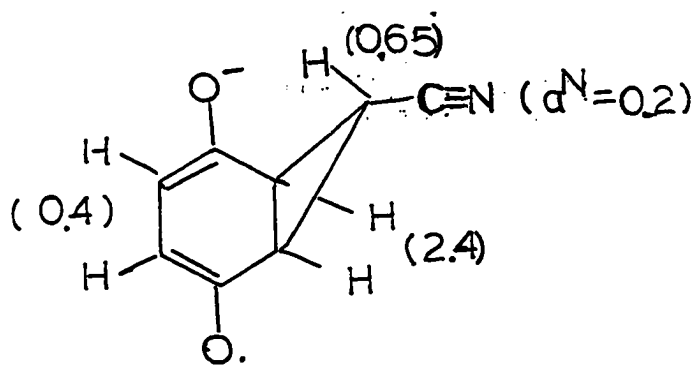


40



41

SOMO is antisymmetric, it was observed that the syn-cyano substituted analogue of 45, semiquinone 42, exhibited a nitrogen splitting. This a^N observed should be solely



42

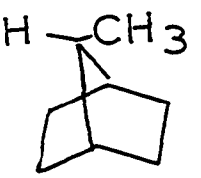
due to spin polarization, since delocalization cannot occur because the coefficients of the HOMO are opposite in sign and consequently cancel out (30,31).

In light of this observation, it is conceivable that the lack of coupling in the semidiones, might be attributable to the fact that spin polarization is not in operation in the aza and phospha bicyclic semidiones studied, where, as previously observed in other semidione systems (6), the more important mechanism in operation is homohyperconjugation.

Long-range coupling does not seem to be important in aza and phospha semidiones, for whatever reasons, and it was therefore decided to focus the attention on other more worthwhile undertakings.

B. Substituent Effects on the Magnitude of a $a^{H}_{7\text{-}\underline{anti}}$ of Bicyclo[2.2.1]-heptane-2,3-semidiones

Russell et al. had previously observed (7) that when the <u>syn</u> hydrogen of <u>1</u> was replaced by a methyl group (compound 43), $a^{H}_{7\text{-}\underline{anti}}$ fell from 6.48 to 3.11 gauss.



<u>43</u>

This observation is consistent with the homohyperconjugation mechanism. Being a through space interaction, it is sensitive to steric interference from the methyl group.

An electronic effect also is a possible explanation for the decrease in $a^{H}_{7\text{-}\underline{anti}}$ observed. The introduction of a methyl group could induce a redistribution of the charge density on this hydrogen, resulting in a change in its

spin density (6).

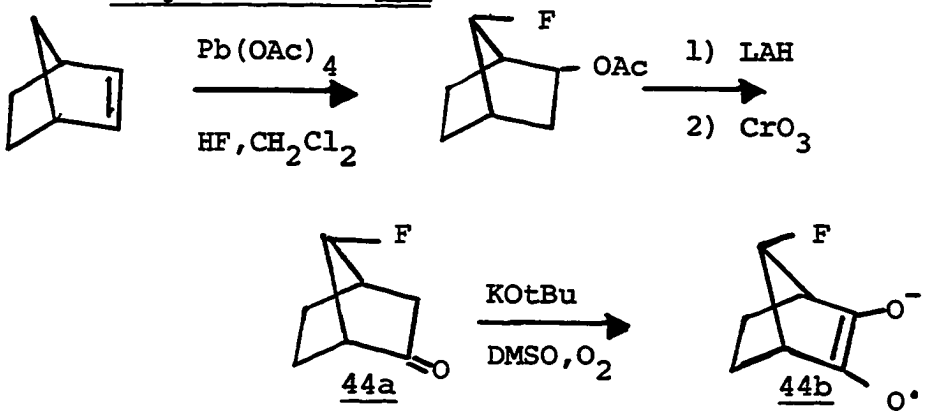
A study of 7, a series of syn substituted 1, with X of varying electronegativity and size could help differentiate between steric and electronic effects. The appropriate monoketone precursors (44a-48a) of the five target semidiones (44b-48b) were prepared according to the procedures shown in Scheme 3 (32-36) and their respective semidiones were generated by their oxygenation in basic DMSO.

The semidiones 44b, 45b and 46b with syn substituents of varying electronegativities could help elucidate the electronic effect while that of 48b could illustrate the steric effect when it shows a greater attenuation of $a^{H}_{7\text{-anti}}$ than 43. The combined effects could be studied with the use of 47b which contains tert-butoxy, a bulky, as well as an electronegative substituent.

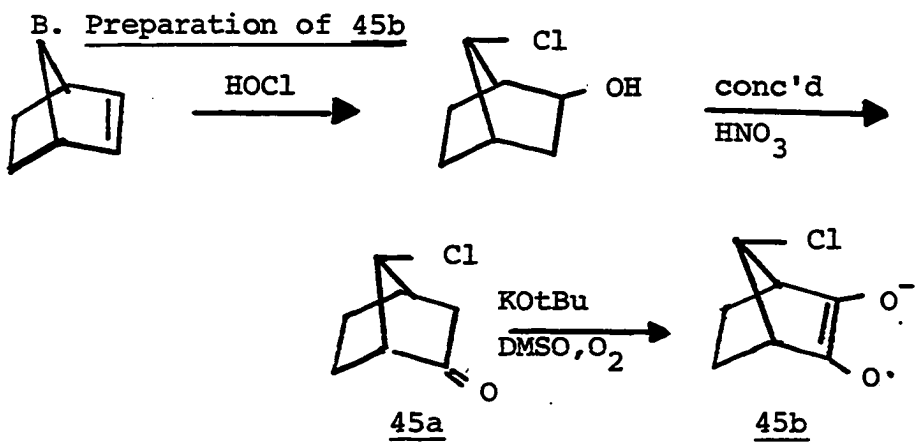
Of the five monoketone precursors, only 44a and 45a successfully generated species which could be attributed to their respective semidiones, 44b and 45b. Both semidiones 44b and 45b exhibited similar spectra, the most notable feature of which was the surprising absence of any $a^{H}_{7\text{-anti}}$. These results were not predicted by the extended Hückel (EH) calculations done on 44b (see Tables 1 and 2).

Scheme 3

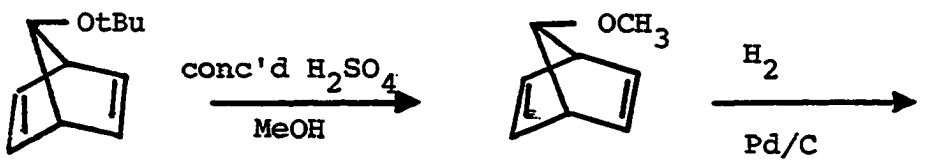
A. Preparation of 44b



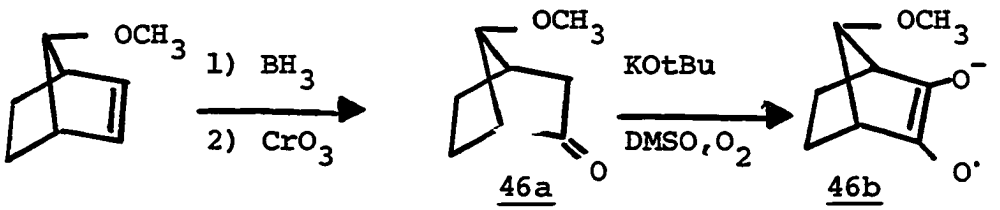
B. Preparation of 45b



C. Preparation of 46b

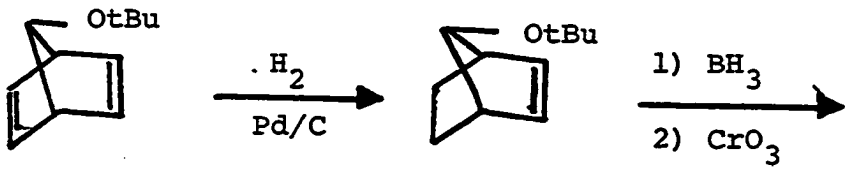


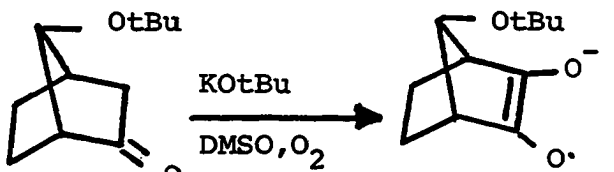
Scheme 3 (continued)



46a 46b

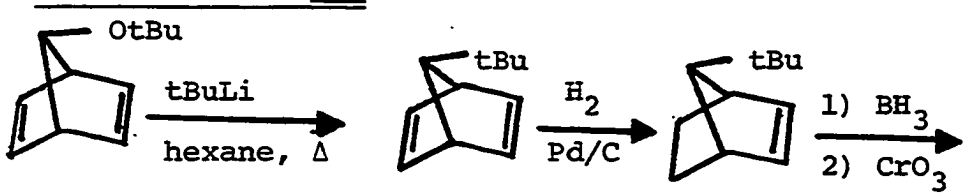
D. Preparation of 47b

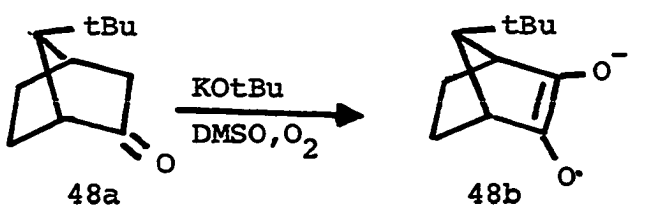




47a 47b

E. Preparation of 48b





48a 48b

Table 1. Extended Hückel calculations[a]

Semidione	Syn substituent	Spin density[b]	$a^{H}_{7\text{-anti}}$	
			calculated[c]	observed
1	H	.0003411	6.8	6.5
43	CH_3	.0000935	1.9	3.1
44b	F	.0002616	5.2	0

[a]Extended Hückel calculations were performed with a program obtained from E. R. Davidson of the University of Washington. This program (37) allows iterative calculations to charge self-consistency and permits the use of three mirror planes in the molecule. The atomic coordinates (Table 2) were obtained using parameters shown in Figure 1. The valence orbital ionization energies for F were calculated (38) from atomic spectral data and zeta exponents were determined from data compiled in Table 4 of the work of Cusachs and Corrington (39).

[b]Spin density = $(\text{coefficient})^2$.

[c]$a^{H}_{7\text{-anti}}$ calculated = spin density x 20,000.

According to these EH calculations, $a^{H}_{7\text{-anti}}$ is expected to be of almost the same magnitude as that of unsubstituted semidione 1. It must be noted that the decrease in $a^{H}_{7\text{-anti}}$ brought about by 7-syn CH_3 substitution in 43 was accurately predicted by EH calculations (7) (see Table 1).

EH calculations, however, are limited in their use, since they can only consider effects due to electron delocalization but not those due to spin polarization. The latter mechanism might be more important in this case.

A possible interaction between the lone pairs of the halogen and the p-orbital of the semidione probe can also cause a distortion in the geometry of the molecule, so as to disturb the W-plan arrangement. This effect could have been investigated by higher levels of calculations.

One can also argue that the electronegativity of the fluorine and chlorine (3.98 and 3.16, respectively, versus 2.2 for hydrogen) (40) might have affected the electron density of the anti hydrogen of carbon 7, so as to give a sizable perturbation in its spin density. This point might possibly have been verified had the study of the other target semidiones 46b-48b been realized.

The results obtained from the study of syn-Cl- and syn-F-bicyclo[2.2.1]heptane-2,3-semidiones helped in further illustrating the fact that substituents can indeed alter the magnitude of long-range coupling.

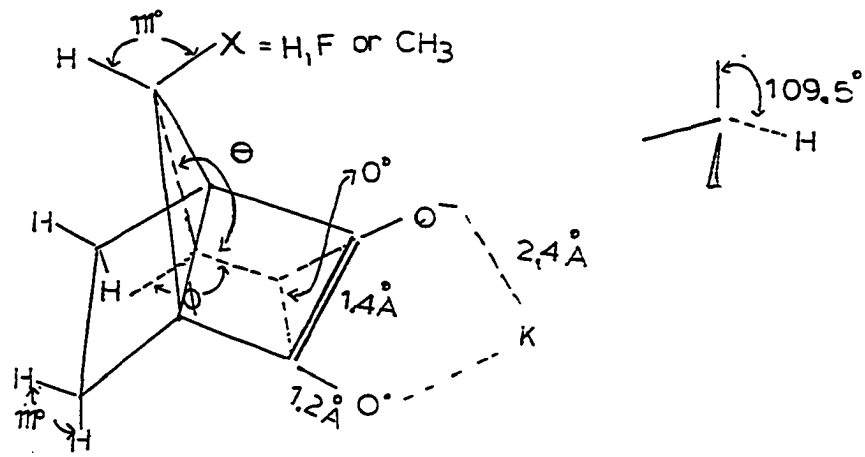


Figure 1. Geometry used in the molecular orbital calculations: d(C-C) = 1.54, d(C-H) = 1.09 Å, d(C-F) = 1.38 Å, θ = 134°, φ = 115 (7). Methylene and methine hydrogens were positioned so that all H-C-C angles for a given group were equal. Substitution of a methyl group or fluorine for C-7 hydrogen atoms was assumed to have no effect on geometry.

Table 2. Parameters for 1, 43 and 44b, used in extended Hückel calculations[a]

Atom[b]	x	y	z
Semidione 1			
X=H	0.5513	1.7954	0
C-1	0	0	-1.143
C-2	1.2439	-0.7925	-0.70
C-3	-1.2601	-0.8028	-0.770
H-anti	-1.2092	-1.4373	0
H-exo	-2.1532	-0.3066	-1.150
H-endo	-1.1878	-1.8218	-1.150
H-bridgehead	0.1911	0.5188	-2.0824
O	2.0868	-1.3295	-1.3998
Semidione 43			
$X=CH_3$			
C	0.8640	2.1192	0.0000
H	0.3776	3.0947	0.0000
H	1.7568	1.7623	-0.8898
Semidione 44b			
X=F	0.7535	2.0048	0

[a]A mirror in the xy plane generated the remainder of the molecule.

[b]The atoms are numbered or identified according to Figure 2.

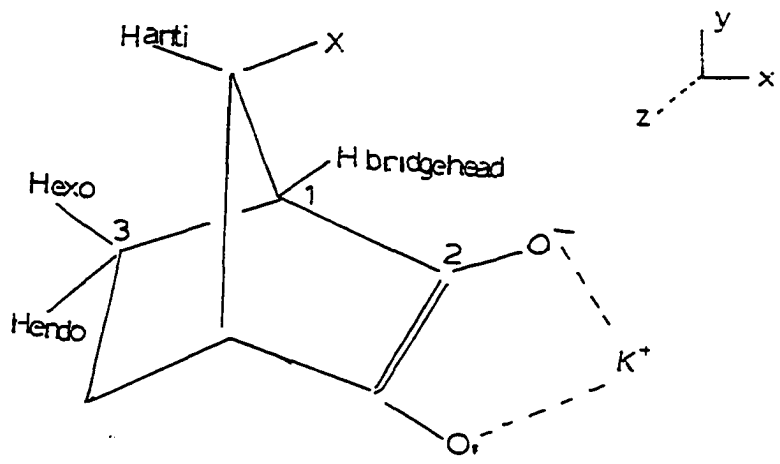


Figure 2. The numbering or identification of atoms of 7-X substituted bicyclo[2.2.1]heptane semidiones

III. CONCLUSION

The results from section 1, "Long-Range Interaction in Bicyclic Semidiones Containing Hetero Atoms", indicate that long-range coupling between the p-orbital of the spin probe and the hetero atom lone pair in aza and phospha bicyclic semidiones does not seem to be important for these systems despite their correct geometry. The arguments put forth to rationalize the lack of coupling were: substitutent effect, valence shell expansion, energy gap difference between the orbitals involved and the necessity of the involvement of the spin polarization mechanism.

In the second section, "The Substituent Effect on the Magnitude of $a^{H}_{7\text{-}\underline{anti}}$ in Bicyclo[2.2.1]heptane-2,3-semidiones", the effect of substituents on the magnitude of long-range coupling in bicyclic semidiones was dramatically illustrated by the complete absence of $a^{H}_{7\text{-}\underline{anti}}$ for 7-<u>syn</u>-chloro and 7-<u>syn</u>-fluoro bicyclo[2.2.1]heptane-2,3-semidiones. However, the limitations of the extended Hückel calculations (which did not predict the observed results) and the failure of their monoketone precursors to generate the other syn-substituted target semidiones did not enable us to properly tell which effect (steric and/or electronic) could be responsible for these observations.

IV. ESR SPECTRA

Figures 3-11 show the ESR spectra of the semidiones mentioned earlier which had not been observed previously.

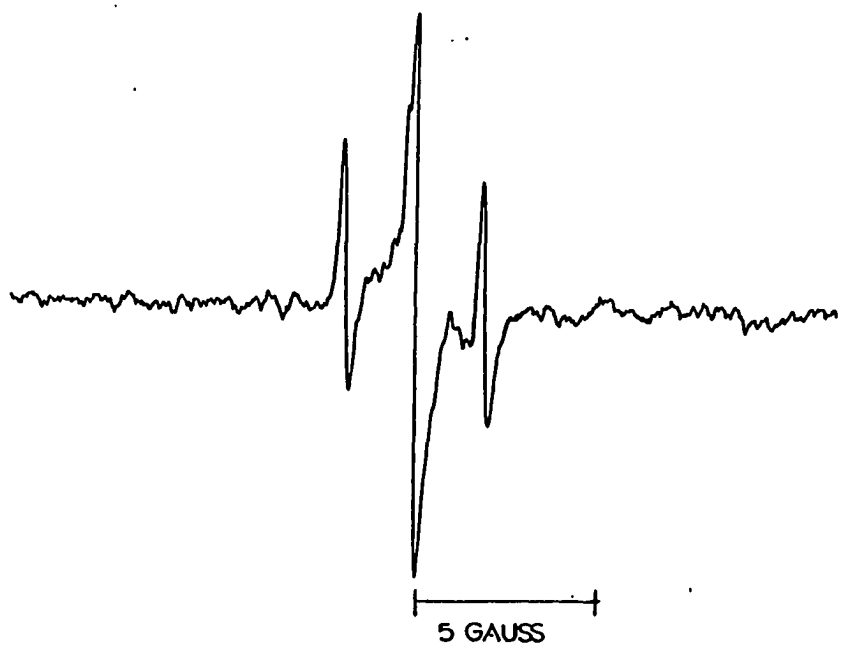


Figure 3. The first derivative ESR spectrum of N-tert-butyl-3,3,6,6-tetramethyl-1-azacycloheptane-4,5-semidione (9)

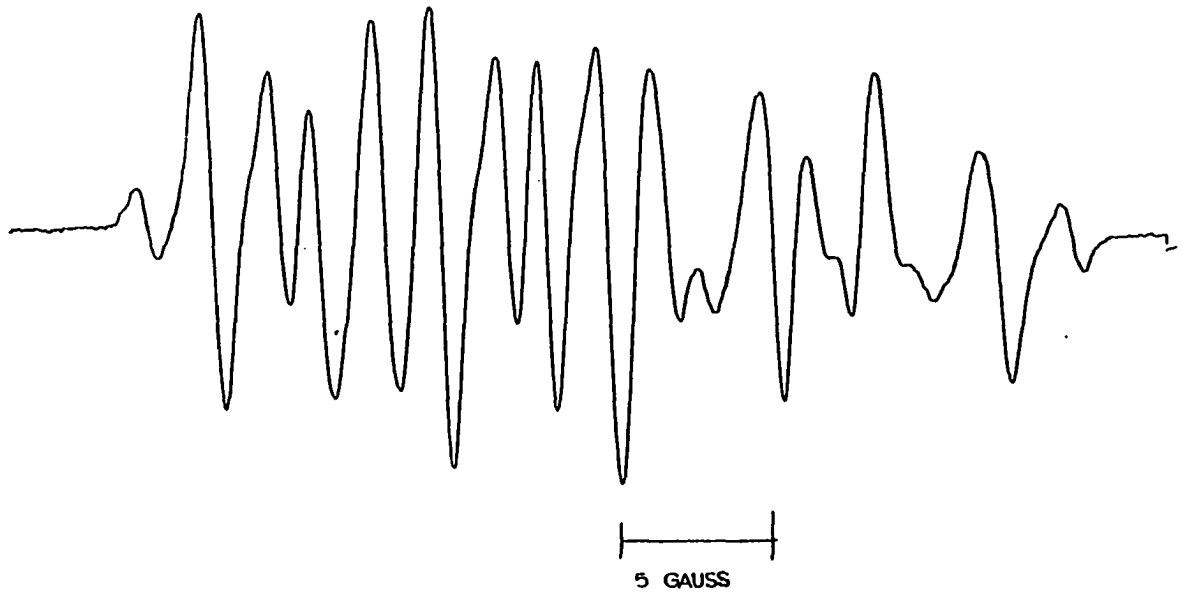


Figure 4. The first derivative ESR spectrum of semidiones (19 and 20) from treatment of α-benzoyloxytropinone with Me_3COK and DMSO with a trace of air

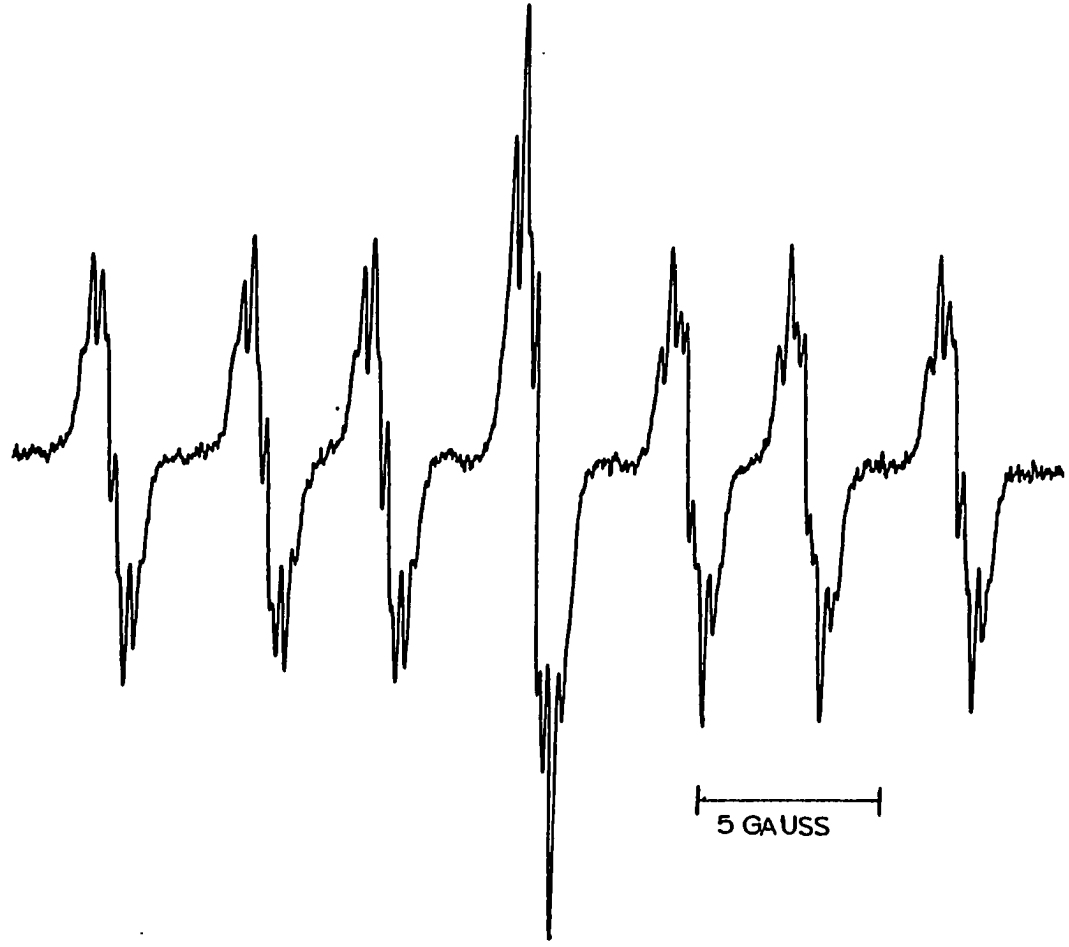


Figure 5. The first derivative ESR spectrum of pseudopelletierine-2,3-semidione (26b)

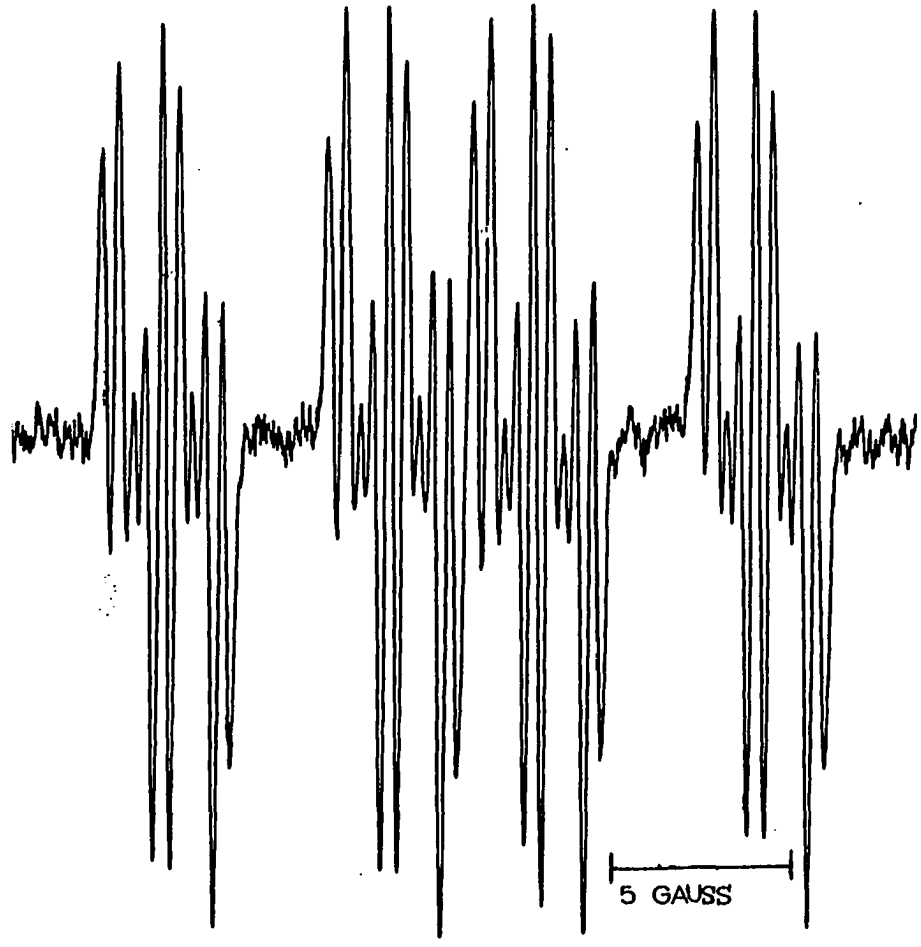


Figure 6. The first derivative ESR spectrum of 9-phenyl-9-phosphabicyclo[3.3.1]-nonane-2,3-semidione (27b)

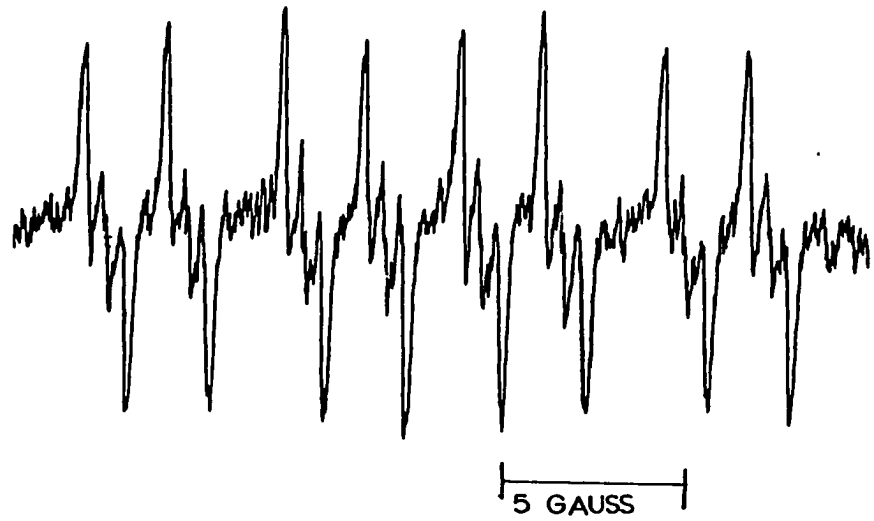


Figure 7. The first derivative ESR spectrum of 9-thiabicyclo[3.3.1]nonane-2,3-semidione (33) or $\Delta^{3,4}$-cyclooctane-1,2-semidione (34)

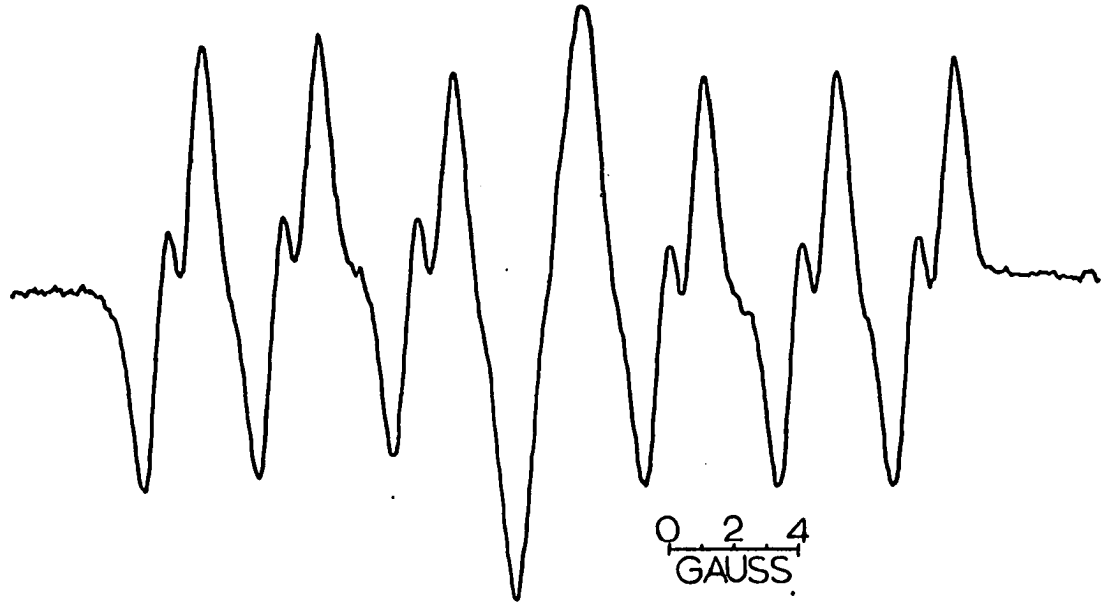


Figure 8. The first derivative ESR spectrum of 6,9-endo-methylenepseudopelletierine-2,3-semidione (36) (Dr. K.-Y. Chang provided this spectrum)

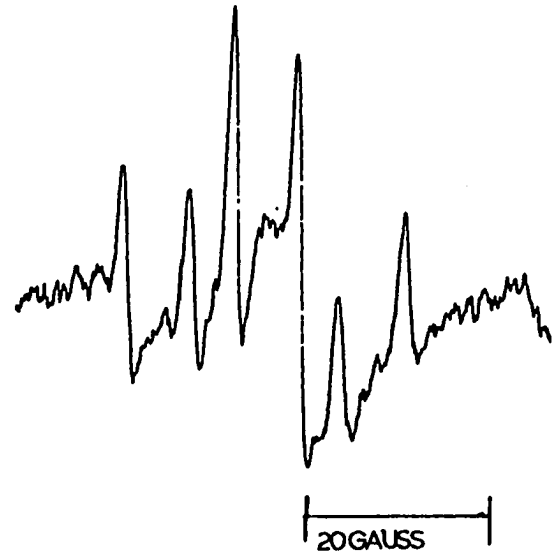


Figure 9. The first derivative ESR spectrum of semidione 37b (Dr. R. V. Stevens supplied the monoketone precursor 37a)

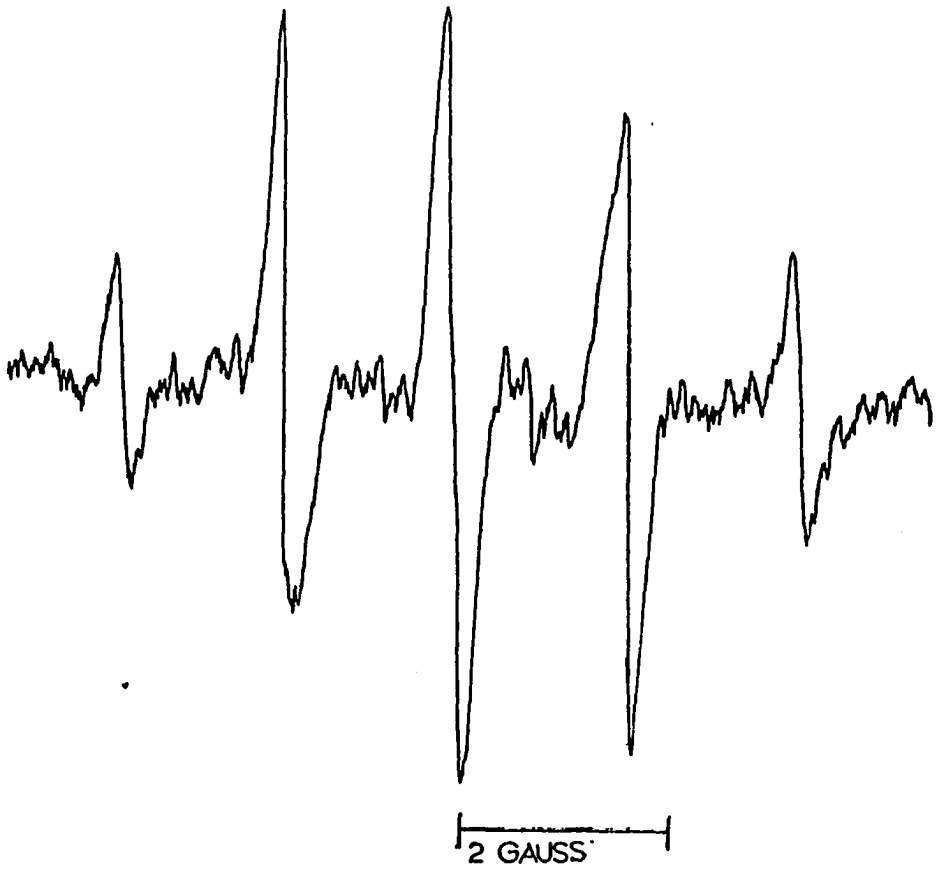


Figure 10. The first derivative ESR spectrum of 7-syn-fluorobicyclo[2.2.1]-heptane-2,3-semidione (44b)

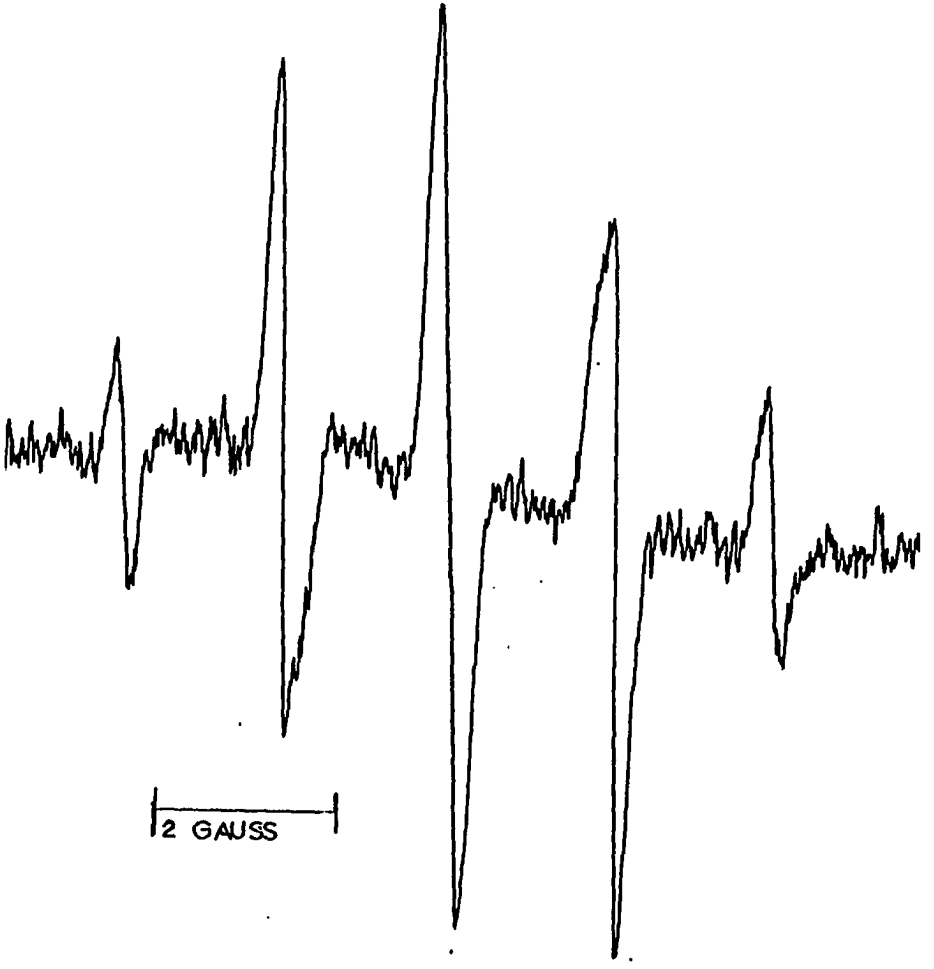


Figure 11. The first derivative ESR spectrum of 7-syn-chlorobicyclo-[2.2.1]heptane-2,3-semidione (45b)

V. EXPERIMENTAL

A. Instrumentation

ESR spectra were recorded on a Varian E-3 spectrometer.

Routine proton NMR spectra were recorded either on a Varian Model A-60, EM 360 or a Hitachi R-20B spectrometer. All chemical shifts were reported as parts per million (δ scale) using tetramethylsilane as standard.

Infrared (IR) spectra were recorded on either a Beckman IR-4250 or a Beckman Acculab-2 infrared spectrometer. All bands are reported in reciprocal centimeters (cm^{-1}).

Gas liquid chromatograph mass spectra (GLC-MS) were obtained on a Finnegan Model 4023 mass spectrometer. Exact mass measurements were obtained on a MS-902 mass spectrometer.

Gas liquid chromatographic data were obtained on a Varian Model 3700 or Beckmann GC 72-5. An Aerograph A-90P was used for the preparative GLC of samples.

All melting points (mp) were obtained on a Thomas-Hoover melting point apparatus and are uncorrected.

B. Generation of Semidiones

The procedure for generating the semidiones depended on the type of precursors used. When hydroxy-ketone, acetoxy-ketone or bis-(trimethylsiloxy)alkene precursors

were used, the semidiones were generated by mixing nitrogen-purged solutions (0.1-1.0 M) of these precursors in dimethyl sulfoxide (DMSO) (distilled from CaH_2 at reduced pressure and stored over molecular sieves) and potassium tert-butoxide (Me_3COK) in dimethyl sulfoxide as described by Holland (41).

When the monoketone precursors were used, the semidiones were generated by mixing first a solution of the monoketone in DMSO and a solution of Me_3COK in DMSO according to the procedure previously described and then adding a measured amount of air with a disposable syringe into the mixed solution.

C. Preparation of Compounds

Preparation of Bis-(n-butoxymethyl)-N-tert-butylamine:

The procedure of Johnson et al. (11) was followed. Paraformaldehyde (60.0 g, 2.0 mol), 1-butanol (149.7 g, 2.02 mol) and 200 ml C_6H_6 were placed into a flask. The mixture was warmed gently with stirring under nitrogen while tert-butylamine (74.9 g, 1.0 mol) was added dropwise over 1 hour. A Dean-Stark trap was attached to the flask and the mixture was heated to reflux. After 6 hours, most of the theoretical amount of water (35 ml) was removed. Benzene was distilled and the remaining liquid was vacuum distilled at 130-135°C

and a pressure of 15-16 mm Hg to give 132.1 g of colorless liquid product (52.8% yield).

^{1}H NMR (CCl_4): δ 0.91 (t, 6H), 1.19 (s, 9H), 1.42 (m, 8H), 3.29 (t, 4H) and 4.32 (s, 4H).

Preparation of diethyl N-tert-butyl-3,3'-imino-2,2,2',2'-tetramethyldipropionate:

Johnson's procedure was used (11). Into a dried flask containing 100 ml of dry ether, Mg (8.1 g, 0.30 mol) was added under N_2 at 10°C. While the mixture was being stirred with an overhead stirrer, ethyl α-bromoisobutyrate (50.35 g, 0.25 mol) in 200 ml dry ether was added dropwise for half an hour. The mixture was stirred for another hour.

Maintaining a 10°C temperature, bis-(n-butoxymethyl)-N-tert-butylamine (26.2 g, 0.11 mol) was added to the reaction mixture over a half-hour period. After allowing the mixture to stir for an hour at 10°C, it was warmed to 32°C and further stirred for another hour. The reaction mixture was quenched with cold aqueous ammonium chloride (approximately 0.6 mol). An acid-base work-up gave 23.5 g of neutral product and 18.91 g of basic crude amine product. Careful distillation (102-106°C, 0.13 mm Hg) of the amine product gave 13.5 g (37.3% yield) of expected product as a light yellow viscous oil.

^{1}H NMR (CCl_4): δ 0.92 (s, 9H), 1.09 (s, 12H), (1.2 (t, 6H), 2.73 (s, 4H), 4.03 (q, 4H).

Neutral product was distilled at 89°C, 0.13 mm Hg to give back starting material.

Preparation of N-tert-butyl-3,3,6,6-tetramethyl-1-azacycloheptan-4-on-5-ol:

Johnson's procedure was used (11). Into a dry 3-necked Morton flask, equipped with an overhead stirrer and condenser, was added 600 ml of dry toluene. After removal of 50 ml toluene from the flask by distillation under N_2, sodium metal (3.0 g, 0.13 mol) was added to the hot toluene and converted to a fine sand using a high-speed stirrer. The solution turned yellow. Diethyl N-tert-butyl-3,3'-imino-2,2,2',2'-tetramethyldipropionate (9.9 g, 0.03 mol) was added dropwise into the flask for a one hour period and the mixture was refluxed for an additional 2 hours after which time it was cooled to 10°C and 50 ml of 5% NH_4Cl was added dropwise under N_2 and with stirring. The organic layer was washed with water until the washings were neutral and the aqueous layer was backwashed with ether. The combined organic washings were dried with $MgSO_4$ and concentrated to give 6.0 g of yellow viscous oil. The crude oil product was stripped of remaining solvent and then sublimed (54°C, 0.18 mm Hg) to give a product, 5.66 g (76% yield), with a mp of 58-59°C.

^{1}H NMR (CCl_4): δ 0.60 (s, 3H), 0.91 (s, 3H), 0.97 (s, 3H), 1.05 (s, 9H), 1.20 (s, 3H), 2.56 (d, J_{AB} = 12 cps, 2H), 2.61 (d, J_{AB} = 14 cps, 2H), 3.57 (s, 1H) (absent in D_2O), and 4.01 (s, 1H).

IR (CCl_4): 3430, 2965, 1700, 1465, 1390, 1365, 1266, 1200 and 1039 cm^{-1}.

The preparation of N-tert-butyl-3,3,6,6-tetramethyl-1-aza-cycloheptane-4,5-dione:

A modification of Johnson's method (11) was used. A mixture of N-tert-butyl-3,3,6,6-tetramethyl-1-azacyclo-heptane-4-on-5-ol (2.0 g, 0.008 mol), pyridine (17.5 ml) and $Pb(OAc)_4$ (3.7 g, .008 mol) was heated to reflux for 24 hours under nitrogen. The solution which was initially brown turned yellow during reflux. The pyridine was removed *in vacuo* to give a brown residue. Water and ether was added to the residue and the pH of the aqueous layer was adjusted to 10. The aqueous phase was extracted five times with ether. The combined organic layer was dried over anhydrous K_2CO_3. The ether was evaporated and the residue distilled at 65-78°C, 0.18 mm Hg to give a light yellow oil. The oil, which was contaminated with starting material, was further purified by column chromatography using silica and 1% hexane in $CHCl_3$ as eluting solvent.

^{1}H NMR (CCl_4): δ 1.08 (s, 12H), 1.09 (s, 9H), 2.62 (s, 4H).

IR (CCl_4): 2970, 1725 (sh, 1700), 1475, 1390 and 1375 cm^{-1}.

Attempted preparation of 2,3-bis(trimethylsiloxy-7-methyl-7-azabicyclo[2.2.1]hept-2-ene 14b:

A modified procedure of Bloomfield's (42) was used. Sodium metal (1.5 g, 0.065 mol) and potassium metal (1.5 g, 0.035 mol) were placed in a 3-necked round-bottomed flask containing 200 ml of dry C_6H_6. The Na/K mixture was heated at about 45°C with vigorous stirring until it turned into greyish sand. Trimethylchlorosilane (11.0 ml, 0.102 mol) and cis-N-methylpyrrolidine-α,α'-bis(ethyl carboxylate)[1] (5 g, 0.022 mol) were mixed together in 40 ml C_6H_6, and the resulting solution added dropwise into the Na/K sand. The reaction mixture was heated to reflux for 8 hours after which the solution was allowed to cool. The Na/K solid was filtred off and the solvent was evaporated. The GLC-MS and NMR of the crude residue was taken and did not contain the data expected for 14b.

---

[1]This was furnished by Gregory Walraff, Iowa State University, Ames, Iowa and can be prepared according to Braun and Seeman's method (43).

Preparation of N-benzylpyrrole:

The procedure described by Josey et al. (44) was followed. 2,5-Dimethoxyfuran (30.6 g, 0.23 mol) and 57 ml of glacial acetic acid were mixed in a 250-ml 3-necked flask fitted with a condenser and addition funnel. Benzylamine (25 ml, 0.229 mol) was added to the mixture which turned warm and yellow in color. The solution was heated to reflux for 1 hour during which the mixture turned brown. The reaction mixture was cooled and the acetic acid was removed by distillation. The resulting dark residue was fractionally distilled through a 10-inch Vigreaux column at 95-100°C, 1.8 mm Hg to give a colorless liquid product, 16.55 g (45% yield).

^{1}H NMR (CCl_4): δ 4.5 (s, 2H), 6.1 (d x t, 2H), 6.4 (t, 2H), 7.0 (m, 5H).

Preparation of acetylenedicarboxylic acid:

The method given by Adams et al. (45) was used. A solution of 40 ml of H_2SO_4 in 159 ml H_2O were mixed with acetylenedicarboxylic monopotassium salt (36.4 g, 0.24 mol). The mixture was extracted about 4 times with 66 ml portions of ether. The ether solution was dried over $MgSO_4$ and stripped of its solvent. The resulting pale yellow solid was dried over anhydrous P_2O_5 *in vacuo* (H_2O aspirator).

Preparation of 2,3-dicarboxy-7-benzyl-7-azabicyclo[2.2.1]-hepta-2,5-diene 15:

The procedure described by Mandell and Blanchard (46) was followed. N-Benzyl pyrrole (14.8 g, .094 mol) and anhydrous acetylene dicarboxylic acid (10.7 g, .094 mol) were mixed with 100 ml of dry ether. The mixture was refluxed for 2 days and the yellow orange solution was filtered through a glass fritted funnel. The filtrate was returned to the reaction pot and refluxed as before. The residue was washed with acetone until it was pale yellow. The process of filtering was repeated four times to give 3.57 g of product (mp 207-210°C).

^{1}H NMR: 4.15 (br s, 2H), 5.6 (t, 2H), 7.35 (br s, 2H), 7.4 (br s, 5H).

The attempted preparation of the anhydride of 2,3-dicarboxy-7-benzyl-7-azabicyclo[2.2.1]hepta-2,5-diene 16:

The procedure was adapted from that of Duckworth's (47). Compound 15 (1 g, 0.003 mol) was added under N_2 to a 3-necked flask, containing 5 ml anhydrous ether. Trifluoroacetic anhydride (0.5 ml, 0.0037 mol) was added dropwise and the reaction mixture allowed to stir for 40 minutes and then heated to reflux for 1 hour. After this time, the reaction mixture was cooled and 19 ml of petroleum ether was added. Pyridine (0.6 ml, 0.0047 mol) was added at one time. The

ether was evaporated by a rotary evaporator and the solid filtered. The petroleum ether of the filtrate was evaporated and the NMR spectrum of the residue did not show any peaks which are characteristic of the expected product.

The solid residue was treated with acetone and filtered. The yellow residue had a mp of 205°C similar to that of the starting material. The NMR of the residue was also characteristic of the reported NMR of the starting material (46).

The preparation of 2-benzoyloxytropinone 18:

n-BuLi in hexane (2.4 M, 2.01 ml, 4.4 mmol) was added to THF (10 ml) in a 50-ml round-bottomed flask under nitrogen. The solution was cooled to -78°C and diisopropylamine (0.57 ml, 4.1 mmol) was added with stirring. After 15 minutes, tropinone (0.57 g, 4.1 mmol) in THF (2 ml) was added to the mixture over a period of 1 minute. After stirring for 15 minutes at -75°C, the mixture was allowed to stir at room temperature for 24 hours. After this period, 7 ml of saturated $NaHCO_3$ was added to the mixture. The two phases were separated, and the aqueous phase was washed with CH_2Cl_2 (3x). The combined organic layers was washed successively with saturated $NaHCO_3$ and NaCl solution and dried over Na_2SO_4. The solvent was evaporated affording 0.80 g crude product which was subjected to Prep TLC (silica, 3x3:1 EtOAc/C_6H_6 eluant). One of the bands was determined to be the product.

^{1}H NMR (CCl_4): δ 1.8-2.9 (m, 8H), 2.6 (s, 3H), 3.9 (broad s, 1H), 7.5-8.0 (m, 5H)

IR (neat): 1750, 1730, 1555 (br s) cm^{-1}

GLC-MS: m/e 259, 154 (loss of PhCOO), 105 (PhC=O), 122 (PhCOOH).

Exact mass: observed; 259.12149; calculated for $C_{15}H_{17}NO_3$; 259.12058 (error +2.5 ppm).

Preparation of cycloheptanone ethylene ketal:

Garbisch's method was followed (48). A solution of cycloheptanone (25.3 g, 0.23 mol), ethylene glycol (14 g, 0.87 mol) and a catalytic amount of p-toluenesulfonic acid in 100 ml C_6H_6 was heated to reflux in a distillation set-up equipped with a Dean Stark trap until approximately 4 ml of H_2O was collected. The reaction mixture was washed with saturated $NaHCO_3$ solution and dried over Na_2SO_4. The solvent was evaporated off to give 19 g of crude ketal.

^{1}H NMR (CCl_4): δ 1.4-2.4 (m, 12H), 3.7 (s, 4H).

Preparation of dibromocycloheptanone ethylene ketal:

Garbisch's procedure was used (48). To a solution of cycloheptanone ethylene ketal (19.0 g, 0.12 mol) in 180 ml of anhydrous ether was added bromine (12 ml), at such a rate as

to obtain a gentle reflux. Extra bromine was added until the bromine color persisted for several minutes.

A solution of monosodium ethylene glycolate prepared from 6.0 g of sodium and 90 ml of ethylene glycol was added slowly. The resulting mixture was poured into water and the ether layer separated and dried. The ether was evaporated under reduced pressure to give the crude product.

Preparation of cycloheptadienone ketal:

Garbisch's method was followed (48). The crude dibromocycloheptanone ethylene ketal (25 g) was added to a mixture of 26.0 g NaOH and 120 ml MeOH and the reaction mixture was heated to reflux for 48 hours.

The reaction mixture was poured into 200 ml of saturated NaCl solution. The product was extracted twice with pentane. The combined extracts were dried and the pentane was evaporated. The residue was distilled at 70°C, 0.15 mm Hg to give the product.

^{1}H NMR (CCl_4): δ 2.25 (m, 4H), 3.85 (s, 4H), 5.7 (m, 4H).

Preparation of cyclohepta-2,6-dienone:

Caution: This is a skin irritant. The procedure given by Garbisch was used (48). The cycloheptadienone ketal was shaken with an equal volume of 3% H_2SO_4 for 5 minutes. The product was extracted with several portions of ether. The

combined ether extracts was washed with dilute sodium bicarbonate and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue distilled at 36°C, 0.15 mm Hg to give the product.

^1H NMR (CCl_4): δ 2.4 (t, 4H), 5.9 (d, $\underline{J}$ = 12 cps, 2H), 7.7 (m, 2H).

Preparation of 8-phenyl-8-phosphabicyclo[3.3.1]octan-3-one, 22:

This was prepared according to Kashman and Benary's procedure (13 and 14). A mixture of cyclohepta-2,6-dienone (1.0 g, 0.0083 mole) and phenylphosphine (1.03 ml, 0.0083 mole) was heated on an oil bath for 8 hours under N_2 at 130-135°C. When the reaction was over, the solution was cooled to room temperature. The unreacted reactants were removed under vacuum. The residue was recrystallized from acetone to give the product.

^1H NMR ($CDCl_3$): δ 1.8 (m, 4H), 2.52-3.0 (m, 6H), 7.3 (m, 5H).

IR: 3020, 1695, 1590, 1430 cm^{-1}.

Preparation of 8-thiabicyclo[3.2.1]octan-3-one, 23:

The procedure described by Sasaki et al. (15) was followed in preparing 23. A mixture of cyclohepta-2,6-dienone (1.89 g) and sodium sulfide nonahydrate (14.7 g) in 80% (v/v) aqueous methanol (264 ml) was stirred for 40 hours at

room temperature. The mixture was diluted with 240 ml of H_2O and extracted 4 times with 80 ml dichloromethane. The combined extracts was washed twice with 20 ml H_2O and dried over anhydrous sodium sulfate. Removal of the solvent gave the crude product which was purified by sublimation (39°C, 0.1 mm Hg) to give the pure product:

^1H NMR ($CDCl_3$): δ 2.1 (broad s, 4H), 2.8 (m, 4H), 3.8 (broad s, 2H).

IR ($CHCl_3$): 1710, 1400, 1330 cm^{-1}.

Preparation of 8-thiabicyclo[3.2.1]octan-3-one-2-acetate, 24:

A mixture of 8-thiabicyclo[3.3.1]octan-3-one, 23, (0.4 g, 0.028 mol) and lead tetraacetate (4.83 g; .012 mol) in 15 ml C_6H_6 was refluxed for 116 hours. The product was extracted with ether. The ether was evaporated and the residue was sublimed.

^1H NMR ($CDCl_3$): δ 2.1 (s, 3H), 2.1-2.8 (m, 4H), 3.3-3.9 (m, 4H), 5.1 (broad s, 1H).

IR (neat): 1740 (broad), 1380, 1235, 1030 cm^{-1}

GLC-MS: m/e (rel. intensity) = 200.02 (24.25), 157.96 (100.00), 113.82 (4.08), 100.82 (43.10), 98.84 (23.80), 96.72 (17.22), 84.86 (14.10), 78.90 (13.48), 73.86 (10.95), 70.86 (20.05), 66.92 (88.02), 64.90 (10.84), 54.92 (19.29), 52.92 (10.56), 45.06 (40.49).

Preparation of pseudopelletierine 26a:

The method described by Cope et al. (12) was used. To glutaraldehyde (72 g of a 25% aqueous solution) were added, in order, 126 ml H_2O, methylamine hydrochloride (98%, 18.0 g, 0.26 mol) dissolved in 180 ml H_2O, acetone dicarboxylic acid (30.0 g, 0.195 mol) dissolved in 299 ml H_2O and a solution of disodium hydrogen phosphate heptahydrate (27 g, 0.1 mol) and NaOH (2.7 g, .068 mol) dissolved in 72 ml H_2O by heating. The mixture was stirred under N_2 for 24 hours during which CO_2 was evolved and the pH of the solution which started as 2.5 increased to 4.5. Concentrated HCl (36 ml) was added to the solution and heated for 1 hour at 80°C. The solution turned orange brown. After the solution was cooled to room temperature, 27 g of NaOH in 36 ml of H_2O was added and the basic mixture was extracted promptly 8 times with 90 ml of CH_2Cl_2. The combined organic extracts was dried over Na_2SO_4, and the solvent evaporated. The residue was sublimed at 40°C, 0.3 mm Hg to give a white product.

Preparation of cyclooctan-2,7-dienone:

Garbisch's procedure (48) used for the preparation of cyclohepta-2,6-dienone, as previously described, was followed.

^1H NMR (CCl_4): δ 1.5-2.6 (m, 6H), 6.2 (m, 4H).

Preparation of 9-phenyl-9-phosphabicyclo[3.3.1]nonan-3-one, 29a:

A procedure similar to that previously described for the preparation of 8-phenyl-8-phosphabicyclo[3.2.1]octan-3-one was employed using cycloocta-2,7-dienone (3.0 g, 0.025 mole) and phenylphosphine (2.8 g, 0.025 mole).

^{1}H NMR: δ 1.22-2.50 (m, 6H), 2.54-3.02 (m, 4H), 3.02-3.12 (m, 2H), 7.32 (m, 5H).

IR ($CHCl_3$): 1690 (C=O) cm^{-1}.

Preparation of 9-oxo-9-phenyl-9-phosphabicyclo[3.3.1]-nonan-3-one, 31a:

The procedure used was adapted from Kashman and Benary's method (14). A stream of air was passed through a solution of 29a in $CHCl_3$ for 48 hours. The solvent was evaporated to give 31.

^{1}H NMR ($CDCl_3$): δ 1.4-2.3 (m, 8H), 2.53-3.4 (m, 6H), 7.5-7.9 (m, 5H).

IR: 1710 (C=O), 1100, 1120, 1150 cm^{-1}.

Preparation of 9-thiabicyclo[3.3.1]nonan-3-one, 32:

The method used for preparing 32 was similar to that used in the previously described preparation of 23 (15).

^{1}H NMR: δ 1.03-2.35 (m, 6H), 2.81 (q, J = 16.8 cps, 4H), 3.24 (broad s, 2H)

IR($CHCl_3$): 1710 (C=O), 1300, 1120 cm^{-1}.

Preparation of 1-(bromomethyl)allyl methyl ether:

The modified procedure by DeGraw et al. (49) was used. To a flask equipped with an overhead stirrer, a dry ice condenser, addition funnel, and a drying tube was added 340 ml of MeOH. The flask was cooled to -10°C and 1,3-butadiene (360 ml, 223 g, 4.1 mol) was condensed into the flask. Methanol (1400 ml)was added and with good stirring N-bromosuccinimide (350 g, 2.01 mol) was added through a funnel in portions over a 2-1/2 hour period while maintaining the temperature at -8 to 12°C. The solution was allowed to warm to room temperature after being stirred for an additional 3-1/2 hours and the mixture was poured into 4 l of water. The aqueous mixture was extracted with 700 ml portions of pentane (4x), the extract dried over $MgSO_4$ and filtered. Pentane was removed by distillation at atmospheric pressure. The residue was distilled (42°C, 18 mm Hg) to give 100 g of product (collected in a cooled receiver).

^{1}H NMR: δ 3.0 (m, 2H), 3.33 (s, 3H), 3.75 (m, 1H); 5-6 (m, 3H).

Preparation of 2-methoxybuta-1,4-diene:

The procedure described by DeGraw et al. (49) was used. To a hot (95-100°C) solution of KOH (63 g, 1.1 mol), in diethylene glycol (750 ml) in a flask equipped for distillation, was added 1-(bromomethyl)allyl methyl ether (120.4 g) over a period of 75 minutes. The temperature was slowly raised to 130°C over a 2 hour period and some distillate was colleted. Water (37.4 ml) was added to the glycol solution and the steam distillate (4.5 ml) was collected. The two layers of the combined distillates were separated and the aqueous phase discarded. The organic layer was dried over $MgSO_4$, leaving 21.1 g crude product which was distilled using a Vigreaux column at 68°C, to give 15.6 g of product.

^1H NMR: δ 3.4 (s, 3H), 4.15 (s, 2H), 5.0-6.3 (m, 3H).

Preparation of ethyl 4-methoxy-3-cyclohexenecarboxylate:

A modification of the procedure of Fiesselmann was followed (50). A mixture of 2-methoxybuta-1,4-diene (11.4 g, 0.136 mol), ethyl acrylate (22 ml, 23.8 g, 0.238 mol) and 1 gram hydroquinone in benzene (28.5 ml) was heated to reflux overnight under nitrogen. Benzene was distilled and the residue was distilled by the Kugelrohr technique to give 11.95 gm (47.8%) of product.

^1H NMR (CCl_4): δ 1.3 (t, 3H), 1.7-2.5 (m, 7H),
3.45 (s, 3H), 4.1 (q, 2H), 4.5 (broad t, 1H).

Preparation of N-methyl-4-methoxy-3-cyclohexenylcarboxamide:

The method of Furtoss et al. (26) was used. Methylamine (approximately 6.25 g, 0.20 mol) was condensed into a flask fitted with a dry ice condenser, which contained MeOH (21.7 ml), sodium methoxide (0.869 g, 0.01 mol) and ethyl-4-methoxy-3-cyclohexenecarboxylate (3.0 g, 0.0763 mol). The flask was stoppered and stirred with a magnetic stirrer for 72 h at room temperature. Methanol and remaining methylamine were evaporated and the white solid residue dissolved in CH_2Cl_2 (20 ml) containing a small amount of water. The two layers were separated and the methylene chloride phase was washed with a small volume of brine. The aqueous layers were extracted with CH_2Cl_2 and the combined organic layers were dried and evaporated. The residue was recrystallized from cyclohexane to give 1.77 g of product.

^1H NMR ($CDCl_3$): δ 1.7-2.5 (m, 7H), 2.85 (d, 3H), 3.55 (s, 3H), 4.6 (m, 1H), 5.8 (m, 1H).

Preparation of 1-methoxy-4-(N-methylaminomethyl)cyclohexene:

The procedure by Furtoss et al. (26) was used. N-Methyl-4-methoxy-3-cyclohexenylcarboxamide (4.4 g, 0.026 mol) dissolved in dry THF (41 ml) was added slowly to a rapidly stirred slurry of $LiAlH_4$ (1.65 g, 0.043 mol) in THF (55.5 ml). Stirring was continued and the mixture heated to reflux for 20 h. After cooling in an ice bath, the mixture was

hydrolyzed by adding dropwise H_2O (1.64 ml), NaOH (15%, 1.6 ml), and H_2O (4.93 ml) followed by rapid stirring for 15 min. The solution was filtered and the remaining residue carefully washed with ether. The combined organic layers were dried ($MgSO_4$) and evaporated and the residue distilled by the Kugelrohr technique (0.1 mm/67°C). The yield of product was 2.75 g (68.7%).

^1H NMR (CCl_4): δ 0.8 (s, 1H), 1.2-2.2 (m, 7H), 2.4-2.6 (m, 2H), 2.35 (s, 3H), 3.45 (s, 3H), 4.5 (m, LH).

Preparation of 1-methoxy-4-(N-chloro-N-methylaminomethyl)-cyclohexane:

The method of Furtoss et al. (26) was used. A heterogeneous mixture of 1-methoxy-4-(N-methylaminomethyl)cyclohexene (0.93 g, 0.006 ml), CH_2Cl_2 (4.0 ml) and sodium hypochlorite solution (5%, 0.671 M, 7.9 ml, 0.01 mol) was vigorously stirred for 90 min at room temperature in the absence of light. The two phases were separated and the aqueous layer was extracted with CH_2Cl_2. The combined dichloromethane solutions were washed with brine, dried ($MgSO_4$) and evaporated in the rotary evaporator without heat and light to yield 0.94 g of product. The chloramines were subjected to cyclization without purification.

Preparation of N-methyl-6-azabicyclo[3.2.1]octan-4-one, (39a):

The method of Furtoss et al. was followed (26). The enol ether N-chloramine (0.81 g, 4.27 mmol) was added dropwise to a ten-fold quantity (8.45 ml) of cooled (0°C) and stirred anhydrous CF_3COOH. Addition was done slowly since the reaction was highly exothermic. The mixture was warmed to room temperature and the acid evaporated *in vacuo*. The brown residue was dissolved in MeOH (14 ml) and solid potassium bicarbonate (1.4 g) was added portionwise to pH 10. After heating to reflux for 1 hr, the MeOH was evaporated without heating, and a small portion of H_2O was added and the mixture extracted with CH_2Cl_2 (3-4 times). The combined organic layers was dried ($MgSO_4$), solvent evaporated and the residue was distilled by Kugelrohr at 40-50°C to give 0.12 g product (80% pure, contaminated with enol ether).

^1H NMR: δ 1.5-3.3 (m, 10H), 2.32 (s, 3H).

IR (neat): 1720 (C=O) cm^{-1}.

The preparation of 7-syn-fluoro-2-exo-norbornyl acetate:

The modified method of Tanner and van Bostelen (32) was followed. Hydrogen fluoride (10 ml, 0.5 mol) was added to the solution of $Pb(OAc)_4$ (62.9 g, 0.14 mol) in 200 ml CH_2Cl_2 in a 2 liter polyethylene bottle equipped with a $CaCl_2$ drying tube at -80°C. The mixture was stirred for 3 hours. The

reaction mixture was quenched by pouring the mixture into a cold, 0°C saturated K_2CO_3 solution. The organic layer was filtered through Celite-Filter Aid. The aqueous layer was extracted with CH_2Cl_2 and the combined organic phases was washed in succession with H_2O, saturated $NaHCO_3$ solution and H_2O and finally dried over anhydrous sodium sulfate. The solvent was evaporated to give 8.25 grams of crude product. The crude residue was distilled by Kugelrohr to afford 0.65 grams of a mixture of diacetates, difluorides, and fluoroacetate isomers. The syn and anti fluoro acetates were separated from the rest of the mixture by preparative GLC (20% Carbowax 6000, 6 ft x 1/4 inch), 155°C oven temp.). The syn and anti fluoroacetates had retention times of 20 and 13.6 minutes, respectively.

^1H NMR (CCl_4): syn-fluoroacetate: δ 4.68 (d of broad s, J = 56 cps, $W_{\frac{1}{2}}$ = 5 cps, 1H), 4.64 (t, J = 5 cps, 1H), 1.94 (s, 3H), 0.9-2.4 (m, 8H).

^1H NMR (CCl_4): anti-fluoroacetate: δ 5.00 (d of broad s, J = 58 cps, $W_{\frac{1}{2}}$ = 4.5 cps, 1H), 4.45 (m, 1H), 4.91 (s, 3H), 1.1-2.4 (m, 8H)

Preparation of 7-syn-fluoro-exo-norborneol:

The method of Tanner and von Bostelen was followed (32). 7-syn-Fluoro-2-exo-norbornyl acetate (153.6 mg, 0.8 mmol) was dissolved in 10 ml anhydrous ether. The solution was added slowly with stirring to a solution of $LiAlH_4$ (52.6 mg, 1.39 mmol) in 5 ml anhydrous ether. After the addition of the ester, the excess $LiAlH_4$ was decomposed with water-saturated ether. The resulting mixture was poured into 20 ml of 6N HCl. The solvent layers were separated and the aqueous portion extracted with ether. The combined ether fractions was washed successively with water, saturated sodium bicarbonate solution, and water, and finally dried over anhydrous Na_2SO_4. The ether was removed by distillation giving 30.7 mg product.

^1H NMR: δ 4.83 (d of d; J = 56 cps, 2 cps, respectively, 1H), 3.75 (broad s, $W_{\frac{1}{2}}$ = 14 cps, 1H), 0.8-2.5 (9H).

^{19}F NMR (CCl_4, $CFCl_3$, as reference):

δ 200.8 (d, J = 47.3 cps)

literature (32): 200.7 (d, J = 54 cps)

Preparation of 7-syn-fluoronorbornan-2-one, 44b:

The method of Tanner and van Bostelen (32) was followed. 7-syn-Fluoro-exo-norborneol (80 mg, 6.2×10^{-4} mole) was dissolved in 3 ml ether and a chromic acid solution (0.062 g, $Na_2Cr_2O_7 \cdot 2H_2O$ and 0.0465 ml 96% H_2SO_4 diluted to 0.3 ml with H_2O) was added over 15 minutes with stirring. The reaction mixture was stirred for 2 hours at room temperature. The layers were separated and the acid layer extracted twice with ether and combined ether layers washed with saturated $NaHCO_3$ solution and finally with water.

The ether was evaporated and the components of the residue separated by preparative GLC (20% Carbowax 6000, 6 ft x 1/4 inch, 155°C oven temperature) to give pure 44b.

^1H NMR: 4.9 (doublet of quadruplets, J = 56 cps, J = 2 cps, 1H), 1.3-2.7 (8H).

Preparation of hypochlorous acid:

THe procedure of Coleman and Johnstone was used (51). Cracked ice (80 g) was added to a solution of mercuric chloride (2.5 g) in 50 ml of H_2O in a 500-ml 3-necked flask. A cold solution of NaOH (19 g) in H_2O (50 ml) was added and a rapid stream of chlorine gas was passed into the mixture which was kept below 5°C. The addition of chlorine was continued until the yellow precipitate of HgO disappeared. Nitric acid (1.5 N, 160 ml) was slowly added into the stirred

reaction mixture. The HOCl was not titrated and was assumed to be 4%. (Literature reports that the concentration was found to be usually 3.5-4%). This was immediately used for the preparation of syn-7-chlorobicyclo[2.2.1]heptan-2-ol.

Preparation of syn-7-chlorobicyclo[2.2.1]heptan-2-ol:

The procedure described by Roberts et al. (33) was used. Norbornene (20 g, 0.21 mole) and HOCl (4%, 278 ml) were alternately added in four portions to an ice-cooled 3-necked flask equipped with an efficient mechanical stirrer. The reaction was kept at approximately 5°C. Fresh portions of the reactants were added when drops of reaction mixture did not give purple color on KI starch indicator. Additional HOCl (80 ml) was added. After the addition was completed, the reaction was stirred for 1/2 hour and the mixture was extracted with six 100 ml portions of ether. The combined ether extracts was shaken with aqueous sodium bisulfite until the aqueous wash was no longer yellow and then extracted with H_2O. The organic layer was dried (Na_2SO_4) and the solvent evaporated at atmospheric pressure. Distillation of the residue by Kugelrohr technique (60-70°C/1 mm Hg) gave 12.85 g of a clear, colorless liquid product.

^1H NMR: δ 1.0-3.0 (complex, 12) 3.9 (m, 1H), 4.2 (broad s, 1).

IR (neat): 3400 cm^{-1}.

Preparation of 7-syn-chlorobicyclo[2.2.1]heptan-2-one, 45b:

The procedure according to Roberts et al. (33), was followed. A mixture of syn-7-chloro-exo-norborneol (5 g, 0.034 mol) and 25 ml 65% concentrated HNO_3-35% H_2O was heated under reflux over 10 minutes. The reaction was vigorous and was accompanied by evolution of oxides of nitrogen. The reaction mixture was cooled and then extracted with ether. The combined ether layers were washed with H_2O, NaOH (1.5 N) and dried over $MgSO_4$. The ether was distilled at atmospheric pressure and the residue distilled by the Kugelrohr technique at 50-70°C/0.5 mm Hg to give 2.21 g of crude product.

For further purification, the ketone was converted to the semicarbazone (mp 183.5-185°C), recrystallized from ethanol-water and regenerated by steam distillation from an oxalic acid solution. The steam distillate was extracted with ether and the etheral extract dried over $MgSO_4$. The residue was sublimed at atmospheric pressure to give 45b as a waxy white solid.

^1H NMR ($CDCl_3$): δ 1.2-2.8 (complex, 8H),
4.1 (t, 1H).

IR (neat): 1740 (C=O) 1280 cm^{-1}.

General procedure for the hydrogenation of 7-alkyl substituted norbornadienes:

A modification of the method reported by Franzus et al. (34) was followed. The substituted norbornadiene (0.01 mole) was dissolved in a flask containing ether (40 ml) and 10% Pd/C (0.6 g) as catalyst and attached to a gas buret hydrogenator. After the apparatus was purged with hydrogen, the reductions were carried out at room temperature and with vigorous stirring with a magnetic stirrer. When 50% of the calculated hydrogen (215 ml) was consumed (i.e., the amount sufficient enough to reduce one double bond), the reaction mixture was filtered through Celite-Filter Aid and the ether distilled at atmospheric pressure to give usually a mixture of syn-and anti-substituted norbornene and the saturated norbornane. The components of the mixture were separated by preparative gas liquid chromatography or used as a crude mixture for the next step, the oxidation of the double bond to the ketone.

General procedure for the oxidation of the 7-substituted norbornenes to the 7-substituted norbornan-2-one:

The procedure according to Brown and Gary (52) was used. Diborane in THF (1 M, 0.9 ml, 0.9 mmol) was added over a period of 5 minutes to a solution of a mixture of norbornene isomers (approximately 1.99 mmole) in 3 ml THF. The mixture was stirred for 3 hours after which the excess hydride was

destroyed with H_2O (3 ml). A chromic acid solution prepared from 0.43 g $Na_2Cr_2O_7 \cdot 2H_2O$ and 0.33 ml 96% H_2SO_4 diluted to 3.5 ml with H_2O was added over a period of 15 minutes at 25-30°C. After heating the mixture to reflux for 2 hours, the layers were separated and the aqueous layer extracted with ether (2x10 ml). The combined ether layers was washed successively with saturated $NaHCO_3$ solution, NaCl solution, H_2O and dried. Solvents were distilled off at atmospheric pressure. The desired isomer was usually isolated by preparative gas liquid chromatography.

Preparation of 7-methoxynorbornadiene:

To a solution of 7-tert-butoxynorbornadiene (4.15 g, 0.025 ml) in MeOH (40 ml) was slowly added concentrated H_2SO_4 (2.18 ml). The mixture was stirred for 5 hr at 30°C. At the end of this period, the reaction mixture was added to ice (40 g) and was extracted with CH_2Cl_2 (4x10 ml). The extract was successively washed with saturated $NaHCO_3$, NaCl solution and dried ($MgSO_4$ and Na_2SO_4). After concentration, distillation at 45°C/0.5 mm Hg afforded 1.14 g of the pure proudct.

^1H NMR (CCl_4): δ 6.51 (t, 2, J = 1 Hz), 6.34 (t, 2, J = 1 Hz), 3.38 (m, 3H), and 1.11 (t, 3, J = 4 Hz).

Preparation of 7-methoxynorbornene isomers:

The compounds were prepared through the hydrogenation of 7-methoxynorbornadiene according to the general procedure described on p.68.

The NMR of the crude reaction mixture featured a peak at δ 5.9 (multiplet) which is the characteristic chemical shift of both syn and anti vinylic hydrogens.

Preparation of syn-7-methoxynorbornan-2-one, 46b:

Compound 46b was prepared according to the general procedure on p. 68 from the mixture of 2 isomers. Preparative GLC (Carbowax 2000 (6 ft x 1/4 inch, 167°C oven temperature) of the crude reaction mixture afforded the syn isomer.

^{1}H NMR (CCl_4): δ 2.21-1.1 (m, 8H), 3.2 (s, 3H), 3.65 (t, 1H).

IR: 1740 (C=O), 1090 and 1100 (doublet, C-O-C) cm^{-1}.

GLC-MS: m/e 140, 124 (loss of O), 108 (loss of MeOH).

Preparation of syn-7-tert-butoxynorbornene:

7-tert-Butoxynorbornadiene was hydrogenated according to the general procedure described on p. 68. 0.25 Grams of crude mixture of syn and anti 7-tert-butoxynorbornene and 7-tert-butoxynorbornane was obtained. Analytical GLC analysis on a 5% OV-3 column at 90°C and 20 ml of He/min showed 2 peaks with the retention times from air of 1.75 min and 2.25 min. The first peak (retention time, 1.75 min), was a mixture

of 7-tert-butoxynorbornane and anti-7-tert-butoxynorbornene The NMR spectrum had the characteristic triplet at 5.9 for the vinyl hydrogens split by the syn-bridge hydrogen of the anti isomer (34). The second peak (retention time of 2.25 min) was the syn-isomer and its NMR spectrum contained a multiplet (doublet of triplet in the literature) at 5.9 ppm. The components of the mixture were also separated by preparative GLC using a 6 ft x 1/4 inch 20% Carbowax 6000 column, at 150°C and 40 ml He/minute and the second peak, the syn-7-tert-butoxynorbornene was isolated.

^{1}H NMR: δ 5.9 (m, 2H), 3.6 (m, 1H), 1.3 (s, 9H), 0.8-2.0 (complex, 6H).

Preparation of syn-7-tert-butoxynorbornan-2-one, 47b:

Compound 47b was prepared by oxidizing syn-7-tert-butoxynorbornene according to the general procedure described on p. 68.

^{1}H NMR: δ 4.0 (m, 1H), 2.3 (m, 2H), 1.0-2.6 (complex, 6H), 1.2 (s, 9H).

IR: 1750, 1090 cm^{-1}.

Preparation of 7-tert-butylnorbornadiene:

Baird and Surridge's procedure was followed (36). To a 250 ml round-bottom flask, equipped with a stirrer, a thermometer, a dropping funnel and a reflux condenser were added under nitrogen tert-butyllithium in pentane (1.24 M,

40.5 ml, 0.050 mole) and dry n-pentane (80 ml). A solution of 7-tert-butoxynorbornadiene (0.82 g, 0.05 mol) in dry n-heptane (5 ml) was added dropwise with stirring at -20°C over a period of 2 hrs. The reaction mixture was allowed to warm to room temperature. The pentane was removed by distillation, and simultaneously 50 ml of dry heptane was added. The reaction was stirred and refluxed for 2 hrs. The reaction was cooled to -0°C and 5 ml isopropyl alcohol was added. The heptane solution was washed twice with 2 ml portions of water and dried over $MgSO_4$. The solvent was removed by distillation and the residue was distilled, b.p. 98-100°C (85 mm).

^{1}H NMR: (neat) δ 6.80 (t, 2H), 6.34 (t, 2H), 3.40 (m, 2H), 2.48 (m, 1H), 0.80 (s, 9H).

Preparation of 7-syn-tert-butylnorbornene:

The general procedure on p. 68 was followed. The crude reaction mixture was obtained containing a mixture of 7-tert-butylnorbornadiene, syn-7-tert-butylnorbornene, 3-tert-butylnortricyclane and 7-tert-butylnorbornane. syn-7-tert-Butylnorbornene was isolated by preparative GLC.

^{1}H NMR: δ 5.66 (t, 2H), 2.68 (m, 2H), 1.46-1.72 (m, 2H), 1.39 (m, 1H), 0.82-1.00 (m, 2H), 0.78 (s, 9H).

Preparation of 7-syn-tert-butylnorbornan-2-one, 48b:

The general procedure on p. 68 was used.

^{1}H NMR: δ 1.4 (s, 9H), 2.4-0.8 (m, 9H).

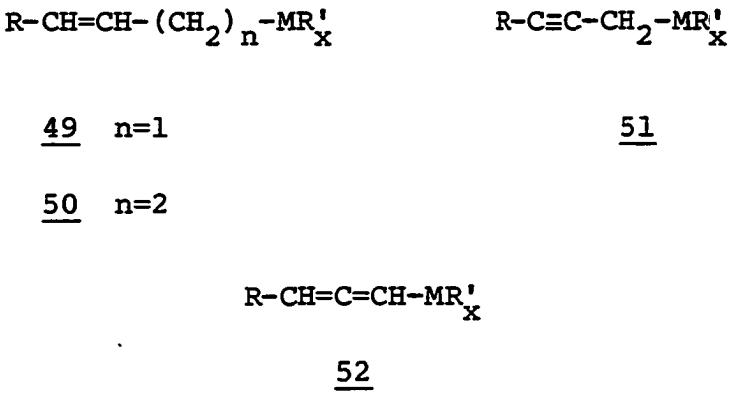
IR: 1750 (C=O) cm^{-1}.

GLC-MS: m/e (rel. intensity) = 167(2.16), 166(18), 124(4.3), 123(7.5), 122(10.7), 110(18), 109(63), 108(5), 107(10), 97(20), 96(12), 95(15), 83(13), 82(46), 81(24), 79(11), 70(19), 69(23), 68(11), 67(47), 66(29), 57(100), 55(68), 53(17).

PART II: THE FREE RADICAL REACTIONS OF UNSATURATED ORGANOSTANNANES

I. INTRODUCTION

Numerous examples (Table 3) of heterolytic displacement of a metal from unsaturated organometallic compounds such as 49-52 have been reported in the literature. In recent years, several research groups have discovered that such displacement can also occur homolytically with certain substrates which are capable of generating an electrophilic radical, E· (Table 3).



$R\text{-}CH{=}CH\text{-}(CH_2)_n\text{-}MR'_x$ (49 n=1; 50 n=2)

$R\text{-}C{\equiv}C\text{-}CH_2\text{-}MR'_x$ (51)

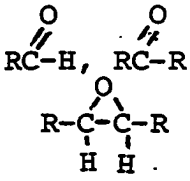
$R\text{-}CH{=}C{=}CH\text{-}MR'_x$ (52)

So far, free radical reactions of this type have been observed with unsaturated derivatives of Sn, Co, Rh and Ir using substrates such as alkyl halides, polyhalogenomethanes, dialkyl disulfides, dialkyl diselenides and alkylsulfonyl halides as sources of E· (Table 3).

Table 3. The mechanism of the reaction of unsaturated organometallic derivatives with different substrates

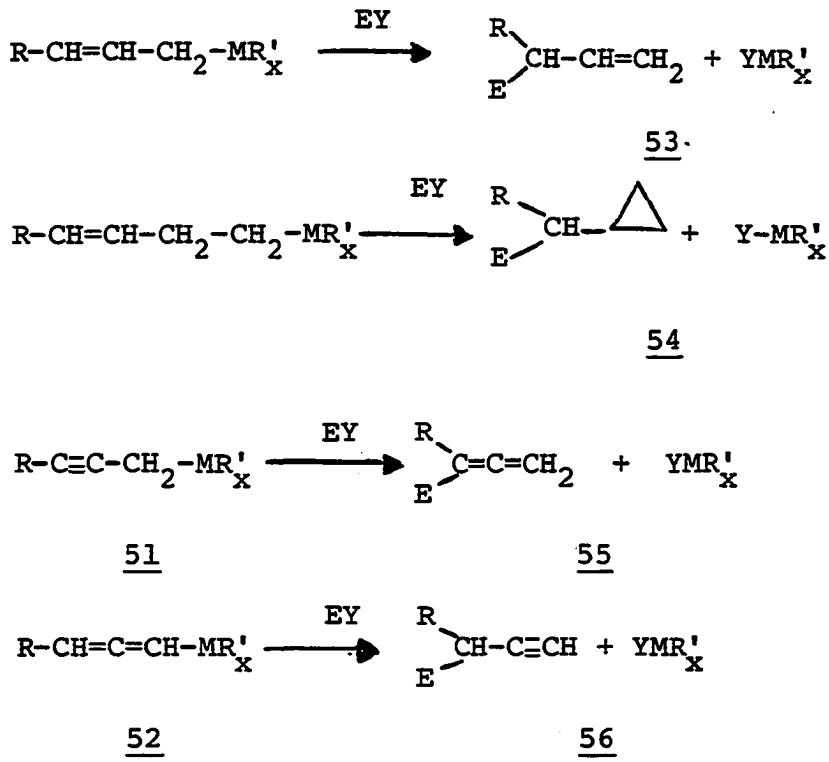
Substrate	Organometallic derivative	Mechanism	Reference
Br_2,Cl_2	but-3-enyl Sn	S_E2'	53
	propadienyl Sn	S_E2'	54
CNBr	propadienyl Ag	S_E2', S_E2	55
CO_2	propadienyl Ag	S_E2	55
CS_2	propadienyl Ag	S_E2', S_E2	55
HCl	propadienyl Sn	S_E2', S_E2	56
$HgCl_2$	allyl, but-3-enyl, propadienyl Sn	S_E2'	53
I_2	propadienyl Ag	S_E2	55
	but-3-enyl Sn	S_E2'	53
	propadienyl Sn	S_E2'	57
	propargyl Sn	S_E2'	53
NBS,NCS	propadienyl Ag	S_E2', S_E2	55
XC_6H_4Cl	allyl, but-3-enyl Co	S_E2'	58
	allyl, but-3-enyl Sn	S_E2'	53
polyhalogenomethane	allyl, propadienyl Co	S_H2' or addn.-elim.	59
	allyl, propadienyl Ir	S_H2' or addn.-elim.	60
	allyl, propadienyl Rh	S_H2' or addn.-elim.	60
	allyl Sn	S_H2' or addn.-elim.	61,62

Table 3 (Continued)

Substrate	Organometallic derivative	Mechanism	Reference
Quinone	allyl Sn	S_E2'	63
	allyl, propadienyl and propargyl Sn	S_E2', S_Ei'	64,65,66,67
	alkenyloxy Sn	aldol condensation	68,69
R_3MCl M=Si,Ge,Sn	propadienyl Ag	S_E2	53
RSH	allyl Sn	addition	70
RSSR	allyl, propadienyl Co	S_H2' or addn.-elim.	71
RSSR	allyl, propadienyl Co	S_H2' or addn.-elim.	71
RSO_2X	allyl Co	S_H2' or addn.-elim.	72
RX	propadienyl Ag	S_E2	55
	allyl Sn	S_H2' or addn.-elim.	61,62,73
	alkenyloxy Sn	S_E2	74,75,76
SCl_2	but-3-enyl Sn	S_E2'	53
SO_2	propargyl and propadienyl Sn	S_E2'	77
SO_3	allyl, but-3-enyl Sn	S_E2'	53

The attack of the electrophilic radical (E·) has been found to take place regiospecifically at the most nucleophilic part, i.e., the unsaturated end of the molecule, to give rearranged products such as 53-56 in Scheme 4.

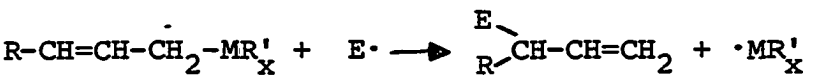
Scheme 4:



Two types of free radical attack have been postulated for these systems, namely: a) the synchronous S_H2' pathway (bimolecular homolytic substitution involving a double bond transposition) (Mode 1, Scheme 5) or b) the two-step addition-elimination process (Mode 2, Scheme 5).

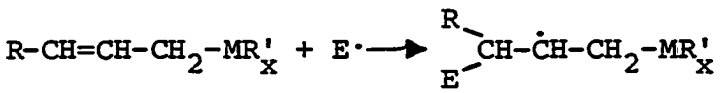
Scheme 5:

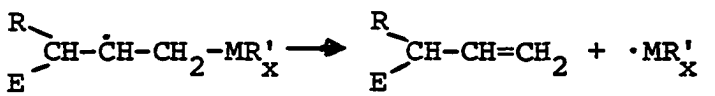
Mode 1: S_H2'



or

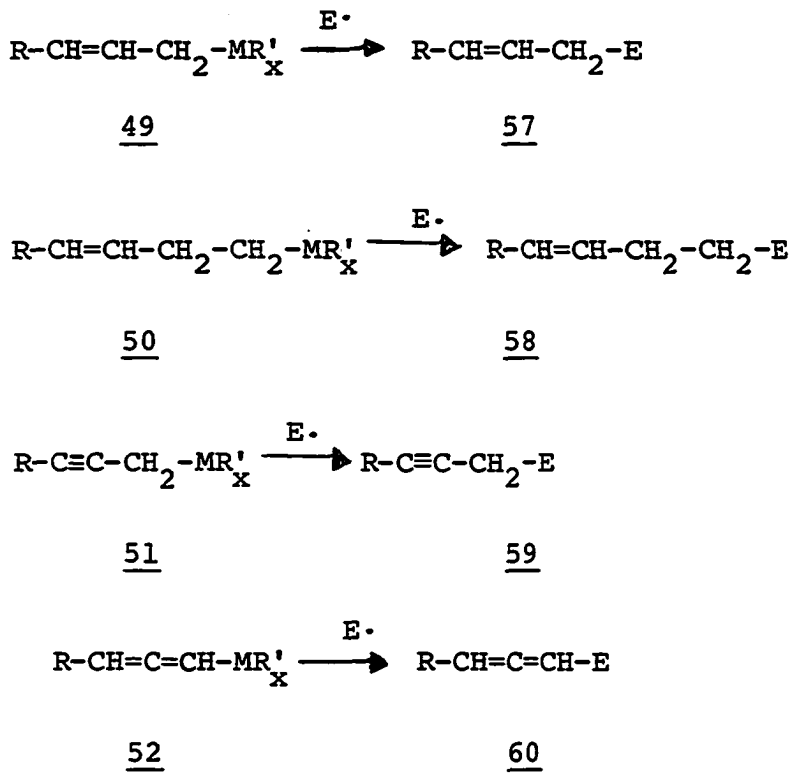
Mode 2: Addition-elimination





Interestingly, the homolytic cleavage of the C-Sn bond, which gives the products 57-60 (Scheme 6), instead of the expected products, has not been found to compete with the previously mentioned mechanisms in any of the systems studied.

Scheme 6:

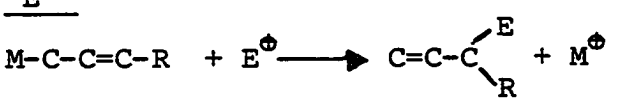


However, products of this type were observed in the reaction of PhSSPh and PhSeSePh with allyl and propadienyl cobaloxime (71) but they arose from the thiyl or selenyl promoted rearrangement of initially formed regiospecific products.

Furthermore, mixed mechanisms involving both homolytic and heterolytic processes, S_E2' and S_E2 (Scheme 7), have not been reported in any of the systems studied, even though some of the electrophilic radical precursors used were, themselves, also potential electrophilic substrates.

Scheme 7:

S_E2'



S_E2

Part II of this dissertation, The Free Radical Reactions of Unsaturated Organostannanes, is engaged in the task of investigating the homolytic displacement of Sn from different types of unsaturated organostannanes using various possible sources of electrophilic radicals ($E^{\bullet}$).

Chapter II in Part II of this dissertation has been divided into three main sections, namely:

A) The Free Radical Reactions of Allylstannanes with Hetero Atom-Centered Radicals;

B) The Free Radical Reactions of Propargylstannanes with Alkylsulfonyl Halides and Polyhalogenomethanes; and

C) The Free Radical Reactions of Alkenyloxystannanes with Polyhalogenomethanes.

II. RESULTS AND DISCUSSION

A. The Free Radical Reactions of Allylstannanes with Hetero Atom-Centered Radicals

M. D. Johnson's research group has extensively investigated the homolytic reactions of unsaturated derivatives of transition metals Co, Rh and Ir (Table 3). This group has observed that carbon-centered radicals derived from polyhalogenomethanes react with allyl derivatives of Co, Rh, and Ir (Scheme 8) via a free radical chain mechanism (59, 60).

Scheme 8

Init. $RMLn \rightarrow R^{\cdot} + {\cdot}MLn$

Prop. ${\cdot}MLn + XCY_3 \rightarrow XMLn + {\cdot}CY_3$

$${\cdot}CY_3 + RMLn \rightarrow RCY_3 + {\cdot}MLn$$

Term. ${\cdot}CY_3 + {\cdot}MLn \rightarrow Y_3CMLn$

$MLn = Ir(Co)P_2X_2$, $Rh(Co)P_2X_2$, $Co(dmgH)_2L'$

X = Br, Cl

$P = PPh_3$, PMe_2Ph

L' = pyridine, imidazole

R = allyl, 2 or 3-methylallyl, 3,3-dimethylallyl, benzyl

$CY_3 = CCl_3$, $CHBrCN$, CCl_2CN, CCl_2CHO, CCl_2CO_2R

They also found that hetero atom-centered radicals from RSO_2Cl (71) and PhSSPh and PhSeSePh (70) reacted in a similar fashion with allylcobalt. The same group has also

$$ArSO_2\cdot + RCH{=}CH{-}CH_2CO(dmgH)_2py$$
$$ArSO_2RCH{-}CH{=}CH_2 + .Co^{II}(dmgH)_2py$$

studied the reaction of PhSCl but it was found to prefer to react heterolytically through an S_E2' process with allyl, as well as but-3-enyl cobaloxime (58).

Kosugi et al. (61) and Grignon et al. (62), in independent studies, have discovered what could be considered to be the first known homolytic displacement of a metal from an unsaturated organometallic compound, i.e., the free radical reaction of organoallylstannanes with alkyl halides and polyhalogenomethanes.

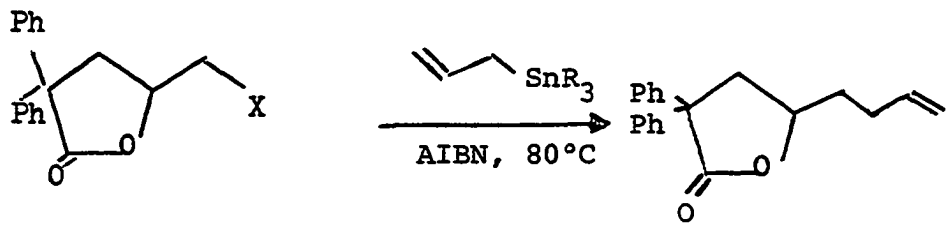
$$R{-}CH{=}CH{-}CH_2{-}SnR'_3 + CH_3CH_2CH_2I \xrightarrow{h\nu} R{-}\underset{\displaystyle CH_3CH_2CH_2}{\underset{|}{CH}}{-}CH{=}CH_2 + R'_3SnI$$

32% yield

$$R{-}CH{=}CH{-}CH_2{-}SnR'_3 + CCl_4 \xrightarrow{h\nu} R{-}\underset{\displaystyle CCl_3}{\underset{|}{CH}}{-}CH{=}CH_2 + R'_3SnCl$$

70% yield

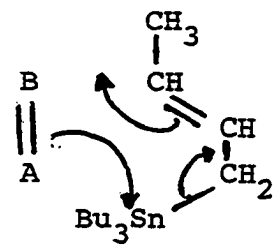
Recently, Keck and Yates (73) extended this particular study by using alkyl halides which are natural product precursors bearing other functionalities such as aldehyde, ketone or epoxide groups. They found that the azobis(isobutyronitrile) (AIBN) initiated reactions were extraordinarily tolerant of both steric hindrance and complex functionality in the substrates.



X=Br, SePh

Aldehydes, ketones and epoxides have also been reacted with allylstannanes, but they reacted heterolytically through an S_E2' or S_Ei process (64, 65, 66).

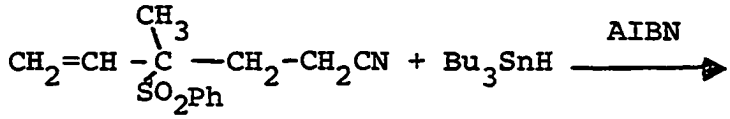
S_Ei



The encouraging results from the reactions of carbon-centered radicals with organoallylstannanes made us investigate the possibility of extending its reaction with hetero atom-centered radicals. This section carries out this task.

Hetero atom-centered radicals from PhSCl and RSH have been reacted with allylstannanes but it resulted in reactions which proceed via an S_E2' and addition mechanism, respectively (53, 69).

However, Ueno et al. has reported that Equation 3 occurred very readily in high yield (78). It is conceivable that the

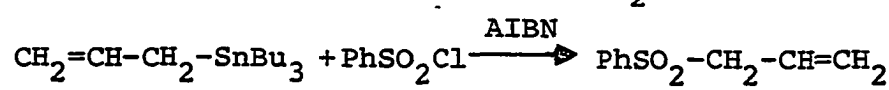


$$CH_2=CH-\underset{SO_2Ph}{\overset{CH_3}{C}}-CH_2-CH_2CN + Bu_3SnH \xrightarrow{AIBN}$$

$$Bu_3Sn-CH_2-CH=\overset{CH_3}{C}-CH_2-CH_2-CN$$

$$+ PhSO_2H \quad \text{(Equation 3)}$$

reaction of an allyl sulfone with $Bu_3Sn^{\bullet}$ is reversible and that the reaction of Equation 4 could possibly occur. This observation makes RSO_2Cl an ideal sulfur-



$$CH_2=CH-CH_2-SnBu_3 + PhSO_2Cl \xrightarrow{AIBN} PhSO_2-CH_2-CH=CH_2$$

$$+ Bu_3SnCl \quad \text{(Equation 4)}$$

centered E· precursor for this type of reaction.

RSSR and RSeSeR are promising free radical precursors also, considering their earlier cited successful reactions with allylcobaloximes. Furthermore, Russell and Hershberger (79) have found that these substrates reacted readily with vinylmercurials in a free radical fashion.

1. The preparation of allylstannane derivatives:

Allyltri-n-butylstannane 61 and crotyltri-n-butylstannane 62 were the two organoallylstannanes used for

$$R\text{-}CH{=}CH\text{-}CH_2\text{-}SnBu_3$$

61 R=H

62 R=CH_3

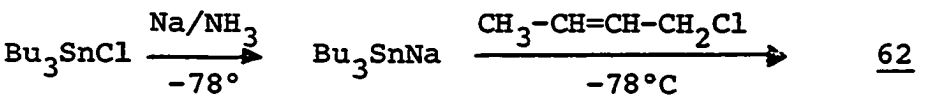
this study. Compound 61 was synthesized through the Grignard route using a modified version of Abel's method (80).

$$CH_2{=}CH\text{-}CH_2Cl \xrightarrow[THF]{Mg} CH_2{=}CH\text{-}CH_2MgCl \xrightarrow{Bu_3SnCl} MgCl_2 + \cdot 61$$

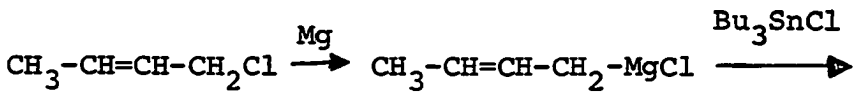
Three pathways are available in the literature (81-83) for the generation of 62 (Scheme 9). All three were tried, and the first procedure, Mode 1, was found to be the most convenient (81). Mode 2, the Grignard route, has the disadvantage of also generating the secondary isomer (82), whereas, mode 3 was found to be sensitive to the duration and temperature of the reaction (83).

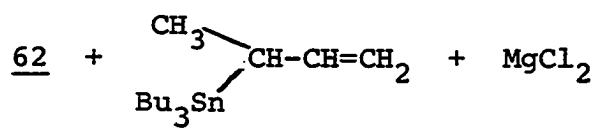
Scheme 9:

Mode 1

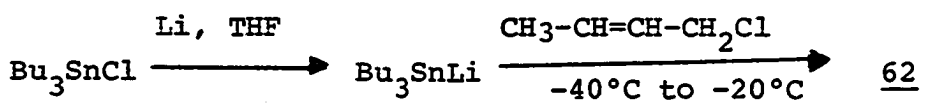


Mode 2:





Mode 3:



2. The reaction of allystannanes with hetero atom-centered radicals:

Compounds 61 and 62 reacted under sunlamp irradiation with sulfur-centered radicals derived from R'SSR' and $R'SO_2Cl$ in good yields (Table 4), to give regiospecific products 63-70 (Scheme 10).

Scheme 10:

$$R\text{-}CH{=}CH\text{-}CH_2\text{-}SnBu_3 + R'SSR' \xrightarrow[\text{irradiation}]{\text{sunlamp}} \underset{SR'}{\overset{R}{\diagdown}}\!\!>CH\text{-}CH{=}CH_2$$

63 R=H, R'=Ph

64 R=H, R'=$PhCH_2$

65 R=CH_3, R'=Ph

66 R=CH_3, R'=$PhCH_2$

$$R\text{-}CH{=}CH\text{-}CH_2\text{-}SnBu_3 + R'SO_2Cl \xrightarrow[\text{irradiation}]{\text{sunlamp}} \underset{R'SO_2}{\overset{R}{\diagdown}}\!\!>CH\text{-}CH{=}CH_2$$

61 R=H

62 R=CH_3

67 R=H, R'=Ph

68 R=H, R'=n-Pr

69 R=CH_3, R'=Ph

70 R=CH_3, R'=n-Pr

Table 4. Photochemical[a] reaction of allylstannanes with hetero atom-centered radicals

$$R\text{-}CH{=}CH\text{-}CH_2\text{-}SnBu_3 + EY \xrightarrow{h\nu} \begin{matrix} R \\ E \end{matrix}\!\!>CH\text{-}CH{=}CH_2$$

Allylstannane	Substrate	Duration	% Yield of $\begin{matrix} R \\ E \end{matrix}\!\!>CH\text{-}CH{=}CH_2$	Structure number
61	PhSSPh	6 h	77[b]	63
	$PhCH_2SCH_2Ph$	6 h	77[b]	64
	$PhSO_2Cl$	6 h	76[b]	67
	n-$PrSO_2Cl$	6 h	74[b]	68
	CCl_3SO_2Cl	6 h	31[c,d]	76
	PhSeSePh	6 h	94[d]	75
62	PhSSPh	-[e]	-[f]	65
	$PhCH_2SCH_2Ph$	1.5 h	34	66
	$PhSO_2Cl$	9 min	72[d]	69
	n-$PrSO_2Cl$	3 min	46[d]	70

[a]Sunlamp irradiation.

[b]Isolated yield.

[c]Product isolated was $\sim\!\!\!\!\diagup\!\!\!\!\sim CCl_3$, not the sulfone product.

[d]NMR yield.

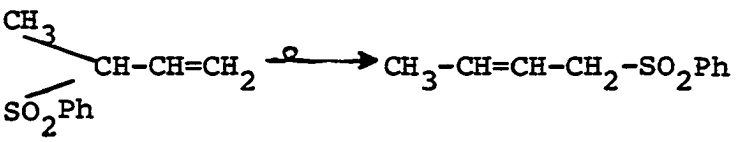
[e]A mixture of 65 and CH_3-CH=CH-CH_2-SPh (72) started appearing according to the NMR spectrum after 2 hrs of irradiation.

[f]50:50 mixture of 65 and 72 after 2 hours.

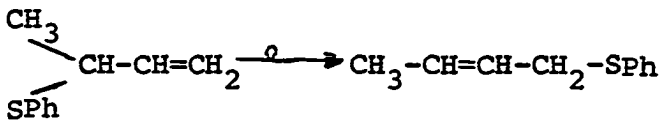
The yield of the reaction does not seem to be dependent on whether the substituents on the dialkyl disulfides and alkylsulfonyl halides are aromatic or aliphatic. Allylcobaloximes, on the other hand, have been reported to react poorly with aliphatic sulfonyl halides (71), as do the vinyl mercuric halides (84). However, the stability of the regiospecific products towards thiyl or sulfonyl promoted rearrangements (Scheme 11) was found to be dependent on the type of alkyl substituents in the substrates used.

When R'= phenyl, the rearrangement of 65 and 69 to 71 and 72, respectively (Scheme 11), was more facile than the corresponding transformation with R'= aliphatic. The phenyl substituted products rearranged in minutes, whereas, the aliphatic substituted ones rearranged only after several days.

Scheme 11:



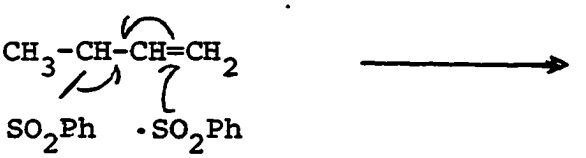
71



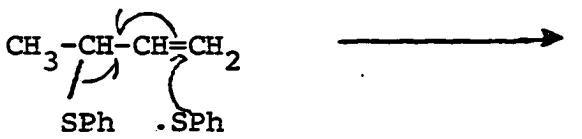
72

The rearrangements were conveniently followed by ^1H NMR which showed a dramatic and distinct change in the proton spectrum of the allylic region as the reaction progressed (see Figure 12, Experimental).

It was originally believed that the rearrangements were promoted by the thiyl or sulfonyl radical generated during the reaction (85). Recent studies on thia-allylic

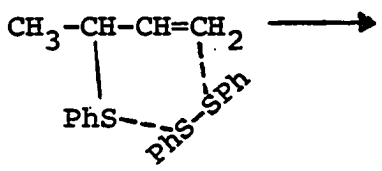


71



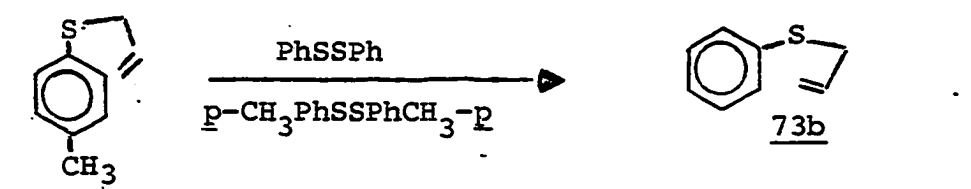
72

rearrangements by Kwart and Johnson (86), however, indicate that the rearrangements probably go through a bimolecular process as depicted in Equation 5 involving a trigonal-bipyramidal intermediate.

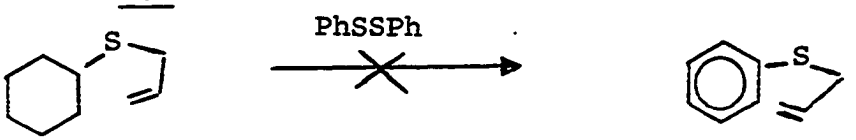


72 (Equation 5)

The difference in stability between phenyl and aliphatic substituted allylsulfides have been previously observed in the literature. Kwart and Johnson (86) have reported that whereas, allyl-p-tolyl sulfide 73a underwent thia-allylic promoted rearrangement to give the crossed product 73b, the cyclohexylsulfide 74a did not give the corresponding product 74b.



73a



74a 74b

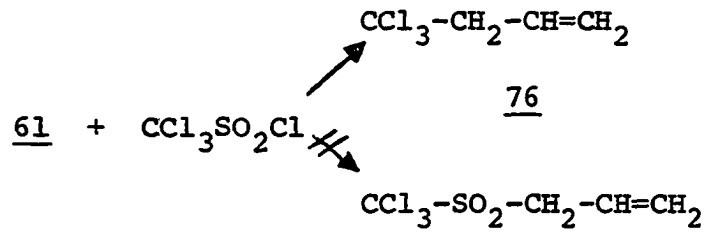
Thiyl and selenyl promoted rearrangements have also been seen with the phenyl sulfides and selenides

generated from organoallylcobaloximes (70). Unfortunately, the studies did not include the corresponding aliphatic substituted allyl sulfides and selenides to warrant a complete comparison with the stannane case. Phenylsulfonyl promoted rearrangements have been earlier described in the literature by Cope et al. (87). However, similar phenylsulfonyl rearrangements were not observed in the organoallylcobaloxime reactions with $PhSO_2Cl$. The products obtained with both aromatic and aliphatic sulfonyl chlorides were resistant to the rearrangements described with the organoallylstannanes (71). It should be noted that products from the reaction of carbon-centered radicals with allyl Sn, Rh, Ir and Co (59, 60, 61, 62, 72) compounds were all stable towards the rearrangements observed in this study. As can be seen from Table 4, allyl selenides 75 can be synthesized in good yields by the reaction of allyl-tri-n-butylstannane with PhSeSePh.

$$\underline{61} + PhSeSePh \xrightarrow{h\nu} CH_2{=}CH{-}CH_2{-}SePh$$

75

Interestingly, the reaction of 61 with CCl_3SO_2Cl gave 4,4,4-trichlorobutene 76 and not the sulfone product 77. Similar results were obtained by Johnson's group in



76

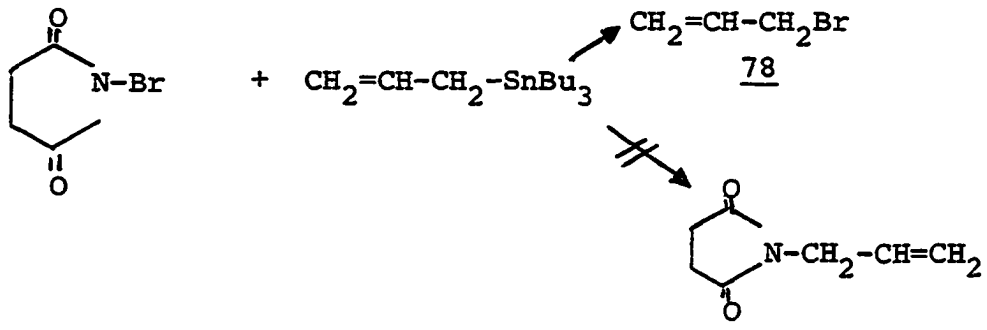
77

their study of organoallylcobaloximes (71). The product observed most likely comes from the attack of the $CCl_3\cdot$ radical species generated by the unstable $CCl_3SO_2\cdot$ radical on 61 (71). The appearance of this product 76 is additional

$$CCl_3SO_2\cdot \longrightarrow CCl_3\cdot + SO_2\cdot$$

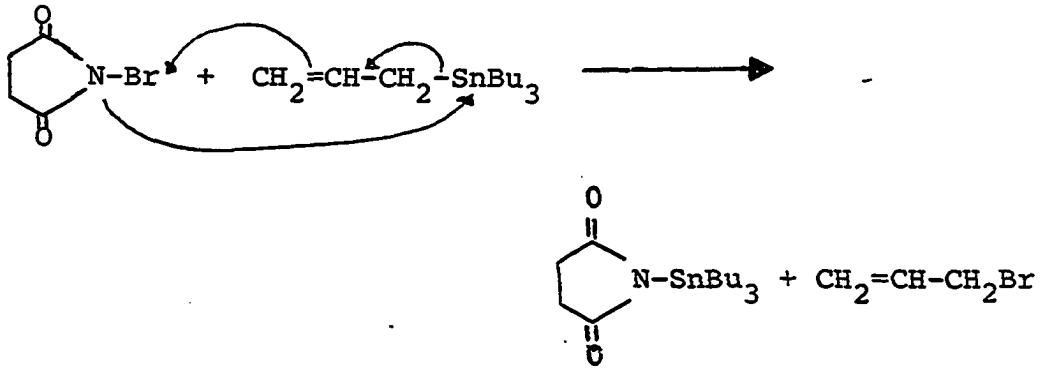
support for the free radical nature of the reaction of organoallylstannanes with sulfonyl chlorides.

The use of N-bromosuccinimide (NBS) as a source of a nitrogen-centered radical to react with allylstannanes was attempted. However, NBS was found to give allyl bromide 78 as the product, and not the expected compound 79.



79

The unexpected product 78 was proposed to arise from an S_Ei type of mechanism as shown in Equation 6.



(Equation 6)

3. The effect of light, dark, initiator and inhibitors on the reaction:

Photochemical initiation was found to be necessary for the reactions of Table 5 to proceed. No product was observed when the reaction was conducted in the dark, namely with the reaction vessel covered with aluminum foil. The reaction can also be initiated by AIBN at 70-80°C and the yields obtained using these conditions were comparable with those achieved under photochemical initiation. Radical inhibitors such as di-tert-butyl nitroxide and galvinoxyl retarded the formation of the product. (Please see Tables 9 and 10 and Figures 13 and 14, Experimental).

4. Mechanistic considerations:

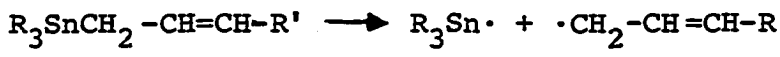
Based on the experimental observations previously described, allylstannanes react via the free radical mechanism shown in Scheme 12. The initiation step can proceed through the generation of $R_3Sn\cdot$ radical, which can be produced by: a) the photochemical dissociation of the organotin bond, or b) the use of a radical Q. from an initiator like AIBN.

In reactions involving RSSR, its photochemical dissociation to RS·, which is precedented in the literature (88), can

$$RSSR \longrightarrow 2RS\cdot$$

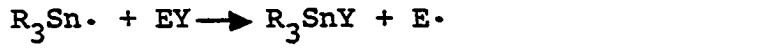
Scheme 12:

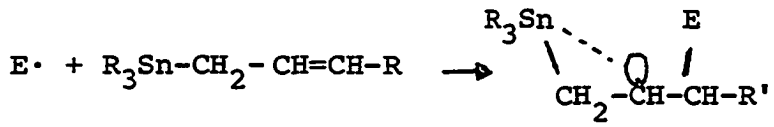
Initiation:

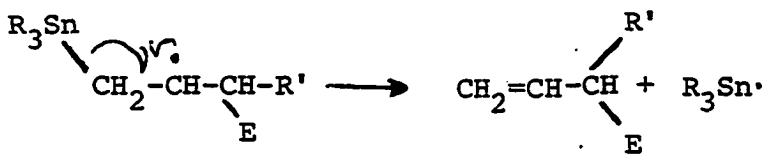


or

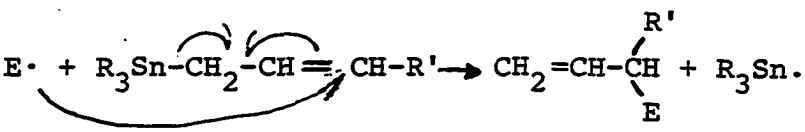
Propagation:



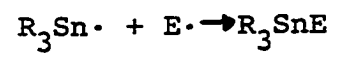




or



Termination:



EY = PhSSPh, $PhSO_2Cl$, . n-$PrSO_2Cl$, $PhCH_2SSCH_2Ph$,

PhSeSePh, CCl_3SO_2Cl

R' = H, CH_3

R = n-Bu

also serve to initiate the reaction.

The propagation step can either proceed in a synchronous manner or by a stepwise addition-elimination process. The two modes, however, are indistinguishable by the techniques employed in this dissertation.

The possibility of the homolytic cleavage of the C-Sn bond (Equation 7) occurring was eliminated by the fact that the products observed were formed in a regioselective manner.

$$R'-CH=CH-CH_2-SnR_3 \xrightarrow{E\cdot} R'-CH=CH-CH_2-E + \cdot SnR_3 \quad \text{(Equation 7)}$$

The electron transfer process (Scheme 13) was thought of as a possible mechanism especially with 2-chloro-2-nitropropane as a reactant.

Scheme 13:

$$R_3Sn\cdot + ClC(Me)_2NO_2 \longrightarrow R_3Sn^{\oplus} + ClC(Me)_2NO_2^{\ominus}$$

$$ClC(Me)_2NO_2^{\ominus} \longrightarrow Cl^{-} + \cdot C(Me)_2NO_2$$

$$\cdot C(Me)_2NO_2 + CH_2=CH-CH_2SnR_3 \longrightarrow NO_2C(Me)_2CH_2-CH=CH_2 + \cdot SnR_3$$

Tanner et al. (89), for example, has observed that the reaction of nitroalkanes with tributyltin hydride proceeded via an electron transfer mechanism shown in Scheme 14.

Scheme 14:

$$R\text{-}NO_2 + Bu_3SnH \longrightarrow RH + Bu_3SnNO_2$$

$$Bu_3Sn\cdot + RNO_2 \longrightarrow Bu_3Sn^{\oplus} + RNO_2^{-}$$

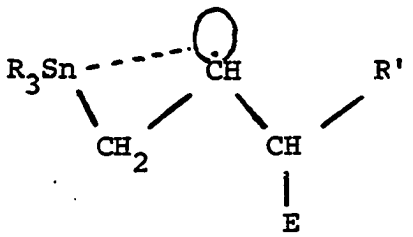
$$RNO_2^{-} \downarrow$$

$$R\cdot + NO_2^{-}$$

$$R\cdot + Bu_3SnH \longrightarrow RH + Bu_3Sn\cdot$$

However, the reactions of allyltri-n-butylstannane with $O_2NC(Me)_2NO_2$ did not occur although $ClC(Me)_2NO_2$ did. The latter probably reacted like the rest of the alkyl halides, through the S_H2' pathway.

The high reactivity of the allylstannanes to free radical addition could be attributed to a resonance effect in the intermediate radical (66, 90). The odd electron can undergo homoconjugation with the 3d orbitals of tin in the manner depicted in 80. It is not surprising, therefore, that the

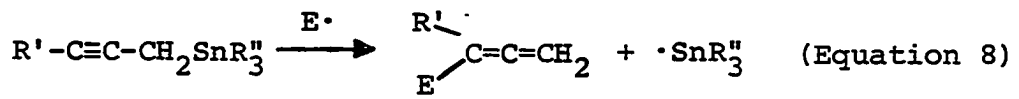


80

tetraalkylstannanes did not react with the substrates used in this section (91).

B. The Free Radical Reaction of Propargylstannanes with Alkylsulfonyl Halides and Polyhalogenomethanes

This section further extends the utility of unsaturated organostannanes by studying the possibility of preparing propadienyl derivatives by the homolytic displacement of Sn from propargylorganostannanes by electrophilic radicals in the manner depicted in Equation 8.



(Equation 8)

Though several studies have already been done on the displacement of Sn from propargyl and propadienylstannanes, they, however, were reactions which went through the heterolytic pathways, i.e., the S_E2' and/or S_E2 process (Table 3). Johnson's group, however, has already shown that

propadienyl derivatives of Co, Rh and Ir can react with polyhalogenomethanes in a free radical chain process (59, 60). They have also observed that the hetero atom-centered radicals from PhSSPh and PhSeSePh (71) can also react in similar fashion with propadienylcobalt.

1. The preparation of the propargylstannanes:

The propargylstannane derivatives, propargyltriphenylstannane 81a and 2-butynyltriphenylstannane 82 were prepared by the Grignard route (Scheme 15) (92).

Scheme 15:

$$CH{\equiv}C\text{-}CH_2\text{-}Br \xrightarrow[THF]{Mg} CH{\equiv}C\text{-}CH_2\text{-}MgBr \xrightarrow{Ph_3SnCl} CH{\equiv}C\text{-}CH_2\text{-}SnPh_3$$

81a

$$+\ CH_2{=}C{=}CH\text{-}SnPh_3$$

81b

$$CH_3\text{-}C{\equiv}C\text{-}CH_2\text{-}Br \xrightarrow[THF]{Mg} CH_3\text{-}C{\equiv}C\text{-}CH_2\text{-}MgBr \xrightarrow{Ph_3SnCl} CH_3\text{-}C{\equiv}C\text{-}CH_2$$

$HgCl_2$ (trace)

Ph_3Sn

82

A trace of $HgCl_2$ (93) was found to be necessary to start the Grignard reaction.

The propadienyltriphenylstannane 81b is also produced during the preparation of 81a, but the two isomers are easily separated from each other by recrystallization from hexane.

2. The reaction of propargylstannanes:

Both derivatives 81a and 82 reacted slowly under sun-lamp irradiation with alkylsulfonyl halides (Scheme 16) to form propadienyl sulfones in modest yields (Table 5). Compound 81a also reacted under thermal conditions using 10 mol percent AIBN as initiator at 72-80°C, overnight, but 82 did not. Polyhalogenomethanes, CCl_4 and $CHCl_3$, reacted fairly well with 81a (Scheme 16) under both AIBN and photochemical conditions, but with 82, they reacted only very slowly and gave lower yields. The reaction of 82 with these substrates was further complicated by the presence of another product. Both 81a and 82 failed to react in the dark with the substrates mentioned.

Aside from the expected products, there was the ubiquitous presence of 81b in the reaction of 81a with some of the substrates. Its presence and the extent of its generation, however, varied according to the substrate, and type of initiation used (Table 6).

When RSO_2Cl reacted with 81a under photochemical stimulation, the expected sulfone product, the isomerized starting material 81b and unreacted starting material were obtained. On the other hand, when the same reaction was initiated by AIBN, no unreacted starting material was observed and only the expected product and isomerized starting material were observed.

Scheme 16:

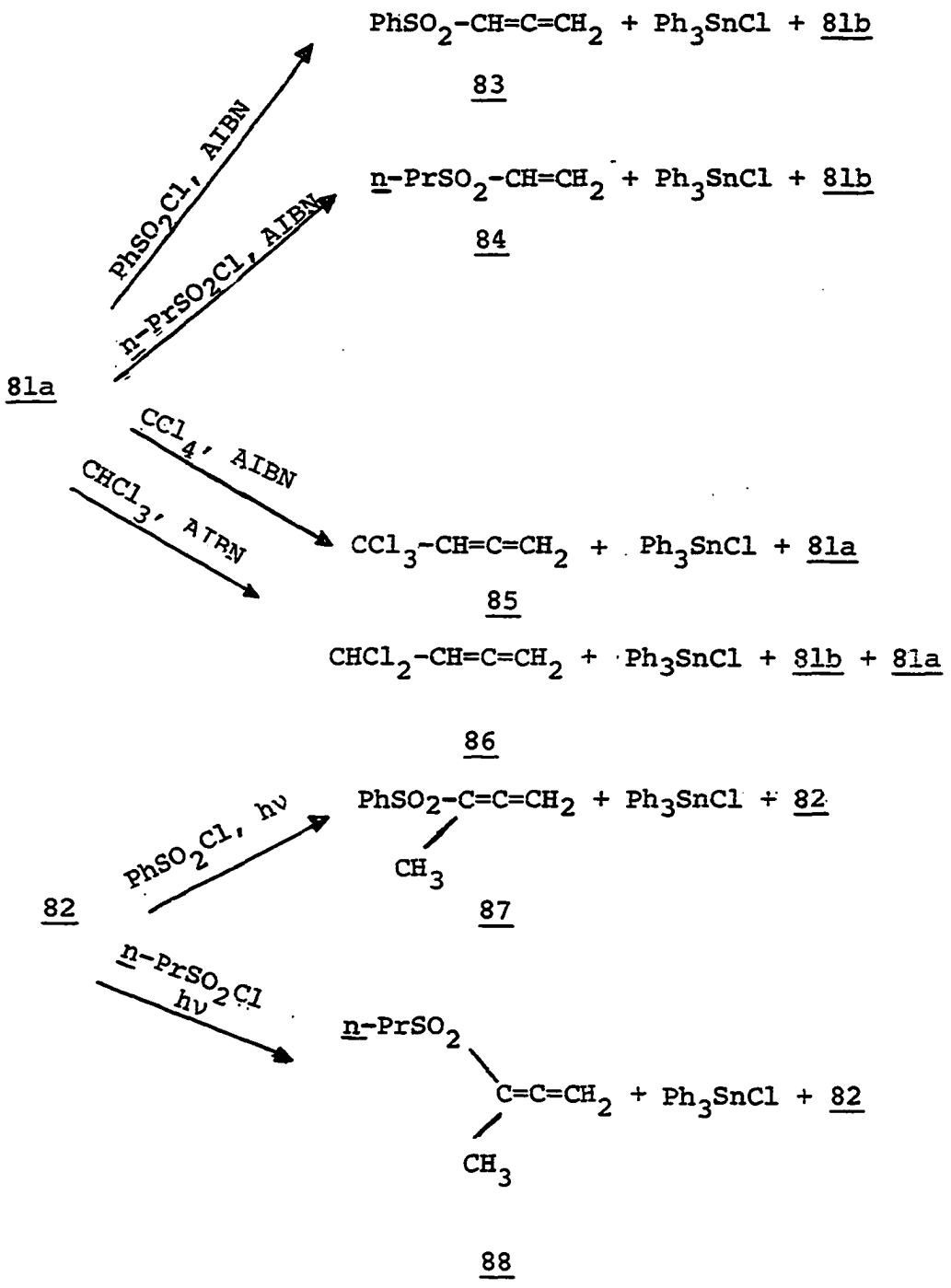

PhSO2-CH=C=CH2 + Ph3SnCl + 81b
83
n-PrSO2-CH=CH2 + Ph3SnCl + 81b
84
PhSO2Cl, AIBN
n-PrSO2Cl, AIBN
81a
CCl4, AIBN
CHCl3, ATRN
CCl3-CH=C=CH2 + Ph3SnCl + 81a
85
CHCl2-CH=C=CH2 + Ph3SnCl + 81b + 81a
86
PhSO2-C=C=CH2 + Ph3SnCl + 82
CH3
87
PhSO2Cl, hν
82
n-PrSO2Cl
hν
n-PrSO2
C=C=CH2 + Ph3SnCl + 82
CH3
88

Table 5. The reaction of propargylstannane with alkylsulfonyl halides and polyhalogenomethanes

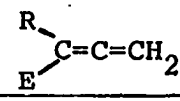
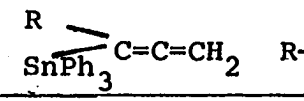
$$R\text{-}C{\equiv}C\text{-}CH_2\text{-}SnPh_3 + EY \longrightarrow \underset{E}{R\text{-}C{=}C{=}CH_2} + Ph_3SnY$$

Propargylstannanes	Substrate	Conditions	% Yield of $R\text{-}\underset{E}{C}{=}C{=}CH_2$	Structure number
81a	$PhSO_2Cl$	10 mol % AIBN/ 70°C/8 h	36[a]	83
	n-$PrSO_2Cl$	10 mol % AIBN/ 70°C/8 h	31[b]	84
	CCl_4	10 mol % AIBN/ 70°C/8 h	46[b]	85
	$CHCl_3$	15 mol % AIBN/ 50°C/21 h	31[b]	86
82	$PhSO_2Cl$	hν, 38 h	42[b]	87
	n-$PrSO_2Cl$	hν, 38 h	31[b]	88

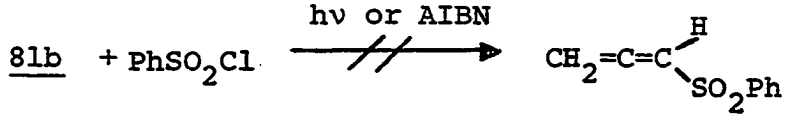
[a]Isolated yield.

[b]NMR yield.

Table 6. The effect of the types of initiator, organostannane and substrate on the composition of the reaction mixture

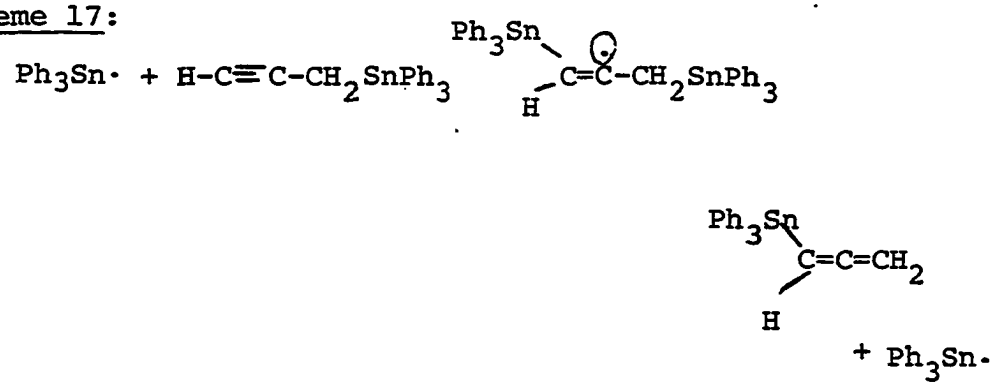
Propargyl-stannane substrate	Sub-strate	Initiator	% Composition of reaction mixture		
					$R-C\equiv C-CH_2SnPh_3$
81a	$PhSO_2Cl$	10 mol % AIBN	50	50	0
		hν	69.1	24.6	9.2
81a	n-$PrSO_2Cl$	10 mol % AIBN	41.6	58.3	0
		hν	20.6	55.1	24.2
81a	CCl_4	10 mol % AIBN	46.0	23.9	0
		hν	64.1	35.9	0
81a	$CHCl_3$	20 mol % AIBN	42.3	15.4	42.3
		hν	26.8	15.4	57.8
82	$PhSO_2Cl$	10 mol % AIBN	0	0	100
		hν	87.5	0	12.5
82	n-$PrSO_2Cl$	10 mol % AIBN	0	0	100
		hν	24.2	0	75.8

When CCl_4 was the substrate, no 81b, surprisingly, was detected. The reaction with $CHCl_3$, however, showed the presence of 81b. Although 81b is produced during the reactions mentioned, it was shown that it is not the precursor of the sulfone nor the polyhalogenomethyl substituted products. When pure 81b was reacted with $PhSO_2Cl$ under both photochemical and AIBN initiated conditions, no propadienyl sulfone 83 was generated.

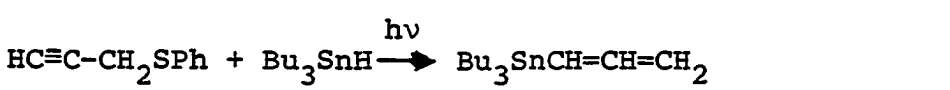


The isomerization of 81a to 81b probably takes place through a free radical chain process shown in Scheme 17.

Scheme 17:



This mechanism is very likely to happen since Ueno et al. (94) has observed similar behavior (Equation 9) in the reaction of Bu_3SnH with propargyl phenyl sulfide.

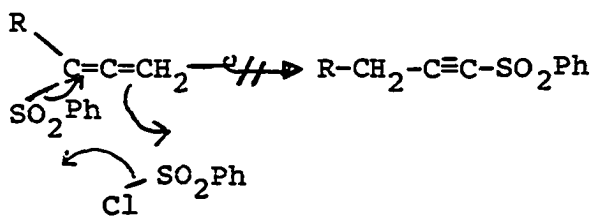


(9)

When 81a was heated at 80°C overnight without an initiator, no 81b was observed. However, the isomerization of 81a to 81b occurred when 81a was heated with AIBN or irradiated with sunlamp.

The isomerization of 82 to 2,3-butadienyl-2-triphenylstannane was not observed during its reaction with alkylsulfonyl halides. This result is not totally surprising since 82 has been found to be resistant to isomerization even under acid-catalyzed conditions (90). Furthermore, as has already been said, it was not produced during its synthesis either, although the preparation of the other propargylstannane derivative 81a did produce 81b (see Scheme 15).

The reaction of 82 with aryl or alkylsulfonyl chlorides proceeded to give regioselective products and, unlike the allylstannanes, did not show the presence of products arising from phenylsulfonyl promoted rearrangements.

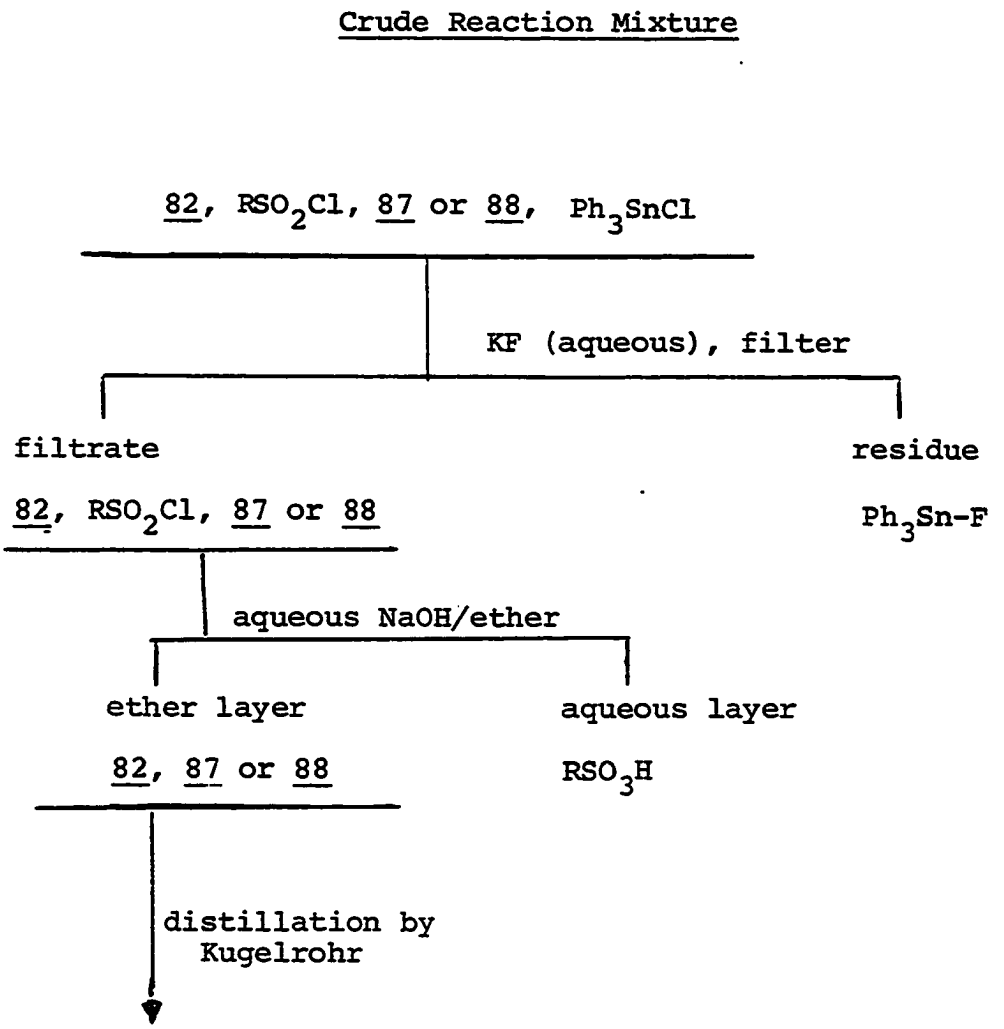


The work-up of the reactions of 81a with the alkyl sulfonyl halides was greatly simplified by using AIBN initiation. Under these conditions, the only compounds that need to be separated are the isomerized starting organostannane 81b and the propadienyl sulfones. Using acetonitrile/hexane partitioning, the propadienyl sulfone, along with unreacted $PhSO_2Cl$, went into the acetonitrile layer while the propadienylstannane 81b went into the hexane layer (95).

The sulfone products were found to be unstable to distillation. Approximately 5-8% of rearranged products were observed even though the reaction mixtures were subjected to work-ups (Scheme 18) which removed possible promoters of rearrangement, such as Ph_3SnCl and RSO_2Cl (96). However, the work-ups used did not eliminate the starting organostannanes. Heat alone is not responsible for the rearrangements, since heating the neat sulfone product did not cause the rearrangement.

Both 81a and 82 failed to react with dialkyl disulfides and, to our surprise, their reaction with alkyl halides did not materialize either. In the reaction of the cobaloximes with PhSSPh and polyhalogenomethanes, the propadienyl derivatives were found to be reactive, whereas, the propargyl were

Scheme 18:

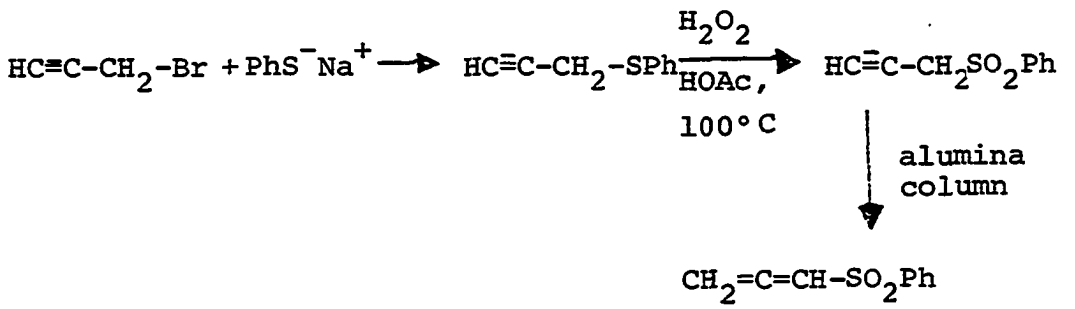

Crude Reaction Mixture
82, RSO2Cl, 87 or 88, Ph3SnCl
KF (aqueous), filter
filtrate
82, RSO2Cl, 87 or 88
residue
Ph3Sn-F
aqueous NaOH/ether
ether layer
82, 87 or 88
aqueous layer
RSO3H
distillation by Kugelrohr

not (59, 71). The studies, however, showed that the propargyl sulfides rearranged and, as a result, a mixture of products was obtained. Propadienyl Rh and Ir have been found to be reactive towards polyhalogenomethanes (60) giving regioselective products.

The reactions discussed can provide a potential synthetic route for substituted allenyl compounds. They have the advantage of being regioselective, efficient and simple in that no special equipment or work-up are needed.

Alternative examples of the synthesis of 84 and 85 have been reported in the literature (97, 98). Truce et al. (97) has reported that 84 can be prepared by a route shown in Scheme 19. Note that Truce's procedure entailed more steps,

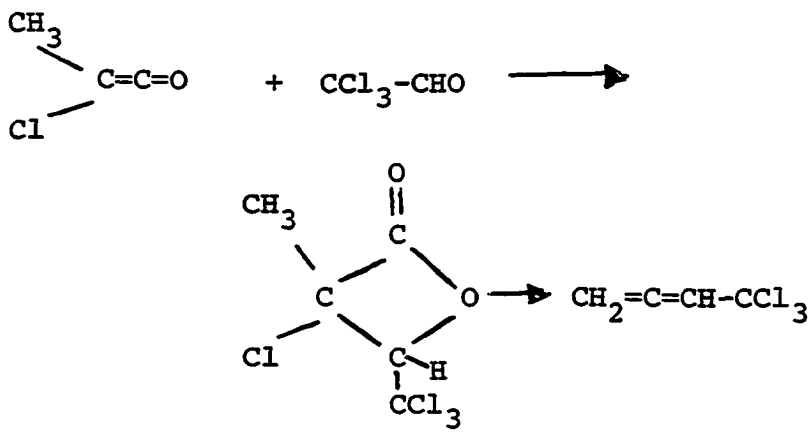
Scheme 19:



and did not necessarily give a higher yield.

Compound 85 has been prepared by Brady and Patel (98) via a method shown in Scheme 20. The procedure required

Scheme 20:



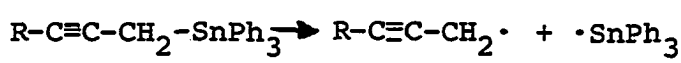
the use of a special set-up, i.e., a ketene generator, which could be inconvenient.

3. Mechanistic considerations:

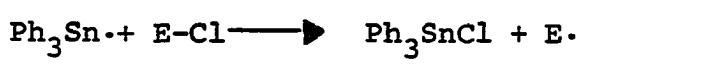
In view of the experimental observations, a free radical chain mechanism (Scheme 21) can be invoked for the reactions of propargylstannanes with alkylsulfonyl halides and polyhalogenomethanes.

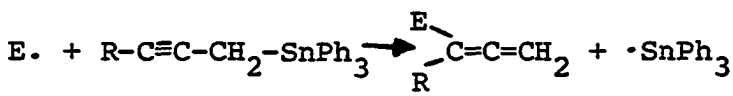
Scheme 21:

Initiation:

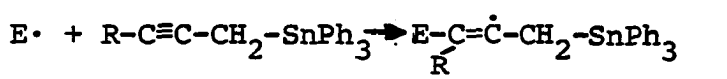


Propagation:

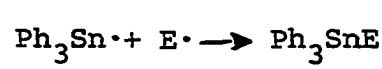




or



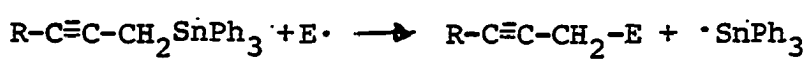
Termination:



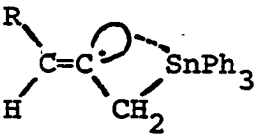
$R = H$ or CH_3

$E\cdot$ = $PhSO_2\cdot$, $\underline{n}$-$PrSO_2\cdot$, $CCl_3\cdot$, $CHCl_2\cdot$

Since only regioselective products were observed, the homolytic attack on the carbon α to Sn is not a competing pathway.

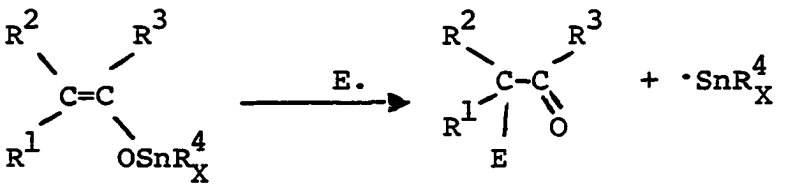


The homoconjugative effect, discussed in the previous section on allylstannanes, can also be utilized to rationalize the reactivity shown by the propargylstannanes, as depicted in 89.



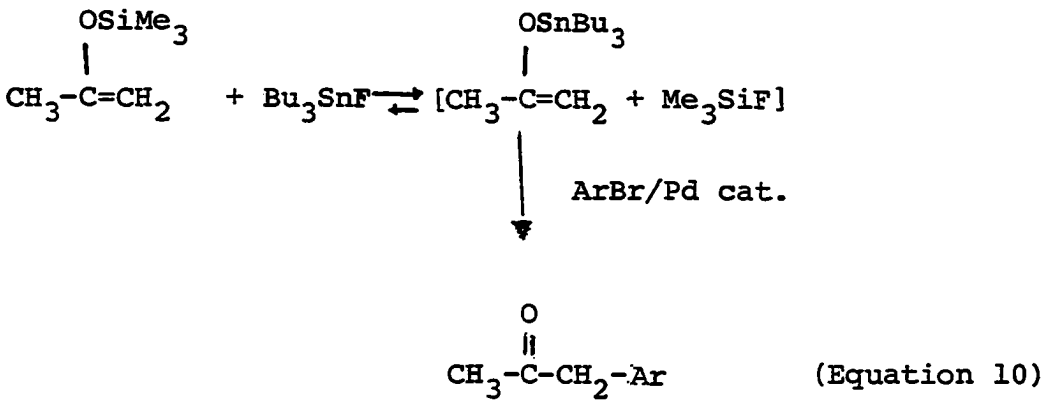
C. The Free Radical Reactions of Alkenyloxystannanes with Polyhalogenomethanes

This section investigates the possibility of using alkenyloxystannanes as ketone or aldehyde equivalents in an S_H2' reaction with electrophilic radicals.



Pereyre's group have already shown that mono α-alkylated ketones and aldehydes could be prepared by a simple nucleophilic substitution of alkyl halides with alkenyloxystannanes (74, 75).

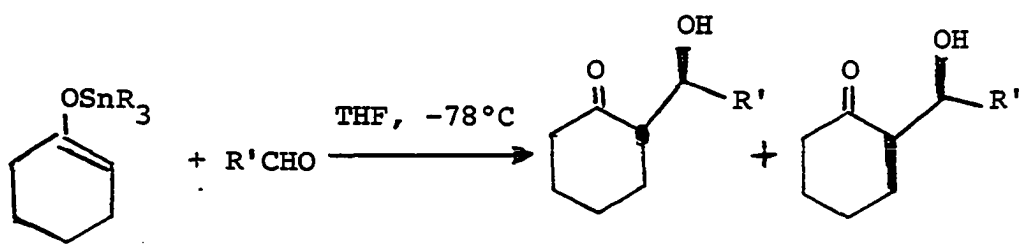
Recently, Pd-catalyzed one-pot reactions between aryl bromides and alkenyloxystannanes generated <u>in situ</u> from silyl enol ethers and Bu_3SnF (Equation 10) have been reported to give high yields of arylated ketones (76).



(Equation 10)

50-65% yield

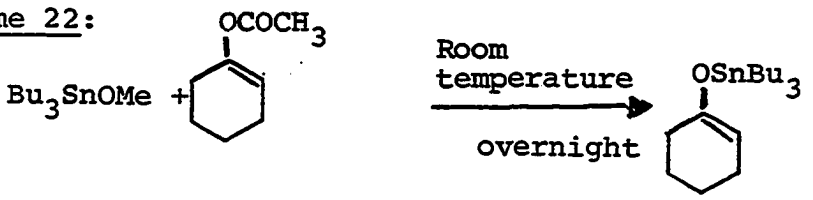
Alkenyloxystannanes have also been reacted with aldehydes and ketones giving aldol condensation products (68, 69).



1. Preparation of alkenyloxystannanes:

1-Cyclohexenyloxytri-n-butylstannane 90 and 2-methylpropenyloxytri-n-butylstannane 91 were prepared through the transesterification procedure shown in Scheme 22 (99, 100). Compounds 90 and 91 were found to be very

Scheme 22:



90

$$Bu_3SnOMe + (CH_3)_2C{=}CH{-}O\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow[\text{overnight}]{\text{Room temperature}} (CH_3)_2C{=}CH{-}OSnBu_3$$

91

sensitive to moisture and should be used immediately after preparation, or a decrease in yield will be observed.

Though some alkenyloxystannanes have been reported to be a mixture of two equilibrating metallotropic forms (carbon and oxy), derivatives 90 and 91 were those which were observed to exist solely in the oxy form (100).

Previous studies (75), however, have found no evidence for any difference in reactivity between the two metallotropic forms.

2. The free radical reaction of alkenyloxystannanes:

Of the various sources of electrophilic radicals studied, which included the alkylsulfonyl halides and dialkyl disulfides, the carbon-centered radicals derived from polyhalogenomethanes were the only ones which successfully produced the expected products.

Bromotrichloromethane ($CBrCl_3$) and carbon tetrachloride (CCl_4) both reacted under sunlamp irradiation with 90 and 91 to give 92 and 93, respectively, in similar yields (Table 7 and Scheme 23). In its reaction with 91, $CBrCl_3$ reacted faster than CCl_4 (5 mins and 2 hrs, respectively). The reactions of 90 and 91 with $CBrCl_3$ and CCl_4 proceeded cleanly, producing only the expected product, 92 and 93 respectively, with only a trace of the α-bromocyclohexanone being observed in the case of the reaction of $CBrCl_3$ with 90.

No evidence of any products arising from an attack on the oxygen was seen. Neither were any compounds obtained which could come from polysubstitution reactions.

Products coming from the further reaction of the

Scheme 23:

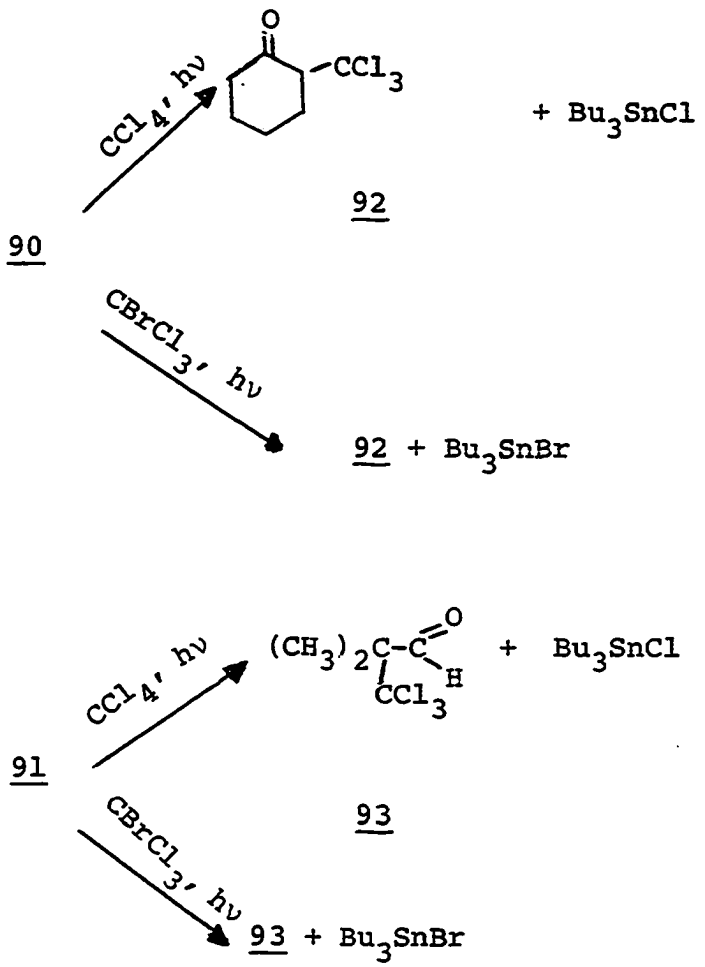

O
CCl3
CCl4, hν
+ Bu3SnCl
92
90
CBrCl3, hν
92 + Bu3SnBr
(CH3)2C-C
O
H
CCl3
CCl4, hν
+ Bu3SnCl
91
93
CBrCl3, hν
93 + Bu3SnBr

Table 7. The photochemical[a] reaction of alkenyloxystannanes with polyhalogenomethanes

Alkenyloxy-stannane	Substrate	Duration	Organic products	(% ^{1}H NMR yield)
90	CCl_4	2 h	92	58.9
90	$CBrCl_3$	3 h	92	64.1
90	$CHBr_3$	1 h	94	28.9
91	CCl_4	2 h	93	53.8
91	$CBrCl_3$	5 min	93	48.1
91	$CHBr_3$	2-4 h	96	17.6
			97	5.9

[a]Sunlamp was used.

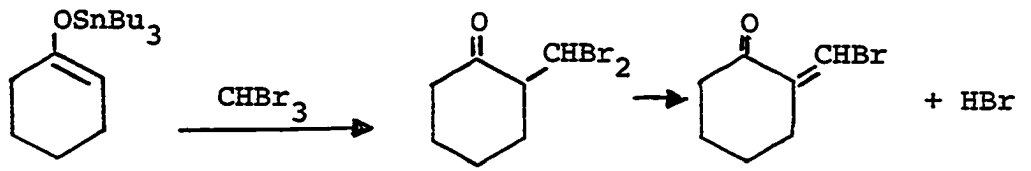
resulting aldehyde or ketone products with the alkenyloxystannanes were not observed either. This is probably unlikely to happen anyway under the photochemical conditions used, since such reactions usually occur at high temperature and have been found to proceed via an S_E2' or S_Ei' mechanism (65, 66, 67).

Compound 92 was found to be very stable, and could be isolated as a pure liquid. However, 93 had appreciable stability only in solution. Surprisingly, the more reactive CBr_4 did not react with either 90 nor 91. Whereas, $CHCl_3$ did not react at all, showing only traces of the expected product, bromoform ($CHBr_3$) reacted with 90 and 91 (Scheme 24) to give the expected products (Table 7) and other interesting results.

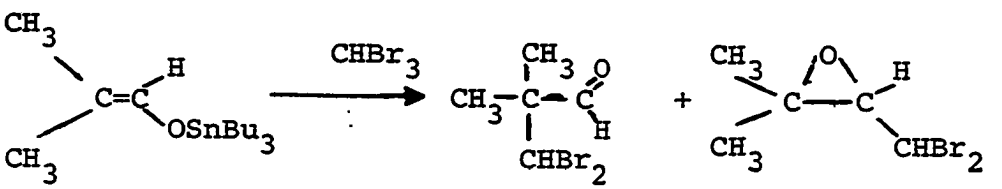
When $CHBr_3$ reacted with 90 (Scheme 24), it generated the expected product 94, which, however, proved to be unstable on standing or upon distillation. The more stable dehydrobrominated form 95 was isolated upon distillation.

Compound 94 can be observed at the end of the reaction. The NMR spectrum of the crude reaction mixture clearly contained a doublet at δ 6.15 (J = 3 cps) which could be atrributed to the $-CHBr_2$ proton. The GLC-MS of the crude

Scheme 24:



90 94 95



91 96 97

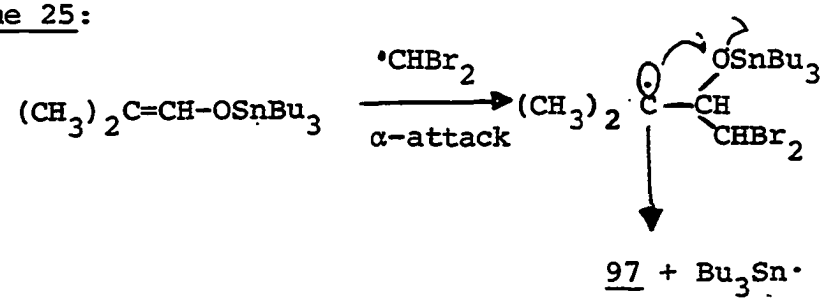
reaction mixture has a component with a parent ion of m/e 268, which corresponds to the molecular weight of 94. GLC analysis of the crude reaction mixture, right after the reaction, and after several hours of standing showed that the amount of a lower retention time component was increasing during standing. The GLC-MS of the crude reaction mixture showed the parent ion of this peak to be 168, which is the molecular weight of 95.

Upon distillation of the crude reaction mixture, the sole product isolated had an NMR spectrum which corresponded to that expected for 95 [C_6D_6 δ 7.3 (t, 1H, J=2 cps), 0.8-2.2 (m, 8H)]. The IR of this product featured a C=O band at 1709 cm^{-1} and a C=C band at 1589 cm^{-1}.

These observations are an indication of the existence of 94 and the fact that it is the precursor of the more stable 95.

In its reaction with the other derivative 91, $CHBr_3$ gave not only the expected product 96, but also product 97, which possibly came (Scheme 25) from the competing attack of the $\cdot CHBr_2$ radical on the α-carbon, followed by epoxide formation via an S_H2' attack on oxygen.

Scheme 25:



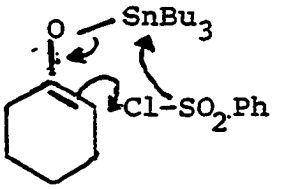
Compounds 96 and 97 are not separable by distillation. The NMR spectrum of the fraction at 46-51°C/3.5 mm Hg during distillation of the crude reaction mixture gave two sets of peaks, i.e., (δ 9.30(s); 5.65(s); 1.1(s); and δ 5.25(d), J=8 cps; 3.35(d), J=8 cps; 1.1(s)) which can be attributed to 94 and 97, respectively. The GLC-MS of this fraction gave two peaks, which both gave a parent ion peak equal to m/e 242.

The GC-IR of the mixture of isomers showed the IR spectrum of the earlier peak to be devoid of any C=O stretching absorption and it was thus assigned as the epoxide product 96. The later peak had a distinct C=O band at 1740 cm^{-1} and the aldehydic C-H bands at 2825 and 2707 cm^{-1} which indicate that it is that of the

aldehydic product 95.

The previously mentioned attack on the less nucleophilic α-carbon (Scheme 25), is apparently the first example of such a reaction in any β,γ-unsaturated organostannane system so far studied. The steric bulk of the attacking radical ($\cdot CHBr_2$) species could be the cause for this unprecedented result.

As previously stated, the alkenyloxystannanes failed to react with hetero atom-centered radical sources such as RSO_2Cl, CCl_3SO_2Cl and PhSSPh to give the expected products. RSO_2Cl and CCl_3SO_2Cl reacted, in the absence of light, with 90, but they generated α-chlorocyclohexanone, probably via an S_E2' mechanism, illustrated in 98.



The reaction of the polyhalogenomethanes with the alkenyloxystannanes was inhibited by di-tert-butyl nitroxide (see Table 14 and Figure 20 in the Experimental section). The reaction did not proceed in the dark.

The reaction of the polyhalogenomethanes with the alkenyloxystannanes was inhibited by di-tert-butyl nitroxide (see

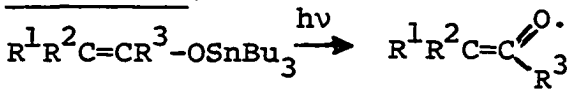
Table 14 and Figure 20 in the Experimental section. The reaction did not proceed in the dark either.

3. Mechanistic considerations:

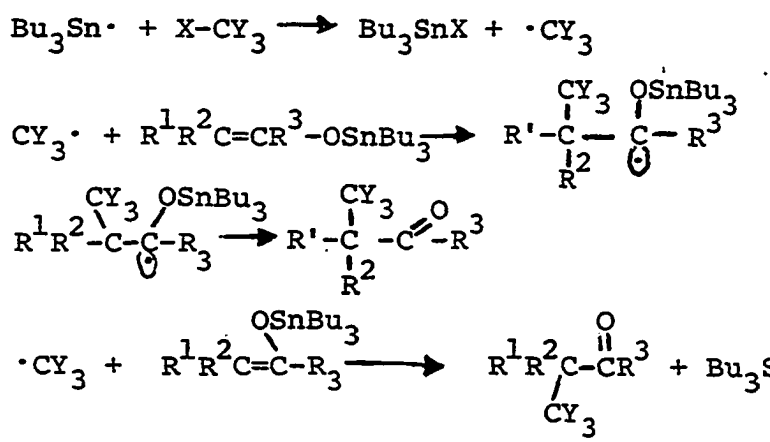
The experimental observations indicate that alkenyloxystannanes react with polyhalogenomethanes by a free radical chain mechanism which is similar to those proposed for the other unsaturated organostannanes studied, the allyl and propargyl derivatives (Scheme 26).

Scheme 26:

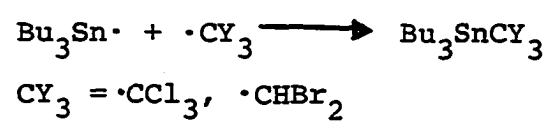
Initiation:



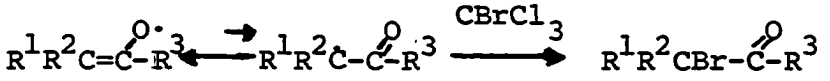
Propagation:



Termination:



The trace amount of α-bromocyclohexanone in the reaction of 90 with $CBrCl_3$ could probably arise from the reaction of $CBrCl_3$ with the enolate radical, perhaps formed in the initiation process Equation 11.



$$+ \cdot CCl_3 \qquad \text{(Equation 11)}$$

III. CONCLUSION

The results in Part II illustrate the fact that the homolytic displacement of metal from an unsaturated organometallic compound is not just a novelty but rather is more common than might previously have been thought. The reactions of allylstannanes with hetero atom-centered radicals, propargylstannanes with alkylsulfonyl halides and polyhalogenomethanes and alkenyloxystannanes with polyhalogenomethanes were all shown to proceed via an S_H2' or addition-elimination free radical chain process.

The investigations carried out in Part II also proved the potential of the reactions of unsaturated organostannanes as convenient and efficient synthetic routes toward allyl sulfides, selenides, and sulfones, sulfonated and polyhalogenomethylated propadienes and α-polyhalogenomethylated ketones and aldehydes.

IV. EXPERIMENTAL

A. Instrumentation

In addition to what was already mentioned in the Instrumentation section of Chapter V of Part I, the following instruments were also used: A Jeol FX-90Q spectrometer was used to obtain the ^{13}C spectra of the pure product of the reaction of propargylstannanes with organosulfonyl halides (Table 13). A Brüker WM-300 spectrometer was used for the double irradiation experiment performed on compound 86, 1,1-dichloro-2,3-butadiene. An IBM IR 198 FT-IR spectrometer was used to obtain the GC-IR data of compounds 96 and 97.

B. Procedure and Results

A typical procedure for the photoreaction of organostannanes on a preparative scale:

Equimolar amounts of the substrate (1.4-6.1 mmol) and organostannane (1.4-6.1 mmol) were introduced into a round-bottomed pyrex flask containing benzene (4-10 ml) as solvent except in the case of the polyhalogenomethanes which were added in excess and were themselves the solvent. The solution was covered with a rubber septum and degassed with nitrogen for a few minutes. The reaction mixture was stirred with a magnetic stirrer while being irradiated with a 275 Watt sunlamp at a distance of approximately 6 inches. At the end of

the reaction, the solvent was evaporated by a rotary evaporator and usually the product was isolated by distillation using the Kugelrohr technique unless otherwise indicated.

A typical procedure for the reaction of organostannanes with substrates using AIBN as initiator on a preparative scale:

The same procedure was used as in the photoreaction of organostannanes on a preparative scale except that 10-20 mol % of AIBN was added and the reaction vessel immersed in an oil bath with a temperature kept between 70-80°C for at least 8 hours.

A typical procedure for the photoreaction of the organostannanes with substrates on an NMR scale:

The substrate (3.0-0.76 mmole) was weighed into and dissolved in deuterated benzene in a vial and then added to the organostannane (3.3-0.76 mmole). The solution was transferred to an NMR tube and capped with a rubber septum. The NMR solution was irradiated with a 275 Watt sunlamp at a distance of approximately 6 inches.

A typical procedure for the reaction of the organostannanes with substrates using AIBN initiation on an NMR scale:

The same procedure described for the NMR scale photoreaction was followed except that 10-20 mol % AIBN was added to the solution and the NMR tube immersed for 8 hours in an oil bath maintained at a temperature between 70-80°C.

General procedure for studying the effect of darkness on the reaction of organostannanes:

The procedure described for conducting a photochemical reaction on an NMR scale was followed except that the NMR tube was covered with a piece of aluminum foil and immersed in a 50°C oil bath for the same length of time as the photochemical reaction but without irradiation with a sunlamp.

General procedure for investigating the inhibitory effect of di-tert-butyl nitroxide or galvinoxyl on the reaction of organostannanes:

The procedure used for the NMR scale photoreaction of organostannane was followed except that 10 mole % of di-tert-butyl nitroxide or galvinoxyl was added to the solution. The NMR solution was irradiated with a sunlamp and the NMR of this solution and another sample which did not contain any inhibitor were taken after the same interval of irradiation had ensued.

Preparation of allyltri-n-butylstannane 61:

A modification of Abel's method (80) was used in preparing 61. Magnesium (6.0 gms, 0.25 mole) and 25 ml dry tetrahydrofuran was added under a nitrogen atmosphere to a 500-ml 3-necked round-bottomed flask furnished with an addition funnel, condenser and magnetic stirrer.

Allyl chloride (19.0 gms, 0.25 mole) dissolved in 72.0

ml THF was added to the mixture at such a rate as to maintain gentle boiling. The reaction mixture turned greyish as the allyl chloride reacted. After all the allyl chloride was added, the reaction mixture was stirred further for 2 hours. The mixture turned into a thick suspension and more THF was added to fill half the flask.

Tri-n-butyltin chloride (10.0 g, 0.03 mole) was added and the reaction mixture was heated to reflux for 1-1/2 hours using an oil bath. The reaction was stirred at room temperature overnight.

Saturated NH_4Cl solution was slowly added to the greyish solution. The solution was filtered and the filtrate was dried over anhydrous magnesium sulfate. The solvent was evaporated in a rotary evaporator and the residue distilled at 106°/0.1 mm Hg to give 6.5 g of clear liquid product.

H NMR (C_6D_6): δ 0.7-2.4 (m, 29), 4.8 (m, 2),
5.9 (m, 1)

IR: (neat) 3080, 2920, 2880, 2840, 2820, 1605, 1445,
1400, 1355, 1170, 1050, 1000, 855.

Preparation of crotyl-tri-n-butylstannane 62:

A modified version of the method reported by Seyferth et al. was used (81). Ammonia gas (250 ml) was condensed into 3-necked flask provided with a dry ice condenser, addition funnel, thermometer, and cooled with a dry ice-acetone

bath. When all the ammonia was added, Na metal (2.5 g, $11x10^{-2}$ mole) in small chunks was added. The solution turned blue. Tri-n-butytin chloride (18.0 g, $5.52x10^{-2}$ mole) was added at dry ice acetone temperature. The reaction mixture was cooled with an acetone dry ice bath and crotyl chloride (5.0 g, $5.52x10^{-2}$ mole) was added. The reaction was quenched with a saturated ammonium chloride solution. The ammonia gas was allowed to evaporate by removing the bath. The solution was shaken with ether and filtered. Ether was evaporated off and the residue distilled at 99°C/0.1 mm Hg to give a clear liquid product.

^{1}H NMR (C_6D_6): δ 0.9-2.5 (m, 29), 5.5 (m, 2)

IR (neat): 2900, 2700, 2850, 2820, 2810, 1640, 1625, 1550, 1450, 1360, 1050, 940, 850 cm^{-1}.

The photoreaction of allyltri-n-butylstannane with sulfur centered radicals:

The general procedure for the photoreaction of organostannanes on preparative scale was followed in obtaining the data on the reactions of allyltri-n-butyl-stannane with RSO_2Cl, RSSR and CCl_3SO_2Cl. Their crude reaction mixtures were distilled by the Kugelrohr technique except in the case of CCl_3SO_2Cl, wherein, a short path distillation set-up which had a receiver flask cooled by an acetone-dry ice bath was used.

The boiling point and NMR spectra of the products of the reactions are given in Table 8. The duration and yield of the reaction have previously been given in Table 4.

The NMR spectra of the products were compared with the NMR spectra of authentic samples prepared by known literature methods (101, 102, 103).

The photoreaction of allyltri-n-butylstannane with PhSeSePh:

The general procedure for the photoreaction of organostannanes on an NMR scale was followed. The reaction lasted 6 hours to give 94% yield of the product.

^{1}H NMR (C_6D_6): δ 3.34 (d, 2, J = 6 cps)

GLC-MS: m/e (rel. intensity) = 175.94 (30.06), 173.76 (62.06), 171.78 (33.48), 94178(83.10), 92.80 (100.00), 90.86 (16.11), 83.98 (30.45), 81.98 (6.97), 80.72 (33.03), 78.84 (30.42), 53.94 (5.89), 51.98 (5.56), 49.86 (2.01).

The photoreaction of allyltri-n-butylstannane with 2-chloro-2-nitropropane:

The general procedure for the photoreaction of organostannanes on an NMR scale was used. The reaction took 6 hours and gave an NMR yield of 90%.

^{1}H NMR (C_6D_6): δ 2.38 (d, 2, J = cps)

GLC-MS: m/e (rel. intensity) = 78.86 (34.05), 76.96 (100), 62.98 (1.51), 62.00 (1.27), 60.98 (4.73), 48.92 (9.74), 46.14 (4.49).

Table 8. The characterization of the products[a] of the reaction of allyltri-n-butylstannane with sulfur centered radicals

Product	Boiling Point (Kugelrohr)	^{1}H NMR (ppm)
63	95-140°C/38 mm Hg	3.45 (d,2) 4.85-6.22 (m, 3) 7.2 (m, 5)
64	140-150°C/0.5 mm Hg	2.95 (d, 2) 3.58 (s, 2) 4.81-6.05 (m, 3) 7.35 (m)
67	80-120°C/0.3 mm Hg	3.77 (d, 2) 4.78-6.11 (m, 2) 7.43-7.97 (m)
68	110-150°C/39 mm Hg	1.1 (t, 3), 1.8 (m, 2) 2.95 (m, 2), 3.74 (d, 2) 5.25-6.35 (m, 3)
76	30-50°C/100 mm Hg	3.2 (d, 2)

[a]The NMR spectra of these products were compared with the NMR spectra of authentic samples prepared by known literature methods (62, 101, 102, 103).

The photoreaction of crotyltri-n-butylstannane with sulfur centered radicals:

The general procedure for the photoreaction of organostannanes on an NMR scale was used. The duration and yield of the reaction are given in Table 4. The formation of regioselective products and their rearrangements were followed by NMR and compared with those of authentic samples. An example of this study is shown in Figure 12 which shows the progress of the reaction of $PhSO_2Cl$ with 62. In all the reactions, an initial formation of regioselective products was observed as shown in Figure 12.

In the case of PhSSPh, the reaction which took 2 h to give the first sign of the characteristic H-C-SPh proton in the NMR, however, showed evidence of immediate rearrangement also. GLC analysis of this sample showed the characteristic retention time of the rearranged product which was formed at the same time as the regioselective product was being produced (54.52% to 45.47% of rearranged product).

The inhibitory effect of di-tert-butyl-nitroxide and galvinoxyl on the reactions of allylstannanes:

The general procedure on p. 130 was used except that the distance of the sunlamp was increased to 20 inches in the case of $(tert\text{-}butyl)_2NO^{\bullet}$. The study was done using the reaction on PhSSPh with allyltri-n-butylstannane. The

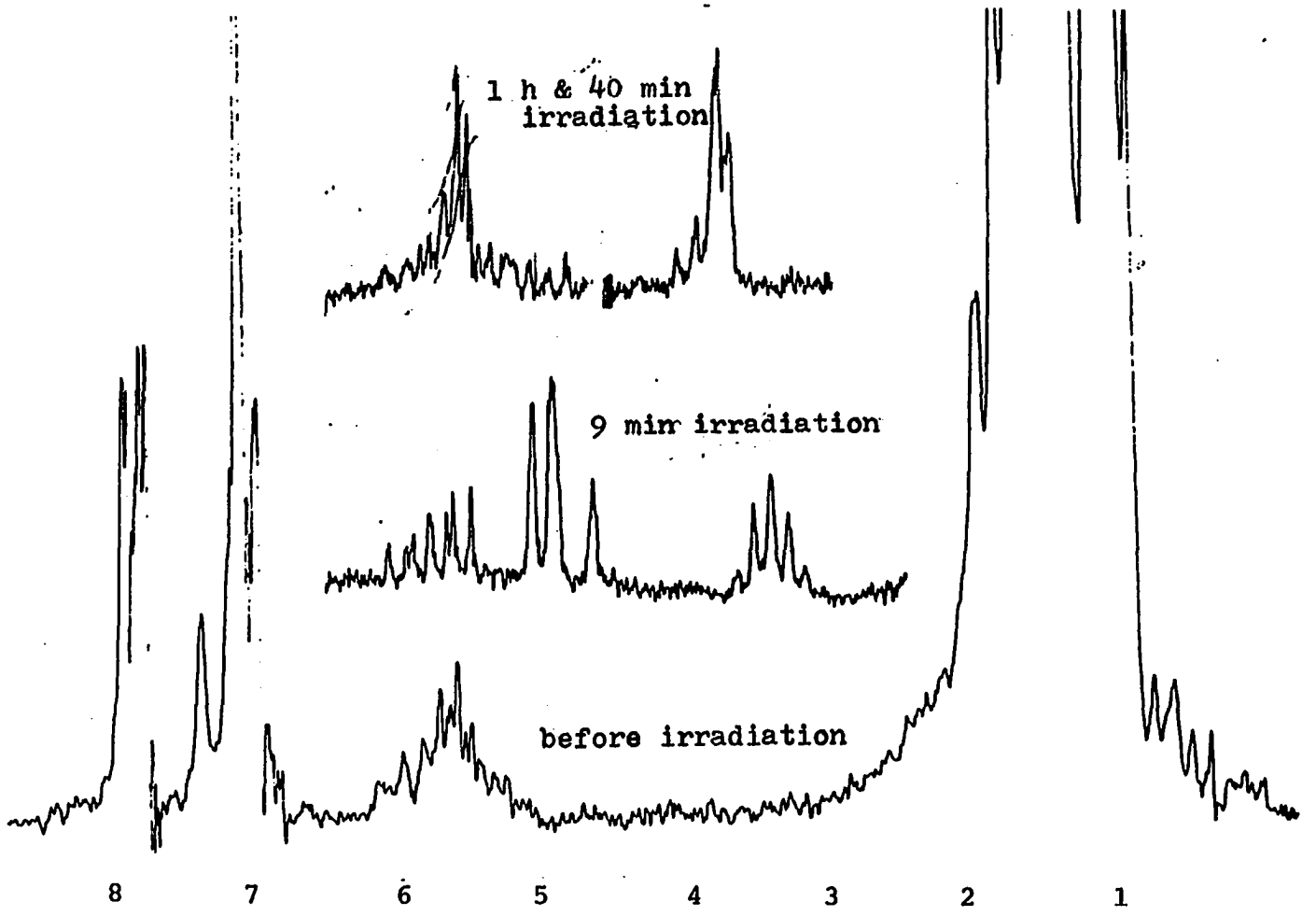


Figure 12. The ^{1}H NMR spectra showing the progress of the reaction of $PhSO_2Cl$ with crotyltri-n-butylstannane

progress of the reaction was followed by comparing the ratio of the CH_2-S protons to the vinyl hydrogens which were assumed to be constant ($-CH=CH_2$).

The results are summarized in Tables 9 and 10 and Figures 13 and 14.

The effect of darkness on the reaction of allylstannanes with hetero atom-centered radicals:

The general procedure on p. 130 was used using PhSSPh as substrate and allyltri-n-butylstannane. The NMR results show the absence of the CH_2-S protons during all the time the reaction was conducted in the dark.

The reaction of allyltri-n-butylstannane with N-bromosuccinimide (NBS):

NBS and allyltri-n-butylstannane were dissolved in C_6D_6 and transferred to an NMR tube. The NMR spectrum of the reaction prior to irradiation was taken and a peak at δ 3.9 was observed. Using the ratio of this peak to the vinyl hydrogens, the reaction was noted to have proceeded 100% even before irradiation.

Comparison of the NMR spectrum of this reaction with that of allyl bromide indicates correspondence of the two spectra.

Table 9. A study of the inhibitory effect of di-tert-butyl nitroxide on the reaction of PhSSPh with allyltri-n-butylstannane

Length of irradiation	Ratio of CH_2-S to -CH=CH_2	
	0 mol % $(tert\text{-}butyl)_2NO\cdot$	10 mol % $(tert\text{-}butyl)_2NO\cdot$
10 min	0	0
20 min	trace	0
30 min	7.8	0
40 min	12.9	0
50 min	15	0
1 h	16.7	0
1.5 h	20.1	0
2 h	37.3	0
3 h	47.2	0
4 h	55.6	0
5 h	67.2	12.9
6 h	85	17.1

Table 10. A study of the inhibitory effect of galvinoxyl on the reaction of PhSSPh with allyltri-n-butylstannane

Length of irradiation	Ratio of $-CH_2S$ to $-CH=CH_2$	
	0 mole % galvinoxyl	10 mole % galvinoxyl
0 min	0	0
10 min	19.5	0
30 min	38.7	0
1 h	46.6	0
2 h	51.4	0
5 h	48.4	0

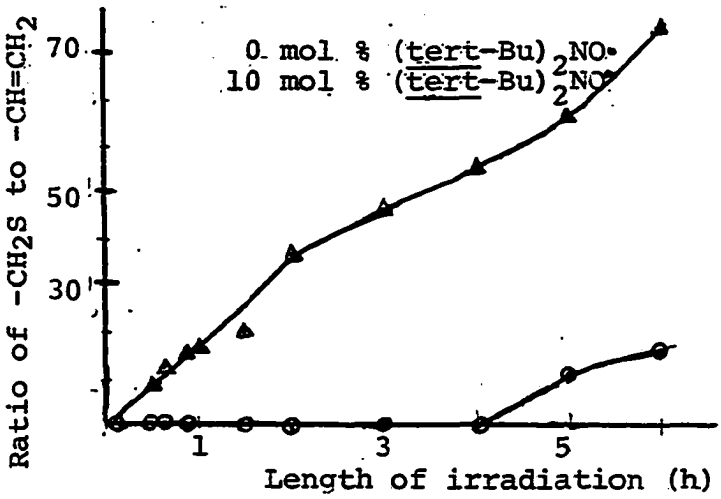


Figure 13. The inhibitory effect of di-tert-butylnitroxide on the reaction of allylstannanes with ϕSSϕ

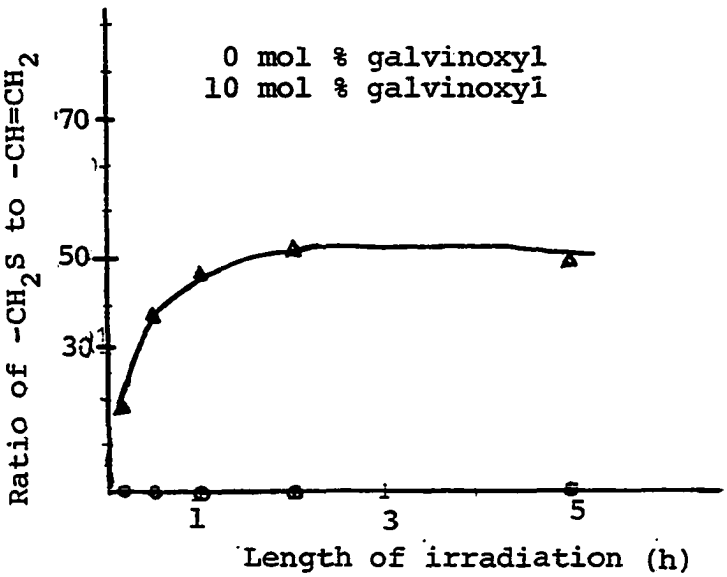


Figure 14. The inhibitory effect of galvinoxyl on the reaction of allylstannanes with PhSSPh

Preparation of 1-propargyltriphenylstannane 81a:

A modified version of LeQuan and Cadiot's procedure was used (92). Magnesium (0.50 g, .002 mole) and 15 ml ether was added under nitrogen atmosphere to 250 ml 3-necked round-bottomed flask provided with an addition funnel, magnetic stirrer, condenser and thermometer. A trace of $HgCl_2$ was added to the mixture. Propargyl bromide (0.4 ml) was added neat to the mixture. The mixture was warmed with a hot tap water bath (a few more traces of $HgCl_2$ were added when the reaction still would not proceed at this point). When the reaction started, the hot bath was removed and replaced with an ice bath. The rest of the propargyl bromide which this time was dissolved in 35 ml ether was added dropwise. The temperature was maintained at 20°C or below. After a few minutes, more proparyl bromide (0.8 g) was added until all the magnesium reacted. The reaction mixture was stirred at 20°C or below. Triphenyltin chloride (3.08 g, 0.0063 mole) was added next while the reaction mixture was cooled by a ice water bath. The reaction was stirred for 3 hours and then quenched with 30 ml saturated ammonium chloride. The aqueous layer was separated from the ether layer. Any mercury was filtered from the aqueous layer and then the layer was extracted twice with ether. The combined ether layers was dried (Na_2SO_4) and the solvent evaporated by rotary evaporator. The

residue was recrystallized in hexane to give 1.2 g of white crystals (mp 80-82°C). The filtrate from the recrystallization contained the other isomer, the propadienyltriphenylstannane 81b.

^{1}H NMR (C_6D_6): δ 1.35 (t, 1, J = 3 cps), 1.55 (d, 2, J = 3 cps), 6.8-7.45 (m, 15)

IR (CCl_4): 3290, 2110 cm^{-1}.

Preparation of propadienyltriphenylstannane 81b:

The procedure of LeQuan and Cadiot was used (92). Compound 81a was dissolved in ethanol in an Erlenmeyer flask and the solution boiled for 15 minutes on a hot plate. Compound 81b was obtained in 100% yield, mp 58-59°C.

^{1}H NMR (CCl_4): δ 4.45 (d, 2, J = 7 cps), 5.51 (t, 1, J = 7 cps), 7.7 (m, 15)

Preparation of 4-bromo-2-butyne (104):

Phosphorous tribromide (36 g, 12.6 mol) was placed under a N_2 atmosphere in a 3-necked round-bottomed flask provided with an addition funnel, low-temperature thermometer and overhead stirrer. The flask was cooled in an ice bath and 0.2 gms of pyridine was added with a syringe. 1-Butynyl-3-ol (0.2 gms) was added at 0°C for 1 hour to the mixture. The reaction mixture was further stirred for

20 minutes at 0°C and allowed to warm to room temperature. The reaction mixture was distilled at 72°C/100 mm Hg to give 5.2 g clear liquid product.

^{1}H NMR: δ 1.91 (t, 3), 4.01 (q, 2)

Preparation of 2-butynyltriphenylstannane 82:

The same procedure used for the preparation of 81a was followed. The product was recrystallized in hexane (mp 68-69°C). None of its allenyl isomer was observed.

^{1}H NMR (CCl_4): δ 1.69 (t, 3, J = 4 cps), 2.16 (q, 2, J = 4 cps)

IR (CCl_4): 2223 cm^{-1}.

Light-induced isomerization of 81a to 81b:

Compound 81a (0.20 gms) was dissolved in 0.4 ml C_6D_6 and transferred to an NMR tube. The solution was degassed and covered with a rubber septum and irradiated with a sun-lamp for 19 hours. The NMR of the solution showed that no 81a remained and only the characteristic peaks of 81b were seen.

The effect of heat on the isomerization of 81a to 81b:

Compound 81a (0.20 gms) was dissolved in 0.4 ml C_6D_6 and transferred to an NMR tube. The solution was degassed and covered with a rubber septum. The NMR spectrum of the solution showed only 81a. No isomerization to 81b was observed.

The effect of AIBN on the isomerization of 81a to 81b:

The same procedure described for the previous experiment was followed except that 10 mol % AIBN was added to the solution.

No 81a was observed in the NMR of the solution. The characteristic NMR peaks of 81b were observed.

The effect of darkness on the reaction of 81a and 82 with alkylsulfonyl halides:

The general procedure given on p.130 was followed using $PhSO_2Cl$ as substrate. The products 83 and 87 from 81a and 82, respectively, were not observed in the NMR spectra of the solutions.

The AIBN initiated reactions of 81a with alkylsulfonyl halides and polyhalogenomethanes:

The general procedure used for AIBN initiated reactions on a preparative scale on p.129 was used. The reaction mixture were stripped of its solvent and distilled by the Kugelrohr technique. The products from the reaction of 81a with $PhSO_2Cl$ and n-$PrSO_2Cl_2$, 83 and 84, respectively, were further purified by preparative GC on a 5 ft x 1/4 inch 15% OV-3 column using a 180°C oven temperature for 83 and 140°C for 84. The characterizations of these products are in Table 11. Their ^{13}C NMR chemical shifts are given in Table 12. The assignments were based on the examples of

allenes in Patai's book (105) and from the partial proton decoupling experiment done on compound 84 (see Figure 15).

The fraction obtained at 35-40°C/110 mm Hg from the reaction of CCl_4 with 81a contained CCl_4 and the expected product 85. The NMR of 85 was compared with the NMR of the compound in the literature (98).

The fraction obtained at 25°C/1.5 mm Hg from the reaction of $CHCl_3$ and 81a was a mixture of $CHCl_3$, the expected product 86 and 81b. A double irradiation, ^1H NMR experiment was done on this fraction (see Figure 16).

The characterization of the products are given in Table 11. The duration and yield of the reactions have been previously given in Table 5.

The photochemical reaction of 82 with alkylsulfonyl halides:

The general procedure for the photoreaction of organostannanes on p. 128 was followed. The crude reaction mixture was subjected to a work-up summarized in Scheme 18. A more detailed description using n-propylsulfonyl chloride as the substrate is as follows:

n-Propylsulfonyl chloride (1.1 gm, 0.0074 mol) and 82 (3 g, .0074 mol) were dissolved in 10 ml C_6H_6 and irradiated for 24 hours.

The solvent was evaporated and 25 ml of 10% aqueous KF was added to the crude residue. The mixture was

stirred for 10 minutes with a magnetic stirrer and filtered. The residue was washed with ether. The ether layer of the filtrate was separated and the solvent was evaporated. The residue was analyzed by NMR spectroscopy and it showed no Ph_3SnCl.

The residue was redissolved in ether and 40 ml 10% NaOH. The two phases were vigorously stirred for 1 day with a magnetic stirrer. The organic layer was separated and the aqueous layer washed with ether (3x). The organic layers were combined and the solvent was evaporated off. The NMR spectrum of the residue showed most of n-$PrSO_2Cl$ gone.

The residue was distilled by Kugelrohr. The NMR of the fraction at 70-110°/1.5 mm Hg showed mostly the product peaks. The residue from distillation by Kugelrohr showed only 82.

All the samples after this work-up were further purified by preparative GLC using a 5 ft x 1/4 inch 15% OV-3 column using 180°C and 140°C for 87 and 88, respectively.

Characterization of the products are given in Table 11 ^{13}C NMR spectral data are shown in Table 12. The duration and yield of the experiments were previously given in Table 5.

Table 11. The characterization of the products of the reaction of 81a and 82 with alkylsulfonyl halides and polyhalogenomethanes

Compound	bp (°C)[a]	NMR (δ)[b]	IR (cm^{-1})[c]	GLC-MS and Exact Mass:
83[d]	130°C/0.8 mm Hg	4.65 (d, 2H, J=6.5 cps) 5.84 (t, 1H), J=6.5 cps) 6.75-7.92 (m, 5H)	1975 1940 doublet	GLC-MS: m/e (rel. intensity) = 180 (1.5), 141 (25), 116 (12), 77 (100), 51 (36), 50 (11) Exact Mass: Meas. 180.02391 Calc'd $C_9H_8SO_2$: 180.02450 Error: 3.3 ppm
84[d]	60-105°C/ 1.3 mm Hg	0.55 (t, 3H) 1.6 (m, 2H), 2.9 (m, 2H) 4.95 (d, 2H, J=6.5 cps) 6.05 (t, 1H, J=6.5 cps)	1985, 1940 doublet	GLC-MS: m/e (rel. intensity) = 104 (100), 103 (11), 81 (25), 79 (20), 76 (71), 75 (13), 67 (99), 63 (12), 55 (30), 54 (30), 53 (31), 47 (14) Exact Mass: Meas.: 146.04015 Calc'd. $C_6H_{10}SO_2$: 146.04016 Error: <1.0 ppm
85	35-40°C/ 100 mm Hg	5.35 (d, 2H, J=6.5 cps) 6.1 (t, 1H, J=6.5 cps)	1960 1550	GLC-MS: m/e (rel. intensity) 162 (0.18), 161 (0.04), 160 (2.2), 159 (0.3), 158 (7), 157 (0.39), 156 (7.8), 125 (10), 123 (63), 121 (100), 87 (10), 86 (10), 85 (50), 61 (11), 60 (15), 51 (434), 50 (75), 49 (33), 47 (10)

86[d,e]	25°C/1.5 mm Hg	6.3 (dxt, 1H, J_d=8, J_t=1) 5.0 (dxt, 1H, J_d=8 cps, J_t=1 cps) 5.25 (dxd, 2H, J_d=8 cps, J_d=1 cps)	1980, 1950 doublet	GLC-MS: m/e (rel. intensity) = 126 (0.86), 124 (6), 122 (10), 89 (28), 87 (100), 61 (9), 52 (10), 51 (77), 50 (38), 49 (12)
87[d]	70-110°C/1.5 mm Hg	1.58 (t, 3H, J=4.0 cps) 4.55 (q, 2H, J=4.0 cps) 6.5-7.75 (m, 5)	1980, 1955, doublet	GLC-MS: m/e (rel. intensity) = 194 (1), 130 (18), 125 (18), 123 (12), 109 (10), 78 (20), 77 (50), 53 (100), 52 (17), 51 (61), 50 (21) Exact mass: Meas.: 194.04033 Calc'd. $C_{10}H_{10}SO_2$: 194.04016 Error: +0.9 ppm

[a] Distillation was done by Kugelrohr.

[b] C_6D_6 was the solvent used except for 85, CCl_4 was used.

[c] The doublet is characteristic of allenes (105).

[d] New compound.

[e] Double irradiation studies done on Brüker WM-300 (see Figure 15).

Table 11 (Continued)

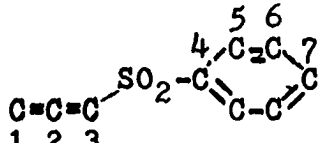
Compound	bp (°C)[a]	NMR (δ)[b]	IR (cm^{-1})[c]	GLC-MS and Exact Mass:
88[d]	130-140°C/ 1.5 mm Hg	0.53 (m, 3H) 1.13 (t, 3H, J=4.0) 1.35 (m, 2H) 4.55 (q, 2H, J=4.0)	1970, 1940, doublet	GLC-MS: m/e (rel. intensity) = 161 (0.07), 160 (0.87), 118 (4), 90 (1.6), 89 (2.5), 81 (3.1), 75 (6), 74 (15), 58 (3), 54 (12), 53 (100), 52 (12), 65 (19), 50 (11), 47 (3). Exact mass: Meas.: 160.05609 Calc'd. $C_7H_{12}SO_2$: 160.00581 Error: 41.8 ppm

Table 12. ^{13}C NMR data for the products of the reaction of 81a and 82 with alkylsulfonyl halides[a]

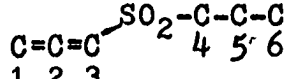
Compound	Carbon Number[b]							
	1	2	3	4	5	6	7	8
83	83.1574	209.1538	101.3915	142.2225	136.0013	132.7119	128.7075	
84	82.871	209.948	98.316	57.371	16.371	13.010		
87	82.013	207.795	108.613	135.111	140.863	132.640	128.564	128.278
88	81.441	207.652	106.756	13.010 or 13.296	54.841	16.157	13.296 or 13.011	

[a]Assignments were based on Munson's previous studies on other types of allenes and on the partial decoupling studies done on compound 84 (see Figure 15).

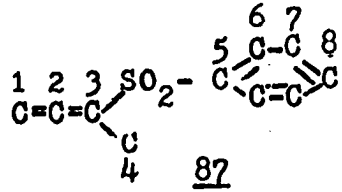
[b]The numbering of carbon atoms of each compound is as follows:



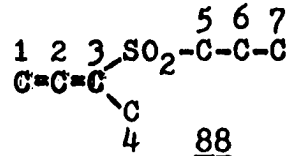
83



84



87



88

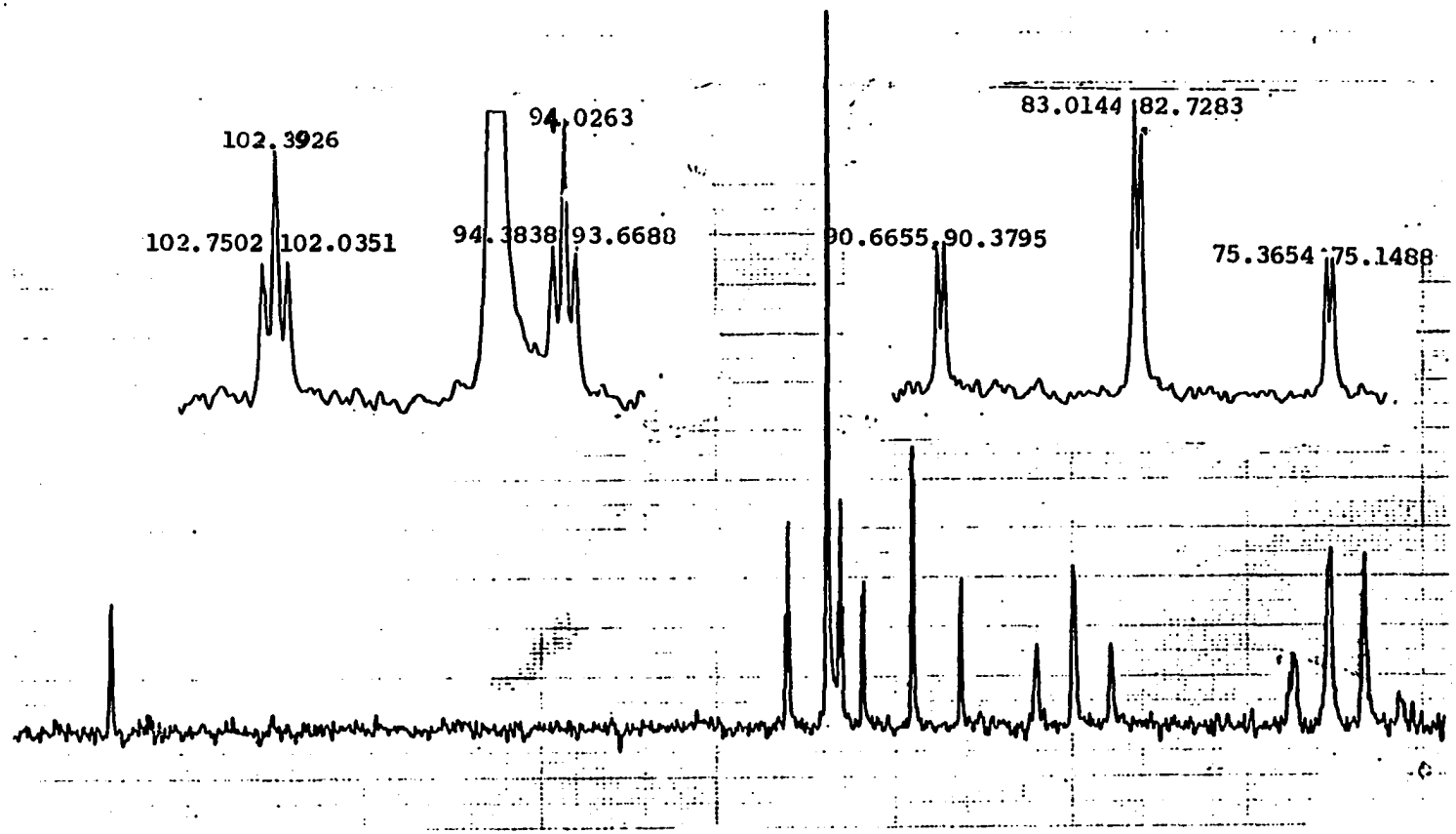


Figure 15. The ^{13}C NMR spectra from the partial decoupling experiment on compound 84

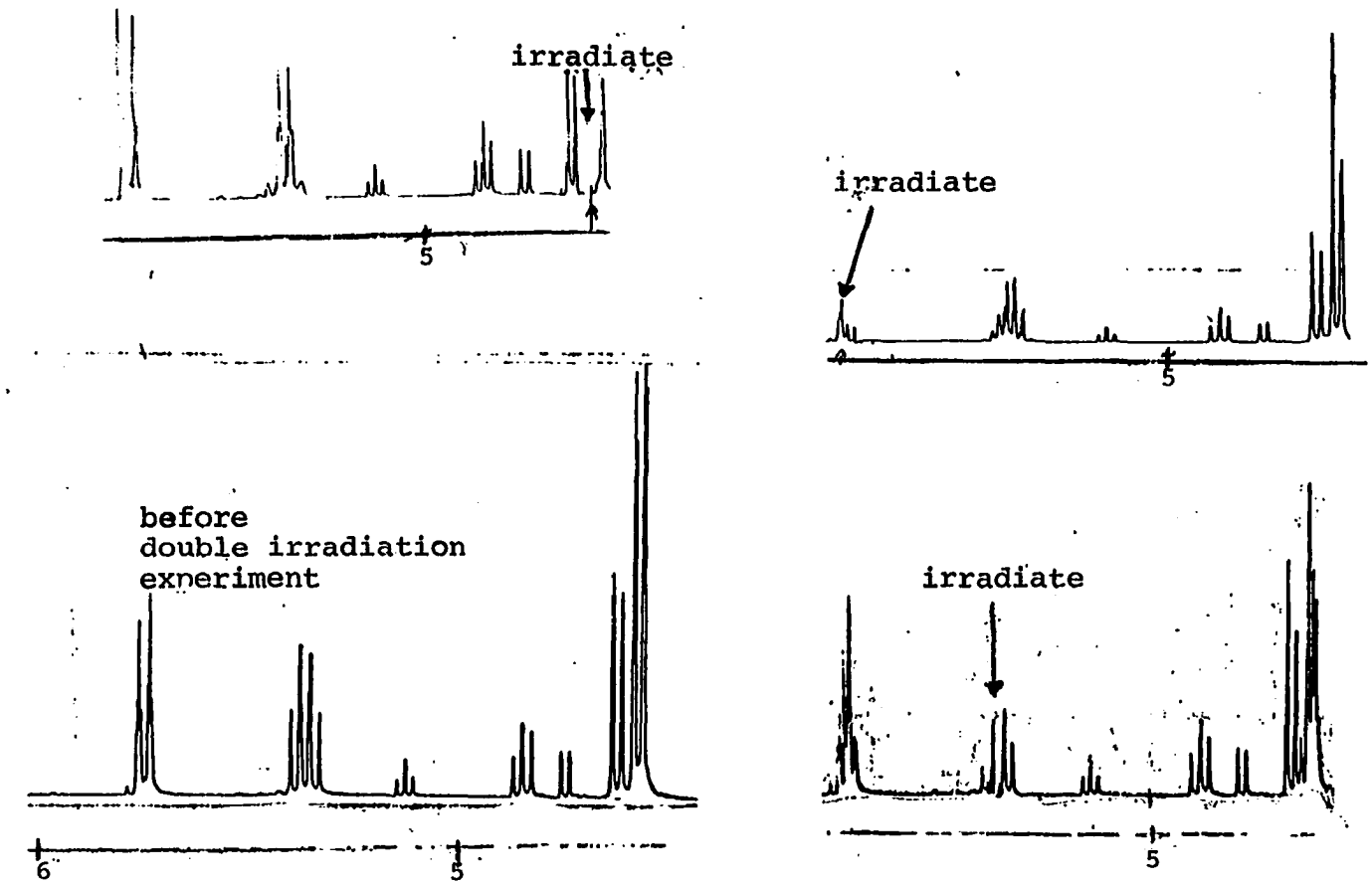


Figure 16. The ^{1}H NMR spectra from the double irradiation experiment done on compound 86

Preparation of tri-n-butylethoxystannane:

The procedure of Davies et al. (106) was followed. $(Bu_3Sn)_2O$ (10.0 g, 1.68×10^{-2} mol) and $(EtO)_2CO$ (5 ml) were mixed in a round-bottomed flask equipped with a reflux condenser and magnetic stirrer. The mixture was heated to reflux for 4 h under nitrogen and distilled at 110°C/1.3 mm Hg (literature 92°C/0.1 mm Hg) to give the product.

Preparation of 2-penten-3-yl acetate:

The procedure of Quattlebaum and Hoffsinger (107) was followed. Isopropenyl acetate (25 g, 0.25 mol), 3-pentanone (10.75 g, 0.125 mol) and concentrated H_2SO_4 (0.12 g, 1.2×10^{-3} mol) were mixed in a round bottomed flask connected to a Vigreaux column and condenser. The reaction mixture was refluxed for 2 hours until 9 ml of acetone distilled off. The crude reaction mixture was distilled to give the product (bp 58°C, 10 mm Hg).

Preparation of 1-cyclohexenyl acetate:

The procedure of Quattlebaum and Hoffsinger (107) was followed. Cyclohexanone (25 g, 0.25 mol) and 2-penten-3-yl acetate (50 g, 0.5 mol) and concentrated H_2SO_4 (0.14 ml, 0.0025 mol) were added to a round-bottomed flask attached to an insulated Vigreaux column and a condenser. After 2 hours of reflux, 10 ml of acetone distilled off.

The reaction mixture was extracted with ether and the organic layer was washed three times with H_2O, and 5% $NaHCO_3$ until the washings were neutral. The solution was dried over Na_2SO_4. The ether was distilled off. The residue was distilled at 77°C/23 mm Hg to give 8.2 g product.

^1H NMR: δ 1.45-2.30 (m, 11), 5.29 (m, 1).

Preparation of 1-cyclohexenyloxytri-n-butylstannane 90:

The method of Ponomarev (99) was used. 4.8 g of 1-cyclohexenyl acetate was added dropwise, under N_2 atmosphere, to 60 g of tri-n-butylethoxystannane at such a rate that the temperature of the reaction mixture did not rise above 25°C. The reaction mixture was stirred with a magnetic stirrer at room temperature overnight. The product was distilled using a short-path distillation set-up without any water running into the condenser. There was usually an initial forerun of hydrolyzed solid product which could clog the condenser. This was easily melted by a heat gun. The product came out as a clear, light yellow product. The product could be stored under nitrogen in a desiccator, but it is preferable that it be used as soon as possible.

^1H NMR (CCl_4): δ 0.5-2.0 (m), 4.5 (m, 1).

Preparation of 2-methylpropenyl acetate:

The procedure of Bedoukian was followed (108). A mixture of isobutyraldehyde (43.5 ml, 36 gms, 0.5 mole) acetic anhydride (76.5 gms, 0.75 mole) and cystalline potassium acetate (6.0 gms, 0.0625 mole) was refluxed on an oil bath for 8 hours under nitrogen atmosphere in a 3-necked flask with an efficient cold finger type of condenser to prevent escape of isobutyraldehyde. The reaction mixture was cooled and excess acid washed out several times with water and finally with 5% Na_2CO_3. The resulting oil was dried over sodium sulfate and distilled through a Vigreaux column.

Preparation of 2-methylpropenyloxytri-n-butylstannane:

5 ml of 1-butenyl acetate was added dropwise under a nitrogen atmosphere to 10 g of Bu_3SnOEt at such a rate that the temperature of the reaction mixture did not rise above 25°C. The reaction mixture was stirred overnight with a magnetic stirrer at room temperature. A short-path distillation set-up with no water running into the condenser was used to distill the product which distilled off at 115°C/8 mm Hg as a clear liquid which immediately solidified on standing. This compound was used immediately.

^1H NMR: δ 0.5-2.0 (m), 6.5 (m, 1H).

The photoreaction of alkenyloxystannane 90 and 91 with polyhalogenomethanes:

The general procedure given on p. 128 was followed using the polyhalogenomethanes as solvents instead of benzene. All the reaction mixtures were distilled either by the Kugelrohr technique or by short-path distillation set-up except for the reaction of CCl_4 with 90 which was purified by recrystallization from hexane.

The duration and yields of the reaction have been previously given in Table 7 while the characterization of the products are given in Table 13. Figure 17 gives the NMR spectrum of the crude reaction mixture between $CHBr_3$ and 90 while Figure 18 gives the NMR spectrum of the distilled fraction (30-50°C/0.2 mm Hg) from the reaction. Figure 19 gives the NMR of the distilled fraction (46-51°C/3.5 mm Hg) from the reaction of 91 with $CHBr_3$.

The effect of darkness on the reaction of alkenyloxystannanes with polyhalogenomethanes:

The general procedure on p. 130 was followed using CCl_4 and 90. After 2 days, no product was observed.

The effect of di-tert butylnitroxide on the reaction of alkenyloxystannanes with polyhalogenomethanes:

The general procedure on p. 130 was followed using CCl_4 and 90. The progress of the reaction was observed by taking the ratio of the integration of the vinyl proton of

Table 13. The characterization of the products from the reaction of 90 and 91 with polyhalogenomethanes

Compound	bp or mp (°C)	IR(cm^{-1})[a]	NMR (δ)[b]	GLC-MS, m/e (rel. intensity)
92[c]	92-93°C (mp)	1720	1.6-2.9 (m,8H) 3, 3 (m,1H)	218(1), 216(4), 214(4), 179(12), 178(10), 137(17), 135(26), 124(14), 122(22), 117(21), 115(66), 114(14), 113(14), 111(65), 109(100), 101(9), 87(16), 85(11), 84(59), 83(26), 79(53), 77(14), 75(13), 73(16), 67(13), 65(12), 55(65), 53(15), 51(31), 49(11)
93	30-50°C/ 0.2 mm Hg (bp)	2840 2720 1745 650	1.09 (s,6H 9.8 (s,1H)	194(0.05), 192(0.52), 190(2.03), 189(0.14), 188(2.22), 161(4), 159(4), 127(11), 126(26), 125(20), 124(40), 123(9), 119(6), 117(8), 111(8), 109(13), 91(29), 89(96), 87(16), 63(13), 53(100), 51(28), 50(9), 49(11)
94[c,d]	-	-	6.15 (d, 1H, J=3 cps)	272(0.27), 270(0.81), 268(0.33), 191(22.4), 189(24), 121(31), 119(32), 109(43), 81(100), 79(21), 67(13), 65(10), 55(13), 53(47), 51(14)
95	40-55°C/ 4 mm Hg (bp)	3085 1709 1589 1442 1288 1137	0.8-2.2 (m,8H) 7.3(t,1H, J=2 cps)	190(13), 188(12), 81(100), 79(34), 53(50), 51(14)

96[c,d]	46-51°C/ 3.5 mmHg	2985,2947 2885,2815 2707,1743 1465,1400 1373,1272 1157,991, 883	1.1(s,6H) 5.65(s,1H) 9.30(s,1H)	246(0.42), 244(0.95), 242(0.40), 217(13.0), 215(26), 213(13), 165(11), 163(12), 137(14), 136(96), 134(100), 133(20), 109(8), 107(9), 95(4), 93(5)
97[c,d,e]	46-51°C/ 3.5 mm Hg (bp)	2993,2978 2939,2889 1508,1458 1423,1384 1315,1245 1192,1138 1091,1034 914	1.1(s,6H) 3.35(d,1H,J= 8 cps) 5.25(d,1H,J= 8 cps)	247(.01), 246(.003), 245(0.03), 244(.01), 243(.01), 242(.002), 219(0.31), 188(1.69), 186(3.37), 184(1.82), 166(1.79), 165(42.67), 163(44.70), 137(0.41), 135(0.40), 137(0.41), 135(0.40), 134(0.02), 133(.06), 125(0.11), 124(0.23), 123(0.49), 122(0.25), 121(0.38), 109(0.26), 107(0.77), 105(0.52), 84(0.13), 83(0.50), 82(0.12), 59(13.53), 56(3.37), 55(100), 53(0.33)

[a] CCl_4 was the solvent.

[b] C_6D_6 was the solvent except for 94 where $CHRb_3$ was the solvent.

[c] New compound.

[d] Characterization done using the crude reaction mixture.

[e] The GC-MS data for this compound were obtained using low electron volt (20 EV). The weakness of the parent peak, and the presence of a (P+1) peak were rationalized as being due to a self-CI (chemical ionization). This proposal was verified by a CI experiment (isobutane), which gave the following results: 247(51.51), 245(100), 243(51.84), 241(0.2), 167(1.84), 166(3.42), 165(30.35), 163(27.63), 151(45), 149(47), 141(3.5), 139(4.8), 137(4.6), 135(4.7), 125(2.2), 125(2.17), 123(1.13), 122(1.01), 121(8.28), 113(9.9), 111(4.4), 109(1.3), 101(1.7), 100(1.13), 99(5.6), 97(7.5), 95(3.9), 93(1.6), 91(1.4), 87(2.3), 86(1.7), 85(16), 83(7.7), 81(9.6), 80(4.5), 75(2.68), 73(6), 72(6.9), 71(27), 69(14), 67(11).

90 to the integration of the added C_6H_6 protons.

Table 14 and Figure 20 summarize the results.

Table 14. Study of the inhibitory effect of di-tert-butyl nitroxide on the reaction of CCl_4 with 90

Time of irradiation	Ratio of integration of =H to ⬡ (22 µl)	
	0 mol % (tert-butyl)$_2$NO·	10 mol % (tert-butyl)$_2$NO·
0 min	0.72	0.60
20 min	0.25	0.55
45 min	0.11	0.48
65 min	0.022	0.32
85 min	0	0.29

The reaction of alkylsulfonyl halides with 90:

The general procedure on p. 129 was followed using $PhSO_2Cl$, n-$PrSO_2Cl$ or CCl_3SO_2Cl and 90. Even before the start of the irradiation, the NMR spectra of the reaction mixtures studied all showed the disappearance of the H\=< proton of the starting material.

The GC-MS of the reaction of 90 with $PhSO_2Cl$, n-$PrSO_2Cl$ and CCl_3SO_2Cl all featured the prominent peak on the GLC which corresponded to α-chlorocyclohexanone. The GLC-MS

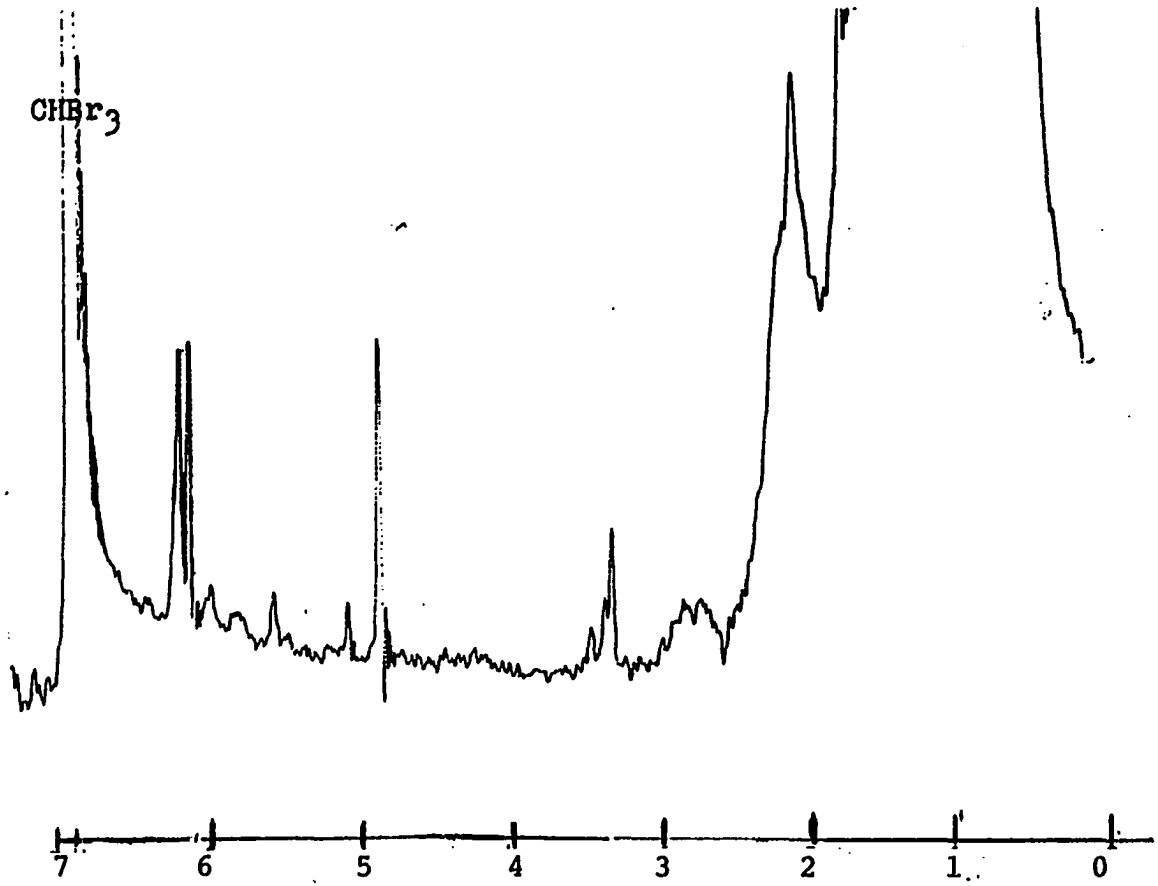


Figure 17. The NMR spectrum of the crude reaction mixture of the reaction of 1-cyclohexenxyloxytri-n-butylstannane with $CHBr_3$

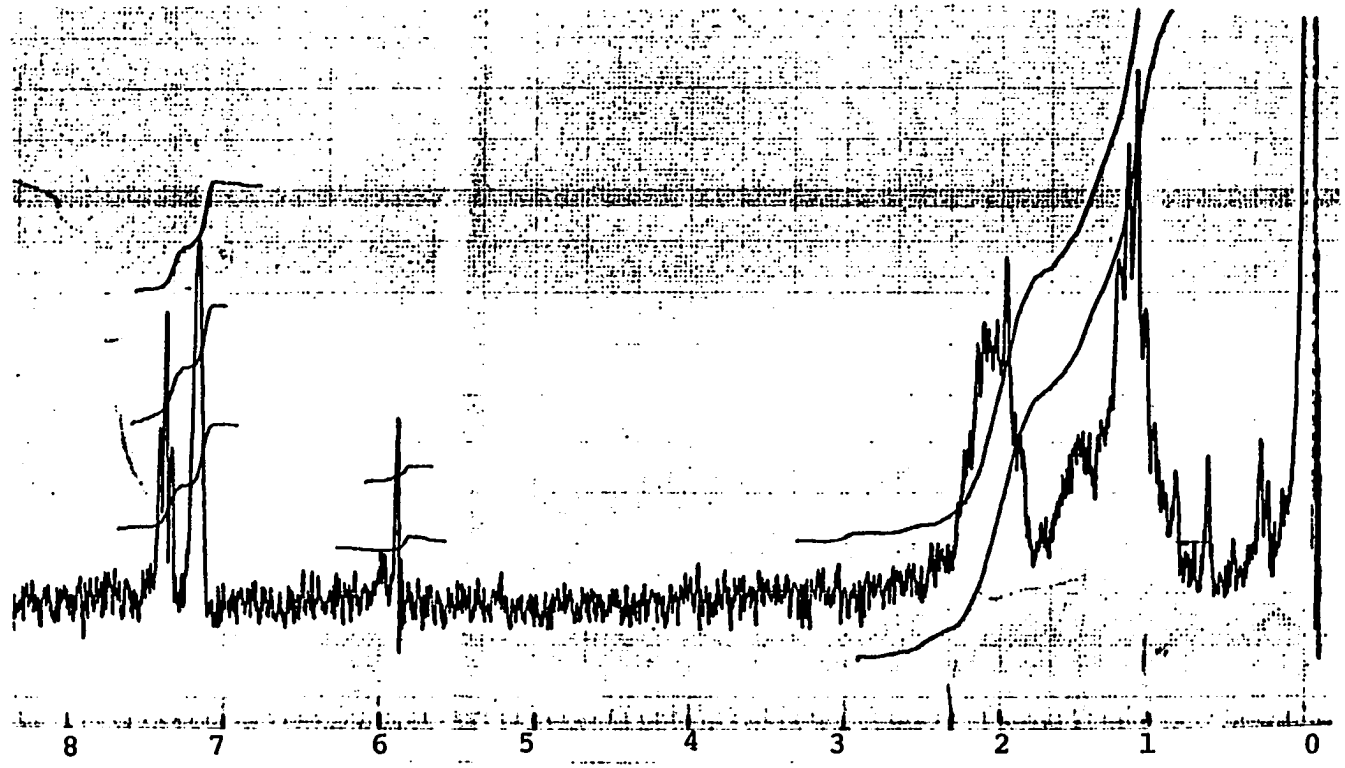


Figure 18. The NMR spectrum of the distillate (30-50°C/0.2 mm Hg) from the reaction of 1-cyclohexenxyloxytri-n-butylstannane with $CHBr_3$. The spectrum of compound 95

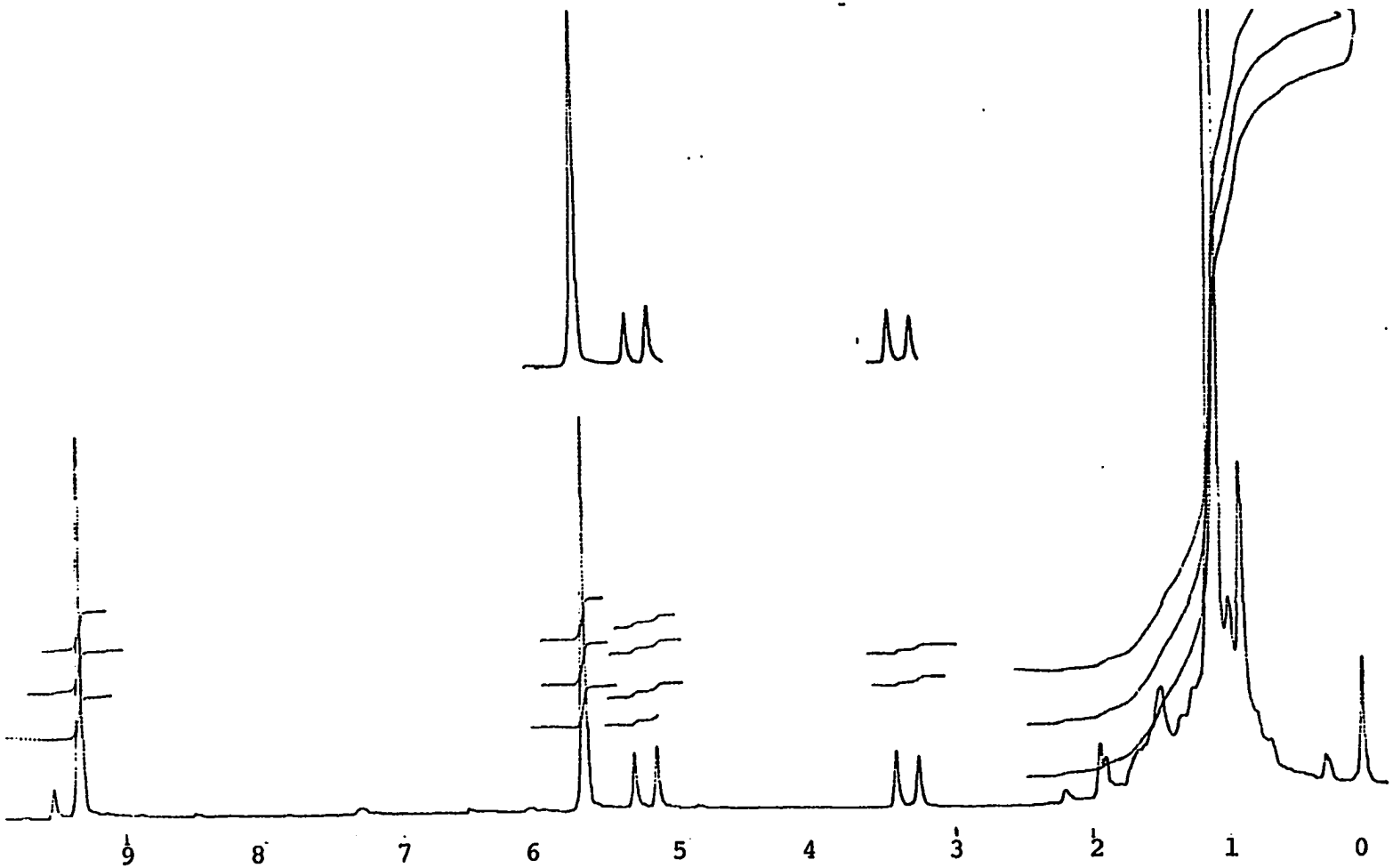


Figure 19. The NMR spectrum of distillate (46-51°C, 3.5 mm Hg) from the reaction of 2-methylpropenyloxytri-n-butylstannane with $CHBr_3$. The spectrum of compound 96 and 97

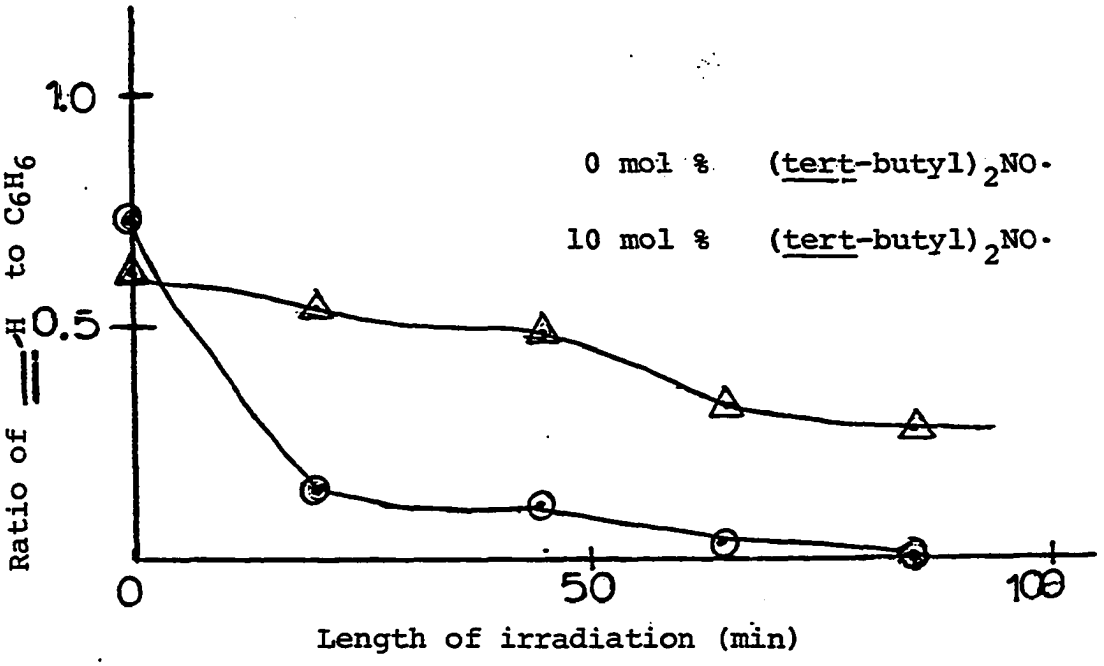


Figure 20. The inhibitory effect of di-tert-butyl-nitroxide on the reaction of 1-cyclohexenyloxytri-n-butyl-stannane with CCl_4

also gave an equal amount of a peak which corresponded to cyclohexanone.

GLC-MS of α-chlorocyclohexanone: m/e (rel. intensity) = 134(6), 132(20), 97(25), 88(22), 69(15), 68(20), 55(100)

GLC-MS of cyclohexanone: m/e (rel. intensity) = 98(30), 70(19), 69(28), 56(11), 55(100).

CONCLUSIONS

The phenomenon of long-range coupling, which has been previously observed between hydrogen atoms and the spin probe in carbocyclic semidiones, is further investigated in Part I of this dissertation. The possibility of a homoconjugative interaction occurring between the spin probe and the hetero atom lone pair of aza and phospha bridge substituted bicyclic semidiones was studied. The lack of nitrogen or phosphorus hyperfine splitting constants (hfsc) in the ESR spectra of several aza and phospha bicyclic semidiones studied suggests that long-range interaction is not important in these systems, despite their correct geometries and highly rigid structures.

The effect of substituents on the magnitude of the $a^{H}_{7\text{-}\underline{anti}}$ in 7-<u>syn</u> substituted bicyclic [2.2.1]heptane-2,3-semidiones was also investigated. The effect was dramatically illustrated when both the <u>syn</u>-chloro and <u>syn</u>-fluoro substituted bicyclo[2.2.1]heptane-2,3-semidiones showed an absence of any hfs by $a^{H}_{7\text{-}\underline{anti}}$.

Part II of this dissertation proved that unsaturated organostannanes are capable of reacting <u>via</u> a free radical chain process. Allylstannanes were found to photochemically react via an S_H2' (bimolecular homolytic substitution with double bond transposition) or addition-elimination process with hetero atom-centered radicals from RSO_2Cl, RSSR and

PhSeSePh to give allyl sulfones, sulfides and selenides, respectively, in good yields. The AIBN initiated or photochemical reaction of propargylstannanes with RSO_2Cl and polyhalogenomethanes also proceeded in similar free radical fashion to give regioselectively substituted propadienyl products.

It was also found that alkenyloxystannanes could serve as aldehyde or ketone equivalents when reacted in an S_H2' mode with polyhalogenomethanes to produce α-polyhalogenomethylated ketones or aldehydes.

BIBLIOGRAPHY

1. Russell, G. A.; Strom, E. T.; Talaty, E. R.; Chang, K.-Y.; Stephens, R. D.; Young, M. C. Rec. Chem. Prog. 1966, 27, 3.

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

3. Russell, G. A. In "Radical Ions"; O. Kaiser, E.; Mokevan, L., Ed. Interscience Publishers, Inc.: New York, 1968; Chapter 3.

4. Russell, G. A. Tech. Chem. (N.Y.) 1972, 4, 441.

5. Russell, G. A. In "Determination of Organic Structures by Physical Methods", Nachod, F. C.; Zuckermann, J. J., Ed.; Academic Press: New York, 1971; Vol. 3, p. 293.

6. King, F. W. Chem. Rev. 1976, 76, 157.

7. Russell, G. A.; Holland, G. W.; Chang, K.-Y.; Keske, R. G.; Mattox, J.; Chung, C. S. C.; Stanley, K.; Schmitt, K.: Blankespoor, R.; Kosugi, Y. J. Am. Chem. Soc. 1974, 96, 7237.

8. Russell, G. A.; Keske, R. G.; Holland, G.; Mattox, J.; Givens, R. S.; Stanley, K. J. Am. Chem. Soc. 1975, 97, 1892.

9. Russell, G. A.; Chang, K.-Y.; Jefford, C. W. J. Am. Chem. Soc. 1965, 87, 4383.

10. Russell, G. A.; Chang, K.-Y. J. Am. Chem. Soc. 1965, 87, 4381.

11. Johnson, P. Y.; Jacobs, I.; Kerkman, D. J. J. Org. Chem. 1975, 40, 2710.

12. Cope, A. C.; Dryden, H. L. Jr.; Howell, C. F. Org. Syn. Coll. Vol. IV 1962, 816.

13. Kashman, Y.; Awenbouch, O. Tetrahedron 1970, 26, 4213.

14. Kashman, Y.; Benary, E. Tetrahedron 1972, 28, 4091.

15. Sasaki, T.; Eguchi, S.; Hioki, T. J. Org. Chem. 1978, 43, 3808.

16. Paquette, L. A.; Heimaster, J. W. J. Am. Chem. Soc., 1966, 88, 763.

17. Ayer, W. A.; Furuichi, K. Can. J. Chem. 1976, 54, 1494.

18. Stevens, R. V.; Lee, A. W. M. J. Am. Chem. Soc. 1979, 101, 7032.

19. Russell, G. A.; Keske, R. G. J. Am. Chem. Soc. 1970, 92, 4458.

20. Russell, G. A.; Ku, T.; Lokensgard, J. J. Am. Chem. Soc. 1970, 92, 3833.

21. Kosman, D.; Stock, L. M. J. Am. Chem. Soc. 1969, 91, 2011.

22. Terabe, S.; Konaka, R. J. Am. Chem. Soc. 1973, 95, 4976.

23. Nelsen, S. F.; Seppanen, E. D. J. Am. Chem. Soc., 1967, 89, 5740.

24. Wiseman, J. R.; Krabbenhoft, H. O. J. Org. Chem. 1976, 41, 389.

25. Wiseman, J. R.; Krabbenhoft, H. O. J. Org. Chem. 1975, 40, 3222.

26. Furtoss, R.; Tadayoni, R.; Esposito, G.; Lacrampe, J.; Heumann, A.; Waegell, B. Can. J. Chem. 1976, 54, 3569.

27. Chandler, G. S.; Thirunamachandran, J. Chem. Phys. 1968, 49, 3640.

28. Cotton, F. A.; Wilkinson, F. R. S. "Advanced Inorganic Chemistry", 3rd ed. Interscience Publishers: New York, 1972; pages 138-140.

29. Russell, G. A.; Suleman, N. K. Unpublished results.

30. Russell, G. A.; Whittle, P. R. J. Am. Chem. Soc. 1967, 89, 6781.

31. Whiffen, D. H. Mol. Phys. 1963, 6, 224.

32. Tanner, D. D.; van Bostelen, P. J. Am. Chem. Soc. 1972, 94, 3187.

33. Roberts, J. D.; Johnson, F. O.; Carbani, R. A. J. Am. Chem. Soc. 1954, 76, 5698.

34. Franzus, B.; Baird, W. C. Jr.; Snyder, E. I.; Surridge, J. H. J. Org. Chem. 1967, 32, 2845.

35. Lustgarten, R. K.; Richey, H. G. J. Am. Chem. Soc. 1974, 96, 6393.

36. Baird, W. C. Jr.; Surridge, J. H. J. Org. Chem. 1972, 37, 304.

37. Schaffer, A. M.; Gouterman, M.; Davidson, E. R. Theoret. Chim. Acta (Berl.) 1973, 30, 9. This program was obtained and modified slightly by Dr. Stephen Elbert.

38. Moore, C. E. "Atomic Energy Levels," Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (US) 1971, No. 35.

39. Cusachs, L. C.; Corrington, J. H. In "Sigma Molecular Orbital Theory"; Sinanoglu, O.; Wiberg, K. B., Eds., Yale University Press: New Haven, Conn., 1970, Chapter VI-4.

40. Allred, A. L. J. Inorg. Nuclear Chem. 1961, 17, 215.

41. Holland, G. Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1969.

42. Bloomfield, J. J. Tetrahedron Lett. 1968, 5, 587.

43. Braun, V., J. Seeman, Chem. Ber. 1923, 56, 1840.

44. Josey, A. D.; Tuite, R. J.; Snyder, H. R. J. Am. Chem. Soc. 1960, 82, 1597.

45. Adams, R.; Chiles, H. M.; Rassweiler, C. F. Org. Syn. Coll. Vol. I, 1941, 9.

46. Mandell, L.; Blanchard, W. A. J. Am. Chem. Soc. 1957, 79, 6198.

47. Duckworth, A. C. J. Org. Chem. 1962, 27, 3146.

48. Garbisch, E. W. J. Org. Chem. 1965, 30, 2109.

49. DeGraw, J. I.; Goodman, L.; Baker, B. R. J. Org. Chem. 1961, 26, 1156.

50. Fiesselmann, H. Chem. Ber. 1942, 75, 881.

51. Coleman, G. H.; Johnstone, H. F. Org. Syn. Coll. Vol. I, 1941, 158.

52. Brown, H. C.; Gary, G. P. J. Am. Chem. Soc. 1961, 83, 2951.

53. Petersen, D. J.; Robbins, M. D.; Hansen, J. R. J. Organomet. Chem. 1974, 78, 237.

54. Barcza, S. J. Org. Chem. 1963, 28, 1914.

55. Westmijze, H. Kleijn, H.; Bos, H. J. T.; Vermeer, P. J. Organomet Chem. 1980, 199, 293.

56. Cochran, J. C.; Kuivila, H. G. Organometallics 1982, 1, 97.

57. Simo, M. S.; Jean, A.; Lequan, M. J. Organomet. Chem. 1973, 35, C23.

58. Ashcroft, M. K.; Gupta, B. D.; Johnson, M. D. J. Chem. Soc., Perkin Trans. 1, 1980, 2021.

59. Bury, A.; Cooksey, C. J.; Funabiki, T.; Gupta, B. D.; Johnson, M. D. J. Chem. Soc., Perkin Trans. 2, 1979, 1050.

60. Crease, A. E.; Gupta, B. D.; Johnson, M. D.; Moorhouse, S. J. Chem. Soc., Dalton Trans. 1978, 1821.

61. Kosugi, M.; Kurino, K.; Takayama, K.; Migita, T. J. Organomet. Chem. 1973, 56, C11.

62. Grignon, J.; Servens, C.; Percyre, M. J. Organomet. Chem. 1975, 96, 225.

63. Naruta, Y. J. Am. Chem. Soc. 1980, 102, 3374.

64. Daude, G.; Pereyre, M. J. Organomet. Chem. 1980, 190, 43.

65. Peruzzo, V.; Taghavini, G. J. Organomet. Chem. 1978, 162, 37.

66. Gambaro, A.; Peruzzo, V.; Plazzogna, G.; Tagliavini, G. J. Organomet. Chem., 1980, 197, 45.

67. LeQuan, M.; Guilerm, G. J. Organomet. Chem., 1973, 54, 153.

68. Shenvi, S.; Stille, J. K. Tetrahedron Lett., 1982, 627.

69. Yamamoto, Y.; Yatagai, H.; Maruyama, K. J. Chem. Soc., Chem. Commun. 1981, 163.

70. Ayrey, G.; Brasington, R. D.; Poller, R. C. J. Organomet. Chem., 1972, 35, 105.

71. Deniau, J.; Duong, K. N. V.; Gaudemar, A.; Bougeard, P.; Johnson, M. D. J. Chem. Soc., Perkin Trans. 2, 1981, 393.

72. Crease, A. E.; Gupta, B. D.; Johnson, M. D.; Bialkowska, E.; Duong, K. N. V.; Gaudemar, A. J. Chem. Soc., Perkin Trans. 1, 1979, 2611.

73. Keck, G. E.; Yates, J. B. J. Am. Chem. Soc., 1982, 104, 5829.

74. Odic, Y.; Pereyre, M. J. Organomet. Chem. 1973, 55, 273.

75. Pommier, J. C.; Pereyre, M. In "Organotin Compounds: New Chemistry and Application", Adv. in Chem. Series, Zuckerman, J. J., Ed.; Am. Chem. Soc., Washington D.C., 1976, 157, p. 82.

76. Kuwajima, I.; Urabe, H. J. Am. Chem. Soc., 1982, 104, 6831.

77. Fong, C. W.; Kitching, W. J. Organomet. Chem., 1970, 22, 107.

78. Ueno, Y.; Ohta, M.; Okawara, M. J. Organomet. Chem., 1980, 197, C1.

79. Russell, G. A.; Hershberger, J. J. Am. Chem. Soc., 1980, 102, 7603.

80. Abel, E. A. J. Organomet. Chem., 1975, 84, 199.

81. Seyferth, D.; Jula, T. F.; Dertouzos, H.; Pereyre, M. J. Organomet. Chem. 1968, 11, 63.

82. Matarasso-Tchiroukhine, E.; Cadiot, P. J. Organomet. Chem., 1976, 121, 169.

83. Matarasso-Tchiroukhine, E.; Cadiot, P. J. Organomet. Chem., 1976, 121, 155.

84. Hershberger, J. Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1981.

85. Brownbridge, P.; Warren, S. J. Chem. Soc., Perkin Trans. 1, 1976, 2125.

86. Kwart, H.; Johnson, N. A. J. Org. Chem., 1977, 42, 2855.

87. Cope, A. C.; Morrison, D. E.; Field, L. J. Am. Chem. Soc., 1950, 72, 59.

88, Kice, J. L. In "Free Radicals", Vol. II; Kochi, J. K., ed. Wiley Interscience: New York, 1973; pages 718-724.

89. Tanner, D. D.; Blackburn, E. V.; Diaz, G. E. J. Am. Chem. Soc., 1981, 103, 1557.

90. Sakurai, H.; Hosomi, A.; Kumada, M. J. Org. Chem., 1969, 34, 1764.

91. Russell, G. A.; Tashtoush, H. Unpublished results.

92. LeQuan, M.; Cadiot, P. Bull. Soc. Chim. Fr., 1965, 45.

93. Gaudemar, M. Ann. Chim. (Paris) [13], 1956, 1, 161.

94. Ueno, Y.; Chino, K.; Okawara, M. Tetrahedron Lett., 1982, 23, 2575.

95. Berge, J. M.; Roberts, S. M. Synthesis, 1979, 471.

96. Seyferth, D.; Lambert, P. L. J. Organomet. Chem., 1975, 91, 31.

97. Truce, W. E.; Heuring, D. L.; Wolf, G. C. J. Org. Chem., 1974, 39, 238.

98. Brady, W. T.; Patel, A. D. J. Org. Chem., 1972, 37, 3536.

99. Ponomarev, S. V.; Baukov, Y. I.; Dudukina, D. V.; Petrosyan, I. V.; Petroskaya, L. I. Zh. Obshch. Khim., 1967, 37, 2204.

100. Pereyre, M.; Bellegarde, B.; Mebdelsohn, J.; Valade, J. J. Organomet. Chem., 1968, 11, 97.

101. Hurd, C. D.; Greengard, H. J. Am. Chem. Soc., 1930, 52, 3356.

102. Kharasch, N.; Cameron, J. L. J. Am. Chem. Soc., 1951, 73, 3864.

103. Kataev, E. G.; Chmutova, G. A.; Yarkova, E. G. Zh. Org. Khim., 1967, 3, 2188.

104. Sharifkanov, A. Sh.; Skhmedova, Sh. S. Khim. i. Khim. Tekhnol. Alma-Ata, Sb I, 1963, 3-5; Chem. Abstr., 1964, 61, 13275a.

105. Munson, J. W. In "The Chemistry of Ketenes, Allenes and Related Compounds, Part I, Patai, S., Ed.; John Wiley & Sons: New York, 1980, Chapter 5.

106. Davies, A. G., Palan, P. P.; Vasishtha, S. C. Chem. and Ind., 1967, 229.

107. Quattlebaum, W. M.; Hoffsinger, C. A. U.S. Patent 2 466 737, 1949; Chem. Abstr., 1949, 43, 7037.

108. Bedoukian, P. J. Am. Chem. Soc., 1944, 66, 1326.

ACKNOWLEDGMENTS

I would like to thank Dr. Glen A. Russell for his help and guidance. I am grateful also to all the past and present members of my research group especially James W. Hershberger, Mary Zaleta, Francisco Ros and Hassan Tashtoush.

I am also grateful to Dr. William Beers for doing the computer work on the semidiones shown in Table 1. I would like to thank Robert Herold for helping with the calculations of the parameters in Table 2 and the gated ^{13}C decoupling study on compound 84.

My thanks also go to my parents, sisters and brothers for their love, prayers and encouragement. I would like to thank my mother-in-law for generously helping in taking care of Wendy, my "graduate-school" baby.

Thank you, Wendy, for being both utterly distracting and highly inspiring.

Lastly, Bob, thanks a lot for listening, loving, helping and encouraging me.