1967

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Iowa State University of Science and Technology, Ph.D., 1967
Chemistry, organic

GENERATION OF SEMIDIONE AND SEMITRIONE RADICAL ANIONS IN DIMETHYL SULFOXIDE

by

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

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1967

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I. INTRODUCTION

Recently a new solvent, dimethyl sulfoxide (DMSO), has become generally available. It is relatively aprotic, pKa 33, has a high dipole moment and dielectric constant, and is known to greatly accelerate anion reactions relative to protic solvents (1-5). DMSO is very often used as a solvent for base catalysed reactions. It has a very high solubility for alkoxide bases. In DMSO the anions are left essentially bare while the cations are highly solvated (6). As a consequence of this type of solvation, the strength of bases in DMSO is increased relative to that in alcohol (7-9). Another consequence is that the carbanions formed in DMSO are much freer and have a greater lifetime than in alcoholic solvents (10,11). Because of these facts, many hydrocarbons are oxidized in basic solutions of DMSO which are not oxidized in alcohol solutions (7-9). Unfortunately DMSO itself will undergo base catalysed oxidation. However it was found that if a mixed solvent of DMSO and alcohol is used, this oxidation is almost completely eliminated. A mixture of 80% DMSO and 20% tertiary butyl alcohol (t-BuOH) has been shown to be a very effective solvent for the base catalysed oxidation of hydrocarbons (7, 9).

Early in 1962, Corey and Chaykovsky reported the preparation of the anion of DMSO (I). This anion

$$CH_3SOCH_2^-$$

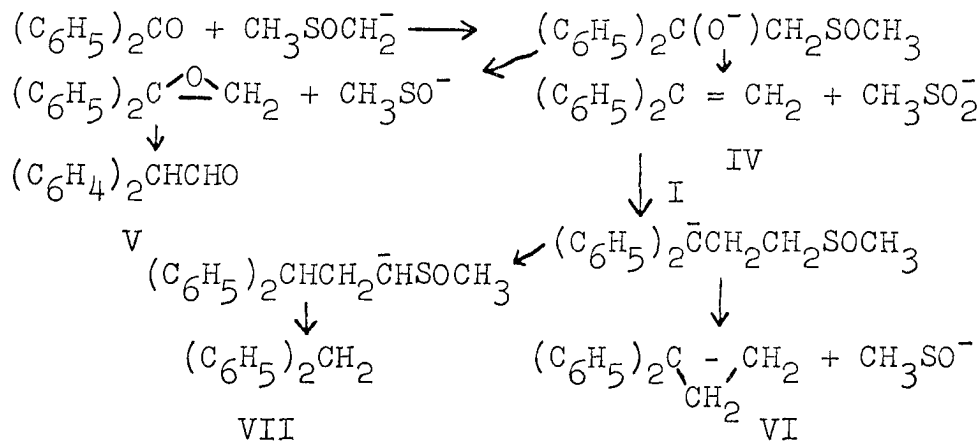
I

was formed by adding sodium hydride to a solution of DMSO under a nitrogen atmosphere. When this was heated to between 60°C and 70°C a vigorous evolution of hydrogen was observed (12). On cooling the resultant solution to room temperature and adding either benzophenone or benzaldehyde, adducts II or III are obtained. If chlorobenzene is added,

$$(C_6H_5)_2C(OH)CH_2SOCH_3 \qquad C_6H_5CH(OH)CH_2SOCH_3$$

II III

the product is benzyl methyl sulfoxide. While I is clearly nucleophilic, it is also a very strong base and will remove a proton from triphenylmethane (12). If instead of cooling solutions of I in DMSO to room temperature, benzophenone is added to the hot solutions II is not isolated (13). A variety of products is obtained and the following scheme is offered in partial explanation.

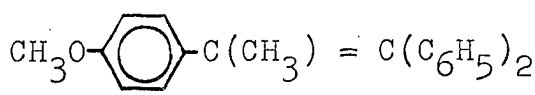


Compounds IV-VII were isolated along with some $C_6H_5CH{=}CHSCH_3$. Walling and Bollyky followed the formation of IV in this reaction (14). With sodium hydride as the base, 32.5% of IV was detected after a reaction time of two minutes at 70°C to 80°C. If potassium tertiary butoxide (t-BuOK) is used as the base, the yield of IV was 6.8% after ten minutes. They therefore proposed the following equilibrium:

$$\text{t-BuO}^- + \text{DMSO} \rightleftarrows CH_3SOCH_2^- + \text{t-BuOH}$$

Russell and coworkers took advantage of this equilibrium by reacting solutions of DMSO containing either sodium hydride or alkali metal alkoxides with a variety of esters (15, 16). In this manner they formed a class of compounds known as β-keto sulfoxides ($ArCOCH_2SOCH_3$). Walling and Bollyky showed that I adds readily to a variety of aryl conjugated olefins (17).

There is evidence to show that I is formed in solutions of 80% DMSO and 20% t-BuOH. Russell and coworkers oxidized diarylmethanes in this solvent using t-BuOK as the base. Instead of isolating ketones from this reaction, they obtained their DMSO adducts (7). In another interesting reaction of diarylmethanes, they observed that solutions of diphenylmethane and p-anisaldehyde when treated with t-BuOK in DMSO yielded VIII (7). They showed that VIII was formed by



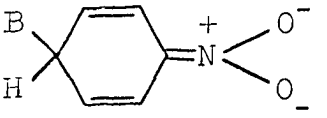
VIII

further reaction of the DMSO adduct of p-anisaldehyde. In fact, if a more acidic methylene compound than diphenylmethane is used, only normal condensation products are obtained.

Russell had shown earlier that 80% DMSO, 20% t-BuOH is an excellent solvent for electron transfer reactions (9). In a later study of these reactions it was pointed out that in solutions of t-BuOK in DMSO containing nitrobenzene, the nitrobenzene radical anion was observed. If 20% t-BuOH is added to the solvent, this reaction is minimized (18). At that time two different mechanisms were offered to explain this result. They are illustrated below where B^- represents an anion present in the solution. More recently it was

I $\quad$ t-$BuO^- + DMSO \rightleftharpoons I$

$$I + C_6H_5NO_2 \rightarrow C_6H_5NO_2^{\cdot-} + CH_3SOCH_2\cdot$$

II $\quad$ $B^- + C_6H_5NO_2 \rightarrow$ 

IX

$$IX + C_6H_5NO_2 \rightarrow C_6H_5NO_2^{\cdot-}$$

shown that if the reaction of nitrobenzene with t-BuOK in DMSO was carried out in an oxygen atmosphere, a mixture of nitrotoluic acids was obtained (19). It is known that these acids are produced when the corresponding nitrotoluene is oxidized under these conditions (20). These results offer another possible explanation for the formation of

nitrobenzene radical anion with t-BuOK in DMSO. This is outlined below.

$$C_6H_5NO_2 + I \rightarrow O\text{-} \text{ (or } P\text{-)} \; CH_3C_6H_4NO_2 + CH_3SO^-$$

$$CH_3C_6H_4NO_2 \rightleftarrows O_2NC_6H_4CH_2^-$$

X

$$X + C_6H_5NO_2 \rightarrow C_6H_5NO_2^{\cdot -}$$

However when the reaction was run in a nitrogen atmosphere no nitrotoluenes were detected. It was felt that this was due to complicating side reactions involving electron transfer. If instead of nitrobenzene, anthracene was treated with I in DMSO either 9-methyl- or 9,10-dimethylanthracene was isolated depending upon the ratio of I to hydrocarbon (19, 21). The reaction was followed by electron spin resonance (e.s.r.) spectroscopy. The initial radical anion was shown to be that of anthracene. At the end of the reaction, the radical anion of 9,10-dimethylanthracene was observed. Clearly I is a capable methylating reagent for some aromatic hydrocarbons (19,21). When anthracene was methylated in DMSO with t-BuOK as the base, the yield of 9-methylanthracene was cut almost in half (22).

Recently a class of compounds known as semidiones (XI) have been generated in basic solutions of DMSO. A few

$$RC(O^-) = C(O^{\cdot})R'$$

XI

hundred such species have been generated in these laboratories and the results have been reviewed (23). It is apparent from the earlier discussion that a solution of t-BuOK in DMSO also contains some I. When such a mixture is used to generate XI from a ketone or substituted ketone, there are many possible intermediates which can be formed. Thus the formation of XI may not even be the major reaction path in solution. Because of the variety of possible products, and the need for low concentrations (less than 0.1 molar) in order to obtain highly resolved e.s.r. spectrums, few attempts have been made to isolate the products from reactions used to produce XI.

Semidione radical anions where both R and R' are aryl groups have been known for some time (24). It is only recently that examples wherein both R and R' are aliphatic or alicyclic (yielding the cis semidione) have been documented (25-28). In fact, if R is an alkyl group, R' can even be hydrogen (29). Moreover, the parent semidione, glyoxal semidione (XI, R = R' = H), has been reported (30). Several methods have been developed for the generation of XI in solution. One of the earliest methods reported involved the mixing of an α-hydroxyketone with the corresponding α-diketone in basic solution. However the authors were unaware of the exact nature of the species produced (31,32). Actually in many cases the diketone is superfluous and semidiones can be produced by the action of base on the α-hydroxyketone (25).

They can be produced by oxidation of the appropriate monoketone(26, 33, 34), by the action of base on an α-bromoketone (29), and by the reduction of an α-diketone (18, 26). However semidiones wherein R or R' is a functional group, or contains a functional group, are not recognized with the exception of the radical anion of pyruvic acid (XII) (23, 29). For this reason it was decided to synthesize

$$CH_3C(O\cdot) = C(O^-)OH \rightleftarrows CH_3C(O^\cdot) = C(O^-)O^-$$

XII

radical anions derived from α-ketoesters. A simple valence bond picture leads to the conclusion that these compounds should be harder to reduce than the corresponding diketones due to the stabilization provided by structure XIII. Another difficulty

$$RCOC(O^-) = \overset{+}{O}R'$$

XIII

in generating such semidiones is indicated by the fact that while the one electron reduction product of benzaldehyde is known to be stable at room temperature (35) the corresponding radical anion of the benzoate esters is a transient intermediate in the acyloin condensation of these esters to benzil. Attempts to produce this ketyl by reduction of ethyl benzoate with potassium metal in hexamethylphosphoramide (HMPA) have led only to diphenyl semidione. However we have found that

the addition of another carbonyl group stabilizes the radical anion to the extent that it is detectable by standard e.s.r. techniques at room temperature.

II. RESULTS AND DISCUSSION

A. Oxidative Approaches to Semidiones Containing the Alkoxy Group ($RC(O^{\cdot}) = C(O^{-})OR'$)

In several cases it is possible to obtain the semidione by direct oxidation of the monoketone in solutions of t-BuOK in DMSO. When this same technique is applied to propionic acid, phenylacetic acid, ethyl propionate, and ethyl phenylacetate no radical anions are observed. In fact even when I is used in place of t-BuOK no radical anions are produced. These results are not too surprising in light of the fact that ethyl acetate is known not to be oxidized by t-BuOK in 80% DMSO, 20% t-BuOH. But under these conditions, ethyl phenylacetate does absorb oxygen (36). However the product of the oxidation with t-BuOK in t-BuOH is benzoic acid (37).

Treatment of ethyl propionate or ethyl phenylacetate with iodine in t-BuOH followed by mixing with either t-BuOK or sodium methoxide (NaOMe) in DMSO does not produce a radical anion. When ethyl α-bromopropionate (XIV) is mixed

$CH_3CHBrCO_2CH_2CH_3$ XIV

$C_6H_5CHBrCO_2CH_2CH_3$ XV

with t-BuOK in DMSO no radical anion is produced. If ethyl α-bromophenylacetate (XV) is similarly treated, a very weak signal which is poorly esolved is obtained. No possible

interpretation could be based on this spectrum. If XIV is heated in DMSO at 70°C for one hour and then mixed with t-BuOK in DMSO no signal is observed. When either α-bromophenylacetic acid or α-bromopropionic acid is treated with t-BuOK in DMSO no radical anion is produced. These results with the bromo-acids and bromoesters are somewhat surprising. It is known that DMSO oxidizes α-bromoketones and α-bromoaldehydes to the corresponding dicarbonyl compounds albeit somewhat slowly at room temperature (38). However a similar oxidation is reported to be catalysed by base (39). Also $BrCH_2CO_2CH_2CH_3$ and XIV are reported to be oxidized to $CHOCH_2CO_2CH_2CH_3$ and ethyl pyruvate respectively at 70°C by DMSO (40). While the former reaction has an induction period of one hour, the latter reacts smoothly at this temperature. In the light of the preceding results, especially the reported time of the reaction for α-bromoketones and α-bromoaldehydes to be oxidized to dicarbonyl compounds, it is possible that the mechanism of conversion of these compounds to semidiones involves hydrolysis of the bromide followed by oxidation of the α-hydroxycarbonyl compound. If this were the mechanism, then the failure of the bromoesters to yield semidiones is easily explained. The hydrolysis of esters is greatly accelerated by the use of DMSO as the reaction solvent (41-43). In either aqueous ethanol or water, it is known that the reaction of XVI with sodium hydroxide yields

$XCH_2CO_2CH_2CH_3$ XCH_2CO_2H X = Br,Cl

XVI XVII

XVII rather than $HOCH_2CO_2CH_2CH_3$ (44). In fact this hydrolysis can even be followed polarographically (45). It has also been shown that in the hydrolysis of α-bromoacids, reaction occurs chiefly via the anions whereas neutral molecules react only slightly, if at all (46, 47).

When a solution of ethyl mandelate (XVIII) is

$C_6H_5CH(OH)CO_2CH_2CH_3$

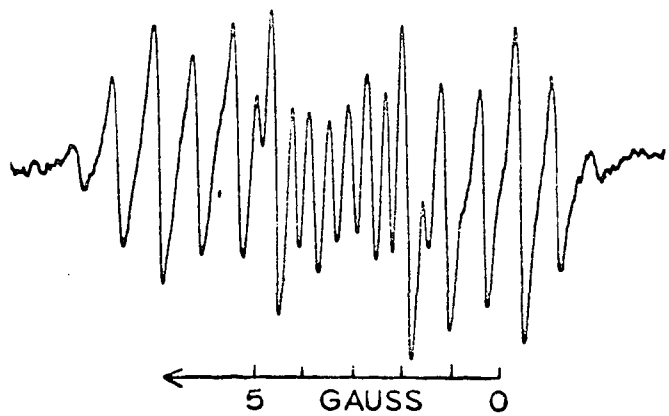
XVIII

mixed with t-BuOK in DMSO, the spectrum shown in Figure 1 is obtained. No attempt was made to introduce oxygen into the system after it had been deaerated by bubbing nitrogen through for a period of fifteen minutes. Either there was sufficient oxygen remaining in the system or the oxidizing agent was DMSO itself. On analysis, the spectrum arises from one proton with splitting constant 2.75 gauss, two protons 2.32 gauss, and five protons 0.78 gauss. These assignments suggest that the radical anion has structure XIX. In semidiones of the type $C_6H_5C(O^-) = C(O^\circ)R$, where R is

$C_6H_5C(O^-) = C(O^\circ)OCH_2CH_3$

XIX

Figure 1. First-derivative e.s.r. spectrum of ethyl benzoylformate radical anion (top) in DMSO; calculated spectrum for Lorentzian line width (bottom) of 0.2 gauss and splitting constants from text performed by Japan Electron Optics Laboratory Co. (JEOLCO) JNM-RA-1 spectrum accumulator.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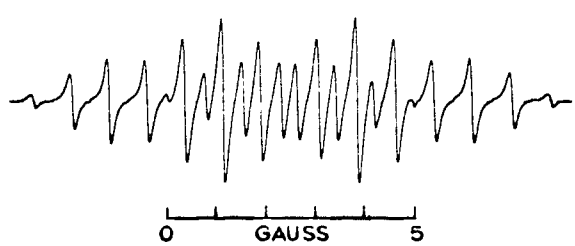
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an alkyl group, the para hydrogen has a splitting constant of about 1.84 gauss, the two ortho hydrogens 1.59 gauss and the two meta hydrogens 0.54 gauss (23). Thus there is a higher spin density in the benzene ring in XIX than in these semidiones. However the distribution of spin within the rings is the same, i.e., the ratios of splitting constants for the various protons are the same in both semidiones. A McLachlan molecular orbital (MO) calculation (48) using parameter values described in detail at the end of this section was done for XIX. This calculation showed a spin density of 0.0819 for the ortho position, -0.0346 for the meta position, and 0.0751 for the para position. The fact that the para proton is predicted to have a smaller splitting constant than the ortho protons is somewhat surprising. However this relationship is also predicted for benzil, where it is known not to occur. If we assume a value of 23 for Q (49) and use the relationship $a_i = \rho_i Q$ (50), then the predicted splitting constants are 1.89 gauss for the ortho position, 0.80 gauss for the meta position, and 1.73 gauss for the para position. While this is in excellent agreement with that found for the meta position, the ortho and para positions are way out of line. It is clear that the predicted value of spin density in the ring is too low overall. Inherent in the assumptions underlying the calculation is the necessity of the spin density in the ring being independent

of the exact nature of the ester function.

When isopropyl mandelate is reacted with t-BuOK in DMSO, the spectrum shown in Figure 2 is obtained. The radical anion is assigned structure XX on the basis of the splitting

$(C_6H_5COCO_2CH(CH_3)_2)^{\cdot-}$

XX

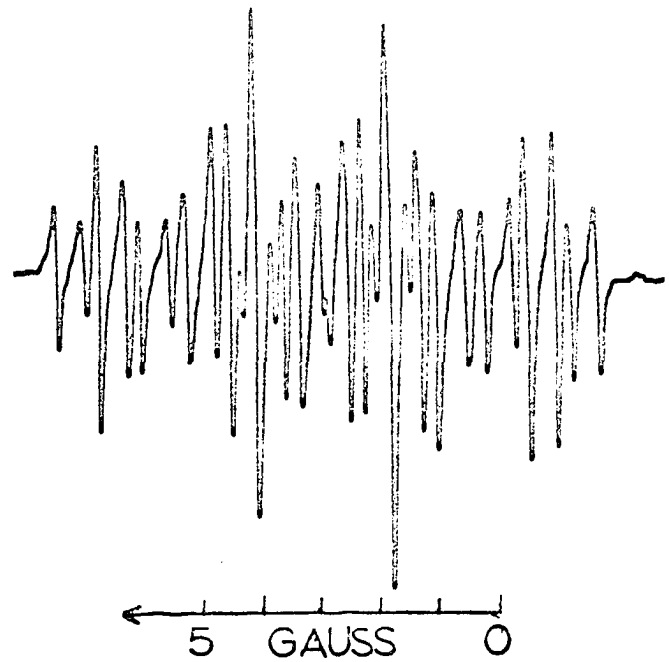
constants. The spectra can be synthesized assuming two protons with splitting constants 2.67 and 0.49 gauss, and two pairs of protons with splitting constants 2.25 and 0.76 gauss. When this is done, all the lines appear in the right places, but the intensities are distorted. However if we use the same splitting constants but assign an intensity ratio of 1:1:1 rather than 1:2:1 for the 2.25 gauss splitting, the relative intensities are in good agreement with the experimental spectrum. This suggests that there might be hindered rotation about the phenyl carbon bond as has been observed for several ketyls (35). When methyl mandelate is mixed with t-BuOK in DMSO, XXI is produced (See Figure 3). Semidione XXI has splitting constants of 2.8 gauss for one

$(C_6H_5COCO_2CH_3)^{\cdot-}$

XXI

proton, 2.46 and 0.74 gauss for two pairs of protons, and 0.83 gauss for three protons.

Figure 2. First-derivative e.s.r. spectrum of isopropyl benzoylformate radical anion (top) in DMSO; calculated spectrum for Lorentzian line width (middle) of 0.2 gauss and splitting constants from text with intensities 1:1:1 for the ortho splitting constants performed by JEOLCO JNM-RA-1 spectrum accumulator; calculated spectrum for Lorentzian line width (bottom) of 0.2 gauss and splitting constants from text with intensities 1:2:1 for the ortho splitting constants performed by JEOLCO JNM-RA-1 spectrum accumulator.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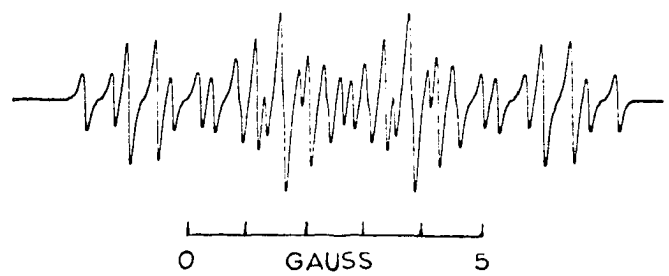
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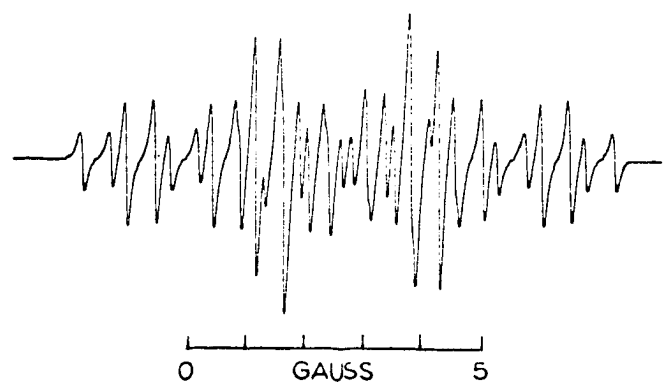
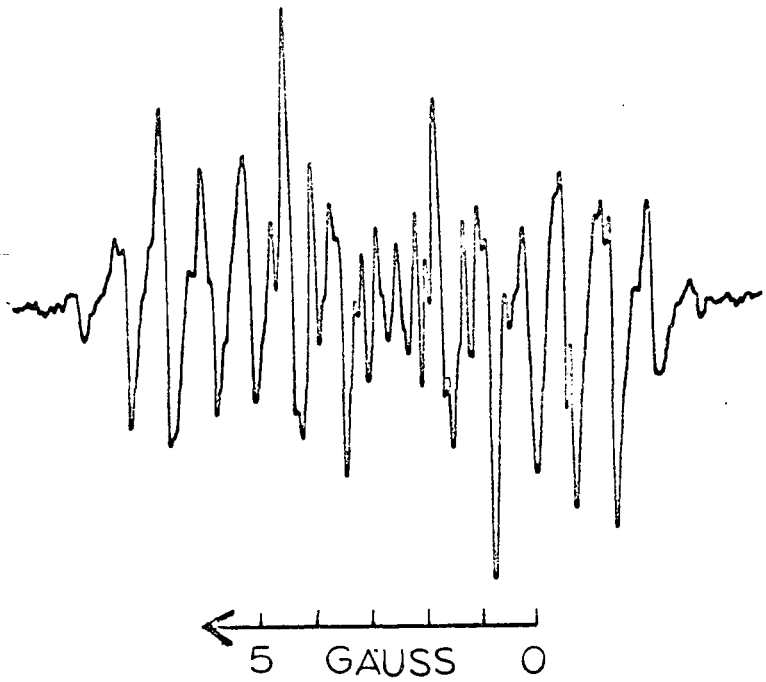

0 GAUSS 5

Figure 3. First-derivative e.s.r. spectrum of methyl benzoylformate radical anion (top) in DMSO; calculated spectrum for Lorentzian line width (bottom) of 0.2 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.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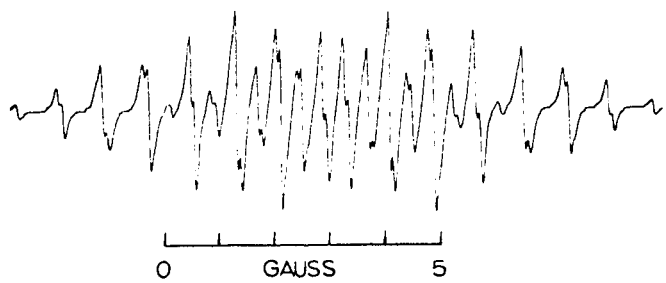
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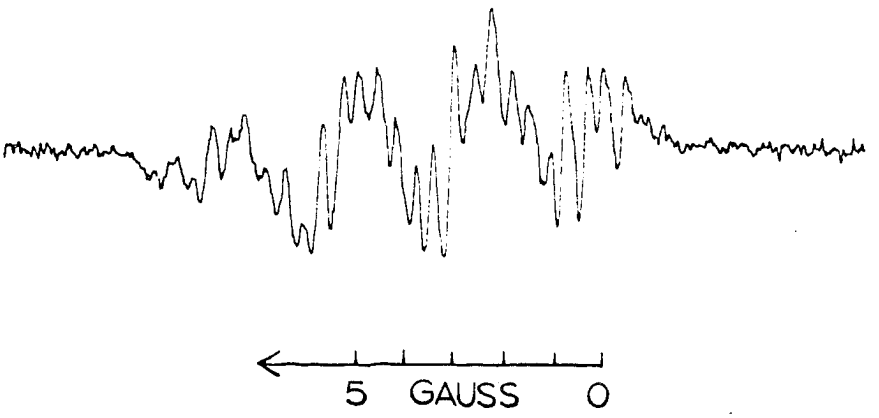
These results show that the spin distribution within the benzene ring is independent of the ester substituent and that there is no ester exchange with t-BuOK in DMSO. If NaOMe is used in place of t-BuOK, then both ethyl and isopropyl mandelate are converted to XXI. This is in agreement with the known ability of DMSO to catalyse ester exchange reactions (5). Semidione XXI is also formed from methyl mandelate with NaOMe in DMSO. This result suggests that ester exchange is occurring prior to the formation of radical anions although there is little evidence on this point. When I is used as the base in DMSO, isopropyl mandelate does not yield XX. The spectrum obtained is shown in Figure 4. On the basis that I is known to attack esters to yield β-ketosulfoxides (15,16), structure XXII has been assigned to the radical anion. Unfortunately the

$$C_6H_5C(O\cdot) = C(O^-)CH_2SOCH_3$$

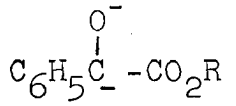
XXII

spectrum is too poorly resolved to allow a complete analysis. It would appear that there is a major quartet with a splitting constant of about 2.5 gauss. At first glance, this could be due to either the para proton and the two ortho protons or the para proton and the two methylene protons. However if the splitting were assigned to the latter, then the ortho protons would have to have a splitting constant less than 1.2 gauss in keeping with the length of the spectrum. This

Figure 4. First-derivative e.s.r. spectrum from isopropyl mandelate (0.05M) and CH_3SOCH_2Na(0.5M) in DMSO.


5 GAUSS 0

is clearly unreasonable in light of the ortho to para ratio in aryl semidiones (30). Furthermore there is some reason to believe that a methylene group adjacent to a sulfoxide has a small splitting constant. (This will be discussed in more detail later.) If the radical anion has structure XXII, then the results with t-BuOK in DMSO demand that the removal of a proton from the mandelate esters be much faster than the formation of I. The second pKa of mandelic acid is reported to be between 15 and 16 (51,52). However the formation of radical anions presumably proceeds through the transfer of an electron from a dianion to some acceptor such as oxygen. Therefore it would appear that the removal of the second proton from the mandelate esters to form XXIII followed by electron transfer must be faster than formation



XXIII

of I followed by attack to yield the β-ketosulfoxide.

When methyl, ethyl, or isopropyl lactate is mixed with a solution of t-BuOK in DMSO, the spectrum obtained has seven equally spaced lines of binomial intensity with a splitting constant of 6.1 gauss. Clearly the known semidione XXIV (29) has been obtained rather than the desired XXV. This is surprising in view of the easy conversion of the

$CH_3C(O^-) = C(O\cdot)CH_3$ XXIV

$CH_3C(O^-) = C(O\cdot)OR$ XXV

mandelate esters to the corresponding semidiones. Exchange studies with ethyl lactate and ethyl mandelate in the presence of D_2O and potassium carbonate in DMSO show that for both compounds the hydroxylic proton is rapidly removed. Clearly then the monoanion is easily formed from lactate esters. However the results can be explained if we assume that the formation of the dianion analogous to XXIII from the lactate esters is slower than the formation and subsequent reaction of the β-ketosulfoxide. From basic principles it is clear that it is easier to remove a proton from $C_6H_5CH(O^-)CO_2R$ than from $CH_3CH(O^-)CO_2R$. The fact that the lactates are not converted to XXV apparently rules out the possibility that the radical anions are formed by loss of an electron from the monoanion followed by removal of a proton. Examination of the β-ketosulfoxide formed from the lactate esters shows that there is a simple mechanism by which it can be converted to XXIV in base. Results with biacetyl itself

$$CH_3CH(OH)CO_2R + I \rightleftarrows CH_3CH(OH)COCH_2SOCH_3 + RO^-$$

XXVI

$$XXVI \rightleftarrows CH_3COCH(OH)CH_2SOCH_3$$

$$CH_3SO^- + CH_3COC(OH) = CH_2 \leftarrow CH_3C\bar{O}C(OH)CH_2SOCH_3$$

$$\downarrow\uparrow$$

$$CH_3COCOCH_3 \rightarrow XXIV$$

show that it will be converted to 2,5-dimethylsemiquinone by t-BuOK in DMSO if it is present in large amounts. However if it is present in low concentrations in the presence of good electron donors, XXIV is easily formed (29). Attempts to isolate either XXVI, biacetyl, or 2,5-dimethylquinone from the reaction of ethyl lactate with either t-BuOK or I as the base in DMSO were all unsuccessful.

In an attempt to determine if radical anions from mandelate esters are inherently different from those from lactate esters, polarographic work with diketones and keto-esters was undertaken. The results were all obtained in DMSO solution which was 0.1 molar in tetra-n-propylammonium perchlorate (TNAP) as the supporting electrolyte. The potentials were all measured relative to an aqeous saturated calomel electrode (SCE). The half-wave potentials so obtained are listed in Table 1. The reduction of 1,2-cyclohexanedione requires a potential of 1.89 volts, 1,2-cyclopentanedione 2.19 volts, whereas biacetyl is reduced at 1.27 volts. This difference probably reflects the difference in energy between cis and trans semidiones (29). The half-wave reduction potential of benzil is 1.16 volts, only slightly lower than that of biacetyl. In fact, this represents an energy difference of only 2.3 kcal/mole between the two. The reduction potential of ethyl pyruvate and ethyl benzoylformate ($C_6H_5COCO_2CH_2CH_3$) is 1.5 volts for both

Table 1. Reduction potential of some carbonyl compounds

Compound	Solvent	$-E_{1/2}$[a]	$E_{calc.}$[b]
1,4-Diphenyl-1,2,3,4-butanetetraone	DMSO[c]	0.78,2.04	0.2443
1,3-Diphenyl-1,2,3-propanetrione	DMSO[c]	0.76,2.25	0.1613
Benzil	DMSO[c]	1.16	0.0000
Benzophenone	-	-	-0.2939
Biacetyl	DMSO[c]	1.27	-0.1221
Ethyl benzoylformate	DMSO[c]	1.48	-0.1024[d]
Ethyl pyruvate	DMSO[c]	1.51	-0.1285
Ethyl formylglyoxylate	-	-	0.1341
Ethyl oxalate	DMSO[c]	1.85	-0.2904
Ethyl mesoxalate	DMSO[c]	0.84	0.0646
Ethyl benzoylglyoxylate	-	-	0.1220
Dehydroascorbic acid	H_2O at pH 3.5	0.42[e]	
Triose reductione (HCOCOCHO)	H_2O at pH 3.5	0.35[e]	-
Dehydroreductic acid	H_2O at pH 3.5	0.27[e]	-
Alloxan	H_2O at pH 3.5	0.05[e]	-

[a]Versus saturated calomel electrode.

[b]Energy of lowest unoccupied orbital in units of β calculated with the Huckel assumptions using the parameter values given in the text.

[c]Solutions 0.1 molar in tetra-M-propylammonium perchlorate.

[d]The ester-ether group (OR) was treated as a heteroatom.

[e]Versus normal calomel electrode, values cited in reference 53.

within experimental error. It is clear therefore that the difference in behavior between the lactates and the mandelates is not due to any inherent differences in the radical anions but rather to differences in the chemical behavior of the starting materials. One result that does emerge from the polarographic work is that while α-ketoesters are harder to reduce than linear α-diketones they are easier to reduce than cyclic α-diketones. Clearly then the reduction potentials of chemically generated species should be sufficient to reduce α-ketoesters.

A useful tool for the analysis of e.s.r. spectra is provided by MO calculations. A simple modification of a computer program for Hückel MO calculations will convert it to one which provides spin densities calculated by the method of McLachlan (48). The parameters chosen for these calculations were those recommended by Streitwieser (54). Because of the complexity of the molecules involved and the inherent difficulties in allowing for alkyl substituents, it was decided to treat esters as ether substituted ketones. In the equations listed below, "O" refers to the carbonyl oxygen while "OR" refers to the ester ether linkage. As in all such calculations the worthiness of the values chosen

$$\alpha_O = \alpha_C + \beta_{CC}; \quad \beta_{CO} = \beta_{CC}$$

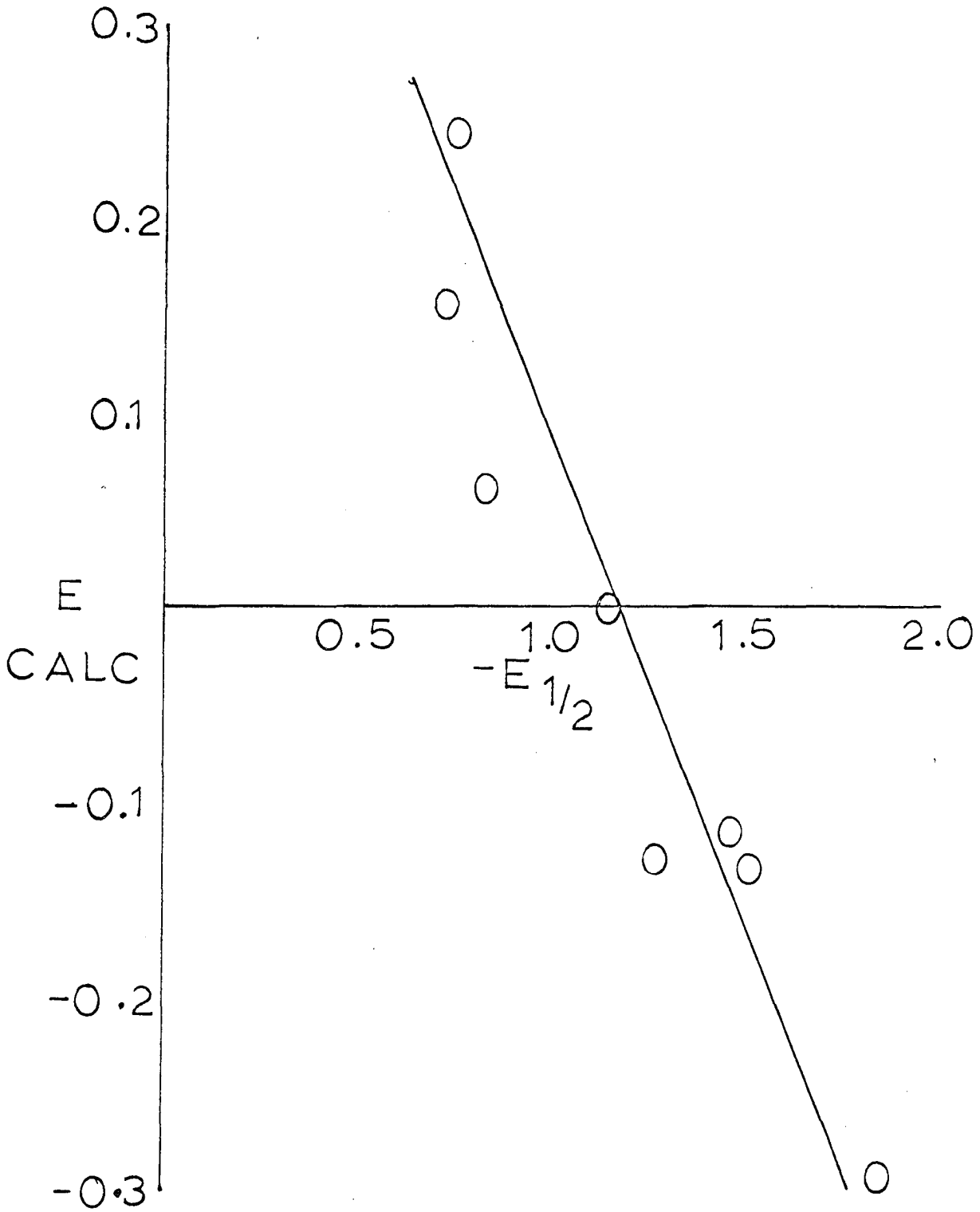
$$\alpha_{OR} = \alpha_C + 1.65\ \beta_{CC}; \quad \beta_{COR} = \beta_{CC}$$

for the parameters is determined by comparison of some calculated value with an experimental measurement of the same variable. Unfortunately it turns out that spin densities are highly dependent on the value chosen for α (49). They are slightly less dependent of the value chosen for β. Rather than juggle the values of α and β to arrive at the experimental spin densities, it was decided to compare the calculated energy for placing an electron in the lowest unoccupied orbital with the reduction potentials determined in DMSO. When this is done, the plot shown in Figure 5 is obtained. As the graph is approximately linear, it would appear that the choices of parameter values lead to reasonable calculated energies and are internally consistent. This method has been used previously by Streitwieser to correlate results with hydrocarbon radical anions (55). This does not mean that the values computed for any one compound must be real but rather the difference between, or ratio of, any two values should be a good measure of the real relationship between these values.

B. Reductive Approaches to Semidiones Containing the Alkoxy Group ($RC(O^{\cdot}) = C(O^{-})OR'$)

In general, the best method for obtaining semidiones is to use a mixture of α-diketone and α-hydroxyketone with t-BuOK in DMSO (23,29). The reaction is presumed to go through a dianion intermediate formed from the α-hydroxyketone

Figure 5. Plot of half-wave reduction potentials in DMSO relative to SCE in volts (abscissa) versus the energy of the lowest unoccupied orbital in units of β (ordinate).

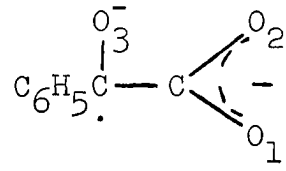

0.3
0.2
0.1
E
CALC
-0.1
-0.2
-0.3
0.5
1.0
1.5
2.0
$-E_{1/2}$

which then reversibly transfers an electron to the diketone to form two molecules of radical anion.

$$RC(O^-) = C(O^-)R' + RCOCOR' \rightleftarrows 2RC(O\cdot) = C(O^-)R'$$

When ethyl, isopropyl, and methyl mandelates and the corresponding benzoylformates were treated with t-BuOK in either DMSO or N,N-dimethylformamide (DMF), XIX, XX, and XXI were formed respectively. Treatment of ethyl and methyl benzoylformate with potassium in HMPA yields XIX and XXI respectively. It is of interest to note that the splitting constants of the radical anions are not solvent dependent.

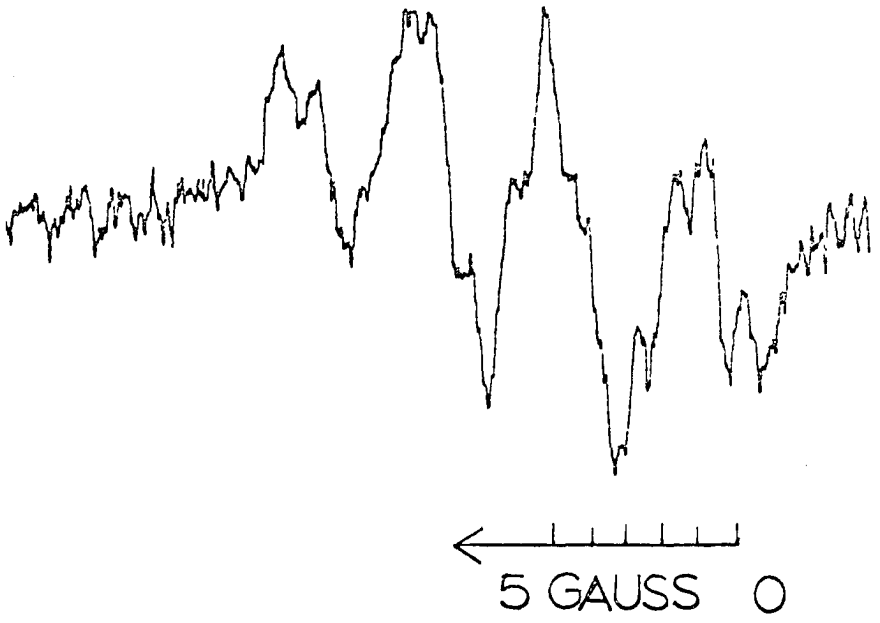
When mandelic acid is mixed with t-BuOK in DMSO, no e.s.r. signal is obtained. The reduction of benzoylformic acid with potassium in HMPA leads to a weak signal which consists of one unresolved peak. A mixture of mandelic and benzoylformic acids when treated with t-BuOK in 100% DMSO yields XXVII. The spectrum is shown in Figure 6. If the



XXVII

solvent contains 10% t-BuOH, no signal is observed. The reduction of tetramethylammonium benzoylformate with potassium in HMPA also produces XXVII. The splitting constants for XXVII are approximately 3.7 gauss for three

Figure 6. First-derivative e.s.r. spectrum of potassium benzoylformate radical anion in DMSO.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0

protons and 0.8 gauss for two protons. When McLachlan calculations of spin density are made for XXVII, the predicted spin densities for the ortho and para positions are too low. These can be raised by changing the value of m in the equation $\alpha_O = \alpha_C + m\beta_{CC}$. The results are shown in Table 2. As might be expected, an increase in the Coulomb integral

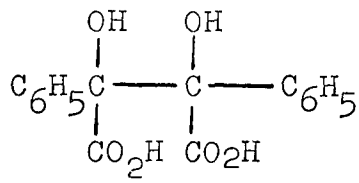
Table 2. Dependence of spin density on parameter value

m		Spin Densities Calculated for XXVII		
O_3	$O_{1,2}$	ortho	meta	para
1.0	1.0	0.090	-0.037	0.085
1.0	1.32	0.081	-0.034	0.074
1.0	2.0	0.065	-0.031	0.054
1.65	1.32	0.103	-0.043	0.088
experimental[a]		0.156	-0.035	0.156

[a]Calculated from $\rho = a/Q$, $Q = 23$.

for the carboxylate oxygens decreases the spin density in the ring, while an increase for the carbonyl oxygen increases the spin density. Because the spin density is so dependent on the value of the parameter, MO calculations are of little help in establishing the reasonableness of the splitting constants in XXVII. It is not too surprising that mandelic acid by itself is not converted to XXVII as it is known that under some conditions wherein benzoin is oxidized to benzil, mandelic acid is not converted to benzoylformic acid (56).

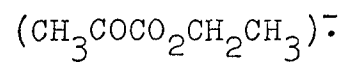
However it is known that the latter is converted to the former under acidic conditions, either on heating (57) or electrically (58). Under basic conditions the electrolytic reduction of benzoylformic acid leads mainly to XXVIII and a



XXVIII

small amount of mandelic acid (59). However XXVIII can easily be imagined as a precurser to XXVII (30).

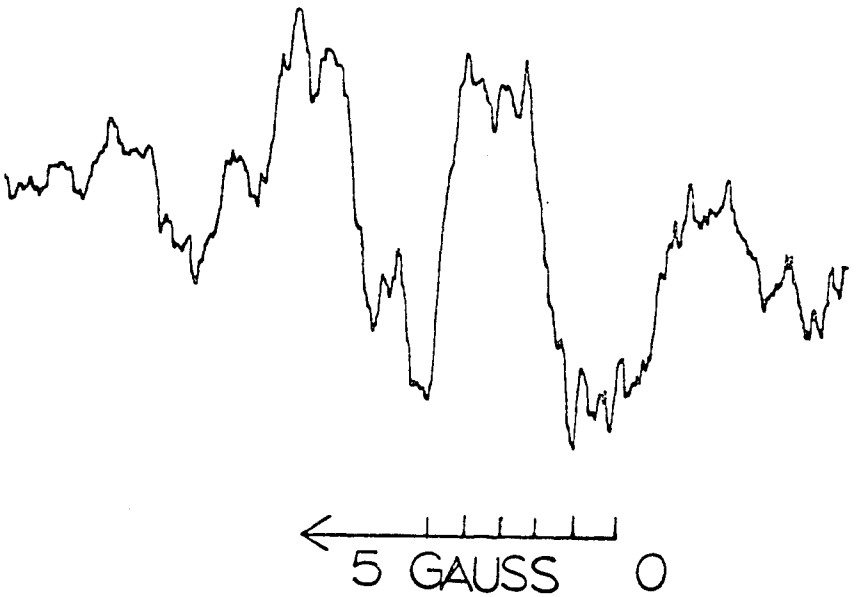
When a mixture of ethyl lactate and ethyl pyruvate is treated with t-BuOK in DMSO, the spectrum shown in Figure 7 is obtained. The large quartet splitting measures about 5.2 gauss. The smaller splitting appears to be a triplet and measures about 0.8 gauss. Therefore the radical anion was assigned structure XXIX.



XXIX

Both values are in excellent agreement with what is expected for such a structure. Mixtures of methyl lactate and methyl pyruvate or isopropyl lactate and isopropyl pyruvate when treated with t-BuOK in DMSO give rise to a signal displaying a major quartet with a splitting of 5.2 gauss with no other hyperfine structure. This is thought to be due to the low

Figure 7. First-derivative e.s.r. spectrum of ethyl pyruvate radical anion in DMSO.


5 GAUSS
0

concentrations of radical anions which causes deterioration of the resolving power of the instrument. However due to the equivalence of the methyl splitting, the radical anions were assigned structures XXX and XXXI respectively. On the other hand, when a mixture of isopropyl lactate and isopropyl

$(CH_3COCO_2CH_3)^{\cdot}$ XXX

$(CH_3COCO_2CH(CH_3)_2)^{\cdot}$ XXXI

pyruvate is reacted with I in DMSO a radical anion is produced which only shows a quartet with a splitting constant of 6.4 gauss. This higher value suggests that this radical anion is $CH_3C(O\cdot) = C(O^-)CH_2SOCH_3$. The lack of splitting from the methylene protons suggests that they have a splitting constant of less than one gauss. This is on the same order as that assigned to these protons in XXII. Again however the evidence is very weak.

If ethyl pyruvate by itself is treated with t-BuOK in DMSO, no e.s.r. signal is obtained. This implies that the enolate anion is not as good a reducing agent as the anion derived from ethyl lactate as it has long been known that pyruvic acid is enolized even under weakly alkaline conditions (60). However ethyl pyruvate is converted to XXIX by potassium metal in HMPA. The fact that XXIX is formed from mixtures of ethyl lactate and ethyl pyruvate is not unexpected. It is known that pyruvic acid is converted to lactic acid electrolytically under basic conditions (61)

and that lactic acid is oxidized to pyruvic acid electrolytically (62,63). Also under basic conditions the latter reaction is reversible (63). In fact these two acid salts maintain a stable potential at an inert electrode (64). It is somewhat surprising that ethyl lactate by itself was not sufficient to generate XXIX as it is known that it is oxidized to ethyl pyruvate on standing in air, albeit somewhat slowly (65, 66).

Attempts were made to obtain nitrogen substituted semidiones from reactions with amides. When either XXXII or XXXIII was treated with t-BuOK in DMSO alone or together, no e.s.r. signal was obtained. This was attributed to the

$C_6H_5COCO_2N(CH_2CH_3)_2$ XXXII

$C_6H_5CH(OH)CO_2N(CH_2CH_3)_2$ XXXIII

hydrolysis of the amides under the conditions employed. To circumvent this, $C_6H_5COCH_2N(CH_3)_2$ was synthesized. When this is mixed with t-BuOK in DMSO, in the presence or absence of iodine, an e.s.r. signal was obtained which was identical in all respects to that obtained from XXXIV (29). It is

$C_6H_5C(O^-) = C(O\cdot)H$ XXXIV

unlikely that the dimethyl amide ion would be the leaving group as sodium hydride preferentially removes a proton from DMSO in solutions of DMSO saturated with dimethylamine.

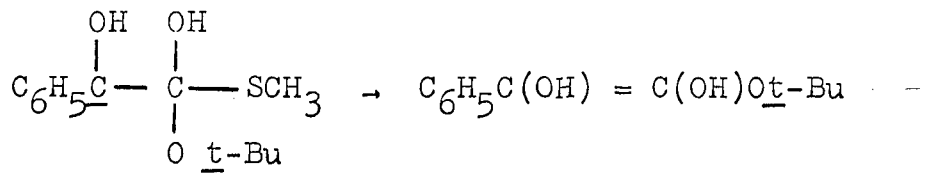
It is possible that there is a concerted reaction to produce $C_6H_5COCH_2OH$ which is converted to XXXIV by t-BuOK in DMSO (29).

When phenylglyoxalhemimercaptal (XXXV) is mixed with

$C_6H_5COCH(OH)SCH_3$

XXXV

t-BuOK in DMSO, a most unusual result is obtained. The radical anion produced has one proton with a splitting constant of 2.90 gauss, and two pairs of protons with splitting constants of 2.45 and 0.80 gauss. It has been shown that this radical anion is the one electron reduction product of t-butyl benzoylformate (30). This identification is discussed in detail in the section dealing with reactions of 1,3-diphenyl-1,2,3-propanetrione. One could understand if XXXV had been converted to XXXIV or radical anions derived from it. However in order to arrive at the observed product it is necessary to postulate either a nucleophilic displacement reaction wherein the mercaptide ion is the leaving group or an addition of t-BuOK to the ene-diol form of XXXV to yield XXXVI followed by elimination to yield XXXVII. However this is just the enolic form of t-butyl



XXXVI XXXVII

mandelate and would be expected to go on to the observed radical anion.

C. Semitrione Radical Anions

1. Introduction

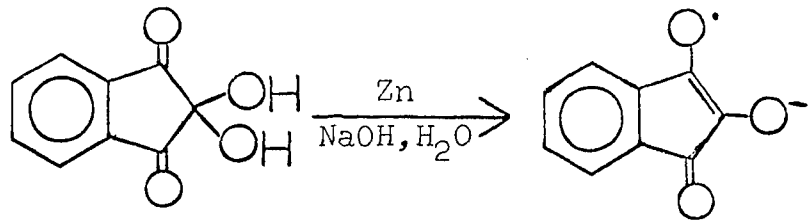
It is obvious from the existence of many kinds of semidiones and the variety of ways in which they can be made, that their stability stems in large measure from the localization of the odd electron on the carbonyl carbon and oxygen atoms. This observation is brought out very clearly by the results of MO calculations (67). Thus even in the case of diphenylsemidione, the spin density in each phenyl ring is only 0.15. Another factor illustrated by these calculations is that the stability of the radical anion increases as the number of carbonyl groups in the molecule is increased. This implies that ketyls should be less stable than semidiones which in turn should be less stable than the corresponding semitriones (23). The stability of ketyls has experimentally been found to be less than that of the corresponding semidione (35). This suggests that there should be a series of semitriones (XXXVIII) corresponding to the known members of the semidione series. The first reported

$$RCOC(O^-) = C(O^\cdot)Y \qquad RC(O^-) = C(O^\cdot)C(Y)O$$

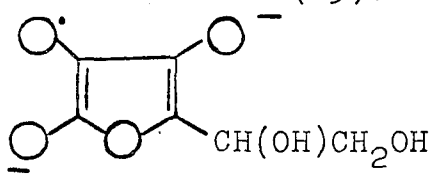
XXXVIII

successful generation of a semitrione was by Adams (68).

He and his coworkers used zinc dust in alkaline solutions to reduce ninhydrin. They reported splitting constants of 1.95



and 1.59 gauss for two pairs of equivalent protons. Several years later Piette reported the semitrione derived from ascorbic acid (XXXIX) and the semitetraone from dihydroxy-tartaric acid (69). However proof of the structure

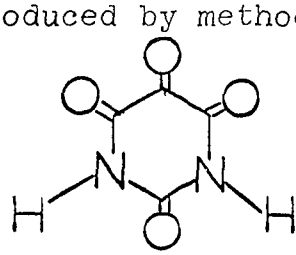


XXXIX

$HOCH_2C(O^{\cdot}) = C(O^{-})OH$

XL

of the latter was based on the fact that the spectrum was a singlet which was somewhat broader than could easily be explained. Lagercrantz also was able to produce XXXIX (70). However his attempts to produce XXXVIII with R = Y = H from a variety of substituted acetones led to what he described as XL (71). This was later shown to be in error (29). More recently semitriones derived from ninhydrin and alloxan (XLI) have been produced by methods used to generate



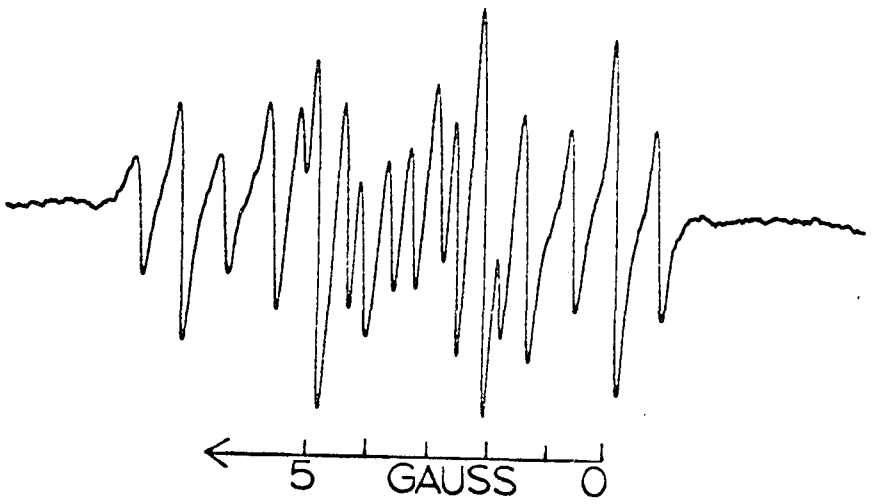
XLI

semidiones (72).

2. Reduction of polycarbonyl compounds

Conceptually, the most straightforward manner to generate XXXVIII is by one electron reduction of the tricarbonyl compound. When 1,3-diphenyl-1,2,3-propanetrione (DPPT) was treated with t-BuOK in DMSO solution, a radical anion (XLII) was produced which did not appear to contain two phenyl groups (see Figure 8). In fact the spectrum was analysed on the basis of two pairs of protons, splitting constants 2.45 and 0.80 gauss, and a single proton, splitting constant 2.90 gauss. When NaOMe was used in place of t-BuOK radical anion XLIII was generated. Its spectrum bore strong resemblance to that of XXI generated from methyl mandelate (See Figure 9). When potassium isopropoxide (i-PrOK) was used as the base, the spectrum obtained was identical with that of the known semidione, XX. These results together with the similarities of the splitting constants of XLII with those of the aromatic protons of XIX, XX, and XXI suggest that XLII is $C_6H_5C(O^-) = C(O^{\cdot})Ot\text{-Bu}$. It is known that alkoxide bases are capable of removing a proton from DMSO (7,12,17,22), yet in the above results there is no indication of the formation of I. When I is formed by the reaction of sodium hydride with DMSO and the resultant solution allowed to cool, and then mixed with DPPT in DMSO the spectrum shown in Figure 10 is obtained. This can be interpreted as two protons with a splitting constant of 0.8 gauss (from the

Figure 8. First-derivative e.s.r. spectrum of t-butyl benzoylformate radical anion (top) in DMSO; calculated spectrum for Lorentzian line width (bottom) and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.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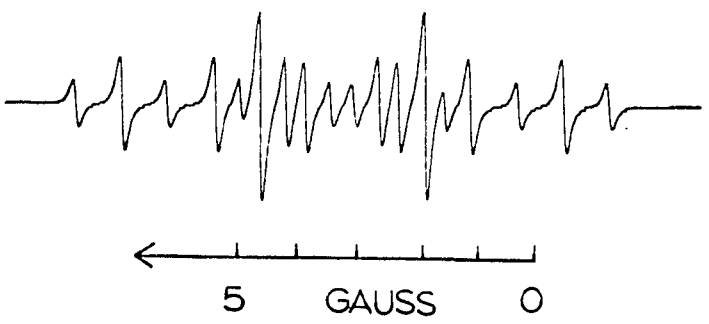
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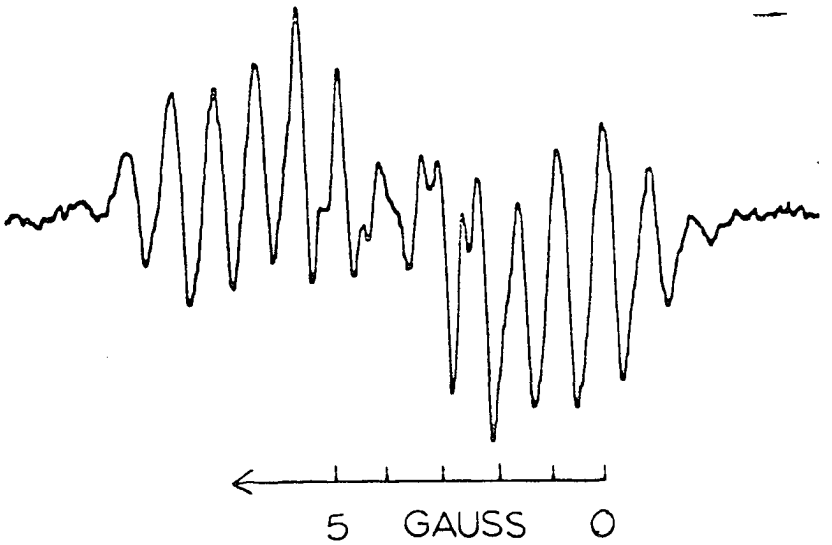
Figure 9. First-derivative e.s.r. spectrum of the radical anion formed by reaction of NaOMe with DPPT (top) in DMSO; first-derivative e.s.r. spectrum of methyl benzoylformate radical anion (bottom) in DMSO.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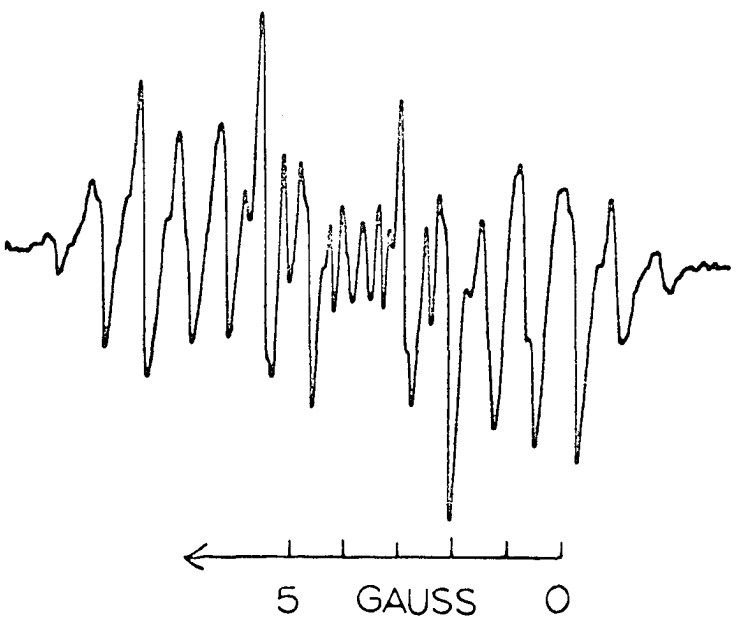
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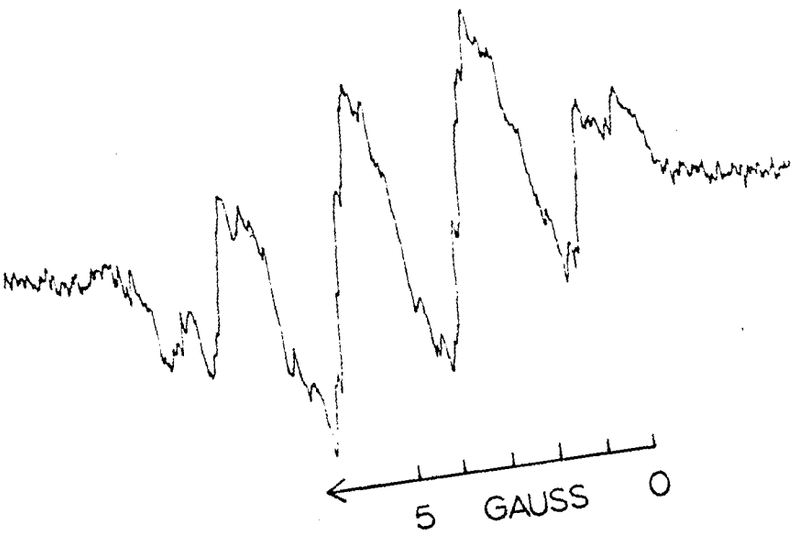
Figure 10. First-derivative e.s.r. spectrum of the radical anion formed by reaction of DPPT with CH_3SOCH_2Na in DMSO.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splitting in the outermost peaks) and three protons with a splitting constant of about 2.6 gauss for the main quartet. This broad envelope of lines is superimposable on the spectrum obtained from isopropyl mandelate under the same conditions (Figure 4) which has been shown to be $C_6H_5(O\cdot) = C(O^-)CH_2SOCH_3$.

When the solvent is changed from DMSO to the alcohol corresponding to the alkoxide base, an unexpected result is obtained. DPPT reacts with i-PrOK in i-PrOH to form the radical anion derived from benzil (XLIV) under these conditions

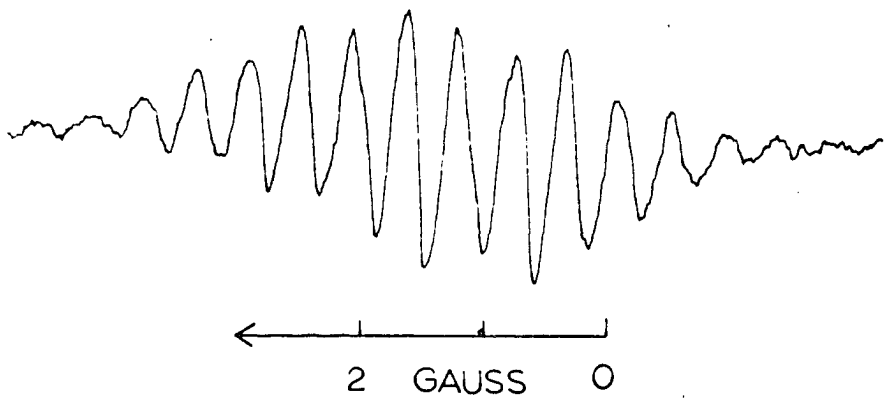
$$C_6H_5C(O^-) = C(O\cdot)C_6H_5$$

XLIV

(See Figure 11). DPPT is also converted to XLIV by the action of t-BuOK in t-BuOH and NaOMe in MeOH. Even where the solvent is 75% DMSO by volume and 25% alcohol, i-PrOK and NaOMe still convert DPPT to XLIV (See Figure 12). In fact, when the solvent contained less than 5% i-PrOH, the spectrum appears to be due mainly to XLIV. It is possible that more than one radical anion is present as the last large upfield peak has too high an intensity for a spectrum due solely to XLIV. This peak appears to be of normal intensity when the solvent is 25% i-PrOH (See Figure 13). Compound XLIV is also produced when DPPT is mixed with t-BuOK in DMF.

As the alkoxide bases did not effect the simple reduction of DPPT, various other reducing agents were tried. When the

Figure 11. First-derivative e.s.r. spectrum of the radical anion formed by reaction of DPPT with i-PrOK (top) in i-PrOH; first-derivative e.s.r. spectrum of the benzil radical anion (bottom) in i-PrOH.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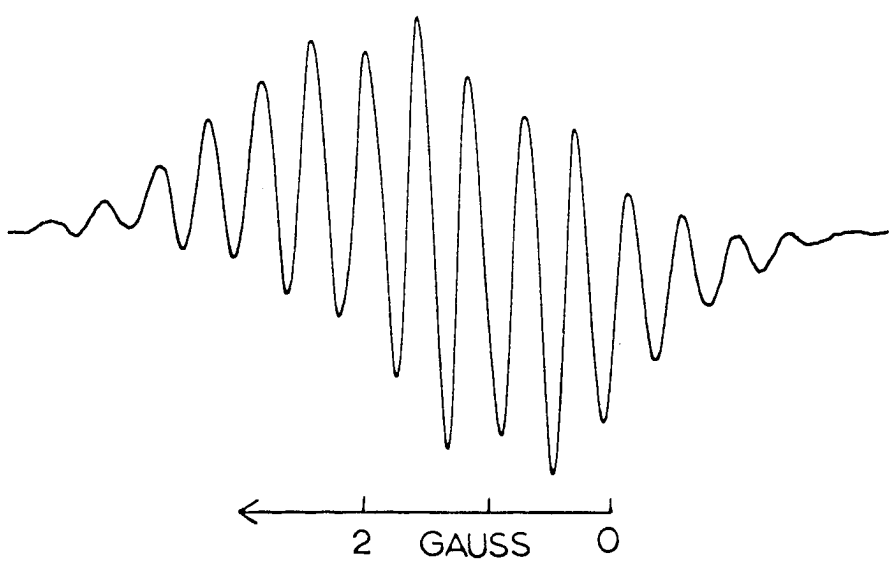
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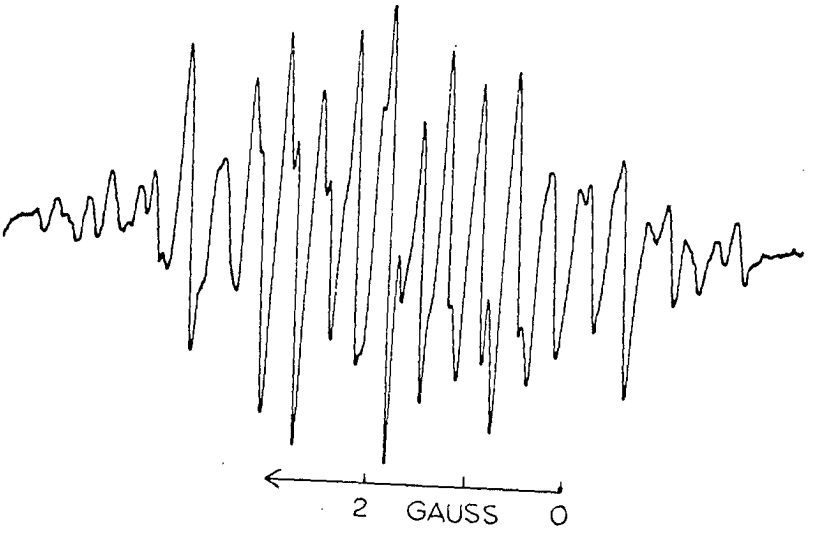
Figure 12. First-derivative e.s.r. spectrum of the radical anion formed by reaction of DPPT with i-PrOK (top) in 95% DMSO, 5% i-PrOH; first-derivative e.s.r. spectrum of benzil radical anion (middle) in DMSO; first-derivative e.s.r. spectrum of the radical anion formed by reaction of DPPT with NaOMe (bottom) in 75% DMSO, 25% methanol.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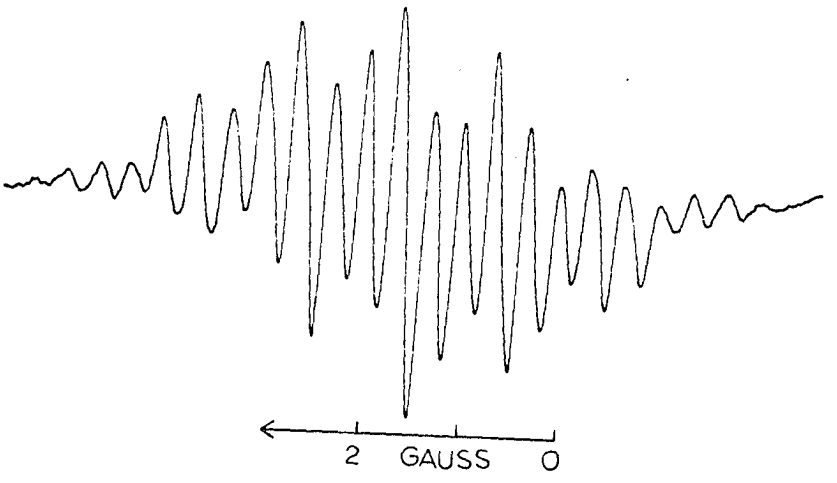
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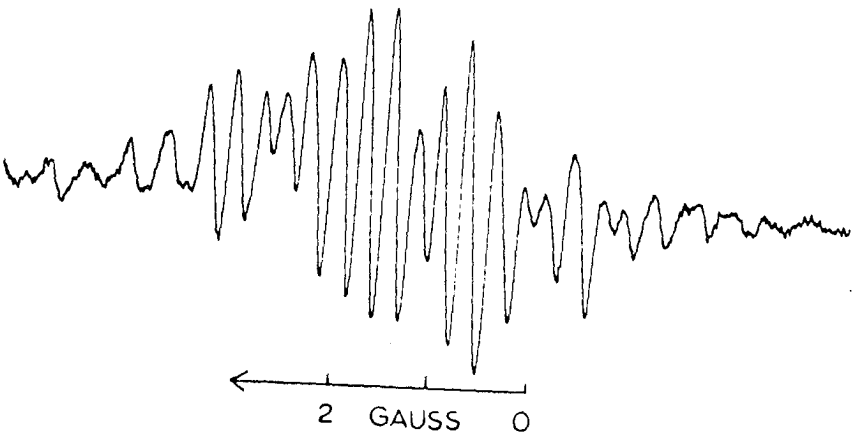
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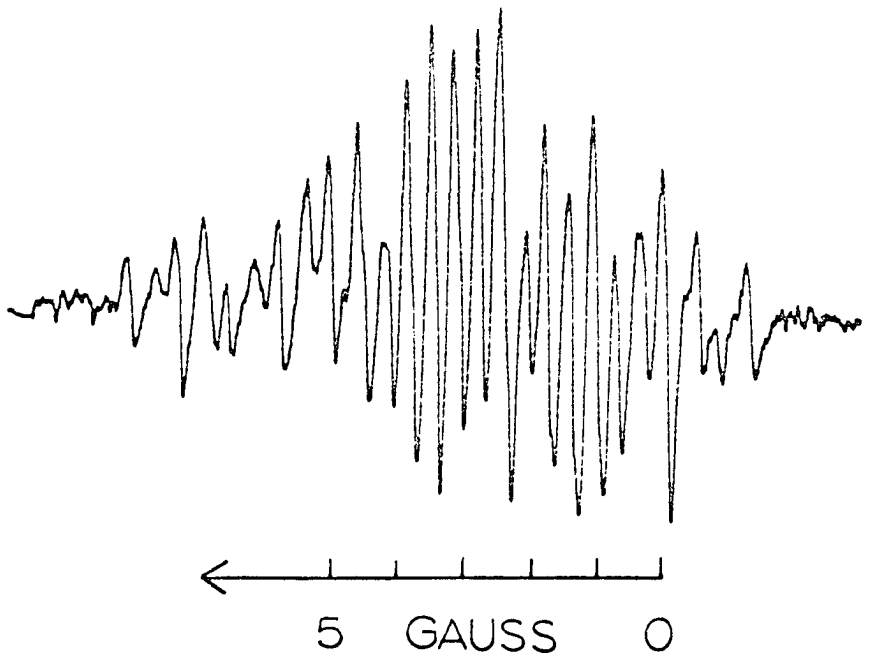
Figure 13. First-derivative e.s.r. spectrum of the radical anion formed by reaction of DPPT with i-PrOK in 75% DMSO, 25% i-PrOH.


5 GAUSS 0

enolate anion of propiophenone, formed by the action of t-BuOK on propiophenone, was mixed with DPPT in DMSO, XLIV resulted. If 9,10-dihydroanthracene was used in place of propiophenone, XLII was produced. When DPPT was reacted with sodium phenoxide, presumably a better electron donor but a weaker base than t-BuOK, XLIV was observed. If a mixture of DPPT and 1,3-diphenyl-2-hydroxy-1,3-propanedione (XLV) is treated with t-BuOH in DMSO, XLIV is produced. Presumably the following occurred:

$$\underset{\text{XLV}}{C_6H_5COCH(OH)COC_6H_5} + 2\text{t-BuOK} \rightleftarrows C_6H_5CO\overset{O^-}{\overset{|}{C}}COC_6H_5 \quad \text{XLIV}$$

$$\text{XLIV} \overset{?}{\rightleftarrows} C_6H_5C(O^-) = C(O^-)COC_6H_5$$

XLVI

$$\text{XLVI} + \text{DPPT} \rightleftarrows C_6H_5C(O^-) = C(O^{\cdot})COC_6H_5 \overset{?}{\rightarrow} \text{XLIV}$$

XLVII

As the spectrum of XLII is wider than that of XLIV, it is clear that no XLII was formed. Dianion XLVI would be expected to react with DPPT to form XLVII. At this stage it is unclear how either or both XLVI and XLVII are converted to XLIV. It is also possible that reaction with XLV produces enough t-BuOH to change the solvent. When aluminum isopropoxide is mixed with DPPT in DMSO the resultant signal is both weak and unresolved and no conclusion can be drawn about the structure of the radical anion. When DPPT is reduced with potassium in HMPA, a spectrum is obtained which

is almost identical to that produced by XLIV in DMSO (See Figure 14). Electrolytic reduction of DPPT in DMSO at 2.5 volts relative to an SCE produced XLIV. When the electrolysis is run at a potential of 1.8 volts, the low field peaks appear to be due to XLIV as they are separated by 0.34 gauss. However, the central and high field regions can best be explained on the basis of four protons with splitting constant 0.17 gauss and six protons with splitting constant 0.54 gauss (See Figure 15). Diphenysemidione has splitting constants of 0.34 gauss for four protons and 1.04 gauss for six protons under conditions where there is sufficient benzil in solution to promote exchange broadening. A McLachlan type calculation (48) predicts the ratio of spin densities of XLVII to XLIV to be 0.40, 0.52, and 0.34 for the ortho, meta, and para positions. This is in excellent agreement with the observed ratio of 0.50 for the four meta protons. While the agreement is poor for the ortho and para positions, the fact that they are predicted to be nonequivalent casts some doubt on the validity of the calculation. However the ratio of meta to ortho-para proton splitting constants is virtually identical in both radical anions. Fortunately radical anions XLVIII and XLIX are both known. The former has a splitting constant of 13.2 gauss for four protons in DMSO (23), while the latter has a value of 6.3 gauss in water (73). Clearly the semitrione to semidione ratio in the diphenyl case is very close to

Figure 14. First-derivative e.s.r. spectrum of benzil radical anion formed by the reduction of DPPT with potassium in HMPA.

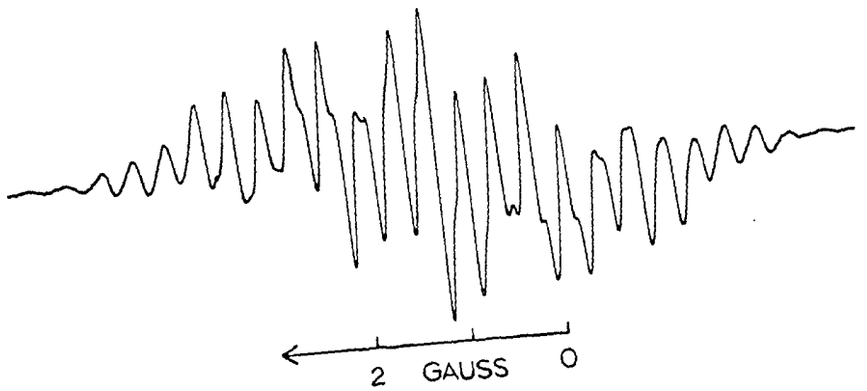
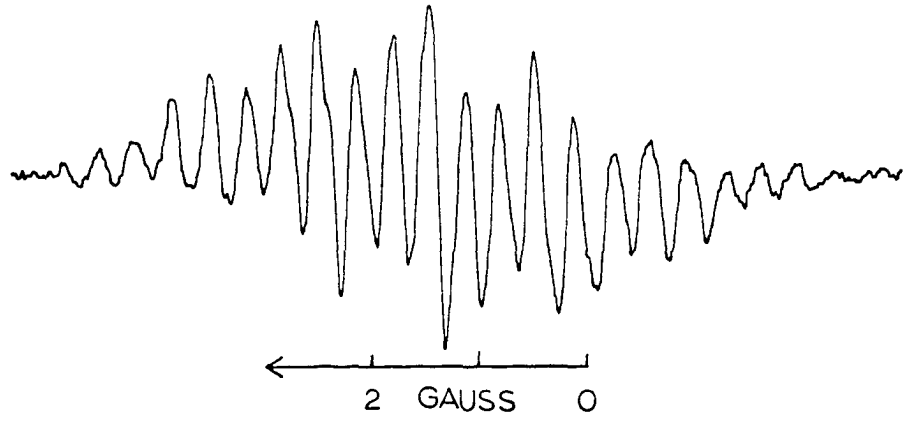

2 GAUSS 0

Figure 15. First-derivative e.s.r. spectrum of benzil radical anion (top) in DMSO; first-derivative e.s.r. spectrum of DPPT radical anion (middle) in DMSO; calculated spectrum for Lorentzian line width (bottom) and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.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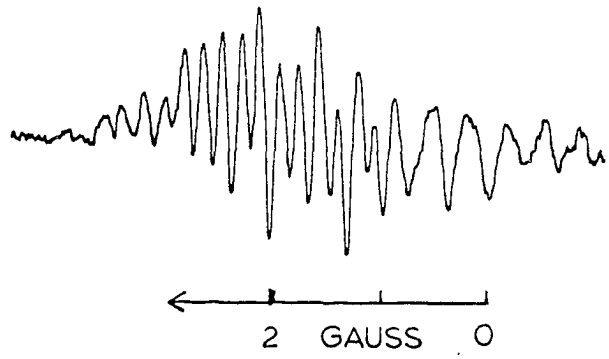
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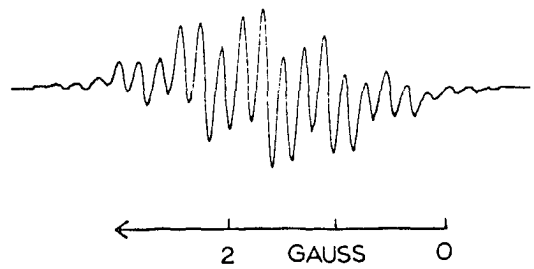
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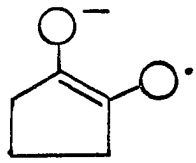
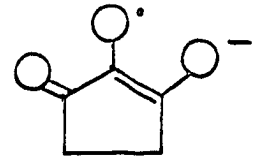


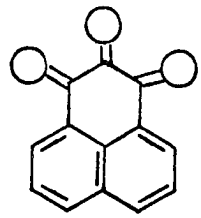
XLVIII



XLIX

what is expected.

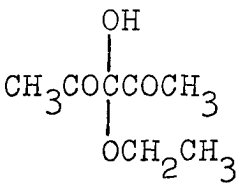
When 1,4-diphenyl-1,2,3,4-butanetetraone (partially hydrated) is reduced electrolytically in DMSO at a potential of 1.7 volts relative to SCE, or by t-BuOK in DMSO XLIV is produced. These spectra are identical with that produced from a mixture of the tetraone and the corresponding dihydro compound on treatment with t-BuOK in DMSO. Treatment of 1,2,3-phenalenetrione (L) with t-BuOK in DMSO resulted in a radical anion which was identical with that produced from acenapthaquinone under these conditions. This result had been



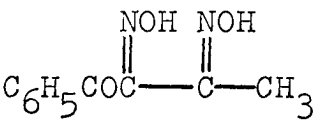
L

obtained previously (74). If 2,3,4-pentanetrione (contaminated with 2,4-pentanedione) is treated with t-BuOK, the anion of propiophenone, or the anion derived from mixing 3-hydroxy-2,4-pentanedione with t-BuOK in DMSO, the resultant e.s.r. spectrum consists of seven lines of binomial intensity which are a distance of 6.1 gauss apart. This is in excellent

agreement with the reported splitting constant of XXIV (29). It is interesting to note that if biacetyl is treated with t-BuOK in DMSO, 2,5-dimethylsemiquinone is produced (29). A similar condensation of 2,3,4-pentanetrione to yield 2,5-diacetylsemiquinone can be imagined. While this may be occurring to some extent, it does not produce the major paramagnetic component. While 2,4-pentanedione does not form a radical anion with tBuOK in DMSO, it might interfere with the condensation reaction or even serve as the reducing agent as the enolate anion. Using the triketone hydrate or the triketone ethyl hemiacetal, XI (75), with t-BuOK in DMSO also produced XXIV as the major radical. When 2,3,4-pentanetrione-3-oxime was similarly treated no radical anion was produced.



LI

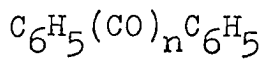


LII

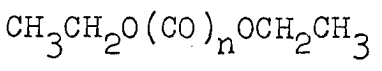
However this failure was found to be rather general as 1,2,3-cyclohexanetrione-1,3-dioxime and palladon, LII, also did not yield radical anions. Presumably this failure is related to the high acidity of the oximes and the stability of the corresponding anions (76).

It is obvious from the preceding results that either the one electron reduction product of these triketones is not formed as easily as had been anticipated, or such products are

not stable. It is also possible that the triketones are too reactive to some form of attack available to the various bases used other than electron transfer. In order to examine the first possibility, Hückel MO calculations were performed on LIII for n = 1,2,3, and 4. The results of Table 1 show that



LIII

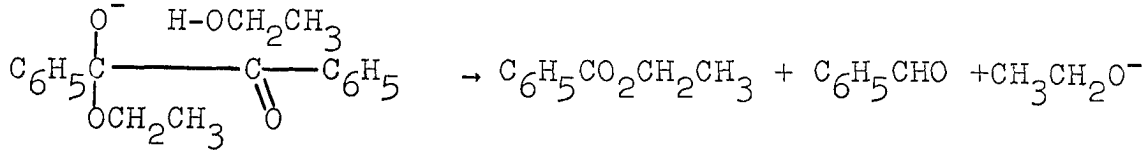


LIV

as n increases, the energy of the lowest unoccupied orbital decreases. This would seem to rule out the first possibility. Further support for this conclusion comes from polarographic measurements (See Table 1). The difference between the half-wave potentials for n = 2 versus n = 3 is 0.40 volts or about 9.2 kcal/mole in favor of the trione. This difference is accentuated if the phenyl groups are replaced by ethoxy substituents (LIV). Here the difference between n = 2 and n = 3 is almost 1 volt (23 kcal/mole). The difference in LIII for n = 3 versus n = 4 is virtually zero for the first reduction but is about 0.20 volts for the second. This suggests that it is very likely that the process of going from the semitetraone to the semitrione is exothermic for the di-phenyl case, and probably of low activation energy. The work of Ono on the reduction of triones in water (54a), shows that these compounds are very easily reduced, with the parent compound, HCOCOCHO, being reduced even more easily

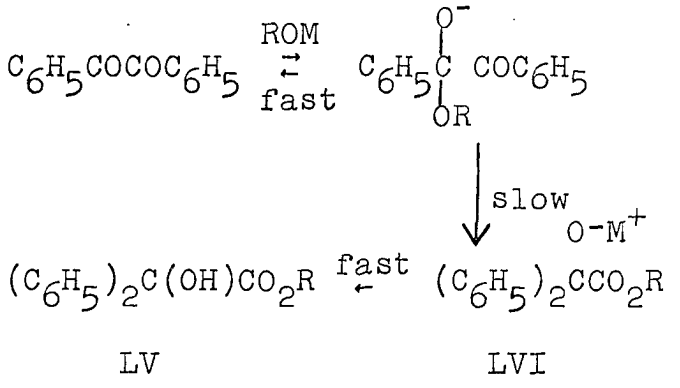
than dehydroascorbic acid.

In examining the second possibility, it is instructive to understand the behavior of benzil under similar conditions. When benzil is treated with a variety of alkoxide bases with either the corresponding alcohol or DMSO as solvent, XLIV is observed spectroscopically (77). However this does not mean that no other reactions are occurring in solution. In fact, it is obvious that the benzilic ester rearrangement must be occurring (78). With t-BuOK as the base and refluxing t-BuOH as the solvent, benzil was converted to t-butyl benzilate (LV, R = t-Bu) and benzilic acid, the former in 76% yield and the latter in 10% yield (79). This also occurs in ether solution (80). With NaOMe in methanol, the products were 68% methyl benzilate (LV, R = CH_3), 9.7% benzilic acid, and 9.6% benzoin (79). With sodium ethoxide in ethanol, ethyl benzoate and benzaldehyde were the major products with only a slight trace of benzilic acid (81). This was thought of as a collapse of the initial benzil-sodium ethoxide adduct with a molecule of ethanol serving as a proton donor (81). With sodamide as



the base in refluxing xylene, benzilic acid was isolated (presumably formed by hydrolysis of the amide on workup) (82). It is now held that with ethoxide or isopropoxide as the base,

benzil undergoes reduction to benzoin rather than the benzilic ester rearrangement (78, 79). The generally accepted mechanism for the benzilic ester rearrangement is outlined below (78, 79). If this rearrangement occurs in



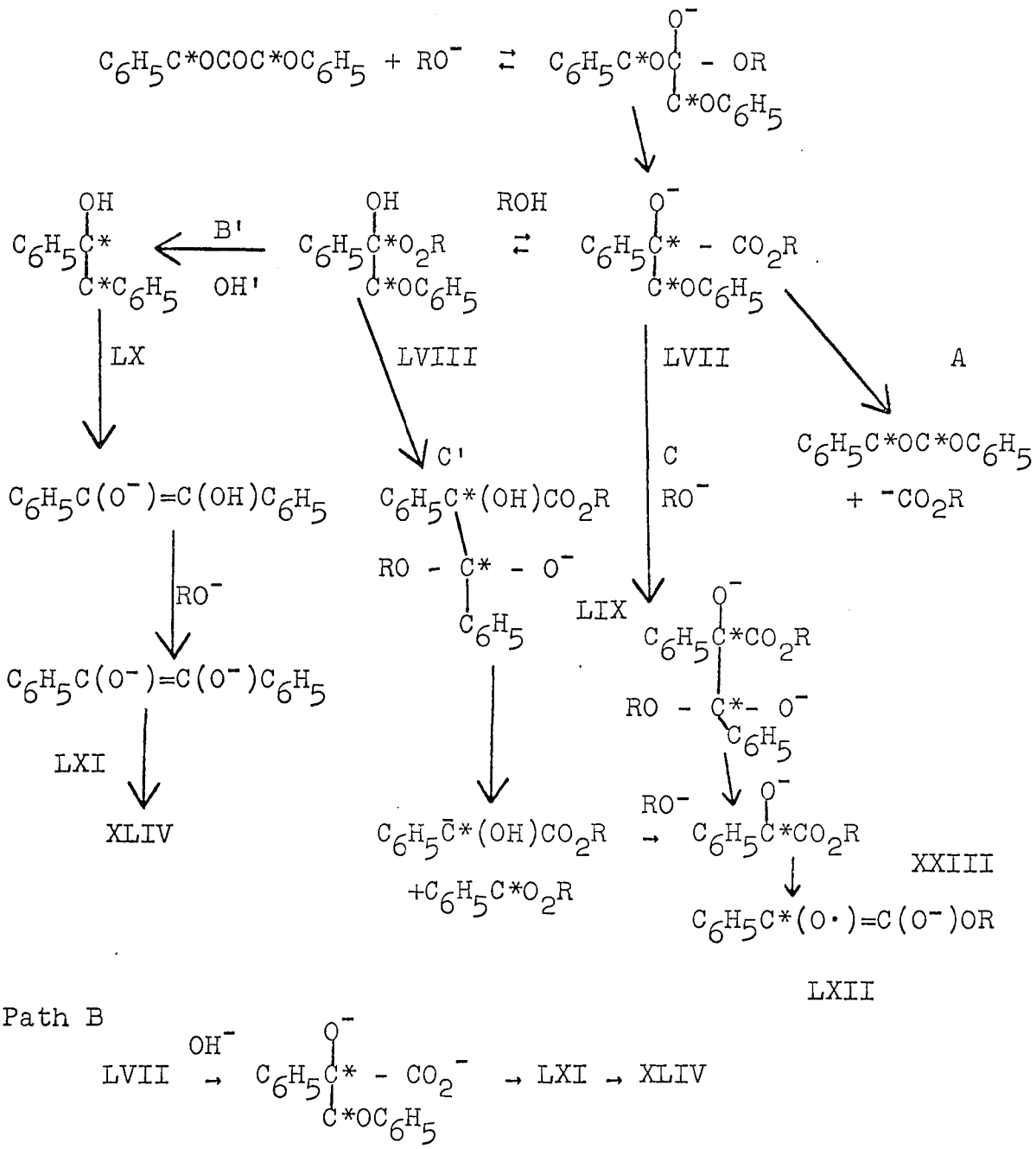
LV LVI

DMSO solutions with t-BuOK, it would not affect the e.s.r. signal unless all of the benzil is rapidly converted to LVI, which is unlikely. Even if LVI were hydrolysed by trace amounts of water followed by decarboxylation to yield benzophenone, this would not be expected to be converted to the ketyl under the conditions employed (18). Also in the presence of benzil, if the ketyl were formed it would probably transfer an electron to form XLIV and benzophenone. It is of some interest to point out that this rearrangement can account for the formation of 9-fluorenone from 5,6-phenanthrenequinone with dilute aqeous sodium hydroxide (83), 9-hydroxyfluorene-9-carboxylic acid with concentrated sodium hydroxide solutions (83,84), and 4,5-diazafluoren-9-one from 1,10-phenanthroline-5,6-quinone (85).

Diaryl triketones are also converted to the corresponding

diketones by the action of base (86-89). In 1890 von Pechman treated DPPT with aqueous sodium hydroxide and found benzoin, benzoic and mandelic acids, and carbon dioxide to be the products (86). More recently, the corresponding products were isolated when 1,3-(2,4,6-trimethyl)-phenyl-1,2,3-propanetrione was treated similarly (90). Pechman suggested that his results were best explained by a rearrangement similar to the benzilic acid rearrangement except that now the migrating group was a benzoyl group with its pair of electrons rather than a phenyl group with its pair of electrons. In the original mechanism R = H and path A was not considered. However in water solutions LVII is almost surely converted to LVIII. The second pKa of mandelic acid is reported to be between 15 and 16 (51,52). It is obvious that for R = H, paths B' and C' lead to the observed products. Clearly path A is untenable for R = H for then LVII would swiftly be converted to LX. If we now let R be an alkyl group, path A must be examined. It is not obvious why path A should not be followed when the solvent is 100% DMSO but is followed when some alcohol is added. Clearly path A and the production of LXII are incompatible as, from polarographic data, LXII would transfer an electron to benzil to produce XLIV. Thus path A is ruled out. If there is some water present, LVII is hydrolysed and goes to LXI, via path B or B', and LXI in turn yields XLIV. However in 100% DMSO which has been

Scheme I



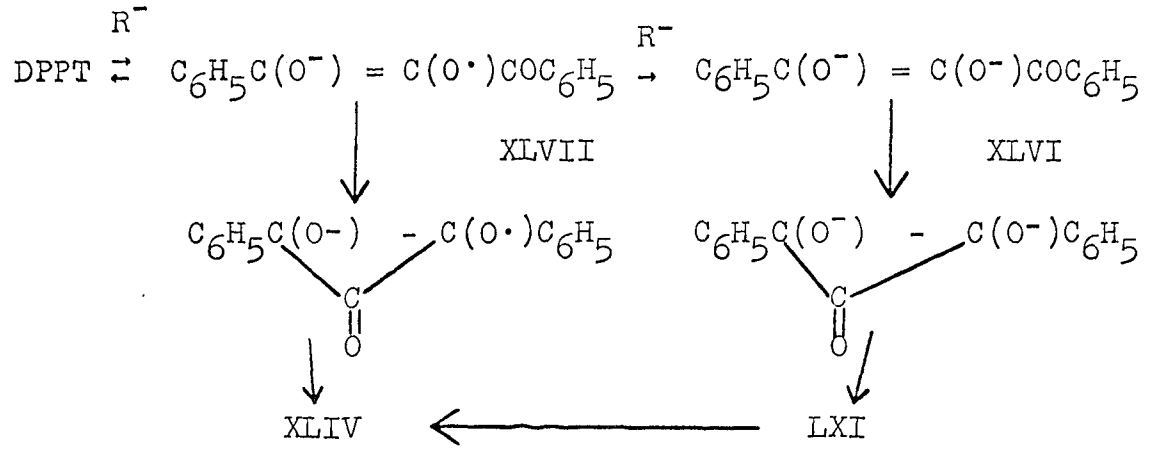
Path B

carefully dried, LVII is converted to XXIII via path C in the presence of an excess of base. But XXIII is known to produce LXII under these conditions (30). Further

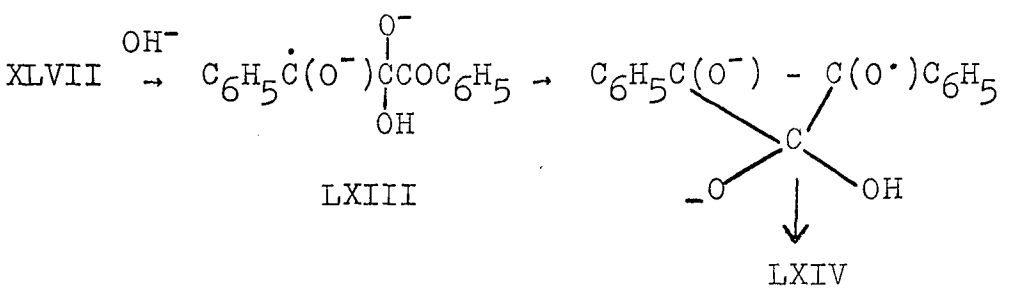
substantiation of this mechanism comes from the more recent work of Roberts (89) who made DPPT labelled at positions 1 and 3 with carbon 14. When this DPPT was decomposed by the action of sodium hydroxide all of the label was retained in the benzoin. The carbon dioxide was not radioactive. Thus the central carbonyl group is lost as is indicated in Scheme I.

However this scheme cannot apply under the conditions employed in the electrolysis of DPPT, the reduction by potassium, nor probably in the presence of propiophenone or XLVII. The inclusion of the latter reagents is supported by Sharp's observation that diethyl sodiomalonate in benzene converts DPPT to benzil (87). Also it is likely that with i-PrOK in i-PrOH, DPPT is reduced to XLV as it is known that benzil is converted to benzoin under these conditions (79). It is also possible that this is the mode of reaction with NaOMe in MeOH (79). A possible mechanism for these transformations is outlined in Scheme II where R^- may be an electron, potassium, or any anion which is capable of transferring an electron to DPPT. The first step involves a simple electron transfer. Any agent capable of reducing benzil (e.g., propiophenone enolate) can also reduce DPPT. In this regard it must be remembered that all of the alkoxide ions are apparently capable of doing so. Depending on the amount of water which would exist almost entirely as the

Scheme II



hydroxide ion under these conditions, it is possible that the reaction proceeds through the dianion radical LXIII as outlined in the following equation. Dianion radicals have



recently been made by the reduction of β-diketone enolate anions with alkali metals in ether solvents (91). It is also possible that XLVI is formed by the disproportionation of two molecules of XLVII. There are many reactions in which a radical anion is presumed to disproportionate to the dianion and starting material (23, 24, 92, 93). It is also conceivable that the dianion arises from a second one electron reduction or from an initial two electron reduction.

Evidence in favor of the disproportionation in this system stems from the fact that the electrolytic reduction of biacetyl in either DMSO or DMF yields 2,5-dimethylsemiquinone as the only detectable intermediate even at potentials just above the half-wave potential (See Figure 16). Furthermore electrolytic reduction of phenylglyoxal in DMSO at potentials of from 1.5 to 4 volts leads only to $C_6H_5C(O^-)=C(O^\cdot)CH_3$ rather than the expected XXXIV (See Figure 17). These reactions are both known to be initiated by base, the latter specifically requiring the dimethyl sulfinyl carbanion (29, 68, 90). Both DMSO and DMF are considered aprotic solvents (6) and it is extremely unlikely that a semidione is capable of removing a proton from either of them (94). It is also unreasonable to expect a semidione to remove a proton from biacetyl. Thus it would appear that dianions had been generated as these are known to be sufficiently basic to remove a proton from DMSO (94). It is possible that the reaction of DPPT with either i-PrOK or NaOMe in 100% DMSO follows this scheme. However if this were the case, radical anion LXII should not have been observed. Even if we allow Schemes I and II to be operable simultaneously, this would predict either the production of XLIV or mixtures of XLIV and LXII. From the reduction potentials in Table 1, it is apparent that if LXII were formed it would transfer an electron to benzil to yield XLIV. Experimentally, it would appear that Scheme II is not

Figure 16. First-derivative e.s.r. spectrum of 2,5-dimethylsemiquinone in DMSO.

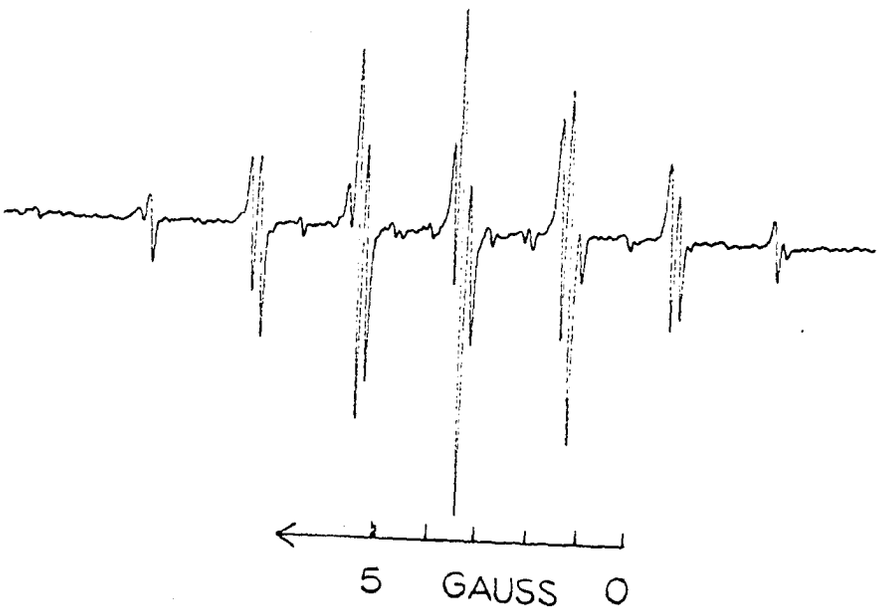
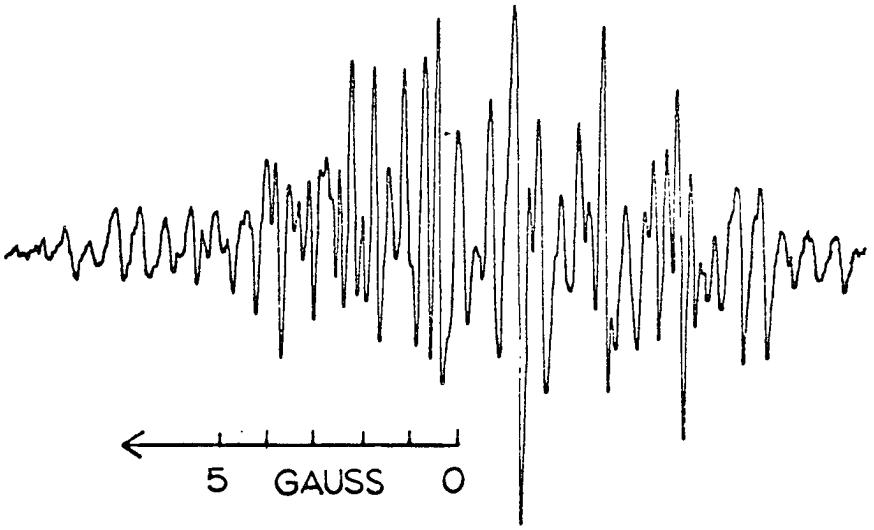
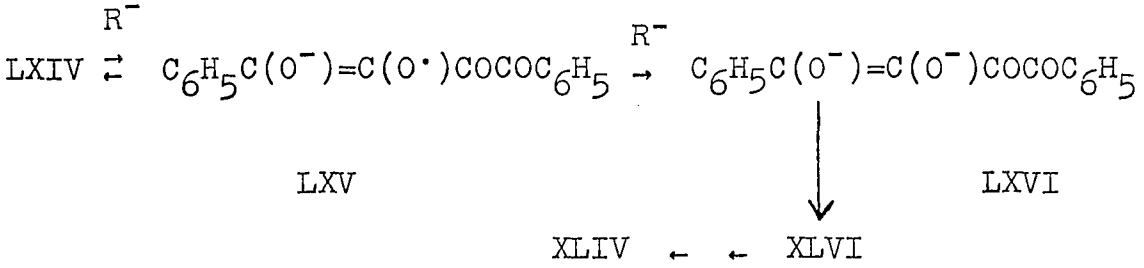

5 GAUSS 0

Figure 17. First-derivative e.s.r. spectrum of the radical anion of 1-phenyl-1,2-propanedione in DMSO.

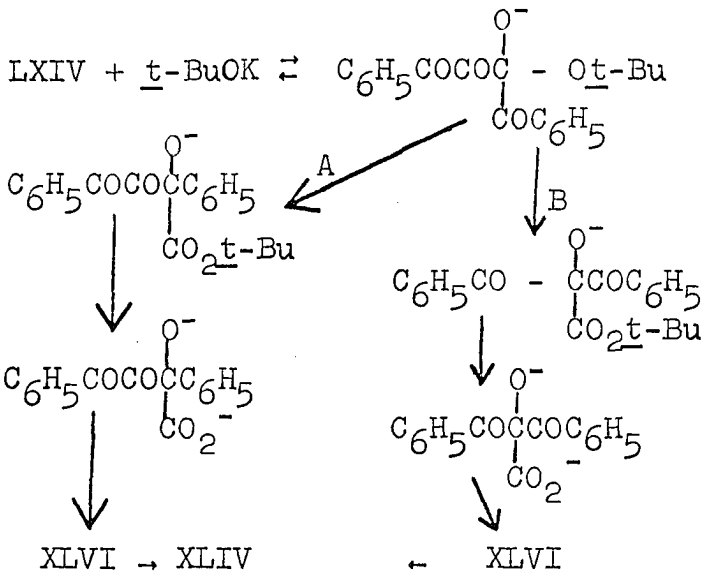

5 GAUSS 0

operable under these conditions. This would seem to demand that the rate of rearrangement of the initial adduct of DPPT with the alkoxide ion to LVII be very much faster than the rate of electron transfer to DPPT (79). Finally the electrolytic reduction of DPPT obviously follows Scheme II. At high potentials only XLIV is observed. At low potentials XLVII is observed as well as a trace amount of XLIV. This is more evidence for the disproportionation of radical anions.

The behavior of 1,4-diphenyl-1,2,3,4-butanetraone (LXIV) when electrolytically reduced or in the presence of its dianion is best explained in a manner similar to Scheme II.



In this case, the dianion LXVI is formed even more readily than from DPPT (see Table 1). Thus the equilibrium between LXV and LXVI would favor LXVI relative to that between XLVI and XLVII. Clearly LXVI would be expected to go on to XLIV. When LXIV is mixed with t-BuOK in DMSO it is possible that LXV or LXVI is formed. But it is more reasonable to suppose that the reaction proceeds by a mechanism analogous to Scheme I.



Path B involves the migration of a benzoyl group while A that of a phenylglyoxyl group. In any case, they both lead to the formation of XLVI which in turn goes on to XLIV as outlined in Scheme II. The possible loss of two molecules of carbon monoxide simultaneously probably does not occur. Fuson has reported that when 1,4-(2,4,6-trimethylbenzene)-1,2,3,4-butanetetraone is decomposed in basic solution the trione is one of the products isolated (90, 95). Presumably the failure to observe any benzoyl formate radical anions is due to the fact that the LXIV used was a mixture of the hydrate and the anhydrous material.

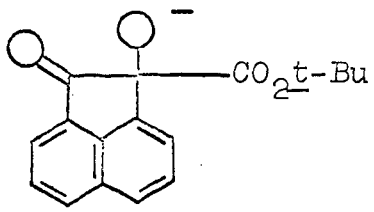
When 2,3,4-pentanetrione is reduced in the presence of propiophenone, 2,4-pentanedione, or 3-hydroxy-2,4-pentanedione in solutions of t-BuOK in DMSO, it is reasonable to assume that the base reacts with these more acidic compounds to form the anion which then transfers an electron to the trione.

Under these conditions, Scheme II is a satisfactory description of the observed behavior. However when the ethyl hemiacetal is reacted with t-BuOK in DMSO, there are several possibilities. Presumably the ethyl alcohol is removed and is converted to the ethoxide ion by t-BuOK. Since there is an excess of t-BuOK, it is likely that this solution contains both alkoxide ions. If either initiates reaction to dimethylsemidione via Scheme II, this would not matter. However Scheme I would predict the formation of LXVII, R = CH_2CH_3, t-Bu which might then be assumed to yield LXVIII. But it has been pointed out earlier that when the

LXVII LXVIII

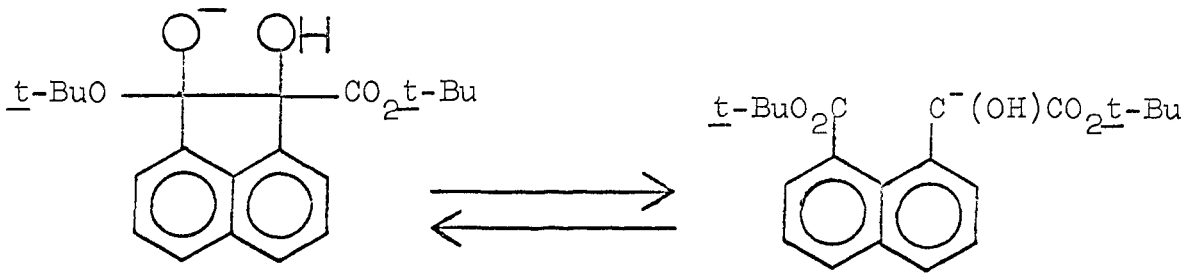
lactate esters, precursors to LXVII, are treated with t-BuOK in DMSO, XXIV is observed rather than LXVIII. Clearly then the behavior of 1,2,3-pentanetrione is consistent with Schemes I and II.

While the decarbonylation of 1,2,3-phenalenetrione, L, to yield acenapthenesemiquinone with t-BuOK in DMSO had been noted previously (74), no mechanism was given. If the reaction proceeds via Scheme II there is no difficulty in explaining the product. However it is felt that Scheme I is the more reasonable path for this reaction. In that case, LXIX becomes the crucial intermediate. Assuming that it does not



XLIX

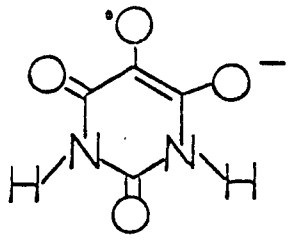
hydrolyse and decarboxylate prior to further attack by t-BuOK, LXX would be formed. But LXXI which is the precursor to



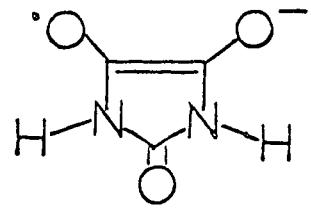
LXX LXXI

any benzoylformate radical anion would be expected to close to LXX rather than the other way round. Thus Scheme I fits this case as well.

At this point it is reasonable to re-examine the evidence in support of the reports that ninhydrin and alloxan, XLI, are converted to the semitriones under basic conditions (68, 72). Alloxan itself is not converted to the radical anion LXXII by t-BuOK in DMSO. However this conversion is effected when propiophenone or 9,10-dihydroanthracene are present. Compound LXXII was reported to have two equivalent nitrogen atoms and two equivalent hydrogen atoms. However there is no evidence to show that LXXII is not LXXIII. Reactions proceeding via

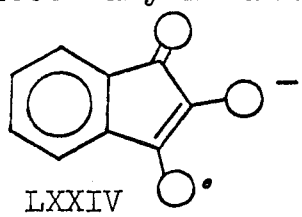


LXXII

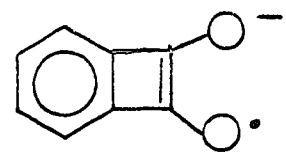


LXXIII

Scheme II have led to decarbonylations in other cases. The ninhydrin radical anion, LXXIV, is formed from ninhydrin by t-BuOK in DMSO both with and without propiophenone in solution. In t-BuOH, propiophenone or 9,10-dihydroanthracene is necessary in addition to t-BuOK to form LXXIV. Adams



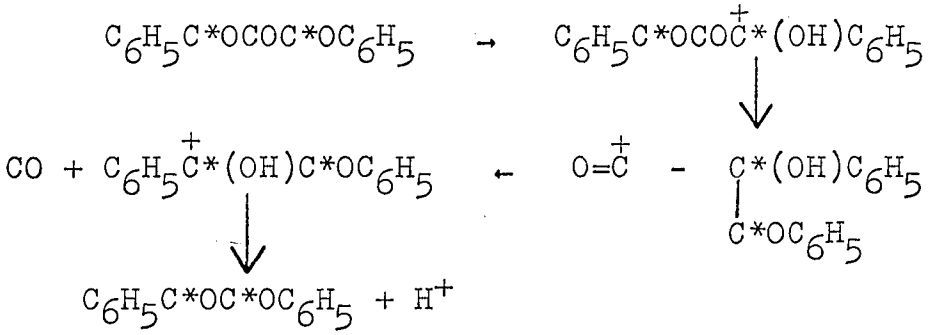
LXXIV



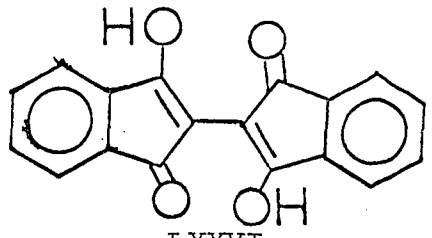
LXXV

reports splitting constants of 1.95 and 1.59 gauss for the two pairs of equivalent protons of LXXIV in aqueous ethanol (68). Russell reports four equivalent protons with a splitting constant of 0.97 gauss in DMSO (72). Fortunately LXXV has been reported (96). In acetonitrile it shows two pairs of equivalent protons with splitting constants of 3.74 and 1.87 gauss. Clearly these values for the splitting constants make it unreasonable to believe that LXXIV was converted to LXXV. It is possible that the failure to eject carbon monoxide stems from the fact that a benzocyclobutadiene would be formed. However there is no indication of any instability

in LXXV other than a slightly high concentration of spin density in the benzene ring (96). More evidence for the unwillingness of ninhydrin to eject carbon monoxide is obtained from the behavior of ninhydrin in acid solutions. A mechanism similar to Scheme I in that the migratory group is a benzoyl group with its pair of electrons has been proposed to explain several acid catalysed decarbonylations (89, 97). The scheme is illustrated for DPPT labelled at the terminal carbons. The labelling work was done by



Roberts (89). In fact when DPPT is heated in sulfuric acid solutions (98), with acetic acid containing either cupric acetate (89) or sulfuric acid (99), or in the presence of aluminum chloride (89, 97) benzil is produced. But when ninhydrin is heated in sulfuric acid solutions LXXVI is the only product isolated (98). It is interesting



LXXVI

to note that LXXVI is converted to LXXIV in solutions of t-BuOK in DMSO (72). Apparently ring contractions to yield the four membered ring from the corresponding benzo substituted five membered ring are difficult to achieve.

3. Oxidation of β-dicarbonyl compounds

Because of the general availability of β-dicarbonyl compounds, LXXVII, an attempt was made to oxidize them by reaction with t-BuOK in DMSO and then carefully admitting small amounts of oxygen to the mixture. When this was done

RCOCHXCOY

LXXVII

LXXVII a. R = Y = CH_3, X = H

b. R = Y = C_6H_5, X = H

c. R = CH_3, Y = OCH_2CH_3, X = H

d. R = C_6H_5, Y = OCH_2CH_3, X = H

e. R = Y = CH_3, X = Cl

f. R = Y = C_6H_5, X = Br

g. R = C_6H_5, Y = CH_3, X = Cl

h. R = Y = OCH_2CH_3, X = Br

i. R = Y = OCH_2CH_3, X = H

with LXXVII a-d, no e.s.r. signal was obtained. These results were not too surprising as it is known that LXXVII d,i, and 5,5-dimethyl-1,2-cyclohexanedione (dimedone) do not absorb oxygen in solutions of t-BuOK in t-BuOH (37). Even in solutions of t-BuOK in t-BuOH containing as much as 80% DMSO

by volume, LXXVII b is known to be inert to oxygen and LXXVII a, c react only sluggishly as measured by oxygen uptake (36). It is known that while some ketones cannot be oxidized to the semidione by t-BuOK in DMSO, the monobromo compound is easily converted to the semidione (29). Accordingly LXXVII a-d and dimedone were placed in a solution of t-BuOH containing either bromine or iodine and these solutions mixed with t-BuOK in DMSO such that the final solution was 75% DMSO by volume. Again no paramagnetic intermediates were observed. In order to eliminate the possibility that the lack of signal was due to some difficulty in effecting in situ halogenation, LXXVII e-h and 2-bromodimedone were isolated and the pure compounds were treated with t-BuOK in DMSO. They too failed to produce radical anions. However there are two paths by which the bromo ketone can conceivably be converted to the semidione. One is by oxidation of the bromo ketone by DMSO to yield the dione or trione (29, 38, 40). However this does not occur immediately with bromo esters at room temperature (38, 40). Apparently the same is true for LXXVII e-g. The other path is simple hydrolysis of the halide by trace amounts of water in solution to yield some hydroxy ketone. However in the case of compounds such as LXXVII, it is possible that they are so highly enolized in the basic medium that the halide could not be replaced (see Table 3) (100, 101a). This might also be the explanation for the failure of DMSO to

Table 3. Enolization of β-dicarbonyl compounds (RCOCHXCOY)

R	X	Y	% Enol	Reference
C_6H_5	H	C_6H_5	100(CCl_4)	100
C_6H_5CO	OH	C_6H_5	57[a]	101b
C_6H_5	OH	C_6H_5	98(pH5)	102a
C_6H_5	H	CH_3	100(CCl_4)	100
C_6H_5	OH	CH_3	48(pH7)	102a
C_6H_5	H	OC_2H_5	22	100
CH_3	H	CH_3	81	100
CH_3	Br	CH_3	46	100
CH_3	Cl	CH_3	94	100
CH_3	OH	CH_3	32(pH6-7)	102b
CH_3	H	OC_2H_5	8	100
CH_3	Br	OC_2H_5	5	100
CH_3	Cl	OC_2H_5	15	100
CH_3	OH	OC_2H_5	47(pH7)	103a
Dimedone			93[b]	103b
α-Bromodimedone			98[b]	103b

[a]Exists as $C_6H_5C(OH) = C(OH)COCOC_6H_5$.

[b]In dilute aqueous solutions, 0.1M $HClO_4$.

oxidize LXXVII e-g. As a test of this hypothesis 2,2,6,6-tetrabromocyclohexan-1-one, 1,4-dibromo-2,3-butanedione, and LXXVIII were reacted with t-BuOK in DMSO. These compounds

$CH_3COCBr_2CO_2CH_2CH_3$

LXXVIII

were not converted to radical anions.

It is apparent at this point that in order to obtain compounds such as LXXVII, X = OH, they or a more direct precursor than the halo compounds must be used. Therefore compounds LXXVII j-h were synthesized.

$RCOCHXCOY$

LXXVII

LXXVII j. R = Y = CH_3, X = OH

k. R = Y = CH_3, X = O_2CCH_3

l. R = Y = C_6H_5, X = OH

m. R = Y = C_6H_5, X = O_2CCH_3

n. R = CH_3, Y = C_6H_5, X = OH

o. R = CH_3, Y = C_6H_5, X = O_2CCH_3

p. R = CH_3, Y = OCH_2CH_3, X = OH

q. R = CH_3, Y = OCH_3, X = OH

r. R = CH_3, Y = OCH_2CH_3, X = O_2CCH_3

s. R = C_6H_5, Y = OCH_2CH_3, X = OH

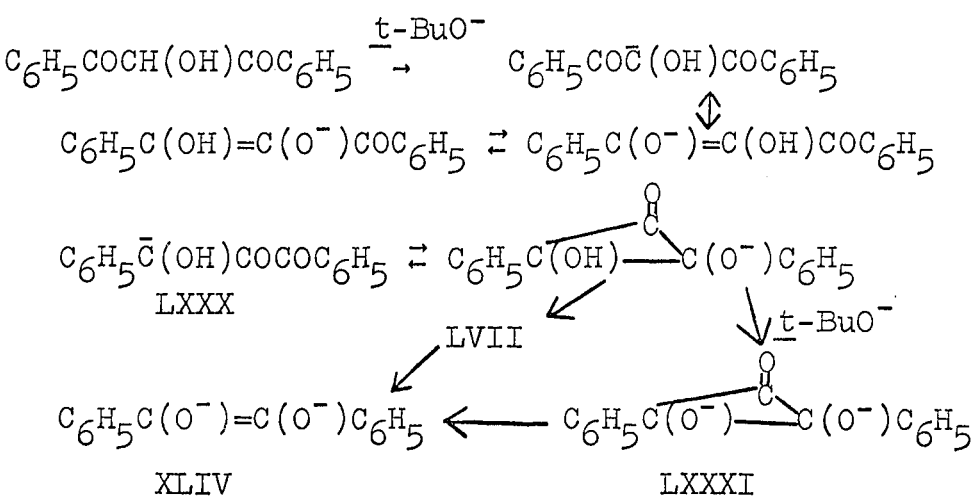
t. R = C_6H_5, Y = OCH2CH_3, X = O_2CCH_3

Both LXXVII j and k produced XXIV when treated with t-BuOK in DMSO. Similarly LXXVII l yielded XLIV. However when LXXVII m was used, $C_6H_5C(O^-) = C(O^\cdot)H$, XXXIV was obtained rather than XLIV. The spectrum was identical with the

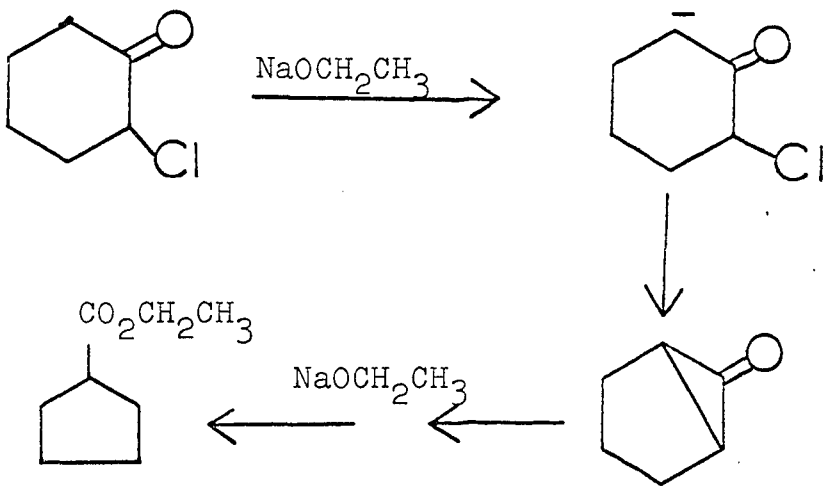
published spectrum of XXXIV (29). Furthermore on standing over several hours, XXXIV was transformed into the radical anion of 1-phenyl-1,2-propanedione, LXXIX (29). This same dichotomy was also observed with LXXVII n and o. Again LXXVII n produced LXXIX while LXXVII o yielded XXXIV. Furthermore if a solution of LXXVII o in DMSO is treated with tetramethylammonium hydroxide in DMSO prior to mixing with t-BuOK in DMSO, LXXIX is produced.

Compounds such as LXXVII j, l, and n are known to be highly enolized (see Table 3). The enediols are known to be very easily oxidized to the corresponding triketones (102-109). Assuming that this oxidation occurs to some extent with t-BuOK in DMSO, the results are best rationalized on the basis of Scheme II with the dianions of LXXVII j, l, and n serving as the reducing agents. However because of this keto-enol tautomerism another mechanism is possible.

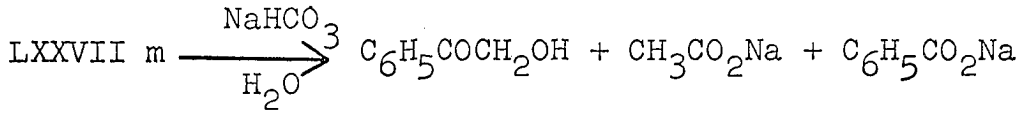
Scheme III



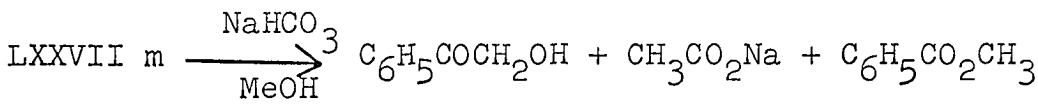
This is illustrated for LXXVII l. Certainly some LXXX is present in solution. If this anion closes as suggested, then LXXXI becomes a logical intermediate. Compound LXXXI also appears as an intermediate in Scheme II. Finally the conversion of LXXX to LXXXI is analogous to the mechanism of the Favorskii rearrangement (78) which is outlined below.



The fact that LXXVII m, o produce XXXIV rather than XLIV would indicate that some reaction is taking place prior to hydrolysis of the acetate. This is clearly shown by the fact that LXXVII o will yield XLIV if treated with $(CH_3)_4NOH$ prior to mixing with t-BuOK. A clue to what is occurring with LXXVII m, o is provided by the observations of Blatt (110) and Karrer (111). They reported the reactions illustrated below. Assuming that t-BuOK in DMSO yields the same products then XXXIV would be the expected radical anion as



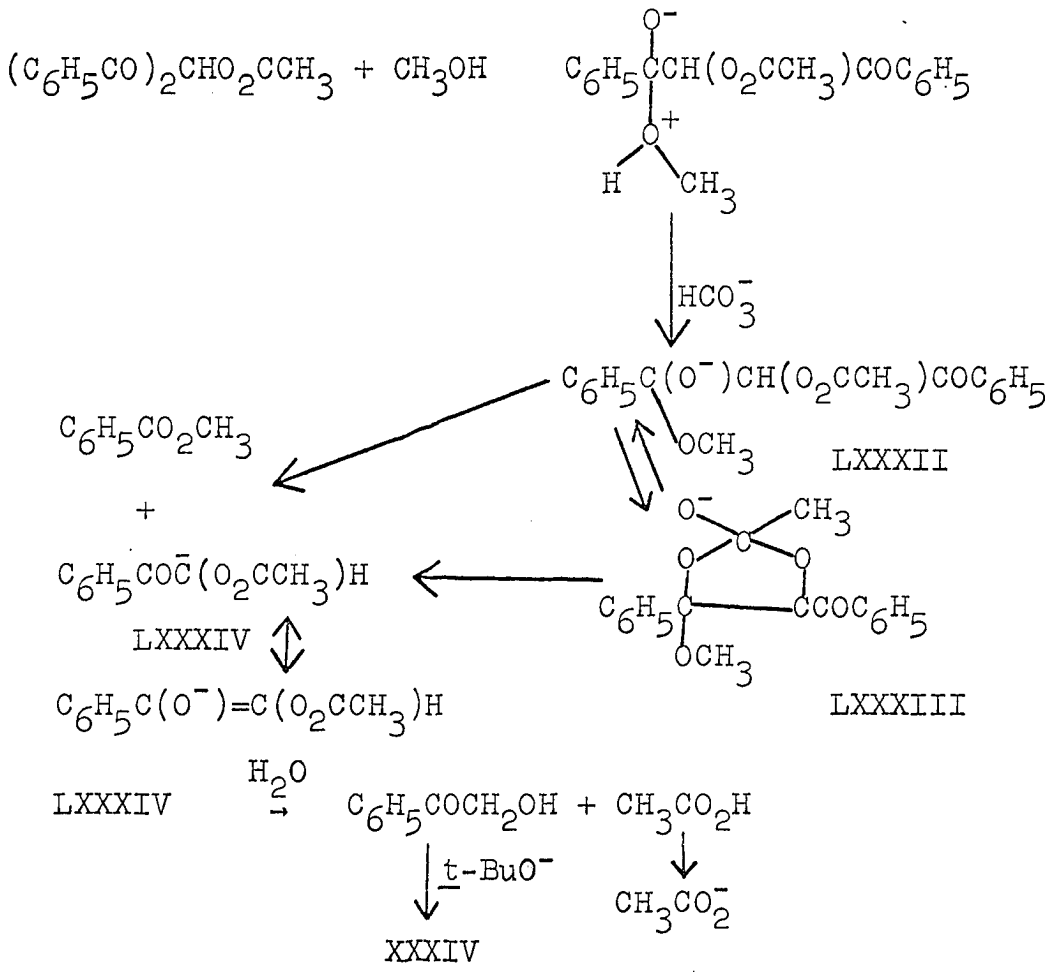
LXXVII m $\xrightarrow[H_2O]{NaHCO_3}$ $C_6H_5COCH_2OH + CH_3CO_2Na + C_6H_5CO_2Na$



LXXVII m $\xrightarrow[MeOH]{NaHCO_3}$ $C_6H_5COCH_2OH + CH_3CO_2Na + C_6H_5CO_2CH_3$

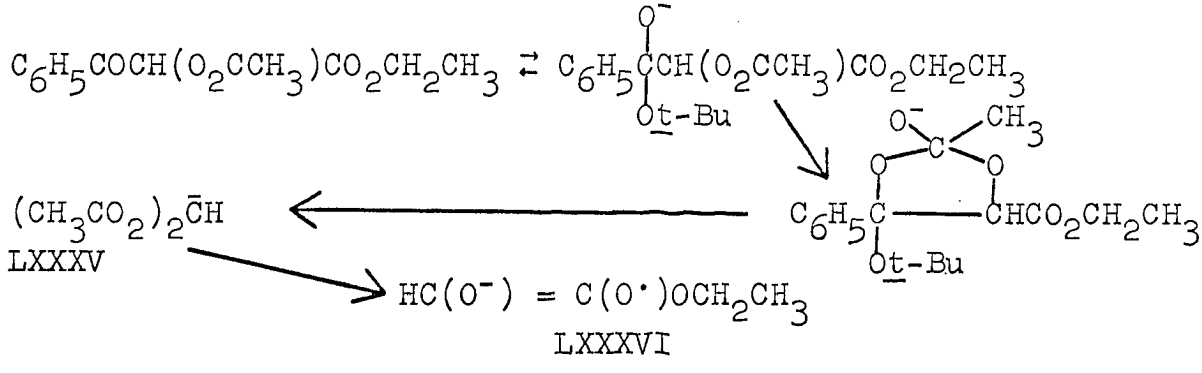
α-hydroxyacetophenone is known to be converted to XXXIV under these conditions (29). A possible mechanism for the conversion of LXXVII m to α-hydroxyacetophenone in methanol is as follows:

Scheme IV



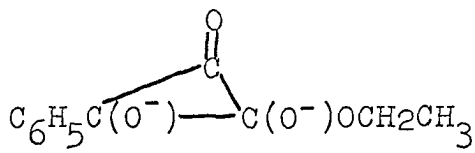
If we envision t-BuOK as the nucleophile instead of methanol, we would expect XXXIV to be produced. Structures similar to LXXXIII have been invoked to account for rate enhancement of solvolyses with acetate as the neighboring group (78). It is very likely that the conversion to LXXXIV proceeds almost entirely through LXXXIII. If this were not the case, LXXVII l would be expected to produce some XXXIV and this is not observed. While this mechanism would appear to apply to the reaction with LXXVII n, it is by no means clear why this should produce only XXXIV and no dimethylsemidione which is known to be produced from acetol under these conditions (29). If any dimethylsemidione were formed, it would be very easy to detect by e.s.r. spectroscopy as its psectrum is much broader than that of XXXIV.

When LXXVII s or t is treated with t-BuOK in DMSO, the known semidione XIX is produced (35). Clearly LXXVII t is converted to LXXVII s prior to production of the semidione. As there is no ester interchange with t-BuOK in DMSO, reaction of t-BuOK with LXXVII t prior to hydrolysis would be expected to yield LXXXV. However no e.s.r. signal was obtained from



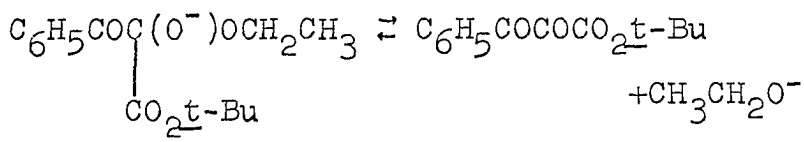
$CH_3OCH_2CO_2CH_3$ under these conditions and LXXXVI would be expected to have a lifetime of less than three seconds (29).

The conversion of LXXVII s to the semidione can proceed via several routes. Scheme III is a very real possibility. With LXXVII s the crucial intermediate in Scheme III is LXXXVII. It is also possible that LXXVII s is oxidized



LXXXVII

to the diketo ester prior to formation of LXXXVII. Reaction according to Scheme I would lead to LXXXVIII. However to

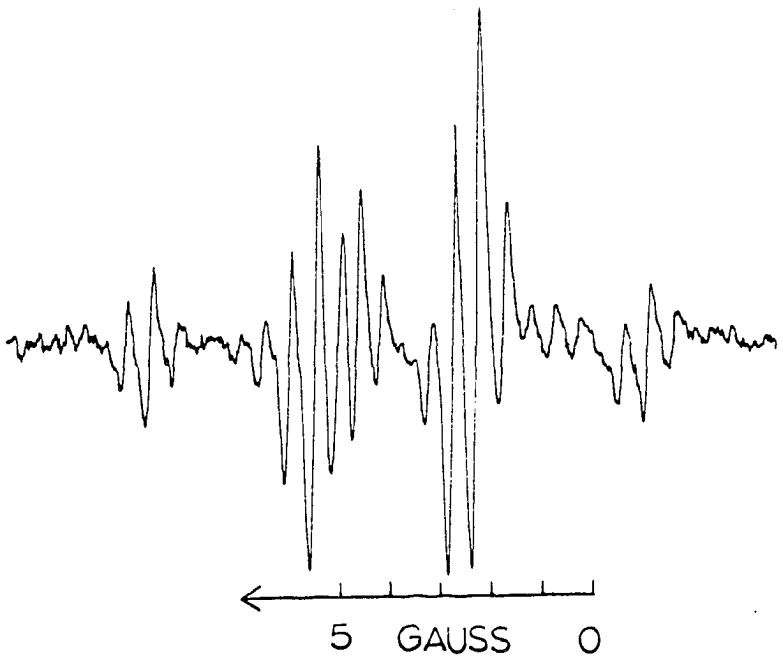


LXXXVIII

get from LXXXVIII to the observed semidione would require reaction along Path A and this has already been shown to be unreasonable. Furthermore if any LXXXVIII were formed it would be expected to produce the t-butyl ester shown, and no radical anions derived from this ester have been observed starting from LXXVII s or t. While Scheme I can thus be ruled out, there is no way to decide whether or not Scheme II is operative under these conditions.

When either LXXVII p or r is treated with t-BuOK in DMSO, the radical anion, LXXXIX, whose e.s.r. spectrum is shown in Figure 18 (top) is obtained. When the solution from LXXVII p was allowed to stand for 20 hours, XC was generated (See Figure 18 (bottom)). Clearly the initial reaction produces two radical anions. Neither however is $CH_3C(O^-) = C(O^\cdot)OCH_2CH_3$, XXIX, as that would require a much broader spectrum than is obtained. The outermost peaks in Figure 18 (top) show a small triplet splitting of 0.5 gauss. Furthermore the spectrum is arranged in four main groups of lines approximately equally spaced. Also the intensities of the groups best fit a 1:3:3:1 pattern. Assuming that this is truly the case and then dividing the distance from the central line of one outermost triplet to the other by three, gives a splitting constant of 3.2 gauss for a methyl group. To test these assignments, LXXVII s was treated with t-BuOK in DMSO and XCI was obtained. The spectrum contained an outermost quartet of lines of binomial intensity with a splitting constant of 0.5 gauss (See Figure 19). Clearly then the ester function has been retained in LXXXIX and XCI. Also the distance from the center of the outermost quartet to its counterpart on the other side of the spectrum divided by three is 3.2 gauss. Again the spectrum breaks down into four main groups approximately 3.2 gauss apart. The middle areas indicate that XC may again be present. A calculated spectrum

Figure 18. First-derivative e.s.r. spectrum of the radical anion of ethyl 2,3-diketobutanoate (top) in DMSO; first-derivative e.s.r. spectrum of the radical anion formed on standing from ethyl 2,3-diketobutanoate (bottom) in DMSO.


5 GAUSS 0

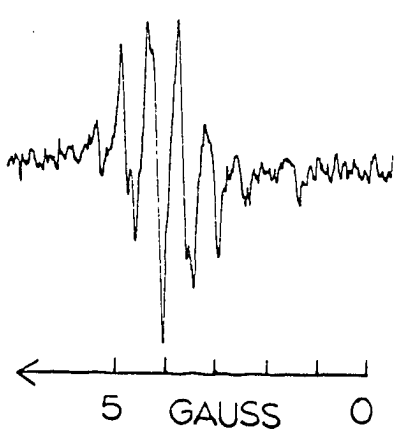
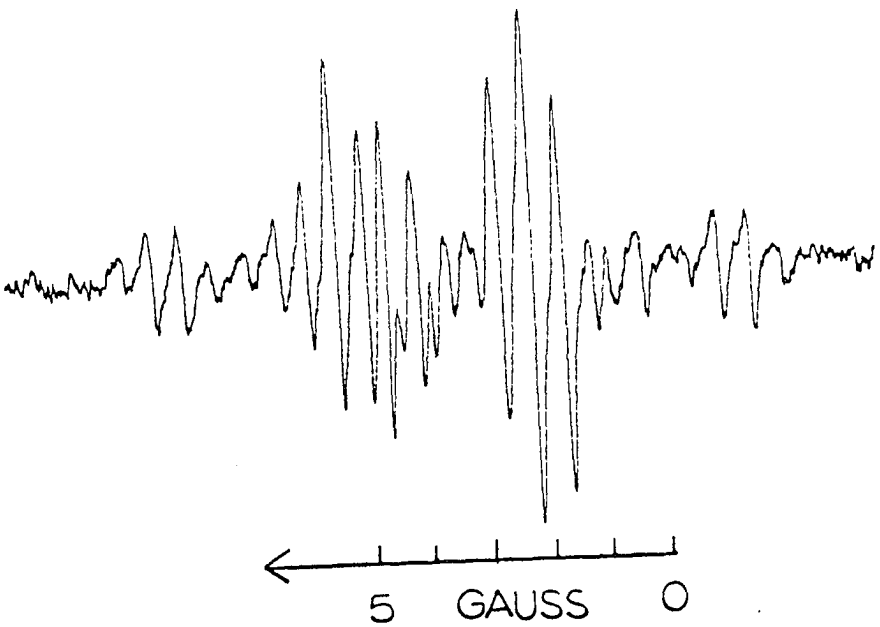
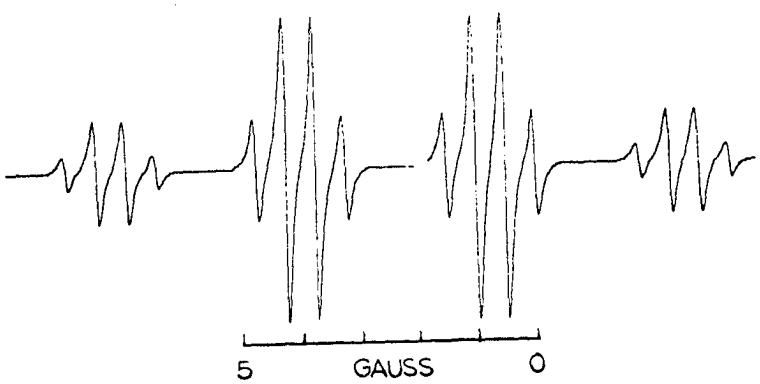

5 GAUSS 0

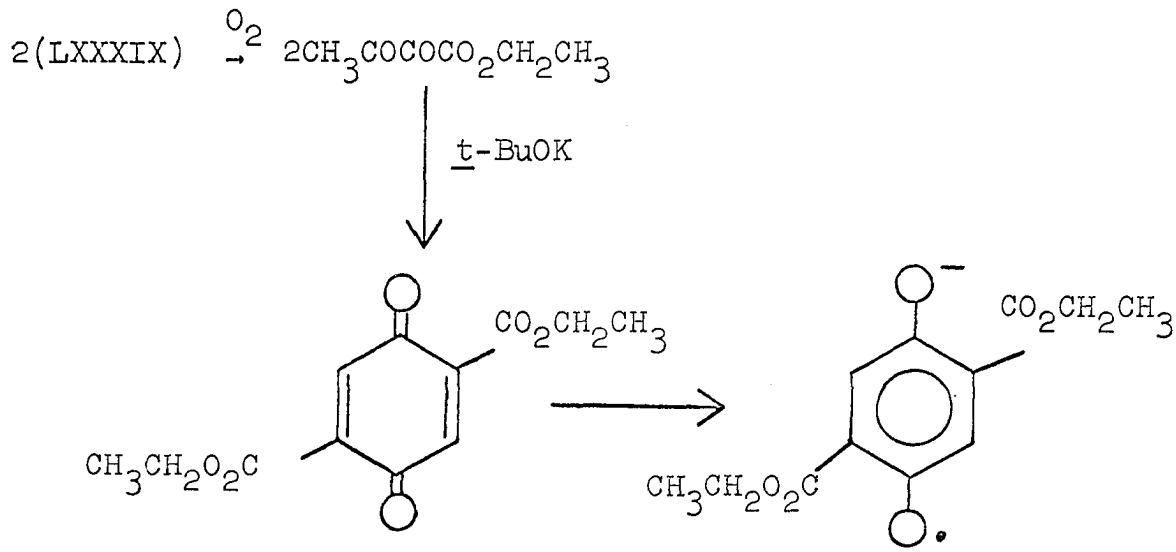
Figure 19. First-derivative e.s.r. spectrum of the radical anion of methyl 2,3-dikobutanoate (top) in DMSO; calculated spectrum for Lorentzian line width (bottom) of 0.2 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.


5 GAUSS 0

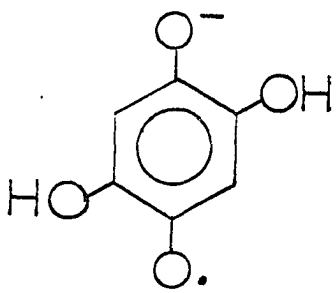

5 GAUSS 0

based on two sets of three protons with splitting constants of 3.2 and 0.5 gauss is also shown in Figure 19. Thus it would appear that LXXVII r-t have generated semitriones. In other words, LXXXIX is $CH_3C(O^-) = C(O^\cdot)CO_2CH_2CH_3$ and XCI is $CH_3C(O^-) = C(O^\cdot)CO_2CH_3$. If we take the ratio of the splitting constants of LXXXIX and XCI to those of the corresponding semidiones, the number turns out to be 0.62. This is certainly in line with that which is to be expected for a semitrione to semidione ratio. The same ratio for the diphenyl radical anions has a value of 0.54 for both sets of splitting constants.

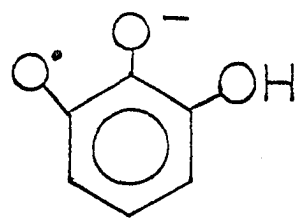
Radical anion XC does not contain two equivalent methyl groups. Also it is highly unlikely that it contains a methyl group next to a carbonyl as the total width of the spectrum is less than 3.5 gauss. The fact that it remains for at least 20 hours, long after LXXXIX has decayed, suggests that it may be a semiquinone. If we assume that all of LXXXIX is converted to the diketo ester than the probable structure of XC becomes obvious. The reactions involved are exactly analogous to the conversion of biacetyl, or even acetoin in the presence of oxygen, to 2,5-dimethylsemiquinone (29). Furthermore when an expansion of the spectrum of XC is compared to a spectrum calculated for two protons with a splitting constant of 0.64 gauss and four protons with a splitting constant of 0.48 gauss, the agreement is good



(See Figure 20). The value of 0.48 gauss for the methylene protons of XC is reasonable in view of the splitting constants of LXXXIX. In XCII, the splitting constant for the two aromatic hydrogens is reported to be 0.81 gauss in water solution (29, 71). If we use this as a model for XC and correct for the difference in solvents by multiplying 0.81 gauss by the ratio of splitting constants of XCIII in water to that in DMSO, then we would expect a value of 0.65 gauss



XCII

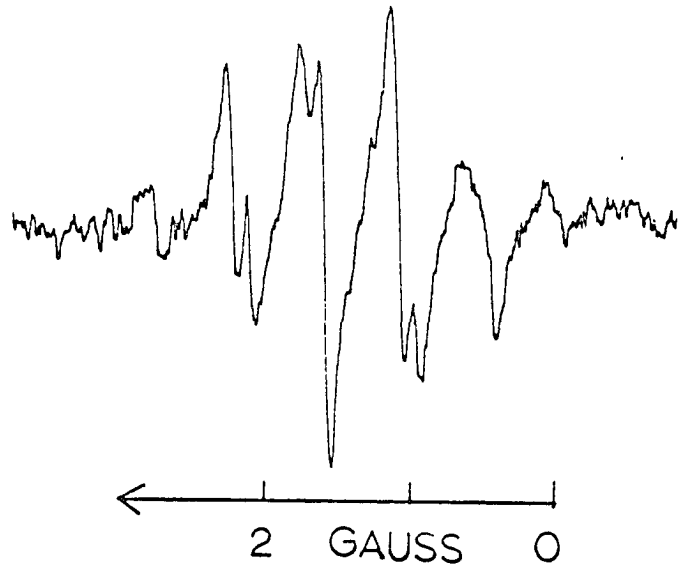


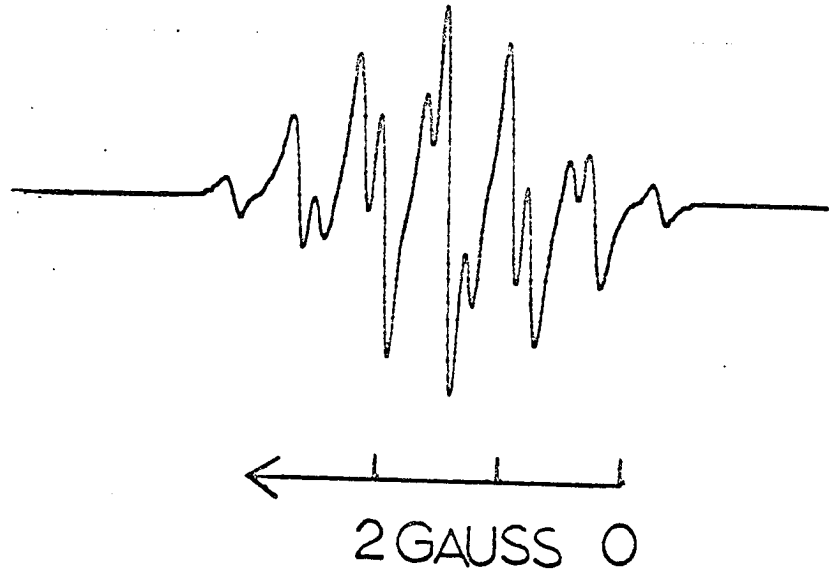
XCIII

for the two protons of XC.

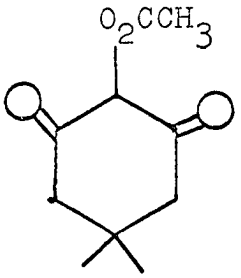
When 2-acetoxydimedone, XCIV, was treated with t-BuOK in DMSO a spectrum was obtained which showed four equivalent

Figure 20. First-derivative e.s.r. spectrum of the radical anion formed on standing from ethyl 2,3-diketobutanoate (top) in DMSO; calculated spectrum for Lorentzian line width (bottom) of 0.15 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.

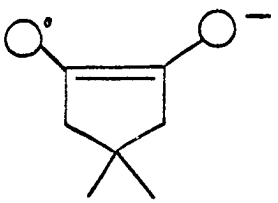

2 GAUSS 0


2 GAUSS 0

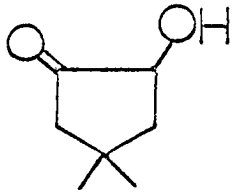
protons with a splitting constant of 12.8 gauss. It was felt that this spectrum was due to XCV. This was shown



XCIV



XCV



XCVI

conclusively when a sample of XCVI was synthesized and mixed with t-BuOK in DMSO. Again the spectrum produced by XCIV was observed (See Figure 21). The reaction of XCIV apparently proceeds by hydrolysis of the acetate followed by cleavage to XCV through Scheme II or III. The reaction of dihydropyrogallol, XCVII with t-BuOK in DMSO led to XCIII. The same spectrum was obtained from pyrogallol (See Figure 22). Semidione XCIII had one proton with a splitting constant of 4.38 gauss and two protons with a splitting constant of 0.8 gauss. The splitting constants are in good agreement with those reported by Adams for XCIII (68). The ratio of the doublet splitting to the triplet splitting in DMSO is equal to that in aqueous solvents. The conversion of XCVII to XCIII can be envisioned as follows:

Figure 21. First-derivative e.s.r. spectrum of the radical anion of 4,4-dimethyl-1,2-cyclopentanedione in DMSO.

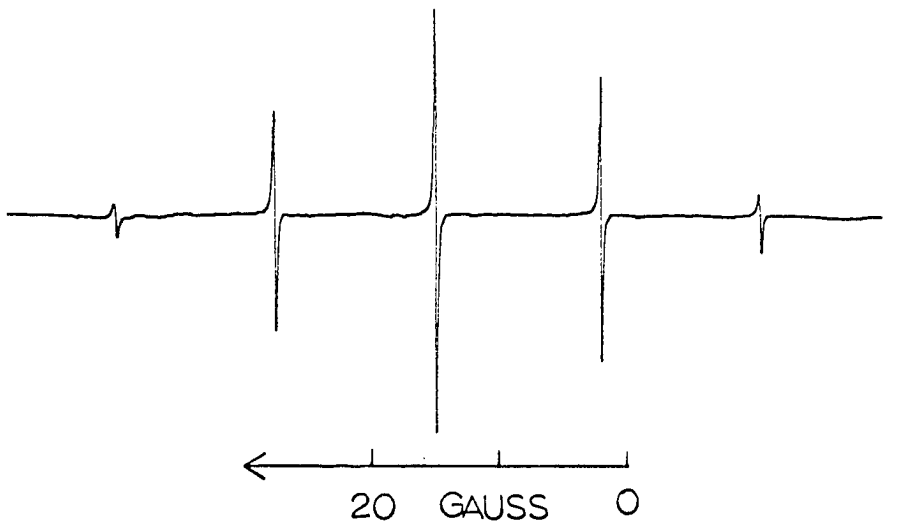
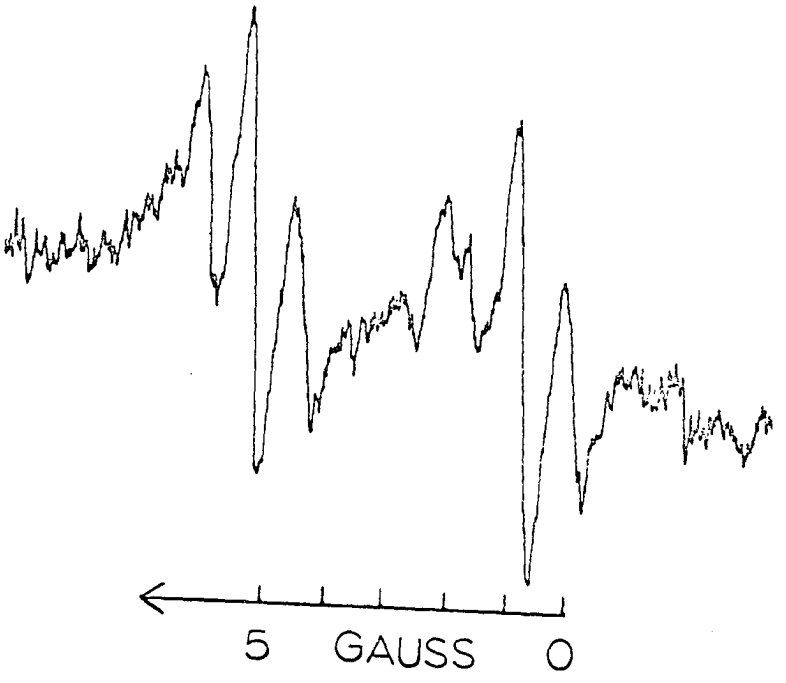
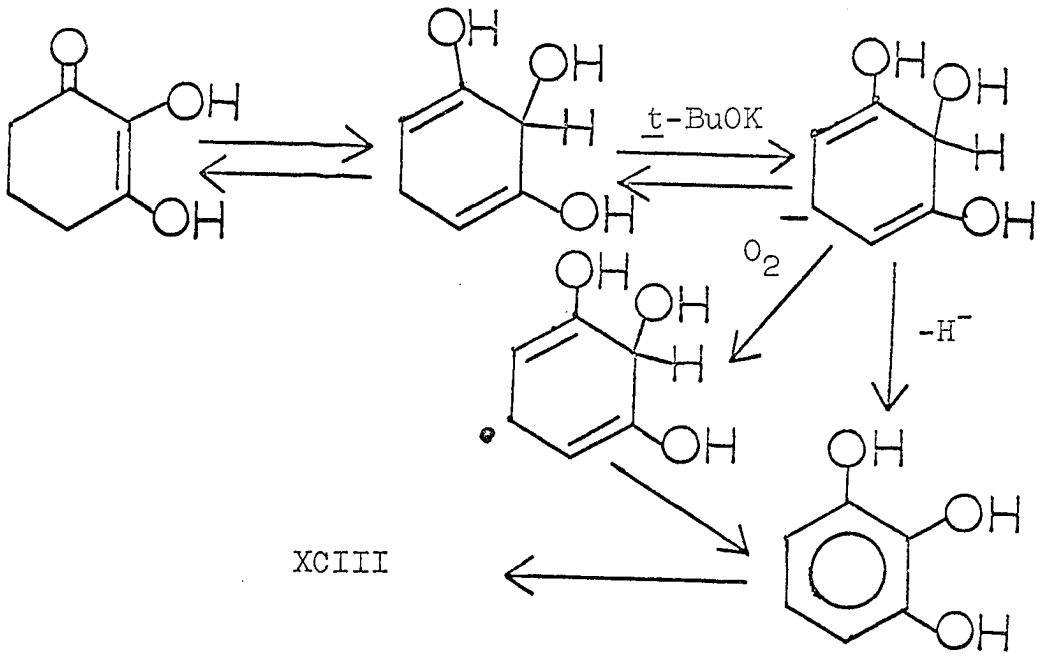

20 GAUSS 0

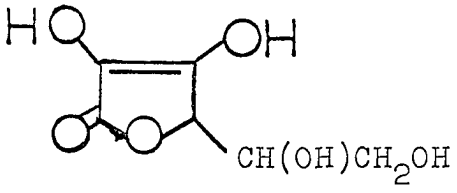
Figure 22. First-derivative e.s.r. spectrum of the radical anion from pyrogallol in DMSO.


5 GAUSS 0

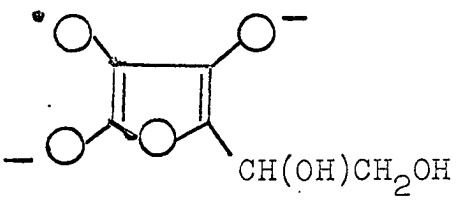


XCIII

The reaction of ascorbic acid, XCVIII with t-BuOK in DMSO led to IC (See Figure 23). The splitting constants



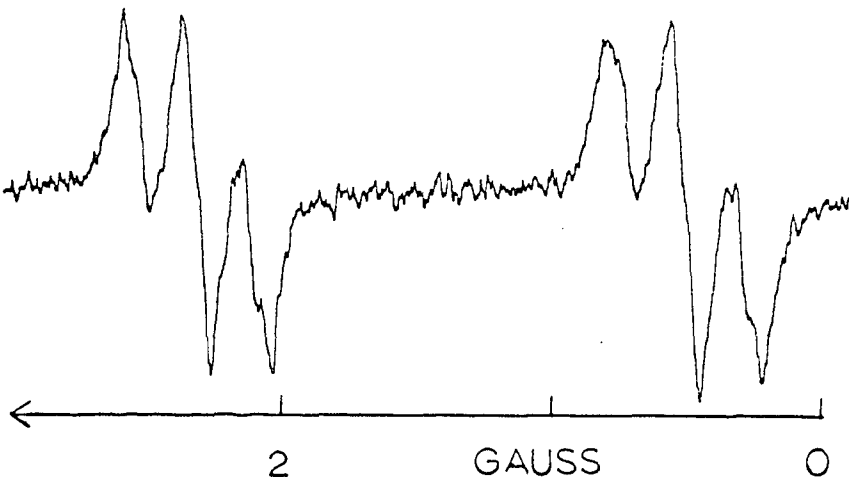
XCVIII



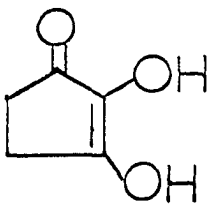
IC

are 0.24 gauss for two protons and 1.84 gauss for one proton. This is in excellent agreement with the values reported for IC in aqueous solutions (69, 70). The fact that XCVIII does not eject carbon monoxide is probably due to the stability derived from the furan ring in IC and may in part be related

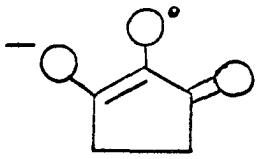
Figure 23. First-derivative e.s.r. spectrum of the radical anion of dehydroascorbic acid in DMSO.


2
GAUSS
0

to the difficulty involved in going from a five to a four-membered ring. The reaction of reductic acid, C, with t-BuOK in DMSO led to a signal which contained only one peak.



C

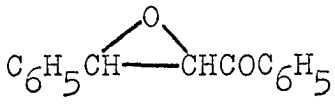


XLIX

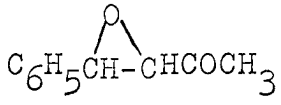
It was hoped that C would be converted to XLIX. Clearly this did not happen. It is unlikely that C would undergo ring contraction and it certainly would not undergo dehydrogenation as dihydropyrogallol had done. It is possible that the one peak is due to an impurity but this is held to be unlikely. Compound C was sublimed prior to use, and no impurities were detected by NMR. This failure to obtain XLIX is especially surprising in view of the fact that Piette had obtained both IC and XLIX starting from XCVIII and C by reaction with H_2O_2 in a solution buffered to pH 4.8 with some horse-radish peroxidase as a catalyst (73). A similar anomaly was encountered by Lagercrantz (71). He was unable to obtain an e.s.r. signal from a solution of HC(OH) = C(OH)CHO in 6N KOH even though $HC(O^-) = C(O^\cdot)CHO$ is known, the latter being obtained by Piette in the manner previously described (73).

An attempt was made to generate semitriones from CI

and CII under basic conditions in DMSO. When CI is mixed



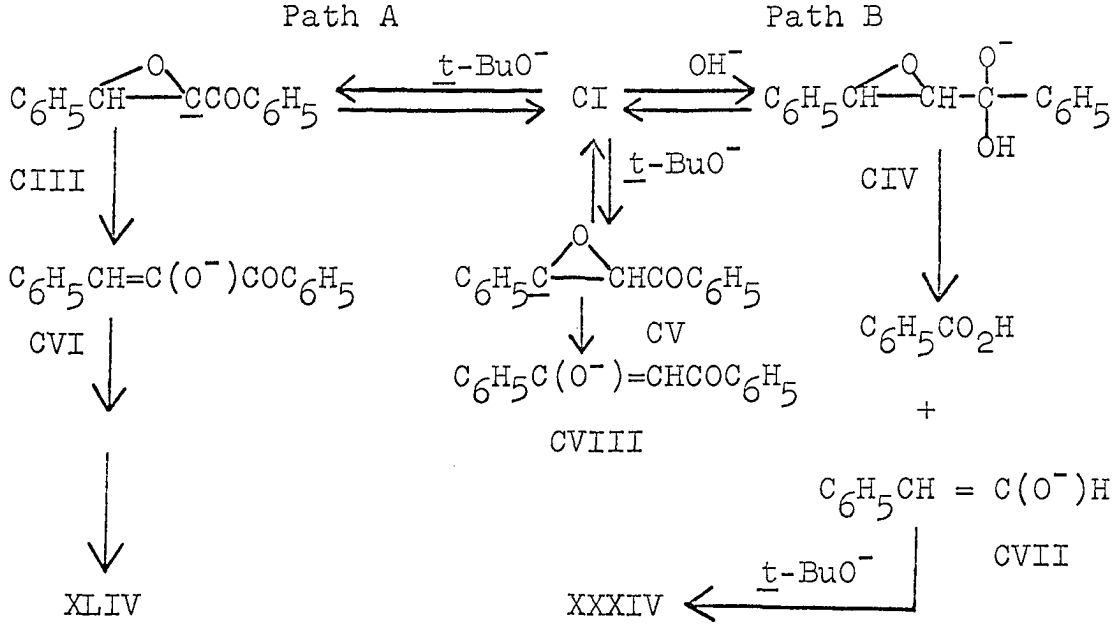
CI



CII

with t-BuOK in DMSO, XLIV is produced. If $(CH_3)_4NOH$ is added to a solution of CI in DMSO prior to reaction with t-BuOK, XXXIV is observed. When CI is hydrolysed under either acidic or basic conditions, 1,3-diphenyl-1,2-propanedione is isolated (112, 113). This latter compound is converted to XLIV by t-BuOK in DMSO. The following scheme is suggested to explain these results. Of the two possible

Scheme V



anions derived from CI, CIII is clearly the more stable.

Furthermore CVIII is the anion of LXXVII b which is known not to be converted to a radical anion with t-BuOK in DMSO. Finally, CVI is the anion of 1,3-diphenyl-1,2-propanedione which is converted to XLIV under these conditions. If we now follow path B, the logical intermediate is CIV. While it is possible that CIV falls apart to styrene oxide as well as, or instead of CVII in a separate experiment it was shown that styrene oxide will not produce XXXIV. Phenylacetaldehyde under these conditions also will not go on to XXXIV. Presumably this is so because it rapidly undergoes self condensation in the strongly basic media. However if CVII were formed either slowly or in very low yield, it is conceivable that it might be converted to XXXIV rather than condense.

When CII is mixed with t-BuOK in DMSO, XXXIV is produced. If $(CH_3)_4NOH$ is added to CII prior to reaction with t-BuOK, LXXIX is produced. In no case is any dimethylsemidione observed. This implies that XXXIV is derived from the epoxy end of the molecule in CI as is indicated in Scheme V. However t-BuOK reacts with CII along path B and $(CH_3)4NOH$ along path A, which is the exact reverse of their behavior with CI. Clearly Scheme V is inadequate as it offers no explanation of this phenomenon. While there are many ways in which the behavior of CII alone can be explained, none is consistent with the behavior of CI and vice versa.

D. Radical Anions Derived from Diesters

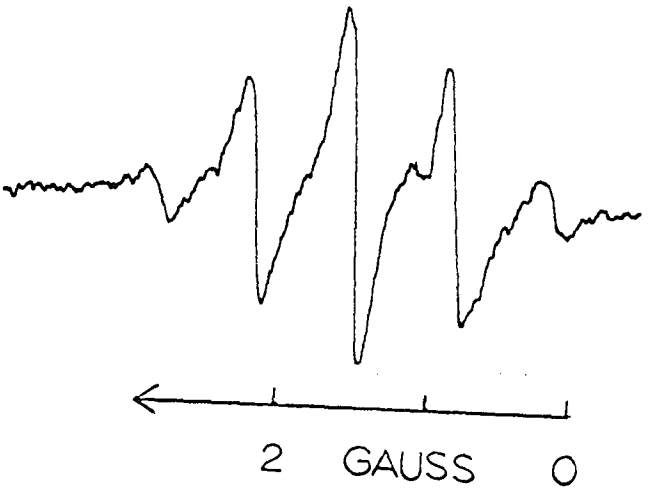
The difficulty in preparing XXIX and its instability relative to dimethylsemidione led us to conclude that the best chance for producing a difunctionally substituted semipolyone would be in the trione series. The reduction of ethyl mesoxalate, CIX, electrolytically in DMF or

$$OC(CO_2CH_2CH_3)_2$$

CIX

acetonitrile, with potassium metal in HMPA, or by the action of t-BuOK in DMSO leads to the same radical anion, CX (See Figure 24). The spectrum consists of a simple quintet of binomial intensity which is due to four equivalent protons with a splitting constant of 0.66 gauss in all of the solvents. If the solvent is changed to 25% i-PrOH or methanol in DMSO with i-PrOK or NaOMe as the respective base, ethyl mesoxalate still yields CX. In the case of i-PrOH there is no noticeable change in the spectrum even after standing for one week. Clearly there is no ester interchange. Surprisingly the reduction of ethyl oxalate with potassium in HMPA also produces CX. If methyl oxalate is similarly treated, CXI is produced. Radical anion CXI contains six equivalent protons with a splitting constant of 0.66 gauss. Isopropyl oxalate yields CXII, which shows two equivalent protons with a splitting constant of 0.44 gauss (See Figure 25). When CX is

Figure 24. First-derivative e.s.r. spectrum of the radical anion of ethyl mesoxalate in DMSO (top) and in HMPA (bottom).


2 GAUSS 0

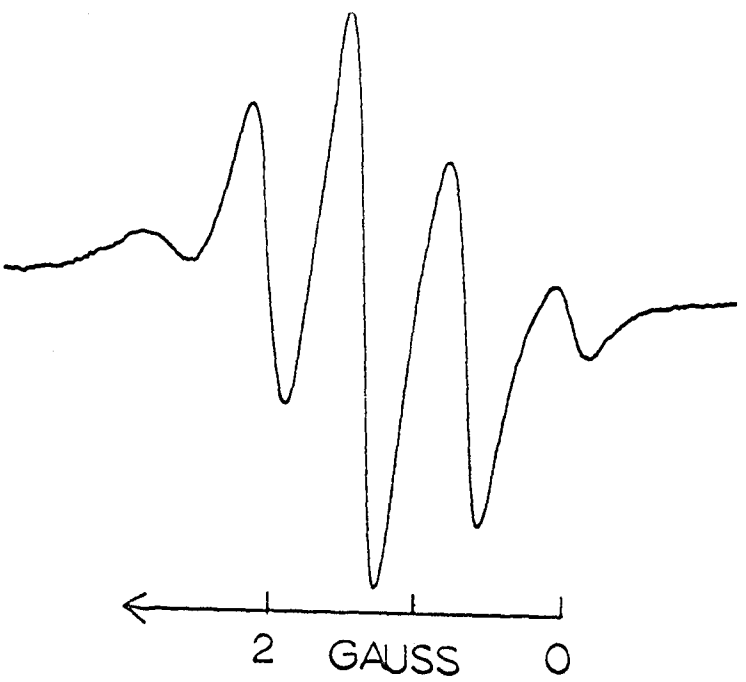
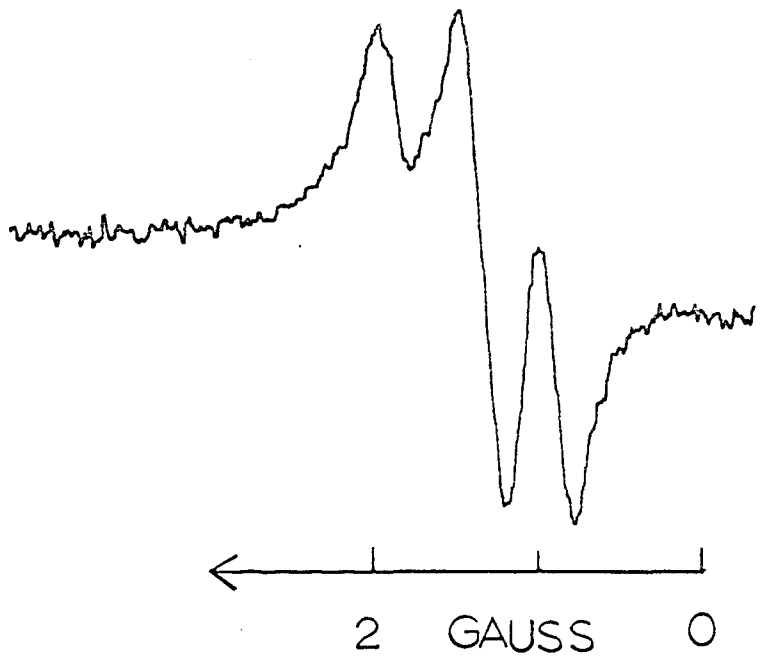

2 GAUSS 0

Figure 25. First-derivative e.s.r. spectrum of the radical anion derived from isopropyl oxalate with potassium in HMPA.


2 GAUSS 0

formed by the reaction of ethyl oxalate with deficient potassium in HMPA and then isorpopyl oxalate is added to the solution, there is no noticeable change in the splitting pattern although there is some loss of intensity. Presumably this loss of intensity is due to the inadvertent addition of oxygen along with the ester. This same loss of intensity is the only noticeable change when ethyl oxalate is added to a solution of CXII which is formed as above. However when a solution containing equimolar amounts of ethyl and isopropyl oxalate is reduced with potassium, a spectrum which is different from both those of CX and CXII is obtained (See Figure 26). This new spectrum contains a major triplet splitting of 0.76 gauss. A careful examination of the spectrum also shows what well could be a doublet splitting of about 0.3 gauss. The oxidation of ethyl tartronate acetate, CXIII, or diethyl dihydroxymaleate, CXIV a, with t-BuOK in DMSO yields CX. Similarly CXIV b is converted to CXI.

$CH_3CO_2CH(CO_2CH_2CH_3)$

CXIII

$RO_2CC(OH) = C(OH)CO_2R$

CXIV a. $R = CH_2CH_3$

b. $R = CH_3$

However, the reaction of ethyl or isopropyl oxalate with t-BuOK in DMSO produces the same spectrum (See Figure 27). This spectrum can be duplicated if we assign four protons a splitting constant of 1.02 gauss and six protons one of

Figure 26. First-derivative e.s.r. spectrum of the radical anion(s) derived from a mixture of ethyl and isopropyl oxalate with potassium in HMPA.

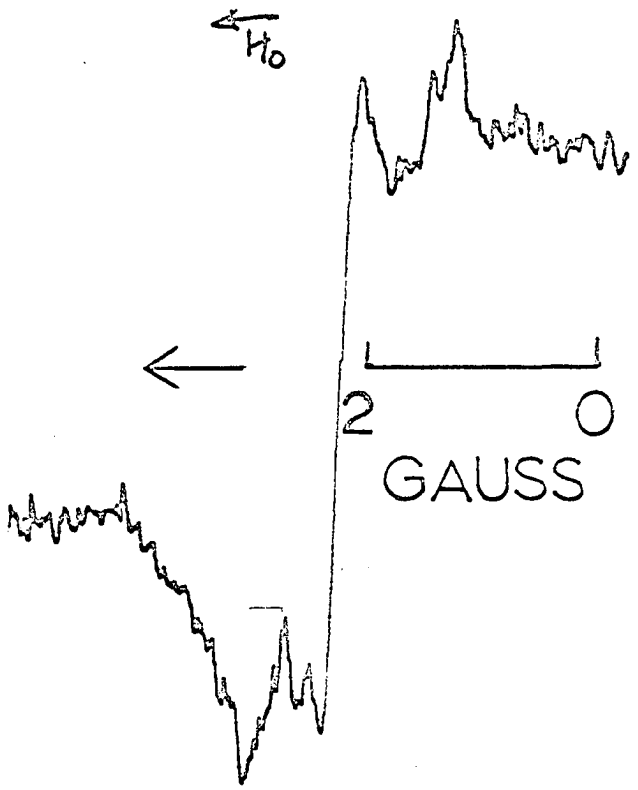
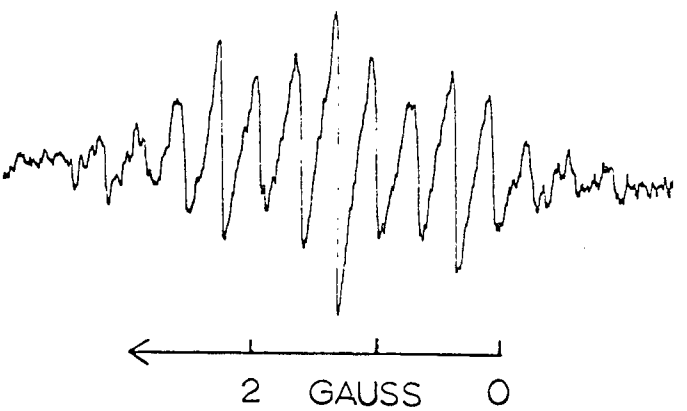
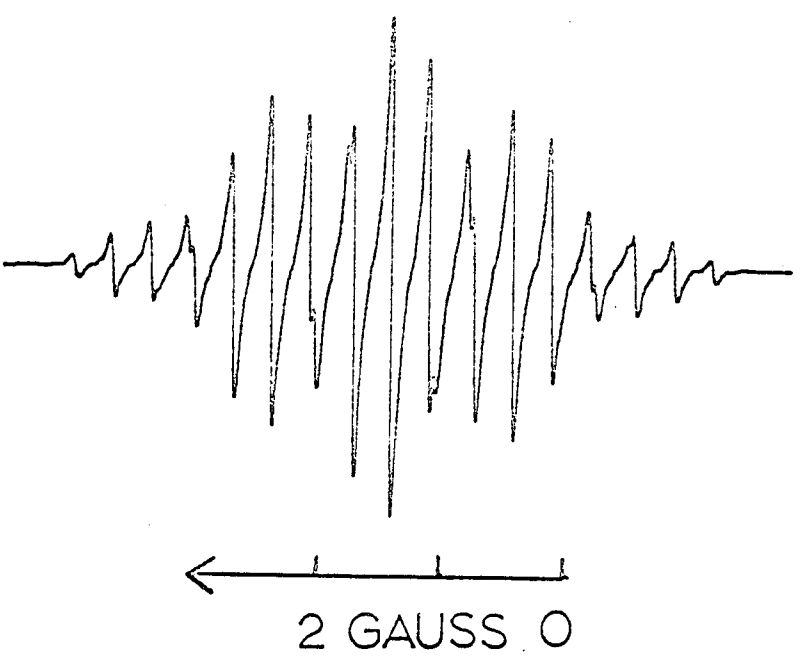

H_0
2
0
GAUSS

Figure 27. First-derivative e.s.r. spectrum of the radical anion derived from ethyl oxalate with t-BuOK in DMSO (top); calculated spectrum for Lorentzian line width (bottom) of 0.2 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.


2 GAUSS 0


2 GAUSS 0

0.32 gauss. It is clear that this radical anion has lost both of its ester functions. Based on this fact and the known ability of t-BuOK in DMSO to generate the dimethylsulfinyl carbanion which will attack esters to yield β-ketosulfoxides (7, 15, 16), structure CXV is proposed for the radical anion.

$$\underset{\text{CXV}}{CH_3SOCH_2C(O^-) = C(O^\cdot)CH_2SOCH_3}$$

If this is the correct structure, then the splitting constant of 1.02 gauss would be the lowest known for a methylene group adjacent to the carbonyl of a semidione. However in two other instances this low value has been suggested. The fact that CXV is not formed from ethyl mesoxalate suggests that it is reduced much more rapidly than ethyl oxalate. This is consistent with the difference in reduction potentials of the esters in DMSO.

Leaving aside this problem, we are faced with determining the number of carbonyl groups in radical anions CX, CXI, and CXII. The size of the splitting constant of CX, 0.66 gauss, is less than that observed for the methylene protons of XIX and XXIX. For the latter two, the splitting constant is 0.8 gauss. It follows from first principles that in an unsymmetric radical anion such as XIX, the concentration of spin density should favor the aromatic ring over the ethoxy group thereby decreasing the methylene splitting constant relative to what it would be in a symmetric molecule. That is, if CX were

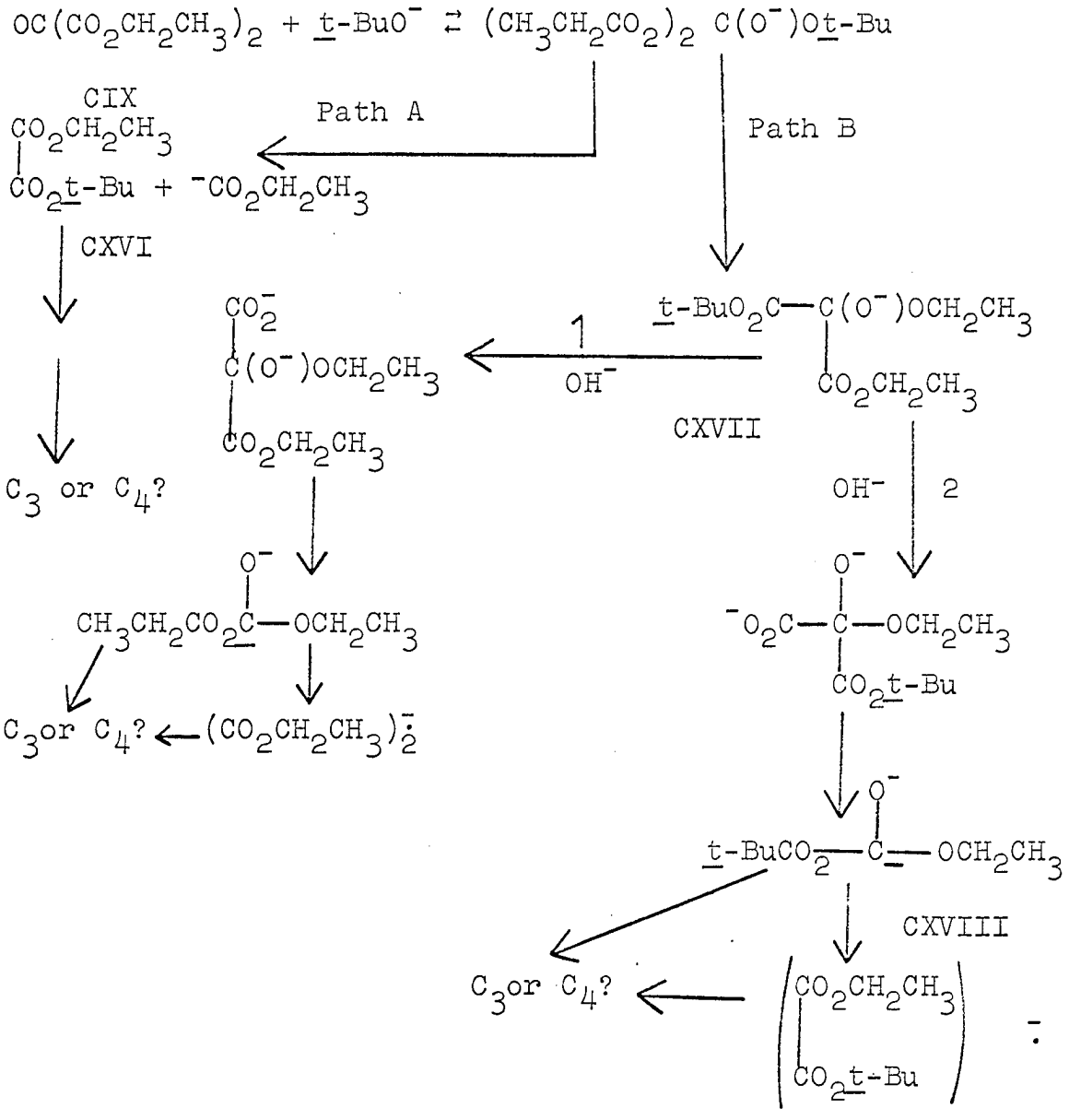
the one electron reduction product of ethyl oxalate then the four protons should have a splitting constant of greater than or at least equal to 0.8 gauss. The fact that the observed splitting constant is 0.66 gauss is strong evidence against CX being a semidione. It is also difficult to explain why reduction of a mixture of oxalates should lead to a different radical anion than that obtained by the addition of one oxalate to the preformed radical anion of another if both are semidiones. Furthermore, it has been reported that the reduction of ethyl oxalate by sodium amalgam in ethyl alcohol produces ethyl mesoxalate and ethyl tartarate among other products (114).

The methylene group of $CH_3C(O^-)=C(O\cdot)CO_2CH_2CH_3$ has a splitting constant of 0.5 gauss. The value of 0.66 gauss is therefore consistent with the structure shown below for CX. The difference in reduction potentials between ethyl mesoxalate

$$CH_3CH_2O_2CC(O^-) = C(O\cdot)OCH_2CH_3$$

CX

and ethyl oxalate is about 1 volt or 23 kcal/mole. Therefore on energetic grounds alone it is highly unlikely that the one electron reduction product of ethyl mesoxalate would be converted to that of ethyl oxalate. Certainly such a conversion would be expected to proceed along the lines of Scheme I rather than Scheme II. If we assume this manner of reaction for ethyl mesoxalate then the following intermediates

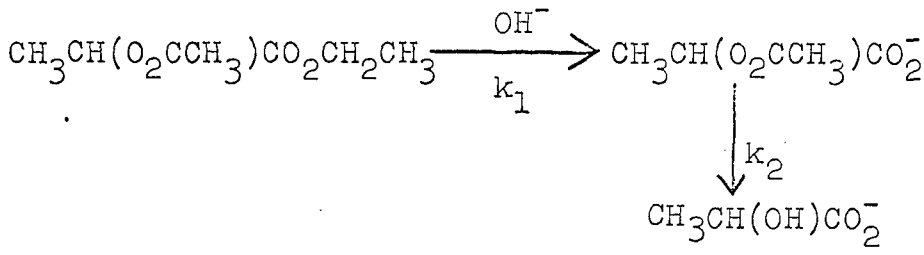


would be formed. The fact that no ester interchange is observed demands initial attack by the nucleophile at the central carbonyl. If CXVI were formed by path A, then either the radical anion should have a triplet e.s.r. spectrum or CXVI must go on to trione or tetrone. In the latter case,

CXVI could give any of three triones or tetrones. However no mixtures of radical anions have been observed. Therefore path A is not allowed. Similarly CXVIII cannot be formed and so only path B1 is allowed. This path is somewhat dubious as the water necessary to hydrolyse CXVII would in all probability have been used up in the hydrolysis of CIX. Thus it is felt that all of the reactions of CIX proceed via Scheme II. Here the energy difference between the reduction products of ethyl mesoxalate and ethyl oxalate as well as the difficulty in adding two electrons to the latter make it unreasonable for the semitrione to be converted to the semidione.

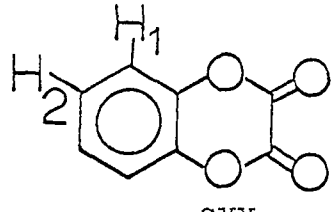
As for the radical anion being the semitetraone, the size of the splitting constant argues against it but is not conclusive. However it is known that mesoxalic acid is produced in the hydrogen peroxide oxidation of tartic acid (115) and in the iron catalysed oxidation of dihydroxymaleic acid (116). In the latter case it is reported that mesoxalic acid is only slowly converted to oxalic acid. Furthermore, heating an alkaline solution of tartaric acid produces tartronic acid (117). Finally for ethyl tartronate acetate, CXIII, to be converted to a semitetraone, the acetate group must first be hydrolysed, the ethyl tartronate oxidized to ethyl mesoxalate, the latter decarbonylated to yield ethyl oxalate which then must undergo a bimolecular acyloin

condensation to form ethyl diketosuccinate. This seems unlikely when it is recalled that the alkaline hydrolysis of CXIX has been shown to proceed in the following manner with $k_1 = 19.6$ and $k_2 = 0.1$ (118). Even if CXIII were decarbonylated prior to hydrolysis, the total number of reactions

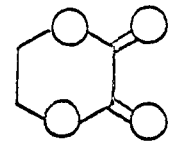


involved makes it unlikely that a semitetraone is produced. For these reasons it is felt that the previous report of dihydroxytartaric acid yielding a semitetraone (69) is in error. Finally mesoxalic acid can be converted to its disodium salt without any apparent decarbonylation (119).

Thus the weight of evidence favors the semitrione structure for CX, CXI, and CXII. However this result is not necessarily applicable to aromatic oxalates. When either phenyl or benzyl oxalate is reduced with potassium in HMPA the resultant signal consists of one strong unresolved peak. When diphenyl carbonate is mixed with t-BuOK in DMSO or potassium in HMPA no signal is observed. The electrolytic



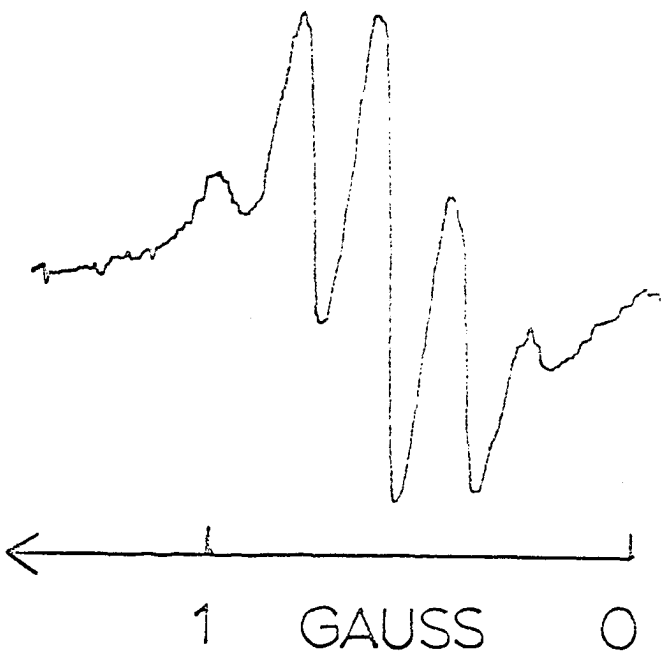
CXX



CXXI

reduction of benzoxalate, CXX, in acetonitrile yields o-benzosemiquinone. However in DMF this electrolysis yields a radical anion containing four equivalent protons with a splitting constant of 0.18 gauss (See Figure 28). The fact that only four protons are observed clearly rules out the possibility that CXX may have dimerized. If we assume a value of 23 for Q, then the experimental spin density for positions 1 and 2 is 0.008. A McLachlan calculation predicts a spin density of 0.032 for position 1 and 0.003 for position 2. However it is known that in ninhydrin radical anion, the four protons are equivalent with a splitting constant of 0.95 gauss (72). A McLachlan calculation predicts splitting constants of 0.16 and 0.22 gauss for this radical anion (72). Attempts to produce a radical anion from CXXI by reduction with potassium in HMPA, t-BuOK in DMSO, or electrolytically in DMSO were unsuccessful.

Figure 28. First-derivative e.s.r. spectrum of the radical anion of benzoxalate in DMF.


1 GAUSS 0

III. EXPERIMENTAL

A. Polarography

All polarograms were run on a Sargent Polarograph Model XXI. DMSO was distilled from alumina under vacuum (B.P. 60°C at 4 mm, lit. B.P. 62-64°C at 4 mm (94)) and stored over molecular sieves. Acetonitrile was obtained as the spectroscopic grade from Matheson, Coleman and Bell and stored over molecular sieves. All potentials were measured relative to an aqueous saturated calomel electrode. Tetra-n-propylammonium perchlorate was purified by the method of Geske and Maki (120) and used as the electrolyte. All solutions were 0.1 molar in electrolyte and 0.001 molar in substrate.

B. Electron Spin Resonance Spectra

The spectra were obtained with a Varian V-4502 spectrometer equipped with a 9-in. magnet with 100-kcps field modulation. In general, the experiments were carried out by treating solutions about 0.1M in substrate with an equal volume of about 1.0M t-BuOK in DMSO (or other solvent). All solutions were deoxygenated prior to mixing. The special cells and techniques used in this work have been described previously (26, 121). The electrolytic generation of radical anions in situ was done using standard techniques

(120, 122, 123). Potentials were measured relative to a non-aqueous reference electrode which has a potential of -0.14 volts relative to an aqueous staturated calomel electrode in acetonitrile.

C. Reagents

DMF and HMPA were distilled under vacuum from calcium hydride and stored over calcium hydride and molecular sieves. All compounds had nuclear magnetic resonance (NMR) spectra and infrared (IR) spectra consistent with their structural assignments. The NMR spectra were obtained on a Varian A-60 spectrometer. All peaks are reported relative to tetramethylsilane as internal standard. The IR spectra were run on a Perkin-Elmer Model 21 Double Beam Infrared Spectrophotometer.

Ethyl mandelate, M.P. 30-32°C, lit. 34-35°C (124), was used without further purification. Its NMR spectrum in carbon tetrachloride (CCl_4) consisted of a multiplet at 7.27 ppm. (intensity 5.3), a singlet at 5.04 ppm (intensity 1.0), a broad quartet at 4.08 ppm (intensity 3.1) and a triplet at 1.15 ppm (intensity 3.2). Its IR spectrum in CCl_4 had absorption bands at 2.85, 5.80, 6.25, 7.85, and 8.45μ. These same bands were present in the IR spectra of methyl and isopropyl mandelate. Methyl mandelate, M.P. 53-55°C, lit. 55°C (124), was made by neutralizing mandelic acid, M.P. 117-121°C, lit. 120.5°C (124), with silver oxide, collecting

the precipitate, and treating it with methyl iodide in a stirred methanol solution. Its NMR spectra in carbon tetrachloride consisted of a multiplet at 7.29 ppm (intensity 5.2), a singlet at 5.04 ppm (intensity 1.0), a broad singlet at 4.39 ppm (intensity 1.0), and a singlet at 3.60 ppm (intensity 2.9). Isopropyl mandelate, B.P. 115-120°C at 4 mm, lit. 97-107°C at 0.01 mm (125), was formed by refluxing a solution of mandelic acid in i-PrOH containing a trace of sulfuric acid. Its NMR spectrum in CCl_4 consisted of a multiplet at 7.30 ppm (intensity 5.0), a complex multiplet at 5.0 ppm (intensity 1.93), a broad doublet at 3.80 ppm (intensity 0.92), and a doublet of doublets at 1.1 ppm (intensity 6.07). Ethyl lactate, B.P. 73-75°C at 35 mm, lit. 72.5°C at 37 mm (126), and methyl lactate, B.P. 70-73°C at 35 mm, lit. 144.8°C (124) were commercial materials which were distilled prior to use. The former had an NMR spectrum in CCl_4 which consisted of a quartet at 4.20 ppm (intensity 3.1), a broad singlet at 3.45 ppm (intensity 1.0), and a badly distorted triplet at 1.29 ppm (intensity 6.2). The latter had an NMR spectrum in CCl_4 which consisted of a quartet at 4.20 ppm (intensity 1.0), a singlet at 3.75 ppm (intensity 3.0), a broad singlet at 3.46 ppm (intensity 1.3) and a doublet at 1.14 ppm (intensity 3.0). The IR spectra of both compounds in CCl_4 as well as that of isopropyl lactate contained bands at 2.82, 5.77, 8.00, 8.25, and 8.88μ.

Isopropyl lactate, B.P. 78-82°C at 35 mm, lit. 75-80°C at 32 mm (127), was obtained by refluxing a solution of ethyl lactate in i-PrOH containing a trace of sulfuric acid. Its NMR spectrum in CCl_4 consisted of a sharp heptet at 5.04 ppm (intensity 1.0), a broad multiplet at 4.13 ppm (intensity 1.06), a broad singlet at 3.23 ppm (intensity 1.06), and doublets at 1.36 ppm (intensity 3.1) and 1.28 ppm (intensity 6.1).

Ethyl benzoylformate, B.P. 97-100°C at 2 mm, lit. 246-8°C (124), was a commercial material which was distilled prior to use. Its NMR spectrum in CCl_4 consisted of multuplets at 7.92 ppm (intensity 2.0) and 7.54 ppm (intensity 3.3), a quartet at 4.39 ppm (intensity 1.99), and a triplet at 1.36 ppm (intensity 3.1). The IR spectra of methyl, ethyl, and isopropyl benzoylformate in CCl_4 contained bands at 5.75, 5.90, 6.25, 8.35, and 8.50μ. A solution consisting of 50 ml. of 40% potassium hydroxide and 170 ml. of ethyl ether was cooled to 5°C with stirring. To this liquid was added 3.3 gms N-nitroso-N-methylurea. The resultant solution of diazomethane in ether was decanted into a stirred solution of 4.7 gms. of benzoylformic acid, M.P. 62-66°C, lit. 66°C (124), in ether. The resultant methyl benzoylformate, B.P. 93-95°C at 2mm, lit. 137°C at 14 mm (128), had an NMR spectrum in CCl_4 consisting of multuplets at 7.98 ppm (intensity 2.0) and 7.50 ppm (intensity 3.2), and a singlet at 3.92 ppm

(intensity 3.0). Isopropyl benzoylformate, B.P. 109-113°C at 2 mm, lit. 153.5-154.4°C at 12 mm (129), was formed by refluxing a solution of benzoylformic acid in benzene containing i-PrOH and a trace of p-toluenesulforic acid. A Dean-Starke trap was used to collect the water. Its NMR spectrum in CCl_4 consisted of multiplets at 8.0 ppm (intensity 2.0) and 7.56 ppm (intensity 3.1), an heptet at 5.24 ppm (intensity 0.98), and a doublet at 1.25 ppm (intensity 6.1). Ethyl pyruvate, B.P. 65°C at 35 mm, lit. 69-71°C at 42 mm (124), was a commercial material distilled before use. Its NMR spectrum in CCl_4 consisted of a quartet at 4.23 ppm (intensity 2.0), a sharp singlet at 2.38 ppm (intensity 3.0), and a triplet at 1.37 ppm (intensity 3.2). The IR spectra of ethyl, methyl, and isopropyl pyruvate in CCl_4 contained broad bands at 5.85, 7.70, and 8.85μ. Methyl pyruvate, B.P. 45-50°C at 12 mm, lit. 53°C at 15 mm (124), was formed by the action of diazomethane on a solution of pyruvic acid in ether. Its NMR spectrum in CCl_4 consisted of two singlets at 3.75 ppm (intensity 3.0) and 2.40 ppm (intensity 3.1). Isopropyl pyruvate (B.P. 80°C at 45 mm, lit. 50.5-51.0°C at 13 mm (129)), was formed by refluxing a solution of pyruvic acid and i-PrOH in benzene containing a trace of p-toluene-sulfonic acid. The water was collected in a Dean-Starke trap. The NMR spectrum of isopropyl pyruvate in CCl_4 consisted of an heptet at 5.08 ppm (intensity 1.0), a singlet at 2.36 ppm (intensity 3.1), and a doublet at 1.33 ppm (intensity 6.3).

Cyclopentanedione, B.P. 50-54°C at 2 mm, lit. 78-86°C at 8 mm (130), was synthesized by the method of Acheson (130) except that potassium chlorate was added to the initial water solution and the final solution was continuously extracted with ether for 48 hours. α-Dimethylaminoacetophenone, B.P. 68-70°C at 8 mm, lit. 83.5-84°C at 15 mm (131), was formed by the reaction of phenacetyl bromide with excess dimethyl amine in ether by the method of Letsinger (131). Its NMR spectrum in CCl_4 consisted of multiplets at 7.95 ppm (intensity 2.0) and 7.40 ppm (intensity 2.97), and sharp singlets at 3.55 ppm (intensity 2.0) and 2.30 ppm (intensity 6.0).

1-Phenyl-1,3-butanedione, sodium salt, and 1,3-diphenyl-1,3-propanedione, sodium salt, were synthesized by the base catalysed condensation of methyl benzoate with acetone (132), and acetophenone (133) respectively. Sodium methoxide was used in place of sodium ethoxide in both cases. 1-Phenyl-1,3-butanedione, sodium salt was dissolved in water and chlorine gas was bubbled into the solution. The solution was extracted with ether, the ether layer dried over anhydrous sodium sulfate and then evaporated. The resultant yellow oil was used without further purification. α-Bromo-1,3-diphenyl-1,3-propanedione was formed similarly. 2,2,6,6-Tetrabromocyclohexanone, M.P. 116°C, lit. 117°C, was prepared according to Bodroux (134) except that preformed aluminum bromide was

used. Dimedon, M.P. 145-147°C, lit. 148-149°C (124), was refluxed with N-bromosuccinimide in CCl_4 to yield α-bromodimedon, M.P. 170-173°C, lit. 174-175°C (135). 3-Chloro-2,4-pentanedione, B.P. 155-160°C, lit. 154-156°C, was formed by the action of sulfuryl chloride on 2,4-pentanedione (136). 2,2-Dibromoacetoacetic acid, ethyl ester, was made by the method of Pedersen (137).

Lead tetraacetate was made according to Bailar (138). All reactions were run in benzene previously distilled from sodium. The β-dicarbonyl compounds were dissolved in benzene and the solution externally cooled with an ice bath. The lead tetraacetate was added at a rate sufficient to keep the temperature below 25°C. In this manner, 2-acetoxybenzoylacetic acid, ethyl ester, B.P. 125-130°C at 0.5 mm, lit. 140-143°C at 1 mm (139), 2-acetoxyacetoacetic acid, ethyl ester, B.P. 120-124°C at 15 mm, lit. 120-122°C at 15 mm (139, 140), 3-acetoxy-2,4-pentanedione, B.P. 112-118°C at 33 mm, lit. 100-106°C at 15 mm (140,141), and 2-acetoxy-1-phenyl-1,3-butanedione, B.P. 120-122°C at 0.4 mm, lit. 123-124°C at 0.4 mm (102a) were prepared. The last two compounds were also prepared by refluxing the corresponding chloro compounds with potassium acetate in glacial acetic acid (102a,b). 2-Acetoxy-1,3-diphenyl-1,3-propanedione, M.P. 90-95°C, lit. 94°C (86), was similarly prepared from the bromo compound. The NMR spectrum of 2-acetoxybenzoylacetic

acid, ethyl ester, in CCl_4 consisted of multiplets at 8.0 ppm (intensity 1.8) and 7.33 ppm (intensity 3.3), a singlet at 6.18 ppm (intensity 1.0), a quartet at 4.25 ppm (intensity 2.2), a singlet at 2.5 ppm (intensity 3.1), and a triplet at 1.3 ppm (intensity 3.2). Its IR spectrum in CCl_4 contained bands at 5.70, 6.00, 6.25, and 8.50μ. The NMR spectrum of 2-acetoxyacetoacetic acid, ethyl ester, in CCl_4 consisted of a singlet at 5.33 ppm (intensity 0.92), a quartet at 4.22 ppm (intensity 2.0), a doublet at 2.2 ppm (intensity 5.9), and a triplet at 1.30 ppm (intensity 3.1). Its IR spectrum in CCl_4 contained bands at 5.70 and 6.00μ and a broad absorption covering the region from 7.5-9.0μ. The NMR spectrum of 3-acetoxy-2,4-pentanedione in CCl_4 consisted of singlets at 5.39 ppm (intensity 1.0), 2.21 ppm (intensity 6.2), and 1.98 ppm (intensity 3.1). Its IR spectrum in CCl_4 showed bands at 5.82 and 8.37μ. The NMR spectrum of 2-acetoxy-1-phenyl-1,3-butanedione consisted of multiplets at 7.95 ppm (intensity 2.0) and 7.40 ppm (intensity 3.5), a singlet at 6.12 ppm (intensity 1.0) and a doublet at 2.18 ppm (intensity 6.5). Its IR spectrum in CCl_4 contained bands at 5.85 (broad), 6.25, and 8.46μ. The NMR spectrum of 2-acetoxy-1,3-diphenyl-1,3-propanedione in CCl_4 consisted of multiplets at 7.98 ppm (intensity 3.9) and 7.52 ppm (intensity 6.3), and singlets at 6.56 ppm (intensity 1.0) and 2.48 ppm (intensity 3.1). Its IR spectrum in CCl_4 contained bands at 5.79, 6.0, 6.25, and 8.43μ.

When dimedone was treated with lead tetraacetate no 2-acetoxydimedone was isolated. The product apparently was a dimer (140). 2-Acetoxydimedone was obtained via the route followed by Eistert (142). 2-Nitrodimedone, M.P. 90°C d., lit. 102°C d., was prepared by adding fuming nitric acid dropwise to a slurry of dimedone in ether with external cooling (143). Despite the low melting point, spectral data and subsequent reactions confirm the proposed structure. The NMR spectrum in deuterochloroform consisted of a broad singlet at 10.7 ppm (intensity 1.0), and singlets at 2.64 ppm (intensity 4.1) and 1.20 ppm (intensity 6.2). The mass spectrum contained peaks at m/e 185 (parent ion), 129 ($(CH_3)_2CCH_2CH(NO_2)CH_2$), and 84 ($(CH_3)_2CCH_2C=O$). The IR spectrum in chloroform contained bands at 2.8-4.5, 5.95, 6.45 (broad), 7.20, 7.45, 7.75, 10.40, and 11.37. 2-Nitrodimedone was reduced with tin and concentrated hydrochloric acid, the solution filtered, the filtrate saturated with hydrogen sulfide and refiltered, and the filtrate diluted with water. This solution was cooled with an ice bath and titrated with sodium nitrite solution until a positive test with starch-iodide paper was obtained. The precipitate which had formed during the titration was filtered and dried. This was 2-diazoniumdimedone chloride, M.P. 103-107°C d., lit. 107-108°C d. (142, 144). This was refluxed in acetic acid containing a little copper powder under a nitrogen atmosphere.

The resultant 2-acetoxydimedone, M.P. 155-160°C, lit. 161°C, was sublimed (142). Its NMR spectrum in deuterochloroform consisted of a broad singlet at 8.7 ppm (intensity 0.9), and singlets at 2.62 ppm (intensity 3.8), 2.32 ppm (intensity 3.1), and 1.10 ppm (intensity 6.0). Its mass spectrum contained peaks at m/e 198 (parent ion), 173 (loss of a methyl group), and 84 ($(CH_3)_2CCH_2C = O$). Its IR spectrum as a potassium bromide pellet contained bands at 2.90-4.40, 5.80, 6.10, 6.40, 8.15, 8.45, and 9.10μ.

3,3-Dimethylglutaric anhydride was refluxed in absolute ethanol containing a small amount of sulfuric acid. The resultant ester was made to undergo an acyloin condensation in liquid ammonia-ether solution to yield 4,4-dimethyl-2-hydroxycyclopentan-1-one, B.P. 67°C at 2.3 mm, lit. 68-70°C at 2 mm (145). Its NMR spectrum in CCl_4 consisted of a complex 1:1:1 triplet centered at 4.17 ppm (intensity 1.0), a broad singlet at 3.50 ppm (intensity 1.0), and complex multiplets at 2.10 ppm (intensity 2.1), 1.6 ppm (intensity 2.1) and 1.18 ppm (intensity 6.0). Its IR spectrum in CCl_4 contained bands at 2.85-3.90, 5.72, and 9.20μ.

2-Hydroxyacetoacetic acid, ethyl ester, B.P. 95-98°C at 15 mm, lit. 98-102°C at 15 mm (111), and methyl ester, B.P. 79-85°C at 15 mm, and ethyl α,β-dihydroxycinnamate, B.P. 119-123°C at 0.1 mm, lit. 90°C at 0.02 mm, were synthesized by the method of Karrer using m-chloroperbenzoic acid

in place of perbenzoic acid (111). 2-Hydroxyacetoacetic acid, ethyl ester, had an NMR spectrum in CCl_4 which consisted of a singlet at 4.68 ppm (intensity 0.9), a quartet at 4.25 ppm (intensity 3.0), a singlet at 2.27 ppm (intensity 2.9), and a triplet at 1.32 ppm (intensity 3.1). Its IR spectrum as a thin film had bands at 2.90, 5.70 (broad), 8.0, and 8.45μ. The methyl ester had an NMR spectrum in CCl_4 which consisted of a singlet at 4.9 ppm (intensity 1.0), a broad singlet at 3.8 ppm (intensity 1.2), and singlets at 3.74 ppm (intensity 3.1) and 2.17 ppm (intensity 3.2). Its IR spectrum in CCl_4 contained bands at 2.90, 5.75 (broad), 8.48, and 8.75μ. The NMR spectrum of ethyl α,β-dihydroxycinnamate in CCl_4 consisted of a broad singlet at 12.2 ppm (intensity 0.4), multiplets at 7.9 ppm (intensity 2.0) and 7.44 ppm (intensity 3.1) a broad singlet at 5.9 ppm (intensity 0.5), a singlet at 5.5 ppm (intensity 0.5), and complex multiplets at 4.2 ppm (intensity 1.96) and 1.20 ppm (intensity 3.1). Its IR spectrum as a thin film contained bands at 2.90, 5.70, 6.10, 7.90, and 8.50μ. 2-Hydroxy-1,3-diphenyl-1,3-propanedione, M.P. 106-110°C, lit. 110-111°C, was obtained by hydrolysis of the corresponding acetate (102a). Its NMR spectrum in CCl_4 consisted of a broad singlet at 11.2 ppm (intensity 1.9), and complex multiplets at 7.96 ppm (intensity 4.0) and 7.53 ppm (intensity 6.2). Its IR spectrum in CCl_4 contained bands at 2.8-3.9, 6.0, and 6.25μ. 3-Hydroxy-2,4-pentanedione,

B.P. 60-70°C at 8 mm, lit. 62-63°C at 8 mm, was obtained by hydrolysis of the chloride (102b). Its NMR spectrum in CCl_4 consisted of a broad singlet at 9.2 ppm (intensity 1.6), and singlets at 5.48 ppm (intensity 0.25), 3.6 ppm (intensity 0.25), 2.15 ppm (intensity 1.7), and 2.03 ppm (intensity 4.3). Its IR spectrum in CCl_4 contained bands at 2.8-4.5, 5.70, 5.85, and 6.15μ. 1,4-Diphenyl-2-hydroxy-1,3,4-butanetrione, M.P. 184-187°C, lit. 187°C was synthesized from ω-isoitroso-acetophenone by the method of Blatt (106). A saturated solution in deuterochloroform was not sufficiently concentrated to obtain a good NMR spectrum. However there appeared to be peaks around the regions of 11.8 ppm, 8.3 ppm, and 7.56 ppm. The IR spectrum in chloroform contained bands at 2.85-4.0, 5.9 (broad), and 6.25μ. The mass spectrum had peaks at m/e 268 (parent ion), 163 ($C_6H_5COCH(OH)CO$), 105 (C_6H_5CO), and 77 (C_6H_5). Dihydropyrogallol, M.P. 107-111°C, lit. 109-112°C, was obtained by reduction of pyrogallol, M.P. 130-132°C, lit. 132.8°C (124), with Raney nickel (146).

Another method used to produce hydroxy dicarbonyl compounds was to make the epoxide from the corresponding α,β-unsaturated carbonyl compound and then heat this with boron trifluoride etherate in DMSO. One drawback to this approach is that the epoxide in part reverts back to the α,β-unsaturated carbonyl compound when so treated. However these compounds were found not to produce a detectable

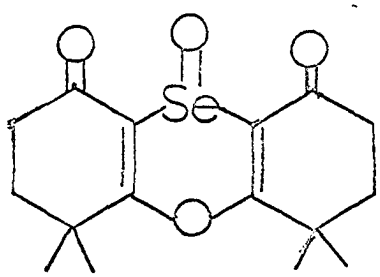
paramagnetic intermediate when mixed with t-BuOK in DMSO. Therefore the crude reaction mixtures were used without purification. In this manner, 2-hydroxy-1,3-diphenyl-1,3-propanedione and 2-hydroxy-1-phenyl-1,3-butanedione were synthesized. To get the required epoxides, 1-phenyl-3-buten-2-one, B.P. 78-80°C at 0.15 mm, lit. 120-130 at 7 mm (147), and chalcone, M.P. 51-57°C, lit. 55-57°C (148), were prepared by the condensation of benzaldehyde with acetone and acetophenone respectively. These enones were treated with alkaline hydrogen peroxide to generate the epoxides. The epoxide of the former, M.P. 35-38°C, lit. 40-42°C (112), had an NMR spectrum CCl_4 which consisted of a singlet at 7.2 ppm (intensity 5.0), doublets at 3.92 ppm (intensity 1.0) and 3.3 ppm (intensity 1.0), and a singlet at 2.03 ppm (intensity 3.0). Its IR spectrum in CCl_4 contained bands at 5.70, 7.30, 8.0, 8.75, and 9.80μ. The epoxide of the latter, M.P. 85-88°C, lit. 87.5-88°C (112), had an NMR spectrum in CCl_4 which consisted of multiplets at 7.95 ppm (intensity 1.9) and 7.52 ppm (intensity 2.9), a singlet at 7.27 ppm (intensity 4.8), and a multiplet at 4.0 ppm (intensity 2.0). Its IR spectrum in CCl_4 contained bands at 5.78, 6.25, 7.50, 8.0, 9.0, and 9.8μ. Chalcone oxide was hydrolysed by reaction with equal volumes of 10% sodium hydroxide and ethanol, followed by acidfication and extraction with benzene. The NMR spectrum of the product in CCl_4 consisted

of multiplets at 7.8 ppm (intensity 2.0) and 7.35 ppm (intensity 3.0), and singlets at 7.17 ppm (intensity 5.0) and 4.05 ppm (intensity 2.0). On this basis, it was decided the product was 1,3-diphenyl-1,2-propanedione.

2,3,4-Pentanetrione-3-oxime, M.P. 73-75°C, lit. 75°C, was synthesized by the method of Wolff (149). Attempts to hydrolyse this oxime by the method of DePuy and Ponder (150) led only to partial recovery of starting material. The oxidation of 2,4-pentanedione with selenium dioxide in the absence of solvent led to a mixture of 2,3,4-pentanetrione and starting material. The NMR spectrum of this mixture in CCl_4 consisted of singlets at 5.4 ppm (intensity 1.0), 2.05 ppm (intensity 4.0), and 1.98 ppm (intensity 6.1). The IR spectrum run as a thin film contained bands at 3.35, 5.80 (broad), and 6.1μ (shoulder). The mass spectrum contained peaks at m/e 100 ($CH_3COCH_2COCH_3$), 86 ($CH_3COCOCH_3$), and 43 (CH_3CO). 2,4-Pentanedione was condensed with N,N-dimethyl-p-nitrosoaniline, M.P. 90-93°C, lit. 92.5-93.5°C (128), and the adduct hydrolysed with sulfuric acid (151-153). This yielded 2,3,4-pentanetrione, B.P. 47-54°C at 12 mm, lit. 54-55°C at 12 mm (153), which existed to a large extent as the ethyl hemiketal. (The solvent in the condensation was ethanol.) The NMR spectrum in CCl_4 consisted of a broad singlet at 5.18 ppm (intensity 1.0), a quartet at 3.42 ppm (intensity 1.8), a doublet at 2.35 ppm (intensity 11.0), and

a triplet at 1.21 ppm (intensity 3.2). When this mixture was left exposed to air, a solid formed which melted at 40-45°C. 2,3,4-Pentanetrione hydrate is reported to have this melting point (154). 1,3-Diphenyl-1,2,3-propanetrione, M.P. 67-69°C, lit. 69-70°C (89), was formed by refluxing 2,2-dibromo-1,3-diphenyl-1,3-propanedione with potassium acetate in glacial acetic acid. The resultant solid was heated under vacuum, giving off acetyl bromide. The DPPT residue was distilled under vacuum and recrystallized from methanol. Its NMR spectrum in CCl_4 consisted of multiplets at 8.02 ppm (intensity 2.0) and 7.55 ppm (intensity 3.2). Its IR spectrum in CCl_4 contained bands at 5.82 (shoulder), 6.00, 6.27, 6.90, 7.06, 9.0, and 11.7μ. Its mass spectrum contained peaks at m/e 238 (parent ion), 210 ($C_6H_5COCOC_6H_5$), 105 (C_6H_5CO), and 77 (C_6H_5). 1,4-Diphenyl-1,2,3,4-butanetetraone was formed by refluxing the dihydro compound in thionyl chloride (106). Attempts to dehydrate the tetraone were only partially successful. The red solid melted at 80-90°C instead of the reported 110-112°C (106) for the anhydrous material. However the NMR spectrum in deuterochloroform consisted of multiplets at 8.06 ppm (intensity 2.0) and 7.48 ppm (intensity 3.1). The IR spectrum in CCl_4 contained bands at 2.89, 5.85, 5.95, 6.25, and 6.90μ. The mass spectrum contained peaks at m/e 266 (parent ion), 238 ($C_6H_5COCOCOC_6H_5$), 210 ($C_6H_5COCOC_6H_5$), 105 (C_6H_5CO), and 77 (C_6H_5). 1,2,3-Phenalenetrione, M.P.

260°C d., lit. 265°C d. (109, 155), was obtained by selenium dioxide oxidation of 1,3-phenaleneclione, M.P. 259°C d., lit. 262°C d. (156). Selenium dioxide oxidation of dimedone produced the known compound CXXII, M.P. 156-158°C, lit. 155°C (157).



CXXII

Ethyl oxalate, B.P. 184-186°C, lit. 185.7°C (124), was commercial material distilled prior to use. Its NMR spectrum in CCl_4 consisted of a quartet at 4.27 ppm (intensity 2.1) and a triplet at 1.33 ppm (intensity 3.0). The IR spectrum of ethyl oxalate as well as those of methyl and isopropyl oxalate in CCl_4 contained bands at 5.75, 8.20, and 8.60μ. Methyl oxalate, M.P. 53-54°C, lit. 54°C (124), was formed by refluxing ethyl oxalate in methanol containing a trace of sulfuric acid. Its NMR spectrum in CCl_4 contained one peak at 3.92 ppm. Isopropyl oxalate, B.P. 118-123°C at 35 mm, lit. 189°C (124), was formed in a similar manner. Its NMR spectrum in CCl_4 contained an heptet at 5.13 ppm (intensity 1.0) and a doublet at 1.34 ppm (intensity 6.1). Diphenyl oxalate, M.P. 132-134°C, lit. 134°C (158), was formed by the reaction of oxalyl chloride with phenol in ether solvent in

the presence of quinoline (158). Its NMR spectrum in deuterochloroform consisted of a multiplet at 7.38 ppm. Its IR spectrum in a potassium bromide disc contained bands at 5.65, 6.30, 6.75, 8.63, 11.85, 13.35, and 14.58μ. Oxalic acid, ethylene ester, M.P. 141-144°C, lit. 144°C was formed from ethyl oxalate and ethylene glycol by the method of Carothers (159).

"Dimethyl dihydroxymaleate", M.P. 178-181°C, lit. 178-180°C (160), was made by the reaction of diazomethane with the acid, M.P. 148-154°C, lit. 155°C (124). However it has been pointed out that this acid is most likely dihydroxyfumaric acid (160). The diethyl ester was made by reaction of the acid with ethanol hydrogen chloride (160). The isomer melting between 54°C and 58°C was used, lit. 54-56°C (160). The NMR spectrum of the dimethyl ester in deuterochloroform consisted of a broad singlet at 9.2 ppm (intensity 1.0) and a sharp singlet at 4.0 ppm (intensity 3.0). The NMR spectrum of the diethyl ester in deuterochloroform consisted of a broad singlet at 7.48 ppm (intensity 1.0), a quartet at 4.25 ppm (intensity 2.1), and a triplet at 1.28 ppm (intensity 3.1). The IR spectra of both esters in chloroform contained bands at 2.8-4.0, 6.0, 6.95, and 8.65μ.

Ethyl mesoxalate and ethyl tartronate acetate were commercial materials used without further purification. The NMR spectrum of the latter in CCl_4 consisted of a singlet

at 5.33 ppm (intensity 1.0), a quartet at 4.20 ppm (intensity 4.0), a singlet at 2.17 ppm (intensity 3.0), and a triplet at 1.30 ppm (intensity 6.2). Its IR spectrum in CCl_4 contained bands at 5.80, 7.42, 8.45, 9.28, and 9.82μ. The NMR spectrum of the former in CCl_4 consisted of a quartet at 4.29 ppm (intensity 2.0) and a triplet at 1.32 ppm (intensity 3.1). Its IR spectrum in CCl_4 contained bands at 5.78 (broad), 7.36, and 8.60μ. Its mass spectrum contained peaks at m/e 174 (parent ion), 146 ($(CO_2CH_2CH_3)_2$), and 73 ($CO_2CH_2CH_3$).

IV. CHEMICALS AND SOURCES

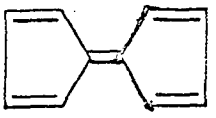
Chemical	Source
potassium t-butoxide	Alpha Inorganics
sodium methoxide	Matheson, Coleman and Bell
sodium hydride	Metal Hydrides Inc.
dimethyl sulfoxide	Crown Zellerbach
N,N-dimethylformamide	Matheson, Coleman and Bell
hexamethylphosphoramide	Eastman
propanoic acid	Eastman
phenylacetic acid	Matheson, Coleman and Bell
mandelic acid	Aldrich
benzoylformic acid	Aldrich
ascorbic acid	Aldrich
reductic acid	Pierce Chemical Co.
dihydroxymaleic acid	Aldrich
dihydroxytartaric acid	Aldrich
ethyl propanoate	Eastman
ethyl phenylacetate	Eastman
ethyl α-bromopropanoate	Aldrich
ethyl α-bromophenylacetate	K and K
ethyl mandelate	K and K
ethyl lactate	Aldrich
ethyl pyruvate	Aldrich
ethyl acetoacetate	Eastman
methyl acetoacetate	Aldrich
diethyl bromomalonate	Aldrich
diethyl tartronate acetate	K and K
diethyl mesoxalate	Aldrich
α-bromopropanoic acid	Aldrich
α-bromophenylacetic acid	Aldrich
ethyl benzoylformate	Eastman
ethyl benzoylacetate	K and K
methyl lactate	K and K
methyl methoxyacetate	Aldrich
3,3-dimethylglutaric anhydride	Aldrich
N,N-diethyl benzoylformamide	Mr. W. C. Danen
N,N-diethyl mandelamide	Mr. W. C. Danen
tetra-n-propylammonium hydroxide	Aldrich
dimethyl amine	Eastman
biacetyl	Aldrich
1,2-cyclohexenedione	Aldrich
phenylglyoxalhemimercaptal	Mr. L. A. Ochrymowicz
1-phenyl-1,3-butanedione	Eastman
1,3-diphenyl-1,3-propanedione	Aldrich
2,4-pentanedione	Aldrich
dimedone	Aldrich

Chemical	Source
1,2,3-cyclohexanetrione-1,3-dioxime	Aldrich
palladon	Aldrich
ω-isonitrosoacetophenone	Aldrich
selenium dioxide	Aldrich
propiophenone	Aldrich
phenalene-1,3[2H,3H]-dione	Aldrich
9,10-dihydroanthracene	Aldrich
pyrogallol	Eastman
catechol	Matheson, Coleman and Bell
cyclohexanone	Matheson, Coleman and Bell
cyclopentanone	Aldrich
ethyl oxalate	Eastman
1,2-benzoxalate	Dr. W. S. Trahanovsky
benzyl oxalate	Dr. W. S. Trahanovsky
oxalyl chloride	Aldrich
α-tropolone	Aldrich
β-tropolone	Aldrich
cycloheptatriene	Shell Development
tropone	Dr. T. H. Kinstle
2-hydroxycyclohexan-1-one	Aldrich
lithium t-butoxide	Alpha Inorganics
sodium t-butoxide	Mine Safety Appliance Corp.
rubidium t-butoxide	Mine Safety Appliance Corp.
cesium t-butoxide	Mine Safety Appliance Corp.

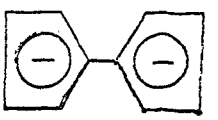
V. APPENDICES

A. Radical Anions Derived from Fulvalene and Heptafulvalene

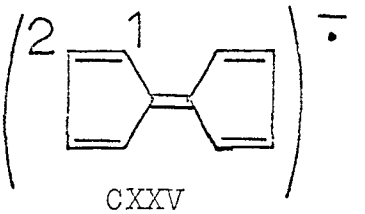
The synthesis of fulvalene, CXXIII, was described by Doering in 1958 (161). Sodium cyclopentadienide, formed



CXXIII



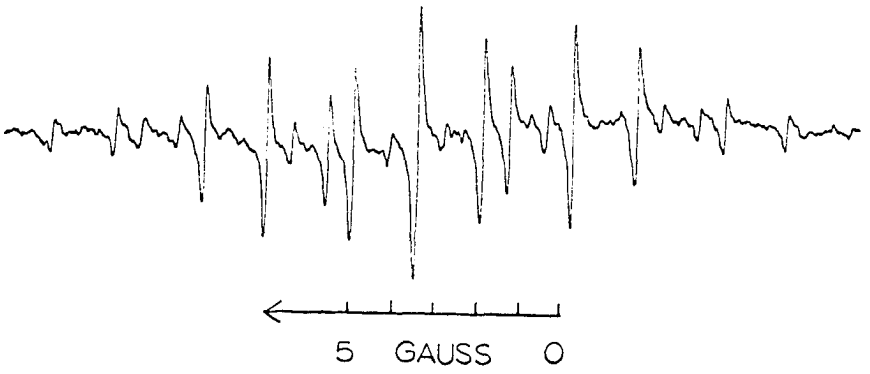
CXXIV

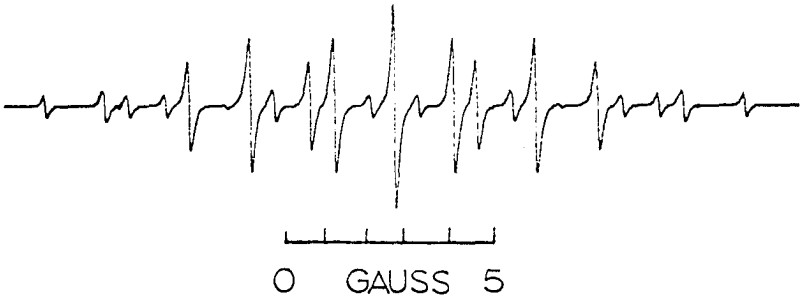


CXXV

by the reaction of sodium metal with cyclopentadiene, was treated with iodine to yield dihydrofulvalene. This was treated with two moles of butyl lithium to yield CXXIV. At low temperatures, CXXIV was converted to CXXIII by bubbling oxygen through the solution. All of the above work was conducted using pentane as the solvent. It would appear that the most likely intermediate in the conversion of CXXIV to CXXIII is CXXV. When a solution of potassium cyclopentadienide, formed by reaction of t-BuOK with cyclopentadiene, is mixed with a trace of iodine, the solvent being DMSO, the radical anion shown in Figure 29 is obtained. A calculated spectrum based on two sets of four equivalent protons with splitting constants of 3.6 and 1.5 gauss is in good agreement with the experimental spectrum. The spin densities predicted for positions 1 and 2 are 0.0614 and 0.1104 by a simple Hückel calculation and 0.0398 and 0.1252 by a McLachlan

Figure 29. First-derivative e.s.r. spectrum of the radical anion of fulvalene (top) in DMSO; calculated spectrum for Lorentzian line width (bottom) of 0.2 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.


5 GAUSS 0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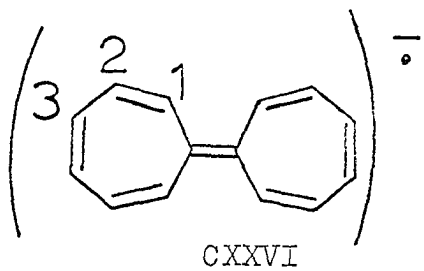
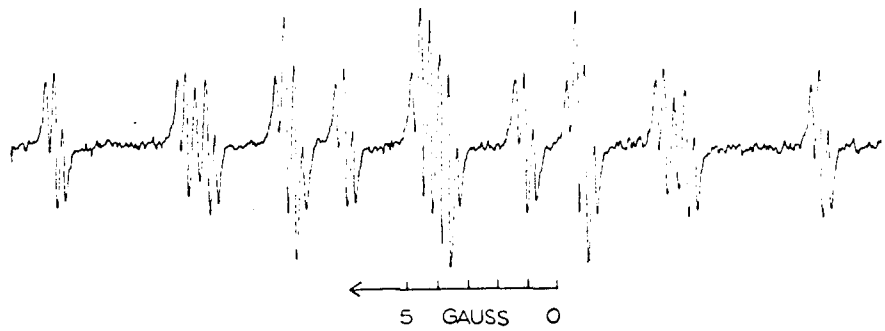
calculation (48). The experimental ratio of spin densities for position 1 to 2 is 0.42, the Hückel ratio is 0.56 and the McLachlan is 0.32. Clearly both calculations are not adequate in this case.



CXXVI

Because CXXV was obtained so readily, it was decided to use the same procedure starting with cycloheptatriene in an attempt to obtain CXXVI. The spectrum obtained is shown in Figure 30. The same spectrum is obtained in the absence of iodine. A calculated spectrum based on four different protons with splitting constants of 8.19, 7.79, 5.19, and 4.62 gauss and two equivalent protons with a splitting constant of 0.31 gauss duplicates the experimental spectrum. Attempts to produce a deuterated radical anion either by adding hexadeutero dimethyl sulfoxide to a solution of the radical anion or by using it as the solvent were unsuccessful. In any case, it is clear that the radical anion is not CXXVI. The size of the splitting constants leads one to conclude that the radical anion is not completely olefinic. The fact that there are five different splitting constants argues against the radical anion being highly symmetric. When the reaction of cycloheptatriene with I in DMSO is run on a large

Figure 30. First-derivative e.s.r. spectrum of the radical anion derived from cycloheptatriene (top) with t-BuOK in DMSO; calculated spectrum for Lorentzian line width (bottom) of 0.2 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.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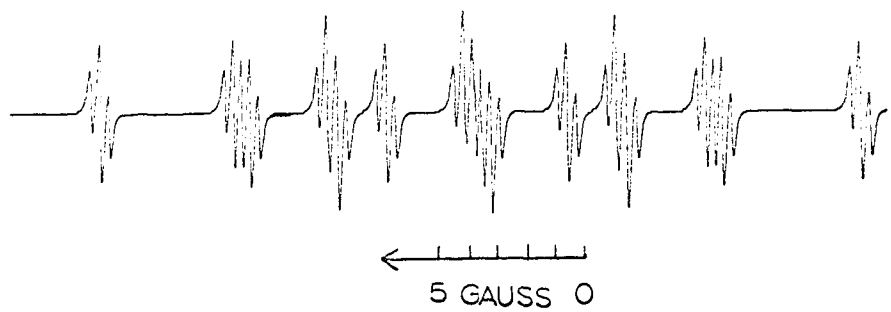
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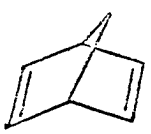
scale in an attempt to isolate the product using techniques described elsewhere (19) some fourteen different traces were detected by gas-liquid chromatography. The major component was collected and from its NMR spectrum (a single peak at 2.18 ppm) and stench it was probably dimethyl sulfide. Attempts to generate radical anions by mixing tropone, or α- or β-tropolone with t-BuOK in DMSO were all unsuccessful. Even though cycloheptatriene was distilled before use, in all likelihood it contained some toluene and some CXXVII (162). However neither produces a radical anion when mixed with

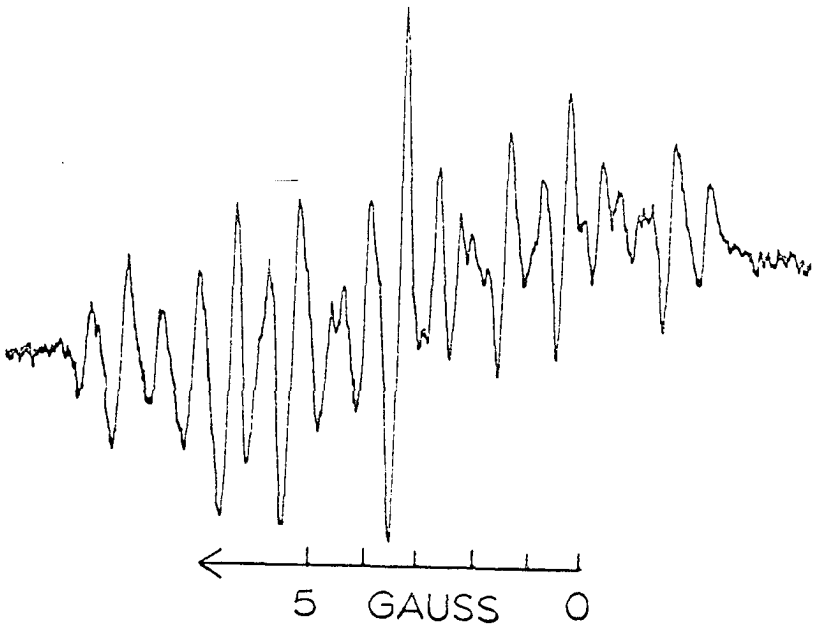


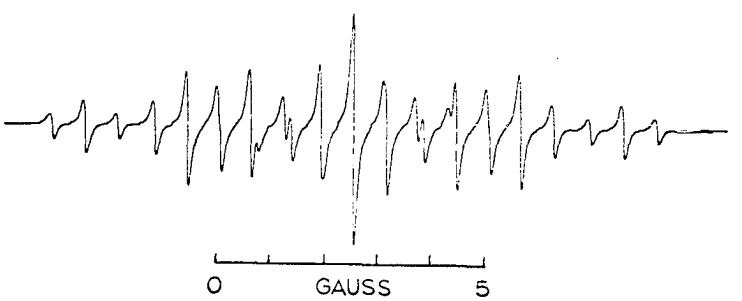
CXXVII

t-BuOK in DMSO. Also the one electron reduction product of CXXVII is known and it's symmetric as its structure implies (163).

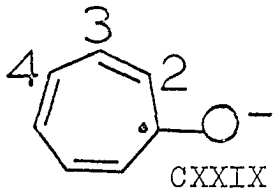
A more direct precurser to CXXVI, dihydroheptafulvalene, CXXVIII, is known and easily synthesized (164, 165). When this is treated with t-BuOK in DMSO, the spectrum shown in Figure 31 is obtained. A spectrum calculated on the basis of three pairs of equivalent protons with splitting constants 3.17, 1.93 and 0.62 gauss is in good agreement with that obtained experimentally. Again it is clear that CXXVI had not been produced. This is not too surprising in light of the fact that Geske had electrolysed a solution of CXXVIII

Figure 31. First-derivative e.s.r. spectrum of the radical anion derived from dihydroheptafulvalene (top) with t-BuOK in DMSO; calculated spectrum for Lorentzian line width (bottom) of 0.2 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.


5 GAUSS 0


0 GAUSS 5

in acetonitrile and shown that the product was the tropylium ion rather than heptafulvalene (166). This result suggests that the radical anion is probably due to some cleavage product of the starting material. The simplest such product consistent with the splitting pattern is the one electron reduction product of tropone, CXXIX. The experimental ratio

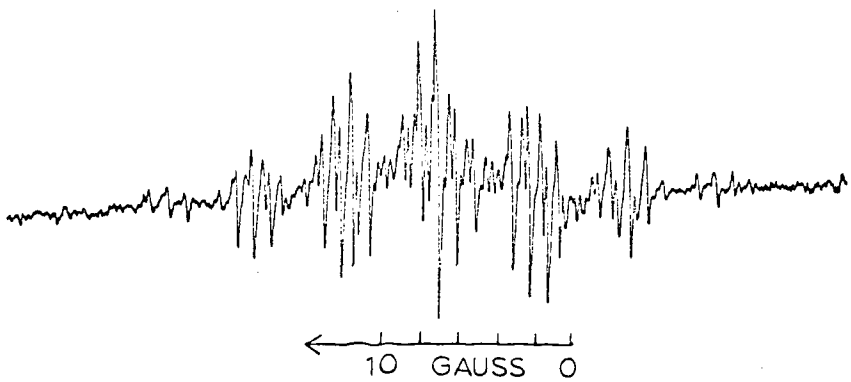


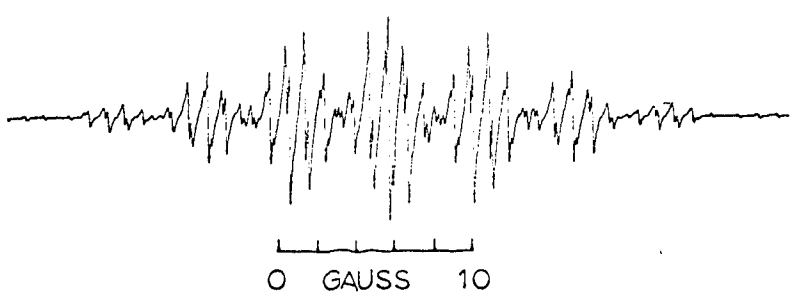
CXXIX

of spin densities of position 4 to 2 is 0.61 while that for 3 to 2 is 0.32. The corresponding ratios as calculated by the Hückel method are 0.64 and 0.20, and 0.50 and 0.05 as calculated by the McLachlan method. While the former values are in reasonable agreement with the experimental, it must be remembered that no radical anion is observed when tropone is mixed with t-BuOK in DMSO.

The best means for generation of a radical anion is to treat a mixture of the compound and its dihydro isomer with base. Fortunately the preparation of heptafulvalene from CXXVIII has been described (161). When a mixture of heptafulvalene and dihydroheptafulvalene is treated with t-BuOK in DMSO, the spectrum shown in Figure 32 is obtained. Assuming three sets of four equivalent protons with splitting constants of 4.46, 3.77, and 0.86 gauss gives a calculated spectrum which is in good agreement with the experimental.

Figure 32. First-derivative e.s.r. spectrum of the radical anion of heptafulvalene (top) in DMSO; calculated spectrum for Lorentzian line width (bottom) of 0.2 gauss and splitting constants from text performed by JEOLCO JNM-RA-1 spectrum accumulator.


10 GAUSS 0


0 GAUSS 10

Calculations of spin densities for CXXVI run into the problem that only the first six molecular orbitals are bonding, with all the rest anti-bonding. Consequently CXXVI contains three electrons in anti-bonding orbitals. The orbital containing the unpaired electron is one of two degenerate orbitals. Therefore the spin densities are obtained by averaging the computed values over the equivalent positions in both rings. When this is done for the Hückel calculation, the spin densities for positions 1, 2, and 3 are 0.1358, 0.0269, and 0.0873 respectively. Assuming a value of Q = 23, these densities predict splitting constants of 3.12, 2.01, and 0.62 gauss. A McLachlan calculation predicts splitting constants of 5.87, 2.99, and 1.42 gauss. The experimental ratios of spin densities for positions 3 to 1, 2 to 1, and 2 to 3 are 0.85, 0.19, and 0.23. Using the Hückel values, the corresponding ratios are 0.64, 0.20, and 0.31. With the McLachlan calculation, these ratios are 0.51, 0.24, and 0.47. Clearly the simple Hückel calculation is in better agreement with experiment. However, it too leaves a lot to be desired.

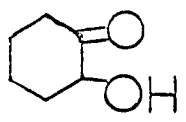
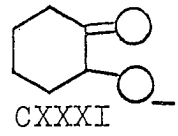
Cyclopentadiene, B.P. 39-41°C, lit. 40.8°C (124), was distilled from the commercially available dimer. Bitropyl was synthesized by the method of Doering (164). It was purified by the method of Dauben (165) to yield crystals, M.P. 61°C, lit. 61°C (164, 165). The NMR spectrum of bitropyl in CCl_4 consisted of complex multuplets at 6.6 ppm (intensity 3.9),

6.18 ppm (intensity 3.9), and 5.2 ppm (intensity 4.0), and a broad singlet at 1.92 ppm (intensity 2.0). 2.9 gms. of bitropyl was dissolved in 18 ml. of CCl_4. To this solution was added 1.6 gms. of bromine in 15 ml. of CCl_4 dropwise with stirring. A precipitate formed, and the CCl_4 was removed. To the solid residue was added 35 ml. of 25% trimethyl amine. This solution was refluxed for one day and extracted with pentane. The pentane extract was chromatographed on alumina. The resultant solid, M.P. 51-54°C, had an NMR spectrum which consisted of all the peaks of bitropyl plus a complex multuplet at 7.18 ppm (intensity 3.3 relative to the broad singlet at 1.92 ppm). This mixture was used without further purification in the e.s.r. experiment.

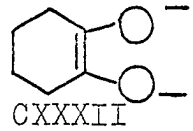
B. Electron Transfer Between 1,2-Cyclohexanedione and 2-Hydroxycyclohexan-1-one in the Presence of Base

It has long been known that electron transfer reactions between dianions and their unsaturated analogs occur readily and are reversible (9, 24). In general these reactions were studied using aromatic compounds wherein base catalysed condensations cannot occur. Consequently it was decided to follow the reaction of 1,2-cyclohexanedione, CXXX with 2-hydroxycyclohexan-1-one in the presence of base in DMSO solution. The bases chosen for this reaction were the alkali metal tertiary butoxides. The general scheme of the

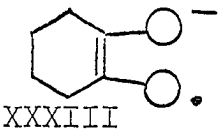
reaction is outlined below. While reactions 1-3 are felt

1.  + t-BuO$^-$ ⇄  + t-BuOH

CXXXI

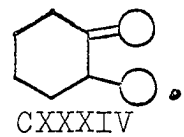
2. CXXXI + t-BuO$^-$ ⇄  + t-BuOH

CXXXII

3. CXXXII + CXXX ⇄ 2 

CXXXIII

4. CXXXII + O_2 → $O_2^{\cdot-}$ + CXXXIII

5. CXXXI + CXXX ⇄ CXXXIII + 

CXXXIV

6. CXXXIV + t-BuO$^-$ ⇄ CXXXIII + t-BuOH

to be the predominant reactions under these conditions, there is no way to rule out reactions 4-6. However reactions 5 and 6 have the same stoichiometry as 2 and 3.

The concentration of CXXXIII as a function of base concentration and alkali metal was followed by both e.s.r. and ultra violet spectroscopy. The solutions of hydrocarbons were 0.01 M while the base solutions were 0.10 M. The final volume of solution was adjusted to four ml. by adding DMSO. The numbers in Table 4 are the peak height of the central peak of the e.s.r. spectrum of CXXXIII at a fixed instrument setting. These numbers were converted to concentrations by comparison with a solution of diphenylpicrylhydrazyl radical

Table 4. Concentration of radical anion as a function of base

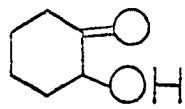
(t-BuOM)/(CXXX)	Relative Concentrations of CXXXIII M					
	Li	Na	K	Rb	Cs(DMSO)	Cs(DMF)
2	0	10	0.5	20	20	--
4	0	18	12	24	45	10
6	0	19	17	25	45	24
8	0	20	21	25	44	24
10	0	18	21	--	--	--
12	0	18	21	25	44	22
16	0	19	21	25	42	22
20	0	18	22	24	--	--
Saturated with base	0.74					
% Conversion	0.2	4.2	4.6	5.5	9.7	5.1
Kx1000	0.004	1.8	2.2	3.2	14	2.8

in DMSO. The per cent conversion was obtained by dividing the concentration of CXXXIII by twice that of CXXX. The value of K was obtained by multiplying the per cent conversion by the concentration of CXXXIII. It follows from these results that t-BuOLi is only poorly dissociated in DMSO. Furthermore t-BuOCs is clearly more dissociated than the other bases. As could be expected if reactions 1-3, and 5 and 6 are predominant, the concentration of CXXXIII as determined by e.s.r. levels out with increasing base concentration. It is possible that the slight fluctuation is due to reaction 4. The results with potassium suggest that the t-BuOK used is contaminated relative to the others, perhaps with the alcohol and/or the

carbonate.

The reaction was also followed by ultra violet spectroscopy. Again the hydrocarbon solutions were 0.01 M and the base solutions 0.10M in DMSO. The absorbance of the peak at 360 millimicrons was measured. The total volume of solution was three ml. The results are listed in Table 5.

Table 5. U.V. absorption as a function of base

Milliliters of Solution				A[360mμ]
CXXX		t-BuOK	t-BuORb	
0.025	0.025	0.005		0.26
0.025	0.025	0.013		0.53
0.025	0.025	0.025		0.76,0.70
0.025	0.025	0.050		0.67,0.74
0.025	0.025		0.100	0.77
0.050	0.025		0.100	1.12,1.11
0.025	0.050		0.100	0.98
0.025	0.025		0.050	0.78
0	0.050		0.100	0.76

The experiments with t-BuOK show the same levelling off of signal as had been indicated by e.s.r. spectroscopy. However it was possible that the absorbance at 360 m_μ was due to CXXXII rather than CXXXIII. In order to check this, the experiments with t-BuORb were performed. The first result again indicates the rough equivalence of base strengths of t-BuOK and t-BuORb. In the second experiment an increase of the concentration of CXXX increases the absorbance. If

the absorbance were due to CXXXII then it should decrease on addition of CXXX due to reaction 3. When the concentration of CXXXII is increased, there is an increase in absorbance but not as great as that caused by CXXX. These results strongly suggest that the absorbance at 360 m_{μ} is due to CXXXIII. The last result in Table 5 indicates reaction 4 can occur under these conditions. While these experiments by no means demand that Equations 1-3 and 5 and 6 are reversible, they are consistent with that hypothesis.

1,2-Cyclohexanedione, M.P. 35°C, lit. 38°C (124), and 2-hydroxycyclohexan-1-one, M.P. 107-111°C, lit. 113°C (128), were commercial materials used without further purification as were the alkali metal tertiary butoxides.

VI. ACKNOWLEDGEMENTS

I would like to thank Dr. G. A. Russell for his kindness and understanding as well as his unstinting support. I would like to thank all the members of the Russell group for their time and advice, especially Dr. E. G. Janzen and Dr. E. T. Strom for introducing me to e.s.r. spectroscopy. I am indebted to Dr. R. W. King, Dr. T. Kinstle, and Mr. R. L. Thrift for many interpretations of spectra. I thank the members of my committee for their time and effort in helping me to obtain an education. I am grateful to the National Aeronautics and Space Administration for support for two years. Finally, I thank my family without whose encouragement this thesis would not have been written.

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