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ELECTRON-TRANSFER REACTIONS OF ORGANIC COMPOUNDS

by

Edwin Thomas Strom

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Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

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Dean of Graduate College

Iowa State University
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Ames, Iowa

1964

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ABSTRACT

The present study was undertaken to determine if electron-transfer could take place between anions (D^{-}) and a variety of unsaturated compounds (A)

$$D{:}^{-} + A \longrightarrow D^{\cdot} + A^{\cdot -}$$

Such electron-transfers would result in the formation of free radicals and radical anions which, if stable, could be detected by electron spin resonance.

The results obtained showed conclusively such electron-transfer reactions take place with relative ease. The rate and extent of electron-transfer between a variety of anions and electron acceptors has been measured. The anions were generated from their conjugate acids by treatment with potassium _t_-butoxide in dimethyl sulfoxide-_t_-butyl alcohol solution. The rate and per cent of electron-transfer was followed by measuring the concentration of stable radical-anions as a function of time by electron spin resonance. The structure of both anions and electron acceptors were varied to determine the scope of such transfers. The results showed that usually dianions are better electron donors than monoanions. Of the monoanions, carbanions proved to be better donors than mercaptide anions, nitranions, or oxanions, although examples could be found of transfer from all of these anions. Organometallic reagents, cyclopentadienide-type anions, and phenone anions were the best donors in the carbanion series. Although it was

not possible in most cases studied to separate those effects due to the rate of ionization from effects due to the electron-transfer, the results were consistent with the least stable anion (as measured by the pK_a of the conjugate acid) giving the most electron-transfer.

The electron acceptors used were a wide variety of unsaturated compounds. Among the most thoroughly investigated were ketones, azo compounds, olefins, aromatics, heteroaromatics, imines, and quinones.

Radical-anions derived from α-diketones and azo compounds were studied in detail. Stable radical-anions of the cyclic α-diketones were formed by base-catalyzed oxidation of the monoketones in dimethyl sulfoxide-*t*-butyl alcohol solution as well as by other methods. Differences between axial and equatorial protons in the α-position were observed for the 4-*t*-butyl cyclohexyl compound and for all rings larger than cyclohexyl. Using known theoretical relationships, the dihedral angles of the axial and equatorial protons and the spin density at the carbonyl carbon atoms were computed. Radical-anions of 1-phenyl-1,2-diketones were also made by oxidation of the corresponding 1-phenyl-1-ketones under the above conditions. Electron-transfer was used to form radical-anions of heterocyclic α-diketones in ethanol. It was found that the radical-anions derived from 2,2'-thenil and 2,2'-furil gave identical spectra.

Radical-anions of a variety of azo derivatives and their vinologs were made by electron-transfer from anions to the azo linkage, by the oxidation of the corresponding dihydro-compound, or in some cases by spontaneous processes occurring in the presence of base.

Molecular orbital calculations were performed on several α-diketones and azo radical-anions. Excellent agreement between experimental and calculated splitting constants was obtained for the azobenzene radical-anion and reasonable, though less successful correlations were obtained for the radical anions of 2,2'-furil and 1-phenyl-1,2-propandione.

The conclusion drawn from this study is that electron-transfer reactions involving carbanions, nitranions, mercaptide anions or organometallic reagents is extremely widespread and of great, but currently unrecognized, importance in organic chemistry. A consideration of electron-transfer reactions can provide an explanation of the mechanism of many organic reactions. Moreover, electron-transfer reactions of the type studied in this work are useful as a means of generating radical-anions for spectroscopic study or synthetic use.

VITAE

The author was born on June 11, 1936, in Des Moines, Iowa. His parents were Mr. and Mrs. Edwin L. Strom. He graduated from North High School of Des Moines in June, 1954. He received the Bachelor of Science in Chemistry degree from the State University of Iowa in June, 1958.

On June 14, 1958, the author married Miss Charlotte Williams of Williamsburg, Iowa. He has two children, Laura Christine, born November 23, 1960, and Eric William, born May 1, 1963.

The author received the Master of Science degree from the University of California at Berkeley in January, 1961. The research was performed in the field of nuclear reactions under the direction of Professor Kenneth Street.

In September, 1960, the author enrolled at Iowa State University. His research was in the field of physical-organic chemistry under the guidance of Professor Glen A. Russell. He received a National Institute of Health fellowship in July, 1962. In February, 1964, he was granted the degree, Doctor of Philosophy, from Iowa State University.

I. INTRODUCTION

Electron-transfer reactions are a part of the general field of oxidation-reduction reactions. Indeed they make up the greater part of the field. Only those cases in which the electrons are transferred by means of an atomic or ionic shift fail to fit easily under this classification.

The Usanovitch acid-base concept is an excellent way of regarding electron-transfer reactions (1). From this viewpoint the electron donor is the Usanovitch base, the electron acceptor is the Usanovitch acid, and electron-transfer is a neutralization reaction.

The excellent work done by Hughes and Ingold on the S_N2 reaction seems to have mesmerized organic chemists. Arrows signifying a two-electron attack are drawn in explaining many chemical reactions. Quite often these reactions could be just as easily written as two one-electron-transfer reactions. Matters have improved somewhat from the days when Hey and Waters, writing a review on free radicals which they obviously feared was too strong for their peers, timidly prefaced their review with the statement,

> It is undoubtedly true, however, that free radicals are only produced in a small minority of reactions in solution, for in most of the reactions of organic chemistry one can demonstrate that ions must intervene. (2)

Nevertheless, the widespread occurrence of free radicals in solution is still not fully appreciated.

The key to the recent advances made in free radical chemistry is the discovery of electron spin resonance absorption (e.s.r.). It is now possible to observe free radicals far more directly than anions or cations. Of course, careful studies must always be made to show that the radicals are a necessary intermediate in the chemical reaction rather than products of a side reaction.

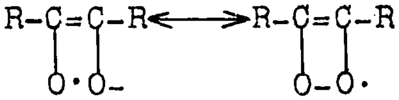
The studies reported herein were concerned with one-electron-transfer reactions in which the donors were organic anions, usually generated in basic solution and usually carbanions, and in which the acceptors were unsaturated linkages of no or little polarity. The chief linkages examined were the $>C=C<$, $-N=N-$, $>C=N-$, and $>C=O$ functions. The latter two examples admittedly have some polar character, but nothing comparable to a semipolar double bond. These functional groups were in generaly highly substituted and/or highly conjugated.

The transfer reactions studied can be divided into two classifications. The more general type consisted of an electron-transfer from a mono- or dianion to one of the previously stated bonds. A special case, studied in some detail, was the case in which the electron donor was the dianion derived from ionizing the two-hydrogen-reduction product of the electron acceptor. Under the first classification the structure of the donor and the acceptor was varied to determine the effect on the ease of electron-transfer.

Most of the e.s.r. work that has been done previously has been concerned with obtaining structural information. Radicals have been made from many classes of compounds solely to compare the experimental results with theoretical predictions. It was decided to study two classes of compounds from this viewpoint. These groups were the radical-anions of azo-compounds (I) and their vinologs and of α-diketones (II).

(I) $\left[R-N\dot{=}N-R\right]^-$

(II)



$$R-\underset{\displaystyle O\cdot}{\overset{|}{C}}=\underset{\displaystyle O^-}{\overset{|}{C}}-R \longleftrightarrow R-\underset{\displaystyle O^-}{\overset{|}{C}}=\underset{\displaystyle O\cdot}{\overset{|}{C}}-R$$

Azo-compounds were of interest because they appeared to be good electron acceptors, while α-diketone radical-anions could possibly provide pertinent information toward the problem of the mechanism of the oxidation of α-hydroxyketones.

In some cases molecular orbital calculations were made to compare experimental spin densities with theoretical predictions.

II. ELECTRON-TRANSFER REACTIONS BETWEEN ANIONS AND UNSATURATED ELECTRON ACCEPTORS

A. Electron-Transfer Reactions between Conjugated Compounds and the Dianions of their Dihydro Derivatives

It is rather surprising that no systematic survey had been made, prior to this study, of electron-transfer reactions between conjugated systems and anions derived from their dihydro derivatives. Dianions can, in principle, be formed from the reduced species, and one would expect a highly favorable equilibrium due to electrostatic considerations. There will be considerable repulsion between the electrons in a poly-negatively-charged ion. The ion can relieve this stress by the transfer of an electron to a suitable acceptor. A dianion must then be a better donor than a monoanion of similar structure. Indeed, theoretical predictions made by Hush and Blackledge predict that the equilibrium lies in favor of the radical-anion for mixtures of aromatic hydrocarbons and the corresponding dianions (3). (This prediction has been criticized by Hoijtink *et al*. (4).)

There are several other reasons for studying electron-transfers of this type. First, there are cases in which the dianion is believed to be a necessary intermediate in the oxidation of a dihydro compound to the dehydro compound. James and Weissberger have shown that the dianion is an intermediate in the oxidation of durohydroquinone to duroquinone

(5). It is thought that the oxidation of 1,4-diones to enediones (6) and hydrazobenzene to azobenzene (7) proceeds through a dianion. James and Weissberger have also suggested a dianion as a possible intermediate in the oxidation of benzoin to benzil (8). Certainly information as to the ease of electron-transfer from these dianions would be of great help in elucidating the mechanism of this type of autoxidation. In the oxidation of durohydroquinone mentioned above, electron-transfer from the dianion to the oxidation product, rather than oxygen, is the rate-determining step. A direct connection of this type can, unfortunately, only be expected in those cases in which the reduction potential of the oxidation product is more positive than that of molecular oxygen. Secondly, this kind of electron-transfer is a very simple method of generating radical-anions. Many of the other techniques for generating radical-anions entail a considerable amount of trouble. If one does an alkali metal reduction, it is necessary to prepare a sodium mirror and to work with a vacuum line. Electrolytic reduction is a good method, but one that is limited to easily reduced materials. Reductions with basic solutions of glucose or sodium dithionite have drawbacks in that glucose is not a very powerful reducing agent and dithionite itself gives a free radical (9). In almost all of the cases to be discussed in which electron-transfer occurs, the radical can also be made by oxidation in basic solution with molecular oxygen, but even this method has limitations. If too much oxygen is added, the radical-anion will be destroyed. Also there will always be dissolved oxygen in the solution, and it has been shown that this causes line broadening in e.s.r. spectra (10). Electron-transfer from dianions to conjugated systems can be performed readily under anaerobic conditions.

To study electron-transfer reactions in general, it seemed advisable to first examine simple systems. Since the best donors are dianions, an electron-transfer to a conjugated system not derived from the dianion could in principle result in two different radical-anions. This would make it extremely difficult to interpret e.s.r. spectra. Electron-transfer from a dianion to an acceptor which is the oxidized form of the dianion should give only one radical-anion.

To keep sentences from becoming unduly cumbersome, conjugated compounds will henceforth be referred to as Π compounds, and the corresponding dihydroderivatives will be referred to as ΠH_2 compounds. The resultant radical-anions will be designated as $\Pi^{\dot{-}}$. The dianion derived from the ΠH_2 compound will be written as $\Pi^{=}$.

Certain isolated examples of electron-transfer from $\Pi^{=}$ anions to Π compounds have been studied. The best known occurs in the oxidation of durohydroquinone to duroquinone, cited previously (5). James and Weissberger found a second order dependence on base concentration and also found the autoxidation to be autocatalytic. Addition of duroquinone enhanced the rate as it should if autocatalysis were taking place. The mechanism was explained in the following manner. The durohydroquinone was doubly ionized. This dianion could transfer electrons to oxygen, although slowly, to give duroquinone. This accounted for the initial dependence on oxygen. With duroquinone, which has a more positive reduction potential than oxygen, a very facile electron-transfer occurred from the dianion to give two durosemiquinone radicals. These react quite readily with oxygen to give duroquinone.

The equilibrium constant for the above reaction was actually measured spectroscopically by Baxendale and Hardy in aqueous solutions (11). They found the value to be 1.28 in the temperature range 15°C. to 30°C.

It is quite possible that such a mechanism might be operative in the oxidation of other hydroquinones. Von Euler and Brunius found a second order dependence on base concentration in the pH range 7.08 to 8.16 in the oxidation of hydroquinone (12). Unfortunately, in this case and many others, matters are complicated because the quinone ring itself is attacked. The recent development of techniques for measuring very fast reactions made it possible for Diebler *et al*. to measure the rate of electron-transfer from hydroquinone dianion to *p*-benzoquinone (13). They found the rate constant to be 2.6 x 10^8 l./Mol.-sec.

Another example of an electron-transfer to a π compound arose from the studies of Weissberger on the oxidation of benzoin (14). A purple color is observed in this oxidation. This color is enhanced by the addition of benzil. Weissberger proposed that this purple color was a bimolecular compound resulting from a combination of the dialkali metal salt of benzoin with benzil. He never did completely exclude the possibility of the ketyl of benzil, however (15). The correct explanation was due to Michaelis and Fetcher (16). They mixed benzoin and benzil anaerobically and observed the purple color in the presence of base. By color intensity and concentration measurements they showed that the purple color was not due to a bimolecular compound. They then proposed that the purple color arose from the radical-anion and postulated, though without experimental data, that the oxidation of benzoin to benzil was two-step, with the benzil radical-anion being the intermediate.

The next logical step was taken by Ihrig and Caldwell, who performed magnetic susceptibility measurements on this system (17). They bubbled oxygen through a benzoin solution until a purple color was observed, measured the magnetic susceptibility, bubbled oxygen through until the solution was colorless, and measured the magnetic susceptibility again. They found a large magnetic susceptibility in the purple solution. They also measured magnetic susceptibilities in solutions of benzoin heated with benzoyl peroxide and benzoin and benzil heated with benzoyl peroxide. The solution containing both benzoin and benzil gave a higher initial susceptibility. Their conclusions were that a paramagnetic species was present in the oxidation of benzoin to benzil and that this species was there in larger amounts in the presence of benzil.

E.s.r. experiments on this system were performed by Venkataraman and Fraenkel (18). They have used the radical formed from benzoin and benzil to check the sensitivity of e.s.r. spectrometer. They did not state whether the experiments were done anaerobically, and the line width reported differs from the one observed in this laboratory. Recently Dehl and Fraenkel obtained an improved spectrum of benzil radical-anion by electrolytic reduction of benzil in dimethyl formamide (19).

Another example of electron-transfer in the π-πH_2 system is the reaction of the dipotassium salt of $\alpha,\alpha,\alpha',\alpha'$-*tetrakis*-(ethyl sulfonyl)-*p*-quino-dimethan in acetonitrile to give the radical-anion (20). The same reaction takes place between the dianion of tetracyanoethylene and tetracyanoethylene (21).

Although dinitrodurene undergoes a two-electron reduction at the dropping mercury electrode, it was found that the dinitrodurene radical-anion could be observed, presumably because of electron-transfer with unreduced dinitrodurene (22).

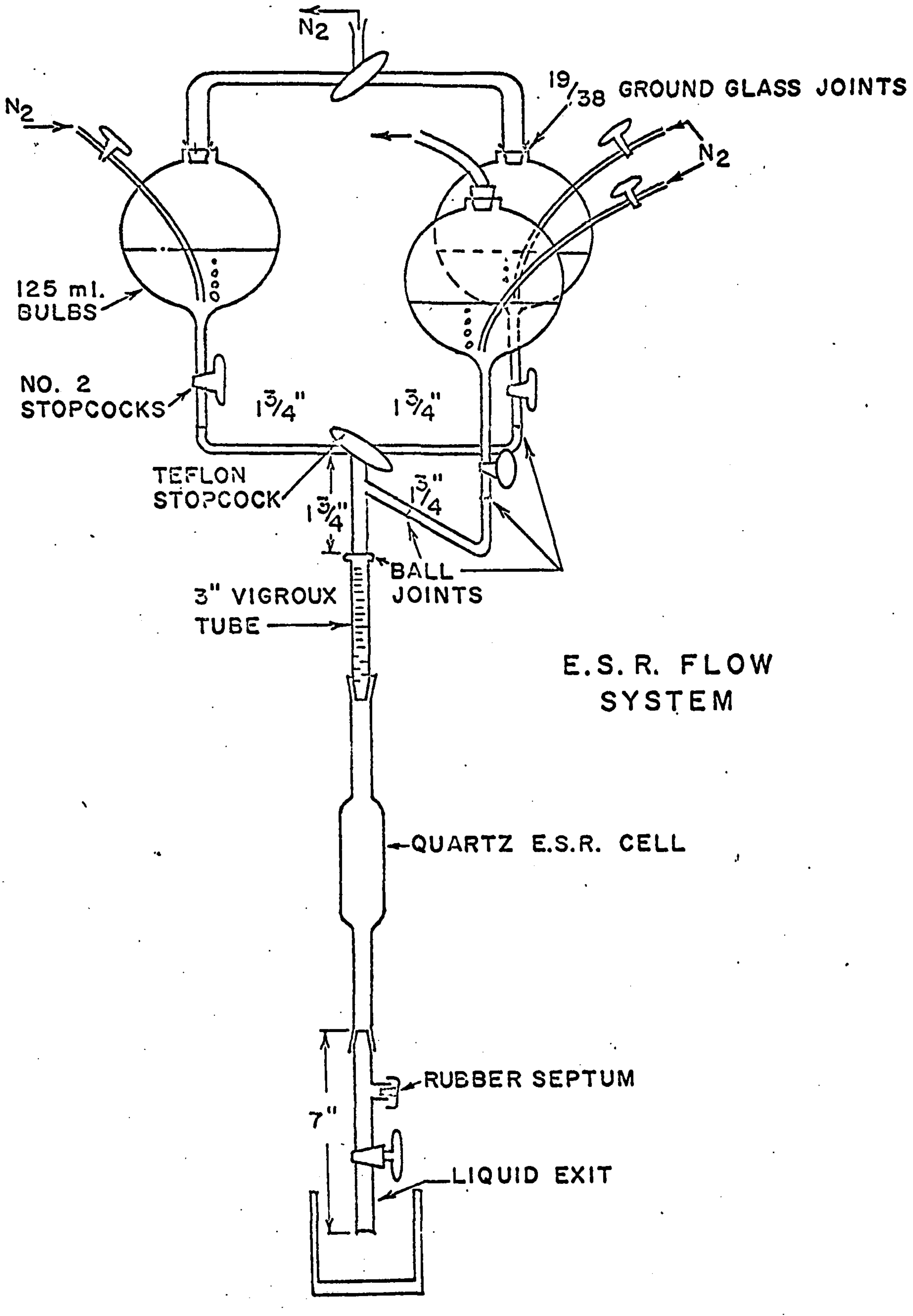
If one goes to nonpolar solvents, a few examples of radical-anion formation from dialkali metal adducts of olefins and olefins have been reported. Cyclooctatetraene very readily adds two moles of alkali metal to give a dianion. This dianion in turn undergoes electron-transfer with unreduced cyclooctatetraene to give cyclooctatetraene radical-anion (23). Although the equilibrium lies far to the left, due to the sensitivity of e.s.r., the radical-anion can be detected. The disodium adduct of tetraphenylethylene undergoes the analogous reaction with tetraphenylethylene, although only in certain aprotic solvents (24). Such behavior is also noted for dimetal adducts of stilbene (25).

The electron-transfer from the dianion to the oxidized compound has actually been used to isolate the lithium salt of the radical-anion of azobenzene (26). Hydrazobenzene readily reacts with two moles of methyllithium to give a dianion soluble in ether. When additional azobenzene is added, the salt of the radical-anion precipitates from solution.

The experiments were performed in two different ways. The earlier experiments were performed on a flow system. A mixture of the Π and ΠH_2 compounds was mixed with a solution of base whose concentration was twice that of the ΠH_2 compound. All solutions were flushed with nitrogen for twenty minutes before mixing. The solutions were in glass vessels mounted above the cavity. Figure 1 shows the arrangement in detail. Radicals could be observed within thirty seconds after mixing. After the mixture was run, the Π and ΠH_2 compounds were run separately. If the amount of radical in the mixture was at least twice as great as the sum of the radical concentration in the separate runs on the Π and ΠH_2 compounds, electron-transfer was judged to have taken place. If the radical was long-lived, an attempt was made to resolve all hyperfine interactions. If the experimental spectrum coincided with that theoretically predicted or with the experimental spectrum of $\Pi^{\cdot}$ made in an unambiguous manner, then one could be certain that the electron-transfer gave the expected product. All the transfers cited herein conform to these criteria. Specific descriptions of the radicals will be given later.

An alternate system was also used. Solutions of Π and ΠH_2 compounds and base were flushed with nitrogen in a special apparatus (see Figure 2) outside the cavity. After degassing, the cell was sealed, the solutions mixed, and the cell placed in the cavity. A radical signal could usually be found within two minutes after mixing. Although a radical could not be observed as quickly as with the flow system, this system proved superior on many other counts. There were fewer

Figure 1. Flow system used for initial experiments



E.S.R. FLOW
SYSTEM

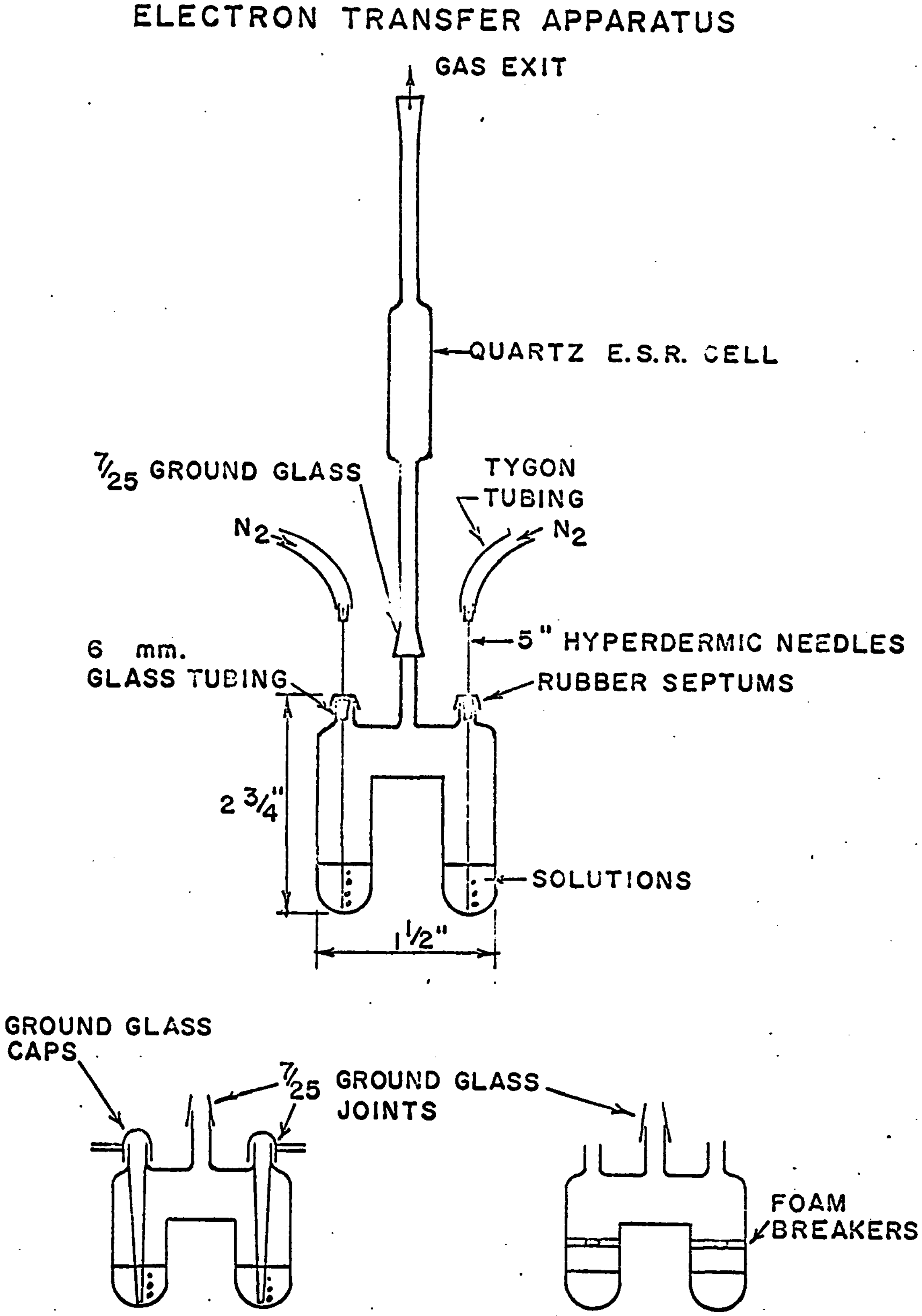


Figure 2. Degassing arrangement and mixing cells used in electron-transfer experiments

joints with correspondingly fewer opportunities for air leakage, and the smaller volumes made possible both better degassing and a great saving of chemicals and solvents. The volume of liquid used was 2 ml. and the volume of the apparatus approximately 15 ml. Experiments could be performed with from one to five milligrams of π or πH_2.

The radical concentration was estimated by comparing the peak-to-peak distance from the maximum to the minimum of the overmodulated first derivative curves of the radical and a standard solution of diphenylpicrylhydrazyl (DPPH) at the same instrument settings and in the same solvents (27, 28). The reproducibility was ± 20%, and the accuracy ± 50%. DPPH has a long line width due to interactions with two nitrogens. Accuracy should be best for those radicals which also have two nitrogen atoms while the concentration was undoubtedly overestimated for those radicals of short line width containing hyperfine interactions with protons.

The e.s.r. spectra were obtained using a Varian V-4500 spectrometer equipped with 100 Kc./s. field modulation and a six inch magnet. Flat fused silica cells (Varian V-4548 aqueous solution sample cells) were used for all experiments.

The following sets of π and πH_2 compounds appeared to undergo electron-transfer reactions when treated with potassium t-butoxide in dimethyl sulfoxide (80%)-t-butyl alcohol (20%): azobenzene-hydrazobenzene, 2,3-diphenylquinoxaline-1,2-

dihydro-2,3-quinoxaline, diethyl azodiformate-diethyl dicarbamate, dibenzoyldiimide-1,2-dibenzoylhydrazine, N,N'-diphenyl-*p*-benzoquinone diimine-N,N'-diphenyl-*p*-phenylene diamine, $\Delta^{9,9'}$-bifluorene-9,9'-bifluorene, and acridine-acridan. Experiments performed by E. G. Janzen show that the following systems undergo analogous reactions: fluoren-9-ol-fluoren-9-one, xanthen-9-ol-xanthen-9-one, and benzhydrol-benzophenone (29). A mixed experiment was also performed with azobenzene and acridan to show the generality of this type of transfer. The more complete study of mixed transfer will be discussed later.

No transfer could be observed under the above conditions for the following Π and ΠH_2 compounds: benzene-1,3-cyclohexadiene, naphthalene-1,4-dihydronaphthalene, anthracene-9,10-dihydroanthracene, phenanthrene-9,10-dihydrophenanthrene, 1,1,4,4-tetraphenyl-1,3-butadiene-1,1,4,4-tetraphenyl-2-butene, tetraphenylethylene-1,1,2,2-tetraphenylethane, azo-bis-isobutyronitrile-hydrazo-bis-isobutyronitrile, 1,2-bis-(4-pyridyl)-ethylene-1,2-bis-(4-pyridyl)-ethane, 1,2-bis-(2-pyridyl)-ethylene-1,2-bis-(2-pyridyl)-ethane, phenylazotriphenylmethane-phenylhydrazotriphenylmethane, N-diphenylmethyleneaniline-N,1,1-triphenylmethylamine, N-benzylideneaniline-N-phenylbenzylamine, and phenanthridine-5,6-dihydrophenanthridine.

Electron-transfer was observed for the following compounds in ethanol containing potassium hydroxide: benzil-benzoin, 2,2'-furil-2,2'-furoin, 2,2'-pyridil-2,2'-pyridoin, 3,3',5,5'-tetra-t-butyl-4,4'-stilbenequinone-3,3',5,5'-tetra-t-butyl-4,4'-stilbenediol, and 3,3',5,5'-tetra-t-butyl-4,4'-diphenoquinone-2,2',6,6'-tetra-t-butyl-p,p'-biphenol. In all cases growth was followed to a maximum (usually 5-10 minutes). The t-butyl derivatives were used to cut down radical blanks.

The results which were obtained are summarized in Table 1. It can be seen that in most of the $\pi - \pi H_2$ systems where transfer is observed, there is a significant amount of radical-anion. An actual equilibrium constant has been measured by Russell and Konaka for the transfer reaction between hydrazobenzene dianion and azobenzene.* This is a particularly favorable case, for the azobenzene radical-anion seems extremely stable in dimethyl sulfoxide-t-butyl alcohol solution. The method used was to mix equimolar amounts of hydrazobenzene and azobenzene under anaerobic conditions and measure the concentration of radical. The base concentration was increased until no further growth of radical-anion was observed. The entirely reasonable assumption was then made that all of the hydrazobenzene was present as the dianion. Under these

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*G. A. Russell and R. Konaka, Department of Chemistry, Iowa State University, Ames, Iowa. Private communication regarding azobenzene radical-anion. 1963.

Table 1. Extent of electron transfer from dihydro compounds to their unsaturated analogs

Acceptor[a]	Solvent	Per cent transfer[b]
Azobenzene	Dimethyl sulfoxide (80%)- *t*-butyl alcohol (20%)	100
2,3-Diphenylquinoxaline	"	46
Diethyl azodiformate	"	0.04
Dibenzoyldiimide	"	0.025
N,N'-Diphenyl-*p*-benzoquinone diimine	"	6.5
$\Delta^{9,9'}$-Bifluorene	"	12.5
Acridine	"	0.33
Fluorenone	"	100
Xanthone	"	100[c]
Benzophenone	"	4×10^{-3}[d]
2,2'-Furil	Ethyl alcohol	100
Benzil	"	2.8
2,2'-Pyridil	"	0.23
3,3',5,5'-Tetra-*t*-butyl-4,4'-stilbenequinone	"	14
3,3',5,5'-Tetra-*t*-butyl-4,4'-diphenoquinone	"	87

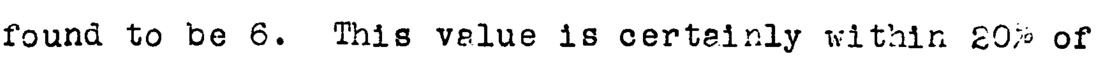
[a] $[\Pi] = 0.01$ *M*., $[\Pi H_2] = 0.01$ *M*. $[\text{Base}] = 0.02$ *M*.

[b] Per cent transfer = $[\Pi^{\overset{-}{\cdot}}] \cdot 100/[\Pi H_2] + [\Pi]$.

[c] $[\Pi] = 0.087$ *M*., $[\Pi H_2] = 0.085$ *M*., $[\text{Base}] = 0.175$ *M*.

[d] $[\Pi] = 2.29$ *M*., $[\Pi H_2] = 2.24$ *M*., $[\text{Base}] = 4.5$ *M*.

conditions the equilibrium constant for the reaction (III)

(III) 

was found to be 6. This value is certainly within 20% of the value given in Table 1.

The amount of electron-transfer observed will be dependent upon three things: the ease of ionization of the πH_2 compound, the ease of reduction of the π compound, and the ease of oxidation of $\pi^=$. One can obtain some idea as to the magnitude of the first two factors, so explanations of the experimental results will be based solely on these factors. Although these effects are not easily separable, one would expect them to be parallel, that is, the ease of ionization of the πH_2 compound will increase as the ease of reduction of the π compound increases. It would be wrong to carry this reasoning too far, for it has been shown that if an anion is extremely stable, it is quite reluctant to give up an electron (29, 30).

Focusing on the results in ethanol first, if we take the per cent electron-transfer as a measure of the reduction potential of the acceptor, the results show that the order of increasing reduction potential is pyridil < benzil < 3,3',5,5'-tetra-t-butyl-4,4'-stilbenequinone < 3,3',5,5'-tetra-t-butyl-4,4'-diphenoquinone < furil. While the experimental uncertainties are such as to preclude a linear relationship, one could hope that experimental reduction potentials would be in the same order. The reduction potential is a function not only of the structure of the reductant but also of the solvent and pH. The ease of reduction usually decreases with increasing pH. Since it was impossible to find data for the very high pH's used in our systems, potentials are compared at pH = 7, ignoring the difference in solvents. The potentials are pyridil, -0.57 v. (31), benzil, -0.27 v. (32) and for 3,3',5,5'-tetra-t-butyl-4,4'-diphenoquinone, 0.65 v. (33). The value for 3,3',5,5'-tetra-t-butyl-4,4'-stilbenequinone can be estimated from the values for 4,4'-diphenoquinone and 4,4'-stilbenequinone, 0.954 v. and 0.854 v., respectively (34). One arrives at a value of 0.55 v. It should be noted that the values for pyridil and the quinones are for two electron reductions. The order predicted is thus the experimental one. Unfortunately there is no good way to estimate what the reduction potential of 2,2'-furil is. If we do assume that ease of reduction of the π compound parallels ease of ionization of the πH_2 compound, there is evidence that furil ought to be more easily reduced than benzil. Weissberger et al. have shown that the rate controlling step in the oxidation of benzoins in basic solution is ionization (35). They found that furoin was oxidized 44 times as rapidly as benzoin. From electronegativity considerations one also would expect furil to be more easily reduced. One would not expect, however, that furil is more easily reduced than the quinones.

It has been shown by Russell and coworkers that many extremely weak acids can be ionized with potassium-t-butoxide in dimethyl sulfoxide (36). Cram and coworkers have found rate enhancements in racemization experiments of the order of 10^9 for a reaction performed in dimethyl sulfoxide as opposed to the same experiment performed in methanol (37). It is thought that enhancement of the basicity of alkoxide ion in dimethyl sulfoxide stems from a lower degree of solvation of the alkoxide ion (37, 38). In fact there is some evidence that in the absence of hydrogen bonding alcohols are really quite weak acids, with acidities of the order of triphenylmethane (39). Dimethyl sulfoxide thus allows the true basicity of alkoxide ion to be detected.

As in ethanol, the per cent of electron-transfer for the reactions in dimethyl sulfoxide-t-butyl alcohol should reflect the ease of ionization of the πH_2 compound, the ease of reduction of the π compound, and the ease of oxidation of the $\pi^=$ compound. Again it will be most convenient to correlate per cent electron-transfer with literature reduction potentials in neutral solution, since more data is available. In general these comparisons will be for different solvents, however. From the electron-transfer experiments it can be predicted that the order of increasing reduction potential is benzophenone $<$ dibenzoyldiimide $<$ diethyl azodiformate $<$ acridine $<$ N,N'-diphenyl-p-benzoquinone diimine $<$ $\Delta^{9,9'}$-bifluorene $<$ 2,3-diphenylquinoxaline $<$ azobenzene, fluorenone, xanthone. The literature values for the reduction potentials and the number of electrons added are as follows: acridine, -0.31 v.

(1) (40); azobenzene, -0.46 v.(2) (41); quinoxaline, -0.64 v.(2) (42); fluorenone, -1.00 v.(1) (43); $\Delta^{9,9'}$-bifluorene, -1.08 v.(1) (44); benzophenone, -1.29 v.(1) (45); and xanthone, -1.30 v.(2) (46). Quinoxaline was chosen as a model for diphenylquinoxaline, but the diphenyl derivative should reduce more easily. It is quite apparent that there is no good correlation.

There are both specialized and general reasons for the discrepancies noted. In the case of dibenzoyldiimide it is known that the π compound is rapidly destroyed by basic hydrolysis (47). The author has observed nitrogen evolution when diethyl azodiformate is reacted with base, while it has been shown that benzophenone reacts rapidly with dimethylsulfinyl carbanion, present in these mixtures to some extent, to form an adduct (36, 48). Furthermore both radical-anions are reactive and undergo further reactions. The radical-anions observed in these cases definitely are not the result of equilibrium processes.

It also appears that the basic postulate as to ease of ionization correlating with ease of reduction breaks down. Acridine supposedly reduces much more easily than fluorenone, but fluorenol is certainly more easily ionized than acridan. It must be remembered, however, that these reduction potentials are determined in a variety of solvents.

The other possible correlation would be with the ease of ionization of the πH_2 compound. If we look at the first ionization constant, then we would predict that fluorenol and xanthydrol would be the best donors. This is what is found experimentally. No difference can be found between the alcohols and hydrazobenzene, presumably because the poorer acidity of hydrazobenzene is made up for by the more positive reduction potential of azobenzene. The quinoxaline derivative, however, ought to transfer as well as the azo-derivative so this difference is unexpected. From acidity considerations one would expect N,N'-diphenyl-*p*-phenylene diamine and 9,9'-bifluorene to transfer as well as hydrazobenzene. The pK_a's of these compounds ought to resemble those of diphenylamine, fluorene, and aniline, respectively. Those pK_a's are 23, 25, and 27 (49). It may be that this is a case of an anion being too stable to lose an electron easily. Russell and Smentowski have found that aniline undergoes base-catalyzed oxidation in dimethyl sulfoxide more readily than diphenylamine.* Fluorene oxidizes readily under these conditions, however (29). In the case of 9,9'-bifluorene steric effects, due to the size and non-planarity of both the π and πH_2 compound, may cut down on electron-transfer.

Further experiments which might be done are of three

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*G. A. Russell and F. J. Smentowski, Department of Chemistry, Iowa State University, Ames, Iowa. Private communication regarding oxidation of aromatic amines. 1961.

types. First of all, the π compounds ought to be reduced polarographically in dimethyl sulfoxide or ethanol to see if these potentials would follow the per cent electron-transfer noted. Next, pK_a's of the πH_2 compounds should be determined in the given solvent. This would be rather difficult because these compounds oxidize in base easily. Finally, attempts should be made to see if monoanion, dianion, or both are the principle electron donors. Although discussion of the results has been based on the premise that the dianion is the donor, no proof has been brought forth. It will be shown later that monoanions can in some cases be good donors. Dianions are probably better, but there are undoubtedly many more monoanions than dianions present under these conditions. The experiments should be repeated using monoalkylated donors such as N-methylhydrazobenzene, benzoin methyl ether, etc. Substitution of a methyl group should not change the acidities of the donors too much. If such substitution cuts down electron-transfer sharply, then the dianion probably is the principle donor. If electron-transfer is almost the same, then a monoanion is the main donor. Finally, by studies performed at a variety of base concentrations, it should be possible to obtain values of K_e (IV). Such experiments will

$$\text{(IV)} \qquad \pi + \pi^{=} \xrightleftharpoons{K_e} 2\pi^{\overline{\cdot}}$$

allow these $\pi^{=}, \pi$ systems to be understood fairly well.

B. Electron-Transfer Reactions between Conjugated Compounds and Mono- and Dianions

The logical step proceeding from investigation of electron-transfer between πH_2 and π compounds was to attempt to find electron-transfer from monoanions to unsaturated systems. Also electron-transfer from a dianion not derived from the unsaturated system was examined. This latter example could have been quite complex in principle because two radical-anions can be produced. In practice it proved to be much simpler.

The unsaturated compounds used as acceptors were as before of the nonpolar double bond type, although the $\gt C=N-$ and $\gt C=O$ functions, which have some polarity, were also investigated. Concurrent investigations were carried out by Janzen (29), using semipolar double bonds as acceptors. His results will be cited here, as they tell a great deal about which systems make good electron acceptors.

It appears that Schlenk _et_ _al_. first recognized the transfer of an electron from a carbanion to an unsaturated organic compound (50, 51). They found that tritylsodium reacts with benzophenone and other diaryl ketones with characteristic color changes to give trityl peroxide and pinacol after hydrolysis and air oxidation. Presumably the transfer resulted in the radical-anion and the triphenylmethyl radical. The radical-anion dimerized to give the pinacol dianion.

Considerable attention has been given to the reduction of benzophenone to benzpinacol or benzhydrol. When trityl Grignard reagents were used, Bachmann found trityl radical and the ketyl present (52). He also observed this process for xanthone, fluorenone, and benzil. The entire process has been attributed to reduction of the ketone by magnesium (53), by magnesium (I) halide (54, 55), by electron-transfer from the incipient carbanion to the ketone (52, 56), and to the decomposition of an initially produced addition product (57). In view of the work to be discussed, the electron-transfer explanation is undoubtedly correct.

Tritylsodium has been found to reduce cyclooctatetraene (58), while the dianion of cyclooctatetraene will transfer an electron to 2,4,6-trimethylpyrylium salts (59) and possibly benzophenone (58). Bachmann found that the "di-Grignard" reagent of hydrazobenzene reduced benzil to benzoin with the formation of azobenzene (52).

Electron-transfer is more prone to occur from anions derived from the heavier elements of a group. Triphenylstannylsodium reduces carbon dioxide, sulfur dioxide, oxygen, or benzophenone to sodium oxalate, sodium dithionite, sodium peroxide, or benzophenone ketyl (60). From electronegativity considerations one would predict that ease of electron-transfer from an anion would decrease as one goes across the periodic table, It is interesting to note that lithium cyclohexylamide reduces 3- or 8-methylfluoranthene and anthracene to the corresponding radical-anions (61, 62), while the very powerful electron acceptor, tetracyanoethylene is reduced by iodide ion (63, 64).

It has been found by Russell and coworkers that nitrobenzene catalyzes the autoxidation of fluorene, benzyl alcohols, nitroalkanes, alkylpyridines, and phenones.* Such catalysis has been attributed to the formation of nitrobenzene radical-anion by electron-transfer from the anion to the catalyst (V). This effect has also been observed in the

$$\text{(V)}\quad RH \rightleftharpoons R^{-};\; R^{-} + ArNO_2 \longrightarrow ArNO_2^{\cdot -} + R\cdot;\; R\cdot + O_2 \longrightarrow RO_2\cdot$$

oxidation of benzoin (14), hindered phenols (65), and mercaptans (66). Smentowski investigated the reaction of mercaptans with such organic acceptors in basic solution and an inert atmosphere and found sizeable yields of disulphides (67). Based on the yield of disulphide, he found the following decreasing order of oxidizing power: azodicarbonamide nitrosobenzene maleic anhydride acrylonitrile nitrobenzene.

The most striking example of electron-transfer from an anion to an unsaturated compound stems from the work of Russell and Janzen (68), who found that a large number of

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*G. A. Russell, E. G. Janzen, E. J. Geels, and S. Mak, Department of Chemistry, Iowa State University, Ames, Iowa. Private communication regarding catalysis of oxidations. 1962.

p-and *o*-nitrobenzene derivatives spontaneously produce the radical-anions of the unionized nitroaromatic in basic solution in the absence of oxygen. This has been attributed to electron-transfer from the anion, or a charge-transfer complex of the anion, to the parent nitro compound.

Foster and Mackie have done extensive work on the Zimmerman and Janovsky reactions (69, 70). In these reactions ketones containing ionizable hydrogens are treated with the nitroaromatic in basic solution. Various colored products are formed, and electron-transfer may play an important part in these reactions.

Amines are isoelectronic with carbanions, so one might expect that they might undergo electron-transfer similar to carbanions. Electron-transfer products have been observed between aliphatic amines and 1,3,5-trinitrobenzene (71), tetracyanoethylene, and tetracyanoquinodimethan (72). However it has been concluded by Briegleb and coworkers that electron-transfer does not occur in the main step of the reaction between amines and di- or trinitrobenzene (73).

Electron-transfer is a distinct possibility in many charge-transfer complexes. The theory of these complexes, first discovered by Benesi and Hildebrand (74), is due to Mulliken (75,76). Mulliken stated that the stability of these complexes was due to resonance between a state in which the two moieties were bonded by Van der Waals forces and a state in which complete electron-transfer had taken place. The lower state, in which the Van der Waals attraction is important is a singlet, while the triplet state, in which complete electron-transfer has taken place, is normally an excited state. If the electron affinity of the acceptor is greater than the ionization potential of the donor, the triplet state can become the ground state. This was first shown by Bijl <u>et al</u>. who demonstrated that certain solid charge-transfer complexes were paramagnetic (77, 78). Matsunaga and McDowell actually detected the presence of two different radicals (79).

Mulliken classified donors into π-type, n-type, or ionic type according to whether the electron came from a bonding molecular orbital, a non-bonding molecular orbital, or from a negatively-charged ion. Acceptors were π-type, v-type, or d-type according to whether the electron went into a π orbital, a vacant orbital, or would dissociate the molecule. Examples of paramagnetism in the π-π (77, 78, 79, 80, 81, 82, 83, 84, 85), π-d (86, 87, 88, 89), n-v (71, 90), and π-v (91, 92, 93, 94) types of charge-transfer complexes are now known. Some of these paramagnetic solids dissociate in polar solvents to give the radical-anions and -cations. Examples are the tetramethyl-*p*-phenylene diamine complexes with quinones or tetracyanoquinodimethan which dissociate in polar solvents to the radical-ions (84, 95, 96). Usually complexes with tetracyanoethylene are diamagnetic (21), but in polar solvents the complex of tetramethyl-*p*-phenylene diamine with tetracyanoethylene dissociates into radical-ions (97).

The first thing to be tested in the present work was the postulate that monoanions could indeed transfer an electron to suitable acceptors. Since this was found to be true, the effect of varying the structure of the carbanion on the amount of electron-transfer was examined. The electron acceptor chosen was azobenzene in the solvent dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%). Potassium *t*-butoxide was used to generate the carbanions. Azobenzene was quite a desirable double-bond acceptor, for the radical-anion was stable under the reaction conditions for many hours, there was no e.s.r. signal in the absence of donor anion, and the characteristic line width made it possible to identify the radical-anion when resolution was impossible. The degassing apparatus and procedure described earlier were used. The concentrations of donor, acceptor, and base are given in Table 2.

Electron-transfer was also studied using fluorenone as an acceptor in dimethyl sulfoxide (20%)-*t*-butyl alcohol (80%). The results for a variety of carbanions are given in Table 2. For experiments using azobenzene as an acceptor the growth of radical was followed to a maximum. No transfer was observed for the anions of *n*-butyl mercaptan, thiophenol, toluene-3,4-dithiol, nitroethane, nitromethane, 2-nitropro-

Table 2. Extent of electron-transfer of carbanions with azobenzene and fluoren-9-one

		% Electron-transfer (time)[a]	
Donor[b]	Acceptor[c]	Azobenzene[d]	Fluoren-9-one[e]
Solvent blank		0.01% (1 hr.)	0.3% (1 hr.)[f]
Cyclopentadiene		0.4 (12 hrs.)	5.6 (1.4 hrs.)[f]
Indene		3 (4.8 hrs.)	74 (5 min.)
Fluorene		56 (5.7 hrs.)[g]	
Diphenylmethane		2 (6 hrs.)	
Triphenylmethane		1.6 (12 hrs.)	
Acetophenone		50 (1.3 hrs.)	
Propiophenone		34 (18 min.)	1.4 (2 hrs.)[f]
Isobutyrophenone		3 (6 hrs.)	
Hydrazobenzene		142 (5 min.)	72[h] (5 min.)
Fluoren-9-ol		100[h] (5 min.)	14[h] (5 min.)
1,4-Diphenyl-1,4-butanedione			9 (54 min.)[i]
9,10-Dihydroanthracene		24[j] (5 min.)	
n-Butyllithium		1.6[k] (5 min.)	50><98[k] (5 min.)

[a] See footnote c, Table 1.

[b] 0.025 *M* in the presence of 0.05 *M* potassium *t*-butoxide.

[c] Acceptor = 0.005 *M*.

[d] In DMSO (80%)-*t*-butyl alcohol (20%).

[e] In DMSO (20%)-*t*-butyl alcohol (80%).

[f] Radical growth not followed to maximum concentration.

[g] Spectrum not consistent with acceptor radical-anion.

[h] Predominant spectrum is that of fluorenone ketyl.

[i] In ethanol containing 0.05 *M* sodium ethoxide.

[j] Radical concentration decreasing.

[k] In tetrahydrofuran (75%)-*n*-hexane (25%).

pane, ethyl acetate, benzhydrol, or 9-phenylfluorene. In every experiment an attempt was made to obtain maximum resolution of the radical in order to obtain unequivocal evidence as to the nature of the radical-anion.

It is interesting to compare results using semipolar double bonds as acceptors. Table 3 gives the results of Janzen for the acceptors nitrobenzene and m-dinitrobenzene. Nitrobenzene gave large blanks in a solvent containing mainly dimethyl sulfoxide, so the solvent system used in this case was dimethyl sulfoxide (20%)-t-butyl alcohol (80%). For analogous reasons experiments performed with m-dinitrobenzene were performed in ethyl alcohol.

Typical graphs of the rate of electron-transfer from several different anions to azobenzene are given in Figure 3.

Electron-transfer was also studied as a function of the structure of the acceptor. Six different donor systems were studied with many different acceptors. These results are given in Table 4. Negative results were obtained when the anions from propiophenone, 1,4-diphenyl-1,4-butanedione, or 9,10-dihydroanthracene with N-diphenylmethyleneaniline, 1,1,4,4-tetraphenyl-1,3-butadiene, 1,8-diphenyl-1,3,5,7-octatetraene, perylene, tetraphenylethylene, phenanthridine, 2-methyl-2-phenylindan-1-3-dione, 2,5-diphenyl-3,4-benzofuran, benzothiazole, or benzooxazole.

Some acceptors which are known to be easily reduced gave

Table 3. Extent of electron-transfer of anions with nitroaromatics

		% Electron-transfer (5 min.)[a]	
Donor[b]	Acceptor[c]	Nitrobenzene[d]	*m*-Dinitrobenzene[e]
Solvent blank		0.1 (10 min.)	0.1 (20 min.)
Fluorene		13	40,80 (20 min.)[f]
9-Phenylfluorene[g]		8	
Indene		36	2[f]
Cyclopentadiene		0.8,1.4 (10 min.)	2.6,10 (1 min.)
Diphenylmethane		3.6,4.8 (10 min.)	
Phenylacetylene		0.4	
Diphenylacetonitrile		2	
Phenylacetonitrile		0.5 (10 min.)	
4-Picoline-N-oxide		0.1 (10 min.)	
Acetophenone		0.8 (20 min.)	2.7
Propiophenone		91	4
Isobutyrophenone		0.2	0.5
1,4-Diphenyl-1,4-butanedione		72[f]	2.6
Cyclohexanone		1.5	
Acetone		0.1	0.8
Ethyl acetate		0.1	0.3,0.5 (20 min.)
Diethyl malonate		0.1	5
1,3-Indanedione			0.1,2.4 (15 min.)
Bindone			0.1,0.8 (25 min.)
Benzoin		100[h]	

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[a] Extent of transfer = [radical-anion](100/0.005); the concentration of radical anion was estimated by comparison of the observed e.s.r. peak heights with those obtained from known concentration of diphenylpicrylhydrazyl in the same solvent.

[b] Donor substrate = 0.025 *M*, [base] = 0.05 *M*.

[c] Acceptor = 0.005 *M*.

[d] In DMSO (20%)-*t*-butyl alcohol (80%) containing potassium *t*-butoxide.

[e] In ethanol containing sodium ethoxide.

[f] Spectrum not consistent with acceptor radical-anion.

[g] Donor-substrate = 0.013 *M*.

[h] Spectrum dominated by radical-anion from donor.

Table 3. (Continued)

	% Electron-transfer (5 min.)	
Donor Acceptor	Nitrobenzene	*m*-Dinitrobenzene
Fluorene-9-ol	100^{h}	
Xanthen-9-ol.	1.0 (10 min.)	
Benzhydrol	0.1	
1,4-Hydroquinone	40^{i}	100^{i}
2,6-Di-*t*-butyl-4-methylphenol	0.1	0.5 (20 min.)
Thiophenol	0 2 (30 min.)	0.6,2 (8 min.)
3,4-Dimerceptotoluene	11	5^{f}
n-Butylmercaptan	0.3 (20 min.)	12^{f}
Nitromethane	0.4 (20 min.)	2
Nitroethane	0.6 (20 min.)	2
2-Nitropropane	0.2 (20 min.)	0.3,2 (40 min.)
Nitrocyclohexane	0.1 (20 min.)	
N-Hydroxybenzene-sulfonamide	92	10^{f} (10 min.)
Hydrazobenzene	2 (40 min.)	7.5^{f} (2 min.)
Triphenylmethane	2.7 (10 min.)	
Diphenylamine	0.1 (10 min.)	
Carbazole	0.1 (10 min.)	
Indole	0.1 (10 min.)	
Benzophenone ketyl[j]	100	6.3 (3 min.)
n-Butyllithium[k]	6^{k}	

[i] Two recognizable radical-anions present.

[j] Produced from dissociation of saturated solution of benzpinacol.

[k] 1 *M* *n*-Butyllithium in tetrahydrofuran (75%) hexane (25%), no further hyperfine resolution of the nitrogen triplet observed.

very large blanks. Such acceptors were *trans*-1,2-dibenzoylethylene, duroquinone, tetracyanoethylene, penchlorofulvalene, tetrachloro-*p*-benzoquinone, benzil, 3,3', 5,5'-tetra-*t*-butyl-4,4'-stilbenequinone and 3,3', 5,5'-tetra-*t*-butyl-4,4'-

Figure 3. Electron-transfer between azobenzene (0.005 *M.*) in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) containing 0.05 *M.* potassium *t*-butoxide and selected donors (0.025 *M.*) at 25°; abscissa is time in minutes; ordinate is concentration of azobenzene radical-anion times 10^{-4} in moles per liter

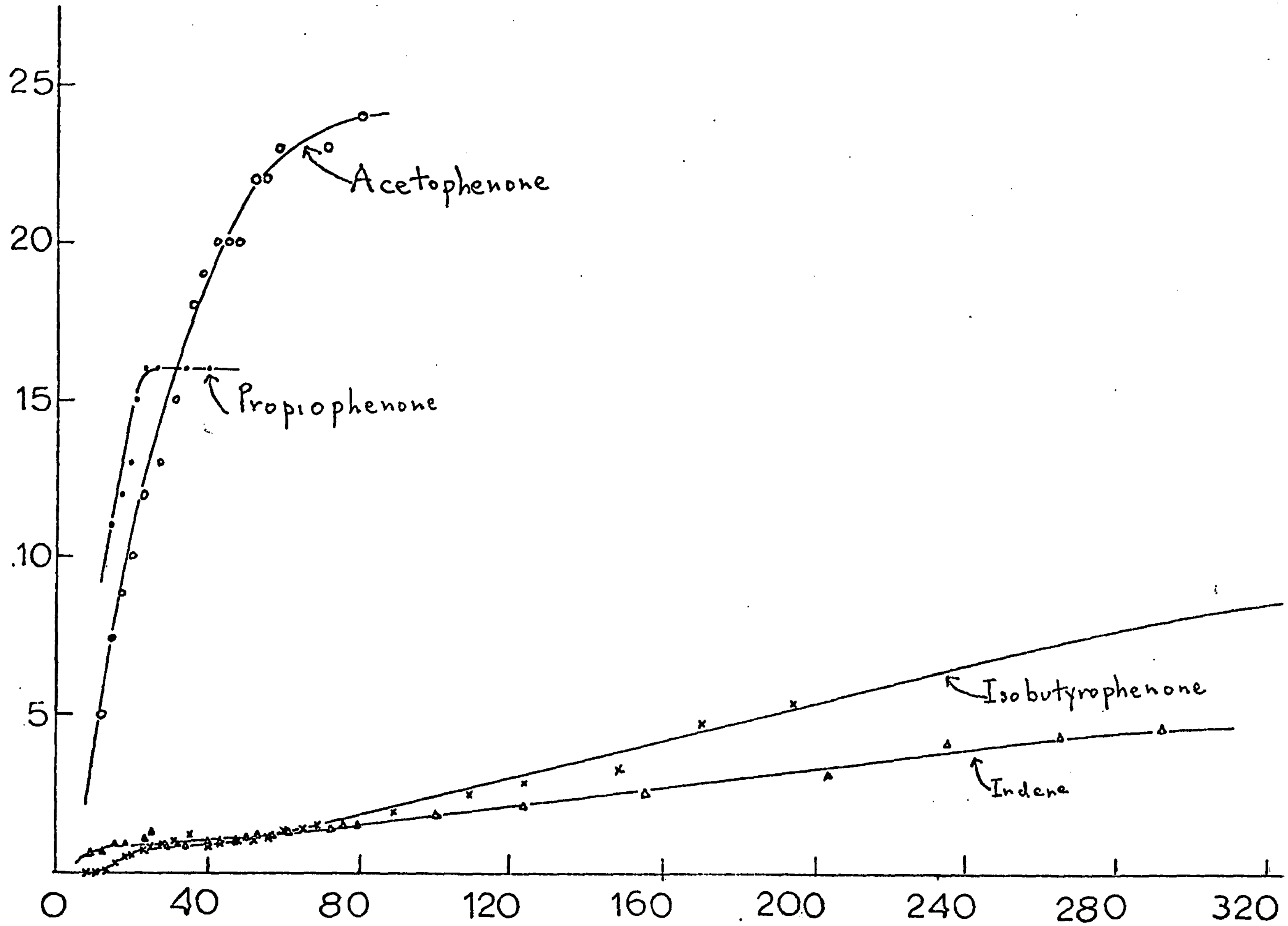
25
20
15
10
5
0
40
80
120
160
200
240
280
320
Acetophenone
Propiophenone
Isobutyrophenone
Indene

Table 4. Electron-transfer from a selected group of carbanions to a variety of unsaturated systems

Acceptor[a]	% Electron-transfer (time)[b]			
Donor (Concn.):	9,10-Dihydro-anthracene (0.025 *M*)	Propiophenone (0.025 *M*)	*n*-Butyl lithium (0.05 *M*)	*n*-Butyl-magnesium bromide (0.25 *M*)
Base (Concn.):	KOC(CH$_3$)$_3$ (0.10 *M*)	KOC(CH$_3$)$_3$ (0.05 *M*)		
Solvent:	DMSO(80%)-*t*-butyl alcohol (20%)	DMSO(80%)-*t*-butyl alcohol (20%)	Tetrahydro-furan(75%)-n-hexane(25%)	Tetra-hydrofuran
-N=N-				
Phenazine	46 (24 min.)	22 (216 min.)	76 (20 min.)	2.5
Azobenzene	25	34 (23 min.)	2.7	0.011
Benzo-[c]-cinnoline	14 (183 min.)[c]	0.3 (123 min.)	2.0 (28 min.)	60
Benzofurazan	2.5	5.4 (10 min.)[c]	0.55	8.4[c]
2,3-Diphenyl-quinoxaline	1.7 (119 min.)[c]		6.1 (65 min.)	No transfer

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[a] Concn. of acceptor = 0.005 *M* with 9,10-dihydroanthracene, propiophenone and 1,4-diphenyl-1,4-butanedione as donors; 0.05 *M* with *n*-butyllithium and *n*-butylmagnesium bromide; 0.01 *M* with dihydro-derivative.

[b] Max. observed concn. of radical-anion, 5 min., unless otherwise noted. Extent of transfer = ([radical-anion] / [acceptor])·100 except for transfer with dihydro-derivative where extent of transfer = ([radical-anion]/2[acceptor])·100.

[c] Radical concn. not followed to max.

Table 4. (Continued)

Acceptor	% Electron-transfer (time)			
N,N'-Diphenyl-*p*-benzoquinone diimine	$--^{d}$	$--^{d}$	30	0.08
Diethyl axodiformate	No transfer	No transfer	0.46	
$>C=C<$				
$\Delta^{9,9'}$-Bifluorene	$--^{d}$	$--^{d}$		
1,2-Bis-(4-pyridyl) ethylene	0.24	No transfer	9.0^{c}	No transfer
$>C=N-$				
Acridine	0.36	No transfer	0.93^{c}	No transfer
$>C=O$				
Fluoren-9-one			$50 > < 98$	0.28
Benzophenone		No transfer	9.5	0.70
[O=O]				
1,4,5,8-Tetrachloro-anthraquinone				
$-N=O$				
Nitrobenzene			14	4.7(93 min.)
Azoxybenzene	2.8	No transfer		

[d] Prohibitive blank in absence of donor.

Table 4. (Continued)

Acceptor	% Electron-transfer (time)		
Donor (Concn.):	1,4-Diphenyl-1,4-butanedione (0.025 M)	Propiophenone (0.025 M)	Dihydro-derivative of acceptor (0.01 M)
Base (Concn.):	$KOC(CH_3)_3$ (0.1 M)	$KOC(CH_3)_3$ (0.05 M)	$KOC(CH_3)_3$ (0.02 M)
Solvent:	DMSO(20%)-*t*-butyl alcohol (80%)	DMSO(20%)-*t*-butyl alcohol (80%)	DMSO(80%)-*t*-butyl alcohol (20%)
-N=N-			
Phenazine	200 (11 min.)[e]	1.5 (188 min.)	
Azobenzene	0.16 (13 min.)[f]	No transfer	100
Benzo-[c]-cinnoline	No transfer	No transfer	
Benzofurazan	No transfer	0.1 (70 min.)	
2,3-Diphenylquinoxaline			46 (47 min.)
N,N'-Diphenyl-*p*-benzoquinone diimine	--[g]	--[g]	6.5
Diethyl azodiformate	No transfer	No transfer	0.04

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[e] Predominant spectrum of acceptor.

[f] Predominant spectrum of donor.

[g] Acceptor not soluble.

Table 4. (Continued)

Acceptor	% Electron-transfer (time)		
>C=C<			
Δ9,9'-Bifluorene		9.6 (87 min.)	12.5 (75 min.)[c]
1,2-Bis-(4-pyridyl) ethylene	No transfer	No transfer	No transfer
>C=N-			
Acridine	No transfer	No transfer	0.33
>C=O			
Fluoren-9-one	76[e]	1.4 (120 min.)[f]	100
Benzophenone	1.8[h]	No transfer	.004[i]
[O=O]			
1,4,5,8-Tetrachloroanthraquinone	110[e]	8.8[j]	
-N=O			
Nitrobenzene		91	
Azoxybenzene	No transfer	No transfer	

[h] Radical-anions from both donor and acceptor detectable.

[i] Benzophenone = 2.29 M, Benzhydrol = 2.24 M, Base = 4.5 M.

[j] Spectrum not consistent with 1,4,5,8-tetrachlorosemiquinone.

stilbenequinone and 3,3',5,5'-tetra-t-butyl-4,4'-diphenoquinone.

The data of these tables reflect the contribution of four different processes: (a) the degree of ionization to give the donor monoanion or dianion; (b) the rate of electron-transfer from the donor anion to the acceptor; (c) side reactions which could consume either donor or acceptor without producing free radicals; or, (d) reactions which might consume the radical-anion after it is formed. So far as azobenzene and fluorenone are concerned, process (d) is probably unimportant since radical concentrations of between 50 and 100% of the theoretical were found to persist over very long periods of time. Whether process (c) is important has not been investigated. One might expect propiophenone, for example, to undergo base-catalyzed condensations. Of course, the condensates themselves might be good donors, and there is no evidence to show that this is not what is going on. This, however, would be outside of the definition of process (c).

With these reservations, the amount and rate of electron-transfer will now be discussed as a function of the structure of the carbanion under the assumption that only processes (a) and (b) are important. It would be helpful if the ionization process could be separated from the electron-transfer process, for then the prediction could be made from the oxidation results cited earlier (29, 30), that the least stable anion should undergo transfer more easily.

In one case the effect of acidity possibly can be separated, for acetophenone, propiophenone, and isobutyrophenone are probably entirely ionized in dimethyl sulfoxide. The order of increasing amount of transfer is isobutyrophenone $<$ propiophenone $<$ acetophenone. We thus have the greatest transfer with the primary carbanion, supposedly the most stable. On the basis of carbanion stability the order expected is acetophenone $<$ propiophenone $<$ isobutyrophenone. If we examine only the initial rate of electron transfer, in increasing order we find isobutyrophenone $<$ acetophenone $<$ propiophenone. Now the primary and secondary carbanions are in the theoretical order, although the tertiary carbanion lags behind. This may be because the assumption of complete ionization is wrong in the case of isobutyrophenone, the least acidic, or it may be that steric effects in the electron-transfer reaction are playing a part, since isobutyrophenone is the bulkiest of the three.

Even though complete ionization can not have taken place for the two series fluorene, indene, cyclopentadiene and diphenylmethane, triphenylmethane, the theoretical expectation of more electron-transfer from the least stable carbanion is realized. Thus fluorene, the least acidic, transfers to an extent of 56% while indene transfers 3% and cyclopentadiene, the most acidic, 0.4%. Also diphenylmethane transfers 2%

while triphenylmethane transfers only 1.6%. In the latter case, the differences are not outside the range of experimental error. This order holds only within the given series, for on this criteria diphenylmethane ought to give the most transfer while fluorene actually does. This discrepancy undoubtedly arises from the differences in acidity of the two compounds.

The results show also that compounds which can be doubly ionized transfer to a greater extent than monoanions. Here transfer is apparently governed by the amount of dianion rather than the stability of the dianion, since the least stable dianion, that of dihydroanthracene, ranks last in per cent electron-transfer.

As one goes to less powerful solvent systems, one would expect the amount of electron-transfer to be increasingly dependent on the amount of carbanion rather than the stability of the carbanion. If we examine the nitrobenzene results on the basis of stability of the carbanion, the order of electron-transfer should be fluorene > indene > 9-phenylfluorene > cyclopentadiene. The actual order is indene > fluorene > 9-phenylfluorene > cyclopentadiene. The amount of transfer is governed neither by the stability nor the amount of carbanion, but by a combination of both effects. Since diphenylacetonitrile transfers more than phenylacetonitrile, we may assume that here the amount of carbanion is the governing factor. In the phenone series, the secondary carbanion, that of propiophenone, gives the most transfer. The difference between this compound and acetophenone and isobutyrophenone is much more pronounced than when azobenzene is used as an acceptor.

Examination of the results with m-dinitrobenzene in ethanol shows no clear-cut trends. The order fluorene > cyclopentadiene > indene is observed. This is consistent neither with trends to be expected from stability of carbanion nor from amount of carbanion.

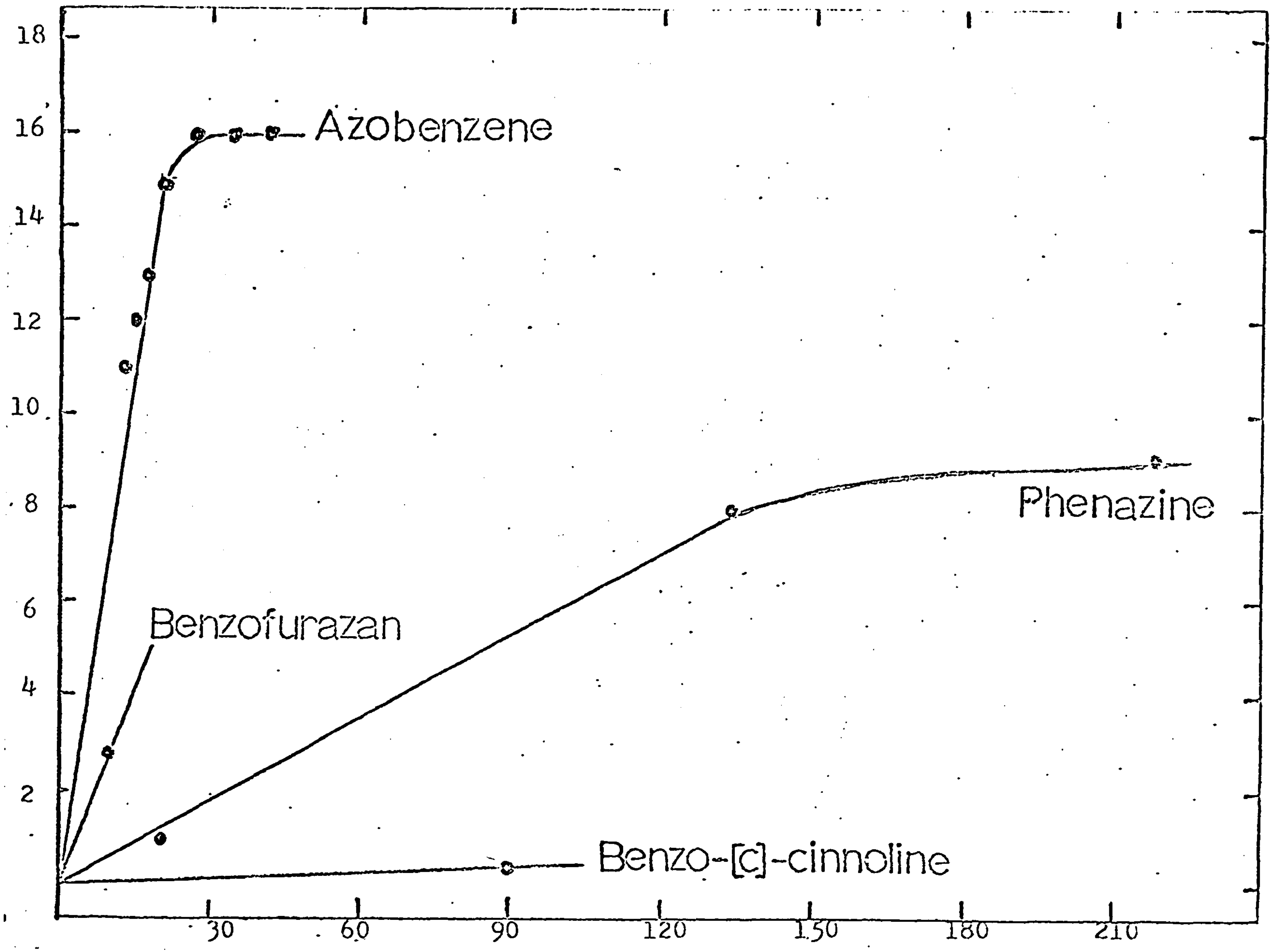
Comparison of the four acceptors is possible even though they were not used in the same solvent systems. 1,3-Indandione should be ionized equally well either in dimethyl sulfoxide-(20%)-t-butyl alcohol (80%) or ethanol. Since transfer was observed only with m-dinitrobenzene, this compound must be a better acceptor than nitrobenzene. Comparison of fluorenone and nitrobenzene is more difficult since the amount of transfer was measured for a longer period of time for fluorenone. The data with propiophenone seems to indicate that nitrobenzene is the better acceptor while the indene data indicate the opposite. Since the nitrobenzene data were gathered over a shorter period of time and since the nitrobenzene radical-anion concentration can be measured more easily than that of fluorenone ketyl, it is the author's belief that nitrobenzene is a better acceptor than fluorenone. There is little doubt that azobenzene is worse than either.

Reduction potentials successfully predict that *m*-dinitrobenzene ought to be the best acceptor (98), but they fail miserably in predicting the order of the other three.

The results obtained in varying the electron acceptor show electron acceptors are not limited to the four just cited. Figure 4 shows typical rates of transfer for propiophenone with several acceptors. Electron acceptors are found in the functional groups $-N=N-$, $>C=C<$, $>C=N-$, $>C=O$, and $[O=O]$. It must be admitted that the most unambiguous results are found with the azo linkage and its vinologs, however, an example of at least one acceptor can be found for each of the functional groups. As before, attempts were made to obtain maximum resolution in every experiment. The radical-anions either were previously known, or else the spectrum was consistent with that to be expected from the one electron reduction of the acceptor. The spectra will be discussed in detail later.

Shifting our attention back to the carbanion momentarily, we see that in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) dihydroanthracene proves to be a better donor than propiophenone, in dimethyl sulfoxide (20%)-*t*-butyl alcohol (80%) 1,4-diphenyl-1,4-butanedione is a better donor than propiophenone, and in tetrahydrofuran *n*-butyllithium is a better donor than *n*-butylmagnesium bromide, although there are some anomalies.

Figure 4. Electron-transfer between propiophenone (0.025 M.) in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) containing 0.05 M. potassium t-butoxide and selected acceptors (0.005 M.) at 25°; abscissa is time in minutes; ordinate is concentration of acceptor radical-anion times 10^{-4} in moles per liter


18
16
14
12
10
8
6
4
2
30
60
90
120
150
180
210
Azobenzene
Benzofurazan
Phenazine
Benzo-[c]-cinnoline

If we compare results in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) with dihydroanthracene as donor we find the following order of electron-transfer: phenazine > azobenzene > benzo-[c]-cinnoline > benzofurazan > 2,3-diphenylquinoxaline > acridine > 1,2-*bis*-(4-pyridyl)-ethylene. One would expect here a dependence only on the reduction potential of the acceptor. The reduction potentials stated before for azobenzene, quinoxaline, and acridine were -0.46 v. (2), -0.64 v. (2), and -0.313 v. (1). One might guess that the reduction potential of 2,3-diphenylquinoxaline would be about -0.54 v. (2). The reduction potential of benzo-[c]-cinnoline at pH 7 is -0.72 v. (2), interpolated from the data of Ross *et al*. (99). Reduction of benzofurazan is a 6 electron reduction, corresponding to reduction of the parent compound, *o*-nitroaniline, and *o*-quinone-dioxime (100). Subtracting the reduction potential of *o*-nitroaniline, we obtain a reduction potential of -0.40 v. (2). By interpolation, the reduction potential of 1,2-*bis*-(4-pyridyl)-ethylene is -0.71 v. (2) (101). Finally, the reduction potential of phenazine is -0.38 v. (2) (102). The order thus predicted is acridine > phenazine > benzofurazan > azobenzene > 2,3-diphenylquinoxaline > 1,2-*bis*-(4-pyridyl)-ethylene > benzo-[c]-cinnoline. The propiophenone data seem to indicate that benzofurazan gave anomalous results with dihydroanthracene and really is a better acceptor than benzo-[c]-cinnoline. Even with this change the reduction potentials do not do a good job of predicting the order. Considering experimental uncertainties of 25 to 50 per cent and the closeness of the various literature reduction potentials, this result is not too surprising.

The large concentrations of radical-anions found when the acceptors were treated with organometallics is quite interesting. Freedman et al. first discovered that polynuclear aromatic hydrocarbons (e.g., anthracene, tetracene, pyrene) yielded the corresponding radical-anions when treated with n-butyllithium (103). These results were duplicated and radical-anions were made by this method from 1,2-benzanthracene, perylene, 1,1,4,4-tetraphenyl-1,3-butadiene, chrysene, and p-quaterphenyl. No clear trend is obvious from the data, but the phenomena of formation of radical-anions is undoubtedly quite widespread.

For organometallic donors the mechanism of radical formation may be different from the other case. One would expect that radical formation here has the same mechanism as the formation of radical from those acceptors which gave too large blanks to be used. Brandon and Lucken explained the formation of semiquinones when quinones were treated with alkoxide as resulting from oxidation of alkoxide to peroxide (104), a rather ridiculous proposal. A more reasonable explanation is that electron-transfer occurs from an adduct (VI). The acceptors which are activated toward electron-

(VI) $\pi + B^{-} \longrightarrow \pi\text{-}B^{-}; \quad \pi\text{-}B^{-} + \pi \longrightarrow \pi^{\overset{\cdot}{-}} + \pi\text{-}B\cdot$

transfer are also activated toward nucleophilic attack, so undoubtedly most of the acceptors are attacked by base. The ensuing adduct might possibly transfer an electron. The resulting radical would have more resonance stabilization than an alkoxy radical or an n-butyl radical. Still another possibility is that electron-transfer is going through a diadduct. Such a diadduct would have a great tendency to lose an electron. It is believed that the formation of tetracyanoethylene radical-anion from tetracyanoethylene and cyanide ion goes through a diadduct (21).

By this reasoning it is now obvious why there are no clear trends with the organometallics. It is necessary that an acceptor be active toward addition for radicals to even be formed. On the other hand, if it is too active, none of the acceptor will remain to be reduced by the adduct. This may account for some of the small amounts of transfer with readily reducible acceptors.

One of the more puzzling aspects is the small amount of radical found when azobenzene is treated with n-butylmagnesium bromide. Previous experiments have shown that Grignard reagents reduce azobenzene to hydrazobenzene with concurrent formation of radical coupling products (105, 106). This is an example where it might be thought that a true electron-transfer from the Grignard reagent to azobenzene takes place.

The data show this is not so. There may be an electron-transfer, but the radical-anion must be reduced immediately.

Nitrobenzene is known to give some azobenzene when treated with Grignard reagents (107). This has been attributed to a radical process, and the data here are supporting evidence.

Further experiments to be done immediately suggest themselves. The most obvious thing to do is to identify the products of the reaction when these experiments are performed on a preparative scale. Such experiments have been carried out by Russell and Chang.* They find that results are clean-cut when dianions are used as donors. A high yield of the oxidized form is obtained. Dihydroanthracene with nitrobenzene, for example, gives a good yield of anthracene and azoxybenzene. The products with monoanions as donors are much more complex. Two products identified when fluorene reacts with nitrobenzene are $\Delta^{9,9'}$-bifluorene and a fluorenylnitrobenzene. In general coupling products are observed. With regard to fluorene as a donor, it should be noted that the predominant radical arising when azobenzene is treated with fluorene is not the radical-anion of azobenzene. A similar pattern is observed when $\Delta^{9,9'}$-bifluorene is used as a donor,

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*G. A. Russell and K. Y. Cheng, Department of Chemistry, Iowa State University, Ames, Iowa. Private communication regarding electron-transfer. 1963.

so the radical is probably the radical-anion of $\Delta^{9,9'}$-bifluorene.

Here, too, it would be quite helpful to determine reduction potentials for all the acceptors in the proper solvents.

Probably the most fruitful approach would entail the use of ultraviolet and visible spectroscopy. Many bright colors are observed in these reactions, colors which do not seem to correspond either to the radical-anion or the carbanion. These colors may be due to charge-transfer complexes. E.s.r. can only give one the concentration of the radical species present, but ultraviolet and visible spectroscopy could, if peaks were widely enough separated, give one the concentration of all the species present. Since in the case of a dianion donor, unionized donor, monoanion, dianion, radical-anion, acceptor, and a change-transfer complex could be present, it is doubtful that all these concentrations could be measured. It might be possible to determine the amount of some of these species, however.

It can be seen that the problem is a difficult one, but it is also a fascinating one.

III. RADICAL-ANIONS OF α-DIKETONES

A. Radical-Anions of Ar'COCOAr'

So far as chemistry is concerned, the chief interest in radical-anions of α-diketones stems from the observation of colors when the α-hydroxyketone in the aromatic and heterocyclic series are treated with base in the presence of oxygen. This represents a color test for aromatic acyloins. Thus benzoin gives a purple color (108), furoin a blue color (109), and 2,2'-thenoin a green color in ethanol (110). The evidence that these colors come from free radicals has already been summarized for benzoin. Presumably the same reasoning holds for the heterocyclic acyloins.

Much of the work that has been done with e.s.r. has dealt with the determination of molecular structure since the hyperfine splitting can be related to the spin density at various positions. These spin densities can also be calculated by simple molecular orbital theory. Adjustment of parameters to give agreement with experimental results thus allows one to determine the values of resonance and Coulomb integrals for heteroatoms relative to carbon. In view of the opportunity to do all these molecular orbital calculations, it is quite surprising that only one α-diketone has been studied in detail. Dehl and Fraenkel have analyzed the spectrum resulting from the reduction of benzil and have performed molecular orbital calculations on this molecule (19). Their results will be discussed later. A brief description of the spectrum of the radical-anion of furil was published by Russell et al. (111), but a complete analysis is now available.

Radical-anions derived from diketones of the series RCOCOR and ArCOCOR have not been reported and are interesting both from the experimental and theoretical viewpoints. The chemistry involved in forming radical-anions of fully aromatic α-diketones is well understood, so the only interest lies in analyzing the spectra and comparing the experimental results with theoretical calculations.

Descriptions will now be given of the radical-anions of the α-diketones 2,2'-thenil, 2,2'-furil, 2,2'-pyridil, and benzil, with an analysis of the spectra when possible. Following this, a presentation of the theory of nuclear hyperfine splitting in e.s.r. will be made. Finally, experimental calculations will be compared to theoretical calculations.

2,2'-Thenoin is difficult to maintain pure in the atmosphere as it oxidizes to 2,2'-thenil. It was decided to let this fact work for the author, for this meant that the radical-anion could be made by electron-transfer without the necessity of the presence of oxygen. The absence of oxygen meant that higher resolution could be attained.

Solutions of impure 2,2'-thenoin and potassium hydroxide, both in ethanol, were placed in the degassing apparatus and flushed with nitrogen for 20 minutes. The concentrations after mixing were 2.5×10^{-3} M. in both base and acyloin. Upon mixing, the solution turned bright green, and an e.s.r. signal was found. The spectrum consisted of what appeared to be a main quintet, breaking down on higher resolution to 19 peaks. This spectrum is shown in Figure 5.

Analysis of the spectrum is straight forward. There is a main interaction with two equivalent protons, a_H=2.29 gauss, a second interaction with two other equivalent protons, a_H=1.84 gauss, and a minor interaction with two protons, a_H=0.39 gauss. (The error in all these measurements is ± 0.05 gauss.) The fact that the smallest splitting is almost equal to the difference between the two larger splittings causes the theoretical 27 lines to coalesce to 19 lines. The ratio of peak heights for this assignment for the first half of the spectrum theoretically would be 1:2:1:2:5:4:1:1:6:10. The experimental ratios are 1:2:0.8:1.6:5.5:5.6:1.2:0.6:5.3: 9.4:5.7:0.8:1.5:5.5:5.7:2:0.9:2:1. The agreement, while not perfect, is good enough to lead one to believe that the assignment is the proper one. The matching of splitting constants with positions in the thenil molecule can only be done by means of isotopic substitution. It seems likely, however, that the smallest splitting is due to position 4, since no normal resonance structures can be drawn with the electron at

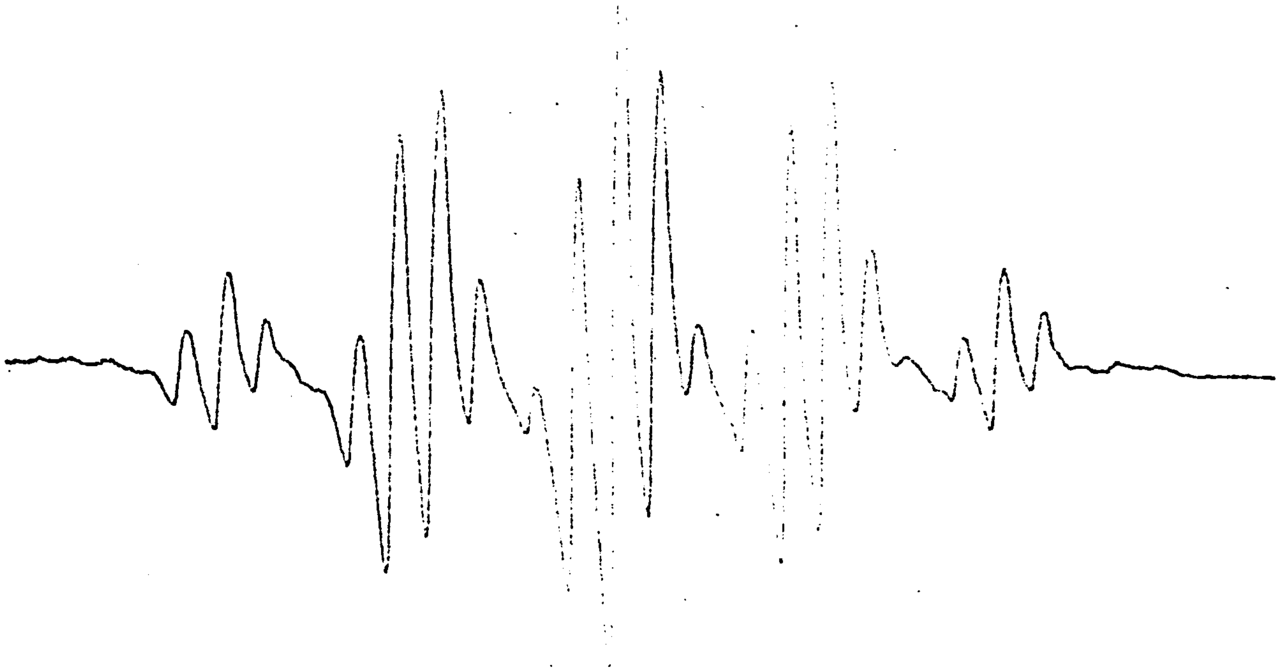

Figure 5. E.s.r. spectrum of 2,2'-thenil radical-anion; generated by electron-transfer from 2,2'-thenoin to 2,2'-thenil with potassium hydroxide in ethanol, 1 cm. = 0.876 gauss

that position.

The radical-anion of furil was first made by Janzen.* He observed a five peak spectrum when furoin was treated with ethanolic potassium hydroxide. These five peaks under higher resolution gave evidence of further structure. To obtain maximum resolution, it is best to use a minimum amount of radical under conditions where a minimum of spin exchange can take place. The author recorded a very well-resolved spectrum when a thoroughly degassed solution of furoin was treated with ethanolic potassium hydroxide. The concentration of furoin was 10^{-2} M. When the radical is formed by electron-transfer betwen furoin and furil, a dark blue solution results, but the color of the degassed furoin solution containing radical is gray-green.

Surprisingly the shape of the spectrum and the splitting constants for the radical-anion of furil are exactly the same as that for 2,2'-thenil radical-anion. This is an astonishing result and not without significance for quantum chemists.

The spectrum of the furil radical-anion is shown in Figure 6. Figure 7 shows this spectrum under highest resolution. Since the smallest splitting constant is not quite equal to the difference between the two larger splitting constants, the center peaks should show further splitting. With

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*E. G. Janzen, Department of Chemistry, Iowa State University, Ames, Iowa. Private communication regarding furil radical-anion. 1961.

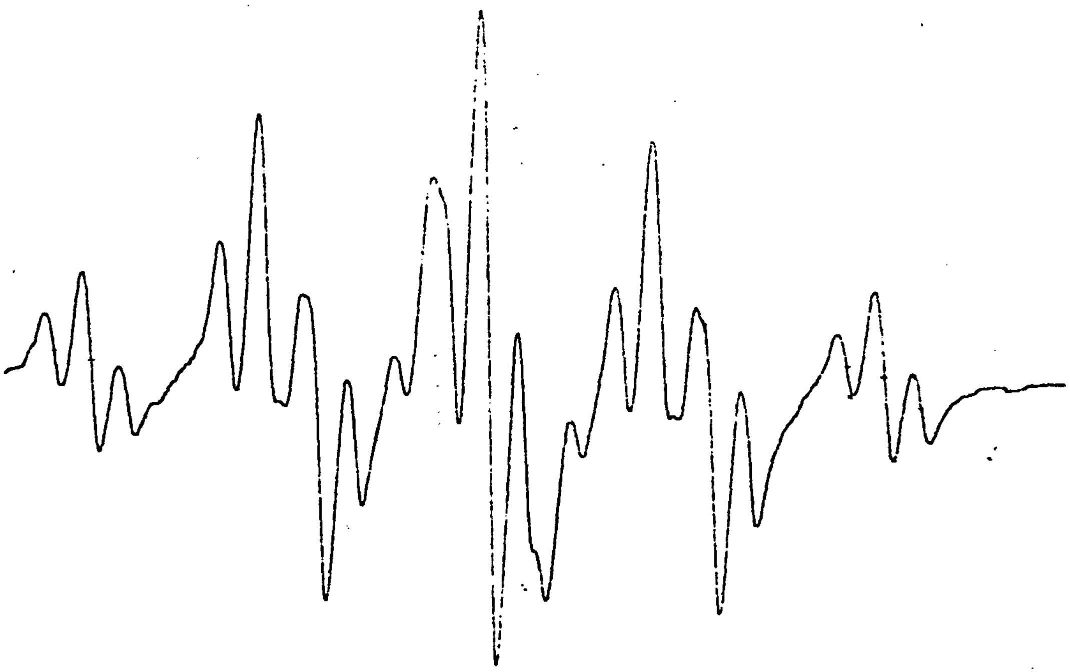
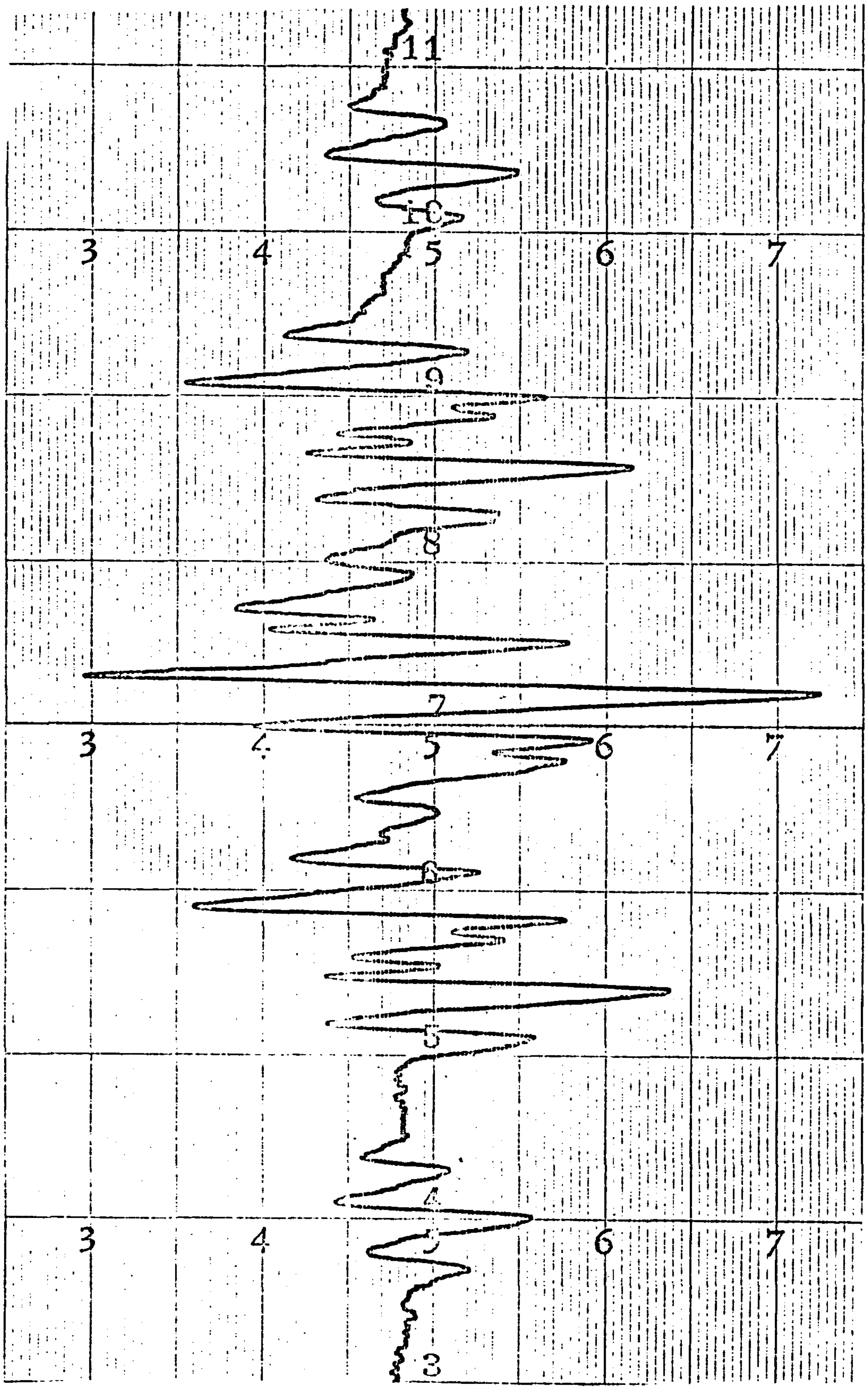


Figure 6. E.s.r. spectrum of furil radical-anion; generated by oxidation of furoin with trace amounts of oxygen in ethanolic potassium hydroxide, 1 cm. = 0.876 gauss

Figure 7. E.s.r. spectrum of furil radical-anion under high resolution; 1 cm. = 0.504 gauss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a little imagination, one can discern all of the possible 27 peaks.

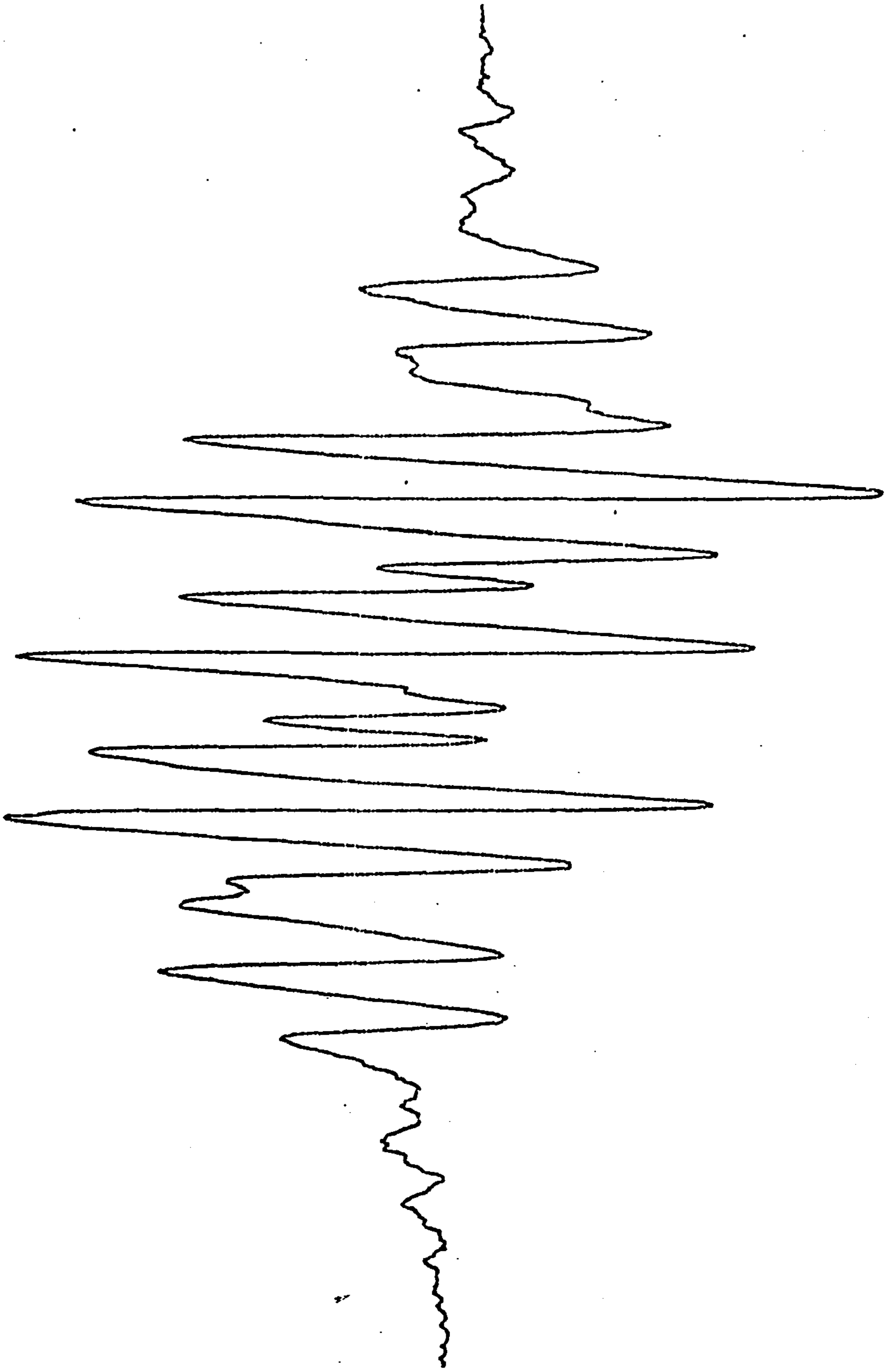
Small amounts of radical were found when 2,2'-pyridoin and 2,2'-pyridil were mixed in the absence of air and the presence of base. In no case did these yellow solutions give enough radical to be resolved.

Benzil radical-anion was made by Dehl and Fraenkel by electrolytic reduction in dimethylformamide (19). They found that reduction took place at -1.0 to -1.1 v. to give a blue solution. In view of the data on reduction potentials given earlier, it seems quite likely that two-electron reduction is actually taking place, and the radical-anion is formed by electron-transfer from the dianion to unreduced benzil. The splitting constants found were $a_{\underline{p}\text{-}H}=1.114$ gauss, $a_{\underline{o}\text{-}H}=0.995$ gauss and $a_{\underline{m}\text{-}H}=0.356$ gauss.

Figure 8 shows the spectrum obtained by the author from a thoroughly degassed solution 2×10^{-2} $\underline{M}$, in benzil, benzoin, and potassium hydroxide. The ethanol solution was purple. Unfortunately, resolution is not sufficient to obtain the splitting constants, but it appears that the largest splittings are very close to those observed by Dehl and Fraenkel.

The theory of hyperfine splitting of aromatic-type protons is due to McConnell (112, 113). He showed that the splitting should be given by the relationship, $a_1 = Q\rho_1$, where Q is a fundamental constant, good for all aromatic-type

Figure 8. E.s.r. spectrum of benzil radical-anion; generated by electron-transfer from benzoin to benzil in ethanolic potassium hydroxide, 1 cm. = 0.504 gauss



protons (e.g., polynuclear aromatics, quinones, heteroaromatics) and ρ_i is the spin density at the carbon to which the hydrogen is attached. It only remains to determine Q and ρ_i, and theoretical splittings can readily be calculated. (Excellent discussions of the theory of electron spin resonance can be found in the books by Ingram (114) and Streitweiser (115).)

Jarrett calculated Q in a semiempirical manner and arrived at a value of 28 gauss (116). Since the spin density at each position of benzene radical-anion is one-sixth, Q ought to be equal to six times the hyperfine splitting for a proton in that radical. When this radical was finally made, the value of Q was found to be 22.5 gauss (117, 118). McLachlan concluded, however, that suitable agreement for larger aromatic radical-anions could only be obtained with a Q of 24.2 gauss (119), while Karplus and Fraenkel calculated 23.7 gauss as the value of Q (120). It appears from theoretical considerations that Q is negative (113). The latter two values of Q seem to be fashionable at present. The splitting of a hydrogen atom is 510 gauss (121), so a Q of 24 gauss means that an unpaired electron in an aromatic system is at the hydrogen nucleus only 5% as much as in a hydrogen atom.

Calculation of spin densities is not straightforward either. This quantity turns out to be the important one so far as obtaining agreement with experiment. For common polynuclear aromatics spin densities can be readily calculated by simple molecular orbital theory, and deBoer and Weissman have found excellent agreement between such spin densities and experimental values (122). Problems arise even here, however, because of the possibility of negative spin density.

If one writes resonance structures for the radical-anion of a polynuclear aromatic, there are certain positions at which it is impossible to put an unpaired electron without drawing charge-separated structure (e.g., the 4-position in 2,2'-thenil radical-anion). Simple Hückel molecular orbital theory (HMO) predicts little or no spin density at these positions; nevertheless, e.s.r. measurements show that these positions do give hyperfine splitting. Measurements on perinaphthyl radical showed that these splittings can be quite sizeable (123).

Brovetto and Ferroni (124) and McConnell and Chesnut (113, 125) showed that these splittings arose from negative spin densities at the given positions. This means that sign of the spin at the meta positions in triphenylmethyl, for example, is opposite to the sign at the ortho and para positions. Such differences in sign cannot be obtained in HMO theory, for the spin densities are obtained by squaring the coefficient for the atom involved of the lowest anti-bonding orbital. McLachlan has developed a simple modification of HMO theory whereby it is possible to obtain negative spin densities (119). His treatment entails introduction of configuration interaction in an approximate fashion.

When a heteroatom (X) is a part of the system, it is impossible to make calculations from first principles. To use HMO theory the Coulomb integral (α) for the heteroatom and the resonance integral (β) for the C-x bond are scaled in terms of the given carbon integrals, using parameters h and k. Thus $\alpha_X = \alpha_C + h\beta_{C-C}$ and $\beta_{C-X} = k\beta_{C-C}$. Usually these parameters are varied to give agreement with theory, even though the values obtained may not be reasonable on the basis of electronegativity differences. Here also McLachlan's modification of HMO theory gives the best results.

In connection with theoretical calculations, it should be pointed out that these splitting constants are not necessarily solvent independent. Deguchi found an increase in the nitrogen splitting constant of diphenyl nitric oxide radical as the dielectric constant of the solvent was increased (126). Stone and Maki found changes in proton splitting constants of semiquinones (127). In comparing results in ethanol-water mixtures with those in dimethyl sulfoxide they found increases of 2.5% in the largest splitting constants in dimethyl sulfoxide and decreases of ~40% for the smallest splittings. These effects have been studied thoroughly by Gendell et al. (128). They arise from solvation of electronegative atoms in the radical. Theoretical calculations should be most significant for solvents in which there is little solvation of the radicals (e.g., tetrahydrofuran, dimethyl formamide, dimethyl sulfoxide, etc.).

With these limitations in mind, theoretical calculations were made on the molecule, 2,2'-furil. These calculations should also hold for 2,2'-thenil. The molecule is described by a real symmetric matrix. This matrix can be multiplied on the left and the right by a matrix such that the product of the multiplication is a matrix with non-zero elements only on the diagonal (129). The diagonal matrix obtained is called the eigenvalue matrix, and in HMO theory the diagonal elements are the energies of the molecular orbitals in terms of α_c and β_c. The matrix by which the input matrix was multiplied is called the eigenvector matrix. In HMO theory the elements of the eigenvector matrix are the coefficients of the molecular orbitals. The eigenvector matrix is the one from which electron densities are calculated, these densities being the squares of the coefficients in the lowest anti-bonding orbital.

The diagonalization procedure was carried out on the Iowa State 7074 computer, using a standard matrix diagonalization procedure.

The results of the HMO calculation were then used as the basis of the McLachlan calculation. This calculation involves the use of self-consistent wave functions. These functions can be arrived at from perturbation methods utilizing Hückel energies and wave functions. In practice all one does is to add the expression $+2\lambda C_{or}^2 \beta_c$ to each diagonal element of the input matrix. The quantity λ can be an adjustable parameter, but it is always taken as 1.2. C_{or} is the coefficient for the given atom in the lowest anti-bonding Hückel orbital (as read from the eigenvector matrix). The modified input matrix is now diagonalized by a computer as before. The spin density for a given atom is found from the expression $\rho_r = C_{or}^2 + \sum_n (C_{nr}'^2 - C_{nr}^2)$. This equation means, to find the spin density for a given atom, add the squares of the coefficients for the lowest antibonding Hückel orbital and the bonding McLachlan orbitals and subtract from this the squares of the coefficients for the bonding Hückel orbitals. The spin density obviously can be either positive or negative.

It takes two computer calculations to determine McLachlan spin densities by using only a simple matrix diagonalization program. A more sophisticated program is certainly called for if a great many calculations are to be done. Johnson and Gutowsky claim that McLachlan's results can be obtained for many radicals merely by adding $2/3(C_{or}^2 - \bar{\rho})$ to the Hückel densities, where $\bar{\rho}$ is the reciprocal of the number of atomic p_π orbitals in the system (130). The author has checked this approximation on several radicals and found it to give very poor results. They are correct, however, in that the

McLachlan procedure usually increases spin density where it is large and decreases it where it is small. Zero or small electron densities derived from HMO calculations are quite often changed to negative spin densities by the McLachlan procedure.

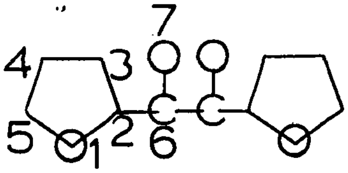
The parameters which one would expect to give the best results are those used by Dehl and Fraenkel for benzil radical-anion (19). These authors reproduced the spin densities for benzil radical-anion by the McLachlan procedure by using the parameters $\alpha_{\dot{o}} = \alpha_c + 1.5\,\beta_{c-c}$, $\beta_{c=o} = 1.6\,\beta_{c-c}$, and $\beta_{c=c}{}^{x} = 0.7\,\beta_{c-c}$. (Experimental spin densities were obtained from the equation $a_1 = -23.7\,\rho_1$.) The last parameter is for the bond between the carbonyl carbon and the ring carbon. These parameters are the same as those used by Rieger and Fraenkel to reproduce the spin densities for benzophenone radical-anion except that $\beta_{c-c}{}^{x}$ has been reduced from 0.9 to 0.7 (131). The latter authors state that $\beta_{c-c}{}^{x}$ is a function of the non-planarity of the benzene ring with the carbonyl group (the greater the non-planarity, the smaller $\beta_{c-c}{}^{x}$), but they do not claim much physical significance for this parameter. Results to be cited later cause the author to emphatically agree.

The only parameters left to be introduced are the Coulomb and resonance integrals for the furanyl oxygen, $\alpha_{\ddot{o}}$ and β_{c-o}. The values of h and k suggested by Streitweiser are

2.0 and 0.8 (115). Orgel et al. in their calculations on dipole moments got excellent agreement with the parameters 3.2 and 1.4 (132). These authors, however, used the same value of k for both carbon-oxygen single and double bonds. This does not seem reasonable, and so a third set of parameters suggest themselves, 3.2 and 0.8.

Molecular orbital calculations were performed on 2,2'-furil (VII) using the parameters of Dehl and Fraenkel along

(VII)



with the Streitweiser parameters, the Orgel parameters, and the modified Orgel parameters in the McLachlan modification. Only the modified Orgel parameters gave reasonable results. The spin densities calculated are ρ_3 = +0.088, ρ_4 = -0.036, and ρ_5 = +0.103. From the formula $a_i = 24.2 \rho_i$ we can calculate splitting constants of 1.94, 0.87, and 2.49 gauss as compared to the experimental values of 1.84, 0.39, and 2.29 gauss. The theoretical ratio of the two larger splitting constants is 0.85 while the experimental ratio is 0.80. A Q of 22.5 gives values of 1.98, 0.81, and 2.32 gauss. Small modifications in the parameters could undoubtedly increase the agreement, but these results are quite good for the larger values. Since the spectra was determined in a complexing solvent, only the larger values should give good agreement with theory. It is actually possible to include the solvent effect in the molecular orbital calculation (128), but this was not done.

This treatment predicts that the smallest splitting is from the 4 position. It also predicts that the largest splitting comes from the 5 position. It should be noted that the calculations with the Streitweiser and unmodified Orgel parameters predict the highest spin density at the 3 position, although both calculations do predict that the 4 position has the least spin density.

It is obvious, of course, that these parameters will give analogous results for 2,2'-thenil radical-anion. Usually thiophene is treated as a modified benzene ring (133), but the differences between the splitting constants of the thenil and benzil radicals show that this is not suitable. Gerdil and Lucken found that the splitting constants for dibenzothiophene radical-anion were considerably larger than those for phenanthrene radical-anion (134). It would be interesting to test whether dibenzofuran radical-anion would give a spectrum identical with that of dibenzothiophene radical-anion. This similarity of sulfur and oxygen is unexpected, and it will be interesting to see how widespread it is in the corresponding free radicals.

The radical-anions of all these α-diketones should also be formed in dimethyl sulfoxide to observe what, if any, changes occur in the splitting constants. Presumably these values would correspond quite closely to those calculated by the McLachlan procedure.

B. Radical-Anions of ArCOCOR

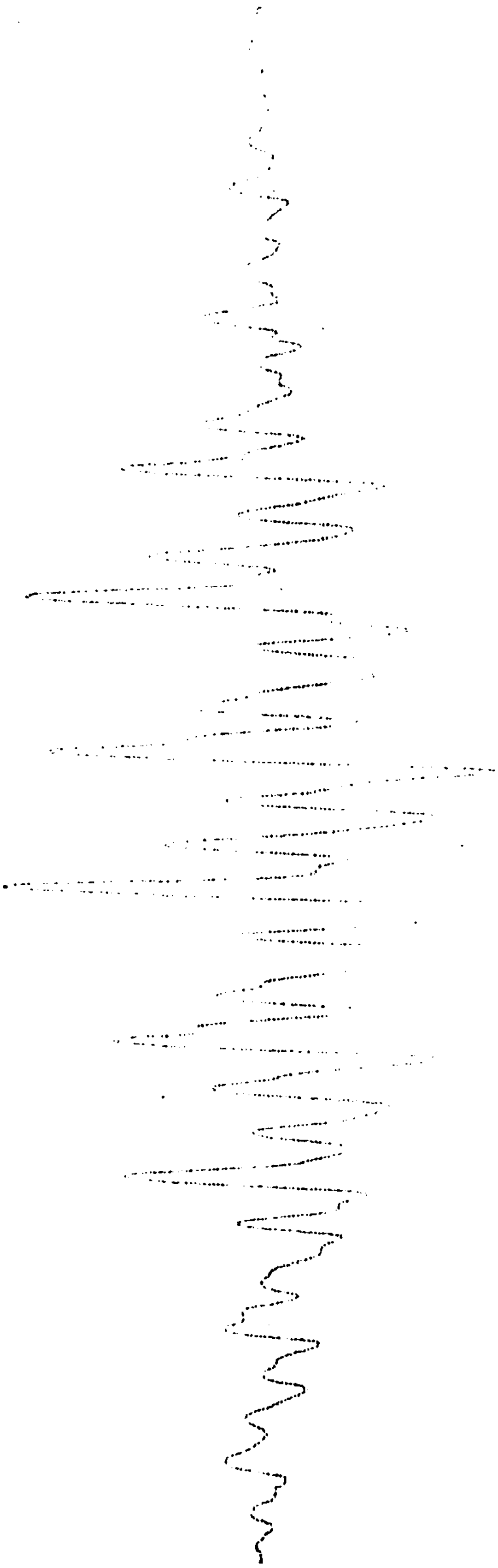
To the author's knowledge, there are no published examples of radical-anions derived from the system ArCOCOR. These are of interest from a theoretical standpoint for they give one a means of detecting and measuring the amount of interaction between the electron and the alkyl group by hyperconjugation.

By analogy with the benzoins, one would expect to generate the radical-anions either by reduction of the diketone, by oxidation of the acyloin, or by electron-transfer between the two compounds. It was quite surprising to find, therefore, that compounds of the type $ArCOCH_2R$ would undergo oxidation with molecular oxygen in the presence of potassium t-butoxide in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) to give radical-anions of the corresponding α-diketones. Typically a solution 5×10^{-2} M. in ketone would be mixed with an equal volume of 10^{-1} M. base after oxygen had been bubbled through the solutions for two minutes. The solutions would turn yellow on mixing, and radicals would be found immediately. Eventually the solutions would turn red-brown. The radicals appeared to be stable for hours. The amount of radical, however, was only about 10^{-4} M.

A solution 2.5×10^{-2} *M*. in propiophenone and 5×10^{-2} *M*. in potassium *t*-butoxide through which oxygen had been bubbled for two minutes gave an e.s.r. signal. The color of the solution was yellow at first. It changed to reddish-brown, but this color could be discharged and the yellow color brought back by shaking. Eventually, however, the reddish-brown color could no longer be discharged.

The spectrum consisted of a main decet. On higher resolution these ten peaks broke into triplets and still smaller splittings could be observed. Figure 9 shows the spectrum under high resolution. The spectrum could be readily analyzed on the basis of a main splitting from the methyl protons and a splitting of half that magnitude from the *ortho* and *para* protons. This accounts for the ten main peaks. Interaction with the two *meta* protons then gives thirty peaks while the additional peaks arise from the differences between the *ortho* and *para* protons. The distances between peaks can be accounted for on the assumption that a_{Me}=3.46 gauss, $a_{\underline{p}-H}$=1.84 gauss, $a_{\underline{o}-H}$=1.66 gauss, and $a_{\underline{m}H}$=0.53 gauss. Assuming exact overlap (which is not the case) one-half of the theoretical peak height ratio are 1:2:1:3:6:3:5:10:5:7:14:7:8:16:8. Since there is not an exact overlap, the experimental peaks intensity ratios would be expected to be close to but somewhat less than the theoretical ratios. The experimental ratios are 1:2.7:1:2:4:1.7:4.7:10.7:4.7:8:14.7:6.3:7.3:18.7:

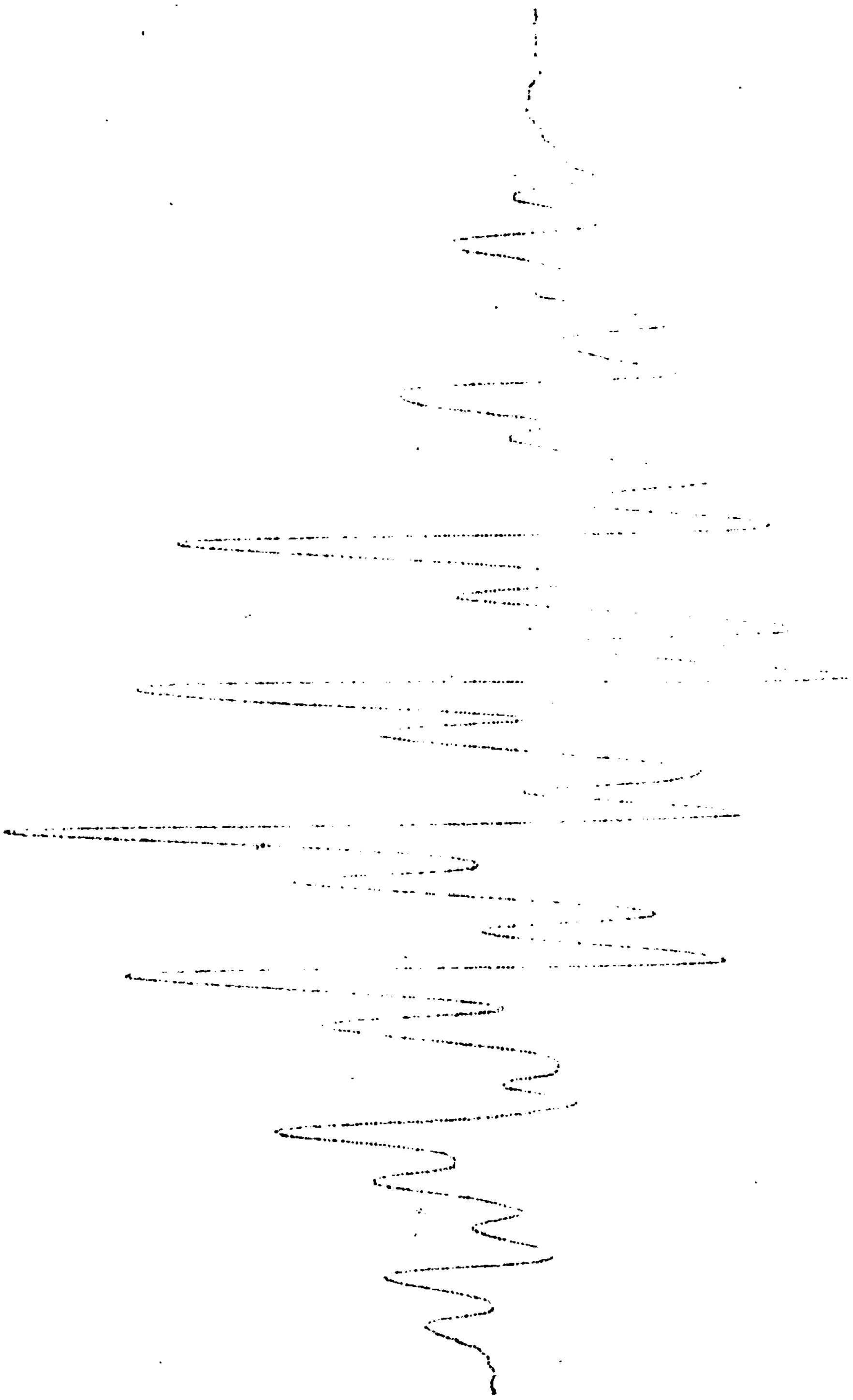
Figure 9. E.s.r. spectrum of 1-phenyl-1,2-propanedione radical-anion; generated by oxidation of propiophenone in dimethyl sulfoxide (80%)-_t_-butyl alcohol (20%) containing potassium _t_-butoxide, 1 cm. = 0.876 gauss



8:9.3:20:8.3:17:5.7:5.3:12:4.7:2:4.7:2:1.3:2.7:1.3. The agreement, while not perfect by any means, is certainly good enough. It was thus concluded that the radical is the radical-anion of 1-phenyl-1,2-propanedione.

A radical was made from n-butyrophenone under exactly the same conditions. The same colors were observed and the radical was presumably 1-phenyl-1,2 butanedione radical-anion. The spectrum consisted of a main octet, each peak of which broke down into triplets. No further hyperfine splitting could be observed. This spectrum is shown in Figure 10. By analogy with the above example, the main interaction is with the methylene group with a splitting of one half the magnitude from the ortho and para protons. The triplets then arise from the meta interaction. Since there is no further splitting, one must conclude that the ortho and para splittings are equal. On this basis the splitting constants are $a_{Me}=3.42$ gauss, $a_{\underline{o},\underline{p}H}=1.71$ gauss and $a_{\underline{m}-H}=0.53$ gauss. The peak height ratios agree with the theoretical ratios about as well as in the case of 1-phenyl-1,2-propanedione radical-anion. Since the methyl and meta splitting constants agree with those from the propanedione within experimental error, it seems quite unlikely that there should be any change in the ortho and para splitting constants. Probably there was no change, and the equality of the two splittings arises from a lack of resolution in this particular case.

Figure 10. E.s.r. spectrum of radical-anion of 1-phenyl-1,2-butanedione; generated by oxidation of n-butyrophenone in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) containing potassium t-butoxide, 1 cm. = 0.876 gauss



In the light of these facts one would expect analogous results from phenylneopentyl ketone. The radical in this case, however, was formed by oxidation of phenylpivaloylcarbinol. The concentrations, after mixing, of carbinol and base were 6.3 x 10^{-3} M. and 2 x 10^{-2} M., respectively. The base was again potassium t-butoxide, and the solvent dimethyl sulfoxide (80%)-t-butyl alcohol (20%). Nitrogen was bubbled through the solutions ten minutes before mixing.

The color of the solution after mixing was purple. An e.s.r. signal was found immediately. A main quartet was observed (Figure 11) which broke into many partly resolved peaks. The spacings between the peaks of the main quartet were 1.66 gauss, while the spacing between the smaller peaks were ∼ 0.18 gauss. This smaller splitting probably arises from the t-butyl protons. The resolution is not good enough so that one can be sure of the *meta* splitting, although it should be about the same as in the other radicals. The large splitting, of course, arises from the *ortho* and *para* protons. One can be quite sure that the radical is the radical-anion of 1-phenyl-3,3-dimethyl-1,2-butanedione.

Acetophenone when treated under the same conditions as propiophenone and n-butyrophenone gave a golden-brown color but no free radical. Apparently stabilization of the radical by hyperconjugation with the alkyl group is extremely important. One might have guessed this would be the case since the

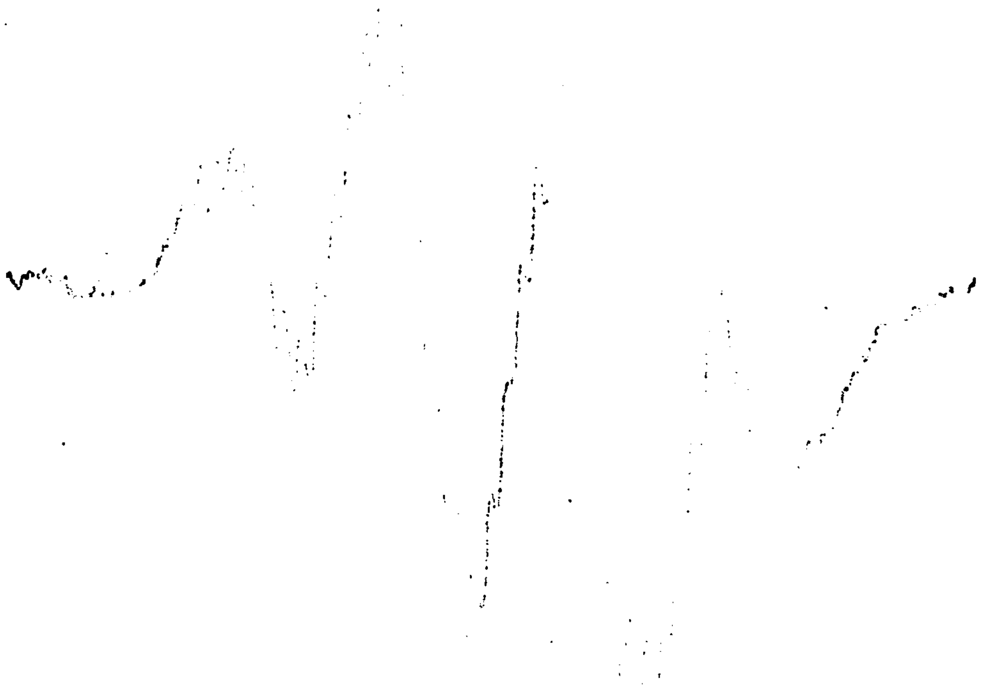


Figure 11. E.s.r. spectrum of the radical-anion of 1-phenyl-3,3-dimethyl-1,2-butanedione; generated by the oxidation of phenylpivalylcarbinol in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) in the presence of potassium *t*-butoxide, 1 cm. = 0.876 gauss

alkyl splitting was so large.

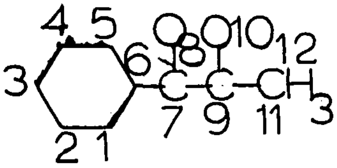
A theoretical treatment of this radical of necessity entails use of the theories of hyperconjugation within the HMO framework. The so-called "conjugation" model treats the alkyl group as a modified vinyl group with suitable changes in the Coulomb and resonance integrals (135). The best parameters to use are those of Coulson and Crawford (136), as modified by Bersohn (137). If we call the methyl carbon atom Y and the three hydrogens atom Z, these parameters are $\alpha_Y = \alpha_c - 0.1\ \beta_{c-c}$, $\alpha_Z = \alpha_c - 0.5\ \beta_{c-c}$ and $\beta_{Y-Z} = 2.5\ \beta_{c-c}$.

After such a calculation is made, the theoretical splitting due to the methyl protons is obtained from the expression $a_{Me} = Q_{Me}\ \rho_i$ (138, 139). In this expression Q_{Me} is believed to be 27-30 gauss. Strauss and Fraenkel propose a value of 27.2 gauss (140), an empirical value obtained from Fessenden and Schuler's work on the ethyl radical (141). Fessenden and Schuler have recently corrected their results for the effect of hyper-conjugation and arrived at a value of 29.25 (142). The value of ρ_i is taken at the carbon atom to which the methyl group is attached. Good results have been achieved using the McLachlan treatment with a Q_{Me} of 27 gauss (143). Although overlap integrals should be included when hyperconjugation is treated (115), so far as radical calculations are concerned, they have been neglected.

The obvious calculation to be made on 1-phenyl-1,2-

propanedione radical-anion (VIII) thus involves using the

(VIII)



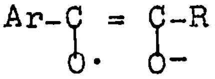
parameters of Dehl and Fraenkel, derived from benzil radical, for the diketone part of the molecule together with the modified parameters of Coulson and Crawford for the methyl group. All this should be done within the framework of a McLachlan calculation. The only parameter which one might feel some trepidation in using is α_Y, for this was derived for the case of methyl group attached to an aromatic carbon. When such calculations are performed, using also a value of β_{c-Y} of 0.70, they fail miserably in predicting splitting constants for either the ring protons or the methyl group. There appears to be too little electron density of the benzene ring. Modification of β_{c-c}^{x} to 0.90, the value which gave good results for benzophenone radical-anion, does give sufficient electron density on the benzene ring. The calculated spin densities are $\rho_1 = +0.076$, $\rho_2 = -0.028$, $\rho_3 = 0.082$, $\rho_9 = 0.207$. Using a Q of 24.2 splitting constants of 1.83, 0.68, and 1.98 gauss are calculated for the ring protons. A Q of 22.5 gives 1.71, 0.63, and 1.85 gauss. The experimental values are 1.66, 0.53, and 1.84 gauss. The most meaningful comparison is the ratio of the two largest splitting constants. The experimental ratio is 0.902 while the theoretical ratio is 0.924. Agreement for the methyl splitting is extremely poor. Using a Q_{Me} of 29.25 one calculates a splitting of 6.05 gauss as compared to the experimental value of 3.46 gauss. Since the hyperconjugation parameters have been used mainly for methyl groups attached to aromatic systems, it appears that the author's earlier reservations were justified. They can not be used for a methyl group attached to a carbonyl carbon without some modification, probably a change in the Coulomb integral of the carbonyl carbon. The ring proton values were very good, it is true, but they are probably insensitive to the hyperconjugation parameters. An HMO calculation for phenyl glyoxal, using the parameters and Q derived by Vincow and Fraenkel for o-quinones (144), gives values within five per cent of the experimental values for 1-phenyl-1,2-propanedione radical-anion.

There is no reason to believe that there should be a different value of $\beta_{c-c}x$ for 1-phenyl-1,2-propanedione radical-anion than for benzil radical-anion. The fact that a larger value had to be used to give agreement leads one to believe that the only significance this integral has is to give an extra parameter for obtaining agreement.

C. Radical-Anions of Aliphatic-α-Diketones

In the examples of stable radical-anions from α-diketones studied thus far, every radical has been conjugated with an aromatic or heteroaromatic ring (IX). Examples of

(IX)



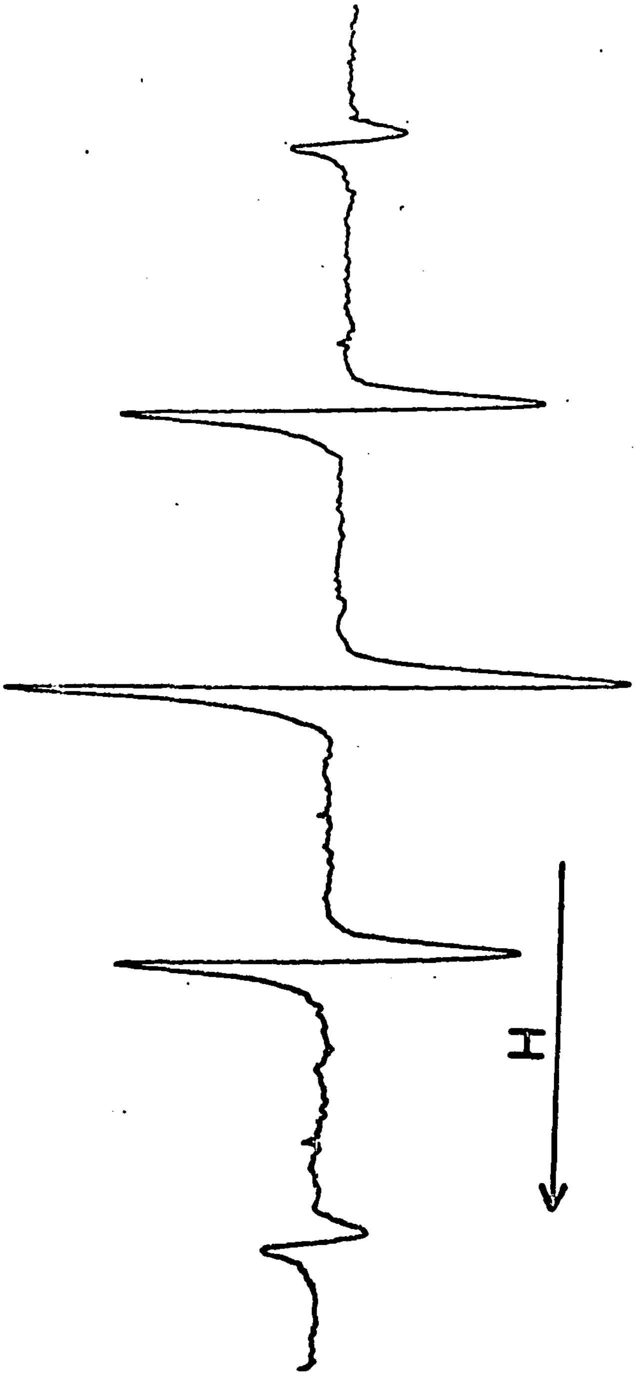
$$\mathrm{Ar{-}}\underset{\mathrm{O\cdot}}{\underset{|}{\mathrm{C}}} = \underset{\mathrm{O^-}}{\underset{|}{\mathrm{C}}}\mathrm{{-}R}$$

purely aliphatic radicals, stable at room temperature in solution, are rare. The only such radicals that readily come to mind are tetracyanoethylene radical-anion (63), di-t-butyl nitroxide (145), mono-t-butyl nitroxide (146), di-n-hexyl nitroxide (146), t-nitrobutyl radical-anion (147) and tetramethyl-1,3-butanedione radical-anion (148). Ketyls of hexamethyl- and pentamethylacetone have been prepared, but these are stable only at very low temperatures (149).

In view of this it was quite surprising that radical-anions of cyclic α-diketones, stable for hours in solution at room temperature, could readily be made. Four basic methods were used: 1) electron-transfer from the acyloin to the diketone in basic media, 2) base-catalyzed oxidation of the acyloin with molecular oxygen, 3) reduction of the diketone with a carbanion and 4) base-catalyzed oxidation of the monoketone. Since the monoketones were most readily available, the last method was generally used. In a typical experiment, equal volumes of air-saturation solutions of the ketone (0.05 M.) and potassium t-butoxide (0.1 M) in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) were mixed in the degassing apparatus. A yellow color immediately developed, and an e.s.r. signal was found at once.

When 2-hydroxycyclohexanone is oxidized, a five peak spectrum is found in the yellow solution (Figure 12). The

Figure 12. E.s.r. spectrum of the radical-anion of cyclohexane-1,2-dione; generated by oxidation of 2-hydroxycyclohexanone in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) in the presence of potassium t-butoxide, 1 cm. = 2.81 gauss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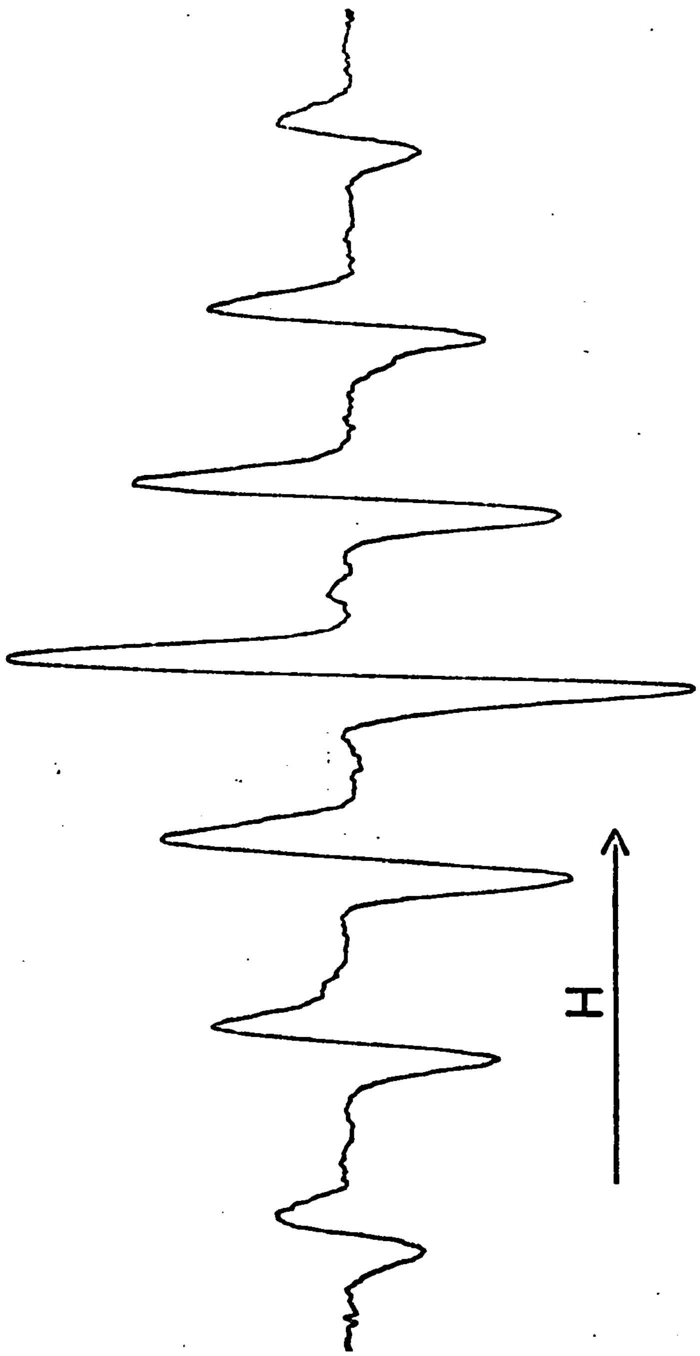
peak height ratios are 1:3.8:6:3.8:1 (theoretical 1:4:6:4:1). An identical spectrum can be obtained either by reduction of 1,2-cyclohexanedione with propiophenone or by oxidation of cyclohexanone with base and air. In all cases the peak separations were 9.82 gauss. The interpretation is simple. There is an interaction with four equivalent protons, and the most reasonable structure for the radical is that of the radical-anion of cyclohexane-1,2-dione. The splitting would arise from the four alpha protons. The radical must either be planar or must not possess conformational stability within the period of measurement (spectrometer frequency $\sim 10^4$ mc./s.).

Substitution of a t-butyl group leads to a truly spectacular result. When the radical anion of 4-t-butylcyclohexane-1,2-dione is made by oxidation of 4-t-butylcyclohexanone, a seven line spectrum is now obtained (Figure 13). This spectrum can be readily analyzed on the base of an interaction with two pairs of protons, with one pair splitting exactly twice as much as the other. On this basis the theoretical peak height intensities should be 1:2:3:4:3:2:1. The experimental intensities are 1:2:3:5.2:3:2:1, which is reasonable agreement. The two splittings measured are 13.10 gauss and 6.55 gauss. The average of these splittings is 9.82 gauss, exactly the value obtained for the four equivalent protons in the unsubstituted radical-anion. The obvious

Figure 13. E.s.r. spectrum of the radical-anion of 4-t-butyl-1,2-cyclohexanedione; generated by the oxidation of 4-t-butylcyclohexanone in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) in the presence of potassium t-butoxide, 1 cm. = 2.81 gauss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conclusion is that the only effect of the t-butyl group is to lock the conformation, and the observed splittings are identical to those of a rigid, unsubstituted cyclohexanedione radical-anion.

The greatest interaction with the π-orbital in which the unpaired electron is located would certainly be with the axial protons. The larger splitting constant must then be due to axial protons while the smaller value arises from equatorial proton splitting. These splittings can be treated quantitatively and will be dealt with later.

Substitution of methyl groups in the alpha positions removes all hyperfine interactions. When a radical-anion is made by electron-transfer between 3,3,6,6-tetramethyl-2-hydroxycyclohexanone and 3,3,6,6-tetramethyl-1,2-cyclohexanedione, only a single peak is observed (Figure 14). Since splitting was observed in the radical-anion of 3,3-dimethyl-1-phenyl-1,2-butanedione, it appears that the removal of a degree of freedom makes it impossible for the methyl groups to rotate in such a manner as to interact with the unpaired electron. The experiment was performed in the absence of oxygen so there should have been no broadening effects associated with dissolved oxygen. The line width of the peak is about 4.8 gauss. The line width of a typical peak from the unsubstituted cyclohexane radical is about 3.3 gauss. If the extra width is assigned to interaction with 12 methyl

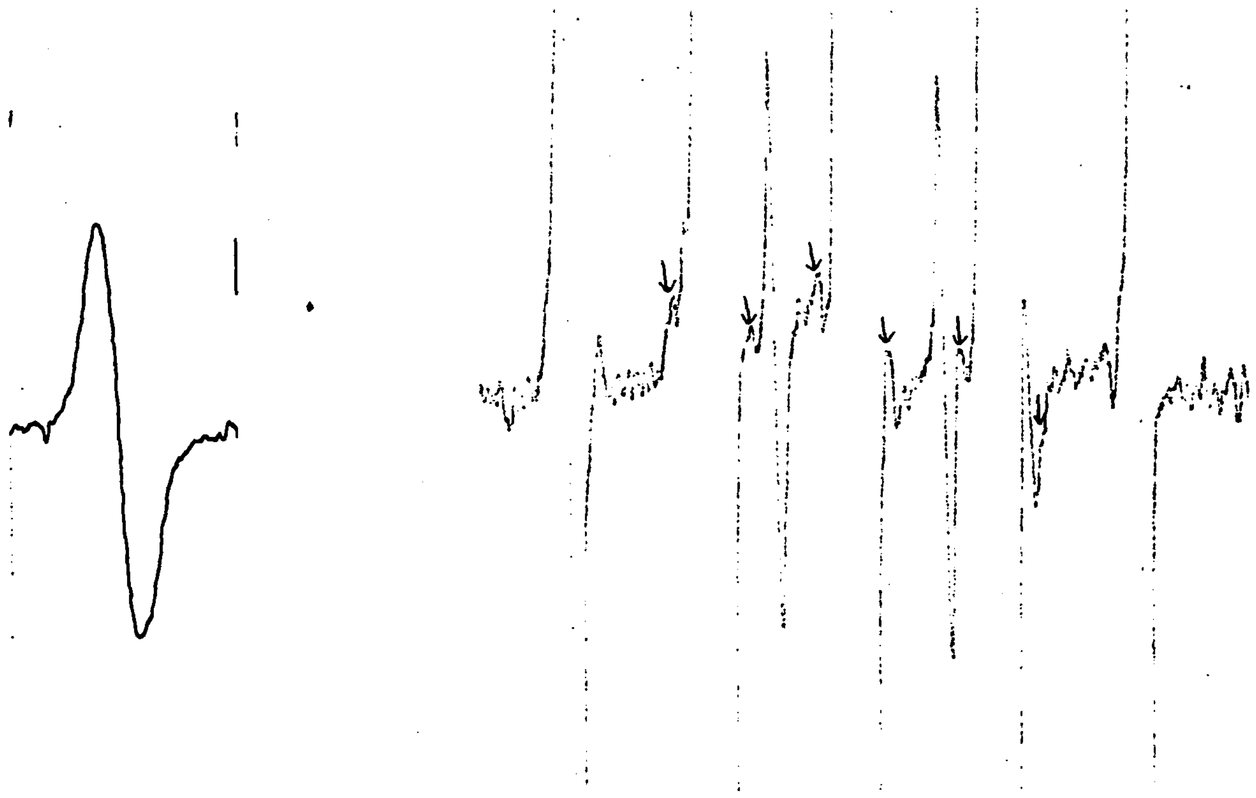

Figure 14. E.s.r. spectrum of radical-anion of 3,3,6,6-tetramethyl-1,2-cyclohexanedione (left, 1 cm. = 2.81 gauss); generated by electron-transfer from the acyloin to the diketone; Carbon 13 splitting in the radical-anion of 1,2-cyclohexane dione (right, 1 cm. = 5.78 gauss); generated by oxidation of cyclohexanone; both spectra taken in dimethyl sulfoxide (80%)-<u>t</u>-butyl alcohol (20%) in the presence of potassium <u>t</u>-butoxide

protons, this would give a splitting of 0.1 gauss per proton which should be resolvable. There may be hyperfine interactions which could be resolved under better conditions, but these interactions are certainly less than in a purely acyclic case.

One anomaly appeared in the spectra of cyclohexanedione radical-anion as formed by oxidation of cyclohexanone. Three small peaks were formed beside the three center peaks, about midway between the peaks. The spacing and intensity of two of these peaks were the same, but the third was smaller and closer to the center peak. Three explanations come to mind. Second order splittings might possibly be showing up. Extra peaks due to this phenomena have been found (142). Without going into the theory, these extra splittings are explained by using a more exact Hamiltonian than is usually used for e.s.r. theory. It is predicted that lines of unit intensity will not be split which fits the experimental results. One would expect the center lines to be split into two equal peaks, however, which does not fit the results.

A second possible explanation is splitting due to the natural abundance of C^{13} at the carbonyl carbon. One would expect all five lines to be split, which is not the case.

The most likely explanation is that some overoxidation is taking place, and a small amount of a second radical, possibly cyclohexane-1,2,3-trione radical-anion, is being observed.

It should be possible to observe C^{13} interaction, however, if the magnitude of the splitting is greater than the line width of the hyperfine components. Figure 14 shows what the author believes to be such an interaction. The proton peaks are off-scale and the taller peaks are undoubtedly due to radicals formed by overoxidation. The peaks marked with an arrow are probably C^{13} satellites. The tallest peak is presumably the best resolved, and so the intensity ratio can be tested here. The theoretical ratio is 11 to 1000 while the experimental ratio is 10 to 1050. The splitting is about 4.9 gauss, presumably due to the carbonyl carbons. Hirota and Weissman (149) and Ward (148) have found C^{13} splitting for carbonyl carbons of 49.6 and 5.0 gauss, respectively. The value here compares well with Ward's result.

This stability of radical-anions of cyclic 1,2-diketones was not limited to six-membered rings. The cyclic monoketones from C_5 to C_{10} and the C_{12} and C_{15} compounds all gave radical-anions upon oxidation. Moreover rings larger than C_6 possessed considerable conformational stability. The results are summarized in Table 5 and will now be discussed in detail.

Oxidation of cyclopentanone gave a yellow solution. A five peak spectrum was obtained which died out rapidly (Figure 15). As the radical disappeared, the solution turned brown. There was no point in comparing experimental peak height ratio

Table 5. Conformation of cycloalkanedione radical-anions

Radical-Anion	Method of Prep.	$a_{\text{alpha-H}}$(gauss)[a] Axial	Equatorial	Axial-H	B'	ρ[b]
Cyclopentane-1,2-dione	1	14.16[c]		(+27)[c,d]	17.8	0.30
4-t-butylcyclohexane-1,2-dione	1	13.10	6.55	+13	13.8	.24
Cyclohexane-1,2-dione	1,2,3,4	9.82		(+43)[c]	13.8[e]	.24
Cycloheptane-1,2-dione	1	6.70	1.97	+3 or -50	6.7 or 16.7	.11 or .29
Cyclooctane-1,2-dione	1	3.33[f]		(+30 or -60)	4.4 or 13.3	.08 or .23
Cyclononane-1,2-dione	1	12.57	5.49	+11	13.0	.22

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[a] In DMSO (80%)--t-butyl alcohol (20%).

[b] B = 58.5 gauss.

[c] Four equivalent protons.

[d] Radical-anion assumed planar and with geometry similar to cyclopentene (ref. 153).

[e] Assumed equal to B for t-butyl compound.

[f] Four nearly equivalent protons.

Table 5. (Continued)

Radical-Anion	Method of Prep.	$a_{\text{alpha-H}}$ (gauss)[a] Axial	Equatorial	Axial-H	B'	ρ[b]
Cyclodecane-1,2-dione	1,2	8.33	0	-30	11.1	.19
Cyclododecane-1,2-dione	1	7.88	0	-30	10.5	.18
Cyclopentadecane-1,2-dione	1	7.23	2.07	+2 or -50	7.2 or 17.5	.12 or .30
Camphorquinone	1,4	$a_{\text{methyl-H}}$ = 2.66[g]				

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[g] Three equivalent protons, probably the 7-syn methyl group.

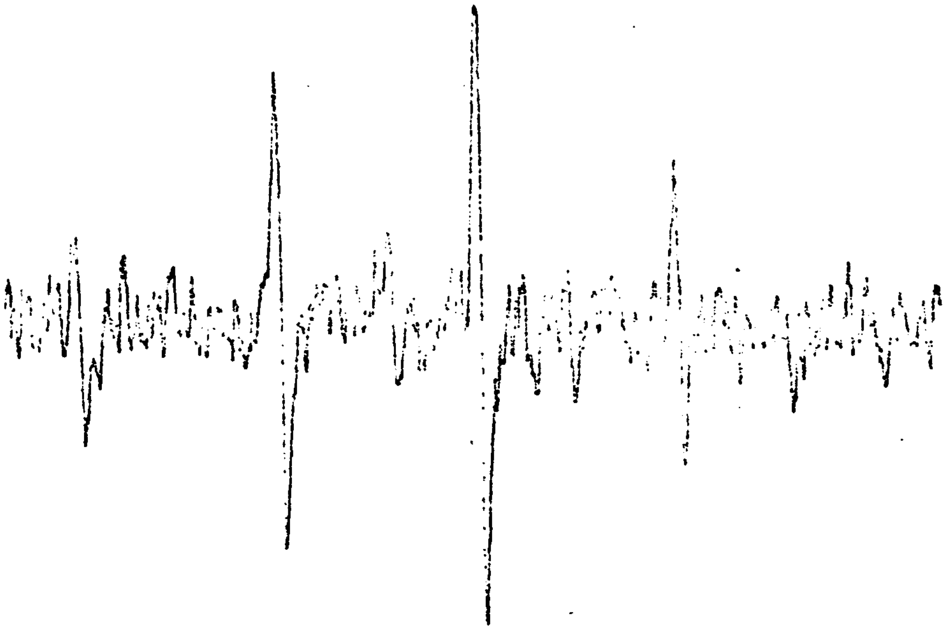


Figure 15. E.s.r. spectrum of the radical-anion of cyclopentane-1,2-dione; generated by oxidation of cyclopentanone in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) in the presence of potassium t-butoxide, 1 cm. = 5.78 gauss

with theoretical values, for the radical diminished rapidly while the spectrum was being recorded. The splitting constant measured for the alpha protons was 14.16 gauss. When a solution of cyclopentanone was treated with base after both solutions were flushed six minutes with nitrogen, there was no color change, and no radical was found.

Cyclobutanone gave a yellow solution on oxidation but no radical-anion. No suitable conditions could be found for the formation of radical. In view of the results with the five-membered ring, this instability of the radical-anion is to be expected.

A nine peak spectrum was obtained from the oxidation of cycloheptanone (Figure 16). The interpretation is that there is a major interaction with two equivalent protons and a minor interaction with two more equivalent protons. The values of the two splittings are 6.70 gauss and 1.97 gauss. The experimental peak height ratios are 1:2.1:0.9:1.8:4.1:1.7:1:2:0.9 (theoretical ratio 1:2:1:2:4:2:1:2:1).

On moderate resolution a five peak spectrum is found when cyclooctanone is oxidized. It would seem that there is an interaction with four equivalent alpha protons. The peak separations are not exactly equal, however, nor do the peak height ratios match the theoretical values. On high resolution the ring peaks split into triplets, as shown in Figure 17. Extra peaks due to nonequivalence of the alpha protons

Figure 16. E.s.r. spectrum of the radical-anion of cycloheptane-1,2-dione; generated by oxidation of cycloheptanone in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) in the presence of potassium *t*-butoxide, 1 cm. = 0.876 gauss

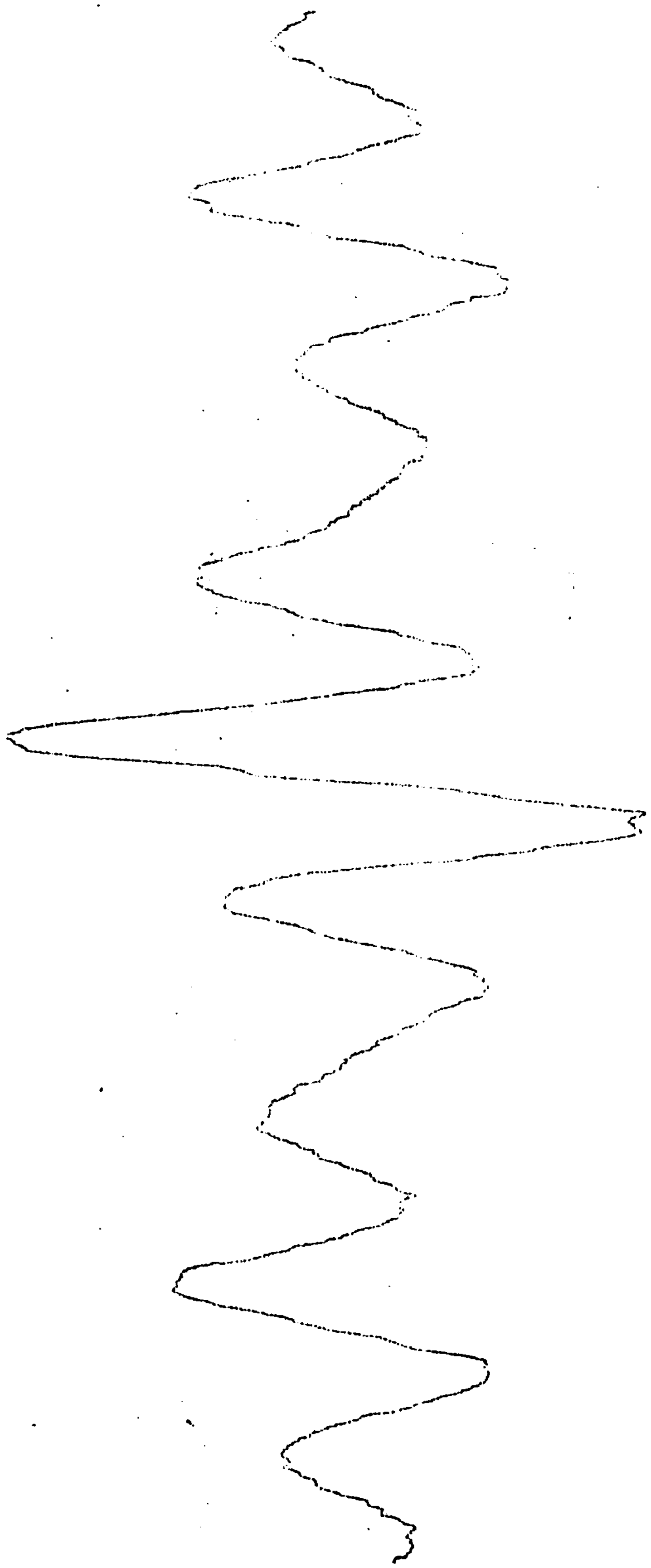
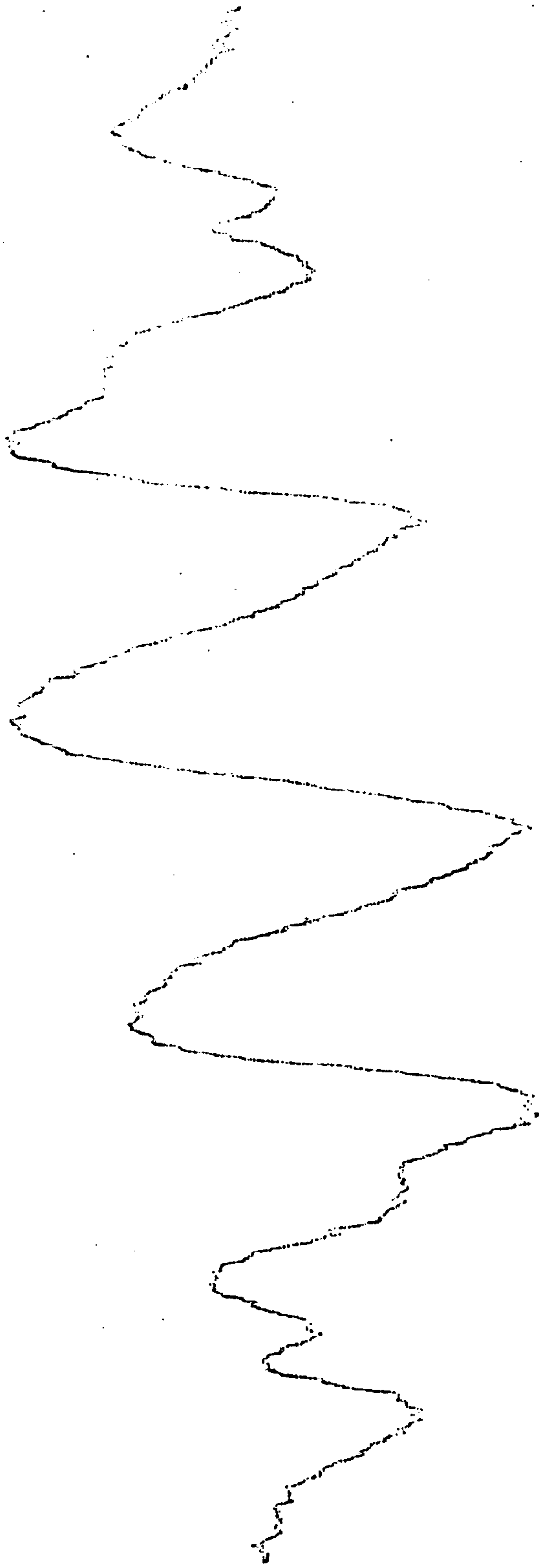


Figure 17. E.s.r. spectrum of the radical-anion of cyclooctane-1,2-dione; generated by the oxidation of cyclooctanone in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) in the presence of potassium t-butoxide, 1 cm. = 0.876 gauss



would show up in the center, not at the wings. The most likely explanation again is that a small amount of overoxidation has taken place.

Seven peaks can be resolved when cyclononanone is oxidized (Figure 18). The interpretation is the same as for the radical-anion of 4-<u>t</u>-butyl-1,2-cyclohexanedione. The two splitting constants, however, are not exactly in a ratio of 2:1 but are almost in that ratio. The values are 12.57 gauss and 5.49 gauss. The broad third and fifth peaks arise from overlap of two peaks. Proper resolution cannot be obtained probably because of the presence of dissolved oxygen. One would expect the peak height ratios for the third and fifth peaks to be less than that predicted for exact overlap. If exact overlap is assumed, the ratios predicted are 1:2:3:4:3:2:1 while the ratios found are 1.1:2:1.7:4:1.7:2:1.

The very simple spectrum obtained from oxidation of cyclodecanone is shown in Figure 18. Apparently there is interaction with only two of the four <u>alpha</u> protons. Extra low intensity peaks are found spaced between the new peaks in the spectrum observed in the oxidation of cyclodecanone, but they have no consistent spacing and probably result from a small amount of overoxidation. The acyloin and ketone gave the same splitting constants.

The oxidation of cyclododecane under the usual conditions gave a three peak spectrum with a_H=7.88 gauss. Trace amounts

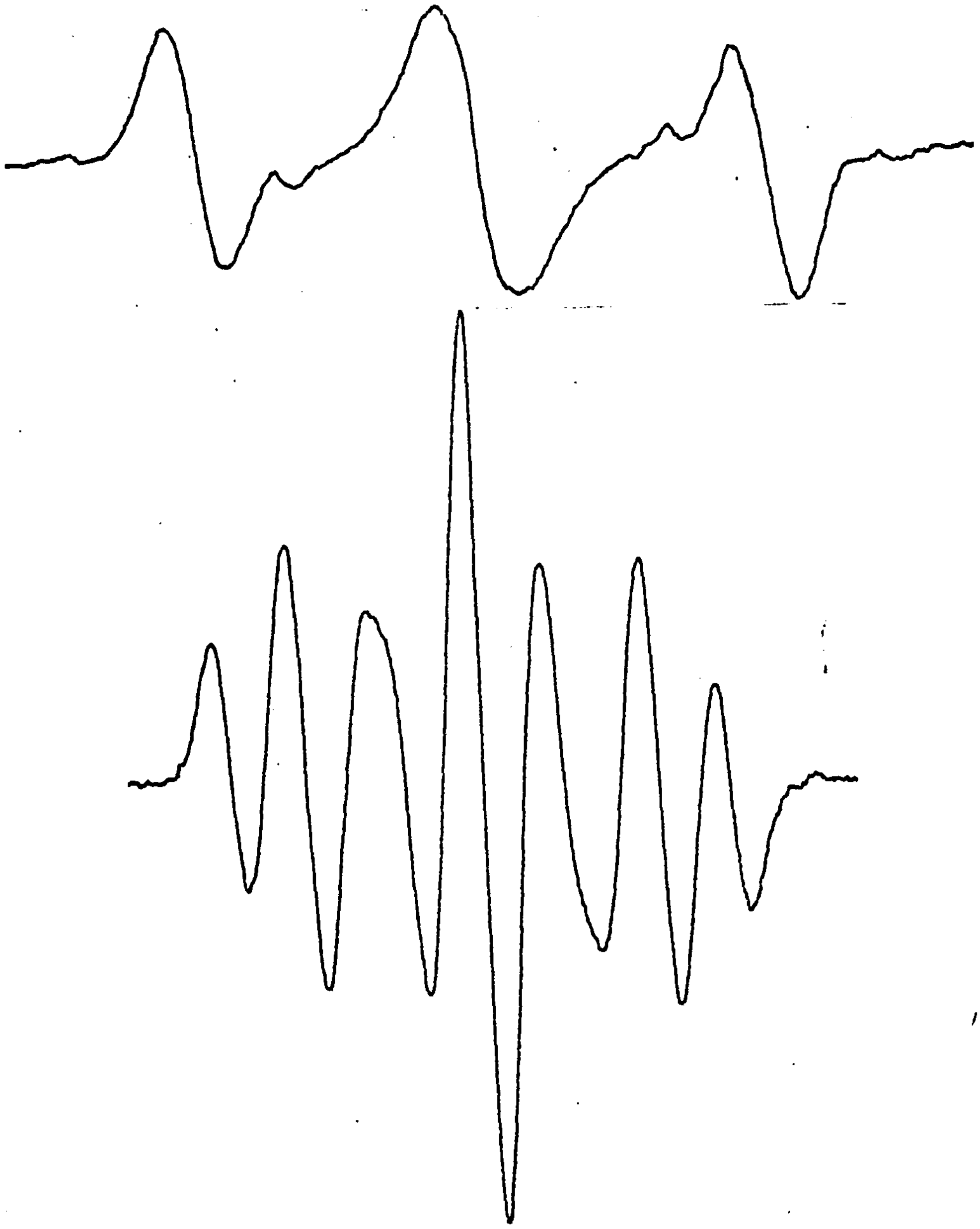


Figure 18. E.s.r. spectra of the radical-anions of cyclodecane-1,2-dione (top, 1 cm. = 2.38 gauss) and cyclononane-1,2-dione (bottom, 1 cm. = 5.78 gauss); generated by oxidation of the corresponding ketones in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) in the presence of potassium t-butoxide

of other radicals were present as shown in Figure 19. The experimental peak height ratios were equal to those predicted from theory.

Interactions with two pairs of protons give a nine peak spectrum (shown in Figure 20) when cyclopentadecanone is oxidized. The major splitting is 7.23 gauss while the minor splitting is 2.07 gauss. The experimental peak height ratios are 1:2:1.2:2.1:4.5:2.3:1.2:2:1 which is in good agreement with the predicted ratios.

It has been proposed that the splitting due to hydrogen on a carbon adjacent to an alkyl radical should follow a $\cos^2 \Theta$ dependence, where Θ is the dihedral angle between the $H-C_\alpha-C_\pi$ and $C_\alpha-C_\pi-p$ orbital planes (150, 151). Heller and McConnell propose that the equation $a_H = A + B \cos^2 \Theta$ holds (151). They find that $A \sim 0$. Since the splittings for hydrogens adjacent to the unpaired electron in alkyl radicals are about 25 gauss and since the average Θ for a freely rotating alkyl group is 45°, it follows that $B \sim 50$ gauss. Using the best value of Q for methyl hyperconjugation, 29.25 gauss, one would predict $B = 58.5$ gauss. It should be noted that for a cyclic radical, the equation predicts that axial protons have a greater splitting than equatorial protons.

The application of the above formula to the radical-anions of cycloalkanediones is not straightforward for there is no longer unit spin density at the carbon atom. We can use

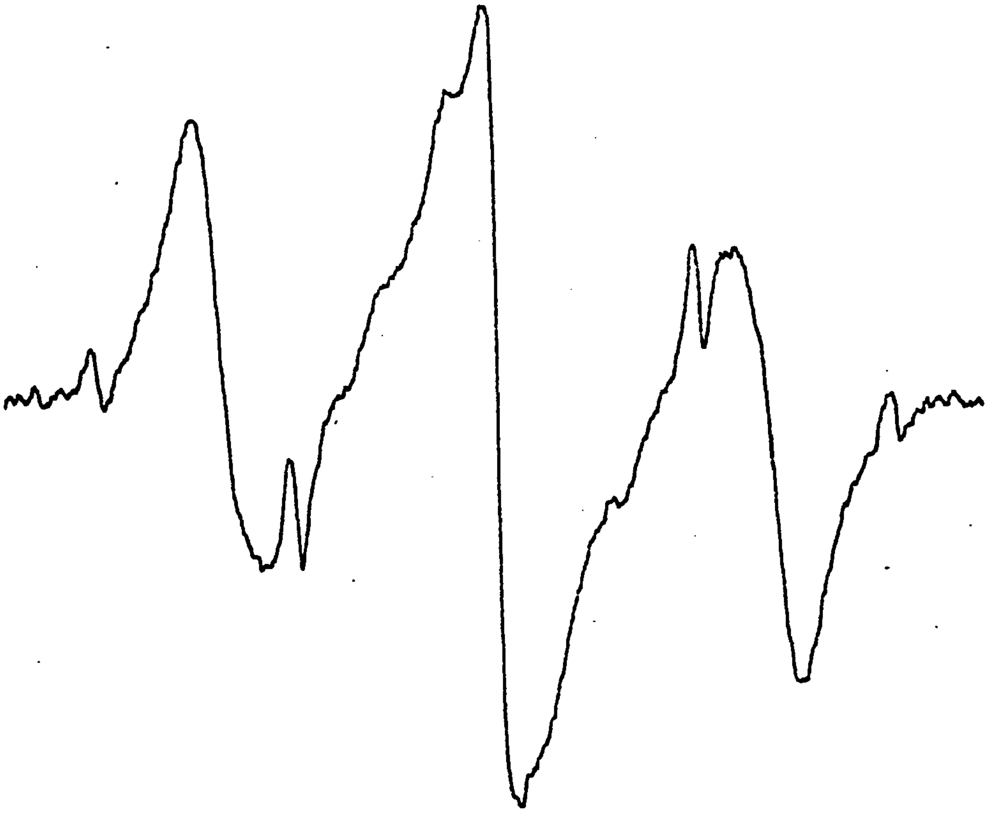
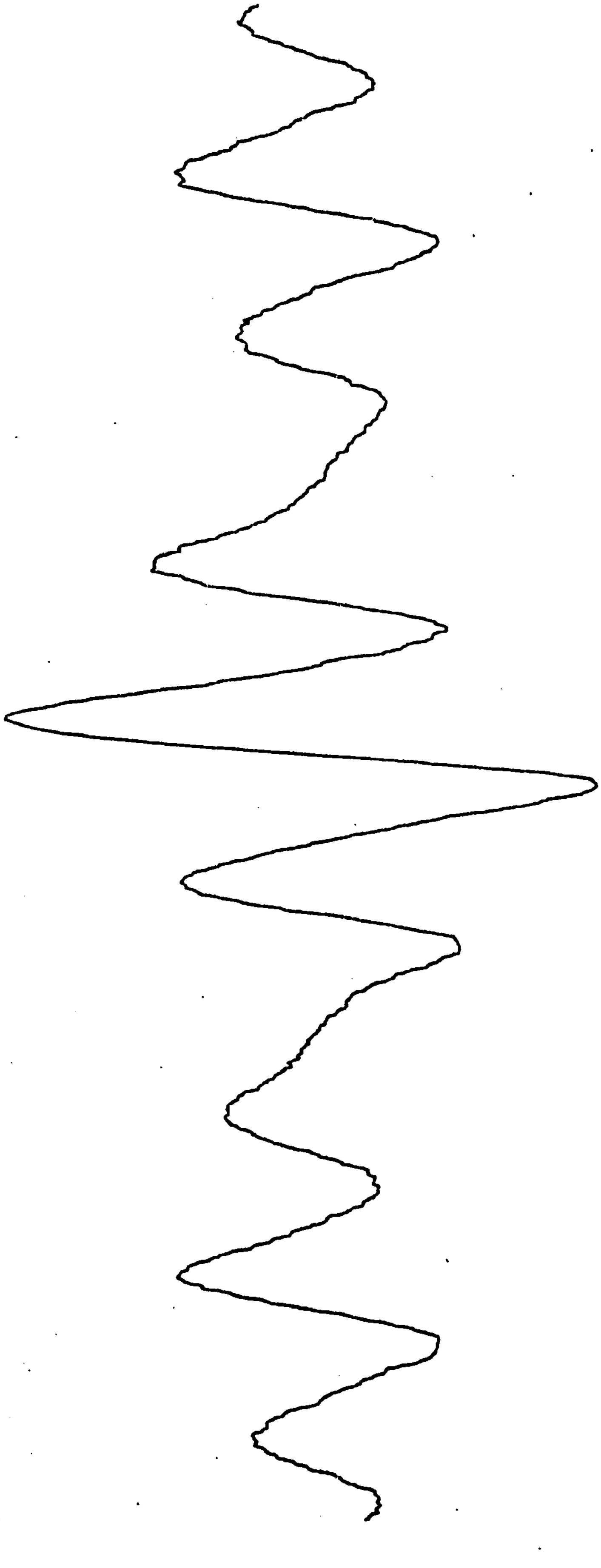


Figure 19. E.s.r. spectrum of the radical-anion of cyclododecane-1,2-dione; generated by oxidation of cyclododecanone in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) in the presence of potassium t-butoxide, 1 cm. = 2.38 gauss

Figure 20. E.s.r. spectrum of the radical-anion of cyclopentadecane-1,2-dione; generated by oxidation of cyclopentadecanone in dimethyl sulfoxide (80%)-t-butyl alcohol in the presence of potassium t-butoxide, 1 cm. = 0.876 gauss



a new equation, however, $a_H = B' \cos^2 \theta$ where $B' = \rho B$. There is no experimental way of measuring the spin density (ρ) on the carbonyl carbon. If B' could be found, one could then work backwards and find ρ. This would entail the assumption that the same B that holds for alkyl radicals also holds for the cycloalkanedione radical-anions. Since this seems to be true for semiquinones (152), it may not be an unreasonable assumption.

B' can only be evaluated when θ is known. Fortunately in all cases but that of the cyclopentyl ring, two splitting constants are known, which means that both B' and θ can be evaluated. These values of B' and θ were tabulated in Table 5. Two values of B' and θ_{ax-H} are obtained by solving the equations $a_{ax-H} = B' \cos^2 \theta_{ax-H}$ and $a_{eq-H} = B' \cos^2 (\theta_{ax-H} + 120°)$. Unrealistic solutions ($B' > 29.25$) have not been listed. The value of θ_{ax-H} for cyclohexanedione radical-anions is exactly equal to that found by n.m.r. for cyclohexene by Smith and Kriloff (153). (These workers use a dihedral angle for axial hydrogens equivalent to $90-\theta_{ax-H}$).

The table shows that B' varies with ring size. This is not unexpected. Brown and coworkers have shown that there is a variation in the stability of <u>exo</u> and <u>endo</u> double bonds in going from five-membered rings to six-membered rings (154). Perhaps an even clearer precedent comes from the work of Leonard and Mader (155). They performed u.v. measurements on a series of cyclic α-diketones, methylated in the alpha positions. The values of $\lambda_{max.}$ decreased in going from the five-membered ring to the seven-membered ring, then increased again at the eight-membered ring. Such a trend is evident in the values of B'. Leonard and Mader attributed this shift to a trend away from coplanarity of the carbonyl groups. The carbonyl groups are cis-coplanar in the five-membered ring. As the ring size increases the carbonyls are increasingly less coplanar until a minimum is reached at the seven-membered ring. Here the two groups are at an angle close to 90°. In the larger rings the carbonyl groups now become trans-coplanar.

Similar reasoning can be applied to the splitting constants. The greatest spin density will be on the carbonyl carbons in those cases when a planar four carbon system can be attained. Otherwise the spin density will be largely at the oxygen atoms. Thus in the five-membered ring where the carbonyl groups are cis-coplanar, the largest value of B' is found. As the carbonyl becomes less coplanar, B' diminishes until a trend toward trans-coplanarity appears. This reasoning is not quite flawless, for B' for the ten-, twelve- and fifteen-membered rings should be greater than or equal to B' for the nine-membered. Instead B' is less for these rings. There seems to be a trend toward decreasing B' from rings C_9 to C_{15}. One would expect B' to eventually be constant with increasing ring size.

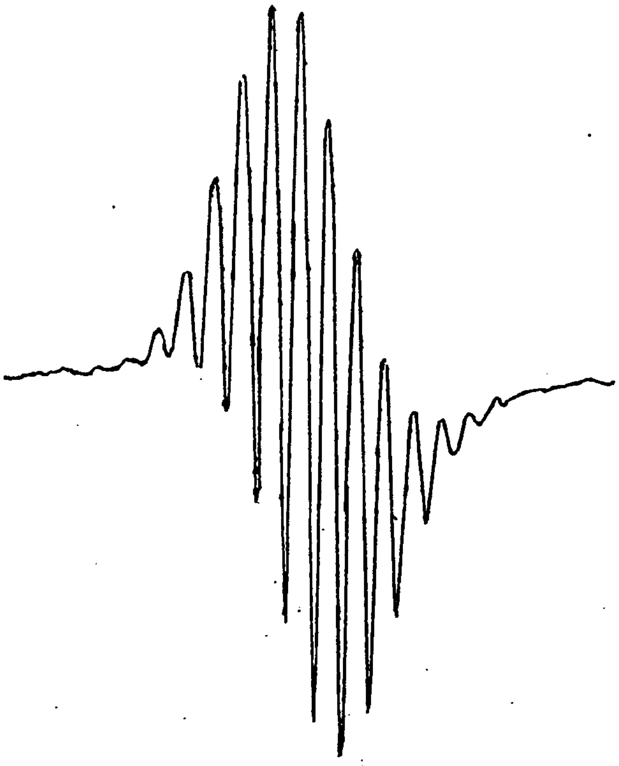
The spin density at the carbonyl carbon for the cis-coplanar radicals will not necessarily be the same as for the trans-coplanar radicals. The experimental data seems to show that the spin density at the carbon is greatest for the cis-coplanar case.

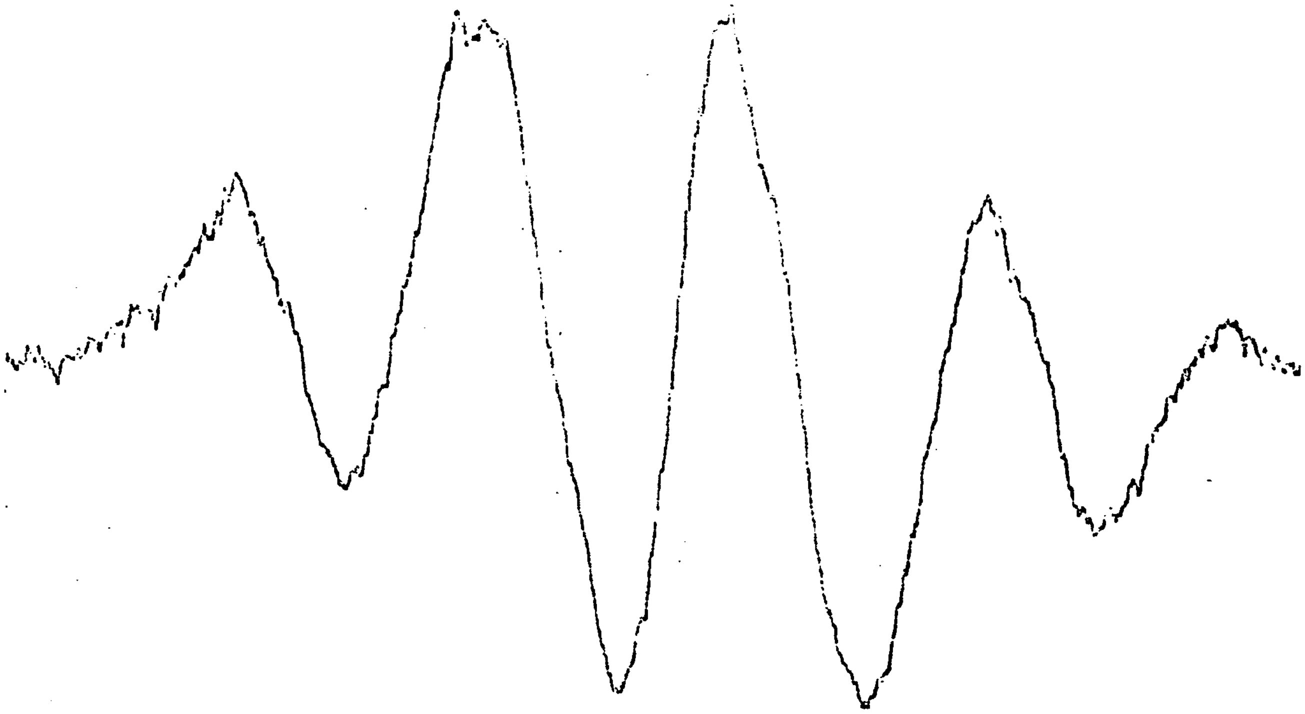
If one assumes that $B' = 58.5\rho$, the carbonyl carbon spin densities can be calculated. These are tabulated in Table 5. The trend in ρ parallels the trend in B', of course.

Oxidation of camphor under the usual conditions also gave a radical-anion. In contrast to the other radicals, it took several hours for a reasonable concentration to be attained. Figure 21 shows the spectrum which is a quartet. On higher resolution some hyperfine structure is observed. The most reasonable interpretation is that the radical is that of camphorquinone, and the splitting is from a methyl group. One would expect the most overlap with the methyl group in the 7-syn position. No splitting from bridgehead protons or methyl groups has been observed in triptycene-1,4-semiquinone (156, 157), nor has the author noticed hyperfine splittings from the bridgehead protons in benzonorbornadiene-1,4-semiquinone. Formation of radicals from α- and β-santenonequinone ought to conclusively show which methyl group is interacting.

Only trace amounts of radical-anions were observed when norcamphor was oxidized. The protons at the bridging position

Figure 21. E.s.r. spectrum of the radical-anion of pivalil (top, 1 cm. = 0.876 gauss); generated by the oxidation of crude pivaloin in dimethyl sulfoxide (80%)-ethyl alcohol (20%) in the presence of potassium _t_-butoxide; e.s.r. spectrum of the radical-anion of camphorquinone (bottom, 1 cm. = 0.876 gauss); generated by the oxidation of camphor in dimethyl sulfoxide (80%)-_t_-butyl alcohol (20%) in the presence of potassium _t_-butoxide





apparently can not interact with the π-orbital. This may have something to do with the lack of stability. Again the author found no splitting due to protons at the bridging methylene group in benzonorbornadiene-1,4-semiquinone.

Corresponding stability is not found among the acyclic acyloins. Oxidation of acetoin, propionoin, and butyroin gave no radicals. Oxidation of crude pivaloin, partially degassed and mixed with pivalil gave a 17 line spectrum (Figure 21). The splitting between components was 0.31 gauss. A reasonable conclusion is that the radical is the radical-anion of pivalil, and the spectrum shows 17 of the expected 19 lines. An examination of theoretical peak height intensities shows that it would be impossible to observe the wing peaks. A reasonable way of expressing the theoretical peak height intensities, since the wing peaks are not observable, is in terms of the ratio of all the peaks to the center peak. Concentrating on the seven center peaks, since they are fully resolved, the theoretical ratios are 2.62, 1.53, 1.11, 1.00, 1.11, 1.53 and 2.62. The experimental ratios are 2.70, 1.52, 1.10, 1.00, 1.13, 1.60, and 2.85. This is quite conclusive. Unfortunately the experiment could not be repeated.

The mode of formation of these radicals is not clear as yet. Radicals could arise from oxidation of the acyloins in the same manner as proposed for the benzoins (16). This would entail the formation of a dianion followed by two one-electron-transfers to oxygen. It does not follow that oxidation of the monoketone goes through an acyloin however. Diketone could be formed in some manner directly from the monoketone, after which radicals could arise from electron-transfer from carbanions undoubtedly present in the solution (X). The fact

(X)

$$R\text{-}CO\overset{\ominus}{C}H\text{-}R+O_2 \longrightarrow RCOCOR;\quad RCO\overset{\ominus}{C}HR+RCOCOR \longrightarrow R\underset{\underset{O\cdot}{|}}{C} = \underset{\underset{O^{\ominus}}{|}}{C}\text{-}R+\text{Products}$$

that the observed amount of radical is far less than the possible amount lends credence to this belief. The monoketones should be oxidized, and the rate of oxygen uptake measured to check this possibility. The growth of diketone could also be followed by taking aliquots, quenching the reaction, and measuring the diketone by u.v.

The stability of the radical-anion in the cyclic case as opposed to the instability of the radical in the acyclic case is somewhat puzzling. This quite possibly has to do with the fact that carbanions of acyclic ketones can undergo condensation reactions much more readily than carbanions of cyclic ketones.

Obvious further experiments to do would be to extend the reaction to more rigid ketones, such as steroids, and to observe the effect of mono- and di-substitution in the <u>alpha</u> positions.

IV. RADICAL-ANIONS OF AZO COMPOUNDS AND THEIR VINOLOGS

The electron-transfer experiments showed quite conclusively that the azo linkage and the vinylogous azo linkage were excellent electron-acceptors. The radicals usually are stable under the strenous conditions employed and give quite characteristic spectra. Some of the spectra were quite interesting in themselves so radicals of a variety of azo-compounds were made, and their spectra were studied. Compounds of interest are listed in Figure 22. Radicals were made from XIII, XIV, XV, XVII, XVIII, XXI, XXIII, XXIV, XXV, XXVI and XXX. Russell and Konaka* made radicals from XXVII and XXVIII. Compound XVI solvoyzed under the reaction conditions while the other compounds have not been tested as yet.

The first published spectra of a radical-anion of a non-cyclic azo compound was that of azobenzene radical-anion (111). During the preparation of this thesis another spectrum was published. This was the spectra of the radical-anion of ethyl azodiformate (158). Two spectra of cyclic azo-compounds have been reported, that of pyridazine (159, 160, 161) and phthalazine (161). There are reports of spectra of several vinylogous cyclic azo-radical-anions in the literature. The spectra of azo radical-anions will now be discussed in detail.

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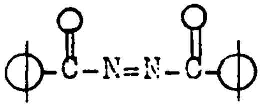
*G. A. Russell and R. Konaka, Department of Chemistry, Iowa State University, Ames, Iowa. Private communication regarding azo radical-anions. 1963.

(XI) R-N=N-R

(XII) ϕ-N=N-R(R=t-butyl)

(XIII) ϕ-N=N-ϕ

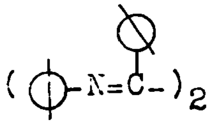
(XIV)



$\phi-\overset{O}{\overset{\|}{C}}-N=N-\overset{O}{\overset{\|}{C}}-\phi$

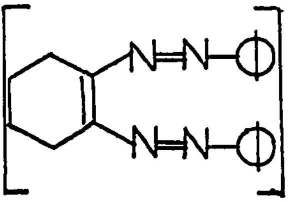
(XV) $EtO_2C-N=N-CO_2Et$

(XVI)

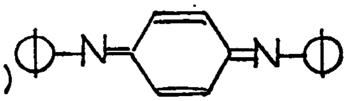


$(\phi-N=\overset{\phi}{C}-)_2$

(XVII)



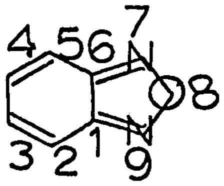
(XVIII)



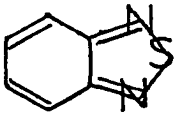
(XIX) $(CH_3)_2-N-N=N-N-(CH_3)_2$

(XX) ϕ-N=C=N-ϕ

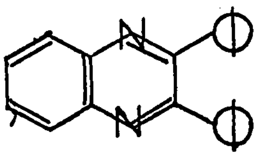
(XXI)



(XXII)



(XXIII)



(XXIV)

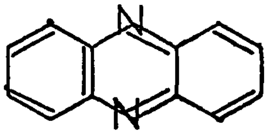
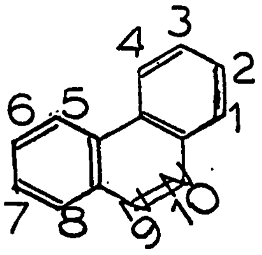
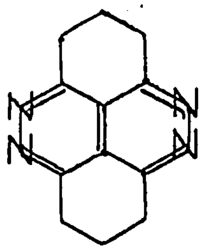


Figure 22. "Vinologs" of azo compounds

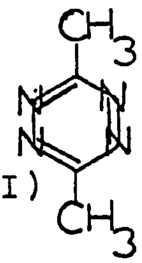
(XXV)



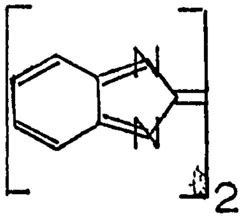
(XXVI)



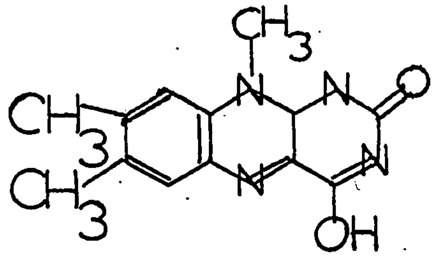
(XXVII)



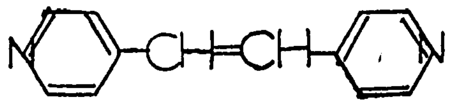
(XXVIII)



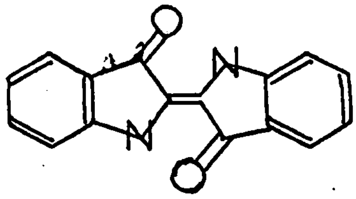
(XXIX)



(XXX)



(XXXI)



(XXXII)

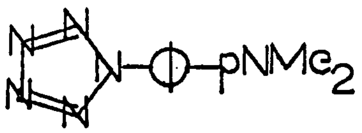


Figure 22. (Continued)

Azobenzene (XIII) radical-anion was first made by Janzen (29), both by oxidation of the hydrazo compound and by electron-transfer from the hydrazo compound to the azo compound. The author investigated the spectrum thoroughly in connection with electron-transfer reactions. The spectrum was finally elucidated by Russell and Konaka* by means of deuterium substitution. The splitting constants were a_N=4.84 gauss, $a_{\underline{p}}=a_{\underline{o}-1}$=2.81 gauss, $a_{\underline{o}-2}$=2.08 gauss and $a_{\underline{m}}$=0.78 gauss in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%). The difference in the *ortho* protons arises because azobenzene occurs in the *trans* form. The radical apparently is also *trans*. A similar example is found in the literature (162). Under the conditions used *cis*-azobenzene immediately is converted to the *trans*-form.

Cyclization of azobenzene gives the molecule benzcinnoline (XXV). E.s.r. spectra of cinnolines have not been reported as yet. Fluorenone is reduced to the radical-anion much more easily than benzophenone, but the analogy does not hold for benzcinnoline and azobenzene. The comparison is probably not too fair, for *cis*-azobenzene would be a better model. In any event, azobenzene is reduced easily by monoanions, while appreciable amounts of benzcinnoline radical-anion are formed only by use of the dianion of dihydroanthracene. The

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***Ibid*.

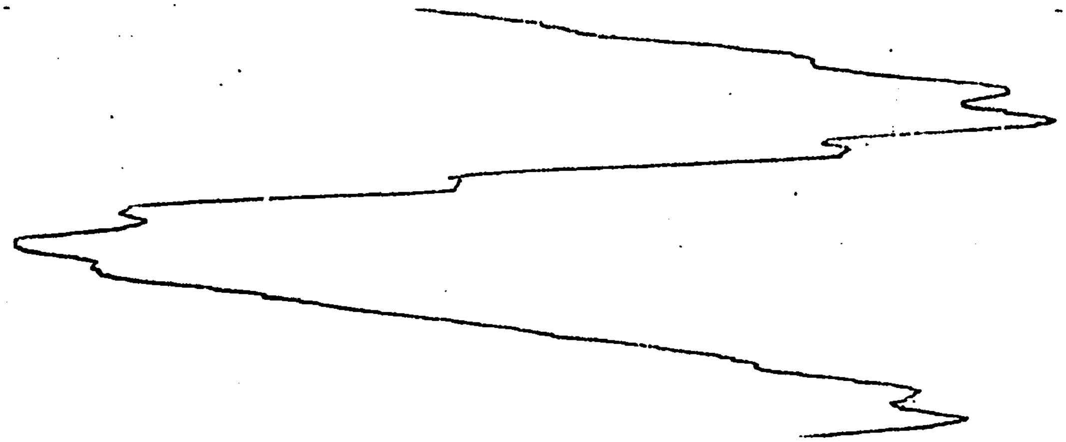
color of the solution was a dark green.

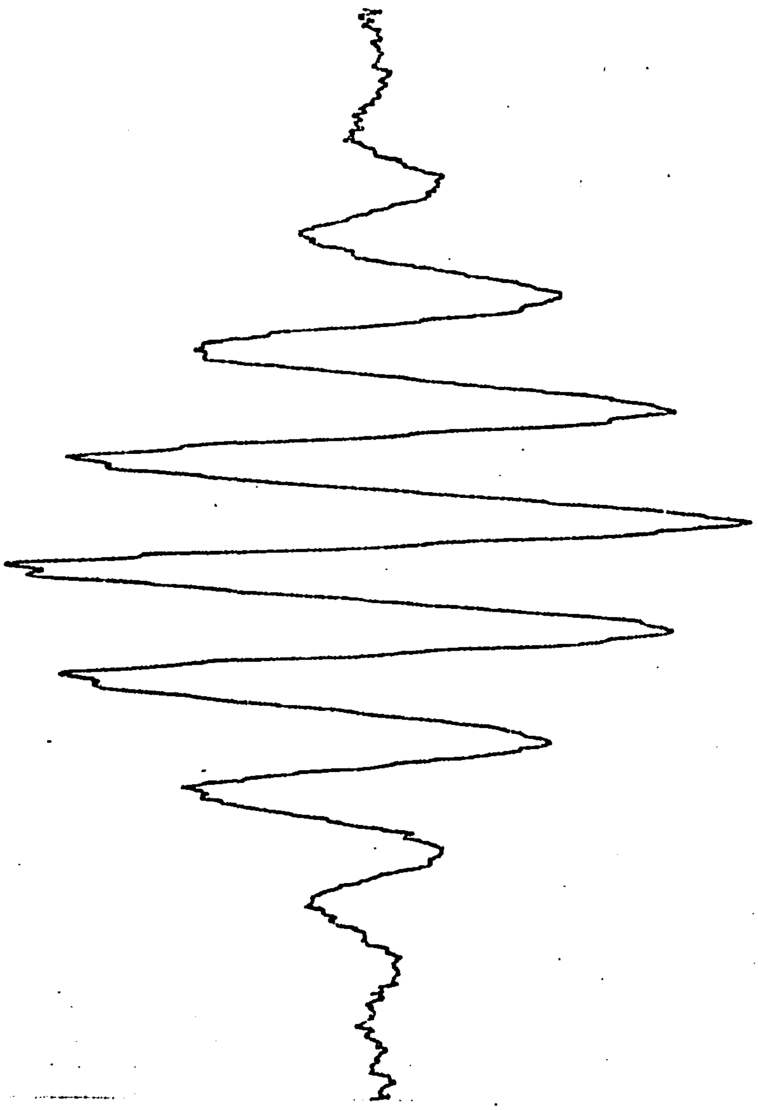
On low resolution thirteen main peaks were observed. These appeared to break into triplets in higher resolution. These triplets had further structure (Figure 23). This spectrum can be explained on the basis of a main nitrogen quintet interacting with four equivalent hydrogens (probably at the 1,3, 6, and 8 positions) with a splitting of one half the nitrogen splitting. This would give thirteen peaks. The triplet then would come from an interaction with two more protons, either the 4 and 5 or 2 and 7 protons. A problem arises in assigning the smallest splittings. The four main protons are certainly not exactly equivalent, although their differences are probably about 0.4 gauss. This means also that the main nitrogen splitting cannot be exactly twice the proton splitting. The smallest splittings could thus arise either from these differences showing up, or they could arise from the interaction of two protons with small splittings. The experimental values are a_H=5.54 gauss, a_1=a_3=2.77 gauss, $a_?$=0.7-0.8 with the smallest spacings 0.2-0.3 gauss.

Still another interesting azo radical-anion is that derived from 1,4,5,8-bis-trimethylenepyridazino-[4,5-d]-pyridazine (XXVI). This radical would be expected to give nine main peaks from four equivalent nitrogens, each of which could be split into nine peaks from the eight methylene protons if there were no overlap. Figure 24 shows the spectrum

Figure 23. E.s.r. spectrum of benzo- c -cinnoline radical-anion; generated by reduction with dihydroanthracene in dimethyl sulfoxide (80%)-_t_-butyl alcohol (20%) in the presence of potassium _t_-butoxide, 1 cm. = 5.78 gauss

Figure 24. E.s.r. spectrum of the radical-anion of 1,4,5,8-bis-trimethylenepyridazino- 4,5-d -pyridazine (left, 1 cm. = 2.38 gauss); spontaneously generated from the parent compound by treatment with potassium t-butoxide in dimethyl sulfoxide (80%)-t-butyl alcohol (20%); center peak (right) is shown under high resolution





obtained. The radical could be formed merely by treating the compound (0.02 *M.*) with potassium *t*-butoxide (0.1 *M.*) in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%). The color of the solution under conditions of maximum radical concentration was brown. As can be seen, the spectrum is quite consistent with that expected. The theoretical peak height intensities to the center peak should be 1:4:10:16:19 while the experimental peak height intensities are 1:3.4:11:15.2:18.4: 15:11:3.4:1. The value of a_n is 3.44 gauss. The methylene proton splittings are approximately 0.2 gauss. Both splitting constants are somewhat less than normal. Figure 24 also shows the center peak under higher resolution.

Radical formation probably occurs in the same manner as radical formation from *p*-nitrotoluene (XXXIII) (68).

$$\text{(XXXIII)}\quad \pi\text{-CH}_2\text{-} + B^- \longrightarrow \pi\text{-}\bar{\text{C}}\text{H-};\quad \pi\text{-}\bar{\text{C}}\text{H-} + \pi\text{-CH}_2\text{-} \longrightarrow$$
$$\text{-CH}_2\text{-}\pi^{\dot{-}} + \pi\text{-}\dot{\text{C}}\text{H-}$$

Difficulties were found in making the radical-anion of ethyl azodiformate (XV), arising mainly from the fact that the compound was prone to decompose with the evolution of nitrogen when treated with strong base. A poorly resolved spectrum could be obtained on treatment of the ester with *n*-butyllithium, but the only good resolution was obtained by mixing equimolar amounts of the hydrazo and azo compound in the presence of base and the absence of air. The concentrations after mixing were azo compound, 0.01 *M.*, hydrazo compound, 0.01 M., and potassium t-butoxide, 0.02 M. The solvent was dimethyl sulfoxide (80%)-t-butyl alcohol (20%). The radical died out rather quickly, but it gave a 25 peak spectrum as shown in Figure 24. This is interpreted as a main quintet, arising from the nitrogens with $a_N=6.31$, each peak of which is split into quintets by the four ethoxy protons. This splitting is 1.07 gauss. The splittings found by Zweig and Hoffman by potassium reduction in dimethoxyethane were $a_N=5.9$ gauss and $a_H=0.9$ gauss (158). The differences in dimethyl sulfoxide solution are in agreement with the results of Deguchi (126) who found that splitting constants for nitrogen increased with increasing dielectric constant of the solvent.

Dibenzoyldiimide is known to be decomposed very quickly by base (46), so one would anticipate difficulty in observing its radical-anion. Nevertheless, the radical-anion can be made by electron-transfer from the dianion of 1,2-dibenzoylhydrazine to dibenzoyldiimide. The experimental conditions were given earlier. There is very little radical in the yellow solution, and it decomposes quickly. A typical spectrum is shown in Figure 25. It appears that there is a main quintet with splitting of 1.2-1.4 gauss. This would be an unusually low nitrogen splitting, particularly when the proton splitting at the analogous position in 1,2-dibenzoylethylene radical-anion is 4.9 gauss. Low nitrogen splittings have been found as in phthalazine (161), but this does not

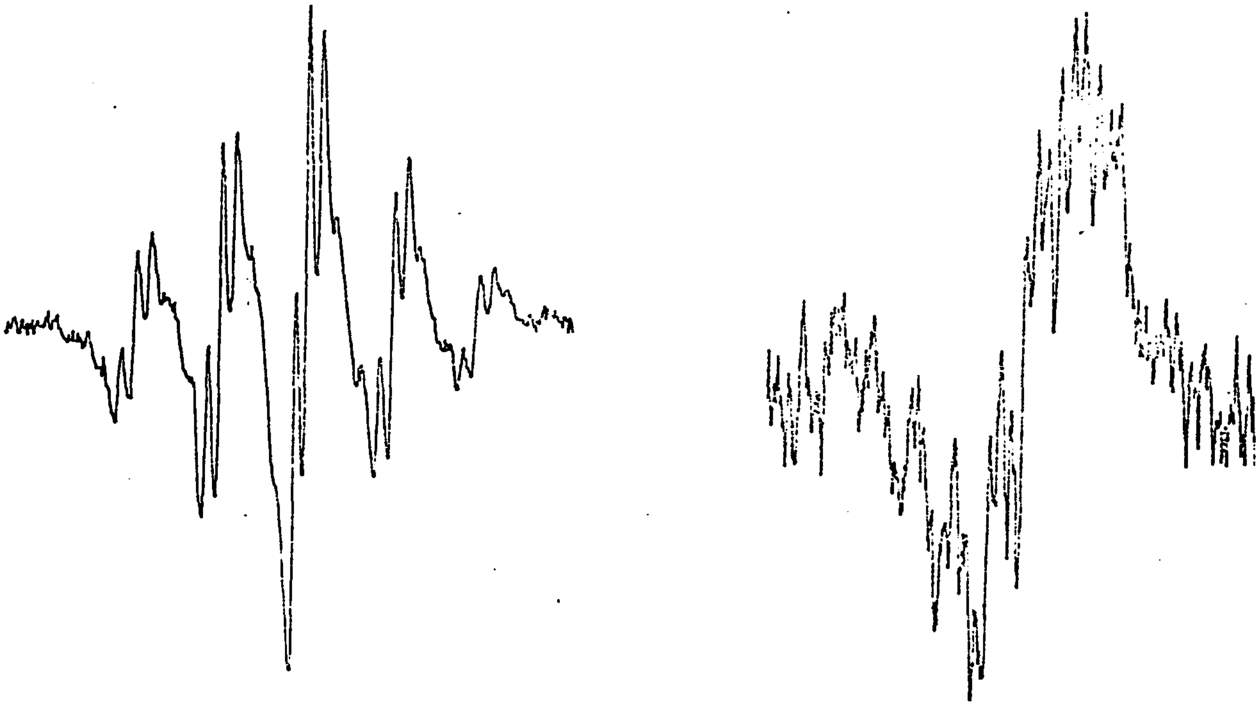


Figure 25. E.s.r. spectra of radical-anions of ethyl azodiformate (left, 1 cm. = 5.78 gauss) and dibenzoyldiimide (right, 1 cm. = 2.38 gauss); generated by electron transfer from the dihydro compounds to the dehydro compounds in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) in the presence of potassium t-butoxide

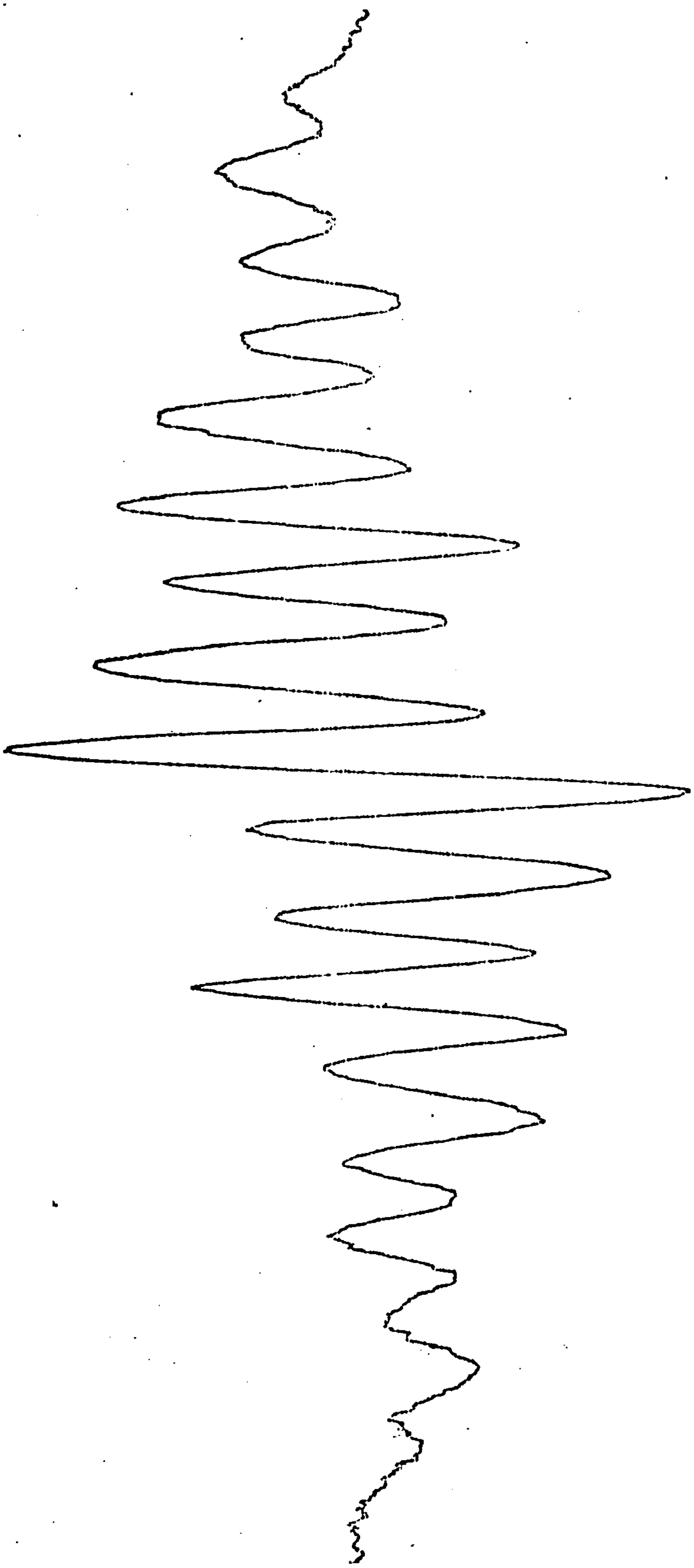
appear to be a similar case. In view of the low concentration of radical, a good deal of the hyperfine structure is lost in the wings, and these splitting constants could be for proton hyperfine splittings on the center peak of a nitrogen quintet, the wing peaks being lost in the noise.

The radical-anion of 2,3-diphenylquinoxaline could be made by oxidation of the 1,2-dihydro compound, by electron-transfer from the dianion of the 1,2-dihydro compound to the parent compound, and by electron-transfer to the quinoxaline from the dianion of dihydroanthracene. In all cases a seventeen line e.s.r. spectrum was obtained from the purple solution (Figure 26). Successive dilutions were performed to attempt to resolve more hyperfine structure, but none of these resulted in any improvement. The interpretation is that of a main quintet, due to two nitrogens, with a_N=5.30 gauss, with a further splitting by four equivalent ring protons. Since the proton splitting is almost one-third of the nitrogen splitting, overlap removes eight of the twenty-five theoretical lines.

The spacing between lines varies from 1.5 to 2.2 gauss. It appears that the average spacing is 1.87 gauss. There may actually be slight differences between the ring protons in the aromatic ring, but the resolution obtained is not sufficient to distinguish this.

The experimental peak height ratios (one half of the

Figure 26. E.s.r. spectrum of the radical-anion of 2,3-diphenyl quinoxaline; generated by electron-transfer from the dihydro compound to the dehydro compound in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) in the presence of potassium *t*-butoxide, 1 cm. = 1.56 gauss



theoretical ratios are 1:4:6:6:9:12:11:14:18) are 1:3.2:4.4:3.6:5.8:10.8:7.6:10.4:18.4:9.8:7.0:10.0:6.0:3.0:3.6:2.6:1. These ratios are less than theoretical in every case except for the centerline and the wing peaks which leads one to believe that the other 14 lines are an envelope.

These values compare well with the previous results of Russell *et al*. (111).

The radical-anion of quinoxaline itself has been made by Ward (160) and by Carrington and Santos-Veiga (163) by alkali-metal reduction in dimethoxyethane. Ward found that a_N=5.7 and a_H for the ring protons was 1.5 gauss. Carrington and Santos-Veiga found a_N=5.64, and they could actually distinguish between the aromatic protons. The values obtained were 2.32 gauss and 1.00 gauss. One should not expect too great a correspondence between quinoxaline and 2,3-diphenylquinoxaline. For example, a_N is greater for quinoxaline in the less polar solvent. This must mean that there is greater electron density in the aromatic ring in 2,3-diphenylquinoxaline. Certainly a difference of 1.32 gauss in the ring protons could have been detected. Probably this shift in spin density tended to average out differences. In an analogous case Vincow and Fraenkel found all the ring protons in the nonsubstituted ring of quinizarin semiquinone equivalent (144).

Phenazine (XXIV) proved to be an excellent electron acceptor. It reduced readily with anions in both dimethyl sulfoxide (80%)-t-butyl alcohol (20%) and dimethyl sulfoxide (20%)-t-butyl alcohol (80%). The color of the radical solutions was purple. Figure 27 shows a spectrum in dimethyl sulfoxide (20%)-t-butyl alcohol (80%). The gross structure of 17 lines can be interpreted as was the spectrum of 2,3-diphenylquinoxaline. All three possible splitting constants can be analyzed, however. The values are a_N=5.15 gauss, a_{H1}=2.03 gauss, and a_{H2}=1.56 gauss for both solvents. The values obtained by Ward (160) and Carrington and Santos-Veiga (163) by alkali-metal reduction in dimethoxyethane are 5.0, 2.0, 1.61 gauss and 5.14, 1.93, and 1.61 gauss, respectively. Stone and Maki (161) made this radical by electrolytic reduction in dimethyl sulfoxide, obtaining splitting constants of 5.15, 1.80, and 1.57 gauss. The agreement obtained is certainly within experimental error.

An interesting variation on the acceptors used previously was the compound benzofurazan (XVI). One would expect this compound to be reduced quite easily, for the addition of an electron would give a radical with a benzenoid structure. Indeed, a stable radical-anion was formed quite easily with anions in dimethyl sulfoxide (80%)-t-butyl alcohol (20%). The color of the solution was brown. A 29 peak spectrum was observed (Figure 28). This could be easily explained on the basis of a_N=5.24 gauss, a_H=3.33 gauss, and a_H=2.02 gauss. One can not tell which of the two pairs of protons gives the

Figure 27. E.s.r. spectrum of the radical-anion of phenazine; generated by reduction with propiophenone in dimethyl sulfoxide (20%)-t-butyl alcohol (80%) in the presence of potassium t-butoxide, 1 cm. = 1.56 gauss

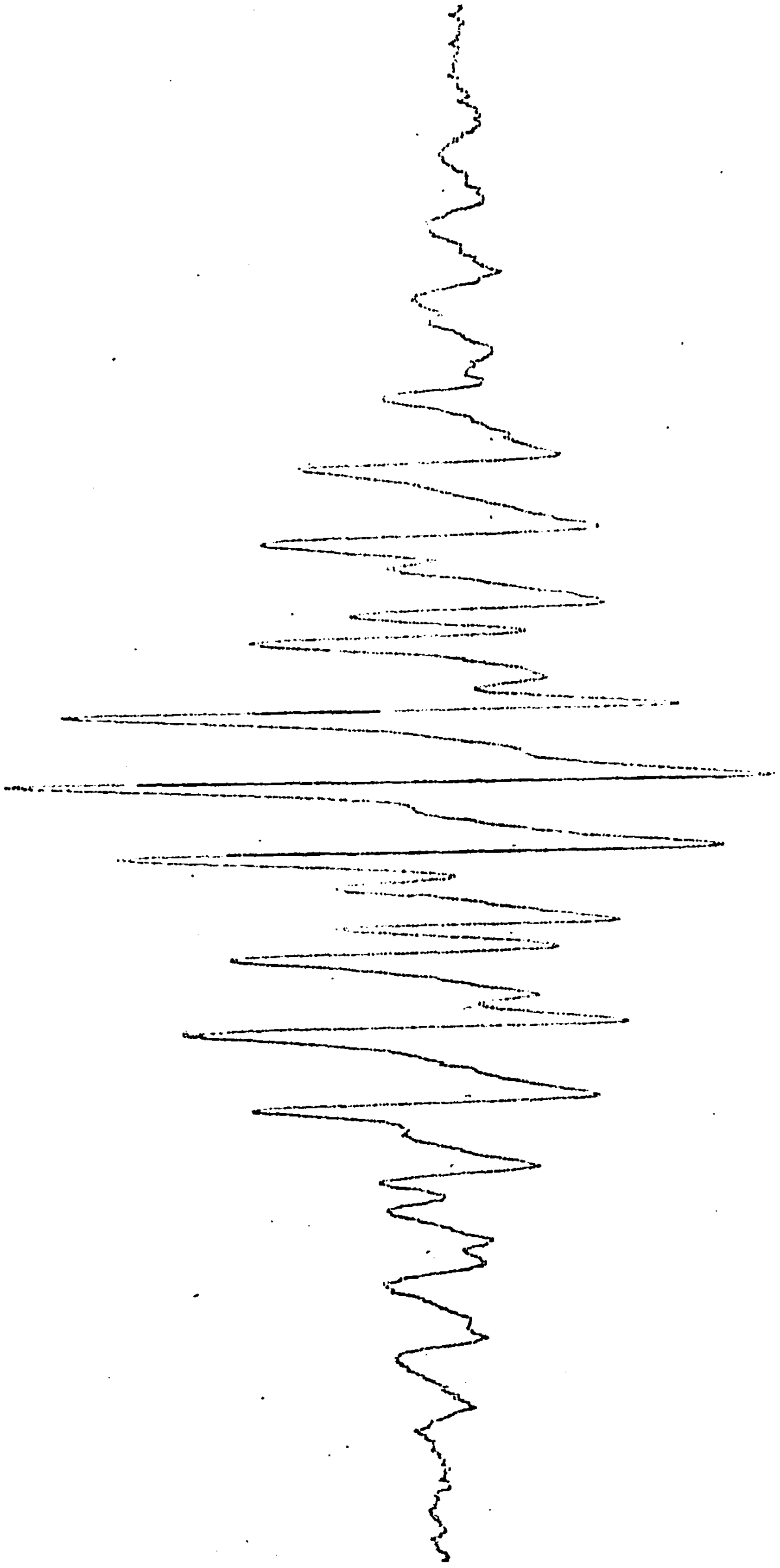
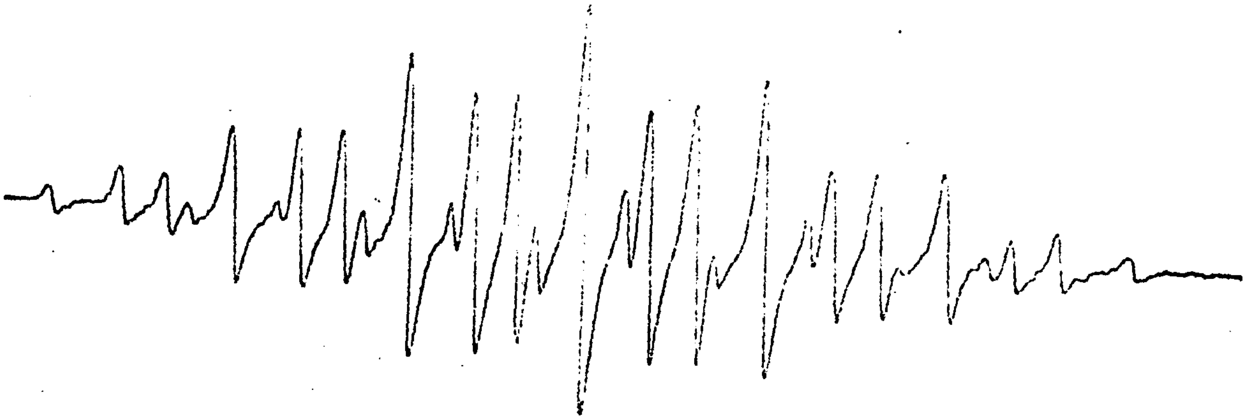
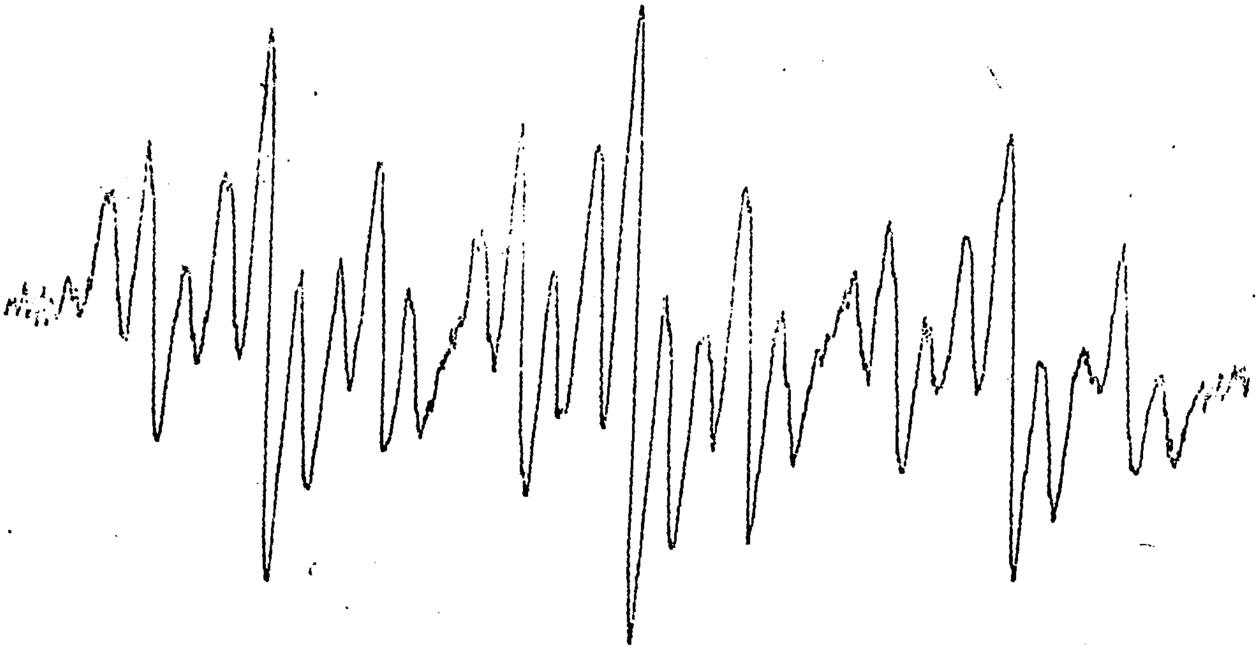


Figure 28. E.s.r. spectra of the radical-anions of benzofurazan (top, 1 cm. = 2.38 gauss), formed by reduction with propiophenone, and 1,2-*bis*-(4-pyridyl)-ethylene (bottom, 1 cm. = 2.38 gauss), formed by reduction with dihydroanthracene; both spectra were taken in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) in the presence of potassium *t*-butoxide



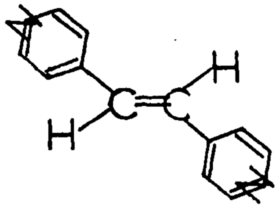


larger splitting, although one would instinctively feel that the positions nearest the heteroatom are the most likely possibility.

The most difficult of the azo vinologs to reduce that could still be reduced was the compound 1,2-(bis-4-pyridyl) ethylene (XXX). This compound could only be reduced using the very powerful donor 9,10-dihydroanthracene in dimethyl sulfoxide (80%)-_t_-butyl alcohol (20%). The spectrum obtained from the colorless solution consisted of a main triplet, each peak of which broke into nine other peaks (Figure 28). The splitting between the triplet components is 10.95 gauss while the separation between the other components is on the average 1.07 gauss. The main triplet almost certainly arises from the ethylenic protons. The nine-fold splitting could arise possibly from an interaction with eight equivalent protons or an interaction with two nitrogens and four protons, all of which are equivalent. The latter possibility seems the more likely, but this can be tested quite easily by an examination of peak height intensity ratios. Such an examination shows that neither explanation is correct. A closer examination of each peak of the triplet reveals that they consist of a triplet, each peak of which is split into a triplet. The splitting for the larger triplet is 3.33 gauss. Each of these triplets appears to have a 1:2:1 peak height ratio. One is thus lead to the inescapable conclusion that this spectrum arises from an interaction with three pairs of protons, with splitting constants of 10.95, 3.33, and 1.07 gauss. The other four protons and the two nitrogens do not appear to split!

The most reasonable explanation is that we here have an example of a <u>trans</u>-planar radical, as with azobenzene (XXXIV).

(XXXIV)

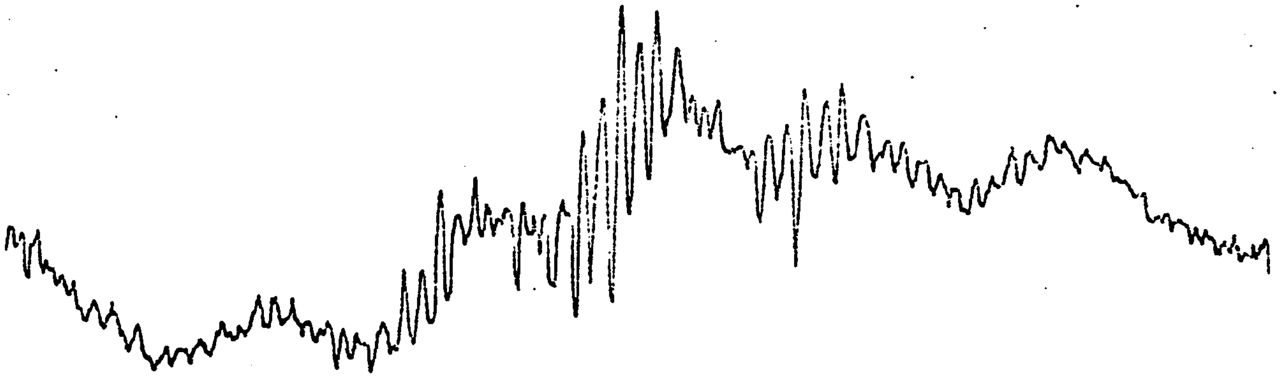


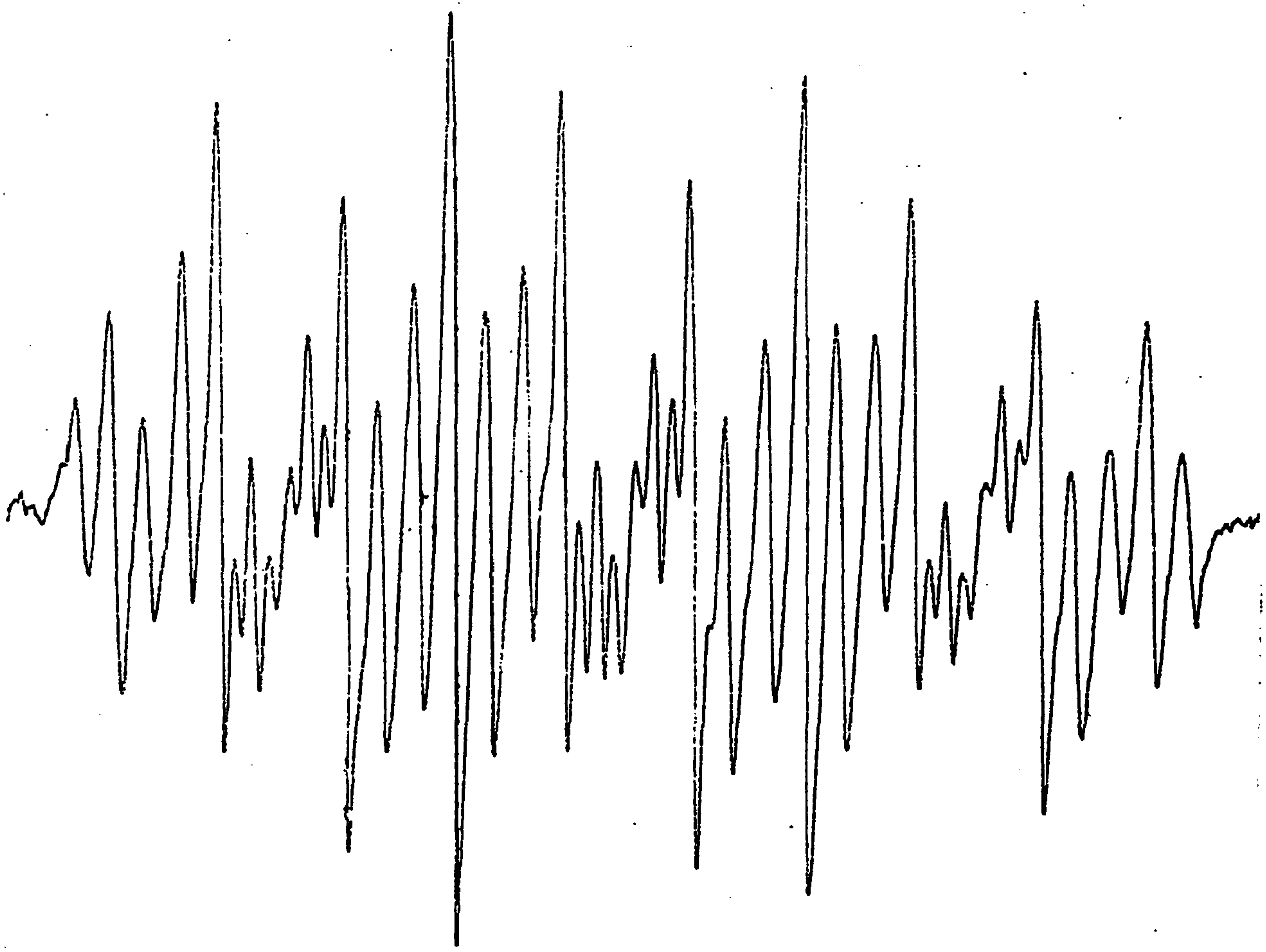
The main splitting thus would be due to the ethylenic protons, the secondary splitting would be due to two <u>meta</u> (with respect to nitrogen) protons, while the minor splitting could come either from the other two <u>meta</u> protons or, less likely, from two <u>ortho</u> protons. If these splittings arise from conjugation with the benzene ring, it is quite surprising that interaction with other protons or the nitrogens are not seen. The scan rate was sufficiently fast that a splitting of 0.3-0.4 gauss might have been missed. It is possible that an interaction through space is taking place, and there is little conjugation with the ring. From the equation $a_H = 24.2 \quad {}_1$ one can calculate that the spin density on each ethylene carbon is 0.452. Unless we assume that there are quite large negative spin densities present, we find that the total spin density is 1.268, an impossibility. This lends substance to an assumption of a spatial interaction. One can make all the assumptions one wishes, but the problem can not be rigorously solved without better resolution to uncover additional splittings and without isotopic substitution to check the splitting assignments.

One would expect the radical-anion of N,N'-diphenyl-p-benzoquinone diimine (more simply known as quinone-dianil) to be quite complex, an expectation which is quite amply realized. Figure 29 shows the spectrum obtained by base-catalyzed oxidation of N,N'-diphenyl-p-phenylene diamine in dimethyl sulfoxide (80%)-t-butyl alcohol (20%). A main quintet due to splitting from two nitrogens can be readily distinguished, but the spectrum becomes quite complex after that. Since there are at least four types of protons, two of one kind and four each of all other types, this complexity is quite understandable. The value of a_N is 5.36 gauss, and it appears that at least one of the proton splittings is $\sim$0.6 gauss.

Oxidation of cyclohexaneosazone in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) gave a dark-brown solution with a strong e.s.r. signal. The spectrum was complex (Figure 29) extending over a distance of 35 gauss. The radical presumably was the radical anion of XVII, but the possibility of a second radical's presence, formed perhaps by ionization of the methylene protons, cannot be excluded. Additional complexity is possible due to non-equivalence of the ortho-protons. The osazone is undoubtedly of the anti-form, with all the ensuing

Figure 29. E.s.r. spectrum of the radical-anion of N,N'-diphenyl-__-benzoquinone diimine (top, 1 cm. = 2.38 gauss); generated by oxidation of N,N'-diphenyl-__-phenylene diamine in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) in the presence of potassium *t*-butoxide; also e.s.r. spectrum of the radical-anion formed when cyclohexaneosazone was oxidized in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) in the presence of potassium *t*-butoxide (bottom, 1 cm. = 2.38 gauss)





complications as in the case of azobenzene.

The calculation of proton splitting constants for azo compounds is exactly the same as for α-diketones. Suitable parameters are chosen for the nitrogen Coulomb integral, the carbon-nitrogen resonance integral, and the nitrogen-nitrogen resonance integral. A McLachlan calculation was carried out for azobenzene, assuming the molecule to be linear. The parameters chosen were those of Ward (160), $\alpha_N = \alpha_C + 0.5\beta_{C-C}$, $\beta_{C-N} = \beta_{C-C}$, and $\beta_{N-N} = 1.25\beta_{C-C}$. The spin densities calculated for the nitrogen, <u>ortho</u> positions, <u>meta</u> positions, and <u>para</u> position are 0.256, 0.096, -0.034, and 0.116, respectively. From the formula $a_i = 24.2\rho_i$ one can calculate splitting constants of 2.32, 0.82, and 2.81 gauss for the ring protons. Assuming that the average of the two experimental <u>ortho</u> protons should be given by the calculation, the corresponding experimental values are 2.45 (average of 2.09 and 2.81 gauss), 0.78, and 2.81 gauss. This agreement is excellent and may actually have some meaning!

Calculations on benz-[c]-cinnoline (XXV) were less successful. The spin densities for the ring protons and nitrogen were calculated using the above parameters. The values obtained were $\rho_1 = 0.147$, $\rho_2 = -0.039$, $\rho_3 = 0.111$, $\rho_4 = 0.222$, and $\rho_9 = 0.249$ (see Figure 22 for numbering). These densities considerably overestimate the experimental values. Hückel calculations predict that position 4 splits more than position 2. The proton splitting constants decrease as h_n is increased, and a value of 0.75, as was used by Carrington and Santos-Veiga for heterocyclic nitrogen radical anions (163), would probably be more suitable. It is not unreasonable that parameters suitable for a non-cyclic molecule would not be proper for a cyclic molecule. It is true that Ward's values were used on cyclic molecules, but they were used in a Hückel rather than a McLachlan calculation. The differences predicted between the two largest proton splittings lead one to wonder if the triplets attributed to a third pair of protons may not instead arise from the differences in the two larger splittings.

Several sets of parameters were used on benzofurazan (XXI). They were the parameters of Orgel _et_ _al_. (132), of Rieger and Fraenkel for nitrobenzene (164), and combinations thereof. None of these were successful in giving the proper magnitude for the proton splitting, and no further attempts were made to find a proper set.

McLachlan calculations were performed on XXVI, neglecting the presence of the methylene groups. The parameters of Ward were used. The calculations predict the largest electron density at the carbons bearing the methylene groups, and a rather small spin density on the nitrogens. This has been observed for a similar molecule, phthalazine (161), but the peak height ratios show that the nitrogens must be the chief splitting nuclei. The calculation thus gives completely erroneous results.

A similar calculation was performed on 1,4-dimethyl tetrazine (XXVII). Russell and Konaka* find that a_N=5.15 gauss and a_{Me}=1.56 gauss in the radical generated spontaneously by base in dimethyl sulfoxide (80%)-t-butyl alcohol (20%). The parameters of Ward *et al*., as modified by Bersohn, were used. The spin density at the methyl-bearing carbon was calculated as -0.072. From the equation a_{Me}=29.25, one arrives at an experimental value of 0.053.

The splitting due to a nitrogen atom is obtained from the following equation (XXXV): $a_N = Q_N^N \rho_N + \sum_i Q_{x_i N}^N \rho_{x_i}$; $Q_N^N = S^N + \sum_i Q_{N x_i}^N$. The splitting includes contributions from both the spin density in the nitrogen p_z orbital and the spin densities in the p_z orbitals of the atoms bonded to the nitrogen. The magnitude of these contributions is controlled by the magnitude of the spin polarization parameters, Q. The theory here was first developed for C^{13} by Karplus and Fraenkel (165).

In principle the determination of the Q parameters is straight forward. If two parameters have to be found, one merely solves two radicals of the particular type rigorously. The spin densities can then be found and with the measured

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*G. A. Russell and R. Konaka, *op. cit*.

nitrogen hyperfine splitting, one can solve two equations with two unknowns. These values should hold for all similar systems.

The problem arises in the choice of the model radical. It should be a radical containing only one type of nitrogen and protons at all carbon positions. The carbon spin densities can be found from the equation $a_H = 24.2\rho_i$, and the nitrogen spin densities can then be found from the normalization condition. Usually, however, some carbon atoms will not be bonded to protons, and the nitrogen spin densities must then be found by molecular orbital calculations. This introduces a great deal of uncertainty.

For the azo linkage the expression reduces to $a_N = (S^N + Q_{NC}^N)\rho_N + Q_{CN}^N\rho_C$ because the parameters $Q_{NN'}^N$ and $Q_{N'N}^N$ are equal and of opposite sign. Stone and Maki (161) have arrived at a value of 21.1 gauss for $(S^N + Q_{NC}^N)$ from the splittings for <u>sym</u>-tetrazine radical-anion. They estimate that $Q_{CN}^N = -2 \pm 2$ gauss. It is interesting to attempt to apply these parameters to some of the azo compounds previously mentioned. Even though azobenzene spin densities are probably known quite well, one would not expect to be able to calculate the nitrogen splitting because Q_{NC}^N is very sensitive to bond angles. The quantity $(S^N + Q_{NC}^N)$ was determined for a cyclic molecule where the bond angles are certainly different than in azobenzene. One can attempt to evaluate Q_{NC}^N for azobenzene, however. The spin density on the carbon to which the azo linkage is attached is 0.003, so the polarization due to the neighboring carbon can be neglected. From the nitrogen spin density of 0.256 and splitting constant of 4.84 gauss, we can calculate ($S^N + Q_{NC}{}^N$) for azobenzene as 18.9 gauss. The parameter S^N should be invariant, and Stone and Maki evaluate it as 11.3 gauss. This means that $Q_{NC}{}^N$ for azobenzene is 7.6 gauss as compared to the value of 9.8 gauss given by Stone and Maki for the cyclic radical-anions. The value of $Q_{NC}{}^N$ for azobenzene is almost within the uncertainty of the value calculated by Stone and Maki.

One would expect this theory to work quite well for 1,4-dimethyl tetrazine radical-anion. The experimental spin density at the methyl-substituted carbon is 0.053. The McLachlan calculation causes one to believe that the spin density at the methyl carbon is zero and at the hydrogens is 0.006. Presumably both spin densities are negative. The nitrogen spin density is thus either 0.280 or 0.221, depending upon whether the carbon spin densities are negative or positive. The parameters of Stone and Maki surprisingly fail to give the proper results. The quantity ($S^N + Q_{NC}{}^N$) is supposedly the most accurate, so any error must derive from $Q_{CN}{}^N$ which is not known very well. If one assumes ($S^N + Q_{NC}{}^N$) is 21.1 gauss, the value of $Q_{CN}{}^N$ can then be calculated. If the carbon spin densities are negative, a value of +14.3 is obtained. If positive spin densities are assumed, then Q_{CN}^{N} is found to be 9.2 gauss. In either case the constant is positive when theory (165) predicts that it should be negative. This anomaly can not be explained as yet. Certainly 1,4-dimethyl tetrazine radical-anion should be formed in pure dimethyl sulfoxide, the solvent used by Stone and Maki, to see if the presence of t-butyl alcohol affects splitting constants.

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VII. APPENDICES

A. Appendix A - Other Free Radicals

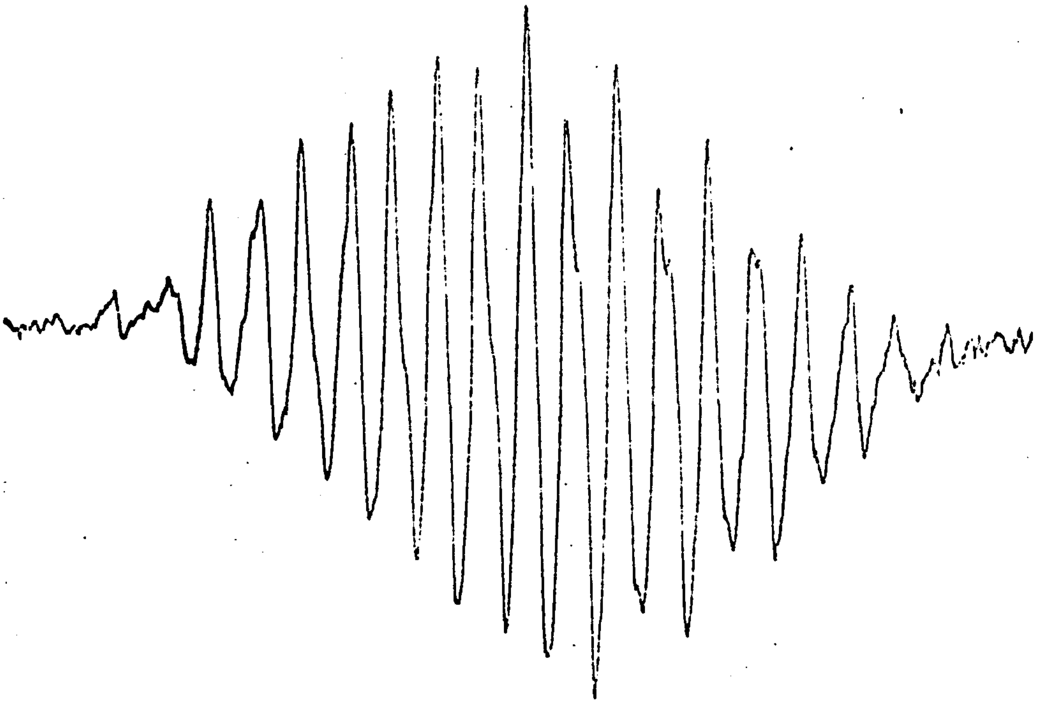
During the course of this research, the author had occasion to study free radicals which do not fit under the classification of radical-anions of α-diketones or azo compounds. Nevertheless, these radicals are quite often interesting in their own right.

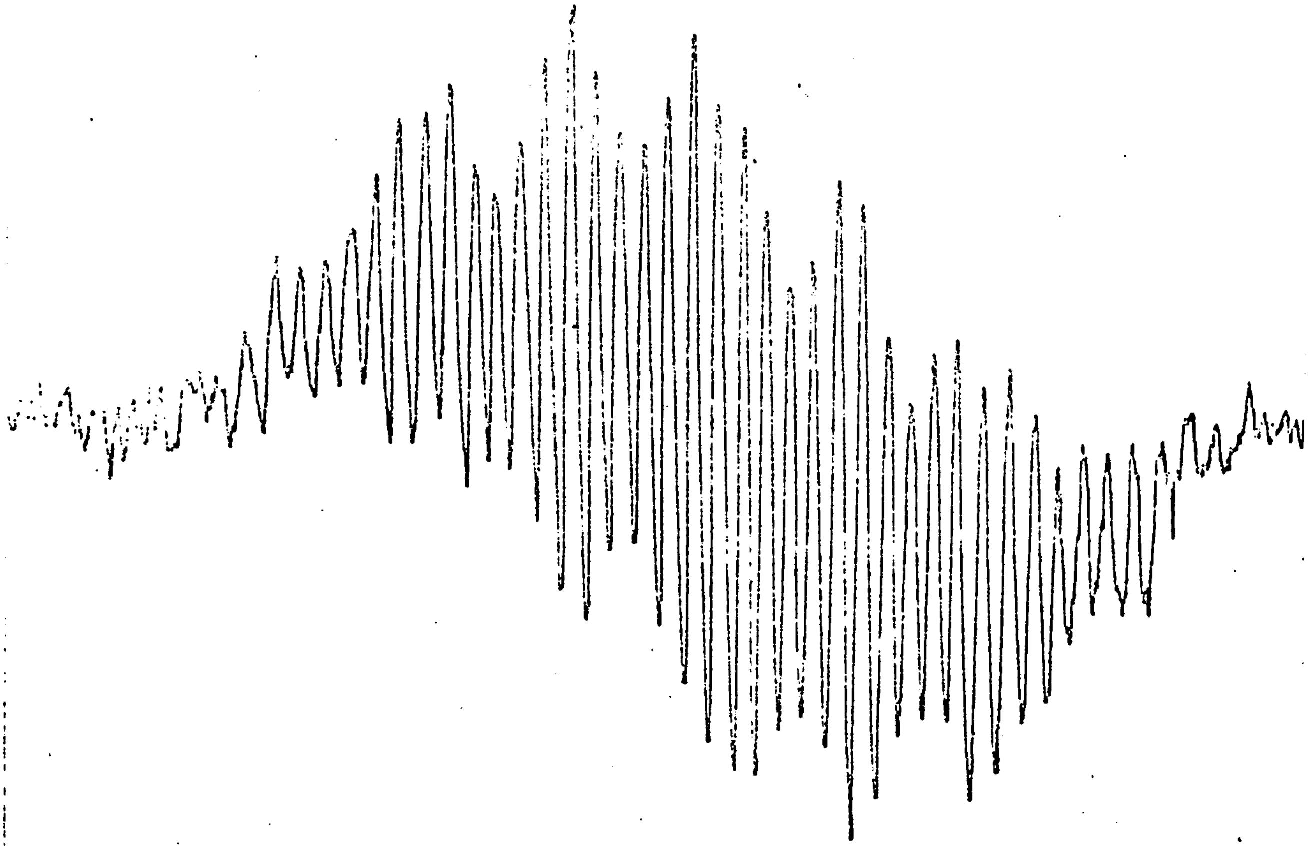
Quite surprisingly no well-resolved spectrum has been published for acridine radical-anion. The lowest member of the series, pyridine, is known to give a dimeric radical-anion when reduced with alkali metals (166). Kuwata *et al.* observed a single broad line when sodium was added to acridine in tetrahydrofuran (167). Markau and Meier obtained a 54 line spectrum when sodium-potassium alloy was added to acridine in tetrahydrofuran (168). They did not publish the spectrum and said that it could not be analyzed. Carrington and Santos-Veiga stated that acridine dimerized when treated with potassium in dimethoxyethane (163). Although some dimerization occurs when acridine is reduced with alkali metals, the reduction gives a sizeable amount of acridan (169), presumably through a radical-anion intermediate. Since dimethyl sulfoxide does not solvate negative ions, there should be no more hinderance to dimerization in dimethyl sulfoxide than in ethereal solvents.

The experiments cited earlier prove that a radical is formed when acridine and acridan are mixed in the absence of air and the presence of base. Figure 30 shows the well-resolved 43 line spectrum obtained from the green dimethyl sulfoxide (80%)-t-butyl alcohol (20%) solution. Also shown (Figure 30) is the spectrum in tetrahydrofuran (75%)-n-hexane (25%). In this case the radical is made by reaction of acridine with n-butyllithium. The line widths are approximately the same, although there is a slightly longer line width in the more highly-resolved spectrum, an understandable result. Janzen (29) found the same radical when acridan was oxidized in dimethyl sulfoxide-t-butyl alcohol solutions.

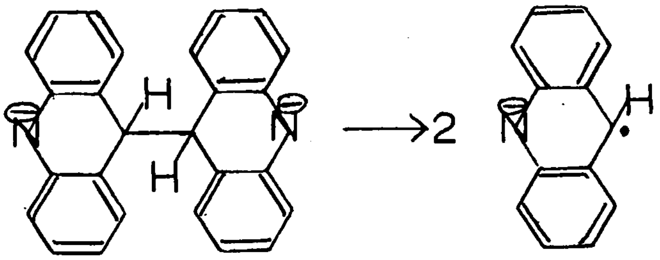
The questions to be decided are whether the radical species is dimeric or monomeric and, if monomeric, whether the radical is indeed the acridine radical-anion. Evidence pointing to the existence of a monomeric species was obtained by treating 9,9'-biacridanyl with potassium-t-butoxide in a thoroughly deoxygenated solution of dimethyl sulfoxide (80%)-t-butyl alcohol (20%). It has been shown by Russell *et al.* (111) that compounds of the type H-π-π-H can be doubly ionized in strong base, the resulting dianion breaking up to give two radical-anions. If the monomeric radical-anion were to be stable under these conditions, then biacridanyl should undergo the analogous reaction (XXXVI). The experiments showed that the same radical was found when biacridanyl was

Figure 30. E.s.r. spectra of the radical anion of acridine; generated spontaneously with _n_-butyllithium (top, 1 cm. = 2.38 gauss) in tetrahydrofuran (75%)-_n_-hexane (25%) and generated by electron-transfer from acridan to acridine (bottom, 1 cm. = 2.38 gauss) in dimethyl sulfoxide (80%)-_t_-butyl alcohol in the presence of potassium _t_-butoxide





(XXXVI)



treated with strong base as when acridine and acridine were mixed in the presence of strong base.

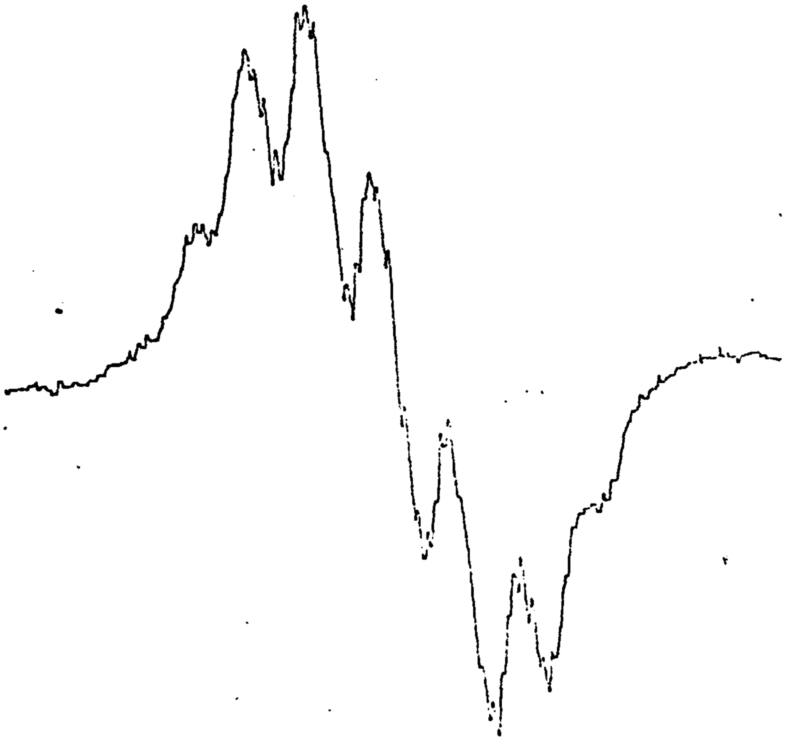
The question as to whether the monomeric radical is acridine radical-anion can only be answered by solving the spectrum. One must be aware of the possibility of nitroxide radical formation. Janzen found, for example, that benzyl aniline when oxidized gave the nitroxide of benzal aniline rather than the radical-anion (29). The formation of the radical in the absence of oxygen precludes the possibility of such a species in the case of acridine, since the electron-transfer experiments described earlier showed that the nitroxide of benzal aniline cannot be formed in the absence of oxygen.

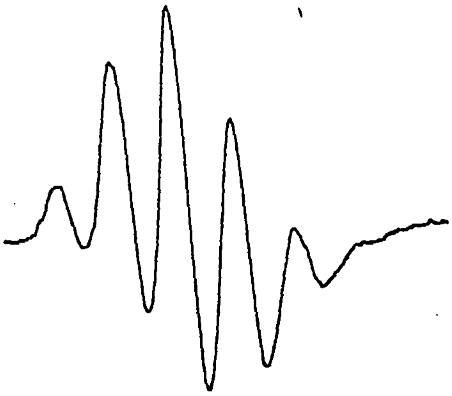
The complexity of the spectrum is such that it can only be solved by deutermic or halogen substitutions. There are five different types of protons as well as a nitrogen present. The spectrum has not been solved up to the present time.

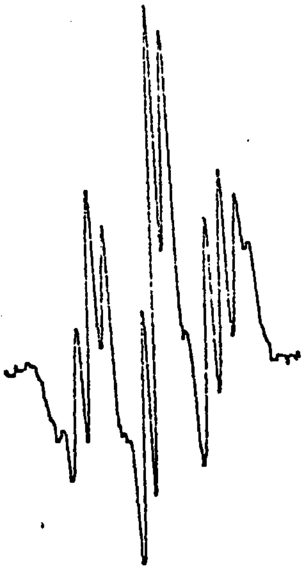
The compound $\Delta^{9,9'}$-bifluorene was prone to give radical spontaneously from base when treated in dimethyl sulfoxide (80%)-t-butyl alcohol (20%). Furthermore, attempts to form the radical by oxidation of 9,9'-bifluorene in dimethyl sulfoxide resulted in large amounts of fluorenone ketyl being formed. A radical could be made, however, by electron-transfer from propiophenone to 9,9'-bifluorene in 20% dimethyl sulfoxide in t-butanol. The solution was yellow, turning green as the radical concentration increased. The spectrum is shown in Figure 31. It certainly is not the spectrum of the fluorenone ketyl. Similar spectra could be obtained by electron-transfer from 9,9'-bifluorene to $\Delta^{9,9'}$-bifluorene in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) and by carefully controlled base-catalyzed oxidation of 9,9'-bifluorene in the same solvent system. The colors ranged from yellow-brown to orange-red, but as the radical concentration increased, the color changed to green.

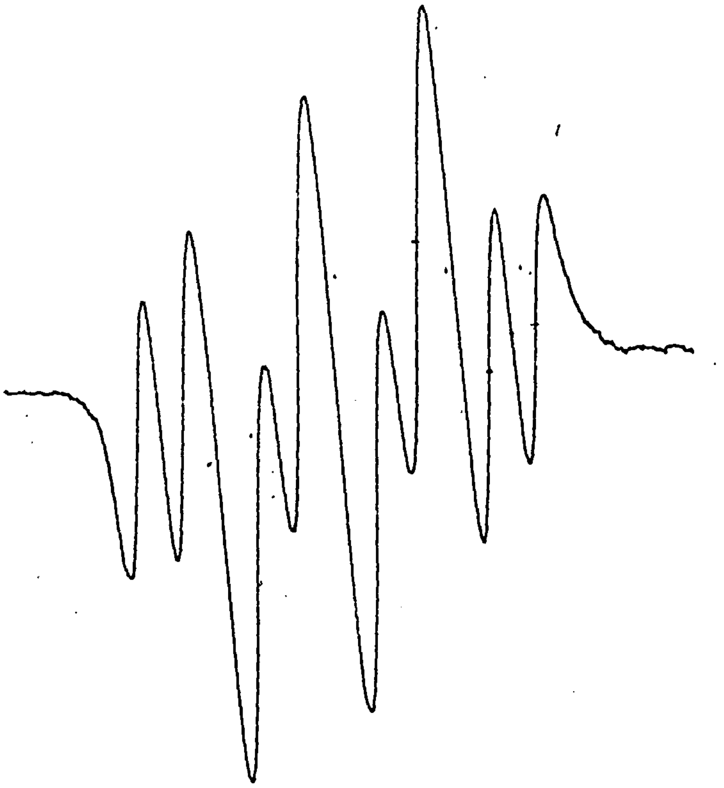
The spectrum observed consists of a main nonet, each peak of which is split further. It appears that the center peaks are split into at least seven peaks. The spacings between the main peaks are 1.93 gauss while the sub-splittings are of the order of 0.26 gauss. A reasonable interpretation is that the main splitting is from the eight protons in the 1,1',3,3',6,6',8,8' positions. The smaller splittings may be due to the other protons or to differences in the 1.6 and 3.8 proton splittings. The splitting constants are quite small for an aromatic hydrocarbon radical-anion and seem to indicate a large spin density at the nine positions. It is not unreason-

Figure 31. E.s.r. spectra of the radical-anions of $\Delta^{9,9'}$-bifluorene (top, left, 1 cm. = 2.38 gauss), 3,3',5,5'-tetra-*t*-butyl-4,4'-diphenoquinone (top, right, 1 cm. = 0.876 gauss), 3,3',5,5'-tetra-*t*-butyl-4,4'-stilbenequinone (bottom, left, 1 cm. = 2.38 gauss), and 2-methyl-2-phenyl-1,3-indandione (?) (bottom, right, 1 cm. = 2.38 gauss); generated by reduction with propiophenone in *t*-butyl alcohol (80%)-dimethyl sulfoxide (20%), by oxidation of the hydroquinones in alcoholic potassium hydroxide, and spontaneously by treatment with *n*-butyllithium in tetrahydrofuran (75%)-*n*-hexane (25%)









able that there is not a great deal of delocalization into the benzene rings, for $\Delta^{9,9'}$-bifluorene is known to be a twisted molecule (170). Theoretical calculations along with polarographic data predict that the two fluorenes are twisted 60° (171), a value not too likely to be different in the radical-anion.

It would be interesting to reduce in the same manner the corresponding butadiene and hexatriene compounds. Their reduction potentials are of the same order of magnitude and in addition they are planar molecules (170). A greater degree of delocalization of the electron should be observed.

The radical-anion of 3,3',5,5'-tetra-t-butyl-4,4'-diphenoquinone was made by electron-transfer from the hydroquinone to the quinone in ethanol, by oxidation of 2,2',6,6'-tetra-t-butyl-4,4'-biphenol, catalyzed with potassium hydroxide in ethanol, and spontaneously by treatment of the quinone with potassium t-butoxide in dimethyl sulfoxide (20%)-t-butanol (80%). The t-butyl derivative was used in the hopes of eliminating spontaneous formation in dimethyl sulfoxide by blocking the carbonyl groups, an attempt which was fruitless. Blanks were not large in ethanol, however, and meaningful experiments could be performed in that solvent. Figure 31 shows the radical obtained by oxidation of the biphenol in alcoholic potassium hydroxide. The peak heights are those that would be expected, and the separation between components is 0.61

gauss. The radical had been reported previously by Fairbourn and Lucken as an intermediate when 2,6-di-t-butyl phenol is oxidized in alcoholic potassium hydroxide (172). These authors report a splitting constant of 0.6 gauss. Matsunaga has reported a splitting constant of 0.78 gauss for the ring protons in the analogous tetramethyl derivative (173).

The radical-anion of 3,3',5,5'-tetra-t-butyl-4,4'-stilbenequinone has not been reported, nor has the radical-anion of any stilbenequinone for that matter. The radical was made under all the conditions that the diphenoquinone radical-anion was. A main triplet is observed at low resolution, and on higher resolution at least 13 peaks are found (Figure 31). A reasonable interpretation is that the triplet arises from the ethylene protons, and each component is then split into five peaks, not all of which are observed. The major splitting constant is 1.90 gauss, and the minor splitting constant is 0.48 gauss. These values are for ethanol solution.

Several attempts were made to test 2-methyl-2-phenylindan-1,3-dione as an electron acceptor in dimethyl sulfoxide solution. No electron-transfer was observed. This was probably due to the low solubility of the compound rather than any inherent low electron affinity. The whole purpose of testing this compound was to see if there might be extra stability imparted to the radical-anion due to homoallylic conjugation of the electron. No such example had been found previously. A radical was finally observed when the compound was treated with n-butyllithium in tetrahydrofuran (75%)-n-hexane (25%). At low resolution it seemed as if a main triplet were present in the orange solution. On better resolution the octet shown in Figure 31 was found. The spacings between the centers of each line are all 1.67 gauss while the spacings between the centers of the main triplet components are 3.3 gauss.

An explanation which gives the correct spacings is a major interaction with two equivalent protons and a minor interaction of one half the magnitude of the major with three equivalent protons. The major interaction could be with the ring protons at the 5 and 6 positions. This would mean a high spin density at the substituted ring carbons. Thus there could be a strong spacial interaction with the methyl group. This would be a true homoallylic interaction and not an interaction of the electron at the carbonyl group with the beta-hydrogens, for the maximum value for such beta-interactions is ~0.5 gauss. According to this reasoning the splitting due to the ring protons at the 4 and 7 positions is small and not resolved. Certainly at this degree of resolution splittings of 0.8 gauss or less could be missed.

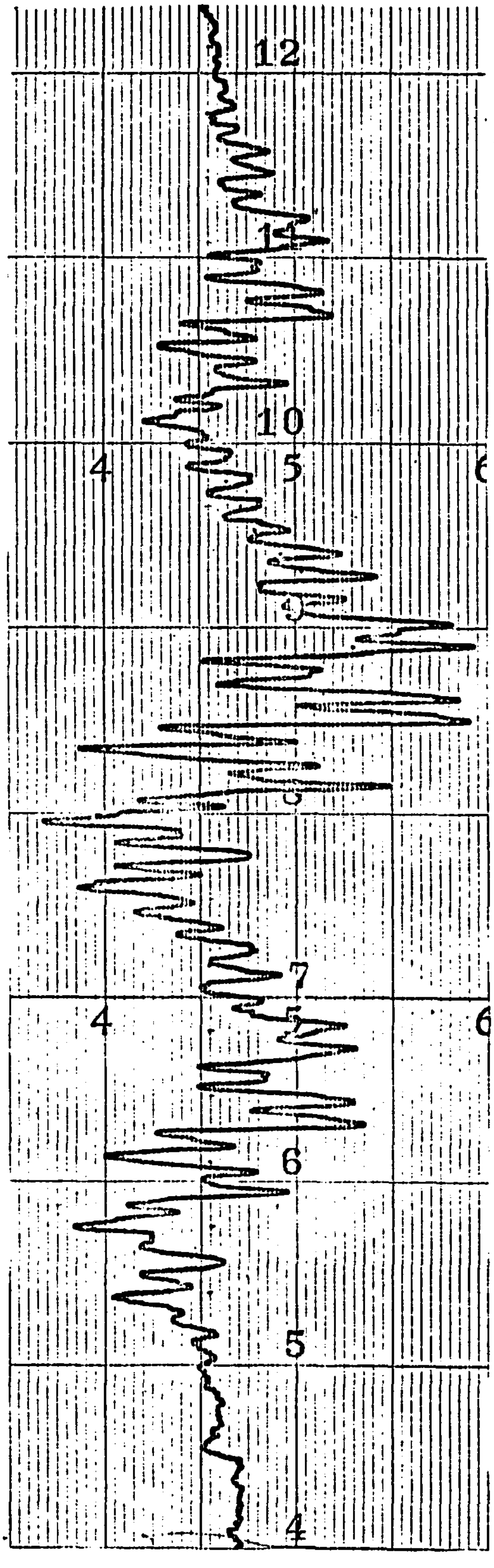
Before speculating too much, however, one should apply some other tests. The theoretical peak height ratios are 1:3:5:7:7:5:3:1 while the experimental values are 1:2.2:0.6:

2.5:0.6:2.2:1. The possibility of the butyl carbanion entering into the radical should not be overlooked either. A final judgment can only be made after a better-resolved spectrum is obtained.

A possible example of a pair of compounds which might undergo electron-transfer were the compounds 1,4-diphenylbutane-1,4-dione and 1,4-diphenylbutene-1,4-dione. It will be recalled that the dihydrocompound was used as donor in previous experiments. Unfortunately in dimethyl sulfoxide solutions the dehydro compounds gave an unacceptable blank while in ethanol solutions only a trace of transfer was observed. The radical decomposes quite swiftly in dimethyl sulfoxide solution. Nevertheless, Figure 32 shows a fairly well-resolved spectrum in dimethyl sulfoxide (80%)-t-butyl alcohol (20%). The main triplet, a_H=4.9 gauss, was undoubtedly due to the ethylenic protons. There are, at the minimum, 56 peaks spread over a distance of 16.6 gauss. No attempt has been made to explain the rest of the spectrum.

It has been speculated that the reaction of 1,4-diketones with base and air to give the corresponding enediones goes through a radical-anion mechanism (6). As a test of this postulate, the Dick-Alder adduct of 1,4-naphthoquinone and 2,3-dimethyl-1,3-butadiene (XXXVII) was made. The base-catalyzed oxidation of this compound was to be run in the e.s.r. cell. Unfortunately, the final product of such an

Figure 32. E.s.r. spectrum of the radical-anion of 1,4-diphenyl-1,4-butenedione; generated by electron-transfer from the dihydro compound to the dehydro compound in dimethyl sulfoxide (80%)-<u>t</u>-butyl alcohol (20%) in the presence of potassium <u>t</u>-butoxide; 1 cm. = 0.876 gauss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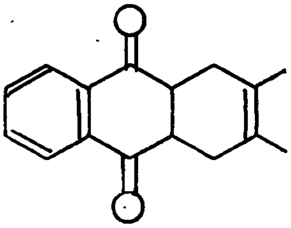
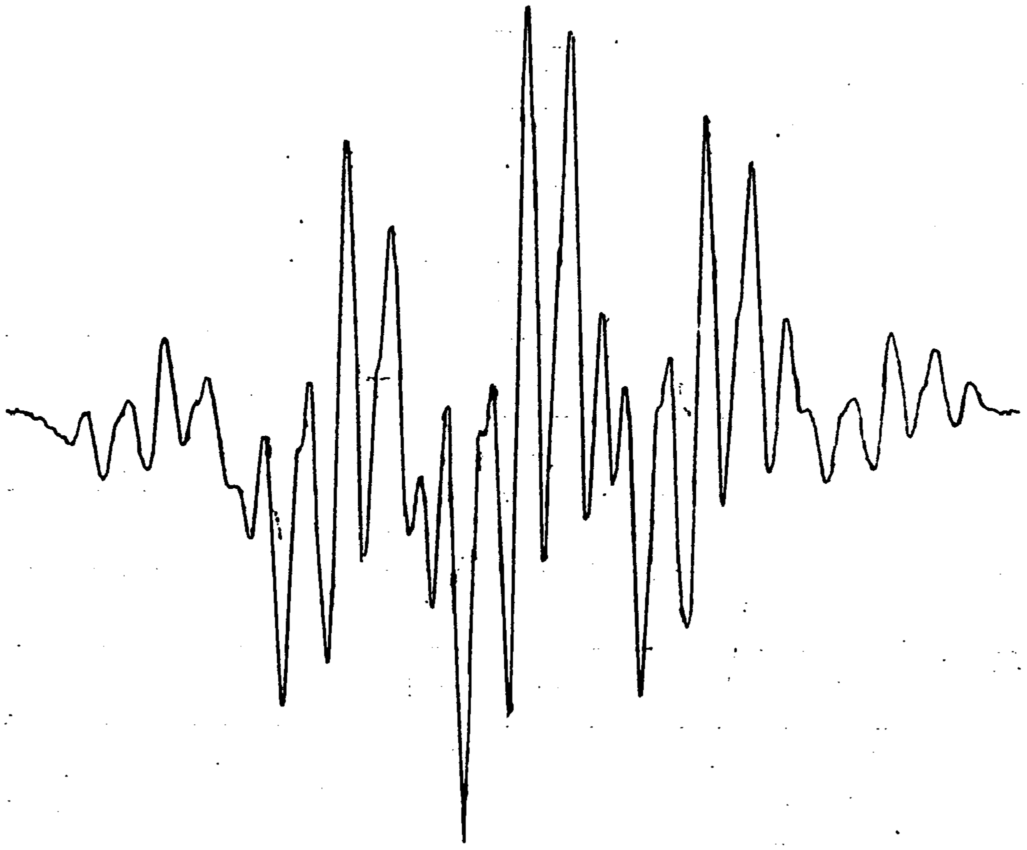
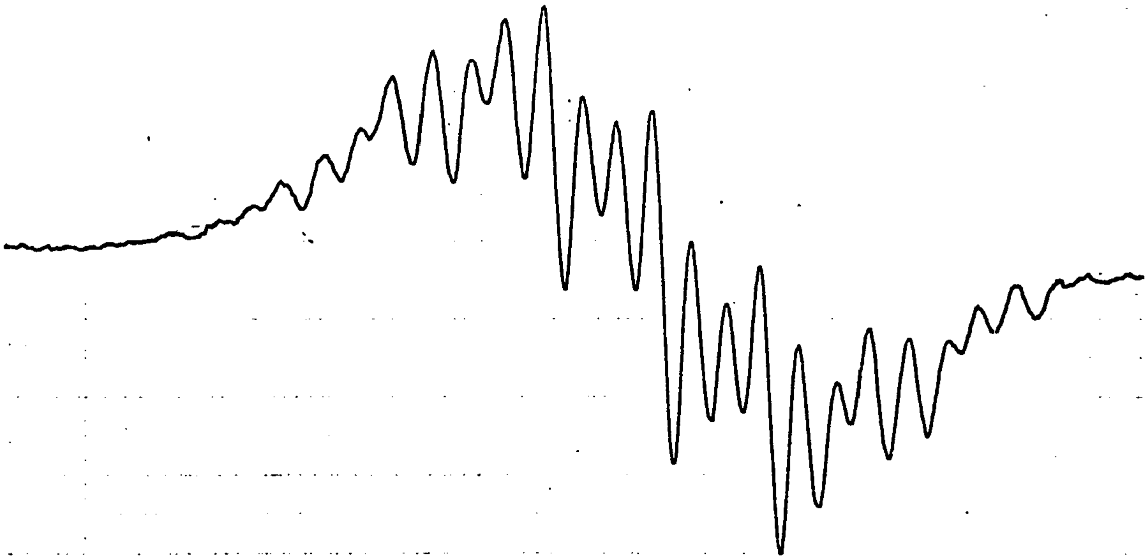
(XXXVII) 

oxidation is 2,3-dimethylanthraquinone. This means that there are two possible radical-anion intermediates, a naphthosemiquinone and an anthrasemiquinone. When the compound was oxidized with potassium hydroxide in ethanol, a red color was observed. A five peak spectrum was observed which broke into 21 lines (Figure 33). This can be attributed to the naphthosemiquinone. The main quintet arises from the four methylene protons, a_H=3.47 gauss, with further splitting due to the ring protons, a_H=0.71 gauss. The methylene splittings are in good agreement with the methyl splittings observed in 2,3-dimethylnaphthosemiquinone although the ring protons splittings are larger (174). Four peaks are apparently lost through overlap. On higher resolution at least 41 peaks appear. These may be due to differences in the ring protons, or they may stem from the appearance of the anthrasemiquinone radical.

In connection with these experiments the semiquinone of 2,3-dimethylanthraquinone was made by a glucose and base reduction in dimethyl sulfoxide. A main septet was observed which broke into 25 peaks (Figure 33). The septet was probably due to the methyl groups. The splitting for the septet was 1.18 gauss while the smallest splitting was 0.39 gauss.

Figure 33. E.s.r. spectra of radical-anions formed by oxidation of the Diels-Alder adduct of 2,3-dimethyl-1,3-butadiene and 1,4-naphthaquinone (top, 1 cm. = 1.56 gauss) and by glucose reduction of 2,3-dimethylanthraquinone (bottom, 1 cm. = 0.876 gauss); reactions performed in alcoholic potassium hydroxide

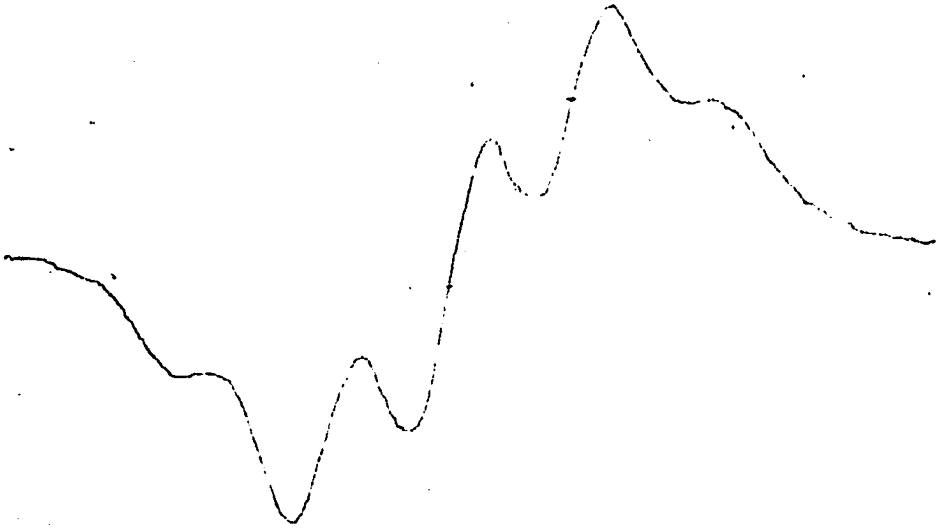


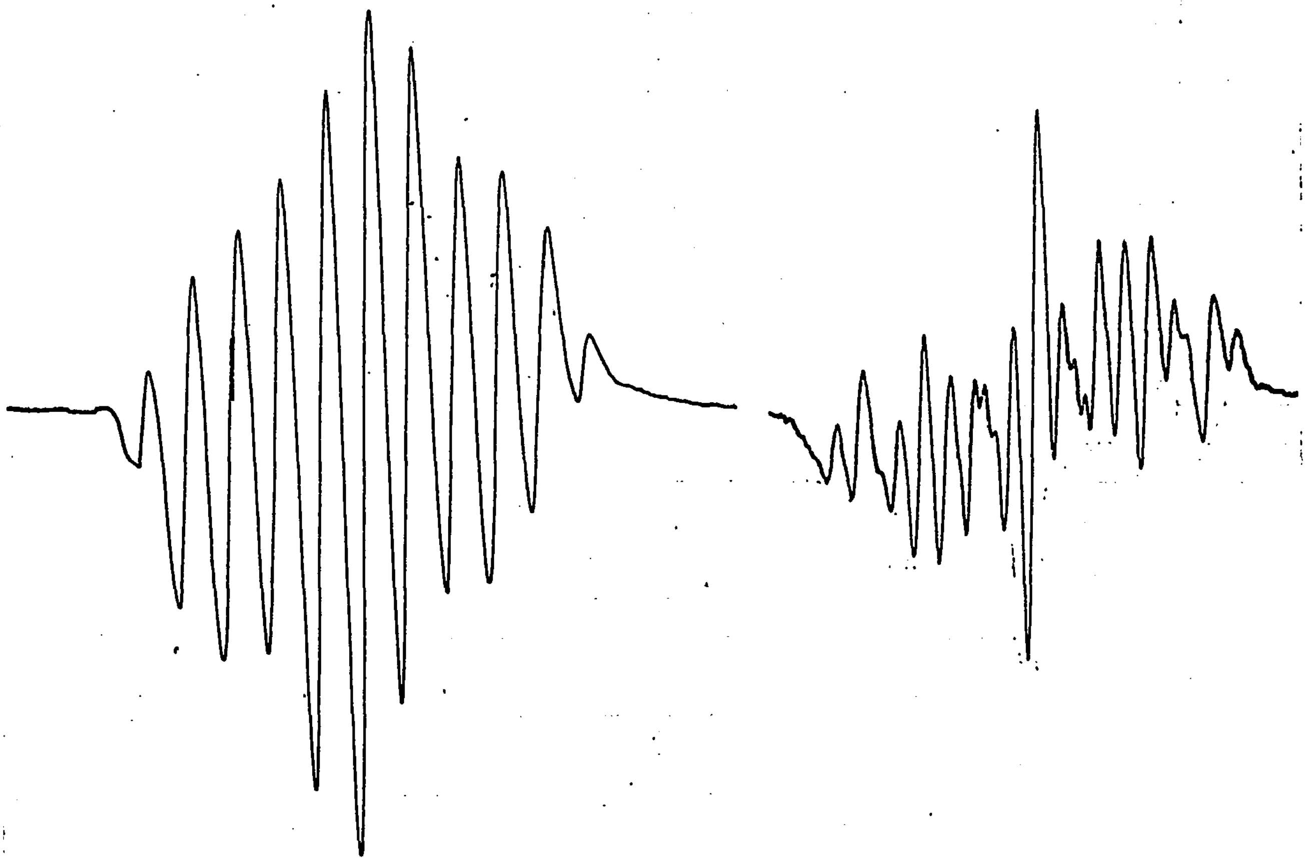


A series of substituted anthraquinones were run in order to check whether the α or β positions in anthrasemiquinone were the predominant splitting positions. The radical-anion of anthraquinone was first made by Adams et al. (175). They observed only 13 lines. Vincow and Fraenkel made this radical and observed all 25 lines (144). The author made the radical by a glucose and base reduction in dimethyl sulfoxide and observed 17 lines. Vincow and Fraenkel predicted from molecular orbital theory that the β positions ought to give the largest splitting. This was checked by substituting sulfonate groups and found to be true. Anthraquinone-2,6-disulfonate when reduced with glucose and sodium hydroxide in water gave an 11 peak spectrum (Figure 34). This could be interpreted as arising from a main interaction of 1.44 gauss with two protons and a minor interaction of 0.48 gauss with four protons. The positions which give the largest splittings are probably the 3 and 7 positions. The 2,7-disulfonate under the same conditions gave a 21 peak spectrum (Figure 34). This can be interpreted as arising from interactions with three pairs of protons, the splitting constants being 1.23, 0.74, and 0.26 gauss. One would guess that these splittings would arise from the 3,6:1,8: and 4,5 positions, respectively.

A spectrum of anthraquinone-1,8-disulfonate radical-anion made by reduction with glucose and base in dimethyl sulfoxide is shown in Figure 34. A main quintet is observed, consistent

Figure 34. E.s.r. spectra of the radical-anions of anthraquinone-2,6-disulfonate (in water), anthraquinone-2,7-disulfonate (in water), and anthraquinone-1,8-disulfonate (in dimethyl sulfoxide); radicals generated by glucose reduction; 1 cm. = 0.876 gauss





with the highest electron density being at the β positions. The splitting is 1.36 gauss. Spectra of the anthraquinone α and β sulfonate radical-anions are shown also in Figure 35. These spectra were also obtained in dimethyl sulfoxide. Note the main quartet with splitting 0.7 gauss in the spectrum of the β-sulfonate. Similar results have been obtained by Elschner et al. (176).

The spectrum of the radical made by treating α-aminoanthraquinone with potassium t-butoxide is shown in Figure 35, as well as the semiquinone of benzonorbornadiene. The latter radical was made by oxidation of the Diel-Alder adduct of cyclopentadiene and p-benzoquinone in benzene with Triton B as base. The splittings are about 2.8 gauss, of the order of quinone ring protons.

The radical-anion of 1,4-naphthoquinone was made by reduction with glucose and base in ethanol. Adams et al. and Wertz and Vivo observed only 15 lines. Vincow and Fraenkel observed all 27 possible lines. The author has seen 25 of the theoretical 25 lines.

B. Appendix B - Chemicals Used

The dimethyl sulfoxide used in these studies was obtained from Crown Zellerbach. The solvent was distilled from calcium hydride at reduced pressure at temperatures from 60-80°C.

The t-butyl alcohol was available from Eastman and was stored over anhydrous sodium sulfate before use. Tetrahydro-

Figure 35. E.s.r. spectrum of the radical-anion formed by reacting 1-aminoanthraquinone with potassium t-butoxide in dimethyl sulfoxide (top, left, 1 cm. = 0.876 gauss); spectra of the radical-anions of anthraquinone-2-sulfonate (top, right, 1 cm. = 0.504 gauss) and anthraquinone-1-sulfonate (bottom, right, 1 cm. = 0.876 gauss); generated by reduction with glucose in dimethyl sulfoxide; spectrum of the radical formed by oxidation of the Diels-Alder adduct of p-benzoquinone and cyclopentadiene (bottom, left, 1 cm. = 13.94 gauss) in benzene containing Triton B

furan was obtained from Matheson Coleman & Bell and was dried over calcium hydride before use. When this solvent was used in making a Grignard reagent, however, it was distilled from sodium and lithium aluminum hydride before use. The absolute ethanol was available from stock.

Potassium _t_-butoxide was either made by the reaction of potassium with _t_-butyl alcohol or else was purchased from MSA Research. The base was dissolved in _t_-butyl alcohol and stored in a dessicator. The potassium and sodium hydroxide were obtained from Mallinckrodt.

In performing experiments, whenever possible the chemicals were weighed directly into the degassing apparatus. Otherwise a solution of the desired concentration was made up and stored in the dessicator.

Most chemicals used were commercially available, and many were used without purification. Numerous compounds were obtained from workers in the group, in other groups, or were available from organic chemicals storage. Table 6 lists the sources and/or melting points or boiling points.

Table 6. Chemicals

Chemical	Purity and sources
Azobenzene	Matheson Coleman & Bell (recryst.)
Hydrazobenzene	Eastman (recryst.)
2,3-Diphenylquinoxaline	M.P. 124-124.5° (177)
1,2-Dihydro-2,3-diphenylquinoxaline	M.P. 143-145° (178)
Diethyl azodiformate	K & K
Diethyl dicarbamate	K & K
Dibenzoyldiimide	M.P. 118-120° (179)
1,2-Dibenzoylhydrazine	Aldrich
N,N'-Diphenyl-*p*-benzoquinone diimine	M.P. 184.5-186.5° (180)
N,N'-Diphenyl-*p*-phenylene diamine	K & K
$\Delta^{9,9'}$-Bifluorene	M.P. 179-183°, Chang
9,9'-Bifluorene	Aldrich
Acridine	Aldrich
Acridan	Aldrich (recryst.)
Benzene	Mallinckrodt
1,3-Cyclohexadiene	Hendry
Naphthalene	B & A
1,4-Dihydronaphthalene	26° (181)
Anthracene	M.P. 220-221°, Lee
9,10-Dihydroanthracene	Aldrich
Phenanthrene	Aldrich
9,10-Dihydrophenanthrene	Aldrich
1,1,4,4-Tetraphenyl-1,3-butadiene	Aldrich
1,1,4,4-Tetraphenyl-2-butene	M.P. 137-138° (182)
Tetraphenylethylene	Aldrich
Sym-Tetraphenylethane	Gilman
Azo-*bis*-isobutyronitrile	Aldrich (recryst.)
Hydrazo-*bis*-isobutyronitrile	Chemical Intermediates
1,2-*bis*-(4-pyridyl)-ethylene	Aldrich
1,2-*bis*-(4-pyridyl)-ethane	Aldrich
1,2-*bis*-(2-pyridyl)-ethylene	Aldrich
1,2-*bis*-(2-pyridyl)-ethane	Aldrich
Phenylazotriphenylmethane	Weibel
Phenylhydrazotriphenylmethane	Weibel
N-Diphenylmethyleneaniline	Gilman
N,1,1-Triphenylmethylamine	Gilman
N-Benzylideneaniline	M.P. 49-51°, Janzen
N-Phenylbenzylaniline	Eastman
Phenanthridine	Aldrich

Table 6. (Continued)

Chemical	Purity and sources
5,6-Dihydrophenanthridine	M.P. 113-119° (183)
Benzil	Matheson Coleman & Bell
Benzoin	Matheson Coleman & Bell
Furil	Eastman
Furoin	Eastman
Pyridil	Aldrich
Pyridoin	Aldrich
3,3',5,5'-Tetra-*t*-butyl-4,4'-stilbenequinone	308-310° (184)
3,3',5,5'-Tetra-*t*-butyl-4,4'-stilbenediol	237-240° (184)
3,3',5,5'-Tetra-*t*-butyl-4,4'-diphenoquinone	237-239.5° (185)
2,2',6,6'-Tetra-*t*-butyl-4,4'-biphenol	187° (185)
1,8-Diphenyl-1,3,5,7-octatetraene	Aldrich
Perylene	Aldrich
2-Methyl-2-phenyl-1,3-indandione	M.P. 154-155°, Young
2,5-Diphenyl-3,4-benzofuran	M.P. 127° (186)
Benzothiazole	Eastman
Benzoxazole	Eastman
Fluorenone	Aldrich
Cyclopentadiene	Rettig
Indene	Aldrich (distil.)
Fluorene	M.P. 113-114°, Janzen
Diphenylmethane	Matheson Coleman & Bell (distil.)
Triphenylmethane	Matheson Coleman & Bell (recryst.)
Acetophenone	Matheson Coleman & Bell
Propiophenone	Eastman
Isobutyrophenone	Eastman
Fluorene-9-ol	M.P. 155-156°, Moye
n-Butyllithium	Foote Mineral
1,4-Diphenyl-1,4-butanedione	M.P. 143-146° (187)
trans-1,2-Dibenzoylethylene	Aldrich
Duroquinone	K & K
Tetracyanoethylene	Aldrich
Perchlorofulvalene	Aldrich
Chloranil	Eastman
n-Butylmercaptan	Eastman
Thiophenol	Matheson Coleman & Bell
Toluene-3,4-dithiol	Aldrich

Table 6. (Continued)

Chemical	Purity and sources
Nitroethane	Eastman
Nitromethane	Eastman
2-Nitropropane	Eastman
Ethyl acetate	Eastman
Benzhydrol	Eastman
9-Phenylfluorene	M.P. 147.5-148°, Moye
Phenazine	Aldrich
Benzo-[c]-cinnoline	M.P. 157-158° (188)
Benzofurazan	M.P. 52-54° (189)
1,4,5,8-Tetrachloroanthraquinone	Aldrich
Benzophenone	Eastman
Nitrobenzene	Matheson Coleman & Bell (distil.)
Azoxybenzene	Eastman
1,2-Benzanthracene	Aldrich
Chrysene	Eastman
p-Quaterphenyl	Eastman
2,2'-Thenoin and thenil	(110)
n-Butyrophenone	Aldrich
Phenylpivalylcarbinol	M.P. 41-42° (190)
Cyclohexanone	Aldrich
3,3,6,6-Tetramethyl-2-hydroxy cyclohexane and diketone	Applequist
2-Hydroxycyclohexanone	Aldrich
Cyclohexane-1,2-dione	Aldrich
4-*t*-Butylcyclohexanone	Aldrich
Cyclopentanone	Aldrich
Cycloheptanone	Aldrich
Cyclooctanone	Aldrich
Cyclononanone	Aldrich
Cyclodecanone	Aldrich
2-Hydroxycyclodecanone	Aldrich
Cyclododecanone	Aldrich
Cyclopentadecanone	Aldrich
Cyclobutanone	Aldrich
Camphor	Welstead
Norcamphor	Aldrich
5,8-Methano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone	M.P. 63-66° (191)
Acetoin	Aldrich
Propionoin	(192)
Butyroin	Chemical storage
Pivaloin	M.P. 76-78° (192)

Table 6. (Continued)

Chemical	Purity and sources
Cyclohexaneosazone	Welstead
Benzil dianil	M.P. 140-141° (193)
1,4,5,8-bis-Trimethylene-pyridazino- 4,5-d -pyridazine	Stille
9,9'-Biacridanyl	Gilman (recryst.)
6,7-Dimethyl-9,10-diketo-5,8,8a,9,10,10a-hexahydro-anthracene	M.P. 147-148° (194)
2,3-Dimethylanthraquinone	M.P. 209-211° (194)
Anthraquinone	Eastman
Anthraquinone-2,6-disulfonate	Aldrich
Anthraquinone-2,7-disulfonate	Aldrich
Anthraquinone-1,8-disulfonate	Eastman
Anthraquinone-1-sulfonate	Chemical storage
Anthraquinone-2-sulfonate	Eastman
1-Aminoanthraquinone	Chemical storage
1,4-Naphthoquinone	Eastman

C. Appendix C - Experimental Data for Electron-Transfer Experiments

Concentrations for electron-transfer experiments were estimated by comparison with standard concentrations of DPPH. Typical procedures were as follows: Measurements of electron-transfer runs were made on certain chosen settings. These were a modulation amplitude (MA) of 1000, a response setting of 2, a scan motor setting of 2, a fine scan setting of 1, a radio frequency power of 10 decibels, and a leakage setting of 300 microamperes. The signal level setting (maximum used 1000, minimum possible 1) was varied in such a manner as to keep the signal at a maximum but on the recorder paper.

Occasionally with extremely concentrated solutions it was necessary to reduce the MA to below 1000 to keep the signal on the chart paper.

The signal observed under these conditions was very broad with usually no hyperfine structure. The distance from the maximum to the minimum point was measured, and the concentration estimated from the distance measured for standard solutions of DPPH at that particular signal level, in the same solvent, and at the standard settings.

The tables following have these distances tabulated as a function of time after mixing and signal level. On those occasions where an MA of less than 1000 is used, it is so noted. In a very few cases the data are presented already converted to concentrations. The very last table presents the analogous distances measured for DPPH, for concentrations 10^{-3} M., 10^{-4} M., 10^{-5} M., and 5 x 10^{-6} M., as a function of signal level, determined in the solvent systems dimethyl sulfoxide (80%)-t-butyl alcohol (20%), dimethyl sulfoxide (20%)-t-butyl alcohol (80%) and tetrahydrofuran (75%)-n-hexane (25%). It should be stated that DPPH had a finite lifetime in these solvents, so the measurements were taken immediately after mixing, the most dilute samples being run first.

Table 7. Data for transfer of carbanions to azobenzene (0.005 M., base conc. = 0.05 M.) (solvent: dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%))

Donor (0.025 M.)	Time (min.) after mixing	Signal level (concentration)	Peak height (mm.)
Cyclopentadiene	33 min.	1000	16 mm.
"	41	1000	42
"	45	500	30
"	52	500	40
"	60	500	51
"	74	250	36
"	83	250	43
"	110	250	60
"	124	100	24
"	720	50	51
Indene	4	100	17
"	9	100	31
"	12	100	37
"	15	100	45
"	18	100	46
"	23	100	53
"	25	80	50
"	29	50	32
"	32	50	34
"	34	50	35
"	37	50	37
"	40	50	39
"	43	50	40
"	47	50	42
"	50	50	43
"	53	50	46
"	57	50	49
"	61	50	51
"	72	50	57
"	75	25	29
"	79	25	30
"	100	25	34
"	123	25	40
"	155	25	47
"	203	25	59
"	235	10	24
"	265	10	25
"	292	10	26

Table 7. (Continued)

Donor (0.025 M.)	Time (min.) after mixing	Signal level (concentration)	Peak height (mm.)
Fluorene	6	250	28
"	8	250	39
"	10	250	55
"	12	100	27
"	14	100	35
"	17	100	48
"	19	100	55
"	21	50	31
"	23	50	40
"	28	50	55
"	29	25	30
"	33	25	37
"	38	25	43
"	44	25	54
"	45	10	21
"	50	10	25
"	53	10	28
"	60	10	32
"	154	5	43
"	234	5	61
"	240	2	25
"	262	2	27
"	280	2	28
"	300	2	29
"	310	2	30
"	340	2	31
Diphenylmethane	6	1000	35
"	9	1000	44
"	12	500	30
"	15	500	35
"	20	500	44
"	25	500	57
"	27	250	31
"	30	250	34
"	35	250	40
"	40	250	43
"	45	250	48
"	51	250	51
"	55	250	55
"	58	100	20
"	70	100	25
"	80	100	26

Table 7. (Continued)

Donor (0.025 M.)	Time (min.) after mixing	Signal level (concentration)	Peak height (mm.)
Diphenylmethane	90	100	30
"	100	100	33
"	120	100	37
"	140	100	43
"	161	100	46
"	185	100	53
"	189	50	27
"	213	50	30
"	240	50	33
"	270	50	36
"	300	50	39
Triphenylmethane	4	1000	54
"	7	500	30
"	9	500	34
"	12	500	37
"	17	500	41
"	23	500	43
"	30	500	45
"	40	500	51
"	50	500	54
"	60	500	59
"	63	250	30
"	71	250	31
"	90	250	36
"	120	250	40
"	150	250	45
"	180	250	49
"	723	100	39
		Concentration	
Acetophenone	12	5×10^{-4}	
"	14	7.4×10^{-4}	
"	17	8.8×10^{-4}	
"	20	10×10^{-4}	
"	23	12×10^{-4}	
"	27	13×10^{-4}	
"	31	15×10^{-4}	
"	36	18×10^{-4}	
"	38	19×10^{-4}	
"	42	20×10^{-4}	
"	45	20×10^{-4}	
"	48	20×10^{-4}	

Table 7. (Continued)

Donor (0.025 M.)	Time (min.) after mixing	Signal level (concentration)	Peak height (mm.)
Acetophenone	52	22×10^{-4}	
"	55	22×10^{-4}	
"	58	23×10^{-4}	
"	71	23×10^{-4}	
"	80	24×10^{-4}	
Propiophenone	14	11×10^{-4}	
"	17	12×10^{-4}	
"	19	13×10^{-4}	
"	21	15×10^{-4}	
"	23	16×10^{-4}	
"	26	16×10^{-4}	
"	34	16×10^{-4}	
"	40	16×10^{-4}	
Isobutyrophenone	8	0.5×10^{-5}	
"	10	0.8×10^{-5}	
"	13	1.7×10^{-5}	
"	15	3.1×10^{-5}	
"	18	5.3×10^{-5}	
"	20	5.8×10^{-5}	
"	23	7.2×10^{-5}	
"	25	8×10^{-5}	
"	28	9×10^{-5}	
"	31	1×10^{-4}	
"	35	1.2×10^{-4}	
"	40	0.85×10^{-4}	
"	43	0.93×10^{-4}	
"	48	1×10^{-4}	
"	52	1.1×10^{-4}	
"	56	1.2×10^{-4}	
"	60	1.3×10^{-4}	
"	65	1.4×10^{-4}	
"	69	1.5×10^{-4}	
"	89	1.9×10^{-4}	
"	109	2.5×10^{-4}	
"	125	2.8×10^{-4}	
"	148	3.3×10^{-4}	
"	170	4.7×10^{-4}	
"	194	5.4×10^{-4}	
"	363	9.1×10^{-4}	

Table 7. (Continued)

Donor (0.025 *M*.)	Time (min.) after mixing	Signal level (concentration)	Peak height (mm.)
Fluoren-9-ol	20	1 (M.A. 200)	61
"	20	1 (M.A. 200)	61

Table 8. Data for transfer of carbanions to fluorenone (0.005 *M*., base conc. = 0.05 *M*.) (solvent: dimethyl sulfoxide (20%)-*t*-butyl alcohol (80%))

Donor (0.05 *M*.)	Time (min.) after mixing	Signal level (concentration)	Peak height (mm.)
Cyclopentadiene	33	1000	33
"	41	1000	42
"	45	500	30
"	52	500	40
"	60	500	51
"	74	250	36
"	83	250	43
"	110	250	60
"	124	100	24
"	720	50	51
		Concentration	
Indene	12	3.7×10^{-3}	
"	14	3.4×10^{-3}	
"	45	2.6×10^{-3}	
Propiophenone	5	1000	45
"	7	1000	46
"	10	1000	53
"	12	500	34
"	15	500	38
"	21	500	52
"	22	250	27
"	25	250	29
"	30	250	34
"	40	250	46
"	44	100	19

Table 8. (Continued)

Donor (0.05 M.)	Time (min.) after mixing	Signal level (concentration)	Peak height (mm.)
Propiophenone	52	100	24
"	60	100	25
"	78	100	33
"	96	100	38
"	120	100	46
Hydrazobenzene	10	2	36
"	29	2	36

Table 9. Rate of transfer of propiophenone (0.05 M.) anions (base = 0.025 M.) to various acceptors (solvent: dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%))

Acceptor (0.005 M.)	Time (min.) after mixing	Signal level	Peak height (mm.)
Phenazine	6	50	17
"	8	50	19
"	10	50	26
"	21	50	44
"	27	50	56
"	144	5	22
"	216	5	26
Benzcinnoline	11	500	32
"	14	500	35
"	19	500	35
"	27	500	38
"	34	500	42
"	50	500	40
"	72	500	39
"	88	500	39
"	123	500	43
Benzofurazan	10	10	17
"	11	25	47

Table 10. Rate of transfer of dihydroanthracene (0.05 M.) anions (base = 0.1 M.) to various acceptors (solvent: dimethyl sulfoxide (80%)-*t*-butyl (20%))

Acceptor (0.005 M.)	Time (min.) after mixing	Signal level	Peak height (mm.)
Phenazine	6	2	25
"	13	2	26
"	24	2	25
Azobenzene	4	2	14
"	9	2	13
Benzo-[c]-cinnoline	8	25	28
"	13	25	32
"	53	25	55
"	88	10	30
"	113	10	32
"	183	10	41
Benzofurazan	9	25	33
"	18	25	33
"	43	25	33
2,3-Diphenylquinoxaline	8	100	17
"	44	100	20
"	59	100	25
"	69	100	26
"	81	100	31
"	119	100	42
1,2-*bis*-(4-Pyridyl)-ethylene	7	100	10
"	33	100	6
Acridine	5	100	15
"	8	100	15

Table 11. Rate of transfer of n-butyllithium (0.5 M.) to various acceptors (solvent: tetrahydrofuran (75%)-n-hexane (25%))

Acceptor (0.05 M.)	Time (min.) after mixing	Signal level	Peak height (mm.)
Phenazine	15	1 (M.A.=200)	38
"	20	1	38
"	30	1	38
Azobenzene	10	2	41
"	15	2	32
"	34	2	27
Benzo-[c]-cinnoline	4	10	18
"	6	10	12
"	21	50	34
"	28	50	56
"	40	50	51
Benzofurazan	4	10	3
"	7	100	26
"	14	100	33
"	21	100	51
"	33	50	27
2,3-Diphenylquinoxaline	8	10	57
"	23	10	63
"	35	5	30
"	65	5	32
N,N'-diphenyl-p-benzoquinone diimine	14	1 (M.A.=500)	21
"	19	1	20
Diethyl azodiformate	8	100	46
"	16	100	44
1,2-bis-(4-Pyridyl)-ethylene	7	10	14
"	17	10	23
"	23	10	27
"	32	10	34
"	53	10	55
"	57	5	29
"	69	5	35
"	79	5	38
"	90	5	47

Table 11. (Continued)

Acceptor (0.05 M.)	Time (min.) after mixing	Signal level	Peak height (mm.)
Acridine	7	10	10
Fluorenone	13	1 (M.A.=250)	53
"	18	1	57
"	24	1	61
"	31	1	61
Benzophenone	10	5	49
"	13	5	46
"	25	5	41

Table 12. Rate of transfer of *n*-butylmagnesium bromide (0.25 M.) to various acceptors (solvent: tetrohydrofuran)

Acceptor (0.05 M.)	Time (min.) after mixing	Signal level	Peak height (mm.)
Phenazine	6	10	28
"	12	10	20
"	35	10	15
Azobenzene	5	1000	13
"	14	1000	4
Benzo-[c]-cinnoline	11	1 (M.A.=250)	37
"	17	1	35
"	20	1	29
Benzofurazan	10	10	15
"	19	10	15
"	44	10	13
N,N'-Diphenyl-*p*-benzoquinone diimine	6	100	7
"	10	100	33

Table 12. (Continued)

Acceptor (0.05 <u>M</u>.)	Time (min.) after mixing	Signal level	Peak height (mm.)
Fluorenone	6	100	37
"	12	100	25
"	38	100	11
Benzophenone	6	100	64
"	16	100	57
"	30	100	54
Nitrobenzene	7	10	19
"	13	10	22
"	22	10	28
"	31	10	32
"	45	10	42
"	61	5	26
"	70	5	26
"	93	5	28
"	118	5	28

Table 13. Rate of transfer of 1,4-diphenyl-1,4-butanedione (0.025 <u>M</u>.) anions (base = 0.1 <u>M</u>.) to various acceptors (solvent: dimethyl sulfoxide (20%)-<u>t</u>-butyl alcohol (80%))

Acceptor (0.005 <u>M</u>.)	Time (min.) after mixing	Signal level	Peak height (mm.)
Phenazine	11	1	53
"	18	1	52
"	31	1	55
Azobenzene	13	20	18
"	14	50	45
"	24	50	32
"	49	50	20
Fluorenone	7	1	35
"	24	1	38
Benzophenone	3	50	45
"	5	50	24
"	13	50	10

Table 14. Rate of transfer of propiophenone (0.025 *M*.) anions (base = 0.05 *M*.) to various acceptors (solvent: dimethyl sulfoxide (20%)-*t*-butyl alcohol (80%))

Acceptor (0.005 *M*.)	Time (min.) after mixing	Signal level	Peak height (mm.)
Phenazine	3	1000	30
"	5	1000	37
"	10	1000	40
"	15	1000	50
"	20	500	26
"	30	500	41
"	40	500	49
"	62	250	35
"	83	250	44
"	135	100	28
"	188	100	36
Benzofurazan	3	1000	31
"	5	1000	28
"	8	1000	23
"	15	1000	30
"	22	1000	30
"	53	1000	37
"	59	500	19
"	70	500	23
"	80	500	24
"	91	500	24
"	120	500	26
"	375	500	15
$\Delta^{9,9'}$-Bifluorene	5	100	25
"	8	100	34
"	11	100	47
"	19	50	45
"	44	20	46
"	50	20	53
"	82	10	43
Fluorenone	5	1000	45
"	7	1000	46
"	10	1000	53
"	12	500	34
"	15	500	38
"	21	500	52
"	22	250	27

Table 14. (Continued)

Acceptor (0.005 *M*.)	Time (min.) after mixing	Signal level	Peak height (mm.)
Fluorenone	25	250	29
"	30	250	34
"	40	250	46
"	44	100	19
"	52	100	24
"	60	100	25
"	78	100	33
"	96	100	38
"	120	100	46

Table 15. Peak heights of DPPH at various signal levels and concentrations

Solvent	Concentration	Signal level	Peak height (mm.)
Tetrahydrofuran (75%)-*n*-hexane (25%)	10^{-5} *M*.	1000	19
"	10^{-5}	500	11
"	10^{-4}	250	48
"	10^{-4}	200	39
"	10^{-4}	125	25
"	10^{-4}	100	18
"	10^{-4}	80	13
"	10^{-4}	50	9
"	10^{-3}	25	63
"	10^{-3}	10	22
"	10^{-3}	8	19
"	10^{-3}	5	11
"	10^{-3}	2	5
Dimethyl sulfoxide (20%)-*t*-butyl alcohol (80%)	5×10^{-6}	1000	28
"	5×10^{-6}	800	22
"	5×10^{-6}	500	14
"	10^{-5}	800	60

Table 15. (Continued)

Solvent	Concentration	Signal level	Peak height (mm.)
Dimethyl sulfoxide (20%)-*t*-butyl alcohol (80%)	10^{-5}	800	60
"	10^{-5}	500	43
"	10^{-5}	250	14
"	10^{-5}	200	11
"	10^{-5}	160	9
"	10^{-5}	100	5
"	10^{-4}	125	68
"	10^{-4}	100	54
"	10^{-4}	80	44
"	10^{-4}	50	27
"	10^{-3}	10	54
"	10^{-3}	8	44
"	10^{-3}	5	27
"	10^{-3}	2	11
Dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%)	5×10^{-6}	1000	21
"	10^{-5}	800	53
"	10^{-5}	500	29
"	10^{-5}	250	13
"	10^{-5}	200	11
"	10^{-5}	160	7
"	10^{-5}	125	6
"	10^{-5}	100	5
"	10^{-5}	80	4
"	10^{-4}	50	40
"	10^{-4}	25	19
"	10^{-4}	10	6
"	10^{-3}	10	57
"	10^{-3}	8	47
"	10^{-3}	5	28
"	10^{-3}	2	11