$$\text{(8)}$$

present understanding of the elimination reaction in carbon compounds.[19]

Experimental

Materials.—Tetrahydrofuran and diglyme were freshly distilled (the latter under vacuum) from lithium aluminum hydride prior to the preparation of each stock solution of diborane. Boron trifluoride etherate was purified by distillation under vacuum. Sodium borohydride from Metal Hydrides, Inc., was used without further purification.

The source or preparative method and physical constants of the allyl compounds used are incorporated in Table V. In addition, the method of preparation and the physical constants of the alcohols required for the gas chromatographic comparison with the alcohol reaction products are included in this table. All the allyl compounds and the alcohols were examined by gas chromatography prior to use and judged to be 98% pure. The compounds obtained commercially were redistilled from calcium hydride, except for the hydroxylic compounds which were distilled after standing over Drierite for several days. Diborane and bis-3-methyl-2-butylborane stock solutions in tetrahydrofuran were prepared following procedures described previously.[20]

General Procedures.—All glassware used in these experiments was flame dried and cooled in a stream of dry nitrogen before use. Throughout the course of the hydroboration a positive pressure of nitrogen was kept above the THF solution. The reactions were carried out in 100-ml., two-neck, round-bottom flasks fitted with a thermometer well, an inlet tube (fitted with a silicone rubber septum), and a magnetic stirrer. In those experiments where the solution was refluxed, the flask was also provided with a water-cooled reflux condenser which had been previously flushed with dry nitrogen.

In a typical hydroboration procedure about 20 mmoles of allyl compound was added dropwise from a hypodermic syringe to the solution of diborane (20 mmoles of BH_3–THF)[21] in the

ice-cooled flask. The temperature was maintained at 0–5° and the amount of allyl compound added determined by weighing by difference. Addition took about 20–30 min.; after allowing the reaction to stand for a further 30 min., excess hydride was destroyed by the dropwise addition of water. Oxidation was carried out by adding 6.7 ml. of a 3 M sodium hydroxide solution (20 mmoles) followed by the dropwise addition of 24 mmoles (a 20% excess) of hydrogen peroxide, keeping the solution cooled in an ice bath. Hydrogen peroxide concentrations were determined from specific gravity measurements. Where ester groupings were present, and in the case of the phenyl ether, addition of base and hydrogen peroxide were carried out simultaneously from two hypodermic syringes. A known weight of internal standard was added at this juncture.

The solution was then saturated with anhydrous sodium carbonate. In order to ensure that any glycols, ethanol, or propanol were completely salted out, it was necessary to add a sufficient excess of potassium carbonate to convert the aqueous layer into a slurry. The tetrahydrofuran layer was decanted off and dried first over anhydrous magnesium sulfate and then over Drierite overnight. The solution was then analyzed by gas chromatography. In order to estimate small quantities of 1-propanol it was necessary fractionally to distil off most of the THF before analysis. In a typical elimination study, 5-ml. aliquots of the reaction mixture were withdrawn and these were oxidized and worked up in exactly the same way as described above.

An Aerograph gas chromatograph Model A90-S (Wilkens Instrument and Research, Inc.) was used for the analyses. The products were identified by a comparison of their retention times with those of authentic samples. A 5-ft. column packed with 20% Carbowax 20M on Chromosorb W was used for the analysis of most of the monohydric alcohols except the phenylthiopropanols. The latter were determined, using a 2-ft. column packed with 2% Carbowax 1540 on Fluorpak 80 at 150°. The propanediols and phenoxypropanols were separated by employing a 5-ft. column packed with d-sorbitol (4%) and Dow silicone 703 (16%) on 60–80 mesh firebrick at 125°.

It was shown that the v.p.c. quantitative determinations were reproducible to ±1% (±2% for the glycols), the results given being the average of three separate analyses. Although it was possible to identify the monobenzoate of 1,3-propanediol using the above columns, the quantitative determination was carried out by first hydrolyzing the ester (by refluxing with aqueous sodium hydroxide) and then analyzing for 1,3-propanediol as before.

(19) E. Eliel, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956.

(20) G. Zweifel, K. Nagase, and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 183, 190 (1962).

(21) The BH₃–THF solutions used in this work varied from 0.3 to 1.3 M in BH₃.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

Electron-Transfer Processes. I. The Scope of the Reaction between Carbanions or Nitranions and Unsaturated Electron Acceptors[1,2]

BY GLEN A. RUSSELL,[3a] EDWARD G. JANZEN, AND E. THOMAS STROM[3b]

The scope of the reaction leading to the products of electron transfer between carbanions and nitranions and unsaturated organic molecules has been investigated. Many carbanions and nitranions, particularly those which are dianions, react with unsaturated molecules such as nitroaromatics, azobenzene, and diaryl ketones to form the radical-anions derived from the unsaturates. The same effect was observed with n-butyllithium and n-butylmagnesium bromide. It is concluded that processes involving one-electron transfer must be important in many reactions involving carbanions.

Introduction

The transfer of an electron from a diamagnetic carbanion to an unsaturated organic molecule was

(3) (a) Alfred P. Sloan Foundation Fellow, 1959–1963; (b) NIH Predoctoral Fellow, 1962–1963.

apparently first recognized by Schlenk who found that tritylsodium reacts with benzophenone and other diaryl ketones with characteristic color changes to produce products which upon hydrolysis and air oxidation yield trityl peroxide and the pinacol.[4]

$$R^-Na^+ + Ar_2CO \rightleftharpoons R\cdot + Ar_2C\text{-}O^-Na^+$$
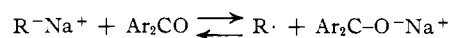
(4) W. Schlenk and R. Ochs, *Ber.*, **49**, 608 (1916); W. Schlenk and E. Bergmann, *Ann.*, **464**, 1 (1928).

The reduction of benzophenone to benzpinacol or benzhydrol by Grignard reagents has received considerable attention.[5] This process in which the trityl radical is produced from trityl Grignard reagents,[5c] and which has also been observed for xanthone, fluorenone, and benzil,[5c] has been attributed to the reduction of the ketone by magnesium,[5a] by magnesium(I) halide,[5b] by electron transfer from the incipient carbanion to the ketone,[5c,e] and from the decomposition of an initially produced addition product.[5d] Tritylsodium has been observed to reduce cyclooctatetraene[6] while the dianion of cyclooctatetraene will transfer an electron to 2,4,6-trimethylpyrylium salts,[7] and possibly to benzophenone.[6]

Bachmann found that the "di-Grignard" reagent of hydrazobenzene reduces benzil to benzoin with the concurrent formation of azobenzene.[5] It is now recognized that many dianions can react with their dehydro derivative or other unsaturated substances, to undergo electronic disproportionation.[8a]

$$\pi^{-2} + \pi \rightleftarrows 2\pi^-$$
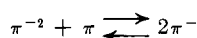
Among the disproportions recognized are benzil–benzoin,[8b] diaryl ketones–diarylcarbinols,[8a,k] quinones–hydroquinones,[8c] azobenzene–hydrazobenzene,[8a,d] tetracyanoethylene–tetracyanoethane,[8e] $\alpha,\alpha,\alpha',\alpha'$-tetrakis-(ethylsulfonyl)-p-xylene–7,7,8,8-tetrakis-(ethylsulfonyl)-p-quinodimethan,[8f] tetraphenylethylene–tetraphenylethane,[8g] cyclooctatetraene–cyclooctatetraene dianion,[8b] stilbene–stilbene dianion,[8i] and benzenoid aromatic hydrocarbons and their conjugate dianions in many instances.[8j]

Apparently anions derived from the heavier elements of a group are more prone to undergo electron transfer. Thus, triphenylstannylsodium reduces carbon dioxide, sulfur dioxide, oxygen, or benzophenone to sodium oxalate, dithionite, peroxide, and benzophenone ketyl.[9] The ease of electron transfer from an anion undoubtedly decreases as a move to the right is made in the periodic table. It is of interest that in the presence of the lithium cyclohexylamide that 3- or 8-methylfluoranthene and anthracene undergo one-electron reduction,[10] while iodide ion undergoes one-electron transfer with tetracyanoethylene.[11]

The catalysis by nitroaromatic compounds of the autoxidation of the anion of benzoin,[8b] hindered phenols,[12a] fluorene,[12b] mercaptans,[12c] xanthen-9-ol,[12d] nitroalkanes,[12d] alkylpyridines,[12d] and phenones[12d] has been attributed[12b] to the formation of free radicals by the transfer of an electron from the anion to the nitroaromatic acceptor. A large number of p- and o-nitrotoluene derivatives spontaneously produce the radical-anions of the un-ionized nitroaromatic in basic solution.[13] In these cases the benzylic anion, or a charge-transfer complex of the ion, undergoes one-electron transfer with the parent nitroaromatic. The colored products produced by the reaction of various ketones containing ionizable protons with m-dinitrobenzene and derivatives in basic solution has been reviewed by Foster and Mackie.[14] In the Janovsky reaction (excess ketone in aqueous base) an addition product is formed in a reversible reaction with the nitroaromatic. When a stronger base is used as in the Zimmermann reaction (e.g., ethoxide ion in ethanol), the initially formed adduct is oxidized, undoubtedly by ionization followed by electron transfer to m-dinitrobenzene to give "irreversibly" the anion of a 2,4-dinitrobenzyl ketone. Numerous weakly acidic materials other than ketones give Janovsky-type colors and ultraviolet spectra in the presence of m-dinitrobenzene and base.[14b] It has not been demonstrated that electron transfer plays a significant role in the Janovsky reaction,[14] but our results demand that consideration be given to this process.

Since amines are isoelectronic with carbanions, they might be expected to undergo electron-transfer reactions similar to those of carbanions, at least with the more potent electron acceptors. Products of electron transfer have been observed between aliphatic amines and 1,3,5-trinitrobenzene,[15] tetracyanoethylene,[8e] and tetracyanoquinodimethan.[16] However, Briegleb has concluded that electron transfer does not occur in the main step of the reaction between aliphatic amines and di- or trinitrobenzene.[17]

The possibility of complete electron transference in the ground state of a charge-transfer complex has received consideration,[18,19] and some complexes of aromatic amines have been found to be paramagnetic in the solid state.[16,18b,19-21] Tetramethyl-p-phenylenediamine complexes with chloranil and other benzoquinones[19] or tetracyanoquinodimethan[16] are not only

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(6) G. Wittig and D. Wittenburg, Ann., **606**, 1 (1957).

(7) K. Conrow and P. C. Radlick. J. Org. Chem., **26**, 2260 (1961).

(8) (a) G. A. Russell, E. G. Janzen, and E. T. Strom, J. Am. Chem. Soc., **84**, 4155 (1962); (b) A. Weissberger, H. Mainz, and E. Strasser, Ber., **62**, 1942 (1929); A. Weissberger, ibid., **65**, 1815 (1932); L. Michaelis and E. S. Fetcher, J. Am. Chem. Soc., **59**, 1246 (1937); J. L. Ihrig and R. G. Caldwell, ibid., **78**, 2097 (1956); (c) T. H. James and A. Weissberger, ibid., **60**, 98 (1938); (d) G. Wittig in "Newer Methods of Preparative Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 571; (e) O. W. Webster, W. Mahler, and R. E. Benson. J. Am. Chem. Soc., **84**, 3678 (1962); (f) W. R. Hertler and R. E. Benson, ibid., **84**, 3474 (1962); (g) J. F. Garst and R. S. Cole, ibid., **84**, 4352 (1962); (h) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, ibid., **85**, 2360 (1963); (i) D. E. Paul, D. Lipkin, and S. I. Weissman, ibid., **78**, 116 (1956); (j) N. S. Hush and J. Blackledge, J. Chem. Phys., **23**, 514 (1955); G. J. Hoijtink, E. deBoer, P. H. van der Meij, and W. P. Weijland, Rec. trav. chim., **75**, 487 (1956); (k) H. Heymann, J. Am. Chem. Soc., **71**, 260 (1949).

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33, 626 (1960); G. Briegleb, W. Liptay, and R. Fick, Z. physik. Chem. (Frankfurt), **33**, 181 (1962).

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(18) (a) R. S. Mulliken, J. Am. Chem. Soc., **74**, 811 (1952); (b) D. Bijl, H. Kainer, and A. C. Rose-Innes, J. Chem. Phys., **30**, 765 (1959); Y. Matsunaga and C. A. McDowell, Nature, **185**, 916 (1960).

(19) G. Briegleb, "Electron-Donator-Acceptor-Komplexe," Springer Verlag, Berlin, 1961, Chapter 11.

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TABLE I

EXTENT OF ELECTRON TRANSFER OF ANIONS WITH NITROAROMATICS

Donor[a]	Acceptor[b] Nitrobenzene[d]	m-Dinitrobenzene[e]
	Electron transfer (5 min.),[c] %	
Solvent blank	<0.1 (10 min.)	<0.1 (20 min.)
Fluorene	13	40, 80 (20 min.)[g]
9-Phenylfluorene[f]	8	
Indene	36	2[g]
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-butane-dione	72[g]	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]	
Fluoren-9-ol	>100[h]	
Xanthen-9-ol	1.0 (10 min.)	
Benzhydrol	<0.1[k]	
1,4-Hydroquinone	40[i]	100[i]
2,6-Di-t-butyl-4-methyl-phenol	<0.1	0.5 (20 min.)
Thiophenol	0.2 (30 min.)	0.6, 2 (8 min.)
3,4-Dimercaptotoluene	11	5[g]
n-Butyl mercaptan	0.3 (20 min.)	12[g]
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[g] (10 min.)
Hydrazobenzene	2 (40 min.)	7.5[g] (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	6.8 (3 min.)
n-Butyllithium[k]	~6[k]	

[a] Donor substrate = 0.025 M, base = 0.05 M. [b] Acceptor = 0.005 M. [c] Extent of transfer = [radical-anion](100/0.005); the concn. of radical-anion was estimated by comparison of the observed e.s.r. peak heights with those obtained from known concentrations of diphenylpicrylhydrazyl in the same solvent. [d] In DMSO (20%)–t-butyl alcohol (80%) containing potassium t-butoxide. [e] In ethanol containing sodium ethoxide. [f] Donor substrate = 0.013 M. [g] Spectrum not consistent with acceptor radical-anion. [h] Spectrum dominated by radical-anion from donor. [i] Two recognizable radical-anions present. [j] Produced from dissociation of saturated solution of benzpinacol.[5a] [k] 1 M n-butyllithium in tetrahydrofuran (75%)–hexane (25%); no further hyperfine resolution of the nitrogen triplet observed.

paramagnetic in the solid state (e.s.r.) but dissociate in polar solvents to produce the radical-anions and the radical-cations.[16,22] Complexes with tetracyanoethylene are mainly diamagnetic,[8e] but in polar solvents the complex with tetramethyl-p-phenylenediamine dissociates extensively into paramagnetic species.[23]

In the present study we have attempted to define the scope (in terms of rate and extent) of electron transfer between a variety of anions and dianions which can be generated in alcohol-containing solvents with nitrobenzene and/or m-dinitrobenzene. On the basis of these results a few anions were selected and the scope of their electron-transfer reactions examined

(22) J. W. Eastman, G. Engelsma, and M. Calvin, J. Am. Chem. Soc., 84, 1339 (1962); I. Isenberg and S. L. Baird, Jr., ibid., 84, 3803 (1962).

(23) W. Liptay, G. Briegleb, and K. Schindler, Z. Elektrochem., 66, 331 (1962).

toward a variety of unsaturated substances containing nitrogen–nitrogen, carbon–carbon, oxygen–oxygen, carbon–nitrogen, carbon–oxygen, and nitrogen–oxygen double bonds or their vinylogs.

Results

Table I lists the extent of electron transfer observed from a variety of anions (generated by ionization of their conjugate acids) in the presence of nitrobenzene and m-dinitrobenzene. The concentration of radical-anions formed was monitored by e.s.r. spectroscopy, a technique which in our hands had a reproducibility of ±20% on a relative basis.
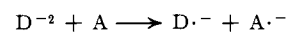
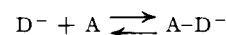The data of Table I reflect (a) the degree of ionization of DH to give the donor anion (D⁻)

$$DH \text{ (or } DH_2) \rightleftarrows D^- \text{ (or } D^{-2})$$
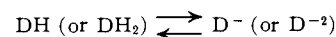
(b) the rate of electron transfer from the donor (D⁻) to the acceptor (A)

$$D^- + A \longrightarrow A\cdot^- + D\cdot \longrightarrow products$$
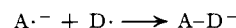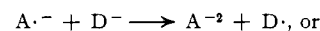
or

$$D^{-2} + A \longrightarrow D\cdot^- + A\cdot^-$$
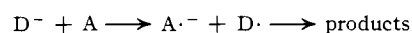
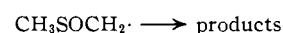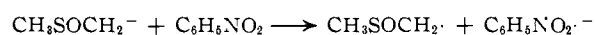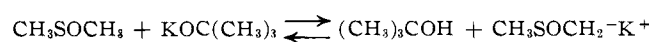(c) possible side reactions that could consume D⁻ and/or A without producing the products of electron transfer, e.g.

$$D^- + A \rightleftarrows A–D^-$$

(d) reactions with might consume A·⁻ after it had been produced, e.g.

$$A\cdot^- + D^- \longrightarrow A^{-2} + D\cdot, \text{ or}$$

$$A\cdot^- + D\cdot \longrightarrow A–D^-$$

In several instances in Table I the donor can be formulated as a dianion (D⁻²). In these cases both A·⁻ and D·⁻ are stable species and the e.s.r. spectrum observed usually showed signals due to each of the radical-anions (e.g., 1,4-hydroquinone with nitrobenzene). In some cases the concentrations of A·⁻ was rather low (e.g., fluoren-9-ol with nitrobenzene) apparently due to the fact that the donor molecule was used in excess and

$$D^{-2} + A\cdot^- \longrightarrow A^{-2} + D\cdot^-$$
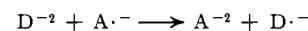
We would have preferred to use a more powerful base–solvent system (such as potassium t-butoxide in dimethyl sulfoxide) for the generation of the donor anions. This would have ensured complete ionization of the more acidic compounds and would have allowed the use of weaker acids, such as toluene. However, nitrobenzene, and to a greater extent m-dinitrobenzene, are not stable and give e.s.r. signals corresponding to the radical-anion (A·⁻) in strongly basic systems. Nitrobenzene gave only a small blank in the presence of 0.05 M potassium t-butoxide in DMSO (20%)–t-butyl alcohol (80%). However, in solvents containing a higher percentage of DMSO the nitrobenzene radical-anion was formed rapidly. This may be due to electron transfer from the methylsulfinyl carbanion, or from the formation of a Meisenheimer or Janovsky

$$CH_3SOCH_3 + KOC(CH_3)_3 \rightleftarrows (CH_3)_3COH + CH_3SOCH_2^-K^+$$

$$CH_3SOCH_2^- + C_6H_5NO_2 \longrightarrow CH_3SOCH_2\cdot + C_6H_5NO_2\cdot^-$$

$$CH_3SOCH_2\cdot \longrightarrow products$$
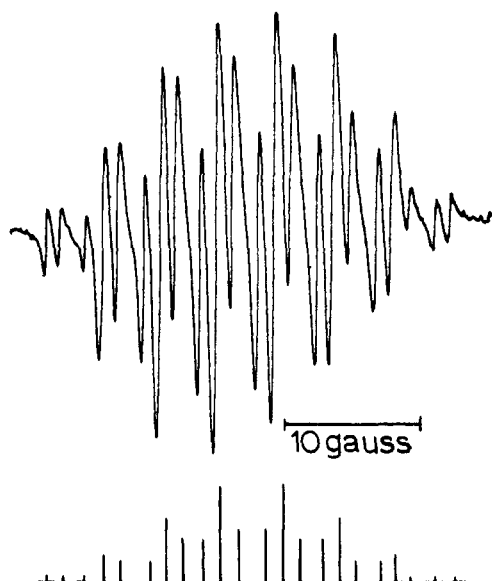
Fig. 1.—E.s.r. spectrum of m-dinitrobenzene radical-anion obtained from 0.01 M m-dinitrobenzene in DMSO (80%)-t-but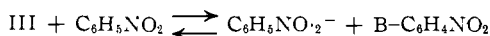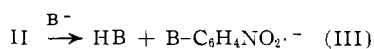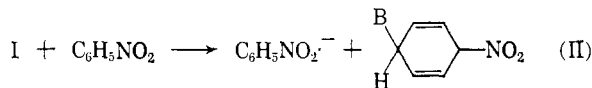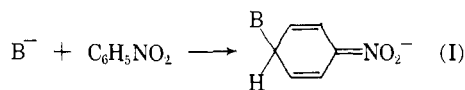yl alcohol (20%) containing 0.005 M potassium t-butoxide. Theoretical spectrum calculated from h.f.s.c. given in text.

Fig. 2.—E.s.r. spectrum of m-dinitrobenzene radical-anion in ethanol from 0.05 M m-dinitrobenzene, 0.025 M ethyl malonate, and 0.050 M sodium ethoxide.

type adduct,[14,24] which can serve as a donor to another nitrobenzene molecule.[25]

$$B^- + C_6H_5NO_2 \longrightarrow \text{(diagram)} =NO_2^- \quad (I)$$

$$I + C_6H_5NO_2 \longrightarrow C_6H_5NO_2^{\cdot-} + \text{(diagram)} -NO_2 \quad (II)$$

$$II \xrightarrow{B^-} HB + B-C_6H_4NO_2^{\cdot-} \quad (III)$$

$$III + C_6H_5NO_2 \rightleftharpoons C_6H_5NO_2^{\cdot-} + B-C_6H_4NO_2$$

Of course, a mechanism of the above type could be invoked to explain all the electron transfers listed in Table I. However, we doubt that this is the case since the e.s.r. spectra observed with nitrobenzene as the acceptor were clearly those of the nitrobenzene radical-anion and showed no effect (other than concentration) of the nature of the donor used. At dilute concentrations the spectra were completely resolved into the theoretical 54 lines with h.f.s.c. of a_N = 10.90, a_{o-H} = 3.28, a_{p-H} = 3.70, and a_{m-H} = 1.06 gauss.[26]

m-Dinitrobenzene is more sensitive to bases than nitrobenzene. Even in potassium t-butoxide–t-butyl alcohol radical-anions are observed,[13] apparently from electron transfer to m-dinitrobenzene from the Meisenheimer adduct with t-butoxide ion[24] or from the dinitrophenyl carbanion.[27] In sodium ethoxide–ethyl alcohol electron transfer is not important and this solvent system was used for the experiments in Table I. As indicated in Table I, in some cases the e.s.r. spectra observed were not consistent with the dinitrobenzene

radical-anion, possibly indicating that electron transfer was a result of oxidation of an adduct of the Meisenheimer or Janovsky type formed between the donor anion and m-dinitrobenzene.

The e.s.r. spectrum observed when m-dinitrobenzene is dissolved in DMSO (80%)-t-BuOH (20%) containing deficient potassium t-butoxide is shown in Fig. 1. This compares favorably with the spectrum reported previously by Maki and Geske[28b] and with the theoretical spectrum calculated with the h.f.s.c. of a_N = $a_{4,6-H}$ = 4.28, a_{2-H} = 3.10, and a_{5-H} = 1.05 gauss. In acetonitrile Maki and Geske have reported a_N = 4.68, $a_{4,6-H}$ = 4.19, a_{2-H} = 3.11, and a_{5-H} = 1.08 gauss. Somewhat different spectra are observed in t-butyl alcohol or ethanol. Figure 2 gives a typical ethanol spectrum obtained by electron transfer with the anion of diethyl malonate. This ten-line spectra, total line width = 35.8 gauss, was obtained with many of the other donors of Table I (acetophenone, etc.) and has been tentatively assigned to the m-dinitrobenzene radical-anion.

Attempts to obtain data using 1,3,5-trinitrobenzene in alcoholic solution were unsuccessful. In t-butyl alcohol a Meisenheimer adduct[24] with the alkoxide ion forms rapidly and precipitates from solution. In DMSO (20%)-t-butyl alcohol (80%) the adduct is more soluble, but only a small amount of electron transfer with potential donor carbanions was observed, presumably because the equilibrium constant for adduct formation is large and the adduct is itself not an acceptor or even a donor toward free 1,3,5-trinitrobenzene. It appears that with excess base the acceptor is completely destroyed giving the Meisenheimer adduct while the excess trinitrobenzene the base is neutralized and the donor substrate not ionized.

The data of Table I indicate, as was expected, that m-dinitrobenzene is a better acceptor than nitrobenzene. This is particularly obvious when the more acidic substrates are considered and the degree of ionization of DH is not a variable. In ethanol-sodium ethoxide solution few of the compounds of Table I would have given any transfer to nitrobenzene.

Table I demonstrates that those substrates which can yield dianions give more extensive electron transfer than most monoanions. Thus, appreciable electron transfer was observed from benzoin, fluoren-9-ol, 1,4-hydroquinone, 1,4-diphenyl-1,4-butanedione, 3,4-

(24) J. Meisenheimer, *Ann.*, **323**, 205 (1902).

(25) Note that when B⁻ is hydroxide ion that this scheme accounts for the well known formation of nitrophenols from nitroaromatics (*e.g.*, m-dinitrobenzene → 2,4-dinitrophenol) in basic solution (A. Wohl, *Chem. Zentr.*, **72I**, 149 (1901).

(26) The spectra were essentially the same as reported by Geske and Maki[28a] in acetonitrile solution except better resolution was obtained in the present work.

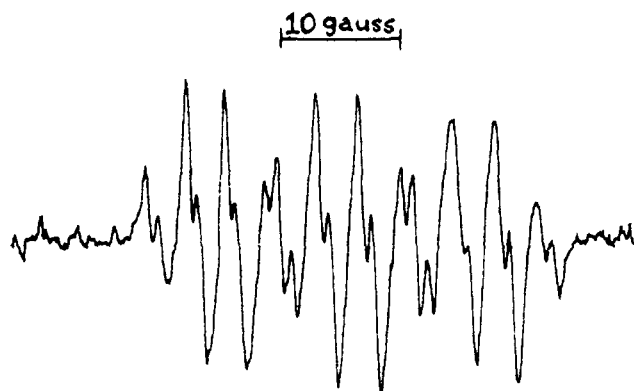(27) R. J. Pollitt and B. C. Saunders, *Proc. Chem. Soc.*, 176 (1962).

(28) (a) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960);
(b) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960).

dimercaptotoluene, N-hydroxybenzenesulfonamide, and hydrazobenzene. Among the monoanions studied those derived from propiophenone, fluorene, and indene are exceptionally good donors. There are indications in Table I that the weaker acids give anions which are better donors. This effect had been observed previously when molecular oxygen was used as the electron acceptor.[29] However, in the present work this effect cannot be completely separated from the degree of ionization of DH. For the cyclopentadienes the extent of transfer observed to nitrobenzene was cyclopentadiene < fluorene < indene, while the acidities are in the order cyclopentadiene > indene > fluorene.

The extensive electron transfer described in Table I is by no means limited to the use of nitroaromatics as electron acceptors. Compounds which might have been better electron acceptors were briefly investigated, but in the presence of alkoxide ions substances like duroquinone and tetracyanoethylene spontaneously produce radical-anions, presumably by nucleophilic addition of the base and electron transfer from the resulting anion. Table II lists the maximum amount of electron transfer observed using somewhat poorer acceptors, azobenzene and fluorenone.

TABLE II

EXTENT OF ELECTRON TRANSFER OF CARBANIONS WITH AZOBENZENE AND FLUOREN-9-ONE

Donor[a]	Azobenzene[d]	Fluoren-9-one[e]
	—————Electron transfer (time),[c] %—————	
Solvent blank	<0.01 (1 hr.)	0.3 (1 hr.)[f]
Cyclopentadiene	0.4 (12 hr.)	5.6 (1.4 hr.)[f]
Indene	3 (4.8 hr.)	74 (5 min.)
Fluorene	56 (5.7 hr.)[g]	
Diphenylmethane	2 (6 hr.)	
Triphenylmethane	1.6 (12 hr.)	
Acetophenone	50 (1.3 hr.)	
Propiophenone	34 (18 min.)	1.4 (2 hr.)[f]
Isobutyrophenone	3 (6 hr.)	
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] 0.025 M in the presence of 0.05 M potassium t-butoxide. [b] Acceptor = 0.005 M. [c] See footnote c, Table I. [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%).

The transfers listed in Table II occurred in general slower than those of Table I, presumably because the ease of one-electron reduction decreases in the order m-dinitrobenzene > nitrobenzene > fluoren-9-one > azobenzene. Fluoren-9-one was used in a solvent of DMSO (20%)-t-butyl alcohol (80%) to avoid the formation of the DMSO adduct (9-hydroxy-9-(methylsulfinylmethyl)fluorene) observed previously.[12b] Azobenzene gave little or no blank in DMSO (80%)-t-butyl alcohol (20%) and the data observed with azobenzene are thus the least complicated from variations in the extent of ionizations of any data so far

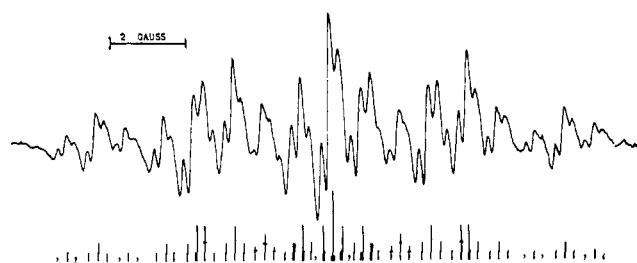(29) G. A. Russell, A. J. Moye, and K. Nagpal, J. Am. Chem. Soc., 84, 4154 (1962).

Fig. 3.—E.s.r. spectrum of fluoren-9-one ketyl in DMSO (20%)-t-butyl alcohol (80%). The ketyl was generated from 0.025 M fluoren-9-ol in the presence of 0.05 M potassium t-butoxide and ca. 0.001 M fluoren-9-one. The theoretical spectrum was calculated with the h.f.s.c. given in the text.

presented. The ease of transfer of fluorene > indene > cyclopentadiene is quite obvious and in agreement with the expectation that the carbanion from the weakest acid should be most readily oxidized.[29] Except when noted otherwise, the spectra observed with azobenzene as the acceptor was the 43-line spectrum described previously.[8a] The h.f.s.c. have been assigned in the azobenzene radical-anion on the basis of a number of deuterium-substitution experiments which will be described elsewhere.[30] In DMSO (80%)-t-butyl alcohol (20%) the h.f.s.c. are $a_N = 4.84$, $a_{p-H} = 2.81$, a_{o-H} (two) = 2.81, a_{o-H} (two) = 2.03, and $a_{m-H} = 0.78$ gauss. The spectrum observed from reduction of fluoren-9-one is given in Fig. 3. Since 2,7-dibromofluorenone ketyl has a spectrum nearly identical with fluorenyl ketyl,[31] the main interaction in fluorenone ketyl involves the protons at carbon atoms 1, 3, 6, and 8 to give a quintet at low resolutions. Higher resolutions gives the spectrum in Fig. 3 which is consistent with $a_{H (1\ and\ 8\ or\ 3\ and\ 6)} = 3.65$, $a_{H (3\ and\ 6\ or\ 1\ and\ 8)} = 2.61$, $a_{H (2\ and\ 7\ or\ 4\ and\ 5)} = 0.81$, and $a_{H (4\ and\ 5\ or\ 2\ and\ 7)} = 0.24$ gauss.

To obtain more information on the reactivity of unsaturated molecules as electron acceptors, six donor carbanions (including n-butyllithium and n-butylmagnesium bromide) were selected and these, as well as the dihydro derivative where available, allowed to react with representative unsaturated systems of the type X(=Q—Q'=)$_n$Y where X and Y are the same or different atoms from the group carbon, nitrogen, or oxygen and Q and Q' were generally carbon. The value of n was usually 0 or 1. Table III lists examples in which at least some electron transfer was observed. In the case of the dianion of 9,10-dihydroanthracene as the donor the anthracene radical anion (D·⁻)

$$DH_2 \rightleftarrows DH^- \rightleftarrows D^{-2}$$

$$D^{-2} + A \rightleftarrows A\cdot^- + D\cdot^-$$
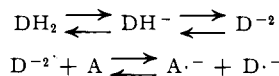
was not stable in the solvent system used and only the A·⁻ radical anion was observed.[32] For 1,4-diphenyl-1,4-butanedione both A·⁻ and D·⁻ were stable and a composite e.s.r. spectrum was often observed.

The spectra of A·⁻ were consistent with previously reported spectra for azobenzene,[8a] phenazine,[33a] 2,3-

(30) Unpublished work with Dr. R. Konaka.

(31) Unpublished work with Dr. E. G. Janzen.

(32) As reported earlier[8a] the anthracene radical-anion can be formed in high yield from anthracene and 9,10-dihydroanthracene in pure DMSO containing potassium t-butoxide. Oxidation of 9,10-dihydroanthracene under these conditions also yields the anthracene radical-anion. However, oxidation in DMSO (80%)-t-butyl alcohol (20%) yields only 9,10-anthrasemiquinone.

(33) (a) A. Carrington and J. Dos Santos-Veiga, Mol. Phys., 5, 21 (1962); R. L. Ward, J. Am. Chem. Soc., 84, 332 (1962); (b) A. Zweig and A. K. Hoff-

TABLE III

ELECTRON TRANSFER FROM A SELECTED GROUP OF CARBANIONS TO A VARIETY OF UNSATURATED SYSTEMS

Acceptor[b]	9,10-Dihydroanthracene (0.025 M) / KOC(CH3)3 (0.10 M) / DMSO (80%)-t-butyl alcohol (20%)	Propiophenone (0.025 M) / KOC(CH3)3 (0.05 M) / DMSO (80%)-t-butyl alcohol (20%)	n-Butyllithium (0.05 M) / Tetrahydrofuran (75%)-n-hexane (25%)	n-Butylmagnesium bromide (0.25 M) / Tetrahydrofuran	1,4-Diphenyl-1,4-butanedione (0.025 M) / KOC(CH3)3 (0.1 M) / DMSO (20%)-t-butyl alcohol (80%)	Propiophenone (0.025 M) / KOC(CH3)3 (0.05 M) / DMSO (20%)-t-butyl alcohol (80%)	Dihydro deriv. of acceptor (0.01 M) / KOC(CH3)3 (0.02 M) / DMSO (80%)-t-butyl alcohol (20%)
—N==N—							
Phenazine	46 (24 min.)	22 (216 min.)	76 (20 min.)	2.5	200 (11 min.)[c]	1.5 (188 min.)	
Azobenzene	25	34 (23 min.)	2.7	0.011	0.16 (13 min.)[d]	No transfer[e]	100
Benzo[c]cinnoline	14 (183 min.)[f]	0.3 (123 min.)	2.0 (28 min.)	60	No transfer[e]	No transfer[e]	
Benzofurazan	2.5	5.4 (10 min.)[f]	0.55	8.4[f]	No transfer[e]	0.1 (70 min.)	
2,3-Diphenylquinoxaline	1.7 (119 min.)[f]		6.1 (65 min.)	No transfer[e]			46 (47 min.)
N,N'-Diphenyl-p-benzoquinonediimine	g	g	30	0.08	h	h	6.5
Diethyl azodiformate	No transfer[e]	No transfer[e]	0.46		No transfer[e]	No transfer[e]	0.04
>C==C<							
Δ^{9,9'} Bifluorene	g	g				9.6 (87 min.)	12.5 (75 min.)[f]
1,2-Bis(4-pyridyl)ethylene	0.24	No transfer[e]	9.0[f]	No transfer[e]	No transfer[e]	No transfer[e]	No transfer[e]
>C==N—							
Acridine	0.36	No transfer[e]	0.93[f]	No transfer[e]	No transfer[e]	No transfer[e]	0.33
>C==O							
Fluoren-9-one			50> <98	0.28	76[c]	1.4 (120 min.)[d]	100
Benzophenone		No transfer[e]	9.5	0.70	1.8[i]	No transfer[e]	0.004[j]
[O==O]							
1,4,5,8-Tetrachloroanthraquinone					110[c]	8.8[k]	
—N==O							
Nitrobenzene			14	4.7 (93 min.)		91	
Azoxybenzene	2.8	No transfer[e]			No transfer	No transfer[g]	

a Maximum observed concentration of radical-anion, 5 min., unless otherwise noted. Extent of transfer = ([radical-anion]/[acceptor]$_0$) × 100 except for transfer with dihydro derivative where extent of transfer = ([radical-anion]/2[acceptor]$_0$) × 100. b Concentration 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. c Predominant spectrum of acceptor. d Predominant spectrum of donor. e Less than 2×10^{-8} M concentration of radical-anion at any time over the 40-min. period after mixing. f Radical concentration not followed to max. g Prohibitive blank in absence of donor. h Acceptor not soluble. i Radical-anions from both donor and acceptor detectable. j Benzophenone = 2.29 M, benzhydrol = 2.24 M, base = 4.5 M. k Spectrum not consistent with 1,4,5,8-tetrachlorosemiquinone.

diphenylquinoxaline,[8a] diethyl azodiformate,[33b] Δ-9,9-bifluorene,[8a] fluoren-9-one,[8a] benzophenone,[33c] 1,4,5,8-tetrachloroquinone,[33d] and nitrobenzene.[28a] From benzo[c]cinnoline, benzofurazan, 1,2-bis(4-pyridyl)-
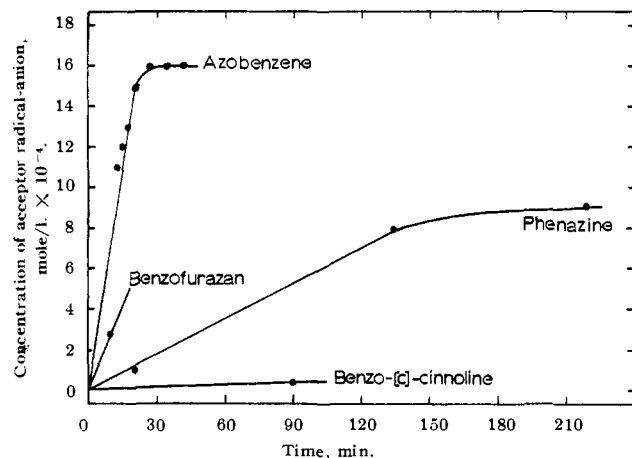
Fig. 4.—Electron transfer between propiophenone (0.025 M) in DMSO (80%)-t-butyl alcohol (20%) containing 0.05 M potassium t-butoxide and selected acceptors (0.005 M) at 25°.

ethylene, N,N'-diphenyl-p-benzoquinonediimine, and 1,2-dibenzoylethylene, e.s.r. spectra obviously consistent with the structure A·⁻ were observed. These spectra will be reported at a later date.

man, J. Am. Chem. Soc., 85, 2736 (1963); (c) P. B. Ayscough and R. Wilson, Proc. Chem. Soc., 229 (1962); (d) R. W. Brandon and E. A. C. Lucker, J. Chem. Soc., 4273 (1961).

The relative ability of the donors to transfer an electron to the acceptors was fairly constant with 9,10-dihydroanthracene > propiophenone (DMSO (80%)-t-butyl alcohol (20%)); 1,4-diphenyl-1,4-butanedione > propiophenone (DMSO (20%)-t-butyl alcohol (80%)); n-butyllithium > n-butylmagnesium bromate (tetrahydrofuran). The relative abilities of the unsaturates to accept an electron was reasonably constant as the donor was varied with the organometallics showing the greatest numbers of irregularities. The data given in Table III are expressed as the maximum concentration of radical-anion observed, except for those cases (labeled) in which the concentration was not followed over an extensive period of time. When considered in graphical form as in Fig. 4, the relative rates of reductions are more easily seen.

Of particular interest in Table III are the large concentrations of A·⁻ formed with the organometallic reagents in certain instances (phenazine, N,N'-diphenyl-p-benzoquinonediimide, and fluoren-9-one with butyllithium[34]; benzo[c]cinnoline with butylmagnesium bromide). Also obvious from Table III is the fact that the dihydro form of a given acceptor is usually a superior donor toward that acceptor.

Numerous other acceptors were examined. No

(34) H. W. Brown and R. C. Jones (J. Chem. Phys., 36, 2809 (1962)) have reported that with H. H. Freedman they have found that the action of butyllithium on polynuclear aromatic hydrocarbons yields the radical-anion of the aromatic hydrocarbons. Similar results involving t-butyllithium and diphenylacetylene have been reported (J. E. Mulvaney, Z. G. Garlund, and S. L. Garlund, J. Am. Chem. Soc., 85, 3897 (1963)).

transfer with the anions from propiophenone, 1,4-diphenyl-1,4-butanedione, or 9,10-dihydroanthracene was observed for N-diphenylmethyleneaniline, 1,1,4,4-tetraphenyl-1,3-butadiene, 1,8-diphenyl-1,3,5,7-octatetraene, perylene, tetraphenylethylene, phenanthridine, 2-methyl-2-phenylindane-1,3-dione, 2,5-diphenyl-3,4-benzofuran, benzothiazole, or benzoxazole.

With propiophenone no electron transfer was observed for phenyl sulfoxide, phenyl sulfone, 4-cyanopyridine, 4-chloropyridine 1-oxide, $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$-hexafluoro-$p$-xylene, $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$-hexafluoro-$m$-xylene, triphenylphosphine oxide, (carbethoxymethylene)triphenylphosphorane, and diphenylphosphonimidotriphenylphosphorane.
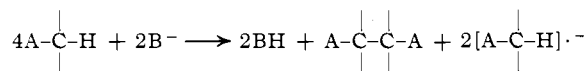
Among the acceptors examined which gave high concentrations of radical-anions in the basic solutions in the absence of any donor under the conditions employed in Table III were nitrosobenzene, m-dinitrobenzene, $trans$-1,2-dibenzoylethylene, duroquinone, tetracyanoethylene, perchlorofulvalene, tetrachloro-p-benzoquinone, benzil, 4-nitropyridine N-oxide, benzofuroxan, 2,2',6,6'-tetra-t-butylstilbenequinone, and 2,2',6,6'-tetra-t-butyldiphenoquinone.

Discussion

The examples of the previous section illustrate that products of electron transfer are quite widely encountered in reactions between carbanions, nitranions, or organometallic reagents and a variety of neutral unsaturated compounds, including, among others, nitroaromatics, azo compounds, and ketones. Apparently much of the chemistry of aromatic nitro, nitroso, and azo compounds in basic solution involves electron-transfer processes. Numerous examples in the literature[35] of dehydrogenations of ionizable substances (DH, DH_2) by such materials (A) in basic solution must involve electron transfer.

$$2DH + 2A + 2B^- \longrightarrow 2BH + D-D + 2A^{.-}$$

$$DH_2 + 2A + 2B^- \longrightarrow 2BH + D + 2A^{.-}$$
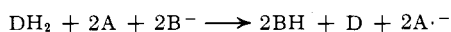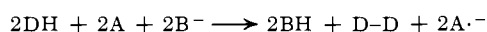
As a special case the acceptor and donor can be present in the same molecule

$$4A-\overset{|}{\underset{|}{C}}-H + 2B^- \longrightarrow 2BH + A-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-A + 2[A-\overset{|}{\underset{|}{C}}-H]^{.-}$$
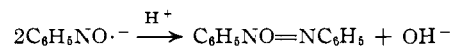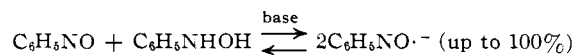
Among the recognized examples of A–C–H are p-nitrotoluene and its derivatives,[13] 3-nitro-4-picoline N-oxide,[35b] p-phenylazotoluene, 1,4-dimethyltetrazine,[30] and 2-amino-9,10-anthraquinone.[36]

It is of interest to speculate on the importance of electron-transfer processes in the synthetically important addition and condensation reactions of carbanions, nitranions, or organometallic reagents. For example, by rapid-flow e.s.r. techniques it can be demonstrated that the base-catalyzed condensation of nitrosobenzene and phenylhydroxylamine to give azoxybenzene is a process involving the nitrosobenzene radical-anion as an intermediate.[37]

$$C_6H_5NO + C_6H_5NHOH \underset{\longleftarrow}{\overset{base}{\rightleftharpoons}} 2C_6H_5NO^{.-} \text{ (up to 100\%)}$$

$$2C_6H_5NO^{.-} \overset{H^+}{\longrightarrow} C_6H_5NO=NC_6H_5 + OH^-$$

It would appear to be of great importance to establish whether the products of one-electron transfer observed in the present work result from decomposition of an initial addition products (the Blicke hypothesis[5d]).

$$D^- + A \rightleftharpoons D-A^- \rightleftharpoons D^. + A^{.-}$$

On the other hand, it is possible to explain the formation of addition products between carbanions or organometallic reagents and unsaturated systems ($e.g.$, carbonyl compounds) solely by electron-transfer reactions.

$$D^- + A \longrightarrow [D^. + A^{.-}]_{solvent\ cage} \longrightarrow D-A^-$$
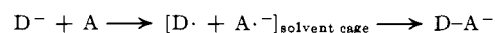
Transfer of one electron from a carbanion, nitranion, mercaptide ion,[12c,38] or organometallic reagent to organic molecules is of course not restricted to the use of neutral unsaturated acceptors. Other substances which undergo facile electrolytic reduction may also react with carbanions by what appear to be electron-transfer processes. The acceptor can be a cation,[39] such as the pyrylium cation,[7] a peroxide,[40] or a disulfide. Alkyl and some aryl halides react with a number of organometallic reagents by an electron-transfer process

$$R:^- + R'X \longrightarrow R^. + [R'-X]^- \longrightarrow R^{.'} + X^-$$

Examples of this type of process are recognized where the donor $(R:^-)$ is a radical-anion,[4,41] a dianion,[41b,42] an alkyllithium reagent,[43] or a Grignard reagent.[44]

Experimental

Apparatus and Procedure.—The e.s.r. spectra were obtained using a Varian V-4500 spectrometer equipped with 100 kc./sec. field modulation. Flat fused silica cells (Varian V-4548 aqueous solution sample cell) were used for all experiments. Initial experiments involved the use of a stopped flow technique in which a thoroughly degassed solution of the base was mixed in a T-tube with a solution of the donor and acceptor. Since this procedure required large volumes of reagents and solvents a simpler procedure was devised. Cells similar to the one shown in Fig. 5 were constructed. After flushing with prepurified nitrogen a solution of the base was added to one leg by syringe through the rubber septum and a solution of the donor and acceptor added to the other leg. The solutions were degassed by introducing prepurified nitrogen through two hypodermic needles extending below the surface of each solution (nitrogen escaped through the open end of the cell). When degassing was complete (20 min.) the exit was closed and the hypodermic needles withdrawn. The solutions were mixed and the resulting mixture forced into the cell by shaking. Initial e.s.r. spectra were recorded about 1
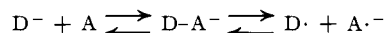
(35) (a) For example, L. A. Pinck and E. G. Hilbert, *J. Am. Chem. Soc.*, **54**, 710 (1932); **68**, 2739 (1946); M. Colonna, *Gazz. chim. ital.*, **90**, 1179 (1960); M. Colonna and L. Zamparello, *ibid.*, **92**, 301 (1962); (b) E. C. Taylor, A. J. Crovetti, and N. E. Boyer, *J. Am. Chem. Soc.*, **79**, 3549 (1957); E. C. Taylor and J. S. Driscoll, *J. Org. Chem.*, **26**, 3796 (1961).

(36) R. Scholl and H. Berblinger, *Ber.*, **36**, 3427 (1903).

(37) Unpublished work with Mr. E. J. Geels.

(38) F. J. Smentowski, *J. Am. Chem. Soc.*, **85**, 3036 (1963).

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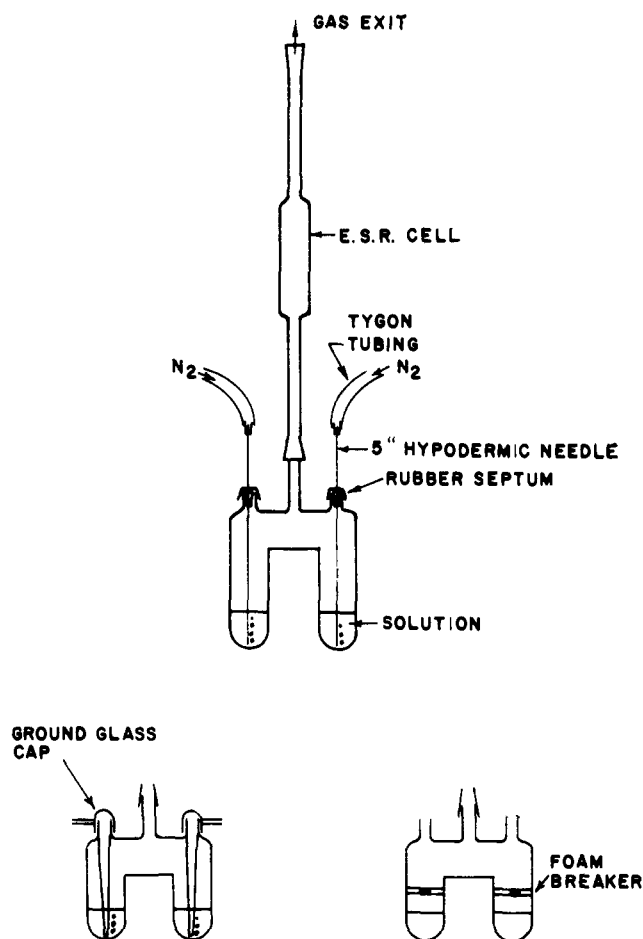
Fig. 5.— Apparatus for electron-transfer experiments under anaerobic conditions.

min. after mixing. Extreme precautions in degassing were required because most of the donors involved (particularly the potential dianions) reacted readily with oxygen to give radical species. The techniques employed consistently gave negligible blanks when used to prepare basic solutions of benzoin, propiophenone, and hydrazobenzene, solutions very prone to produce radical-anions in the presence of oxygen. For each electron-transfer experiment blank experiments using the donor alone and the acceptor alone were performed and for all experiments reported in Tables I–III the concentrations of paramagnetic species were negligible in the blanks when compared to the concentrations observed for the mixture of donor and acceptor. The percentage electron transfer was measured as specified in Tables I–III. This method had a reproducibility of ±20% on a relative basis. Considerably higher percision was possible when the data were expressed in terms of d[radical-anion]/dt for those electron transfers which were slow enough that an initially linear buildup of radical-anion could be observed.

Estimates of the radical concentrations were made by comparing the peak-to-peak distance from the maximum to the minimum of the over-modulated first derivative curves of the radical and a standard solution of diphenylpicrylhydrazyl at the same instrument settings and in the same solvents.[45] The reproducibility was ±20% and the accuracy probably was ±50%. We believe that the accuracy was poorest for those radicals of shorter line width (e.g., fluorenone and benzophenone ketyls) and was best for those radical-anions containing two nitrogen atoms.

Materials.—Dimethyl sulfoxide (Crown Zellerbach Corp.) was distilled under reduced pressure from calcium hydride. Commercial t-butyl alcohol was stored over sodium sulfate and used

without purification. Tetrahydrofuran was distilled from sodium and from lithium aluminum hydride. The potassium t-butoxide used was commercial material (Mine Safety Appliance Corp.).

Benzo[c]cinnoline was prepared by the method of Badger, Seidler, and Thomson[46]; m.p. 157–158°, lit.[46] m.p. 156°.

Benzofurazan synthesized by the method of Hammick, Edwardes, and Steiner[47] had a m.p. 52–54°, lit.[47] m.p. 55°.

Benzofuroxan was prepared according to the procedure of Smith and Boyer[48]; m.p. 69–71°, lit.[48] m.p. 70–71°.

Δ-9,9'-Bifluorene was synthesized from 9,9'-bifluorene by electron transfer to nitrobenzene in the presence of potassium t-butoxide in dimethylformamide solution; m.p. 179–183°, lit.[49] m.p. 187–188°. Thin-layer chromatography showed the presence of only one component.

1,2-Dihydro-2,3-diphenylquinoxaline was prepared by the condensation of o-phenylenediamine with benzoin in glacial acetic acid; m.p. 143–145°, lit.[50] m.p. 148°. 2,3-Diphenylquinoxaline was prepared by a similar condensation between o-phenylenediamine and benzil; m.p. 124–124.5°, lit.[51] m.p. 124°.

2,5-Diphenyl-3,4-benzofuran was made by the method of Allen and Van Allen[52]; m.p. 127°, lit.[52] m.p. 127°.

N,N'-Diphenyl-p-benzoquinonediimine was prepared by the procedure of Hughes and Saunders[53]; m.p. 184.5–186.5°, lit.[53] m.p. 181.5–182.5°.

1,4-Diphenyl-1,4-butanedione was prepared by the reduction of the olefin with sodium dithionite according to the procedure of Conant and Cutter[54]; m.p. 143–146°, lit.[55] m.p. 144–145°.

Fluoren-9-ol was prepared by reducing fluoren-9-one with lithium aluminum hydride; m.p. 155–156°, lit.[56] m.p. 158–159°.

9-Phenylfluorene was prepared by the method of Ullman and von Wurstenberger[57]; m.p. 147.5–148°, lit.[57] m.p. 145°.

Benzpinacol was synthesized by the method of Gomberg and Bachmann[58]; m.p. 185–186° dec., lit.[58] m.p. 192–194° dec.

2-Methyl-2-phenylindan-1,3-dione was prepared by the procedure of Nathanson[59]; m.p. 154–155°, lit.[59] m.p. 154–155°.

3,3',5,5'-Tetra-t-butyl-4,4'-diphenoquinone was prepared by the method of Kharasch and Joshi[60]; m.p. 237–239.5°, lit.[60] m.p. 246°. 3,3',5,5'-Tetra-t-butyl-4,4'-stilbenequinone was synthesized by the procedure of Cook, Nash, and Flanagan[61]; m.p. 308–310°, lit.[61] 315–316°.

n-Butylmagnesium bromide was prepared in tetrahydrofuran solution, filtered through a perforated disk, and stored under nitrogen. The concentration of the Grignard reagent was determined by titration with acid. The freshly prepared reagent gave no e.s.r. signal. n-Butyllithium in hexane solution was obtained from commercial sources (Foote Mineral Corp.) and diluted with tetrahydrofuran immediately before use.

The other potential donors and acceptors were obtained from standard sources and generally recrystallized or distilled before use.

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