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Photochemical Generation of Radical Anions *via* Organolithium Compounds

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Lithium salts of radical anions of polycyclic aromatic hydrocarbons have been prepared under photolytic conditions using organolithium compounds as reducing agents. The scope and usefulness of this reaction is discussed as are implications on reaction mechanism.

In recent years several methods for the production of radical anions have been explored.[1] These have been summarized in eq 1–5. One case of photolytic generation of a benzophenone ketyl involves irradiation of an alkaline solution of benzophenone[2]

$$A\cdot^- + B \rightleftharpoons A + B\cdot^- \qquad (1)$$

$$A^{2-} + A \rightleftharpoons 2A\cdot^- \qquad (2)$$

$$H{-}\pi{-}\pi{-}H \xrightarrow{B^-} {}^-\pi{-}\pi^- \rightleftharpoons 2\pi\cdot^- \qquad (3)$$

$$H_2\pi \xrightarrow{B^-} \pi^{2-} \xrightarrow{O_2} \pi\cdot^- + O_2\cdot^- \qquad (4)$$

$$A + D^- \longrightarrow A\cdot^- + D\cdot \qquad (5)$$

$$(C_6H_5)_2C{=}O + RO^- \longrightarrow (C_6H_5)_2\underset{\cdot}{C}O^- + RO\cdot$$

The concept that this reaction is a photosensitized one-electron reduction has been refuted (eq 5).[3] Instead, the reaction is considered to be another example of a system summarized by eq 3, by which benzophenone dimerizes to the dianion of benzopinacol which then in a subsequent step produces the ketyl.

This proposal was substantiated experimentally; benzophenone did not yield any detectable free radical when photolyzed in the absence of base. Formation of benzophenone ketyl in a subsequent dark reaction with base was evident from esr measurements.[3]

It has been observed that radical anions are formed slowly and spontaneously in the dark from butyllithium and the aromatic hydrocarbon.[4] However, the different type of reaction between aromatic hydrocarbons and butyllithium[5] makes this method of limited practical significance since it readily could lead to erroneous results.

The reaction to be discussed here may be represented as shown.

$$C_6H_5Li + ArH \xrightarrow{h\nu} C_6H_5\cdot + Ar\cdot^-Li^+ \qquad (6)$$

(ArH is an aromatic hydrocarbon)

The novel and fundamental aspect of the work discussed here is the influence of light on reaction 5. The dark reactions in which A is a nitro-substituted aromatic compound and D^- is any of an extensive series of bases (including butyllithium in one example) has been reviewed recently.[1] Furthermore, one-electron transfer has been stated to occur in the reaction of organolithium compounds with sterically hindered dienes.[6]

It is our contention that one-electron transfers occur as a separate step in many reactions of organometallic compounds. The driving force for such steps may, in a simplified manner, be considered to be dependent on two factors: (1) the oxidation potential of the organometallic compound or its anion (eq 7) and (2) the electron affinity of the substrate with which the organometallic compound reacts (eq 8).

$$\begin{gathered} R{-}M \longrightarrow R\cdot + e^- + M^+ \\ \text{or} \\ R^- \longrightarrow R\cdot + e^- \end{gathered} \qquad (7)$$

$$e^- + A \longrightarrow A\cdot^- \qquad (8)$$

The further course of reactions of organometallic compounds involving such a mechanistic step is dependent on the group R, the metal M, and the stability of $A\cdot^-$.

The oxidation of a carbanion (eq 7) is most certainly intimately connected with carbanion stabilities and thus also with the halogen–metal interconversion discussed elsewhere.[7]

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[1] G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **86**, 1807 (1964).

[2] P. B. Ayscough and F. P. Sargent, *Proc. Chem. Soc.*, 94 (1963); R. Wilson, *Can. J. Chem.*, **44**, 551 (1966).

[3] G. A. Russell and E. J. Geels, *Tetrahedron Letters*, 1333 (1963).

[4] H. H. Freedman, *J. Chem. Phys.*, **36**, 2809 (1962).

[5] H. J. S. Winkler, R. Bollinger, and H. Winkler, *J. Org. Chem.*, **32**, 1700 (1967).

[6] R. Waack and M. A. Doran, *J. Organometal. Chem.* (Amsterdam), **3**, 92 (1965).

[7] (a) D. E. Applequist and D. B. O'Brien, *J. Am. Chem. Soc.*, **85**, 743 (1963); (b) H. J. S. Winkler and H. Winkler, *ibid.*, **88**, 964 (1966).

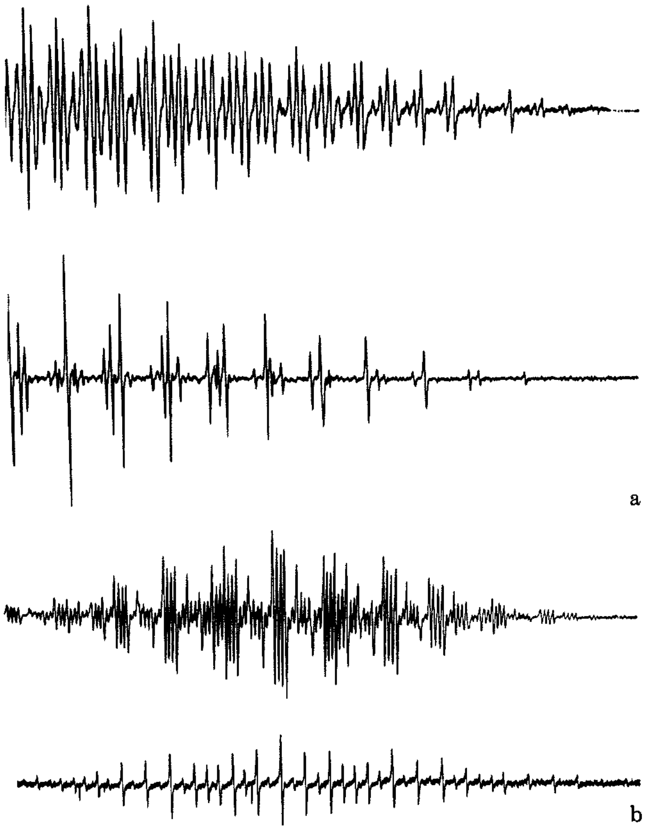

Figure 1.—(a) Electron spin resonance spectra of lithium anthracene radical anion in THF (lower spectrum) and diethyl ether (top spectrum). (b) Electron spin resonance spectra of lithium pyrene radical anion in THF (lower spectrum) and diethyl ether (top spectrum).

From a photochemical standpoint the reaction discussed here is a photoreduction of an aromatic hydrocarbon by the organolithium reagent acting as one-electron-donor or -reducing agent. Choosing electron acceptors, A, of high electron affinity (eq 8), the reaction may proceed spontaneously. We have found that the electron affinity of poorer electron acceptors (such as aromatic hydrocarbons) increases by photoexcitation. Under the proper conditions the product of the one-electron-transfer step, the lithium salts of radical anions, is stable and can be detected either by its ultraviolet or its esr spectrum. The reaction constitutes a new and convenient preparation of radical anions of aromatic hydrocarbons. The method has several advantages over other available methods (eq 1–5, p 1695).

Organolithium compounds such as phenyllithium are effective oxygen and water scavengers. Water destroys radical anions and oxygen usually causes broadening of the esr lines. Hence for the preparation of samples for esr spectra the method is both convenient and effective.

The concentration of the radical anion is readily adjusted by the time of exposure to ultraviolet irradiation. This is a distinct advantage over other methods because of the sensitivity of line width in the esr spectrum to exchange or further reduction of aromatic radical anions to diamagnetic dianions. There is no induction period. In other methods this is caused by time-consuming removal of traces of moisture or oxygen from the solution by reaction with the radical anion initially formed.

Finally the relative freedom in choice of solvent is a distinct advantage. However, a restriction is likewise imposed, the solvent must be inert to the organolithium compound. It should be mentioned that only radical anions with larger electron affinity or lower reduction potential than biphenyl can be prepared by this photolytic method. This is a minor disadvantage since most condensed aromatic hydrocarbons have higher electron affinity than biphenyl.

The following hydrocarbons have been converted to the corresponding radical anions in either diethyl ether (DEE) or THF by the conventional method (A) arene + Li, or the photochemical method (B) arene + C_6H_5Li ($h\nu$): biphenyl (DEE, B), naphthalene (DEE, A, B), anthracene (DEE, THF, A, B), phenanthrene (DEE, THF, A, B), pyrene (DEE, THF, B), perylene (DEE, B, THF, A), chrysene (DEE, B, THF, A), and acenaphthene (DEE, B). In all cases were the hyperfine splitting patterns independent of method of preparation.

Phenyllithium on photolysis gives some biphenyl.[8] The biphenyl could form the radical anion, but since biphenyl is of very low electron affinity it readily gives up an electron to any other hydrocarbon present which has a lower reduction potential[9] (eq 1).

It is significant to note that in the dark the reaction between phenyllithium and anthracene in diethyl ether does proceed extremely slowly; in tetrahydrofuran, however, the reaction is faster; and in hydrocarbon solvents it could not be detected in the absence of light. The importance of being able readily to prepare radical anions in a wide variety of solvents rests mainly in the possibility of studying the variation in hyperfine splitting by the alkali metal cation as a function of the medium. The alkali metal hyperfine splitting has been detected in a variety of salts of radical anions. Alkali metal ketyls[10] and several aromatic hydrocarbon radical anions such as the one from pyracene[11] have been particularly thoroughly studied. It appears that only in the case of intimate ion pairing is it possible to detect alkali metal hyperfine splitting. An interesting study of the conductivity of sodium salts of radical anions[12] reveals details of the equilibrium between ion pairs and free ions, the latter usually being present only in very dilute solutions.

It is immediately apparent from Table I that hyperfine splitting by lithium (^7Li), otherwise only rarely detected,[13] is observed for most lithium salts of aromatic anion radicals in diethyl ether. The larger hyperfine splitting in a solvent of lower dielectric constant is consistent with the increase in contact pairing for poorly solvated species. High alkali metal hyperfine splittings are observed mainly in compounds where the alkali metal is situated in a chelated system.[14] The largest

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(8) The reaction is not so extensive as indicated by E. E. van Tamelen, J. I. Brauman, and L. A. Ellis, *J. Am. Chem. Soc.*, **87**, 4964 (1965).

(9) E. De Boer, F. G. A. Stone, and R. West, *Advan. Organometal. Chem.*, **2**, 115 (1964), and references therein; K. Higasi, H. Baba, and A. Rembaum, "Quantum Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1965; J. M. Fritsch, T. P. Layloff, and R. N. Adams, *J. Am. Chem. Soc.*, **87**, 1724 (1965).

(10) G. R. Luckhurst and L. E. Orgel, *Mol. Phys.*, **8**, 117 (1964).

(11) E. de Boer, *Rec. Trav. Chim.*, **84**, 609 (1965).

(12) R. V. Slates and M. Szwarc, *J. Phys. Chem.*, **69**, 4124 (1965).

(13) W. H. Brunig, G. Henrici-Olivé, and S. Olivé, *Z. Physik. Chem.*, **47**, 114 (1965).

(14) B. J. Herold, A. F. N. Correia, and J. Dos Santos, *J. Am. Chem. Soc.*, **87**, 2661 (1965).

Table I

Hyperfine Splitting Constants for Lithium Salts of Radical Anions[a]

		a, gauss					
Hydrocarbon	Solvent	Li	α	β	γ	δ'	ϵ
Naphthalene	THF	0.180	4.90	1.83			
	Ether	0.51	4.73	1.75			
Anthracene	THF	0.0	5.27	2.71	1.48		
	Ether	1.72	5.41	2.38	1.50		
Biphenyl	THF	0.00	5.47	2.73	0.47		
	Ether	0.06	5.24	2.59	0.34		
Pyrene	THF	0.0	4.75	2.11	1.04		
	Ether	0.165	4.67	2.08	1.00		
Phenanthrene	THF	0.0	4.33	3.62	2.89	0.72	0.32
	Ether	0.12	5.17	4.05	2.91	1.07	0.59

[a] The hyperfine splitting constants, HFSC, were found by comparing spectra computed from estimated HFSC with observed ones. The computations were made by Dr. J. M. Fritsch of Central Research Department, St. Louis, Mo. The average uncertainty of the hyperfine splitting constant is ±0.01 gauss, temperature 25°.

magnitude of lithium splitting in the radical anions studied occurs for anthracene. Figure 1a shows the esr spectra with and without lithium splitting. It appears reasonable to expect the highest hyperfine splitting for salts in which lithium is situated nearest the highest probability of finding the unpaired electron. The symmetry properties of the singly occupied orbital would determine the preferred site of the alkali metal. If the position of the alkali metal per chance coincides with the location of highest unpaired spin density, then one would expect the largest alkali metal splitting. In the ions studied this appears to be borne out. Figure 1b depicts the esr spectra of lithium pyrene radical anion in DEE and THF.

Variation in Wavelength.—Experiments were performed in which the rates of consumption of anthracene and phenyllithium were measured as a function of the wavelength of the light. The results of these studies are summarized in Figure 2. The consumption of anthracene under a given set of conditions and using quartz-filtered, Vycor-filtered, and Pyrex-filtered light was 0.40, 0.41, and 0.08 mM, respectively. This result and the apparent rate of decrease of anthracene and phenyllithium (analyzed by quenching with chlorotrimethylsilane and performing vpc quantitatively using xylene as internal standard[7b]) show little difference in rate using light including the range 230–200 mμ, but, by cutting off light below 300 mμ (Pyrex filter), a significant lowering in rate resulted. It thus appears that the β band (λ 254 mμ) is significant in this photochemical transformation; however, further experiments on the quantum yield of the reaction as a function of wavelength of excitation are underway and will decide this point. Phenyllithium itself shows three absorptions [λ 292, 268, and 261 (log ϵ 2.88, 2.99, and 3.02)] in the region[15] filtered out by Pyrex filters, and it cannot be concluded unequivocally that the phenyllithium is not directly photoexcited. The fact that phenyllithium in the absence of aromatic hydrocarbons as photosensitizer does not decompose to the same extent as in the presence thereof, however, does point in this direction.

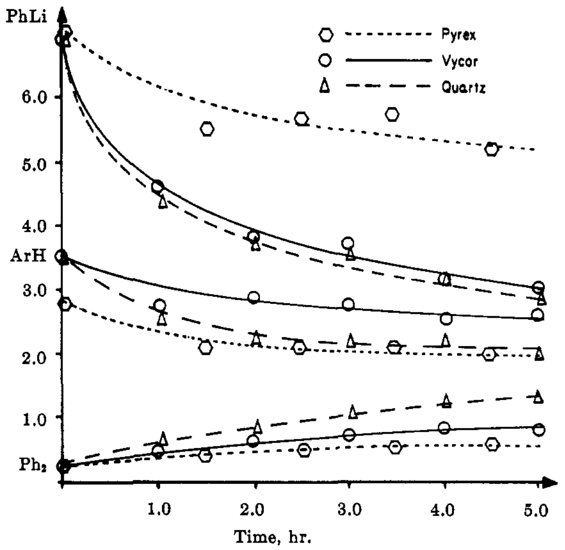
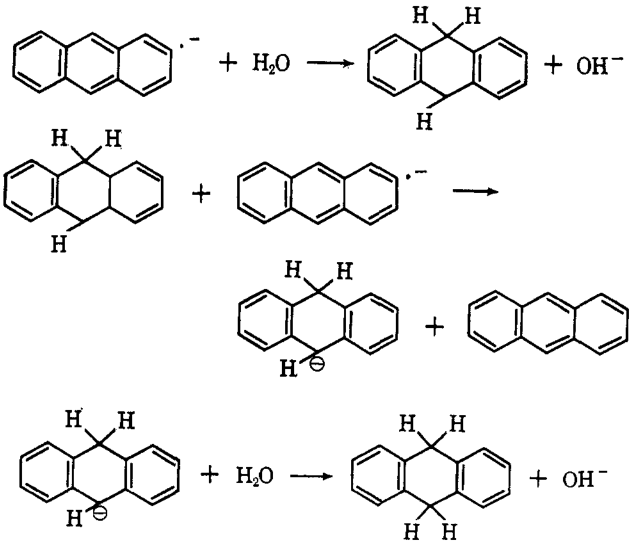


Figure 2.—Change in concentrations of phenyllithium (PhLi), anthracene (ArH), and biphenyl (Ph$_2$) with time of photolysis using Pyrex, Vycor and quartz filters.

Two photochemical reactions of anthracene have been studied extensively, the photodimerization and the photooxidation.[16] The maleic acid addition in the 9,10 positions[17] is less well understood. All three reactions occur across the 9,10 position. There is reasonable agreement that these photochemical reactions occur by $\pi \rightarrow \pi^*$ excitation of anthracene to its lowest triplet state, which than decays to a singlet,[18] and that this is the species which reacts.

Hydrolysis of Photolysis Products.—The hydrolysis of the lithium salt of the dianion of anthracene yields the 9,10-dihydro derivative. From the dianion and the hydrocarbon one can prepare the paramagnetic lithium salt of the anthracene radical anion. When this compound is hydrolyzed one obtains, depending on concentration, an equimolar mixture of anthracene and dihydroanthracene. The mechanism of this reaction postulated by Lipkin[19] has recently been substantiated.[20]



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(15) The data in the literature for THF solution of phenyllithium [R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 1651 (1963)] were confirmed for ether solutions.

(16) E. J. Bowen and D. W. Tanner, *Trans. Faraday Soc.*, **51**, 475 (1955).

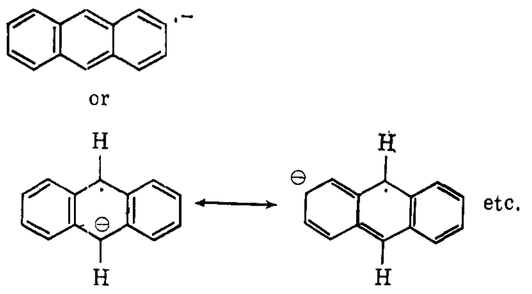
(17) J. P. Simons, *ibid.*, **56**, 391 (1960).

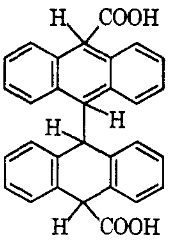
(18) F. D. Greene, S. L. Misrock, and J. R. Wolfe, *J. Am. Chem. Soc.*, **77**, 3852 (1955); J. K. S. Wan, R. N. McCormick, E. J. Baum, and J. N. Pitts, Jr., *ibid.*, **87**, 4409 (1965).

(19) D. E. Paul, D. Lipkin, and S. I. Weissman, *ibid.*, **60**, 951 (1938).

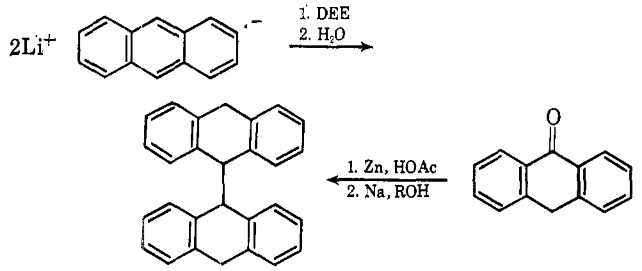
(20) S. Bank and W. D. Closson, *Tetrahedron Letters*, 1349 (1965).

We have found that at relatively high concentrations of lithium anthracene (2×10^{-2} *M*) a solid precipitated which on hydrolysis gave 9,9′,10,10′-tetrahydro-9,9′-dianthryl. This shows that the radical anion does indeed have both radical and anion character, as postulated by Schlenk and Bergmann[21] who, on carbonation of concentrated solution of the radical anion had found a diacid of the following structure.





We have synthesized the tetrahydrodianthryl by an independent procedure and found it to be identical with that obtained from the lithium anthracene anion radical.



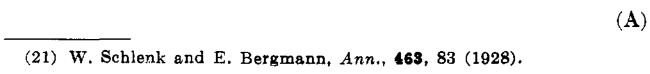
In a typical photolysis experiment on a preparative scale there are obtained, from anthracene and phenyllithium, anthracene (recovered), 80%; 9,10-dihydroanthracene, 17%; and biphenyl, 27%, based on the total number of phenyl groups present at the start as phenyllithium. Photolysis of anthracene in the absence of phenyllithium under the same conditions gave 63% photodimer and 27% recovered anthracene.

Mechanism of Reaction.—A decision had to be made between the two principally different routes: (1) homolytic cleavage of the C–Li bond under photolytic conditions, followed by radical reactions of the phenyl radical and reduction of anthracene by lithium metal, in "*statu nascendi*" (route A) and (2) photosensitization *via* anthracene formally causing a one-electron transfer from the phenyl carbanion to the anthracene (route B).

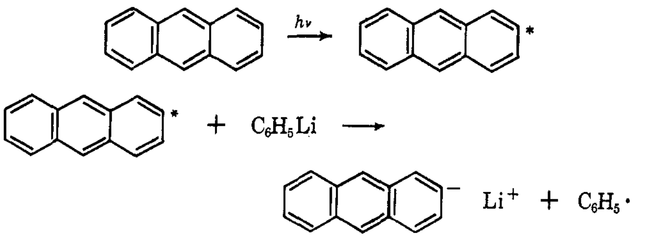
$$C_6H_5Li \xrightarrow{h\nu} C_6H_5\cdot + Li^0$$

$$C_6H_5\cdot + \text{solvent} \longrightarrow C_6H_6$$

$$2C_6H_5\cdot \longrightarrow C_6H_5C_6H_5$$



(A)



(B)

Both these schemes can be written with the phenyllithium as a dimer.[22] This would make more probable the relatively high degree of biphenyl formation. The following points favor the second mechanism. (a) The photolysis of phenyllithium in the absence of anthracene causes only a very slow decomposition. (b) The normal photochemical dimerization of anthracene is almost entirely repressed by the presence of phenyllithium even when this is not in substantial excess. The dimerization process is considered to occur on encounters between singlet-state anthracene and ground-state anthracene. However, the severe geometric restrictions on the transition state lowers the frequency factor for this reaction, whereas the apparent encounter with a phenyllithium molecule causes a fast reaction. (c) Both reaction schemes as written have phenyl radicals as product. Barring the reasonable assumption of dimeric phenyllithium, one would expect the normal radical behavior, *i.e.*, substitution, if the reaction were performed in toluene. The products of this reaction followed by deuterolysis were anthracene, 85% (recovered); 9,10-dideuterioanthracene, 10%; and biphenyl, 26%, based on the total number of phenyl groups from phenyllithium which had reacted. No methyl-substituted biphenyls (the phenyl substitution products on toluene) could be detected. In a second experiment the photolysis of *p*-tolyllithium in the presence of anthracene (in ether) was shown on deuteriolysis to yield anthracene, 81%, recovered partly as the photodimer; 9,10-dideuterioanthracene, 7%; di-*p*-tolyl, 28.2%, based on the total number of tolyl groups introduced; and toluene containing only 20% *p*-deuteriotoluene. This experiment shows clearly that only part of the *p*-tolyl groups give the dimer, whereas the major proportion reacts with the solvent to form undeuterated toluene. (d) The reaction is very slow in the dark and is very solvent dependent.

Experimental Section[23]

Preparation of Lithium Anthracene Radical Anion.—A convenient vessel for the preparation and esr measurements of radical anions is used. It consists of a round-bottomed, 100-ml Pyrex flask connected to a normal quartz tube *via* a sintered-glass plug. The opening to the flask is an inner joint to which can be fitted a vacuum valve which permits either evacuation of the apparatus or filling with an inert gas and also permits the introduction of solvent, lithium metal, or the hydrocarbons.

Example of Photolytic Preparation.—The vessel previously cleaned with organic solvents, chromic acid cleaning solution, and distilled water is dried in an oven (140°) and connected to the vacuum line for evacuation and filling with nitrogen. This process is repeated three times at a minimum, the vessel being

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(21) W. Schlenk and E. Bergmann, *Ann.*, **463**, 83 (1928).

(22) G. Wittig, F. J. Meyer, and G. Lange, *Ann.*, **571**, 167 (1951).

(23) The assistance of Mr. R. Bollinger and Miss U. Feisst is much appreciated.

heated with a hand torch intermittently. The flask is charged with 100 mg of anthracene, 20 ml of ether, and 2–3 ml of approximately 1 *M* phenyllithium solution in diethyl ether, closed, cooled in liquid nitrogen, and evacuated to *ca.* 0.1 mm before the vacuum is closed. The contents are allowed to warm to room temperature, and a small amount of the solution is filtered through the glass plug into the esr tube by cooling. This solution serves the purpose of assuring the removal of trace amounts of moisture of the glass surface. For a measurement it is usually sufficient to filter enough solution into the side tube so that the last 5–10 mm of the tube is filled. The main portion of the flask is covered with aluminum foil, and the esr tube is dipped into a constant-temperature bath kept at 20° containing a high-pressure mercury immersion lamp in such a position that the lamp zone is well introduced into the water and the esr tube is at a distance of *ca.* 10 mm and at a height approximately corresponding to the solution in the tube. The solution is irradiated 1–5 min depending on the intensity of the source. With reasonable sensitivity of the esr spectrophotometer[24] sufficient radical anions remain on the glass walls so that the solution may be emptied out of the esr tube and fresh solvent distilled into the side tube by cooling this in Dry Ice–acetone (caution: the quartz tubes have a tendency to break when cooled in liquid nitrogen if they are filled with solvent). If the solutions are still too concentrated they can readily be diluted by repeating the procedure above and distilling fresh solvent into the tube.

Example of Normal Procedure for Reducing the Aromatic Compound with Lithium Metal.—The flask is charged with 100 mg of anthracene, 20 ml of diethyl ether, and 5–10 very thin slices of lithium metal in a countercurrent of nitrogen. The vessel is closed and evacuated as described above and the solution agitated by a magnetic stirrer until an intense color has developed. A small portion of the solution is filtered into the side tube and the agitation of the main vessel continued. The sample in the esr tube may be diluted either by distillation or by filtration in order to obtain the optimum concentration of the free radical for measurement of the esr spectrum.

Spontaneous Formation of Lithium Anthracene Radical Anion.—To 1.0 g of anthracene in 10 ml of diethyl ether was added 10 ml of 0.85 *M* phenyllithium in diethyl ether. The solution was allowed to stand in the dark for 72 hr, at which time the solution had become red-violet. The esr spectrum obtained from this solution was identical with those obtained from the two above examples.

Phenyllithium and Anthracene in Diethyl Ether. Rates.—A reaction vessel was constructed so that the medium-pressure Hanovia lamp could be surrounded entirely with jackets of different types of glass: high-purity quartz transmitting from the visible to *ca.* 2000 A; Vycor, transmitting from the visible region to 2300 A; and Pyrex, transmitting from the visible region to *ca.* 3000 A. Three identical experiments were performed with the various filters. The starting concentrations in diethyl ether were phenyllithium 0.07 *M*, anthracene 0.035 *M*. Samples were removed at 1-hr intervals and added to excess chlorotrimethylsilane and a known amount of xylene internal standard. The results are depicted in Figure 2.

The work-up was performed by hydrolyzing, extracting with ether, drying the ether layer over calcium chloride, concentrating, and diluting to 100 ml. A 1-ml sample of this solution was analyzed using xylene as internal standard.

Preparative Experiment.—A diethyl ether solution of 1.43 g of anthracene and 32 mmoles of phenyllithium (1:4) was photolyzed with the Hanovia medium-pressure lamp for 5 hr. Hydrolysis and vpc analysis gave the following product distribution: 80% recovered anthracene, 17% dihydroanthracene, and 27% of the phenyl groups present as phenyllithium had been converted to biphenyl.

Preparation of Lithium Anthracene Radical Anion.—A Schlenk tube was charged with 1.0 g of lithium cut into small pieces, 0.5 g of anthracene, and 140 ml of diethyl ether. The solution was shaken for 4 hr and 20 ml of the dark solution was hydrolyzed. The products of this hydrolysis were 9,10-dihydroanthracene, 81%, anthracene, 15%, and an unknown substance, 4%. Part of this solution (100 ml) was mixed in a double Schlenk tube with 0.357 g of anthracene and shaken for 2.5 hr. A sample of the clear solution was hydrolyzed and analyzed: 9,10-dihydroanthracene, 36%, anthracene, 56%, and an unknown substance, 8%. A sample of the precipitate which had formed was hydrolyzed. A solid, mp 260–261°, was filtered and identified by comparison with authentic 9,9′,10,10′-tetrahydro-9,9′-dianthryl. The filtrate contained anthracene and 9,10-dihydroanthracene in molar ratio 1:1.

9,9′,10,10′-Tetrahydro-9,9′-dianthryl.[25,26]—Anthrone (25 g), zinc (15 g, granular), and glacial acetic acid (125 ml) were mixed and heated to boiling; 15 ml of concentrated hydrochloric acid was added dropwise to the boiling solution over 2 hr. The color of the solution turned dark, and then a yellow solid precipitated which was recovered from the hot solution. The solid was washed on the filter with glacial acetic acid, 2 *N* hydrochloric acid, and water. After drying *in vacuo* 8.0 g of yellow 9,9′-dianthryl, mp 298–299°, was obtained.

To 3.5 g of recrystallized 9,9′-dianthryl in 75 ml of boiling amyl alcohol was added 4.6 g of sodium in small portions at a time. The solution changed to red and was hydrolyzed by the addition of 150 ml of 2 *N* hydrochloric acid; the solid precipitating from the organic phase was identified as the title compound, mp 157°, 2.5 g, after recrystallization from xylene.

Anal. Calcd for $C_{28}H_{20}$: C, 93.81; H, 6.19. Found: C, 93.94; H, 6.03.

Phenyllithium and Anthracene in Toluene.—Phenyllithium (50 mmoles) and anthracene (25 mmoles) in 500 ml of toluene and 100 ml of ether were irradiated for 3 hr. Samples taken intermittently showed that the phenyllithium was being consumed in the process of photolysis. The reaction mixture was deuterolyzed by the addition of 3 ml of deuterium oxide. The organic phase was taken to dryness and the anthracene recovered before the mother liquors were chromatographed. There was obtained 85% recovery of anthracene, 10% 9,10-dideuterioanthracene, mp 110°, and 0.976 g of biphenyl, mp 69–70°, 26%, based on the total number of mmoles of phenyllithium which had reacted, and benzene (presumably partly monodeuteriobenzene). Special care was taken to detect any of the methyl-substituted methylbiphenyls, only a trace of which was found.

***p*-Tolyllithium and Anthracene in Ether.**—An ether solution containing 6 g of anthracene and 33 mmoles of *p*-tolyllithium was irradiated with a medium-pressure mercury lamp under nitrogen for 30 min. Hydrolysis was performed by the addition of deuterium oxide. The precipitated anthracene photodimer, 14% of anthracene introduced, was filtered off. From the filtrate was recovered 67% of the anthracene starting material. By careful chromatography over neutral alumina there was obtained 28.2% di-*p*-tolyl, and the toluene isolated by fractional distillation contained 20% *p*-deuteriotoluene. In addition there was obtained *ca.* 7% 9,10-dideuterioanthracene identified by infrared analysis and nmr spectra.

Anal. Calcd for $C_{14}H_{14} = C_{14}H_{10}D_2$: C, 92.26; H, 7.74. Found: C, 92.41; H, 7.40.

In a control experiment the same concentration of anthracene in diethyl ether was irradiated for 30 min. There was isolated 63% anthracene photodimer, and 27% anthracene was recovered.

Registry No.—Naphthalene lithium salt, 4913-80-8; anthracene lithium salt, 10349-28-7; biphenyl lithium salt, 5143-35-1; pyrene lithium salt, 10349-29-8; phenanthrene lithium salt, 10349-30-1; 9,9′,10,10′-tetrahydro-9,9′-dianthryl, 10349-31-2; phenyllithium, 591-51-5; anthracene, 120-12-7; 9,10-dideuterioanthracene, 4484-97-3; biphenyl, 92-52-4; *p*-tolyllithium, 2417-95-0.

Acknowledgment.—The author is indebted to Dr. J. M. Fritsch of the Monsanto Co., Central Research Department, St. Louis, Mo., for his kind cooperation in calculating the theoretical electron spin resonance spectra.

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(24) We wish to express our thanks to Drs. G. Henrici-Olivé and S. Olivé for performing these measurements.

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(26) W. Schlenk and E. Bergman, *Ann.*, **463**, 166 (1928).