Photolytic Alkylation of Aromatic Hydrocarbons Using Alkyllithium Compounds

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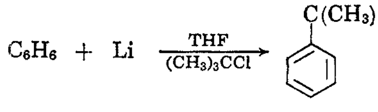
n-Alkyllithium compounds containing from two to ten carbon atoms react under photolytic conditions with anthracene to form 9-alkyl-9,10-dihydroanthracene. In contrast, methyllithium, vinyllithium, and phenyllithium cause only partial reduction of the hydrocarbon. *sec*-Butyllithium undregoes the same alkylation step spontaneously. Photolytic alkylation was observed for naphthalene and phenanthrene but not for biphenyl under the given conditions.

In the course of studying the formation of radical anions photolytically[1b,c] the reaction of butyllithium with anthracene was attempted. It was found that the radical anion was formed, but after hydrolysis an additional oily substance was isolated which was shown to be 9-butyl-9,10-dihydroanthracene.

Recently it has been found that alkyllithium compounds are capable of alkylating aromatic hydrocarbons in hydrocarbon solvents at elevated temperatures,[2] but yields were generally low. Later, better yields were obtained at lower temperatures.[3] The conclusion drawn was that the reactivity of the alkyllithium compound decreased along the series: tertiary > secondary > primary. Whereas tolerable yields of alkylated products were obtained from *t*- and *sec*-butyllithium, primary alkyllithium compounds failed almost entirely to react. In one special instance a condensed aromatic hydrocarbon perylene was alkylated by *n*-butyllithium specifically to give the 1-substituted derivative (13%, using THF as solvent).[4]

Still more recently a perhaps related reaction has been reported.[5] However, the reaction in this instance probably involves the reaction of *t*-butyl chloride with the lithium salt of benzene dianion. Similar reactions

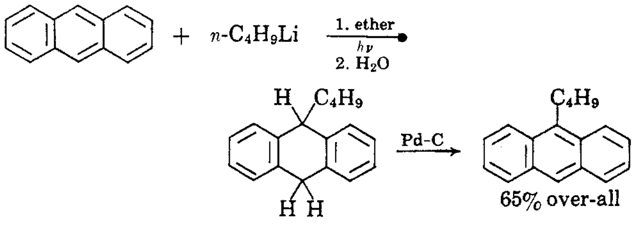


have been studied extensively,[6-10] but in these cases the reaction is most clearly a coupling of an anion radical with an alkyl halide.

Very recent work[11] points toward the possibility of aluminum alkyl compounds adding to aromatic systems in the presence of sodium. The reaction, although similar, does not lead to alkylated aromatics but to mixed aluminum arylalkyls.

Variation in Alkyl Groups

The natural extension to our study of the photolytic production of radical anions[1b] involved the use of alkyllithium compounds. Although radical anions were produced, it soon became evident that other products were formed as well. The most carefully investigated example involved the use of *n*-butyllithium and anthracene. A study of the reaction variables soon led to the most favorable conditions for alkylation, exemplified by the reaction between anthracene and *n*-butyllithium.



Methyllithium.—It was found that methyllithium reacts differently from other alkyllithium compounds in this reaction. No alkylated products were found. Photolysis of a 2:1 molar mixture of methyllithium and anthracene in ether showed only a small extent of reduction to radical anions which on hydrolysis yielded dihydroanthracene. The photodimer was formed in appreciable amounts. On changing to tetrahydrofuran as solvent and photolyzing under the same conditions, much more extensive reduction occurred (37% 9,10-dihydroanthracene was isolated), and the dimerization was suppressed. This result shows that methyllithium in THF acts essentially as phenyllithium in ether.

Ethyllithium.—This alkyllithium compound reacted like *n*-butyllithium. In a typical reaction 9-ethylanthracene was isolated in 74% yield after dehydrogenation of the intermediately recovered 9-ethyl-9,10-dihydroanthracene. The establishment of the structure of this compound will be discussed in a later section.

Vinyllithium.—Vinyllithium as representative for the group of alkenyllithium compounds was prepared by a metal–metal interchange reaction well documented in the literature.[12] Photolysis of anthracene in the presence of the vinyllithium solution, from which the tetraphenyltin had been removed by filtration, caused no apparent change. Work-up showed practially no reaction of anthracene aside from the formation of a trace of 9,10-dihydroanthracene.

***n*-Butyllithium.**—The reaction between anthracene and butyllithium under photolytic conditions has been studied most extensively. In ether as solvent the reaction proceeds smoothly to give 9-butyl-9,10-dihydroanthracene if the reaction mixture is hydrolyzed and 9-butyl-9-hydro-10-deuterioanthracene if deuterolized

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(2) D. H. Fishman, *Dissertation Abstr.*, **25**, 6229 (1965); J. A. Dixon and D. H. Fishman, *J. Am. Chem. Soc.*, **85**, 1356 (1963).

(3) J. A. Dixon, D. H. Fishman, and R. S. Dudinyak, *Tetrahedron Letters*, 613 (1964).

(4) H. Ziegler and J. E. Rosenkranz, *J. Org. Chem.*, **29**, 2469 (1964).

(5) E. P. Kaplan, Z. I. Kazakova, and A. D. Petrov, *Izv. Akad. Nauk USSR*, 537 (1965); *Chem. Abstr.*, **63**, 519 (1965).

(6) D. Weyenberg and L. H. Toporcer, *J. Am. Chem. Soc.*, **84**, 2843 (1962).

(7) D. Weyenberg and L. H. Toporcer, *J. Org. Chem.*, **30**, 943 (1965).

(8) H. Kock and F. Ernst, *Ber.*, **92**, 2732 (1959).

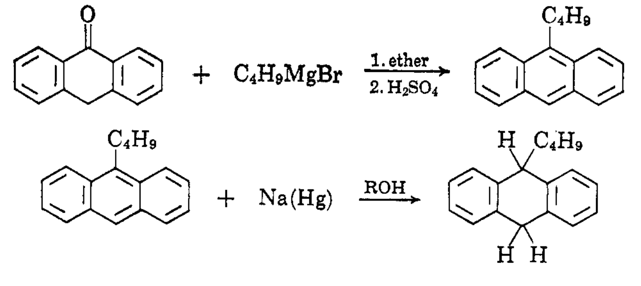
(9) R. Gerdil and E. A. C. Lucken, *Helv. Chim. Acta*, **44**, 1978 (1961).

(10) W. Hückel, J. C. M. Jennewein, and M. Wartini, *Ann.*, **686**, 51 (1965) (a series of 17 publications).

(11) H. Lehmkuhl, *Tetrahedron Letters*, 2817 (1966).

(12) D. Seyferth and M. A. Weiner, *Chem. Ind.* (London), 402 (1959).

(yields ranging from 60 to 80%). Small amounts (6–10%) of 9-butylanthracene were likewise detected in the reaction mixture. The structure of the photolysis product was confirmed by comparison of physical properties with a sample prepared by an unambiguous route.[13] Dehydrogenation of the photolysis product



yielded 9-butylanthracene which was also identical with the independently synthesized sample.

The identity of the samples was established by superimposability of infrared, ultraviolet, and nmr spectra. The benzylic region of the nmr spectra presented in Figure 1 is particularly informative. The integration of all resonance peaks in this region corresponds to three protons for 9-butyl-9,10-dihydroanthracene (I) and two protons for 9-butyl-9-hydro-10-deuterioanthracene (II) when compared with either the aromatic or aliphatic proton regions. The spectrum of I was analyzed to be a composite of a 1:2:1 triplet at τ 6.24 (J = 6.5 cps, combined area corresponding to one proton), and an AB system with intensity ratio *ca.* 0.55:1.45:1.45:0.55 at midpoint, τ 6.14 (J_{AB} = 18 cps, combined area corresponding to two protons); the difference in chemical shift of protons A and B was calculated to be approximately 36 cps. Support for this interpretation was obtained by a decoupling experiment. Figure 1 shows how the triplet at τ 6.24 collapses to a singlet when decoupled to the first methylene of the butyl group. The fact that the protons in the 10 position form an AB system becomes reasonable on inspection of models. One proton is situated toward the inside of the folded molecule whereas the other is on the outside. A similar example has been reported[14] for 9-trimethylsilyl-9,10-dihydroanthracene, which likewise shows an AB system with J_{AB} = 17 cps.

The nmr spectrum of II is also given in Figure 1. Significant is the disappearance of the AB system but the retainment of the 1:2:1 triplet at τ 6.24 (J = 6.8 cps). Again this triplet collapses to a singlet when decoupled to the methylene protons of the butyl group. What remains are two peaks with a difference in chemical shift of approximately 30 cps, in reasonable agreement with the $\Delta\delta$ approximated from the AB system in I. The areas of these two broad singlets are almost equal. This is interpreted to mean that the sample is a 1:1 mixture of two isomers having the deuterium either *cis* or *trans* to the butyl group. In one isomer the deuterium is situated in the position where proton H_A previously was, leaving the proton at the position of H_B. The coupling with the deuterium presumably causes the broad singlet which was not resolved (a 1:1:1 triplet with J_{HD} = ~1–2 cps could have been expected).[15] The other broad singlet is presumably due to an isomer with a proton at the position of H_A and the deuterium at the position previously occupied by H_B.

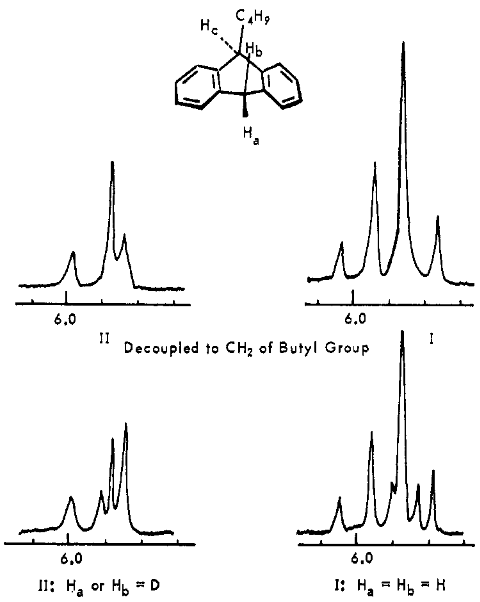
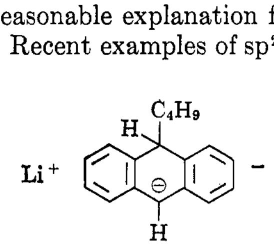


Figure 1.—Benzylic region of nmr spectra of 9-*n*-butyl-9,10-dihydroanthracene.

In contrast 9,10-dihydroanthracene shows only one sharp singlet at τ 6.19. The benzene rings presumably undergo a flip-flap, motion and the average chemical shift is observed in this compound at room temperature. A sample of 9,10-dideuterioanthracene was obtained by deuterolysis of the reaction mixture obtained on photolysis of a mixture of anthracene and phenyllithium in ether.[1] This compound had an nmr showing a broader singlet at τ 6.16. It was possible to show that this singlet is in reality a 1:1:1 triplet (J_{HD} = 2.2) by high-resolution techniques on a 100-Mc instrument.[16] The mass spectra of I and II agreed with this interpretation both in so far as molecular ion peaks and cracking patterns are concerned.[17] The chemical consequence of the interpretation of these spectra is that the 9-butyl-9-hydro-10-deuterioanthracene is formed from an organolithium intermediate which gives equal amounts of the two possible deuterium isomers. If one postulates that the organolithium compound contains an sp²-hybridized carbon in the 10 position, a reasonable explanation for the observed facts is found. Recent examples of sp²-hybridized carbon atoms in benzylic organolithium compounds are available.[18]



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(13) A. Sieglitz and R. Marx, *Ber.*, **56**, 1621 (1923).

(14) H. Gilman and O. Marrs, *J. Org. Chem.*, **27**, 1879 (1962).

(15) C. G. MacDonald, J. S. Shannon, and S. Sternhell, *Australian J. Chem.*, **17**, 38 (1964).

(16) With thanks to Mr. Märki of the Varian Laboratories, Zürich.

(17) Many thanks to Drs. Jackson, D. R. Beasecker, and C. H. Dungan, Monsanto Central Research Department, St. Louis, Mo., for the measurements of the mass spectra.

(18) R. Waack, M. A. Doran, E. B. Baker, and G. A. Olah, *J. Am. Chem. Soc.*, **88**, 1272 (1966).

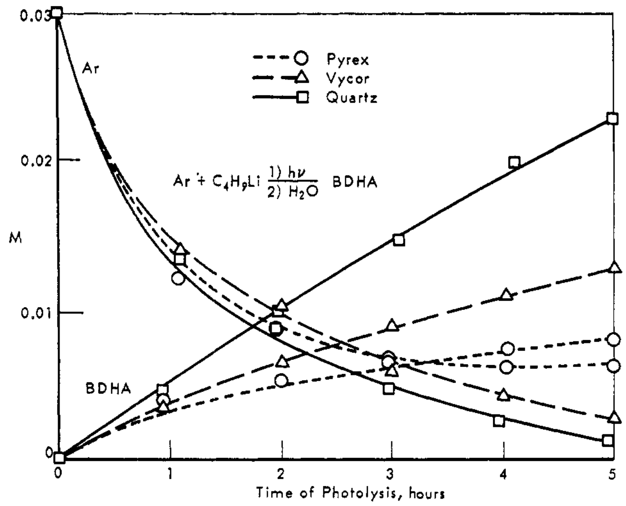

Figure 2.—Variation in concentration of anthracene (Ar) and 9-butyl-9,10-dihydroanthracene (BDHA) with time of photolysis using Pyrex, Vycor, and quartz filters.

***n*-Decyllithium.**—The use of decyllithium in the photolytic alkylation of anthracene bore the promise of showing what the fate of the alkyl groups from the organolithium compounds was. The normal product, 9-decyl-9,10-dihydroanthracene, was obtained in good yield from this reaction. The structure of this compound was confirmed by comparison of infrared and ultraviolet spectra with those of 9-*n*-butyl-9,10-dihydroanthracene. The product obtained by dehydrogenation was in similar fashion shown to be 9-decylanthracene.

In a separate experiment the crude photolysis product was carboxylated. Aside from undecanoic acid and the corresponding ketone, there was isolated a 10:1 mixture of decane and decene-1 (*ca.* 19% decyllithium had been consumed to give these products).

***sec*-Butyllithium.**—Using specialized techniques it was possible (see Experimental Section) to prepare *sec*-butyllithium in ether. This organolithium compound reacted instantaneously with anthracene in the absence of light to give 9-*sec*-butyl-9,10-dihydroanthracene, which was identified by analysis and comparison of physical properties and spectra with the isomeric *n*-butyl compound.

Variation in Solvent

The importance of the solvent is striking in the case of *sec*-butyllithium which in ether underwent reaction very rapidly even at 0° to give 9-*sec*-butyl-9,10-dihydroanthracene in good yields, compared with the reaction conditions for the dark reaction in hydrocarbon solvent for 41 hr at 160°.[2] When the reaction was performed in hexane under similar conditions to those used with ether (ultraviolet source and time of photolysis), 96% of the anthracene was recovered on hydrolysis. In benzene under similar conditions a 13% yield of 9-butyl-9,10-dihydroanthracene was obtained (in ether 60–80% had been isolated).

Variation in Hydrocarbon

A series of four parallel photolyses were performed employing anthracene, phenanthrene, naphthalene, and biphenyl in ether containing *n*-butyllithium. It was found that the reactivity of the hydrocarbons decreased in the following order: anthracene > phenanthrene > naphthalene > biphenyl. This may be a consequence of the difference in the ultraviolet spectra (relative to the high-pressure mercury emission spectrum) or of the variation in electron affinity of these hydrocarbons.[1b]

From phenanthrene there was obtained 45% 9-butyl-9,10-dihydrophenanthrene containing *ca.* 30% 9-butylphenanthrene. This compound was identified by its ultraviolet, infrared, and nmr spectra.

Naphthalene reacted slower under comparable conditions to give a 2:1 mixture of compounds indentified by their infrared, ultraviolet, and nmr spectra to be 1-butyl-1,2-dihydronaphthalene and 2-butylnaphthalene (combined yield 30%; 56% naphthalene was recovered). Dehydrogenation of a portion of the crude product gave a 2:1 mixture of 1-butylnaphthalene and 2-butylnaphthalene. The butylnaphthalenes were prepared by independent routes and compared with those obtained from the photoalkylation. The dihydro derivative was identified by its nmr and ultraviolet spectrum (see Experimental Section). Under identical conditions biphenyl was only consumed to *ca.* 16% after 4-hr photolysis in ether in the presence of butyllithium, and no alkylated biphenyl could be detected.

Elucidation of Mechanism

The photolytic alkylation of anthracene by butyllithium was chosen as a standard reaction since it proceeded to one reasonably pure product at a convenient rate.

Electron Spin Resonance.—Samples were removed at various times of photolysis and the esr spectra of any radicals present in these samples measured. Although there was a steady increase in intensity of the spectrum, the free radical in the solution was identified to be pure lithium anthracene radical anion[1b,c] throughout the time of the photolysis. This important observation shows that the product of hydrolysis, 9-butyl-9,10-dihydroanthracene, does not result from a radical-anion intermediate related to 9-butylanthracene.

Influence of Wavelength of Irradiation.—Figure 2 depicts the results of three experiments in which 0.030 *M* solutions of anthracene in ether 0.12 *M* in *n*-butyllithium were exposed to light from a medium-pressure lamp filtered through quartz (transparent to 200 mμ), Vycor (transparent to 230 mμ), and Pyrex (transparent to 300 mμ). Although the anthracene consumption does not appear to vary significantly with the difference in wavelength of irradiation, the increase in concentration of 9-butyl-9,10-dihydroanthracene is decidedly more rapid for the unfiltered light and intermediate when the region 200–230 mμ is excluded. An exact study of the variation in quantum yield with wavelength of irradiation will be decisive in elucidating the details of the photolytic process.

Rate Studies.—Under carefully controlled conditions (constant temperature, 15°, and constant intensity of irradiation) it was possible to follow the rate of the reaction by the increase in product (of hydrolysis) formation (Table I). These data do not take into account the parallel consumption of anthracene by the formation of the radical anion. A sample of the evaluation of the order of the reaction (exclusion of second- and third-order processes) is given in Figure 3.

TABLE I

RATES OF PHOTOALKYLATION

$$\underset{a-x}{C_4H_9Li + \text{anthracene}} \xrightarrow[2.\ H_2O]{1.\ h\nu} \underset{x}{\text{BDHA}^a}$$

Initial concn, M		Molar	$k_1 \times 10^4$
C_4H_9Li	Anthracene	ratio	sec^{-1}
0.135	0.0268	5:1	1.74
0.216	0.0265	8:1	1.83
0.109	0.0267	4:1	1.81
0.050	0.0247	2:1	0.63
0.054	0.0128	4:1	2.00

[a] BDHA = 9-butyl-9,10-dihydroanthracene; temperature 15°; solvent, diethyl ether; $k_1t = \ln a/(a - x)$.

The conclusions drawn from the rate data are (1) the specific rate of product formation is approximately inversely proportional to the anthracene concentration; (2) the formation of 9-butyl-9,10-dihydroanthracene obeys a first-order rate law; (3) the rate of product formation decreases markedly below a molar ratio of 2:1 for butyllithium/anthracene; (4) the rate of by-product formation (dialkylation) is directly proportional to the butyllithium concentration.

Two inherently different schemes may be postulated for the reaction, mechanisms A and B.

Mechanism A

$$C_4H_9Li + C_{14}H_{10} \xrightarrow{h\nu} [C_{14}H_{10}]\cdot^-Li^+ + C_4H_9\cdot$$

$$[C_{14}H_{10}]\cdot^-Li^+ + C_4H_9Li \xrightarrow[\text{or}\ h\nu]{\text{dark}} Li^0 + [C_4H_9C_{14}H_{10}]^-Li^+$$

In this case the lithium anthracene radical anion is postulated as an intermediate in the formation of 9-butyl-9-hydro-10-lithioanthracene, $Li^+ [C_4H_9C_{14}H_{10}]^-$.

Mechanism B

$$C_4H_9Li + C_{14}H_{10} \xrightarrow{h\nu} Li^+[C_{14}H_{10}]\cdot^- + C_4H_9\cdot$$

$$C_4H_9Li + C_{14}H_{10} \xrightarrow{h\nu} [C_4H_9C_{14}H_{10}]^-Li^+$$

This scheme involves two different photochemical reactions of anthracene.

Anthracene has been observed to copolymerize with butadiene. Analysis of the spectra of these copolymers indicates that anthracene was incorporated across the 9,10 position.[19] Recently anthracene has been used as a scavenger of benzyl radicals.[20] The products of the reactions were mainly dimeric in nature and not, as in this case, monomeric organolithium compounds. It is unlikely that the 9-butyl-9,10-dihydroanthracene is formed by independent attack of a free butyl radical on a separate anthracene molecule, but a concerted radical attack during one-electron transfer is conceivable.

To test mechanism A, lithium anthracene radical anion was prepared by an independent route and allowed to react both in the dark and under photolytic conditions with butyllithium. In the dark a very slow reaction did occur, but the rate was far from comparable with that of the photolytic alkylation. Under the influence of ultraviolet irradiation, however, the reaction to produce 9-butyl-9,10-dihydroanthracene did occur, but 9,10-dihydroanthracene was formed to a much larger extent than under normal photolytic alkylations. It thus appears more reasonable that it is the anthracene formed in the following equilibrium which is reacting with the butyllithium.

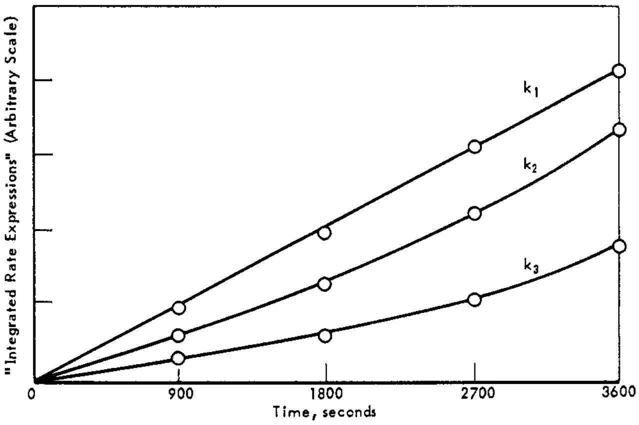

Figure 3.—Determination of order of photolytic alkylation reaction.

$$2[C_{14}H_{10}]\cdot^-Li^+ \rightleftarrows [C_{14}H_{10}]^{2-}2Li^+ + C_{14}H_{10}$$

Finally, the possiblility that the photodimer of anthracene was formed initially and that this was an intermediate was rejected by demonstrating the inertness of the photodimer to butyllithium both in the dark and under photolytic conditions.

It is thus most reasonable to suggest that two different photolytic reactions of anthracene occur (mechanism B). Evidence for this is apparent in the faster rate of removal of anthracene (on a molar scale) than the rate of formation of butyldihydroanthracene. The first-order dependency in anthracene (triplet excited) is also in accord with this proposal, as is the apparent dependency of the rate of reaction on the butyllithium concentration at ratios of butyllithium/anthracene below 2:1. The lack of an initiation period disfavors the scheme involving the radical anion as an intermediate (mechanism A).

The main difference in reaction between aryl- and alkyllithium reagents may have its origin in a difference in oxidation potential of the two types of C–Li bonds but also in the increased activity (lower selectivity) of the phenyl radical compared to the methyl and larger alkyl radicals; on a relative reactivity scale the radicals may be arranged as follows: $\cdot C_6H_5$, +4.0; $\cdot CH_3$, 0.0; $\cdot C_3H_7$, −3.0.[21]

Experimental Section

Gas Chromatography.—The purity of the liquid samples isolated in the following experiments was checked by gas chromatographic analysis at the appropriate temperatures using silicone rubber, Carbowax, Apiezon L, and Bentone–didecyl phthalate as liquid phases.

Photolysis of Methyllithium in the Presence of Anthracene.—Methyllithium was prepared from methyl iodide and lithium in diethyl ether. The concentration was found to be 0.375 M by double titration (residual base determined with ethylene bromide). Photolysis of 66 mmoles of methyllithium and 33 mmoles of anthracene in 660 ml of diethyl ether with a water-cooled high-pressure mercury lamp (Heraeus Q 700) for 3, 5, 8, and 12 hr and analyzing using biphenyl as internal standard gave the following amounts (milligrams/milliliter) of anthracene and dihyroanthracene, respectively, in solution after hydrolysis

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(19) C. S. Marvel and W. S. Anderson, *J. Am. Chem. Soc.*, **75**, 4600 (1953).

(20) R. O. C. Norman and W. A. Waters. *J. Chem. Soc.*, 950 (1957).

(21) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Pergamon Press Ltd., London, 1958, p 37.

[hours of photolysis (yields)]: 0 (8.9, 0); 3 (3.50, 0.40); 5 (3.50, 0.43); 8 (2.78, 0.47); and 12 (2.62, 0.47).

The reaction mixture was hydrolyzed and the solid precipitate, bianthryl, mp 260–270°, 1.30 g, was filtered off. From the filtrate 1.70 g of anthracene, mp 207–208°, and 2.1 g of a mixture of anthracene and dihydroanthracene were recovered.

The experiment was repeated using the Hanovia medium-pressure lamp and a 0.1 *M* methyllithium and 0.05 *M* anthracene solution in diethyl ether. After 3 and 5 hr of irradiation the amounts of 9,10-dihydroanthracene and anthracene were 0.238, 0.244 and 3.51, 3.50 mg/ml, respectively. The corresponding amounts in the beginning were 0 and 8.6 mg, respectively. The bianthryl isolated after hydrolysis taken together with the anthracene and dihydroanthracene agreed with the amount of anthracene originally present in the reaction solution.

Methyllithium and Anthracene in Tetrahydrofuran.—The experiment described for diethyl ether was repeated using tetrahydrofuran as solvent and the aliquots were analyzed using biphenyl as internal standard giving the following yields of 9,10-dihydroanthracene and anthracene, respectively [hours of photolysis (yields)]: 0 (0, 8.9); 3 (1.19, 3.87); 4 (1.82 3.80); 5 (2.38, 2.89); 6 (2.47, 2.83); and 7 (2.45, 2.38).

On hydrolysis there was isolated 43% anthracene, 37% 9,10-dihydroanthracene, and no anthracene photodimer.

Ethyllithium and Anthracene in Ether.—To 66 mmoles of ethyllithium in 660 ml of ether was added in three portions a total of 5.6 g of anthracene over 2 hr. During the addition period the solution was photolyzed. Samples removed at various time intervals were analyzed by the internal standard technique, giving (milligram/milliliter) the following yields of anthracene and 9-ethyl-9,10-dihydroanthracene [hours of photolysis (yields)]: 0 (8.5, 0); 3 (3.6, 1.6); 4 (2.5, 2.3); 5 (2.5, 2.2); 6 (33 mmoles of ethyllithium was added) (1.5, 3.5); and 7 (1.1, 3.7). Work-up was effected as usual giving 11% recovered anthracene and an oil distilled at 110° (0.08 mm).

Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.46; H, 7.50.

The oil was dehydrogenated in boiling mesitylene using palladium-on-carbon catalyst to give 74% 9-ethylanthracene, bp 170° (0.05 mm).

Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 92.59; H, 7.29.

Vinyllithium and Anthracene.—To an ether solution containing 2.01 g of tetravinyltin was added 20 ml of 1.77 *M* salt-free phenyllithium dropwise. The reaction mixture was stirred at room temperature for 1 hr before the tetraphenyltin was filtered off, and the vinyllithium solution (containing 35.4 mmoles of vinyllithium) was added to a total of 610 ml of ether in which 3.15 g of anthracene had been dissolved. During the 4-hr photolysis the solution did not change appreciably. On hydrolysis 1.70 g of anthracene photodimer was filtered off and from the filtrate was recovered 1.40 g of anthracene and a trace of dihydroanthracene.

Butyllithium and Anthracene in Ether.—A total of 5.6 g of anthracene was added in three equal portions to a mixture of 565 ml of diethyl ether and 95 ml of 1.47 *M* butyllithium. The reaction mixture was irradiated with a water-jacketed high-pressure lamp. After 4-hr irradiation a sample was removed for measurement of the esr spectrum of lithium anthracene radical anion. The work-up was performed by hydrolysis, removal of the 30% recovered anthracene partly as photodimer, and distillation of the remaining oil at 115° (0.03 mm). The distillate was a 10:1 mixture of 9-butyl-9,10-dihydroanthracene and 9-butylanthracene in 60 and 6% yields, respectively, based on introduced anthracene.

The experiment was repeated but samples were removed and analyzed by hydrolysis and addition of a given amount of biphenyl as internal standard, giving (milligram/milliliter) the following yields of anthracene and BDHA (9-butyl-9,10-dihydroanthracene) [hours of photolysis (yields)]: 0 (8.8, 0); 3 (3.82, 3.08); 4 (2.20, 3.17); 5 (2.03, 4.07); and 6 (1.42, 4.17).

The reaction mixture was worked up by hydrolysis and concentration followed by trituration with hexane to yield 15% recovered anthracene and an oil which was chromatographed from neutral alumina. The similar fractions were combined and distilled to give 60% BDHA and 6% 9-butylanthracene.

A second experiment was performed using 140 mmoles of butyllithium and 33 mmoles of anthracene in 660 ml of absolute ether. The reaction was again followed by the standard technique. The work-up of the main portion of the reaction mixture by deuterolysis gave a 12% recovery of anthracene and 50% yield of purified 9-butyl-9-hydro-10-deuterioanthracene, bp 120° (0.005 mm). Anthracene and BDHA, respectively (milligram/milliliter) were formed as follows [hours of photolysis (yields)]: 0 (9.0, 0); 3 (3.1, 4.5); 4 (2.2, 4.2); 5 (1.5, 4.8); and 6 (1.4, 5.7).

Anal. Calcd for $C_{18}H_{19}D$: C, 91.08; H, 8.91. Found: C, 91.09, 91.17; H, 8.87, 8.77.

Preparation of 9-Butyl-9,10-dihydroanthracene.—The procedure by Sieglitz and Marx[13] was followed closely. The product from the reaction of anthrone with butylmagnesium bromide was recrystallized from ethanol, 9-butylanthracene, mp 49–50°, picrate mp 80–82°.

Reduction of this compound with sodium amalgam and ethanol gave the desired 9-butyl-9,10-dihydroanthracene, a viscous liquid, bp 120–125° (0.1 mm).

A sample of 9-butyl-9,10-dihydroanthracene prepared by photolysis was dehydrogenated using palladium-on-carbon catalyst in boiling mesitylene. The product, bp 150–155° (0.1 mm), had identical retention time (also as mixed vpc on silicone rubber) as the synthetic 9-butylanthracene, mp 46–48°; mixture melting point was not depressed; picrate melting point was 76–78°.

Rates of Photolysis Reactions.—The water circulating in the photolysis apparatus was maintained at 15° using a thermostatic bath. A mixture of 0.415 g of biphenyl (internal standard), 0.792 g of anthracene, and 9 mmoles of butyllithium in a total of 180 ml of ether were exposed to the medium-pressure lamp; 1-ml aliquots were removed with 15- or 30-min intervals and analyzed by vpc techniques using separatedly determined response factors.

Dependence of Rate on Wavelength of Irradiation.—Three experiments were performed using 19.5 mmoles of butyllithium and 4.8 mmoles of anthracene in a total of 160 ml of ether and irradiating with the same source of light but using filters made out of quartz, Vycor, and Pyrex glass with the relative cutoffs at 200, 230, and 300 mμ, respectively. The results are summarized in Figure 2.

Lithium Anthracene Radical Anion and Butyllithium.—The lithium salt of the radical anion of anthracene was prepared *via* the dilithio salt and the hydrocarbon in equimolar amounts. A solution containing 30 mmoles of this salt was treated with 32 mmoles of butyllithium. A small sample was removed and placed in the dark. During the subsequent photolysis samples were taken with 1-hr intervals and analyzed by the standard vpc techniques. By filtration of the hydrolysate there was obtained 22% of a compound which was probably 9,9′-dianthryl, mp 238–240°, remelts at 205–206°, and does not depress the melting point of anthracene after the first remelt. The other components of the reaction mixture were 9,10-dihydroanthracene, 23%; anthracene, 20% recovered; 9-butyl-9,10-dihydroanthracene, 27%.

Preparation of 9-Butylanthracene by Photolysis and Dehydrogenation.—Anthracene (5.6 g added in three portions with 1-hr intervals of photolysis in between) and 95 ml of 1.6 *M* butyllithium (in hexane) in a total of 565 ml of ether was photolyzed for 3 hr (1.69 mg/ml of anthracene and 1.84 mg/ml of BDHA). After standing overnight (1.87 and 2.11 mg/ml, respectively) an additional 50 ml of butyllithium was added and photolysis was continued for 3 hr (0.93 and 4.45 mg/ml of anthracene and BDHA, respectively) and 3 hr more (final analysis: 0.4 and 3.2 mg/ml, respectively). Work-up by hydrolysis, concentration, and direct dehydrogenation by the use of palladium on carbon in boiling mesitylene yielded 12% recovered anthracene and 65% isolated 9-butylanthracene, bp 136–140° (0.07 mm).

Butyllithium and Anthracene in Hexane.—Photolysis of a solution of 5.7 g of anthracene and 24 mmoles of butyllithium in 160 ml of purified hexane for 4.5 hr and decomposition with water yielded 93% recovered anthracene, mp 205–206°.

In Benzene (0.2 and 0.1 *M*).—The experiment was repeated using the same amounts but benzene as solvent. There was obtained 1% photodimer, 90% recovered anthracene, and 4% each of 9-butylanthracene and 9-butyl-9,10-dihydroanthracene, after 5 hr of photolysis with the medium-pressure lamp.

A large-scale experiment in more dilute solution was performed photolyzing a benzene solution 0.1 *M* in butyllithium and 0.05 *M* in anthracene for 5 hr. The compounds obtained were 25% photodimer, 51% recovered anthracene, 7% 9-butylanthracene, 13% 9-butyl-9,10-dihydroanthacene, and 2% 9,10-dihydroanthracene.

In a control experiment a mixture of butyllithium and anthracene was kept in the dark and agitated by bubbling a current of nitrogen through the solution for 3 hr. Work-up of the solution yielded a 94% recovery of anthracene and only a trace of 9-butylanthracene.

Preparation of *sec*-Butyllithium in Ether.—In a steel crucible, equipped with a metal lid and a high-speed stirrer, was placed under argon 50 ml of paraffin oil, 0.1 g of sodium, and 4.3 g of lithium, and 1 drop of oleic acid as emulsifier. The oil was heated on a hot plate to 220° and the high-speed stirrer (Ultra Turrax) was started. The crucible was cooled and the stirrer flushed with ether. A total of 200 ml of ether was used for washing the paraffin oil off the lithium metal which was then transferred to a three-necked reaction vessel. This had been charged with 75 ml of ether during the transfer process. Now 13.3 ml of *sec*-butyl bromide in 25 ml of ether was added dropwise to the reaction vessel cooled in Dry Ice–acetone. The inner temperature was $-55°$ during the 2-hr addition time. The reaction mixture was kept cold during 16 hr before removal of aliquots for the double titration, 0.3 M.

***sec*-Butyllithium and Anthracene.**—Using the freshly prepared solution of *sec*-butyllithium in diethyl ether, three parallel experiments were performed.

A.—To 178 mg of anthracene in 25 ml of ether was added 10 ml of 0.25 M *sec*-butyllithium. A green color developed during the first seconds of the reaction. Samples were taken after 5 and 30 min. The ratios of anthracene/butyldihydroanthracene in these two samples were 0.68 and 0.52, respectively.

B.—The experiment described under method A was repeated, but the temperature was kept at 0° and samples were taken at 5, 30, 65, and 120 min after mixing. The ratio of anthracene/butyldihydroanthracene changed as follows: 1.79, 0.54, 0.91, 0.57.

C.—Same conditions as in method A but the double amount of butyllithium was used. After 5- and 30-min reaction time at room temperature the ratio of anthracene/butyldihydroanthracene changed from 0.225 to 0.179.

The products from the reactions A, B, and C were combined and worked up to give, aside from recovered anthracene, 9-*sec*-butyl-9,10-dihydroanthracene, bp 120° (0.05 mm).

Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.35; H, 8.63.

The compound was identified as 9-*sec*-butyl-9,10-dihydroanthracene by comparison of its infrared and ultraviolet spectra with those of the *n*-butyl isomer.

***n*-Decyllithium and Anthracene in Ether.**—A solution (660 ml) containing 5.6 g of anthracene and 66 mmoles of *n*-decyllithium was photolyzed under the standard conditions and samples were taken, yielding anthracene and 9-decyl-9,10-dihydroanthracene (in milligrams/milliliter), respectively: 0 (8.5, 0); 3 (2.8, 2.7); 4 (1.7, 3.1); 5 (1.9, 3.4); and 6 hr (1.4, 3.2). Hydrolysis was performed after 6 hr of photolysis to give 27% recovered anthracene. The mother liquors were carefully distilled to give a large ether fraction and 5.6 g of decane containing 2–3% decene-1. The residue was chromatographed from neutral alumina to yield poorly separated 9-decylanthracene and 9-decyl-9,10-dihydroanthracene mixtures. A sample of such a mixture was dehydrogenated to give a viscous oil, bp 170° (0.001 mm).

Anal. Calcd for $C_{24}H_{30}$: C, 90.51; H, 9.49. Found: C, 90.35; H, 9.60.

Repeat of Decyllithium Experiment (Carbonation).—The experiment was repeated with a solution containing 17.5 mmoles of anthracene and 70 mmoles of decyllithium which was photolyzed for 6 hr. After 3 hr a 10-ml sample was removed and poured onto Dry Ice. The ether layer was extracted with 10% sodium hydroxide and analyzed on a Carbowax column. It contained 3.58 mg of decane and 0.27 of decene-1/milliliter. After complete photolysis the entire solution was poured onto Dry Ice and a sample analyzed as before. The solution now contained 4.99 mg of decane and 0.35 of decene-1/milliliter. The organic phase was extracted with 10% aqueous sodium hydroxide. Careful fractionation of the ether phase gave a prefraction consisting of ether and ethanol, whereas the next fraction, 1.8 g, was identified by vpc to be a mixture of decane and decene-1, *ca.* 10:1 (13 mmoles out of 70 mmoles was used up in this way!). The mother liquors gave 0.3 g of didecyl ketone, mp 65–66°. The alkaline extracts were acidified and extracted with ether. The extracts were dried over sodium sulfate and concentrated and distilled: bp 120° (0.15 mm), undecanoic acid, $n^{25}{}_{\mathrm{D}}$ 1.4295 (lit.[22] 1.4294), 16–20 mmoles out of 70. The residue from the distillation did not give the expected 9-decyl-9,10-dihydroanthracene-10-carboxylic acid in crystalline form.

Photodimer and Butyllithium.—A slurry of anthracene photodimer, 0.443 g in 45 ml of ether, was treated with 10 mmoles of butyllithium for 3 hr. There was no visible change, and a sample of the slurry did not show any BDHA or anthracene. The solution was then photolyzed for 3 hr again with no visible change nor any detectable products in the vpc. After hydrolysis the photodimer was recovered without change.

Butyllithium and Naphthalene in Ether.—Naphthalene (3.6 g) and butyllithium, 100 ml (1.24 M) in 550 ml of diethyl ether, was irradiated for 7 hr while samples were removed and analyzed by use of biphenyl as internal standard, yielding naphthalene and butyldihydronaphthalene (milligrams/milliliter), respectively [hours of photolysis (yields)]: 0 (5.5, 0); 3 (5.1, 0.8); 4 (3.4, 1.3); 5 (3.4, 1.3); 6 (4.3, 1.6); and 7 (3.8, 1.5).

Hydrolysis yielded a 56% recovery of naphthalene and a viscous oil which was distilled, 60° (0.05 mm). Two major components were recognized in the distillate. These were collected by vpc techniques in *ca.* 20 and 10% yields, respectively, based on naphthalene.

Anal. Calcd for $C_{14}H_{18}$ (component A, 1-butyl-1,2-dihydronaphthalene): C, 90.26; H, 9.74. Found: C, 90.07; H, 9.80.

The ultraviolet spectrum in hexane showed $\lambda_{\max}$ 262 mμ (log ϵ 3.81); nmr,[16] τ 2.8–3.3 (4 aromatic H); 3.6, one vinylic proton (position 4), two doublets coupled to the other vinylic proton, $J_1 \sim 5$ cps, established by decoupling experiment; 4.2, multiplet from the second vinylic proton (position 3) likewise coupled to the first vinylic proton, $J_2 \sim 6$ cps, the multiplet collapsed to the high-field doublet of an AB system when decoupled to the allylic protons; 4.7, one benzylic proton (position 1), multiplet not affected by decoupling to the vinylic proton; 7.5–7.9, two allylic protons (position 2), complex pattern coupled to the second vinylic proton, but still complex pattern when decoupled to the proton at position 3; 8.2–8.9, six methylene protons; and 9.0–9.3, three methyl protons. The pattern substantiated the structure of the compound as 1-*n*-butyl-1,2-dihydronaphthalene and could not be assigned to the other isomers.

Anal.. Calcd for $C_{14}H_{16}$ (component B, 2-butylnaphthalene): C, 91.25; H, 8.75. Found: C, 90.83; H, 9.15.

An 0.2-g sample of a mixture of component A and B was dehydrogenated using palladium-on-carbon catalyst in mesitylene solvent. The product was distilled at 120° (0.01 mm).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.18; H, 8.80.

The ultraviolet spectrum showed $\lambda_{\max}$ 276 mμ (log ϵ 3.91), 305 (2.87), and 319 (2.84, hexane). A Bentone column (350 cm, 5% Bentone–5% didecyl phthalate on Chromosorb W, 180°) separated 1-butylnaphthalene and 2-butylnaphthalene. The dehydrogenated sample was shown to be a 2:1 mixture of 1-butyl- and 2-butylnaphthalene, whereas the dihydro derivative on dehydrogenation produced 82% 1-butyl- and 6% 2-butylnaphthalene.

Prepartion of 1-Butyl- and 2-Butylnaphthalene.—The 1 isomer was prepared by standard procedures from α-tetralone and *n*-butylmagnesium bromide *via* the dehydrated product which was dehydrogenated with sulfur: bp 96–98° (0.1 mm), $n^{20}{}_{\mathrm{D}}$ 1.5809; ultraviolet spectrum, $\lambda_{\max}$ 283 mμ (log ϵ 3.83, hexane) [lit.[23] bp 141.5 (12 mm), $n^{20}{}_{\mathrm{D}}$ 1.58993].

2-Butylnaphthalene was likewise prepared by standard procedures from 2-bromonaphthalene *via* halogen–metal interconversion with butyllithium at low temperature and reaction with butyraldehyde. The secondary alcohol was reduced with platinum in acetic acid to 2-butylnaphthalene: bp 120–122° (0.1 mm), $n^{20}{}_{\mathrm{D}}$ 1.5678; ultraviolet spectrum, $\lambda_{\max}$ 275 mμ (log ϵ 3.68, hexane) [lit.[23] bp 133° (5 mm), $n^{20}{}_{\mathrm{D}}$ 1.57774].

Butyllithium and Naphthalene in Hexane (0.1 and 0.05 M).—The solution defined in the title was irradiated with the medium-pressure lamp for 4 hr. The color of the solution changed to dark yellow. Work-up yielded a 90% recovery of naphthalene.

Butyllithium and Phenanthrene in Ether.—To 547 ml of absolute ether was added 112.6 ml of 1.24 M butyllithium and 5.9 g

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[22] H. Lange, "Handbook of Chemistry," 9th ed, Sandusky, Ohio, 1956.

[23] H. Luther and G. Wächter, *Ber.*, **82**, 161 (1949).

of phenanthrene (in three portions with 1-hr intervals in between). Samples were analyzed during the photolysis, yielding phenanthrene and 9-butyl-9,10-dihydrophenanthrene (milligrams/milliliter) [hours of photolysis (yields)]: 0 (9.0, 0); 3 (5.2, 1.5); 4 (5.1, 1.9); 5 (4.8, 2.0); 6 (4.1, 1.9); and 7 (4.1, 2.4).

After a total of 6.75 hr of photolysis the reaction mixture was hydrolyzed and worked up by column chromatography (neutral alumina) after distillation: bp 122° (0.005 mm). By collection from a gas chromatograph (silicone rubber) there was obtained two liquid compounds pure, the amounts constituting yields of 45% *based on starting phenanthrene.*

Anal. Calcd for $C_{18}H_{20}$ (constituent A (*ca.* 60%), 9-butyl-9,10-dihydrophenanthrene): C, 91.47; H, 8.53. Found: C, 91.41, 91.47; H, 8.56, 8.59.

The ultraviolet spectrum in heptane showed λ_{max} 261 mμ (log ϵ 4.58), 299 sh (3.5), 270 (4.5), 253 (4.50), and 241 (4.45).

Anal. Calcd for $C_{18}H_{18}$ (constituent B (*ca.* 30%), 9-butylphenanthrene): C, 92.26; H, 7.74. Found: C, 92.15; H, 7.78.

The ultraviolet spectrum in heptane showed λ_{max} 253 mμ (4.80), 297 sh (4.2), 284 (4.0), 277 (4.2), 247 (4.7), 224 (4.4), and 214 (4.6).

Constituent C could be a butylphenanthrene with the butyl group in the A ring (*ca.* 10% of mixture).

Registry No.—Methyllithium, 917-54-4; ethyllithium, 811-49-4; vinyllithium, 917-57-7; *n*-butyllithium, 109-72-8; *n*-decyllithium, 4416-59-5; *sec*-butyllithium, 598-30-1; anthracene, 120-12-7; 9,10-dihydroanthracene, 613-31-0; 9-ethyl-9,10-dihydroanthracene, 605-82-3; 9-ethylanthracene, 605-83-4; 9-butylanthracene, 1498-69-7; 9-*sec*-butyl-9,10-dihydroanthracene, 10394-54-4; 9-decyl-9,10-dihydroanthracene, 10394-55-5; naphthalene, 91-20-3; 1-butyl-1,2-dihydronaphthalene, 10394-56-6; 2-butylnaphthalene, 1134-62-9; phenanthrene, 85-01-8; 9-butyl-9,10-dihydrophenanthrene, 10406-91-4; 9-butylphenanthrene, 10394-57-7; 9-butylanthracene picrate, 10394-58-8; lithium anthracene, 10349-28-7; I, 10394-60-2; *cis* II, 10394-61-3; *trans* II, 10394-62-4.

Quaternary Benzylammonium Ion Rearrangements with Organolithium Compounds. III. Dimethyldibenzylammonium Chloride Reaction with *n*-Butyllithium[1a]

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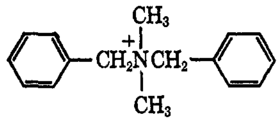
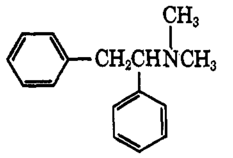
The reaction between N,N-dimethyldibenzylammonium chloride and *n*-butyllithium gave hydrocarbon and amine products from displacement, rearrangement, and elimination reactions. In addition to the known rearrangement products, N,N-dimethyl-1,2-diphenylethylamine and *o*,N,N-trimethylbenzhydrylamine, *o*,N-dimethyldibenzylamine was observed in significant quantities. The displacement products, dimethylbenzylamine, *n*-pentylbenzene, toluene, and 1,2-diphenylhexane, were detected. Stilbene from elimination reactions was also formed. The routes to these products were found to be consistent with the reaction mechanisms previously postulated in benzylammonium ion rearrangements with organolithium compounds.

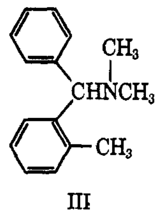
Dimethyldibenzylammonium ion (I) undergoes rearrangement when treated with strong base.[2-6] N,N-Dimethyl-1,2-diphenylethylamine (II) was observed as a 1,2-shift product at temperatures from 100 to 150° with sodium methoxide,[2] sodium amide,[2,5] and potassium hydroxide.[6] Only *o*,N,N-trimethylbenzhydrylamine (III) was produced with sodium amide in liquid ammonia,[4] while both II and III were obtained when phenyllithium was treated with I in boiling ether.[3]



I

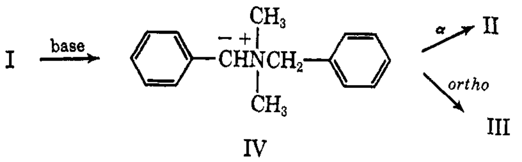


II



III

Both these arrangement products can be formed through a single intermediate, the benzyl ylid IV. However, even in the case of the simplest known benzyl ammonium salt, benzyltrimethylammonium ion,[4,7,8] rearrangement gives appreciable amounts of products which involve reaction at the methyl rather than benzyl group.



IV

Since other rearrangement products seemed reasonable, we have reinvestigated the reaction of dimethyldibenzylammonium chloride with the strong base, butyllithium, in aprotic solvents. It is hoped that this more detailed analysis, accomplished by the use of modern instrumentation, has led to a better understanding of the reaction routes in quaternary ammonium salt rearrangements.

Results

The reaction of N,N-dimethyldibenzylammonium chloride with *n*-butyllithium gave a complex mixture of

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(1) (a) Part II: A. R. Lepley and R. H. Becker, *J. Org. Chem.*, **30**, 3888 (1965). (b) To whom reprint requests should be sent at Marshall University.

(2) T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 1932 (1932).

(3) G. Wittig, H. Tenhaeff, W. Schoch, and G. Koenig, *Ann.*, **572**, 1 (1951).

(4) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951).

(5) C. R. Hauser, R. M. Manyik, W. R. Brasen, and P. L. Bayless, *J. Org. Chem.*, **20**, 1119 (1955).

(6) M. G. Indzhikyan and A. T. Babayan, *Izv. Akad. Nauk. Arm. SSR, Ser. Kim. Nauk.*, **10**, 313 (1957); *Chem. Abstr.*, **52**, 16256*f* (1958).

(7) G. Wittig, R. Mangold, and G. Felletschin, *Ann.*, **560**, 116 (1948).

(8) A. R. Lepley and R. H. Becker, *Tetrahedron*, **21**, 2365 (1965).