Photolysis of Lithium Aryls

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Abstract: In connection with a program concerned with carbanion photolysis, the behavior of excited lithium aryls was studied. Ultraviolet irradiation of lithium aryls in ethyl ether results in aryl coupling. For example, lithium phenyl is converted to biphenyl in greater than 80% yield. Coupling is specific at the carbon–lithium bond, 2-naphthyllithium giving exclusively 2,2-binaphthyl, and 4-methylphenyllithium giving exclusively 4,4′-dimethylbiphenyl. Only small amounts of products resulting from radical attack on solvent were detected. Addition of deuterium oxide in the work-up of a phenyllithium photolysis resulted in no incorporation of deuterium in the biphenyl, and thus biphenyl and not biphenylyllithium is the product of the primary reaction. Phenyl radicals generated by the thermal decomposition of phenylazotriphenylmethane in ether produced only benzene and no biphenyl. Consequently the formation of biphenyl in the photolysis reaction is probably not a "simple" ground-state free-radical coupling reaction. A reaction sequence, featuring conversion of excited lithium aryl dimer to the anion radical of coupling product, is proposed.

Motivated by interests in both valence bond isomerism of aromatic systems and ultraviolet irradiation of charged carbon species, we chose to study the chemical behavior of excited lithium aryls, a class representative of organometallic species possessing carbon–metal bonds with considerable covalent character. As pointed out elsewhere, at the outset of this work nothing was known about the nature of irradiation products formed from carbanions; in the same respect, very little concerning organometallics (covalent) had been recorded, and in particular no examples of group I organometallic behavior could be located. While in our work no evidence for valence bond isomerism could be uncovered, lithium aryls were observed to undergo an efficient photoinduced coupling reaction in which biaryls are generated by unique mechanistic means.

Previously, ultraviolet irradiation studies have been carried out on aryl mercury,[1,2] bismuth,[3] and lead[2,4] compounds. In all these cases, the free metal is liberated, and organic products apparently are formed by way of intermediate phenyl radicals. Furthermore, the phenyl radicals resulting from ultraviolet excitation of these organometallics appear to behave in essentially the same manner as those generated by thermal means. As indicated by observations described and interpreted in more detail below, the biaryls isolated after photolysis of lithium aryls seemingly are not derived from free phenyl radicals, but rather from a biaryl radical anion, itself arising by a novel carbon–carbon bond forming process undergone by a lithium aryl dimer.[5]

In the experiments, lithium aryls in ether solution were prepared in good yield according to known procedures,[6] and photolyses were executed with the organometallic in the original solvent. In the latter reactions, a Hanovia quartz immersion well apparatus (equipped with 450-W high-pressure mercury arc lamp) was used. The photolysis normally was monitored by vpc and uv spectral means. After completion of the reaction, water was added, and the product was analyzed by vpc (volatile components) and tlc (nonvolatile components). A nonirradiated solution of reactant was examined in each case for thermal product.

The ultraviolet irradiation of phenyllithium gave biphenyl and (apparently) metallic lithium in high yield.

$$2C_6H_5Li \xrightarrow[-2Li^0]{h\nu} (C_6H_5)_2$$

During photolysis, the medium darkened while a suspension formed, and light transmission decreased rapidly. The dark brown photolysis solution instantly became colorless on contact with water. Nonvolatile organic material from the photolysis included small amounts of polymer, in addition to the main product. The presence of lithium metal was indicated by color and by its reaction with water to give hydrogen. The only volatile photoproduct observed was *sec*-butyl ethyl ether, identified by its nmr spectrum, and by ir comparison and vpc coinjection with authentic material.

Although most experiments were carried out using 0.04 *M* phenyllithium in ether, solutions ranging in concentration from 0.02 to 0.4 *M* were found to give essentially the same photochemical results. Photolysis of 0.04 *M* phenyllithium at 10° gave the same results as photolysis at room temperature. When 67% of the original phenyllithium had disappeared during the irradiation of a 0.04 *M* solution, 80% of consumed starting material appeared as biphenyl. Even higher percentage yields are realized earlier in the photolysis since biphenyl is not completely stable to ultraviolet light. The photochemical reaction is less efficient for more concentrated solutions; after photolysis of a 0.4 *M* solution for 72 hr, only 14% of the phenyllithium had been converted to biphenyl.

The rate of biphenyl formation is rapid at first and then decreases as photolysis proceeds. A first-order kinetic plot of the data shows curvature which reflects the decreasing light transmission of the solution, a result consistent with the observation of lower yields of biphenyl in the photolysis of more concentrated phenyllithium solutions.

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(1) G. A. Razubaev, B. G. Zateev, and V. N. Myakov, *Proc. Acad. Sci. USSR*, **154**, 37 (1964), and earlier papers.

(2) J. M. Blair and D. Bryce-Smith, *J. Chem. Soc.*, 3174 (1959).

(3) D. H. Hey, D. A. Shingleton, and G. H. Williams, *ibid.*, 5612 (1963).

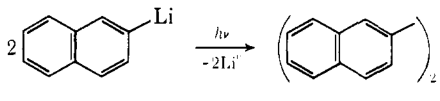
(4) P. A. Leighton and R. A. Mortensen, *J. Amer. Chem. Soc.*, **58**, 448 (1936).

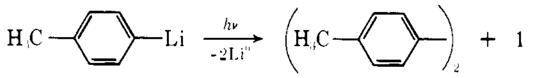
(5) The results of research described in this paper first appeared as a Communication to the Editor: E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *ibid.*, **87**, 4964 (1965).

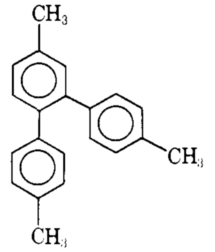
(6) H. Gilman, E. A. Zoellner, and W. M. Selby, *ibid.*, **54**, 1957 (1932).

In order to determine whether or not the intermediate product of the coupling reaction is organometallic, deuterium oxide was added in the work-up of the reaction. The biphenyl isolated in this experiment did not contain deuterium, as indicated by ir and mass spectral analysis.

In attacking the problem of site specificity in the coupling reaction, the photochemical behavior of 2-naphthyllithium was examined. A 0.05 *M* solution of 2-naphthyllithium in ether was prepared and was irradiated as previously described. The coupled product from the photolysis was exclusively 2,2′-binaphthyl. Presence of other binaphthyls in the reaction mixture was ruled out by uv analysis of all trace photoproducts. Complementary to the above inquiry was the photolysis of 4-methylphenyllithium. A 0.04 *M* solution of 4-methylphenyllithium in ether, on ultraviolet irradiation, gave 4,4′-dimethylbiphenyl as the only dimeric photoproduct. Also isolated from this reaction was a trace of trimeric photoproduct, which is believed to be an *o*-terpenyl-1-methyl-3,4-bis(4′-methylphenyl)-benzene (**1**). Interpretation of the nmr spectrum was the sole basis for identification. There are three hydrogens at δ 7.18, eight hydrogens at 6.9 (aromatic region), three hydrogens at 2.4, and six hydrogens at 2.3 (methyl region). This spectrum is consistent with the *o*-terphenyl structure **1**, assuming that hydrogens of the *o*-toluyl groups are shifted upfield due to the shielding effects of ring current[7] in the juxtaposed aromatic ring.







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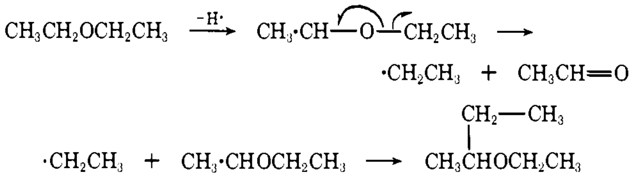
Phenyl radicals generated by the thermal decomposition of phenylazotriphenylmethane in ether produced only benzene and no biphenyl. Consequently the formation of biphenyl in the present photolysis reaction is probably not a simple ground-state free-radical coupling reaction. The *sec*-butyl ethyl ether, which is formed in the thermal decomposition of phenylazotriphenylmethane and in trace amounts in the photolysis reaction, probably arises from radical attack on solvent according to the following scheme. That the addition of deuterium oxide in the work-up of the reaction resulted in no incorporation of deuterium in the biphenyl demonstrated that biphenyl, and not biphenylyllithium, is the product of the primary reaction.

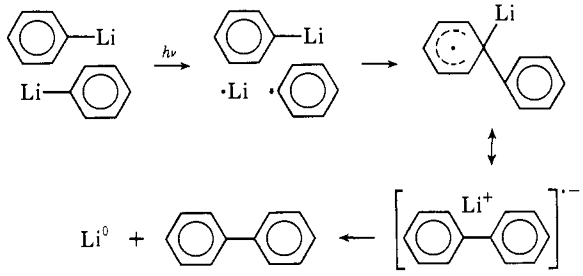


$$CH_3CH_2OCH_2CH_3 \xrightarrow{-H\cdot} CH_3\cdot CH—O—CH_2CH_3 \longrightarrow \cdot CH_2CH_3 + CH_3CH{=}O$$

$$\cdot CH_2CH_3 + CH_3\cdot CHOCH_2CH_3 \longrightarrow CH_3\overset{CH_2—CH_3}{\overset{|}{C}}HOCH_2CH_3$$

Exclusive photoinduced formation of 2,2′-binaphthyl from 2-naphthyllithium and 4,4′-dimethylbiphenyl from 4-methylphenyllithium reveals that this coupling is specific at the carbon–lithium bond. 2-Naphthyllithium was selected intentionally for this study since homolytic aromatic substitution usually occurs at the 1 position of naphthalene. Failure to observe any dimeric product coupled at the 1 position serves as evidence that the present reaction is not an ordinary homolytic aromatic substitution. The fact that 4,4′-dimethylbiphenyl is the exclusive photoproduct from 4-methylphenyllithium indicates that no unusual rearrangements are taking place, *i.e.*, aromatic valence bond isomerizations.

A possible pathway leading to biphenyl is the reaction of a phenyl radical with phenyllithium. This need not be a typical radical reaction, however, since phenyllithium has been shown to be associated as dimers in ether,[8,9] and production of a phenyl radical by homolysis of the carbon–lithium bond would probably occur in the immediate vicinity of another molecule of phenyllithium. The specificity of radical attack on the carbon–lithium bond is understandable in terms of the intermediate which would result from this reaction. Unlike the usual homolytic aromatic substitution intermediates, which are simply resonance-stabilized free radicals,[10] this intermediate is, in effect, the considerably more stable biphenyl radical anion and lithium cation. Because the biphenyl radical anion is unstable in ether, lithium metal and biphenyl result.[11] The postulated reaction sequence is



The proposed mechanism need not be exclusive—some radicals may escape from the solvent cage and cause formation of trace amounts of such products as *sec*-butyl ethyl ether and 1-methyl-3,4-bis(4′-methylphenyl)-benzene.

Alternatively, direct formation of biphenyl or synchronous generation and coupling of two phenyl radicals from the dimer would account for these results. Since it is unlikely that a given dimer absorbs two photons simultaneously, the photochemical event in such a

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(7) See J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 180, for a discussion of ring current.

(8) G. Wittig, *Angew. Chem.*, **62**, 231 (1950); G. Wittig, F. J. Meyer, and G. Lange, *Justus Liebigs Ann. Chem.*, **571**, 167 (1951).

(9) T. V. Talalaeva, A. N. Rodionow, and K. A. Kocheskov, *Proc. Acad. Sci. USSR*, **154**, 47 (1964).

(10) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, New York, N. Y., 1960.

(11) N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Amer. Chem. Soc.*, **58**, 2442 (1936).

process would have to be due to the absorption of a single photon.[12]

The coupling reaction does not appear to be generally applicable to monovalent organometallic compounds. Under conditions which produced biphenyl from phenyllithium, neither phenylsodium nor phenylmagnesium bromide gave coupled product. The failure of phenyllithium to give either biphenyl or *n*-butylbenzene when photolyzed in the presence of *n*-butyllithium suggests that *n*-butyllithium may prevent biphenyl formation by interfering with the association of phenyllithium dimers. Formation of *n*-butylbenzene by the proposed mechanism could occur only by initial dissociation of the nonabsorbing *n*-butyllithium and would proceed through a resonance-stabilized free-radical intermediate instead of the considerably more stable radical anion intermediate.[13]

Experimental Section

Melting points were taken on a Büchi capillary tube melting point apparatus or a Reichert microscope hot stage and are uncorrected. Boiling points are uncorrected. Infrared (ir) spectra were measured on a Perkin-Elmer 137 sodium chloride spectrophotometer, a Perkin-Elmer 237B grating spectrophotometer, or a Perkin-Elmer 421 grating spectrophotometer. Ultraviolet (uv) spectra were taken on a Bausch and Lomb spectronic 505. Nuclear magnetic resonance (nmr) spectra were obtained with a Varian A-60 spectrometer or a Varian HR-100 spectrometer (carbon tetrachloride with tetramethylsilane as an internal standard). Chemical shifts are given as in parts per million relative to tetramethylsilane at δ 0.00. Mass spectra were taken on a CEC 103-C mass spectrometer with an all-glass heated inlet system.

Vapor phase chromatography (vpc) was carried out with a Perkin-Elmer Model 154D vapor fractometer using thermal conductivity detection with helium as carrier gas. A polypropylene glycol column ($^1/_4$ in. × 2 m, UCON-Oil LB-550-X, oven at 50°) was used for both analytical and preparative work. Analytical thin-layer chromatography (tlc) was carried out with Merck silica gel H using iodine for compound detection. Preparative tlc utilized Merck silica gel GF_{254} (1 mm thick) with petroleum ether as eluent and uv light for compound detection.

Preparation of Anionic Solutions (Illustrated by Phenyllithium). Apparatus for the preparation of anionic solutions was made entirely of glass. The solutions were prepared in a 50-ml, three-necked flask fitted with a pressure equalizing dropping funnel, Friedrichs condenser, magnetic stirrer, and a specially constructed glass tube for transferring the solution to the photolysis vessel. A nitrogen train constructed from Tygon tubing and glass Y-tubes with mercury U-type valves and a drying tower of Drierite was used to introduce prepurified nitrogen at the top of the Friedrichs condenser and at one side of the photolysis vessel. Since both nitrogen inlets were part of the same system, pinch clamps could be used to direct a flow from either inlet.

Glassware was dried overnight in an oven at 120° and was assembled under a nitrogen flush. Approximately 220 ml of ethyl ether was distilled from lithium aluminum hydride into the reaction flask and degassed at −78° for 1 hr by vacuum pump. Lithium metal ribbon was cut into small pieces in a brisk nitrogen stream from the reaction flask. It was necessary to use prepurified nitrogen because water-pumped nitrogen caused the freshly cut lithium metal surfaces to turn black. An excess of lithium metal was added. The 50-ml pressure equalizing dropping funnel was put in place as soon as the lithium metal had been added and was flushed with nitrogen for several minutes. Ethyl ether (40 ml) (distilled from lithium aluminum hydride and stored under nitrogen) and 1.5 g (0.0095 mol) of bromobenzene were placed in the dropping funnel by pipet and stirred until homogeneous. The dropping funnel was flushed with nitrogen for another minute, and the system was sealed. The bromobenzene solution was added to the reaction flask at the approximate rate of 30 drops/min with brisk stirring. Enough heat was generated during the addition of bromobenzene to maintain the ether at refluxing temperature. The solution was stirred for approximately 12 hr and allowed to stand until the lithium bromide precipitate had settled. The yield of phenyllithium was 90–95%.

Transfer of Solution to Photolysis Vessel. The Pyrex photolysis vessel and quartz immersion well were dried in an oven overnight at 120° and were assembled under a nitrogen flush. The assembled apparatus was flushed with nitrogen for 20 min and then connected to the transfer tube of the reacton flask. A plug of glass wool was used as a filter in the transfer tube when necessary. Approximately 160 ml of the anion solution was transferred to the photolysis vessel by nitrogen pressure and was maintained under nitrogen until the end of the photolysis.

Photolysis of Anionic Solutions. All photolyses were carried out with a Hanovia immersion well photochemical apparatus. The 450-W high-pressure mercury arc lamp was placed vertically inside a double-walled water-cooled quartz immersion well. No filters were used. The immersion well was positioned inside a Pyrex outer vessel leaving a cavity of ~160 ml for the photolysis solution.

Samples were taken by syringe during photolysis and were hydrolyzed by injecting into rapidly stirred saturated salt solutions (sodium chloride) in small stoppered Erlenmeyer flasks. The samples were examined for changes in the uv and were analyzed by vpc for volatile products.

Work-up of Photolyzed Solution. The photolyzed phenyllithium solution was poured into 100 ml of water in a separatory funnel. The ether layer was washed several times with water and dried over sodium sulfate. Aliquots were analyzed by vpc for volatile products. The solvent was removed, and the residue was analyzed by tlc for nonvolatile products.

Preparation of Materials. Bromobenzene (Eastman grade) was refluxed overnight with excess calcium hydride, distilled (boiling range 150–152°), and stored in a vacuum desiccator. Analysis by vpc under conditions used for sample analysis indicated a trace of benzene (retention time 20.5 min) and one other volatile impurity (retention time 12.5 min).

Lithium metal was pounded into sheets (0.5 cm thick), cut into strips (1 cm × 5 cm × 0.5 cm), and stored under ethyl ether.

Photolysis of Phenyllithium. Upon irradiation, the light yellow phenyllithium solution quickly became dark brown. The transmission oft he solution decreased rapidly as a suspension of finely divided metallic lithium particles was formed. Samples were withdrawn during photolysis, hydrolyzed, and analyzed by uv and vpc. As photolysis proceeded, the increasing ultraviolet spectrum of biphenyl (λ_{max} 284 nm (ϵ_{max} 18,000)) became superimposed on the decreasing spectrum of benzene (λ_{max} 255 nm (ϵ_{max} 215)). Analysis by vpc indicated decreasing concentrations of benzene and extremely slow buildup of a volatile photoproduct of retention time 10.7 min (identified as *sec*-butyl ethyl ether). The volatile impurity from the bromobenzene (retention time 12.5 min) remained. When 0.02 *M* phenyllithium solutions were photolyzed, the biphenyl produced during initial photolysis was eventually destroyed by the uv light and polymeric material resulted.

The dark brown color of the photolysis mixture disappeared immediately on contact with water and hydrogen was given off. A white precipitate (presumed to be lithium hydroxide) formed for a few seconds in the aqueous layer and then dissolved, leaving two clear, colorless phases.

Identification of Products. Biphenyl. The biphenyl isolated from the photolysis solution was recrystallized from ethyl alcohol–water and identified by its ultraviolet and infrared spectra. Identification was confirmed by mixture melting point with authentic material (photoproduct mp 67.5–70°; authentic mp 68–70°; mmp 67.5–70°).

Lithium Metal. The dark brown color generated by photolysis appeared to be due to a finely divided solid which could be partially removed from the solution by filtration under nitrogen through a sintered glass funnel. The brown color disappeared on exposure to air. The ether was removed in one experiment without exposing the brown solution to air. The gas which was formed on addition of water to the brown residue gave a positive hydrogen test.

***sec*-Butyl Ethyl Ether.** A dilute phenyllithium solution (0.02 *M*) was photolyzed for 15 days, and the slow but steady buildup of a volatile photoproduct (retention time 10.7 min) was followed by vpc. After photolysis the hydrolyzed ether solution was concen-

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[12] H. J. S. Winkler, H. Winkler, and R. Bollinger (*Chem. Commun.*, 70 (1966)) more recently have reported the generation of radical anions by photolysis of the parent aromatic hydrocarbon in the presence of phenyllithium, and have proposed that the reaction is a "photosensitized one-electron transfer from the anion of the organolithium reagent to the hydrocarbon."

[13] W. H. Glaze and T. L. Brewer (*J. Amer. Chem. Soc.*, **91**, 4490 (1969)) have described the irradiation with a mercury lamp of ethyllithium, which produces ethylene and ethanes, but no butane.

trated to 0.5 ml in a bulb-to-bulb vacuum distillation. The concentrated solution was injected into the vapor fractometer, and the photoproduct was collected at −78°. The nmr spectrum (A-60 and HR-100 in carbon tetrachloride) exhibited a complex multiplet at δ 3.0–3.7 corresponding to hydrogens on carbon next to oxygen (3 H), a complex multiplet at 1.4–1.8 (2 H), an overlapping doublet and triplet at 1.0–1.4 (3 H, each), and a triplet at 0.7–1.0 (3 H). Analysis of the nmr spectrum permitted tentative assignment as *sec*-butyl ethyl ether.

Authentic *sec*-butyl ethyl ether was prepared by dissolving 1 g (0.04 mol) of sodium metal in 15 ml of *sec*-butyl alcohol and adding 1.4 g (0.013 mol) of ethyl bromide. The reaction mixture was refluxed for 1 hr and the product was collected by vpc as described above. Identification of the photoproduct was confirmed by coinjection with authentic material on vpc and by comparison of infrared spectra (16 out of 16 peaks correspond).

Photolysis of Phenyllithium at Reduced Temperature. A phenyllithium solution (0.04 *M*) was irradiated for 2 hr at approximately 10° by immersing the entire photolysis apparatus in a larger Dewar flask of ice water. The results of this experiment were the same as those of photolyses done at room temperature.

Yield of Biphenyl and Efficiency of Conversion. Phenyllithium (0.04 *M*) was prepared in the usual manner using 1.5 g (0.0095 mol) of bromobenzene and excess lithium metal in 240 ml of ethyl ether. *n*-Octane (1 ml) was added to serve as an internal standard for vpc analysis. The solution was photolyzed for 114 hr and worked up in the usual manner. The concentration of benzene in the hydrolyzed photolysis solution was determined by vpc analysis (comparison with a standard solution of benzene and *n*-octane in ether calibrated by vpc). The concentration of biphenyl was determined by uv analysis (comparison with a standard solution of biphenyl calibrated by uv). Reasonably accurate uv analysis of biphenyl ($\lambda_{\max}$ 248 nm ($\epsilon_{\max}$ 18,000)) is possible in the presence of a relatively small concentration of benzene ($\lambda_{\max}$ 255 nm ($\epsilon_{\max}$ 215)). Under the conditions of this experiment 67% of the original phenyllithium was allowed to react, and an 80% yield of biphenyl was obtained (corrected for recovered starting material).

A more concentrated phenyllithium solution (0.40 *M*) was prepared in the usual manner using 15 g (0.095 mol) of bromobenzene and excess lithium metal in 240 ml of ether. A portion of the solution (155 ml) was photolyzed for 72 hr and worked up in the usual manner (an extremely vigorous evolution of gas occurred during work-up). The crude biphenyl (0.64 g) isolated from the photolyzed solution accounted for 13% of the original bromobenzene.

Rate of Biphenyl Production. Phenyllithium (0.04 *M*) was prepared and photolyzed in the usual manner. Samples were taken at intervals during the 20-hr photolysis, were hydrolyzed as previously described, and were analyzed for biphenyl in the ultraviolet (248 mμ) [time, hr (absorbance, 248 mμ)]: 0.5 (0.33); 1 (0.47); 2 (0.71); 4 (0.88); 6 (1.07); 8 (1.05); 20 (1.40).

Deuterium Oxide Work-up of Photolysis Solution. A phenyllithium solution (0.04 *M*) was prepared in the usual manner, and a 175-ml portion was photolyzed for 25 hr. Deuterium oxide was added with stirring to the photolyzed solution in 5 portions of 50 μl each. The photolysis solution was then worked up in the usual manner. The biphenyl was recovered and recrystallized from ethyl alcohol–water and was dried in a vacuum desiccator. The infrared spectrum of the biphenyl, identical with that of an authentic sample, provided no evidence for carbon–deuterium absorption. Likewise, the mass spectrum was, within experimental error (less than 1%), identical with that of an authentic sample.

Thermal Decomposition of Phenylazotriphenylmethane in Ethyl Ether. Into a 125-ml Erlenmeyer flask were placed 2.0 g (0.0056 mol) of phenylazotriphenylmethane and 75 ml of anhydrous ethyl ether. The solution was stored for 1 week at room temperature. Analysis of the resulting solution and the nonvolatile material from the solution by uv, ir, vpc, and tlc revealed considerable benzene (75% based on starting material by comparison with a calibrated benzene solution), but no biphenyl. A small amount of *sec*-butyl ethyl ether was detected by vpc and was confirmed by coinjection with authentic material.

Photolysis of 2-Naphthyllithium. 2-Bromonaphthalene was recrystallized twice from absolute ethyl alcohol. 2-Naphthyllithium (0.05 *M*) was prepared in the manner described for phenyllithium, using 2.25 g (0.011 mol) of 2-bromonaphthalene and excess lithium metal in 225 ml of ethyl ether. The solution became dark purple as it was refluxed for 5 hr. The solution was allowed to settle for 12 hr; then a 150-ml portion was transferred to the photolysis vessel. During work-up of the remaining solution the dark purple color became colorless on contact with water and a white, water-soluble precipitate (lithium hydroxide) formed for a few seconds, then dissolved. The ether layer from the unphotolyzed solution contained mainly naphthalene with a trace of polar or polymeric material (tlc) which was not examined further.

The ultraviolet spectrum of a sample taken after 24 hr of photolysis exhibited a strong new absorption at 253 mμ. The photolysis was terminated after 72 hr. The ether solution was worked up in the usual manner and was found to contain naphthalene and polymeric material. A ring of brown solid material, presumably lithium metal, scraped from the top of the photolysis vessel, bubbled vigorously on contact with water leaving a water-insoluble white crystalline solid (mp 182–184°) identified as 2,2′-binaphthyl. Careful analysis of the product mixture by continuous preparative tlc (GF_{254} silica gel, 30–60° petroleum ether eluent) revealed a number of trace materials.

Naphthalene was identified by its uv spectrum and by mixture melting point with authentic material (mp 78–80°, authentic mp 78–80°, mmp 78–80°). 2,2′-Binaphthyl, the major product, was identified by its melting point and uv spectrum, and by the melting points of its picrate and 2,4,7-trinitrofluorenone derivatives. Identification was confirmed by comparison of its ir spectrum with the ir spectrum of authentic material and by mixture melting point with authentic material (mp 182–184°; authentic mp 183–185.5°; mmp 182–185.5°).[14]

Photolysis of 4-Methylphenyllithium. 4-Methylphenyllithium (0.038 *M*) was prepared in the usual manner as previously described for phenyllithium using 1.4 g (0.0082 mol) of *p*-bromotoluene, excess lithium metal, and 215 ml of ethyl ether. A 160-ml portion of the solution was photolyzed for 13 hr and worked up in the usual manner. The remaining unphotolyzed solution was worked up and examined for products. Analysis of nonvolatile material from the photolysis solution by tlc revealed 0.120 g of a major photoproduct, mp 114–119°, identified as 4,4′-dimethylbiphenyl (lit.[15] mp 120.7–121.5°), and 0.010 g of a minor photoproduct, mp 103–115°, tentatively identified by nmr as 1-methyl-3,4-bis(4′-methylphenyl)-benzene.

The nmr spectrum of the minor photoproduct exhibited signals at δ 7.11 (3 H, broad singlet), 6.92 (8 H, singlet), 2.37 (3 H, singlet), and 2.29 (6 H, singlet). The possibility of the minor photoproduct being one of the other dimethylbiphenyl isomers was ruled out on the basis of its nmr spectrum and its melting point.

Photolysis of a Mixture of Phenyllithium and *n*-Butyllithium. Solutions of phenyllithium (0.04 *M*) and *n*-butyllithium (0.04 *M*) were prepared individually in the usual manner, and an 85-ml portion of each solution was transferred to the photolysis vessel. The two nearly colorless solutions formed a red-colored solution when combined. Samples were withdrawn and analyzed in the ultraviolet as the mixture was photolyzed for 21 hr. At the end of photolysis the solution was yellow instead of red. There was no evident of finely dispersed lithium metal. Analysis of the photolysis solution and nonvolatile material from the soluton by uv, ir, tlc, and vpc gave no evidence for formation of either biphenyl or *n*-butylbenzene. *sec*-Butyl ethyl ether was identified as a trace photoproduct by coinjection with authentic material on vpc. The nonvolatile material appeared to be polymeric.

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(14) The authors thank Dr. W. M. Padgett, Hyman Laboratories, Berkeley, Calif., for a sample of 2,2′-binaphthyl.

(15) E. A. Johnson, *J. Chem. Soc.*, 4155 (1957).