Organometallic Photochemistry. III. The Photolysis of *o*-Anisyllithium[1]

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The photolysis of *o*-anisyllithium (**1**) in diethyl ether with high-pressure mercury arc radiation yields, after hydrolysis, 17% 2-methoxybiphenyl (**3**). Smaller quantities (1%) of 2,2′-dimethoxybiphenyl (**4**) are also found. Reaction of the photolysis mixture with deuterium oxide yields 2-methoxybiphenyl-d_1, of uncertain structure, and carbonation gives 2′-methoxy-2-biphenylcarboxylic acid. Photolysis of a mixture of **1** and *n*-butyllithium results in no **3** or **4**; *n*-butylbenzene is the major aromatic product. Various mechanistic pathways are discussed for the rationalization of these results. Under similar conditions, the photolysis of *m*-anisyllithium gives lithium metal and the simple coupling product, 3,3′-dimethoxybiphenyl (8%).

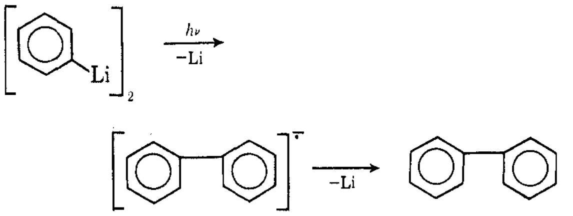
In 1965, van Tamelen and coworkers reported biphenyl yields of 80% from the photolysis of phenyllithium in ether.[2] Although their work suggested a potentially useful synthetic method for the preparation of various biphenyls, no further reports on the photolysis of aryllithiums are known to us. In this paper, we report the results of the photolytic studies of *o*- and *m*-anisyllithium which illustrate two possible photolytic pathways available to substituted aryllithiums.

Results

Preparation of Anisyllithiums.—*o*-Anisyllithium (**1**) was synthesized initially by the metalation of anisole with *n*-butyllithium in ether–hexane. However, the maximum yield of this reaction is only approximately 60%,[3] which we have verified, and the presence of by-products and unreacted anisole is detrimental to the photolysis process. Therefore, we adopted an alternate route to *o*-anisyllithium in the latter stages of this work, namely, the halogen–lithium exchange reaction. When carried out in hexane solvent, the reaction of *o*-bromoanisole and *n*-butyllithium yields crystalline *o*-anisyllithium which may be separated and redissolved in ether for photolytic studies. This procedure has been used previously for the preparation of phenyllithium[4] and methyllithium,[4] as well as a variety of aryllithiums in the hands of Fraenkel and coworkers.[5] The reaction is of quite high yield (80–90%) and the white, powdery *o*-anisyllithium is uncontaminated except for a trace of lithium bromide. So far, we have applied the technique only for the preparation of *o*- and *m*-anisyllithium, but in view of Fraenkel's work, the method appears to be quite general.

Photolytic Studies.—Photolyses were carried out in all cases with radiation from mercury arc lamps filtered only through quartz. In most cases, a quartz high-pressure mercury arc lamp was used which had usable ultraviolet output from 3660 to 2224 Å. Some photolyses were carried out in a photochemical reactor with low-pressure Hg lamps (2537 Å), but the yields were generally lower. Care was taken to keep the aryllithium solution from contact with air and each photolysis was carried out under an argon blanket. After irradiation of *o*-anisyllithium in ether for an hour or two, the solution began to color pink, and after 12 hr a small amount of precipitate was present. Hydrolysis of the solution and work-up yielded 2-methoxybiphenyl (**3**, 17%), 2,2′-dimethoxybiphenyl (**4**, 1%), as well as 63% recovered anisole. On work-up, the aqueous layer yielded a small quantity (*ca.* 2–3%) of phenolic materials consisting of phenol and various cresols.[6] When allowed to react with deuterium oxide, the photolysis mixture yielded anisole containing 74 and 26% of d_0 and d_1 species, respectively, 2-methoxybiphenyl (16 and 84% d_0 and d_1), and undeuterated 2,2′-dimethoxybiphenyl. Carbonation of the photolysis mixture with Dry Ice–ether slurry gave 2′-methoxy-2-biphenylcarboxylic acid (**5**). This acid was characterized by coversion to the methyl ester **6** with ether–diazomethane, and the nmr and ir spectra of the ester were identical with those of an authentic sample[9] (see Experimental Section).

The results summarized in Scheme I suggest the primary photolytic product to be 2-lithio-2′-methoxybiphenyl (**2**) and are in contrast to the results of van Tamelen, *et al.*,[2] where only biphenyl-d_0 was obtained by deuterolysis of the photolysis mixture from phenyllithium. These workers suggested two possible mechanisms: (a) a route involving the unstable biphenyl radical anion (eq 1) and, (b) synchronous generation and coupling of two phenyl radicals.



(1)

For the present case, the process shown in eq 1 would yield 2,2′-dimethoxybiphenyl radical anion. Although we are uncertain as to the fate of this species under our photolytic conditions, some clue may be derived from the behavior of anisole radical anion, which has been

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[1] Paper II in this series: W. H. Glaze, T. L. Brewer, and A. C. Ranade, *J. Organometal. Chem.*, **26**, C6 (1971).

[2] E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *J. Amer. Chem. Soc.*, **87**, 4965 (1965).

[3] (a) G. Wittig, U. Pockels, and H. Dröge, *Chem. Ber.*, **71**, 1903 (1938); (b) H. Gilman and R. L. Bebb, *J. Amer. Chem. Soc.*, **61**, 109 (1939); (c) D. A. Shirley, J. R. Johnson, Jr., and J. P. Hendrix, *J. Organometal. Chem.*, **11**, 209 (1968); (d) D. W. Slocum, G. Book, and C. A. Jennings, *Tetrahedron Lett.*, 3443 (1970).

[4] T. L. Brown and M. T. Rogers, *J. Amer. Chem. Soc.*, **79**, 1859 (1957).

[5] G. Fraenkel, S. Dayagi, and S. Kobayashi, *J. Phys. Chem.*, **72**, 953 (1968).

[6] The phenolic products may be attributed to the photolysis of anisole,[7] which accumulates at long exposure times.[8]

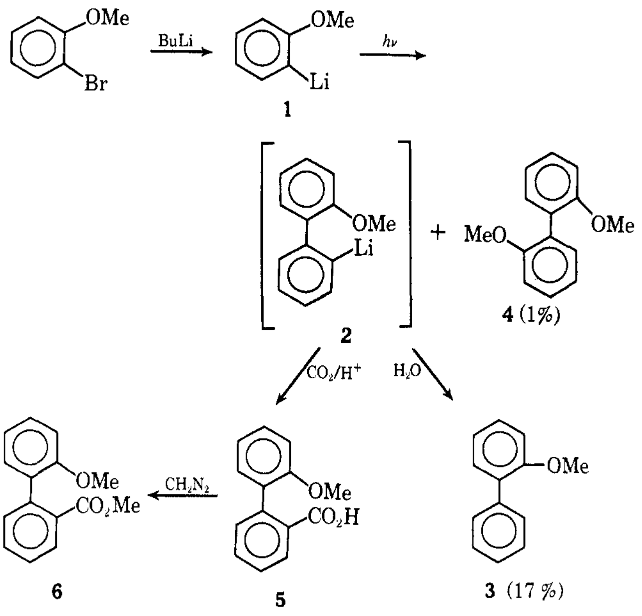
[7] J. J. Houser and M.-C. Chen, *Chem. Commun.*, 1447 (1970).

[8] The large amount of anisole-d_0 and the smaller quantity of 2-methoxybiphenyl-d_0 probably results from the cleavage of ether by the corresponding lithiated species **1** and **2**.

[9] We are grateful to Dr. D. I. Davies for supplying an authentic sample of 2′-methoxy-2-biphenylcarboxylic acid,[10] which upon esterification with diazomethane yielded a methyl ester with identical ir and nmr spectra with the ester obtained from the photolysis of **1**.

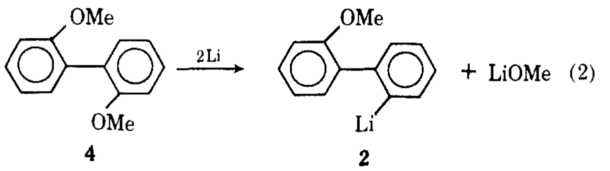
[10] D. I. Davies and C. Waring, *J. Chem. Soc. C*, 1639 (1967).

SCHEME I



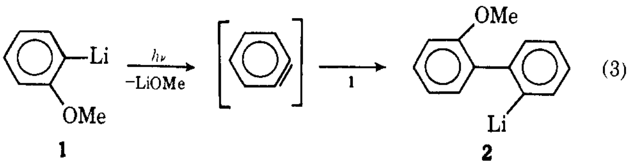
studied.[11] Esr spectra indicate that the latter decomposes at room temperature in THF to yield biphenyl radical anion. However, phenol is the major product obtained after hydrolysis.[11] In view of the low yield of phenolic materials which we obtain, it is doubtful that the principal photolytic product **2** would be produced by this route.

Synchronous coupling to yield 2,2′-dimethoxybiphenyl (and lithium metal) may account for the small amount of this material. Moreover, one might propose that the dominant product **2** is produced by cleavage of lithium methoxide from **4** under the photolytic conditions. Some precedent for the cleavage of *o*-methoxy



groups in polysubstituted aromatics has been established for Birch reductions,[12] although we are unaware of the occurrence of the reaction with the type of compounds and under the rather mild conditions employed here. To investigate the point further, a sample of **4** was photolyzed in ether with a dispersion of lithium metal. After 24 hr of irradiation under conditions similar to those used for **1**, 90% of **4** was recovered unchanged. Glc of the reaction mixture indicated only a trace of one component which may be attributed to 2-methoxybiphenyl (**3**). In another experiment, the concentrations of **3** and **4** were monitored by removing and hydrolyzing aliquots from the photolysis of **1** at various times. Beginning at 1 hr and observing at 1-hr intervals thereafter, the ratio of **3**:**4** was found by glc to increase from 6 to 21 after 48 hr. In no case was the ratio less than that observed at 1 hr. Thus, reaction 2 must be rather rapid on this time scale if it is to account for the production of **2**.

An attractive alternative mechanism would be the photolytic elimination of lithium methoxide to yield benzyne. We expect under these conditions that this intermediate would react with *o*-anisyllithium to yield **2** directly (eq 3).[13,14] Moreover, the probable dimeric



nature of the starting material[15] would provide easy access of the *o*-anisyllithium to the benzyne species before the latter could escape. Unfortunately, the reactive nature of the aryllithiums, as well as the photolytic conditions, makes it difficult to employ the usual benzyne traps. However, photolysis of a mixture of *o*-anisyllithium with *n*-butyllithium (1:2.4) in ether does result in a complete alteration of the photolytic products. Most important, a moderate yield of *n*-butylbenzene (**7**) is observed, as would be expected if the benzyne intermediate were trapped by the excess *n*-butyllithium.[13,14] However, the latter is also undergoing photolysis to some degree under these conditions,[16] and the isolation of **7** cannot be taken as definitive evidence for a benzyne mechanism. Moreover, it appears that the majority of **7** isolated after deuterolysis of the reaction mixture contains two deuterium labels.

While in the process of these trapping experiments, we have discovered a hydrocarbon-soluble complex of *o*-anisyllithium and *n*-butyllithium. This complex, prepared by the reaction of solid **1** with a 1.6 *M* solution of *n*-butyllithium in hexane, has unusual chemical and spectral properties which are presently under investigation.

The photolysis of *m*-anisyllithium has also been investigated and, in accordance with our expectations, yields 3,3′-dimethoxybiphenyl as the only major product (8%) (see Experimental Section). Thus, elimination may be restricted to aryllithiums with polar ortho substituents and may not represent a significant restriction to the use of the photolytic method for the preparation of certain disubstituted biphenyls. Further experiments to explore the method are in progress.[17]

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[11] J. K. Brown, D. R. Burnham, and N. A. J. Rogers, *Tetrahedron Lett.*, 2621 (1966); *J. Chem. Soc. B*, 1149 (1969).

[12] O. L. Chapman and P. Fitton, *J. Amer. Chem. Soc.*, **85**, 41 (1963).

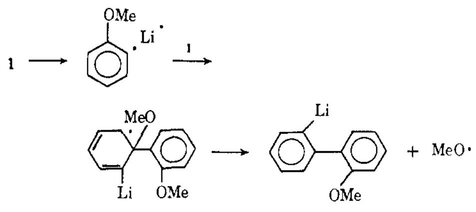
[13] V. Franzen and H. I. Joschek, *Angew. Chem.*, **72**, 564 (1960).

[14] G. Wittig and L. Pohmer, *Chem. Ber.*, **89**, 1334 (1956).

[15] P. West and R. Waack, *J. Amer. Chem. Soc.*, **89**, 4395 (1967).

[16] W. H. Glaze and T. L. Brewer, *ibid.*, **91**, 4490 (1969).

[17] A referee has suggested that a radical mechanism should also be considered.



We have no evidence to eliminate this mechanism; in fact, it would be very difficult to distinguish between a "caged radical" and a "caged benzyne" process. However, the marked difference in the behavior of *o*- and *m*-anisyllithium is best explained, we believe, in terms of a benzyne process for the former and a synchronous coupling process for the latter.

Experimental Section

Materials.—Phillips Petroleum Co. pure grade *n*-pentane was redistilled from $LiAlH_4$. Anhydrous diethyl ether obtained from J. T. Baker Co. was dried similarly. *o*- and *m*-bromoanisole were obtained from Eastman Organic Chemicals and were used without further purification. *n*-Butyllithium in hexane (1.6 *M*) was obtained from Foote Mineral Co.

Spectral Measurements.—Spectra were obtained with a Perkin-Elmer Hitachi RMU-7 mass spectrometer, Perkin-Elmer 237 or 621 infrared spectrometers, Cary 14 uv–visible spectrometer, and JEOLCO MH-60 and PS-100 nmr spectrometers.

Preparation of *o*-Anisyllithium.—To a solution of *o*-bromoanisole (23.2 ml, 0.200 mol) in pentane (200 ml) was added a hexane solution of *n*-butyllithium (126 ml, 0.200 mol). The solution was stirred overnight in an argon atmosphere. The reaction vessel was stoppered and taken into a drybox, and the precipitated *o*-anisyllithium was filtered, washed with pentane, and dried. The yield of pure *o*-anisyllithium was 20.0 g (84%). To test the purity, a small portion of *o*-anisyllithium was dissolved in ether and treated with D_2O. This gave 98% of anisole-d_1, as evidenced by mass spectroscopy. Glc of the organic layer after hydrolysis showed no evidence of benzene or other impurities.

Preparation of *m*-Anisyllithium.—*m*-Bromoanisole (18.7 g, 0.10 mol) was treated with 63 ml of 1.6 *M* *n*-butyllithium (0.10 mol) in hexane as described above. *m*-Anisyllithium was isolated as a white powder and redissolved in dry ether. Glc of an aliquot of the solution showed only anisole after hydrolysis. Deuteriolysis yielded anisole-d_1 (96% isotopic purity).

Photolysis of *o*-Anisyllithium.—A solution of *o*-anisyllithium (11.0 g, 0.096 mol) in ether (450 ml) was irradiated in an immersion photochemical reactor (Ace Glass Co.) with a 450-W Hanovia Model 679A-36 high-pressure Hg arc lamp. The radiation was filtered only through quartz and therefore consisted of a wide distribution of uv wavelengths with maxima at 3660 and 3130 Å. The solution was irradiated for 12 hr under an argon atmosphere, while stirring with a magnetic bar. Deuterium oxide (10 ml) was added slowly through a septum. Glc analysis of a portion of the aqueous layer indicated the presence of methanol. The aqueous layer, on acidification, gave a phenolic material (0.2 g, 2.4%) which was a mixture of phenol and cresols. Removal of volatiles from the dried ether layer gave 8.2 g of a viscous liquid, which upon distillation under vacuum furnished anisole (6.45 g, 0.060 mol), bp 100° (15 mm), and 2-methoxybiphenyl (1.5 g, 0.0082 mol), bp 108° (3 mm). Analysis by mass spectroscopy indicated that the anisole contained 26.1% of anisole-d_1 and 73.9% of anisole-d_0 compounds. The 2-methoxybiphenyl contained 83.5% of d_1 and 16.5% d_0 compounds. The yield of 2-methoxybiphenyl based on initial *o*-anisyllithium is 16.6%, but this amounts to a yield of 45%, based on the *o*-anisyllithium which was photolyzed. Glc analysis of the crude product mixture on a 5 ft × 0.125 in. SE-30 column at 150°, 50-ml/min flow of He, showed the presence of 2,2′-dimethoxybiphenyl (1%). Comparisons of retention times and spectra were made with an authentic sample of 4 collected by preparative glc.[18] In this photolysis, a small amount of polymeric material was also formed.

Carbonation of the mixture after photolysis (0.10 mol of **1** in 300 ml of ether) was accomplished by pouring the mixture over Dry Ice–ether slurry in a glove bag. The alkaline aqueous layer was separated, acidified with hydrochloric acid, and extracted with ether. The mixture of acids (**5** and *o*-methoxybenzoic acid) was converted to the corresponding methyl esters with diazomethane–ether and the ester **6** was isolated by preparative glc (5 ft × 0.25 in. SE-30, 220°, 50 ml/min). Mass, nmr, and ir spectra were identical with those of the corresponding ester prepared by treatment of a sample of acid **5** prepared by Davies.[9,10]

Photolysis of *m*-Anisyllithium.—A solution of *m*-anisyllithium (11.0 g, 0.096 mol) in ether (450 ml) was irradiated for 12 hr as described in the previous section. A finely divided dispersion of lithium metal was observed to form during the course of the irradiation. Water (15 ml) was added slowly thereafter. Separation of the organic layer and removal of solvent gave 8.0 g of a dark viscous liquid which upon distillation gave anisole (6.0 g, 0.055 mol), bp 100° (15 mm). Preparative glc of the pot residue yielded 3,3′-dimethoxybiphenyl, the identity of which was established by comparison of ir,[19] nmr,[19] and mass spectra[20] with reported values. The yield of 3,3′-dimethoxybiphenyl (8%) and recovered anisole (52%) was determined by glc. with biphenyl internal standard in a separate run. Thus, the yield of 3,3′-dimethoxybiphenyl based on reacted anisole is 19%.

Control Experiments.—Before photolysis of an ether solution of *o*-anisyllithium, two 20-ml aliquots were removed. Reaction of one with D_2O yielded only anisole-d_1 of 98% isotopic purity. The other aliquot was allowed to stand at room temperature for 12 hr, after which reaction with D_2O gave only anisole-d_1 of 96% isotopic purity. A similar experiment with *m*-anisyllithium resulted in the recovery of anisole-d_1 of 96% isotopic purity immediately after preparation of the solution. However, after standing for 12 hr, the solution gave, upon reaction with D_2O, anisole-d_1 (80%) and anisole-d_0 (20%). The more rapid rate of reaction of *m*-anisyllithium with solvent is apparently responsible for the lower yield of photolysis product, 3,3′-dimethoxybiphenyl.

Photolysis of *o*-Anisyllithium-*n*-Butyllithium Complex.—A mixture of *o*-anisyllthium and *n*-butyllithium (1:2.4 ratio) in ether was photolyzed as in the first experiment. Treatment of the photolysis product with D_2O gave *n*-butylbenzene (2.4% yield), identified by spectral comparison after preparative glc collection. The majority of the *n*-butylbenzene appears to be dideuterated (mass spectroscopy). No 2-methoxybiphenyl was observed by glc from this run; the major products appear to be high polymers of unknown structure.

Preparation of a Soluble Complex of *o*-Anisyllithium and *n*-Butyllithium in Hexane.—A solution of *n*-butyllithium in hexane was added under an argon atmosphere to a suspension of *o*-anisyllithium (4.0 g) in 25 ml of dry pentane. Even after adding 50 ml of *n*-butyllithium some *o*-anisyllithium was still not dissolved. The solution was filtered and evaporated to dryness in a drybox. A crystalline material was obtained which redissolved in dry pentane. Comparison of the integrated areas of aromatic protons of *o*-anisyllithium and of methylene protons α to the lithium atom in *n*-butyllithium indicated that the complex contained 2.4 mol of *n*-butyllithium for each mole of *o*-anisyllithium.

Registry No.—**1**, 31600-86-9; **3**, 86-26-0; *m*-anisyllithium, 31600-88-1; anisole, 100-66-3.

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(18) D. A. Shirley and W. L. Dean, *J. Amer. Chem. Soc.*, **79**, 1205 (1957).

(19) Sadtler Research Laboratories, Inc., Standard IR Spectrum No. 19573, NMR Spectrum No. 2210M.

(20) C. S. Barnes, D. J. Collins, J. J. Hobbs, P. I. Mortimer, and W. H. F. Sasse, *Aust. J. Chem.*, **20**, 699 (1967).