[Contribution from the Chemistry Department of Iowa State College]

Reactions of Lithium with Some Aromatic Hydrocarbons in Tetrahydrofuran

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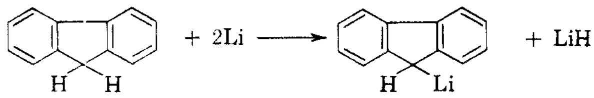
Certain aromatic hydrocarbons have been found to react with lithium metal in tetrahydrofuran to give compounds having a carbon—lithium bond. 9,9-Diphenylfluorene has been cleaved by lithium in tetrahydrofuran to give 9-phenylfluorenyllithium and phenyllithium.

Aromatic hydrocarbons like fluorene and 9-phenylfluorene[1] have been metalated in high yields by a variety of organolithium compounds. On the other hand, cyclopentadienyllithium has been successfully prepared from the reaction of cyclopentadiene with lithium in liquid ammonia.[2] It has also been obtained by the metalation of cyclopentadiene by phenyllithium[3] and *n*-butyllithium.[4]

We are now reporting convenient methods for synthesizing some organolithium compounds by the direct reaction of aromatic hydrocarbons with lithium metal in tetrahydrofuran (THF). To our knowledge this is the first reported example wherein an aromatic hydrocarbon reacts with lithium metal in an ethereal solvent. Fluorene and 9-phenylfluorene,



when treated with lithium in THF, yielded 72 and 38% of 9-fluorenecarboxylic acid and 9-phenylfluorenecarboxylic acid, respectively, subsequent to carbonation. Likewise, cyclopentadiene reacted with lithium in a similar fashion to give a 45% yield of diphenylfulvene after treatment of the reaction mixture with benzophenone. Thus, this appears to be a well-suited method for preparing certain organolithium compounds, which are free of halide salts, in an organic solvent.

The open-chained model of 9-phenylfluorene, triphenylmethane, did not react with lithium in THF.

9-Phenylfluorenyllithium was also prepared by another method. 9,9-Diphenylfluorene underwent almost a quantitative cleavage in 15 hr. by lithium in THF to give 9-phenylfluorene subsequent to hydrolysis of the reaction mixture. This reaction is not novel since Koelsch[5] found that stirring 9-benzyl-9-phenylfluorene with sodium amalgam in diethyl ether for 5 days afforded, after hydrolysis, 40% of 9-phenylfluorene; but it does emphasize that THF has a pronounced effect on facilitating the cleavage.

In connection with the synthesis of 9,9-diphenylfluorene, we have found that the intermediate carbinol, 2-biphenylyldiphenyl carbinol, can be obtained in a higher yield from the reaction of 2-biphenylyllithium with benzophenone than by a previously reported[6] procedure in which 2-phenylbenzophenone was treated with phenylmagnesium bromide. The former method also involves fewer steps.

EXPERIMENTAL[7]

Reaction of lithium with fluorene. A solution of 5 g. (0.03 mole) of fluorene in 35 ml. of tetrahydrofuran (THF) was added, during 1.5 hr., to a stirred suspension of 1.23 g. (0.178 g. atom) of finely cut lithium wire contained in 10 ml. of THF. The color of the mixture which was periodically cooled by a water bath during the addition changed from green to orange. When the addition was complete, the mixture was stirred at room temperature for 50 min. and was poured through a glass wool plug onto a slurry of Dry Ice and diethyl ether. Following hydrolysis with water, the aqueous layer was separated, boiled to expel THF and diethyl ether, filtered, and acidified with hydrochloric acid to give a solid which was crystallized from acetic acid to yield 4.46 g. (71%) of needles, m.p. 230–232°, which showed no depression in melting point when admixed with an authentic sample of 9-fluorenecarboxylic acid.

Reaction of lithium with 9-phenylfluorene. A mixture of 4.0 g. (0.0165 mole) of 9-phenylfluorene, 1.7 g. (0.245 g. atom) of lithium, and 45 ml. of tetrahydrofuran was stirred at room temperature for 4 hr. before carbonating and working the reaction mixture up as described in the preceding experiment. The yield of acid, m.p. 180–182°, was 1.81 g. (38%). The melting point was undepressed when the compound was admixed with an authentic sample of 9-phenylfluorenecarboxylic acid.

Reaction of lithium with triphenylmethane (attempted). A mixture of 5.0 g. (0.02 mole) of triphenylmethane, 0.8 g. (0.115 g. atom) of lithium wire, and 40 ml. of tetrahydrofuran was stirred at room temperature for 5 days. Work-up of the organic layer gave 4.71 g. (94%) of triphenylmethane, m.p. 90–92°, identified by mixed melting point.

Reaction of lithium with cyclopentadiene. A solution of 4.03 g. (0.061 mole) of cyclopentadiene in 30 ml. of tetrahydrofuran (THF) was added to a rapidly stirred suspension

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(1) Metalation of these compounds as well as other types has been reviewed recently; H. Gilman and J. A. Morton, Jr., *Org. Reactions*, **VIII**, 258 (1954).

(2) E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. anorg. allgem. Chem.*, **282**, 59 (1955).

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(6) R. G. Clarkson and M. Gomberg, *J. Am. Chem. Soc.*, **52**, 2881 (1930).

(7) All melting points are uncorrected. Reactions involving organolithium compounds were carried out under an atmosphere of dry, oxygen-free nitrogen in sodium-dried solvents.

of 2.0 g. (0.288 g. atom) of lithium in 40 ml. of THF. Initially about 5 ml. of the cyclopentadiene solution was added. After 20 min. bubbles began to evolve around the pieces of lithium. The remaining cyclopentadiene solution was added, during 45 min. while cooling at 0°. The mixture was stirred at room temperature for 30 min. before filtering it into a stirred solution of 10.9 g. (0.06 mole) of benzophenone in 35 ml. of THF. The orange mixture was stirred at room temperature for 21 hr. and was poured into a mixture of ice and water. The organic layer was separated, dried, and most of the solvent was evaporated under a stream of dry air. The red residue was refluxed in petroleum ether (b.p. 28–38°) and filtered to leave a brown, gummy material. The petroleum ether was slowly evaporated under reduced pressure to leave orange crystals which were washed with 95% ethanol, filtered, and dried to give 4.88 g. (35%) of diphenylfulvene, m.p. 75–77°, identified by mixed melting point.

In another run using 8.05 g. (0.122 mole) of cyclopentadiene and 2.85 g. (0.41 g. atom) of lithium, a 45% yield of diphenylfulvene was obtained.

2-Biphenylyldiphenylcarbinol. An ethereal solution containing 0.344 mole of 2-biphenylyllithium[8] was added to a solution of 62.6 g. (0.344 mole) of benzophenone. The mixture was hydrolyzed with water and the organic layer was worked up in the usual fashion. Evaporation of the solvent under a stream of dry air left a solid which was crystallized from ethanol to give 97 g. (84%) of product, m.p. 86–88°.

2-Biphenylyldiphenylcarbinol, m.p. 87–88°, has previously been prepared in 63% yield from phenylmagnesium bromide and 2-phenylbenzophenone.[6] Refluxing the carbinol in acetic acid gave 9,9-diphenylfluorene.

Reaction of lithium with 9,9-diphenylfluorene. A mixture of 6.0 g. (0.019 mole) of 9,9-diphenylfluorene, 2.0 g. (0.29 g. atom) of lithium wire, and 50 ml. of tetrahydrofuran was stirred at room temperature for 15 hr. The organic layer was separated and dried over sodium sulfate after hydrolyzing with water. Distillation of the solvent left a material which was crystallized from a minimum of ethanol to give 3.88 g. (85%) of colorless needles, m.p. 143–144°, which showed no depression in melting point when admixed with an authentic sample of 9-phenylfluorene.

When the reaction time was limited to 1.75 hr., only a 25% yield of 9-phenylfluorene was obtained.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Addition of Ethyl Mercaptan to Acetylenic Compounds[1]

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The free-radical addition of two equivalents of ethyl mercaptan to several acetylenic compounds has been studied. These comprised propargyl alcohol, propargyl acetate, 2-butyn-1,4-diol diacetate, 1-hexyne, 2-methyl-3-butyn-2-ol, propiolic acid, dimethyl acetylenedicarboxylate, and phenylacetylene. Vicininal *bis*-ethylmercapto derivatives were obtained in all but two instances. Phenylacetylene afforded phenylacetaldehyde diethyl mercaptal while from dimethyl acetylenedicarboxylate only a monoadduct was realized.

These bisethylmercapto derivatives were not active when tested *in vivo* against *M-tuberculosis* infection in mice.

Although the literature abounds with reports of studies of the addition of thiols to ethylenic substances, relatively little attention has been given to such additions involving acetylenic compounds.[2,3]

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[1] The work reported here was done as part of a general research program in organic chemistry at Cornell University, sponsored by the B. F. Goodrich Co.

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