This experiment was repeated in essentially the same manner except that a 20% excess of n-butyl bromide was added to the refluxing solution immediately after the n-butyllithium and 1-bromonaphthalene were mixed. It was necessary to reflux the reaction for only 24 hr. before Color Test I was negative. The product was worked up and purified as before to obtain an 87% yield of the pure 1-n-butylnaphthalene.

In another run, the ether was replaced by benzene immediately after the n-butyllithium had been added. Color Test I was negative after refluxing the mixture for 15 hr., but the yield of pure product was only 38%.

1-n-Hexylnaphthalene. An ethereal solution of 0.41 mole of n-hexyllithium was prepared by the usual method[12] in 70% yield and was added to 85.0 (0.41 mole) of 1-bromonaphthalene. A 20% excess of 1-bromohexane was then added; even after refluxing the mixture for 5 days, Color Test I remained positive. The mixture was poured onto a dry ice–ether slurry and the acid was isolated in the customary manner by basic extraction. A 4.2% yield of 1-naphthoic acid (mixture melting point) melting at 155–156° was obtained. The neutral ether solution was worked up by fractional distillation in essentially the same manner as that described above for 1-n-butylnaphthalene to obtain a 61% yield of 1-n-hexylnaphthalene, n_D^{20} 1.5652, d_{20}^{20} 0.957. These physical constants are in good agreement with the reported values:[3] n_D^{20} 1.5652, d_4^{20} 0.958.

Reaction of 1-naphthyllithium with benzyl chloride. To 207.1 g. (1.0 mole) of 1-bromonaphthalene was added, at −5°, an ethereal solution containing 1.0 mole of n-butyllithium; the mixture was stirred for 30 min. and then 190 g. (1.5 moles) of freshly distilled benzyl chloride was slowly added. Color Test I was negative immediately after all of the benzyl chloride had been added. After pouring into water and separating the layers, the organic material was distilled at reduced pressure. The fraction boiling from 250–270° (3.5 mm.) was digested with petroleum ether (b.p. 30–60°) and the solution was allowed to crystallize undisturbed. After 2 days, 33 g. of white solid melting at 81–83° was removed. Recrystallization from ethanol raised the melting point to 82–83°.

The expected product, 1-benzylnaphthalene, melts at 58°.[8] A sodium fusion test showed halogen to be absent. The compound was insoluble in concentrated sulfuric acid, and a picrate could not be made. The ultraviolet absorption spectrum of the compound showed maxima at 273, 283.5, 292.5 and 276 mμ. On the basis of these data and the report by other investigators of a similar reaction,[9] the compound is believed to be 1-naphthylphenylbenzylmethane.

Anal. Calcd. for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.86, 93.96; H, 5.99, 6.21.

Attempted addition of 1-naphthyllithium to stilbene. An ethereal solution of 5.0 g. (0.028 mole) of stilbene and 0.056 mole of 1-naphthyllithium (prepared in 86% yield) was refluxed for 16 hr. Following hydrolysis and separation of the layers, the organic material was distilled at 3.0 mm. The fraction boiling from 240–305°, a red oil, was digested with 4 ml. of petroleum ether (b.p. 30–60°) and cooled to give 2.3 g. of stilbene (mixture melting point) melting at 118–120°. The remaining oil was dissolved in petroleum ether (b.p. 30–60°) and the petroleum ether solutions were combined and chromatographed on alumina. Six distinct bands developed on the column. After extruding and separating the 6 bands, the organic material was eluted with methanol. Evaporation of all fractions gave only colored oils which could not be crystallized.

1,2-Diphenyl-1-(1-naphthyl)ethylene (attempted). A number of substituted stilbenes have been prepared by distilling the corresponding carbinol at reduced pressure in the presence of a trace of sulfuric acid.[14] 1-Naphthylphenylbenzylcarbinol, m.p. 148–149°, was prepared by the method of Bauer.[15] Seven grams (0.021 mole) of 1-naphthylphenylbenzylcarbinol was distilled at 0.1 mm., after adding 3 drops of 50% sulfuric acid to the dry solid. The fraction boiling at 215–220°, 6 g. of a yellow viscous oil, was collected and dissolved in petroleum ether (b.p. 60–80°). Only oils were obtained from methanol, ethanol, petroleum ether, and various combinations of these solvents.

Attempted dehydration of 1-naphthylphenylbenzylcarbinol by Chugaev's method. Although this reaction was carried out in essential accordance with the procedure of Alexander and Mudrak[16] for use with a similar carbinol, a 92% recovery of starting alcohol was obtained. Since it was believed that the sodium salt of the carbinol was not formed initially in the 3-step reaction, the lithium salt was made by adding an equivalent amount of n-butyllithium to the alcohol. The above procedure was then followed but an 84% recovery of the carbinol was obtained.

1-Naphthylphenylbenzylmethyl chloride (attempted). A mixture of 2.0 g. (0.006 mole) of 1-naphthylphenylbenzylcarbinol and thionyl chloride (freshly distilled from quinoline) in benzene was refluxed for 2 hr. The solvent and excess thionyl chloride were removed by distillation at reduced pressure to give a yellow oil. This material could not be crystallized from petroleum ether (b.p. 60–80°), ethanol, or benzene.

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(14) W. Tadros, K. Farahat, and J. M. Robson, *J. Chem. Soc.*, 439 (1949).

(15) H. Bauer, *Ber.*, **42**, 2588 (1909).

(16) E. R. Alexander and A. Mudrak, *J. Am. Chem. Soc.*, **72**, 1810 (1950).

An Improved Metalation Procedure for Dibenzofuran

HENRY GILMAN AND RICHARD D. GORSICH

Received December 14, 1956

Dibenzofuran has been metalated successfully in the past with various organolithium compounds.[1] A comparative metalation study of dibenzofuran with n-butyllithium has been carried out in diethyl ether, di-n-butyl ether and petroleum ether (b.p. 28–38°) to give yields of 56%, 76%, and 1%, respectively, of 4-dibenzofurancarboxylic acid after carbonation of the metalated product. In all of these cases the reaction mixtures were refluxed for 4–24 hr. with the yields of 4-dibenzofuryllithium increasing slightly with increased refluxing periods.[2] The use of organolithium compounds other than n-butyllithium generally results in smaller yields of 4-dibenzofuryllithium.[2,3] It might be mentioned that 4-dibenzofuryllithium has been derived in rather good yields with O-methylhydroxylamine and with oxygen to give the amine and hy-

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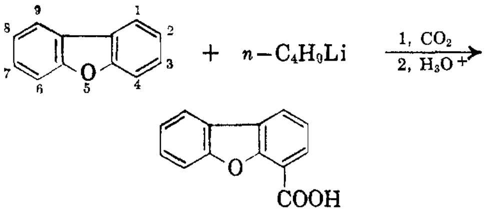
(1) For a general discussion of metalation reactions see H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **VIII**, Chap. 6 (1954).

(2) H. Gilman, F. W. Moore, and O. Baine, *J. Am. Chem. Soc.*, **63**, 2479 (1941).

(3) H. Gilman and C. G. Stuckwisch, *J. Am. Chem. Soc.*, **67**, 877 (1945).

droxy compound, respectively.[4] Although the yields of the latter two compounds were higher than that of the corresponding carboxylic acid, the conditions for preparing the 4-dibenzofuryllithium were quite similar.

We have metalated dibenzofuran with *n*-butyllithium in yields (83–86%) higher and under conditions much milder than ever described previously. The *n*-butyllithium, prepared in diethyl ether, was added to a tetrahydrofuran solution of dibenzofuran at −60° and then the reaction mixture was stirred between 0–5° for 1 hr. before carbonating. For our present investigations we have purposely selected tetrahydrofuran because it is a more basic solvent than any utilized in previous studies.[5]



In order to examine further the pronounced effect of tetrahydrofuran on the metalation of dibenzofuran, a run was made at −50°. A significant 11% yield of acid was obtained after stirring at −50° for 1 hr. followed by carbonation. In contrast, a diethyl ether solution of dibenzofuran and butyllithium stirred at 0° for 1 hr. afforded only a 5% yield of acid.

It was hoped that the exclusion of diethyl ether from the reaction might result in the metalation occurring under even milder conditions than already mentioned. For this purpose the *n*-butyllithium was prepared *in situ* at −25° from butyl chloride.[6,7] The highest yield of acid obtained with this method was 30%. The use of butyl bromide instead of butyl chloride did not result in any better yields. The studies are being extended to other systems.

EXPERIMENTAL[8]

Metalation of dibenzofuran in tetrahydrofuran with preformed n-butyllithium (*A*) *at 0°*. To a stirred solution of 4.2 g. (0.025 mole) of dibenzofuran in 35 ml. of tetrahydrofuran[9] was added, during 10 min., 22 ml. of a diethyl ether solution containing 0.03 mole of *n*-butyllithium.[10] The temperature of the reaction mixture was maintained between −55 and −60° during the addition. On completion of the addition, the mixture was stirred between −45 and −50° for 5 min. before being allowed to warm to 0° during 15 min. The brown solution was stirred in an ice bath for 1 hr., cooled to −50° and carbonated by pouring the solution jetwise into a slurry of Dry-Ice and ether. Prior to separation of the two layers, 50 ml. of diethyl ether was added to the mixture to reduce the solubility of water in the organic layer. The aqueous layer was boiled until most of the tetrahydrofuran had been expelled and then was acidified with concentrated hydrochloric acid. The organic layer was extracted with two 30-ml. portions of 5% sodium hydroxide. The combined extracts were boiled and acidified. The combined crude acid was dried and then crystallized from a mixture of ethanol and water to give 4.56 g. (86%) of 4-dibenzofurancarboxylic acid, m.p. 213–214°. A mixed melting point with an authentic sample showed no depression. After drying the organic layer over anhydrous sodium sulfate and distilling the solvents, no unchanged dibenzofuran was recovered.

In another run the reaction mixture was stirred at 0° for 2.5 hr. After working up the mixture as described above there was obtained an 83% yield of the acid.

At −50°. In another experiment the temperature was kept between −55 and −60° during the addition. After completing the addition, the mixture was stirred at the minimum temperature afforded by dry ice-acetone for 15 min., and then between −50 and −55° for 70 min. The mixture was cooled to −70° and carbonated in the manner described in the preceding experiment. Work-up of the reaction mixture as described in the last run yielded 0.65 g. of crude acid melting over the range 208–212°. Crystallization from ethanol-water gave 0.58 g. (11%) of 4-dibenzofurancarboxylic acid, m.p. 212–214°. The yield of unchanged dibenzofuran was 3.41 g. (81%).

In a similar run employing the same quantities of reactants, the reaction mixture was stirred between −35 and −40° for 15 min. after adding the butyllithium during 9 min. at the same temperature. From the aqueous layer and basic extracts there was finally obtained 0.42 g. (7.9%) of acid, m.p. 212.5–214°. Distillation of the solvents from the organic layer left 3.80 g. (90%) of unchanged dibenzofuran.

Metalation of dibenzofuran with n-butyllithium prepared in situ. To a mixture of 0.60 g. (0.086 g. atom) of lithium wire cut into small pieces, 4.2 g. (0.025 mole) of dibenzofuran, and 40 ml. of tetrahydrofuran was added, during 18 min., a solution of 2.60 g. (0.028 mole) of *n*-butyl chloride in 5 ml. of tetrahydrofuran. The addition was carried out between −25 and −30°. The mixture became bright orange after adding a few drops of butyl chloride. Subsequent to stirring between −25 and −30° for 13 min., 20 ml. of diethyl ether was added; the mixture was cooled to about −60° and carbonated as described previously. Work-up of the reaction mixture in the usual manner gave 1.64 g. of crude acid which was recrystallized to give 1.60 g. (30%) of 4-dibenzofurancarboxylic acid, m.p. 210–212°.

There was obtained from the neutral organic layer 1.62 g. (39%) of starting material.

In a similar run *n*-butyl bromide was used in place of *n*-butyl chloride and the reaction mixture was stirred be-

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(4) H. Gilman and R. K. Ingham, **75**, 4843 (1953); H. Gilman and R. V. Young, *J. Am. Chem. Soc.*, **57**, 1121 (1935).

(5) The base strength of tetrahydrofuran toward boron trifluoride is greater than that of diethyl ether; H. C. Brown and R. M. Adams, *J. Am. Chem. Soc.*, **64**, 2557 (1942).

(6) The butyllithium was prepared in this manner to avoid loss of the RLi compound. It has been observed that the yield of butyllithium decreases more rapidly in tetrahydrofuran than in diethyl ether; B. Gaj, unpublished studies.

(7) The mixture was not warmed to 0° since it is possible to cleave dibenzofuran with lithium in tetrahydrofuran at warmer temperatures; H. Gilman and J. J. Dietrich, *J. Org. Chem.*, in press.

(8) All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen and all melting points are uncorrected.

(9) The tetrahydrofuran was dried and purified by shaking with sodium hydroxide pellets, refluxing over sodium metal for several hours and finally distilling, immediately before use, from lithium aluminum hydride.

(10) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949). The yield was determined according to a procedure described by H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

tween −30 and −35° for 35 min. rather than between −25 and −30°. In this run the yield of 4-dibenzofurancarboxylic acid was 1.32 g. (25%).[11]

From the neutral organic layer there was isolated 2.51 g. (60%) of starting dibenzofuran.

Metalation of dibenzofuran in diethyl ether at 0°. Twenty milliliters of a diethyl ether solution containing 0.028 mole of butyllithium was added rapidly to a stirred solution of 4.2 g. (0.025 mole) of dibenzofuran in 35 ml. of dry diethyl ether cooled to *ca* −10°. The reaction mixture was stirred in an ice bath for 1 hr., cooled to −20° and carbonated. Work-up in the usual manner afforded 0.26 g. (4.9%) of 4-dibenzofurancarboxylic acid, m.p. 210–212°.

The organic layer, after drying and distilling the ether, gave 3.32 g. (79%) of starting dibenzofuran.

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[11] The low yield of acid obtained when using butyl bromide may be due in part to the tendency of butyl bromide to couple in tetrahydrofuran. Butyllithium can be prepared only in very small yields from butyl bromide and lithium in tetrahydrofuran; B. Gaj, unpublished studies.

Reaction of Triphenyltin-Lithium with Some Esters

HENRY GILMAN AND LEWIS A. GIST, JR.[1]

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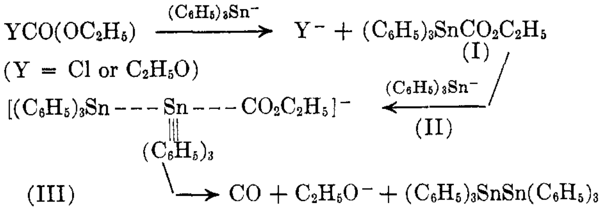
In the course of investigations in this laboratory, the reactions of triphenyltin-lithium with diethyl carbonate and with ethyl chloroformate have been explored as a possible route for preparing ethyl triphenylstannylcarboxylate and bistriphenyltin ketone. The products obtained, however, were not the desired ester and ketone. Instead, carbon monoxide was vigorously evolved, and hexaphenylditin was obtained as the principle product along with a lesser amount (*ca.* 20%) of tetraphenyltin.

The mechanism of this reaction was not determined. It is believed, however, that ethyl triphenylstannylcarboxylate was first formed, then decarbonylated in a manner similar to that proposed earlier for esters of triphenylsilanecarboxylic acid,[2] and for methyl triphenylgermanecarboxylate.[3] The proposed mechanism would involve the attack of the triphenyltin anion (II) on the tin atom of the intermediate ethyl triphenylstannylcarboxylate (I) with the formation of a transition state (III), which leads to the products obtained.



$$YCO(OC_2H_5) \xrightarrow{(C_6H_5)_3Sn^-} Y^- + \underset{(I)}{(C_6H_5)_3SnCO_2C_2H_5}$$

$$(Y = Cl \text{ or } C_2H_5O)$$

$$[(C_6H_5)_3Sn---\underset{(C_6H_5)_3}{\overset{}{Sn}}---CO_2C_2H_5]^- \xleftarrow[(II)]{(C_6H_5)_3Sn^-}$$

$$(III) \longrightarrow CO + C_2H_5O^- + (C_6H_5)_3SnSn(C_6H_5)_3$$

It is reasonable to expect the intermediate ethyl triphenylstannylcarboxylate to be rather unstable in the presence of a base. The electropositive triphenyltin radical attached directly to a pseudo-positive carbon atom should be highly susceptible to an anionic attack of this type. Furthermore, the large atomic radius of the tin atom coupled with its low electron density renders it vulnerable to nucleophilic attack. It is also possible that a radical mechanism might be proposed for this reaction.

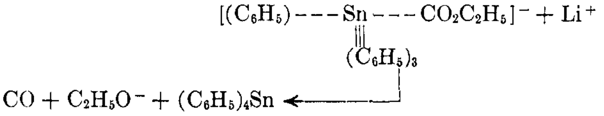
After carbonation of the product obtained from the reaction of triphenyltin-lithium with fluorene, d'Ans and co-workers[4] obtained approximately a 20% yield of 9-fluorenecarboxylic acid. These investigators[4] concluded, therefore, that triphenyltin-lithium was approximately 20% dissociated according to the equation:

$$(C_6H_5)_3Sn^-\,Li^+ \rightleftarrows (C_6H_5)_2Sn + C_6H_5Li$$

Conversely, the reactions of triphenyltin-lithium with gaseous carbon dioxide, Dry Ice, benzophenone, and benzalacetophenone were investigated in this laboratory earlier,[5,6] and no evidence of such an equilibrium could be found.

The reaction of triphenyltin-lithium with diethyl carbonate and with ethyl chloroformate offered an opportunity to investigate again the possibility of this equilibrium. None of the compounds which might be expected from the reaction of phenyllithium with diethyl carbonate or with ethyl chloroformate could be found among the products of the reaction.

The presence of tetraphenyltin in these reaction mixtures could conceivably have resulted from the reaction of ethyl triphenylstannylcarboxylate (I) with phenyllithium as follows:



$$C_6H_5^-Li^+ + \underset{(I)}{(C_6H_5)_3SnCO_2C_2H_5} \longrightarrow [(C_6H_5)---\underset{(C_6H_5)_3}{Sn}---CO_2C_2H_5]^- + Li^+$$

$$\longrightarrow CO + C_2H_5O^- + (C_6H_5)_4Sn$$

However, tetraphenyltin is believed to have resulted as a by-product in the preparation of triphenyltin-lithium, and not from a reaction of the type proposed above, since it is invariably obtained

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[1] General Education Board Fellow at Iowa State College, 1952–1954.

[2] A. G. Brook and H. Gilman, *J. Am. Chem. Soc.*, **77**, 2322 (1955).

[3] H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **77**, 4675 (1955).

[4] J. d'Ans, H. Zimmer, E. Endrulat, and K. Lübke, *Naturwissenschaften*, **39**, 450 (1952).

[5] H. Gilman and S. D. Rosenberg, *J. Org. Chem.*, **18**, 680 (1953).

[6] H. Gilman and S. D. Rosenberg, *J. Org. Chem.*, **18**, 1554 (1953).