Diphenyl-*p*-tolylsilane is reported[4a] to melt at 176–177° and the accompanying analysis given is acceptable for this compound. It is possible that the reported compound might be a mixture of tetraphenyl- and tetra-*p*-tolylsilane. If two equivalents of the first-added organolithium reagent are mixed too rapidly with silicon tetrachloride, a substantial quantity of the corresponding tetrasubstituted silane may be formed. This would leave a proportionate amount of unreacted silicon tetrachloride to react with the second organolithium reagent forming the tetrasubstituted silane. The resulting mixture of tetraphenyl- and tetra-*p*-tolylsilane might form a eutectic mixture and give a correct silicon analysis for diphenyldi-*p*-tolylsilane. In order to check this possibility, equivalent amounts of the two pure tetrasubstituted silanes were recrystallized together from ethyl acetate. Even after three recrystallizations, the melting point had not changed from that of the original mixture, which melted at 199–201°.

Phenyltri-*p*-tolylsilane.—To a stirred mixture of 6.5 g. (0.031 mole) of phenyltrichlorosilane was added 88.5 ml. of a 1.13 *N* ethereal solution of *p*-tolyllithium (0.10 mole). No attempt was made to cool the reaction flask and the addition was made at such a rate as to permit gentle refluxing. After the mixture was poured onto water, the organic layer was washed well with dilute hydrochloric acid and the layers were separated. The solvent was removed to yield 10.2 g. of gray solid melting from 176–180°. Two recrystallizations of this material from petroleum ether (b.p. 90–110°) gave 3.85 g. of white crystals melting at 182–183°.[15] This melting point was not improved after two recrystallizations from ethyl acetate. After removing the solvent from the combined mother liquors and recrystallizing the residue from petroleum ether (b.p. 60–80°), an additional 4.5 g. of product melting at 180–181° was obtained. The yield of good quality phenyltri-*p*-tolylsilane was 71%.

Since phenyltri-*p*-tolylsilane has been reported[4b] to melt at 127–128°, the material melting at 182–183° was analyzed.

Anal. Calcd. for $C_{27}H_{26}Si$: Si, 7.42. Found: Si, 7.40, 7.39.

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[15] The use of this compound for a mixed m.p. was reported by A. G. Brook and H. Gilman, This Journal, **76**, 2333 (1954).

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The Preparation of *o*-Fluorophenyllithium

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Previously *o*-fluorophenyllithium had been postulated as an intermediate in the reaction of fluorobenzene with phenyllithium.[1,2] Evidence indicated that the fluorobenzene was metalated in the *ortho* position and that the *o*-fluorophenyllithium thus formed reacted further with phenyllithium to give 2-biphenylyllithium which was identified by derivatization with benzophenone. However, in no case was any derivative obtained indicating that *o*-fluorophenyllithium was an intermediate in the sequence of reactions mentioned above. Since *o*-fluorophenyllithium could not be detected it was concluded that the fluorine in *o*-fluorophenyllithium was so mobile that the *o*-fluorophenyllithium reacted further with phenyllithium or itself although no evidence was found to substantiate the latter possibility.

Although *o*-fluorophenyllithium appears to be a very reactive compound as correctly stated earlier by Wittig and co-workers, we have been able to prepare it in very high yields at −70° by the interaction of *o*-fluorobromobenzene and *n*-butyllithium. The *o*-fluorophenyllithium was treated subsequently with benzophenone to give an 84% yield of *o*-fluorophenyldiphenylcarbinol. All the reactions were carried out at about −70° and despite this low temperature the reaction of the organolithium compound with benzophenone was almost instantaneous as was evidenced by a negative Color Test I[3] immediately following the addition of the benzophenone.

$$o\text{-FC}_6\text{H}_4\text{Br} \xrightarrow{n\text{-C}_4\text{H}_9\text{Li}} o\text{-FC}_6\text{H}_4\text{Li} \xrightarrow{(\text{C}_6\text{H}_5)_2\text{CO}} o\text{-FC}_6\text{H}_4\text{C(OH)(C}_6\text{H}_5)_2$$

The *o*-fluorophenyldiphenylcarbinol was identified by a mixed melting point determination with a specimen synthesized unambiguously by the reaction of *o*-fluorobenzoyl chloride with phenylmagnesium bromide.

An attempt to prepare *o*-fluorophenyllithium at −15° proved unsuccessful, for only a trace of unidentified acidic material was obtained after carbonating the reaction mixture. Apparently, even at −15° the compound is too reactive to exist in appreciable quantities under these conditions. Further results concerning the stability of *o*-fluorophenyllithium at higher temperatures and its role as a possible intermediate in other reactions will be presented later.

Experimental[4]

Reaction of *o*-Fluorophenyllithium and Benzophenone.—To a 250-ml., three-necked flask fitted with a mechanical stirrer, addition funnel and thermometer was added 38 ml. of a 1.315 *N* *n*-butyllithium solution.[5] An additional 35 ml. of anhydrous ether was added and the resulting solution was cooled to −70° by means of a Dry Ice–acetone-bath. To the rapidly stirred solution was added, over a period of 4 minutes, 8.74 g. (0.05 mole) of *o*-fluorobromobenzene dissolved in 60 ml. of ether, always maintaining the temperature below −65° during the addition. Immediately on completion of the addition, a solution of 9.1 g. (0.05 mole) of benzophenone in 50 ml. of ether was added while keeping the temperature of the reaction mixture between −65 and −70°. Color Test I was negative immediately following the addition of benzophenone. Subsequently, the reaction mixture was poured into iced 5% hydrochloric acid. The ethereal layer was separated from the aqueous layer and then dried over anhydrous sodium sulfate. The mixture was filtered and the ether was distilled from the filtrate on a steam-bath. The residue, 13.7 g., was crystallized from a minimum of petroleum ether (b.p. 60–70°) to yield after air-drying 10.6 g. of *o*-fluorophenyldiphenylcarbinol melting at 117.5–118.5°. Concentration of the mother liquor gave an additional 1.05 g. of white powder melting at 115–116°. The total yield of *o*-fluorophenyldiphenylcarbinol based on *o*-fluorobromobenzene was 83.8%.

***o*-Fluorophenyldiphenylcarbinol from *o*-Fluorobenzoyl Chloride and Phenylmagnesium Bromide.**—The *o*-fluorobenzoyl chloride was prepared by heating 2.3 g. (0.0164 mole) of *o*-fluorobenzoic acid and 3.9 g. (0.0328 mole) of thionyl chloride on a steam-bath for one hour. The excess thionyl chloride was removed by distillation between 70 and 80°. The product was distilled at 92–93° at 11 mm. to give 2.0 g. (76.7%) of *o*-fluorobenzoyl chloride. The boiling point of *o*-fluorobenzoyl chloride has been reported as 99° at 13 mm.[6]

The *o*-fluorobenzoyl chloride described above was added[7] to

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[1] G. Wittig, G. Pieper and G. Fuhrmann, *Ber.*, **73**, 1193 (1940).

[2] G. Wittig and W. Merkle, *ibid.*, **75**, 1491 (1942).

[3] H. Gilman and F. Schulze, This Journal, **47**, 2002 (1925).

[4] All melting points reported herein are uncorrected and all reactions involving organometallic compounds were carried out under an atmosphere of dry, oxygen-free nitrogen.

[5] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, This Journal, **71**, 1499 (1949).

[6] J. B. Cohen, *J. Chem. Soc.*, **99**, 1062 (1911).

[7] For a general procedure on a related reaction see H. Gilman, R. E. Fothergill and H. H. Parker, *Rec. trav. chim.*, **48**, 748 (1929).

phenylmagnesium bromide prepared from 10.3 g. (0.066 mole) of bromobenzene and 1.64 g. (0.067 g. atom) of magnesium turnings. After working up the reaction mixture according to the method described previously there was obtained 1.9 g. (54.3%) of *o*-fluorophenyldiphenylcarbinol melting at 113–115°. An additional crystallization from petroleum ether (b.p. 60–70°) raised the melting point to 116–117°.

A mixed melting point of this compound with that obtained from the reaction of *o*-fluorophenyllithium and benzophenone showed no depression.

The melting point of *o*-fluorophenyldiphenylcarbinol prepared from methyl *o*-fluorobenzoate and phenylmagnesium bromide has been reported as 116°.[8]

Attempted Preparation of *o*-Fluorophenyllithium at −15°.—Thirty-seven milliliters of a 0.98 *N* *n*-butyllithium solution was added over a period of 6 minutes to a rapidly stirred solution of 6.0 g. (0.0342 mole) of *o*-fluorobromobenzene in 55 ml. of anhydrous ether. The temperature was not permitted to rise above −15° during the addition. Immediately on completion of the addition, Color Test I was positive while Color Test II[9] was negative. The reaction mixture was poured jetwise over a Dry Ice–ether slurry. The carbonated mixture was hydrolyzed with water and then the ethereal layer was separated. The organic layer was washed twice with two 50-ml. portions of 5% sodium hydroxide and the extracts were combined with the original aqueous layer. The residual ether was boiled from the aqueous solution and then the solution was acidified with hydrochloric acid. A milky solution resulted and after cooling a fine precipitate settled out. This precipitate was filtered and air-dried to yield 0.20 g. of light brown powder melting over the range 200–210° with decomposition. Attempts to recrystallize the unknown material have been unsuccessful.

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(8) E. Bergmann, *Rec. trav. chim.*, **58**, 863 (1939).

(9) H. Gilman and J. Swiss, This Journal, **62**, 1847 (1940).

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The Nitration of Some 2- and 3-Amino Derivatives of Dibenzothiophene

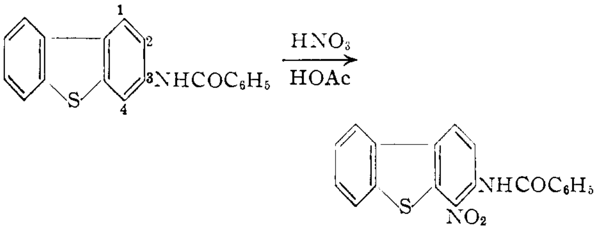
By Henry Gilman and Gene R. Wilder

Received March 11, 1955

2-Carbethoxyaminodibenzothiophene[1] and 2-acetaminodibenzothiophene[2] have been shown to nitrate predominantly in the 1-position as opposed to the structurally similar 2-acetaminodibenzofuran, which nitrates in the 3-position.[3] 2-Benzenesulfonamidodibenzothiophene,[4] as well as 2-benzamidodibenzothiophene, however, nitrate almost exclusively in the 3-position, indicating that steric factors may play a significant role in the direction of electrophilic attack on the 2-substituted aminodibenzothiophene derivatives.

The nitration of 3-acetaminodibenzothiophene affords a 77% yield of 4-nitro-3-acetaminodibenzothiophene[1] as opposed to the nitration of 3-acetaminodibenzofuran which gives the 2-nitro-3-acetamino derivative in a 75% yield.[2]

In a similar fashion then, it was thought that nitration of 3-benzamidodibenzothiophene would yield mostly the 2-nitro product; however, a 79.5% crude yield of 4-nitro-3-benzamidodibenzothiophene was obtained, indicating that steric factors do not have so strong an effect in influencing entering groups in the 4-position.



Experimental[5]

2-Benzamidodibenzothiophene.—Seven grams (0.0352 mole) of 2-aminodibenzothiophene[6] was dissolved in 100 ml. of benzene to which had been added 3.0 ml. of pyridine. This solution was warmed slightly and treated with 5.0 ml. of benzoyl chloride giving rise to a precipitate. The mixture then was cooled and the precipitate filtered and washed with small portions of dil. hydrochloric acid. This crude material was crystallized from methyl Cellosolve to yield 6.0 g. (60.0%) of 2-benzamidodibenzothiophene melting at 199–200°.

Anal. Calcd. for $C_{19}H_{13}NOS$: S, 10.57. Found: S, 10.42.

3-Benzamidodibenzothiophene.—This material was prepared in a similar fashion as above from 3-aminodibenzothiophene[7] to yield 96.7% of 3-benzamidodibenzothiophene melting at 227–228°.

Anal. Calcd. for $C_{19}H_{13}NOS$: S, 10.57. Found: S, 10.51.

4-Nitro-3-benzamidodibenzothiophene.—Into a 250-ml. round-bottomed, three-necked flask equipped with a mechanical stirrer and reflux condenser were placed 3.5 g. (0.015 mole) of 3-benzamidodibenzothiophene and 100 ml. of glacial acetic acid. To the stirring mixture was added over a period of 15 min., 8.0 ml. of nitric acid (90%). A precipitate formed during the addition of the nitric acid and the reaction mixture was stirred for 15 min. The resulting precipitate was filtered and dried to yield 3.2 g. (79.5%) of crude, orange product, m.p. 225–233°. This material was crystallized from methyl Cellosolve to yield 2.1 g. (52.0%) of orange, fiber-like needles of 4-nitro-3-benzamidodibenzothiophene melting at 246–247°.

Anal. Calcd. for $C_{19}H_{12}N_2O_3S$: S, 9.21. Found: S, 8.91.

4-Nitro-3-aminodibenzothiophene.—Into a 125-ml. erlenmeyer flask equipped with a reflux condenser were placed 1.0 g. (0.00288 mole) of 4-nitro-3-benzamidodibenzothiophene, 5.0 g. of potassium hydroxide, 25 ml. of water and 25 ml. of ethanol. The reaction mixture was allowed to reflux for a period of two hours at which time 50 ml. of water was added to the system and the contents cooled. The reddish-orange material was filtered and dried to yield 0.57 g. (81.0%) of 4-nitro-3-aminodibenzothiophene melting at 244–245° and giving no depression in melting point when admixed with an authentic specimen of 4-nitro-3-aminodibenzothiophene.

3-Nitro-2-benzamidodibenzothiophene.—Into a 250-ml. round-bottomed, three-necked flask equipped with a mechanical stirrer and reflux condenser were placed 5.5 g. (0.0182 mole) of 2-benzamidodibenzothiophene, 50 ml. of glacial acetic acid and 7.0 ml. of nitric acid (90%). A precipitate formed almost immediately; however, stirring was continued for a period of 15 min. The resulting precipitate was filtered and crystallized from methyl Cellosolve to yield 4.2 g. (67.0%) of golden needles melting at 213–214°.

Anal. Calcd. for $C_{19}H_{12}N_2O_3S$: S, 9.21. Found: S, 9.30.

A small sample of this material was hydrolyzed in a manner described for the hydrolysis of the 3-benzamido product to yield a compound which corresponds to the nitro-amine obtained from the nitration of 2-benzenesulfonamidodibenzothiophene[4] followed by hydrolysis, which melted at 246–247°.

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(1) E. Sawicki, *J. Org. Chem.*, **18**, 1492 (1953).

(2) H. Gilman and G. R. Wilder, This Journal, **76**, 2906 (1954).

(3) H. Gilman, G. E. Brown, W. G. Bywater and W. H. Kirkpatrick, *ibid.*, **56**, 2473 (1934).

(4) E. Sawicki, *J. Org. Chem.*, **19**, 608 (1954).

(5) All melting points are uncorrected.

(6) H. Gilman and J. F. Nobis, This Journal, **71**, 274 (1949).

(7) H. Gilman and J. F. Nobis, *ibid.*, **67**, 1479 (1945).

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