removed under reduced pressure. The residual acetic acid concentrate was allowed to evaporate on watch glasses overnight. Adding water to the oil induced crystallization. The water-washed crystals weighed 53.3 g. The oily material in the filtrate was hydrolyzed with dilute aqueous hydrochloric acid to yield 9 g. of crude glucuronolactone. The crystalline mixture was separated into its components by taking advantage of the differences in ether solubility of the pyridine salts of the anomers. It was dissolved in 55 ml. of hot pyridine, the brown solution cooled and diluted with ca. 150 ml. of ether. The crystalline salt of the β-anomer separated, wt. 31.8 g. The filtrate was taken to an oil under reduced pressure, the red oil dissolved in water and the solution acidified with hydrochloric acid. The precipitated oil crystallized to give 20.2 g. of the α-anomer. The β-anomer–pyridine salt was dissolved in 50 ml. of warm water, the solution cooled and the salt decomposed with a small excess of hydrochloric acid; the β-anomer separated crystalline in a hydrated form which was freed of water by refluxing in toluene with a water collector. It separated crystalline from the cooled toluene solution but was contaminated by an oil which was removed with ether, leaving 20.0 g. of the β-anomer melting at 146–152°. The oil, 4.6 g., proved to be an α–β mixture and was separated into its components by repassage through the pyridine salt. The β-anomer was further purified by means of toluene and had m.p. 152–154°, [α]²⁰D +16.3° (c 0.5 in chloroform).

Anal. Calcd. for $C_{14}H_{18}O_{11}$: C, 46.41; H, 5.01. Found: C, 46.62; H, 5.20.

By the action of diazomethane in ether this acid gave an ester which melted at 172–174° and did not depress the melting point of a sample of methyl tetra-O-acetyl-β-D-glucopyranuronate, m.p. 173–176°, prepared by acetylation of methyl glucuronate. For this compound Goebel and Babers[2a] reported m.p. 178°, [α]²⁰D +8.7° (c 1.0 in chloroform).

The α-anomer was recrystallized from ethanol, and appeared to contain solvent. Dried in an Abderhalden tube at 80° under reduced pressure, one sample melted at 118–119°. Under the same conditions another portion of the same sample melted at 116–119°. Another dry sample melted at 105–117°, but after moistening with alcohol and redrying, it melted at 114–118°. More than one crystalline form is thereby indicated. The material had [α]¹⁹D +111° (c 0.7 in chloroform).

Anal. Calcd. for $C_{14}H_{18}O_{11}$: C, 46.41; H, 5.01. Found: C, 46.28; H, 4.90.

The methyl ester was prepared as above. The ester likewise had a broad melting range, from 113–118°. The melting point was not depressed by admixture with a sample, m.p. 117–119°, prepared by acetylation of methyl glucuronate. This compound is reported[2a] to melt at 111–112° with [α]²⁵D +98° (c 1.3 in chloroform).

[The material obtained by the acetolysis of β-pachyman in the presence of perchloric acid[4] melting at 103–107°, [α]²⁰D +66.2° (chloroform), could be a mixture of the anomeric acids. Tetra-O-acetyl-β-D-glucose on potassium permanganate oxidation is reported to yield an oil consisting mainly of tetra-O-acetyl-D-glucuronic acid, [α]D +6° (c 1.1 in chloroform).[5]]

Tri-O-acetyl-β-D-glucopyranurono-6,1-lactone. A.—A solution of 13.2 g. of tetra-O-acetyl-β-D-glucopyranuronic acid in 550 ml. of benzene in a flask equipped with a water trap was refluxed until all visible water was removed. The solution was rapidly cooled to 38° and 5.7 ml. of stannic chloride added. A small amount of flocculent precipitate formed. The temperature dropped to 29° in 40 minutes, when it was reduced to 20° and 13 g. of sodium carbonate in 50 ml. of aqueous solution was added with stirring. The benzene layer was separated, the solvent removed under reduced pressure and the crystalline product filtered from an alcohol suspension. A total of 8.4 g. (76%), m.p. 122–124°, was recovered. Recrystallized from alcohol, it melted at 122.5–124° and had [α]¹⁹D −78.6° (c 0.9 in chloroform).

Anal. Calcd. for $C_{12}H_{14}O_9$: C, 47.68; H, 4.67. Found: C, 47.86; H, 4.56.

Under similar conditions 80% of the α-anomer was recovered from the aqueous solution after acidification and 10%

(4) K. Takeda, *J. Agr. Chem. Soc. Japan*, **10**, 1111 (1934); *Bull. Agr. Chem. Soc. Japan*, **10**, 160 (1934); *C. A.*, **29**, 831 (1935).
(5) M. Stacey, *J. Chem. Soc.*, 1529 (1939).

by weight of an unidentified oil was present in the benzene.

B. (Tri-O-acetyl-α-D-glucopyranosyl bromide)-uronic acid (see below) was heated in pyridine solution for five minutes. Dilution of the cooled red solution with water gave the lactone in 8% yield. The recovery was increased to 10% by heating the solution for 30 minutes. Identity with the lactone described above was established by melting point and mixture melting point determinations.

(Tri-O-acetyl-α-D-glucopyranosyl bromide)-uronic Acid (IIIa).—A suspension of 1.0 g. of tetra-O-acetyl-β-D-glucopyranuronic acid in 2.0 ml. of hydrobromic acid–acetic acid solution containing 0.11 mole of hydrogen bromide was shaken for ten minutes to give a yellow solution. Crystals began to separate in an hour and after two hours water was added to the chilled suspension. The product was removed by filtration and water-washed, wt. 0.85 g. (80%). Recrystallization was effected by adding petroleum ether (30–60°) to a solution in ethyl acetate. It melted with decomposition ca. 165°, the temperature of decomposition varying with the rate of heating; [α]²⁰D +209° (c 0.4 in chloroform).

Anal. Calcd. for $C_{12}H_{15}BrO_9$: C, 37.61; H, 3.95; Br, 20.86. Found: C, 37.39; H, 3.87; Br, 21.06.

Under similar conditions this compound was also obtained from the α-anomer and the 6,1-lactone in ca. 60% yields. The optical rotations and decomposition points were in agreement with the above data but in order to get proof of identity the samples were kept separate and individually converted into the uronic acid described in the next paragraph.

Methyl Tri-O-acetyl-β-D-glucopyranosiduronic Acid.—Two grams of (tri-O-acetyl-α-D-glucopyranosyl bromide)-uronic acid in a cooled methanolic solution with silver carbonate reacted in the usual manner to give a crystalline product. Contaminating oil was removed by cold ether. It weighed 0.83 g. (47%), and was recrystallized by adding petroleum ether (30–60°) to a concentrated ethereal solution. After several recrystallizations it melted at 124–127° with a slight previous sinter; [α]¹⁹D −20.3° (c 1.0 in chloroform).

Anal. Calcd. for $C_{13}H_{18}O_{10}$: C, 46.71; H, 5.43. Found: C, 46.85; H, 5.46.

Samples of this material derived from the anomeric tetraacetylglucopyranuronic acids and from the 6,1-lactone were identical as determined by melting points and mixture melting points.

By the action of diazomethane in ether this acid was converted into methyl (methyl tri-O-acetyl-β-D-glucopyranosid)-uronate identical by melting and mixture melting point determinations with a sample prepared from methyl tetra-O-acetyl-β-D-glucopyranuronate.[2b]

Methyl (Tri-O-acetyl-α-D-glucopyranosyl bromide)-uronate (IIIb) resulted from the action of diazomethane in ether on (tri-O-acetyl-α-D-glucopyranosyl bromide)-uronic acid. It recrystallized from alcohol solution in prisms melting at 80–82°. Recrystallization from ether gave prisms which sintered at 80°, resolidified and melted at 103–104°. Goebel and Babers[2b] reported a partial collapse at 85° with melting at 104–105°.

Methanolysis of the Lactone II.—The action of hot methanol on the lactone in the presence of either pyridine, pyridine-p-toluenesulfonic acid salt or silver carbonate, in no case yielded the product of abnormal ring-opening, namely, methyl tri-O-acetyl-β-D-glucopyranosiduronic acid. Instead the ring opened normally to give an oil which after acetylation yielded methyl tetra-O-acetyl-β-D-glucopyranuronate (Ib).

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Some Tetrasubstituted Naphthyl- and Tolylsilanes

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Some of the steric factors concerned with naphthylsilanes have been discussed previously.[1] We

(1) (a) H. Gilman and C. G. Brannen, This Journal, **72**, 1280 (1950); (b) **73**, 1610 (1951).

are reporting the synthesis of additional compounds in an extension of the study of steric hindrance in arylsilanes.

Tri-1-naphthylphenylsilane has been prepared[2] from diethoxy-1-naphthylphenylsilane and 1-naphthyllithium; the reported melting point for this compound is 160–161°. This compound now has been synthesized by treating phenyllithium with tri-1-naphthylchlorosilane, with tri-1-naphthylsilane and with tri-1-naphthylethoxysilane; the pure tri-1-naphthylphenylsilane obtained by these methods has a melting point of 192–193°.

Tri-1-naphthyl-p-tolylsilane was prepared for comparative purposes and to provide a means of introducing functional groupings into the molecule. Another compound of this series, 1-naphthyltri-p-tolylsilane, recently has been reported.[3]

Tri-1-naphthyl-p-tolylsilane was prepared by the action of p-tolyllithium on tri-1-naphthylsilane, -chlorosilane, -bromosilane or -ethoxysilane, but only the last of these gave high yields. Probably this was due to the ease of purification and not because the other compounds failed to react completely.

Triphenyl-p-tolylsilane,[4a] diphenyldi-p-tolylsilane[4a] and phenyltri-p-tolylsilane[4b] have been reported.[5] We are describing new syntheses and corrected melting points (see Table I) for these compounds. It was not possible to obtain the reported high yields[4a] of diphenyldi-p-tolylsilane by the reaction of silicon tetrachloride with two equivalents of phenyllithium and two equivalents of p-tolyllithium; a method of choice for the synthesis of this compound is the reaction of diphenyldichlorosilane with p-tolyllithium.

TABLE I

Compound	M.p., °C.	M.p. prev. reptd., °C.	Ref.
$(C_6H_5)_3SiC_6H_4\text{-}Me\text{-}p$	140–141	134–135	4a
$(C_6H_5)_2Si(C_6H_4\text{-}Me\text{-}p)_2$	121–122	176–177	4a
$C_6H_5Si(C_6H_4\text{-}Me\text{-}p)_3$	182–183	127–128	4b
$(1\text{-}C_{10}H_7)_3SiC_6H_5$	192–193	160–161	2

Experimental[6]

Tri-1-naphthylphenylsilane. A. From Tri-1-naphthylchlorosilane and Phenyllithium.—To a solution of 15.0 g. (0.034 mole) of tri-1-naphthylchlorosilane in 200 ml. of dry benzene was added 0.24 mole of an ethereal solution of phenyllithium[7] (made in 96% yield in the usual manner but filtered through a pressure filter[8] immediately before use). Most of the ether was removed by distillation and the mixture was refluxed at 54° for 30 hours. Color Test I[9] was still positive after this treatment. Following hydrolysis with dilute hydrochloric acid and extraction of the inorganic salts,

(2) A. D. Petrov and V. S. Chugunov, *Doklady Akad. Nauk S.S.S.R.*, **77**, 815 (1951) [*C. A.*, **46**, 480 (1952)].

(3) V. S. Chugunov and A. D. Petrov, *Izvest. Akad. Nauk S.S.S.R.*, *Otdel. Khim. Nauk*, 713 (1953) [*C. A.*, **48**, 12716 (1954)].

(4) (a) H. Gilman and R. N. Clark, THIS JOURNAL, **68**, 1675 (1946); (b) R. N. Clark, Doctoral Dissertation, Iowa State College (1946).

(5) After this work was completed and written up for publication, an article appeared reporting the preparation of these three compounds; see M. Maienthal, M. Hellmann, C. P. Haber, L. A. Hymo, S. Carpenter and A. J. Carr, THIS JOURNAL, **76**, 6392 (1954). These authors report the following melting points: triphenyl-p-tolylsilane, 141–143°; diphenyldi-p-tolylsilane, 119–120°; and phenyltri-p-tolylsilane, 185.5–186.5°.

(6) All melting points are corrected.

(7) R. G. Jones and H. Gilman in R. Adams, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 353.

(8) A Hormann laboratory filter was used with a No. 1 asbestos pad.

(9) H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

the organic layer was set aside to crystallize, the solvent being allowed to evaporate slowly. After seven days, 11.25 g. of white solid melting from 135–150° was collected in two portions. Recrystallization from benzene, ethyl acetate, petroleum ether (b.p. 90–110°), and ethanol failed to change the melting point. Chromatography using the combination of alumina and petroleum ether (b.p. 60–80°) did not improve the melting point. This material was finally purified by exhaustive digestion[10] of the finely pulverized solid with four 20-ml. portions of ethanol. This procedure gave a yield of 8.7 g. (53%) of white solid melting at 192–193°.

Anal.[11] Calcd. for $C_{36}H_{26}Si$: Si, 5.76. Found: Si, 5.75, 5.84.

This experiment was repeated several times in an effort to obtain higher yields and to isolate other compounds. In all cases the crude product melted from 135–150° and this material resisted attempts at purification by all of the common laboratory methods except by digestion or crystallization from chlorobenzene (see section D). The yields varied from 40–60%. Silicon analysis of the low-melting material indicated it to contain 5.29% silicon. A sodium fusion test indicated the absence of halogen. The expected impurities would contain a higher percentage of silicon than does trinaphthylphenylsilane.

B. From Tri-1-naphthylsilane and Phenyllithium.— Ten grams (0.024 mole) of tri-1-naphthylsilane was dissolved in 250 ml. of dry ether and 0.02 mole of phenyllithium (prepared in 92% yield) was added to the refluxing mixture. Even after stirring and refluxing for four days, Color Test I was positive. An additional 0.02 mole of phenyllithium was added, the ether was replaced with benzene, and the resulting mixture was refluxed at 60° for three days. Although Color Test I was still positive, the material was worked up in the usual manner to obtain 12.8 g. of white solid melting from 140–150°. Purification by digestion with six 20-ml. portions of ethanol gave 7.3 g. (63%) of crude product melting at 187–189°. After three recrystallizations from benzene, a pure sample of tri-1-naphthylphenylsilane melting at 192–193° was obtained. A mixed melting point with the product of method A showed no depression. Attempts to fractionate the remaining solids by crystallization were unsuccessful and only impure low-melting solids were obtained.

C. From Tri-1-naphthylethoxysilane and Phenyllithium. —To a solution of 5.0 g. (0.011 mole) of tri-1-naphthylethoxysilane in about 100 ml. of dry xylene was added 0.022 mole of phenyllithium in ether. After refluxing for 36 hours, the opaque purple mixture gave a positive Color Test I. Following hydrolysis and removal of the inorganic salts, the solvent was removed by distillation to yield a yellow semi-solid. Digestion of this oil with several small portions of ethanol followed by three recrystallizations from benzene gave 0.8 g. (14%) of tri-1-naphthylphenylsilane melting at 189–190°. Identification was made by a mixed melting point determination.

D. Complex with Chlorobenzene.—Five grams (0.011 mole) of tri-1-naphthylphenylsilane, m.p. 190–191°, was dissolved in about 40 ml. of hot chlorobenzene and the solution was allowed to cool slowly. After 4 hours, 2.6 g. of large colorless crystals melting at 108–109° were removed by filtration. Recrystallization from the same solvent did not change the melting point.

Anal. Calcd. for $C_{42}H_{31}ClSi$: Cl, 5.92; Si, 4.68. Found: Cl, 5.80; Si, 4.61.

Three recrystallizations of 1.3 g. of this material from petroleum ether (b.p. 90–110°) were necessary before the melting point was constant at 192–193°. A 60% recovery of material was realized.

Attempts to purify the crude product, melting from 135–150°, (obtained by the treatment of tri-1-naphthylchlorosilane with phenyllithium) by crystallization from chlorobenzene gave inferior yields to those obtained by the exhaustive digestion treatment although some of the complex was isolated.

Triphenyl-2-naphthylsilane.—An ethereal solution of 20.7 g. (0.1 mole) of 2-bromonaphthalene in 25 ml. of ether

(10) See A. A. Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1938, p. 228.

(11) The silicon analyses were carried out by the procedure of H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, THIS JOURNAL, **72**, 5767 (1950).

was added, at room temperature, to 132 ml. (0.1 mole) of a 0.76 N solution of n-butyllithium.[12] After stirring this mixture for 10 minutes, an ethereal solution of 15.1 g. (0.051 mole) of triphenylchlorosilane was added over a period of 20 minutes. Even after refluxing the resulting solution for 17 hours, Color Test I was positive. The reaction mixture was poured onto dilute hydrochloric acid to yield considerable white solid floating between the layers. The aqueous layer was drained off, keeping the solid with the ethereal layer. Removal of the solvent from the organic material gave a yellow oil. Digestion of this oil with 50 ml. of petroleum ether (b.p. 60–80°) gave 12.4 g. of white solid, m.p. 130–133°, and a second portion of 3.1 g., m.p. 120–125°. The solids were combined and recrystallized from 100 ml. of petroleum ether (b.p. 90–110°) to give 12.2 g. (32%) of white crystals melting at 150–151°.

Anal. Calcd. for $C_{28}H_{22}Si$: Si, 7.26. Found: Si, 7.23, 7.22.

Since the melting point of triphenyl-2-naphthylsilane is the same as that of triphenylsilanol, a mixed melting point determination was run to furnish additional proof that this material was not triphenylsilanol formed by hydrolysis of the triphenylchlorosilane. A large depression of the melting point resulted.

Tri-1-naphthyl-p-tolylsilane. A. From Tri-1-naphthylethoxysilane and p-Tolyllithium.—A solution of 110 g. (0.24 mole) of tri-1-naphthylethoxysilane in 1 liter of dry benzene was effected by heating, and an ethereal solution containing 0.34 mole of p-tolyllithium was added. Color Test I was positive after refluxing the mixture for four days. The brown mixture was poured onto dilute hydrochloric acid, the inorganic salts were removed by extraction and the solvent was removed from the organic layer. The hard, brittle brown solid was melted, poured into a large mortar and, after cooling, pulverized. The material thus obtained weighed 112 g. (92%) and melted from 220–223°. Exhaustive digestion with small portions of boiling acetone gave 98 g. (80%) of pure tri-1-naphthyl-p-tolylsilane melting at 232–233°. The analytical sample was recrystallized twice from ethyl acetate with no change in the melting point.

Anal. Calcd. for $C_{37}H_{28}Si$: Si, 5.60. Found: Si, 5.68, 5.72.

In another run xylene rather than benzene was used for a solvent in an attempt to reduce the reaction time. Although Color Test I was negative after 20 hours when equivalent quantities of silicon compound and organolithium reagent were used, the mixture turned dark brown and the final product was difficult to purify with an attendant decrease in yield. A check run of p-tolyllithium, when refluxed in xylene for 20 hours, gave the same color change and a brown to yellow ether solution after hydrolysis.

B. From Tri-1-naphthylchlorosilane and p-Tolyllithium.—Preparations starting with tri-1-naphthylchlorosilane gave variable results. The procedure used was essentially the same as that outlined above (method A). From some of these runs only the corresponding silanol was isolated, while in others fair yields (40–60%) of the expected product were isolated. In all of the instances where the silanol was isolated the yield of p-tolyllithium was between 50 and 60%. Perhaps the organolithium reagent was consumed by coupling with the unused p-bromotoluene and the starting chlorosilane was hydrolyzed incidental to the process of isolation. Here again the use of xylene as a solvent gave colored impurities that were difficult to remove. A reaction period of three days in benzene appeared to give optimal results.

C. From Tri-1-naphthylbromosilane and p-Tolyllithium.—Equivalent quantities of tri-1-naphthylbromosilane and p-tolyllithium reacted in only 2 hours in refluxing ether to give a 60% yield of the expected product. Again the crude product, melting from 190–195°, was difficult to purify by crystallization and this yield was isolated by digestion with small portions of acetone.

D. From Tri-1-naphthylsilane and p-Tolyllithium.—Tri-1-naphthylsilane did not react appreciably with one equivalent of p-tolyllithium until the mixture, in benzene, had refluxed for six days. After this treatment the product was contaminated with colored impurities. The digestion procedure was not effective in this case probably due to

the extreme insolubility of tri-1-naphthylsilane in acetone. Only after a long systematic crystallization procedure using ethyl acetate was a 12% yield of tri-1-naphthyl-p-tolylsilane isolated from the colored oils and low-melting solids.

Triphenyl-p-tolylsilane.—To a solution of 80.0 g. (0.27 mole) of triphenylchlorosilane, m.p. 96–97°, in about 300 ml. of ether was added 0.4 mole of p-tolyllithium in 300 ml. of ether; the mixture was cooled with an ice-bath during the 20-minute addition period. After stirring overnight, Color Test I was positive. The mixture was poured onto crushed ice, about 50 ml. of dilute hydrochloric acid was added to dissolve the inorganic salts, and the insoluble white solid was removed by filtration. The solvent was removed from the ether layer of the filtrate and the residue, a white solid, was added to the previously obtained solid. After drying under a heat lamp for two hours, the crude product melted at 137–139° and weighed 97.0 g. (100%). Recrystallization from ethyl acetate gave 89.0 g. (92%) of pure triphenyl-p-tolylsilane, m.p. 140–141°.

Although this melting point is higher than that (134–135°) reported earlier,[4a] a mixed melting point determination of the two compounds showed no depression.

Diphenyldi-p-tolylsilane. A. From Diphenyldichlorosilane and p-Tolyllithium.—To a vigorously stirred solution of 12.6 g. (0.05 mole) of diphenyldichlorosilane in 300 ml. of dry ether was added, over a period of 20 minutes, 0.13 mole of p-tolyllithium in 325 ml. of ether. The mixture was stirred for 3 hours at room temperature and then poured onto about 400 ml. of 1% hydrochloric acid. The layers were separated, the solvent was removed from the ethereal layer, and the residual oil was dissolved in 40 ml. of boiling ethyl acetate. About 80 ml. of methanol was added to the refluxing solution; the mixture was filtered hot and set aside to crystallize. After 6 hours, 14.8 g. (87%) of white crystals melting at 118–119° were removed by filtration. Recrystallization from ethyl acetate–petroleum ether (b.p. 90–115°) (1:1) gave 13.1 g. (77%) of product melting at 121–122°. This melting point could not be raised by two more recrystallizations from ethyl acetate.

Diphenyldi-p-tolylsilane is reported[4a] to have a melting point of 176–177°; consequently this material was analyzed.

Anal. Calcd. for $C_{26}H_{24}Si$: Si, 7.70. Found: Si, 7.70, 7.73.

B. From Silicon Tetrachloride, Phenyllithium and p-Tolyllithium.—This experiment was undertaken to check the results of the previous report.[4a]

To a mixture of 17.8 g. (0.105 mole) of freshly distilled silicon tetrachloride and 1.5 liters of dry ether was added 600 ml. of 0.35 N phenyllithium (0.21 mole) while the reaction flask was cooled with an ice-salt-bath. The phenyllithium solution was added at a rate of 100 ml. per hour. Immediately after this addition was completed, 0.29 mole of p-tolyllithium[13] in 300 ml. of ether was added over a period of 30 minutes. Color Test I was positive after stirring the mixture for 1 hour under gentle reflux conditions. The mixture then was poured onto about 1 liter of water and the organic layer was separated. The solvent was removed from the ethereal layer and the resulting residue was subjected to systematic fractional crystallization.[14] Thus there was obtained 3.7 g. of crude diphenyldi-p-tolylsilane, m.p. 111–112°. A mixed melting point with a sample, m.p. 118–119°, prepared by method A was 112–117°. Also obtained were several other fractions of widely varying melting points. No further crystallizations were attempted since it seems impossible to obtain high yields of the desired compound by existing directions for the stepwise addition of two organolithium reagents to silicon tetrachloride.

This experiment was repeated except that the p-tolyllithium was added first, followed by phenyllithium. Essentially negative results were obtained from the systematic fractional crystallization. The only identifiable solids isolated were a trace of p,p'-bitolyl and 6% of triphenyl-p-tolylsilane, m.p. 134–136°.

(13) An excess of p-tolyllithium was used in order to avoid the formation of silanols which might have complicated subsequent crystallization.

(14) R. S. Tipson in A. Weissberger, "Technique of Organic Chemistry," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1950, p. 420ff.; A. A. Morton, "Laboratory Technique in Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1938, p. 162.

(12) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, 71, 1499 (1949).

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 C27H26Si: Si, 7.42. Found: Si, 7.40, 7.39.

(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

BY HENRY GILMAN AND RICHARD D. GORSICH

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 inter-

(1) G. Wittig, G. Pieper and G. Fuhrmann, *Ber.*, **73**, 1193 (1940).
(2) G. Wittig and W. Merkle, *ibid.*, **75**, 1491 (1942).

action 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

$$o\text{-}FC_6H_4Br \xrightarrow{n\text{-}C_4H_9Li} o\text{-}FC_6H_4Li \xrightarrow{(C_6H_5)_2CO} o\text{-}FC_6H_4C(OH)(C_6H_5)_2$$

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.

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

(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).