phenyltin acetate, m.p. 122–124° (reported[14]: m.p. 122–124°.

Anal. Calcd. for $C_{24}H_{18}O_2Sn$: molecular weight, 409. Found: mol. wt., 398 (ebulliosopic in benzene).

Extraction of the initial waxy residue with benzene gave 0.29 g. of diphenyltin oxide, infusible.

B. A solution of 20.0 g. (0.0570 mole) of I and 1.71 g. (0.0285 mole) of acetic acid was allowed to react in heptane at reflux temperature for 2 hr. The solvent was removed by distillation and the residue extracted with 250 ml. of ether, leaving a pasty residue.

Distillation of the ether and two recrystallizations of the residue from benzene gave 9.6 g. (85%) of triphenyltin acetate, m.p. 123.0–124.8°. No further compounds could be isolated.

Triphenyltin hydride and benzoic acid. A. A solution of 10.0 g. (0.0285 mole) of I and 1.75 g. (0.0142 mole) of benzoic acid was allowed to react for 3 hr. in heptane at 60°. The solvent was distilled, and the remaining solid extracted with 300 ml. of ether, leaving an oily residue. The ether was removed by distillation and the solid, 2.1 g., m.p. 177–183° (dec.), recrystallized from benzene to give 1.6 g. (46%) of *sym*-tetraphenyldibenzoyl oxyditin m.p. 184–185° (dec.) [reported[15]: m.p. 184–185° (dec.)].

Anal. Calcd. for $C_{38}H_{30}O_4Sn_2$: Sn, 30.13; molecular weight, 788. Found: Sn, 30.10; mol. wt., 820 (ebullioscopic in chloroform).

A flammable gas (hydrogen) was observed during the first 30 to 45-minutes' reaction. In a parallel experiment the heptane was distilled and subjected to vapor phase chromatographic analysis. Peaks for benzene and for heptane were observed.

The oily residue was extracted with benzene, which, upon standing, deposited 0.1 g. of infusible diphenyltin oxide. The mother liquor was concentrated, leaving an intractable oil (8. g.).

B. A solution of 10.0 g. (0.0285 mole) of I and 3.47 g. (0.0285 mole) of benzoic acid was allowed to react in heptane at 60° for 3 hr. The solvent was removed by distillation and the white residue extracted with 300 ml. of ether leaving a yellow waxy residue. Distillation of the ether left 1.5 g. of a white solid, m.p. 180–185° (dec.), which was recrystallized from benzene to give 1.2 g. (10%) of *sym*-tetraphenyldibenzoyloxyditin, m.p. 184–185° (dec.).

The yellow residue was dissolved in benzene and kept in an ice bath for 4 hr. Filtration afforded 1.2 g., (10%) of the ditin, m.p. 184–185° (dec.). The remaining solution was concentrated to a yellow oil (7 g.). Infrared analysis indicated the presence of I and trace amounts of carbonyl containing compounds. Attempts at isolation were unsuccessful. The total yield of the ditin was 20%.

Triphenyltin hydride and fuoric acid. A. A solution of 10 g. (0.0284 mole) of I and 3.2 g. (0.0284 mole) of furoic acid was allowed to react in heptane for 2 hr. at 65°. The reaction mixture was cooled and the mixture filtered. Concentration of the solvent left a clear oil. An infrared spectrum indicated the presence of I and carbonyl compounds. Standing at Dry Ice temperature for 6 hr. produced 1.5 g. of a white solid, m.p. 175–180° (dec.). Recrystallization from chloroform gave 1.3 g. (17%) of *sym*-tetraphenyldifuroyloxyditin, m.p. 184–186° (dec.).

Anal. Calcd. for $C_{34}H_{26}O_6Sn_2$: Sn, 30.91. Found Sn, 30.72.

The remaining oil was left at Dry Ice temperature overnight. Filtration afforded 3.4 g. of impure triphenyltin furoate, m.p. 190°. Recrystallization from benzene gave 3.25 g. (70%) of white solid, m.p. 192–193° (dec.).

Anal. Calcd. for $C_{23}H_{18}O_3Sn$: Sn, 25.74. Found: Sn, 25.72.

The original residue from the solvent filtration was recrystallized from benzene to give 1.0 g. of white needles, m.p. 131–133°. A mixture melting point with furoic acid was not depressed. The oily residue was dissolved in 10 ml. of benzene and allowed to stand at Dry Ice temperature for 2 hr. Filtration afforded 1.0 g. of hexaphenylditin, m.p. 229–231° (reported[12]: 231°).

B. A solution of 5.0 g. (0.0142 mole) of I and 0.8 g. (0.0071 mole) of furoic acid was allowed to react in heptane for 19 hr. at 65°. The solvent was distilled and the residue extracted with ether leaving a residue. The ether was distilled and the solid recrystallized from benzene to give 1.0 g. (31%) of the furoate, m.p. 192–193° (dec.).

The residue was recrystallized from chloroform to give 1.9 g. (35%) of the ditin, m.p. 184–186° (dec.). The mother liquor from this recrystallization was concentrated to an intractable oil (1.5 g.).

Triphenyltin hydride and propionic acid. A solution of 10.0 g. (0.0285 mole) of I and 1.0 g. (0.0142 mole) of propionic acid was heated in heptane for 3 hr. at 60°. The solvent was removed by filtration to leave a white solid. This was extracted with ether leaving a residue. Crystallization of the solid from ether gave 5.5 g. (90%) of triphenyltin propionate, m.p. 122–124°. An infrared spectrum of the inextractable concentrated solvent indicated I and decomposition products of I.

Anal. Calcd. for $C_{21}H_{20}O_2Sn$: Sn, 28.05. Found: Sn, 27.84.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF IOWA STATE UNIVERSITY]

Metalation Reactions by Organolithium Derivatives of Triaryl Group IV-B Elements

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The relative reactivity of triphenylsilyl-, triphenylgermyl-, triphenyltin-, and triphenylleadlithium has been studied by allowing tetrahydrofuran solutions of these anions to metalate fluorene under similar conditions. Fluorene-9-carboxylic acid was obtained after carbonation decreasing in the order $(C_6H_5)_3Si^-$, $(C_6H_5)_3Ge^-$, $(C_6H_5)_3Sn^-$, $(C_6H_5)_3Pb^-$. Compared to other organometallic reagents, triphenylsilyllithium has been found to be of moderate metalating ability.

Although the lithium derivatives of triaryl group IVb elements of the general formula $(C_6H_5)_3MLi$, were M═Si, Ge, Sn, and Pb, have been utilized in numerous studies,[1] little is known about the relative reactivity of these four anions.[1a] Until recently, the triaryl group IVb lithium derivatives were prepared under different conditions, and, therefore, a fair comparison of their reactivity could not be made. The recently reported preparation of these lithium derivatives in tetrahydrofuran[2] made it possible to study reactions of these organometallic compounds under similar conditions. This paper reports a study of the relative proton affinity that the lithium derevatives of the triaryl Group IVb elements exhibit toward fluorene. Also, the metalating ability of triphenylsilyllithium toward various hydrocarbons and heterocycles has been investigated.

Previous work has shown that compounds containing the more acidic hydrogens are metalated rapidly by silylmetallic reagents. Triphenylsilyllithium, -potassium, and -sodium have been reported to metalate triaylmethanes in good yields,[3] and phenylacetylene was readily metalated by triphenylsilylpotassium.[4] Triphenylgermyllithium in ethylene glycol dimethyl ether was an effective metalating reagent toward fluorene giving fluorene-9-carboxylic acid in a 69% yield subsequent to carbonation.[5] Dibenzofuran was not metalated by this reagent.[5] Triphenyltinlithium and triphenylleadlithium have been reported to metalate fluorene in 22 and 52% yields, respectively.[6] However, it was proposed that these two reagents were part of the equilibrium systems

$$(C_6H_5)_3SnLi \rightleftarrows (C_6H_5)_2Sn + C_6H_5Li$$
$$(C_6H_5)_3PbLi \rightleftarrows (C_6H_5)_2Pb + C_6H_5Li$$

with triphenyltinlithium and triphenylleadlithium dissociated about 20 and 50%, respectively, and it was concluded that phenyllithium was actually metalating the fluorene. Furthermore, benzoic acid was obtained in a 49% yield when triphenylleadlithium, prepared from phenyllithium and lead dichloride at −10° in ether, was carbonated. The equilibrium system was suggested as being displaced 80% toward the triphenylleadlithium.[7] Carbonation of triphenyltinlithium, prepared from phenyllithium and stannous chloride in ether at −10°, failed to give any benzoic acid,[8] indicating that triphenyltinlithium is not part of an equilibrium system in ether.

We have found, however, that triphenyltinlithium and triphenylleadlithium, prepared directly from triphenyltin chloride and triphenyllead chloride and lithium in tetrahydrofuran,[2c] metalate fluorene to the extent of only 17.4 and 0.5%, respectively (Table I).

TABLE I

METALATION OF FLUORENE BY $(C_6H_5)_3MLi$ IN TETRAHYDROFURAN[a]

$(C_6H_5)_3MLi$ M=	Yield of Fluorene-9-carboxylic Acid		Other Products (%, Pure) (R = C_6H_5)
	%, Crude	%, Pure	
Si	81.2	68.8	R_3SiH (46.1) Fluorene (5.6)
Ge	88.8	65.6	R_3GeH (49.6) R_6Ge_2 (0.6) $R_3GeOGeR_3$ (8.8) Fluorene (17)
Sn	19.5	17.4	R_6Sn_2 (46.6) Fluorene (62.4)
Pb	10.9	0.5	Fluorene (64.7)

[a] All reactions stirred 18 hr. at room temperature with a molar ratio of 1:1.

Moreover, carbonation of the tin-lithium or the lead-lithium solutions did not afford any acidic material.[2c] Therefore, the low yields of fluorene-9-carboxylic acid illustrate the low basic properties of these two anions. The absence of benzoic acid upon carbonation, particularly in the case of the triphenylleadlithium, suggests the equilibrium systems, if they exist under these conditions, are displaced principally toward triphenyltinlithium and triphenylleadlithium.

Triphenylsilyllithium and triphenylgermyllithium metalated fluorene with about equal magnitude giving the acid in yields of 68.8 and 65.6%, respectively. It has been shown, however, in these laboratories triphenylsilyllithium readily metalates triphenylgermane, whereas triphenyltinlithium failed to react with the germane.[9]

$$(C_6H_5)_3SiLi + (C_6H_5)_3GeH \longrightarrow (C_6H_5)_3SiH + (C_6H_5)_3GeLi$$

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TABLE II

REACTION OF TRIPHENYLSILYLLITHIUM WITH VARIOUS HETEROCYCLES AND HYDROCARBONS FOLLOWED BY CARBONATION

Hydrocarbon	Conditions Hr.	Conditions Temp.	Acid	Yield, % Crude	Yield, % Pure	Other Products (%, Pure) (R = C_6H_5)
Xanthene	0.5 4	0 25	Xanthene-9-carboxylic	90.2	36.5	[a]
Xanthene	16	25	Xanthene-9-carboxylic	53.2	25.9	Xanthene (6)[a]
Thiaxanthene	16	25	Thiaxanthene-10-carboxylic	64.5	44.6	R_3SiOH (20), Thiaxanthene (6.3)
Dibenzofuran	18	25		None		R_3SiOH (25.3), Dibenzofuran (68.2)
9,10-Dihydroanthracene	4	25	9,10-Dihydroanthracene-9-carboxylic		71.8	Oil
Indene	0.5 3.5	0 25	Indene-1-carboxylic	87.3	56.8	R_3SiH (64.4)
10-Ethylphenothiazine	24	Reflux	10-Ethylphenothiazine-4-carboxylic	5.6	1.7	R_3SiOH and $R_3Si(CH_2)_4OH$ (4 g.), 10-Ethylphenothiazine (30)
10-Ethylphenothiazine-5-oxide[b]	9	0		None		R_3SiH (27), R_3SiOH (11), 10-ethylphenothiazine (35)
10-Ethylphenothiazine-5,5-dioxide	4	25	[c]	None		10-Ethylphenothiazine-5,5-dioxide (48.3)
Diphenylmethane	18	25	Diphenylacetic	67.8	56.5	R_4Si (2.5), R_3SiH (55), R_3SiOH (11.3)
Diphenylmethane	18 24	25 Reflux	Diphenylacetic	8.5	5.9	R_4Si (16.2), R_3SiH (61), R_2CH_2 (38.7)
Phenylacetylene	18	25	Phenylpropiolic	50	40	R_3SiH (52.3), Solid[d] (0.08 g.)
sym-Tetraphenylethane	5[e]	25		None		R_2CHCHR_2 (95.4), R_3SiOH (72.6)
Toluene	75[e]	25	[f]			

[a] Organic layers combined. [b] Ratio triphenylsilyllithium to hydrocarbon, 3:1. [c] Reaction mixture hydrolyzed. [d] Unidentified, m.p. 146–148°. [e] Red color developed which is indicative of metalation. [f] Chlorotriphenylsilane added to the reaction mixture. Benzyltriphenylsilane could not be isolated.

It was concluded that the relative proton affinities of these anions decreased in the order

$$(C_6H_5)_3Si^- > (C_6H_5)_3Ge^- > (C_6H_5)_3Sn^-$$

The relative ability of the anions to metalate fluorene are in agreement with this conclusion.

In addition, triphenylsilyllithium readily metalated xanthene, thiaxanthene, indene, diphenylmethane, phenylacetylene, and 9,10-dihydroanthracene, the respective acids being formed upon carbonation (Table II). 9-Lithioxanthene was also characterized by reaction with chlorotriphenylsilane to give 9-triphenylsilylxanthene in a 14.4% yield.

Apparently the metalation reaction proceeds only to a limited extent with less acidic systems. Refluxing 10-ethylphenothiazine with triphenylsilylithium gave a trace of 10-ethylphenothiazine-4-carboxylic acid subsequent to carbonation. The sulfoxide group of 10-ethylphenothiazine-5-oxide was reduced by triphenylsilyllithium as evidenced by a 35% yield of 10-ethylphenothiazine. Triphensilane was also isolated which may be indicative of some metalation. It is known that a simultaneous reduction of the sulfoxide grouping and metalation of the nucleus take place when 10-ethylphenothiazine-5-oxide is treated with *n*-butyllithium.[10] There was no reaction between 10-ethylphenothiazine-5,5-dioxide and triphenylsilyllithium.

Metalation of still "less acidic" systems by triphenylsilyllithium is rarely observed. Although a red color developed (indicative of metalation) when toluene was allowed to react with triphenylsilyllithium, benzyltriphenylsilane could not be isolated when the reaction mixture was treated with chlorotriphenylsilane. However, a small amount of benzyltriphenylsilane has been obtained by allowing the silylmetallic compound to react with toluene in the presence of hexaphenyldisilane.[11] It was assumed the benzyllithium, formed by metalation of toluene, cleaved the disilane to give the observed product.[12]

Triphenylsilyllithium has also been reported to metalate diphenyl ether to give, subsequent to carbonation, a trace of 2,2′-dicarboxydiphenyl ether.[13] However, none of the acid could be isolated when

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TABLE III

REACTIONS OF ORGANOLITHIUM REAGENTS WITH TRIPHENYLSILANE FOLLOWED BY CARBONATION

Organolithium Reagent	Conditions	Yield of Acid %, Crude	 %, Pure	Other Products (%, Pure) ($R = C_6H_5$)
Diphenylmethyl	18 hr. at 25°; 24 hr. reflux	None		R_4Si (12.5), R_2CH_2 (26), R_3SiH (48), Oil
9-Fluorenyl	18 hr. at 25°	64.4[a]	54	R_3SiH (82.2)
9-Fluorenyl	18 hr. at 25°; 24 hr. reflux	62.8[a]	39	R_3SiH (76.3), red resin

[a] Fluorene-9-carboxylic acid.

dimethylphenylsilyllithium was allowed to react with the same ether. In addition, dibenzofuran, *N*,*N*-dimethylaniline, 1,1-diphenylethane, cumene, and *sym*-tetraphenylethane did not appear to be metalated by triphenylsilyllithium under the experimental conditions employed. Cumene also was not metalated by dimethylphenylsilyllithium.

By relating the metalating ability of triphenylsilyllithium with the various hydrocarbons and the acid strengths of these hydrocarbons, a qualitative evaluation of the relative proton affinity of triphenylsilyllithium can be ascertained. Conant and Wheland[14] and McEwen[15] have shown that by allowing the anion of a weak acid to react with another weak acid the following order of acid strengths was observed:

$$n\text{-}C_4H_{10} < C_6H_6 < (C_6H_5)CH(CH_3)_2 < C_6H_5CH_3 < (C_6H_5)_2CHCH_3 < (C_6H_5)_2CH_2 < (C_6H_5)_3CH < (C_6H_5)_2(\alpha\text{-}C_{10}H_7)CH < \text{xanthene} < \text{fluorene} < \text{9-phenylfluorene} < \text{indene} < C_6H_5C{\equiv}CH$$

As discussed above, triphenylsilyllithium metalates phenylacetylene, indene, fluorene, xanthene, triphenylmethane, and diphenylmethane quite rapidly. Toluene was metalated only in poor yield. Cumene and 1,1-diphenylethane did not appear to react with the silylmetallic compound. Therefore, triphenylsilyllithium probably should be considered as possessing greater nucleophilic activity than the diphenylmethyl anion and less than the 1,1-diphenylethyl anion.

The reaction of diphenylmethane with triphenylsilyllithium at room temperature gave, in addition to the metalation products diphenylmethyllithium and triphenylsilane, tetraphenylsilane (2.5%). Refluxing of the reaction mixture increased the yield of tetraphenylsilane to 16.2%, with an accompanying decrease in the yield of diphenylacetic acid (Table II). Also, when preformed diphenylmethyllithium and triphenylsilane were refluxed for the same length of time, the diphenylmethyllithium was completely utilized or destroyed as no diphenylacetic acid was obtained subsequent to carbonation of the reaction products (Table III). The yield of tetraphenylsilane was 12.5%. Diphenylmethyltriphenylsilane, a type of product arising from a reaction common with other organolithium reagents and triphenylsilane,[16] could not be isolated.

$$(C_6H_5)_2CHLi + (C_6H_5)_3SiH \not\longrightarrow (C_6H_5)_2HCSi(C_6H_5)_3 + LiH$$

Chlorotriphenylsilane did react with diphenylmethyllithium to give the expected diphenylmethyltriphenylsilane.[17]

The first step in the reaction of triphenylsilyllithium with diphenylmethane is metalation (reaction 1). This reaction is rapid and nearly quantitative, which has also been observed with triphenylsilylpotassium and triarylmethanes.[3] Tetraphenylsilane probably results from triphenylsilyllithium and the triphenylsilane that has been formed (reaction 2). The same product was formed from triphenylsilane and triphenylsilylpotassium in diethyl ether[18a] and triphenylsilyllithium in tetrahydrofuran.[18b] The mode of formation of the tetraphenylsilane has not been rigorously established.[18]

$$(C_6H_5)_3SiLi + (C_6H_5)_2CH_2 \longrightarrow (C_6H_5)_3SiH + (C_6H_5)_2CHLi \quad (1)$$

$$(C_6H_5)_3SiLi + (C_6H_5)_3SiH \longrightarrow (C_6H_5)_4Si \quad (2)$$

As tetraphenylsilane was obtained from triphenylsilane and preformed-diphenylmethyllithium, reaction 1 may be an equilibrium system. Although other reaction mechanisms may be envisaged, metalation of triphenylsilane (reverse of reaction 1) has been postulated in the reaction of this silane with triphenylmethylsodium.[3] In the same report, triphenylmethane was isolated, after carbonation, from triphenylmethyllithium and triphenylsilane. Also, a small amount of tetraphenylsilane was obtained from *n*-butyllithium and triphenylsilane.[19] This could have arisen if triphenylsilane were first metalated, followed by reaction of

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the silylmetallic reagent as depicted in reaction 2.[20]

9-Fluorenyllithium proved to be more stable and less reactive than diphenylmethyllithium as refluxing of 9-fluorenyllithium and triphenylsilane did not materially affect the yield of fluorene-9-carboxylic acid; nor could tetraphenylsilane be isolated.

EXPERIMENTAL[21]

Reagents. Triphenylsilyl-,[2a] triphenylgermyl-,[22] triphenyltin-,[2c] triphenyllead-,[2c] diphenylmethyl-,[17] and 9-fluorenyllithium[23] were prepared according to published directions.

General Method. The organometallic reagent in tetrahydrofuran (THF) was added to the hydrocarbon or heterocycle dissolved in a small quantity of THF in 1:1 molar ratios unless noted otherwise, and the reaction allowed to proceed under the conditions listed in Tables I–III. Carbonation was then effected by pouring onto a Dry Ice–ether slurry followed by the usual work-up for isolation of the organic acid from the aqueous layer and basic extracts, and the neutral products from the organic layer. Some selected representative procedures are described below in detail.

Reaction of triphenyltinlithium with fluorene (Table I). A solution of 0.03 mole of triphenyltinlithium, prepared from 11.56 g. (0.03 mole) of triphenyltin chloride and 0.7 g. (0.1 g. atom) of cut lithium wire in 75 ml. of tetrahydrofuran (THF) was added to 5.0 g. (0.03 mole) of fluorene dissolved in 15 ml. of THF. A red color slowly developed and after 18 hr. of stirring at room temperature, Color Test I[24] was positive. The mixture was poured onto a Dry Ice–ether slurry and hydrolyzed with dilute hydrochloric acid. The aqueous layer was separated, extracted twice with ether, and discarded. The organic layer was filtered to give 3.25 g. (31%) of hexaphenylditin, m.p. 228–231°, identified by mixture melting point.

The organic layer was extracted with 300 ml. of 5 % sodium hydroxide, followed by boiling of the extracts to expel THF and acidification to give 1.23 g. (19.5%) of slightly crude fluorene-9-carboxylic acid, melting 221–224°. Washing with petroleum ether (b.p. 60–70°) gave 1.1 g. (17.4%) of the acid, m.p. and mixed m.p. 225–227°.

The organic layer was dried and distilled. The residue was treated with methanol to give 4.11 g. (82.2%) of fluorene, m.p. 108–111°. Recrystallization from methanol yielded 3.12 g. (62.4%) of pure product, m.p. 112–114°, identified by mixture melting point.

Reaction of triphenylleadlithium with fluorene (Table I). Triphenylleadlithium (0.03 mole), prepared from 15.89 g. (0.03 mole) of triphenyllead chloride and 0.7 g. (0.1 g. atom) of finely cut lithium wire in 100 ml. of tetrahydrofuran (THF), was added to 5.0 g. (0.03 mole) of fluorene dissolved in 15 ml. of THF. There was no apparent reaction, but after stirring 18 hr. at room temperature, the solution had turned from the dark green color of the lead-lithium derivative to brown color. The reaction mixture was carbonated, hydrolyzed with water, and filtered to remove 6.95 g. of a powdery white solid which melted above 360°. The organic layer was separated and extracted with 100 ml. of 5% sodium hydroxide. The aqueous layer and basic extracts were combined, boiled and acidified. Filtration gave 0.69 g. of a solid which softened slightly below 350°. Recrystallization from glacial acetic acid gave 0.03 g. (0.48%) of fluorene-9-carboxylic acid, m.p. and mixed m.p. 230–232°, and a small amount of insoluble material which did not melt below 360°.

The organic layer was dried and concentrated. Addition of methanol to the residue gave 3.95 g. (79.2%) of slightly crude fluorene, m.p. 109–112°. The crude fluorene was recrystallized from methanol to give 3.25 g. (64.7%) of solid, m.p. 111–113° (mixture melting point).

Reaction of triphenylsilyllithium with xanthene. (a) *Carbonation.* Ten grams (0.055 mole) of xanthene was dissolved in 50 ml. of tetrahydrofuran (THF) and the reaction mixture was cooled to ice-bath temperature. To the solution was added slowly 0.055 mole of triphenylsilyllithium in THF. The dark-red solution was stirred at ice-bath temperature for 0.5 hr. and at room temperature for 4 hr. Color Test I was slightly positive. A 50 ml. aliquot (about 1/3 of the total reaction mixture) was carbonated by pouring into a Dry Ice–ether slurry. The remaining solution was allowed to stir overnight at room temperature. The next morning, it was carbonated in a similar manner.

(*i*) *4-Hr. aliquot.* After the solution had warmed to room temperature, it was extracted with 2.5% sodium hydroxide solution. The basic extracts were acidified with 10% hydrochloric acid solution to give 3.70 g. (90.2% based upon 1/3 total volume aliquot) of crude acid, melting range 215–222°. This was recrystallized from ethanol-water to give 1.50 g. (36.5%) of xanthene-9-carboxylic acid, m.p. 216–220° (mixture melting point). The literature value[25] is 222°. The infrared spectrum was identical with that of an authentic sample.

(*ii*) *16-Hr. aliquot.* The same isolation procedure was carried out as described above to give 4.30 g. (53.2%) of crude acid, m.p. 205–210° dec. A recrystallization from petroleum ether (b.p. 60–70°) gave 2.10 g. (25.9%) of relatively pure acid, m.p. 217–220° (mixture melting point).

The combined crude acid represents a 64.0% yield; while the pure acid represents a yield of 29.2%. No attempt was made to work up the mother liquors.

The original organic layers from the basic extractions were combined, and the solvent evaporated to leave a yellow oil. The oil was chromatographed on alumina to recover 0.60 g. (6.0%) of xanthene, m.p. 97–99° (mixture melting point).

(*b*) *Derivatization with chlorotriphenylsilane.* Ten grams (0.055 mole) of xanthene was metalated by 0.055 mole of triphenylsilyllithium as described in the previous reaction and was subsequently brought into reaction with 16.5 g. (0.056 mole) of chlorotriphenylsilane dissolved in 50 ml. of THF. There was no spontaneous refluxing, but the color of the solution changed to black. Color Test I was negative. Aqueous hydrolysis was followed by the usual work-up. Evaporation of the solvent left a dark brown solid which was chromatographed on alumina. Elution of this column with petroleum ether (b.p. 60–70°) gave, after several recrystallizations from ethanol, 0.90 g. (9.0%) of recovered xanthene, m.p. 100–102° (mixture melting point). Elution of the column with benzene gave, subsequent to several recrystallizations from ethanol, 3.50 g. (14.4%) of 9-triphenylsilylxanthene,[26] m.p. 164.5–166° (mixture melting point). Elution of the column with ethanol gave a solid which was recrystallized from petroleum ether (b.p. 80–100°) to give 7.55 g. (48.7%) of triphenylsilanol, m.p. 151–153.5° (mixture melting point).

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[20] See R. A. Benkeser and D. J. Foster, *J. Am. Chem. Soc.*, **74**, 5314 (1952), and references therein, for a discussion of the reaction of triphenylsilane with various alkali metals.

[21] All melting points and boiling points are uncorrected. Reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. Tetrahydrofuran, boiling at 65–66°, was freed from peroxides and moisture before use by refluxing over sodium and then distilling from lithium aluminum hydride.

[22] H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **77**, 5740 (1955).

[23] H. Gilman and R. D. Gorsich, *J. Org. Chem.*, **23**, 550 (1958).

[24] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

[25] R. R. Burtner and J. W. Cusic, *J. Am. Chem Soc.*, **65**, 1582 (1943).

[26] H. Gilman, J. W. Diehl, and W. J. Trepka, Unpublished studies.

Reaction of triphenylsilyllithium with diphenylmethane. (a) *Room temperature for 18 hr.* (Table II). Diphenylmethane (5.04 g., 0.03 mole) was treated with 0.03 mole of triphenylsilyllithium in 50 ml. of tetrahydrofuran and the mixture stirred 18 hr. at room temperature. The red solution was carbonated and worked up as described above. There was isolated by basic extraction 4.31 g. (67.8%) of crude diphenylacetic acid, m.p. 134–141°. The crude acid was recrystallized from an ethanol-water mixture yielding 3.59 g. (56.5%), m.p. 143–145°, identified by mixture melting point.

The organic layer was dried and distilled. The residual material was treated with methanol and filtered to give 0.41 g. (4.05%) of solid, m.p. 197–217°. Recrystallization from benzene yielded 0.25 g. (2.5%) of tetraphenylsilane, m.p. 232–235°, which was identified by mixture melting point and by comparison of the infrared spectra.

The methanolic filtrate was cooled and seeded with triphenylsilane. There was obtained 3.54 g. of triphenylsilane, m.p. 42–44°. The filtrate was stripped of the solvent, and ethyl acetate added to the residue. Filtration gave 0.37 g. of triphenylsilanol, m.p. 148–151°. The ethyl acetate was removed and the oily residue chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 0.75 g. of triphenylsilane (total yield: 4.29 g. or 55%). A small amount of oil was eluted with benzene, and elution with ethyl acetate gave an additional 0.62 g. of triphenylsilanol after crystallization from petroleum ether. The crude triphenylsilanol (0.99 g., 12%) was recrystallized from petroleum ether to give 0.93 g. (11.3%) of pure product, m.p. and mixed m.p. 150–153°.

(*b*) *Room temperature for 18 hr., then 24 hr. at reflux* (Table II). Triphenylsilyllithium (0.04 mole) was allowed to react with 6.72 g. (0.04 mole) of diphenylmethane in 80 ml. of tetrahydrofuran for 18 hr. at room temperature, followed by 24 hr. at reflux. The red reaction mixture was carbonated and then hydrolyzed with dilute acid. Ether was added, and the layers separated. The organic layer was filtered to afford 2.24 g. of tetraphenylsilane, m.p. 234–237°. Extraction of the organic layer with dilute sodium hydroxide, followed by acidification of the extract gave 0.72 g. (8.5%) of crude diphenylacetic acid. The yield of pure acid was 0.5 g. (5.9%), which melted at 142–144°.

The organic layer was dried and distilled to give 2.6 g. (38.7%) of diphenylmethane, b.p. 75–76°/0.09 mm., n_D^{20} 1.5774, and 6.33 g. (61%) of triphenylsilane, identified by comparison of the infrared spectra. A higher boiling fraction and the distillation residue yielded an additional 0.93 g. of tetraphenylsilane after treatment with ethyl acetate. The yield of crude tetraphenylsilane was 3.17 g. (25.4%). Recrystallization from an ethyl acetate-benzene mixture afforded 2.02 g. (16.2%) of pure product, m.p. and mixed m.p. 236–238°. The infrared spectra were superimposable.

Reaction of triphenylsilyllithium with indene (Table II). To 5.80 g. (0.05 mole) of indene dissolved in 50 ml. of ether, cooled to ice-bath temperature, was added a tetrahydrofuran solution of 0.05 mole of triphenylsilyllithium. The reaction mixture was stirred at ice-bath temperature for 30 min., and then at room temperature for 3.5 hr. The solution was dark brown at first but gradually turned to a yellow brown. The reaction mixture was carbonated by pouring jet-wise into a Dry Ice–ether slurry. After the carbonation mixture had warmed to room temperature, the usual organic acid work-up was carried out. There was obtained 7.00 g. (87.3%) of crude indene-1-carboxylic acid, m.p. 134–151° (lit. value[27] 159.5–161°). Sublimation and subsequent recrystallization from benzene–petroleum ether (b.p. 80–110°) raised the melting point of the acid to 158–160°; 4.55 g. (56.8%).

Work-up of the organic layer and chromatography on alumina of the resulting brown oil gave 8.40 g. (64.4%) of triphenylsilane.

Reaction of triphenylsilyllithium with 10-ethylphenothiazine-5-oxide (Table II). Triphenylsiyllithium (0.018 mole) was cautiously added during 0.5 hr. to 4.37 g. (0.018 mole) of 10-ethylphenothiazine-5-oxide suspended in 30 ml. of tetrahydrofuran at 0°. After stirring for 4 hr., two additional equivalents of triphenylsilyllithium were added and the reaction mixture agitated for 5 hr. at 0°. The light-green solution was carbonated by pouring onto a Dry Ice–ether slurry, and then the usual work-up was carried out.

None of the desired 10-ethylphenothiazine-4-carboxylic acid has yet been isolated from the acid fraction. Chromatography on alumina of the green oil obtained subsequent to evaporation of the organic fraction gave a 27.0% yield of triphenylsilane, m.p. 41–45°; a 35.0% yield of 10-ethylphenothiazine, m.p. 103–105°; and an 11.0% yield of triphenylsilanol, m.p. 149–153°. All of the compounds were identified by mixed melting points and comparison of their infrared spectrum with authentic samples.

Reaction of diphenylmethyllithium with triphenylsilane (Table III). A solution of 0.08 mole of diphenylmethyllithium in 88 ml. of ether was divided into two equal portions; one portion was added to 10.42 g. (0.04 mole) of triphenylsilane in 40 ml. of tetrahydrofuran (THF) and the second to 11.80 g. (0.04 mole) of chlorotriphenylsilane dissolved in 40 ml. of THF. There was no evidence of a reaction after 24 hr. of stirring at room temperature. The ether was distilled from the reaction mixture and 30 ml. of THF added. The red solution was set at reflux and after 24 hr., Color Test I was positive. The reaction mixture was poured onto a slurry of Dry Ice and ether and hydrolyzed with dilute acid. The organic layer was separated and filtered to give 1.0 g. of crude tetraphenylsilane, m.p. 222–230°. Extraction of the organic layer gave no acid products upon acidification of the basic extracts.

Addition of methanol to the residue from removal of the organic solvents yielded 1.6 g. of crude tetraphenylsilane, m.p. 210–220°. The solvent was removed from the filtrate and the oily residue chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave an oil which was distilled to give 1.77 g. (26%) of diphenylmethane, b.p. 79.5–83°/0.005 mm., $n_D^{19.4}$ 1.5780, and 4.98 g. (48%) of triphenylsilane, identified by infrared spectrum. Elution with cyclohexane gave 0.2 g. of tetraphenylsilane. The total yield of crude tetraphenylsilane was 19.3% and after recrystallization from an ethyl acetate–benzene mixture the melting point was raised to 231–233°. A mixed melting point with an authentic sample was not depressed. The yield of pure product was 12.5%.

Further elution of the column with benzene and ethanol gave an oil which could not be purified by chromatography, crystallization, or distillation.

The diphenylmethyllithium-chlorotriphenylsilane mixture was stirred 20 hr. at room temperature at which time Color Test I was negative. Hydrolysis and filtration gave 6.7 g. of diphenylmethyltriphenylsilane,[17] m.p. and mixed m.p. 155–158°. Work-up of the organic layer gave an additional 2.34 g. of diphenylmethyltriphenylsilane. Some of the product was mechanically lost during concentration of the organic layer. The yield of product was 53%.

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