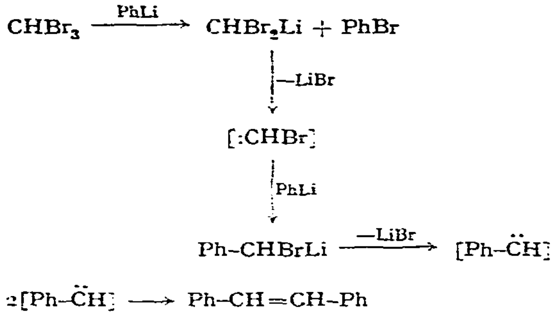
REACTIONS OF TRIPHENYLSILYLLITHIUM WITH POLYHALOMETHANES*

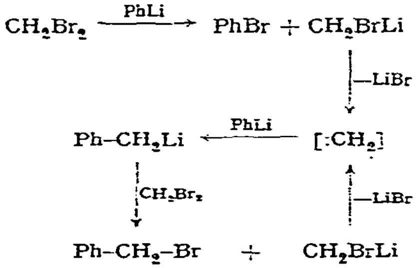
HENRY GILMAN AND DAN AOKI
Chemical Laboratory of Iowa State University, Ames, Iowa (U.S.A.)

(Received December 16th, 1963)

In 1939 Wittig and Pockels[2] reported the reaction of phenyllithium and bromoform. These workers demonstrated that the halogen–metal interconversion reaction is the major reaction between these two compounds as a result of isolation of bromobenzene in a 45% yield. The other product obtained was stilbene (34% maximum). In the light of carbene chemistry[3,4,5,6] the formation of the latter compound can easily be accounted for:



Two years later, Wittig and Witt[7] reported the reactions of phenyllithium with various polyhalomethanes. Reactions of carbon tetrachloride and carbon tetrabromide gave relatively small amounts of chlorobenzene (27.6%) and bromobenzene (33.2%), respectively. The fact that no other product could be isolated from the residue indicates the occurrence of complex secondary reactions, possibly involving carbene intermediates. The reaction of methylene bromide and phenyllithium in a



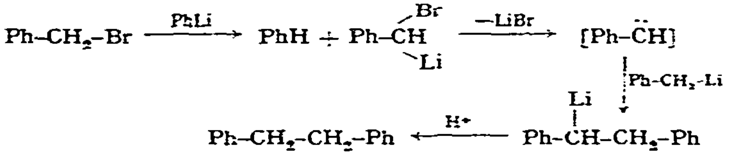
---

[*] Reported in part in a preliminary communication[1].

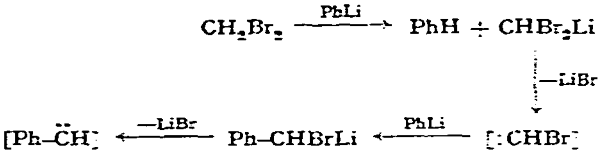
J. Organometal. Chem., 1 (1964) 449–463

1:1 ratio yielded bromobenzene (25%), benzyl bromide (21%), bibenzyl (18.9%), and the starting material (11.5%). Direct coupling reaction between phenyllithium and methylene bromide was proposed by Wittig for the formation of benzyl bromide. Although this reaction scheme may not be ruled out, there is another possibility; that is, the halogen–metal interconversion between methylene bromide and benzyllithium. The latter compound would be formed by the reaction of carbene and phenyllithium. (For equations see at the bottom of p. 449.)

Benzyl bromide would be expected to undergo three possible reactions with RLi compounds: halogen–metal interconversion[8], metalation[7,9] and coupling[6]. The coupling reaction with benzyllithium may account for the formation of bibenzyl. The metalation reaction, however, can also give rise to bibenzyl[1,5]:



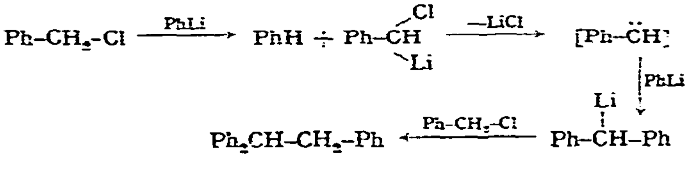
Although Miller and Kim[10] isolated only norcarane from the reaction of methylene bromide with methyllithium in the presence of cyclohexene, methylene bromide may undergo a metalation reaction with phenyllithium. The bromocarbene formed can react with phenyllithium to give phenylcarbene:



The reaction of phenylcarbene and benzyllithium would give bibenzyl as shown above.

Methylene chloride has been shown to give a coupling product with sodium diphenylmethide[11], whereas organolithium compounds react with methylene chloride exclusively by metalation[5].

It is interesting that in one case[7] 1,1,2-triphenylethane was isolated as the major product from the reaction of benzyl chloride and phenyllithium. Phenylcarbene might have been an intermediate in this case also.



The diphenylmethyllithium would be expected to react with benzyl chloride in all possible ways, but under the conditions employed the coupling reaction seemed to be favored.

The halogen–metal interconversion reaction is the major reaction between triphenylsilyllithium and polyhalomethanes, as evidenced by the isolation of hexaphenyldisilane[12] in large yields. In the case of chloroform a metalation reaction occurs to some extent, as indicated by the presence of triphenylsilane among the products. It has been shown that chloroform reacts exclusively by metalation with organo-alkali-metal compounds[13]. A coupling reaction may be occurring between methylene chloride and triphenylsilyllithium.

However, the reactions are complex because of the different behavior of halides toward carbene intermediates and organolithium compounds.

The reaction of methylene chloride with triphenylsilyllithium gave hexaphenyldisilane (35–56%), methyltriphenylsilane (15.5–34.2%), (chloromethyl)triphenylsilane (0–11.7%), and bis(triphenylsilyl)methane (5.4–17.4%).

The fact that (chloromethyl)triphenylsilane was not isolated when methylene chloride was added to triphenylsilyllithium, as well as when excess triphenylsilyllithium was added to methylene chloride in the normal addition, suggested that bis(triphenylsilyl)methane was formed by a coupling reaction between the silyllithium compound and (chloromethyl)triphenylsilane. Independently, triphenylsilyllithium and (chloromethyl)triphenylsilane were allowed to react under similar conditions. It was noted that extensive halogen–metal interconversion (36.8% of hexaphenyldisilane) accompanied the coupling reaction [32.4% of bis(triphenylsilyl)methane]. Steric hindrance appears to be responsible for the occurrence of halogen–metal interconversion. (Chloromethyl)trimethylsilane did not give any hexaphenyldisilane, whereas neopentyl chloride gave a 62% yield of the same compound[14].

It is somewhat surprising that a relatively lower yield (35.2%) of hexaphenyldisilane was obtained when reverse addition was employed. This may be explained by the fact that two competing reactions exist in the system; namely, the reactions of triphenylsilyllithium with chlorotriphenylsilane and with carbene, both of which involve halogen–metal interconversion:

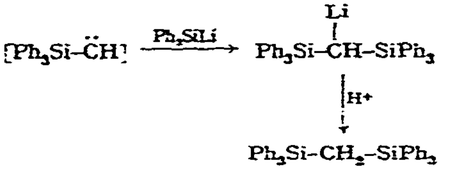
$$\begin{tikzcd}
\mathrm{Ph_3SiLi + CH_2Cl_2} \arrow[r] & \mathrm{Ph_3SiCl + CH_2ClLi} \arrow[d, "-\mathrm{LiCl}"] \\
\mathrm{Ph_3Si{-}CH_2Li} & {[:\mathrm{CH_2}]} \arrow[l, "\mathrm{Ph_3SiLi}"']
\end{tikzcd}$$

The resulting triphenylsilylmethyllithium may compete with triphenylsilyllithium in reactions with chlorotriphenylsilane and with methylene chloride.

There are three possible reactions that triphenylsilylmethyllithium can undergo with methylene chloride: coupling, halogen–metal interconversion, and metalation. The last reaction results in the formation of methyltriphenylsilane and chlorocarbene:

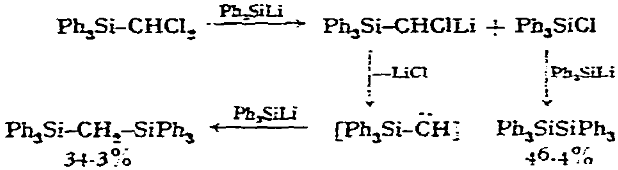
$$\begin{tikzcd}
& \mathrm{Ph_3Si{-}CH_2Li + CH_2Cl_2} \arrow[r] & \mathrm{Ph_3Si{-}CH_3 + CHCl_2Li} \arrow[d, "-\mathrm{LiCl}"] \\
{[\mathrm{Ph_3Si{-}\ddot{C}H}]} & \mathrm{Ph_3Si{-}CHClLi} \arrow[l, "-\mathrm{LiCl}"'] & {[:\mathrm{CHCl}]} \arrow[l, "\mathrm{Ph_3SiLi}"']
\end{tikzcd}$$

The chlorocarbene may react with triphenylsilyllithium to give triphenylsilylcarbene. Likewise, the latter carbene might be expected to react with triphenylsilyllithium to yield bis(triphenylsilyl)methyllithium, which would result in the formation of bis(triphenylsilyl)methane:



$$\begin{tikzcd}
{[Ph_3Si\text{-}\ddot{C}H]} \arrow[r, "Ph_3SiLi"] & Ph_3Si\text{-}\overset{Li}{C}H\text{-}SiPh_3 \arrow[d, "H^+"] \\
 & Ph_3Si\text{-}CH_2\text{-}SiPh_3
\end{tikzcd}$$

The reaction of (dichloromethyl)triphenylsilane with triphenylsilyllithium gave hexaphenyldisilane (46.4%) and bis(triphenylsilyl)methane (34.3%). Triphenylsilylcarbene appears to be an intermediate:



$$\begin{tikzcd}
 & Ph_3Si\text{-}CHCl_2 \arrow[r, "Ph_3SiLi"] & Ph_3Si\text{-}CHClLi \arrow[d, "-LiCl"] & + Ph_3SiCl \arrow[d, "Ph_3SiLi"] \\
\underset{34.3\%}{Ph_3Si\text{-}CH_2\text{-}SiPh_3} & & {[Ph_3Si\text{-}\ddot{C}H]} \arrow[ll, "Ph_3SiLi"'] & \underset{46.4\%}{Ph_3SiSiPh_3}
\end{tikzcd}$$

Methyltriphenylsilane may have arisen at least in part by the reaction of triphenylsilylmethyllithium with the solvent (tetrahydrofuran)*.

The reaction of methylene bromide with triphenylsilyllithium gave hexaphenyldisilane (42.5–59.4%), methyltriphenylsilane (trace–40.0%), and (bromomethyl)triphenylsilane (0–9.6%).

The significant point in this reaction is that bis(triphenylsilyl)methane was not isolated. Probably methylene bromide does not undergo coupling or metalation reactions to any appreciable degree with either triphenylsilyllithium or triphenylsilylmethyllithium under the conditions employed. The same may be true for (bromomethyl)triphenylsilane. If these reactions should take place to any significant degree, bis(triphenylsilyl)methane would be isolated.

(Bromomethyl)triphenylsilane was probably formed as a result of halogen–metal interconversion between triphenylsilylmethyllithium and methylene bromide. Methyltriphenylsilane may very well have resulted by the metalation reaction of triphenylsilylmethyllithium with the solvent.

The reaction of methylene iodide gave hexaphenyldisilane (42.5–65%), methyltriphenylsilane (16.4–28.3%), (iodomethyl)triphenylsilane (6.3–23.0%), and bis(triphenylsilyl)methane (0–5.6%).

Three runs were carried out under similar conditions (ratio of reactants, temperature, mode of addition, and solvent), yet the product ratio was significantly altered. Probably the rate of addition as well as concentration of reactants had an important influence on the course of the reaction. Higher yields of (iodomethyl)triphenylsilane than those of the corresponding (bromomethyl)triphenylsilane may indicate that methylene iodide is more susceptible than methylene bromide to halogen–metal interconversion with triphenylsilylmethyllithium.

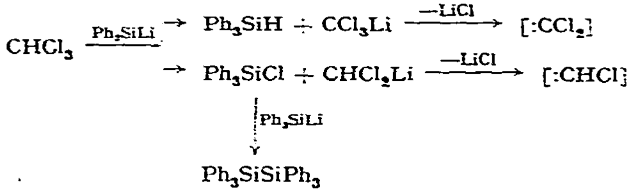
The reaction of chloroform with triphenylsilyllithium gave hexaphenyldisilane

---

* For metalation and cleavage reactions of ethers by organometallic compounds, see, for example, ref. 15.

(51.6–60.5%), triphenylsilane (5.3–13.0%), (chloromethyl)triphenylsilane (3.2–6.5%), (dichloromethyl)triphenylsilane (0–11.7%), and bis(triphenylsilyl)methane (1.7–10.3%).

Isolation of hexaphenyldisilane and triphenylsilane indicates occurrence of both halogen–metal interconversion and metalation reactions:



$$\mathrm{CHCl_3} \xrightarrow{\mathrm{Ph_3SiLi}} \begin{cases} \mathrm{Ph_3SiH} + \mathrm{CCl_3Li} \xrightarrow{-\mathrm{LiCl}} [:\mathrm{CCl_2}] \\ \mathrm{Ph_3SiCl} + \mathrm{CHCl_2Li} \xrightarrow{-\mathrm{LiCl}} [:\mathrm{CHCl}] \end{cases}$$

$$\mathrm{Ph_3SiCl} \xrightarrow{\mathrm{Ph_3SiLi}} \mathrm{Ph_3SiSiPh_3}$$

The dichlorocarbene and chlorocarbene would then react with triphenylsilyllithium to give chloro(triphenylsilyl)carbene and triphenylsilylcarbene, respectively. The reaction of the latter carbenes with chloroform* may have yielded (dichloromethyl)triphenylsilane and (chloromethyl)triphenylsilane:

$$[\mathrm{Ph_3Si{-}\ddot{C}{-}Cl}] + \mathrm{CHCl_3} \longrightarrow \mathrm{Ph_3Si{-}CHCl_2} + [:\mathrm{CCl_2}]$$

$$[\mathrm{Ph_3Si{-}\ddot{C}{-}H}] + \mathrm{CHCl_3} \longrightarrow \mathrm{Ph_3Si{-}CH_2Cl} + [:\mathrm{CCl_2}]$$

(Dichloromethyl)triphenylsilane and (chloromethyl)triphenylsilane may undergo further reaction with triphenylsilyllithium giving hexaphenyldisilane and bis(triphenylsilyl)methane.

From the reaction of bromoform there was obtained hexaphenyldisilane (48.7–62.5%), methyltriphenylsilane (0.9–10.3%), (bromomethyl)triphenylsilane (20.5–34.0%), and (dibromomethyl)triphenylsilane (0–13.9%). Triphenylsilane was obtained only in trace amounts. Bis(triphenylsilyl)methane was not isolated as in the case of methylene bromide reactions.

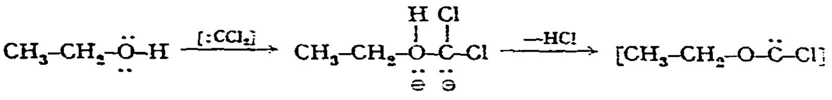
Isolation of (dibromomethyl)triphenylsilane gives some support to the mechanism advanced earlier that triphenylsilylcarbene may react with haloform by dehydrohalogenation yielding (halomethyl)triphenylsilane and dihalocarbenes. The latter carbenes follow paths similar to halocarbenes to give (dihalomethyl)triphenylsilanes.

Methyltriphenylsilane was probably the result of halogen–metal interconversion between (bromomethyl)triphenylsilane and triphenylsilyllithium, followed by proton abstraction from the solvent on the part of the resulting triphenylsilylmethyllithium.

When triphenylsilyllithium was added to iodoform at room temperature until the solution gave a positive Color Test[17] I, three products were isolated: hexaphenyldisilane (60.5% based on triphenylsilyllithium); methyltriphenylsilane (23.7% based on iodoform); and bis(triphenylsilyl)methane (19.5% based on iodoform). The ratio

---

* Hine *et al.*[16] postulated electrophilic attack of dichlorocarbene on the oxygen atom of alcohol:



$$\mathrm{CH_3{-}CH_2{-}\ddot{\underset{\cdot\cdot}{O}}{-}H} \xrightarrow{[:\mathrm{CCl_2}]} \mathrm{CH_3{-}CH_2{-}\underset{\oplus}{\overset{H}{O}}{-}\underset{\ominus}{\overset{Cl}{C}}{-}Cl} \xrightarrow{-\mathrm{HCl}} [\mathrm{CH_3{-}CH_2{-}O{-}\ddot{C}{-}Cl}]$$

of the reactants was approximately 3 (triphenylsilyllithium) to 1 (iodoform). When the ratio was 2 to 1, methyltriphenylsilane and bis(triphenylsilyl)methane were not isolated, but (iodomethyl)triphenylsilane (15.6%) and (diiodomethyl)triphenylsilane (14.5%) were obtained in addition to a 60% yield of hexaphenyldisilane.

In the first case sufficient triphenylsilyllithium is added to react with the intermediates, (mono- and diiodomethyl)triphenylsilane, to form methyltriphenylsilane and bis(triphenylsilyl)methane by the mechanisms postulated for the reactions of (bromomethyl)triphenylsilane and (dichloromethyl)triphenylsilane.

When the reverse addition was employed until all of triphenylsilyllithium was used (indicated by a negative Color Test I), the yield of hexaphenyldisilane was 64.7%. The other products were methyltriphenylsilane (11.0%), bis(triphenylsilyl)-methane (3.1%), and 1,2-bis(triphenylsilyl)ethane (2.4%). The last compound is expected in all reactions which involve triphenylsilylmethyllithium as an intermediate; however, this is the only case in which this compound was actually isolated.

In the reaction of carbon tetrachloride with triphenylsilyllithium at —60°, only two products were isolated: hexaphenyldisilane (56.6–73.5% based on triphenylsilyllithium) and (dichloromethyl)triphenylsilane (11.2–42.2% based on carbon tetrachloride). The reaction of carbon tetrabromide under similar conditions, however, gave (bromomethyl)triphenylsilane (0–2.8%), (dibromomethyl)triphenylsilane (0–1.4%), bromo(triphenylsilyl)acetylene (0–2.0%), bis(triphenylsilyl)acetylene (2.8–4.3%), and hexaphenyldisilane (64.1–67.5%).

This suprising difference might very well be due to the difference in nature of the postulated intermediates, chloro(triphenylsilyl)carbene and bromo(triphenylsilyl)-carbene. It appears that the former carbene can abstract a chloride atom from carbon tetrachloride by way of a free-radical mechanism, whereas the latter has little tendency to undergo such a reaction.

EXPERIMENTAL

Reactions involving organometallic reagents were carried out under an atmosphere of dry, oxygen-free nitrogen. All melting points are uncorrected.

Reaction of triphenylsilyllithium with methylene chloride

(*a*) *Normal addition*

(*1*) *1:1 Ratio*. A solution of triphenylsilyllithium[13] (0.08 mole) was added dropwise to 6.8 g (0.08 mole) of methylene chloride at —60°. The reaction mixture was stirred at this temperature for 2 h after the addition. It was black and formed a tar-like material. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 11.7 g (56.4%), was separated by filtration. The organic layer was dried with sodium sulfate. The solvent was removed and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave in the first fraction 5.70 g (26.0%) of methyltriphenylsilane, m.p. 68–70°, after recrystallization from petroleum ether (b.p. 60–70°). A mixed melting point with an authentic sample was not depressed and the infrared spectra were superimposable. Further elution with the same solvent gave in the second fraction 0.90 g (3.6%) of (chloromethyl)triphenylsilane, m.p. 116–118°, after recrystallization from petroleum ether (b.p. 60–70°). Another recrystallization from the same solvent raised the melting point to 120–122°. Elution with carbon tetrachloride gave 1.10 g (5.2%) of bis(triphenylsilyl)methane, m.p. 141–142°, after recrystallization from petroleum ether (b.p. 60–70°). (Found: Si, 10.49, 10.39. $C_{37}H_{32}Si_2$ calcd.: Si, 10.54%.)

(*2*) *2:1 Ratio*. A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 3.40 g (0.04 mole) of methylene chloride at —60°. Color Test I was negative after the addition. The reaction mixture was black as in the case of (*1*). It was worked up by the same procedure as in (*1*) and the following compounds were isolated: hexaphenyldisilane, 9.45 g (45.5%); methyltriphenylsilane, 3.75 g (34.2%); (chloromethyl)triphenylsilane, 1.05 g (8.5%); and bis(triphenylsilyl)methane, 1.15 g (5.4%).

(*3*) *2:1 Ratio*. A solution of triphenylsilyllithium (0.08 mole) was added dropwise to a mixture of 3.40 g (0.04 mole) of methylene chloride and 8.1 g (0.1 mole) of cyclohexene at —60°. Color Test I was slightly positive when the addition was completed. The reaction mixture was a light brown. It was stirred at this temperature for 2 h at which time Color Test I became negative. Subsequent to hydrolysis, hexaphenyldisilane, 8.30 g (40.0%), was separated by filtration. The yellow organic layer was dried with sodium sulfate. The solvent was removed by distillation. The mixture was then subjected to fractional distillation, but no product distilled even at 250°. The residue was chromatographed on alumina. The following compounds were isolated: methyltriphenylsilane, 1.70 g (15.5%); (chloromethyl)triphenylsilane, 1.45 g (11.7%); and bis(triphenylsilyl)methane, 1.30 g (6.1%).

(*4*) *5:2 Ratio*. A solution of triphenylsilyllithium was added dropwise to 1.70 g (0.02 mole) of methylene chloride in 20 ml of THF at room temperature. When 0.04 mole of triphenylsilyllithium had been added, Color Test I was negative, but the color test became positive when 0.052 mole of triphenylsilyllithium had been added. The reaction mixture was worked up by the same procedure as in (*1*). The compounds isolated were hexaphenyldisilane, 4.50 g (43.5%); methyltriphenylsilane, 1.20 g (21.9%); and bis(triphenylsilyl)methane, 1.85 g (17.4%). In addition, a mixture of triphenylsilane and methyltriphenylsilane (1.35 g) was obtained. (Chloromethyl)triphenylsilane was not isolated.

(*b*) *Reverse addition*

A solution of methylene chloride in tetrahydrofuran (THF) was added dropwise to 0.04 mole of triphenylsilyllithium cooled in an ice bath. When 0.02 mole of methylene chloride had been added, Color Test I became negative. The reaction mixture was a brownish black. A work-up by the same procedure as in (*1*) of the previous section gave hexaphenyldisilane, 3.65 g (35.2%); methyltriphenylsilane, 1.40 g (25.6%); and bis(triphenylsilyl)methane, 1.25 g (11.7%).

Reaction of triphenylsilyllithium with methylene bromide

(*a*) *Normal addition*

(*1*) *2:1 Ratio*. A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 6.96 g (0.04 mole) of methylene bromide at —60°. The reaction mixture was stirred for 5 h. Color Test I was negative. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 12.30 g (59.4%), was separated by filtration. The organic layer was worked up in the usual manner and the residue was chromatographed on alumina.

Elution with petroleum ether (b.p. 60–70°) gave in the first fraction 3.55 g (32.4% based on methylene bromide) of methyltriphenylsilane, m.p. 64–67° (mixed m.p.). Further elution with the same solvent gave 1.35 g (6.9%) of (bromomethyl)triphenylsilane, m.p. 121–122.5°, after recrystallization from petroleum ether (b.p. 60–70°). (Found: C, 63.10, 63.06; H, 4.77, 4.76; Si, 8.04, 7.96. $C_{19}H_{17}BrSi$ calcd.: C, 64.58; H, 4.58; Si, 7.95%.)

(2) *2:1 Ratio, in the presence of cyclohexene.* A solution of triphenylsilyllithium (0.08 mole) was added dropwise to a mixture of 6.96 g (0.04 mole) of methylene bromide and 24 g (0.3 mole) of cyclohexene at —60°. Color Test I was negative after the addition. A work-up by the same procedure as in (1) gave hexaphenyldisilane, 8.90 g (42.5%), and methyltriphenylsilane, 4.35 g (40.0%).

(*b*) *Reverse addition*

A solution of methylene bromide in THF was added to 0.08 mole of triphenylsilyllithium at —60°. Color Test I became negative when 0.028 mole of methylene bromide had been added. Subsequent to hydrolysis, hexaphenyldisilane, 11.90 g (57.5%), was separated by filtration. The organic layer was dried with sodium sulfate. The solvent was removed. The residue was treated with petroleum ether (b.p. 60–70°). An insoluble material was separated by filtration. A part of this material melted at 254–260°. This compound has not been identified. The mother liquor was poured onto an alumina column. Elution with the same solvent gave only a trace amount of methyltriphenylsilane.

Reaction of triphenylsilyllithium with methylene iodide

A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 10.7 g (0.04 mole) of methylene iodide at —60°. After stirring for 1 h, Color Test I was only slightly positive. Subsequent to hydrolysis, hexaphenyldisilane, 11.80 g (57.0%), was separated by filtration. The organic layer was worked up in the usual manner and subsequently chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave in the first fraction 3.10 g (28.3% based on methylene iodide) of (iodomethyl)triphenylsilane, m.p. 117–119°, after recrystallization from ethanol. (Found: Si, 7.07, 6.97. $C_{19}H_{17}ISi$ calcd.: Si, 7.02%.)

Elution with carbon tetrachloride gave 1.20 g (5.6%) of bis(triphenylsilyl)methane, m.p. 138–140°. A mixed melting point with a sample obtained from the reaction of triphenylsilyllithium with methylene chloride was not depressed and the infrared spectra were superimposable.

In another run under similar conditions the products isolated were hexaphenyldisilane, (50.0%); methyltriphenylsilane (16.4%); and (iodomethyl)triphenylsilane (23.0%).

In still another run, when the reaction was carried out at room temperature, the yield of hexaphenyldisilane increased (65.1%), while only small amounts of other products were obtained.

Reaction of triphenylsilyllithium with chloroform

(*a*) *Normal addition*

(1) *1:1 Ratio, room temperature.* A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 9.55 g (0.08 mole) of chloroform at room temperature. The

reaction was exothermic and Color Test I was negative immediately after the addition. The mixture was black. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 10.7 g (51.6 %), was separated by filtration. The residue obtained after a work-up of the organic layer in the usual manner was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave in the first fraction 2.35 g (11.3 %) of triphenylsilane. Further elution with the same solvent gave in the second fraction 0.80 g (3.2 %) of (chloromethyl)triphenylsilane, m.p. 119–120° (mixed m.p.). Elution with carbon tetrachloride gave 0.70 g (1.7 %) of bis(triphenylsilyl)methane, m.p. 137–139° (mixed m.p.).

(2) 2:1 Ratio, —60°. A solution of triphenylsilyllithium (0.08 mole) was added dropwise to 4.78 g (0.04 mole) of chloroform at —60°. This reaction mixture was stirred for 3 h at this temperature, during which time Color Test I became negative. It was black and formed a tar-like material. Subsequent to hydrolysis, hexaphenyldisilane, 11.0 g (53.0 %), was separated by filtration. The residue after work-up was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave a mixture of compounds from which 1.60 g (11.7 %) of (dichloromethyl)triphenylsilane, m.p. 147–148°, was separated by crystallization from petroleum ether (b.p. 60–70°). A mixed melting point with the product obtained from the reaction of triphenylsilyllithium with carbon tetrachloride was not depressed. The mother liquor was poured onto an alumina column to be rechromatographed. Elution with petroleum ether (b.p. 60–70°) gave 0.55 g (5.3 %) of triphenylsilane and 0.80 g (6.5 %) of (chloromethyl)triphenylsilane. Elution with carbon tetrachloride gave 0.60 g (2.8 %) of bis(triphenylsilyl)methane, m.p. 140–141.5° (mixed m.p.).

(b) Reverse addition

A solution of 4.78 g (0.04 mole) of chloroform in 20 ml of THF was added to 0.08 mole of triphenylsilyllithium at —60°. Color Test I was negative at the end of the addition and the reaction mixture was black. Subsequent to hydrolysis, hexaphenyldisilane, 12.55 g (60.5 %), was separated by filtration. The organic layer was worked up in the usual manner and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave in the first fraction 1.35 g (13.0 %) of triphenylsilane. Further elution with the same solvent gave in the second fraction 1.60 g of a mixture of (chloro- and dichloromethyl)triphenylsilane, m.p. 130–140°. No attempt was made to separate these two. The combined yield was approximately 12 %. Further elution with carbon tetrachloride gave 2.20 g (10.3 %) of bis(triphenylsilyl)methane, m.p. 140–141° (mixed m.p.).

Reaction of triphenylsilyllithium with bromoform

(a) Normal Addition

(1) 2:1 Ratio. A solution of triphenylsilyllithium (0.08 mole) was added dropwise over a period of 40 min to 10.1 g (0.04 mole) of bromoform at —60°. Color Test I was negative immediately after the addition. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 12.55 g (60.5 %), was separated by filtration. The black organic layer was dried with sodium sulfate. The solvent was removed and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 0.35 g (3.3 %) of methyltriphenylsilane which was identified by a comparison

of its infrared spectrum with that of an authentic sample. Elution with carbon tetrachloride gave an oily material in two fractions. The first fraction was treated with petroleum ether (b.p. 60–70°) to give 2.90 g (20.5 %, based on bromoform) of (bromomethyl)triphenylsilane, m.p. 122–123.5°, after recrystallization from the same solvent. A mixed melting point with a sample obtained from the reaction of triphenylsilyllithium with methylene bromide was not depressed. The second fraction was also treated with petroleum ether (b.p. 60–70°) to produce a solid with a wide melting point range, 128–140°. This solid was recrystallized from the same solvent to give 0.70 g (4.0 %) of a compound, possibly (dibromomethyl)triphenylsilane, m.p. 137–140°. Two more recrystallizations from the same solvent raised the melting point to 150–152°. (Found: Si, 6.77, 6.69. $C_{19}H_{16}Br_2Si$ calcd.: Si, 6.51 %.)

In another run under identical conditions the following products were isolated: hexaphenyldisilane (54 %); methyltriphenylsilane (0.9 %); (bromomethyl)triphenylsilane (34.0 %); and triphenylsilane (0.5 %). (Dibromomethyl)triphenylsilane, however, was not isolated.

(2) *8:3 Ratio.* A solution of triphenylsilyllithium (0.08 mole) was added slowly to 7.6 g (0.03 mole) of bromoform in 50 ml of ether at —60°. Color Test I was slightly positive at the end of the addition. The reaction mixture, however, was hydrolyzed immediately with dilute acid. Hexaphenyldisilane, 10.1 g (48.7 %), was separated by filtration. The straw colored organic layer was worked up by the same procedure as in (*1*). The products isolated were: methyltriphenylsilane, 0.80 g (9.7 %), m.p. 66–67° (mixed m.p.); (bromomethyl)triphenylsilane, 2.60 g (24.5 %), m.p. 121–122.5° (mixed m.p.); and (dibromomethyl)triphenylsilane, 1.80 g (13.9 %), m.p. 150–152° (mixed m.p.).

(*b*) *Reverse addition*

An ethereal solution of bromoform was added dropwise to 0.08 mole of triphenylsilyllithium at —60°. When 0.03 mole of bromoform had been added, Color Test I became negative. Subsequent to hydrolysis, hexaphenyldisilane, 12.9 g (62.5 %), was separated by filtration. The organic layer was worked up by the same procedure as in (*1*) to give 0.15 g (1.9 %) of triphenylsilane, which was identified from its infrared spectrum; 0.85 g (10.3 %) of methyltriphenylsilane, m.p. 65–67° (mixed m.p.); and 2.55 g (24.0 %) of (bromomethyl)triphenylsilane, m.p. 122.5–123.5° (mixed m.p.).

Reaction of triphenylsilyllithium with iodoform

(*a*) *Normal addition*

(*1*) *Until positive with Color Test I.* A solution of triphenylsilyllithium was added dropwise to 7.88 g (0.02 mole) of iodoform in 50 ml of ether at room temperature. Slight heat was evolved during this addition. When 0.069 mole of triphenylsilyllithium had been added, Color Test I became positive. The reaction mixture was stirred for 2 h, at which time Color Test I became negative. The reaction mixture was hydrolyzed with dilute acid. Hexaphenyldisilane, 10.80 g (60.5 % based on the silyllithium compound), was separated by filtration. The dark organic layer was dried with sodium sulfate. The solvent was removed and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 1.30 g (23.7 % based on iodoform) of methyltriphenylsilane, which was identified by a mixed melting point determination with an authentic sample. Further elution with carbon tetrachloride gave 2.10 g (19.7 % based on iodoform) of bis(triphenylsilyl)methane, m.p. 137–140° (mixed m.p.).

(2) *2:1 Ratio, in the presence of triphenylsilane.* A solution of 0.08 mole of triphenylsilyllithium was added dropwise to a mixture of 15.8 g (0.04 mole) of iodoform and 5.20 g (0.02 mole) of triphenylsilane dissolved in 50 ml of THF. The reaction mixture was cooled to −60° by means of a Dry Ice–acetone bath when one-third of the silyllithium compound had been added. Color Test I was negative when the addition was completed. A work-up of the reaction mixture as in (1) gave 12.40 g (60.0 %) of hexaphenyldisilane and an oil, which was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave in the first fraction 4.50 g (86.5 % recovery) of triphenylsilane. Further elution with the same solvent gave in the second fraction 2.50 g (15.6 %) of (iodomethyl)triphenylsilane, m.p. 117.5–119° (mixed m.p.), after recrystallization from petroleum ether (b.p. 60–70°). Elution with carbon tetrachloride gave 3.05 g (14.5 %) of crude (diiodomethyl)triphenylsilane. Three recrystallizations from petroleum ether (b.p. 60–70°) gave a sample with a melting point of 151.0–152.5°. (Found: C, 44.00, 43.97; H, 3.31, 3.10; Si, 5.41, 5.33 $C_{19}H_{16}I_2Si$ calcd.: C, 43.36; H, 3.07; Si, 5.34 %.)

(b) Reverse addition

A solution of 11.82 g (0.03 mole) of iodoform in THF was added dropwise to 0.08 mole of triphenylsilyllithium at room temperature. When 0.026 mole of iodoform had been added, Color Test I became negative. The reaction mixture was hydrolyzed with dilute acid. Hexaphenyldisilane, 13.40 g (64.7 %), was separated by filtration. The residue after a work-up of the organic layer was chromatographed on alumina. Elution with petroleum ether gave 0.90 g (11.0 %) of methyltriphenylsilane, m.p. 67–68° (mixed m.p.). Further elution with carbon tetrachloride gave a solid, which was treated with petroleum ether (b.p. 60–70°). The insoluble material was filtered off. There was no attempt made to purify this compound, m.p. 185–205°, (0.20 g, 2.4 %). Its infrared spectrum was identical with that of 1,2-bis(triphenylsilyl)ethane, m.p. 211–212°. From the mother liquor there was isolated 0.50 g (3.1 %) of bis(triphenylsilyl)methane, m.p. 140.5–142° (mixed m.p.).

Reaction of triphenylsilyllithium with carbon tetrachloride

(a) Normal addition

A solution of triphenylsilyllithium was added dropwise to 3.19 g (0.021 mole) of carbon tetrachloride in 50 ml of ether at −60°. When 0.04 mole of triphenylsilyllithium had been added. Color Test I was negative, but it became positive when 0.054 mole of the silyllithium compound had been added. The reaction mixture was black. Subsequent to hydrolysis, hexaphenyldisilane, 8.0 g (57.2 %), was separated by filtration. The organic layer was dried with sodium sulfate. The solvent was removed and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave a trace amount of triphenylsilane. Further elution with carbon tetrachloride gave 3.0 g (42.2 % based on carbon tetrachloride) of (dichloromethyl)triphenylsilane, m.p. 147–148.5°, after recrystallization from petroleum ether (b.p. 60–70°). (Found: C, 66.54, 66.50; H, 4.95, 4.72; Si, 8.04, 7.95. $C_{19}H_{16}Cl_2Si$ calcd.: C, 66.46; H, 4.70; Si, 8.18 %.)

In another run 0.06 mole of triphenylsilyllithium was reacted with 0.03 mole of carbon tetrachloride under the same conditions to give hexaphenyldisilane, 8.8 g (56.6%) and (dichloromethyl)triphenylsilane, 1.35 g (13.0%).

(b) Reverse addition

A solution of carbon tetrachloride in THF was added dropwise to 0.08 mole of triphenylsilyllithium at —60°. When 0.026 mole of carbon tetrachloride had been added, Color Test I became negative. The reaction mixture was black. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 15.25 g (73.6%), was separated by filtration. The organic layer was worked up as in the case of the normal addition. The only product isolated and identified was (dichloromethyl)triphenylsilane, m.p. 147–148.5° (mixed m.p.), 1.0 g (11.2%).

Reaction of triphenylsilyllithium with carbon tetrabromide

(a) Normal addition

A solution of triphenylsilyllithium (0.08 mole) was added over a period of 55 min to 13.3 g (0.04 mole) of carbon tetrabromide in 50 ml of ether at —60°. The color of the reaction mixture changed from yellow to gray as the addition proceeded. Color Test I was slightly positive at the end of the addition. The mixture was allowed to warm to room temperature. After 1 h of stirring, Color Test I was negative. By this time the mixture was black. Subsequent to hydrolysis with dilute acid, hexaphenyldisilane, 11.0 g (53.1%), was separated by filtration. The organic layer was dried with sodium sulfate. The solvent was removed and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave only a trace amount of a material which was not identified. The following elution with carbon tetrachloride gave an oily material which was treated with petroleum ether (b.p. 60–70°). A material which crystallized out first was separated by filtration. It was recrystallized from the same solvent and was identified as (dibromomethyl)triphenylsilane, m.p. 148–150° (mixed m.p.). The mother liquor was concentrated and a second compound, m.p. 154–157.5°, was crystallized out. This compound was identified as bis(triphenylsilyl)-acetylene by a mixed melting point determination with an authentic sample prepared from dilithium acetylide and chlorotriphenylsilane. The yields of (dibromomethyl)-triphenylsilane and bis(triphenylsilyl)acetylene were 0.30 g (1.7%) and 0.50 g (4.6%) respectively.

(b) Reverse addition

An ethereal solution of carbon tetrabromide was added slowly to 0.08 mole of triphenylsilyllithium at —60°. When 0.03 mole of carbon tetrabromide had been added, the color of the reaction mixture changed from yellow to pale green and Color Test I was negative. An excess of carbon tetrabromide was added, making a total of 0.08 mole. The reaction mixture was stirred at —60° for 1 h; then it was allowed to warm to room temperature. Its color changed to gray, but Color Test I remained negative. It was stirred at room temperature for 2.5 h before it was worked up. Subsequent to hydrolysis, hexaphenyldisilane, 15.3 g (73.9%), was separated by filtration. The black organic layer was dried with sodium sulfate. The solvent was removed and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave

0.22 g (2.0 %) of bromo(triphenylsilyl)acetylene, m.p. 108–110°, after recrystallization from ethanol. This compound was identified by a mixed melting point determination with an authentic sample prepared from bromoethynyllithium and chlorotriphenylsilane and by a comparison of infrared spectra. Further elution with carbon tetrachloride gave an oil in two fractions. The first fraction was treated with petroleum ether (b.p. 60–70°). Most of the oil dissolved leaving a small amount of solid, m.p. 168–250°, which was obtained by filtration. This solid was recrystallized from the same solvent to give 0.07 g of a compound with a melting point of 185–190°. Its infrared spectrum was very similar to that of bis(triphenylsilyl)acetylene. The mother liquor was concentrated and a second compound, m.p. 119–122°, crystallized out. A mixed melting point with (bromomethyl)triphenylsilane was not depressed. The yield was 0.03 g (2.8 %). The second fraction was treated with petroleum ether (b.p. 60–70°) to give 0.70 g (4.3 %) of bis(triphenylsilyl)acetylene, which was identified by a mixed melting point determination with an authentic sample and a comparison of infrared spectra.

Reaction of triphenylsilyllithium with (chloromethyl)triphenylsilane

A solution of triphenylsilyllithium was added dropwise to 0.90 g (0.0029 mole) of (chloromethyl)triphenylsilane in 25 ml of THF at room temperature. Color Test I was negative when 0.004 mole of triphenylsilyllithium had been added, but it became positive upon the addition of another 0.001 mole. The reaction mixture was hydrolyzed with dilute acid after a stirring of 30 min. Hexaphenyldisilane, 0.55 g (36.8 %), was separated out by filtration. The organic layer was worked up in the usual manner and the residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave only a trace amount of triphenylsilane. Further elution with carbon tetrachloride gave 0.50 g (32.4 %) of pure bis(triphenylsilyl)methane, m.p. 140.5–142° (mixed m.p.).

Reaction of triphenylsilyllithium with (dichloromethyl)triphenylsilane

A solution of triphenylsilyllithium was added dropwise to 1.40 g (0.0041 mole) of (dichloromethyl)triphenylsilane in 45 ml of THF at —60°. The reaction appeared to be slow at this low temperature; therefore, the cooling bath was removed and the reaction mixture was allowed to reach room temperature. When 0.0125 mole of triphenylsilyllithium had been added, Color Test I was found to be slightly positive. The reaction mixture was hydrolyzed with dilute acid after 10 min of stirring. Hexaphenyldisilane, 1.50 g (46.4 %), was separated by filtration. The residue after a work-up of the organic layer was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave a trace amount of methyltriphenylsilane, identified from its infrared spectrum. Further elution with carbon tetrachloride gave 0.75 g (34.3 %) of bis(triphenylsilyl)methane, m.p. 140.5–142° (mixed m.p.).

Reaction of triphenylsilyllithium with (chloromethyl)trimethylsilane

A solution of triphenylsilyllithium (0.08 mole) was added to 13.0 g (0.12 mole) of (chloromethyl)trimethylsilane. The reaction mixture was cooled in an ice-bath during the addition. Color Test I was negative when the addition was completed. A work-up in the usual manner gave an oily residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 22.7 g (82 %) of an oil. Upon distillation under reduced pressure it solidified immediately, m.p. 70–71°, after recrystallization from a mixture of petroleum ether (b.p. 60–70°) and ethanol. (Found: Si, 16.09, 16.02. $C_{22}H_{24}Si_2$ calcd.: Si, 16.21 %.)

Reaction of triphenylsilyllithium with (chloromethyl)dimethylvinylsilane

A solution of triphenylsilyllithium (0.08 mole) was added to 10.8 g (0.08 mole) of (chloromethyl)dimethylvinylsilane at an ice bath temperature. Color Test I was negative immediately after the addition. A work-up in the usual manner, followed by chromatography on alumina, gave an oil, 18.2 g (63.5 %), which was distilled under reduced pressure, b.p. 158–159°/0.01 mm, $n_D^{21.5}$ 1.5890. (Found: Si, 15.43, 15.38. $C_{23}H_{26}Si_2$ calcd.: Si, 15.67 %.)

Reduction of (dichloromethyl)triphenylsilane with lithium aluminum hydride

A solution of 0.70 g (0.002 mole) of (dichloromethyl)triphenylsilane in 25 ml of THF was added to 0.70 g (0.018 mole) of lithium aluminum hydride in 25 ml of THF at room temperature. The reaction mixture became slightly warm during the addition. It was stirred for 35 min before the excess lithium aluminum hydride was destroyed by adding dropwise 25 ml of ethyl acetate.

The reaction mixture was worked up in the usual manner, followed by chromatography on alumina. Elution with petroleum ether (b.p. 60–70°) gave 0.08 g (14.6 %) of methyltriphenylsilane, m.p. 69–70° (mixed m.p.). Further elution with carbon tetrachloride gave 0.40 g (64.6 %) of (chloromethyl)triphenylsilane, m.p. 117.5–119° (mixed m.p.).

Reduction of (diiodomethyl)triphenylsilane with lithium aluminum hydride

This reduction was carried out essentially in the same manner as the reduction of (dichloromethyl)triphenylsilane. Using 1.10 g (0.0021 mole) of (diiodomethyl)triphenylsilane, there was obtained 0.45 g (78.5 %) of methyltriphenylsilane, m.p. 70–71° (mixed m.p.).

Reaction of (bromomethy)triphenylsilane with lithium in THF

To (bromomethyl)triphenylsilane, 2.0 g (0.00566 mole), and finely cut lithium wire, 1.2 g (0.17 mole), was added tetrahydrofuran (45 ml) in small portions at room temperature. An immediate reaction occurred evolving some heat, and the reaction mixture turned black. Color Test I was positive. The reaction mixture was worked up in the usual manner after 20 min of stirring. The residue obtained was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 0.15 g (9.7 %) of methyltriphenylsilane. Further elution with carbon tetrachloride gave 0.60 g (38.8 %) of 1,2-bis(triphenylsilyl)ethane, which was identified by a mixed melting point determination with an authentic sample, m.p. 210–211°, and by comparison of infrared spectra.

ACKNOWLEDGMENT

This research was supported in part by the United States Air Force under Contract AF 33(616)-6463 monitored by the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio.

SUMMARY

Reactions of methylene halides, haloforms, and carbon tetrahalides with triphenylsilyllithium have been investigated. The primary reaction was found to be halogen–metal interconversion, except in the case of chloroform where a metalation reaction was also observed. Secondary reactions seem to involve carbene intermediates. The products in most cases were methyltriphenylsilane, (mono- and dihalomethyl)-triphenylsilane, and bis(triphenylsilyl)methane. Mechanisms of these transformations are considered.

REFERENCES

1 H. Gilman and D. Aoki, *Chem. Ind. (London)*, (1960) 1165.
2 G. Wittig and V. Pockels, *Ber.*, 72 (1939) 884.
3 J. Hine, *J. Am. Chem. Soc.*, 72 (1950) 2438.
4 W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, 76 (1954) 6162.
5 G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, 81 (1959) 4996.
6 W. Kirmse, *Angew. Chem.*, 73 (1961) 161.
7 G. Wittig and H. Witt, *Ber.*, 74 (1941) 1474.
8 H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, 66 (1944) 1515.
9 G. L. Closs and L. E. Closs, *Tetrahedron Letters*, (1960) (24) 26.
10 W. P. Miller, Jr., and C. S. Y. Kim, *J. Am. Chem. Soc.*, 81 (1959) 5008.
11 C. R. Hauser, C. F. Hauser and P. J. Hamrick, Jr., *J. Org. Chem.*, 24 (1959) 397.
12 H. Gilman and D. Aoki, *J. Org. Chem.*, 24 (1959) 426 and references cited there.
13 C. R. Hauser, W. G. Kofron, W. R. Dunnavant and W. F. Owens, *J. Org. Chem.*, 26 (1961) 2627; G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, 82 (1960) 5723.
14 H. Gilman and G. Dappen, unpublished studies.
15 K. Ziegler and H. G. Fellert, *Ann. Chem.*, 567 (1950) 185; R. L. Letsinger and D. F. Pollart, *J. Am. Chem. Soc.*, 78 (1956) 6079.
16 J. Hine, E. L. Pollitzer and H. Wagner, *J. Am. Chem. Soc.*, 75 (1953) 5607.
17 H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, 47 (1925) 2002.
18 H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, 80 (1958) 608.