[Contribution from the Chemical Laboratories of Tuskegee Institute]

# THE ADDITION OF ORGANOLITHIUM COMPOUNDS TO VINYLTRIPHENYL- AND VINYLTRIMETHYL-SILANES

LOUIS F. CASON and HOUSTON G. BROOKS

*Received January 18, 1954*

In a previous publication (1), it was shown that phenyllithium and *n*-butyllithium add to the unsaturated linkage of vinyltriphenylsilane in such a manner as to produce β-phenylethyltriphenylsilane and *n*-hexyltriphenylsilane. The continuation of this study has been undertaken first, in order to show that prior to hydrolysis a new intermediate organolithium agent capable of further reaction is formed; next, to demonstrate that the reaction is general for alkyl and aryl lithium compounds; and finally, to determine the effects of the substituents about the silicon atom and the position of the ethylenic bond in the side chain on additions of this type.

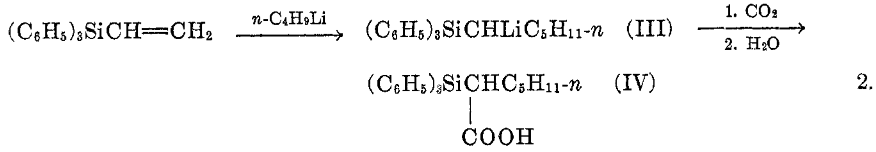
Reference to early work on the addition of lithium alkyls to olefins was summarized in the first paper of this series (1), but quite recently, reactions of isopropyllithium and *tert*-butyllithium with simple olefins have been reported (2), and a somewhat related addition has been shown to take place between triphenylsilylpotassium and *trans*-stilbene (3).

Although the direction of the addition of organolithium compounds to vinyltriphenylsilane was established earlier, no attempt was made to demonstrate that this process involves the intermediate formation of 1-triphenylsilyl-2-phenylethyllithium (I) as postulated by equation 1.

$$(C_6H_5)_3SiCH{=}CH_2 + C_6H_5Li \rightarrow [(C_6H_5)_3SiCH(Li)CH_2C_6H_5] \quad (I)$$
$$\xrightarrow{H_2O} (C_6H_5)_3SiCH_2CH_2C_6H_5 \quad (II) \qquad 1.$$

Preliminary evidence for I was indicated by a negative reaction with Gilman's Color Test III reagent (4). This test differentiates between alkyl- and aryllithium compounds in metalation reactions and is positive for the latter class of compounds. Hence, if according to equation 1, phenyllithium adds quantitatively to the silane, intermediate I should not respond to the test prior to hydrolysis.

Oxidation of I to the corresponding carbinol or reactions with benzaldehyde or benzoyl chloride were unsuccessful. While silane II resulted from the attempted carbonation of the unhydrolyzed reaction mixture, the possibility of the transitory existence of lithium 2-triphenyl-3-phenylpropionate and subsequent decarboxylation upon hydrolysis is not remote since it has been shown that lithium α-triphenylsilylphenylacetate, produced by metalating benzyltriphenylsilane and carbonating the lithium derivative, decomposes on hydrolysis to triphenylsilanol and phenylacetic acid (5). Further examples of the instability of α-trialkylsilyl substituted aliphatic acids have been reported by Hance and Hauser (6). These investigators were able to secure the ethyl esters of α-trimethylsilylacetic and α-trimethylsilylisobutyric acids by alkylating the corresponding unsubstituted ester with trimethylchlorosilane in the presence of sodium triphenylmethide. However, on attempted hydrolysis, these compounds yielded the siloxane and the unsubstituted acid. Nevertheless, in the present investigation, a low yield of α-triphenylsilylheptanoic acid (IV) resulted when an ether solution of 1-triphenylsilyl-*n*-hexyllithium (III) from the addition of *n*-butyllithium to vinyltriphenylsilane was treated with carbon dioxide.



$$(C_6H_5)_3SiCH{=}CH_2 \xrightarrow{n\text{-}C_4H_9Li} (C_6H_5)_3SiCHLiC_5H_{11}\text{-}n\ \text{(III)} \xrightarrow[2.\ H_2O]{1.\ CO_2} (C_6H_5)_3Si\underset{\displaystyle COOH}{\underset{|}{C}}HC_5H_{11}\text{-}n\ \text{(IV)} \qquad 2.$$

Although this substance was not appreciably soluble in base, its analyses for carbon, hydrogen, and silicon agreed with the calculated values.

Results of the second aspect of this investigation are summarized in Table I. The variation in yields of the addition products may be attributed possibly to two factors: steric interference offered by the triphenylsilyl group toward an entering substituent and the relative reactivity of the organolithium compound. Since it had been shown that steric factors are important in reactions leading to the formation of highly substituted organosilanes containing *o*-tolyl, *alpha*- and *beta*-naphthyl groups (7, 8), the limited addition of *o*-tolyllithium and α-naphthyllithium to vinyltriphenylsilane might be explained on the same basis.

TABLE I

TRIPHENYLALKYLSILANES FROM THE ADDITION OF ORGANOLITHIUM COMPOUNDS TO VINYLTRIPHENYLSILANE

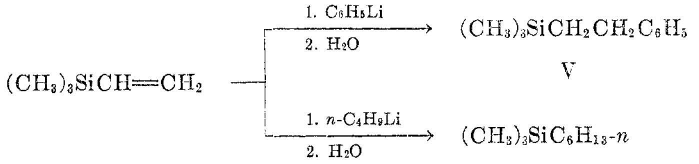
$(C_6H_5)_3SiCH{=}CH_2 + RLi \rightarrow (C_6H_5)_3SiCH_2CH_2R$

| RLi | Reaction Time (hrs.) | Recrystallization Solvent | Yield, % | M.p., °C.[i] | Formula | Analyses, Si | |
|---|---|---|---|---|---|---|---|
| | | | | | | Calc'd | Found |
| Methyl[a] | 6 | Ethanol | —[b] | — | — | — | — |
| *n*-Propyl | 6 | Ethanol | —[c] | — | — | — | — |
| *n*-Butyl | 44 | Ethanol | 67 | 77–78 | $C_{24}H_{28}Si$ | 8.14 | 8.20 |
| *n*-Hexyl | 18 | Ethanol | —[d] | — | — | — | — |
| Phenyl | 6 | 1-Propanol | 84 | 146–148 | $C_{26}H_{24}Si$ | 7.70 | 7.65 |
| *p*-Tolyl | 16 | 1-Propanol | 27 | 140–141 | $C_{27}H_{26}Si$ | 7.41 | 7.57 |
| *o*-Tolyl[e] | 6 | 1-Propanol | 17 | 118–119 | $C_{27}H_{26}Si$ | 7.41 | 7.66 |
| α-Naphthyl[e] | 10 | 1-Propanol | 8[f] | 136–138 | $C_{30}H_{26}Si$ | 6.77 | 6.97 |
| *p*-Dimethylaminophenyl[g] | 18 | *n*-Butyl acetate | 7[h] | 153–154 | $C_{28}H_{31}ClNSi$ | 6.32 | 6.12 |

[a] Ziegler, German Patent 512,882 (1929); *Chem. Abstr.*, **25,** 2154 (1931). [b] The starting material was largely recovered (60%), and a small amount of an oil which could not be recrystallized was secured. [c] Most (90%) of the starting material was recovered. [d] The crude product, an oil, could not be further purified. [e] Gilman, *et al.*, *J. Am. Chem. Soc.*, **54,** 1957 (1932). [f] A polymer resulted which hindered the isolation of the addition product. [g] Austin, *J. Am. Chem. Soc.*, **54,** 3726 (1932). [h] Isolated as the hydrochloride. *Anal.* Calc'd for $C_{28}H_{31}ClNSi$: N, 3.15. Found: N, 3.25. (Semimicro Dumas method). [i] The melting points are uncorrected.

According to Gilman and Moore (9), the order of decreasing reactivities of organolithium compounds (in interconversion and metalation reactions) follows the pattern *n*-propyl- > ethyl- > *n*-butyl- > phenyl- > methyl-. Our results are partially consistent with this scheme although, in the alkyl series, a satisfactory addition product was secured only with *n*-butyllithium. The recovery of 60 and 90% of the unsaturated silane from reactions with methyl- and *n*-propyl-lithium, respectively, indicated that little or no addition took place with these reagents. Although no starting material was recovered, the failure to isolate an addition compound from *n*-hexyllithium and vinyltriphenylsilane was due perhaps to difficulties in purifying the crude product.

In the examination of the effect of the nature of the substituted silyl group, vinyltrimethylsilane was used instead of the corresponding phenyl compound. Under conditions specified earlier, β-phenylethyltrimethylsilane (V) and trimethyl-*n*-hexylsilane (VI) were produced in 6 and 10% yields from the respective addition of phenyl- and *n*-butyl-lithium to vinyltrimethylsilane. These products were identified through comparisons with physical properties reported earlier (10, 11). Higher-boiling fractions and viscous, intractable resins accompanied the products which suggest that reactions of organolithium compounds with the simpler vinylsilanes are predominantly those of polymerization rather than addition.



$$(CH_3)_3SiCH{=}CH_2 \xrightarrow[2.\ H_2O]{1.\ C_6H_5Li} (CH_3)_3SiCH_2CH_2C_6H_5 \qquad 3.$$

V

$$(CH_3)_3SiCH{=}CH_2 \xrightarrow[2.\ H_2O]{1.\ n\text{-}C_4H_9Li} (CH_3)_3SiC_6H_{13}\text{-}n \qquad 4.$$

Interestingly enough, trisubstituted allylsilanes are unaffected by *n*-butyllithium, and their reaction with phenyllithium is not of the addition type. The results of these studies will be reported in detail elsewhere.

The authors are grateful to the Research Corporation for a grant-in-aid to the Carver Foundation of Tuskegee Institute for the support of this work.

## EXPERIMENTAL

*Reactions of organolithium compounds with vinyltriphenylsilane.* The procedure which follows is general for the reactions listed in Table I. Molar equivalents of vinyltriphenylsilane and the organolithium compound in ether and in an atmosphere of nitrogen were stirred for the specified length of time. Color Test I (12) was positive throughout the reaction. The mixture was poured into ice water, the layers separated, and the organic portion dried over calcium chloride. After removing the solvent by distillation, the residue was purified by recrystallization from a suitable solvent.

*Attempted oxidation of the postulated organometallic intermediates from the addition of phenyllithium and n-butyllithium to vinyltriphenylsilane.* A mixture of 9 g. (0.032 mole) of vinyltriphenylsilane and 0.033 mole of phenyllithium was stirred for 6 hours. The solution was then transferred under nitrogen to a flask cooled by an ice-salt mixture and pure oxygen was passed into it until Color Test I was negative (20 minutes). The mixture was hydrolyzed with ice and dilute hydrochloric acid, and the organic layer was separated and dried over magnesium sulfate. After removing the excess solvent, the residue was recrystallized from 1-propanol. A product identified as β-phenylethyltriphenylsilane (m.p. and mixture m.p.) was obtained; yield, 5 g. (44%).

When 5 g. (0.018 mole) of the unsaturated silane was treated with 0.025 mole of *n*-butyllithium, 1.5 g. (22%) of the starting material was recovered from the attempted oxidation. There resulted also 2.5 g. of an oil which could not be identified.

*Attempted carbonation of 1-triphenylsilyl-2-phenylethyllithium* (I). A mixture of 10 g. (0.035 mole) of vinyltriphenylsilane and 0.036 mole of phenyllithium in ether was stirred for 6 hours, then poured slowly over 100 g. of solid carbon dioxide. The mixture was allowed to stand until all of the carbon dioxide had evaporated. Following hydrolysis with ice and hydrochloric acid, the organic layer was separated while the aqueous portion was extracted with fresh ether, and the combined extracts were dried over magnesium sulfate. After removing the solvent and recrystallizing the residue from 1-propanol, 6 g. (47%) of β-phenylethyltriphenylsilane was recovered (m.p. and mixture m.p. 146–148°).

*α-Triphenylsilylheptanoic acid* (IV). A solution of 0.029 mole of *n*-butyllithium and 5 g. (0.018 mole) of vinyltriphenylsilane in ether was stirred at room temperature for 20 hours, then poured onto 100 g. of Dry Ice and allowed to stand overnight. The reaction was hydrolyzed and worked up in the manner described above. Recrystallization of the crude product from petroleum ether (boiling range 30–65°) yielded 0.5 g. (7%) of a crystalline substance melting at 138–139°. This material was insoluble in 10% and 20% base, but analyses corresponded to the calculated values for the free acid.

*Anal.* Calc'd for $C_{25}H_{28}O_2Si$: C, 77.27; H, 7.26; Si, 7.22.
Found: C, 77.12, 77.09; H, 7.25, 7.48; Si, 7.20.

*β-Phenylethyltrimethylsilane* (V). Vinyltrimethylsilane (17.5 g., 0.175 mole) (13) and 0.175 mole of phenyllithium in ether was stirred at room temperature for 7 hours. After hydrolysis, the reaction was worked up in the usual manner. An oil was obtained which on distillation yielded a liquid boiling over a range of 100–120°/8 mm. On redistillation, 2 g. (6.4%) of a substance was collected at 74–78°/3 mm. The physical constants for the compound were in agreement with those reported earlier (10): $n_D^{20}$ 1.4867, reported $n_D^{20}$ 1.4869. Calc'd for $C_{11}H_{18}Si$: Mol. wt., 178.3. Found: Mol. wt., 172.

*n-Hexyltrimethylsilane* (VI). A mixture of 12.9 g. (0.129 mole) of vinyltrimethylsilane and 0.131 mole of *n*-butyllithium in ether was stirred for 22 hours. After hydrolysis the ether layer was separated and dried over calcium chloride. The excess solvent was removed by distillation, and the residue was distilled *in vacuo*. The fraction boiling over the range of 76–94°/150 mm. amounted to 2.1 g. (10%) and was identified as *n*-hexyltrimethylsilane; $n_D^{20}$ 1.4152, reported (11) $n_D^{20}$ 1.4154. An unidentified liquid (5 g.) was collected over the range of 109–120°/31 mm.

## SUMMARY

The reaction of organolithium compounds with vinyltriphenylsilane has been shown to proceed by way of addition involving the formation of an intermediate organometallic compound.

Apparently, additions of this type are general for alkyl and aryllithium compounds, but the extent of the reaction depends somewhat on the relative reactivity and structure of the organometallic agent.

Vinyltrimethylsilane reacts with *n*-butyllithium and phenyllithium in a similar fashion; however, polymerization of the unsaturated silane as well as addition occurs. Since organolithium reagents do not interact with trisubstituted allylsilanes in this manner, the addition is influenced by the position of the unsaturated linkage in the alkylene side-chain.

Tuskegee Institute, Alabama

## REFERENCES

(1) CASON AND BROOKS, *J. Am. Chem. Soc.*, **74,** 4582 (1952).
(2) BARTLETT, FRIEDMAN, AND STILES, *J. Am. Chem. Soc.*, **75,** 1771 (1953).
(3) GILMAN AND WU, *J. Am. Chem. Soc.*, **75,** 2509 (1953).
(4) GILMAN AND YABLUNKY, *J. Am. Chem. Soc.*, **63,** 839 (1941).
(5) GILMAN AND HARTZFELD, *J. Am. Chem. Soc.*, **73,** 5878 (1951).
(6) HANCE AND HAUSER, *J. Am. Chem. Soc.*, **75,** 994 (1953).
(7) GILMAN AND SMART, *J. Org. Chem.*, **15,** 720 (1949); *J. Org. Chem.*, **16,** 424 (1950).
(8) SUNTHANKAR AND GILMAN, *J. Am. Chem. Soc.*, **72,** 4884 (1950).
(9) GILMAN AND MOORE, *J. Am. Chem. Soc.*, **62,** 1843 (1940).
(10) GILMAN AND MARSHALL, *J. Am. Chem. Soc.*, **71,** 2066 (1949).
(11) WHITMORE, *et al.*, *J. Am. Chem. Soc.*, **68,** 475 (1946).
(12) GILMAN AND SCHULZE, *J. Am. Chem. Soc.*, **47,** 2002 (1925).
(13) BURKHARD, *J. Am. Chem. Soc.*, **72,** 1078 (1950); NAGEL AND POST, *J. Org. Chem.*, **17,** 1379 (1952).