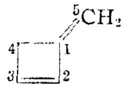
species, although the differences in *DE* are considerably smaller. With the benz-derivatives none of the ionic species is predicted to have a lowest triplet state.

The cyclobutadienylcarbinyl radical (XXX) is interesting in that it is calculated to have a *DE* more than twice that of the benzyl radical. The difference between the radicals is particularly striking when it is remembered that methylcyclobutadiene would have a *DE* of 2 β less than that of toluene. The calculations suggest that methylenecyclobutene XXXII should be readily attacked by free-radical, anionic or cationic reagents at the 4-position.



XXXII

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF TUSKEGEE INSTITUTE]

An Interesting Side-Reaction in the Preparation of Triphenylvinylsilane[1a]

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When vinyltrichlorosilane was allowed to react with phenyllithium in ether, the expected coupling product, triphenylvinylsilane (I) and triphenyl-(β-phenylethyl)-silane (II) resulted. (II) was obtained when phenyllithium was added to (I) in ether, and likewise, triphenyl-*n*-hexylsilane (III) was formed from (I) and *n*-butyllithium. The configurations of (II) and (III) were established by alternate syntheses.

In connection with investigations on the syntheses and properties of some triarylalkenylsilanes, it was observed that on treatment of vinyltrichlorosilane with an excess of phenyllithium in ether, two principal products are formed in addition to considerable amounts of polymer: the expected coupling product, triphenylvinylsilane (I) and triphenyl-(β-phenylethyl)-silane (II). Convincing evidence for the structures of (I) and (II) was achieved through analysis and molecular weight determination, and speculations as to how (II) was formed in the reaction ultimately led to a hypothesis suggesting the addition of the organometallic compounds to the unsaturated silane.

$$\mathrm{3C_6H_5Li + CH_2{=\!=}CHSiCl_3 \longrightarrow (C_6H_5)_3SiCH{=\!=}CH_2\ (I) + LiCl} \quad (1)$$

$$\mathrm{(C_6H_5)_3SiCH{=\!=}CH_2 + C_6H_5Li \longrightarrow [(C_6H_5)_3SiCH(Li)CH_2C_6H_5]} \quad (2)$$

$$\xrightarrow{\mathrm{H_2O}} \mathrm{(C_6H_5)_3SiCH_2CH_2C_6H_5} \quad \mathrm{(II)}$$

Organolithium compounds are known to undergo addition to the carbon–carbon double bonds of highly conjugated molecules like 1,1-diphenylethylene, the fulvenes, and $\Delta^{9,9'}$-bifluorene and to simple conjugated dienes in the initiation of polymerization.[2] Recently it has been reported that cyclooctatetraene undergoes a similar reaction with certain organolithium compounds.[3]

As far as we have been able to ascertain, the addition of alkyl and aryl lithium compounds to comparatively simple olefins is a relatively rare phenomenon. Thus, in order to test our hypothesis, triphenylvinylsilane was stirred at room temperature for six hours with an equivalent amount of phenyllithium in ether. Subsequent to hydrolysis and purification (II) was isolated in 84% yield. In addition, triphenyl-*n*-hexylsilane (III) was formed in 67% yield when the procedure was repeated with *n*-butyllithium.

Although, at present, it has not been positively demonstrated that a new organometallic compound is formed as an intermediate in this reaction, the structures of (II) and (III) have been confirmed through unequivocal syntheses. First, triethoxy-(β-phenylethyl)-silane (IV) was formed from tetraethoxysilane and β-phenylethylmagnesium bromide. Refluxing (IV) with three equivalents of phenyllithium in ether produced (II).

$$\begin{tikzcd}[column sep=small]
\mathrm{(C_2H_5O)_4Si + C_6H_5CH_2CH_2MgBr \longrightarrow} & \\
\mathrm{(C_2H_5O)_3SiCH_2CH_2C_6H_5(IV) + C_2H_5OMgBr} \quad (3) \arrow[dr, "\mathrm{C_6H_5Li}"] & \\
\mathrm{(C_6H_5)_3SiCH{=\!=}CH_2\ (I)} \arrow[r, "\mathrm{1,\ C_6H_5Li}", "\mathrm{2,\ H_2O}"'] & \mathrm{(C_6H_5)_3SiCH_2CH_2C_6H_5}\ \mathrm{(II)}
\end{tikzcd}$$

Then, on treatment of triphenylchlorosilane with *n*-hexyllithium in ether, an excellent yield of (III) resulted. The identity of the addition products was established by mixed melting point determinations with the authentic samples.

$$\begin{tikzcd}[column sep=small]
\mathrm{{\mathit{n}\text{-}C_6H_{13}Li} + (C_6H_5)_3SiCl} \arrow[r] & \mathrm{(C_6H_5)_3SiC_6H_{13}\text{-}\mathit{n}\ (III) + LiCl} \quad (4) \\
\mathrm{(C_6H_5)_3SiCH{=\!=}CH_2 + {\mathit{n}\text{-}C_4H_9Li}} \arrow[ur, "\mathrm{H_2O}"] &
\end{tikzcd}$$

It is of interest to note that the formation of (I) from vinyltrichlorosilane and phenylmagnesium bromide required more drastic conditions and, apparently, without the addition of the Grignard reagent to the ethylenic linkage. On the other hand,

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[1] (a) Abstracted from a thesis submitted to the graduate faculty of Tuskegee Institute by H. G. Brooks in partial fulfillment of the requirement for the Master of Science Degree. (b) Frederick Gardner Cottrell Fellow, George Washington Carver Foundation, Tuskegee Institute, Alabama.

[2] H. Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, Chap. V. Wittig (translated and revised by J. R. Thirtle) in "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 585. See also E. Krause and A. von Grosse, "Die Chemie der Metallorganischen Verbindungen," Photo-lithoprint Reproduction, Edwards Brothers, Inc., Ann Arbor, Mich., 1943, pp. 82, 94–96.

[3] A. C. Cope and M. R. Kintner, THIS JOURNAL, **73**, 3424 (1951).

the unsaturated silane reacted vigorously with phenyllithium at room temperature yielding a mixture of products. When the procedure was carried out at −45 to −30° and the reagents added in reverse order, the reaction was much smoother, and (I) was the predominant product. It is therefore apparent that the three competing reactions, *e.g.*, coupling, addition and polymerization, might be controlled by the proper selection of temperature conditions, reagents and their mode of addition.

An examination of the broad applications and limitations of these reactions has not been completed. The investigation is being extended to the study of the addition of other organolithium compounds to triphenylvinylsilane and additional aryl- and alkylalkenylsilanes.

Acknowledgment.—The authors are grateful to the Research Corporation for their partial support of this investigation.

Experimental[4]

Reaction of Vinyltrichlorosilane with Phenyllithium.—A solution of 32 g. (0.2 mole) of redistilled vinyltrichlorosilane[5] in 100 ml. of anhydrous ether was added over a period of one hour to a solution of 0.7 mole of phenyllithium in approximately 350 ml. of ether. After refluxing for an hour, Color Test I[6] was positive and remained so on continued refluxing for an additional hour. Subsequent to hydrolysis, the organic layer was separated and dried over anhydrous calcium chloride. On removing the solvent by distillation, a viscous oil remained. This substance was dissolved in ligroin, and after allowing the solution to remain in the refrigerator for several days, a crystalline product separated. Recrystallization of this crude material from a mixture of benzene and ligroin produced 3 g. (4% based on the chlorosilane) of a pure crystalline product melting at 147 to 148° and identified later as triphenyl-(β-phenylethyl)-silane (II).

Anal. Calcd. for $C_{26}H_{24}Si$: C, 85.62; H, 6.61; Si, 7.67; mol. wt., 364.5. Found: C, 85.87; H, 6.75; Si, 7.65, 7.81; mol. wt., 353.0 (cryoscopic method in benzene).

The mother liquors from the above separation and recrystallizations were combined and concentrated. Since the residue could not be made to solidify, it was subjected to distillation under reduced pressure, and the fraction boiling over the range of 175–220° (7 mm.) was collected. Nine and two-tenths grams (16%) of a crude product (m.p. 54–58°) was obtained, and careful recrystallization from petroleum ether (boiling range 30–60°) yielded 8 g. (14%) of the pure product, m.p. 64–65°, identified as triphenylvinylsilane (I).

Anal. Calcd. for $C_{20}H_{18}Si$: Si, 9.79; mol. wt., 286. Found: Si, 9.59; mol. wt., 282.

Triphenylvinylsilane (I). A. (From Phenyllithium).—To an ethereal solution of 43.1 g. (0.27 mole) of vinyltrichlorosilane cooled by means of an ice–salt mixture there was added 0.88 mole of phenyllithium in ether at such a rate as to cause the slightest refluxing of the solvent. Since Color Test I was negative at the end of the addition, the reaction was hydrolyzed by ice and dilute hydrochloric acid and worked up as described above. The crude product was distilled over the range of 190–210° (3 mm.) and yielded 44.5 g. (60%) of the pure silane (m.p. 67–68°) on recrystallization from 95% ethanol.

A subsequent run was made in the same manner but at −45 to −30° (solid carbon dioxide and trichloroethylene). The crude yield was 57 g. (91%). Recrystallization from ethanol produced 30 g. (43%) of the pure product.

B. (**From Phenylmagnesium Bromide**).—Two moles of phenylmagnesium bromide was added with stirring to 105 g. (0.65 mole) of vinyltrichlorosilane dissolved in 300 ml. of ether (Color Test I positive). The reaction was then stirred and refluxed for 16 hours, hydrolyzed and worked up in the customary manner. The yield of the pure product was 108 g. (58%). The products secured from these procedures were identical (m.p. and mixed m.p.).

Triethoxy-(β-phenylethyl)-silane (IV).—To a solution of 23 g. (0.12 mole) of tetraethoxysilane in 55 ml. of ether there was added with stirring, and at such a rate as to cause moderate refluxing, 0.11 mole of β-phenylethylmagnesium bromide. After the complete addition of the Grignard reagent, the mixture was refluxed for four hours, then filtered and the residue washed with a small amount of ether. The excess solvent was removed, and the oily residue distilled at 129–134° (3 mm.). The yield was 5 g. (17%), $n^{20}{}_D$ 1.4669; d^{20}_{20} 0.98136.

Anal. Calcd. for $C_{14}H_{24}O_3Si$: Si, 10.45; MR_D,[7] 75.32. Found: Si, 10.37; MR_D, 75.86.

Triphenyl-(β-phenylethyl)-silane (II). A. From the Addition of Phenyllithium to Triphenylvinylsilane.—A mixture of 5 g. (0.0175 mole) of triphenylvinylsilane and 0.018 mole of phenyllithium in ether was stirred for six hours at room temperature (Color Test I was positive). After hydrolysis and working up the product in the usual manner, 5.4 g. (84%) was obtained; m.p. 146–148° (from 1-propanol).

B. **From Triethoxy-(β-phenylethyl)-silane and Phenyllithium.**—Into a solution of 5 g. (0.0186 mole) of triethoxy-(β-phenylethyl)-silane dissolved in 25 ml. of ether there was dropped 0.05 mole of phenyllithium, and the mixture stirred for several hours. On hydrolysis with dilute hydrochloric acid and ice, some of the product separated from the solvent. The remainder of the material was secured after separating the organic layer, drying over anhydrous calcium chloride and removing the excess solvent. The yield of the pure product after recrystallization from 1-propanol was 1.3 g. (19%); m.p. 147–148°.

Triphenyl-*n*-hexylsilane (III). A. Addition of *n*-Butyllithium to Triphenylvinylsilane.—Ten grams (0.035 mole) of triphenylvinylsilane was added to 0.044 mole of *n*-butyllithium[8] in ether. The mixture was stirred for 44 hours then hydrolyzed and worked up in the usual manner. Eight grams (67%) of the pure product was obtained after recrystallization from ethanol; m.p. 77–78°.

B. **From *n*-Hexyllithium and Triphenylchlorosilane.**—A solution of 0.0123 mole of *n*-hexyllithium[8] in ether was added to an ethereal solution of 1.5 g. (0.0123 mole) of triphenylchlorosilane. (Color Test I was negative after the addition.) The mixture was stirred for several hours, then hydrolyzed and worked up according to the customary procedure. Two grams (47%) of the pure product resulted after recrystallization from ethanol; m.p. and mixed m.p. with product from (A) 77–78°.

Anal. Calcd. for $C_{24}H_{28}Si$: Si, 8.14. Found: Si, 8.20.

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[4] All melting points and boiling points are uncorrected. All reactions employing organometallic compounds and the silanes were conducted in an atmosphere of nitrogen. The silicon analyses were performed according to the procedure of H. Gilman, *et al.*, THIS JOURNAL, **72**, 5767 (1950).

[5] Purchased from the Linde Air Products Company, New York, N. Y.

[6] H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

[7] Bond refractions for organosilicon compounds are reported by E. L. Warrick, *ibid.*, **68**, 2455 (1946).

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