

boiling at 100–120° was redistilled through an 8-inch vacuum jacketed glass helices packed column and the fractions boiling at 110–112° (I), and 112–113° (II) were collected. Fraction I had n_D^{24} 1.4475, while Fraction II gave n_D^{24} 1.4473. Yield, 18.7 g. (41.9%).

Anal. Calcd. for $C_7H_6F_2$: C, 65.63; H, 4.72; F, 29.66. Found: C, 65.89; H, 4.22; F, 30.21.

3,4-Difluorobenzoic acid. 3,4-Difluorotoluene (0.9 g.) was oxidized to the corresponding acid according to procedure 32B in "Identification of Organic Compounds," 2nd edition, Shriner and Fuson, John Wiley & Sons, p. 164. The product, recrystallized from toluene, melted at 184–185° and had a neutral equivalent of 158 (theory, 158).

Anal. Calcd. for $C_7H_4F_2O_2$: F, 24.03. Found: F, 23.72.

BIOCHEMICAL RESEARCH LABORATORY
DOW CHEMICAL CO.
MIDLAND, MICH.

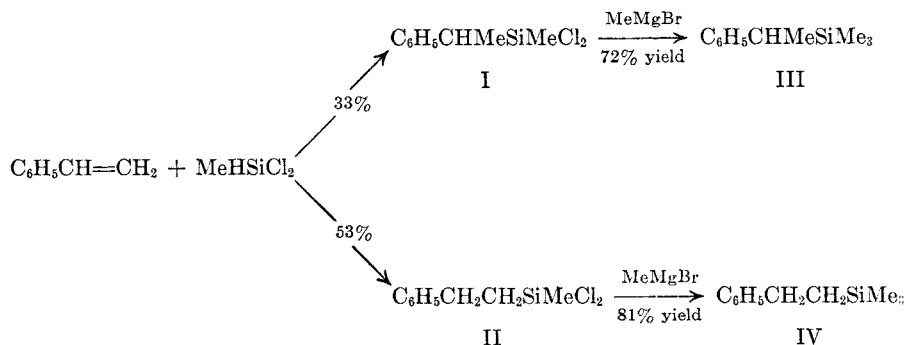
Addition of Silicon Hydrides to Olefinic Double Bonds. IV. The Addition to Styrene and α -Methylstyrene

JOHN W. RYAN AND JOHN L. SPEIER

Received July 9, 1959

Styrene with methylchlorosilane in the presence of platinized carbon has recently¹ been described as giving only (2-phenylethyl)methylchlorosilane. Careful experiments repeated several times now indicate two isomeric products form with either platinized carbon or chloroplatinic acid. The two products are the 1- and the 2-phenylethylmethylchlorosilane in a ratio of approximately 33 to 53. The mixture has physical properties very nearly coinciding with those previously reported¹ as those of 2-phenylethylmethylchlorosilane.

Careful distillation separated the isomers which were methylated to form obviously different derivatives (see Table I).



The structure of IV was confirmed by the agreement of its physical properties with those of an authentic sample prepared from trimethylchlorosilane and 2-phenylethylmagnesium bromide.^{1,2}

(1) Part II of this series; J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).

(2) H. Gilman and F. J. Marshal, *J. Am. Chem. Soc.*, **71**, 2066 (1949).

The NMR proton spectra of I, II, III, and IV were consistent with the structures assigned.³

From these data we conclude that styrene forms two adducts. However, experiments indicated that only one product formed with α -methylstyrene under the same conditions. Only one product (V) was detected by distillation. This product was methylated to form apparently pure VI (2-phenylpropyl)trimethylsilane as judged by distillation, gas liquid phase chromatography and by a NMR proton spectrum. The spectrum clearly showed the presence of phenyl, SiCH_3 , $-\text{CH}_2-$, and $-\text{CHCH}_3-$ groups.

Methylcyclosiloxanes $(\text{MeHSiO})_n$ react very well with α -methylstyrene in the presence of chloroplatinic acid to form nearly quantitative yields of (2-phenylpropyl)methylcyclosiloxanes. The structure of these was established by the NMR proton spectra and also in one case by converting the adduct to VI by way of (2-phenylpropyl)methylchlorosilane and methylmagnesium bromide.

Hydrolysis of (2-phenylpropyl)methylchlorosilane gave a polysiloxane mixture from which was isolated a cyclic trimer (VII). The trimer (VII) was also isolated as the most volatile product formed in the alkaline depolymerization of the adduct obtained with 1,3,5,7,9-pentamethylcyclopentasiloxane.

sym-Tetramethyldisiloxane gave an 81% yield of 1,3-bis(2-phenylpropyl)tetramethyldisiloxane (IX) and trichlorosilane gave 67% (2-phenylpropyl)trichlorosilane (X). These products were assigned their structures largely on the basis of their NMR proton spectra. All of the adducts had spectra clearly indicative of (2-phenylpropyl) structures free of any detectable impurities.

EXPERIMENTAL

Styrene and methylchlorosilane. Styrene (921 g., 8.85 mol.), *t*-butylcatechol (0.1 g.) and 8×10^{-5} mol. of chloro-

platinic acid (added as a 0.06M solution in dioxane ethanol) was heated to 90° in a 3-l., three necked flask equipped with an addition funnel, reflux condenser, and thermometer. Methylchlorosilane (1120 g., 9.73 mol.) was added during 2 hr. so that the heat of reaction maintained the mixture between 90 and 130°. Distillation then gave: (I), 642 g.,

(3) All NMR spectra and their interpretation were obtained by P. C. Lauterbur, Mellon Institute, Pittsburgh, Pa.

TABLE I

| No. | Structure | B.P. | Mm. Hg | n _D ²⁵ | | R _D | | % Si | | Neut. Equiv. | |
|------|--|------------------|-----------|------------------------------|------------------------------|----------------|---------------------|-------|--------|------------------------------|--------|
| | | | | n _D ²⁵ | D ₄ ²⁵ | Found | Calcd. ^a | Found | Calcd. | Found | Calcd. |
| I | C ₆ H ₅ MeCHSiMeCl ₂ | 121-122 | 25 | 1.5197 | 1.1321 | 0.2684 | 0.2650 | 12.6 | 12.8 | 109.8 | 109.6 |
| II | C ₆ H ₅ CH ₂ CH ₂ SiMeCl ₂ | 137-138 | 30 | 1.5107 | 1.1216 | 0.2669 | 0.2650 | 12.7 | 12.8 | 109.9 | 109.6 |
| III | C ₆ H ₅ MeCHSiMe ₃ | 111.3 | 38 | 1.4959 | 0.8738 | 0.3345 | 0.3307 | 15.4 | 15.7 | | |
| IV | C ₆ H ₅ CH ₂ CH ₂ SiMe ₃ ^b | 117 | 40 | 1.4840 | 0.8582 | 0.3329 | 0.3307 | 15.6 | 15.7 | | |
| V | C ₆ H ₅ MeCHCH ₂ SiMeCl ₂ | 148-149 | 42 | 1.5082 | 1.100 | 0.2708 | 0.2690 | 12.0 | 11.8 | 117.2 | 116.6 |
| VI | C ₆ H ₅ MeCHCH ₂ SiMe ₃ | 217 | 750 | 1.4841 | 0.8619 | 0.3320 | 0.3308 | 14.3 | 14.6 | | |
| VII | (C ₆ H ₅ MeCHCH ₂ SiMeO) ₃ | 228 ^c | 1 | 1.5220 | 1.041 | 0.2926 | 0.2924 | 16.0 | 15.8 | Viscosity 88-91 cs. at 25° | |
| VIII | (C ₆ H ₅ MeCHCH ₂ SiMeO) ₄ | 270 ^c | 1 | 1.5262 | 1.051 | 0.2923 | 0.2924 | 16.0 | 15.8 | Viscosity 198-202 cs. at 25° | |
| IX | (C ₆ H ₅ MeCHCH ₂ SiMe ₂) ₂ O | 162 | 1 | 1.5043 | 0.9487 | 0.3123 | 0.3124 | 15.2 | 15.1 | | |
| X | C ₆ H ₅ MeCHCH ₂ SiCl ₃ | 141 | 30 | 1.5140 | 1.218 | 0.2471 | 0.2457 | 11.3 | 11.1 | 83.6 | 83.6 |

^a Calculated according to the bond values of A. I. Vogel, W. T. Cresswell, G. H. Jeffrey, and J. Leicester, *J. Chem. Soc.*, 514 (1952); A. I. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954). ^b Ref. 1 cites for an authentic sample, b.p. 101° at 20 mm., n_D²⁵ 1.4842, D₄²⁵ 0.8591. ^c Ebulliometric boiling points. The other boiling points are condensation temperatures taken during distillation.

33% yield with the properties given in Table I, and (II), 1019 g., 53% yield. A viscous polymer (128 g.) remained as residue.

2-Phenylpropylmethylchlorosilane (V). α -Methylstyrene (354 g., 3.0 mol.) and methylchlorosilane (380 g., 3.3 mol.) with 2×10^{-5} mol. of chloroplatinic acid were treated as above, and kept overnight at about 140°. Careful fractionation gave 38 g. boiling between the excess methylchlorosilane and a constant boiling plateau described as V in Table I, 631 g., 90% yield.

2-Phenylpropyltrimethylsilane (VI). Excess methylmagnesium bromide in ether with V formed VI in 85% yield.

(2-Phenylpropyl)methylpolysiloxanes. Hydrolysis of V (700 g., 3.0 mol.) in 2500 ml. of toluene with 1 l. of water was followed by a thorough washing with dilute sodium carbonate and then with water. Distillation at 1 mm. gave 190 g., 36% of the cyclotrisiloxane (VII) n_D²⁵ 1.5220-1.5222, viscosity, 88-91 cs. at 25°.

α -Methylstyrene (1182 g., 10.0 mol.) with 2×10^{-4} mol. of chloroplatinic acid was heated to 110° and 1,3,5,7,9-pentamethylcyclopentasiloxane (601 g., 10.0 equivalents) was added slowly. The mixture was kept at 110° overnight and then distilled rapidly from 1 g. of potassium hydroxide at 1 mm. The distillate (1704 g., 96% yield) was a mixture of cyclosiloxanes, n_D²⁵ 1.5242, viscosity, 216 cs. at 25°.

On redistillation of a portion of this material the trisiloxane (VII) was again isolated, n_D²⁵ 1.5220, D₄²⁵ 1.041, viscosity 88 cs. at 25° (45% yield). After recovering an intermediate portion, presumably a mixture of cyclic trimer and tetramer, there was recovered the cyclotetrasiloxane (VIII), n_D²⁵ 1.5262, D₄²⁵ 1.051, viscosity 200 cs. at 25° (18% yield). The condensation temperatures recorded during the low pressure distillations were variable and unreliable. The progress of the distillation was followed chiefly by the index of refraction and viscosity of each fraction.

A second portion of this adduct (50 g., 0.28 mol.) was dissolved in 200 ml. of cold concentrated sulfuric acid and saturated with hydrogen fluoride. The upper layer which was assumed to be (2-phenylpropyl)methyldifluorosilane was added to excess methylmagnesium bromide in ether. In the usual way, 2-phenylpropyltrimethylsilane (VI) was isolated in 34% yield. By vapor-liquid phase chromatography this product was judged to be not less than 99% the same as VI, made by methylation of V.

α -Methylstyrene (1040 g., 8.8 mol.), chloroplatinic acid (9×10^{-5} mol.) and 1,3,5,7-tetramethylcyclotetrasiloxane (481 g., 8 equiv.) were heated at 110° overnight. The excess α -methylstyrene was removed at 1 mm. up to a temperature of 315°. The residue then had a viscosity of 211 cs. at 25°. Distillation without the potassium hydroxide gave

1355 g., 95% of a distillate boiling at a flask temperature of 315-320° at 1 mm., n_D²⁵ 1.5258-1.5267, viscosity 184-203 cs. at 25°. Most of the distillate had n_D²⁵ 1.5263-1.5266, viscosity 193-203 cs. at 25°.

1,3-Bis(2-phenylpropyl)tetramethyldisiloxane (IX). α -Methylstyrene (591 g., 5.0 mol.) and chloroplatinic acid (1 ml. of 0.06M solution in dioxane ethanol) were heated to 110° and *sym*-tetramethyldisiloxane (336 g., 2.5 mol.) was added in 50 ml. portions. The reaction proceeded slowly. The mixture was maintained at 110° overnight and distilled through a 1-inch by 3-inch vacuum-jacketed column containing no packing to yield a low boiling fraction (37 g.), b.p. 80° at 1 mm., which gave a positive test for Si-H. This material presumably is 1-(2-phenylpropyl)-1,1,3,3-tetramethyldisiloxane. On continued distillation there was recovered 1,3-bis(2-phenylpropyl)tetramethyldisiloxane (747 g., 81% yield) having the properties given in Table I.

2-Phenylpropyltrichlorosilane (X). α -Methylstyrene (354 g., 3.0 mol.) containing 6×10^{-5} mol. H₂PtCl₆ was kept at 100-110° in a flask equipped with a reflux condenser and a dropping funnel as trichlorosilane (330 ml., 3.3 mol.) was added during 6 hr. The mixture was then maintained at 110° overnight.

Fractionation of the mixture gave 2-phenylpropyltrichlorosilane (505 g., 67% yield) of X.

The residue from the above fractionation (137 g.) contained little hydrolyzable chloride, indicating that it was principally a polymer of α -methylstyrene.

RESEARCH DEPARTMENT
DOW CORNING CORP.
MIDLAND, MICH.

Action of Trifluoroacetic Acid on Peptide Bonds

KENNETH D. KOPPLE AND ELISABETH BÄCHLI

Received July 13, 1959

In view of the utility of anhydrous trifluoroacetic acid as a protein solvent, a report on its reactivity toward peptide bonds may be of interest. Simple amides such as *N*-acetyl- β -phenylethylamine and acetanilide can be recovered unchanged