

148. Organosilicon Compounds. Part XXIII.¹ The γ -Radiation-catalysed Addition of Some Organosilicon Hydrides to Some Organovinylsilanes.

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Some organosilicon hydrides have been shown to add to some organovinylsilanes under γ -irradiation.

THERE have been many studies of the addition of silicon hydrides to olefins under a variety of conditions and with several types of catalyst,² but only two, rather limited, investigations have been reported of additions catalysed by γ -radiation. The first involved addition of trichlorosilane and methyldichlorosilane to several olefins under irradiation from a 3·0 kc. ⁶⁰Co source,³ and the second the addition of trichlorosilane to cyclohexene and non-1-ene, and of triphenylsilane to the latter, under similar irradiation at a dose rate of 123 rad./sec.⁴

We examined the reaction between the organosilicon hydrides, R¹R²R³SiH, and vinylsilicon compounds, R⁴R⁵R⁶Si·CH:CH₂, under irradiation from a 100 c. ⁶⁰Co source, and although this source is much weaker than those used in the two studies mentioned above we observed formation of the expected compounds, R⁴R⁵R⁶Si·CH₂·CH₂·Si⁹R¹R²R³ in several cases. In some typical cases, reactants (with molar proportions in parentheses), irradiation times, and yields of addition products were as follows: (i) Ph₃SiH (1) + Ph₃Si·CH:CH₂ (1), 64 hr., 13%; (ii) Ph₃SiH (1) + Ph₃Si·CH:CH₂ (1), 128 hr., 20%; (iii) Ph₂MeSiH (2) + Ph₃Si·CH:CH₂ (1), 97 hr., 6%; (iv) (*p*-Cl·C₆H₄)₃SiH (1) + Ph₃Si·CH:CH₂ (1), 128 hr., 0% [while no addition product was isolated, the residue after distillation of unchanged reactants had an infrared spectrum consistent with formation of the product in very low (<3%) yield]; (v) (*p*-Cl·C₆H₄)₃SiH (1) + Ph₃Si·CH:CH₂ (1) + light petroleum b. p. 100—120° (40 wt. % of reactants), 120 hr., 29%; (vi) Ph₂SiH₂ (2) + Ph₃Si·CH:CH₂ (1), 81 hr., 70%; (vii) PhSiH₃ (3) + Ph₃Si·CH:CH₂ (1), 97 hr., 64% (impure) (a little diphenylsilane was also isolated); (viii) Ph₂SiH₂ (1) + (*p*-Me·C₆H₄)₃Si·CH:CH₂ (1), 98 hr., 29%. Further, (ix), the compounds Ph₂HSi·CH:CH₂ and PhMeHSi·CH:CH₂ gave the polymers [\cdot Ph₂Si·CH₂·CH₂·]_x and [\cdot PhMeSi·CH₂·CH₂·]_x in 18% and 25% yield, respectively, after 98 hr. irradiation. (It should be noted that all the yields quoted are calculated from the amounts of reactants taken. Recovery of unchanged reactants was usually good, so that yields based on unrecovered reactants would be much higher.) Triphenylvinylsilane alone was unchanged after irradiation for 64 hr.

Some features of these results, and some additional observations are as follows:

(a) Catalysis by γ -radiation provides a practicable process for adding arylsilicon hydrides to arylvinylsilanes. While yields were frequently low, use of stronger sources, such as the 1—3 kc. sources now fairly commonly available, would lead to higher yields in shorter times.

(b) As would be expected, the yield of product from triphenylsilane and triphenylvinylsilane was increased by longer irradiation. This result, along with the observation that little or no addition product was obtained from tri-*p*-chlorophenylsilane and triphenylvinylsilane unless some light petroleum was also added [see (c) below], can be taken as confirmation that the observed additions took place under irradiation and not during heating in the working-up.

(c) Mixtures of solids were fused together and allowed to cool before irradiation. It

¹ Part XXII, Canavan and Eaborn, *J.*, 1962, 592.

² Eaborn, "Organosilicon Compounds," Butterworths Scientific Publns., London, 1960, pp. 45—55; Petrov, Mironov, Ponomarenko, and Chernyshev, "Sintez Kremniorganicheskikh Monomerov," Soviet Acad. Sciences, Moscow, 1961, pp. 434—448.

³ El-Abbady and Anderson, *J. Amer. Chem. Soc.*, 1958, **80**, 1737.

⁴ Dzhagatspanyan, Zetkin, and Filippov, *Zhur. Vsesoyuz. Khim. obsch. im. D.I. Mendeleeva*, 1961, **6**, 231; *Chem. Abs.*, 1961, **55**, 21013.

seems that the mixture must be at least partly liquid for reaction to occur; very little change occurred in the solid mixture of tri-*p*-chlorophenylsilane and triphenylvinylsilane, but when sufficient light petroleum was present to render the mixture liquid, 29% of the addition product was obtained. The other reactant mixtures in the cases (i)—(ix) above were liquid or partly so, with the exception of the 1 : 1 mixture of triphenylsilane and triphenylvinylsilane. This is solid at room temperature but melts a few degrees above room temperature, and probably local melting occurred during the irradiation. The solidity of the reaction mixture probably accounts for the absence of reaction between tri-*p*-tolylsilane and triphenylvinylsilane during 28 hours' irradiation, and possibly also for that between tribenzylsilane and triphenylvinylsilane under the same conditions. A liquid reactant mixture is not sufficient to ensure addition, however, for no reaction occurred in the partly liquid mixture of triethylsilane and triphenylvinylsilane during 51 hours' irradiation, or in the liquid mixture of phenyldimethylsilane and triphenylvinylsilane during 65 hours' irradiation.

(d) The polymer from phenylmethylvinylsilane seemed similar to that obtained by Curry using a platinum catalyst,⁵ but was presumably free from the branched-chain structures present in Curry's product.

For comparison, some reactions were carried out for 44 hr. in refluxing light petroleum (b. p. 100—120°) with benzoyl peroxide as catalyst. Reactant pairs and yields of addition products were as follows: Ph₃SiH (1) + Ph₃Si·CH:CH₂ (1), 41%; Ph₂MeSiH (2) + Ph₃Si·CH:CH₂ (1), 66%; (*p*-Cl·C₆H₄)₃SiH (1) + Ph₃Si·CH:CH₂ (1), 25%; Ph₃SiH (2) + (*p*-Cl·C₆H₄)₃Si·CH:CH₂ (1), 73%; Ph₂SiH₂ (2) + Ph₃Si·CH:CH₂ (1), 85%; PhSiH₃ (3) + Ph₃SiCH:CH₂, 70% (impure); Ph₂SiH₂ (2) + (*p*-Me·C₆H₄)Si·CH:CH₂ (1), 35%. No reaction occurred between triphenylvinylsilane and 1-triphenylsilyl-2-diphenylsilylethane.

The purified products were identical in infrared spectra and, where solid, in m. p. with those from the corresponding radiation-catalysed addition. The extent of reactions were greater than in the latter processes in similar reaction times, but the products were usually dark and we formed the impression that formation of by-products is probably more serious. If this is so, the radiation-catalysis with stronger sources could be the more satisfactory process.

EXPERIMENTAL

Preparation of Reactants.—The organosilicon compounds were made by standard methods. Only two were new, and these were made as follows:

(a) The Grignard reagent from *p*-bromochlorobenzene (60 g.) in ether was boiled with trichlorovinylsilane (40 g.) for 7 hr. Treatment with dilute hydrochloric acid followed by the usual working-up and fractionation, gave an oil, b. p. 220—225°/0.4 mm., which crystallized from methanol to give *tri-p-chlorophenylvinylsilane* (38 g., 40%), m. p. 72° (Found: C, 61.6; H, 3.9. C₂₀H₁₅Cl₃Si requires C, 61.6; H, 3.9%).

(b) A similar preparation from *p*-bromotoluene, but with replacement of most of the ether by toluene before the refluxing, gave an oil, b. p. 200—210°/1 mm., which crystallized from ethanol to give *tri-p-tolylvinylsilane*, m. p. 79° (Found: C, 83.9; H, 7.3. C₂₃H₂₄Si requires C, 84.1; H, 7.4%).

Radiation-catalysed Reactions.—A glass vessel containing the reactant mixture (12—16 g.) was placed within 1 cm. of the base of a ⁶⁰Co disc (100 c.) 1.2 cm. in diameter and 1 mm. thick. The estimated dose rate was ca. 10⁵ rad./hr.

After the irradiation, the infrared spectrum of the mixture was examined to see if any reaction had occurred. Unchanged reactants were then recovered by distillation at low pressure, and the residue was either distilled or recrystallized. When little reaction had taken place recovery of unchanged reactants was good.

Peroxide-catalysed Additions.—A solution of the reactants (combined wt., 12—16 g.) and benzoyl peroxide (ca. 0.5 g.) in light petroleum (b. p. 100—120°; 100 ml.) was refluxed for 44 hr., additional peroxide (ca. 0.5 g.) being added after 18 hr. Removal of the solvent was followed by working-up as described in the preceding paragraph.

⁵ Curry, *J. Amer. Chem. Soc.*, 1956, **78**, 1686; *J. Org. Chem.*, 1961, **26**, 1308.

Products.—Products from corresponding radiation- and peroxide-catalysed reactions were shown to be identical by their infrared spectra, and, where appropriate by mixed m. p.s. The spectra were in all cases consistent with the structures assigned; peaks at 8.8 and 9.5 μ , characteristic of the Si-CH₂-CH₂-Si system were particularly useful.

Physical properties and analytical data were as follows: 1,2-bistriphenylsilylethane, m. p. 216—217° (from benzene-light petroleum) (Found: C, 83.3; H, 6.3; Si, 10.5. C₃₃H₃₄Si₂ requires C, 83.5; H, 6.3; Si, 10.3%); 1-(methyldiphenylsilyl)-2-triphenylsilylethane, m. p. 135—136° (from ethanol) (Found: C, 81.9; H, 6.7. C₃₃H₃₂Si₂ requires C, 81.8; H, 6.65%); 1-tri-p-chlorophenylsilyl-2-triphenylsilylethane, m. p. 136—138° (from ethanol) (Found: C, 70.0; H, 4.9; Si, 8.6. C₃₆H₃₁Cl₃Si₂ requires C, 70.2; H, 4.8; Si, 8.6%); 1-diphenylsilyl-2-triphenylsilylethane, m. p. 125—126° (from ethanol) (Found: C, 81.9; H, 6.7. C₃₂H₃₀Si₂ requires C, 81.65; H, 6.4%); 1-diphenylsilyl-2-tri-p-tolylsilylethane, m. p. 66—68° (from ethanol) (Found: C, 81.95; H, 7.05; Si, 10.8. C₃₅H₃₆Si₂ requires C, 82.0; H, 7.1; Si, 10.9%).

The *polymer* from diphenylvinylsilane was washed with ethanol and dried to give a glass (Found: C, 79.9; H, 6.65; Si, 13.2. [$\text{Ph}_2\text{Si-CH}_2\text{-CH}_2$]_x requires C, 79.9; H, 6.7; Si, 13.4%), soluble in benzene and carbon tetrachloride.

The polymer from methylphenylvinylsilane was a viscous oil, n_D^{25} 1.5820, with an infrared spectrum similar to that of the oil, n_D^{25} 1.5870, obtained by Curry. It was not analysed.

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