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Abstract

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Addition of Triphenyl Radicals to 1,3-Enyne Organotin Hydrocarbons

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In our laboratory, in order to study the influence of tin on the reactivity of the 1,3-enyne system, trialkylstannylvinylacetylenes and several of their closest homologs were synthesized ([1]). However, in studying transformations of the enyne system in these compounds we encountered considerable difficulties. Hydrogenation over Pd/$CaCO_3$ did not proceed, apparently because of steric hindrance. Electrophilic reagents, bromine and hydrogen halides, cleaved primarily the C –Sn bond. Reagents with nucleophilic activity, for example alkyllithiums, behaved similarly. The action of radical reagents remained uninvestigated. The literature contains data on the free-radical addition of polyhalomethanes to triethyl- and triphenylvinyltin, and also of trichlorosilane to the former compound ([2,3]). In all cases the element-containing radical formed a bond with the terminal carbon atom.

We investigated the addition to triethyltin vinylacetylene (I) and triethyltin isopropenylacetylene (II) of free triphenylmethyl radicals from a solution of hexaphenylethane in benzene.

Triphenylmethyl radicals add to 1,3-enyne hydrocarbons in the 1,4-position with formation of allenes ([4,5]). At the same time, enyne silicon hydrocarbons give different adducts depending on structure: trialkylsilylvinylacetylenes—predominantly at the double bond; trialkylsilylisopropenylacetylenes—in the 1,4-position; trimethylsilylpropenylacetylene, apparently, at the acetylenic bond ([6]).

The direction of addition of triphenylmethyl radicals to the 1,3-enyne organotin hydrocarbons (I) and (II) proved analogous to the direction of their addition to the corresponding silicon hydrocarbons.

In the infrared spectrum (Fig. 1, 1) of the adduct of triphenylmethyl radicals to the organotin hydrocarbon (I) there was a rather intense band of a triple bond (2142 cm^{-1}). In the region 1940 cm^{-1} only slight absorption was observed, which might also have been unrelated to the presence of an allene hydrocarbon impurity, since polyphenyl hydrocarbons also absorb weakly in this region ([4]). On hydrolytic cleavage, which in this case proceeds comparatively readily, the adduct gave the previously described acetylenic hydrocarbon with a terminal acetylenic bond:

Fig. 1. IR transmission spectra

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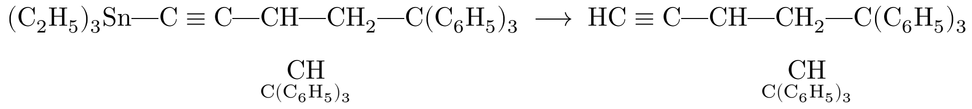


$$(C_2H_5)_3Sn—C \equiv C—\underset{\substack{\text{CH}\\ C(C_6H_5)_3}}{\text{CH}}—CH_2—C(C_6H_5)_3 \longrightarrow HC \equiv C—\underset{\substack{\text{CH}\\ C(C_6H_5)_3}}{\text{CH}}—CH_2—C(C_6H_5)_3$$

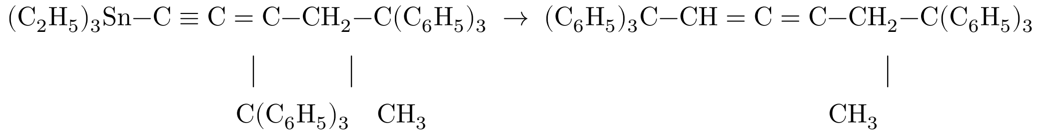
In the infrared spectrum of this hydrocarbon (Fig. 1, 4) there was an intense band at 3312 cm^{-1}, characteristic of monosubstituted acetylenes.

Thus, it was established that the organotin hydrocarbon (I) added triphenylmethyl radicals exclusively or almost exclusively at the double bond. Addition of triphenylmethyl radicals to organo-

hydrocarbon (II) proceeded considerably more slowly. In the IR spectrum of the adduct obtained there was an intense band of the allene grouping at 1920 cm^{-1}, and absorption in the region of 2140 cm^{-1} was absent. Hydrolysis of the adduct proceeded with great difficulty: complete reaction could be achieved only by fusing the substance with solid alkali. As a result of hydrolytic cleavage, the allenic hydrocarbon described in the literature—1,1,1,6,6,6-hexaphenyl-4-methylhexadiene-2,3 (5)—was obtained; in its IR spectrum (Fig. 1, 5) there was a band at 1950 cm^{-1} and no absorption at 3300 cm^{-1}.

Fig. 1. IR transmission spectra: 1 —1-triethylstannyl-3-triphenylmethyl-5,5,5-triphenylpentyne-1, 2 —1-triethylstannyl-1-triphenylmethyl-5,5,5-triphenyl-3-methylpentadiene-1,2, 3 —the same with an admixture of a mercury derivative, 4 —3-triphenylmethyl-5,5,5-triphenylpentyne-1, 5 —1,1,1,6,6,6-hexaphenyl-4-methylhexadiene-2,3 (5-7% solutions in CCl_4, layer thickness 224 μ).

Consequently, in this case the triphenylmethyl radicals added in the 1,4-position



$$(C_2H_5)_3Sn{-}C \equiv \underset{\substack{|\\ C(C_6H_5)_3}}{C} = \underset{\substack{|\\ CH_3}}{C}{-}CH_2{-}C(C_6H_5)_3 \rightarrow (C_6H_5)_3C{-}CH = C = \underset{\substack{|\\ CH_3}}{C}{-}CH_2{-}C(C_6H_5)_3$$

Variation of the method of carrying out the reaction, changing the temperature, and using triphenylchloromethane and mercury as the source of free radicals instead of hexaphenylethane did not affect the direction of addition. However, when the reaction was carried out by the latter method, we observed partial cleavage of the starting hydrocarbon at the C–Sn bond, with formation of triethylchlorostannane and the ethynyl derivative of mercury. Triethylchlorostannane was distilled off together with an excess of the starting hydrocarbon. The mercury compound contaminated the main product.

Experimental Part

Organotin hydrocarbons (I) and (II) were prepared by the action of vinyl- or *iso*-propenylbromoacetylenes on triethylsodium stannide in liquid ammonia (^{1}). A solution of hexaphenylethane in benzene was obtained by the usual method. Its concentration was determined from the dry residue after distilling benzene off from a measured volume of the solution in vacuo. All operations, except isolation of the adducts, were carried out in an atmosphere of purified nitrogen.

Addition of triphenylmethyl radicals to organotin hydrocarbon (I). a) A solution of 1.4 g of hexaphenylethane and 9 g (an 11-fold excess) of organotin hydrocarbon (I) in 25 ml of benzene was left at room temperature for 10 days, after which the benzene and the excess organotin hydrocarbon (I) were distilled off in vacuo. The remaining crystalline mass was washed with petroleum ether. 1.5 g of product was obtained, from which crystallization from dimethylformamide gave 1 g (44.5%) of 1-triethyltin-3-triphenylmethyl-5,5,5-triphenylpentyne-1. Mp 171.5–172.5° (from dimethylformamide).

Found, %: C 77.63; 77.65; H 6.64; 6.70; Sn 16.04; 15.56
$C_{48}H_{48}Sn$. Calculated, %: C 77.53; H 6.51; Sn 15.96

From the petroleum ether, about 0.15 g of triphenylcarbinol with mp 163–164° was also isolated. A mixed-melting-point test with authentic triphenylcarbinol melted at the same temperature. The residue was a resin. From dimethylformamide about 0.1 g of 3-triphenyl-5,5,5-triphenylpentyne-1 with mp 210–214° was isolated. It was identified by a mixed-melting-point test and by its IR spectrum.

b) A solution of 2.1 g of hexaphenylethane and 12.8 g of triethylvinylacetylenyltin in 40 ml of benzene was boiled on a water bath for 4 h. The golden color of the benzene solution of hexaphenylethane disappeared immediately. From the reaction mixture, by the method described above, 1.47 g (47.5%) of adduct with mp 171–172°, 0.26 g of triphenylcarbinol, and 0.06 g of an acetylenic hydrocarbon with mp 217–221° were isolated.

c) 0.74 g of the adduct with mp 171.5–172.5° was boiled with a solution of 5 g of KOH in 50 ml of ethanol for 35 h. The mixture was diluted with water; the precipitate was filtered off, washed with dilute hydrochloric acid and with water, dried, and crystallized from dimethylformamide. 3-Triphenylmethyl-5,5,5-triphenylpentyne-1 with mp 222–222.5° was obtained. It was identified by a mixed-melting-point test with an authentic sample and by its IR spectrum.

Addition of triphenylmethyl radicals to organotin hydrocarbon (II). a) From 4.5 g of hexaphenylethane and 27 g (an 11-fold excess) of organotin hydrocarbon (II) in 100 ml of benzene, with the reaction carried out at room temperature for 10 days and with the usual work-up of the mixture, 0.82 g (11.7%) of 2-triethyltin-1,1,1,6,6,6-hexaphenyl-4-methylhexadiene-2,3 was obtained. Mp 150–150.5° (from dimethylformamide).

Found, %: C 77.30; 77.70; H 6.61; 6.65; Sn 15.75; 15.50
$C_{49}H_{50}Sn$. Calculated, %: C 77.68; H 6.65; Sn 15.67

From the mother liquor, 1.35 g of triphenylcarbinol with mp 160-162° (from ethanol) was isolated. The residue was a resin (3.6 g).

b) A solution of 2.1 g of hexaphenylethane and 13.5 g of organotin hydrocarbon (II) in 40 ml of benzene was boiled on a water bath for 8 h. 1.8 g (54.6%) of adduct with mp 150-150.5°, 0.72 g of triphenylcarbinol, and 1.6 g of resin were obtained.

c) From 3.5 g of triphenylchloromethane, 13.5 g of organotin hydrocarbon (II), and 15 g of mercury in benzene (room temperature, 10 days), 0.94 g (19.7%) of the usual adduct was obtained, as well as crystalline products with mp from 101 to 134° containing mercury, and also a crystalline product with mp 128-130° containing tin and not containing phenyl radicals. Mercury was determined by emission analysis. The presence of a mercury bond with the acetylenic group—

by pipetting—according to the IR spectrum (Fig. 1, 3; the band at 2133 cm^{-1} is characteristic of mercury-acetylene compounds (7)). These substances were not investigated further.

The starting organotin hydrocarbon distilled off from the mixture contained triethylchlorotin: in its various fractions from 1 to 10% chlorine was found.

g) On fusing 0.38 g of the adduct with 1 g of KOH in an oil bath at 220°, followed by dilution of the melt with water, 0.07 g (25.3%) of 1,1,1,6,6,6-hexaphenyl-4-methylhexadiene-2,3 with m.p. 185-185.5° (from dimethylformamide) was obtained. The residue was a resin.

Cleavage by boiling with alcoholic KOH could not be effected. On boiling with 45% sulfuric acid for 3 hours, the adduct underwent only partial cleavage: the hydrocarbon was isolated in 21.4% yield. The residue was the starting organotin hydrocarbon (II).

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