Addition of Methyldichlorosilane to Allene Hydrocarbons

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Abstract

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Addition of Methyldichlorosilane to Allene Hydrocarbons

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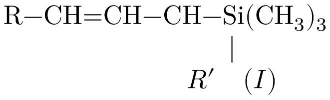
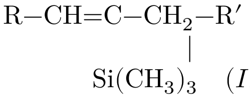
Allene hydrocarbons add water and hydrogen halides in such a way that the hydrogen is directed to the terminal atoms of the allene system ($^{1-3}$). Continuing the study of reactions of allene hydrocarbons, we became interested in the direction of addition to them of silicon hydrides, i.e., compounds with a different (hydride) character of the hydrogen atom. Data on this question were absent from the literature.

We investigated the direction of addition of methyldichlorosilane to two monosubstituted allenes (propyl- and butylallene) and two symmetrically disubstituted allenes (methylpropyl- and methylamylallene) in the presence of chloroplatinic acid. The addition product was also isolated in the case of ethylpropylallene; however, its structure was established only partially.

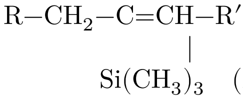
All the adducts obtained were methylated with magnesium bromomethyl without isolation. As a result of the reaction, in the case of monosubstituted allenes, mono- and diadducts were obtained. The latter were not studied. In the case of disubstituted allenes the amounts of diadducts were insignificant. In each case, the formation of four isomers of the monoadduct could be expected:



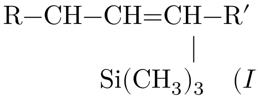
$$R{-}CH{=}CH{-}\underset{\substack{|\\ R'}}{CH}{-}Si(CH_3)_3 \quad (I)$$



$$R{-}CH{=}\underset{\substack{|\\ Si(CH_3)_3}}{C}{-}CH_2{-}R' \quad (III)$$



$$R{-}CH_2{-}\underset{\substack{|\\ Si(CH_3)_3}}{C}{=}CH{-}R' \quad (II)$$



$$R{-}\underset{\substack{|\\ Si(CH_3)_3}}{CH}{-}CH{=}CH{-}R' \quad (IV)$$

$$(I{-}IV\,a)\quad R' = H,\ R = C_3H_7; \qquad (I{-}IV\,b)\quad R' = H,\ R = C_4H_9;$$
$$(I{-}IV\,v)\quad R' = CH_3,\ R = C_3H_7; \qquad (I{-}IV\,g)\quad R' = CH_3,\ R = C_5H_{11}.$$

The structure of the compounds obtained was established from the IR spectra, by hydrogenation to known saturated silicon hydrocarbons, or by ozonolysis.

In the case of monosubstituted allenes, the IR spectra of the methylated addition products (Fig. 1, *1,2*) had intense bands in the region of 1620 cm^{-1},

Fig. 1

Figure 1: Fig. 1

characteristic of a double bond with a silicon atom in the β-position (^{4}). Absorption in the region 1590-1600 cm^{-1}, characteristic of a double bond in the α-position with respect to the silicon atom, was not observed. The spectra also lacked bands of a terminal methylene group. Consequently, formulas IIa and IIb, as well as IIIa and IIIb, for the compounds obtained were excluded. On hydrogenation, both investigated substances absorbed amounts of hydrogen close to the calculated values, with formation, respectively, of trimethylhexyl- and trimethylheptylsilanes. The latter had IR spectra identical with the spectra of authentic samples, and constants close to those given in the literature (^{5}).

The structure of the silicon hydrocarbon obtained from propylallene was confirmed by obtaining butyric acid upon its ozonolysis.

IR spectra of the silicon hydrocarbons obtained from disubstituted allenes (Fig. 1, 3-5), on the same grounds as in the case of monosubstituted allenes, made it possible to reject formulas II and III (c, d).

Ozonolysis of the first two substances gave, respectively, butyric and caproic acids, which indicated the preferential formation of adducts (Ib) and (Ig). However, in both cases acetic acid was also isolated (about 30% of the acid mixture), which testified to the presence of an admixture of the isomers (IVb) and (IVg).

Fig. 1

Thus, the direction of addition of silicon hydrides to allenes proved to be opposite to the direction of addition to them of hydrogen halides and water.

For the reaction of addition of methyldichlorosilane to olefins, a nucleophilic mechanism is assumed (6). In the case of allenes, the reaction apparently begins with attack by a hydride ion at the central atom of the allene system. The direction of addition of the silicon-containing cation is determined chiefly by the steric factor. In the case of monosubstituted

Table 1

Substance	B.p., °C	d_4^{20}	n_D^{20}	Note
Hydrogenation product of adduct (Ia)	162, 163	0.7458	1.4170	Our data
Trimethylhexylsilane	161-163	0.7434	1.4160	(4)
Trimethylhexylsilane	163	0.7422	1.4154	(4)

Substance	B.p., °C	d_4^{20}	n_D^{20}	Note
Hydrogenation product of adduct (Ib)	76-77 (20 mm)	0.7543	1.4231	Our data
Trimethylheptylsilane	77-77.5 (20 mm)	0.7512	1.4210	(5)
Trimethylheptylsilane	184	0.7506	1.4201	(5)

allenes the terminal methylene group is the most accessible, which explains the 1,2-addition. In the case of disubstituted allenes, the silicon-containing cation is directed predominantly toward the smaller radical.

Experimental part

Propylallene was obtained by reduction of 3-chlorohexyne-1(7), butylallene by the action of butylmagnesium bromide on propargyl bromide(8). Disubstituted allenes were obtained by addition of lithium alkyls to vinylalkylacetylenes(9).

Propylallene. To a mixture of 0.1 g-mole of propylallene and 0.6 ml of catalyst (a 0.1 *M* solution of chloroplatinic acid in isopropyl alcohol), 0.1 g-mole of methyldichlorosilane was added dropwise with vigorous stirring. After heating for 1.5 hours on a water bath, the chloride obtained was methylated with an ethereal solution of methylmagnesium bromide. The reaction mixture was then treated with a 5% HCl solution. The ether layer was washed with a sodium bicarbonate solution and dried over $CaCl_2$. On distillation of the substance through a Widmer column, two main fractions were obtained: 1) 60-61° (20 mm)—5 g (monoadduct), and 2) 93-95° (20 mm)—3.5 g (predominantly diadduct). Residue 1.5 g. Constants and analytical data for all monoadducts are given in Table 2.

On **hydrogenation** of the monoadduct (1.6 g) in methanol over $Pd/CaCO_3$ for 2 hr, more than 90% of the calculated amount of hydrogen was absorbed. The reaction product—trimethylhexylsilane—was washed with sulfuric acid and distilled. Constants of this and other hydrogenation products are given in Table 1. A counter synthesis of trimethylhexylsilane was carried out by the usual method—by the action of hexylmagnesium bromide on trimethylchlorosilane in ethereal solution(5).

On **ozonization** of the monoadduct (2.5 g) in ethyl chloride and decomposition of the ozonide with hydrogen peroxide on heating, 0.66 g of butyric acid was obtained.

Table 2

Main product	b.p., °C	Pressure, mm	d_4^{20}	n_D^{20}	MR found	MR calc.	Found C, %	Found H, %	Found Si, %	Gross formula	Calculated C, %	Calculated H, %	Calculated Si, %
C_3H_7–CH=C=CH–$CH_2Si(CH_3)_3$	60–61	20	0.7563	1.4241	52.75	52.90	69.33 69.20	12.76 12.89	18.05 18.19	$C_9H_{20}Si$	69.23	12.82	17.95
C_4H_9–CH=C=CH–$CH_2Si(CH_3)_3$	56–57	8	0.7683	1.4339	57.62	57.60	70.50 70.49	12.64 12.69	16.40 16.52	$C_{10}H_{22}Si$	70.59	12.94	16.47
C_3H_7–CH–CHSi$(CH_3)_3$	50–51	6	0.7808	1.4430	57.72	57.60	70.53 70.43	13.07 13.14	16.12 16.10	$C_{10}H_{22}Si$	70.59	12.94	16.47
C_5H_{11}–CH=C–CHSi$(CH_3)_3CH_3$	81–82	6	0.7893	1.4450	66.76	66.89	72.92 72.36	13.39 13.41	14.23 13.96	$C_{12}H_{26}Si$	72.73	13.13	14.14
C_2H_5–CH=C–CH–C_3H_7 +CHHSi$(CH_3)_3$	60–61	6	0.7805	1.4440	62.63	62.25	71.06 70.93	13.55 13.57	14.91 15.50	$C_{11}H_{24}Si$	71.74	13.04	15.22

B.p. 60–62° (20 mm), d_4^{20} 0.9513, n_D^{20} 1.4010. Ag salt.

Found, %: C 24.76; 24.93; H 3.96; 3.85; Ag 55.45; 55.36
C_4H_7AgO. Calculated, %: C 24.61; H 3.59; Ag 55.38

Butylallene. From 0.1 g-mol of hydrocarbon, by the procedure described above, there were obtained: 1) monoadduct–5 g, 2) diadduct–2.5 g. Residue 3 g.

Methylpropylallene (heptadiene-2,3). From 0.1 g-mol of hydrocarbon, 6.5 g of monoadduct and 2.5 g of residue were obtained. On distillation of the products of ozonolysis of the monoadduct, the following fractions were obtained: 1) 52–58° (30 mm), n_D^{20} 1.3849, 0.5 g (acetic acid). Ag salt.

Found, %: C 14.33; 14.09; H 1.84; 1.95; Ag 64.27; 64.02

$C_2H_3AgO_2$. Calculated, %: C 14.37; H 1.80; Ag 64.67

2) 60–64° (20 mm), n_D^{20} 1.3760, 2.0 g (butyric acid). Anilide. M.p. 94.5° (from 50% alcohol).

Found, %: N 8.85; 8.87
$C_9H_{11}ON$. Calculated, %: N 8.59

Methylamylallene (nonadiene-2,3). Fractionation of the products obtained from 0.15 g-mol of hydrocarbon gave 9.5 g of monoadduct and 5 g of residue (above 90° at 6 mm). On ozonization of the monoadduct (7.8 g), there were obtained: 1) acetic acid (0.5 g), 50–60° (100 mm), n_D^{20} 1.3810. Anilide: m.p. 113–114° (from 40% alcohol).

Found, %: N 10.51; 10.70
C_8H_9NO. Calculated, %: N 10.37

2) Caproic acid (2.7 g), 85-90° (15 mm), n_D^{20} 1.4170. Anilide: m.p. 97° (from 50% alcohol).

Found, %: N 7.40; 7.56
$C_{12}H_{17}NO$. Calculated, %: N 7.33

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Note: Figure translations are in progress. See original paper for figures.