Interaction of Diazoacetic Ester with Tetraallylsilane

1964

SovietRxiv

Abstract

Full Text

Chemistry

I. E. Dolgii, A. P. Meshcheryakov

Interaction of Diazoacetic Ester with Tetraallylsilane

(Presented by Academician A. A. Balandin, 11 II 1964)

The number of described examples of the interaction of diazoacetic ester with dienes is small. At the same time, information on reactions of diazoacetic ester with polyene compounds is completely absent from the literature. In this connection, it seemed interesting to us to study the interaction of diazoacetic ester with such a tetraene as tetraallylsilane. Our choice of an organosilicon tetraene was due to the fact that, as is known, the barrier effect of the silicon atom, which separates the C=C bonds and thereby hinders their interaction, at the same time hinders side reactions of isomerization, polymerization, etc., which would have been difficult to avoid in the case of hydrocarbon polyenes. Using the reaction of diazoacetic ester with dimethyldiallylsilane as an example, we showed that under the selected conditions (temperature 100–110°, eightfold excess of diene) addition of carbethoxycarbene occurs only to one double bond of the starting unsaturated compound, i.e., only dimethylallyl-[(2-carbethoxycyclopropyl)-methyl]-silane is formed. On this basis, the reactions of diazoacetic ester with tetraallylsilane and with the ethyl esters of unsaturated acids obtained from it were also carried out at a temperature of 100–110° and with an eightfold excess of the unsaturated compound.

As a result of the interaction of diazoacetic ester with tetraallylsilane, we obtained, in 80% yield, only [(2-carbethoxycyclopropyl)-methyl]-triallylsilane; upon its further treatment with diazoacetic ester, bis-[(2-carbethoxycyclopropyl)-methyl]-diallylsilane was likewise formed exclusively, in 70% yield. By successive interaction of diazoacetic ester with the bis-[(2-carbethoxycyclopropyl)-methyl]-diallylsilane and tris-[(2-carbethoxycyclopropyl)-methyl]-allylsilane synthesized in this way, tris-[(2-carbethoxycyclopropyl)-methyl]-allylsilane and tetrakis-[(2-carbethoxycyclopropyl)-methyl]-silane, respectively, were obtained in yields of ~40%. In the reaction with tris-[(2-carbethoxycyclopropyl)-methyl]-allylsilane, diazoacetic ester was introduced with a 1.6-fold molar excess in order to ensure the most complete utilization of the unsaturated component. During distillation of the resulting reaction mixture in vacuum down to 0.4 mm Hg, decomposition began; therefore the tetrakis-[(2-carbethoxycyclopropyl)-methyl]-silane formed was isolated by molecular distillation in vacuum at $1.5\text{–}2 \cdot 10^{-4}$ mm Hg, with heating in a bath at a temperature of 185–190°.

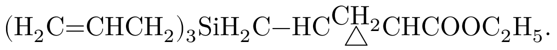
All the esters obtained—mono-, bis-, tris-, and tetrakis-[(2-carbethoxycyclopropyl)-methyl]-silanes—are oily and mobile liquids, despite their high molecular weight; they are evidently resistant to thermal polymerization, since we did not observe a single case of their polymerization under prolonged heating and at relatively high temperatures (up to 200-250°).

By saponifying the synthesized esters for ~20 hours with a 10% alcoholic solution of KOH, the corresponding acids were obtained; they proved to be viscous oils, which in the case of the di-, tri-, and tetracarboxylic acids solidified to glass.

Experimental Part

Tetraallylsilane was synthesized by the Grignard reaction from silicon tetrachloride and allyl bromide in 78% yield, b.p. 102°/13 mm, n_D^{20} 1.4860. Literature data (^{1}): yield 37%, b.p. 90.5°/10 mm, n_D^{20} 1.4840.

((2-Carbethoxycyclopropyl)methyl)triallylsilane.



$$(H_2C{=}CHCH_2)_3SiH_2C{-}HC\overset{CH_2}{\triangle}CHCOOC_2H_5.$$

To a mixture of 355 g of tetraallylsilane and 1 g of $CuSO_4$ was added at 100-110° a solution of 25 g of diazoacetic ester in 25 g of tetraallylsilane. After distilling off the excess tetraallylsilane, 50 g of [((2-carbethoxycyclopropyl)methyl)triallyl]silane was isolated, yield 82%, b.p. 148-148.5°/4.5 mm, n_D^{20} 1.4893, d_D^4 0.9420.

Found, %: C 68.76, 68.78; H 9.53, 9.73; Si 10.17, 9.87;
MR_D 85.31

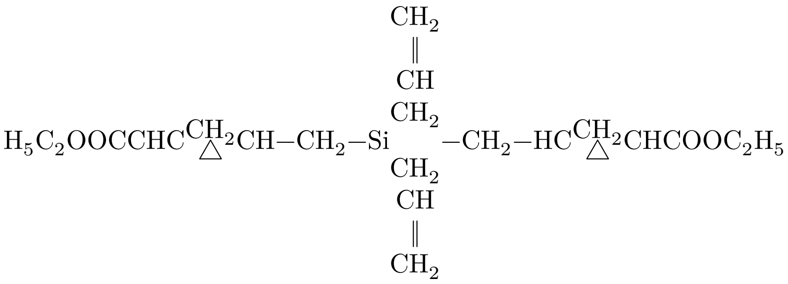
$C_{16}H_{26}O_2Si$. Calculated, %: C 69.04; H 9.37; Si 10.08;
MR_D 84.81

((2-Carboxycyclopropyl)methyl)triallylsilane. A mixture of 28 g of the ethyl ester of ((2-carboxycyclopropyl)methyl)triallylsilane, 6 g of KOH, and 60 ml of alcohol was heated for 20 h at 100-110° with stirring, after which 19 g (76%) of the acid was isolated, b.p. 152-154°/0.7 mm, n_D^{20} 1.5065, d_4^{20} 0.9791.

Found, %: C 66.55, 66.80; H 8.70, 8.77; Si 11.08, 10.96;
acid number 257.189; MR_D 76.03

$C_{14}H_{22}O_2Si$. Calculated, %: C 67.15; H 8.85; Si 11.20;
acid number 250.376; MR_D 75.40

Bis-(2-carbethoxycyclopropyl)-methyl-diallylsilane.



To a mixture of 200 g of ((2-carbethoxycyclopropyl)methyl)triallylsilane and 1 g of $CuSO_4$ was added at 100-110° with stirring a solution of 12 g of diazoacetic ester in 15 g of the starting unsaturated compound. After completion of the reaction, the mixture was distilled, and 179 g of ((2-carbethoxycyclopropyl)methyl)triallylsilane and 27 g of bis-((2-carbethoxycyclopropyl)methyl)-diallylsilane were obtained, yield 71%, b.p. 173.5-175°/1 mm, d_4^{20} 1.0069, n_D^{20} 1.4890.

Found, %: C 65.69, 65.98; H 9.04, 8.85; Si 7.95, 7.63; MR_D 104.48

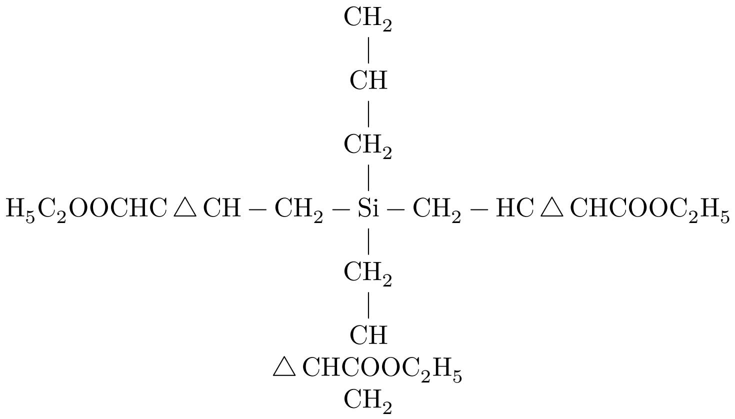
$C_{20}H_{32}O_4Si$. Calculated, %: C 65.96; H 8.85; Si 7.70; MR_D 104.16

Bis-((2-carboxycyclopropyl)methyl)-diallylsilane. A mixture of 36 g of the diethyl ester of bis-((2-carboxycyclopropyl)methyl)-diallylsilane, 14 g of KOH, and 140 ml of alcohol was heated for 20 h at 100-110°. Thirty grams of the dicarboxylic acid were obtained, n_D^{20} 1.5232; n_D^{45} 1.5152.

Found, %: C 61.26, 61.65; H 7.69, 7.72; Si 9.13, 9.54

$C_{16}H_{24}O_4Si$. Calculated, %: C 62.30; H 7.84; Si 9.10

Tris-((2-carbethoxycyclopropyl)-methyl)-allylsilane.



To a mixture of 92 g of bis-((2-carbethoxycyclopropyl)-methyl)-diallylsilane and 1 g of $CuSO_4$ at 100—110°, a solution of 5 g of diazoacetic ester in 10 g of bis-((2-carbethoxycyclopropyl)-methyl)-diallylsilane was added. The reaction mixture was then distilled, and 8 g of tris-((2-carbethoxycyclopropyl)-methyl)-allylsilane was isolated, yield 40%; b.p. 182.5—183.5° at 0.45 mm, n_D^{20} 1.4893, d_4^{20} 1.0507.

Found, %: C 63.32, 63.47; H 8.53, 8.71; Si 6.40, 6.61;

$$MR_D\ 123.83$$

$C_{24}H_{38}O_6Si$. Calculated, %: C 63.97; H 8.50; Si 6.22;

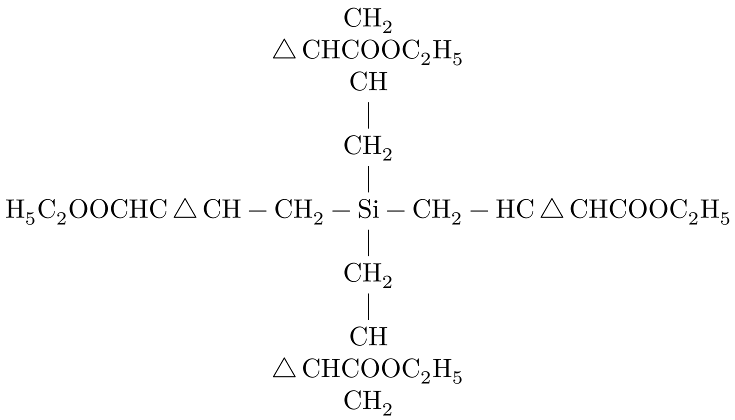
$$MR_D\ 123.51$$

Tris-((2-carboxycyclopropyl)-methyl)-allylsilane.
10 g of the starting triethyl triester, 5 g of KOH, and 50 ml of alcohol were heated for 20 hr at 100—110°, after which 7.5 g of the named tricarboxylic acid was isolated.

Found, %: C 57.78, 57.89; H 7.34, 7.21; Si 7.59, 7.84;
acid number 127.739

$C_{18}H_{26}O_6Si$. Calculated, %: C 58.99; H 7.15; Si 7.66;
acid number 122.155

Tetrakis-((2-carbethoxycyclopropyl)-methyl)-silane.



$$\begin{array}{c} CH_2 \\ \triangle\, CHCOOC_2H_5 \\ CH \\ | \\ CH_2 \\ | \\ H_5C_2OOCHC\,\triangle\, CH - CH_2 - Si - CH_2 - HC\,\triangle\, CHCOOC_2H_5 \\ | \\ CH_2 \\ | \\ CH \\ \triangle\, CHCOOC_2H_5 \\ CH_2 \end{array}$$

To a mixture of 7 g of tris-((2-carbethoxycyclopropyl)-methyl)-allylsilane and 0.5 g of $CuSO_4$ at 100—110°, with stirring, a solution of 3 g of tris-((2-carbethoxycyclopropyl)-methyl)-allylsilane in 5 g of diazoacetic ester was added dropwise. After the reaction was complete, the mixture was diluted with ether and filtered. The solvent and volatile impurities were distilled off in vacuum at 0.5 mm Hg with the bath temperature up to 150°. From the residue, by molecular distillation in vacuum at 1.5—$2 \cdot 10^{-4}$ mm Hg with the bath temperature 185—190°, 5 g of tetrakis-((2-carbethoxycyclopropyl)-methyl)-silane was isolated, yield 41%, n_D^{20} 1.4880, d_4^{20} 1.0842.

Found, %: C 62.11, 62.83; H 8.25, 8.33; Si 5.02, 4.63; MR_D 142.57

$C_{28}H_{44}O_8Si$. Calculated, %: C 62.65; H 8.26; Si 5.23; MR_D 142.85

Tetrakis-((2-carboxycyclopropyl)-methyl)-silane. A mixture of 4 g of the tetraethyl ester of the named acid, 2 g of KOH, and 20 ml of alcohol was heated for 20 h at 100–110°. This gave 2 g of tetrakis-2-carboxycyclopropyl)-methyl)-silane, m.p. 64–66°.

Found, %: C 55.93, 55.85; H 7.26, 6.99; Si 6.29, 6.51;
acid number 111.263

$C_{20}H_{28}O_8Si$. Calculated, %: C 56.58; H 6.65; Si 6.61;
acid number 106.126

Institute of Organic Chemistry
named after N. D. Zelinsky
Academy of Sciences of the USSR

Received
20 I 1964

REFERENCES

1. A. D. Petrov, L. L. Shchukovskaya, *Izv. AN SSSR, OKhN*, 1952, 564.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.