AN INVESTIGATION OF THE SYNTHESIS AND TRANSFORMATION OF UNSATURATED SILICON-CONTAINING COMPOUNDS

COMMUNICATION 1: ESTERIFICATION WITH ADIPIC ACID OF PRIMARY AND TERTIARY ACETYLENIC ALCOHOLS WHICH CONTAIN SILICON IN THE GAMMA POSITION

M. F. Shostakovskii, N. V. Komarov, V. P. Kuznetsova and I. I. Igonina

The Irkutsk Institute of Organic Chemistry, Siberian Division of the Academy of Sciences, USSR

Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
No. 4, pp. 699-703, April, 1961
Original article submitted December 15, 1959

The present investigations which we conducted earlier [1-6] on the synthesis and transformation of silicon- and germanium-containing organic acetylenic alcohols have made it possible to obtain much interesting data from the point of view of the reactivity of these compounds, and to obtain from them very interesting derivatives. The reactions investigated included hydrogenation, acetylation, vinylation, dehydration, cyanoethylation, esterification and the exchange of hydroxyl for halogen. A systematic study of the properties of the hetero-organic acetylenic alcohols with the alluring prospect of obtaining from them interesting new substances has compelled us to investigate intensively the esterification of these compounds.

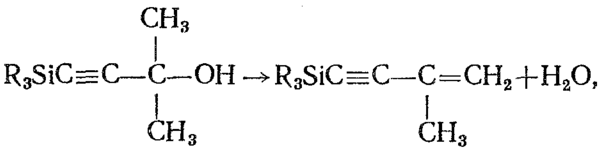
The present investigation is devoted to the study of the esterification with adipic acid of the primary and tertiary acetylenic alcohols which contain silicon in the gamma position. The esterification of these alcohols was carried out by the reaction of the alcohols or of their magnesium derivatives with adipyl chloride. The study of the esterification with adipic acid of the primary acetylenic alcohols which contain silicon in the gamma position in the absence of catalyst showed that depending on the conditions of the synthesis and the ratios of the starting materials, the reaction could proceed to form either the acid esters

$$R_3SiC{\equiv}C{-}CH_2OH + HOOC(CH_2)_4COOH \rightarrow R_3SiC{\equiv}C{-}CH_2OOC(CH_2)_4COOH,$$
$$\text{where } R = CH_3,\ C_2H_5 \text{ and } C_6H_5,$$

or the full esters of adipic acid

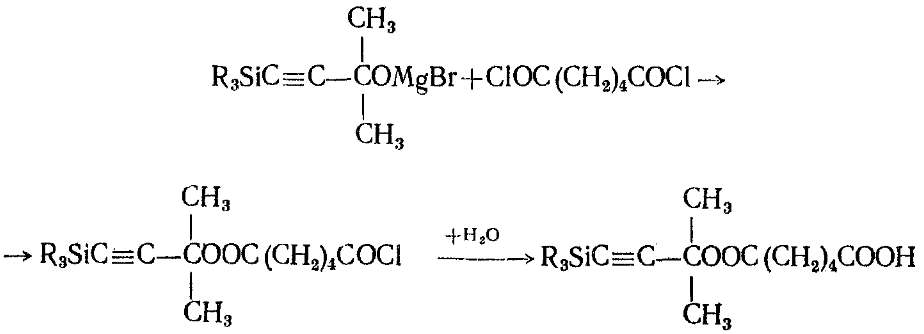
$$2R_3SiC{\equiv}C{-}CH_2OH + HOOC(CH_2)_4COOH \rightarrow R_3SiC{\equiv}C{-}$$
$${-}CH_2OOC(CH_2)_4COOCH_2C{\equiv}CSiR_3,$$
$$\text{where } R = CH_3 \text{ and } C_6H_5.$$

However, this method turned out to be useless for the esterification of the tertiary acetylenic alcohols with adipic acid both in the presence of acid catalysts (p-toluenesulfonic acid, boric acid and others), and in their absence it led to the dehydration of the alcohol to form the corresponding vinylacetylenic silicon-containing hydrocarbon.



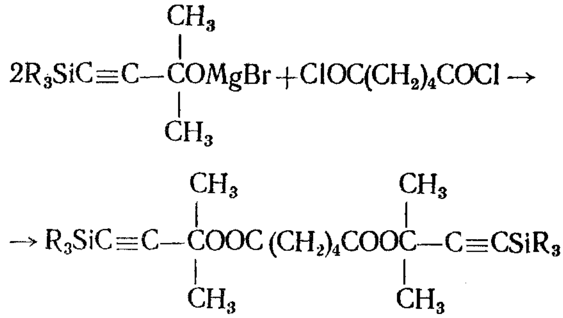
$$R_3SiC{\equiv}C{-}\underset{CH_3}{\overset{CH_3}{C}}{-}OH \rightarrow R_3SiC{\equiv}C{-}\underset{CH_3}{C}{=}CH_2 + H_2O,$$
$$\text{where } R = CH_3 \text{ and } C_2H_5.$$

An attempt to realize the esterification of the tertiary acetylenic alcohols containing silicon in the gamma position by means of their interaction with adipyl chloride in the presence of pyridine was unsuccessful, as was also an attempt at ester exchange with these alcohols and dimethyl adipate under the influence of sodium ethylate. We succeeded in synthesizing the acid and full esters of the tertiary acetylenic alcohol containing silicon in the gamma position through the interaction of the magnesium alcoholates with adipyl chloride



$$\mathrm{R_3SiC{\equiv}C{-}\underset{CH_3}{\overset{CH_3}{C}}OMgBr + ClOC(CH_2)_4COCl} \rightarrow$$

$$\rightarrow \mathrm{R_3SiC{\equiv}C{-}\underset{CH_3}{\overset{CH_3}{C}}OOC(CH_2)_4COCl} \xrightarrow{+\mathrm{H_2O}} \mathrm{R_3SiC{\equiv}C{-}\underset{CH_3}{\overset{CH_3}{C}}OOC(CH_2)_4COOH}$$



$$\mathrm{2R_3SiC{\equiv}C{-}\underset{CH_3}{\overset{CH_3}{C}}OMgBr + ClOC(CH_2)_4COCl} \rightarrow$$

$$\rightarrow \mathrm{R_3SiC{\equiv}C{-}\underset{CH_3}{\overset{CH_3}{C}}OOC(CH_2)_4COO\underset{CH_3}{\overset{CH_3}{C}}{-}C{\equiv}CSiR_3},$$

where $\mathrm{R = CH_3}$ and $\mathrm{C_2H_5}$.

EXPERIMENTAL PART

1. The following starting materials were used in carrying out the investigations: 4-trimethylsilyl-2-methylbutyne-3-ol-2 [1], b.p. 78° (25 mm) m.p. 42.5°; 4-triethylsilyl-2-methylbutyne-3-ol-2, b.p. 91° (2 mm); n^{20}_D 1.4462; d^{20}_4 0.8571; 3-trimethylsilylpropyne-2-ol-1 [7], b.p. 61° (2 mm); n^{20}_D 1.4523; d^{20}_4 0.8806; 3-triethylsilylpropyne-2-ol-1 [7], b.p. 109° (6 mm); n^{20}_D 1.4670; d^{20}_4 0.8932; 3-dimethylphenylsilylpropyne-2-ol-1 [7], b.p. 131° (2 mm); n^{20}_D 1.5335; d^{20}_4 0.9996; adipic acid, m.p. 151°; adipyl chloride, b.p. 116° (7 mm).

The synthesis of mono-3-dimethylphenylsilylpropene-2 adipate $\mathrm{(CH_3)_2C_6H_5SiC \equiv C{-}CH_2OOC(CH_2)_4COOH}$. Adipic acid, 3.65 g (0.025 M) was placed in a three necked 25 ml round bottomed flask furnished with a reflux condenser, a mechanical stirrer, a thermometer, a dropping funnel, and an exit tube. The contents of the flask were heated to the melting point, and to the melted acid was added drop-wise 4.76 g (0.025 M) of 3-dimethylvinylsilylpropyne-2-ol-1. The reaction mixture was stirred and heated for 3 hours at 160°. The water formed in the synthesis was collected via the exit tube in a tared receiver. At the end of the synthesis, the reaction mass was filtered on a glass filter to separate the unreacted adipic acid. The residue was washed several times with dry ether. The filtrate and the residue left from the removal of the dry ether were distilled in vacuo. The substance isolated by distillation weighed 2.0 g (25%), 210° (4 mm); n^{20}_D 1.4960; d^{20}_4 1.067. Found: Si 8.87%; MR 87.18, $\mathrm{C_{17}H_{22}SiO_4}$. Calculated: Si 8.85%; MR 88.70.

The synthesis of di-(3-dimethylphenylsilylpropyne-2) adipate* $\mathrm{(CH_3)_2C_6H_5SiC \equiv C{-}CH_2OOC(CH_2)_4COOCH_2C \equiv {\equiv} CSi(C_6H_5)(CH_3)_2}$. In the apparatus described above were placed 9.52 g (0.05 M) of 3-dimethylphenylsilylpropyne-2-ol-1 and 3.65 g (0.025 M) of adipic acid. The mixture was heated to 170-175° and stirred for 3 hours. The water formed during the synthesis was collected via the exit tube in a tared receiver. At the end of the synthesis, the

---

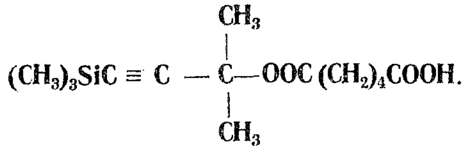
*The mono- and the di-(3-dimethylphenylsilylpropyne-2) adipates were apparently contaminated with disproportionation products.

reaction mixture was filtered through a glass filter from the unreacted adipic acid. The precipitate and the filtrate were worked up in a manner analogous to that described above. As a result of the synthesis, 1.23 g (33%) of adipic acid was regained and 4.84 g (39%) of di-(3-dimethylphenylsilylpropyne-2) adipate with b.p. 260° (5 mm); $n^{20}D$ 1.5112; d^{20}_4 1.0700. Found: Si 10.86%; MR 137.47. $C_{23}H_{34}Si_2O_4$. Calculated: Si 11.44%; MR 144.39.

The synthesis of mono-3-triethylsilylpropyne-2 adipate $(C_2H_5)_3SiC{\equiv}C{-}CH_2OOC(CH_2)_4COOH$. The synthesis was carried out in a manner analogous to the synthesis of mono-3-dimethylphenylsilylpropyne-2 adipate. Adipic acid, 3.65 g (0.025 M) and 3-triethylsilylpropyne-2-ol-1, 4,4 g (0.025 M) were used. The yield was 3 g (41%), b.p. 215° (6 mm); $n^{20}D$ 1.4650; d^{20}_4 1.010. Found: Si 9.39%; MR 81.62. $C_{15}H_{13}SiO_4$. Calculated: Si 9.42%; MR 82.92.

The synthesis of mono-3-triethylsilylpropyne-2 adipate $(CH_3)_3SiC{\equiv}C{-}CH_2OOC(CH_2)_4COOH$. The synthesis was carried out as described above. The quantities used were 3.65 g (0.025 M) of adipic acid and 3.2 g (0.025 M) of 3-trimethylsilylpropyne-2-ol-1. The yield was 3.2 g (53%), b.p. 184-185° (4 mm); $n^{20}D$ 1.4604; d^{20}_4 1.012. Found: Si 11.83%; MR 65.10. $C_{12}H_{10}SiO_4$. Calculated: Si 11.70%; MR 69.03.

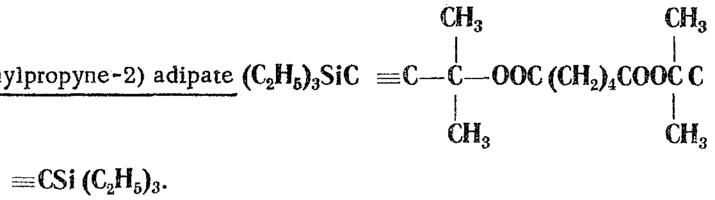
The synthesis of mono-3-trimethylsilyl-1,1-dimethylpropyne-2 adipate



$$(CH_3)_3SiC \equiv C - \underset{CH_3}{\overset{CH_3}{C}}{-}OOC(CH_2)_4COOH.$$

To the Grignard reagent prepared from 2.4 g (0.1 M) of Mg and 10.9 (0.1 M) of ethyl bromide with cooling and stirring, was added drop-wise 15.6 g (0.1 M) of 4-trimethylsilyl-2-methylbutyne-3-ol-2 in 20 ml of absolute ether. The mixture was heated on a water bath for 1 hour. Then 9.2 g(0.05 M) of adipyl chloride was added with cooling and stirring. The reaction mixture was heated on a water bath for 1 hour, and was then treated with a 1 N solution of hydrochloric acid until the residue was completely dissolved. The ether layer was separated from the aqueous layer, and the latter was extracted 3 times with ether. The ether layer and the ether extract were washed with water to free them from HCl, and they were then dried over anhydrous calcium chloride. The ether was removed, and the residue was distilled in vacuo. The yield was 10 g (36%), b.p. 178-180° (4 mm); $n^{20}D$ 1.4548; d^{20}_4 0.9902, Found: Si 9.88%; MR 77.87; $C_{14}H_{24}SiO_4$. Calculated: Si 9.89%; MR 78.29.

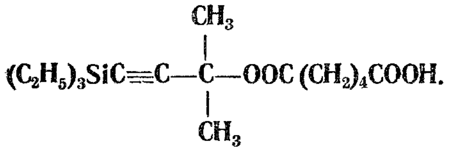
The synthesis of di-(triethylsilyl-1,1-dimethylpropyne-2) adipate



$$(C_2H_5)_3SiC \equiv C{-}\underset{CH_3}{\overset{CH_3}{C}}{-}OOC(CH_2)_4COO\underset{CH_3}{\overset{CH_3}{C}} \equiv CSi(C_2H_5)_3.$$

The synthesis was carried out in the manner described above. Mg, 0.84 g (0.035 M) and 3.8 g (0.035 M) of ethyl bromide, were used, followed by 6.9 g (0.35 M) of 4-triethylsilyl-2-methylbutyne-3-ol-2 and 3.2 g (0.0175 M) of adipyl chloride. The yield was 3.1 g (18%), b.p. 198° (2 mm); m.p. 131°. Found: Si 11.47%. $C_{28}H_{50}Si_2O_4$. Calculated: Si 11.09%.

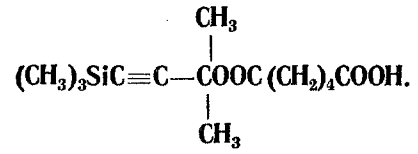
The attempted synthesis of mono-3-triethylsilyl-1,1-dimethylpropyne-2 adipate



$$(C_2H_5)_3SiC{\equiv}C{-}\underset{CH_3}{\overset{CH_3}{C}}{-}OOC(CH_2)_4COOH.$$

The synthesis was carried out analogously to that used for obtaining mono-3-dimethylphenylsilyl-1,1-dimethyl propyne adipate. Adipic acid, 7.3 g (0.05 M), and 4-triethylsilyl-2-methylbutyne-3-ol-2, 10 g (0.05 M) were used. The substances isolated from the synthesis were adipic acid, 7 g and 3 g (32%) of a substance of b.p. 63-65° (14 mm); $n^{20}D$ 1.4610; d^{20}_4 0.8135. Found: Si 15.52%; MR 60.71. $C_{11}H_{10}Si$. Calculated: Si 15.59%; Mr 60.61. The analytical data correspond to 4-triethylsilyl-2-methylbutene-1-yne-3 $(C_2H_5)_3SiC\equiv C-\underset{CH_3}{\underset{|}{C}}=CH_2$ – the product of the dehydration of the alcohol. On standing, the silicon-containing hydrocarbon polymerized to a glass.

The attempted synthesis of mono-3-trimethylsilyl-1,1-dimethylpropyne-2 adipate



$$(CH_3)_3SiC\equiv C-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}OOC(CH_2)_4COOH.$$

The synthesis was carried out in a manner analogous to that given above. Adipic acid, 3.65 g (0.025 M) and 4-trimethylsilyl-2-methylbutyne-3-ol-2, 3.9 g (0.025 M) were used. From the products were isolated 1.77 g of adipic acid and 1.1 g (29%) of substance $(CH_3)_3SiC\equiv C-\underset{CH_3}{\underset{|}{C}}=CH_2$ with b.p. 31° (12 mm); $n^{20}D$ 1.4445; d^{20}_4 0.7736. Found: Si 20.30%; MR 46.59. $C_8H_{14}Si$. Calculated: Si 20.31%; MR 46.72. The data from the literature [5] are: b.p. 32-32.5° (15 mm); $n^{20}D$ 1.4465; d^{20}_4 0.7854. On standing, the product polymerized to a glass.

4-Trimethylsilyl-2-methylbutene-1-yne-3 was obtained also by the interaction of 4-trimethylsilyl-2-methylbutyne-3-ol-2 with adipic acid under the influence of p-toluenesulfonic acid and of boric acid.

SUMMARY

1. The esterification with adipic acid of primary and tertiary acetylenic alcohols which contain silicon in the gamma position was investigated. Methods were worked out for the synthesis of the half and the full adipic esters of the acetylenic alcohols containing silicon in the gamma position.

2. The following compounds were obtained and characterized for the first time: mono-3-dimethylphenylsilylpropyne-2 adipate, di-(3-dimethylphenylsilylpropyne-2) adipate, mono-3-triethylsilylpropyne-2 adipate, mono-3-trimethylsilpropyne-2-adipate, mono-3-trimethylsilyl-1,1-trimethylpropyne-2 adipate, di-(triethylsilyl-1,1-dimethylpropyne-2) adipate, 4-triethylsilyl-2-methylbutene-1-yne-3.

LITERATURE CITED

1. M. F. Shostakovskii, I. A. Shikhiev, and N. V. Komarov, Izv. AN SSSR. Otd. khim. n. 1271 (1956); Dokl. AN SSSR 109, 344 (1956).
2. I. A. Shikhiev, M. F. Shostakovskii, N. V. Komarov, and L. A. Kayutenko, Izv. AN SSSR. Otd. khim. n. 1139 (1957).
3. M. F. Shostakovskii, I. A. Shikhiev, N. V. Komarov, I. A. Aslanov, Avt. svid. 117493 (1958); Zh. obshch. khimii 29, 1549 (1959).
4. I. A. Shikhiev, and L. A. Kayutenko, Izv. AN SSSR. Otd. khim. n. 991 (1957).
5. I. A. Shikhiev, M. F. Shostakovskii, and L. A. Kayutenko, Dokl. AzSSR 14, 687 (1958).
6. I. A. Shikhiev, M. F. Shostakovskii, and L. A. Kayutenko, Zh. obshch. khimii 29, 2137 (1959).
7. N. V. Komarov, and M. F. Shostakovskii, Izv. AN SSSR, Otd. khim. n. 1300 (1960).