Chemistry

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Abstract

Full Text

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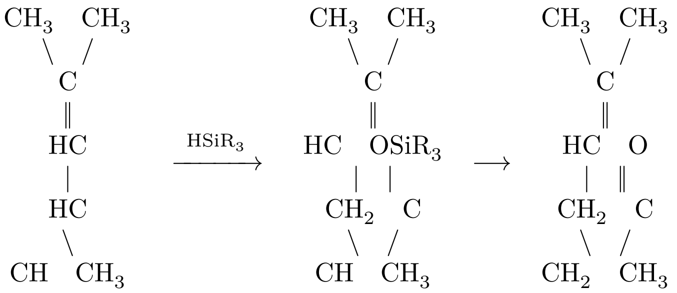
SELECTIVE REDUCTION OF 6-METHYLHEPTA-3,5-DIEN-2-ONE WITH TRIALKOXY- AND TRIALKYLSILANE HYDRIDES

The ability of silicon hydrides to add to olefins under the influence of platinum, palladium, potassium chloroplatinate, and chloroplatinic acid is known (^{1,2}). One of us, jointly with S. I. Sadykh-Zade (^{3}), has described the addition of trialkyl- and trialkoxysilanes to the conjugated system of α, β-unsaturated carbonyl compounds.

In the present work we have studied the addition of triethoxy- and triethylsilanes to the conjugated diene system of 6-methylhepta-3,5-dien-2-one (I) under the influence of catalytic amounts of chloroplatinic acid, and a strictly selective 1,4-addition was observed, which first leads to substituted vinyl ethers (II)

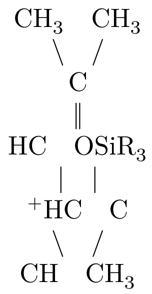


(I) (II) (III)

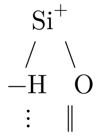
Hydrolysis of (II) in the presence of acidified alcohol gives 6-methylhept-5-en-2-one (III).

The observed selective direction of the reaction forming silico ethers II may be represented, in simplified form, as the result of the initial electrophilic attack ($^{5-7}$) of the ion $Si(OC_2H_5)_3^+$ or, respectively, $Si(C_2H_5)_3^+$ formed on the carbonyl oxygen, with formation of a carbonium ion (IV), stabilized by conjugation with two double bonds, toward which the hydride hydrogen is directed.

It is also possible that, sterically, the most favorable is the six-membered cyclic transition complex (V)



(IV)



conjugated diene ketone fragment

(V)

The reaction begins under the influence of a very small amount of catalyst and proceeds with strong heating, which may indicate its ionic-chain character.

Experimental Part

Formation of silyl ethers. 2-(6-Methylheptadien-2,5)-oxytriethoxysilane (II, $R = OC_2H_5$). To 12.4 g (0.1 mole) of 6-methylheptadien-3,5-one-2 (I), heated to 90°, 18 g (0.11 mole) of triethoxysilane and 1.5 ml of a 0.1 M solution of H_2PtCl_6 in absolute isopropyl alcohol are added simultaneously dropwise. Heating to 162° occurs. The mixture is then heated at 155–160° for 15 min, centrifuged from the catalyst, and distilled. 21.5 g (74.6%) of the silyl ether is obtained. B.p. 89–91°/1 mm; n_D^{20} 1.4310, d_4^{20} 0.9466; MR_D found 78.72, calculated 78.92.

Found, %:	C 58.27; 57.94;	H 9.87; 9.97;	Si 9.77; 10.07
$C_{14}H_{28}O_4Si$. Calculated, %:	C 58.33;	H 9.72;	Si 9.72

2-(6-Methylheptadien-2,5)-oxytriethylsilane (II, $R = C_2H_5$) is obtained at a temperature not above 100°. Yield 73.2%. B.p. 109–112°/5 mm; n_D^{20} 1.4605, d_4^{20} 0.8646; MR_D found 76.08, calculated 76.54.

2-(6-Methylheptadien-2,5)-oxymethyldiethylsilane is obtained at 60–70°. Yield 66.2% of theory. B.p. 73–74°/3 mm; n_D^{20} 1.4600; d_4^{20} 0.8590; MR_D found 72.07, calculated 71.89.

Hydrolysis. 10 g (0.35 mole) of the silyl ether (II, $R = OC_2H_5$) is added to 100 ml of ethyl alcohol acidified with 2.5 ml of concentrated hydrochloric acid and heated at reflux for 30 min. The alcohol is removed in vacuo, the residue is extracted with ether, the extract is washed with water and dried, and the solvent is removed. The substance is distilled. 3.4 g (76.6%) of 6-methylhepten-5-one-2 (III) is obtained. B.p. 75–77°/25 mm; n_D^{20} 1.4410.

By gas-liquid chromatography, there is one peak, which increases upon addition of authentic 6-methylhepten-5-one-2. Semicarbazone, m.p. 134–135.5°.

Found, %: C 59.00; 58.85; H 9.58; 9.35; N 23.00
$C_{19}H_{17}N_3O$. Calculated, %: C 58.98; H 9.35; N 22.92

A mixed sample with the semicarbazone of authentic 6-methylhepten-5-one-2 gives no depression of the melting point.

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

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