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Abstract

Full Text

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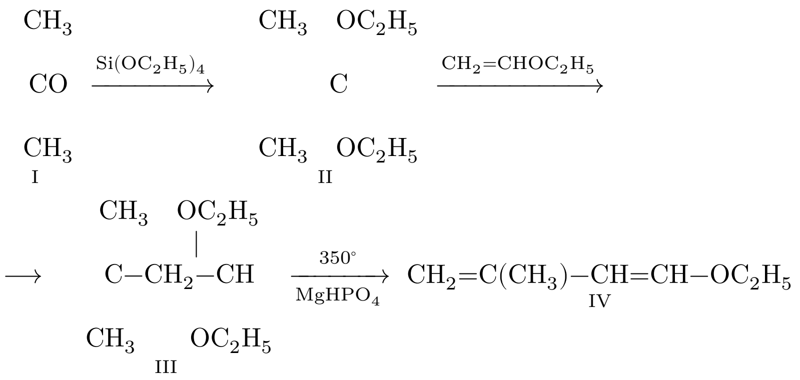
SYNTHESIS OF ETHOXYISOPRENE

Alkoxydienes are of unquestionable interest for organic chemistry. The presence in alkoxydienes of two conjugated double bonds and a reactive alkoxyl group makes it possible to use them for the synthesis of a variety of compounds. Of particular interest is ethoxyisoprene (1-ethoxy-3-methylbutadiene-1,3) (IV), which, owing to the presence of a methyl branch in the 3-position, possesses an isoprenoid structure, making it possible to use it for the synthesis of important isoprenoids (citral, vitamin A, carotene, etc.).

We have for the first time carried out and developed the synthesis of ethoxyisoprene (IV) by the following reactions:



$$\underset{\text{I}}{\overset{CH_3}{\underset{CH_3}{CO}}} \xrightarrow{Si(OC_2H_5)_4} \underset{\text{II}}{\overset{CH_3\quad OC_2H_5}{\underset{CH_3\quad OC_2H_5}{C}}} \xrightarrow{CH_2=CHOC_2H_5}$$

$$\longrightarrow \underset{\text{III}}{\overset{CH_3\quad OC_2H_5}{\underset{CH_3\qquad OC_2H_5}{C-CH_2-CH}}} \xrightarrow[MgHPO_4]{350^\circ} \underset{\text{IV}}{CH_2=C(CH_3)-CH=CH-OC_2H_5}$$

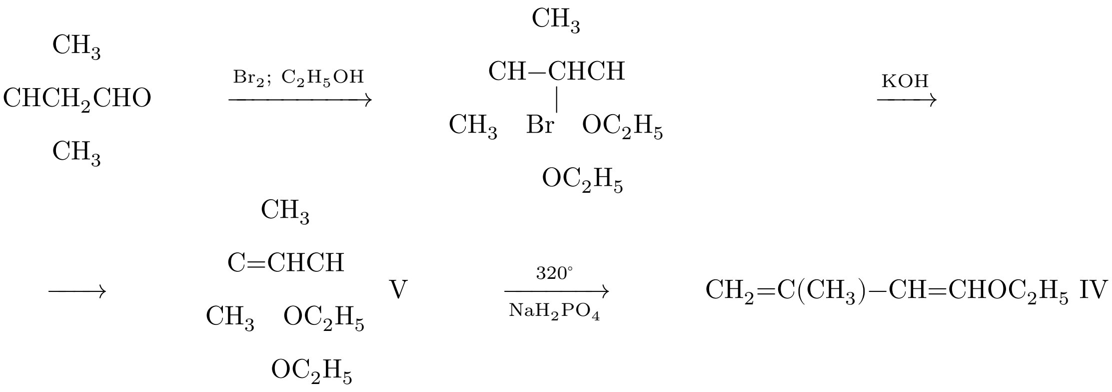
By the action of tetraethoxysilane on acetone we obtained the diethyl ketal of acetone (II). The literature contains a report by Helferich (^{1}) on the preparation of the diethyl ketal of acetone from acetone and tetraethoxysilane in a medium of threefold excess ethyl alcohol in the presence of hydrogen chloride as catalyst. However, in numerous experiments under these conditions we obtained only an insignificant yield of ketal (10–15%). A high yield of acetone ketal (92%) was obtained when 85% phosphoric acid was used as catalyst, in the presence of a small amount of ethyl alcohol (0.5 mole of alcohol per 1 mole of tetraethoxysilane).

We then introduced the diethyl ketal of acetone into a condensation reaction with vinyl ethyl ether. It is known from the literature that acetals of aldehydes readily enter into condensation with vinyl ethyl ether in the presence of zinc chloride or boron trifluoride catalysts (^{2}). However, the addition of ketals to vinyl ethers has hardly been studied. There are only patent data on the addition of ketals of acetone and cyclohexanone to vinyl methyl ether with low yield ([3]). We succeeded in carrying out the condensation of the diethyl ketal of acetone with vinyl ethyl ether at 0° in the presence of catalytic amounts of boron trifluoride etherate, with a yield of 3-methyl-1,1,3-triethoxybutane (III) of 85% based on the diethyl ketal of acetone that entered into the reaction. To avoid further condensation reaction

of 1,1,3-triethoxy-3-methylbutane with vinyl ethyl ether it is necessary to take a one-and-a-half-fold excess of acetone diethyl ketal into the reaction.

It was shown earlier that 1,1,3-trialkoxybutanes and acetals of crotonaldehyde at 250–350° over certain contact catalysts are converted into 1-alkoxybutadienes ([4],[5]). We have established that, when vapors of 1,1,3-triethoxy-3-methylbutane (III) are passed through a contact tube filled with an $MgHPO_4$ catalyst at 350° under a vacuum of 15–20 mm, two molecules of alcohol are split off, and ethoxyisoprene (IV) is obtained in 77% yield.

Ethoxyisoprene was also obtained by us in good yield by passing vapors of the diethyl acetal of β-methylcrotonaldehyde (V) over a contact catalyst, NaH_2PO_4. The diethyl acetal of β-methylcrotonaldehyde required for this reaction was obtained from isovaleraldehyde ([6]).



$$\begin{array}{c} CH_3 \\ CHCH_2CHO \\ CH_3 \end{array} \xrightarrow{Br_2;\ C_2H_5OH} \begin{array}{c} CH_3 \\ CH{-}CHCH \\ CH_3 \quad Br \quad OC_2H_5 \\ OC_2H_5 \end{array} \xrightarrow{KOH}$$

$$\longrightarrow \begin{array}{c} CH_3 \\ C{=}CHCH \\ CH_3 \quad OC_2H_5 \\ OC_2H_5 \end{array} \text{V} \xrightarrow[NaH_2PO_4]{320^\circ} CH_2{=}C(CH_3){-}CH{=}CHOC_2H_5 \ \text{IV}$$

Experimental Part

Acetone diethyl ketal (II). A mixture of 3120 g of tetraethoxysilane, 1200 ml of dry acetone, 450 ml of anhydrous ethyl alcohol, and 30 ml of 85% phosphoric acid was boiled for 10 h and then left for 24 h at room temperature. The reaction mass was treated with sodium methylate until alkaline and subjected to distillation. The fraction collected within 70–150° (1900 g) was shaken for 10–15 min with 30% caustic soda (1200 ml), and then washed three times with water. The substance was dried with potash and distilled. 1735 g of acetone diethyl ketal with b.p. 112–114° was obtained. From the wash waters, by extraction with ether, an additional 100 g of ketal was isolated. Total yield 1835 g (92.5% of theory).

1,1,3-Triethoxy-3-methylbutane (III). To a mixture of 1300 g of acetone diethyl ketal and 5.2 ml of boron trifluoride etherate, with cooling by ice water and vigorous stirring for 3.5 h, 500 g of vinyl ethyl ether was added. The mixture was stirred at 4–5° for another 3.5 h and then neutralized with sodium ethylate. After two distillations the following was obtained:

1. 615 g of starting acetone diethyl ketal (II) with b.p. 110–114°.
2. 903 g of 1,1,3-triethoxy-3-methylbutane (III) with b.p. 78°/7 mm; n_D^{20} 1.4145; d_4^{20} 0.8813; MR found 58.01; calculated 57.92.

Found, %: C 64.55; 64.45, H 11.80; 11.77
$C_{11}H_{24}O_3$. Calculated, %: C 64.66; H 11.84

Yield based on ketal entering into the reaction 85%.

3. Residue 207 g.

Preparation of the $MgHPO_4$ **catalyst.** 100 g of $MgHPO_4 \cdot 7H_2O$ was mixed in a porcelain dish with 190 g of water glass (sp. gr. 1.384) to the consistency of a thick paste. The resulting mass was formed with the aid of a metal syringe (orifice diameter 2 mm) into "worms," which were then cut into lengths of 3–4 mm. The catalyst was dried at 200° under a vacuum of 10–15 mm.

Ethoxyisoprene (1-ethoxy-3-methylbutadiene-1,3) (IV). a. From 1,1,3-triethoxy-3-methylbutane. Through a porcelain contact tube 60 cm long and 20 mm in diameter,

packed with 100 ml of $MgHPO_4$ catalyst, under vacuum of 15–20 mm at a temperature of 350–390° for 8 h, 600 g of 3-methyl-1,1,3-triethoxybutane (III) was passed through. The reaction product, collected in a trap cooled with a mixture of dry ice and acetone, was washed with water, dried over anhydrous potassium carbonate, and distilled under vacuum. This gave 254 g (77% yield) of ethoxyisoprene (IV), b.p. 75–77°/90 mm; n_D^{20} 1.4618; d_{20}^{20} 0.8345; MR found 36.87; calculated 35.23.

Found, %: C 75.23; 75.25; H 10.85; 10.71
$C_7H_{12}O$. Calculated, %: C 75.00; H 10.71

b. From the diethyl acetal of β-methylcrotonaldehyde (V). Through the contact tube described above, packed with 60 g of NaH_2PO_4 catalyst ([5]), under vacuum of 25 mm at a temperature of 320° for 50 min, 30 g of the diethyl acetal of β-methylcrotonaldehyde (V) was passed; the condensate was collected in a trap cooled with a mixture of dry ice and acetone. After the usual workup and distillation under vacuum, 11.6 g (54%) of ethoxyisoprene (IV) was obtained, b.p. 75–77°/20 mm.

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named after M. V. Lomonosov

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