CONDENSATION OF UNSATURATED THIOETHERS OF TERPENE SERIES WITH ORTHOFORMIC ESTER

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G. S. Ter-Sarkisyan and B. M. Mikhailov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

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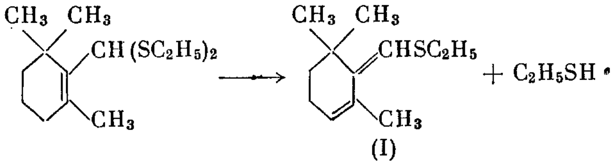
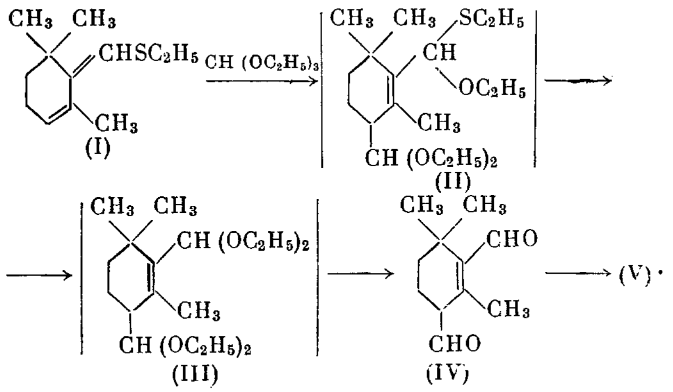
In a previous paper [1] we described the synthesis of unsaturated sulfides of general formula RCH = CH $-C(SC_2H_5) = CH_2$, formed in the decomposition of the diethyl thioketals of α- and β-ionone. Continuing this study, we found that the diethyl thioacetal of β-cyclocitral can also undergo a similar transformation. When heated in the presence of boron trifluoride etherate, the diethyl mercaptal of β-cyclocitral loses a molecule of ethyl mercaptan and is converted to 1-ethylmercaptomethylene-2,6,6-trimethyl-2-cyclohexene (I)



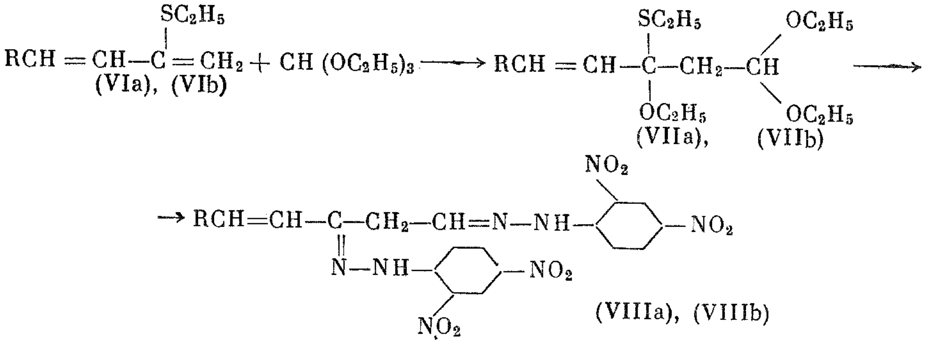
In this paper we studied the reaction of the polyene sulfides, obtained from the diethyl thioacetals of β-cyclocitral, α-ionone and β-ionone, with ethyl orthoformate. The reaction between 1-ethylmercaptomethylene-2,6,6-trimethyl-2-cyclohexene (I) and orthoformic ester goes with the formation of addition product (II), which when treated with an alcohol solution of mercuric chloride is converted to the tetraethoxy compound, representing the bis-acetal of the dialdehyde (III). Hydrolysis of the bis-acetal enabled us to isolate the dialdehyde (IV) and prepare its bis-2,4-dinitrophenylhydrazone (V)



The results obtained in the hydrolysis of 1-ethylmercaptomethylene-2,6,6-trimethyl-2-cyclohexene (I) in the presence of 2,4-dinitrophenylhydrazine testify in support of the fact that the dialdehyde is a derivative of β-cyclocitral and represents 1,3-diformyl-2,6,6-trimethyl-1-cyclohexene. Only the 2,4-dinitrophenylhydrazone of β-cyclocitral [with m.p. 172-173° (from the literature [2]: m.p. 172-173°)] was isolated when the compounds formed here were chromatographed on aluminum oxide, and we failed to obtain any of the 2,4-dinitrophenylhydrazone of α-cyclocitral, which could have been formed in the case of water adding to the semicyclic double bond.

The unsaturated sulfides with conjugated double bonds, obtained from the diethyl thioketals of α-ionone and β-ionone, add orthoformic ester in the 1,2-position, analogous to the ethers of the enols of α- and β-ionone [3]. The reaction of 1-(2,6,6-trimethyl-2-cyclohexenyl)-3-(ethylmercapto)-1,3-butadiene (VIa) and orthoformic ester goes with the formation of 5-(2,6,6-trimethyl-2-cyclohexenyl)-3-(ethylmercapto)-1,1,3-triethoxy-4-pentene (VIIa), which when hydrolyzed in the presence of 2,4-dinitrophenylhydrazine hydrochloride is converted to the bis-2,4-dinitrophenylhydrazone of 5-(2,6,6-trimethyl-2-cyclohexenyl)-4-penten-3-on-1-al (VIIIa). 5-(2,6,6-Trimethyl-1-cyclohexenyl)-3-(ethylmercapto)-1,1,3-triethoxy-4-pentene (VIIb) and the bis-2,4-dinitrophenylhydrazone of 5-(2,6,6-trimethyl-1-cyclohexenyl)-4-penten-3-on-1-al (VIIIb) were synthesized in a similar manner from 1-(2,6,6-trimethyl-1-cyclohexenyl)-3-(ethylmercapto)-1,3-butadiene (VIb) and orthoformic ester.

The end reaction products—the β-aldehyde ketones—were not isolated as the pure compounds due to their instability and tendency to polymerize [4]



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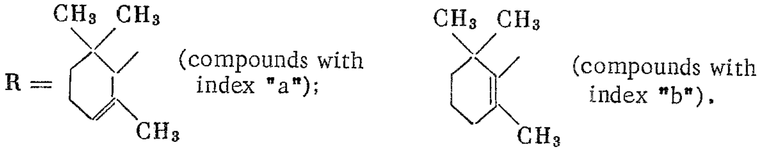

EXPERIMENTAL

1-Ethylmercaptomethylene-2,6,6-trimethyl-2-cyclohexene (I). A mixture of 31 g of β-cyclocitral diethyl mercaptal and 0.09 ml of $BF_3 \cdot O(C_2H_5)_2$ was vacuum-distilled from a Favorskii flask; after fractional distillation we obtained 15.6 g (67.2%) of (I) as a colorless mobile liquid with a disagreeable odor; b.p. 79-80° (0.1 mm), n_D^{20} 1.5510; d_4^{20} 0.9634; λ_{max} (in alcohol) 275 mμ (log ε 2.2). Found: C 72.90; 72.98; H 10.16; 10.40; S 16.37; 16.55%. MR 64.07. $C_{12}H_{20}S$. Calculated: C 73.40; H 10.27; S 16.33%; MR 62.33. 6.6 g of ethyl mercaptan was collected in the trap, cooled with liquid nitrogen.

1,3-Diformyl-2,6,6-trimethyl-1-cyclohexene (IV). To a mixture of 99 g of orthoformic ester and 5.5 ml of 10% $ZnCl_2$ solution in ethyl acetate was added 33 g of (I) in 4.5 h at 50-52°. The reaction mass was treated with 5% caustic solution and then extracted with ether. After distilling off the solvent and fractional distillation of the residue we obtained 4.9 g (8.3%) of 1-ethoxy-1-(ethylmercapto)methyl-3-(diethoxymethyl)-2,6,6-trimethyl-1-cyclohexene (II) with b.p. 125-128° (0.18 mm) and n_D^{20} 1.5290.

To a mixture of 10 ml of absolute alcohol, 11 g of dry $CdCO_3$ and 4 g of compound (II) heated to 60°, was added an alcohol solution of 11 g of $HgCl_2$ in 1 h. The ethylmercaptomercury chloride precipitate was filtered, and the filtrate was poured into a mixture of water and chloroform. After the usual workup and removal of the chloroform we obtained 3.06 g of 1,3-(diethoxymethyl)-2,6,6-trimethyl-1-cyclohexene (III), which was heated with 30 ml of 5% phosphoric acid for 1 h. After working up the reaction mixture in the usual manner, followed by distillation of the reaction product, we obtained 0.7 g (38.5%) of 1,3-diformyl-2,6,6-trimethyl-1-cyclohexene (IV) with b.p. 103-105° (5 mm). Found: C 72.84, 72.97; H 9.25, 9.39%. $C_{11}H_{16}O_2$. Calculated: C 73.31; H 8.95%. After recrystallization from pyridine, the bis-2,4-dinitrophenylhydrazone (V) was obtained as dark red crystals with m.p. 269-270°. Found: C 50.92, 50.93; H 4.15, 4.27; N 21.09, 21.23%. $C_{23}H_{24}N_8O_8$. Calculated: C 51.11, H 4.48; N 20.75%.

Reaction of 1-(2,6,6-trimethyl-2-cyclohexenyl)-3-(ethylmercapto)-1,3-butadiene (VIa) and ethyl orthoformate. To a mixture of 10.6 g of orthoformic ester and 0.2 ml of BF_3 etherate was added 8.5 g of (VIa) in 30 min at 19°. The reaction mass was stirred for another 30 min, after which 5% NaOH solution and ether were added. After the usual workup, distilling off the solvent, and fractional distillation of the residue, we obtained 2.1 g (15.2%) of (VIIa) with b.p. 150-155° (0.16 mm) and n_D^{20} 1.5330.

After recrystallization from a mixture of alcohol and ethyl acetate, and subsequent chromatographing on Al_2O_3, the bis-2,4-dinitrophenylhydrazone (VIIIa) was obtained as slender orange-red needles with m.p. 201-203°. Found: C 53.52; H 5.01; N 19.05%. $C_{26}H_{28}N_8O_8$. Calculated: C 53.79; H 4.86; N 19.30%.

Reaction of 1-(2,6,6-trimethyl-1-cyclohexenyl)-3-(ethylmercapto)-1,3-butadiene (VIb) and ethyl orthoformate. To a mixture of 18.8 g of orthoformic ester and 1 ml of BF_3 etherate was added 15 g of (VIb) in 30 min at 25°. The reaction mixture was stirred for another hour and then worked up in the same manner as described above. After removal of the solvent and fractional distillation of the residue we obtained 3.34 g (13.7%) of (VIIb) with b.p. 160-168° (0.18 mm) and n_D^{20} 1.5585. After recrystallization from a mixture of ethyl acetate and acetic acid the bis-2,4-dinitrophenylhydrazone (VIIIb) had m.p. 247-248°. Found: C 53.34; H 4.60; N 19.24%. $C_{26}H_{26}N_8O_8$. Calculated: C 53.79; H 4.80; N 19.30%.

SUMMARY

1. The diethyl mercaptal of β-cyclocitral when heated in the presence of boron trifluoride etherate is converted to 1-ethylmercaptomethylene-2,6,6-trimethyl-2-cyclohexene.

2. Dicarbonyl compounds of the terpene series, which were isolated as the bis-2,4-dinitrophenylhydrazones, were synthesized by the condensation of unsaturated sulfides, obtained from the diethyl acetals of α-ionone, β-ionone and β-cyclocitral, with orthoformic ester.

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