SOME TRANSFORMATIONS OF β-IONONE DIMETHYL KETAL

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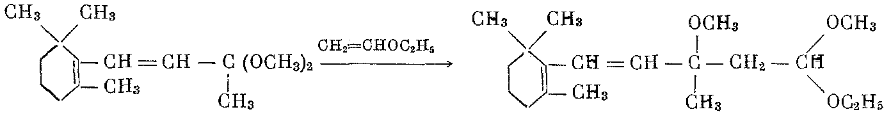
β-Ionone dimethyl ketal (I), synthesized by the general method of obtaining ionone ketals [1] the same as β-ionone diethyl ketal [2], reacts with vinyl ethyl ether to give the acetal of methoxydihydro-β-ionylideneacetaldehyde (II).



(I) (II)

The hydrolysis of acetal (II) gives trans-β-ionylideneacetaldehyde, which contains a small amount of retroionylideneacetaldehyde as impurity [3]. Both aldehydes were isolated as the 2,4-dinitrophenylhydrazones (III, IV), which were identified by their mixed melting points with authentic samples. β-Ionone dimethyl ketal when heated with p-toluenesulfonic acid [2] is converted to 1-(2,6,6-trimethylcyclohexen-1-yl)-3-methoxy-1,3-butadiene (V). The reaction of (V) with the methyl and ethyl esters of orthoformic acid gives 1-(2,6,6-trimethylcyclohexen-1-yl)-3,5,5,5-tetramethoxy-1-pentene (VI) or 1-(2,6,6-trimethylcyclohexene-1-yl)-3,5,5-triethoxy-3-methoxy-1-pentene (VII). The hydrolysis of bis-acetals (VI) and (VII) in the presence of 2,4-dinitrophenylhydrazine hydrochloride gave the bis-2,4-dinitrophenylhydrazone of 5-(2,6,6-trimethylcyclohexen-1-yl)-4-penten-3-on-1-al (VIII), identical with the compound isolated by us when studying the analogous reaction with the thioether of the enol form of β-ionone [4].

EXPERIMENTAL

β-Ionone Dimethyl Ketal (I). A mixture of 90 g of β-ionone [b.p. 128-129° (10 mm); n_D^{20} 1.5195], 300 ml of methyl orthoformate, 450 ml of absolute methanol and 0.5 ml of a 12% solution of hydrogen chloride in absolute alcohol was allowed to stand at room temperature for 24 h. The reaction mass was neutralized with sodium methylate. The alcohol and orthoformic ester were removed by distilling under a slight vacuum, and the residue was fractionally distilled. We obtained 80.5 g (yield 72.5% of theory) of (I) with b.p. 95-97°C (1.5 mm); n_D^{20} 1.4905; d_4^{20} 0.9441. Found %: C 75.31, 75.50; H 10.79, 10.96. $C_{15}H_{26}O_2$. Calculated %: C 75.57; H 11.01.

1-(2,6,6-Trimethylcyclohexen-1-yl)-3-methyl-3,5-dimethoxy-5-ethoxy-1-pentene (II). To 60 g of (I), in 20 min, was simultaneously added from two dropping funnels, 20 ml of a 10% solution of zinc chloride in ethyl acetate and 7.2 g of vinyl ethyl ether. The mixture was stirred for 2.5 h, and then 50 ml of ether and 85 ml of 10% NaOH solution were added, after which the ether solution was separated, dried over potassium carbonate, the ether was distilled off, and the residue was fractionally distilled in vacuo. We obtained 42.5 g of starting (I) and 8 g (yield 25.8% of theory, or 35.1% when based on reacted ketal) of (II) with b.p. 105-107° (0.2 mm); n_D^{20} 1.4810; d_4^{20} 0.9624. Found %: C 72.82, 73.01; H 10.91, 10.95. MR 91.79. $C_{19}H_{34}O_3$. Calculated %: C 73.50; H 11.04. MR 91.73.

β-Ionylideneacetaldehyde. A mixture of 4.4 g of ether acetal (II), 5 ml of 90% phosphoric acid, 40 ml of dioxane and 10 ml of water was heated in a nitrogen stream, in the presence of a trace of hydroquinone, at 85-90° for 3.5 h. The dioxane and water were distilled off during the heating. At the same time, a mixture of dioxane and water (4 : 1) was added to the flask at such a rate that the volume remained constant. The solution was cooled to room temperature, poured into cold water, and shaken with ether. The ether solution was washed with sodium bisulfite solution, then with water, dried over magnesium sulfate, the ether was distilled off, and the residue was fractionally distilled. We obtained 0.95 g (28.6%) of β-ionylideneacetaldehyde with b.p. 100-115° (0.4 mm); n_D^{20} 1.5470. We obtained 0.5 g of the 2,4-dinitrophenylhydrazone from 0.4 g of the aldehyde. Chromatographing on Al_2O_3 and subsequent recrystallization from a mixture of alcohol and ethyl acetate gave: 1) 0.2 g of dark cherry-red crystals of the 2,4-dinitrophenylhydrazone of trans-β-ionylideneacetaldehyde (III) with m.p. 195-196° (from the literature [5]: m.p. 195-196°); 2) 0.02 g of orange-red needles of the 2,4-dinitrophenylhydrozone of retroionylideneacetaldehyde (IV) with m.p. 186-188°; the mixed melting point with the previously synthesized sample of (IV) [3] was not depressed.

1-(2,6,6-Trimethylcyclohexen-1-yl)-3-methoxy-1,3-butadiene (V). A mixture of 12.8 g of (I)., 0.5 ml of quinoline and 0.04 g of p-toluenesulfonic acid was heated under a vacuum of 1 mm for 3 h at 80-90°, and then it was distilled. We obtained 7.9 g (yield 70% of theory) of (V) with b.p. 81-82° (1 mm); n_D^{20} 1.5485. Found %: C 81.11, 81.01; H 10.64, 10.75. $C_{14}H_{22}O$. Calculated %: C 81.50; H 10.75. 1.4 g of methyl alcohol was collected in the trap, cooled with liquid nitrogen.

Reaction of 1-(2,6,6-trimethylcyclohexen-1-yl)-3-methoxy-1,3-butadiene with Orthoformic Esters. To 35 ml of methyl orthoformate was simultaneously added in 2 h, at 20-22°, 8.5 g of (V) and 10 ml of a 10% solution of zinc chloride in ethyl acetate, and then 50 ml of 5% NaOH solution and ether were added. The ether solution was washed with water and then dried over potassium carbonate. After removal of the ether and fractional distillation of the residue we obtained 2.95 g (yield 20.5% of theory) of (VI) with b.p. 123-125° (0.3 mm); n_D^{20} 1.4990. Found %: C 70.02, 70.16; H 9.86, 9.89. $C_{18}H_{32}O_4$. Calculated %: C 69.19; H 10.32. When alcohol solutions of 0.5 g of (VI) and 0.8 g of 2,4-dinitrophenylhydrazine hydrochloride were mixed we obtained 0.85 g of the bis-2,4-dinitrophenylhydrazone (VIII), which after recrystallization from a mixture of chloroform and pyridine had m.p. 245-248°. The mixed melting point with the previously obtained sample of (VIII) [4] was not depressed.

To 28 g of ethyl orthoformate was simultaneously added in 45 min, at 20-22°, 9.8 g of (V) and 10 ml of a 10% solution of zinc chloride in ethyl acetate. The mixture was stirred for 1 h and then worked up in the same manner as described above. We obtained 2.15 g (yield 14.8% of theory) of the bis-acetal (VII) with b.p. 140-145° (0.4 mm); n_D^{20} 1.4905. The bis-2,4-dinitrophenylhydrazone (VIII) had m.p. 246-248° (from pyridine).

CONCLUSIONS

1. β-Ionone dimethyl ketal reacts with vinyl ethyl ether to give the acetal of methoxydihydro-β-ionylideneacetaldehyde, from which the 2,4-dinitrophenylhydrazone of β-ionylideneacetaldehyde was obtained.

2. 1-(2,6,6-Trimethylcyclohexen-1-yl)-3-methoxy-1,3-butadiene, obtained by heating β-ionone dimethyl acetal with p-toluenesulfonic acid, reacts with the methyl and ethyl esters of orthoformic acid to give the corresponding bis-acetals of 5-(2,6,6-trimethylcyclohexen-1-yl)-4-penten-3-on-1-al.

LITERATURE CITED

1. B. M. Mikhailov and L. S. Povarov, Soviet Author's Application No. 778097/23-4.
2. B. M. Mikhailov and L. S. Povarov, Izv. AN SSSR, Ser. khim., 1963, 1144.
3. B. M. Mikhailov and G. S. Ter-Sarkisyan, Izv. AN SSSR, Ser. khim., 1965, 1197.
4. G. S. Ter-Sarkisyan and B. M. Mikhailov, Izv. AN SSSR, Ser. khim., 1965, 561.
5. I. N. Nazarov and Zh. A. Krasnaya, DAN SSSR, 121, 1034 (1958).
