SYNTHESIS OF HYDROTHIOXANTHENES. III*

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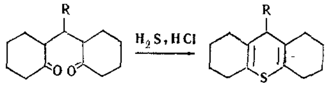
Reaction of alkylidenedicyclohexanones with hydrogen sulfide in polar solvents under the influence of hydrogen chloride or hydrochloric acid has been studied. A preparative route to the synthesis of sym-octahydrothioxanthenes has been established and some of their chemical properties have been studied.

sym-Octahydrothioxanthenes are formed, together with other six-membered tricyclic sulfides, by the reaction of alkylidenedicyclohexanones with sulfides of phosphorus [1–4]. On studying the behavior of methylene-, ethylidene-, and propylidenedi(α, α'-cyclohexanones) to hydrogen sulfide in polar solvents under the influence of hydrogen chloride or hydrochloric acid, we have established that this reaction can be used as a simple preparative method for obtaining sym-octahydrothioxanthenes [1, 5]. The reaction of the alkylidenedicyclohexanones with hydrogen sulfide takes place smoothly at 20° C with a yield of sulfides of 45–77%.



I–III

I R = H; II R = CH$_3$; III R = C$_2$H$_5$

We have already reported the synthesis of the thioxanthene II under the conditions of this reaction [1]; here we deal only with the synthesis and chemical properties of compounds I and III. Compound I has previously [4] been identified as a liquid, and only now have we isolated it in the crystalline state. It forms pale yellow rhombic crystals with mp 38–39.5° C (from nitromethane). On storage in the air and under the influence of light the crystals readily change, deliquescing to form an orange oil. Thin-layer chromatography on alumina of the liquid and crystalline products gives spots at the same level. 9-Ethyloctahydrothioxanthene (III) forms colorless low-melting crystals. The thioxanthenes I and II have absorption maxima in the same region of the UV spectrum as γ-thiopyran [6] (IV): I—λ_{max} 234 nm (log ε 3.82); II—λ_{max} 238 nm (log ε 3.79); IV—λ_{max} 236–238 nm (log ε 3.72).

With perchloric acid, sym-octahydrothioxanthene (I) forms octahydrothioxanthylium perchlorate, a colorless crystalline substance which explodes upon heating but is relatively stable to hydrolysis. As in the case of dehydrogenation over sulfur [4], the dehydrogenation of I over Pd/C at 290° C smoothly yields thioxanthene [7]. The Clemmensen reduction of I gives perhydrothioxanthene [4]. The oxidation of III with hydrogen peroxide in acetic acid solution forms 9-ethyloctahydrothioxanthene 10-dioxide.

The chemical properties of I show that the sym-octahydrothioxanthenes may serve as starting materials for obtaining the previously inaccessible or difficultly accessible sulfides of the perhydrothioxanthene and thioxanthene series which are found in the high-boiling fractions of petroleum [8]. In view of this they are important as model compounds for studying the composition of the organosulfur components of petroleum. The thioxanthenes are also of great interest for the synthesis of important pharmaceutical preparations [9].

EXPERIMENTAL

The alkylidenedicyclohexanones were obtained by the diketone condensation method [1].

Octahydrothioxanthene (I). A solution of 45.3 g (0.22 mole) of methylenedicyclohexanone in 80–100 ml of acetic acid was treated with 0.2 g of hydroquinone and was then saturated with hydrogen sulfide at +4° C until the increase in weight was 3.4 g (~0.1 mole), after which 0.2 ml of concentrated hydrochloric acid was added and saturation with hydrogen sulfide was continued at room temperature until the increase in weight was 7.7 g (~0.22 mole). The colorless oily layer that formed was separated off, the acetic acid solution was poured into water and neutralized with sodium carbonate, and the reaction product was extracted with ether. The combined ethereal extract and oily product were washed with sodium carbonate solution and with water and dried with sodium sulfate. The ether was distilled off. The residue either crystallized directly or the I was isolated by cooling a solution of the reaction mixture in a mixture of methanol and ether (2 : 1) to from −50° to −60° C. Yield 35 g (77%); mp 38–39.5° C (from nitromethane). Readily soluble in benzene, ether, and dioxane. Found, %: C 76.29; 75.47; H 8.51, 8.98; S 15.53, 15.83. Calculated for $C_{13}H_{18}S$, %: C 75.72; H 8.73; S 15.55.

9-Ethyl-sym-octahydrothioxanthene (III). A solution of 11.8 g (0.05 mole) of propylidenedicyclohexanone in 100 ml of ethanol was saturated with hydrogen sulfide at 0° C for 100 minutes. Then hydrogen chloride and hydrogen sulfide simultaneously were passed in for 4 hr. The reaction product was isolated in a similar manner to I. Yield 45%, mp 23–25° C (from a mixture of ethanol and ether, 2 : 1). Found, %: C 76.40, 77.77; H 9.30, 9.17; S 13.01, 13.07. Calculated for $C_{15}H_{22}S$, %: C 76.92; H 9.40; S 13.67. (IR spectrum, ν, cm^{-1}: 675, 768, 820, 845, 1008, 1050, 1075, 1105, 1140, 1178, 1245, 1272, 1342, 1350, shoulder, 1380, 1455, 1650, 1675, 2830–2890 intense broad band with peaks at 2840, 2860, and 2935 with a shoulder at 2970).

sym-Octahydrothioxanthylium perchlorate. One gram of I was dissolved with ice water cooling in a mixture of 7.5 ml of glacial acetic acid and 4 ml of acetic anhydride, and then 1.2 ml of 70% perchloric acid was added dropwise. After 48 hr, 20 ml of ether was added and the crystalline precipitate was separated off and washed with benzene and ether. Mp 120–122° C (from water). Found, %: C 51.31, 51.04; H 5.81, 5.62; Cl 11.96, 11.82. Calculated for $C_{13}H_{17}ClO_4S$, %: C 51.23; H 5.63; Cl 11.66.

Dehydrogenation of I over Pd/C. A mixture of 1 g of I and 1 g of 5% Pd/C was heated in an atmosphere of nitrogen to 290° C over 45 min and at 290° C for 2 hr. The reaction product was extracted with ethanol and then with benzene to give 0.77 g of colorless crystals of thioxanthene which, after recrystallization from ethanol, had mp

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*For part II, see [1].

128–130° C. According to the literature [7], mp 128° C. A mixture with authentic thioxanthene gave no depression of the melting point.

Reduction of sym-octahydrothioxanthene (I). With vigorous stirring, 20 g of zinc dust was added in small portions over 1 hr to 2 g of I emulsified in 150 ml of concentrated hydrochloric acid. The temperature of the reaction mixture rose to 50° C. After all the zinc dust had been added, the mixture was heated in the boiling water bath for another 2 hr. After cooling the reaction mixture to room temperature, a crystalline "crust" formed on the surface. The crystals were separated off and washed with water. A thin-layer chromatogram in alumina showed the presence of two substances in the crystalline product. One gave an intense spot at the level of perhydrothioxanthene, and the other was unidentified. After recrystallization from ethanol, 0.7 g of colorless crystals with mp 68–70° C were isolated. A mixture with authentic perhydrothioxanthene gave no depression of the melting point.

9-Ethyl-sym-octahydrothioxanthene 10-dioxide. A solution of 0.2 g of III in 22 ml of acetic acid was treated with 0.7 ml of hydrogen peroxide (33%). The reaction mixture was heated in the water bath for 15 min and left at 20° C for 24 hr, after which it was poured into water and the colorless crystals that deposited were separated off. Yield 0.13 g, mp 126–127° C (from petroleum ether). Found, %: C 67.70; 67.63; H 8.13, 8.29; S 11.70. Calculated for $C_{15}H_{22}O_2S$, %: C 67.67; H 8.27; S 12.03. IR spectrum: ν, cm^{-1}: 1115, 1130, 1170, 1230, 1265, 1290, 1335, 1390, 1455, 1465, 1680, 2870–2985 broad intense band.

The UV spectra were recorded on SF-4 and SP-700 spectrophotometers in octane and hexane. The IR spectra were recorded on a UR-10 spectrophotometer in paraffin oil.

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