SYNTHESIS OF HYDROTHIOXANTHENES. II*

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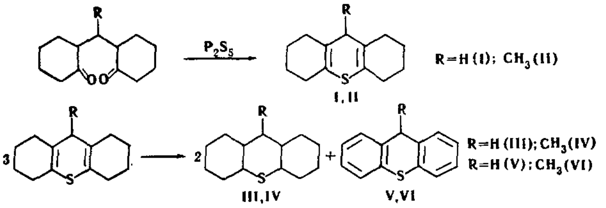
Ethylenedicyclohexanone and phosphorus pentasulfide give 9-methyloctahydrothioxanthene (II) (yield ~37%), a small amount of 9-methylperhydrothioxanthene (IV) (~2%), and 9-methylthioxanthene (VI) (~1%). Reaction with hydrogen sulfide gives a high yield of thioxanthene II (64–65%). The behavior of II in dehydrogenation over Pd/C, and of II and IV to oxidation are investigated. IR spectrum data are given for II and its sulfone.

Up to recently no sym-octahydrothioxanthenes and perhydrothioxanthes had been known. We first prepared the simplest members of the homologous series of these compounds by reacting alkylidenedicyclohexanones with phosphorus sulfides [1, 2]. Alkylidenedicyclohexanones and phosphorus pentasulfide give mixtures of sulfides of the sym-octahydrothioxanthene, perhydrothioxanthene, and thioxanthene series, and it is found that in the case of methylenedicyclohexanone the yield of perhydrothioxanthene is relatively high (25%) [2]. It is possible that the octahydrothioxanthenes first formed can undergo disproportionation:

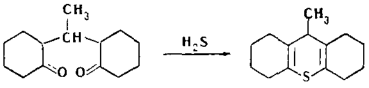


However that is only a preliminary hypothesis.

The present paper gives results, obtained in a study of the reaction of α, α'-ethylidenedicyclohexanone with phosphorus pentasulfide and hydrogen sulfide.

α, α'-Ethylidenedicyclohexanone, like methylenedicyclohexanone, reacts with phosphorus pentasulfide, to give a mixture of sulfides II, IV, and VI, but the main reaction product is 9-methyl-sym-octahydrothioxanthene (II) (yield ~37%); IV and VI are formed only in small amounts (2% and 1% respectively). Such insignificant yields of IV and VI can be explained by the stabilizing effect of the electron-donating methyl group (at C-9) on the molecule of sym-octahydrothioxanthene. This may also explain the stability of thioxanthene II as compared with thioxanthene I towards oxygen of the air and light. Under ordinary conditions I is a compound of low stability. While II is oxidized at 20° C by hydrogen peroxide to the corresponding sulfone, I under similar conditions suffers more profound change, and gives a resinous product. Xanthene II is readily dehydrogenated at 300° C over Pd/C to the known 9-methylthioxanthene (VI), thus confirming the structure. The IR spectrum of II shows the following main frequencies which confirm its structure: 1380, 1445, 1458, 2840, 2870, 2890, 2950, 1690, 1115, 1290 cm^{-1}.*

Ethylidenedicyclohexanone and hydrogen sulfide in ethanol at 20° C are reacted smoothly with hydrogen chloride, to give a high yield (~65%) of hydrothioxanthene II:



II

IV and VI were not formed, as was shown by chromatographing the reaction products.

EXPERIMENTAL

Ethylidenedicyclohexanone was prepared by diketone condensation [3]; n_D^{20} 1. 5180 (the literature gives 1. 5184).

Behavior of α, α'-ethylidenedicyclhexanone towards phosphorus pentasulfide. 111 g (0. 5 mole) α, α'-ethylidenecyclohexanone was dissolved in 111 ml toluene under N at 0° C, and 111 g (0. 5 mole) P_2S_5 added, with vigorous stirring, over a period of 30 min. Then the mixture was carefully heated on a water bath until the onset of a vigorous reaction, and when the reaction ceased, heating was continued for about 2 hr on a water bath. After cooling the top layer which separated was decanted and the thickened portion treated with conc Na_2CO_3 solution, then extracted with benzene. The benzene extract and the decanted part of the reaction products were combined, the solution washed with Na_2CO_3 and water, dried over $MgSO_4$, the solvent distilled off, and the residue vacuum distilled at 127°–143° C (2. 5 mm). 49. 8 g oily material, n_D^{20} 1. 5647, was isolated, and this on cooling solidified almost completely to colorless crystals. 38 g crystalline 9-methyl-svm-octahydrothioxanthene (II) was isolated. TLC on alumina showed the uncrystallized part (11. 8 g) of the reaction product to consist mainly of the 3 sulfides I, IV, and VI. 2 g Oily reaction product was column chromatographed on alumina grade II activity, using octane as eluent and II, IV, and VI were isolated in their individual states.

9-Methyl-sym-octahydrothioxanthene (II), colorless rodlets, mp 61°–62° C (ex EtOH), readily soluble in benzene, ether, and acetone, rather less soluble in MeOH and EtOH. Found: C 76. 40; 76. 36; H 9.06; 9. 015; S 14. 43; 14. 67%; M 210; 215, calculated for $C_{14}H_{20}S$: C 76. 30; H 9. 15; S 14. 55%; M 220. 4.

9-Methylperhydrothioxanthene (IV), also obtained by fractional crystallization of the fraction n_D^{20} 1. 5728, obtained by redistilling the oily material. Yield 20%, colorless plates, mp 128°–129° C (ex EtOH). Found: C 74. 53; 74. 47; H 10. 94; 10. 88; S 14. 00; 13. 94%; M 220; 227, calculated for $C_{14}H_{24}S$: C 75. 00; H 10. 71; S 14. 22%; M 224. 4.

9-Methylthioxanthene (VI) was obtained in 1% yield by chromatographing on alumina, colorless plates, mp 81°–82. 5° C (ex MeOH). The literature gives mp 84. 5° C [4], 74° C [5]. Found: C 78. 98; 79. 04; H 5. 81; 5. 72; S 15. 00; 15. 27%, calculated for $C_{14}H_{12}S$: C 79. 24; H 5. 66; S 15. 09%.

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*For Part I see [2]

*The spectra were measured in CCl_4 solution, and again in vaseline, using a UR-10 instrument.

Dehydrogenation of 9-methyl-sym-octahydrothioxanthene (II). 1.35 g II was mixed with 1.35 g 10% Pd/C in a test tube fitted with a reflux condenser and gas take-off-tube. The dehydrogenation was run in a current of N. The temperature of the reactants was slowly raised (over a period of 1-1/2 hr to 300° C, and held there for 2 hr. The dehydrogenation product was extracted, first with EtOH, then with benzene, and the solvent removed, leaving 1.05 g oily material which crystallized on standing. Yield 0.4 g crystals, which were hexahedral plates, mp 81°-82.5° C (ex MeOH). Undepressed mixed mp with 9-methylthioxanthene, obtained by column chromatography.

Sulfone (VIII) from 9-methyl-sym-octahydrothioxanthene. 0.95 g II was dissolved in 10 ml glacial AcOH, and 3.2 ml 30% H_2O_2 added. The mixture was heated for 5 min on a water bath, kept for 21 hr at room temperature, then poured into water. The crystalline solid was washed with water, and dried. Mass 0.9 g, yield 84.1%, mp 139.5°-141° C (benzene—petrol ether 1:1). Found: C 66.36; 66.56; H 7.70; 8.02; S 12.89; 12.70%, calculated for $C_{14}H_{20}SO_2$: C 66.62; H 7.98; S 12.70%.

Sulfone (VIII) from 9-methylperhydrothioxanthene. 0.25 g VI was dissolved in 6 ml glacial AcOH, 3 ml 30% H_2O_2 added, and the whole heated on a boiling water bath for 2-1/2 hr. The crystals that came down on cooling were filtered off, washed with water, and dried, yield 0.164 g (57.6%), mp 246°-248° C (ex EtOH). Found: C 65.52; 65.36; H 9.52; 9.56; S 12.34; 12.36%, calculated for $C_{14}H_{24}SO_2$: C 65.62; H 9.32; S 12.50%.

Reaction of ethylidenedicyclohexanone to hydrogen sulfide. 111 g (0.5 mole) ethylidenedicyclohexanone was dissolved in 250 ml dry MeOH, and the solution saturated with H_2S for 3 hr at 20° C, after which HCl was passed in as well as H_2S at 20° C for 3 hr. The crystalline precipitate was separated off by decanting the liquid, the crystals washed with Na_2CO_3 solution, then with water, and finally extracted with ether. The ether solution was also washed with Na_2CO_3 solution and water, after which it was dried, and the ether distilled off. The residue partly crystallized. Total mass of crystals isolated 70.55 g (64.1%), colorless rodlets, mp 61°-62° C (ex EtOH), undepressed mixed mp with known II. TLC on alumina showed the oily part of the reaction product isolated to also contain II, as well as unidentified impurities.

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