

SYNTHESIS OF HYDROTHIOXANTHENES. I.

V. G. Kharchenko and T. I. Krupina

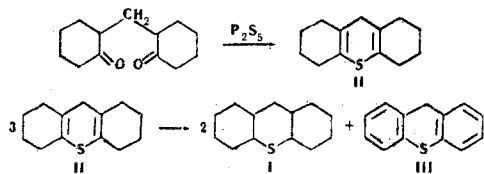
Khimiya Geterotsiklicheskikh Soedinanii, Vol. 3, No. 3, pp. 468-470, 1967

UDC 547.818.6.07

It is shown that methylene dicyclohexanone reacts with phosphorus sulfides to give a mixture of tricyclic 6-membered ring sulfides: perhydrothioxanthene, 1, 2, 3, 4, 5, 6, 7, 8-octahydrothioxanthene, and thioxanthene. The behaviors of perhydrothioxanthene and sym-octahydrothioxanthene toward oxidation, mercuric chloride, and dehydrogenation are investigated.

Continuing research on the chemistry of 1,5-diketones, we showed that alkylidenedicyclohexanones react with phosphorus sulfides to give tricyclic sulfides with 6-membered rings [1]. The present paper gives results obtained in a study of the reaction of methylenedicyclohexanone with phosphorus pentasulfide. The products of this reaction were perhydrothioxanthene (I) (25% yield), thioxanthene (III) (very small amount), and sym-octahydrothioxanthene (II).

The following is one of the possible views of the chemistry of the process. Initially the methylenedicyclohexanone reacts with phosphorus pentasulfide to give sym-octahydrothioxanthene (II), further transformed by irreversible catalysis into perhydrothioxanthene (I) and thioxanthene.



Methylenedicyclohexanone and formamide react similarly when undergoing the Leuckart reaction to give perhydro- and sym-octahydroacridine [2].

Under the reaction conditions II may undergo reduction as well as disproportionation.

The nature of the perhydrothioxanthene obtained is shown by its analytical data, and its dehydrogenation to thioxanthene, and is confirmed by the IR spectrum. A study of some of the chemical properties of I gave results agreeing with its structure. It is readily oxidized quantitatively to a sulfone, forms a mercuric chloride complex, and forms a colorless perchlorate with perchloric acid. It is important to note that perhydrothioxanthene is almost undehydrogenated by sulfur, but is smoothly dehydrogenated by Pd/C, to thioxanthene, though the temperature required is rather high (300°-320°).

Unlike perhydrothioxanthene, sym-octahydrothioxanthene (II) is readily dehydrogenated by sulfur to thioxanthene, hydrogen sulfide being detected even at 138°, which is characteristic of unsaturated cyclic sulfides [3]. An attempt to obtain a sulfone, using the conditions employed for perhydrothioxanthene, was unsuccessful.

Thioxanthene (III) was identified from its analytical data and mixed melting point with authentic synthetic material [4]. The results obtained are of considerable interest, since hitherto tricyclic sulfides have remained difficult to obtain synthetically. We have now demonstrated the possibilities of 1-stage syntheses of the hitherto unknown perhydrothioxanthene and sym-octahydrothioxanthene, the first representatives of hitherto uninvestigated series of tricyclic sulfides.

EXPERIMENTAL

Methylenedicyclohexanone was prepared by diketone condensation [5]. 48.8 g (0.22 mole) P_2S_5 was added, in a N atmosphere, to a solution of 41.2 g (0.2 mole) methylenedicyclohexanone (bp 60°-61.5°) in 60-100 ml of toluene, xylene, or the like. The mixture was heated on a water-bath for 1-2 hr, then the product extracted with ether or benzene.

The solid residue was treated with saturated Na_2CO_3 solution, and also extracted. The bulked extracts were washed with Na_2CO_3 solution, then with water, dried over $MgSO_4$, the solvent distilled off, and the residue vacuum-distilled. The main portion, comprising mixed sulfides, distilled at 117°-128° C (2 mm), yield 20 g (50% reckoning it as tricyclic sulfides). The oily reaction product isolated partly crystallized, either immediately, or after repeated distillation. The crystals obtained corresponded to I, yield 25%. The part which did not crystallize was vacuum-distilled; II distilled at 132°-143° (3 mm), yield 20% (see below); the next cut was taken at 134°-156° (3 mm), n_D^{20} 1.5908, mass 4.1 g, and this partly solidified, giving 0.4 g (1%) III, mp 129°-130° (ex EtOH), undepressed mixed mp with authentic thioxanthene. Found: C 79.04; 78.51; H 5.19; 5.31; S 16.08; 15.82%. Calculated for $C_{13}H_{10}S$, C 78.78; H 5.05; S 16.16%.

Perhydrothioxanthene (I) was a colorless crystalline compound, forming rodlets, mp 70°-71.5° C (ex EtOH), readily soluble in all the ordinary organic solvents: acetone, benzene, dioxane, etc. Found: C 74.41; 74.26; H 10.56; 10.53; S 15.09; 15.03%; M 203; 207. Calculated for $C_{13}H_{22}S$: C 74.29; H 10.48; S 15.24%; M 210. IR spectrum*: 668, 701, 1334, 1474, 2845, 2915 cm^{-1} .

Dehydrogenation of perhydrothioxanthene (I). 1.0115 g I and 1 g Pd/C (5%) were heated together in CO_2 ,

*IR spectra were determined in CCl_4 , using an IKS-14 instrument.

in a vessel attached to a gasometer. The H_2S evolved was absorbed in a $Cd(OAc)_2$ solution. Dehydrogenation was effected at $300^\circ-320^\circ C$, for 2 hr. The hydrogen collected amounted to 651 ml (STP), calculated 647 ml (STP). 0.5 g crystalline material mp $129^\circ-130^\circ$ (ex EtOH) was isolated from the reaction products, mixed up with authentic thioxanthene $129^\circ-130^\circ$. An attempt to dehydrogenate I with sulfur at $200^\circ-210^\circ$ led to its being recovered almost completely from the end products.

Perhydroxanthene sulfone. Prepared by adding 4 ml 30% H_2O_2 to a solution of 1.05 g (0.005 mole) I in 20 ml glacial AcOH. The mixture was heated on a boiling water-bath for 2 hr. The product formed colorless crystals mp $146^\circ-147^\circ C$ (ex EtOH). Yield 100%. Found: C 64.13; 64.03; H 9.19; 8.92; S 12.90; 12.57%. Calculated for $C_{13}H_{22}SO_2$: C 64.46; H 9.09; S. 13.22%.

I mercuric chloride complex. 0.39 g (1.5 mmole) $HgCl_2$ in 12 ml ether was added to a solution of 0.2 g (1 mmole) perhydrothioxanthene in 2 ml dry ether. There was immediate formation of a copious precipitate, which was filtered off and washed with ether, yield 0.43 g, mp $192^\circ-193.5^\circ C$. Found: Hg 41.66; 41.60%. Calculated for $C_{13}H_{22}S \cdot HgCl_2$: Hg 41.51%.

Perhydrothioxanthene perchlorate. A solution of 0.5 g (2.5 mmole) I in 5 ml ether was mixed with 3 ml Ac_2O , the mixture cooled to -70° , and 0.6 g (4 mmole) 70% $HClO_4$ added. Yield 0.53 g, colorless prisms, mp $186^\circ-187^\circ C$ (ex AcOH). Found: Cl 10.80; 10.83%. Calculated for $C_{13}H_{22}S \cdot HClO_4$: Cl 11.45%.

Sym-octahydrothioxanthene (II). This was an unstable pale-yellow liquid, which readily underwent change in air, turning yellow, bp $132^\circ-134^\circ$ (3 mm).

Found: C 75.78; 75.31; H 9.10; 9.17; S 15.88; 15.54%; M 200; 204. Calculated for $C_{13}H_{18}S$: C 75.73; H 8.74; S 15.53%; M 206. IR spectrum, cm^{-1} : 683, 746, 1459, 2845, 2915, 1588 weak, 1618 weak, 1664 weak.

Dehydrogenation of sym-octahydrothioxanthene (II). 0.8 g (4 mmole) II and 0.6 g (0.019 g-at) finely powdered S were heated together in CO_2 for 2 hr. Evolution of H_2S started at 138° , the temperature was gradually raised to 250° , and held at that temperature for about 5 min. 0.016 mole H_2S was evolved (calculated 0.0155 mole). During the dehydrogenation, long acicular crystals sublimed, mp $126^\circ-128^\circ C$ (ex EtOH). Mixed mp with authentic thioxanthene was not depressed.

Investigation of the bactericidal properties of sym-octahydrothioxanthene (II), showed it to be somewhat bactericidal in respect of Gram-positive bacteria (*Staph. aureus*) at dilution 1:200.

REFERENCES

1. V. G. Kharchenko, T. I. Krupina, S. K. Klimenko, and A. A. Rassudova, *ZhOrKh*, **1**, 2245, 1965.
2. M. N. Tilichenko, V. I. Vysotskii, and V. G. Kharchenko, *Uch. zap. SGU, vyp. khim.*, **71**, 159, 1959.
3. P. Plattner, *New Methods of Preparative Organic Chemistry* [Russian translation], IL, Moscow, 172, 1950.
4. C. Graebe and O. Schultets, *Ann.* **263**, 1, 1891.
5. M. N. Tilichenko and V. I. Vysotskii, *Uch. zap. Yakutsk. univ.*, **8**, 27, 1961.

4 October 1965

Saratov Polytechnic Institute