SYNTHESIS OF HYDROTHIOXANTHENES

IX.* DISPROPORTIONATION OF 9-ALKYL- AND 9-ARYL-sym-OCTAHYDROTHIOXANTHENES WITH HYDRIDE ION TRANSFER

V. G. Kharchenko and A. A. Rassudova

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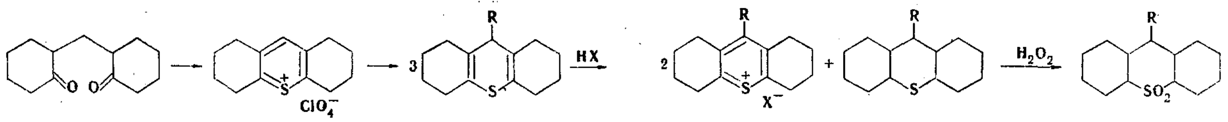
9-Alkylaryl- and 9-aryl-sym-octahydrothioxanthenes disproportionate with hydride ion transfer under the influence of protic acids to give 9-methyl-, 9-ethyl-, 9-propyl-, 9-phenyl-, and 9-(p-tolyl)perhydrothioxanthenes and their sulfones.

To date only a small number of two-ring 1,5-diketones are known. Only methylene-2,2'-dicyclohexanone is preparatively accessible [1].



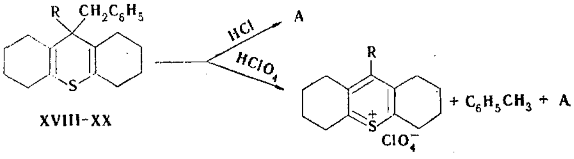
I II III-VII XIII-XVII VIII-XII VIIIa-XIIa

Considering the importance of perhydrothioxanthenes for petrochemistry as standard compounds for the study of the sulfurous composition of oils and products obtained from the refining of them [2], we studied the possibility of synthesizing them from methylenedicyclohexanone (I). Compound I reacts with hydrogen sulfide and perchloric acid to give sym-octahydrothioxanthylium perchlorate (II), which readily reacts with the Grignard reagent to give 9-R-sym-octahydrothioxanthenes (III-VII). sym-Octahydrothioxanthylium iodide and chloride are also capable of reacting with the Grignard reagent. 9-R-sym-Octahydrothioxanthenes III-VII disproportionate under the influence of HCl, $HClO_4$, CF_3COOH, and $FeCl_3$/HCl with hydride ion transfer to give mixtures of the corresponding salts (XIII-XVII) and perhydrothioxanthenes VIII-XII.

This method is a general one and can be used to obtain both 9-alkyl- and 9-arylperhydrothioxanthenes.

9-Phenyl- and 9-(p-tolyl)-sym-octahydrothioxanthenes (VI and VII) do not change under the influence of hydrogen chloride. They disproportionate only under the influence of CF_3COOH and $HClO_4$.

9-Benzyl-9-R-sym-octahydrothioxanthenes (XVIII-XX) and 9-cyclohexyl-sym-octahydrothioxanthene (XXII) do not form the corresponding perhydrothioxanthenes under the influence of $HClO_4$ and $FeCl_3$/HCl, but the benzyl group is cleaved to give the corresponding sym-octahydrothioxanthylium salt, toluene, and a 9-benzyl-9-R-sym-octahydrothioxanthene isomer (A). The A isomer of the corresponding 9-benzyl-9-R-



XVIII-XX II, XVI, XXI

II, XVIII R=H; XIX, XXI R=CH_3; XVI, XX R=C_6H_5

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*See [7] for communication VIII.

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TABLE 1. 9-R-Perhydrothioxanthenes and Their Sulfones

Comp.	R	mp, °C	Empirical formula	Found, %			Calc., %			νSO, cm^{-1}	Yield, %
				C	H	S	C	H	S		
IX	C_2H_5	111,5—113	$C_{15}H_{26}S$	75,5	10,6	13,5	75,6	10,9	13,4	1100, 1138, 1150,	20
IXa	C_2H_5	196—197	$C_{15}H_{26}O_2S$	66,3	9,5	11,7	66,7	9,6	11,8	1288, 1312	74
X	C_3H_7	Liquid n_D^{20} 1,5333	$C_{16}H_{28}S$	76,7	10,7	12,2	76,2	11,1	12,7	1100, 1140, 1150, 1288, 1308,	11
Xa	C_3H_7	147—149	$C_{16}H_{28}O_2S$	67,5	10,0	10,9	67,6	9,9	11,3	1312	41
XI	C_6H_5	172,5—174	$C_{19}H_{26}S$	79,5	9,0	11,0	79,7	9,1	11,2		12
XIa	C_6H_5	180—183	$C_{19}H_{26}O_2S$	71,8	8,5	9,7	71,7	8,2	10,2	1100, 1138, 1145,	80
XII	$C_6H_4CH_3$	165—167	$C_{20}H_{28}S$	80,5	9,7	10,3	80,0	9,3	10,7	1278, 1308	10

sym-octahydrothioxanthene is obtained in high yield by the action of hydrogen chloride, and cleavage of the benzyl group is not observed. The nature of the A isomer is under investigation.

The structures of perhydrothioxanthenes VIII-XII were confirmed by the IR spectra and by chemical means. In contrast to the spectra of sym-octahydrothioxanthenes III-VII, the spectra of perhydrothioxanthenes VIII-XII and their sulfones (VIIIa-XIa) do not contain absorption bands of double bonds at 1600-1700 cm^{-1}. The IR spectra of sulfones VIIIa-XIa contain several very intense absorption bands at 1100-1150 and 1288-1327 cm^{-1} and were assigned to the symmetrical and asymmetrical stretching vibrations of S$-$O in SO_2 (see Table 1).

The structures of these compounds are confirmed by the conversion of 9-methyl- and 9-phenylperhydrothioxanthenes to the known corresponding thioxanthenes [3] during dehydrogenation over Pd/C. 9-R-sym-Octahydrothioxanthylium salts XIII-XVII and XXI were identified by comparison with genuine samples [4].

EXPERIMENTAL

Disproportionation of 9-Ethyl-sym-octahydrothioxanthene (IV). A solution of 3 g of ferric perchlorate in 10 ml of concentrated HCl was added by drops to 1.4 g (0.066 mole) of sulfide IV in 2 ml of acetic anhydride, and the mixture was heated for 1 h and allowed to stand for 20-24 h. The precipitated 9-ethyl-sym-octahydrothioxanthylium chloroferrate (XIV) was separated and washed with acetic acid and ether to give 1.6 g (62%) of a product with mp 101-102° (from acetic acid). Evaporation of the mother liquor and the ether solutions gave 0.29 g (20%) of colorless crystals of 9-ethylperhydrothioxanthene (IX) with mp 111.5-113° (from alcohol). sym-Octahydrothioxanthenes III and V disproportionate with hydride ion transfer under similar conditions. The yields of products of the disproportionation of III and V were as follows: 9-methylperhydrothioxanthene (VIII) 15%, 9-methyl-sym-octahydro-9-methylperhydrothioxanthene tetrachloroferrate (XIII) 47%, 9-propylperhydrothioxanthene (X) 11%, and 9-propyl-sym-octahydrothioxanthylium tetrachloroferrate (XV) 60%.

Disproportionation of 9-Phenyl-sym-octahydrothioxanthene (VI). A total of 22 ml of 70% perchloric acid was added in small portions to 10 g (0.035 mole) of sulfide VI in 80 ml of acetic acid, and the mixture was heated on a water bath for 30 min. It was then allowed to stand for 20-24 h and diluted with ether to give a colorless precipitate. The precipitate was separated and washed with ether to give 6.5 g (48%) of 9-phenyl-sym-octahydrothioxanthylium perchlorate (XVI) with mp 173-175° (reprecipitation from chloroform by the addition of ether). The ether filtrate was washed with sodium carbonate solution and water and dried. The ether was evaporated, and the residue was crystallized to give 1.2 g (12%) of 9-phenylperhydrothioxanthene (XI) with mp 172.5-174° (from alcohol).

9-(p-Tolyl)-sym-octahydrothioxanthene (VII) disproportionated under similar conditions to give 9-(p-tolyl)perhydrothioxanthene (XII) in 10% yield and 9-tolyl-sym-octahydrothioxanthylium perchlorate (XVII) in 60% yield.

9-Phenylperhydrothioxanthene S,S-Dioxide (XIa). A 10-ml sample of hydrogen peroxide was added to a suspension of 0.8 g of sulfide XI in 9 ml of acetic acid, and the mixture was heated on a water bath for 30-40 min and allowed to stand for 24 h. The precipitate was removed by filtration and washed with water and cold alcohol to give 0.71 g (80%) of a product with mp 180-183°.

9-Ethylperhydrothioxanthene S,S-dioxide (IXa) and 9-propylperhydrothioxanthene S,S-dioxide (Xa) (Table 1) were similarly obtained.

Isomerization of 9-Benzyl-sym-octahydrothioxanthene (XVIII). A solution of 0.296 g (0.001 mole) of 9-benzyl-sym-octahydrothioxanthene in 15 ml of acetic acid was saturated with hydrogen chloride for 1.5 h, after which the mixture was allowed to stand at 20° for 48 h. The precipitate of isomer A was removed by filtration, and the filtrate was poured into water. The aqueous mixture was extracted with ether, and the ether extracts were washed with water and dried. The ether was removed by distillation to give an additional amount of isomer A. The yield of product with mp 136.5-138° (from alcohol) was 0.26 g (89%). Found,%: C 81.0; H 8.4; S 11.2. Mol. wt., 294. Calculated,%: C 81.1; H 8.1; S 10.8. Mol. wt., 296.

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