SYNTHESIS OF HYDROTHIOXANTHENES. VII*.

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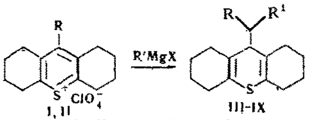
On reaction with Grignard compounds, sym-octahydrothioxanthylium and 9-methyl-sym-octahydrothioxanthylium perchlorates form 9-mono- and 9,9-disubstituted sym-octahydrothioxanthenes. The reactions of the new sym-octahydrothioxanthene with perchloric acid and ferric chloride has been studied. The elimination of the benzyl group of 9-benzyl-sym-octahydrothioxanthene on salt formation has been observed.

We have previously shown that 9-substituted sym-octathioxanthenes are formed by the reaction of bicyclic 1,5-diketones with hydrogen sulfide [2,3] or phosphorus pentasulfide [3–5]. However, at the present time only a few bicyclic 1,5-diketones are preparatively accessible. In order to broaden the possibility of the synthesis of 9-substituted sym-octahydrothioxanthenes, we have studied the reaction of the readily accessible sym-octahydrothioxanthylium and 9-methyl-sym-octahydrothioxanthylium perchlorates (I and II) with Grignard reagents.



I, II III–IX

R = H, CH$_3$; R' = Alk, Ar

By means of thin-layer chromatography on alumina it was found that the nucleophilic addition of a Grignard reagent takes place without the formation of the possible isomeric sulfides.

The structure of the sym-octahydrothioxanthenes III–V was confirmed by their identity with the authentic sulfides [1–4] and the identity of the respective sulfones.

When IV–IX were oxidized with hydrogen peroxide in acetic acid solution with heating, the corresponding sulfones XIX–XXIV were obtained for the first time. We previously discovered a disproportionation reaction with the transfer of hydrogen in 9-alkyl-sym-octahydrothioxanthenes [6] on reaction with perchloric acid and ferric chloride. We have attempted to extend these reactions to the octahydrothioxanthenes VI, VII, and IX. The reaction of VI and IX gave high yields of the corresponding salts XII and XV. It is possible that the nature of the salt-forming reaction between VI and IX and HClO$_4$ and FeCl$_3$ is different from that in 9-alkyl-sym-octahydrothioxanthenes.

Instead of undergoing disproportionation with hydrogen transfer, with perchloric acid and ferric chloride 9-benzyl-sym-octahydrothioxanthene (VIII) lost its benzyl group, forming the perchlorate I and sym-octahydrothioxanthylium tetrachloroferrate (X) and a sulfide isomeric with 9-benzyl-sym-octahydrothioxanthene. We have not yet definitively established the nature of the isomerization of VII. The elimination of the benzyl group in the reaction of VII with HClO$_4$ and FeCl$_3$ is similar to the known [7] elimination of the benzyl group in the reaction of 9-benzylthioxanthene with ferric chloride. The tetrachloroferrates XI, XII, and XVIII smoothly take part in exchange reactions with potassium iodide, forming the corresponding sym-octa-hydrothioxanthylium iodides (XIV, XV, XVIII).

The structure of 9-benzyl-sym-octahydrothioxanthene (VII) was confirmed by its dehydrogenation over Pd/C at 220–290° C to the known [7] 9-benzylthioxanthene.

EXPERIMENTAL

The 9-mono- and 9,9-disubstituted sym-octahydrothioxanthenes III–IX (see Table 1). Over a period of 20 min, 0.037 mole of the perchlorate I or II [6] in the dry form or as a suspension in ether was added to a Grignard reagent (from 0.075 g-at. of magnesium and 0.076 mole of halogen derivative) in 150 ml of ether. The reaction mixture was boiled for 2–4 hr, the ethereal solution was decanted off, and the residue was decomposed with ammonium chloride and extracted with ether. The ethereal solutions were combined, washed with water, and dried, and the ether was

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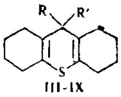
*For part VI, see [1].

Table 1


III-IX

and


XIX-XXIV

Compound	R	R′	Mp, °C	Empirical formula	Found, %			Calculated, %			IR spectra* in the 1700-1500-cm^{-1} region, and ν_{SO} in SO_2	Yield, %
					C	H	S	C	H	S		
III	H	CH_3	60—61**	$C_{14}H_{20}S$							1650. 1674	55
IV	H	C_2H_5	23—25	$C_{15}H_{22}S$	76.4 77.8	9.3 9.2	13.0 13.1	76.9	9.4	13.7	1650. 1675	88
V	H	n-C_3H_7	Liquid n_D^{20} 1,5540	$C_{16}H_{24}S$	77.38 77.50	9.4 9.3	13.2 13.2	77.4	9.7	12.9	1642. 1682	87
VI	H	C_6H_5	101.5—103	$C_{19}H_{21}S$	80.71 80.86	7.8 7.9	11.6 11.4	80.9	7.8	11.4	1550. 1575, 1599, 1638. 1660	66
VII	H	$C_6H_5CH_2$	109—110	$C_{20}H_{24}S$	81.52 81.46	7.8 8.2	10.4 10.7	81.0	8.2	10.8	1500. 1560, 1610, 1640. 1655	95
VIII	CH_3	$C_6H_5CH_2$	52—53	$C_{21}H_{26}S$	81.52 81.61	8.4 8.4	9.9 10.3	81.2	8.4	10.3		80
IX	H	p-$CH_3C_6H_4$	133—135	$C_{20}H_{24}S$	81.31 80.97	8.4 8.4	11.1 11.2	81.0	8.2	10.8		51
XIX	H	C_2H_5	126—127**	$C_{15}H_{22}SO_2$							1680. 1295, 1275, 1140. 1120	60
XX	H	n-C_3H_7	144—146	$C_{16}H_{24}SO_2$	68.5 68.3	8.7 8.6	11.6 11.7	68.6	8.5	11.4		79
XXI	H	C_6H_5	192—193	$C_{19}H_{21}SO_2$	72.5 72.4	7.2 7.4	10.0 10.1	72.6	7.1	10.2		58
XXII	H	$C_6H_5CH_2$	173—175	$C_{20}H_{24}SO_2$	73.5 73.2	7.7 7.6	9.4 9.4	73.2	7.3	9.8		96
XXIII	CH_3	$C_6H_5CH_2$	138.5—140.5	$C_{21}H_{26}SO_2$	73.4 73.4	7.9 7.9	9.3 9.2	73.6	7.7	9.4		84
XXIV	H	p-$CH_3C_6H_4$	226—227.5	$C_{20}H_{24}SO_2$	73.0 73.1	7.3 7.3	10.0 10.1	73.2	7.3	9.8		76

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*The IR spectra were taken on a UR-10 spectrometer in Nujol.

**Identified by mixed melting points with authentic samples.

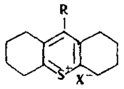
distilled off. The residue was crystallized or distilled in vacuo. The sulfides VI–IX were recrystallized from ethanol.

The oxidation of the sulfides IV–IX with hydrogen peroxide [3] gave the colorless sulfones XIX–XXIV, which were purified by recrystallization from ethanol. The sulfides III–IX and the sulfones XIX–XXIV are readily soluble in benzene, ether, tetrahydrofuran, chloroform, dichloroethane, and acetone. They are sparingly soluble in ethanol and gasoline.

9-Propyl-sym-octahydroxanthylium tetrachloroferrate (XI). A solution of 2 g (0.008 mole) of V in 2.9 mole of acetic anhydride was treated with 4.28 g (0.026 mole) of ferric chloride in 14.5 ml of conc HCl and the reaction mixture was allowed to stand for 24 hr. Then the precipitate was separated off and washed on the filter with acetic acid and ether. This gave 2.2 g (61%) of yellow-green needles.

The tetrachloroferrates XII and XVII were obtained similarly (Table 2).

Table 2



Compound	R	X	Mp, °C*	Empirical formula	Found, %			Calculated, %			Yield, %
					Cl	I	S	Cl	I	S	
XI	n-C_3H_7	$FeCl_4$	85—86	$C_{16}H_{23}Cl_4FeS$	32,2; 32,0		7,0; 7,1	31,9		7,2	61
XII	C_6H_5	$FeCl_4$	102—103.5	$C_{19}H_{21}Cl_4FeS$	29,6; 29,3		7,0; 6,7	29,7		6,7	60
XIII	C_6H_5	ClO_4	115—116	$C_{19}H_{21}ClO_4S$	9,4; 9,5		8,5; 8,8	9,3		8,4	85
XIV	n-C_3H_7	I	120—123	$C_{16}H_{23}IS$		33,9; 34,1	8,8; 8,8		33,7	8,6	60
XV	C_6H_5	I	141—143	$C_{19}H_{21}IS$		31,4; 31,6	7,6; 7,6		31,1	7,8	54
XVI	p-$CH_3C_6H_4$	ClO_4	186—188	$C_{20}H_{23}ClO_4S$	9,0; 8,9		8,5; 8,4	9,0		8,1	60
XVII	p-$CH_3C_6H_4$	$FeCl_4$	144—146	$C_{20}H_{23}Cl_4FeS$	28,8; 28,8		6,5; 6,6	28,8		6,5	45
XVIII	p-$CH_3C_6H_4$	I	120—122	$C_{20}H_{23}IS$		30,2; 30,3	7,6; 7,8		30,1	7,6	56

*The perchlorates consisted of colorless, the tetrachloroferrates of yellow-green, and the iodides of brown or light brown crystals insoluble in ether, benzene, or gasoline, and soluble in chloroform, dichloroethane, and acetic acid.

9-Propyl-sym-octahydrothioxanthylium iodide (XIV). To a solution of 0.3 g (0.67 mole) of XI in 2 ml of acetone was added a solution of 0.56 g (3.4 mM) of KI in 1.5 ml of water, and then 30 ml of water. The brown crystalline precipitate of the iodide XIV was separated off and washed with water. The iodides XV and XVIII were obtained similarly (Table 2).

9-Phenyl-sym-octahydrothioxanthylium perchlorate (XIII). With ice cooling, 1.75 ml of 70% perchloric acid was added to a solution of 0.5 g (1.8 mM) of VI in 6 ml of acetic acid and 5 ml of acetic anhydride. The reaction mixture was heated at 40–50° C for 10 min and was kept at 20° C for 12–15 hr, and then 50 ml of ether was added, and 0.57 g (85%) of the perchlorate XIII separated out. The perchlorate XV was obtained similarly (Table 2).

9-Benzylthioxanthene. A mixture of 1 g (0.32 mM) of VII and 1.5 g of 5% Pd/C was heated in an atmosphere of nitrogen at 220–290° C for 3 hr 30 min. The reaction product was extracted with ethanol, and evaporation of the extract yielded 0.8 g of residue. After several recrystallizations, 0.15 g (16%) of colorless crystals with mp 131–133.5° C (from ethanol) were obtained; according to the literature [7], mp 127° C. Found, %: C 83.03; 83.13; H 5.06, 5.40; S 10.98, 10.80. Calculated for $C_{20}H_{16}S$, %: C 83.33; H 5.55; S 11.11.

Reaction of 9-benzyl-sym-octahydrothioxanthene (VII) with perchloric acid. With stirring, 1.4 ml of 70% perchloric acid was added in small portions to a suspension of 0.5 g (1.7 mM) of VII in 6.2 ml of acetic acid and 2.1 ml of acetic anhydride, and the mixture was heated in a water bath until VII had dissolved (~20 min), and, after cooling, the nonsalt part of the reaction product was extracted with petroleum ether. The petroleum ether was separated off and the acetic acid solution was treated with a mixture of ether (50 ml) and benzene (10 ml), which gave a precipitate of 0.25 g (49%) of colorless crystals of the perchlorate I, mp 119–121° C (reprecipitated with ether from dichloroethane). A mixture with authentic sym-octahydrothioxanthylium perchlorate [6] melted without depression. Evaporation of the petroleum ether extract yielded a substance with mp 137.5–139° C (ethanol), yield 0.12 g (25%). Found, %: C 81.01, 81.00; H 8.42, 8.20; S 10.83, 11.16. Mol wt (cryoscopy in benzene) 294, 291. Calculated for $C_{20}H_{24}S$, %: C 8.11; H 8.11; S 10.81. Mol wt 296. IR spectrum (in Nujol), cm^{-1}: 1500, 1592, 1605, 1620, 1655–1660. Oxidation with hydrogen peroxide formed a sulfone with mp 222–224° C (petroleum ether). Found, %: C 73.65, 73.60; H 7.61, 7.70; S 9.32, 9.40. Calculated for $C_{20}H_{24}SO_2$, %: C 73.17; H 7.32; S 9.75.

Reaction of 9-benzyl-sym-octahydrothioxanthene (VII) with ferric chloride. With stirring, 1.4 g of ferric chloride in 2.6 ml of conc HCl was added in small portions to a suspension of 0.3 g (0.001 mole) of VII in 6 ml of acetic anhydride, and the mixture was heated in the water bath for about 10 min until the VII had dissolved. On cooling, yellowish green crystals deposited in an amount of 0.18 g (44%), mp 85–86.5° C (from acetic acid). A mixture with authentic [6] sym-octahydrothioxanthylium tetrachloroferrate melted without depression. The filtrate yielded 0.1 g (33%) of a substance with mp 137.5–139° C identical with that obtained by the reaction of VII with perchloric acid.

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