SYNTHESIS OF HYDROTHIOXANTHENES

VIII.* REACTION OF ALKYLIDENEDICYCLOHEXANONES WITH PHOSPHORUS PENTASULFIDE

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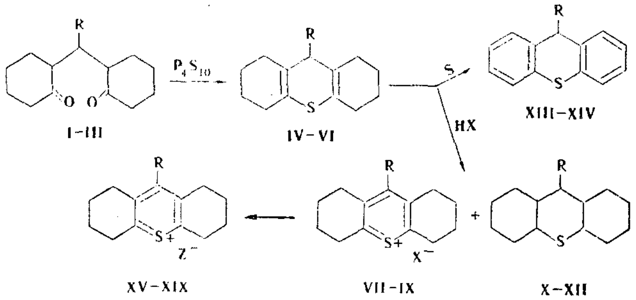
Alkylidenedicyclohexanones I-III react with phosphorus pentasulfide in an inert solvent to form sym-octahydrothioxanthenes, which, under the influence of the acid products of the decomposition of phosphorus pentasulfide, are converted to perhydrothioxanthenes and sym-octahydrothioxanthylium salts.

As was previously reported [2], the corresponding sym-octahydrothioxanthenes and thioxanthenes were isolated from the reaction of phosphorus pentasulfide with toluene solutions of alkylidenedicyclohexanones.

A further study of the reactions of alkylidenedicyclohexanones I-III with phosphorus pentasulfide in pyridine, toluene, and xylene with hydrogen sulfide and hydrogen chloride in acetic acid made it possible to specify more accurately the mechanism of the reaction. The data obtained are evidence that the disproportionation of sym-octahydrothioxanthenes (IV-VI) proceeds with transfer of a hydride ion during salt formation rather than via the principle of irreversible catalysis [2]. It was established that the primary products of the reaction of diketones I-III with phosphorus pentasulfide in an inert solvent (toluene, etc.) are sym-octahydrothioxanthenes (IV-VI). Under the influence of the acidic reagents (H_3PO_3S, $H_3PO_2S_2$, etc.) that are produced during the hydrolysis of phosphorus pentasulfide under the reaction conditions, they disproportionate with hydrogen transfer, and sym-octahydrothioxanthylium salts (VII-IX) and perhydrothioxanthenes (X and XI) are formed. The presence of a small amount (about 1%) of thioxanthenes (XIII and XIV) in the reaction products can evidently be explained by the ease of dehydrogenation of IV and V over sulfur, which may be present in the phosphorus pentasulfide or may develop during its decomposition. In fact, IV undergoes dehydrogenation over sulfur at about 130°C [2].



I, IV, VII, X, XIII, XV, XVII R=H; II, V, VIII, XI, XIV, XVI, XVIII $R=CH_3$; III, VI, IX, XII, XIX $R=C_2H_5$; XV, XVI $Z^-=ClO_4^-$; XVII-XIX $Z^-=FeCl_4^-$

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*See [1] for communication VII.

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TABLE 1. Conditions and Products of the Reaction of sym-Octahydrothioxanthenes (IV-VI) with Acids*

Starting compound	Solvent	Amt. of solvent, ml	Amount of acid	Reaction temp., °C	React. time, h	Reaction products (yield, %)
IV	Acetic anhydride	3	1,5 ml 70% $HClO_4$	20	24	X (20); XV (51)
IV	Acetic acid	8,5	3g $FeCl_3 \cdot 3H_2O$ in 6 ml conc.HCl	90—100	5 min	X (19); XVII (52)
IV	Acetic acid Acetic anhydride	12 2	1 ml 85% H_3PO_4	20	24	X (20); VII†
IV	Without a solvent	—	3 g P_2O_5 in 1,5 ml H_2O	100	1,5	X (25); VII†
IV	Acetic acid	5	Saturation with gaseous HCl for 2 h	20	48	X (15); XX (60)
V	Without a solvent	—	10 ml 60% $HClO_4$	90—100	6,5	XI (15); XVI (54)
V	Acetic anhydride	2	3 g $FeCl_3 \cdot 3H_2O$ in 6 ml conc.HCl	100	1	XI (16); XVIII (51)
V	Acetic acid	5	Saturation with gaseous HCl for 2 h	20	48	XI (15); XXI (57)
VI	Acetic acid	2	2,8 g $FeCl_3 \cdot 3H_2O$ in 10 ml of conc. HCl	90—100	1	XII (21); XIX (58)

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*Data calculated on the basis of 0.005 mole of the starting sulfide are presented in the table.

† The mixture of sym-octahydrothioxanthylium phosphates and thio- and dithiophosphates that develops is converted to sym-octahydrothioxanthylium perchlorate (XV), the yield of which is 40-50% based on the starting sym-octahydrothioxanthene (IV).

TABLE 2. Characteristics of the Compounds Obtained

Comp.	Name	mp, °C	Empirical formula
IV	sym-Octahydrothioxanthene	38—39,5	$C_{13}H_{18}S$
V	9-Methyl-sym-octahydrothioxanthene	61—62	$C_{14}H_{20}S$
VI	9-Ethyl-sym-octahydrothioxanthene	23—25	$C_{15}H_{22}S$
X	Perhydrothioxanthene	70—71,5	$C_{13}H_{22}S$
XI	9-Methylperhydrothioxanthene	127—129	$C_{14}H_{24}S$
XII	9-Ethylperhydrothioxanthene	111,5—113	$C_{15}H_{26}S$
XIII	Thioxanthene	129—130	$C_{13}H_{10}S$
XIV	9-Methylthioxanthene	81—82,5	$C_{14}H_{12}S$
XV	sym-Octahydrothioxanthylium perchlorate	120—122	$C_{13}H_{17}ClO_4S$
XVI	9-Methyl-sym-octahydrothioxanthylium perchlorate	90—92	$C_{14}H_{19}ClO_4S$
XVII	sym-Octahydrothioxanthylium tetrachloroferrate	85—86,5	$C_{13}H_{17}Cl_4FeS$
XVIII	9-Methyl-sym-octahydrothioxanthylium tetrachloroferrate	97,5—99	$C_{14}H_{19}Cl_4FeS$
XIX	9-Ethyl-sym-octahydrothioxanthylium tetrachloroferrate	101,5—102	$C_{15}H_{21}Cl_4FeS$
XX	sym-Octahydrothioxanthylium chloride	95—97	$C_{13}H_{17}ClS$
XXI	9-Methyl-sym-octahydrothioxanthylium chloride hydrochloride	155—157	$C_{14}H_{19}ClS \cdot HCl$

TABLE 2 (continued)

Comp.	Found, %				Calculated, %				Yield, %
	C	H	S	Cl	C	H	S	Cl	
IV	75,8	9,1	15,9	—	75,7	8,7	15,3	—	65
V	76,4	9,1	14,5	—	76,3	9,2	14,6	—	52
VI	76,4	9,3	13,2	—	76,9	9,4	13,7	—	45
X	74,3	10,6	15,1	—	74,3	10,5	15,2	—	20
XI	74,5	10,9	14,0	—	74,9	10,8	14,3	—	15
XII	75,5	10,6	13,5	—	75,6	10,9	13,4	—	21
XIII	78,6	5,3	16,1	—	78,8	5,1	16,2	—	~1
XIV	79,1	5,8	15,1	—	79,2	5,7	15,1	—	~1
XV	51,3	5,6	11,8	—	51,2	5,6	11,7	—	51
XVI	—	—	9,7	11,1	—	—	10,1	11,1	54
XVII	—	—	7,6	35,3	—	—	7,9	35,2	52
XVIII	—	—	7,5	34,5	—	—	7,7	34,1	51
XIX	—	—	7,4	32,8	—	—	7,4	32,9	58
XX	—	—	13,0	15,1	—	—	13,3	14,8	60
XXI	—	—	10,9	14,1	—	—	11,0	14,4	57

The 9-R-sym-octahydrothioxanthylium salts (VII-IX) are quite soluble in water and are apparently a complex mixture of phosphates and thio- and dithiophosphates. Compounds VII-IX were identified through the corresponding perchlorates (XV and XVI) and tetrachloroferrates (XVII-XIX) of the sym-octahydrothioxanthylium ion.

The only products from the reaction of P_4S_{10} with pyridine solutions of diketones I-III are sulfides IV-VI. Pyridine ties up the acid products of the decomposition of phosphorus pentasulfide and excludes the possibility of disproportionation of sulfides IV-VI.

The reaction of 9-R-sym-octahydrothioxanthenes (IV-VI) with perchloric acid, a hydrochloric acid solution of ferric chloride, polyphosphoric acid, and other acids leads to disproportionation with hydrogen transfer. Data on the conditions and products of the reaction of IV-VI with acids are presented in Table 1.

In our opinion, the disproportionation of sym-octahydrothioxanthenes with acids (including the acid products of the decomposition of P_4S_{10}) is associated with the protonation of the double bonds in sulfides IV-VI and with the formation of carbonium ions, which are hydride-ion acceptors during salt formation [3]. The duration of the reaction depends on the chemical nature of the acid used as the salt-forming reagent and on the reaction conditions, primarily the temperature and the solvent. Thus the complete conversion of sym-octahydrothioxanthenes IV-VI with perchloric acid occurs after 2-3 h, but takes 48 h or longer with hydrogen chloride [4].

The yields of sym-octahydrothioxanthylium salts (XV-XIX) and of the corresponding perhydrothioxanthenes (X-XII) do not strictly correspond to the 2 : 1 ratio that should have been expected for quantitative disproportionation via the scheme presented above. The reason for this is the unavoidable loss during the preparative isolation of the reaction products.

It can also be assumed that the disproportionation of IV-VI proceeds with the participation of only one double bond [5] and with the formation of decahydroxanthenes, but we were unable to detect them even by chromatography.

EXPERIMENTAL

Reaction of Alkylidenedicyclohexanones I-III with Phosphorus Pentasulfide in Pyridine. A 0.05-mole sample of pulverized P_4S_{10} was added in the course of 1 h under nitrogen at 0° to a solution of 0.05 mole of the diketone in 20-22 ml of pyridine. The reaction mixture was heated on a boiling water bath for 2 h, cooled, and treated with water and ether. The ether extract was dried, and the ether was removed by distillation. Vacuum distillation of the residue gave the corresponding sulfides (IV-VI) in 45-65% yields. Sulfide IV was obtained in the crystalline state by freezing out (at −70°) an ether−methanol solution (1 : 3) of the fraction with bp 135-143° (5 mm). Sulfides IV-VI were identified by determining the melting points of mixtures with authentic samples of the appropriate 9-R-sym-octahydrothioxanthenes [2].

Reaction of Alkylidenedicyclohexanones I-III with Phosphorus Pentasulfide in an Inert Solvent. The reaction was carried out in toluene or xylene via the method described above with strict observance of the quantitative ratio of the reagents and the reaction time. As previously described [2] (Table 2), sulfides IV-VI (20-35%), X-XII (10-20%), and XIII and XIV (about 1%) were isolated from the ether extracts. The aqueous layer containing the sym-octahydrothioxanthylium salt (VII-IX) was treated with excess perchloric acid. Extraction with dichloroethane and dilution of the extract with ether or benzene [or ether−benzene (2 : 1)] gave the corresponding perchlorates (XV, XVI). Similar treatment of the aqueous layer with a hydrochloric acid solution of ferric chloride gave the corresponding tetrachloroferrates (XVII-XIX, Table 2).

Disproportionation of 9-R-sym-Octahydrothioxanthenes (IV-VI) with Acids. Excess mineral acid ($HClO_4$, HCl, $FeCl_3$ + HCl, H_3PO_4, and PPA) was allowed to act on solutions of IV-VI in glacial acetic acid or in a mixture of the latter with acetic anhydride at 20-100° (Table 1). At the end of the reaction, the mixture was diluted with ether (with absolute ether in the case of the chlorides), upon which the corresponding 9-R-sym-octahydrothioxanthylium salts (XV-XXI) precipitated; perhydrothioxanthenes X-XII were isolated from the ether extracts. The results of the disproportionation are presented in Table 1.

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