ACID SOLVOLYSIS OF 1,3,5,7-TETRAMETHYL-2,4,6,8-TETRATHIOADAMANTANE AND 1,3,5,7-TETRAMETHYL-2,4,6,8-TETRATHIOPROTOADAMANTANE DERIVATIVES

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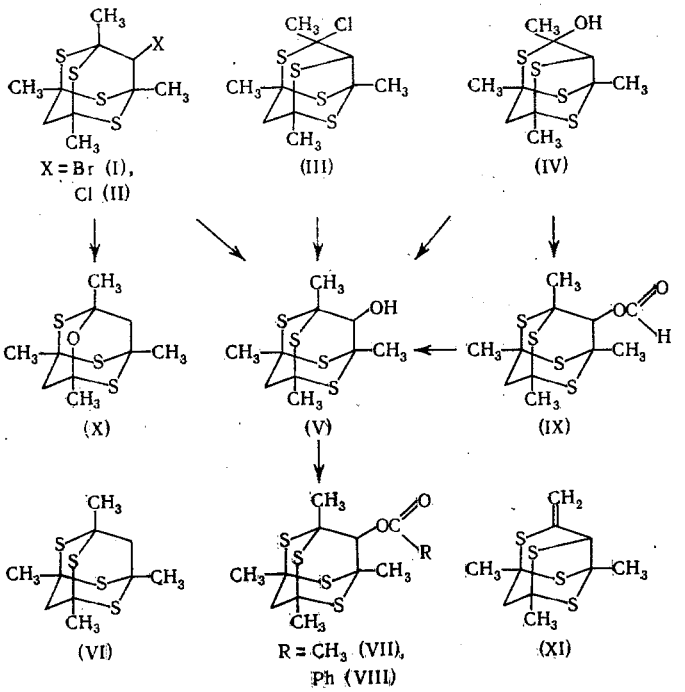
Previously [1] we described the synthesis and basic solvolysis of the halides of 1,3,5,7-tetramethyl-2,4,6,8-tetrathioadamantane (I, II) and 1,3,5,7-tetramethyl-2,4,6,8-tetrathioprotoadamantane (III), and also of 1-hydroxy-1,3,5,7-tetramethyl-2,4,6,8-tetrathioprotoadamantane (IV). The present paper is devoted to a study of the transformations of compounds (I)-(IV) under acid solvolysis conditions.



Halides (I)-(III) are hydrolyzed when reacted with aqueous HCOOH, while alcohol (IV) is isomerized to give 9-hydroxy-1,3,5,7-tetramethyl-2,4,6,8-tetrathioadamantane (V). The IR spectrum of (V) has the bands of the OH group (1050, 3440 cm^{-1}); in the NMR spectrum the signal of the proton at C^9 appears as a doublet at 3.3 ppm, which is caused by splitting due to spin–spin coupling with the OH group. The addition of CF_3COOH led to disappearance of the doublet and the appearance of a singlet at 3.8 ppm. The UV spectrum of (V) resembles the spectra of 1,3,5,7-tetramethyl-2,4,6,8-tetrathioadamantane (VI) and its derivatives (I) and (II). The esterification of (V) gave its acetate (VII) and benzoate (VIII). The reaction of (IV) with 100% HCOOH led to the formate (IX), the structure of which as being the ester of alcohol (V) [and not of alcohol (IV)] is confirmed by the NMR spectrum, which contains the signal of a proton at 5.21, which is characteristic for the HCOCOH grouping. Hydrolysis without rearrangement occurs when formate (IX) is chromatographed on Al_2O_3 with the formation of (V). From the structure of (V) and (IX) it follows that in aqueous HCOOH the hydrolysis of the halo derivatives of 2,4,6,8-tetrathioadamantane (I) and (II) proceeds without

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TABLE 1. Composition of Acetolysis Products of Halides (I) and (III) as a Function of Aqueous CH_3COOH Concentration

Starting compound	CH_3COOH, %	Composition of products, %					
		(II)	(IV)	(V)	(VI)	(X)	(XI)
Bromide (I)*	92	—	—	6	34	56	—
	80	—	—	26	34	40	—
	70	—	—	33	46	18	—
	60	—	7	27	42	10	11
	50	—	15	15	22	2	30
Chloride (III)†	95	8	7	—	8	—	73
	85	4	64	—	7	—	22
	75	6	91	—	0	—	0

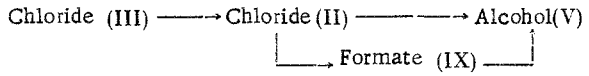
*At solvent reflux.
†At 20°C.

rearrangement, whereas the compounds with a proto structure, (III) and (IV), undergo skeletal rearrangement.

The formolysis of bromide (I) proceeds successfully in 50-92%, and that of chloride (III) in 60-95% aqueous HCOOH. In the indicated concentration range the HCOOH has little effect on the yield, and also on the time required to complete the reaction in the case of (I); the hydrolysis of (II) and (III) is completed faster in 60% than in 85-95% aqueous HCOOH. It should be mentioned that in the formolysis of compounds (I)-(III), together with hydrolysis, dehalogenation also occurs, which leads to (VI), the yield of which varies in the range 20-40% in the case of (I), and 10-20% in the formolysis of (III).

A study of the formolysis of chloride (III) disclosed the intermediate formation of the isomerized chloride (II) and formate (IX). Thus, the formolysis of (III) in 95% aqueous HCOOH for 20 min gives a mixture of 26% of (II), 29% of (IX), and 32% of (V), after 1 h the mixture contains 9% of (IX) and 77% of (V), and after 3 h only alcohol (V) is present. In turn, the formolysis product of (II) in 85% aqueous HCOOH (20 min) contains, together with (IV), also 10% of (IX). Bromide (I) gives only alcohol (V) under analogous conditions.

The obtained data make it possible to propose the following scheme for the formolysis of chloride (III).



A study of the acetolysis of bromide (I) in 50-92% aqueous CH_3COOH disclosed that at solvent reflux the reaction is completed in 3 h and gives a mixture of 1,3,5,7-tetramethyl-2-oxa-4,6,8-trithioadamantane (X), alcohol (V), and compound (VI). The relative amount of (V) and (X) in the mixture depends on the CH_3COOH concentration (Table 1). We employed mass, IR, and NMR spectroscopy to identify (X). The characteristics obtained for (X) were in full agreement with the data given in [2], where (X) was isolated from the mixture of products of the reaction of acetylacetone with H_2S in conc. HCl. It may be assumed that the formation of (X) in the acetolysis of (I) occurs via the fragmentation of (I), while the cleavage of SBr and the subsequent cyclization of the intermediate compound with the involvement of the oxygen in the skeleton of the molecule.

The reaction of chloride (II) with 92% aqueous CH_3COOH at reflux also leads to (X), but in contrast to (I), the acetolysis of (II) proceeds with much greater difficulty. Thus, only 20% of (II) reacts in a time that is sufficient to complete the acetolysis of (I). Under analogous conditions the acetolysis of chloride (III) leads only to chloride (II); however, alcohol (IV) and olefin (XI) are formed if the acetolysis is run at 20°, in a ratio that depends on the CH_3COOH concentration (see Table 1). When the solvolysis of chloride (III) is run in 75% aqueous CH_3COOH the hydrolysis proceeds selectively without rearrangement, while the acetolysis of bromide (I) in 50-60% aqueous CH_3COOH leads, together with (V) and (X), also to the rearrangement products, namely alcohol (IV) and olefin (XI).

A comparison of these data with the previously reported data [1] makes it possible to trace an analogy in the transformations of halides (I) and (III) in dilute CH_3COOH solution and under basic solvolysis conditions.

EXPERIMENTAL

The NMR spectra were recorded on a Varian A-56-60A spectrometer in CCl_4 solution using HMDS as the internal standard. The mass spectra were taken on an MKh-1303 instrument under standard conditions in an ion source with an energy of 70 eV for the ionizing electrons. The IR spectra were taken on a UR-20 instrument. The UV spectra were measured on a Specord UV-VIS spectrophotometer in isooctane solution. The chromatographic analysis was run on a Chrom-31 chromatograph equipped with a flame-ionization detector at 200°; the column was 5.5 mm × 0.7 m; the statinary plase was 15% Silicone Elastomer E-301 deposited on Celite 545; and the carrier gas was nitrogen.

The preparation of the starting halides (I)-(III) and compounds (IV), (VI), and (XI) was described in [1].

Solvolysis of Halides (I)-(III). A mixture of 0.2 g of the halide and 10 ml of aqueous acid was refluxed: in the case of (I) and (II) with 50-95% HCOOH for 1 h, and in the case of (III) with 60-95% HCOOH for 1-3 h; in the case of (I) with 50-92% CH_3COOH for 3 h, while the mixture of (III) with 75-95% CH_3COOH was kept at 20° for 3 h. Then the mixture was diluted with water, and the obtained precipitate was separated, washed with water, and dried. We obtained 0.1-0.17 g of products, the composition of which, determined by GLC and NMR spectroscopy, is given in the general section and in Table 1.

9-Hydroxy-1,3,5,7-tetramethyl-2,4,6,8-tetrathioadamantane (V). A mixture of (V) and (VI) (1.23 g), obtained by the formolysis of (I), was chromatographed on Al_2O_3 using a 1:1 hexane–ether mixture as the eluant. We isolated 0.6 g of (V), mp 150-152°. Found: C 42.6; H 5.7; S 45.2%. $C_{10}H_{16}S_4O$. Calculated: C 42.8; H 5.7; S 45.7%.

Infrared spectrum (ν, cm^{-1}, KBr pellet): 650, 1050, 1105, 1235, 1355, 1370, 1440, 3430. NMR spectrum (δ, ppm): 1.41, 1.45, 1.55 ($4CH_3$), 2.04 (CH_2), 3.3 d (1H, J = 13 Hz, CHOH); the doublet at 3.3 ppm disappears when CR_3COOH is added and a singlet appears at 3.8 ppm (1H). Mass spectrum (m/e): 280 (30, M^+), 247 (3), 191 (25), 159 (18), 133 (22), 131 (40), 127 (33) ...59 (100). Ultraviolet spectrum (λ_{max}, nm): 218 (ε 2990), 250 (ε 1430).

9-Acetoxy-1,3,5,7-tetramethyl-2,4,6,8-tetrathioadamantane (VII). A solution of 0.1 g of (V) in 7.5 ml of Ac_2O was refluxed for 4 h, poured into water, and extracted with benzene. After removal of the benzene we obtained 0.11 g (91%) of (VII), mp 195-198°. Infrared spectrum (ν, cm^{-1}): 1220, 1740 ($OCOCH_3$). NMR spectrum (δ, ppm): 1.32, 1.51, 1.61 ($4CH_3$), 2.04 (CH_2), 2.05 ($OCOCH_3$), 5.06 (CH). Mass spectrum (m/e): 322 (20, M^+), 289 (4), 197 (6), 191 (20), 159 (15)...59 (100). Ultraviolet spectrum (λ_{max}, nm): 220 (ε 2640), 254 (ε 1230).

1,3,5,7-Tetramethyl-2,4,6,8-tetrathioadamantane 9-benzoate (VIII). A mixture of 0.1 g of (V) and 0.5 ml of benzoyl chloride in 5 ml of pyridine was refluxed for 3 h, poured into water, and extracted with ether. The extract was washed with 5% aqueous NaOH solution, then with water, and dried over $MgSO_4$. Evaporation of the ether gave 0.09 g (65.5%) of (VIII). After chromatography on Al_2O_3 (1:1 hexane–ether), mp 146-147°. Infrared spectrum (ν, cm^{-1}): 1120, 1270, 1730, 3080 ($OCOC_6H_5$). NMR spectrum (δ, ppm): 1.32, 1.52, 1.65 ($4CH_3$), 2.12 (CH_2), 5.32 (CH), 7.4, 8.2 (C_6H_5). Mass spectrum (m/e): 384 (26, M^+), 351 (3), 191 (18), 159 (13)...104 (100), 59 (65).

Solvolysis of (IV). 1) A mixture of 0.3 g of (IV) and 15 ml of 85% aqueous HCOOH was refluxed for 15 min. After the usual workup and chromatography on Al_2O_3 (1:1 hexane–ether) we obtained 0.1 g of (V).

2) A mixture of 0.4 g of (IV) and 10 ml of 100% HCOOH was refluxed for 10 min in an argon atmosphere. After the usual workup we obtained 0.19 g of (IX), which when heated above 100° is converted to (V). Infrared spectrum (ν, cm^{-1}): 1180 (COCOH), 1720 (CO). NMR spectrum (δ, ppm): 1.32, 1.47, 1.57 ($4CH_3$), 2.05 (CH_2), 5.21 (CHOCOH), 8.05 (COH).

1,3,5,7-Tetramethyl-2-oxa-4,6,8-trithioadamantane (X). A mixture (2.15 g) of (V), (VI), and (X) (respectively 6, 34, and 56%), obtained by the acetolysis of (I) in 92% aqueous CH_3COOH, was chromatographed on Al_2O_3 (hexane). We obtained 1.2 g of (X), mp 103-104°. Infrared spectrum (ν, cm^{-1}): 645, 820, 870, 970, 990, 1115, 1175, 1380, 1460. NMR spectrum (δ, ppm): 1.40 ($2CH_3$), 1.46 ($2CH_3$), 1.91 ($2CH_2$). Mass spectrum (m/e): 248 (34, M^+), 215 (8), 184 (10), 183 (24), 157 (3), 139 (6), 133 (7), 132 (15), 131 (34)...117 (100)...59 (67) (cf. [2]).

CONCLUSIONS

1. It was found that a rearrangement of the 2,4,6,8-tetrathioprotoadamantane skeleton to that of 2,4,6,8-tetrathioadamantane occurs in the reactions that proceed in HCOOH, while the reverse rearrangement takes place when treatment is with dilute CH_3COOH solution.

2. The principal direction of the solvolysis of the halides of 1,3,5,7-tetramethyl-2,4,6,8-tetrathioadamantane (I)-(II) and 1,3,5,7-tetramethyl-2,4,6,8-tetrathioprotoadamantane (III) by aqueous HCOOH is hydrolysis.

3. The direction of the acetolysis of halides (I)-(III) in aqueous CH_3COOH depends on the acid concentration. Cleavage reactions predominate when the acetolysis is run in 90-95% aqueous CH_3COOH; dilution of the acid facilitates the progress of hydrolysis.

LITERATURE CITED

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