SYNTHESIS OF 1,3-DIOXANIUM HEXACHLOROANTIMONATES

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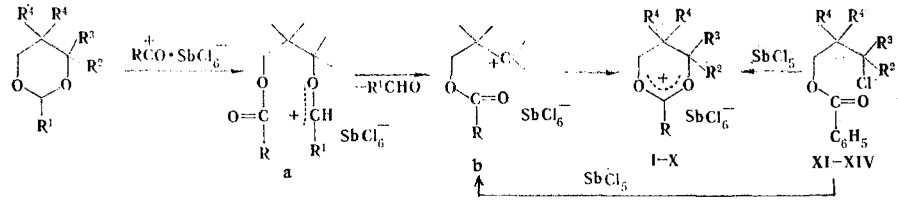
2-Alkyl(aryl, 2-furyl, and β-vinylphenyl)-1,3-dioxanium hexachloroantimonates were obtained by acylation of 1,3-dioxanes with carboxylic acid chlorides in the presence of antimony pentachloride.

We have previously investigated the reaction of 1,3-dioxanes with aliphatic acid anhydrides in the presence of 70% perchloric acid [1] and have established the formation of 2-alkyl-substituted 1,3-dioxanium perchlorates. It seemed of interest to study the behavior of 1,3-dioxanes with various structures in acylation with carboxylic acid chlorides. It is known that 2-phenyl-1,3-dioxanium salts are stable compounds [2]. In a continuation of the synthesis of new stable salts with various substituents in the ring we used (in addition to aliphatic acid, pyromucic, and cinnamic acid chlorides) benzoyl chloride as the principal acylating reagent.

A number of 2-alkyl(aryl, 2-furyl)-1,3-dioxanium hexachloroantimonates (I-X) were obtained by reaction of 1,3-dioxanes, acid chlorides, and antimony pentachloride in chloroform in a ratio of 1:1:1 via the scheme



$R^1 = H$, C_6H_5; I—VII $R^2 = R^3 = CH_3$, $R^4 = H$; I $R = CH_3$; II $R = C_2H_5$; III $R = C_3H_7$; IV $R = C_6H_5$; V $R = p\text{-}C_6H_4Br$; VI $R = CH{=}CH-C_6H_5$; VII $R = C_4H_3O$; VIII—X $R = C_6H_5$; VIII $R^2 = R^3 = R^4 = H$; IX $R^2 = CH_3$; $R^3 = R^4 = H$; X $R^2 = R^3 = H$, $R^4 = CH_3$

Intermediates *a* and b are not detected, but the formation of an aldehyde from *a* and salts IV and VIII-X from chlorohydrin benzoates XI-XIV serves as convincing evidence in favor of the reaction scheme presented above. The production of benzaldehyde was proved by gas—liquid chromatography (GLC) in the case of the reaction of 2-phenyl-4-methyl-1,3-dioxane with benzoyl chloride and $SbCl_5$. Benzaldehyde was detected chromatographically in the filtrate after separation of salt IX.

The reaction time and temperature depend on the structure of the 1,3-dioxane. The presence of donor substituents in the 4 position of the ring promotes the formation of salts I-VII and IX in high yields (Table 1) at −5°C after 15-30 min. The synthesis of salts VIII and X takes place at 40°C in chloroform after 4 h, i.e., the reactivities of 4- and 6-unsubstituted 1,3-dioxanes are considerably lower; this is done to the formation of less stable cation b.

Compounds IV and VIII-X were obtained in 55-70% yields by alternative cyclization of chlorohydrin benzoates XI-XIV by the action of antimony pentachloride under the conditions of the synthesis of the salts from 1,3-dioxanes. 1,3-Dioxanium salts were obtained by this

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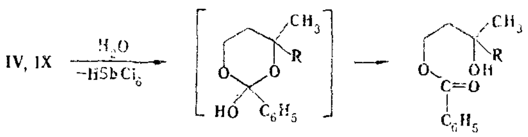
TABLE 1. 1,3-Dioxanium Hexachloroantimonates

Compound	mp, °C	IR spectrum, cm^{-1}	Found, %		Empirical formula	Calc., %		Yield, %
			C	H		C	H	
I	74—75	1570, 1525, 1460, 1440, 1380, 1290, 1180, 1140, 1050, 1010, 900, 770	18,3	3,1	$C_7H_{13}Cl_6O_2Sb$	18,1	2,8	95
II	116—118	1575, 1520, 1470, 1445, 1385, 1295, 1180, 1140, 1045, 1000, 900, 780	20,45	3,6	$C_8H_{15}Cl_6O_2Sb$	20,2	3,15	92
III	62—64	1575, 1520, 1460, 1445, 1380, 1280, 1170, 1140, 1040, 1000, 900, 780	22,3	3,9	$C_9H_{17}Cl_6O_2Sb$	21,95	3,45	81
IV	94	1595, 1530, 1500, 1440, 1430, 1330, 1180, 1160, 1110, 1025, 710	27,95	2,98	$C_{12}H_{15}Cl_6O_2Sb$	27,6	2,9	93
V	94	1595, 1530, 1500, 1445, 1440, 1335, 1180, 1160, 1110, 1025, 800, 710	26,75	2,8	$C_{12}H_{14}BrCl_6O_2Sb$	26,1	2,5	95
VI	96	1620, 1570, 1520, 1500, 1470, 1420, 1380, 1330, 1260, 1210, 1120, 1070, 980, 770	29,5	2,5	$C_{14}H_{15}Cl_6O_2Sb$	29,98	2,7	90
VII	52—54	3040, 1580, 1550, 1510, 1480, 1425, 1295, 1170, 1020, 820, 710	23,05	2,1	$C_{10}H_{13}Cl_6O_3Sb$	23,2	2,5	70
VIII	176—178	1605, 1595, 1500, 1510, 1480, 1430, 1290, 1180, 1040, 1020, 820, 720	24,35	2,5	$C_{10}H_{11}Cl_6O_2Sb$	24,0	2,2	55
IX	130	1605, 1590, 1555, 1510, 1470, 1400, 1300, 1290, 1250, 1190, 1170, 1150, 1110, 880, 720	25,1	2,1	$C_{11}H_{13}Cl_6O_2Sb$	25,7	2,5	70
X	146—148	1600, 1560, 1505, 1480, 1400, 1380, 1300, 1280, 1190, 1165, 1100, 920, 840, 770	27,7	2,8	$C_{12}H_{15}Cl_6O_2Sb$	27,3	2,8	25

method for the first time in [3]. The reaction temperature and time were also a function of the structures of the starting chlorohydrin benzoates XI-XIV. These facts make it possible to assume that the rate-determining step in the reaction is detachment of a molecule of aldehyde or a chloride anion to give carbonium ion b, which precedes the 1,3-dioxanium cation in the direct and alternative syntheses.

It is known [3] that the hydrolysis of salts IV and VIII-X leads to 1,3-diol monoesters (XV-XVIII). One structural isomer (XV and XVI, respectively), the individuality of which was determined by GLC, was obtained in each case from hexachloroantimonates IV and IX; this constitutes evidence for the regioselectivity of the reaction, in contrast to the benzoylation of the 1,3-dioxane ring, which leads to two structural isomers.



R = H, CH$_3$

XV, XVI

The structure of the synthesized compounds (both the previously known VIII [2] and the newly obtained compounds) were confirmed by data from IR and NMR spectroscopy. The IR spectra of the salts contain absorption bands of an $O\text{—}C^{+}\text{—}O$ fragment at 1590 and 1510 cm^{-1}. The spectra of the 2-phenyl-substituted salts contain absorption bands of C=C bonds at 3080 and 1600 cm^{-1}. The bands at 3400 and 1725 cm^{-1}, which correspond to the O—H bond and the C=O bond of the ester group of the products of hydrolysis (XV-XVIII) of the salts constitute convincing evidence in favor of their structure. The PMR spectrum of salt IV confirms the 1,3-dioxanium cation structure.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the crystalline substances or thin layers of the liquid compounds were recorded with a Specord spectrometer. The PMR spectrum was recorded with a C-60-HL spectrometer with tetramethylsilane as the internal standard. Analysis by GLC was carried out with a Khrom-4 chromatograph with a flame-ionization detector under isothermal conditions with a 2.5-m-long column with a diameter of 4 mm. In the case of XV-XVIII the column was packed with 15% Apiezon L on Chromaton N-AW DMCS (grain size 0.250-0.315 mm), the vaporization temperature was 320°C, the recorder chart speed was 600 mm/h, and the sample volume $\eta = 1$ µl. In the analysis of the mother liquor in the synthesis of salt IX the column was packed with 5% SE-30 on Chromaton N-AW DMCS (grain size 0.250-0.315 mm), the vaporization temperature was 240°C, the recorder chart speed was 2400 mm/h, and the sample volume $\eta = 0.2$ µl.

2-Phenyl-4,4-dimethyl-1,3-dioxanium Hexachloroantimonate (IV, Table 1). A 1.3-ml (0.01 mole) sample of $SbCl_5$ was added to a cooled (to 0°C) solution of 1.16 g (0.01 mole) of 4,4-dimethyl-1,3-dioxane and 1.5 ml (0.01 mole) of benzoyl chloride in 4 ml of chloroform, and the resulting crystals were removed by filtration and washed with glacial acetic acid and ether to give 4.9 g of salt IV. PMR spectrum (in CF_3COOH, 26°C): 2.24 [6H, s, $(CH_3)_2$], 3.08 (2H, t, 5-CH_2), 5.56 (2H, t, 6-CH_2), and 7.83-8.58 ppm (5H, m, C_6H_5). Salts I-III, V-VII, and IX were similarly obtained.

2-Phenyl-1,3-dioxanium Hexachloroantimonate (VIII). A) A solution of 2.6 ml (0.02 mole) of $SbCl_5$ in 10 ml of methylene chloride (or chloroform) was added at 0°C to a solution of 3.28 g (0.02 mole) of 2-phenyl-1,3-dioxane and 2.32 ml (0.02 mole) of benzoyl chloride in 10 ml of methylene chloride (or chloroform), after which the reaction mixture was heated to 40°C and stirred for 1 h. The precipitated crystals were removed by filtration and washed with glacial acetic acid and ether to give 5.4 g (55%) of salt VIII, which was identical to the salt described in [2]. Salt X, which, because of its high solubility in chloroform, was additionally precipitated with ether, was similarly obtained.

B) A solution of 2.6 ml (0.02 mole) of $SbCl_5$ in 10 ml of chloroform was added dropwise at 0°C to a solution of 3.97 g (0.02 mole) of 3-chloro-1-benzoxypropane in 10 ml of chloroform, and the reaction mixture was heated to 40°C and stirred for 4 h. The resulting crystals were removed by filtration and washed with glacial acetic acid and ether to give 6.9 g (70%) of product. Salts IX and X were similarly obtained.

2-Methyl-4-benzoxy-2-butanol (XV). Water (20 ml) was added to 5.26 g (0.01 mole) of salt IV, and the mixture was heated to the boiling point. The resulting oil was extracted with ether, and the ether extract was washed with 5% KOH solution and dried over Na_2SO_4. The solvent was evaporated, and the residue was distilled at 121°C (29.3 hPa) to give 1.8 g (93%) of a product with n_D^{20} 1.5100. IR spectrum: 3400 (O–H); 1720 (C=O); 1600, 1580 cm^{-1} (C_6H_5). Found: C 62.4; H 10.2%. $C_9H_{18}O_3$. Calculated: C 62.1; H 10.3%. Monoesters XVI-XVIII were similarly obtained.

4-Benzoxy-2-butanol (XVI). This compound, with bp 146-147°C (6.66 hPa) and n_D^{20} 1.5118, was obtained in 75% yield. IR spectrum: 3450 (O–H); 1720 (C=O); 3030, 1610, 1580 cm^{-1} (C_6H_5). Found: C 67.8; H 7.5%. $C_{11}H_{14}O_3$. Calculated: C 68.1; H 7.5%.

2,2-Dimethyl-3-benzoxy-1-propanol (XVII). This compound, with bp 164-166°C (10.7 hPa) and n_D^{20} 1.5101, was obtained in 55% yield. IR spectrum: 3477 (O–H); 1730 (C=O); 3030, 1610, 1590 cm^{-1} (C_6H_5). Found: C 69.8; H 7.5%. $C_{12}H_{16}O_3$. Calculated: C 69.3; H 7.7%.

3-Benzoxy-1-propanol (XVIII). This compound, with bp 176-178°C (29.3 hPa) and n_D^{20} 1.5180, was obtained in 70% yield. IR spectrum: 3400 (O–H); 1725 (C=O); 3050, 1610, 1580 cm^{-1} (C_6H_5). Found: 66.5; H 6.7%. $C_{10}H_{12}O_3$. Calculated: C 66.7; H 6.7%.

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