

# THE CHEMISTRY OF 1,3-BIFUNCTIONAL SYSTEMS, XXVIII\* A NEW DIRECT SYNTHESIS OF 1,3-DIOXAN-2-YLIUM SALTS FROM 1,3-DIOLS

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2-Phenyl-1,3-dioxan-2-ylum hexachloroantimonates (5—8) can be prepared in good yield from 1,3-diols (1—4) with the use of benzoyl chloride and antimony pentachloride (Scheme 1). Conclusions may be drawn with regard to the mechanism of the process.

## Introduction

MEERWEIN et al. [1] were the first to prepare a 1,3-dioxan-2-ylum cation as its tetrafluoroborate or hexachloroantimonate, well-defined crystalline compounds, by the cleavage of the ethoxy anion of a cyclic orthoester. The existence of this cation was confirmed by other authors, in studies of the Prins reaction [2,3] the solvolysis of 1,3-dioxane derivatives [4] and the reactions of 1,3-diols and acid chlorides [5]. The existence of the 1,3-dioxan-2-ylum cation in the reaction between acetyl chloride and 1,3-butanediol could be confirmed by comparison of the rotations of the optically active starting 1,3-butanediol and the chloroacetate end-product [5].

Examples of the preparative separation of the 1,3-dioxan-2-ylum cation are syntheses starting from the esters of 1,3-diols [6, 7] or other 1,3-diol derivatives [8—11], in the course of which the cation can be separated in the form of its hexachloroantimonate, perchlorate or tetrafluoroborate. The synthesis and properties of salts of this type have been reviewed [12].

In the literature examples of the synthesis of 1,3-dioxan-2-ylum salts the corresponding diol derivative was prepared in every case in a separate reaction step, and the salts were then precipitated [2, 6—11].

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### Results and discussion

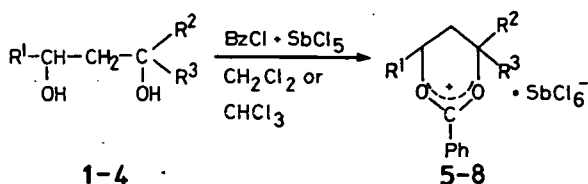
In the method we propose, a 1:2:1 mixture in chloroform or dichloromethane of antimony pentachloride, benzoyl chloride (BzCl) and 1,3-diols containing hydroxy groups of different orders (1—4) is allowed to stand or is boiled, when 2-phenyl-1,3-dioxan-2-ylum hexachloroantimonates (5—8) can be separated in crystalline form in one step after cooling of the mixture and its treatment with ether (Scheme 1).

1,5  $R^1, R^2, R^3=H$

2,6  $R^1, R^2=H, R^3=Me$

3,7  $R^1=H, R^2, R^3=Me$

4,8  $R^1, R^2, R^3=Me$



Scheme 1

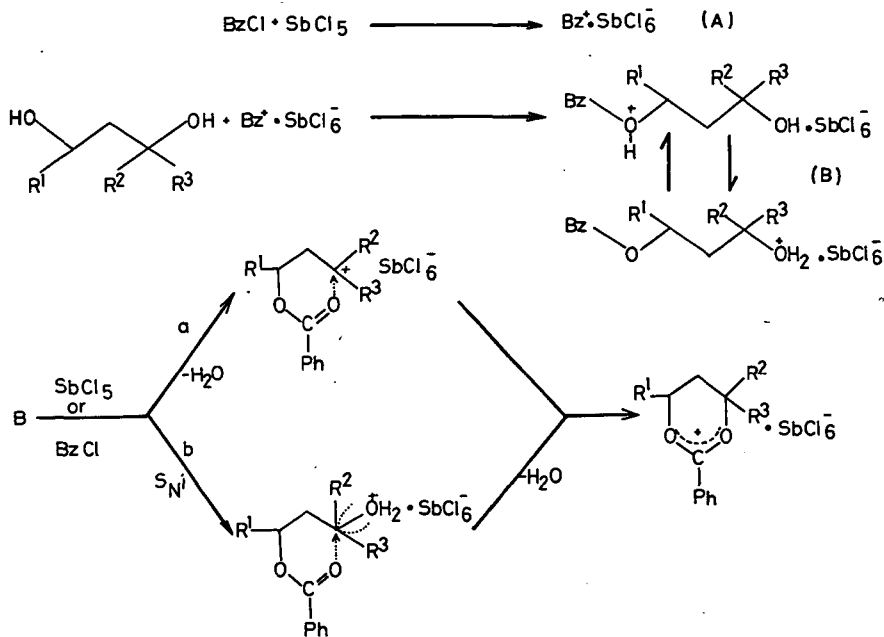
The yields of the 1,3-dioxan-2-ylum salts (5—8) and the reaction rates are influenced appreciably by the reaction conditions, *e.g.* the ratio of the components, the structure of the diol, and the temperature and duration of the reaction. In syntheses starting from 1,3-diols, a two-fold quantity of benzoyl chloride in all cases resulted in an increased yield of the salt. A few characteristic experimental results are to be seen in the following Table:

The yields of the salts (5—8) increase with increase of the order of the carbon atom bearing one of the hydroxy groups in the 1,3-diols (1—4). A higher temperature results in higher yields of the salts (5, 6), even with a shorter reaction time. In the syntheses starting from the corresponding primary monobenzoates as intermediates, the yields of the salts (5, 6) are comparable to those with the 1,3-diols (1, 2) as starting materials.

Table I

Methods	Ratio of reagents	Yield of 2-phenyl-1,3-dioxan-2-ylum salt, % (reaction time)			
		5	6	7	8
1	1,3-diol: BzCl: SbCl <sub>5</sub> 1:2:1	12 (40 h)	70 (40 h)	80 (15 min)	95 (15 min)
2	1,3-diol: BzCl: SbCl <sub>5</sub> 1:2:1	30 (1 h)	72 (3 min)	—	—
3	1,3-diol-monobenzoate: BzCl: SbCl <sub>5</sub> 1:1:1	10 (1 h)	79 (3 min)	—	—

On the basis of the experimental data, the formation of the 2-phenyl-1,3-dioxan-2-ylum hexachloroantimonates (5—8) can be interpreted by the reaction sequence given in Scheme 2.

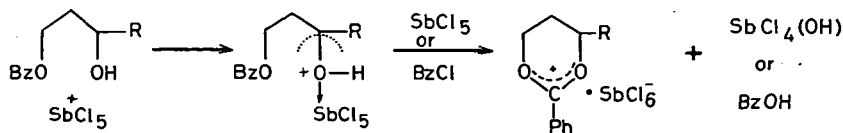


Scheme 2

The reaction begins with the interaction of the 1,3-diol and the acylating agent (A), when the faster acylation of the primary hydroxy group is to be expected [2,13]. In acylation with BzCl this is all the more characteristic [14], and the migrational ability of the Bz group is lower too [15]. The salt formation takes place with water elimination via the protonated forms of the monobenzoates (B); depending on the order of the second hydroxy group of the 1,3-diol, this can be interpreted as proceeding via a carbonium ion (route "a") in the case of 2, 3 and 4, or by a slower cyclization with an  $S_{\text{N}}\text{i}$  mechanism in the case of the primary hydroxy group (1) (route "b"). This reaction pathway is supported by the experiments with 1,3-diol monobenzoates (Table I, line 3).

Thus, the larger yields and rates of formation of the salts (6—8) originating from the higher 1,3-diols (2, 4) also containing a hydroxy group can be brought into correlation with the favoured water elimination preceding the ring closure (Scheme 2, route "a").

The 1,3-dioxan-2-ylum salts (6) can be obtained in a yield of 50% from 1-benzoyloxybutanol-3 in the presence of an equimolar quantity of antimony pentachloride. On this basis a general scheme can be proposed to interpret the synthesis shown in row 3 of Table I (Scheme 3).



Scheme 3

The formation of the 2-phenyl-1,3-dioxan-2-ylum hexachloroantimonates from the corresponding 1,3-diols can be explained by the water-elimination ring-closure reaction of the intermediate monobenzoates.

### Experimental

**General observations.** The 1,3-diols **1**, **2** and **4** were products of Fluka. **3** was prepared according to [16], and 1-benzoyloxy-propanol-3 and 1-benzoyl-oxybutanol-3 according to [17]; they were identified by chromatographic, analytical and spectroscopic methods.

The 2-phenyl-1,3-dioxan-2-ylum salts were recrystallized from  $\text{CH}_2\text{Cl}_2$ . Melting points (m.p.) of salts are not corrected.  $^1\text{H}$  NMR spectra ( $\text{CD}_6\text{N}_5\text{O}_2$  if not otherwise stated): JEOL C—60 HL NMR spectrometer. Chemical shifts are given in ppm; abbreviations: s singlet, d doublet, dd doublet of doublets, t triplet, m multiplet; J spin-spin coupling constant in MHz. IR spectra (KBr): Unicam SP 200 IR spectrometer;  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ .

### Synthesis methods

1. 2.30 ml (0.02 mol) benzoyl chloride and 0.01 mol of the appropriate 1,3-diol (**1**, **2**, **3**, **4**) are added at  $0^\circ\text{C}$  to a solution of 1.28 ml (0.01 mol) antimony pentachloride in 5 ml chloroform, and the mixture is left to stand at room temperature. After 40 h in the case of **1** and **2**, or after 15 min in the case of **3**, and **4**, 30 ml ether is added to the mixture, and the resulting crystals are filtered off, and washed with a cold 1:2 mixture of ethyl acetate and ether, and then with ether. Yields calculated for the starting diol: **5**: 0.59 g (12%); **6**: 3.58 g (70%); **7**: 4.2 g (80%); **8**: 5.12 g (95%).

2. A solution of 0.01 mol of the appropriate 1,3-diol (**1**, **2**), in 5 ml chloroform is added to a mixture of 1.28 ml (0.01 mol) antimony pentachloride and 2.30 ml (0.02 mol) benzoyl chloride. The mixture is boiled for 60 min or for 3—5 min in the case of **1** and **2**, respectively. After cooling, 30 ml ether is added, the salt separating out is filtered off, and it is washed with cold ethyl acetate, and then with ether. Yields: **5**: 1.49 g (30%); **6**: 3.68 g (72%).

3. A solution of 1.94 g (0.01 mol) 1-benzoyloxybutanol-3, 1.28 ml (0.01 mol) antimony pentachloride and 1.15 ml (0.01 mol) benzoyl chloride in 10 ml chloroform is boiled for 3 min, then cooled and diluted with 30 ml ether. The work-up is the same as in 2. Yield: **6**: 4 g (79%) (2.55 g (50%) if the reaction is carried out without benzoyl chloride). In an analogous way, **5** can be obtained from 1-benzoyloxypropanol-3 if the reaction mixture is boiled for 60 min. Yield: **5**: 0.5 g (10%).

- 5: m.p.: 180°; <sup>1</sup>H NMR: 3.05 (m): 5 CH<sub>2</sub>; 5.6 (m): 4 and 6 CH<sub>2</sub>; 7.66—8.46 (m): aromatic protons; IR (cm<sup>-1</sup>): 1600, 1590, 1550, 1510, 1450, 1440, 1380, 1290; C<sub>10</sub>H<sub>11</sub>O<sub>2</sub> SbCl<sub>6</sub> (497.66), Calc.: C 24.13 H 2.23, Found: C 23.70 H 2.28.
- 6: m.p.: 140°, <sup>1</sup>H NMR: 1.9 (d): 4 CH<sub>3</sub>; 2.83 (m): 5 CH<sub>2</sub>; 5.83 (m): 6 CH<sub>2</sub>; 5.92 (m): 4 CH; 7.5—8.2 (m): aromatic protons; IR (cm<sup>-1</sup>): 1600, 1590, 1540, 1510, 1470, 1450, 1390, 1350, 1280; C<sub>11</sub>H<sub>13</sub>O<sub>2</sub> SbCl<sub>6</sub> (511.70), Calc.: C 25.82 H 2.56, Found: C 25.75 H 2.59.
- 7: m.p.: 108°; <sup>1</sup>H NMR: 2.00 (s): 4 (CH<sub>3</sub>)<sub>2</sub>; 2.96 (t): 5 CH<sub>2</sub>; 5.4(t): 6 CH<sub>2</sub>; 7.5—8.3 (m): aromatic protons; IR (cm<sup>-1</sup>): 1600, 1540, 1510, 1470, 1440, 1430, 1340, C<sub>12</sub>H<sub>15</sub>O<sub>2</sub> SbCl<sub>6</sub> (525.70), Calc.: C 27.40 H 2.87, Found: C 26.45 H 3.09.
- 8: m.p.: 111°; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 1.9 (s): 4 (CH<sub>3</sub>)<sub>2</sub>; 1.83 (d): 6 CH<sub>3</sub>; 2.75 (dd): 5 CH<sub>2</sub>; 5.8 (m): 5 CH<sub>2</sub>; 7.7—8.4(m): aromatic protons; IR (cm<sup>-1</sup>): 1600, 1540, 1510, 1450, 1430, 1400, 1300; C<sub>13</sub>H<sub>17</sub>O<sub>2</sub> SbCl<sub>6</sub> (539.70), Calc.: C 28.93 H 3.14, Found: C 28.54 H 3.23.

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#### ХИМИЯ 1,3-БИФУНКЦИОНАЛЬНЫХ СИСТЕМ, XXVIII. НОВЫЙ НЕПОСРЕДСТВЕННЫЙ СИНТЕЗ 1,3-ДИОКСАН-2-ИЛИЕВЫХ СОЛЕЙ ИЗ 1,3-ДИОЛОВ

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Гексахлоро свинцовые соли 2-фенил-1,3-диоксан-2-илия (5—8) могут быть приготовлены с хорошим выходом из 1,3-диолов (1—4) при использовании бензоилхлорида и пятихлористого свинца (схема I). Сделаны заключения относительно механизма происходящих процессов.