Neighbouring Benzoyl Group Participation in 1,2- and 1,3-Diol System

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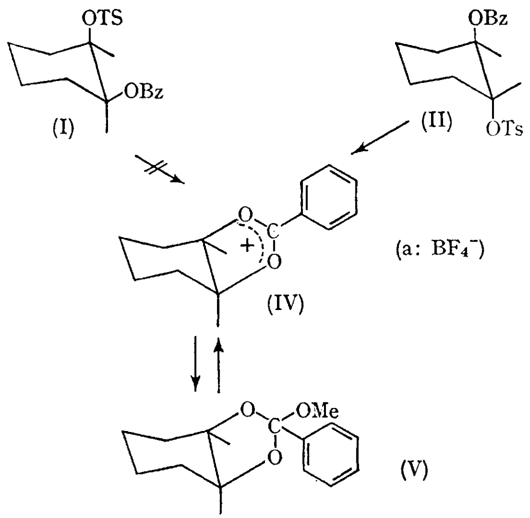
THE neighbouring acetyl group participation through a five-membered acetoxonium ion (AcO-5) is well known since the investigations of Winstein and co-workers.[1] In the past, we considered that the neighbouring acetyl group participation occurred through a six-membered acetoxonium ion (AcO-6).[2]

Recently we have been interested in the neighbouring benzoyl group participation. In order to study the (BzO-5) participation, the *cis*- and *trans*-2-benzoyloxycyclohexyl toluene-*p*-sulphonate (I and II) have been prepared. The relative rate of the acetolysis of compound (I) in dry acetic acid at 100° in the presence of potassium acetate was found to be $4 \cdot 6 \times 10^{-4}$, as compared to that of cyclohexyl-*p*-sulphonate (III) chosen as standard, while the reaction rate of the corresponding *trans*-isomer (II) proved to 0·26. The considerable increase in the reaction rate of (II), relative to that of *cis*-isomer (I), was explained by the participation of the neighbouring benzoyl group and the formation of a five-membered benzoxonium cation (IV) intermediate assumed to have been formed in the course of solvolysis.

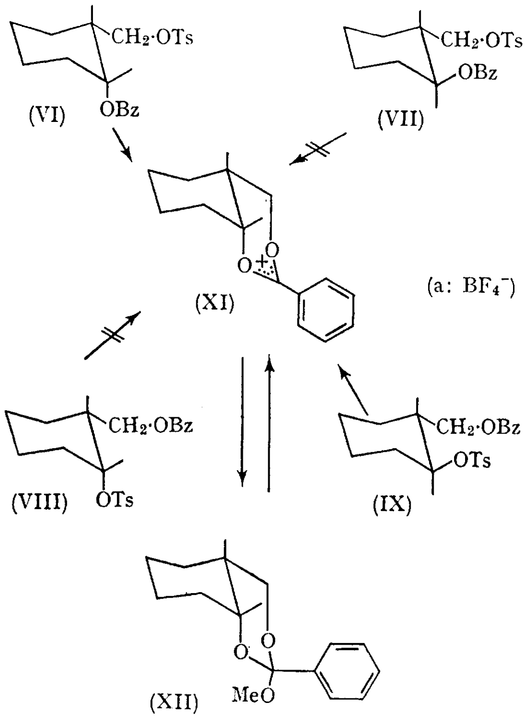
2-Phenyl-*cis*-4,5-tetramethylene-1,3-dioxolenium cation (IV), the presumed intermediate of the acetolysis of (II) could be isolated as 2-phenyl-2-methoxy-*cis*-4,5-tetramethylene-1,3-dioxolan (V)



from the preparative-scale methanolysis product, subsequently its fluoroborate salt (IVa) was also precipitated.

The examination of the benzoyl group participation arising at 1,2-diol toluenesulphonate–benzoate mixed esters has been extended also to 1,3-systems. To study further this (BzO-6) participation, the *cis*- and *trans*-2-toluene-*p*-sulphonyloxymethylcyclohexyl benzoate (VI and VII), and the *cis*- and *trans*-2-benzoyloxymethylcyclohexyl-toluene-*p*-sulphonate (VIII and IX) have been prepared. The acetolysis of (VI) in dry acetic acid at 100° in the presence of potassium acetate was 353·6 times faster than that of toluene-*p*-sulphonyloxymethylcyclohexane (X), considered as the basic compound. The increase in the rate of acetolysis was explained by the participation of the neighbouring benzoyl group and the formation of the ambident 2-phenyl-*cis*-4,5-tetramethylene-1,3-dioxonium cation (XI), as a possible intermediate. This cation could be isolated in good yields as 2-phenyl-2-methoxy-*cis*-4,5-tetramethylene-1,3-dioxan (XII) in the course of methanolysis carried out on a preparative scale, and its fluoroborate salt (XIa), too, could be precipitated. The formation of the same ambident cation (XI) and of the *ortho*ester derivative (XII) was observed in the methanolysis of (IX) too.

On the contrary, (BzO-6) participation was not found in either the case of (VII), nor (VIII). Similarly to those experiences obtained with the



acetoxy-group (1) in the case of the latter two compounds (VII and VIII) the neighbouring benzoyl group did not participate in the solvolysis of toluene-*p*-sulphonyl group.

TABLE

Acetolysis in dry acetic acid at 100°

Compound	10^4k_1 (sec.$^{-1}$)	$\tau_{\frac{1}{2}}$ (min.)	Rel. rate	
(X)	0·0506	2279·00	1	
(VI)	17·894	6·45	353·60	
(VII)	0·345	339·90	6·80	
(VIII)	1·972	58·56		0·30
(IX)	0·857	134·60		0·13
(I)	0·003	38,500·00		$4·6 \times 10^{-4}$
(II)	1·725	66·90		0·26
(III)	6·420	17·99		1

The recognised rules for benzoyl group participation can be studied in the above compounds with various substituted benzoyl derivatives.

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[2] (a) Ö. K. J. Kovács, G. Schneider, and L. K. Láng, *Proc. Chem. Soc.*, 1963, 374; (b) G. Schneider and Ö. K. J. Kovács, *Chem. Comm.*, 1965, **10**, 202.