The Directing Effect of the S → O Configuration on the Pyrolysis of Cyclic Sulphites

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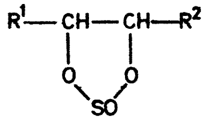
Summary Cyclic sulphites (**4a**,**b**,**c**) on pyrolysis give greater ketone : aldehyde product ratios than the *S*-epimeric compounds (**5a**,**b**,**c**).

ALDEHYDES (**2**) and ketones (**3**) are assumed[1] to be formed by a heterolytic process on pyrolysis of disubstituted cyclic sulphites (**1**). We now report the results of an examination of the influence of the configuration of the S→O group on the product distribution for the *S*-epimeric cyclic sulphites derived from *meso*-hydrobenzoins.

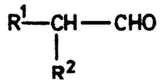
The cyclic sulphites were prepared in each case by reaction of the *meso*-hydrobenzoins[2] with thionyl chloride in C_5H_5N–CH_2Cl_2.[3] The major isomer (**4a**,**b**,**c**) was isolated by crystallisation from the mixture (*ca.* 20 : 1) of epimeric sulphites (**4**) and (**5**). Samples of the minor components (**5a**,**b**,**c**) were obtained from the crystallisation residues by chromatography on silica. The assignment of configuration at the sulphur atom for the epimeric cyclic sulphites (**4**) and (**5**) followed from the known deshielding effect of the sulphite S→O on *syn*-substituents on the heterocyclic ring[4] (Table).

Pyrolysis of each cyclic sulphite at 270° for 20 min under nitrogen gave mixtures of the corresponding aldehyde and ketone (total >85% yield) together with traces of other minor unidentified products. The relative yields of the major products, identified by comparison (n.m.r., g.l.c.) with authentic samples, were determined by g.l.c. (Table). For each series of cyclic sulphites (**4a**,**b**,**c**) and (**5a**,**b**,**c**) aryl migration to yield aldehyde (**2**) was favoured by 4,4′-methyl substituents and significantly suppressed by 3,3′-chloro-substituents.

Comparison of aldehyde : ketone product ratios for epimeric cyclic sulphites reveals a markedly higher yield of ketone from that epimer in which the S→O is *syn* to the hydrogen atoms on the heterocyclic ring. It seems probable that this increased yield of ketone arises as a result of proton capture by the *syn* sulphite oxygen to give the ketone *via* an enol mechanism (Scheme).



(1)

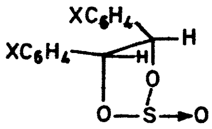


$R^1{-}\underset{R^2}{\underset{|}{CH}}{-}CHO$

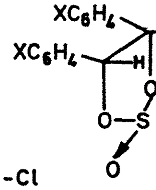
(2)

$R^1{-}CH_2{-}CO{-}R^2$

(3)



(4)



(5)

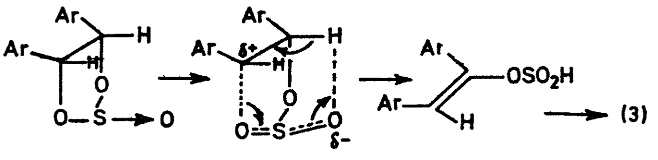
a; X = 3-Cl
b; X = H
c; X = 4-Me

N.m.r. data[a] *and pyrolysis product compositions*[b] *for cyclic sulphites* (**4**) *and* (**5**)

Cyclic sulphite	–C*H*–O–S–O signal (p.p.m.)	Aldehyde	Ketone
(**4a**)	6·13	18	82
(**5a**)	5·83	36	64
(**4b**)	6·12	36	64
(**5b**)	5·79	67	33
(**4c**)	6·10	64	36
(**5c**)	5·77	85	15

[a] Determined at 60 MHz for 10% solutions (w/v in $CDCl_3$ with $CHCl_3$ and Me_4Si as internal standards.

[b] Ratio obtained by g.l.c. on a 1·85 m column packed with 5% SE 30 on Aeropak 30.



SCHEME

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[2] L. F. Fieser, "Organic Experiments," D. C. Heath and Co., New York, 1965, p. 213.
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[4] M. D. Brice, J. M. Coxon, E. Dansted, M. P. Hartshorn, and W. T. Robinson, *Chem. Comm.*, 1969, 356.