Carbon–Sulphur Bond Cleavage in the Reaction of Benzyl and t-Butyl Sulphoxides with *N*-Halogenosuccinimides

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Summary Benzyl and t-butyl alkyl or aryl sulphoxides react with NBS or NCS in $CHCl_3$–ethanol (1%) at 25° to give benzyl or t-butyl halides and ethyl esters of alkyl or aryl sulphinic acids.

The reaction of sulphoxides with positive halogen species,[1] including *N*-bromo-[2,3] and *N*-chloro-succinimide,[3] either in the presence or absence of added base, generally results in the introduction of a halogen α to the sulphoxide function.

We have found that instead of α-halogenation, the reaction of sulphoxides with NXS results in cleavage of the carbon–sulphur bond [R^1–S in (**1**)], if such a cleavage leads to a relatively stable carbocation *e.g.* PhMeCH$^+$ or Me_3C^+.

Thus the sulphoxides (**1**) (R^1 = PhMeCH or Bu^t, R^2 = alkyl or aryl) react with NBS or NCS at room temperature in $CHCl_3$ containing an equivalent of an alcohol according to equation (1).

$$\underset{(\mathbf{1})}{R^1S(O)R^2} \xrightarrow[CHCl_3,R^3OH]{NXS} R^1X + R^2S(O)OR^3 \quad (1)$$

This cleavage, which represents a new reaction of sulphoxides, has considerable potential for the synthesis of a variety of cyclic and acyclic sulphinic and sulphonic acid derivatives. Carbon–sulphur bond cleavage in some benzylic,[4,5] t-butyl,[5] and ring sulphoxides[6] has been known for some time.

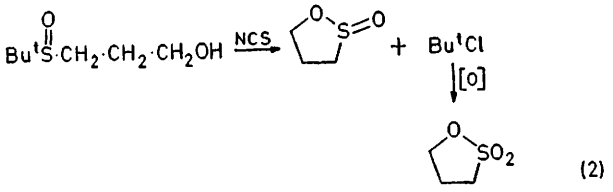
TABLE. $R^1S(O)\cdot CHR^2R^3 \xrightarrow[CHCl_3\text{–EtOH(1\%)}]{NXS} R^2R^3CH\cdot S(O)$

R^1	R^2	R^3	Ester (%)
Bu^t	H	Pr	60
Bu^t	Me	Me	85
Bu^t	Me	Pr	94
Bu^t	Et	Pr	95
Bu^t	Et	Pr	50[a]
$PhCH_2\cdot S(O)Ph \longrightarrow PhS(O)Et$			95
$PhCH(Me)\cdot S(O)Ph \longrightarrow PhS(O)\cdot OCEt$			95

[a] After chromatography through SiO_2.

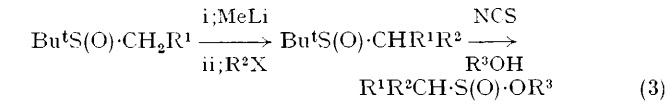
A number of examples of the cleavage reaction are shown in the Table. The sulphinate esters produced according to equation (1) could be isolated if desired, but were generally oxidized to the corresponding sulphonate esters by addition of *meta*-chloroperbenzoic acid to the reaction mixture. The n.m.r. spectra of the crude esters thus obtained were virtually identical with those of the purified products. When the alcohol was incorporated into the sulphoxide, as in the γ-hydroxy-sulphoxide (**2**), reaction with NCS gave

cyclic sulphinic esters and, after oxidation, sultones [equation (2)].



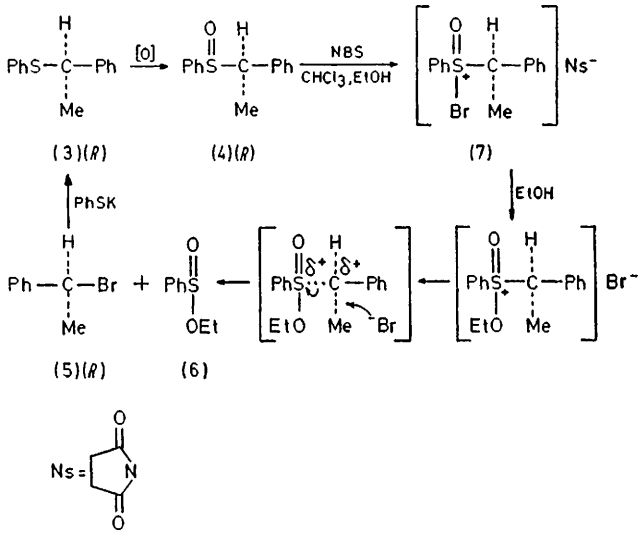
(2)

Cleavage of t-butyl alkyl sulphoxides, prepared by treatment of the lithio-derivatives of simpler sulphoxides with electrophilic reagents, affords substituted sulphinate esters and thus represents a general synthesis of these substances [equation (3)].



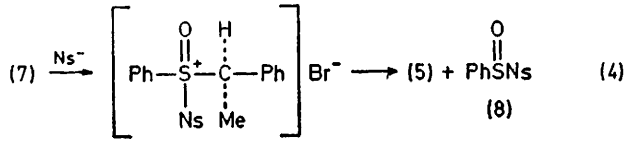
(3)

The mechanism of the fragmentation has also been briefly investigated by studying the stereochemical course of the cleavage reaction using the optically active sulphoxide (**4**), prepared by oxidation of *R*-α-methylbenzylphenyl sulphide (**3**), $\alpha_D = +167°$ (*c* 2·8, $CHCl_3$).[7] Treatment of (**4**) with NBS in $CHCl_3$–EtOH (1%) at 0° for 90 min afforded, in virtually quantitative yield, a mixture of α-phenethyl bromide (**5**) and ethyl benzenesulphinate (**6**). Because of the ease with which the bromide (**5**) is racemized,[8] the crude reaction product was treated with PhS^-K^+ in methanol. The sulphide (**3**) thus obtained had $\alpha_D = +11·5°$ (*c* 2·8, $CHCl_3$). Since the sign of the rotation of the sulphide (**3**) thus obtained was the same as that of the starting sulphide, the fragmentation must have occurred with net inversion of configuration at the benzylic carbon. The low optical yield, *ca.* 6%, indicates that the cleavage reaction is essentially an S_N1 type process (Scheme). In agreement with this conclusion is the observation that the major product of the cleavage in methanol is α-methylbenzyl methyl ether. The mechanism suggested in the Scheme



SCHEME

for the sulphoxide cleavage is entirely analogous to that proposed by Tuleen and Stephens[5a] for the cleavage of benzylic sulphides. In the Scheme, succinimide anion (NS^-) could also displace Br^- from the bromo-oxosulphoxonium salt (**7**). The intermediate thus obtained could fragment to (**5**) and the sulphinamide (**8**) [equation (4)]. Reaction of (**8**) with ethanol would be expected to form ethyl benzenesulphinate and succinimide.



(4)

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