Selective Oxidation of 2-Benzylidene-2,3-dihydro-5-methylbenzo[*b*]thiophen-3-one by Sodium Hypochlorite–Hypochlorous acid

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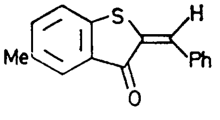
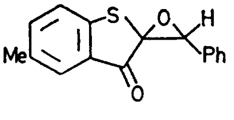
Summary Aqueous sodium hypochlorite, adjusted to various pHs, was found to be a versatile reagent for the controlled oxidation of 2-benzylidene-2,3-dihydro-5-methylbenzo[*b*]thiophen-3-one to the epoxide, *S*-oxide, and isomeric *S*-oxide epoxide derivatives.

PERACIDS are the usual reagents of choice for the stereospecific epoxidation of olefins[1] including in some cases $\alpha\beta$-unsaturated ketones.[1] These reagents cannot be used directly for this purpose when the system contains a sulphide group as in benzylidenebenzothiophenones because of the greater susceptibility of this group to electrophilic attack over that of the olefin bond.[1] We have now found that sodium hypochlorite, which had previously been shown to be a stereospecific nucleophilic reagent in the epoxidation of the geometrical isomers of 3-arylideneflavanones,[2] may be used effectively for this purpose with such a system. Thus, *trans*-2-benzylidene-2,3-dihydro-5-methylbenzo[*b*]thiophen-3-one (**3**) on treatment with freshly prepared sodium hypochlorite (pH 13)† gave the *trans*-epoxide (**4**) in high yield, while treatment of the *cis*-isomer (**1**) gave a mixture of the *cis*-epoxide (**2**; 44%) and the *trans*-epoxide (**4**; 48%).

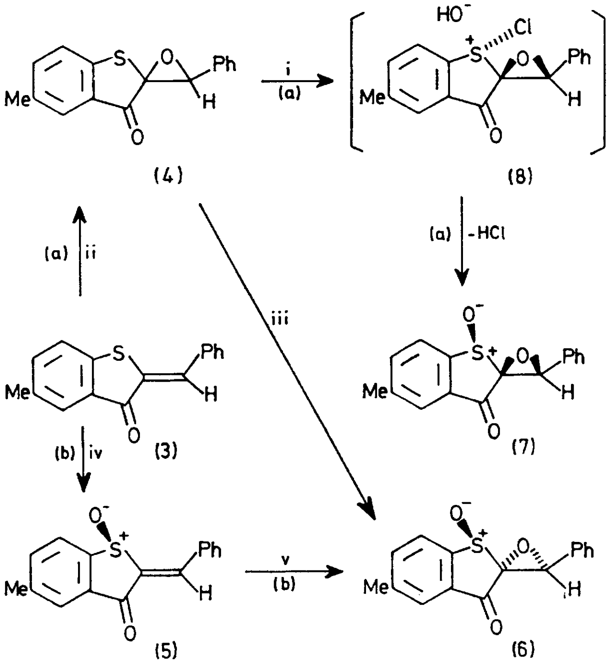

(1)


(2)

Compound (**3**) on reaction with sodium hypochlorite which had been adjusted to pH 4 or pH 6 (hypochlorous acid)† gave the *S*-oxide (**5**)[3] (>80% in <16 s) resulting, presumably, from electrophilic attack by HOCl. Treatment of (**4**) in the same way with hypochlorous acid (pH 6) afforded the *S*-oxide epoxide (**7**) together with a small quantity of the isomeric *S*-oxide epoxide (**6**) (ratio, *ca.* 50:1). Further reaction of (**5**) with sodium hypochlorite (pH 13) yielded a mixture of the same isomeric compounds (**7**) and (**6**) in a ratio of 1:3. When alkaline hydrogen peroxide was used as the epoxidising agent (**6**; 67%) was the sole product isolated.‡ Compound (**6**) was assigned the *trans,trans*-configuration on the basis of steric approach control[4] of the major product in each reaction (Scheme). This conclusion was supported when *m*-chloroperbenzoic acid, on reaction with (**4**), afforded (**6**) as the major product [ratio of (**6**) to (**7**), *ca.* 6:1].

The practically stereoselective formation of the *trans,cis*-sulphoxide epoxide (**7**) on reaction of hypochlorous acid (pH 6) with (**4**) suggests initial attack by the HOCl on the side of the molecule *trans* to the epoxide oxygen to give an intermediate 1,2-*trans*-chlorosulphonium ion (**8**) followed by displacement of the chloride ion to yield (**7**). This reaction is analogous to that of the *S*-oxidation of certain substituted thians by means of t-butyl hypochlorite to give *cis*-sulphoxides,[4] in which it was shown[5] that chlorosulphonium ions were intermediates.

When (**3**) was oxidised by aqueous sodium hypochlorite having intermediate pH (pH 8), a mixture of the two isomeric compounds (**7**) and (**6**) (ratio *ca.* 2:1) was obtained. This presumably results from two competing consecutive reactions; initial attack on the sulphur atom of (**3**) by hypochlorous acid to give (**5**) followed by reaction with the hypochlorite ion to yield mainly the *trans,trans*-*S*-oxide epoxide (**6**) (Scheme, path b), and initial attack on the olefin bond by the hypochlorite ion to produce (**4**), with subsequent oxidation by hypochlorous acid to give mainly the *trans,cis*-*S*-oxide epoxide (**7**) (Scheme, path a).



SCHEME. All reactions were carried out in dioxan at room temperature. Only the major product of each reaction is shown. i, HOCl (pH 6); ii, NaOCl (pH 13); iii, ClC$_6$H$_4$CO$_3$H-*m*; iv, HOCl (pH 4 or 6); v, NaOCl (pH 13) or H$_2$O$_2$-NaOH.

(*Received, 2nd September* 1976; *Com.* 1013.)

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† Freshly prepared aqueous sodium hypochlorite had pH 13 which was adjusted to appropriate levels (pH meter) by the addition of glacial acetic acid. Using $3{\cdot}8 \times 10^{-8}$ as ionisation constant for hypochlorous acid (M. W. Lister, *Canad. J. Chem.*, 1962, **30**, 879) the percentage hypochlorite ion of the total hypochlorite ion and hypochlorous acid in solution is calculated to be 100% at pH 13, 79·2% at pH 8, 3·7% at pH 6, and 0·38% at pH 4.

‡ All new compounds were identified by satisfactory analytical and spectral data.

[1] See A. Rosowsky in 'Heterocyclic Compounds with Three- and Four-membered Rings,' ed. A. Weissberger, Interscience, New York, 1964, pt. 1, p. 1, and H. O. House, 'Modern Synthetic Reactions,' 2nd edn. Benjamin, California, 1972, p. 293.

[2] D. D. Keane, W. I. O'Sullivan, E. M. Philbin, R. M. Simons, and P. C. Teague, *Tetrahedron*, 1971, **27**, 3535.

[3] The sulphoxide (5) was recently reported (L. S. S. Réamonn and W. I. O'Sullivan, *J.C.S. Chem. Comm.*, 1976, 642) in connection with a novel additive Pummerer reaction which this compound undergoes.

[4] C. R. Johnson and D. McCants, *J. Amer. Chem. Soc.*, 1965, **85**, 1109.

[5] C. R. Johnson and J. J. Rigau, *J. Amer. Chem. Soc.*, 1969, **91**, 5398.