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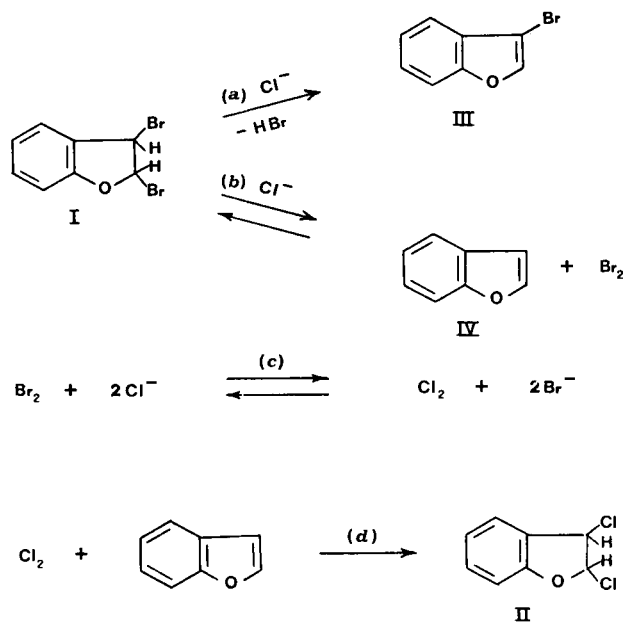
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Treatment of the title compound with chloride ions in acetonitrile leads mainly to the formation of *trans*-2,3-dichloro-2,3-dihydrobenzofuran. Since a nucleophilic displacement of bromide anion by chloride anion can be excluded, a mechanism involving the equilibrium  $2\text{Cl}^- + \text{Br}_2 \rightleftharpoons 2\text{Br}^- + \text{Cl}_2$  is suggested.

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Sir:

Our continuous interest in the role played by addition compounds in the mechanism of the halogenation of aromatic and heteroaromatic substrates (1) has led us to investigate the decomposition pattern of *trans*-2,3-dibromo-2,3-dihydrobenzofuran (I) in different solvent-base systems. In this communication we wish to report that an indirect halogen exchange takes place in the reaction of I with chloride ions in acetonitrile.



When I (0.05 M) reacts, in the presence or in the absence of 2,4,6-collidine, with tetra-*n*-butylammonium chloride (0.75 M) at 30° for 4 hours, *trans*-2,3-dichloro-2,3-dihydrobenzofuran (II) (2) is formed as the main reaction product, together with a small amount (ca. 10%) of 3-bromobenzofuran (III) [nmr and glc analysis: comparison with authentic specimens (3)]. However, when the reaction is carried out in the presence of stannous chloride or solid sodium thiosulfate (both of which do not react with I in the absence of chloride anion) the only product observed is benzofuran (IV).

Since the latter result rules out the possibility that II is formed from I by a direct nucleophilic displacement of

bromide anion by chloride anion, we suggest that the reaction of I with chloride ions occurs by the mechanism reported in the scheme.

Chloride ions act both as dehydrohalogenating, reaction (a), and dehalogenating, reaction (b), agents leading to III and IV, respectively. However, whereas debromination is a favoured *anti*-elimination reaction, the loss of hydrogen bromide must necessarily take place *via* a *syn*-elimination process, which is energetically unfavoured, especially when promoted by halide ions (4). Therefore, the occurrence of reaction (a) is to be related to the fact that it is an irreversible process, whereas equilibrium (b) is shifted far to the left (1). The addition product II is then formed by the reaction of IV with molecular chlorine deriving from equilibrium (c), which has already been shown to play a significant role in the bromination of some aromatic compounds (5). Reaction (d) is irreversible and extraordinarily fast (2), and should take place even though the equilibrium concentrations of chlorine and IV are probably very small (6).

Addition of a bromine scavenger (such as sodium thiosulfate or stannous chloride) has the twofold effect of making reaction (b) irreversible and of not allowing the establishing of equilibrium (c). Thus, the exclusive formation of benzofuran is observed in line with the above reasonings.

The peculiarity of the reaction with chloride ions is shown by the fact that, in contrast, when bromide ions are used as the base, under the same conditions, the only reaction product found is benzofuran (IV), clearly formed by the favoured *anti*-dehalogenation process (4).

Similarly, the expected *syn*-elimination reaction, leading to the exclusive formation of 3-bromobenzofuran, is generally observed using alkaline alcoxides in the corresponding alcohols.

Acknowledgements.

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#### REFERENCES AND NOTES

- (1) E. Baciocchi, S. Clementi, and G. V. Sebastiani, *J. Chem.*

*Soc. Perkin Trans. II*, 266 (1976).

(2) E. Baciocchi, S. Clementi, and G. V. Sebastiani, *J. Heterocyclic Chem.*, **14**, 359 (1977).

(3) The glc analysis of the reaction mixture shows the presence of benzofuran, 3-bromobenzofuran, 3-chlorobenzofuran, and 2-chlorobenzofuran. The absence of the peak of 2-bromobenzofuran is a clear evidence of the complete absence of I in the reaction mixture, as the latter is known to give, by thermal decomposition, an appreciable amount (25%) of 2-bromoderivative, together with 70% of IV and 5% of III. The relative amount of benzofuran (25%), 2-chlorobenzofuran (40%), and 3-chlorobenzofuran (35%) is in agreement with the pattern obtained by

thermal decomposition of an authentic specimen of *trans*-2,3-dichloro-2,3-dihydrobenzofuran. On the other hand the nmr spectrum of the reaction product is compatible with that previously reported for the latter compound (2).

(4) W. H. Saunders, Jr. and A. F. Cockerill, "Mechanisms of Elimination Reactions", New York, N.Y., 1973, p. 194 ff.

(5) E. Baciocchi and L. Mandolini, *Tetrahedron Letters*, 1659 (1971).

(6) Control experiments have shown that in acetonitrile the addition of chlorine to IV actually leads to the formation of the *trans* adduct only, whereas in non polar solvents a mixture of *cis* and *trans* isomers had been obtained.