Formation of Thiobenzophenones by the Alkoxide Cleavage of Substituted Diphenylmethyl Phenyl Disulphides

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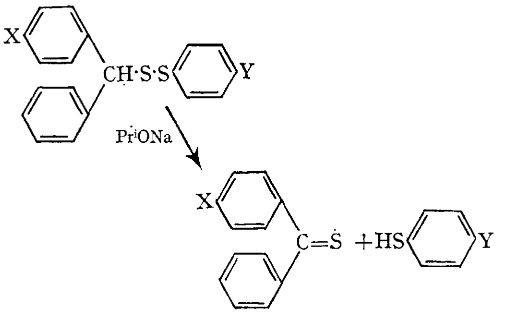
THE mechanism of the alkaline cleavage of organic disulphides has been extensively discussed.[1] In the case of disulphides with a hydrogen atom attached to one of the α-carbon atoms, a mechanism involving a β-elimination has been suggested[2] as an alternative to direct attack of the base on one of the sulphur atoms. The elimination reaction would involve proton removal by base followed by loss of mercapto-ion to give a thioaldehyde or thioketone. However, no conclusive evidence for the formation of thiocarbonyl derivatives has been reported in such a reaction. In general they are only implied as reactive precursors of the carbonyl compounds identified as the final products.

We report an example of the formation of thiocarbonyl compounds from disulphides by such an elimination, together with a preliminary kinetic study of the reaction. We have found that diphenylmethyl phenyl disulphides† are converted into thiobenzophenones and thiophenols by base. Both thioketone and thiophenol have been isolated and identified in one experiment in which 4-chlorophenyl-4-phenyldiphenylmethyl disulphide ($1{\cdot}24 \times 10^{-3}$ mol.) was treated with sodium isopropoxide ($2{\cdot}46 \times 10^{-3}$ mol.) in isopropyl alcohol–benzene (50—50 v/v)‡ at 25° under nitrogen. At the end of the reaction water was added and acidification of the aqueous alcoholic layer gave the crude 4-chlorothiophenol which was purified by sublimation under vacuum, m.p. 50—52° (60%). On the other hand 4-phenylthiobenzophenone was recovered from the organic layer and purified by chromatography on a silica gel column developed with CCl_4, (50%), m.p. 124—125°. The visible, u.v., and i.r. spectra correspond to those of the authentic thioketone prepared from the oxygen analogue.[3]



A number of differently substituted disulphides (Table) have been investigated at a reagent concentration ($2—3 \times 10^{-3}$ M) in isopropyl alcohol–benzene (95—5 v/v). The thioketones were identified by comparison of the absorption spectra of the final solutions with those of authentic samples. The thiophenols were isolated by sublimation and identified by v.p.c. The yields and the rate constants have been spectrophotometrically determined using the absorption band near 600 mμ, characteristic of the thioketones.§

The conversion of disulphide into thioketone is not quantitative. The yields are in the range of 68—87% (Table) depending on the nature of the substituents X and Y; the remainder of the disulphide is consumed in a concurrent reaction, likely to involve attack by the base on one of the sulphur atoms. Both the elimination and the concurrent reaction are irreversible and parallel second-order rate processes (first in disulphide and first in base respectively) as shown by the constancy of the yields of thioketone despite substantial variation of base and substrate concentrations. Kinetic data show (*a*) the reaction occurs readily, presumably because of the strength of the base and the marked acidity of the diphenylmethyl hydrogen atom which is activated by the α-sulphur atom as well as the two aryl groups.¶ However, it is

Rate constants and product yields for the thiocarbonyl elimination from diphenylmethyl phenyl disulphides promoted by sodium isopropoxide in isopropyl alcohol–benzene (95—5 v/v) *at* 25°.

Substituents X[a]	Y[b]	m.p.	Thioketone yields (%)[c]	k_{1e}[d], (M^{-1} sec.$^{-1}$ $\times 10^2$)
Cl	Cl	oil	87	71
Ph	Cl	106—107°	77	15
H	Cl	58—59°	77	7·5
Ph	H	88—89·5°	69	4·1
Ph	CH_3	110—111°	68	2·3

[a] diphenylmethyl substituent; [b] thiophenyl substituent; [c] calculated from the maximum value of the optical density reached at the end of the reaction using the extinction coefficient determined with authentic samples in isopropyl alcohol: ϵ 187 (600 mμ) for *p*-Cl, 267 (603 mμ) for *p*-Ph (we previously reported a lower value of 232), and 167 (600 mμ) for the unsubstituted thiophenones. Deviations of 0·5—2% from the reported values have been observed; [d] averaged over 3 or more runs carried out at different initial substrate concentrations ($3—5 \times 10^{-3}$ M) and base ($2—5 \times$ disulphide concentration). The deviations from the reported values range between 2—5%.

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† Diphenylmethyl phenyl disulphides have been prepared by reaction of diphenylmethyl thiols with sulphenyl chlorides and purified by chromatography on silica gel. Satisfactory elemental analyses have been obtained for all new compounds.

‡ Benzene was added because of the low solubility of some disulphides in isopropyl alcohol.

§ Authentic thioketones are stable in the reaction medium at least for 4—5 half-lifes. However, as the ratio isopropoxide: thioketone is higher than 5—6, thioketones undergo decomposition at a significant rate. Addition of thiophenols does not appreciably affect the rate of decomposition.

¶ The same factors have been suggested to account for the closely related reaction, hydrogen cyanide eliminaton from diphenylmethyl thiocyanates, A. Ceccon, U. Tonellato, and U. Miotti, *Chem. Comm.*, 1966, 586; A. Ceccon, U. Miotti, U. Tonellato, and M. Padovan, to be published.

remarkable that a large fraction of the disulphide is consumed in a competitive reaction, in spite of the above-mentioned factors, all of which favour the high reactivity in the elimination reaction. This could mean that for the other systems, such as aliphatic disulphides, the elimination route can hardly compete with the direct attack on one of the sulphur atoms unless very acidic α-hydrogens are present; (*b*) the elimination rate is markedly affected by substituents both in the diphenylmethyl and in the thiophenyl moiety. Electron-withdrawing groups accelerate the rate and the effect is larger for substituents on the diphenylmethyl group.

(*Received, February 29th*, 1968; *Com.* 248.)

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[2] N. A. Rosenthal and G. Oster, *J. Soc. Cosmetic Chemists*, 1954, **5**, 286; *J. Amer. Chem. Soc.*, 1961, **83**, 4445.

[3] A. Schönberg, "Methoden der Organische Chemie", ed. Houben-Weyl, Thieme, Stuttgart, 1955, vol. 9, p. 710.