Preparation and Reversible Polymerisation of Monothiobenzil

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Summary A new preparation is described of monothiobenzil which in the solid state turns to a green polymeric glass; the latter, in solution in inert solvents, reverts during several hours to monomeric monothiobenzil.

IN connection with syntheses of sulphur-containing enophiles we are interested in routes to monothiobenzil (I), a substance only recently described, and prepared in an impure state, by Dittmer,[1] *via* 1,2-dibenzoylstilbene episulphoxide.

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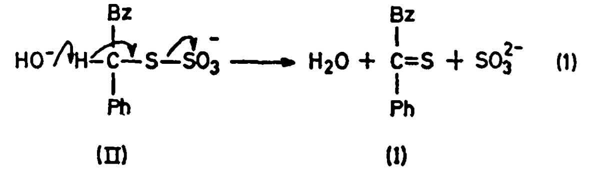
The base-catalysed decomposition of Bunte salts, in which transient formation of thiocarbonyl species seems mechanistically implicated,[2] and which are mentioned in a paper[3] on the conceptually similar base-fission of diarylmethyl thiocyanates, might be usefully and specifically applied in the case of the ion (II) to provide another route to monothiobenzil [reaction (1)]. However, in preparations of (I) by this means in aqueous systems it would be important to minimize competitive reactions, which would destroy or suppress formation of the product thione. These include (i) bisulphite addition across the carbonyl or thiocarbonyl groups, (ii) alkaline hydrolysis of (I) to benzil, and (iii) reaction of sulphide ion [liberated in (ii)] with 2 mol. equiv. of (II)[4] to yield didesyl trisulphide [desyl = Ph-(PhCO)CH] and would all occur in the aqueous phase.



$$HO^- + H\text{–}C(Bz)(Ph)\text{–}S\text{–}SO_3^- \longrightarrow H_2O + (Bz)(Ph)C{=}S + SO_3^{2-} \quad (1)$$

(II) (I)

Accordingly an aqueous solution of sodium *S*-desylthiosulphate[5] was added to aqueous alkali in the presence of a partitioning solvent which would separate the expected monothiobenzil (I) from the aqueous nucleophiles. In practice, dichloromethane was chosen as co-solvent, and we find the following conditions for the formation of monothiobenzil most suitable.

To vigorously stirred aqueous NaOH (1N; 25 ml) and CH_2Cl_2 (40 ml) in air at room temperature 0·1N aqueous sodium *S*-desylthiosulphate (25 ml)[5]‡ was added during 5 min. The blue dichloromethane layer, was then washed and dried (Na_2SO_4). It had u.v.-visible absorptions at 248 (s), 327 (s), and 608 (C=S n–π^* transition) ($\epsilon \sim 40$) nm, identical with the solution data of Dittmer.[1] I.r. data showed the expected carbonyl bands, also in agreement with Dittmer's reports.[1] T.l.c., using the perpendicular repeat technique, differentiated impurities (<5%) indigenous to the sample from those formed by reaction of (I) with the support material. Finally, the weight of product remaining after removal of solvent was within 2% of that expected from equation (1), whilst that product gave a satisfactory analysis for sulphur.

The dichloromethane extract of monothiobenzil showed remarkable behaviour as solvent was removed: the deep blue colour continued to intensify until, with the solvent practically removed, it changed to a lighter emerald green as a glassy polymer was rapidly deposited. When this polymer, which can be stored apparently unchanged for several weeks, was rapidly redissolved in dichloromethane, or other inert solvents, its colour was at first unchanged in solution and may be attributed to a weak residual n–π^* absorption at 608 nm together with short wavelength visible region absorptions.

However, after 2—3 h in the dark or in daylight, the absorption of these solutions at 608 nm grows substantially so that in the limit a spectrum identical with that of the presumably monomeric monothiobenzil extract from the parent reaction mixture is obtained. Typical spectra indicating this change are given in the Figure, whilst study still in progress shows that the rate of this 'depolymerisation' is slightly reduced by bases and is somewhat sensitive to the choice of solvent. It is clear that the polymerisation–depolymerisation cycle is completely reversible, and the green polymer may provide a useful source of monothiobenzil for future studies of its enophilic and dienophilic nature.

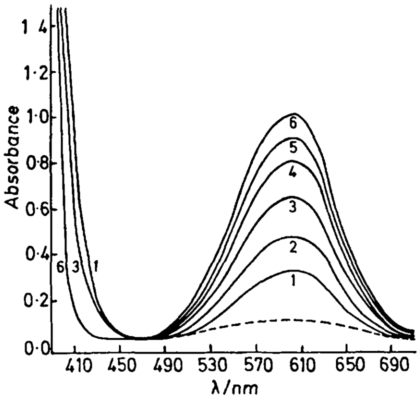


FIGURE. *Visible spectra of monothiobenzil* (0·03M) *at various times after dissolution of the green polymeric form in dichloromethane at room temperature* (1 *cm cell*). *Dashed curve: extrapolated zero time spectrum of green polymer. Spectra of same solution after* 10 *min* (*curve* 1), 25 *min* (2), 35 *min* (3), 50 *min* (4), 70 *min* (5), *and* 100 min (6). *Curve* 6 *is practically superimposable on the spectrum of monomeric monothiobenzil* (0·03M) *prepared in solution as described in the text.*

Of some theoretical interest are the facts that, unlike other thiones, monothiobenzil does not seem to be particularly unstable towards oxygen, and that the depolymerisation represents the easy formation of thiocarbonyl groups (of presumably low π-bond energy) from –C–S–C–S– systems of formally strong σ-bond description, no doubt owing to the influence of the neighbouring benzoyl group.

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‡ In the absence of co-solvent no thione can be isolated after a transient blue–green coloration, whilst t.l.c. of the products indicates a complex decomposition pattern. If the system in the presence of co-solvent is not vigorously stirred, or if the concentration of alkali is near to or below 0·1N emulsification is a problem.

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[5] R. H. Baker and C. Barkenbus, *J. Amer. Chem. Soc.*, 1936, **58**, 262.