Reaction of Thiobenzophenone with Various Amines giving 3,3,5,5-Tetraphenyl-1,2,4-trithiolan

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Summary Reaction of thiobenzophenone with certain amino-compounds afforded the title compound, together with low yields of the expected Schiff bases.

IT has been assumed in the literature[1] that thioketones react with suitable amines to form Schiff bases. We report that thiobenzophenone (Ia), when treated with certain amines, afforded the thio-ozonide, 3,3,5,5-tetraphenyl-1,2,4-trithiolan (II).

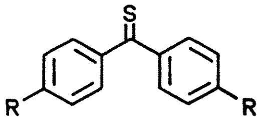
A solution of thiobenzophenone in amines (a)—(e) (Table) was stirred briefly at ambient temperature under nitrogen. The deep blue colour was discharged rapidly by the primary amines (a)—(c), slowly by diethylamine (d), and not at all by triethylamine (e). Removal of the excess of amine under vacuum at low temperature gave an oily solid which on heating or prolonged exposure to the atmosphere decomposed to a blue oil. T.l.c. in each case indicated a significant amount of a non-polar product (R_F 0·9; Kieselgel G; 90% benzene–10% light petroleum) which gradually acquired the deep blue colour of thiobenzophenone if left on the chromatography plate. Only small quantities of imino-compounds were estimated to be present. Careful preparative t.l.c. of the crude products afforded modest yields of the thio-ozonide, identical with authentic material[2] (elemental analysis, t.l.c., i.r., and m.p.).

TABLE

	Reactant	Yield[a] of thio-ozonide
(a)	$MeNH_2$	31%
(b)	$PhNH_2$	30%
(c)	$Me_2N{\cdot}NH_2$	27%
(d)	Et_2NH	26%
(e)	Et_3N	Trace
(f)	$H_2N{\cdot}O{\cdot}SO_3H$	13%
(g)	$p\text{-}MeC_6H_4{\cdot}SO_2{\cdot}NNaCl,3H_2O$ ..	90%
(h)	$p\text{-}MeC_6H_4{\cdot}SO_2{\cdot}NH_2$	Zero

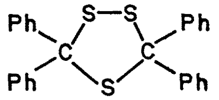
[a] Estimated by preparative t.l.c. separation following removal of amine under vacuum, at low temperature. Quoted as weight percent isolated from total crude product.

Excess of reactants (f)—(h) were removed by aqueous extraction.

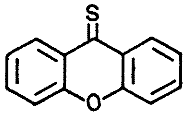


(I)

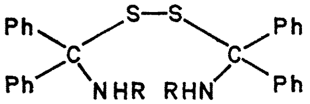
a, R = H
b, R = NMe_2
c, R = OMe



(II)



(III)



(IV)

In the i.r. spectrum, (KBr disc), strong absorption bands at 1490, 1080, 1025, and 920 cm^{-1} were observed. Mass spectral examination was complicated by the thermal lability of the compound. Superimposed mass spectra of thiobenzophenone[3] and sulphur were obtained. An ion at *m/e* 332 was attributed to tetraphenylethylene (obtained by extrusion in the mass spectrometer† of sulphur from the thio-ozonide).

Addition of radical inhibitors with reactants (a)—(f) or exclusion of light did not significantly affect product formation but addition of mineral acid inhibited thio-ozonide formation. Compound (IV) may be an intermediate.

Thiobenzophenone reacted with hydroxylamine-*O*-sulphonic acid (f) at room temperature only in the presence of sodium ethoxide and gave a low yield of thio-ozonide, other major products being benzophenone oxime and sulphur.

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† It is not known at this stage whether extrusion is due to thermal or electron bombardment processes.

Reaction at ambient temperature with chloramine-T (g) (benzene or carbon tetrachloride suspension) afforded almost quantitative conversion of thione into thio-ozonide (no nitrene insertion product was observed).

Preliminary studies of other aromatic thiones (Ib), (Ic), and (III), indicate that under similar conditions thio-ozonides are not obtained.

When the unstable thio-ozonide (II) was heated under reflux in cyclohexene, thiobenzophenone was formed, together with sulphur and traces of cyclohexene sulphide (comparative t.l.c. and g.l.c. on polar and non-polar stationary phases).

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[1] For reviews of the reactivity of the thioketone group see E. Campaigne, *Chem. Rev.*, 1946, 1; R. Mayer, *Angew. Chem. Internat. Edn.*, **1964, 4**, 277 (aliphatic thioketones); E. E. Reid, "Organic Chemistry of Bivalent Sulphur," vol. 3, Chemical Publishing Co., New York, 1960; E. Campaigne, "Chemistry of the Carbonyl Group," ch. 17, ed. S. Patai, Interscience, New York, 1966.

[2] H. Staudinger and H. Freudenberger, *Chem. Ber.*, 1928, **61B**, 1836; E. Campaigne and W. Bradley Reid, *J. Org. Chem.*, 1947, **12**, 807; A. Schönberg and B. Konig, *Chem. Ber.*, 1968, **101**, 725.

[3] D. Schumann, E. Frese, and A. Schönberg, *Chem. Ber.*, 1969, **102**, 3192.