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SOME REACTIONS OF BENZOTHIAZOLE-2-SULPHENAMIDES

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Abstract—Thermal reactions of N-cyclohexylbenzothiazole-2-sulphenamide, alone and in admixture with 2-mercaptobenzothiazole, have been studied. Among the products is N-benzothiazolylcyclohexylamine; this compound can also be obtained in high yield by the reaction of cyclohexylammonium benzothiazolyl-2-mercaptide and 2,2'-dithiobisbenzothiazole. Benzothiazole-2-sulphenamides react in solution with thiols at ambient temperature to give disulphides and amine thiolates.

BENZOTHIAZOLE-2-sulphenamides form an important class of delayed-action rubber vulcanization accelerators.[1] Of these sulphenamides N-cyclohexylbenzothiazole-2-sulphenamide (I) appears to be the most widely used, but those of other amines, e.g. morpholine, t-butylamine, are also important. The technological properties are affected by the amine involved.

There is a substantial amount of patent literature concerned with the preparation of these compounds, and with their technological application, but little has been published concerning the chemistry of benzothiazole-2-sulphenamides, or for that matter, of sulphenamides in general. The field has been recently reviewed.[2]

This paper describes part of a programme of investigation into the chemistry of benzothiazole-2-sulphenamides, with particular emphasis on reactions of relevance to the application of these materials as vulcanization accelerators.

It was reported by Carr, *et al.*[3] that benzothiazole-2-sulphenamides decompose on heating to give 2,2'-dithiobisbenzothiazole(II) and the amine salt of 2-mercaptobenzothiazole.

More recently Eitingon *et al.*[4] isolated and identified 2,2'-dithiobisbenzothiazole, cyclohexylammonium benzothiazolyl-2-mercaptide (III) and 2-mercaptobenzothiazole (IV) from the products of decomposition of N-cyclohexylbenzothiazole-2-sulphenamide at 140°. The reaction exhibited an induction period; free radicals were detected by electron spin resonance, after the induction period.

In this present work it was found that when held at 180° in a thermogravimetric balance, N-cyclohexylbenzothiazole-2-sulphenamide exhibited an induction period of 60 min after which time an accelerating loss of weight to a maximum of 20% occurred. A larger sample, held at 140° for $3\frac{1}{2}$ hr gave a tar, from which was isolated 2-mercaptobenzothiazole, 2,2'-dithiobisbenzothiazole, cyclohexylammonium benzothiazolyl-2-mercaptide (isolated as 2-mercaptobenzothiazole and cyclohexylamine), and a solid, m.p. 103–105° which was shown by elementary analysis, IR comparison, and mixed m.p. with an authentic sample to be N-benzothiazolylcyclohexylamine (V). This latter compound has not been previously reported as a product of the decomposition. Thus:

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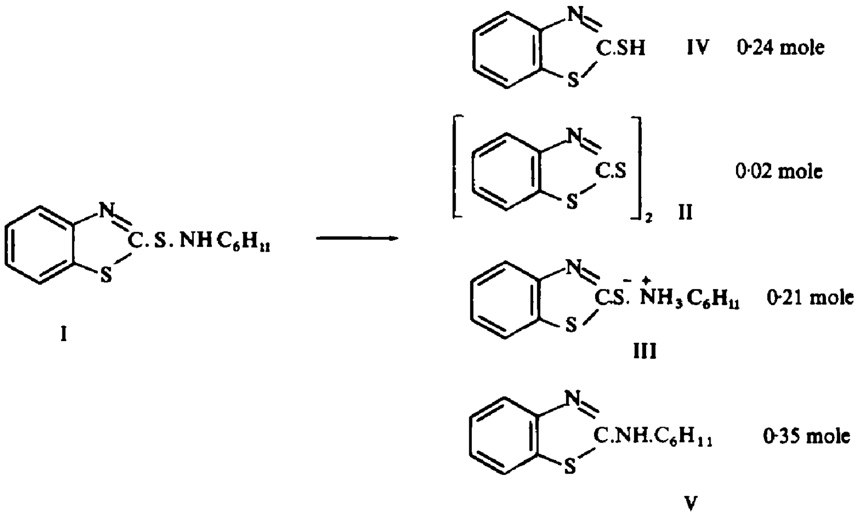

I

IV 0·24 mole

II 0·02 mole

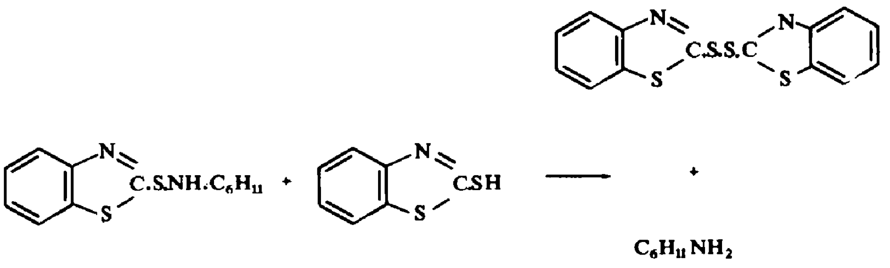
III 0·21 mole

V 0·35 mole

Contrary to previous reports, under the conditions used above, 2,2′-dithiobisbenzothiazole is only a minor product of this reaction.

It has been suggested[4] that the formation of 2-mercaptobenzothiazole is responsible for the autocatalytic nature of this decomposition. We found that N-cyclohexylbenzothiazole-2-sulphenamide and 2-mercaptobenzothiazole underwent rapid reaction at 140–150°. Thus, when a mixture of these compounds, in molar ratio 1·2:1 was held at 150° for 5 min the sulphenamide was completely reacted, the products identified being mainly 2,2′-dithiobisbenzothiazole and N-benzothiazolylcyclohexylamine.

The facility of this reaction suggested that benzothiazole-2-sulphenamides and thiols might react at lower temperatures. On mixing equimolar amounts of 2-mercaptobenzothiazole and N-cyclohexylbenzothiazole-2-sulphenamide in ether solution, and allowing the mixture to stand at room temperature, a precipitate, which was shown to be mainly 2,2′-dithiobisbenzothiazole, was obtained after about 5 min; cyclohexylamine was liberated in the ether solution.



Similar reactions occurred between N-morpholino- and N-t-butylbenzothiazole sulphenamide and 2-mercaptobenzothiazole and between N-cyclohexylbenzothiazole-2-sulphenamide and benzyl thiol and *p*-nitrothiophenol. Thus, equimolar quantities of benzyl thiol and N-cyclohexylbenzothiazole-2-sulphenamide gave

2,2′-dithiobisbenzothiazole, cyclohexylammonium benzothiazolyl-2-mercaptide, dibenzyldisulphide and cyclohexylamine.

The time taken before the development of a precipitate, which gives an approximate indication of the rate of reaction, was dependent on the thiol used.

TABLE 1. REACTION OF 0·042 MOLAR N-CYCLOHEXYLBENZOTHIAZOLE-2-SULPHENAMIDE AND 0·042 MOLAR THIOLS IN ETHER

Thiol	p*Ka*	Time to first precipitate
p-Nitrothiophenol	5·1[5]	20 sec
2-Mercaptobenzothiazole	8·0[6]	5 min
Benzylthiol	11·8[6]	4 hr

It has been shown for a series of thiols that the higher the acid dissociation constant of a thiol, the less nucleophilic it is.[7] In the reaction under consideration, presumably a nucleophilic displacement from sulphur of amine by thiol, the more acid the thiol, the more rapid was the reaction. This tends to suggest that the first step in this reaction is protonation of sulphenamide by thiol, the overall rate of reaction being controlled by the position of this equilibrium.

$$\mathrm{RSNHR' + R''SH \rightleftharpoons RS\overset{+}{N}H_2R' + R''S^-}$$

The disulphide isolated will not necessarily be that first formed. Disulphides are known to undergo disproportionation reactions with both thiols and other disulphides.[8]

The facile reaction of benzothiazole sulphenamides with thiols suggests that in the thermal decomposition of sulphenamides, this is the main reaction leading to cleavage, after the induction period, 2-mercaptobenzothiazole being formed by participation of 2,2′-dithiobisbenzothiazole in dehydrogenation reactions. Eitingon *et al.* have suggested that azocyclohexane is formed during the decomposition of N-cyclohexylbenzothiazole-2-sulphenamide.[4] A possible overall scheme for the decomposition of this compound to disulphide and amine salt is thus:

$$\begin{array}{ll}
\mathrm{C_6H_4.NSC.S.NH.C_6H_{11} + C_6H_4.NSC.SH} & \mathrm{\rightarrow (C_6H_4.NSC.S)_2 + C_6H_{11}NH_2} \\
\mathrm{(C_6H_4.NSC.S)_2} & \mathrm{\rightarrow 2C_6H_4.NSC.S.} \\
\mathrm{C_6H_4.NSC.S. + C_6H_{11}NH_2} & \mathrm{\rightarrow C_6H_4.NSC.SH + C_6H_{11}NH.} \\
\mathrm{2C_6H_{11}NH.} & \mathrm{\rightarrow C_6H_{11}NH.NHC_6H_{11}} \\
\mathrm{(C_6H_4.NSC.S)_2 + C_6H_{11}NH.NHC_6H_{11}} & \mathrm{\rightarrow 2C_6H_4.NSC.SH + C_6H_{11}\,N{=}NC_6H_{11}} \\
\mathrm{C_6H_4.NSC.SH + C_6H_{11}NH_2} & \mathrm{\rightarrow C_6H_4.NSC.S^-\overset{+}{N}H_3C_6H_{11}}
\end{array}$$

2-Mercaptobenzothiazole is likely to be present in small amounts in samples of sulphenamide prepared by the methods normally used.[3]

The route by which N-benzothiazolylcyclohexylamine is formed in this system is not at present clear. A number of reactions are known in which a sulphur atom is extruded from sulphur containing compounds,[9] and it is possible that this is a similar reaction, involving extrusion of sulphur from N-cyclohexylbenzothiazole-2-sulphenamide. However, N-benzothiazolylcyclohexylamine was also produced in a yield of 91% theory (based on amine) by heating a mixture of cyclohexylammonium benzothiazolyl-2-mercaptide and 2,2′-dithiobisbenzothiazole, indicating that the amine may be formed via these compounds.

EXPERIMENTAL

M.ps are uncorrected. IR spectra were recorded on a Perkin–Elmer No. 137 "Infracord" instrument.

Materials used. Commercial N-cyclohexylbenzothiazole-2-sulphenamide (ICI Ltd.) was recrystallized from petroleum to constant m.p., m.p. 103–104° (Lit.[10] m.p. 103–104°). Commercial N-morpholinobenzothiazole-2-sulphenamide (Monsanto Chemicals Ltd.) was recrystallized from petroleum to constant m.p., m.p. 111–112° (Lit.[12] m.p. 112–113°). Commercial 2-mercaptobenzothiazole (ICI Ltd.) was purified by solution in dil NaOHaq and precipitation with acid, m.p. 178–180° (Lit.[10] m.p. 177–179°). Commercial 2,2′-dithiobisbenzothiazole (ICI Ltd.) was recrystallized from benzene to constant m.p., m.p. 178–180° (Lit.[13] m.p. 180°).

Thermal decomposition of N-*cyclohexylbenzothiazole-2-sulphenamide* (I). I (2·64 g; 0·01 mole) was heated at 140°, under reflux for 3½ hr and the products poured into cold water. The solid products were extracted with ether (100 ml). Extraction of the ethereal soln with NaOHaq, and subsequent acidification gave 2-mercaptobenzothiazole (0·710 g) m.p. 174–177°, mixed m.p. with authentic sample 176–178°. Extraction of the ether soln with dil HCl gave a soln which when made alkaline yielded a viscous green liquid (0·812 g) which crystallized slowly. Recrystallization from ether gave a solid, m.p. 103–105° which was shown, by IR comparison and mixed m.p. with an authentic sample to be V (Lit.[14] m.p. 103–104°). Evaporation of the ether soln gave a solid (0·358 g) which was shown by TLC (silica-gel, benzene–acetone, 10:1) to contain no I, and was not investigated further.

The IR spectrum of the ether insoluble solid indicated that it was a mixture of II and III. The latter was estimated by steam distilling a sample of the solid and determining the cyclohexylamine in the distillate by titration. This indicated that the solid consisted of 0·062 g III and 0·065 g II.

The water into which the decomposition products had been poured was combined with the aqueous filtrate from the isolation of V and the whole was distilled to give cyclohexylamine (0·183 g estimated by titration), benzoate m.p. 146–147° (Lit.[10] m.p. N-benzoylcyclohexylamine, 147°).

Reaction of N-*cyclohexylbenzothiazole-2-sulphenamide* (I) *and* 2-*mercaptobenzothiazole* (IV) *at* 150°. I (2·54 g; 0·0096 mole) and IV (1·30 g; 0·0078 mole) were heated together at 150° for 5 min. The products were extracted with ether (50 ml). The IR spectrum of the ether-insoluble portion (0·342 g) indicated that it was II containing a small amount of III. Recrystallization from benzene gave crystals m.p. 176–178°, mixed m.p. with authentic II, 176–179°. Extraction of the ether soln with NaOHaq and HCl gave IV (0·700 g), m.p. 173–177°, and V (1·400 g) m.p. 100–103°.

Evaporation of the remaining ether soln gave an oily brown solid (0·991 g) which was shown by TLC (aluminium oxide, benzene–petroleum 100–120, 5:1) to contain no I.

Reaction of cyclohexylammoniumbenzothiazolyl-2-mercaptide (III) *and 2,2′-dithiobisbenzothiazole* (II) *at* 145°. III (2·66 g, 0·01 mole) and II (6·64 g; 0·02 mole) were heated at 145° for 15 min. The products were extracted with ether (300 ml), leaving a solid (1·77 g). Compounds IV (2·66 g) m.p. 176–178°, and V (2·12 g) m.p. 101–104°, 91·5% yield based on III, were isolated from the ether soln by extraction with dil NaOHaq and with dil HCl.

Reaction of N-*cyclohexylbenzothiazole-2-sulphenamide* (I) *and* 2-*mercaptobenzothiazole* (IV) *at* 20°. The ether used as solvent for the reaction in this and subsequent experiments was dry and peroxide free. Compound I (0·660 g; 0·0025 mole) in ether (30 ml) was mixed with IV (0·417 g; 0·0025 mole) in ether (30 ml). The ppt which started to form after 5 min, was filtered off after 3 hr and was recrystallized from benzene to give II (0·420 g) m.p. 180–182°. Compound IV (0·075 g), m.p. 175–179° was isolated by extraction of the ether soln with dil NaOHaq. Extraction of the ether soln with dil HCl, and distillation of the extract after making alkaline gave aqueous cyclohexylamine (0·176 g, by titration), benzoate m.p. 145–147°, mixed m.p. with authentic benzoylcyclohexylamine 145–147°. Solubility of II in ether, ca. 0·1 g/100 ml.

Reaction of N-*cyclohexylbenzothiazole-2-sulphenamide* (I) *and benzyl thiol* (VI). I (0·526 g; 0·0020 mole) in ether (24 ml) was mixed with VI (0·247 g; 0·0020 mole) in ether (24 ml). The ppt (0·172 g) which started to form after 4 hr was filtered off after 3 days. Its IR spectrum indicated that it was a mixture of II and III. III was estimated by steam-distillation as before (0·098 g), giving, by difference, II (0·074 g). Cyclohexylamine in soln in the ether (0·101 g) was estimated by extraction with dil HCl and back-titration. TLC (aluminium oxide, benzene) indicated that the ether contained dibenzyl disulphide and unchanged I. No VI was detected. Solubility of III in ether, ca. 0·3 g/100 ml.

Reaction of N-*cyclohexylbenzothiazole-2-sulphenamide* (I) *and* p-*nitrothiophenol* (VII). I (0·660 g; 0·0025 mole) in ether (30 ml) was mixed with VII (0·387 g; 0·0025 mole) in ether (30 ml). The ppt, which started to form after 20 sec, was filtered off after 3 hr (0·184 g). Its IR spectrum indicated that it was mainly di-*p*-nitrophenyl disulphide containing small quantities of II and III (0·044 g estimated as above). Cyclohexylamine (0·155 g) and IV (0·020 g) were isolated from the ether, as previously described, and TLC aluminium oxide, benzene) indicated that the ether contained unchanged I and di-*p*-nitrophenyldisulphide. Solubility of di-*p*-nitrophenyldisulphide in ether, ca. 0·3 g/100 ml.

Reaction of N-*t-butylbenzothiazole-2-sulphenamide* (VIII) *with 2-mercaptobenzothiazole* (IV). VIII (0·595 g; 0·0025 mole) in ether (30 ml) was mixed with IV (0·417 g; 0·0025 mole) in ether (30 ml). The ppt (0·491 g) which started to form after 17 min was filtered off after 20 hr. It was recrystallized from benzene to give II m.p. 180–182°. IV (0·027 g) m.p. 175–179°, was isolated from the ether soln, and t-butylamine (0·098 g) was estimated by distillation and titration.

Reaction of N-*morpholinobenzothiazole-2-sulphenamide* (IX) *and 2-mercaptobenzothiazole* (IV). IX (0·630 g; 0·0025 mole) in ether (30 ml) was mixed with IV (0·417 g; 0·0025 mole) in ether (30 ml). The ppt which started to form after 30 min was filtered off after 20 hr. It was shown by mixed m.p. and IR comparison to be II (0·496 g). The ether contained IV (0·033 g).

Preparation of N-*benzothiazolylcyclohexylamine* (V). Chlorine was passed into a suspension of IV (16·7 g; 0·10 mole) in water (120 ml) and AcOH (60 ml) for 4 hr, the temp being maintained at 5°. The mixture was steam-distilled and the dense, colourless liquid which separated from the distillate was dried and distilled to give 2-chlorobenzothiazole,[15] (2·1 g; 0·0124 mole) b.p. 246–248° (Lit.[16] b.p. 248°). This product was heated under reflux at 100° for 3 hr with cyclohexylamine (5·2 g, 0·0525 mole). The reaction mix was extracted with dil HCl; addition of NaOH and recrystallization of the product from ether gave V, m.p. 105–107° (Lit.[14] m.p. 103–104°). (Found: C, 67·5; H, 7·1; N, 12·0; S, 13·6; Calc. for $C_{13}H_{16}N_2S$: C, 67·3; H, 6·9; N, 12·1; S, 13·8%), picrate, m.p. 234–236° (Lit.[14] m.p. 233–234°) yield, 2·76 g, 96% based on 2-chlorobenzothiazole.

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