6. *Reactions of Benzthiazole Derivatives. Part IV.* 1-*Thiocyanobenzthiazole.*

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1-Thiocyanobenzthiazole is readily converted by many reagents into derivatives of 1-thiolbenzthiazole. With alcohols, however, it gives the thioncarbamates derived from 1-aminobenzthiazole. The mechanism of this is discussed.

When alcoholic potassium thiocyanate was heated with 1-chlorobenzthiazole, approximately the theoretical amount of potassium chloride was precipitated but only a small amount of the expected 1-thiocyanobenzthiazole was isolated. This thiocyano-compound was therefore prepared from cold alcoholic sodio-1-thiolbenzthiazole and cyanogen bromide (Levi, *Gazzetta*, 1931, **61**, 383). The yield was excellent and the crude product could readily be purified by crystallisation from ether, but attempted crystallisation from hot alcohols, as recommended by Levi, gave mixtures containing a considerable amount of higher-melting material. These unexpected results led us to investigate more closely the stability of 1-thiocyanobenzthiazole to heat and to chemical reagents.

1-Thiocyanobenzthiazole is not stable to prolonged storage and decomposes fairly rapidly on heating. With aqueous sodium hydroxide and sulphide, sodio-1-thiolbenzthiazole was formed in good yield. With sodium methoxide in methyl alcohol, a vigorous reaction gave sodio-1-thiolbenzthiazole, sodium cyanate, and 1-methylthiobenzthiazole. Similarly, sodium ethoxide in ethyl alcohol gave the same sodium salts, together with 1-ethylthiobenzthiazole. Analogous sulphides have been reported from the reaction between thiocyanobenzene and sodium ethoxide (Ross, *J. Amer. Chem. Soc.*, 1934, **56**, 727), and the formation of cyanate was observed by Levi (*loc. cit.*) in the reaction between dibenzthiazyl disulphide and excess of alcoholic potassium cyanide.

When 1-thiocyanobenzthiazole was heated in benzene or, better, toluene, an orange amorphous precipitate (presumably " pseudocyanogen sulphide "; see, *e.g.*, Wheeler and Johnson, *J. Amer. Chem. Soc.*, 1902, **24**, 680) was formed and from the solution dibenzthiazyl monosulphide was isolated; there was no evidence of the formation of an *iso*thiocyano-compound. With a benzene suspension of sodio-1-thiolbenzthiazole, the same products were obtained, together with a small amount of dibenzthiazyl disulphide. The yield of monosulphide was, however, much higher in this case, and this fact, together with the qualitative detection of SCN′ in the product, indicates that some of the monosulphide was derived by direct action of the thiocyano-compound with the sodio-derivative with elimination of sodium thiocyanate. In this case, the SCN group is functioning as a pseudo-halogen.

When 1-thiocyanobenzthiazole was heated in alcohol, no trace of " pseudocyanogen sulphide " was observed.

With methyl alcohol, a small amount of dibenzthiazyl disulphide was isolated, but the main product was *methyl benzthiazyl-1-thioncarbamate*, which was characterised by analysis, solubility in alkali, stability to dilute alkali and acid, and hydrolysis with strong acid to 1-aminobenzthiazole. Homologous derivatives were obtained with higher alcohols [Chi and co-workers (*J. Amer. Chem. Soc.*, 1930, **52**, 1580; 1932, **54**, 2056; 1933, **55**, 418) found that certain thiocyanopyrimidines react with alcohols to give thioncarbamates].

A possible mechanism for this reaction as well as for the formation of alkylthiobenzthiazoles in the reaction with sodium alkoxides might involve the formation of the unstable intermediate imino-thiocarbonic esters (I). [Although the formation of imino-ethers from nitriles and alcohols is usually carried out in the presence of an acid, the reversible addition of alcohols to nitriles with a sodium alkoxide catalyst is also well established (Marshall, jun., Acree, and co-workers, *Amer. Chem. J.*, 1913, **49**, 127, 369).] Such an imino-ether would be expected to lose cyanic acid and give the alkyl sulphide (II), this being analogous to the loss of cyanamide from the hypothetical intermediate (III) derived from thiourea and 1-chlorobenzthiazole (Scott and Watt, *J. Org. Chem.*, 1937, **2**, 148; Watt, *ibid.*, 1939, **4**, 436) and to the thermal decomposition of methyl iminodithiocarbonate [NH:C(SMe)$_2$] to methylthiol and methyl trithiocyanurate (Delépine, *Bull. Soc. chim.*, 1903, **29**, 55). Alternatively the imino-ether (I) might rearrange to give the thioncarbamate (IV), such migrations of a group from sulphur to nitrogen in the system ·N:C·SR having been previously reported (Reed, Robertson, and Sexton, J., 1939, 473).

$$\underset{\text{(II.)}}{\text{HO·CN} + \text{R·SR'}} \longleftarrow \underset{\text{(I.)}}{[\text{RS·C(:NH)·OR'}]} \longrightarrow \underset{\text{(IV.)}}{\text{NHR·CS·OR'}}$$

$$\text{R·SH} + \text{NH}_2\text{·CN} + \text{HCl} \longleftarrow \underset{\text{(III.)}}{[\text{RS·C(:NH)·NH}_2\text{,HCl}]} \xrightarrow{\text{RCl}} \text{R}_2\text{S} + \text{NH}_2\text{·CN} + 2\text{HCl}$$

R = 1-Benzthiazyl.

Little is known of the properties of iminothiocarbonates of type (I). Knorr (*Ber.*, 1916, **49**, 1735; 1917, **50**, 229, 767) prepared hydrochlorides in which R was alkyl, but the free bases were too unstable to be isolated and even the hydrochlorides, in the presence of water or an alcohol, decomposed to give the thiolcarbamates (NH$_2$·CO·SR) and an alkyl chloride. 1-Thiocyanobenzthiazole in excess of methyl alcohol was treated with hydrogen chloride; when the product was poured into water, 1-methylthiobenzthiazole was obtained in good yield but no 1-benzthiazyl thiolcarbamate, analogous to the products obtained from alkyl thiocyanates (Knorr, *loc. cit.*), was detected. This suggests that the mode of decomposition of the iminothiocarbonates differs, as might be expected, according to their substituents and that, in the case of the benzthiazyl derivative at least, decomposition by elimination of cyanic acid is possible.

If the mechanism suggested for these reactions is correct, it would imply that the formation of iminothiocarbonates from thiocyanates may be fairly general (cf. reactions with thiocyanobenzene; Ross, *loc. cit.*) but that the subsequent isomerisation to thioncarbamates is rarer, being dependent on the nature of the radical attached to the thiocyano-group.

Experimental.

1-Thiocyanobenzthiazole.—A specimen prepared according to Levi (*loc. cit.*) and crystallised from ether had m. p. 87—88°.

Stability. (i) A sample stored in a glass vessel for 3½ years had become yellow and had m. p. 82—87° (softening at 77°).

(ii) Resinous material was formed on heating at 70° for 4 hours. In boiling benzene, an amorphous orange solid was precipitated during 48 hours. 1-Thiocyanobenzthiazole (1·92 g.) was heated in boiling toluene (50 c.c.) for 24 hours: the amorphous orange precipitate (0·49 g.) was removed, and the filtrate concentrated to yield, on cooling, dibenzthiazyl sulphide (0·94 g., 64%), m. p. 101° after crystallisation from alcohol, not depressed by an authentic specimen (Watt, *loc. cit.*).

Reactions. (i) *With sodium hydroxide.* 1-Thiocyanobenzthiazole (2·0 g.) and 2N-sodium hydroxide (10 c.c.) were stirred at 70—80° for 2 hours, cooled, and filtered. Addition of 2N-hydrochloric acid (10 c.c.) precipitated 1-thiolbenzthiazole (1·54 g., 88%). The filtrate contained sodium cyanate, which was indicated by evolution of carbon dioxide on acidification and the presence of ammonia in the acidified liquor.

(ii) *With sodium sulphide.* 1-Thiocyanobenzthiazole (3·84 g.) dissolved exothermally in the calculated quantity of aqueous sodium sulphide. On acidification, 1-thiolbenzthiazole (3·34 g., 100%) was precipitated, m. p. 177—178°.

(iii) *With alcoholic sodium methoxide.* 1-Thiocyanobenzthiazole (4·8 g.) was added during 10 minutes to a stirred solution of sodium methoxide (sodium, 0·6 g., in methyl alcohol, 30 c.c.) maintained at about 0°. After a further 15 minutes at 0°, the solution was filtered from sodium cyanate (0·62 g., 37·5%), poured into water, and separated into neutral and alkali-soluble fractions, from which were isolated 1-methylthiobenzthiazole (1·61 g., 35%), m. p. 38—43°, mixed m. p. with authentic material 39—45°, and 1-thiolbenzthiazole (2·37 g., 57%), m. p. and mixed m. p. with authentic material, 176—177°.

(iv) *With alcoholic sodium ethoxide.* This was carried out as for the methoxide reaction but at 10° instead of 0°. The products were sodium cyanate (0·46 g., 38%), 1-thiolbenzthiazole (2·48 g., 55%), and 1-ethylthiobenzthiazole (1·78 g., 42%).

(v) *With sodio-1-thiolbenzthiazole in methyl alcohol.* 1-Thiocyanobenzthiazole (3·84 g.) was added to a solution of sodio-1-thiolbenzthiazole (3·78 g.) in methyl alcohol (30 c.c.) with good stirring; the temperature rose slowly from 22° to 27°. After 2 hours' stirring, the precipitate (2·0 g.) of sodium cyanate and dibenzthiazyl disulphide was collected and washed with water to remove the cyanate; the residue was identified as the disulphide (1·26 g., 37·5%). The weight of sodium cyanate (identified in the filtrate by the usual tests) was therefore 0·74 g. (57%). The alcoholic filtrate was poured into water and separated with alkali to give 1-methylthiobenzthiazole (2·56 g.), m. p. 37—41°, and 1-thiolbenzthiazole (2·23 g.), m. p. and mixed m. p. with authentic material 175—177°.

(vi) *With sodio-1-thiolbenzthiazole in benzene.* 1-Thiocyanobenzthiazole (1·92 g.) and sodio-1-thiolbenzthiazole (1·89 g.) were heated in boiling benzene (50 c.c.) for 24 hours, and the solution filtered hot from the orange insoluble

material (1·8 g.). This orange product was extracted with water, and the extract acidified to precipitate 1-thiolbenzthiazole (0·6 g.), m. p. and mixed m. p. with authentic material, 176—178° : the aqueous filtrate gave qualitative reactions for SCN'. The benzene filtrate, on cooling, gave plates (0·3 g.), m. p., after crystallisation from benzene, 178—179°, alone or mixed with dibenzthiazyl disulphide. The benzene filtrate was evaporated to dryness to give a yellow solid (1·7 g.), m. p. 89—92°, which, after two crystallisations from alcohol to remove the sparingly soluble dibenzthiazyl disulphide, gave dibenzthiazyl monosulphide in pale yellow needles, m. p. 97—98°, not depressed by an authentic sample (m. p. 101°).

(vii) *With methyl alcohol.* 1-Thiocyanobenzthiazole (20 g.) was heated in boiling methyl alcohol (150 c.c.) for 24 hours, a further 350 c.c. of alcohol being added gradually to prevent separation of solid. After clarification with charcoal and cooling, crystals (6·0 g.) separated, m. p. 166—168°, raised by successive crystallisation from methyl alcohol, benzene, and light petroleum to 175°. From the original alcoholic mother-liquors, more of this material (crude) as well as dibenzthiazyl disulphide, m. p. and mixed m. p. with authentic material, 177—178°, were obtained. The new compound dissolved in dilute alkali solution and was precipitated unchanged on acidification. Heating for 2 hours with dilute alcoholic sodium hydroxide did not affect it, but boiling with 30% aqueous sodium hydroxide caused profound decomposition. The compound was also soluble in hot 36% hydrochloric acid. It resisted the action of 15% methyl-alcoholic sulphuric acid, but when the material (1 g.) was boiled for 1 hour with 5% sulphuric acid (14 g.) a white solid separated. This was dissolved by addition of water and a base was precipitated on addition of alkali. The base (0·45 g.), m. p. 126—128°, was identified as 1-aminobenzthiazole by mixed m. p. with authentic material and by its characteristic colour reactions with hypochlorite and sulphuric acid. On the basis of these reactions, the methyl alcohol reaction product is identified as *methyl benzthiazyl-1-thioncarbamate* (Found : C, 48·5; H, 3·4; N, 12·5; S, 27·9. $C_9H_{10}ON_2S_2$ requires C, 48·2; H, 3·6; N, 12·5; S, 28·6%).

(viii) *With other alcohols.* With ethyl alcohol, 10 hours' heating sufficed to convert 1-thiocyanobenzthiazole into *ethyl benzthiazyl-1-thioncarbamate*, m. p. 163° after crystallisation from alcohol (Found : C, 50·2; H, 4·5; N, 12·1; S, 27·0. $C_{10}H_{12}ON_2S_2$ requires C, 50·0; H, 5·0; N, 11·7; S, 26·7%). This ester was hydrolysed to 1-aminobenzthiazole as in the case of the lower homologue.

By heating 1-thiocyanobenzthiazole on the steam-bath with the appropriate alcohols, the following esters of benzthiazyl-1-thioncarbamic acid were prepared : *n*-butyl, m. p. 105°; *iso*propyl, m. p. 174°; *cyclo*hexyl, m. p. 146°; amyl, m. p. 116°; and β-ethoxyethyl, m. p. 125°.

(ix) *With methyl-alcoholic hydrogen chloride.* 1-Thiocyanobenzthiazole (3·8 g.) was added to methyl alcohol (50 c.c.) at 0°; with good stirring, the suspension was saturated with hydrogen chloride at 0°. After several days, the solution was filtered, poured into water, and basified. The neutral material, isolated by extraction with ether, was 1-methylthiobenzthiazole (2·23 g., 61%), m. p. and mixed m. p. with authentic material 43—47°. Only traces of acid-soluble and alkali-soluble products were obtained.

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