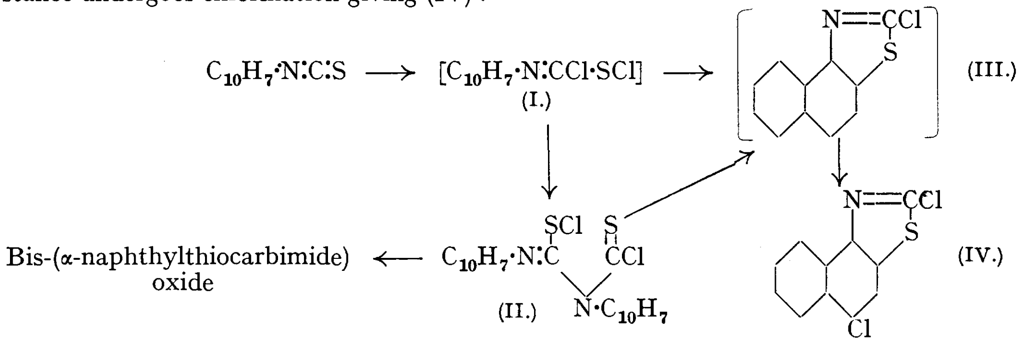
63. *The Action of Chlorine on Aryl Thiocarbimides and the Reactions of Aryl* iso*Cyanodichlorides. Part III. The Addition of Chlorine to α-Naphthylthiocarbimide and the Structure of the Compounds obtained.*

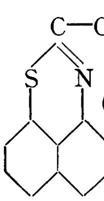
By G. Malcolm Dyson and Thomas Harrington.

The action of chlorine upon α-naphthylthiocarbimide yields an unstable chloro-addition compound, which forms *bis-(α-naphthylthiocarbimide) oxide* when exposed to the air. Further addition of chlorine produces 2 : 4′-*dichloronaphtha*(1′ : 2′ : 4 : 5)*thiazole* and prolonged chlorination yields a compound of empirical formula $C_{11}H_2NCl_5S$. α-Naphthyl *iso*cyanodichloride was not obtained.

When chlorine is passed into a chloroform solution of α-naphthylthiocarbimide, the additive compound (I), which is presumably the first product formed, may either pass into (II) or undergo loss of hydrogen chloride to give the thiazole (III). It is considered that (II) also may pass directly into (III). This substance undergoes chlorination giving (IV) :



Compound (II) is rapidly converted by moisture into the corresponding *oxide* (cf. Dyson and Harrington, J., 1940, 191; this vol., p. 150). That the product of ring-closure of (I) is probably the thiazole (III) and not the *peri*naphthathiazine (V) is based on the observation that 2-phenyl*peri*naphthathiazine (V with Ph for Cl; Reissert, *Ber.*, 1922, **55**, 858) is not identical with the product of oxidation of thiobenz-α-naphthalide (cf. Jacobson, *Ber.*, 1887, **20**, 1898), which is therefore evidently 2-phenylnaphtha(1′ : 2′ : 4 : 5)thiazole (III with Ph for Cl).


(V.)

The position of the nuclear chlorine atom in (IV) is established by the preparation of this compound by the action of chlorine on 4-*chloro-α-naphthylthiocarbimide.*

Prolonged action of chlorine on α-naphthylthiocarbimide gives a substance of probable formula $C_{11}H_2NCl_5S$.

Experimental.

α-Naphthylthiocarbimide.—α-Naphthylamine (145 g.) in chloroform (500 ml.) was added during 2 hours to thiocarbonyl chloride (115 g.) suspended by vigorous stirring in water (800 ml.). Stirring was continued for a further ½ hour. The white solid formed was removed (a portion crystallised from alcohol had m. p. 215°, and was probably *s*-di-α-naphthylthiourea, recorded m. p. 212—214°), the chloroform solution separated and dried by calcium chloride, and the chloroform and the excess of thiocarbonyl chloride distilled off from a water-bath. An oil remained which set solid on cooling and crystallised from aqueous acetone in white needles (100 g.), m. p. 57°

4-*Chloro-α-naphthylthiocarbimide.*—4-Chloro-α-naphthylamine (18 g.) (Reverdin and Crépieux, *Ber.*, 1900, **33**, 682) in chloroform (100 g.) was added slowly with shaking to thiocarbonyl chloride (12 g.) suspended in water (100 ml.). The mixture turned apple-green and a solid was deposited; this crystallised from alcohol (charcoal) in pale blue needles (5 g.), m. p. 230° (decomp.), and was probably *s*-di-(4-chloro-α-naphthyl)thiourea.

The chloroform layer was separated and dried over calcium chloride, and the chloroform and the excess of thiocarbonyl chloride distilled off. The residual oil solidified on cooling and then formed colourless needles (14 g.), m. p. 87°, from acetone (Found : N, 6·3; S, 14·4; Cl, 16·3. $C_{11}H_6NClS$ requires N, 6·4; S, 14·6; Cl, 16·1%).

Bis-(α-naphthylthiocarbimide) Oxide.—α-Naphthylthiocarbimide (50 g.) in chloroform (100 g.) was slowly treated with chlorine for 3 hours; the increase in weight was 40 g. Yellow needles were deposited, which crumbled within 5 minutes after collection to a white powder, m. p. 79°, at the same time evolving hydrogen chloride. It was obtained from alcohol in white needles (30 g.), m. p. 80° (Found : N, 7·2. $C_{22}H_{14}ON_2S_2$ requires N, 7·3%).

2 : 4′-*Dichloronaphtha*(1′ : 2′ : 4 : 5)*thiazole.*—(1) α-Naphthylthiocarbimide (50 g.) in chloroform (100 g.) was treated with chlorine more rapidly than in the preparation of bis-(α-naphthylthiocarbimide) oxide; the increase in weight was 50 g. in 2 hours and hydrogen chloride was evolved. After 12 hours the pink solid was collected and crystallised from alcohol, forming blue needles (25 g.) which became colourless after prolonged boiling with alcohol and charcoal; m. p. 113°. The chloroform filtrate deposited a further 5 g. of 2 : 4′-*dichloronaphtha*(1′ : 2′ : 4 : 5)*thiazole* (Found: C, 51·7; H, 2·3; N, 6·0; S, 12·8; Cl, 28·5. $C_{11}H_5NCl_2S$ requires C, 52·0; H, 2·0; N, 5·5; S, 12·6; Cl, 28·0%).

Prolonged addition of chlorine to α-naphthylthiocarbimide in chloroform produced a solution which deposited yellow crystals on standing. These were obtained from benzene in small white needles, m. p. 235° (decomp.) (Found : N, 3·9. $C_{11}H_2NCl_5S$ requires N, 3·9%).

(2) In order to confirm its structure 2 : 4′-dichloronaphtha(1′ : 2′ : 4 : 5)thiazole was prepared as follows : 4-Chloro-α-naphthylthiocarbimide (10 g.) in chloroform (50 g.) was treated with chlorine for 2 hours so that the increase in weight was 5 g. The needles deposited after 2 days had m. p. 110°; after recrystallisation from alcohol (yield, 1 g.), the m. p. and mixed m. p. with the compound obtained by method (1) were 113°.

Thiobenz-α-naphthalide (cf. Jacobson, *loc. cit.*).—Benz-α-naphthalide (120 g.) was heated with phosphorus pentasulphide (70 g.); a vigorous effervescence took place. Ethyl alcohol (500 ml.) was immediately added in small amounts because of frothing. The product was heated on a water-bath, made strongly alkaline with sodium hydroxide, diluted with water (1500 ml.), and filtered after 12 hours from a large amount of tar. Acid-free carbon dioxide was passed through the clear solution for 24 hours and the precipitated yellow solid was washed with water and crystallised from alcohol, forming colourless needles (70 g.), m. p. 150°.

2-Phenylnaphtha(1′ : 2′ : 4 : 5)thiazole, prepared from thiobenz-α-naphthalide (70 g.) by Jacobson's method (*loc. cit.*), formed almost colourless needles (35 g.), m. p. 103° to a red liquid (Found : N, 5·2; S, 12·6. Calc. for $C_{17}H_{11}NS$: N, 5·4; S, 12·3%).

2-Phenyl*peri*naphthathiazine, prepared from α-naphthylsulphonyl chloride (Erdmann and Süvern, *Annalen*, 1893, **275**, 230) by Reissert's method (*loc. cit.*), formed yellow-brown needles, m. p. 106° (Found : N, 5·3; S, 12·2. Calc. for $C_{17}H_{11}NS$: N, 5·4; S, 12.3%), mixed m. p. with 2-phenylnaphtha(1′ : 2′ : 4 : 5)thiazole, 80—85°.

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