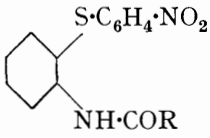
299. *Derivatives of* o-*Thioldiphenylamine.*

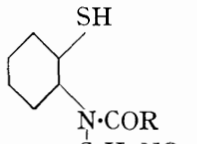
By WILFRID J. EVANS and SAMUEL SMILES.

PREVIOUS experiments (this vol., p. 181) showed that rearrangement of sulphides of type (I) leads to thiols of type (II). The thiol obtained from the acetyl derivative (I; R = Me) behaved as a pseudo-base, and with hydrochloric or perchloric acid yielded salts to which the structure (III) was assigned. Confirmation of this view has now been obtained from the conversion of (III) by usual methods into the *thiocarbocyanine iodide* (IV; X = I). Since the formation of stable thiazolinium salts containing the *N*-*o*-nitrophenyl group was unexpected, the behaviour of other thiols of type (II) has been examined.

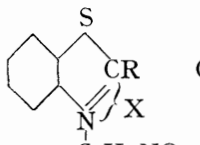
In thiols derived from type (II; R = Me) by replacement of 2-nitrophenyl by 4-chloro-2-nitrophenyl or 2 : 4-dinitrophenyl, the function of pseudo-base is suppressed; no stable salts of type (III) have been obtained from them. On the other hand, mononitrophenyl derivatives such as (II; R = Ph or CHPh:CH) readily yielded salts of type (III), the phenyl compound being converted into the thiol by alkaline agents.



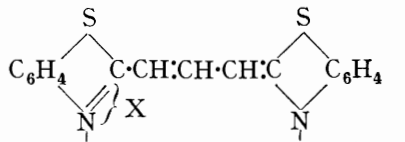
(I.)



(II.)



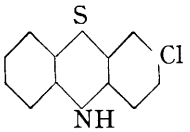
(III.)



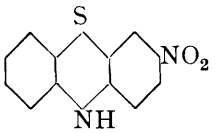
(IV.)

The thiols derived from 4-chloro-2-nitro- or 2 : 4-dinitro-*N*-acetyldiphenylamine (as II) are easily attacked by warm alkaline media, the first thiol yielding a *chlorothiodiphenylamine* evidently of structure (V). Conversion of 2 : 4-dinitro-2′-acetamidodiphenyl sulphide (as I; R = Me) into the thiol (as II) by rearrangement has already been demonstrated by isolation of the methyl ether of the latter (this vol., p. 187); but attempts to isolate

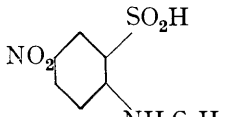
the thiol in a pure condition have not succeeded owing to the ease with which the thiazine is formed from it. Proof that the latter has the structure (VI), and is therefore formed from the thiol and not from the dinitro-sulphide before rearrangement, is afforded by its synthesis from the sulphinic acid (VII) by reduction with hydrogen iodide. This convenient method of synthesising derivatives of thiodiphenylamine appears to be capable of wider application. The sulphinic acid (VII) also serves as a convenient source of other heterocyclic systems; *e.g.*, the 1-derivatives of 2-phenylbenzthiazoline dioxide (VIII) are



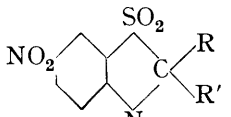
(V.)



(VI.)



(VII.)



(VIII.)

obtained from it by condensation with aldehydes or ketones. Attempts to convert the 1-methyl derivative (VIII; R = H, R′ = CH_3) by oxidation in acid media into salts analogous to (III) (compare Claasz, *Ber.*, 1916, **49**, 619) were unsuccessful.

Experimental.

2 : 2′-*Di*-o-*nitrophenylthiocarbocyanine Iodide* (IV; X = I).—A solution of the iodide (XIV, this vol., p. 187; 5 g.), ethyl orthoformate (2·5 c.c.), acetic anhydride (50 c.c.), and pyridine (2·5 c.c.) was boiled (30 mins.); more ethyl orthoformate (2·5 c.c.) was added and boiling was continued for 1 hr. The *iodide* separated as purple plates with a metallic lustre, m. p. 269° (decomp.) (Found: C, 51·3; H, 3·1; N, 8·4; S, 9·2. $C_{29}H_{19}O_4N_4IS_2$ requires C, 51·3; H, 2·8; N, 8·3; S, 9·4%).

2-o-*Nitrophenyl*-1-*phenylthiazolinium Iodide* (III; R = Ph; X = I).—Alcoholic sodium hydroxide (*N*, 1·25 mols.) was slowly added to a boiling solution of the sulphide (I, R = Ph; 6 g.) in acetone (40 c.c.). After 45 mins.' boiling, the solution was cooled and diluted, insoluble material being then removed. The thiol (II; R = Ph) was isolated from this solution of its sodium salt by addition of dilute sulphuric acid; when hydriodic acid (*d* 1·7) was added to its warm solution in acetone, the required *iodide* separated in yellow plates, m. p. 195° (Found: C, 49·9; H, 2·9; N, 6·3. $C_{19}H_{13}O_2N_2IS$ requires C, 49·6; H, 2·8; N, 6·1%). The thiol was regenerated from this iodide by warm aqueous sodium hydroxide, and methylation of it in alkaline solution yielded the methylthiol previously described (this vol., p. 340).

2-*Nitro*-2′-*cinnamamidodiphenyl sulphide* (I; R = CHPh:CH) was obtained from the amine with cinnamoyl chloride in acetone in presence of sodium bicarbonate, and formed needles from propyl alcohol, m. p. 132° (Found: C, 66·9; H, 4·4. $C_{21}H_{16}O_3N_2S$ requires C, 67·0; H, 4·3%). Rearrangement of this sulphide was effected in the usual manner with hot alcoholic sodium hydroxide (*N*, 1·25 mols.). The thiol formed (II; R = CHPh:CH) was not isolated in the pure condition but was characterised by methylation, which furnished 2-*cinnamo*-o-*nitrophenylamidophenyl methyl sulphide*, yellow needles, m. p. 170—171° (Found: C, 67·6; H, 4·9; S, 8·1. $C_{22}H_{18}O_3N_2S$ requires C, 67·7; H, 4·6; S, 8·2%), decomposed by warm hydriodic acid into methylthiol.

2-o-*Nitrophenyl*-1-*styrylthiazolinium iodide* (III; R = CHPh:CH) was obtained from the cinnamoyl derivative of 2-nitro-2′-aminodiphenyl sulphide by the process described in the case of the benzoylated amine. It formed yellow plates and had m. p. 225° (decomp.) (Found: C, 51·9; N, 5·8. $C_{21}H_{15}O_2N_2IS$ requires C, 52·0; N, 5·7%).

Bis-2-*aceto*-p-*chloro*-o-*nitrophenylamidophenyl Disulphide.*—Rearrangement of 4-chloro-2-nitro-2′-acetamidodiphenyl sulphide was effected in boiling acetone in presence of alcoholic sodium hydroxide (1 mol.). The thiol was isolated as usual, but was not obtained in the pure condition owing to rapid conversion into the *disulphide*, which had m. p. 187—188° (Found: C, 52·1; S, 9·7; *M*, 641. $C_{28}H_{20}O_6N_4Cl_2S_2$ requires C, 52·2; S, 9·9%; *M*, 643).

3-*Chlorothiodiphenylamine* (V) was formed when a solution of the above thiol in acetone containing alcoholic sodium hydroxide was boiled; it was also obtained, together with the thiol, from the product of rearrangement of the chloro-nitro-sulphide. From propyl alcohol, it formed needles, m. p. 199° (Found: N, 6·1; Cl, 15·5. $C_{12}H_8NClS$ requires N, 6·0; Cl, 15·2%).

3-*Nitro*-N-*acetylthiodiphenylamine* was formed in boiling (30 mins.) acetone (100 c.c.) which contained 2 : 4-dinitro-2′-acetamidodiphenyl sulphide (10 g.) and alcoholic sodium hydroxide

(1 mol.). Part of the solvent was removed, and the required product separated from the cooled residue. It formed yellow plates from alcohol, m. p. 146° (Found : C, 58·9; N, 10·0. $C_{14}H_{10}O_3N_2S$ requires C, 58·7; N, 9·8%).

3-Nitrothiodiphenylamine (VI) was obtained (*a*) by hydrolysis of the above acetyl derivatives with alcoholic sodium hydroxide, (*b*) by adding hydriodic acid to a warm aqueous solution of 4-nitrodiphenylamine-2-sulphinic acid (VII) containing sulphurous acid. The impure material which separated was treated successively with aqueous sodium thiosulphate, alcohol, and warm benzene. The residue after purification from hot xylene had m. p. 218°, not depressed by admixture with a sample obtained from process (*a*). Kehrmann and Nossenko (*Ber.*, **1913**, **46**, 2809) give m. p. 218° (Found : N, 11·2. Calc. : N, 11·5%).

4-*Nitro*-2-*methanesulphonyldiphenylamine* (as VII).—Sodium 4-nitrodiphenylamine-2-sulphonate (100 g.) was converted into the chloride by reaction with phosphorus pentachloride (200 g.). When the product was shaken (1·5 hrs.) with a weakly alkaline solution (250 c.c.) of sodium sulphite (200 g.), the required sodium sulphinate separated (60 g.). The unstable sulphinic acid was characterised as the *methylsulphone*, which formed yellow needles, m. p. 170—171°, from acetic acid (Found : C, 53·5; H, 4·3; N, 9·6; S, 10·8. $C_{13}H_{12}O_4N_2S$ requires C, 53·4; H, 4·1; N, 9·6; S, 11·0%).

The preparation of the following derivatives of 2-phenylbenzthiazoline dioxide was effected by warming a solution of the sulphinic acid (VII) in the requisite aldehyde or ketone. The required product separated after the solvent had been partly evaporated. 5-*Nitro*-2-*phenylbenzthiazoline* S-*dioxide* (VIII; R, R′ = H, H), from methylal and the sulphinic acid, formed yellow prisms from alcohol, m. p. 147° (Found : C, 53·6; N, 9·7. $C_{13}H_{10}O_4N_2S$ requires C, 53·8; N, 9·7%); the 1-*methyl* homologue (VIII; R = H, R′ = CH_3), from acetal and the sulphinic acid, had m. p. 150° (Found : C, 55·4; N, 9·2; S, 10·3. $C_{14}H_{12}O_4N_2S$ requires C, 55·3; N, 9·2; S, 10·5%); the 1 : 1-*dimethyl* compound (VIII; R = R′ = CH_3) had m. p. 200° (Found : C, 56·5; N, 9·0. $C_{15}H_{14}O_4N_2S$ requires C, 56·6; N, 8·8%). 5-*Nitro*-1-p-*hydroxyphenyl*-2-*phenylbenzthiazoline* S-*dioxide* (VIII; R = H, R′ = C_6H_4·OH), from the sulphinic acid and *p*-hydroxybenzaldehyde in alcohol, had m. p. 220° (decomp.) (Found : C, 59·4; N, 7·4. $C_{19}H_{14}O_5N_2S$ requires C, 59·7; N, 7·3%).

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