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BY

Praphulla Chandra Guha and Tejendra Nath Ghosh.

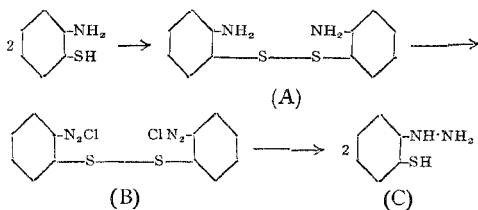
DR. M. O. FORSTER, F.R.S., CHAIRMAN OF EDITORIAL BOARD,

ATTEMPTS TO SYNTHESISE *Ortho*-THIOLPHENYLHYDRAZINE

By Praphulla Chandra Guha and Tejendra Nath Ghosh.

o-Derivatives of benzene, namely, dihalogen, diamino-, dihydroxy-, dithiol, aminohydroxy-, halogenamino-, thiolamino-, etc., are well known for their extensive reactivity with suitable agents to form heterocyclic compounds. The hydrazino-group also combines freely with a large number of organic types to form diverse open and closed chain compounds. *o*-Hydroxyphenylhydrazine and *o*-thiolphenylhydrazine, if obtainable, would open out a new field for investigation among heterocyclic compounds containing nitrogen and oxygen, or sulphur; accordingly, various attempts to prepare the thiolhydrazine have now been made.

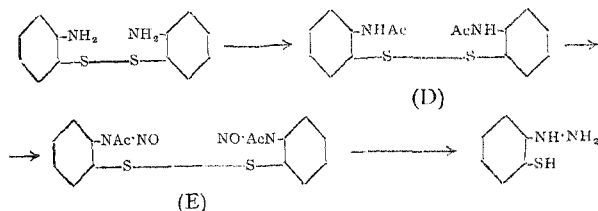
o-Thiolphenylhydrazine cannot be prepared from *o*-thiolaniline by diazotisation and subsequent reduction of the diazonium group. In fact Jacobson (*Annalen*, 1893, **277**, 208) studied the action of nitrous acid upon *o*-aminothiophenol and obtained *o*-phenylenediazosulphide with a very small quantity of thianthrene. It was expected that if the tendency to ring-closure between the diazo- and mercaptanic groups were prevented by converting the thiol group into a disulphide, the resulting diaminodiphenyl disulphide might be converted into the desired *o*-thiolphenylhydrazine according to the following scheme :



The diazonium salt (B) was found to be abnormal, however, inasmuch as it could not be reduced to the compound (C), nor could it be coupled with aniline, potassium ethyl xanthate, etc. The diazo-compound suffered decomposition on keeping or in presence of coupling and reducing agents, producing in every case a brownish tarry matter which furnished on steam distillation a pale yellow oil with empirical formula C₁₂H₈OS₂. It is thus evident that the diazonium compound (B) does not react with any of the above agents and is slowly decomposed in presence of water yielding the unstable *oo'*-dihydroxydiphenyl disulphide; this loses a molecule of water to yield the oxy-

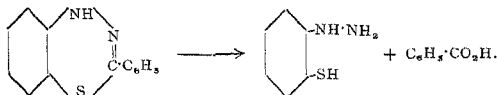
diphenylene disulphide, C₆H₄ $\begin{matrix} \text{O} \\ \diagup \quad \diagdown \\ \text{S}_2 \end{matrix}$ C₆H₄.

This is the first instance of a seven-membered ring containing one oxygen and two sulphur atoms being synthesised. Failing in the reduction of the tetrazonium salt of the disulphide (B), it was thought worth while to proceed as follows:—

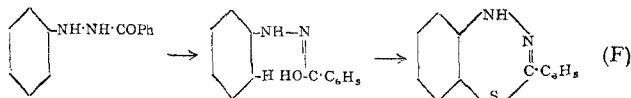


Diaminodiphenyl disulphide readily forms the diacetyl derivative (D) which, however, could not be made to yield a nitroso-derivative, though different possible methods (*Ber.*, 1876, 9, 464; 1877, 10, 959) for introducing the nitroso-group were tried (see below). This reluctance of an imino-group to yield a nitroso-derivative resembles the inert character of the diazonium salt (B), and in both cases some steric influence may be responsible.

Benzenyl-*o*-aminothiophenol yields *o*-aminothiophenol when heated with fused potash (*Annalen*, 1881, 208, 291; *Ber.*, 1880, 13, 1223 and 1887, 20, 2259); it was thought advisable to apply this treatment to 2:3-benzo-6-phenyl-1:4:5-thiodiazine which might yield *o*-thiophenylhydrazine thus:—



Phenylbenzothiodiazine was prepared from benzoylphenylhydrazine by heating with sulphur (compare *Ber.*, 1880, 13, 1223, for the preparation of benzenyl-*o*-aminothiophenol).



Contrary to expectation, not only is the thiodiazine ring disrupted in fusion with potash, but the sulphur atom is eliminated by the alkali, and an aqueous solution of the fused mass yields benzoic acid and hydrogen sulphide on acidification.

EXPERIMENTAL.

Benzenyl-*o*-aminothiophenol was prepared according to the method of Hofmann (*Ber.*, 1880, **13**, 1223, footnote), the yield being 50 per cent. The disulphide of *o*-aminothiophenol was also prepared by Hofmann's method (*Ber.*, 1887, **20**, 2259) with a slight modification in the final oxidation which was more conveniently carried out by iodine solution. Yield 35 per cent.

Diazotisation and Attempted Reduction by Stannous Chloride.—*oo'*-Diaminodiphenyl disulphide (6 gms.) was dissolved in 15 c.c. of concentrated hydrochloric acid (d., 1.19) and diazotised in the usual manner with 3.6 gms. of sodium nitrite dissolved in 30 c.c. of water. To the ice-cold mixture, an ice-cold solution of stannous chloride (30 gms.) in 30 c.c. of concentrated hydrochloric acid was gradually added. The brownish yellow precipitate was allowed to stand in the freezing mixture for about an hour and then quickly filtered at the pump; otherwise the precipitate tends to become oily. On transferring it to a beaker containing water, a brownish oil separated and was distilled in steam. The light yellowish oil thus obtained was extracted with ether, dried with fused calcium chloride and freed from ether; it is insoluble in acid and alkali, possesses a peculiar smell, does not contain nitrogen and produces a reddish-pink coloration with strong sulphuric acid.

Reduction of the Diazo-compound by Sodium Sulphite.—According to the method of Fischer (*Annalen*, 1878, **190**, 71) *oo'*-diaminodiphenyl disulphide (10 gms.) dissolved in 25 c.c. of concentrated hydrochloric acid was diazotised with 5.6 gms. of sodium nitrite when a brownish yellow precipitate was obtained. To the reaction mixture was added a cold saturated solution of sodium sulphite (50 gms., i.e., 2 mols. of sodium sulphite for each amino-group). After the mixture had remained in the freezing mixture for an hour, the precipitate was very rapidly filtered by suction and washed with ice-cold water. It decomposed to a reddish-brown oil at 20–21° and was distilled in steam when tarry matters were left behind and a heavy, pale yellow oil collected; it was extracted with ether, dehydrated over fused calcium chloride, and found to be in all respects identical with the oil obtained in the previous operation.

Coupling with Aniline.—*oo'*-Diaminodiphenyl disulphide (6 gms.) was diazotised in the usual manner and an ice-cold solution of freshly distilled aniline (4.5 gms.) in 5 c.c. of concentrated hydrochloric acid was gradually added. The precipitate did not change in colour, but began to decompose at 20–22° giving rise to an oil which was purified as before and was found to be identical with the product obtained in the previous operations (Found: C, 61.84; H, 3.56;

S, 25·87. $C_{12}H_8OS_2$ requires C, 62·07; H, 3·45; S, 27·59 per cent). The estimation of sulphur in this compound by the method of Carius always gave a deficiency (see below. Compare also Ray, Guha and Das, *J.C.S.*, 1919, 115, 1310; Ray and Guha, *loc. cit.*, 271 and 546).

Coupling with Potassium Ethyl Xanthate.—*oo'*-Diaminodiphenyl disulphide (6 gms.) was diazotised, the diazonium salt being quickly filtered and added to potassium ethyl xanthate (7·7 gms.) dissolved in the minimum quantity of water; the mixture was well stirred, kept in the freezing mixture for about an hour and then filtered. The precipitate gradually changed to a reddish brown oil which on steam-distillation yielded a product identical with that obtained previously (Found: C, 61·79; H, 3·62; S, 26·01. $C_{12}H_8OS_2$ requires C, 62·07; H, 3·45; S, 27·59 per cent.).

Decomposition of the Diazonium Salt.—*oo'*-Diaminodiphenyl disulphide (10 gms.) in 22 c.c. of concentrated hydrochloric acid was diazotised and after one hour in the ice-bath yielded a brownish yellow precipitate of the diazonium salt. This was very quickly filtered, washed with ice-cold water and allowed to attain the room-temperature, when it decomposed at 20–22°. The same change occurred in a beaker containing water, the resulting brownish oil yielding on distillation in steam a product identical with that previously obtained, the yield being 3·7 gms. The oil boiled and decomposed at 231°, evolving pungent fumes at 200–210° (Found: C, 61·94; H, 3·47; S, 25·18. $C_{12}H_8OS_2$ requires C, 62·07; H, 3·45; S, 27·59 per cent.).

Reduction of Oxydiphenylene Disulphide.—The oxydisulphide (1·5 gms.) was reduced with tin and hydrochloric acid and the product subjected to steam distillation. A colourless oil possessing characteristic mercaptanic properties and smell was thus obtained in quantity too small for further purification. An alcoholic solution of this oil, however, gave an insoluble yellow precipitate with lead acetate and a white precipitate with mercuric chloride. It was also soluble in dilute alkali. All these facts show that this oil is different from oxydiphenylene disulphide and is probably a mercaptan.

Diacetaminodiphenyl Disulphide.—Diaminodiphenyl disulphide (3 gms.) was heated on a sand-bath under reflux with acetic anhydride (10 c.c.) and fused sodium acetate (1·5 gms.) for 2–3 minutes only when a clear solution was obtained and immediately poured into cold water which precipitated a colourless semi-solid; on partial neutralisation with concentrated sodium carbonate the product solidified. It was filtered, washed with acetone and ether to remove any tarry matter and finally crystallised from acetone; m.p. 154°. Yield 3 gms. (Found: S, 19·21; $C_{16}H_{16}N_2O_2S_2$ requires S, 19·28, per cent.).

Attempts to prepare the Nitroso-derivative.—(1) To an ice-cold suspension of the acetyl derivative (2 gms.) in moderately strong hydrochloric acid was added an aqueous solution of sodium nitrite (1 gm.) drop by drop with constant stirring; there was no change. (2) The acetyl derivative was suspended in moderately strong hydrochloric acid and treated with the gas from strong nitric acid and arsenious oxide; in this case also the acetyl derivative was left unchanged. (3) The same gas was passed into the crystalline paste obtained by rapidly cooling in ice a solution in hot glacial acetic acid. A green coloration appeared, but the crystals did not dissolve. The clear filtrate from glass-wool was diluted with ice-cold water, and the colourless precipitate shown to be unchanged acetyl derivative.

2: 3-Benzo-6-phenyl-1: 4: 5-*thiodiazine* (F).—Benzoylphenylhydrazine (80 gms.) was intimately mixed with sulphur (30 gms.) and heated in an oil-bath at 190–200° for about 24 hours. The black tarry mass thus obtained was transferred to a porcelain basin, heated with strong hydrochloric acid, filtered and poured into a large quantity of water which produced a yellowish flocculent precipitate. This extraction was repeated several times, the precipitate being filtered, washed with water and finally crystallised from alcohol, forming yellowish plates melting at 109°. Yield 5–6 gms. It is soluble in alcohol, acetone and acetic acid (Found: C, 68·61; H, 4·30; N, 12·09; S, 14·57. $C_{13}H_{10}N_2S$ requires C, 69·02; H, 4·42; N, 12·38; S, 14·18 per cent.).

Action of Melted Potash.—The foregoing compound (20 gms.) and powdered caustic potash (100 gms.) moistened with a small quantity of water was heated in a nickel basin until frothing and fuming ceased when the flame was removed and the fused mass allowed to cool. The reddish-brown aqueous solution of the melt was neutralised with dilute hydrochloric acid in a bath of ice-cold water, much sulphuretted hydrogen being evolved and benzoic acid precipitated with some black tarry matter. The solution did not give any precipitate with mercuric chloride, lead acetate, or iodine nor did it react with benzaldehyde, proving the absence of any compound containing the thiol or hydrazino-group.

The University, Dacca.
Department of Organic Chemistry,
Indian Institute of Science,
Bangalore.

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