

OXIDATION OF *NN'*-DIARYL- AND *NN*-ALKYLARYL-SUBSTITUTED
THIOCARBAMIDES. PART I. THE SO-CALLED 2:5-
DIARYLIMIDO-3:4-DIARYL-1:3:4-THIODIAZOLES

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Hydrogen peroxide oxidation of certain symmetrical diarylthiocarbamides in alcoholic medium has been found to afford the respective diarylcarbamides and not thiodiazoles, as reported earlier (this *Journal*, 1928, 5, 661). The unsymmetrical diaryl or alkylaryl compounds, however, yield sulphur containing products, probably thiodiazoles of yet undecided constitution.

Oxidation of thiocarbamide and its *N*-alkyl-substituted homologues leads to "formamidine disulphide" salts as the primary products of oxidation (Werner, *J. Chem. Soc.*, 1912, 101, 2180; Sahasrabudhey and co-workers: A series of papers in this *Journal* since 1949). *N*-Aryl-substituted thiocarbamides on the other hand have been reported to form thiazoles (Hunter, *J. Chem. Soc.*, 1925, 127, 2023, 2270, *et seq*; Sahasrabudhey and Krall, this *Journal*, 1944, 21, 17; Sahasrabudhey, *ibid.*, 1950, 27, 433; Allen and Allen, "Org. Syntheses", 1942, 22, p. 16; Sahasrabudhey, Miss Mukherjee and Suresh, *Proc. Ind. Sci. Cong.*, 1958, Part III, p. 135) and thiodiazoles (Hector, *Ber.*, 1889, 22, 1177; 1890, 23, 357; Hugershoff, *Ber.*, 1903, 36, 3121; Fromm and Heyder, *Ber.*, 1909, 42, 3804; Lal and Krall, this *Journal*, 1939, 16, 32; Sahasrabudhey and Krall, *ibid.*, 1945, 22, 37) depending on the conditions of reaction.

By hydrogen peroxide oxidation in alcoholic medium of a few (i) symmetrical and (ii) unsymmetrical, aryl and mixed disubstituted thiocarbamides, De and Chakravarty (this *Journal*, 1928, 5, 661) claimed to have obtained certain 2:5-diarylimido-3:4-diaryl-1:3:4-thiodiazoles and 2:5-di(aryllkylamino)-1:3:4-thiodiazoles respectively. In this oxidative process, the formation of intermediate disulphide products akin to formamidine disulphide has been envisaged, as indeed was done by earlier workers also (Hector, *loc. cit.* Cf. Sahasrabudhey and Krall, *loc. cit.*).

A reinvestigation of the work of De and Chakravarty (*loc. cit.*) was carried out in the hope of isolating, if possible, the disulphide intermediate products and also the thiodiazoles for further study. In the cases of four *NN'*-diarylthiocarbamides examined, the products, although agreeing in m. p. and %nitrogen content with those reported by these authors, are sulphur-free, and these have now been identified with the respective *NN'*-diarylcarbamides. In the other two remaining cases also, they are probably identical with the respective diarylcarbamides, as indicated by agreement in the melting points (*vide* Experimental; Table I).

NN-Methylphenylthiocarbamide gave a product, m.p. 93-94°, as reported. It is found identical with the thiodiazole obtained earlier by Hofmann and Gabriel (*Ber.*, 1892, 25, 1578) who refer to it as an 1:2:4-thiodiazole. In absence of any definite proof for the 2:5-di(phenylmethylamino)-1:3:4-thiodiazole structure, suggested by De and Chakravarty (*loc. cit.*), the question of the structure of this compound should be considered open.

Oxidation of *NN*-ethylphenylthiocarbamide gave a compound melting at 58°. From its basic nature, non-desulphurisability, molecular weight and sulphur content, it also appears to belong to the same class to which the above compound from methylphenylthiocarbamide belongs. No compound with m.p. 107-109°, reported by De and Chakravarty, could be isolated.

Thus, it appears that the hydrogen peroxide oxidation of symmetrical diarylthiocarbamides leads to the respective carbamides, whereas asymmetrical diaryl or alkylaryl compounds give sulphur-containing derivatives, probably thiodiazoles of yet undecided structures. Further work is in progress.

EXPERIMENTAL

Oxidation of s-Diphenyl-, s-Di-p-tolyl-, s-Di-o-tolyl-, s-Di- α -naphthyl- and s-Di- β -naphthyl-thiocarbamides with Hydrogen Peroxide in an alcoholic medium.—The procedure followed was the same as described by De and Chakravarty (*loc. cit.*). Thiocarbamide (5 g.) was finely powdered and dissolved in about 50-60 c.c. of alcohol by boiling under reflux. The solution was then allowed to cool and when crystals had just begun to appear, hydrogen peroxide (4 g.) in 70-80 c.c. solution was added gradually within a short time. Heat was evolved and turbidity developed due to separation of sulphur. Some time after all the hydrogen peroxide had been added, a white crystalline mass was thrown out. It was filtered and crystallised from glacial acetic acid as well as from alcohol.

Due to poor solubility of di- β -naphthyl- and di- α -naphthylthiocarbamides in alcohol, a fine suspension of these in hot alcohol was used, as recommended by the above authors. No product could be isolated in the case of di- α -naphthyl compound. Melting points of products from other thiocarbamides are recorded in Table I (column 4). For comparison, melting points of the products obtained by the above authors are also recorded (column 3).

On analysis it was found that all these products were sulphur-free and therefore could not be thiodiazoles. The nitrogen content, as reported by De and Chakravarty (*loc. cit.*), and the nearness, verging almost on identity, of the melting points with those of the respective *s*-diarylcarbamides suggested that these compounds might be identical with the latter.

Authentic samples of the appropriate *s*-diarylcarbamides were therefore prepared by the method recommended by Vogel ("A Text-Book of Practical Organic Chemistry", 2nd ed., 1954, p. 618) or by a modification of it in the case of *s*-di- α - and - β -naphthylcarbamides which were obtained by heating α -naphthylamine and β -naphthylamine respectively with urea in the ratio 2:1 at 180° for 1½ hours. The melting points of these authentic samples on crystallisation from alcohol or glacial acetic acid are recorded in Table I (column 5) along with the melting points of the supposed thiodiazoles (column 3).

TABLE I
[T denotes thiocarbamide]

	Oxidation product of thiocarbamides.	Supposed 1:3:4-thiodiazole.	M.P.*	M.P.†	M.P.‡
1.	<i>s</i> -Diphenyl-T	2:5-Diphenylimido-3:4-diphenyl-	228-30°	235-36°	236-37°
2.	<i>s</i> -Di- <i>p</i> -tolyl-T	2:5-Di- <i>p</i> -tolylimido-3:4-di- <i>p</i> -tolyl-	261°	26°	261°
3.	<i>s</i> -Di- <i>o</i> -tolyl-T	2:5-Di- <i>o</i> -tolylimido-3:4-di- <i>o</i> -tolyl-	249°	249-50°	249-50°
4.	<i>s</i> -Di- β -naphthyl-T	2:5-Di- β -naphthylimido-3:4-di- β -naphthyl-	288°	289-90°	293-95°
5.	<i>s</i> -Di- α -naphthyl-T	2:5-Di- α -naphthylimido-3:4-di- α -naphthyl-	283-85°	...	285°
6.	<i>s</i> -Di- <i>m</i> -xylyl-T	2:5-Di- <i>m</i> -xylylimido-3:4-di- <i>m</i> -xylyl-	250-52°	...	247°

N.B. No depression in m.p. of the mixtures of thiodiazole and the *s*-di-carbamide was noticed.

*. De and Chakravarty (*loc. cit.*).

†. Recorded by the present author

‡. M.P. of the respective carbamide according to Srl. number.

Oxidation of NN-Methylphenyl- and NN-Ethylphenyl-thiocarbamides.—Oxidation of *NN*-methylphenylthiocarbamide under conditions similar to those outlined above gave an oily product which solidified on standing. Crystallised from alcohol, it melted at 93-94°. It was found to contain both sulphur and nitrogen and its identity with Hofmann and Gabriel's thiodiazole (*loc. cit.*) was established by un-depressed mixed m.p. with an authentic sample of the latter. It also gave a picrate, m.p. 142°, as reported (Sahasrabudhey and Krall, *loc. cit.*, 1945).

NN-Ethylphenylthiocarbamide on similar oxidation gave an oil which solidified on standing. It was crystallised from methyl alcohol, m.p. 58°. It gave a picrate from alcoholic solution, m.p. 129-30°. The compound contained both sulphur and nitrogen but was not desulphidable with alkaline lead oxide. [Found: S, 10.15; M.W. (cryoscopic), 314. C₁₆H₂₀N₄S requires S, 9.87% ; M.W., 324].

No product with a m.p. 107-109° could be isolated and the compound reported earlier by De and Chakravarty (*loc. cit.*) might have been the unchanged impure *NN*-ethylphenylthiocarbamide, m.p. 113°. No properties or derivatives have been mentioned.

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