Tetrahedron Letters No. 1, pp. 5-8, 1961. Pergamon Press Ltd. Printed in
United States of America

REACTIONS OF ETHYLENE-DI-ISOTHIOCYANATE WITH AMINES

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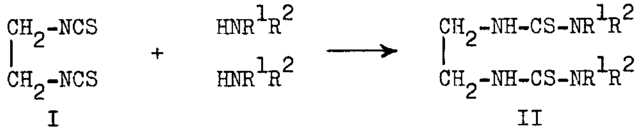
(Received 28 November 1960)

PREVIOUSLY ethylene-di-isothiocyanate (I) has been shown to react with aniline giving the substituted ethylene-dithiourea (II; R^1=H R^2=C_6H_5);[1] analogous products have been obtained from $(CH_2)_4(NCS)_2$ with aniline, NH_3 and CH_3NH_2 [2] and from $(CH_2)_6(NCS)_2$ with $(CH_2)_2NH$.[3] We are studying the behaviour of I towards NH_3 and primary and secondary amines using various molecular ratios, and give here the results of some reactions made in water or aqueous medium, at room temperature. With dimethylamine and piperidine the substituted dithioureas are formed as primary products [II R^1=R^2=CH_3; R^1R^2=$(CH_2)_5$]; secondary products are formed in very small amounts and have not yet been fully identified.



$$\begin{array}{c} CH_2\text{-}NCS \\ | \\ CH_2\text{-}NCS \\ \mathrm{I} \end{array} + \begin{array}{c} HNR^1R^2 \\ HNR^1R^2 \end{array} \longrightarrow \begin{array}{c} CH_2\text{-}NH\text{-}CS\text{-}NR^1R^2 \\ | \\ CH_2\text{-}NH\text{-}CS\text{-}NR^1R^2 \\ \mathrm{II} \end{array} \qquad (1)$$

In the reactions hitherto studied with primary amines - CH_3NH_2 and $C_2H_5NH_2$ - the substituted di-thioureas (II) have on the contrary been

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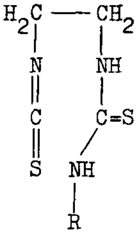
[1] A.Ya. Yakubovic and V.A. Klimova *J.Chem. Soc. U.S.S.R.* **9**, 1777 (1939); *Chem.Abstr*. **34**, 3685 (1940).

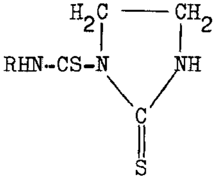
[2] J.v. Braun and G. Lemke *Ber.* **55**, 3552 (1922).

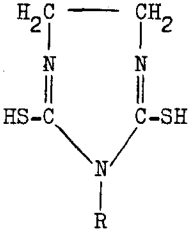
[3] A.G. Bayer, Brit. Pat. 753,247; *Chem. Abstr.* **51**, 9681 (1957).

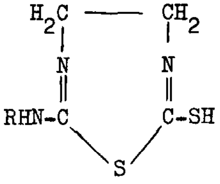
obtained only as secondary products, even using excess of amine. The main products are originated, according to the analytical results, in a reaction of I with a sole molecule of amine; namely, with CH_3NH_2; A: m.p. 202-203° (Found: C, 34.10; H, 5.37; N, 23.96; S, 36.30. $C_5H_9N_3S_2$ requires C, 34.28; H, 5.18; N, 23.99; S, 36.54%); with $C_2H_5NH_2$; B: m.p. 166-167° (Found: N, 21.98; S, 34.00. $C_6H_{11}N_3S_2$ requires: N, 22.21; S, 33.84%).

Structures III to VI could be theoretically thought to fit with


III

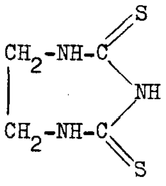

IV

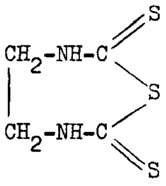

V


VI

the analytical figures of A and B.

III can be ruled out since the I.R. spectra of the compounds do not show the characteristic absorption of the isothiocyanate grouping in the


V'


VII

range of 2100 cm^{-1}.* Formula V' has been given to a compound obtained both from reaction of I with NH_3, and of the hypothetic ethylen-thiuram-monosulphid (VII) with NH_3[4]; (in the latter reaction, the AA have also isolated II. $H_2O(R^1=R^2=H)$. Structure V is furthermore related to the 1,5 di- and 1,3,5-

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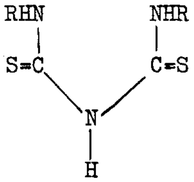
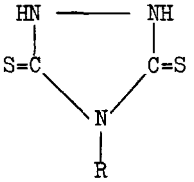
* We are indebted to Dr. C. Pecile and to the Institute of Physical Chemistry of the University of Padua for the I.R. spectra.

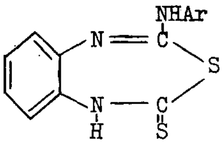
[4] G.D. Thorn and R.A. Ludwig, Canad.J.Chem. 32, 872 (1954).

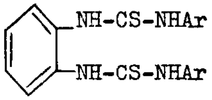
trialkyl-dithiobiurets (VIII) and less directly to the 1,2,4 triazolidine-3,5-dithiones (IX); VI may be related to X, a structure given to the hydrolysis product of XI.[5] The structure given to VII is,

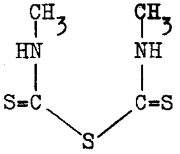

VIII

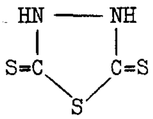

IX

on its side, related to 1,5-dimethyl-thiuram-monosulphide (XII)[6] and less directly to 1,3,4-thia-imidazolidine-2,5-dithiones (XIII). We assign to compounds A and B obtained from I with CH_3NH_2 and $C_2H_5NH_2$, the structures of 1-methyl- and 1-ethyl- thiocarbamyl-imidazolidine-2-thione (IVA and IVB)

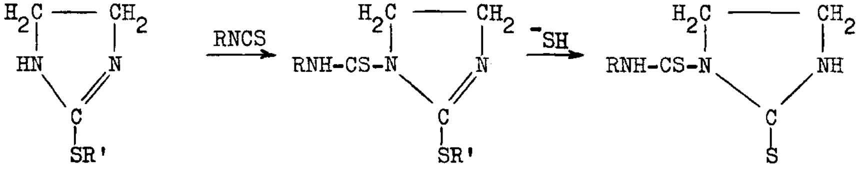

X


XI


XII


XIII

because they are identical with the ones obtained, by purpose of comparison, following equation (2). The identity has been checked by m.p.s and mixed m.p.s, I.R. spectra, chromatographic behaviour (R_f and colour reactions with Grote's reagent and with $AgNO_3$), solubilities and other physical properties.



XIV IV' IV (2)

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[5] T.N. Ghosh and P.C. Guha, J.Indian Chem.Soc. 6, 181 (1929); T.N. Ghosh, Ibid. 10, 583 (1933).

[6] F. D'Angeli and A. Iliceto Gazz.Chim.Ital. 89, 2095 (1959).

Reactions of equation (2) are an application of the synthesis of 1,5-di-alkyl-2,4-dithiobiurets (VIII) [7,8] which are the open chain analogs of structure IV; it seems unlikely that in the mild conditions in which both steps are performed (0° or room temperature) the five atom ring of 2-alkyl-mercapto-2-imidazoline (XIV) would undergo any transformation besides the expected 1-thio-carbamilation and subsequent thio-hydrolysis. Research is progressing to give further evidence to the permanence of such ring.

Both amidic nitrogens and the thiolic tautomeric sulphur of thioureas are known to fail to react with alkyl- or aryl-isothiocyanates;[7] should compound III be the first product of reaction between I and a single mole of a primary amine, its transformation into IV (or V and VI) would only be made possible by the favouring steric situation leading to a cycle; a different intermediate might in any case be involved.

Some of the properties previously described for 1,5-dimethyl-thiuram-monosulphide XII [6] and the evidence given here for the structure of compounds IVA and IVB offers some doubt as to whether the assigned seven membered ring structures[4] really belong to compounds V' and VII.

We gratefully acknowledge the support by Shell Internationale Research Maatschappij, N.V. The Hague, Holland, for the investigation.

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[7] F.H.S. Curd, D.G. Davey, D.N. Richardson and R. de B. Ashworth, J.Chem.Soc. 1739 (1949).

[8] A.E.S. Fairfull and D.A. Peak, J.Chem.Soc. 796 (1955).