Tetrahedron Letters No.45, pp. 3931-3932, 1970. Pergamon Press. Printed in Great Britain.

THE REACTION OF DICYCLOHEXYL CARBODIIMIDE WITH THIOUREAS

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(Received in UK 5 August 1970; accepted for publication 27 August 1970)

During recent years a number of reports have appeared$^{(1-4)}$ describing reactions of acylated carbodiimides with thioamides. In the case of N, N^{1} disubstituted thioureas, carbodiimides are formed in good yield$^{(3)}$ and a general carbodiimide synthesis has been claimed$^{(4)}$. Unexpectedly, no mention could be found in the literature regarding the reaction of carbodiimides themselves with substituted thioureas. When thioureas bearing at least two hydrogen atoms are reacted with dicyclohexyl carbodiimide under mild conditions, dicyclohexyl thiourea is formed in excellent yield together with a new carbodiimide or alkyl cyanamide as below.

$$\text{i)}\quad RN{=}C{=}NR + H_2N\,CSNH_2 \longrightarrow RNHCSNHR + H_2NC \equiv N$$

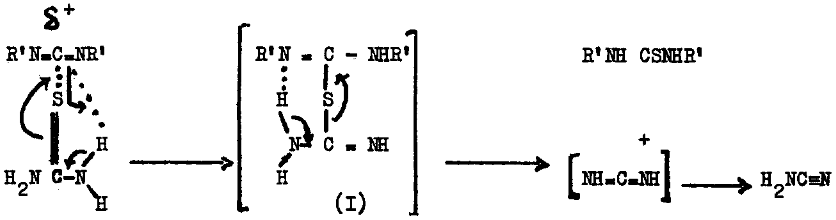
$$\text{ii)}\quad RN{=}C{=}NR + R'NHCSNH_2 \longrightarrow RNHCSNHR + R'NHC \equiv N$$

$$\text{iii)}\quad RN{=}C{=}NR + R'_2NCSNH_2 \longrightarrow RNHCSNHR + R_2'NC \equiv N$$

$$\text{iv)}\quad RN{=}C{=}NR + R'NHCSNHR' \rightleftharpoons RNHCSNHR + R'N = C = NR'$$

Thus, when equimolar amounts of dicyclohexylcarbodiimide and thiourea were reacted at 80 - 85° for 15 hr. in dimethyl formamide solution, dicyclohexyl thiourea (m.p. 180 - 182°) was obtained in 85% yield. Because of the ease with which cyanamides polymerise to dicyandiamides, iso-melamines, melamines etc.$^{(5-7)}$ it is not surprising that under these conditions the compounds could not be isolated in a pure form. The crude by-product exhibited bands at 2212cm^{-1}(-C≡N), 1639 cm^{-}1(-C=N-) and 3330 cm^{-1}(-NH) in the I.R. spectrum, in broad agreement with those expected for cyanamide or its dimer dicyandiamide. Both symmetrically and unsymmetrically disubstituted thioureas reacted in an analogous manner. When N,N-dimethyl and N,N'-di-t-butyl thioureas were used, dicyclohexyl thiourea was isolated in 75% and 36% yields respectively. Once again, under the conditions of reaction, the alkyl cyanamides formed underwent further reaction to form mixtures although both dimethyl cyanamide (I.R. absorption at 2212 cm^{-1} due to C≡N) and di-t-butyl carbodiimide could be separated from the respective by-products by preparative gas-chromatography (Pye 105 instrument, 12'x^{3}/8" Apiezon L column). It is significant that, where cyanamides are necessarily formed (reactions (i)-(iii)), the new thiourea is obtained in excellent yield suggesting that the reverse reaction does not occur to any appreciable extent. On the other hand, in the case of reactions of type (iv) it is clear that mixtures of carbodiimides and thioureas will always be formed.

The nucleophilicity of the thione sulphur atom will be enhanced by contributions from the nitrogen lone pairs and it is likely that initial attack occurs at the relatively electron poor carbon atom of the carbodiimide. Although the mechanism has not been fully investigated it seems possible that the process is of the type outlined below



In the intermediate (I), the basicity of the alkylimino nitrogen atom may be enhanced by participation of the sulphur lone pair and the movement of electrons facilitated. However, it is clear, since either N, N or N,N' disubstituted thioureas react, that the hydrogen atom to be transferred can come from either the amino or imino groups.

The work described above was incidental to an entirely unrelated theme. Consequently, no attempt has been made to optimise reaction parameters (e.g. solvent, temp. etc.) and it may be that, under the correct conditions, good yields of substituted cyanamides could be isolated circumventing the normal route to these compounds which utilises the rather dangerous cyanogen halides.

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