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A NOVEL METHOD FOR THE PREPARATION OF CARBODIIMIDES

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The preceding paper (1) has described that the oxidation of mercaptans to disulfides by means of diethyl azodicarboxylate is extremely promoted by triphenyl phosphine without being changed itself.

A tautomeric pair of thiol and thiocarbonyl structures exists in a thiourea. Thus, the reaction of thioureas with diethyl azodicarboxylate (I) and triphenyl phosphine (II) would be expected to result in an initial formation of bis(carbamidino) disulfides (III)* which might be in turn desulfurized by II to give corresponding carbodiimides, diethyl hydrazodicarboxylate (IV) and triphenyl phosphine sulfide (V) (Scheme 1). The reproduced thiourea reacts again through the same process.

When N, N'-diphenylthiourea was allowed to react with equimolar amounts of I and II in tetrahydrofuran (THF) at room temperature, the orange-red color of the solution immediately disappeared. After the solution was kept stand overnight at room temperature, N, N'-diphenylcarbodiimide, IV and V were obtained in 65%, 72% and 81% yields, respectively. Similarly, N, N'-di-p-tolylcarbodiimide was obtained in a 42% yield.

It is noteworthy that the formation of carbodiimides by this process couples to redox system, i. e., I is reduced to IV and II is oxidized to V.

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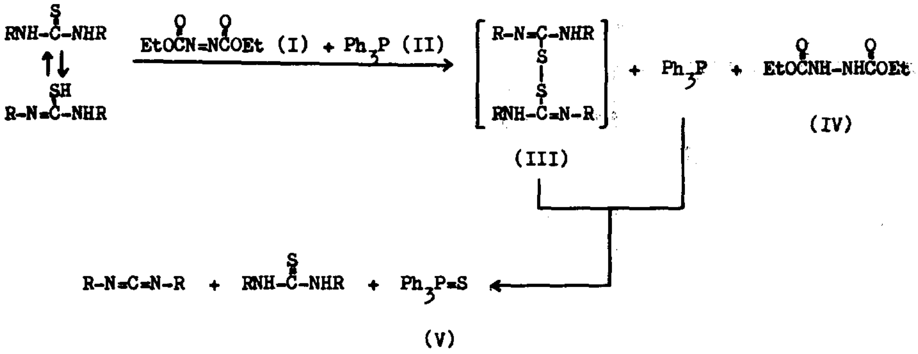
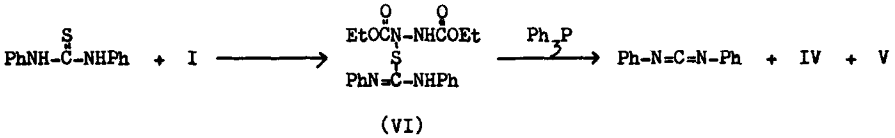
* Although several bis(carbamidino) disulfides have been prepared (2, 3), desulfurization of them by using trivalent phosphorus compounds has not been attempted. Srivastava and Saleem (2) have demonstrated that bis(diphenylformamidino) disulfide dihydrobromide on treatment with absolute ethanol extrudes an atom of elemental sulfur to give bis(diphenylformamidino) sulfide.

Scheme 1



In order to isolate the proposed intermediate, bis(N, N'-diphenylcarbamidino) disulfide (III; R = C_6H_5), N, N'-diphenylthiourea was allowed to react with an equimolar amount of I in THF at room temperature for 1 day. Slow fading of the solution was noted over a period of 3 hrs. Contrary to our expectation, no disulfide (III) could be isolated but was obtained an unexpected product which was formulated as 1 : 1 adduct (VI)* of I with the thiourea. The adduct was purified by reprecipitation from ether-petroleum ether at room temperature. The THF solution of the adduct, when further treated with II at room temperature, afforded N, N'-diphenylcarbodiimide (66%), IV (91%) and V (74%) (Scheme 2).

Scheme 2



These results suggest that the reaction of thiourea with I in the presence of II also proceeds through initial formation of VI. As shown in the previous paper (1), however, II extremely promotes the oxidation of mercaptans to disulfides. Thus, at the present stage of the investigation, the course of the reaction involving III can not be excluded, when II coexists with I.

Further studies on the reactions of these compounds involving thioamides are being done.

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* Anal. Calcd. for $C_{19}H_{22}N_4O_4S$: C, 56.71; H, 5.51; N, 13.92; S, 7.97. Found: C, 56.90; H, 5.65; N, 14.21; S, 8.03.
Infrared spectrum (KBr): no C=S, 3290 cm^{-1} (NH), 1730, 1710 cm^{-1} (C=O), 1640 cm^{-1} (C=N).

References

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3. T. Kodama, K. Uehara, K. Hisada and Y. Kodama, Yuki Gosei Kagaku Kyokai-shi, **26**, 674 (1968).