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ISOMERIZATION OF CARBODIIMIDES INTO CYANAMIDES

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Isomerization of carbodiimides I into cyanamides II constitutes a new molecular rearrangement reminiscent of the thermal (1) and photochemical (2) isomerization of ketenimines into nitriles. Table I summarizes our results on the photoisomerization I → II. Phenylbenzylcyanamide, m.p. and mixture m.p. 59-60°, also has been detected in trace amount after pyrolysis of N-phenyl-N'-benzylcarbodiimide at 260° for 7 hours in diphenyl ether. Its i.r. and n.m.r. absorption were each identical with authentic spectra.

$$\underset{\text{I}}{RN{=}C{=}NR'} \xrightarrow[h\nu]{\text{heat or}} \underset{\text{II}}{RR'NC{\equiv}N}$$

The photoreactions in dilute degassed dioxane were run in quartz tubes under oxygen free nitrogen in a Rayonet Reactor with irradiation from 16 lamps (2537A). The formation of diphenylcyanamide during photolysis of diphenylcarbodiimide is assumed; however, this product has not been detected. By separate experiment it was found that diphenylcyanamide under similar irradiation undergoes rapid decomposition into unknown products. Irradiation of dicyclohexylcarbodiimide by a high-pressure Hanovia immersion lamp (100 w) for 7 hours produced dicyclohexylcyanamide in nearly the same yield as that reported in Table I.

Each product II was identified by melting-point, by identical comparison of both n.m.r. and i.r. spectra with authentic spectra, and by glc retention times which were identical with those for authentic material. The amount of each unreacted carbodiimide after photolysis was determined by quantitative hydrolysis in 3N hydrochloric acid at 25° to the known urea derivative III (see Table I). Under these conditions the cyanamides were unreactive.

$$\text{I} \xrightarrow[H_2O]{HCl} \underset{\underline{\text{III}}}{\text{RNHCONHR}'}$$

Conceivably cyanamide formation may result from either bond-cleavage and radical recombination within the solvent cage or an intramolecular cyclic reorganization of σ and π electrons. Either process may account for the apparent absence of formation of R_2, R_2', $(RNCN)_2$, $(R_2'NCN)_2$, R_2NCN and $R_2'NCN$ and is not inconsistent with the failure of irradiation in the presence of acetophenone to reveal a photosensitization effect for the rearrangement.

$$\underline{\text{I}} \longrightarrow R\cdot \; + \; \cdot N{=}C{=}NR' \quad \text{or} \quad R\cdot' \; + \; \cdot N{=}C{=}NR$$

$$RN{=}C{=}N\cdot \longleftrightarrow R\dot{N}CN \xrightarrow{R\cdot'} \underline{\text{II}} \xleftarrow{R\cdot} R'\dot{N}CN \longleftrightarrow R'N{=}C{=}N\cdot$$

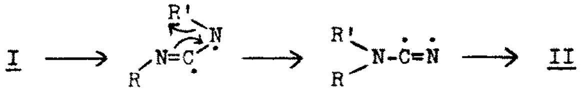

TABLE I

Photoisomerization of Carbodiimides I into Cyanamides II

I	R R'	C_6H_5 C_6H_5	C_6H_5 $C_6H_5CH_2$	C_6H_5 CH_3	cyclo C_6H_{11} cyclo C_6H_{11}
conc. m/1		0.013	0.033	0.1	0.019
irradiation time		36 hr.	36 hr.	80 hr.	1 week
II yield (%)		0	13.8	2.0	11.0
unreacted I (%)		82	2.6	33	92

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