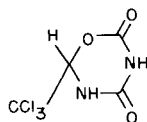


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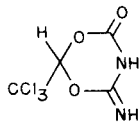
Structure of the Reaction Product of Chloral Hydrate and Isocyanic Acid

Bernard Loev and Gerald Dudek

In a recent article describing the reactions of isocyanic acid with carbonyl compounds, Hoover, Stevenson, and Rothrock (1) observed that chloral reacted slowly with free isocyanic acid at 0° to give $\text{CCl}_3\text{CH}(\text{OH})\text{NCO}$, m. p. 25°. On stirring with water, this was converted to a solid, m. p. 190–200°, assigned structure A. This latter substance was also produced by reaction of isocyanic acid directly with chloral hydrate.



A



B

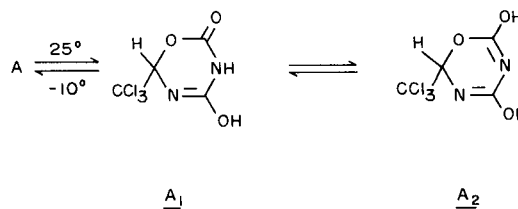
Independently, Loev and Kormendy (2) in the course of a study of the synthesis of carbamates by reaction of an alcohol with sodium cyanate and trifluoroacetic acid in an inert solvent, observed that 1,3-glycols gave bis-carbamates, and 1,2-glycols gave a mixture of carbonate and carbamates, but that a 1,1-glycol such as chloral hydrate gave a product, m. p. 240°, which was assigned structure B on the basis of infra-red and nuclear magnetic resonance spectra (3).

Despite the difference in melting points (4), the two compounds seemed to be identical, as shown by a comparison of the infra-red spectra (5). Although the infra-red spectra and possible mechanisms of formation were compatible with either structure, nuclear magnetic resonance spectra, determined at room temperature, appeared to exclude structures, such as A, in which there would be two adjacent hydrogens. Thus, the sharpness of the peak at 5.8 p.p.m. in such diverse solvents as dioxan- d_8 , acetone- d_6 , or methanol- d_4 supported a structure in which the hydrogen on the carbon in the ring was not adjacent to any element having a hydrogen attached (*i.e.* structure B).

Following the appearance of the article by Hoover, *et al.*, further n.m.r. studies were carried out. It was found that significant splitting occurred at low temperatures (5). At -10° (in acetone- d_6) the

sharp peak which at room temperature appeared at 5.8 p.p.m., now manifested itself as a doublet occurring at 6.32 p.p.m. ($J = 3.6$ Hz). The two acidic proton signals ($\delta = 9.07, 10.19$ p.p.m.) narrowed as the temperature was lowered. At -54°, the acidic proton signal at $\delta = 9.42$ p.p.m. showed evidence of being a poorly resolved doublet. The signal at $\delta = 10.63$ p.p.m. remained a singlet. These splittings can only be accounted for by the oxadiazine structure (A), originally proposed by Hoover, Stevenson, and Rothrock.

The occurrence of a single sharp peak in the n.m.r., carried out at room temperature, which originally led us to favor structure B, is probably due either to the existence, at room temperature, of A predominantly in the tautomeric forms A₁ or



A₂, whereas at low temperatures form A predominates, or to the possibility that hydrogen exchange occurs at room temperature but becomes unimportant as the temperature is lowered.

REFERENCES

- (1) F. W. Hoover, H. B. Stevenson, and H. S. Rothrock, *J. Org. Chem.*, 28, 1825 (1963).
- (2) B. Loev and M. F. Kormendy, *ibid.*, 28, 3421 (1963).
- (3) B. Loev, K. M. Snader, and M. F. Kormendy, *ibid.*, 29, 245 (1964).
- (4) The compound melts with decomposition, and the temperature of decomposition varies with the rate of heating.
- (5) We wish to thank Dr. Hoover for providing us with some of his spectra and for helpful discussions. In a private communication, Dr. F. W. Hoover has informed us of similar low temperature n.m.r. studies conducted by Mr. C. B. Matthews.

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