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EVIDENCE OF TAUTOMERISM IN IMINO-URETHANES

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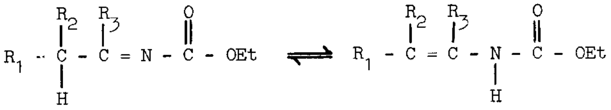
It has recently been reported (1) that tautomerism has been observed in unconjugated azomethines revealing a measurable amount (~5%) of secondary enamine tautomer. We here report our results for the related case of the imino-urethanes (A) where the azomethine grouping is conjugated with a carboxyester function. We have found evidence for the presence of a substantial amount of enamide tautomer (B), considerably greater than for the unconjugated cases (1).

The imino-urethanes were prepared by condensation of the corresponding ketals with ethyl carbamate according to the method of Hoch (2). The infra-red spectrum of cyclohexylidene-urethane (IA) included a single NH stretch peak at 3360 cm^{-1}, as expected for a monosubstituted urethane (3). Urethane itself shows more than one peak in the NH stretch region (4). The n.m.r.spectrum of the product included a broad singlet at 3.72 τ (NH) and a triplet at 4.24τ , J = 3 c./sec. (olefinic H). The ester CH_2 gave rise to a quartet centred at 5.92τ . The integral value for this absorption (the same for both tautomers) allowed estimation of the amount of enamide present by comparison with the integrals for the NH and olefinic CH protons (only present in tautomer IB). This revealed that 64-71% of the compound was in the enamide form (IB).



$$R_1-\underset{\displaystyle H}{\overset{\displaystyle R_2}{C}}-\overset{\displaystyle R_3}{C}=N-\overset{\displaystyle O}{\overset{\|}{C}}-OEt \rightleftharpoons R_1-\overset{\displaystyle R_2}{C}=\overset{\displaystyle R_3}{C}-\underset{\displaystyle H}{N}-\overset{\displaystyle O}{\overset{\|}{C}}-OEt$$

(A) (B)

Example	R_1	R_2	R_3
I	H	$-(CH_2)_4$	$-$
II	H	$-(CH_2)_3$	$-$
III	H	H	C_6H_5

In cyclopentylidene-urethane (IIA) the NH stretch absorption in the infra-red spectrum was again a single band, at 3320 cm^{-1}. In the n.m.r. spectrum the NH singlet (broad) occurred at 3.16 τ and the olefinic proton triplet at 4.50 τ, J = 2 c./sec. Integration showed 60-66% enamide tautomer (IIB) present. Thus in this case there is less compound with the double bond endo than for the six carbon ring case, which is as might be expected from stereochemical considerations (5).

In the case of the urethane from acetophenone diethyl ketal (IIIA) spectroscopic information again revealed tautomerism to be present, the n.m.r. spectrum including bands at 4.18 τ and 4.43 τ assignable to the methylene protons of the enamide form (IIIB, cf. the n.m.r. spectrum of α-methyl styrene (6)). Integration revealed approximately 31% of enamide tautomer present. This lower value, compared with the other cases cited, is perhaps not surprising as the enamide structure supports in this case an unsubstituted methylene group.

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