Cycloaddition of Isocyanates to Ketenimines. Formation of 4-Iminoacetidin-2-one Derivatives

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Summary Isocyanates undergo thermal [2+2] cycloaddition to ketenimines with the formation of 4-iminoacetidin-2-one derivatives in high yields.

HETEROCUMULENES readily undergo thermally induced cycloaddition reactions.¹ Recently, ketenimines have also been shown to take part in such reactions although isocyanates have been claimed to be unreactive.² We have found that diphenyl-N-p-tolylketenimine (1) and dimethyl-N-ptolylketenimine (2) react thermally with the isocyanates (3) to give the corresponding 4-iminoacetidin-2-one derivatives $(4)^3$ in high yields. In order to achieve a reasonable rate of reaction it was necessary to heat the ketenimines and aryl isocvanates at $140-150^\circ$, while with p-tosyl isocvanate heating at 80° was sufficient. The reactions were usually run overnight, although some reactions were complete in a shorter time.

 $R_2^1C=C=N-p-Tol + R^2NCO$ ŃR² 07 (3) (1) $R^{1} = Ph$ (2) $R^1 = Me$ (4) Yield(%) $a; R^1 = Ph; R^2 = Ph$ 83 b; $R^1 = Ph$; $R^2 = p$ -Tolyl 78 c; $R^1 = Ph$; $R^2 = p$ -Anisyl R¹CH-78 NHR² d; $R^1 = Ph$; $R^2 = p - Tosyl$ 72 $e_j R^1 = Me_j R^2 = Ph$ (5) 76 $f_1 R^1 = Me_1 R^2 = p - Tosyl$ 73 (6)

Structural assignments were based primarily on spectral evidence but also on the fact that basic hydrolysis led to the acetamidine derivatives (5).4 Conclusive evidence for structure (4) was provided by m.s. data. Fragmentation of the molecule into halves can take place in two ways thereby giving rise to four different fragments. Such a fragmentation occurred in all cases and it was thus possible unequivocally to establish the structures. All but one of the reactions yielded exclusively the cycloaddition product (4). From reactions of the ketenimine (1) with p-tosyl isocyanate small and variable amounts of diphenyl-N-ptolyl-*N*-*p*-tosylacetamidine (5; $R^1 = Ph$; $R^2 = p$ -Tos) were always isolated along with some unchanged ketenimine. The presence of p-tosylamide in the p-tosyl isocyanate was unavoidable and addition of the former to the ketenimine would account for the presence of (5); such an addition was proved by a separate experiment. The presence of unchanged ketenimine was explained when we discovered that compound (4d) reverts thermally to ketenimine and isocyanate. Under the above conditions cyclohexyl and alkyl isocyanates were unreactive. Chlorosulphonyl isocyanate reacted readily with the ketenimine (1) at 0° yielding an unstable product from which the chlorosulphonyl group was reductively removed with thiophenol-pyridine.⁵ One compound, m.p. 201°, was obtained in 84% overall yield. The molecular formula, C43H35N3O, corresponds to a combination of two molecules of the ketenimine with one of the isocyanate. The fragmentation pattern of the mass spectrum and other spectral data are consistent with structure (6). It remains to establish whether the thermal [2+2] cycloaddition is concerted or stepwise.⁶ There is ample evidence which suggests a concerted reaction path for thermal [2+2] cycloaddition reactions involving certain heterocumulenes;1 we believe, however, that the present reaction is stepwise. The formation of compound (6) can best be explained by a two-step process in which a dipolar intermediate, formed from (1) and the isocyanate, would react with a second molecule of ketenimine to give the observed product.

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