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

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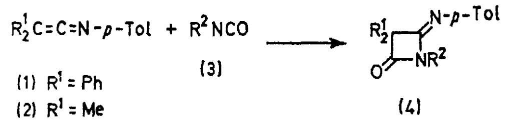
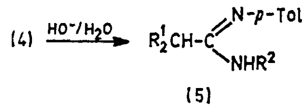
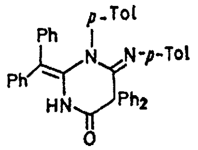
Summary Isocyanates undergo thermal [2 + 2] cycloaddition to ketenimines with the formation of 4-iminoacetidin-2-one derivatives in high yields.

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*-*p*-tolylketenimine (**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 isocyanates at 140—150°, while with *p*-tosyl isocyanate heating at 80° was sufficient. The reactions were usually run overnight, although some reactions were complete in a shorter time.



	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	78
d; R^1 = Ph; R^2 = *p*-Tosyl	72
e; R^1 = Me; R^2 = Ph	76
f; R^1 = Me; 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*-*p*-tolyl-*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, $C_{43}H_{35}N_3O$, 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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