Cycloadditions of Extended Dipoles: Reaction of Imidoylazimines with Ketens

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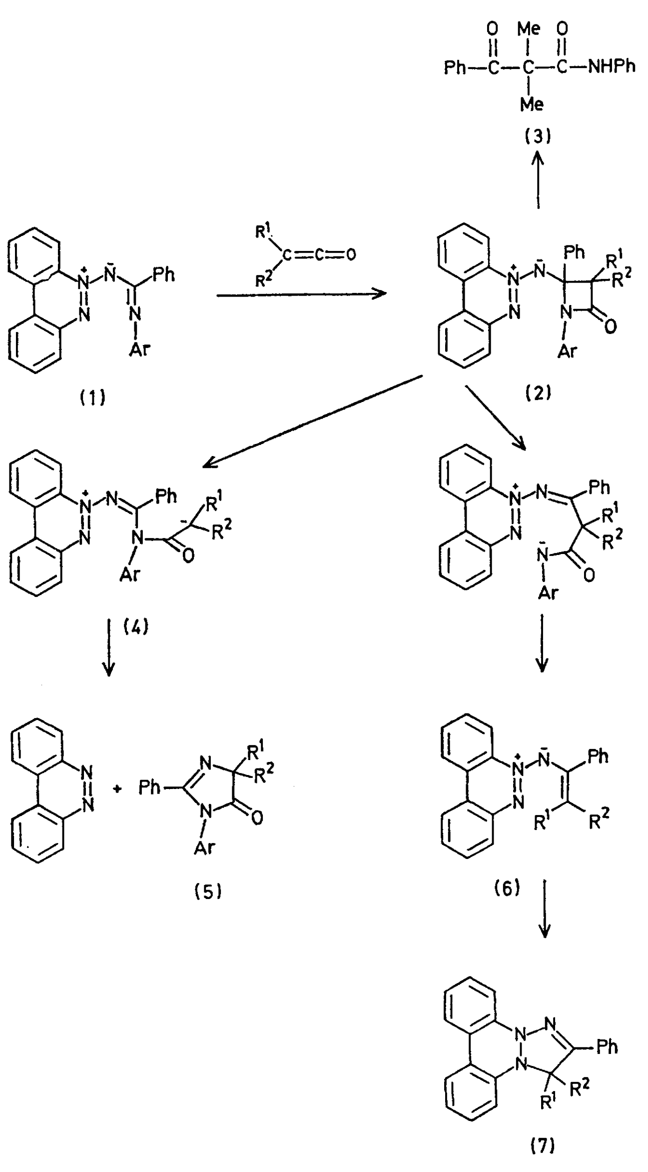
Summary Ketens undergo 2+2 cycloaddition to the C=N bond of the imidoylazimines (**1**) to give the β-lactams (**2**) which are cleaved on heating to give either benzocinnoline and 1,2,4,4-tetrasubstituted imidazolin-5-ones (**5**) or the triazolines (**7**), depending on the keten substituents.

CYCLOADDITIONS involving extended dipolar systems offer the possibility of a simple route to medium ring heterocycles; the periselectivity observed in such processes is therefore of practical, as well as of current theoretical interest.[1]



The imidoylazimines (**1**)[2] can in principle undergo 5+2, 3+2, or 2+2 cycloaddition with ketens. However, addition of diphenyl-, phenylmethyl-,† and dimethylketens† to the imidoylazimines (**1**; Ar = Ph, *o*-tolyl, and *p*-$NO_2 \cdot C_6H_4$) in benzene at room temperature gave the yellow 2+2 cycloadducts (**2**) quantitatively. Evidence for the β-lactam structure is the i.r. carbonyl absorption at 1750—1730 cm^{-1}, retention of the characteristic benzocinnoline *N*-imide ^1H n.m.r. absorption pattern,[3] and the ready hydrolysis of the adduct (**2**; Ar = Ph, $R^1 = R^2 =$ Me) to give benzocinnoline *N*-imide and the ketoamide (**3**).

The adducts (**2**) are unstable and decompose on prolonged standing or heating to give products which depend on the keten substituents R^1 and R^2. The diphenylketen adducts (**2**; Ar$=R^1=R^2=$Ph and Ar$=$*o*-tolyl, $R^1=R^2=$Ph) in refluxing benzene gave benzocinnoline quantitatively and the imidazolinones (**5**; Ar$=R^1=R^2=$Ph and Ar$=$*o*-tolyl, $R^1=R^2=$Ph), m.p. 158° (70%), and m.p. 138° (75%), respectively. These imidazolinones were also produced unambiguously but in lower yields from diphenylglycine and the *N*-arylbenzimidoyl chloride. Formation of the imidazolinones is readily explained in terms of the highly stabilised zwitterionic intermediate (**4**) resulting from C–C bond cleavage of the β-lactam. Significantly, in the overall sequence (**1**) → (**2**) → (**5**) the imidoylazimine has functioned effectively as an imidoylazide. Such reactivity is precluded for the latter which exist as the very stable tetrazoles.

The dimethylketen adduct (**2**; Ar = Ph, $R^1 = R^2 =$ Me), although hydrolytically less stable than the diphenyl analogue, is somewhat more stable thermally and undergoes a different mode of breakdown. Heating in dry toluene gives the triazoline (**7**; $R^1 = R^2 =$ Me), m.p. 165° (20%), presumably by C–N bond cleavage in the β-lactam leading to loss of isocyanate and formation of the 1,5-dipole (**6**) which cyclises. In this case C–C bond cleavage would give a zwitterion (**4**; $R^1 = R^2 =$ Me) in which the carbanionic centre is less stabilised than in the diphenyl analogue and none of the imidazolinone (**5**; $R^1 = R^2 =$ Me) was detected. On further heating in toluene the triazoline (**7**), a rare type of dihydro-1,2,3-triazole with two saturated nitrogen atoms, undergoes fragmentation to give benzocinnoline and benzonitrile. Predictably the methylphenylketen adducts show intermediate behaviour. Thus (**2**; Ar = R^1 = Ph, R^2 = Me) gave the imidazolinone (**5**) (30%) and the triazoline (10%) whereas (**2**; Ar = *p*-$NO_2 \cdot C_6H_4$, R^1 = Ph, R^3 = Me) gave only the triazoline (50%). As expected the more electron-withdrawing substituent on the terminal nitrogen favours cleavage of the C–N bond.

Formation of adducts (**2**) can be readily rationalised by a stepwise cycloaddition through the zwitterion (**4**) formed by nucleophilic attack of the terminal ylide nitrogen on the keten, although concerted ${}_{\pi}2_s + {}_{\pi}2_a$ addition, or ${}_{\pi}2_s + {}_{\pi}2_s$ addition favoured by configuration interaction,[4] are also formal possibilities. Rare examples of 5 + 2 (possibly concerted ${}_{\pi}6_s + {}_{\pi}2_a$) additions of conformationally fixed

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† Generated *in situ* by the action of triethylamine on the appropriate acid chloride.

cisoid 1,5-dipoles to cumulenes have been observed;[5] however, the preferred configuration and conformation of the acyclic 1,5-dipoles (**1**) are uncertain and may militate against formation of the 5 + 2 adduct by either stepwise or concerted modes of addition.

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