Action of *N*-Phenylmaleimide and 1-Diethylaminopropyne on a 1,3-Oxazin-2-one

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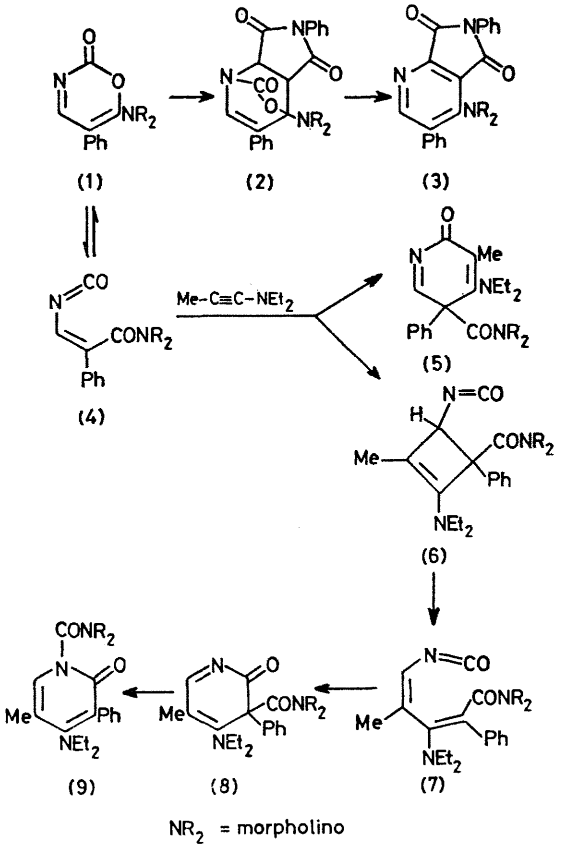
Summary Whereas *N*-phenylmaleimide and 6-morpholino-5-phenyl-1,3-oxazin-2-one (**1**) yield the pyridine derivative (**3**) by a Diels–Alder reaction, the action of 1-diethylaminopropyne on the oxazinone results in the isomeric adducts (**5**) and (**9**), which are thought to be formed by initial 1,4- and 1,2-cycloaddition, respectively, of the ynamine to the acyclic valence isomer (**4**) of the oxazinone; the 1,2-cycloadduct rearranges to the final product by a sequence of pericyclic reactions.

THE 1-azabuta-1,3-diene system is incorporated in the structure of 1,3-oxazin-2-ones, *e.g.* the morpholino derivative (**1**).[1] These compounds were therefore expected to function as dienes in Diels–Alder reactions and we did observe this kind of behaviour with electron-deficient dienophiles. Thus compound (**1**) reacted with *N*-phenylmaleimide to give a yellow product, m.p. 148 °C (decomp.),† which is assigned the pyridine structure (**3**) on the basis of its molecular weight and its i.r. (ν_{max} 1720 and 1610 cm^{-1}) and ^{1}H n.m.r. spectra [δ 8·6 (s, 1H), 7·6—7·3 (m, 2 × Ph), and 3·86 (br s, 8H, morpholino H)]. It is probably formed by loss of carbon dioxide and hydrogen from the initial Diels–Alder adduct (**2**).

The reaction with ynamines took an entirely different course. Treatment of compound (**1**) with 1-diethylaminopropyne in boiling benzene gave a yellow and a colourless adduct in 35 and 37% yield, respectively, which were separated by fractional crystallisation. The i.r. spectrum of the yellow adduct, m.p. 179—181 °C, exhibited carbonyl absorptions at 1652 and 1615 cm^{-1} and its ^{1}H n.m.r. spectrum indicated the presence of methyl, diethylamino, morpholino, and phenyl groups and of an isolated olefinic proton. The colourless isomer, m.p. 158—160 °C, showed



NR$_2$ = morpholino

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† All new compounds gave satisfactory analyses and mass spectra.

ν_{max} 1695, 1652, and 1610 cm^{-1}; its n.m.r. spectrum resembled that of the first compound, except that it exhibited allylic coupling (*J* 1 Hz) between the olefinic proton and the methyl group.

The structures of the two adducts were solved by *X*-ray crystallography. The yellow compound was shown to be the 2(5*H*)-pyridone (**5**) and the colourless isomer the 2(1*H*)-pyridone (**9**).

We suggest that the formation of both products proceeds by initial valence isomerisation of the oxazinone to the isocyanate (**4**), which has recently been observed to occur on flash-vacuum pyrolysis.[2] The isocyanate then undergoes a Diels–Alder reaction with the ynamine to form the yellow adduct (**5**). $2\pi + 2\pi$ cycloaddition[3] of the ynamine to the olefinic double bond of the isocyanate produces the cyclobutene (**6**), which undergoes electrocyclic ring-opening to the azahexatriene (**7**). Electrocyclisation of the latter results in the 2(3*H*)-pyridone (**8**), which is converted into the more stable, fully conjugated colourless product (**9**) by a [1,5]-sigmatropic shift of the morpholinecarbonyl group.[4] Compound (**5**) may not undergo an analogous rearrangement because the required suprafacial [1,3]-shift is forbidden by the rules of orbital symmetry.

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[2] P. W. Manley, R. C. Storr, A. E. Baydar, and G. V. Boyd, *J.C.S. Chem. Comm.*, 1978, 902.

[3] J. Ficini, *Tetrahedron*, 1976, **32**, 1449.

[4] [1,5]-Migrations of acyl groups from carbon to carbon (D. J. Field, D. W. Jones, and G. Kneen, *J.C.S. Chem. Comm.*, 1976, 873) and from carbon to nitrogen (M. Franck-Neumann and C. Dietrich-Buchecker, *Tetrahedron Letters*, 1976, 2069) occur readily.