

Ring-transformation Reactions of 4-Imino-1,3-4H-oxazoles

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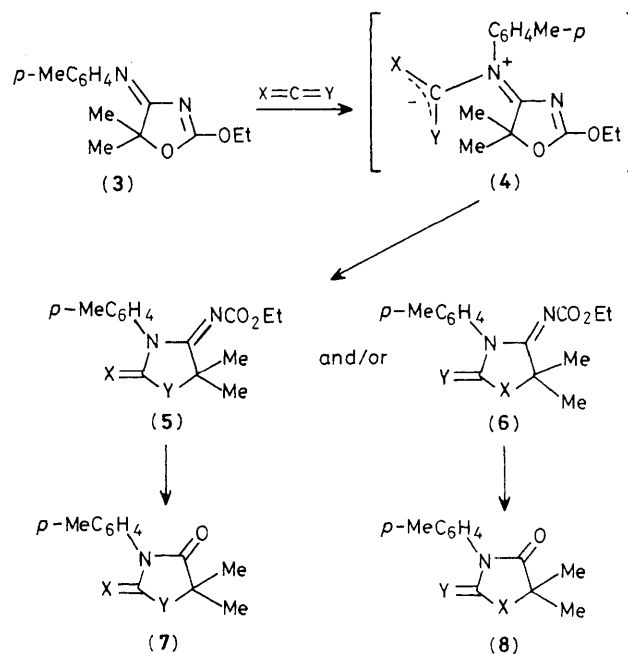
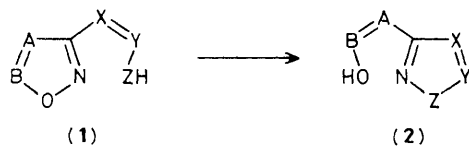
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The 4-imino-1,3-4H-oxazole (3) undergoes ring-opening cycloaddition reactions with electrophilic heterocumulenes by way of an extended Boulton-Katritzky scheme.

A general rearrangement in heterocyclic chemistry involving the participation of three side-chain atoms is the azole-azole interconversion (1) → (2), generalized by Boulton and Katritzky.¹ This scheme is limited to heterocycles containing the N-O bond; the nucleophilic C-3 substituent (XYZ) in principle is a heteroallyl moiety, although the reaction has been extended to saturated chains.²

We have now found that the 4-imino-1,3-4H-oxazole (3) undergoes cycloaddition reactions with electrophilic heterocumulenes (X=C=Y) to give (5) and/or (6) via the intermediacy of the dipolar species (4).† The rearrangement (4) → (5) and/or (6) bears some analogy with the Boulton-Katritzky scheme (1) → (2), but differs basically in that the electrophilic centre is carbon instead of nitrogen. The reactions occur under mild conditions (refluxing benzene) because of the presence of a good leaving group in the starting molecule. This extension of the Boulton-Katritzky scheme has not so far been recognized, although a single example exists in the literature.³

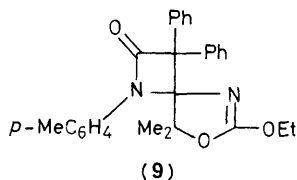
Compound (3) was prepared by cycloaddition of ethyl azidoformate with dimethylketen-*N*-(tolyl)imine according to the literature procedure.⁴ Treatment of (3) with two equivalents of tosyl isocyanate in benzene at 90 °C for 7 days led to



	X	Y
a	TosN	O
b	ClSO ₂ N	O
c	PhCON	O
d	O	O
e	PhSO ₂ N	S
f	TosN	S
g	(EtO ₂ C) ₂ C	O

Tos = *p*-Me-C₆H₄SO₂-

† All compounds gave satisfactory C, H analyses and spectral data (i.r., ¹H and ¹³C n.m.r., and mass spectra) in agreement with the assigned structures.



the isolation of two products which were characterized as (**5a**) (11%, m.p. 189 °C) and (**6a**) (47%, m.p. 168 °C). When the reaction was followed in CDCl_3 solution at 70 °C by integration of the ring methyl signals in the ^1H n.m.r. spectrum [at δ 1.53 for (**3**), 1.73 for (**5a**), and 1.97 for (**6a**)], (**5a**) was observed as the major product at the early stage of the reaction, whereas (**6a**) predominated at the end of the reaction. Thus, (**5a**) reached a maximum concentration of 65% after 20 h, but then decreased in favour of (**6a**). After 600 h, the concentrations of (**5a**) and (**6a**) were 47% and 53% respectively. The isomerization of an isourea structure (**5a**) into a more stable urea structure (**6a**) is a typical Dimroth rearrangement,⁵ known to occur under these reaction conditions.

Distinction between (**5a**) and (**6a**) is easily made on the basis of the positions of the C-5 carbon resonances in the ^{13}C n.m.r. spectra. These are situated at δ 88.1 for (**5a**) and 66.7 for (**6a**) as expected for oxygen and nitrogen respectively in the α -position.³

When (**3**) was heated with chlorosulphonyl isocyanate in benzene solution at 70 °C, the n.m.r. spectrum indicated the presence of (**5b**) along with 20% of the hydrolysed product (**7b**). Attempted purification by column chromatography on silica gel furnished the hydrolysed product (**7b**) (33%, m.p. 191 °C) exclusively. Compound (**5b**) (m.p. 144 °C), however, could be isolated in the pure state (25%) by fractional crystallization of the crude reaction mixture from chloroform-diethyl ether.

Similarly, the reaction of (**3**) with benzoyl isocyanate at 80 °C in acetonitrile yielded (**5c**) (34%, m.p. 150 °C), but treatment of the crude reaction mixture on a silica gel column furnished (**5d**) (36%, m.p. 115 °C). Both (**5b**) and (**5c**) are the kinetic products of the reaction.

The strongly electrophilic phenylsulphonyl isothiocyanate and tosyl isothiocyanate reacted with (**3**) at 75 °C to give (**6e**) (76%, m.p. 227 °C) and (**6f**) (71%, m.p. 235 °C) respectively as the sole reaction products. Cyclization thus occurred at nitrogen as shown by the C-2=S and C-5 carbon resonances at δ 179 and 70 respectively in the ^{13}C n.m.r. spectrum.³ Compound (**6f**) remained unchanged when treated with 1,4-diazabicyclo[2.2.2]octane, but hydrolysed to (**8f**) (100%, m.p. 231 °C) in dilute hydrochloric acid.

Whereas (**3**) reacted with bis(ethoxycarbonyl)ketene⁶ at 80 °C to give (**7g**) (17%, m.p. 158 °C) after column chromatography on silica gel, diphenylketene reacted in a different manner and furnished the spiro-cycloadduct (**9**) (30%, m.p. 179 °C). Its structure was established by spectral methods, in particular by the occurrence of two different ring methyl absorptions in the ^1H (δ 0.95 and 1.45) and ^{13}C n.m.r. spectra (δ 23.4 and 26.6). This is because of the presence of an asymmetric carbon atom in the α -position.

No cycloadducts were obtained when (**3**) was treated with phenyl isocyanate, phenyl isothiocyanate, benzoyl isothiocyanate, methyl acrylate, methyl vinyl ketone, or acrylonitrile.

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