Studies dealing with the Dipolar Cycloaddition Reactions of 2-Diazo-4,5-dicyanoimidazole

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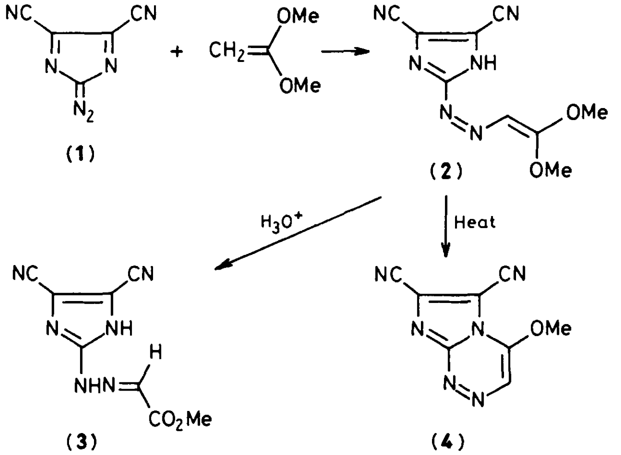
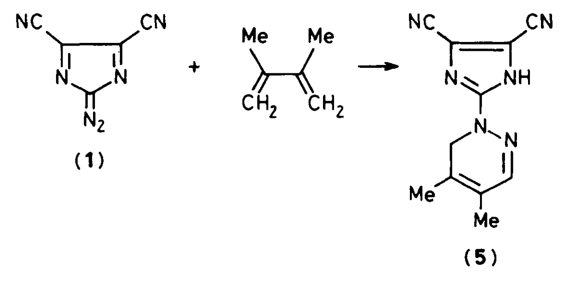
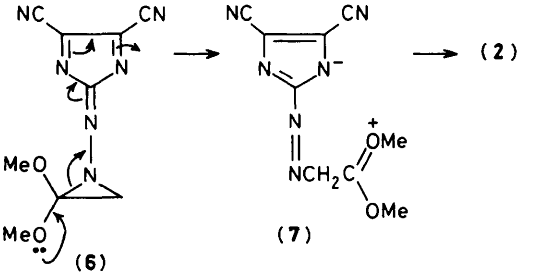
The dipolar cycloaddition reactions of 2-diazo-4,5-dicyanoimidazole with 1,1-dimethoxyethylene and 2,3-dimethylbuta-1,3-diene have been studied; it is proposed that the reaction proceeds *via* the nitrene form of the diazo compound.

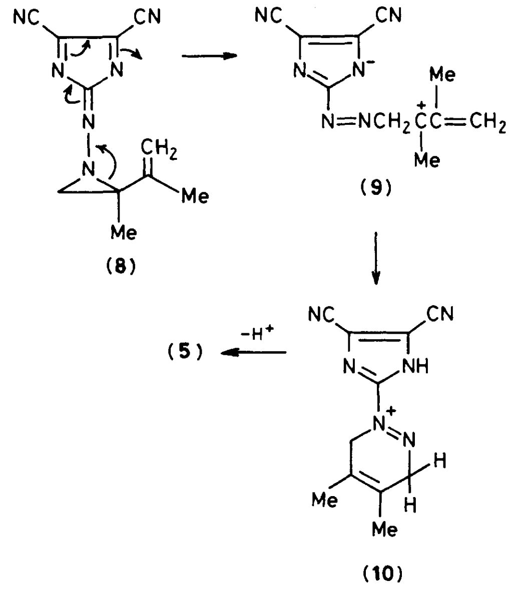
Diazoalkanes are a long known and thoroughly investigated class of 1,3-dipoles.[1,2] The diazo group possesses two mutually perpendicular π-systems. One of these (π_z) is delocalized over the entire π framework and, like the allyl anion, contains four electrons. The other π system (*i.e.* π_y) is localized on the two nitrogen atoms, each of which provides an electron. The terminal nitrogen atom also bears a lone pair of electrons which is sp hybridized. The nitrene character of the diazo group, like a carbene, is derived from the mutually perpendicular frontier molecular orbitals which are energetically accessible and possess sizeable eigenvectors at the atomic centre. For the nitrene type of 1,1-cycloaddition to proceed effectively, it is necessary for the diazo group to possess a high-lying occupied π_z orbital with a sizeable coefficient on N-1. The nitrene form of a diazo compound could become quite important if the attached R group is π-donating and σ-withdrawing. MO calculations at the 4-31G level indicate that a phenyl group fulfils these requirements whereas hydrogen, alkyl, or π-electron withdrawing groups do not.‡ In fact, the 1,1-cycloaddition reaction has recently been reported for a series of phenyl substituted β,γ-unsaturated diazoalkenes.[3,4] 2-Diazo-4,5-dicyanoimidazole (**1**)[5] may represent another example of a system where 1,1-cycloaddition could occur since the dicyanoimidazole ring is a strong electron acceptor while the ring nitrogen lone pairs may donate electrons into the diazo π_y system. Here we report on studies of the cycloaddition behaviour of the diazoimidazole (**1**).

Treatment of 1,1-dimethoxyethylene with (**1**) in benzene at 25 °C resulted in a clean reaction to give the dimethyl acetal (**2**), m.p. 192—193 °C, in 82% yield. The structure of (**2**) was suggested by the molecular ion at *m/z* 232 and by characteristic resonances [δ 2.90 (s, 6H) and 6.61 (s, 1H)] in its mass and ^{1}H n.m.r. spectra, respectively. This assignment was further supported by the acid hydrolysis of (**2**) to methyl glyoxylate (*Z*)-2-[(4,5-dicyanoimidazol-2-yl)hydrazone] (**3**), m.p. 199—200 °C; ^{1}H n.m.r. (CD$_3$CN, 90 MHz) δ 3.81 (s, 3H) and 7.30 (s, 1H). Thermolysis of (**2**) in benzene at 150 °C for 11 h gave 4-methoxyimidazo[2,1-*c*]-*as*-triazine-6,7-dicarbonitrile (**4**) in 85% yield, m.p. 218—219 °C; ^{1}H n.m.r. (CD$_3$CN, 90 MHz) δ 4.02 (s, 3H) and 7.72 (s, 1H).









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‡ *Ab initio* calculations at the 4-31G level were carried out by Dr. T. Fukunaga (DuPont Co.) using the program Gamess and standard geometries.

Compound (**1**) also reacted with 2,3-dimethylbutadiene in benzene at 25 °C in a clean cycloaddition without elimination of nitrogen to give 2-[4,5-dimethyl-(6*H*)-pyridazin-1-yl]imidazole-4,5-dicarbonitrile (**5**) in 90% yield, m.p. 235—236 °C; ^{1}H n.m.r. {[$^2H_6$]Me_2SO, 90 MHz} δ 1.70 (s, 6H), 4.21 (m, 2H), and 6.92 (s, 1H).

The products obtained from the above reactions are different from those obtained from other diazo compounds. It is very likely that the cycloadditions proceed by a mechanism similar to that proposed for phenyl substituted β,γ-unsaturated diazoalkenes.[3,4] Thus, attack of the terminal nitrogen atom of (**1**) on the π-system of dimethoxyethylene affords a transient aziridine (**6**) which undergoes a subsequent ring opening reaction [to (**7**)] followed by a hydrogen atom transfer. An analogous mechanism nicely accounts for the formation of (**5**) from the reaction of (**1**) with 2,3-dimethylbutadiene [*via* (**8**)—(**10**)]. Although the experimental results are consistent with a 1,1-cycloaddition process, it should be noted that attack of the terminal nitrogen atom on the olefinic double bond may occur in a stepwise manner.

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