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SYNTHESIS OF A MESOIONIC IMIDAZOLE SYSTEM AND STUDIES OF ITS PARTICIPATION IN 1:3 DIPOLAR CYCLOADDITION REACTIONS

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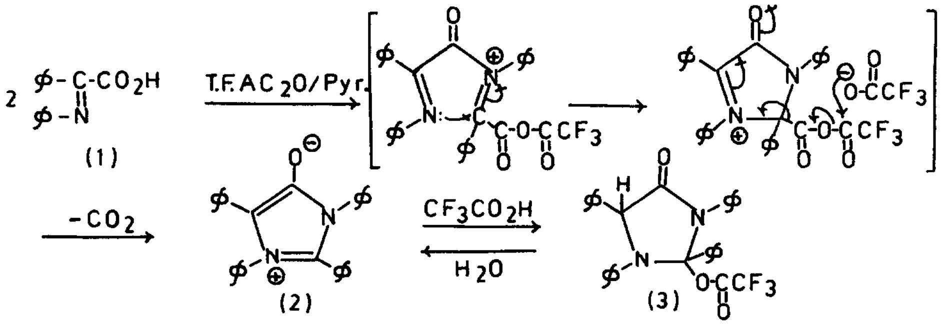
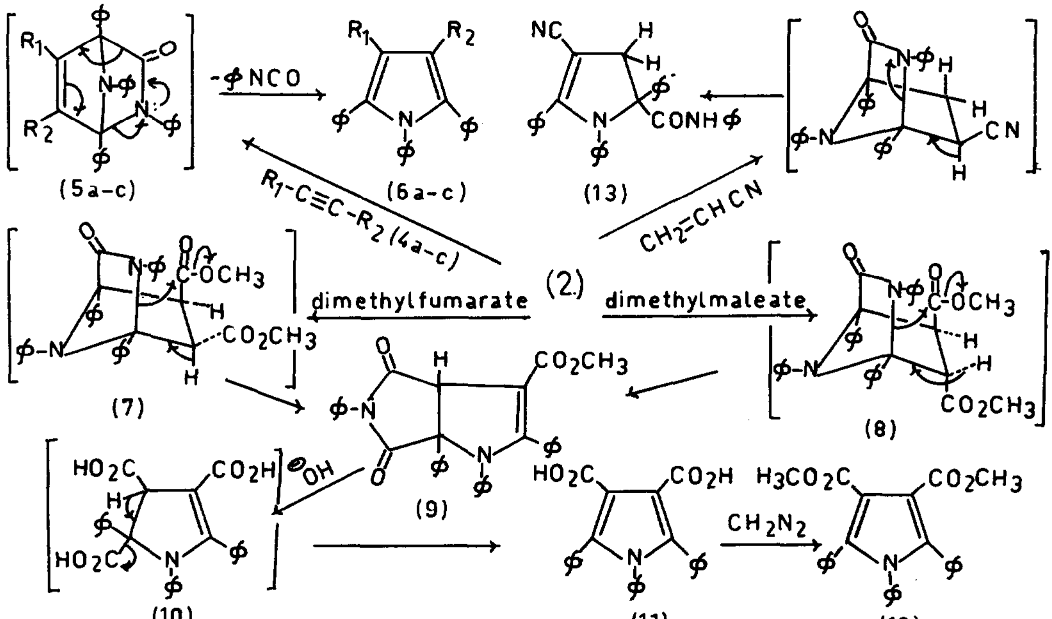
The monocyclic mesoionic imidazole system has previously been described only as its 5-acyl derivatives.[1,2] These were found to be unreactive towards dipolarophiles due to the internal stabilization of the system through resonance participation with the acyl carbonyl function.[3] We now wish to report the synthesis of the mesoionic 5-phenyl imidazole system (2) and its 1:3 dipolar cycloaddition reactions with various dipolarophiles. Treatment of benzoylformic acid-anil (1)[4,5] with trifluoroacetic anhydride in dry pyridine at 0°C results in dimerization and evolution of carbondioxide leading to the formation of (2), isolated as its trifluoroacetate derivative (3), m.p. 150°C. The latter on treatment with water undergoes hydrolysis and yields the more stable, mesoionic system (2) as bright yellow microcrystalline powder, m.p. 167-68°C (decomp.). λ_{max}^{EtOH} 358 nm (ϵ, 11,800). IR ($CHCl_3$): 1630 cm^{-1}. The compound (2) was found to be weakly basic and forms acid salts, which, however, dissociate readily to the parent compound on contact with water.



The 1:3 dipolar cycloaddition reactions of (2) have been studied with various alkynes and alkenes. Thus, treatment with alkynes (4a: $R_1=R_2=CO_2CH_3$; 4b: $R_1=H$, $R_2=CO_2C_2H_5$ and 4c: $R_1=H$, $R_2=C_6H_5$) in refluxing benzene for 12 hr

affords the corresponding pyrrole derivatives (6a–c) as white crystalline solids in almost quantitative yields. The reaction is presumed to proceed through the bicyclic adduct (5a–c) followed by the extrusion of the elements of phenyl isocyanate. Treatment of (2) with either dimethyl fumarate or maleate in refluxing xylene for 48 hr gave the same product (9) as white crystalline solid, m.p. 228°C. Its formation can be rationalized as a β-elimination of the initially formed adducts (7 or 8) followed by recyclization. Hydrolysis of (9) with refluxing 15% potassium hydroxide water dioxane solution, furnished the dicarboxylic acid (11), m.p. 248°C. The corresponding dimethyl ester (12) melted at 198°C. This transformation may be envisaged as proceeding through the initially formed tricarboxylic acid (10) followed by loss of formic acid, to the more stable pyrrole system (11).[6] Similar treatment of (2) with acrylonitrile gave the dihydropyrrole system (13), m.p. 123°C, directly. All the products have been fully characterized on the basis of analytical and spectral data.



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