A Novel Heterocyclic Rearrangement: Extrusion of Carbon Dioxide from Non-adjacent Carbonyl Groups

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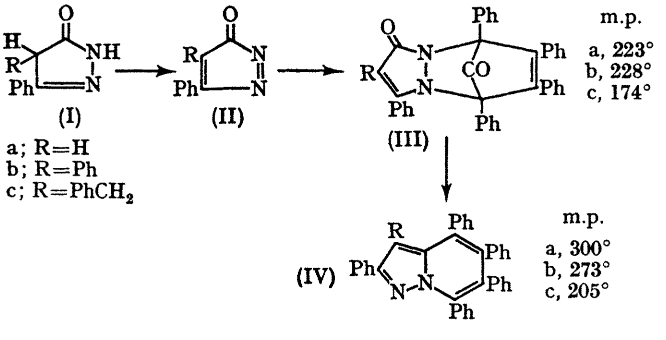
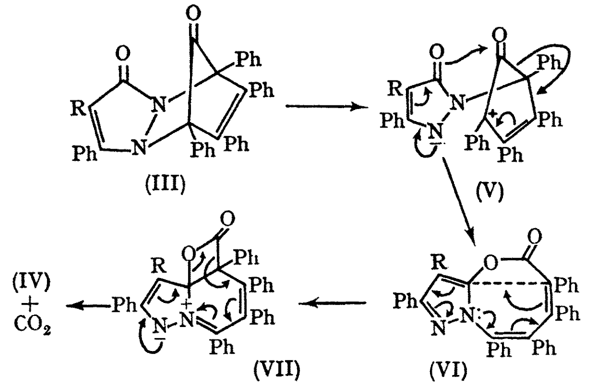
Summary Thermolysis of 1,4-carbonopyrazolo[1,2-*a*]-pyridazin-6-ones to pyrazolo[1,5-*a*]pyridines, which is paralleled in the mass spectrometer, is a new, unusual rearrangement involving the elimination of carbon dioxide from two non-adjacent carbonyl groups.

OXIDATION of 4-substituted-3-phenylpyrazolin-5-ones (I) with lead tetra-acetate in methylene chloride containing tetraphenylcyclopentadienone gave good yields of the Diels–Alder adducts (III) of the unstable pyrazolones (II). Similar adducts have recently been made in the same way with various cyclic and acyclic dienes.[1] The mass spectra of the adducts (III) all showed a strong molecular ion and a strong $M - 44$ peak for the loss of carbon dioxide, in spite of the two oxygen atoms in the molecule being well separated. Similar loss of carbon dioxide under electron impact from molecules with non-adjacent carbonyl groups appears to be rare, but has been reported for *N*-substituted phthalimides,[2] and the photodimers of 1,4-naphthaquinone.[3]



However, with the adducts (III) this extrusion of carbon dioxide also occurred on quite mild thermolysis. When they were heated at 210°/1 mm. for 16 hr., carbon dioxide was evolved and the pyrazolo[1,5-*a*]pyridines (IV) were formed in 30—45% yield. Their structures were based on analytical and spectral data and the striking chemical inertness of the hexaphenyl derivative (IVb). The u.v. spectrum was very similar to that of the 2-phenyl derivative,[4] and the lone hydrogen in (IVa), which appeared as a singlet in the n.m.r. spectrum at τ 3·3, was readily replaced by bromine to give the monobromo-derivative, m.p. 302°. The pyrazolopyridine (IVb) was also formed (45%) from (IIIb) in 1,2,4-trichlorobenzene at 220° for 4 hr. Attempts to decarbonylate (IIIb) in milder thermal conditions, or by photolysis, only slowed down the rate of "decarboxylation".

A mechanism for this unusual rearrangement is outlined. Heterolytic N–C bond fission (the first part of a stepwise retro-Diels–Alder reaction) would give the stabilised zwitterion (V), in which nucleophilic attack by the pyrazolone oxygen of the other carbonyl group is possible.



Subsequent ring opening would give the lactone (VI). This can now lose carbon dioxide by, first, the extended pericyclic process shown [arrows in (VI)] facilitated by the terminal nucleophilic and electrophilic nitrogen atoms, followed by the reverse process [arrows in (VII)] in which, by extrusion of carbon dioxide, the very stable aromatic system (IV) is formed.

The other major product in each of the above thermolyses was tetraphenylcyclopentadienone (35—40%), the stable product of the normal retro-Diels–Alder reaction; this could, of course, also have been formed from the zwitterion (V).

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