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DIAZAARYNES: 3,4- AND 4,5-DIDEHYDROPYRIDAZINE BY ELECTRON IMPACT AND THERMOLYTIC FRAGMENTATION OF THE CORRESPONDING DICARBOXYLIC ANHYDRIDES

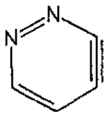
Francesco De Sio,* Stefano Chimichi, and Rodolfo Nesi
Centro di Studio del CNR sulla Chimica e la Struttura dei Composti Eterociclici e loro Applicazioni, presso l'Istituto di Chimica Organica dell'Università, Via Gino Capponi 9, 50121 Firenze, Italy

Lucia Cecchi
Istituto di Chimica Farmaceutica, Università di Firenze, Via Gino Capponi 9, 50121 Firenze, Italy

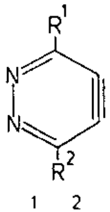
Abstract- The new hetarynes (1) and (2) have been advanced as intermediates in the vapour phase both for the electron impact and the pyrolytic fragmentation pattern of pyridazine-3,4- and 4,5-dicarboxylic acid anhydrides (10) and (11), respectively. The presence of a peak at m/e 78 in the mass spectra of these compounds, as well as the formation of the diazanaphthalenes (12) and (13), respectively, from their thermolysis in benzene, appeared to support this proposal.

After the discovery of the first hetarynes at the beginning of the sixties[1], only more recently the intermediacy of the didehydropyridazine derivatives (3)[2-4] and (4)[5] was unambiguosly substantiated[6].

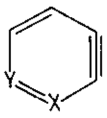
However, to our knowledge, no experimental data have been ever reported for the parent didehydropyridazines (1) and (2) although, according to EHT (Extended Hückel Theory) calculations[7], they should be more stable than the widely investigated monoaza analogues 2,3- and 3,4-didehydropyridines (5) and (6).



(1)

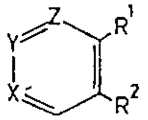


(2) $R^1 = R^2 = H$
(3) $R^1 = R^2 = Ph$
(4) $R^1 = CH_2OMe, R^2 = Me$

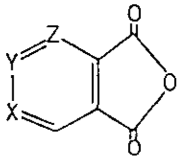


(5) X=N, Y=CH
(6) X= $\dot{C}$H, Y=N

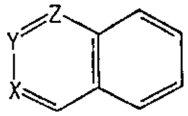
Recent attempts to synthesize pyridazine-5-diazonium-4-carboxylate (7), a potential precursor of (2), were unsuccessful[8]. On the other hand it has been shown that several aromatic and heterocyclic dicarboxylic anhydrides could be advantageously employed for generating arynes and hetarynes, respectively[9-11]. On these grounds the pyridazine dicarboxylic anhydrides (10) and (11), easily available from the corresponding acids (8) and (9)[12], appeared very attractive and, in order to ascertain the potential of these products as sources of the new intermediates (1) and (2) in the gas phase, we investigated their mass spectral and pyrolytic behaviour; the preliminary results of such a study are reported herein.



(7) $X=Y=N, Z=CH, R^1=CO_2^-, R^2=N_2^+$
(8) $X=CH, Y=Z=N, R^1=R^2=CO_2H$
(9) $X=Y=N, Z=CH, R^1=R^2=CO_2H$



(10) $X=CH, Y=Z=N$
(11) $X=Y=N, Z=CH$



(12) $X=CH, Y=Z=N$
(13) $X=Y=N, Z=CH$

Likewise for pyrazine-2,3-dicarboxylic anhydride[13], both the spectra of compounds (10) and (11) clearly showed, beside peaks at m/e 150 (M) and 106 ($M-CO_2$), a signal at m/e 78 ($M-CO_2$ and CO) attributable to a species having the composition of 3,4- and 4,5-didehydropyridazine molecular ion, respectively. However, whereas this signal represented the base peak in the spectrum of the anhydride (10), it exhibited in the fragmentation pattern of (11) a relative abundance of only 7% with respect to the predominant peak at m/e 50, corresponding to butadiyne[14].

This remarkable difference led us to argue that, at least under electron impact, 3,4-didehydropyridazine (1) appeared more stable than the 4,5-isomer (2); according to a feature previously emphasized for the diphenyl derivative (3)[2,3], the intermediate (2) could easily give rise to a subsequent fragmentation by a highly favourable extrusion of molecular nitrogen.

In the hope of confirming the intermediacy of the hetarynes (1) and (2) in the gas phase, we tried to duplicate the above fragmentations thermally. Accordingly, 0.01 molar solutions of compounds (10) and (11) in benzene were pyrolyzed at 700°C through a Pursil silica tube packed with silica powder (40-60 mesh), under dry nitrogen (30-40 mmHg pressure) at a steady rate of 25 ml/h. The pyrolysates recovered from three traps cooled between 0° and -10°C, were carefully analysed by gas chromatography [10% Apiezon L or 3% OV 17 on Anachrom-Q (80-100 mesh) columns, flame ionization and nitrogen detectors]; beside products coming from benzene pyrolysis [biphenyl as the largely predominant component (96-97%) and naphthalene (0.5-0.7%)], cinnoline (ca. 1%) and phthalazine (ca. 0.3%) were also detected, respectively, on the basis of the retention times of authentic samples[15].

These results were regarded as a good indication for the occurrence of the title intermediates since the formation of the heterocyclic ring systems (12) and (13) from (10) and (11), respectively, could be easily accounted for through a 1,4-addition of the diazaarynes (1) and (2) with benzene, followed by rearomatization.

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14. The mass spectra were determined with a Perkin-Elmer 270 mass spectrometer and samples were introduced by direct inlet probe at 70°C. Operating conditions: ion accelerating voltage 2.5 kV, electron energy 70 eV, and ion source temperature 110°C.
15. Other unidentified compounds were also present in small amounts.

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