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PARTICIPATION OF CONCERTED N_2 - ELIMINATION IN THE PHOTOLYSIS OF 1 - PYRAZOLINES

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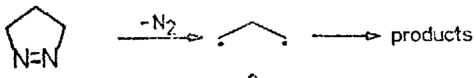
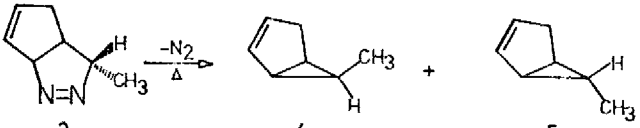
1-Pyrazolines undergo thermal and photochemical decomposition presumably *via* the intermediacy of biradicals, whose detailed structure is still a matter of discussion [1]. If both C—N-bonds in 1 are broken simultaneously, we obtain a nitrogen free intermediate, which could be either a conventional diradical or assume the structure of a 0,0-diradical [2].



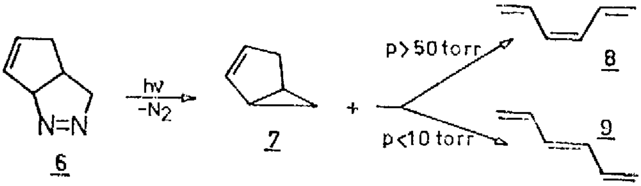
1 2

Earlier we studied a series of bicyclic 1-pyrazolines which, because of their rigidity, could not readily achieve the geometry of a 0,0-diradical. The gas phase thermolysis of exo-4-methyl-2,3-diazabicyclo[3.3.0]octa-2,7-diene 3 produces only the exo- and endo-6-methylbicyclo[3.1.0]hex-2-enes 5 and 4. No open chain or other rearrangement products were observed [3].



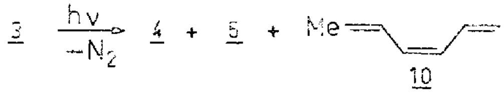
3 4 5

We have now undertaken a study of the photochemistry of these compounds. Monochromatic irradiation ($n \rightarrow \pi^*$ transition at 328 nm, 450 W xenon lamp, Bausch&Lomb high intensity grating monochromator) of a hexane solution of the unsubstituted compound 6 did not only yield the expected bicyclo[3.1.0]hex-2-ene 7, but additionally 8 — 10 % (Z)-1,3,5-hexatriene 8, the yield being temperature independent between - 60 and 30°C. No (E)-1,3,5-hexatriene 9 was observed under these conditions. 8 was identified by comparison with an authentic sample [4].

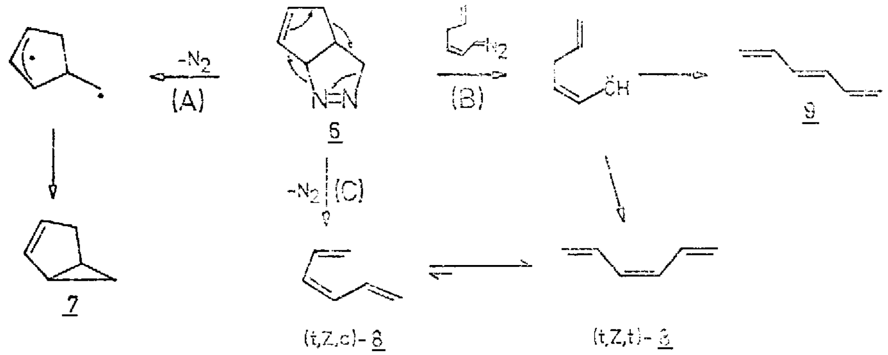


6 7 8 9

The gas phase photolysis of 6, however, is pressure dependent. At inert gas (N_2) pressures between 50 and 760 torr in addition to 7 only 8, which can be clearly identified by its gas phase UV-spectrum[5], is observed. At low pressures ($p < 10$ torr), however, only 9 is produced. It is reasonable to assume that in this case primarily formed 8 is deactivating its excess vibrational energy *via* isomerisation to 9, in contrast to the collisional deactivation at higher pressures or in solution. In similar gas phase and solution experiments we found the photolysis behaviour of 3 to be identical to that of 1: the λ_{max} - dependence on gas pressure is the same and in solution we could detect only one isomer[6] 10 in 8-10% yield in addition to 4 and 5. The position of the methyl group is still uncertain.



The stereospecific formation of the (Z)-1,3,5-hexatrienes 8 and 10 in the photochemical decomposition of 6 and 3 cannot be explained by the intermediacy of a 1,3-diradical (A) alone and must be derived either *via* a retro-1,3-dipolar cycloaddition (B)[7] or *via* a concerted N_2 elimination (C). In order to test for possible carbene intermediates, all irradiation experiments were also carried out in solutions of methanol, *cis*- and *trans*-2-butene and tetramethylethene. No measurable changes in the production of 1,3,5-trienes were observed under those conditions. Moreover the reactions are strictly stereospecific and no stereochemical scrambling is occurring. This would support the participation of pathway (C) which would to our knowledge be the first example of an electrocyclic N_2 elimination in the decomposition of 1-pyrazolines. A detailed study with a series of 1-pyrazolines is in progress.



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