

MATRIX ISOLATION AND IR SPECTROSCOPIC STUDY OF THE PYROLYSIS PRODUCTS OF
2-METHYL-3,4-DIAZAPENTA-1,3-DIENE. CLEAVAGE OF N=N-BOND IN UNSATURATED AZO
COMPOUNDS

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Abstract: Under very low-pressure pyrolysis (VLPP) conditions the decomposition of 2-methyl-3,4-diazapenta-1,3-diene proceeds via: (a) homolytic cleavage of C-N-bonds with the formation of methyl and 1-methylvinyl radicals (1); (b) cleavage of double N=N-bond with the formation of N-methyl methyleneimine (3) and acetonitrile. A mechanism involving decomposition of the intermediate 1,4-diazacyclobutene has been suggested for (b).

Azo alkanes are believed to be good starting compounds for thermal and photochemical generation of alkyl radicals:



Recently it has been ascertained that reaction (1) proceeds in two steps, i. e. elimination of nitrogen is preceded by the formation of diazenyl radical¹ $R-N=N^\circ$. With a view to obtain the earlier unknown IR spectrum of 1-methylvinyl radical (1), the decomposition products of 2-methyl-3,4-diazapenta-1,3-diene (2)²⁻⁴ were studied using the matrix isolation technique. A typical spectrum is shown in the figure. The reaction was carried out between 775 and 1175 K and at 10^{-2} - 10^{-3} Torr. Matrix gas (argon or nitrogen) was used in amounts exceeding 500 times than 2. For experimental details see ref. 5.

The pyrolysis products of 2 were not found to be the result of mere reaction⁶ (1). Even at pyrolysis temperatures below 850 K, besides the absorption band of the methyl radical (614 cm^{-1})⁷ and the absorption bands tentatively assigned to 1-methylvinyl radical (856 , 1342 , and 1614 cm^{-1}) we ob-

served the absorption bands of other products, viz.: N-methyl methyleneimine (3) (482, 952, 1030, 1224, 1402, 1475, and 1662 cm^{-1}) and acetonitrile (1041 and 2265 cm^{-1}). The latter was identified by the matrix IR spectrum of an authentic sample. Unlike other absorption bands, those of acetonitrile were reproduced when the pyrolysis products were evaporated and re-condensed on the target. The correctness of assigning frequencies to 3 was confirmed by their good agreement with the matrix IR spectrum of N-methyl methyleneimine⁸.

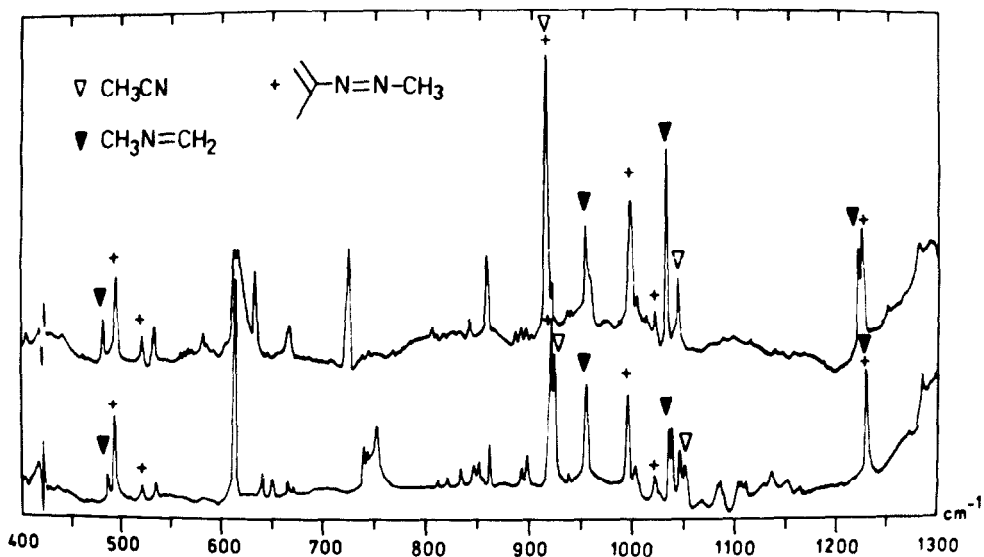
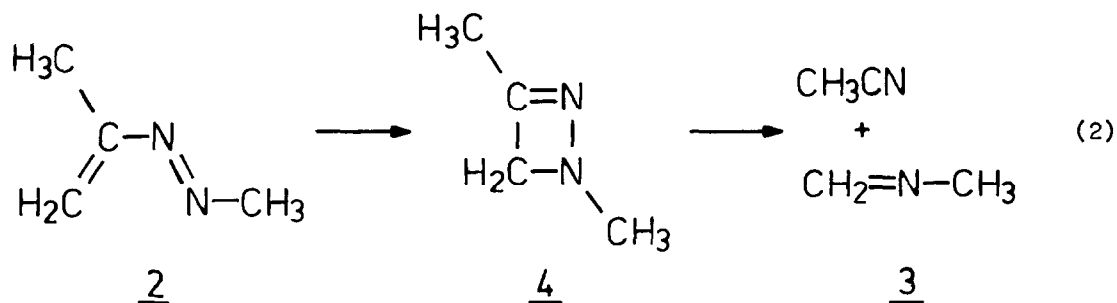


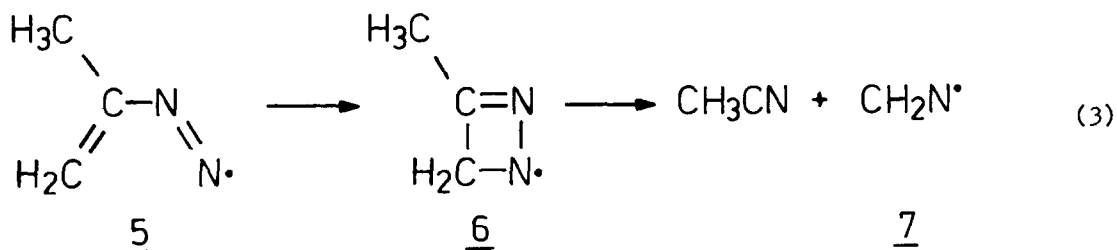
Figure. Matrix isolation IR spectra of VLPP products of 2-methyl-3,4-diazapenta-1,3-diene produced at 823 K and $5 \cdot 10^{-3}$ Torr (the lower spectrum - 10 K, N_2 matrix; the upper spectrum - 10 K, Ar matrix).

Between 775 and 930 K the selectivity of formation⁹ of 3 and CH_3CN was about 50. At higher temperatures, homolytic cleavage of C-N-bonds dominated. However, the secondary reaction products: allene (846 cm^{-1}), propyne (632, 3330 cm^{-1}), methane (1310 cm^{-1}), ethane (826 cm^{-1}), propene (582, 913, 937, and 996 cm^{-1}), and a small amount of isobutene (892 cm^{-1}) appeared. Thus, our results show that in pyrolysis of 2 the reaction (1) is accompanied by a process that yields CH_3CN and 3. We believe that the latter products are produced by decomposition of 1,4-diazacyclobutene (4) which is the transient cyclization product of 2:

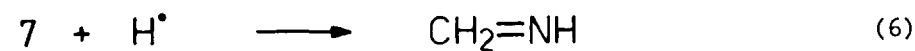
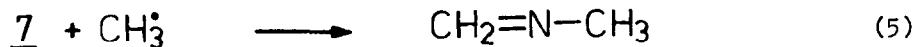
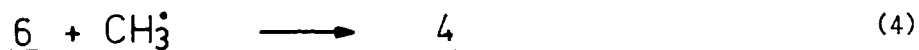


An analogous reaction mechanism has been suggested for the formation of HCN and N,N-dimethyl-N'-phenylformamidine in the thermal decomposition of 5,5-dimethyl-1-phenyl-1,2,5-triazapentadiene¹⁰. It is supported also by the products of thermal decomposition of condensed 1,4-diazacyclobutenes¹¹. Under the pyrolysis conditions 4 immediately decomposes yielding CH₃CN and 3, both being thermally more stable than 4. For this reason 4 does not reach the target and cannot be isolated in the nitrogen or argon matrix at 10 K.

We failed to detect the reaction products that would have pointed towards cyclization of the diazenyl radical¹² (5):



At low pressure the contribution of the bimolecular reaction (4) cannot be significant. For similar reasons the bimolecular reactions (5) and (6) cannot proceed.



Indeed, neither the $\text{H}_2\text{C}=\text{NH}$ - recombination product (reaction (6)) - nor HCN, which would have formed by unimolecular decomposition of radical 7 in reaction (7), were noticed. Therefore, the diazenyl radical 5, if it participates at all in the process, is not responsible for the formation of 3 and CH_3CN . With regard to the methyldiazenyl radical $\text{CH}_3-\text{N}=\text{N}^\circ$, its ease of decomposing to N_2 and CH_3 at these pyrolysis temperatures does not permit observation by the matrix IR spectroscopy method¹³.

References and Notes

- † Deceased.
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 6. Absorption bands of 2 are 494, 520, 914, 996, 1020, 1219, 1372, 1436, 1450, 1530, and 1648 cm^{-1} (Ar matrix, 10 K).
 7. In parentheses are shown typical absorption bands (Ar matrix) which are distinct from the absorption bands of other products.
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 12. An alternative mechanism suggested by the reviewer of *Tetrahedron Letters*.
 13. Analogously, due to decomposition, it is not possible to detect the absorption bands of $\text{C}_3\text{H}_7^\circ$ produced by pyrolysis.

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