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COMPETITIVE DIRADICAL AND DIAZOALKANE FORMATION IN THE THERMOLYSIS AND PHOTOLYSIS OF THE AZOALKANE 7,7,8-TRIMETHYL-2,3-DIAZATRICYCLO[4.2.1.$0^{4,8}$]NON-2-ENE

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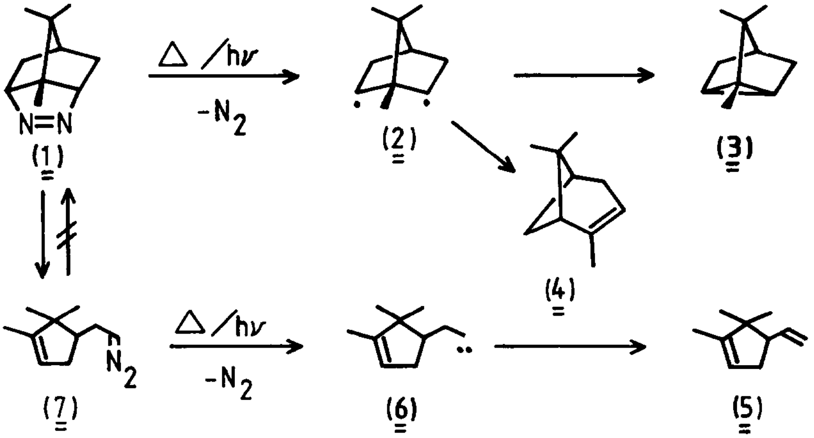
SUMMARY: On laser photolysis of azoalkane 1 at elevated temperature, besides the expected denitrogenation into the tricyclane 3 via 1,3-diradical 2, the diazoalkane 7 is directly observed, denitrogenating into vinylcyclopentene 5.

The bicyclo[2.2.1]heptane-2,6-diyl diradical 2, in principle accessible via denitrogenation of the azoalkane 1 [1], would be expected to generate a variety of products (Eq. 1), of which



(Eq. 1)

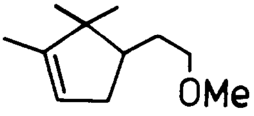
the tricyclane 3, α-pinene (4) and the vinylcyclopentene 5 are likely ones. For example, analogous to the 5,6-benzobicyclo[2.2.2]oct-5-ene-2,7-diyl diradical [2], ring closure of 2 would afford 3, while migration of the C_1-C_7 bond to either radical site would lead to α-pinene (4). Alternatively, the 1,3-diradical 2 could suffer fragmentation into the carbene 6, which on 1,2-shift of hydrogen would produce the vinylcyclopentene 5. However, such a process is more likely to be observed in 185-nm photolyses.[3] Since 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) cycloaddition to α-pinene (4) gave the urazole precursor to the azoalkane 1, the latter was prepared and its denitrogenation investigated in order to explore the chemical transformations of the 1,3-diradical 2.[4,5]

The results of the thermal and photochemical denitrogenations are collected in Table I. These data show that varying amounts of the tricyclane 3 and the vinylcyclopentene 5 are formed, but in all cases α-pinene (4) is lacking.[5] Its thermal and photochemical stability under the reaction conditions was confirmed through control experiments.

Vacuum flash pyrolysis (VFP) required very high temperatures (Entry 1, Table I) in view of the high thermal stability of azoalkane 1. The tricyclane 3 was formed essentially exclusively in this thermal denitrogenation, since only traces of 5 could be detected by capillary GC. Similarly, the triplet sensitized denitrogenation with benzophenone (Entry 2, Table I) gave exclusively tricyclane 3. This implies that if the 1,3-diradical 2 intervenes as product precursor, both its singlet state (thermal) and its triplet state (benzophenone-sensitized) suffer only cyclization.

The product composition was, however, considerably more complex in the direct photolysis of azoalkane 1 (Entries 3 - 6, Table I). Depending on the solvent and temperature, variable amounts of tricyclane 3 and vinylcyclopentene 5 were produced. For example, in THF at -78°C (Entry 4, Table I) only 3 was formed, while in THF at 60°C (Entry 6, Table I) ca. 70% of 3 and 30% of 5 were produced. Clearly, the relative yield of 5 increased with increasing temperature. This temperature dependent product branching point required an additional intermediate in the direct photolysis of azoalkane 1.

Since photo-cleavage of azoalkanes into diazoalkanes is a precedented process[6,7], we suspected that diazoalkane 7 was a viable intermediate in the photolysis of azoalkane 1, which would lead to the vinylcyclopentene 5 via carbene 6 on denitrogenation. For this reason the experiments with methanol (Entry 7, Table I), acetic acid (Entry 8) and methyl acrylate (Entry 9) were conducted. Indeed, on photolysis of 1 in methanol the amount of vinylcyclopentene product 5 was reduced (cf. Entries 6 and 7, Table I); but more important, ca. 4% of ether 8 was detected by capillary GC (comparison with authentic material). With acetic acid (Entry 8, Table I) the trapping was still more efficient since 19% of acetate 9 was detected by capillary GC. But since the ether 8 and acetate 9 are also trapping products of the carbene 6 [8], the experiment with methyl acrylate (Entry 9, Table II) was carried out in the hope that 1,3-dipolar cycloaddition products such as the pyrazoline 10 (or its tautomers) would be formed, thereby providing definitive proof that the diazoalkane 7 intervened. In the presence of methyl acrylate no vinylcyclopentene 5 was formed in the photolysis of azoalkane 1; however, although GC-MS analysis suggested that trapping products such as 10 were formed, a full characterization was not possible because of the complex product mixture.



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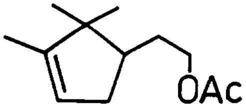

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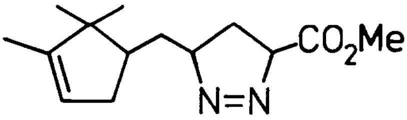

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In view of this difficulty, authentic diazoalkane 7 was prepared analogous to standard synthetic methods.[7] It is an extremely unstable material (loses nitrogen even at room temperature), which exhibits a characteristic diazo band at 2060 cm^{-1} and a yellow color with λ_{max} = 462 nm. Indeed, thermal as well as photochemical denitrogenation affords the vinylcyclopentene 5, but no tricyclane 3. It is also of interest to mention that diazoalkane 7 does not cyclize into azoalkane 1. In the presence of methanol and acetic acid the ether 8 and acetate 9 were produced as expected. However, in the presence of methyl acrylate a complex, intractable product mixture was formed, quite similar to that observed in the photolysis of azoalkane **1** and methyl acrylate (Entry 9, Table I).

A definitive answer on this mechanistic problem could be provided by means of laser photolysis of azoalkane **1**, using a Coherent 18W Argon Ion Laser. On irradiation of a 0.10 *M* solution of **1** in benzene at room temperature, after 8 min the colorless solution turned yellow, which on prolonged irradiation turned colorless again. IR and UV analysis of the yellow solution confirmed that the transient species was the photolabile diazoalkane **7**.[9] The mechanistic scheme in Eq. 1 explains most effectively the experimental results described herein on the thermal and photochemical denitrogenation of azoalkane **1**.[10]

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9. It was possible, albeit difficult, to generate barely detectable amounts of the transient diazoalkane color by irradiation either in the Rayonet Photoreactor or with a 1000-W Hanovia lamp, coupled to a monochromator. In fact, laser photolysis of azoalkane **1** constitutes the most convenient preparation of diazoalkane **7**.
10. Preliminary results show that on laser photolysis the azoalkanes **11** - **14** also give transient diazoalkanes and we are elucidating these in detail.

TABLE I: Product Distribution of the Denitrogenation of Azoalkane 1.

Denitrogenation Conditions	Products (%)^{a} (1)	(3)	(5)	Product Balance (%)^{b}
1. VFP (450°C at 18 Torr)	0	100	trace	100
2. hν (300 nm, pentane; Ph_2CO; 30°C)^{c}	7	100	0	100
3. hν (350 nm; C_6H_6; 30°C)^{d,e}	0	81	19	100
4. hν (350 nm; THF; -78°C)^{d,f}	88	100	0	91
5. hν (350 nm; THF; 0°C)^{d,f}	83	94	6	100
6. hν (350 nm; THF; 65°C)^{d,f}	47	74	26	100
7. hν (350 nm; MeOH; 65°C)^{d,g}	39	88	12	100^{h}
8. hν (350 nm; C_6H_6; HOAc; 70°C)^{d,i}	24	89	11	100^{j}
9. hν (350 nm; C_6H_6; MA; 65°C)^{d,k}	1	100	0	100^{l}

a) Determined by capillary GC on a 50-m OV-101 column, operated at injector, column and detector temperatures of 200, 100-180 and 200°C, respectively, and a nitrogen pressure of 0.7 kg/cm^2; product yields are within 10% of the stated values; products 3 and 5 are normalized to 100%.

b) Sum of absolute yields of 1, 3 and 5; remainder are unidentified products, unless specified.

c) [1] = 0.011 M; [$Ph_2C{=}O$] = 0.19 M; Rayonet Photoreactor.

d) Rayonet Photoreactor.

e) [1] = 0.0074 M.

f) [1] ∿ 0.01 M.

g) [1] = 0.014 M.

h) Includes 4% ether 8.

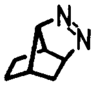
i) [1] = 0.014 M; [HOAc] = 0.35 M.

j) Includes 19% acetate 9.

k) [1] = 0.012 M; [MA] = 1.2 M; MA = methyl acrylate.

l) Includes ca. 37% isomeric products with long retention times; MS shows that these products contain nitrogen and the acrylate moiety.


(11)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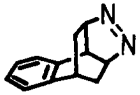
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