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PREPARATIVE UV-LASER PHOTOCHEMISTRY OF THE AZOALKANE SPIRO(2,3-DIAZABICYCLO-[2.2.1]HEPT-2-ENE-7',1-CYCLOPROPANE):
TRAPPING OF THE 1,4-DIRADICAL 2-(3-CYCLOPENTENYL)ETHYL BY MOLECULAR OXYGEN

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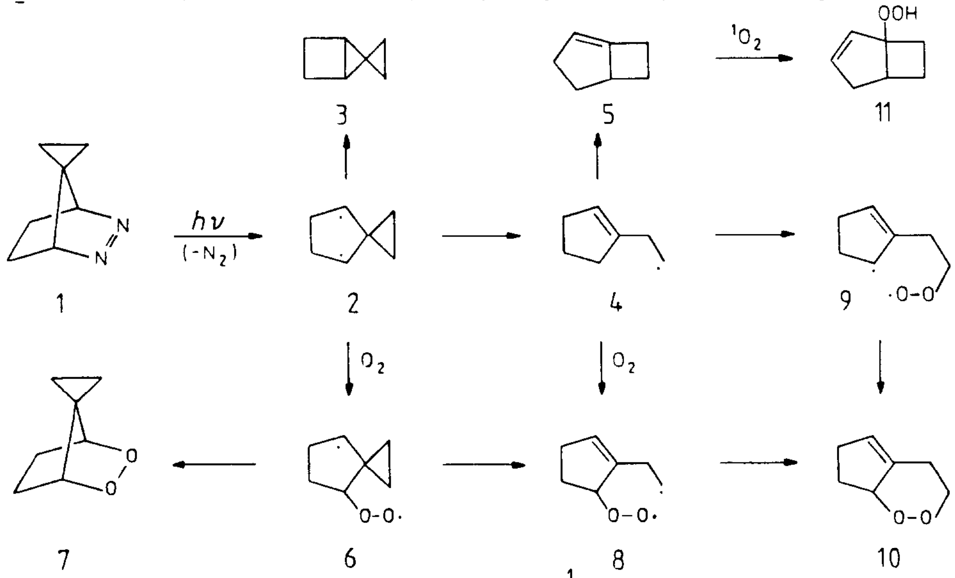
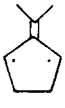
SUMMARY: Photo-extrusion of nitrogen from the azoalkane 1 in the presence of molecular oxygen gave besides the hydrocarbons 3 and 5, the endoperoxide 10 and hydroperoxide 11, the former via trapping of the 1,4-diradical 4 by triplet oxygen, the latter by ene-reaction of hydrocarbon 5 with singlet oxygen.

The photolysis of the azoalkane 1 affords the two hydrocarbons spiro(bicyclo[2.1.0]pentane-5',1-cyclopropane) (3) and bicyclo[3.2.0]hept-1-ene (5), postulated to be derived from the 1,3-diradical spiro[2.4]hepta-4,7-diyl (2) and the 1,4-diradical 2-(3-cyclopentenyl)ethyl (4), respectively, as illustrated in Eq.1.[1] Direct photolysis gave predominantly the cyclization product 3, while benzophenone-sensitized photolysis gave mainly the rearranged product 5. To rationalize this spin state selectivity, it was argued[1] that in its singlet state the 1,3-diradical 2 preferred cyclization into 3, but in its triplet state ring-opening to the 1,4-diradical 4 predominated, followed by cyclization into 5. Stereolabeling experiments of the cyclopropane ring in azoalkane 1 showed that the intervention of the 1,4-diradical 4 was plausible.



The recent success of trapping 1,3-diradicals 12 - 14[2,3] and 1,4-diradicals 15 - 17[4] by molecular oxygen to form of the corresponding peroxides encouraged us to apply this useful

12



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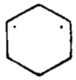

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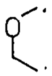

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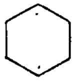

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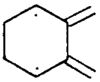

17

diradical probe in the photolysis of azoalkane 1. The spirocyclopropane moiety in diradical 2 was particularly interesting and significant in that the built-in cyclopropylcarbinyl "free radical clock"[5] provided us with a means of estimating lifetime limits of the transient species of the photolysis of azoalkane 1. We anticipated that the triplet 1,3-diradical 2 would ring-open faster to the triplet 1,4-diradical 4 than being trapped with triplet oxygen to form endoperoxide 7, but that oxygen trapping of the 1,4-diradical 4 would give the 1,2-dioxane 10 faster than cyclization into the hydrocarbon 5. The need of monochromicity at high intensities for the triplet sensitization and the expected short lifetimes of the diradical intermediates, especially the spiro[2.4]hepta-4,7-diyl (2), dictated making use of laser photochemistry at elevated oxygen pressure[4a] to optimize diradical trapping.

Irradiation of a $CFCl_3$ solution of azoalkane 1 (0.1 M) and benzophenone (0.13 M), contained in a Griffin-Worden tube under a 10 atm pressure of oxygen gas, was carried out at -20°C with the 363.7-nm line (ca. 1 Watt intensity) of a Coherent Supergraphite Model CR-18 argon ion laser for 3 h. TLC (silica gel, CH_2Cl_2) monitoring revealed the presence of two peroxides, spotted by means of the ferrous thiocyanate spray.[6] Silica gel chromatography at -20°C and eluting with CH_2Cl_2 gave 8% of a mixture of hydrocarbons 3 and 5, 30% unreacted azoalkane 1, the 1,2-dioxane 10[7] and the hydroperoxide 11[8], in 21% and 32% yields, respectively. Structural assignment of these peroxides rested on positive peroxide test, elemental composition and spectra data, particularly the characteristic ^{13}C- and ^{1}H-NMR spectra. The latter were exceedingly complex, but with the help of decoupling and computer simulation the observed spectra were consistent with the proposed structures. In addition, the hydroperoxide 11 could be independently prepared in 74% yield by tetraphenylporphine-sensitized photooxygenation of hydrocarbon 5 in CH_2Cl_2 at -20°C.

Control experiments revealed that not even traces of the endoperoxide 7 could be detected in the laser photolysis mixture of azoalkane 1. For this purpose authentic endoperoxide 7 was prepared by photooxygenation and diimide reduction.[9] Under the benzophenone-sensitized conditions the hydrocarbon 5 was converted to the hydroperoxide 11, but in the dark the hydrocarbon 5 was stable towards triplet oxygen. Thus, the hydroperoxide 11 was the product of the ene-reaction of hydrocarbon 5 with *in situ* singlet oxygen that was generated via quenching of benzophenone triplets by oxygen.[10]

The *bona fide* oxygen trapping product in the laser photolysis of azoalkane 1 was the 1,2-dioxane 10. The hydroperoxide 11 was a secondary product, derived from singlet oxygenation of of hydrocarbon 5. Since in the laser photolysis ca. 32% hydroperoxide 11 and ca. 8% hydrocarbons 3 and 5 were formed, the effective yield of the latter is ca. 40%. Thus, the 1,4-diradical 4 predominantly cyclizes to hydrocarbon 5, but oxygen trapping is competitive since substantial amounts (ca. 21%) of 1,2-dioxane 10 were isolated. Since no endoperoxide 7 could be detected, the 1,3-diradical **2** must be significantly shorter lived (about 10- to 100-fold) than the 1,4-diradical **4**. Trapping of diradicals by oxygen is essentially diffusion controlled, within the confines of spin statistics as evidenced by the measured bimolecular rate constant k= 2.4×10^{9} m^{-1}sec^{-1}.[11] Thus, under the trapping conditions employed here, the lifetime (τ) of the 1,4-diradical **4** must be at least 1 nsec and consequently that of the 1,3-diradical **2** less than 0.1 nsec, possibly as short as 0.01 nsec.

Of the two possible trapping routes **4** → **8** → **10** and **4** → **9** → **10** (Eq.1) clearly the latter is preferred in view of the allylic stabilization in the 1,6-diradical **9**, which is absent in the 1,6-diradical **8**. However, the latter could in principle arise via the path **2** → **6** → **8**. In view of the fact that the rate constant of the cyclopropylcarbinyl rearrangement is only 2.0×10^{8} sec^{-1},[5] the ring-opening of the 1,5-diradical **6** is much too slow compared to oxygen trapping and cyclization. We should have detected endoperoxide **7** under the conditions employed here. Thus, the **2** → **6** → **8** → **10** route cannot be important because the 1,3-diradical **2** is too short-lived on account of its facile ring-opening to the 1,4-diradical **4**. The gain in allylic stabilization and the release in cyclopropane strain must be responsible for the very fast (ca. 10^{11} sec^{-1}) ring-opening **2** → **4**.

The present investigation demonstrates that diradical trapping by molecular oxygen under laser photolysis conditions provides a powerful mechanistic tool for characterizing such elusive intermediates and estimating their lifetimes. Particularly advantageous for this purpose is the monochromatic and intense light output of the argon ion laser[12], optimal requisites for generating and trapping diradical intermediates.

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≠ Undergraduate research participant during spring 1983.

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7. Endoperoxide **10**, colorless liquid, b.p. 100°C/14 Torr (Kugelrohr).-
   IR (CCl_4): 3050, 2950, 2920, 2870, 1460, 1440, 1435, 1355, 1040, 1010 cm^{-1}.-
   ^1H-NMR ($CDCl_3$), 400 MHz: δ = 1.49 - 1.59 (m, $J_{1,9'}$= 6.4, $J_{8,9'}$= 10.1, $J_{8',9'}$= 6.7, $J_{9,9'}$= 13.4 Hz; 1H, 9'-H), 2.21 - 2.30 (m, $J_{1,9}$ = 7.9, $J_{8,9}$ = 1.8, $J_{8',9}$ = 8.1 Hz; 1H, 9-H), 2.30 - 2.46 (m, $J_{1,8}$ = 2, $J_{1,8'}$= 1.8, $J_{5,8}$ = 2.5, $J_{5,8'}\sim$ 3, $J_{7,8}$ = 2.3, $J_{7,8'}$= 2.3, $J_{8,8'}$= 13.5 Hz; 2H, 8-H and 8'-H), 2.48 - 2.53 (m, $J_{1,5'}$= 0.6, $J_{4,5'}$= 1.0, $J_{4',5'}$= 3.0, $J_{5,5'}$= 13.5, $J_{7,5'}$= 0.4 Hz; 1H, 5'-H), 2.60 - 2.70 (m, $J_{4,5}$ = 6.1, $J_{4',5}$ = 12.2, $J_{7,5}$ = 1.8 Hz; 1H, 5-H), 4.07 - 4.21 (m, $J_{4,4'}$= 12.2 Hz; 2H, 4-H and 4'-H), 5.12 - 5.17 (m; 1H, 1-H), 5.59 - 5.63 (m, $J_{1,7}$ = 0.8 Hz; 1H, 7-H).-
   ^{13}C-NMR ($CDCl_3$), 100.6 MHz: δ = 27.3 (t), 27.6 (t), 29.2 (t), 72.9 (t), 88.4 (d), 125.2 (d), 136.9 (s).-
   MS (70 eV): m/e = 126 (6%, M^+), 108 (20%), 97 (46%), 80 (20%), 79 (100%), 77 (66%), 41 (44%).-
   $C_7H_{10}O_2$ (126.12): Calcd. C 66.64 H 7.99
   Found C 66.69 H 7.96

8. Hydroperoxide **11**, colorless liquid, b.p. 20°/0.1 Torr (Kugelrohr).-
   IR (CCl_4): 3590, 3110, 3040, 2990, 2960, 2890, 1445, 1370, 1330, 1250 cm^{-1}.-
   ^1H-NMR ($CDCl_3$), 400 MHz: δ = 1.09 - 1.19 (m, $J_{6,6'}$= 12.1, $J_{6',7'}\sim$ 10, $J_{6',7}$ = 9.7, $J_{5,6'}$= 5.4, $J_{4,6'}$= 0.4, $J_{2,6'}$= 0.4 Hz; 1H, 6'-H), 2.00 - 2.18 (m, $J_{7,7'}\sim$ 12, $J_{6,7}$ $\sim$ 9, $J_{6,7'}\sim$ 9.5 Hz; 3H, 4'-H, 6-H and 7'-H), 2.35 - 2.45 (m, $J_{4,7}$ = 1, $J_{5,7}$ = 0.4 Hz; 1H, 7-H), 2.61 - 2.71 (m, $J_{4,4'}$= 17.0, $J_{4,5}$ = 6.9, $J_{3,4}$ = 1.8, $J_{2,4}$ = 2.7 Hz; 1H, 4-H), 2.79 - 2.89 (m, $J_{4',5}$ = 0.6, $J_{5,6}\sim$ 9, $J_{3,5}$ = 0.9, $J_{2,5}$ = 0.7 Hz; 1H, 5-H), 5.71 - 5.75 (m, $J_{2,3}$ = 5.5, $J_{2,4'}$= 1.8 Hz; 1H, 2-H), 6.11 - 6.15 (m, $J_{3,4'}$= 2.5 Hz; 1H, 3-H), 7.87 (br.s, 1H, -OOH).-
   ^{13}C-NMR ($CDCl_3$), 100.6 MHz: δ = 20.1 (t), 30.4 (t), 39.6 (t), 39.5 (d), 96.5 (s), 130.0 (d), 137.9 (d).-
   MS (70 eV): m/e = 126 (1%, M^+), 110 (22%), 82 (95%), 79 (55%), 68 (45%), 54 (47%), 39 (100%).-
   $C_7H_{10}O_2$ (126.16): Calcd. C 66.64 H 7.99
   Found C 66.50 H 8.18

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11. Gisin, M.; Rommel, E.; Wirz, J.; Burnett, M. N.; Pagni, R. M. *J. Am. Chem. Soc.* 1979, **101**, 2216; private communication from Professor J. Wirz (University of Basel) related to us by Professor R. M. Wilson (University of Cincinnati).
12. An attempt of such trapping experiments in the case of azoalkane **1**, using a Rayonet photoreactor or 1000-W Xenon lamp with appropriate filter, provided inconclusive results.

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