

REARRANGEMENTS OF FREE RADICALS IX ¹⁾ THERMAL AND PHOTOCHEMICAL ISOMERIZATIONS OF BICYCLO(3.2.0)HEPTENYL RADICALS

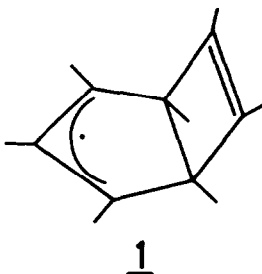
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Summary Bicyclo(3.2.0)heptenyl radicals rearrange in matrix to cyclopentadienyl and cyclohexadienyl radicals.

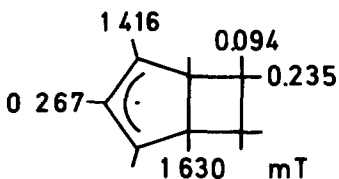
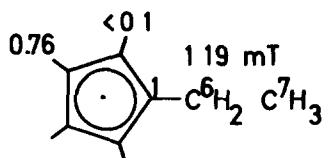
Rearrangements of free radicals in solution can be observed if they can compete successfully with termination reactions. Therefore most of the reported isomerizations require low free energies of activation ²⁾. The investigation of free radicals in an adamantane matrix ³⁾ which prevents combination and disproportionation reactions allows the observation of processes with higher activation barriers.

Bicyclo(3.2.0)heptadienyl radical (1) undergoes an electrocyclic ring opening to tropylium radical ⁴⁾. In order to see whether the formation of the resonance stabilized tropylium system enables the disrotatory ring opening we



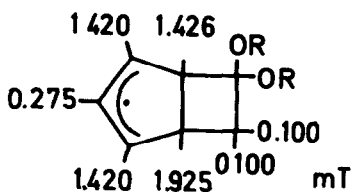
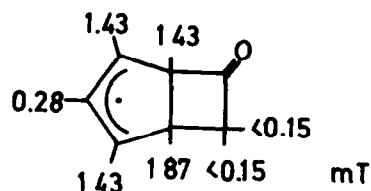
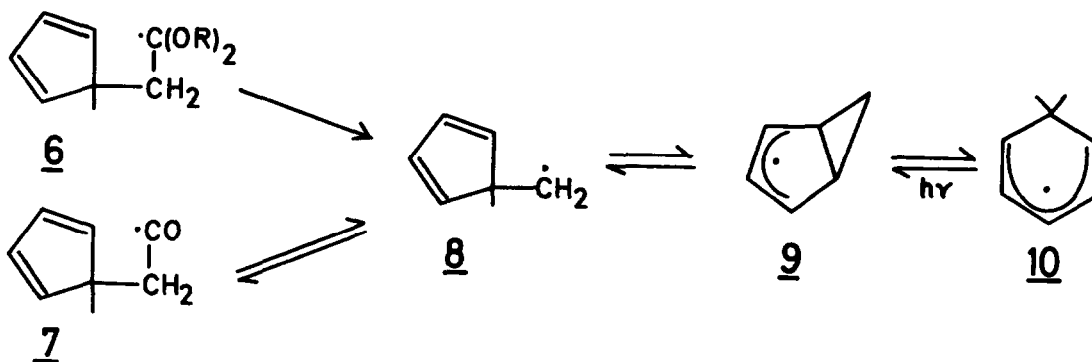
investigated the bicyclo(3.2.0)heptenyl radical (2). Ring opening of the central bond would lead to cycloheptadienyl radical.

X-ray irradiation (W-Anode, 125 kV, 20 mA, 3.4 mA/kg) of an adamantane matrix doped with bicyclo(3.2.0)hept-2-en at a temperature of -196°C gave 2. Its ESR-spectrum could be simulated with the parameters which were obtained from the solution spectrum (photolysis of di-tert-butyl peroxide in presence of bicyclo(3.2.0)hept-2-en, cyclopropane as solvent at -128°C). By comparison with bicyclo(3.1.0)hexenyl radical ⁵⁾ we assign the allylic coupling constants and

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attribute the coupling constant of 0.235 mT to the exo protons of the four membered ring. This is in accord with the W-arrangement of the p-orbital at C-2 and the exo C-H bond. All other assignments follow from symmetry and multiplicity. The ESR-spectrum of 2 in adamantane matrix can be observed up to +10°C. At this temperature a new spectrum begins to appear which finally replaces that of 2 completely. It consists of nine broad lines and can be interpreted with two coupling constants (mT): $a_1 = 0.76$ (2H) and $a_2 = 1.19$ (2H). The spectrum is attributed to ethyl cyclopentadienyl radical 3. INDO calculations assuming a regular pentagon for cyclopentadienyl (bond length 140 pm) and a conformation of the ethyl group in which the five membered ring is perpendicular to the plane formed by C-1, C-6 and C-7 support this assignment. The calculated couplings are $a_{H-2} = a_{H-5} = 0.114$ mT, $a_{H-3} = a_{H-4} = -0.712$ mT and $a_{H-6} = 0.875$ mT. Due to the line width in matrix the splitting of protons H-2 and H-5 can not be resolved. Recently ethyl cyclopentadienyl radical has been detected in solution ⁶). A discrepancy in coupling is found for the methylene protons (1.582 mT in solution). A difference of this kind for coupling constants in solution and adamantane matrix had been observed before for conformationally non rigid radicals ⁷). As a result of our investigation we conclude that the radical 2 prefers the cleavage of an exocyclic bond followed by a 1,3-hydrogen shift. Similar results were obtained in a study of the bicyclo(3.2.0)hept-2-yl radical in solution ⁸).

Radicals 4 and 5 were generated by x-ray irradiation in adamantane matrix from 6,6-diethoxy bicyclo(3.2.0)hept-2-en and from bicyclo(3.2.0)hept-2-en-6-on respectively. 4 could also be obtained by hydrogen abstraction with tert-butoxy-radicals in solution. The coupling constants in formula 4 are those from the solution spectrum whereas the couplings in formula 5 were deduced from the matrix spectrum. In both cases the assignment of the bridgehead protons couplings is arbitrary. 4 and 5 undergo rearrangements above 0°C to cyclohexadienyl radical (10). Its spectrum can be recognized easily by the large methylene coupling constant. Rationalisation of the results leads to intermediate radicals 6 and 7

4 R = C₂H₅5

formed by cleavage of an exocyclic cyclobutane bond. Loss of carbon monoxide or diethoxycarbene respectively gives 8 which in turn rearranges to bicyclo(3.1.0)hexenyl radical (9). This undergoes ring opening to cyclohexadienyl radical (10). Whereas decarbonylation of acyl radicals is a known process fragmentation of a radical with formation of a carbene has not been observed so far. An interconversion 8 \rightleftharpoons 9 has been established earlier for the endo-exo isomerization of 6-substituted bicyclo(3.1.0)hexenyl radicals ¹⁾.

Due to their transient nature photochemical reactions of reactive free radicals can not be detected in solution. In adamantane matrix however we were able to induce photochemical transformations. Thus cyclohexadienyl radical yields under UV illumination bicyclo(3.1.0)hexenyl radical (9) ⁹⁾. This also seems to happen with 10 when it was obtained from 5. However a thermal process follows by which 5 is formed again. Thus after UV-illumination of 10 in matrix at low temperatures (-70°C) we observed the ESR-spectrum of 5 again. This is interpreted in terms of reversible attachment of carbon monoxide to 8 and sub-

sequent ring closure to 5. Obviously carbon monoxide can not escape from the cage in the matrix. Prolonged illumination of 5 at low temperatures (-70°C) gives still another radical as is shown by the appearance of a strong singlet ($g = 2.0012$). The structure of this radical is still under investigation.

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