

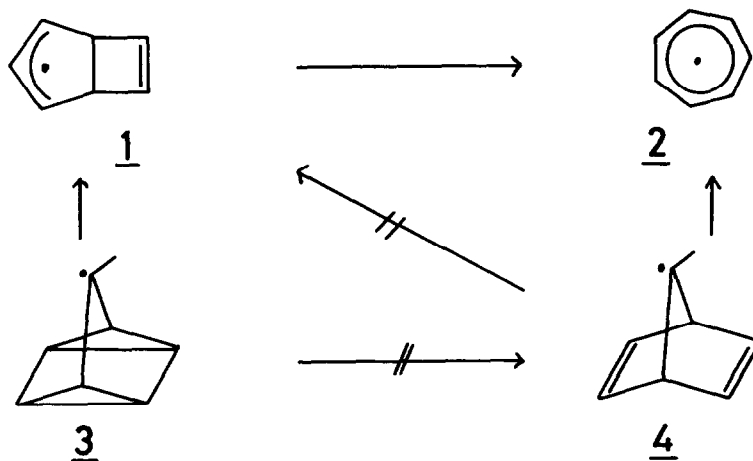
REARRANGEMENTS OF FREE RADICALS X¹⁾: C₇H₇ - RADICALS AND RELATED SYSTEMS

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Summary 7-Norbornadienyl radical rearranges in matrix to tropylium radical. Deuterated and cyano substituted bicyclo(3.2.0)heptadienyl radicals do not undergo 1.2-vinyl shifts prior to electrocyclic ring opening.

Under conditions of long lifetime in adamantane matrix we observed some time ago²⁾ the rearrangement of bicyclo(3.2.0)heptadienyl radical (1) to tropylium radical (2). Two other members on the C₇H₇-hypersurface are 3-quadracyclanyl radical (3) and 7-norbornadienyl radical (4). Both 3 and 4 have been observed in solution recently^{3,4)}. 3 undergoes even at very low temperatures in solution a rearrangement to 1. As a cyclopropyl carbinyl radical it behaves similar to



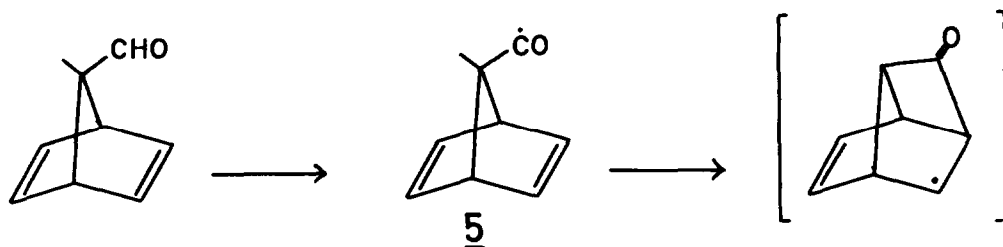
tetracyclo(3.3.0.0^{2,6}.0^{4,8})oct-7-yl radical, for which we had found an isomerization to bicyclo(3.2.1)octadienyl-2.5 radical at -145°C⁵⁾. No transformation of 3 to 4 does take place in solution even though this might be possible by two consecutive cyclopropyl carbinyl - homo allyl rearrangements. This seems to indicate that 4 is less stable than 3 which in turn is less stable than 1. Investigations of rearrangement reactions of free radicals in solution are hampered by the competition with low activation energy processes like combination and

disproportionation. We therefore undertook a study of 3 and 4 under conditions of long lifetime in adamantane matrix.

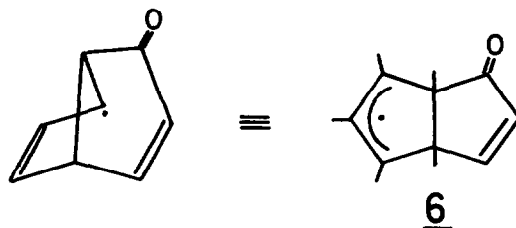
X-ray irradiation (W-anode, 125 kV, 20 mA, 3.4 mA/kg) of quadricyclane in adamantane matrix at $+10^{\circ}\text{C}$ gives as expected from Kawamura's result ³⁾ directly the ESR-spectrum of 1. A similar x-ray irradiation of norbornadiene in adamantane matrix does not give any of the radicals 1-4. Instead an intense ESR-spectrum is recorded which can be interpreted in terms of the following coupling constants (mT): $a_1=2.04$ (2H), $a_2=1.42$ (2H) and $a_3=0.30$ (1H). The structure of this radical is still under investigation. Formation of radicals by x-ray irradiation of compounds having only C-H bonds of similar energy or having double bonds is sometimes not very selective. Several radicals may be formed by H-abstraction or H-addition. A more selective way for radical formation can be envisaged by introducing a substituent carrying a distinctly weaker C-H bond. Such a substituent is the formyl group. We tested the feasibility of this group as a radical precursor by x-ray irradiating 3-formyl quadricyclane ⁶⁾ at room temperature in adamantane matrix. As anticipated the acyl radical is formed and loses immediately carbon monoxide. The resulting 3 rearranges to 1.

As a result of x-ray irradiation of 7-formyl norbornadiene in adamantane matrix at -196°C we obtained below -30°C an ESR-spectrum which consisted of a single line with g -value 2.0002. Above -30°C this line disappeared while a new spectrum emerged which can be interpreted in terms of the coupling constants (mT): $a_1=0.28$ (1H), $a_2=1.425$ (2H), $a_3=1.91$ (1H) and $a_4=2.19$ (1H). The g -value of the primary radical proves it to be an acyl radical (5), the coupling constants of 1.425 and 0.28 mT of the secondary radical disclose its allylic nature (6) and its relation to some of our other bicyclic radicals ¹⁾. We interpret the results in terms of Scheme I. The assignment of the coupling constants of 1.91 mT (1H) and 2.19 mT (1H) to either proton 1 or 5 in 6 or vice versa has not been proven. Instead of losing carbon monoxide to give 4 the radical 5 adds intramolecularly to a double bond. This difficulty to split off carbon monoxide may be taken as further indication for the instability of 4.

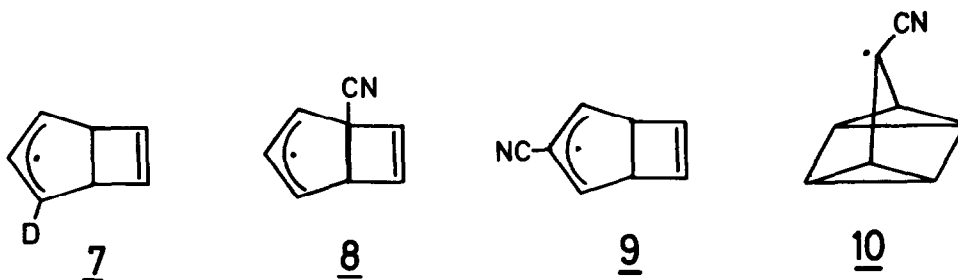
Using halogen compounds one can generate radicals by x-ray irradiation through dissociative electron capture ⁷⁾. 7-Chloronorbornadiene in adamantane matrix was subjected to two kinds of x-rays (W-anode and Be-anode). Only after irradiation at room temperature with the softer x-rays from the Be-anode we obtained an ESR-spectrum. Besides some unresolved lines of an unknown radical one recognized the typical pattern of the tropylium radical 2. Thus under the conditions of formation 4 rearranges to 2. The transformation does not proceed by way of 1 as an intermediate because 1 would have been stable at room temperature. While there is no detectable equilibrium between 1 and 4 the 7-norbornadienyl radical might be a high energy intermediate or transition state in a rearrangement in which the C-atoms of the five membered ring in 1 equilibrate. Successive 1,2-vinyl shifts in the corresponding cation where the equilibrium



Scheme 1



is in favor of 7-norbornadienyl system lead to such an equilibration ⁸⁾. To test this in the radical case we prepared d-labeled 7. In adamantane matrix however no scrambling of deuterium is found. Formation of deuterated tropylium radical shows that the electrocyclic ring opening requires less energy of activation than the 1.2-vinyl shift.



In order to see whether substituents might affect an equilibrium between 1 through 4 we prepared cyano substituted analogs 8 - 10. The radical stabilizing power of a cyano group ^{9,10)} could lead to a shift in the position of equilibrium. 1-cyano-bicyclo(3.2.0)hepta-3,6-diene was obtained by photochemical ring contraction of 1-cyano-cycloheptatriene-2,4,6 ¹¹⁾. 3-cyano-quadracyclane was prepared from quadracyclanone by reaction with tosylmethylisocyanide ¹²⁾. X-ray irradiation of 3-cyano-quadracyclane in adamantane at -60°C gives 9. Thus cyano stabilization does not stabilize 10 sufficiently to prevent its isomerization at low temperatures. X-ray irradiation of 1-cyano-bicyclo(3.2.0)hepta-3,6-diene in adamantane leads to 8. If 1.2-vinyl shifts would occur in the cyano substituted radicals 8 and 9 would be interconverted. However no such transformation takes place. The process of lowest energy of activation for both 8 and 9 is ring opening to cyano tropylium radical. We therefore conclude that a radical stabilizing group like cyano neither does change the order of stability nor does it enable a

1.2-vinyl shift in these systems.

While we found that cyclohexadienyl radical cyclizes to bicyclo(3.1.0)hexenyl radical photochemically ¹³⁾ tropylium radical can not be induced to cyclize to 1 by light (high pressure Hg-light). However 1 transforms photolytically to 2 at temperatures where the thermal ring opening can not be observed yet.

Acknowledgement: This work was supported by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie. We thank Prof. W. Dittrich, Institut für Strahlenbiologie, Universität Münster, and Prof. C. Streffer, Institut für Strahlenbiologie, Universität Essen für the possibility to carry out the x-ray irradiations.

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(Received in Germany 7 November 1979)