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Rearrangements of Free Radicals, XI[1]

Sigmatropic and Electrocyclic Reactions of Bicyclo[3.2.0]heptadienyl Radicals, 3-Quadricyclanyl Radicals, and 7-Norbornadienyl Radical

Reiner Sustmann, Dieter Brandes, Fritz Lange,* and *Ursula Nüchter*

Institut für Organische Chemie der Universität Essen,
D-4300 Essen 1, Postfach 103764

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The rearrangement of matrix-isolated organic radicals with bicyclo[3.2.0]heptadienyl structure (**2**, **5**, **11a,b**), 3-quadricyclanyl structure (**16**, **26**, **27**), and of 7-norbornadienyl radical **15** is studied. Final rearrangement products are radicals with tropylium structure. **16**, **26**, and **27** isomerize to radicals with bicyclo[3.2.0]heptadienyl skeleton before electrocyclic ring opening to tropylium radicals takes place. 7-Norbornadienyl radical **15** is the least stable radical on the C_7-hypersurface. Sigmatropic 1,2-vinyl shifts in bicyclo[3.2.0]heptadienyl radicals could not be observed. Substituents do not influence the rearrangement behaviour.

Umlagerungen von Freien Radikalen, XI[1]

Sigmatrope und elektrocyclische Reaktionen von Bicyclo[3.2.0]heptadienyl-Radikalen, 3-Quadricyclanyl-Radikalen und des 7-Norbornadienyl-Radikals

Die Umlagerung matrixisolierter organischer Radikale mit Bicyclo[3.2.0]heptadienyl-Struktur (**2**, **5**, **11a,b**), 3-Quadricyclanyl-Gerüst (**16**, **26**, **27**) und von 7-Norbornadienyl-Radikal **15** wurde untersucht. Alle Systeme führen letztlich zu Radikalen mit Tropylium-Struktur. **16**, **26** und **27** isomerisieren zunächst in Radikale mit Bicyclo[3.2.0]heptadienyl-Gerüst, bevor Tropylium-Radikale gebildet werden. 7-Norbornadienyl-Radikal **15** ist der instabilste Vertreter auf der C_7-Hyperfläche. Sigmatrope 1,2-Vinylverschiebungen von Radikalen mit Bicyclo[3.2.0]heptadienyl-Gerüst wurden nicht beobachtet. Substituenten ändern die relativen Stabilitäten der Radikale nicht.

Free radical rearrangements of bicyclic model systems under conditions of long life time have been the subject of several electron spin resonance investigations and a part of the work presented here has been published in preliminary form[1–3]. The purpose of studying rearrangements of matrix isolated free radicals is to demonstrate that sofar unknown radical reactions can take place with activation energies similar to reactions of comparable ionic species. Eventually this may lead to the application of such reactions in the synthesis of complex organic molecules.

In solution bicyclo[3.2.0]hepta-2,6-diene (**1**) is converted by hydrogen abstraction of an allylic hydrogen atom with photolytically generated *tert*-butoxy radicals to bicyclo[3.2.0]heptadienyl radical (**2**). Its ESR spectrum can be interpreted in terms of four different coupling constants. Due to the molecular symmetry hy-

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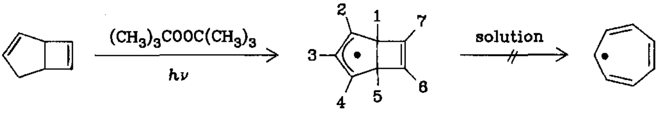
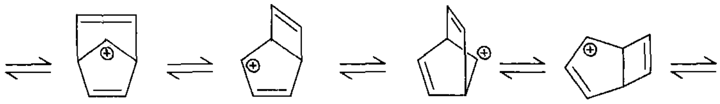
drogen atoms 1,5, 2,4, and 6,7 show equivalent hyperfine splitting constants. The assignment of the coupling constants follows from a comparison with the ESR spectra of bicyclo[3.1.0]hexenyl radical[4] and cyclopentenyl radical[5] (Table 1). The spectrum could be recorded in solution between −65 and +104°C without showing any indication of a rearrangement to tropylium radical **3**. This observation does not exclude, however, the possibility of an electrocyclic ring opening, it only demonstrates that it does not take place under the conditions of short life times due to competing reactions of minimal barrier to activation like combination reactions.



1 **2** **3**

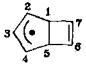
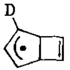
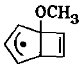
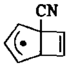
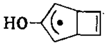
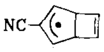
Under these circumstances the generation of free radicals in adamantane matrix by hydrogen abstraction with X-rays has proven to be a valuable tool[6,7]. If an adamantane matrix with **1** as host is X-ray irradiated at room temperature, the spectrum of **2** is obtained. It can be simulated with the coupling parameters of the solution spectrum by increasing the line width to 0.14 mT, which is caused by the restricted mobility of **2** in the matrix. An increase in temperature above +20°C initiates changes in the spectrum. A decrease in signal intensity of **2** is followed by the appearance of eight new lines with equal spacings of 0.39 mT. This new spectrum can be assigned unambiguously to tropylium radical **3**[8]. A kinetic analysis of the unimolecular disappearance reaction of **2** gives a free enthalpy of activation of $\Delta G^{\neq} = 90.0 \pm 2.1$ kJ/mol at +50°C (Table 2). Such a $\Delta G^{\neq}$ value explains why the rearrangement was not detected in solution: As consequence of fast bimolecular termination reactions the isomerization can not compete.

The investigation of the bicyclo[3.2.0]heptadienyl system was conceived partly because the corresponding cation had been produced in superacidic medium, where it rearranged even at −120°C to 7-norbornadienyl cation[9], a more stable species on the $C_7H_7^+$-hypersurface. It also was shown that other rearrangements like 1,2-vinyl shifts occur in 7-norbornadienylcation. Even though a bicyclo[3.2.0]-heptadienyl cation could not be detected it was postulated as an intermediate in this rearrangement.



Whereas in the ionic system 7-norbornadienyl cation is thermodynamically more stable than bicyclo[3.2.0]heptadienyl cation the inverse seems to be true for the radical. This, however, does not preclude the possibility of a 1,2-vinyl shift in **2**. Suitable substitution might reveal this reaction. For this purpose [2-^{2}H]bicyclo-

Table 1. ESR parameters for radicals with bicyclo[3.2.0]heptadienyl skeleton (mT)

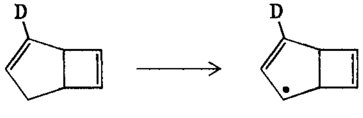
Radical		Conditions	T[°C]	$a_{1\text{-H}}$	$a_{2\text{-H}}$	$a_{3\text{-H}}$	$a_{4\text{-H}}$	$a_{5\text{-H}}$	$a_{6\text{-H}}$	$a_{7\text{-H}}$	a_D	a_N	g
	**2**	neat	−65	2.000	1.414	0.275	1.416	2.000	0.175	0.175	–	–	–
	**5**	adamantane[a]	−40	1.97	–	0.265	1.41	1.97	0.175	0.175	0.216	–	2.0027
	**11a**	adamantane	−42	–	1.43	0.26	1.43	1.71	>0.15	>0.15	–	–	–
	**11b**	CFCl$_3$ adamantane[a]	−89 −48	– –	1.41 1.41	0.276 0.276	1.492 1.492	1.93 1.93	0.121 0.121	0.203 0.203	– –	– –	2.0027 –
	**28**	adamantane	+41	2.00	1.38	–	1.38	2.00	0.18	0.18	–	–	–
	**29**	adamantane	20	1.97	1.39	–	1.39	1.97	0.20	0.20	–	–	2.0028

[a] In cases, where solution spectra were obtained, matrix spectra were interpreted on the basis of solution coupling parameters with increased line width (ca. 0.15 mT).

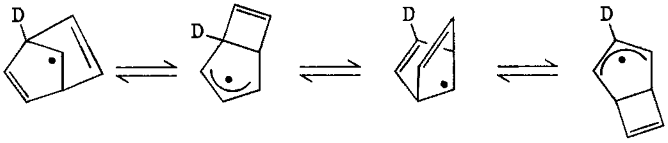
Table 2. Rate constants and free energy of activation for the rearrangement of **2**

T [K]	k [s^{-1}] [±5%]	ΔG^{+} [kJ/mol]	T [K]	k [s^{-1}] [±5%]	ΔG^{+} [kJ/mol]
312	0.00726	89.3	332	0.0367	90.7
318	0.0112	89.9	335	0.0552	90.5
323	0.0178	90.0	337	0.0679	90.4
328	0.254	90.6			

[3.2.0]hepta-2,6-diene (**4**) was synthesized by reducing bicyclo[3.2.0]hept-6-en-2-one with lithium aluminum deuteride and transforming the alcohol by xanthate pyrolysis to **4**. *X*-Ray irradiation of **4** in an adamantane matrix at −60°C leads to the ESR spectrum of **5**, observable between −50 and −10°C. Simulation of the spectrum (Table 1) was carried out with the coupling constants of the undeuterated radical by replacing one hyperfine coupling constant by the calculated deuterium coupling according to the relation $a_{\mathrm{D}} = 0.15354 \cdot a_{\mathrm{H}}$[10].



4 **5**

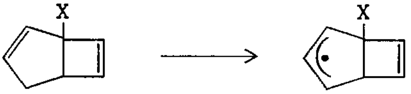


6 **7** **8** **9**

Keeping the probe at −10°C for 45 min and then raising the temperature gradually to 20°C caused initially small and then drastic changes in the center of the spectrum. The spectrum of [1-^{2}H]tropylium radical resulted. Thus **5** behaves like the undeuterated system **2**. The ESR spectrum of **5** does not show any indication of becoming a superposition of signals due to the presence of **5**, **7**, and **9** prior to ring opening. In order to be able to recognize the presence of **7** and **9** in the experimental spectrum we simulated spectra with different admixtures of radicals **7** and **9** to **5** by using the coupling constants of the undeuterated radical and replacing one hyperfine coupling constant by the deuterium hyperfine splitting. The comparison of these with the experimental spectra gave no indication of a 1,2-vinyl shift. The conclusion therefore is: electrocyclic ring opening needs less energy of activation than sigmatropic rearrangement. The activation energy for formation of 7-norbornadienyl radical, an intermediate in the vinyl shift reaction, must therefore be higher than 90.0 kJ/mol, the required energy of isomerization for **2** to **3**.

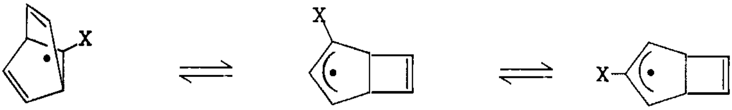
Free radicals may be stabilized by substituents and this may influence the equilibrium between isomers and the ease of their interconversion. A cyano group at a radical center shows a stabilization of 20−30 kJ/mol[11], a methoxy group of about 6 kJ/mol[12]. In order to test the effect of substituents on the equilibrium between **5**−**9** we prepared 1-methoxy- (**10a**) and 1-cyanobicyclo[3.2.0]hepta-2,6-diene (**10b**) by photocyclization of 1-substituted cycloheptatrienes. The presumption was that the substituent does not affect the stability of radicals **11** but should exert its full power in radicals **12** and a somewhat diluted effect in the delocalized radicals **13** and **14**.

Both radical precursors when *X*-ray irradiated in adamantane matrix at ca. $-50\,^\circ C$ gave at temperatures $<0\,^\circ C$ ESR spectra (hyperfine coupling constants and their assignment see Table 1). An ESR spectrum of **11b** with high resolution was also recorded, when di-*tert*-butyl peroxide was photolyzed in solution in the presence of **10b**. The matrix spectrum was successfully interpreted on the basis of the solution hyperfine splittings. Temperature increase ($>10\,^\circ C$) transformed the spectra slowly into those of the corresponding tropylium radicals[13]. As in the case of unsubstituted **2** no sign of a sigmatropic rearrangement has been observed. Thus even the strong radical stabilizing effect of a cyano group does not favour the 1,2-vinyl shift over the electrocyclic ring opening.



10a: X = OCH_3
10b: X = CN

11a: X = OCH_3
11b: X = CN

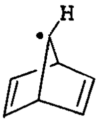


12a: X = OCH_3
12b: X = CN

13a: X = OCH_3
13b: X = CN

14a: X = OCH_3
14b: X = CN

The question, which relation exists between 7-norbornadienyl radical and the other radicals on the C_7-hypersurface can only be answered by independent generation of 7-norbornadienyl radical (**15**). In this connection we also wanted to study 3-quadricyclanyl radical (**16**) in matrix. Both **15** and **16** have been investigated in solution[14]. Whereas an ESR spectrum of **15** was obtained and analyzed, radical **16** undergoes even in solution at very low temperatures ($<-146\,^\circ C$) twice a cyclopropylcarbinyl-homoallylic rearrangement to **2**.



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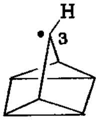
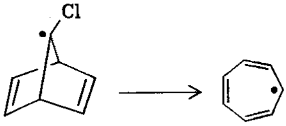


16



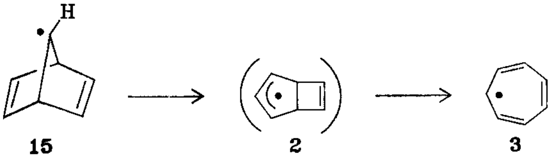
17

3

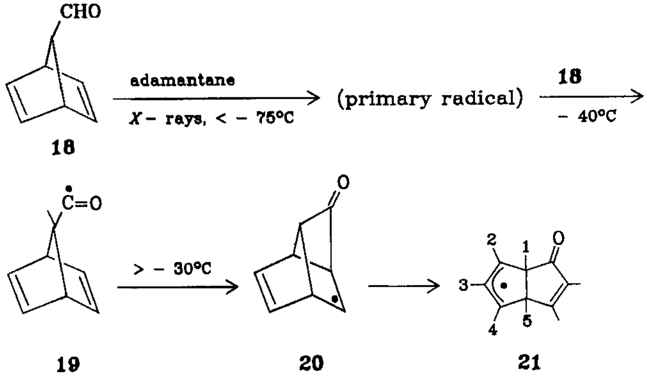
In solution **15** was prepared by the photolysis of di-*tert*-butyl peroxide in the presence of 7-bromonorbornadiene and triethylsilane. In adamantane matrix we used as precursor 7-chloronorbornadiene (**17**). Free electrons produced by *X*-ray irradiation of adamantane can add to the antibonding orbital of the C-halogen bond and may lead to dissociative electron capture[15-17]. Irradiation of an adamantane matrix of **17** with soft *X*-rays at room temperature produced an intense ESR spectrum of tropylium radical **3**. Additional signals, neither due to **2** nor to **15**, could not be interpreted.

A more selective method of radical production consists in the reaction of halogen compounds with sodium in the gas phase. If applied in combination with low temperature equipment to trap the radicals, this is an elegant way of studying free radicals by ESR spectroscopy. We used for this purpose a Displex cryogenic system attached to a high vacuum line (see experimental part). A mixture of **17** and argon was brought together with sodium vapor close to the cooled sapphire rod (20 K) of the cryogenic system. The material condensed on the cool sapphire rod and was analyzed by ESR spectroscopy. A spectrum of high signal to noise ratio of **3** was recorded proving that the primary radical **15** rearranges under the reaction conditions to **3**. As the rationalization might be that **15** is produced in a vibrationally excited state in the gas phase and therefore needs no further activation for rearrangement to **3** we attempted yet another method of preparation. A matrix of alternating layers of **17** and sodium was prepared by depositing at 20 K in turn the two reactants. This process was repeated three times. Without irradiation with UV- or visible light this matrix exhibited the ESR lines of sodium and unidentified signals of low intensity in the center of the spectrum. Photoionization of electrons from sodium at 20 K and dissociative electron capture[18], a process similar to the production and capture of electrons by *X*-rays in adamantane, may lead to the formation of free radicals. Irradiation with light >320 nm for a few seconds bleached the blue sodium matrix and generated an intense ESR spectrum of **3**. Even through the process is carried out at ca. 20 K a primary radical can not be detected. The rearrangement of a primary radical therefore must have either a very low barrier to activation or occurs via a photochemical reaction. All these experiments demonstrate that on the C_7H_7-radical hypersurface norbornadienyl radical is very unstable. It is hard to conceive a one step process for the isomerization of **15** to **3**. It seems more plausible that **2** is an intermediate.

Even though the barrier for electrocyclic ring opening of **2** to **3** requires 90 kJ/mol activation, the postulate of **2** as an intermediate in the low temperature work can be supported. It was shown that **2** photoisomerizes to **3** at temperatures where no thermal reaction takes place.



Formyl hydrogen atoms are sensitive to abstraction, yielding acyl radicals[19], which may undergo further reactions, for instance decarbonylation to an alkyl radical. This reaction sequence seemed also to be appropriate to produce 7-norbornadienyl radical **15** from norbornadiene-7-carbaldehyde (**18**). **18** was subjected in adamantane matrix to *X*-rays at −196°C. Below −100°C a poorly resolved ESR spectrum (8 mT broad) was recorded, the resolution of which improved at higher temperatures. At −40°C an additional singlet apppeared with simultaneous disappearance of the primary radical. The *g*-value of 2.0006 for this signal proves it to derive from an acyl radical[20]. Above −27°C the singlet and the primary spectrum had disappeared completely in favour of a new spectrum. In matrix the radical is stable to greater than +100°C. Its coupling constants a_1 = 0.28 mT (1H), a_2 = 1.425 mT (2H), a_3 = 1.91 mT (1H), and a_2 = 2.19 mT (1H) are in accordance with structure **21**. Particular support for this proposal is given by the comparison with the spectrum of **2** and cyclopentenyl radical[21,22]. The coupling constants a_3 and a_4 stem from the interaction of the unpaired electron with protons 1 and 5, respectively, the other two are typical for the allylic part of the radical.

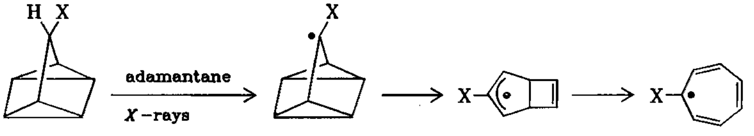


18

19 **20** **21**

The observation of poorly resolved primary radicals, if *X*-ray irradiation is carried out at liquid nitrogen temperature, is not uncommon. This is a feature of the radical producing reactions in adamantane matrix. It is assumed[23] that *X*-ray irradiation first leads to ionization of adamantane, leading after deprotonation to adamantyl radical which then reacts with the substrate to give a substrate radical and adamantane[24]. Support for this hypothesis is found in the fact that stabilized radicals, as most of our systems are, can be studied most easily. In the production sequence for a specific radical there may be additional radicals after the adamantyl radical has reacted, as seems to be the case in the above experiment. The lower the temperature, however, the greater is the anisotropy of the spectra. The concurrent line broadening makes an interpretation in these cases difficult.

Kawamura[14] reported the rearrangement of 3-quadricyclanyl radical in solution at low temperature to bicyclo[3.2.0]heptadienyl radical **2**. *X*-Ray irradiation of quadricyclane at +10°C in adamantane confirms the easy rearrangement of **16** to **2**. The only ESR signals observable are those from **2**. Similarly radical **2** was



22: X = H
23: X = CHO
24: X = OH
25: X = CN

16: X = H
26: X = OH
27: X = CN

28: X = OH
29: X = CN

30: X = OH
31: X = CN

obtained if 3-quadricyclanecarbaldehyde (**23**) was *X*-ray irradiated in adamantane matrix at room temperature. Contrary to **19**, where the acyl radical adds to the double bond of the norbornadiene system, the acyl radical from **23** looses carbon monoxide. This is plausible as no intramolecular competition reaction can take place.

Similarly to the 7-substituted norbornadienyl radicals we examined the influence of a hydroxy group and a cyano group on the rearrangement behaviour of 3-substituted **16**. If **25** (X = CN) is treated with *X*-rays at low temperature in adamantane, one observes between −60 and 0°C only signals due to the 1- and 2-adamantyl radical[24]. At room temperature these signals disappear in favour of those of **29** and a doublet with splitting of 1.34 mT. Assignment of the spectrum to structure **29** is based on the coupling constants (Table 1) which are very similar to those of the other radicals with bicyclo[3.2.0]heptadienyl structure. Above room temperature **29** isomerizes to cyanotropylium radical[13] as was observed for the structurally related radical **11b**. At +85°C both the signals of **29** and of the doublet, which could not be identified structurally, had completely disappeared, leaving only the spectrum of cyanotropylium radical.

3-Quadricyclanol (**24**) yielded analogous results on irradiation of an adamantane matrix with *X*-rays at room temperature. Two primary radicals are formed, the major one being **28**. The minor component shows splittings of $a_1 = 0.35$ mT (1H), $a_2 = 1.43$ mT (2H), and $a_3 = 2.49$ mT (1H). The structure of this radical is unknown so far. Above +50°C a rapid isomerization of **28** to **30** is found[3], the signals of the minor radical remain in this case however visible even at +125°C.

Discussion of the Results

The isomerization of radicals on the C_7H_7-hypersurface was analyzed under conditions of long life time. In similar fashion the behaviour of corresponding cations in superacidic media has been investigated extensively. A comparison of the results in both series of compounds may contribute to a better understanding of similarities and differences.

In superacidic medium at −80°C *Winstein*[9,25] was able to observe by NMR spectroscopy the rearrangement of 3-quadricyclanyl cation to 7-norbornadienyl cation. Bicyclo[3.2.0]hepta-2,6-dienyl cation isomerized under these conditions at −125°C to norbornadienyl cation. The latter finally gives tropylium cation with a free energy of activation of $\Delta G^{+} = 98$ kJ/mol at +47°C. As mentioned earlier 7-norbornadienyl cation undergoes a 1,2-vinyl shift. At −47°C the free energy of activation for the sigmatropic rearrangement is 69 kJ/mol. As intermediate a bicyclo[3.2.0]hepta-2,6-dienyl cation is postulated[9,26] (see above). UV-irradiation of tropylium cation in fluorosulfonic acid at −70°C gives 7-norbornadienyl cation[27]. If the irradiation is carried out in water containing 5% sulfuric acid, one can isolate products derived from bicyclo[3.2.0]hepta-2,6-dienyl cation[28,29].

C_7H_7-radicals behave differently. 3-Quadricyclanyl radical isomerizes at < -145°C in solution to bicyclo[3.2.0]heptadienyl radical **2**, which transforms to tropylium radical. 7-Norbornadienyl radical rearranges under various conditions to tropylium radical **3**, without evidence for any intermediates. Irradiation of bicyclo[3.2.0]heptadienyl radical also yields **3**.

In both systems the final product has the monocyclic tropylium structure. Within the bicyclic molecules a difference is observed. The most stable cation is 7-norbornadienyl cation, the most stable radical has bicyclo[3.2.0]hepta-2,6-dienyl structure. A simple MO-theoretical argument provides an explanation.

In Fig. 1 an orbital diagram is constructed for 7-norbornadienyl cation using as basis the π-orbitals of norbornadiene and an isolated p-orbital in position 7. In the cationic system orbitals ψ_1 and ψ_2 are occupied. 7-Norbornadienyl cation therefore is stabilized by the interaction of the diene-π-orbitals with the p-orbital at C-7. The radical has one additional electron in ψ_3. The stabilization of the cation brought about by the interaction of ψ_2 and p will be counterbalanced. Assuming a symmetrical splitting this destabilisation amounts to 50%. The discussion is somewhat oversimplified as the cation does not have the symmetrical structure but an even more stable tilted structure. The conclusion therefore is that the radical certainly is less stable than the cation.

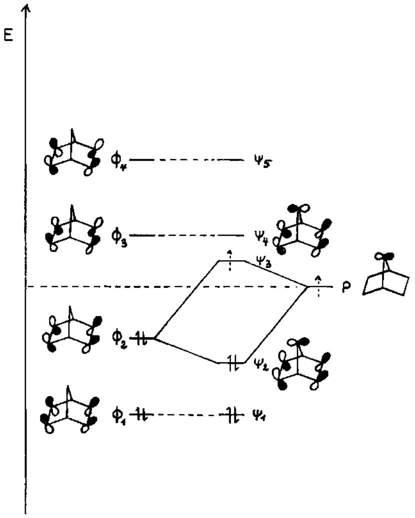


Fig. 1. Orbital interaction diagram of norbornadiene with a p-orbital at C-7

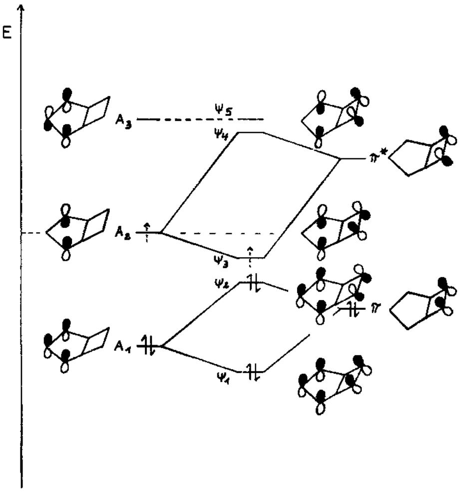


Fig. 2. Orbital interaction diagram for an allyl radical and a double bond in bicyclo[3.2.0]heptadienyl radical

Fig. 2 provides a similar interaction diagram for the bicyclo[3.2.0]hepta-2,6-dienyl system. In the cation ψ_1 and ψ_2 are each doubly occupied. In the case of a symmetrical orbital splitting due to the interaction of A_1 and π the molecule will not be stabilized by the interaction. The additionol electron in the radical occupies ψ_3 which is lowered compared to A_2. Thus the interaction of the allylic system with a double bond provides stabilization for the radical and not for the cation. This difference between cation and radical seems to be the reason for the observed stability trends.

The attempted stabilization of various radicals by substituents did not lead to a change in rearrangement behaviour. An interchange of energy minima on the hypersurface can therefore not be effected by substituents.

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Experimental Part

Analytical Instruments: ^1H and ^{13}C NMR spectra (internal standard TMS): Varian XL 200 and EM 360 A. – Mass spectra: Finnigan MAT 312/188, coupled with Varian gaschromatograph 3700. – IR spectra: Perkin Elmer 397. – ESR spectra: Bruker ER 420 and Varian E3. – GLC analysis: Varian 3700 with CDS 111 data system. – Preparative GLC: Varian P 90.

ESR Measurements: The preparation of adamantane matrices and the method of *X*-ray irradiation has been described elsewhere[4,7]. *X*-Ray irradiations were carried out with instruments of C.H.F. Müller-company using a tungsten anode (2500 W at 125 kV and 20 mA, 800 R/min) and a stabilipan instrument of Siemens with a copper anode (3600 W at 240 kV and 15 mA, 240 R/min). Except where noted "soft *X*-rays" (beryllium anode), all irradiations were carried out with the above instruments.

Bicyclo[3.2.0]hepta-2,6-diene (**1**)[30]: The compound was purified by preparative GLC, using a 2.5 m glass column with 15% SE 30 on chromosorb W. Column: 80°C, injector 120°C, collector 110°C.

[2-^2H]Bicyclo[3.2.0]hept-6-en-2-ol: Following a procedure of *Svenson*[31] 4.6 g (42 mmol) of bicyclo[3.2.0]hept-6-en-2-one[32] were added to 600 mg (14 mmol) of lithium aluminum deuteride in 50 ml of ether at such a rate that the solution refluxed slowly. After reflux for 1 h the solution was hydrolyzed with 30 ml of water and 30 ml of 10% sulfuric acid at 0°C. The ethereal layer was separated and dried over sodium sulfate. After removing ether distillation yielded 3.6 g (77%) of [2-^2H]bicyclo[3.2.0]hept-6-en-2-ol, b.p. 75°C/16 mbar (undeuterated compound b.p. 70°C/12 mbar[31]). Degree of deuteration >99% by NMR. – ^1H NMR ($CDCl_3$): δ = 1.1–1.6 (m, 2H), 1.8–2.1 (m, 2H), 3.0–3.2 (m, 2H), 3.3 (m, 1H), 5.9–6.1 (m, 2H). – IR (film): 2120 cm^{-1} (C–D). – MS (70 eV): m/e = 111 (M^+, 20%), 110 (M^+ – H, 25), 96 (M^+ – CH_3, 80), 95 (30), 93 (M^+ – H_2O, 70), 92 (75), 82 (60), 79 (80), 68 (65), 53 (50), 39 (100).

Methyl ([2-^2H]Bicyclo[3.2.0]hept-6-en-2-yl)xanthate: Analogously to ref.[33] 1.8 g (78 mmol) of sodium were pulverized at –78°C in 150 ml of absol. ether with an Ultra-Turrax stirrer. To this suspension were added at room temperature 2.45 g (22 mmol) of [2-^2H]bicyclo[3.2.0]hept-6-en-2-ol and stirred for 30 h. After addition of 5.6 ml (7.05 g, 92 mmol) of carbon disulfide the solution was stirred for 1 h. 12 ml (27.2 g, 191 mmol) of methyl iodide were added and the solution was stirred for 12 h before another 4.0 ml (63 mmol) of methyl iodide were added. After 1 h sodium iodide was filtered off and the solvent removed under vacuum at room temperature. 4.4 g (93%) of the product were obtained and used for the next step without further purification.

[2-^{2}H]Bicyclo[3.2.0]hepta-2,6-diene (**4**): 4.4 g (21 mmol) of methyl ([2-^{2}H]bicyclo-[3.2.0]hept-6-en-2-yl)xanthate was pyrolyzed in a micro distillation apparatus, connected to a 10 cm vigreux column at 210 °C. The apparatus was continuously purged with a slow stream of nitrogen to remove the product which was collected at −78 °C, yield 1.1 g (54%). – ^{1}H NMR (CCl_4): δ = 6.35 (d, J = 3 Hz, 1 H), 6.05 (d, J = 3 Hz, 1 H), 5.6 (s, 1 H), 3.55 – 3.75 (m, 1 H), 3.1 – 3.4 (m, 1 H), 2.15 – 2.45 (m, 2 H). – ^{13}C NMR ($CDCl_3$): δ = 33.14 (t), 44.82 (d), 55.79 (d), 130.92 (d), 130.98 (t), 140.29 (d), 145.30 (d). – MS (70 eV): *m/e* = 93 (M^+, 40%), 92 (M^+ − H, 100). 91 (M^+ − D, 15), 67 ($C_6H_5D^+$, 30), 51 (10), 39 (20), 38 (30).

Bicyclo[3.2.0]hepta-2,6-diene-1-carbonitrile (**10b**): 3.0 g (25.6 mmol) of 2,4,6-cycloheptatriene-1-carbonitrile$^{34)}$ were cyclized photochemically in 560 ml of ether with a high pressure mercury lamp (Heraeus TQ 718). After 9.5 h of irradiation at room temperature no signals of the educt could be detected by NMR. After removal of the solvent "Kugelrohr" distillation yielded 1.85 g (62%) of **10b** with b.p. 50 °C/0.8 mbar. – ^{1}H NMR ($CDCl_3$): δ = 2.2 – 2.6 (m, 2 H), 3.5 – 3.9 (m, 1 H), 5.8 (s, 2 H), 6.2 (m, 1 H), 6.4 (m, 1 H). – ^{13}C NMR ($CDCl_3$): δ = 32.24 (t, C-2), 50.82 (d, C-5), 51.9 (s, C-1), 119.48 (s, CN), 128.05 (d, C-3 or C-4), 134.82 (d, C-3 or C-4), 140.99 (d) and 141.23 (d) (C-6 and C-7). – MS (70 eV): *m/e* = 117 (M^+, 70%), 116 (M^+ − H, 100), 91 (M^+ − CN, 40), 90 (116 − CN, 60), 89 (116 − HCN, 45).

1-Methoxybicyclo[3.2.0]hepta-2,6-diene (**10a**)$^{35)}$
7-Chloro-2,5-norbornadiene (**17**)$^{36,37)}$
Bicyclo[2.2.1]hepta-2,5-diene-7-carbaldehyde (**18**)$^{38)}$
Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**22**)$^{39)}$
Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-3-ol (**24**)$^{40)}$

Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-3-carbonitrile (**25**): Following a procedure of *Oldenziel* and *van Leusen*$^{41)}$ to a suspension of 1.0 g (8.9 mmol) of freshly sublimed potassium *tert*-butoxide in 8 ml of absol. *tert*-butyl alcohol and 8 ml of tetrahydrofuran was given dropwise a solution of 480 mg (4.52 mmol) of tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-3-one and 1.0 g (4.74 mmol) of tosylmethyl isocyanide (TOSMIC) in 70 ml of absol. tetrahydrofuran at 0 to −10 °C. The solution was stirred for 45 min at 0 °C, then added to 35 ml of ice-water which was extracted twice with 100 ml of *n*-pentane. After drying over sodium sulfate and removal of the solvent at normal pressure "Kugelrohr" distillation yielded 50 mg (10%) of **25** of m.p. 41 °C (ref.$^{42)}$ 44 °C). The IR spectrum was identical with that reported for **25**$^{42)}$.

Kinetics of the Rearrangement of **2**: The free energy of activation $\Delta G^{\neq}$ was determined by following the decrease in signal intensity of the most intense signal of the two outermost quartets at a certain temperature as function of time. The data were evaluated on the basis of a first order reaction. This is fulfilled to > 80% turnover. Table 2 lists the rate constants at seven different temperatures and the corresponding $\Delta G^{\neq}$ values. The standard deviation amounts to ±4.0 kJ/mol.

Low Temperature Experiments: A closed-cycle helium cryostat, comprising a compressor CW 202, an expander DMX 1A/15, and a temperature controller ADP-F of AIR-Products was connected to a high vacuum line.

For the reaction of vaporized sodium with 7-chloro-2,5-norbornadiene we used the reaction cell of fig. 3. It was connected at one side to the expander part of the cryostat and on the other side to the high vacuum system. From a storage flask, which contained vaporized 7-chloronorbornadiene and argon in a ratio of 1:500, 10^{-4} – 10^{-5} mol/min of the mixture were released through a needle valve to the vacuum line at 10^{-5} mbar and guided through stainless steel flexible tubes to the reaction cell close to the cooled sapphire rod.

Purified sodium, which was kept in fused melting point tubes[43] (ca. 5 mg) and which were opened prior to introduction into the cell, was heated with a resistance wire to ca. 200°C. Vaporized sodium and alkyl halide reacted close to the cooled sapphire rod and the products of this reaction were deposited. The dimensions of the reaction cell were kept as small as possible. Limiting factor for the size are the stainless steel-glass connections.

The reaction cell for the production of alternating layers of 7-chloronorbornadiene and sodium is shown in fig. 4.

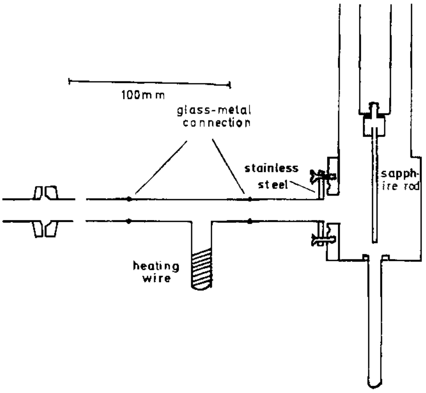

Fig. 3. Cell for the reaction of vaporized sodium with an alkyl halide

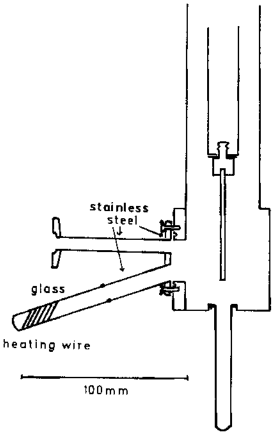

Fig. 4. Cell for the alternating deposition of sodium and alkyl halide

30—50 mg of the gas mixture (7-chloronorbornadiene and argon) and sodium were deposited alternately on the sapphire rod at 20 K. The amount of sodium is controlled by the colour of the sapphire rod. If this takes on an intense blue colour (approximately 10—15 min deposition time), the heating is stopped and the gas mixture is deposited again until the matrix becomes colourless. The final layer consists of sodium.

The sapphire rod is then lowered in the quartz tube of the expander which in turn is introduced in the cavity of the ESR spectrometer. The matrix is illuminated with light from a 1000 W-HG-Xe-lamp (Hanovia 977-B). The light is filtered through a water cooled uranium glass filter (UG 5 Schott) and a 320 nm filter (WG 320 Schott), which removes light of wave lengths <320 nm. To bleach the blue matrix an irradiation time of ca. 20 s is required. Simultaneously the ESR spectrum of sodium disappears completely[18].

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