# Energy Barriers to the Diels–Alder Cycloadditions and Cycloreversions of Cation-radicals in the Gas Phase

**František Tureček**[a]* **and Zdeněk Havlas**[b]
[a] *The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Máchova 7, 121 38 Praha 2, Czechoslovakia*
[b] *Institute of Organic Chemistry and Biochemistry, 166 10 Praha 6, Czechoslovakia*

The mechanism of the retro-Diels–Alder reaction of substituted bicyclo[2.2.1]hept-2-ene cation-radicals can be related to the energetics of the fragmentation. Concerted synchronous or asynchronous mechanisms are operative in reactions which occur at their thermochemical thresholds. The reverse process, tne Diels–Alder reaction of a cation-radical with a molecule, has a negligible activation energy for symmetrical and slightly unsymmetrical systems, $[(Z)\text{-1,2-dihydroxyethene}]^{+\cdot}$ + cyclopentadiene, $[\text{cyclopentadiene}]^{+\cdot}$ + vinyl alcohol, $[(E)\text{-1-hydroxybuta-1,3-diene}]^{+\cdot}$ + cyclopentadiene, and $[(Z)\text{-1-hydroxybuta-1,3-diene}]^{+\cdot}$ + cyclopentadiene. The retro-Diels–Alder decomposition of the highly unsymmetrical 2-vinylbicyclo[2.2.1]hept-5-en-2-ol cation-radical proceeds in two steps and overcomes a barrier of 58—67 kJ mol$^{-1}$ above the thermochemical threshold. The effect of bond-dissociation energies on the reaction mechanism is discussed.

The Diels–Alder (DA) reaction of cation-radicals with neutral molecules in solution[1] and the retro-Diels–Alder (RDA) decomposition of cation-radicals in the gas phase[2] have been shown to proceed through highly asymmetric transition states, in contradiction to the predictions of the symmetry-conservation rules.[3,4] Theory[5,6] and experiment[6–8] have indicated that the RDA and DA reactions in asymmetric systems, *e.g.* $[\text{vinylcyclohexene}]^{+\cdot} \longrightarrow [\text{butadiene}]^{+\cdot}$ + butadiene[5] and *vice versa*,[7,8] favoured stepwise routes in which the open-ring distonic intermediate (**A**) (Figure 1) represented a stable structure (local minimum) on the energy hypersurface.[5]

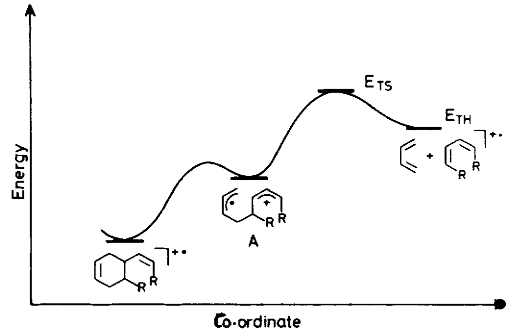
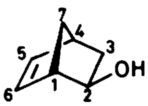
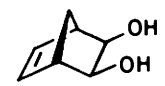


Figure 1. Schematic energy profile for stepwise RDA decomposition of cation-radicals

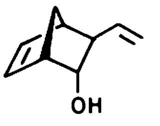
A typical feature of such a two-step process is the presence of an energy barrier[5,6] to the DA reaction of 44—76 kJ mol$^{-1}$, depending on the system in question.[5,7] The molecular-orbital interpretation of the stepwise mechanism[2,5] follows from the hyperconjugative stabilization of the reactant and the intermediate (**A**); this disfavours the transition state of the concerted process in which the stabilization is largely removed, resulting in the high activation energy of the concerted reaction. The question has remained, however, as to whether or not the overall preference for the stepwise route is due to the pronounced stability of the ring-opened intermediate (**A**) or, in general, to the dissymmetry in the dissociation energies of the allylic bonds to be broken. In order to clarify this point we have now examined the RDA decomposition of the bicyclo[2.2.1]-hept-2-ene (norbornene) derivatives (**1**)—(**5**) in which the bond dissociation energies (BDE) can be varied by substitution, and in which the hyperconjugative stabilization of the norbornene double bond by the bridgehead C–H orbitals should be negligible in their cation-radicals because of their geometry.[5]



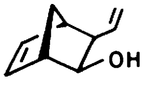
(1)



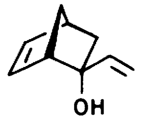
(2)



(3)



(4)



(5)

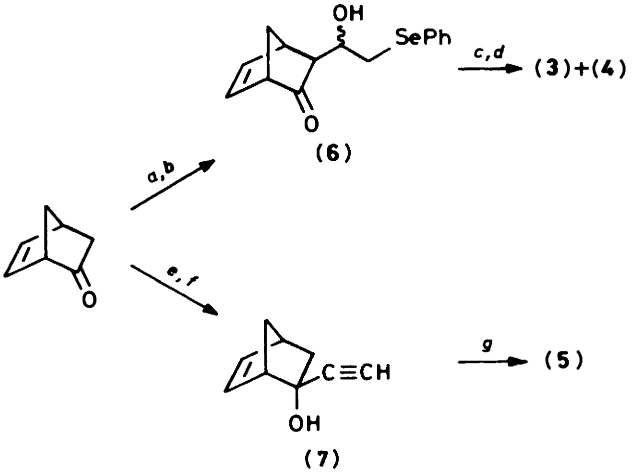
## Experimental

*Methods.*—Mass spectra were measured on a Jeol D-100 spectrometer (75 eV, 300 μA) by a direct inlet or in coupling with a gas chromatograph (column SE-30, 3% on Chromosorb W). The ionization (i.e.) and appearance (a.e.) energies were measured with 50 μA emission current and the repeller voltage set to 0.00 ± 0.01 V. The ion intensities were measured by a data system in 50 meV steps from *ca.* 0.5 eV below the onset up to 2—3 eV above it. The raw data were processed according to Vogt and Pascual,[9] and the deconvoluted ionization efficiency curves were truncated at 0.1—0.15% of the nominal intensity at 20 eV. For ionization energy measurements the linear portions of the deconvoluted curves were fitted with least-squares lines. The reported values are averages of 8—10 measurements. Methyl iodide (i.e. = 9.545 eV) was used for energy-scale calibration. The unstable enols (*Z*)-1,2-ethenediol, (*E*)-1-hydroxybuta-1,3-diene, and (*Z*)-1-hydroxybuta-1,3-diene were generated from the corresponding norbornene precursors (**2**), (**3**), and (**4**), respectively in a molecular-flow micro-oven[10] coupled to a mass spectrometer. The details of their preparation will be published separately. $^1$H N.m.r. spectra (δ, p.p.m.) were

**Table.** Energy data for the RDA and DA reactions in $[1]^{+\cdot}$—$[5]^{+\cdot}$

| Precursor | Products | Appearance energy (eV) | $E_{TS}$[a] | $E_{TH}$[a] | Reverse activation energy[a] |
|---|---|---|---|---|---|
| (1) | $[C_5H_6]^{+\cdot} + CH_2{=}CH{-}OH$ | 9.37 ± 0.05 | 829 | 834 | ~0 |
| (2) | $[HO{-}CH{=}CH{-}OH]^{+\cdot} + C_5H_6$ | 9.38 ± 0.04 | 656 | 651 | ~5 |
| (3) | $[(E){-}CH_2{=}CH{-}CH{=}CH{-}OH]^{+\cdot} + C_5H_6$ | 9.00 ± 0.05 | 870 | 868 | ~2 |
| (4) | $[(Z){-}CH_2{=}CH{-}CH{=}CH{-}OH]^{+\cdot} + C_5H_6$ | 8.95 ± 0.06 | 865 | 866 | ~0 |
| (5) | $[CH_2{=}C(OH){-}CH{=}CH_2]^{+\cdot} + C_5H_6$ | 9.95 ± 0.05 | 955 | 897 | ~58 |
|  | $[C_5H_6]^{+\cdot} + CH_2{=}C(OH){-}CH{=}CH_2$ | 9.92 ± 0.05 | 952 | 885 | ~67 |

[a] In kJ mol$^{-1}$.



**Scheme 1.** *Reagents:* [a] $\mathrm{Pr^i_2NLi}$, THF; [b] $\mathrm{PhSeCH_2CHO}$; [c] MsCl, $Et_3N$; [d] $LiAlH_4$, ether; [e] $Me_3SiC{\equiv}CLi$, THF; [f] NaOH, MeOH; [g] $LiAlH_4$, THF

measured on a Varian XL-200 spectrometer (200.058 MHz, FT-mode) at 22 °C in deuteriochloroform with tetramethylsilane as internal reference.

*Preparations.*—Compounds (**1**)[10] and (**2**)[11] were prepared according to literature procedures. The preparation of compounds (**3**)—(**5**) is depicted in Scheme 1.

3-exo-*Vinylbicyclo*[2.2.1]*hept-5-en-2-ol* (**3**,**4**).—Bicyclo[2.2.1]hept-5-en-2-one[12] (1 g, 9.2 mmol) in tetrahydrofuran (THF) (5 ml) was added dropwise under argon to a stirred solution of lithium di-isopropylamide (10.3 mmol) in THF (10 ml) under cooling to −78 °C. After 1 h at −78 °C, a solution of phenylselenylacetaldehyde[13] (1.89 g) in THF (5 ml) was added and the mixture was stirred for 1 h at −78 °C and 10 min at 0 °C. It was then acidified with acetic acid (2 ml), and the solvent was evaporated off under reduced pressure and the residue diluted with ether (30 ml) and water. The ethereal solution was washed successively with 5% hydrochloric acid, 5% potassium hydrogencarbonate, and water, dried ($Na_2SO_4$) off and the solvent evaporated, under reduced pressure. The crude aldol (**6**) (2.56 g, 90% of a 2:1 mixture of two diastereoisomers by t.l.c.) was dissolved in dichloromethane (10 ml) and treated at 0 °C with triethylamine (20 mmol) and methanesulphonyl chloride (15 mmol) for 2 h.[14] The mixture was diluted with pentane (20 ml), washed successively with 5% hydrochloric acid and water, dried ($Na_2SO_4$), and the solvents were distilled off through a short Vigreux column. The residue was flash-distilled from the selenium compounds under reduced pressure to yield 3-*exo*-vinylbicyclo[2.2.1]hept-5-en-2-one (850 mg, 76%) which was immediately reduced with lithium aluminium hydride (100 mg) in ether at room temperature. The usual work-up afforded a mixture of (**3**), (**4**), and another minor isomer which were separated by column chromatography (silica gel, elution with light petroleum–ether, 1:1). Compound (**3**) (320 mg after vacuum distillation) $\delta$ 6.52 (dd, 1 H, *J* 5.8, 3.2 Hz), 6.16 (ddd, 1 H, *J* 5.8, 3.0, 0.4 Hz), 5.88 (ddd, 1 H, *J* 17.2, 10.1, 7.9 Hz), 5.11 (ddd, 1 H, *J* 17.2, 1.8, 1.2 Hz), 5.04 (ddd, 1 H, *J* 10.2, 1.8, 1.1 Hz), 4.14 (m, 1 H, *W* 10 Hz), 2.97 (m, 1 H, *J* 8 Hz), 2.65 (m, 1 H, *W* 7 Hz), 1.72 (dm, 1 H, $J_d$ 4 Hz), 1.57 (ddd, 1 H, *J* 9.2, 1.4, 1.4 Hz), 1.50 (ddd, 1 H, *J* 9.2, 4.4, 2.0 Hz), and 1.37 (m, 1 H); *m/z*, rel. intensity 136 ($M^{+\cdot}$, 0.4), 117 (3), 107 (2), 91 (6), 79 (8), 77 (7), 70 (100), 69 (18), 67 (27), 66 (37), 55 (4), 53 (3), 51 (4), 42 (10), 41 (13), and 39 (14) (Found: C, 79.25; H, 8.7. $C_9H_{12}O$ requires C, 79.37; H, 8.88%). Compound (**4**) (45 mg after vacuum distillation) $\delta$ 6.25 (dd, 1 H, *J* 6.0, 3.2 Hz), 6.04 (dd, 1 H, *J* 6.0, 3.2 Hz), 5.77 (ddd, 1 H, *J* 17, 10.4, 8.8 Hz), 5.22 (ddd, 1 H, *J* 17, 2.2, 1.0 Hz), 5.15 (ddd 1 H, *J* 10.4, 2.2, 0.7 Hz), 3.84 (m, 1 H), 2.79 (m, 1 H), 2.63 (m, 1 H), 2.31 (ddm, 1 H, *J* 8.8, 7.2 Hz), 1.90 (dm, 1 H, $J_d$ 8.9 Hz), 1.62 (m, 1 H), and 1.55 (dddd, 1 H, *J* 8.9, 3.3, 1.8, 1.8 Hz); mass spectrum identical with that of compound (**3**) (Found: C, 79.4; H, 8.85%). The third isomer (*endo-endo*) was isolated only in a mixture with (**4**).

5-exo-*Vinylbicyclo*[2.2.1]*hept-5-en-2-ol* (**5**).—Bicyclo[2.2.1]hept-5-en-2-one (1 g, 9.2 mmol) in THF (5 ml) was added to a solution of lithium trimethylsilylacetylide (11 mmol, from trimethylsilylacetylene[15] and butyl-lithium) at −78 °C under argon. After being kept for 1 h at −40 °C the reaction mixture was quenched with water and worked up. The semicrystalline crude product (1.62 g, 85%) was desilylated[16] to yield 2-*exo*-ethynylbicyclo[2.2.1]hept-5-en-2-ol (**7**) (790 mg, 75%), m.p. 28—30 °C after sublimation; $\delta$ 6.44 (dd, 1 H, *J* 5.6, 3.2 Hz), 6.12 (dd, 1 H, *J* 5.6, 3.1 Hz), 3.11 (m, 1 H), 2.92 (m, 1 H), 2.55 (s, 1 H), 2.35 (dd, 1 H, *J* 12.6, 3.9 Hz), 1.80 (s, 1 H), 1.77 (dm, 1 H, $J_d$ 10.0 Hz), 1.63 (dm, 1 H, $J_d$ 10 Hz), and 1.34 (dd, 1 H, *J* 12.6, 3.6 Hz); *m/z*, rel. intensity 134 ($M^{+\cdot}$, 1), 133 (7), 119 (4), 105 (3), 91 (5), 79 (5), 77 (6), 66 (100), 53 (8), 51 (5), 40 (9), 39 (14), and 27 (5). Alcohol (**7**) (500 mg) was reduced with lithium aluminium hydride (150 mg) in refluxing THF (5 ml) for 6 h. The excess of hydride was destroyed with saturated aqueous sodium sulphate, the mixture was diluted with ether, dried, and the solvents were distilled off through a Vigreux column. The residue was distilled under reduced pressure to afford compound (**5**) (450 mg, 90%) (Found: C, 79.6; H, 8.8. $C_9H_{12}O$ requires C, 79.37; H, 8.88%). The $^1H$ n.m.r. spectrum of (**5**) has been reported.[17] Mass spectrum (*m/z*, rel. intensity) 136 ($M^{+\cdot}$, 4), 133 (2), 117 (1), 115 (1), 95 (4), 93 (9), 79 (8), 77 (6), 70 (25), 66 (100), 65 (12), 55 (19), 51 (4), 43 (6), 40 (8), 39 (13), and 27 (12).

## Results and Discussion

The energies of the transition states ($E_{TS}$, Table) were constructed from the heats of formation of the neutral reactants (**1**)—(**5**) and the experimental appearance energies for the given RDA channels. The heats of formation of the precursors were estimated according to the additivity rules[18] and adjusted to the experimental $\Delta H^{\circ}_{f,298}$ of norbornene[19] to allow for ring strain: $\Delta H^{\circ}_{f,298}(\mathbf{1}) = -75$ kJ mol$^{-1}$; $\Delta H^{\circ}_{f,298}(\mathbf{2}) = -249$ kJ mol$^{-1}$; $\Delta H^{\circ}_{f,298}(\mathbf{3}) = +1$ kJ mol$^{-1}$; $\Delta H^{\circ}_{f,298}(\mathbf{4}) = +1$ kJ mol$^{-1}$; and $\Delta H^{\circ}_{f,298}(\mathbf{5}) = -5$ kJ mol$^{-1}$. The values of $E_{TS}$ are compared with the thermochemical thresholds ($E_{TH}$) represented by the heats of formation of products. These were obtained from the literature data, *e.g.* $\Delta H^{\circ}_{f,298}(C_5H_6) = 136$ kJ mol$^{-1}$(lit.,[20]); $\Delta H^{\circ}_{f,298}([C_5H_6]^{+\cdot}) = 962$ kJ mol$^{-1}$ (lit.,[20]); $\Delta H^{\circ}_{f,298}([CH_2{=}CH{-}C(OH){=}CH_2]^{+\cdot}) = 761$ kJ mol$^{-1}$ (lit.,[21]); $\Delta H^{\circ}_{f,298}(CH_2{=}CH{-}OH) = -128$ kJ mol$^{-1}$ (lit.,[10,22,23]); or estimated from the $\Delta H^{\circ}_f$ of the neutrals as calculated by the MNDO method[24] and combined with experimental ionization energies:* $\Delta H^{\circ}_{f,298}([HO{-}CH{=}CH{-}OH]^{+\cdot}) = 515$ kJ mol$^{-1}$ (from $\Delta H^{\circ}_{f,298}(HO{-}CH{=}CH{-}OH) = -316$ kJ mol$^{-1}$ and i.e. = $9.62 \pm 0.04$ eV); $\Delta H^{\circ}_{f,298}([(E){-}CH_2{=}CH{-}CH{=}CH{-}OH]^{+\cdot}) = 732$ kJ mol$^{-1}$ {from $\Delta H^{\circ}_{f,298}[(E){-}CH_2{=}CH{-}CH{=}CH{-}OH] = -89$ kJ mol$^{-1}$ and i.e. $= 8.51 \pm 0.03$ eV}; and $\Delta H^{\circ}_{f,298}$-($[(Z){-}CH_2{=}CH{-}CH{=}CH{-}OH]^{+\cdot}) = 730$ kJ mol$^{-1}$ {from $\Delta H^{\circ}_{f,298}[(Z){-}CH_2{=}CH{-}CH{=}CH{-}OH] = -87$ kJ mol$^{-1}$ and i.e. $= 8.47 \pm 0.03$ eV}. Taking into account the inaccuracies inherent to these measurements (± 10 kJ mol$^{-1}$), the difference ($E_{TS} - E_{TH}$) gives us an estimate of the activation energy of the DA reaction between the particular cation-radical and molecule.

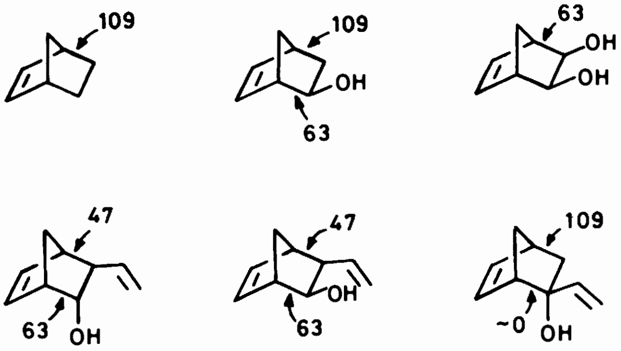
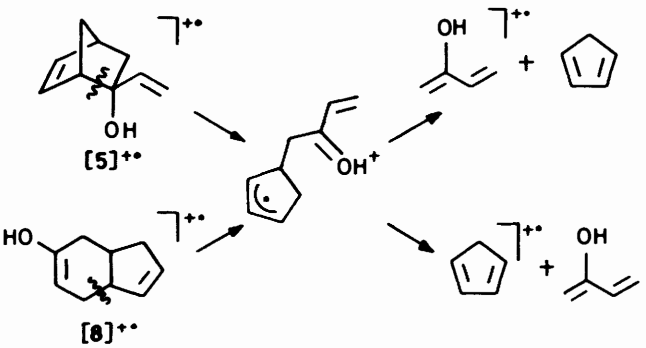


Figure 2. Estimated bond dissociation energies (kJ mol$^{-1}$) in [norbornene]$^{+\cdot}$ and $[\mathbf{1}]^{+\cdot}$—$[\mathbf{5}]^{+\cdot}$



Scheme 2.

The data show that the RDA decomposition of $[\mathbf{1}]^{+\cdot}$—$[\mathbf{4}]^{+\cdot}$ proceeds at the thermochemical threshold, as also reported for the parent norbornene.[25] By contrast, in $[\mathbf{5}]^{+\cdot}$ the formation of either ion *via* an RDA reaction occurs at an energy above the threshold, suggesting that there is a considerable barrier (58—67 kJ mol$^{-1}$) to the reverse (DA) reaction. Since the molecules of (**1**) and (**3**)—(**5**) are unsymmetrical, it is of interest to estimate the BDE of the ring allylic bonds to be broken in the RDA or formed in the DA reactions. We have used 3-substituted cyclopentenes as related models for which the corresponding BDE values can be extracted from the available thermochemical data. Thus, [3-ethylcyclopentene]$^{+\cdot}$ ($\Delta H^{\circ}_{f,298} = 13$ kJ mol$^{-1}$, i.e. = 8.90 eV)[26] decomposing to [cyclopentenyl]$^{+}$ ($\Delta H^{\circ}_{f,298} = 847$ kJ mol$^{-1}$)[20] and ethyl radical ($\Delta H^{\circ}_{f,298} = 107.5$ kJ mol$^{-1}$)[20] gives BDE = 109 kJ mol$^{-1}$ as an estimate for the C(3)–C(4) bond in [norbornene]$^{+\cdot}$, $[\mathbf{1}]^{+\cdot}$, and $[\mathbf{5}]^{+\cdot}$. Similarly, [3-(1-hydroxyethyl)cyclopentene]$^{+\cdot}$ ($\Delta H^{\circ}_{f,298} = -176$ kJ mol$^{-1}$, i.e. *ca.* 9.1 eV)[26] decomposing to cyclopentenyl radical ($\Delta H^{\circ}_{f,298} = 158$ kJ mol$^{-1}$ from the $\Delta H^{\circ}_f$ of cyclopentene[18] and the BDE of the allylic HCH bond[27]) and $CH_3CH{=}OH^+$ ($\Delta H^{\circ}_{f,298} = 607$ kJ mol$^{-1}$)[20] gives BDE = 63 kJ mol$^{-1}$ for the C(1)–C(2) bond in $[\mathbf{1}]^{+\cdot}$—$[\mathbf{4}]^{+\cdot}$. The BDEs of the doubly allylic bonds C(3)–C(4) in $[\mathbf{3}]^{+\cdot}$ and $[\mathbf{4}]^{+\cdot}$ were estimated from [3-(but-3-enyl)cyclopentene]$^{+\cdot}$ ($\Delta H^{\circ}_{f,298} = 69$ kJ mol$^{-1}$, i.e. *ca.* 8.9 eV) decomposing to [cyclopentenyl]$^{+}$ and methylallyl radical ($\Delta H^{\circ}_{f,298} = 128$ kJ mol$^{-1}$)[20] as 47 kJ mol$^{-1}$. These values are summarized in Figure 2. A similar estimate for the decomposition of [3-(1-hydroxyallyl)cyclopentene]$^{+\cdot}$ ($\Delta H^{\circ}_{f,298} = -66$ kJ mol$^{-1}$, i.e. *ca.* 9.1 eV) to cyclopentenyl radical and $CH_2{=}CH{-}CH{=}OH^+$ ($\Delta H^{\circ}_{f,298} = 649$ kJ mol$^{-1}$)[28] gives a negative value for the BDE of a doubly allylic bond $\alpha$-to a hydroxy group, which suggests that the analogous C(1)–C(2) bond in $[\mathbf{5}]^{+\cdot}$ should be extremely weak.

The comparison of the BDE for the allylic bonds and the critical energies for the decomposition of the symmetrical ions ([norbornene])$^{+\cdot}$ and $[\mathbf{2}]^{+\cdot}$ reveals that the energies of the open-ring intermediates would lie above those of the corresponding transition states for the RDA decompositon. Hence we conclude that these symmetrical ions undergo a concerted synchronous RDA reaction which follows the lowest-energy path. Slight asymmetry in the BDE (ions $[\mathbf{1}]^{+\cdot}$, $[\mathbf{3}]^{+\cdot}$, and $[\mathbf{4}]^{+\cdot}$) has no effect on the energetics of the RDA reaction which still occurs at the thermochemical threshold. Rough estimates of the heats of formation of the cation-radicals $[\mathbf{1}]^{+\cdot}$ ($\Delta H^{\circ}_f$ *ca.* 803 kJ mol$^{-1}$) and $[\mathbf{3}]^{+\cdot}$, $[\mathbf{4}]^{+\cdot}$ ($\Delta H^{\circ}_f$ *ca.* 860 kJ mol$^{-1}$) indicate that even breaking the weaker allylic bond to produce an open-ring intermediate would require more energy than the overall RDA decomposition. Hence one can conclude that even in asymmetric cation-radicals the RDA reaction can proceed *via* a concerted, but probably asynchronous,[29] mechanism. The asynchronicity of the bond dissociation in the RDA, or bond formation in the DA reaction, can be assessed from the corresponding BDE. For instance, the interaction between a cyclopentadiene cation-radical and a vinyl alcohol molecule is expected to commence with the development of the C(3)–C(4) bond for which a greater BDE is predicted. We note here that the calculated[30] charge distribution in vinyl alcohol predicts that the terminal carbon atom will carry a negative charge, so that the interaction of this terminus with the cylopentadiene cation-radical could be energetically favourable.

The situation is dramatically changed in the RDA decomposition of $[\mathbf{5}]^{+\cdot}$. Owing to the weakness of the C(1)–C(2) bond the parent cation-radical is forced to undergo ring opening, which produces an intermediate of type (**A**) (Scheme 2). The same intermediate could be, however, expected[7] for an RDA decomposition of the 3-hydroxybicyclo[4.3.0]nona-3,7-diene

---

* For instance the fragmentation of $[3]^{+\cdot}$ requires $E_{TH} = \Delta H^{\circ}_{f,298}([(E){-}CH_2{=}CH{-}CH{=}CH{-}OH]^{+\cdot}) + \Delta H^{\circ}_{f,298}(C_5H_6)$, where $\Delta H^{\circ}_{f,298}([(E){-}CH_2{=}CH{-}CH{=}CH{-}OH]^{+\cdot}) = \Delta H^{\circ}_{f,298}(\text{neutral}) + \text{i.e.}_{exp}(\text{neutral})$. The $\text{i.e.}_{exp}$ obtained from threshold energy measurements approaches the adiabatic ionization energy which should be used to evaluate the $\Delta H^{\circ}_f$ of the ion.

cation-radical [**8**]$^{+\cdot}$, in which the subsequent rate-determining step overcomes the energy barrier, affording vibrationally excited products.

*Conclusions.*—The thermochemical data summarized in this paper and the discussion of the reaction mechanisms allow us to arrive at two conclusions. First, norbornene derivatives that decompose *via* a concerted RDA reaction following ionization can serve as reliable precursors for the determination of the $\Delta H_f^\circ$ of the cation-radical products. The substitution pattern of the ene part should be designed so as not to overly destabilize one of the allylic bonds, which would drive the system towards stepwise RDA fragmentation. Since norbornene derivatives are useful precursors for a number of unstable compounds,[31] ion thermochemistry based on the RDA reaction may also be helpful in establishing the heats of formation of the corresponding neutral molecules.[10,17,32,33]

Secondly, the existence of the concerted mechanism of the RDA fragmentation in [**1**]$^{+\cdot}$—[**4**]$^{+\cdot}$, as also deduced from stereochemical studies of substituted cyclohexene derivatives,[34] points out the importance of the substituents located in the allylic positions.[2] In the absence of substituents, the RDA[5,7] and DA[8] reactions avoid the concerted paths. Symmetrical substitution, however, highly favours the concerted mechanism, save for systems in which one of the allylic bonds is extremely weak. The very low activation energies for the concerted DA reaction of cation-radicals with molecules are remarkable and unprecedented in the gas-phase chemistry of analogous neutral molecules.[35] Rather, they are reminiscent of transition-metal-catalysed cycloadditions[36] for which very low activation energies have also been reported.[37]

## References

1 N. L. Bauld and R. Pabon, *J. Am. Chem. Soc.*, 1983, **105**, 633, and references therein.
2 F. Tureček and V. Hanuš, *Mass Spectrom. Rev.*, 1984, **3**, 85.
3 R. B. Woodward and R. Hoffmann, *Acc. Chem. Res.*, 1968, **1**, 17.
4 I. R. Dunkin and L. Andrews, *Tetrahedron*, 1985, **41**, 145.
5 J. Pancíř and F. Tureček, *Chem. Phys.*, 1984, **87**, 223.
6 N. L. Bauld, D. J. Bellville, R. Pabon, R. Chelsky, and G. Green, *J. Am. Chem. Soc.*, 1983, **105**, 2378.
7 F. Tureček, J. Pancíř, D. Stahl, and T. Gäumann, *Org. Mass. Spectrom.*, 1985, **20**, 360.
8 G. S. Groenewold and M. L. Gross, *J. Am. Chem. Soc.*, 1984, **106**, 6569.
9 J. Vogt and C. Pascual, *Int. J. Mass Spectrom. Ion Phys.*, 1972, **9**, 441.
10 F. Tureček and V. Hanuš, *Org. Mass Spectrom.*, 1984, **19**, 423.
11 V. Van Rheenen, R. C. Kelly, and D. Y. Cha, *Tetrahedron Lett.*, 1976, 1973.
12 P. D. Bartlett and B. E. Tate, *J. Am. Chem. Soc.*, 1956, **78**, 2473.
13 R. Baudat and M. Petrzilka, *Helv. Chim. Acta*, 1979, **62**, 1406.
14 H. J. Reich, F. Chow, and S. K. Shah, *J. Am. Chem. Soc.*, 1979, **101**, 6638.
15 E. Colvin, *Chem. Soc. Rev.*, 1978, **7**, 15.
16 S. J. Harris and D. R. M. Walton, *Tetrahedron*, 1978, **34**, 1037.
17 F. Tureček, *Tetrahedron Lett.*, 1984, **25**, 5133.
18 S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279.
19 D. W. Rodgers, L. S. Chol, R. S. Girellini, T. J. Holmes, and N. L. Allinger, *J. Phys. Chem.*, 1980, **84**, 1810.
20 H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem., Ref. Data*, 1977, **6**, Suppl. 1.
21 J. K. Terlouw, W. Heerma, J. L. Holmes, and P. C. Burgers, *Org. Mass Spectrom.*, 1980, **15**, 582.
22 J. L. Holmes and F. P. Lossing, *J. Am. Chem. Soc.*, 1982, **104**, 2648.
23 B. Albrecht, M. Allan, E. Haselbach, L. Neuhaus, and P.-A. Carrupt, *Helv. Chim. Acta*, 1984, **67**, 216.
24 M. J. S. Dewar and W. J. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899.
25 J. L. Holmes and D. McGillivray, *Org. Mass Spectrom.*, 1971, **5**, 1349.
26 R. D. Levin and S. G. Lias, 'Ionization Potential and Appearance Potential Measurements 1971—1981' U.S. Department of Commerce–National Bureau of Standards, NSRDS-NBS 71, 1982.
27 D. M. Golden and S. W. Benson, *Chem. Rev.*, 1969, **69**, 125.
28 J. Hegedüs-Vajda and A. G. Harrison, *Int. J. Mass Spectrom., Ion Phys.*, 1979, **30**, 293.
29 F. K. Brown and K. N. Houk, *Tetrahedron Lett.*, 1985, **26**, 2297.
30 G. Frenking, N. Heinrich, J. Schmidt, and H. Schwarz, *Z. Naturforsch., Teil. B*, 1982, **37**, 1597; N. Heinrich and H. Schwarz, personal communication, February 1985.
31 M.-C. Lasne and J.-L. Ripoll, *Synthesis*, 1985, 121.
32 F. Tureček, *J. Chem. Soc., Chem. Commun.*, 1984, 1374.
33 F. Tureček and V. Hanuš, *Org. Mass Spectrom.*, 1984, **19**, 631.
34 A. Mandelbaum, *Mass Spectrom. Rev.*, 1983, **2**, 223.
35 G. B. Kistiakowski and J. R. Lacher, *J. Am. Chem. Soc.*, 1936, **58**, 123.
36 F. D. Mango, *Coord. Chem. Rev.*, 1975, **15**, 109.
37 J. Poláček, H. Antropiusová, V. Hanuš, L. Petrusová, and K. Mach, *J. Mol. Catal.*, 1985, **29**, 165.

*Received 9th September* 1985; *Paper* 5/1536