The Cation-radical Cope Rearrangement of 2,5-Diphenylhexa-1,5-dienes Under Electron Ionization

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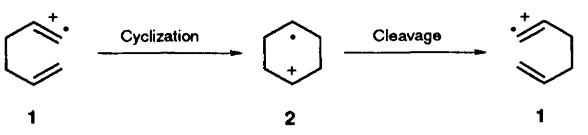
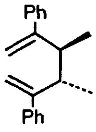
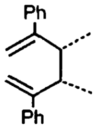
Mass spectrometry of 2,5-diphenylhexa-1,5-dienes provides evidence for the cation-radical Cope rearrangement in the gas phase, in which the reaction directionality is different from that in a thermal process.

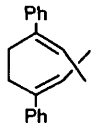
Comparison of skeletal rearrangements of cation radicals with those of the corresponding neutral molecules is currently of interest from the point of view of understanding the nature of cation radical species.[1] The Cope rearrangement of the hexa-1,5-diene cation radical **1** is among the most intriguing. A MINDO/3 calculation by Bauld and coworkers[2] suggested that the reaction would proceed in a stepwise manner, in which the initial cyclization of **1** to cyclohexane-1,4-diyl cation radical **2** would occur with a low-energy barrier but the successive cleavage process of **2** to **1** would have too large an endothermic energy requirement (Scheme 1). In fact, electron paramagnetic resonance (EPR) studies of **1** generated in a low-temperature matrix[3a–c] and the Ce^{IV}-catalysed reaction of 1,4-diphenyl-2,3-diazabicyclo[2.2.2]oct-2-ene[4] showed that **2** and its 1,4-diphenyl derivative did not undergo cleavage.† In sharp contrast, 2,5-diphenyl-3,4-dimethylhexa-1,5-dienes (±-**3**, *meso*-**3**) and 3,6-diphenylocta-2,6-dienes (*Z,Z*-**4**, *E,Z*-**4**, and *E,E*-**4**) underwent the Cope rearrangement through cyclohexane-1,4-diyl cation radical intermediate **5** under the 9,10-dicyanoanthracene (DCA)-sensitized electron-transfer conditions.[5] A possible explanation for the characteristic photochemical process is that a facile back electron transfer (BET) from DCA$^{-\bullet}$ to **5** may occur to yield 2,3-dimethyl-1,4-diphenylcyclohexane-1,4-diyl, which, in turn, undergoes cleavage to complete the electron-transfer Cope rearrangements of **3** and **4**.[6] In order to gain insight into the different reactivities of cyclohexane-1,4-diyl cation radical derivatives under photochemical and nonphotochemical electron-transfer conditions, it is necessary to explore whether or not the cation-radical Cope rearrangements of **3** and **4** occur in the gas

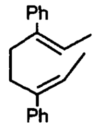


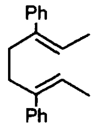
Scheme 1 The cation-radical Cope rearrangement

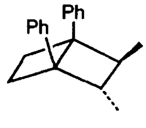

±-**3**

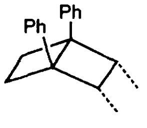

meso-**3**

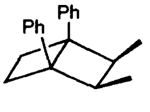

Z,Z-**4**


E,Z-**4**


E,E-**4**


trans-**13**


endo,cis-**13**


exo,cis-**13**

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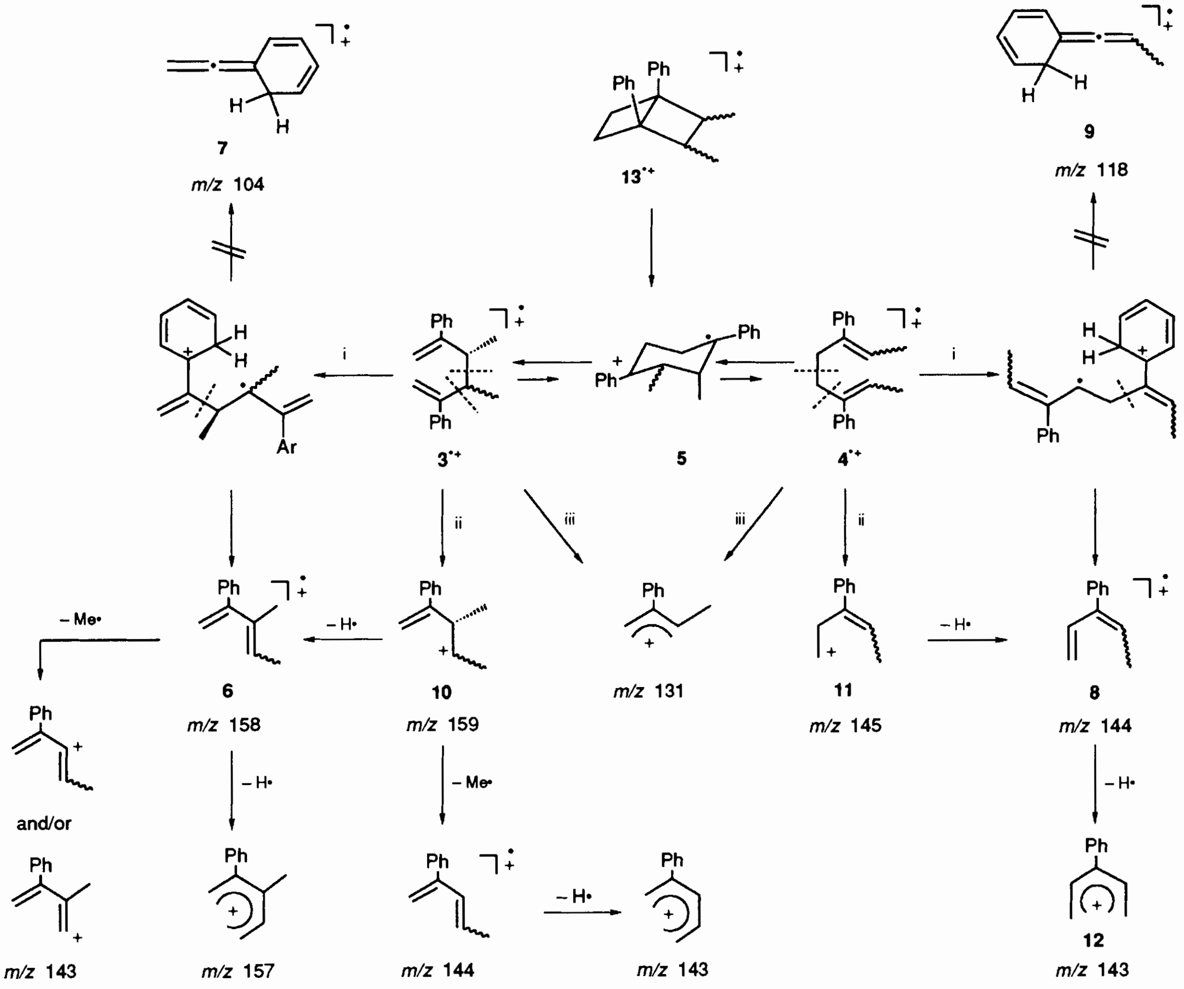
† Recently, Williams reported the cation-radical Cope rearrangement of *endo*-5-vinylbicyclo[2.2.1]hept-2-ene in a low temperature matrix.[3d]



Scheme 2 i, γ-Hydrogen rearrangement; ii, α,β-cleavage; iii, β,γ-cleavage

Table 1 EI spectra of **3**, **4** and **13**[a]

	m/z								
Compound	262(M^+)	159	158	157	145	144	143	131	91
±-**3**	74	13	100	13	2	10	53	36	33
meso-**3**	62	13	100	12	2	8	52	37	34
Z,Z-**4**	97	14	100	15	2	10	59	39	37
E,Z-**4**	95	13	100	14	2	11	61	38	38
E,E-**4**	95	13	100	15	3	10	61	41	40
trans-**13**	58	11	100	12	1	8	55	31	29
endo,cis-**13**	52	13	100	13	2	10	59	34	33
exo,cis-**13**	47	13	100	12	1	8	49	30	24

[a] 70 eV, 42–58 °C.

phase where **5** is not affected by BET. Herein, we report the cation-radical Cope rearrangements of **3** and **4** under electron ionization (EI, 70 eV).‡

It is well known that aromatic molecules possessing γ-hydrogen in a substituted side-chain undergo the γ-hydrogen rearrangement[7] involving a bond cleavage through a distonic cation radical under EI. We used this fragmentation as a probe into the cation-radical Cope rearrangements of **3** and **4**. The rearrangement of $\mathbf{4}^{+\cdot}$ to $\mathbf{3}^{+\cdot}$ can be confirmed by the observation of an inherent ion peak at *m/z* 158 for a fragment **6** or at *m/z* 104 for **7**, whereas an ion peak at *m/z* 144 for **8** or at *m/z* 118 for **9** should be observed if $\mathbf{3}^{+\cdot}$ rearranged to $\mathbf{4}^{+\cdot}$ (Scheme 2).

As shown in Table 1, hexa-1,5-dienes (±- and *meso*-**3**) and octa-2,6-dienes (*Z,Z*-, *E,Z*-, and *E,E*-**4**)§ gave almost the same spectra with a common base peak at *m/z* 158, though molecular ion peaks were somewhat intense for **4**. The base peak cation was exactly composed of $C_{12}H_{14}$ (calc. *m/z* 158.1096, obs. *m/z* 158.1096 for ±-**3**, *m/z* 158.1086 for *meso*-**3**,

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‡ High- and low-resolution mass spectrometries were performed on a JEOL JMS-HX110 double focusing mass spectrometer (42–58 °C, 70 eV). To the best of our knowledge, there is no report on the cation-radical Cope rearrangement of hexa-1,5-diene systems in mass spectrometry except for Banks' study on germacranolides.[9] In ref. 9, the reaction was suggested to occur through a six-membered transition state.

§ Upon refluxing in toluene, diene ±-**3** and *meso*-**3** rearranged to *Z,Z*-**4** and *E,Z*-**4**, respectively, in quantitative yields. Under the same conditions, all isomers of **4** were quantitatively recovered. Consequently, we can easily exclude the possibility of thermal Cope rearrangement of **3**, of course **4**, during short interval at the temperature employed in the mass spectrometric studies.

m/z 158.1103 for *Z,Z*-**4**, *m/z* 158.1116 for *E,Z*-**4**, and *m/z* 158.1096 for *E,E*-**4**) and was confirmed by linked scannings¶ to be formed through the γ-hydrogen rearrangement. These observations directly demonstrated that gaseous cation radical **4**$^{+\bullet}$ was efficiently converted to **3**$^{+\bullet}$ through **5** in the Cope-type rearrangement. A particularly intriguing result was that a low intensity peak at *m/z* 144 and a moderately intense peak at *m/z* 143 observed for both **3** and **4** did not always mean the formation of **4**$^{+\bullet}$. In short, the linked scannings¶ revealed that both peaks were mainly originated from cation **6** and **10**, but not from **8** and **12**. In addition, neither ion peak at *m/z* 104 for **7** nor that at *m/z* 118 for **9** was observed for **3** and **4**. Those results suggest that the gas-phase Cope rearrangement of **4**$^{+\bullet}$ to **3**$^{+\bullet}$ occurred much more efficiently than that of **3**$^{+\bullet}$ to **4**$^{+\bullet}$. It is of interest to note that the directionality of the Cope rearrangement under EI is different from an irreversible thermal rearrangement of **3** to **4**.§ Because **3**$^{+\bullet}$ and **4**$^{+\bullet}$ are essentially styrene-type cation radicals, which, in general, readily cyclize at the β-carbon under various electron-transfer conditions,[8] it is reasonable for **3**$^{+\bullet}$ and **4**$^{+\bullet}$ to form distonic cation radical **5**. In favour of the formation of **5** from **3**$^{+\bullet}$ and **4**$^{+\bullet}$ were results obtained from mass spectrometry of 1,4-diphenyl-2,3-dimethylbicyclo[2.2.0]hexanes (*trans*-**13**, *endo,cis*-**13**, and *exo,cis*-**13**). If cation radical **5** truly serves as an intermediate in the rearrangement sequence, **13** should give a similar spectrum to those of **3** and **4**. In fact, the spectrum of **13** was almost identical with those of **3** and **4** under the same conditions (Table 1). The successive cation-radical cleavage step would be facilitated by good overlap of the orbitals of the spin and positive charge with the C(2)–C(3) or C(5)–C(6) bonds in **5**. Because a characteristic ion peak at *m/z* 91 for tropylium cation was observed, there must be pathways that **3**$^{+\bullet}$, **4**$^{+\bullet}$ and **5** form cation radical species having a cycloheptatrienyl ring to some degree under the conditions employed. However, this cation-radical Cope rearrangement followed by the γ-hydrogen rearrangement is almost independent of such fragmental pathways, because at 13.5 eV|| all ion peaks except for that of tropylium cation were observed with similar intensities to those at 70 eV.

In conclusion, gaseous cation radicals of 2,5-diphenylhexa-1,5-dienes (**3** and **4**) underwent the Cope rearrangement in a cation-radical cyclization–cleavage mechanism. These results do not always mean that cation radical **5** cleaves to **3**$^{+\bullet}$ or **4**$^{+\bullet}$ in the photosensitized electron-transfer process. However, cation radical **5** activated vibrationally under EI easily undergoes cleavage to complete the cation-radical Cope rearrangements, even if the energy barrier of cleavage step is so high as calculated.[2]

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¶ Meta-stable ion spectra were collected by using a Shimadzu/Kratos Concept 1S double focusing mass spectrometer under *B/E* or B^2/E constant conditions. Linked scannings (*B/E* constant) spectra of ±-**3**, *Z,Z*-**4**, and *trans*-**13** gave nearly the same results for an ion peak at *m/z* 158. The linked scannings also suggested the α,β-cleavage–hydrogen atom elimination pathways through **10** at *m/z* 159 and **11** at *m/z* 145. Judging from the even-electron rule, however, ion peaks at *m/z* 159 and 145 may be merely M^{+}+1 ion peaks of **6** and **8**, respectively.

|| Mass spectral data at 13.5 eV were collected by using a Hitachi M-52 mass spectrometer.