

Figure 1. Potential energy diagram for acetaldehyde loss from benzyl ethyl-1,1- d_2 ether.

hand, this is not true for the closely similar $\text{CH}_3(\text{CH}_2)_3\text{C}_6\text{H}_5^+$ (3), which is more stable than its distonic isomer $\text{CH}_3\text{CHCH}_2\text{CH}_2\text{C}_6\text{H}_6^+$ (4) by $\sim 12 \text{ kcal mol}^{-1}$.¹⁵ Despite this, the formation of C_7H_8^+ from 3 apparently proceeds through a stepwise mechanism.^{3b}

Ion isomerizations such as $1 \rightarrow 2$ and $3 \rightarrow 4$ can be studied by comparing mass spectra from 70-eV electron ionization (EI)¹⁷ and spectra from collisionally activated dissociation¹⁸ (CAD). EI spectra show ion dissociations occurring in $\ll 1 \mu\text{s}$, while CAD spectra represent dissociations induced in ions that have had a much longer time (25 μs for the 10-keV ions used here)¹⁹ to isomerize. C_7H_7^+ (eq 1) and C_7H_8^+ (eq 2) represent the major fragment ions in both the EI and CAD spectra of benzyl ethyl ether and *n*-butylbenzene;²¹ isomerization of 1 to 2, or of 3 to 4, should increase the formation of C_7H_8^+ relative to C_7H_7^+ . Consistent with the greater stability of 3 vs. 4 for *n*-butylbenzene this time delay makes little difference, with $[\text{C}_7\text{H}_8^+]/[\text{C}_7\text{H}_7^+] = 0.6$ for EI and 0.8 for CAD. However, for benzyl ethyl ether the similar EI value of 0.8 increases to 6 for CAD, indicating that a substantial proportion of the 1 ions have isomerized to 2 before undergoing CAD. The $[\text{C}_7\text{H}_8^+]/[\text{C}_7\text{H}_7^+]$ value of this CAD spectrum is reduced to 4 by reducing the ionizing electron energy to 15 eV, apparently lowering the proportion of 1 ions formed with sufficient energy to isomerize to 2 in 25 μs .

In further support of the intermediacy of 2, the spontaneous dissociation of metastable benzyl ethyl-1,1- d_2 ether ions of $\sim 25\text{-}\mu\text{s}$ lifetime yields $[(\text{M} - \text{C}_2\text{H}_4\text{O})^+]/[(\text{M} - \text{C}_2\text{H}_3\text{DO})^+] = 2.4\%$ (10% for 2-keV ions, lifetime $\sim 60 \mu\text{s}$). Also for these data a stepwise exchange involving the reversible isomerization $1 \rightleftharpoons 2$ (eq 3) appears to be the only logical explanation.

Finally, the unusual isotope effects of Bowie et al.⁴ could also be consistent with a stepwise mechanism. If (Figure 1) the transition-state energy for $1 \rightarrow 2$ is slightly less than that for 2

(14) We calculate $1 \rightarrow \text{C}_7\text{H}_8^+$ (eq 2) to be 6 kcal mol⁻¹ endothermic overall; $\Delta H_f^\circ(\text{CH}_3\text{CHO}) = -40 \text{ kcal mol}^{-1}$ ^{11b} and $\Delta H_f^\circ(\text{C}_7\text{H}_8^+) = 229 \text{ kcal mol}^{-1}$ (Burgers, P.C.; Terlouw, J. K.; Levsen, K. *Org. Mass Spectrom.* 1982, 17, 295).

(15) $\Delta H_f^\circ(3) = 197 \text{ kcal mol}^{-1}$.¹⁶ $\Delta H_f^\circ(\text{CH}_3\text{CHCH}_2\text{CH}_2\text{C}_6\text{H}_5) = \Delta H_f^\circ(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5)$ ¹⁶ + $D(\text{R}-\text{H}) - \Delta H_f^\circ(\text{H}\cdot)$ ^{13b} = $-3 + 95 - 52 = 40 \text{ kcal mol}^{-1}$, if $D(\text{R}-\text{H})$ is the same as for $(\text{CH}_3)_2\text{CH}-\text{H}$.^{11b} $\Delta H_f^\circ(4) = \Delta H_f^\circ(\text{CH}_3\text{CHCH}_2\text{CH}_2\text{C}_6\text{H}_5) + \Delta H_f^\circ(\text{H}\cdot)$ ^{13b} - $\text{PA} = 40 + 366 - 197 = 209 \text{ kcal mol}^{-1}$, assuming that the proton affinities of $\text{CH}_3\text{CHCH}_2\text{CH}_2\text{C}_6\text{H}_5$ and *n*-butylbenzene are the same.^{13cd} The formation of C_7H_8^+ from 3 is endothermic by 37 kcal mol⁻¹: $\Delta H_f^\circ(\text{C}_7\text{H}_8^+) + \Delta H_f^\circ(\text{CH}_3\text{CH}=\text{CH}_2)$ ^{11b} - $\Delta H_f^\circ(3)$ ¹⁶ = $229 + 5 - 197 = 37 \text{ kcal mol}^{-1}$.

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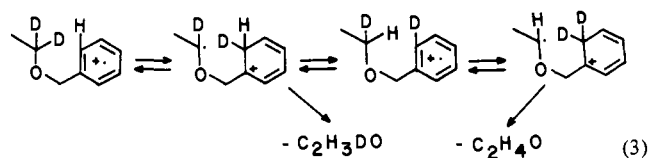
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(19) Experiments utilized a tandem double-focusing mass spectrometer described previously²⁰ with 10-kV ion acceleration and ion source temperature $< 150^\circ\text{C}$. In the CAD experiment the collision gas (helium) pressure was adjusted to give 50% transmittance of the precursor ions.

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(21) For both 1 and 3 the formation of C_7H_7^+ (eq 1) requires more energy than formation of C_7H_8^+ (eq 2).



\rightarrow products (the latter reaction should have the looser transition state), both reactions should be subject to an isotope effect.²²

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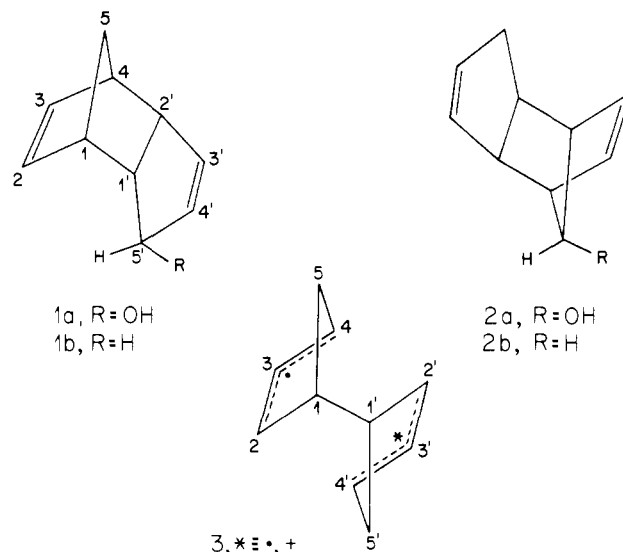
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Radical Cation of Dicyclopentadiene. Evidence for a Singly Bridged Structure

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Twenty-five years ago, Woodward and Katz reported the remarkable rearrangement of α -1-hydroxydicyclopentadiene (**1a**) to *syn*-8-hydroxydicyclopentadiene (**2a**) which occurs with com-



plete stereochemical selectivity and with complete retention of optical integrity.¹ These observations were interpreted as "evidence which shows with special clarity that the thermal dissociation of dicyclopentadiene derivatives takes place in two discrete and experimentally separable stages".¹ This interpretation implies the involvement of a doubly allylic species, 3, or of its mechanistic equivalent as an intermediate or transition state. In the paper presented here, we discuss evidence for a radical cation of the general structure type, 3, discussed by Woodward and Katz.

We studied the reaction of photoexcited chloranil with *endo*-dicyclopentadiene (**1b**) and observed strong nuclear spin polarization effects for the hydrocarbon. As in many other systems,²⁻⁴

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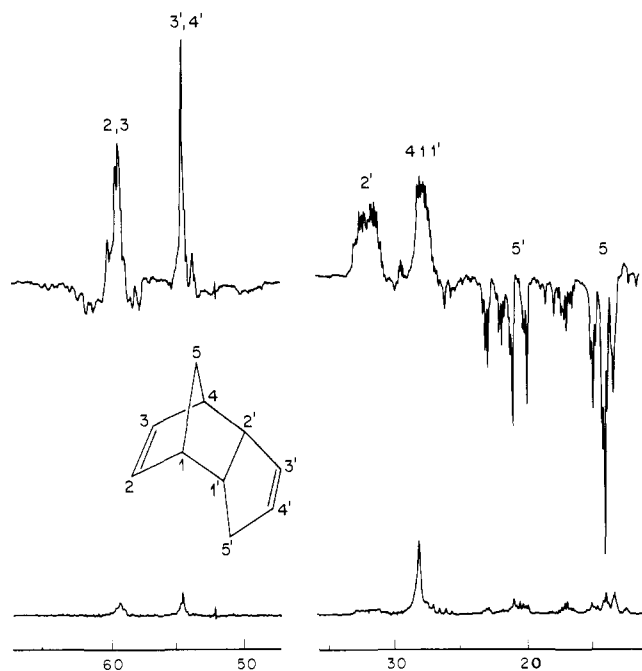
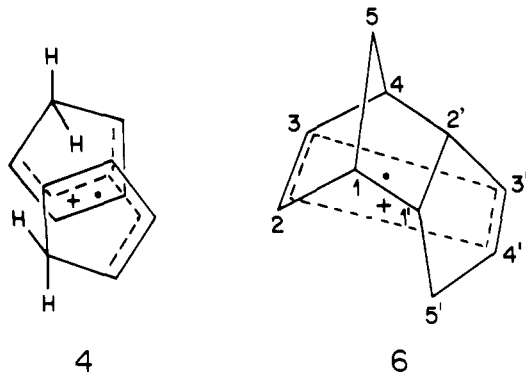


Figure 1. PMR spectra, 90 MHz, observed during the UV irradiation of an acetone- d_6 solution containing 0.02 M each of chloranil and *endo*-dicyclopentadiene (top) and of the same solution in the dark (bottom). The numbering was chosen to reflect the origin of the protons in the two cyclopentadiene fragments. The assignments agree fully with those of Ramey and Lini¹³ and of Sergeev et al.¹⁴

the polarization is ascribed to a radical ion pair, which is generated by electron transfer from the hydrocarbon to the triplet quinone.⁵ These pairs undergo hyperfine induced intersystem crossing leading to an overpopulation of some nuclear spin states (and to an underpopulation of others) in the resulting singlet pairs. The recombination of singlet pairs transfers the unbalanced spin populations to the "product" dicyclopentadiene.

The polarization pattern observed for this product (Figure 1) reflects the absolute signs and the relative magnitude of the hyperfine coupling constants (hfc) of the individual nuclei in the paramagnetic intermediate, D^+ , and allows an insight into its structure. In addition to the singly linked species **3**, we have considered a π complex **4**, without any σ link between the five-membered rings, and a doubly linked radical cation, in which spin and charge are either localized in one π bond (**5**) or shared by the four olefinic carbons (**6**). Structure **6** is remotely related to



(5) Both the generation of the pair and the recombination are energetically feasible. The pair energy is calculated according to $\Delta G = E_{D/D^+} - E_{A^-/A} - e^2/\epsilon a$ from the oxidation potential of the donor (1.95 V vs. SCE),⁶ the reduction potential of the acceptor (-0.02 V vs. SCE),⁷ and a Coulomb term (~ 0.2 V) accounting for ion pairing: Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*, 257. The calculated pair energy, $\Delta G = 1.8$ eV, lies well below the triplet energy of the acceptor, $E_T = 2.7$ eV (Kasha, M. *Chem. Rev.* **1947**, *41*, 401).

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Table I. Hyperfine Coupling Patterns of $C_{10}H_{12}$ Radical Cations and CIDNP Effects Observed during Electron-Transfer Quenching of Chloranil by *endo*-Dicyclopentadiene^a

proton	3	4	5a ^b	5b ^c	6	CIDNP
H ₁	+	-	+		+	E
H ₂	-	-	-		-	A
H ₃	<i>d</i>	-	-		-	
H ₄	-	-	+		+	A
H _{5a,b}	+	+	<i>e</i>		<i>e</i>	E
H _{1'}	+	-		<i>e</i>	<i>e</i>	E
H _{2'}	-	-		+	+	A
H _{3'}	<i>d</i>	-		-	-	
H _{4'}	-	-		-	-	A
H _{5a,b'}	+	+		+	+	E

^a For the reaction discussed here, a positive (negative) hfc would result in emission (enhanced absorption). ^b Spin and charge are assumed to be localized in the norbornene-like π bond of **1b**. ^c Spin and charge are assumed to be localized in the cyclopentene-like π bond of **1b**. ^d hfc is small and positive, but NMR signals are not resolved from H₂ and H₂. ^e Small or negligible hfc.

the radical cation of norbornadiene (**7**)⁸ although the interaction of the π orbitals in **6** cannot be nearly as favorable as in **7**. This conclusion is based on the photoelectron spectrum of **1b**, which shows a π ionization at 8.79 eV,⁹ shifted insignificantly relative to the corresponding transition in norbornene (8.83 eV).¹⁰ In contrast, one of the π transitions in norbornadiene is lowered to 8.42 eV.¹⁰ The π complex **4** is somewhat analogous to the complexes of naphthalene¹¹ or benzene¹² with their respective radical cations.

The hfc patterns of the four species can be expected to differ substantially (Table I) so that the CIDNP pattern observed for **1b** should allow an unambiguous identification of the preferred intermediate. Indeed, the results are incompatible with three of the four structures considered. The π complex **4** can be eliminated because its involvement requires enhanced absorption for eight protons, one of which clearly shows emission (H₁). Any one localized radical cation can be eliminated, because it can account for only four (or five) polarized protons whereas at least eight protons are actually polarized. Finally, the diolefin radical cation **6** (or the simultaneous involvement of two localized ones) can be eliminated because H_{1'} and H_{5a,b} show emission while no polarization is expected and because H₄ and H_{2'} show enhanced absorption instead of the emission expected for **6**.

Only the singly connected intermediate **3** is fully compatible with every facet of the CIDNP results. The opposite signal direction observed for the two pairs of bridgehead protons is particularly revealing. Proton H_{1'} appears in emission, a result expected for allylic protons (and an intact link C₁-C_{1'}), whereas protons H₄ and H_{2'} show enhanced absorption indicative of positions bearing positive spin density (and a ruptured link C₄-C₂). Two minor ambiguities concerning this assignment remain. An intermediate of structure **3** would generate weak emission of H₃ and H_{3'} and strongly enhanced absorption for H₂ and H_{4'}. However, this prediction cannot be verified, because the NMR signals of H₂ and H₃, and of H₃ and H_{4'}, are not resolved. The observed net effect is in agreement with the major polarization predicted. The second ambiguity is due to severe overlap of H₄ with H₁ and H_{1'}. The latter two protons are allylic in **3**, but at unfavorable angles relative to the π system. Accordingly, only

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small hfc's and weak CIDNP effects can be expected. During the CIDNP experiment part of the H_1 spectrum clearly shows emission whereas H_1 is obscured by the strong enhanced absorption of H_4 . We note further that a localized radical cation, **5a,b**, although incompatible with the observed polarization, cannot be ruled out as a primary oxidation product, which rearranges rapidly ($\tau \leq 10^{-9}$ s) to the doubly allylic, resonance stabilized **3**.

The formation of **3** requires a rehybridization of C_4 and C_2 . This structure may permit some overlap between the π orbitals of the two allylic systems at C_4 and C_2 or at C_2 and C_4 . However, significant overlap can be achieved only at the expense of severe distortion.

The radical cation **3** is an interesting example of an emerging family of radical cations, which have structures quite unlike their parent molecules. In fact, the radical cations resemble the geometries of transition states of the corresponding thermal isomerizations. A detailed discussion of these radical cations is in preparation.

F-2,4-Dimethyl-3-ethyl-3-pentyl and F-2,4-Dimethyl-3-isopropyl-3-pentyl: Stable tert-Perfluoroalkyl Radicals Prepared by Addition of Fluorine or Trifluoromethyl to a Perfluoroalkene

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Addition of F_2 , at ambient temperature and pressure, to *F*-3-isopropyl-4-methyl-2-pentene (**1**) or *F*-2,4-dimethyl-3-ethyl-2-pentene (**2**)¹⁻³ gives the hindered free radical *F*-2,4-dimethyl-3-ethyl-3-pentyl (**3**) in concentrations as high as 3 M! Radical **3** is stable at room temperature to dimerization, disproportionation, O_2 , Cl_2 , Br_2 , I_2 , or aqueous acid or base, and, at 70 °C, GC and decomposes by β -scission with a half-life of 1 h at 100 °C. This easy synthesis of **3**, the first air-stable alkyl radical,⁴ and its clean thermolysis at 80–120 °C make it an attractive new source of CF_3 .⁶ While evidence for radical intermediates in the fluorination of alkenes is not new,^{7,8} such radicals have not previously been observed directly.

We discovered **3** while repeating the fluorination of **1** and **2** at 30 and 100 °C as described by von Halasz, Kluge, and Martini³

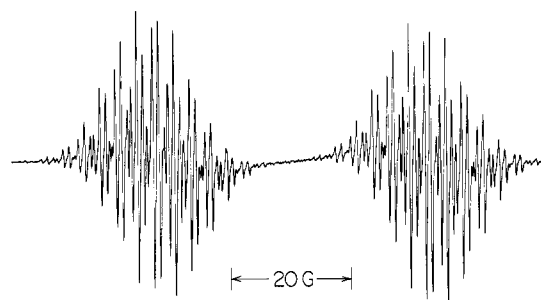


Figure 1. ESR spectrum of radical **3**.

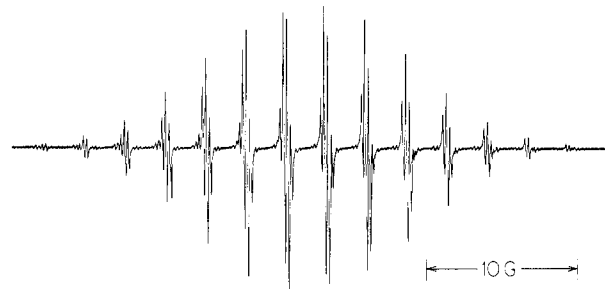
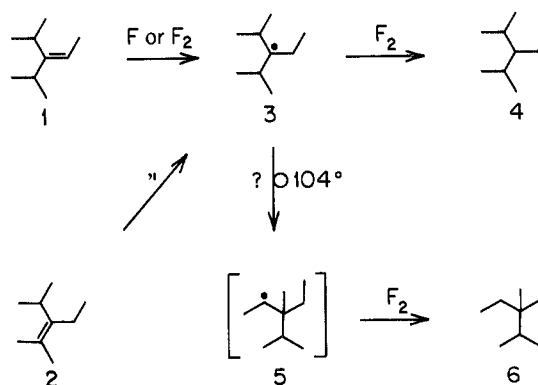


Figure 2. ESR spectrum of radical **7**.

Scheme I



(Scheme I). We wanted samples of **4** and **6** for another study, but doubted structure **6** because of the novel 1,2- CF_3 shift proposed by the authors to explain its formation. We did, however, obtain **6** as described by von Halasz et al. and concluded, based on F NMR and negative ion MS,⁹ that the structure was correct. In following the fluorination at room temperature by F NMR, we noted line broadening suggesting the presence of a paramagnetic species. ESR examination revealed a strong signal, $G = 2.00286$, and upon diluting and degassing we obtained the spectrum shown in Figure 1 and assigned to **3**. This spectrum shows >90 lines and is not yet completely analyzed, but its main feature is a 45.0-G doublet, consistent with a conformationally locked structure in which one β -fluorine of the C_2F_5 group is nearly eclipsed with the half-filled p orbital, while the other lies near its nodal plane.¹⁰ A space-filling (CPK) model of **3** cannot be assembled unless the in-plane β -F's are replaced by H's, and "decomposes" if rotation of the C_2F_5 is attempted. The 45-G coupling is too low for an α -F in a 2° radical but is within the range reported for β -couplings.^{11,12} Radical **3** gives an intense M^- in its negative ion MS⁹ and reacts slowly with F_2 at room temperature to give **4**. These data, plus the fact that **3** is the only radical detected by ESR during fluorination of either **1** or **2** at room temperature, conclusively establish its structure.

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