Scheme II. Norrish type I cleavage followed by the loss of a molecule of carbon monoxide generates diradical **12** which is a common intermediate for products **9–11**; recombination of diradical **12** yields epoxy ketone **9**; extrusion of a molecule of carbon monoxide followed by electrocyclic transformation gives oxepin **10**; opening of the epoxide ring of **12** accompanied with the loss of a molecule of carbon monoxide and hydrogen shift affords β-naphthol **11**.

In summary, our findings show that the photochemistry of **3** and **4** is subject to the stereoelectronically controlled ring opening of the epoxide rings of different configurations and demonstrate that the photolysis of bicyclic unsaturated α-diketones, at least in the present cases, proceeds in a stepwise manner. The detailed mechanism of these reactions and the extension of the studies of the effects of small ring systems other than epoxide are under current active investigation.

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Registry No. 3, 79898-89-8; **4**, 79952-34-4; **7**, 79898-90-1; **9**, 79898-91-2; **10**, 79898-92-3; **11**, 79898-93-4; **11** benzoate, 79898-94-5.

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(10) Compound 9: IR 1775 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.12 (t, 6 H, J = 7 Hz), 1.46–2.28 (m, 8 H), 3.64 (s, 2 H), 7.04–7.40 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 15.06 (q), 18.40 (t), 27.07 (t), 48.11 (d), 56.48 (s), 120.82 (d), 127.20 (d), 136.70 (s), and 194.47 (s); mass spectrum, *m/e* (rel intensity) 228 (M^+, 100), 199 (32), 186 (30), 185 (25) and 157 (26). **10**: IR 1630, 1130, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.80 (t, 6 H, J = 7.0Hz), 1.30 (sextet, 4 H, J = 7.0 Hz), 2.38 (t, 4 H, J = 7.0 Hz), 6.39 (s, 2 H), and 7.00–7.44 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 13.42 (q), 21.62 (t), 32.05 (t), 126.15 (d), 128.14 (s), 136.87 (s) and 144.67 (d); mass spectrum *m/e* (rel intensity) 228 (M^+, 100), 199 (49), 186 (38), 185 (43), 157 (82), 143 (32), 129 (47), 128 (23), 115 (22), 85 (27), 69 (21), 57 (66), 55 (22), 43 (38), and 41 (26); UV $\lambda_{max}^{n\text{-hexane}}$ (ϵ) 260 (3.1×10^3, shoulder), and 234 (2.8×10^4) nm. Compound **11** was not easily purified and thus characterized as its benzoate. Benzoate of **11**: IR 1745, 1283, 1270, 1253, 1120 and 725 cm^{-1}; ^{1}H NMR ($CDCl_3$) 0.98 (t, 3 H, J = 7.0 Hz), 1.04 (t, 3 H, J = 7.0 Hz), 1.72 (sextet, 2 H, J = 7.0 Hz), 1.80 (sextet, 2 H, J = 7.0 Hz), 2.98 (t, 2 H, J = 7.0 Hz), 3.02 (t, 2 H, J = 7.0 Hz), 7.12 (s, 1 H), 7.28–7.68 (m, 5 H), 7.84-8.38 (m, 4 H); mass spectrum *m/e* (rel intensity) 332 (M^+, 20) and 105 (100).

Twisting in Alkene Ion Radicals

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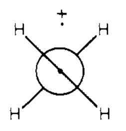
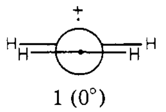
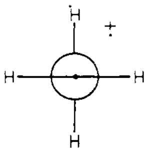
In 1947, R. S. Mulliken and C. C. J. Roothan proposed the ethene cation radical (**1**) as an example of isovalent hyperconjugation in which major hyperconjugative stabilization would be evident prima facie from the ground-state structure of the species, which they predicted to be twisted 30° from planarity.[1] The latter is the result of a compromise between normal π bonding, which is optimized in the planar structure [**1** (0°)], and hyperconjugative π bonding, which is optimized in the perpendicular structure [**1** (90°)]. This prediction was to receive strong support from vacuum ultraviolet studies of the series of Rydberg states of ethene, which converge to the ethene cation radical.[2] These states are found to be twisted by ca. 25°. Very recently, a careful analysis of the vibrational structure of the photoelectron spectrum of ethene has confirmed a 25° twist for ethene cation radical.[3] On the other hand, a planar structure has been determined for the Rydberg states and preesumably the cation radical (**2**) of tetrachloroethene.[4] Somewhat surprisingly, planarity has also been ascribed to the cation radicals of tetraalkylethenes.[5] Although several semiempirical[6–8] and ab initio[9] SCF MO studies of **1** have been published, none of these appear to predict its torsional potential well enough to justify confidence in their extension to substituted alkene cation radicals, and no such extensions have been reported. Several reasonably extensive SCF MO CI calculations have even been reported which likewise fail to generate a twisted ethene cation radical minimum,[10,11] but the excellent CI calculation of Buenker, Peyerimhoff, and Hsu does predict a 23° twist.[12] Extension of this approach to highly substituted ethene cation radicals is, however, impractical. It is the purpose of this communication to report that MNDO reproduces the structure and torsional potential of **1** exceptionally well. The structure and planar minimum of **2** are also accurately predicted, but the tetramethylethene cation radical (**3**) is calculated to be even more strongly twisted than **1**. Reexamination of the PES evidence suggests that the planar assignment is probably in error. Extension of the study to include a variety of alkene cation radicals affords additional significant insights into cation radical structures. Comparison of the MNDO and ab initio torsional potentials of the ethene anion radical to those of the corresponding cation radical reveal that hyperconjugation is at most only moderately attenuated in the anion.



1 (25°; ground state)



1 (0°)



1 (90°)

Table I. MO and MO/CI Torsional Studies of Ethene Cation Radical

method	twist angle at energy min, deg	energy at planar geometry, kcal mol^{-1}	energy at perpendicular max, kcal mol^{-1}
Mulliken[6]	30		
CNDO[7]	37	2.3	20.7
MINDO/3[8]	44	3.4	15.3[a]
ab initio MO (4-31G)[9]	0	0.0;[b] 1.6 (30°)[a]	27.2[a]
6-31G*	0[a]	0.0;[b] 2.1 (30°)[a]	29.2[a]
ab initio SCF MO/CI[12]	23		
many body[3]	9	0.16	
MNDO[a]	20	0.05	17.3
MNDO/UHF[a]	25	0.20	13.9
experiment[3]	25	0.67	

[a] This work. [b] Planar minimum.

The torsional potential data are summarized in Table I. All calculations except the original Mulliken one are optimized. In several instances the earlier studies had calculated only the minimum energy structure. In these cases the requisite additional data were obtained in this work (see entries designated by asterisk). All of the calculations reflect the softness of the torsional potential and hence the potency of hyperconjugation. Also, in each case the perpendicular conformation is the absolute torsional maximum.

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Table II. MNDO and ab Initio Torsional Potentials of Ethene Ion Radicals

species	method	twist angle, deg	relative energy, kcal mol^{-1}
1	MNDO/UHF (MNDO)	0	0.20 (0.05)
1	MNDO/UFF (MNDO)	25	0.00 (~0.00)
1	MNDO/UHF (MNDO)	45	0.98
1	MNDO/UHF (MNDO)	65	5.22
1	MNDO/UHF (MNDO)	90	13.90 (16.8)
6	MNDO	0	0.00
6	MNDO	25	1.18
6	MNDO	45	4.44
6	MNDO	65	10.86
6	MNDO	90	24.35
1	4-31G (6-31G**)[a]	0	0.00 (0.00)
1	4-31G (6-31G**)[a]	45	5.86 (5.05)
1	4-31G (6-31G**)[a]	90	29.12 (27.26)
6	4-31G (6-31G**)[b]	0	0.00 (0.00)
6	4-31G (6-31G**)[b]	45	4.40 (4.35)
6	4-31G (6-31G**)[b]	90	21.94 (21.56)

[a] Geometry optimized in 6-31G**. [b] Point calculation at 4-31G optimized geometry.

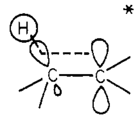
Under transient or low-energy conditions this barrier is high enough that cis ⇄ trans isomerization of labeled **1** would not be expected. The ab initio SCF MO methods, even with quite extended basis sets and in some cases fairly extensive CI, fail to generate a realistic, twisted minimum. The semiempirical SCF MO methods are qualitatively more successful but generally exaggerate the extent of twisting and the barrier height. The Dewar methods in general are by far the most convenient, and MNDO (UHF), in particular, gives an excellent account of the potential. The MNDO structure of **1** (R_{C-C} = 1.423 Å, R_{C-H} = 1.093 Å, H–C–H = 116.6°) is also in very good accord with the experimental structure (R_{C-C} = 1.405 Å, R_{C-H} = 1.091 Å, H–C–H = 117.5°). Even the ab initio SCF MO/CI structure is slightly inferior to that generated by MNDO (R_{C-C} = 1.425 Å, R_{C-H} = 1.092 Å, H–C–H = 119.2°).[3]

For **2** the MNDO optimum structure is planar and again agrees well with experiment [R_{C-C} = 1.435 Å (1.41 Å experimentally), R_{C-Cl} = 1.704 Å (1.69 Å); Cl–C–Cl = 116.2° (116°)]. Two factors appear to be responsible for the shift to planarity in **2**. Cationic hyperconjugation in twisted **2** is somewhat suppressed because of the necessity of involving C–Cl bonds and of situating positive charge on electronegative chlorine. In addition, the π bond order in planar **2** (0.565 in MNDO) is greater than in planar **1** (0.500) because delocalization of the chlorine lone pairs contributes to the bond order of **2**. Nevertheless, the torsional potential in **2** is still relatively soft (the energy at 25° is only 0.7 kcal higher than that at 0°; the barrier height is 15.2 kcal mol^{-1}). Substituents, other than chlorine, which possess lone pair electrons should be expected to exert similar effects in favor of planarity as should conjugating groups. The 1,3-butadiene cation radical, e.g., is neither predicted nor found to be twisted.[13,14]

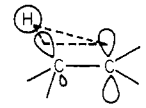
The isobutene cation radical (**4**) is an interesting case to compare with **2**. The electronegativity factor mentioned in the latter connection is absent in **4**, but the bond order factor is still present in some measure. Hyperconjugative delocalization of the methyl C–H electron pairs elevates the bond order in planar 2 to 0.534. Accordingly this species is less twisted (15°) than is **1** and has a smaller calculated barrier to planarization (0.01 kcal mol^{-1}).

The tetramethylene cation radical (**3**), in contrast, is calculated to be more highly twisted (40°) than **1** and to have a much higher barrier to planarization (5.1 kcal). This result appears quite reasonable and predictable on the basis of a simple steric effect. Without doubt the barrier should be much larger for a more hindered species, such as the tetraisopropylethene cation radical (**5**). The experimental assignment of planarity of tetraalkylakene cation radicals was made on the qualitative basis that the PES vibrational structures of **3** and **5** (and related species) are quite similar.[5] It was therefore concluded that these species have similar torsional minima. The (apparently unsupported) assumption was then made that **3** has a planar structure and that, thus, **5** is also planar. In view of the present results the similarity of the vibrational structure could better be seen as reflecting the circumstance that both species are highly twisted. In view of the softness of the ethene cation radical torsional potential, as affirmed by all theoretical methods and by experiment, and of the significant steric repulsions known to be present in the neutral alkenes corresponding to **3** and especially **5**, it seems clear that, as predicted by MNDO, these species must both be twisted.

Comparison of the torsional potentials of **1** and the corresponding anion radical (**6**, Table II) develops a further point of interest. Although **6** is predicted by both MNDO and ab initio (6-31G**) methods to be planar, the torsional potential is still remarkably soft, revealing that hyperconjugation in the anion is still strong and only modestly decreased (MNDO) or even increased (ab initio) relative to the cation. This is not unexpected, since hyperconjugation in its simplest MO representation (**7**) is merely an allylic resonance type. It is well-known that the HMO



7, * = +, −



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delocalization energies of the allyl cation and anion are identical. It is perhaps, less well-known that this is also true in ZDO SCF MO (MINDO/3, PPP, etc.) MO/CI methods, so long as long-range interactions are neglected (i.e., for purely a linear allyl ribbon).[15] Inclusion of the next nearest neighbor (1,3 carbon–hydrogen interaction (**8**) converts the linear allylic ribbon to a perturbed cyclopropenyl ribbon and should introduce a modest cation preference, as found by MNDO. The fact that the ab initio calculation finds a 90° rotation more facile in **6** than in **1** presumably arises from the circumstance that the bond order in planar **6** is less than that of planar **1** in a non-ZDO SCF MO method.

Finally, the soft torsional potentials of **1** and **6** should certainly not be construed as reflecting extremely attenuated π bonding in these species. Qualitatively, this is obvious from the MNDO π bond orders which are 0.500 in planar **1** and **6** and which remain high in the perpendicular forms. In these latter, however, strong π bonding occurs involving both the p_y and p_z orbitals (assuming p_x lies along the C–C σ bond axis). The magnitude of the π bonding in either planar or perpendicular form can be estimated by using a procedure referred to in this laboratory as "deperturbation".[16] After carrying out a normal optimized calculation (e.g., MINDO/3), a new calculation is made which is identical with the previous one except that the static geometry of the normal calculation is maintained and appropriate resonance integrals are set to zero. The heat of formation of a hypothetical version of planar (for example) **1** with no π bond is obtained by setting the resonance integral for the p_z–p_z interaction to zero. This heat is 43.7 kcal higher than that obtained in the initial, normal calculation. Similarly, with the resonance integrals for both the p_z–p_z and p_y–p_y interactions set to zero, the corresponding increase for perpendicular **1** is 43.2 kcal.

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Registry No. **1**, 34470-02-5; **2**, 79952-33-3; **3**, 34512-36-2; **4**, 34526-44-8; **5**, 79898-67-2; **6**, 34527-91-8.

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