

Figure 1. Synthetic route used for synthesis of 9-aneN₂O. (Ts = tosyl, i.e., *p*-toluenesulfonyl)

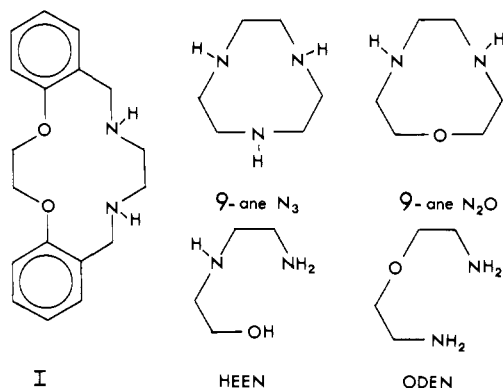


Figure 2. Ligands discussed in this paper.

Table I. Log *K* for 9-ane Macrocycles and Their Linear Analogues^a

metal ion		Cu(II)	Ni(II)	Zn(II)
9-aneN ₂ O ^b	log <i>K</i> ₁	10.85	8.59	6.32
	log <i>K</i> ₂	8.64	7.27	5.07
HEEN ^c	log <i>K</i> ₁	10.09	6.82 (6.85) ^d	4.75
	log <i>K</i> ₂	7.53	5.62 (5.49) ^d	
ODEN ^c	log <i>K</i> ₁	8.70	5.62	(3.5) ^e
	log <i>K</i> ₂	4.4	3.39	
9-aneN ₃ ^f	log <i>K</i> ₁	15.52	16.24	11.62
	log <i>K</i> ₁	15.9	10.5	8.8

^a At 25 °C at ionic strength 0.1. ^b This work, 0.1 M NaNO₃. ^c Reference 8. ^d This work, run as a check on potentiometric system. ^e Estimated by comparison with Cu(II) and Ni(II) complexes. ^f Reference 7.

N,O-donor macrocycles have greater potential application than their all-nitrogen analogues.

The complex [Ni(9-aneN₂O)₂]²⁺ gives a purple solution, as compared with [Ni(HEEN)₂]²⁺, which is the blue color typical of Ni(II) with four aliphatic nitrogen and two oxygen donors. The electronic spectrum shows bands at 11 600, 12 500 (shoulder), 18 800, and 28 250 cm⁻¹. This gives 10*Dq* (*Dq* = ligand field parameter) 11 600 and *B* (Racah parameter) = 820 cm⁻¹, assuming octahedral symmetry, whereas 10*Dq* and *B* for [Ni(HEEN)₂]²⁺ are only 10 950 and 870 cm⁻¹. It is remarkable that 10*Dq* in the bis(9-aneN₂O) complex is larger than for complexes such as [Ni(en)₃]²⁺ (11 200 cm⁻¹) with six nitrogen donor atoms. The increase in 10*Dq* of 650 cm⁻¹ on cyclization to form 9-aneN₂O may be compared with 1000 cm⁻¹ for 9-aneN₃ (10*Dq* for the bis complex⁷ of Ni(II) with 9-aneN₃ is 12 500 cm⁻¹ and for dien 10 *Dq* = 11 500 cm⁻¹). Increases in 10*Dq* on cyclization are thought⁴ to be due to the formation of more basic secondary from primary nitrogens, without the usual increase in strain. The smaller increase of 650 cm⁻¹ for the 9-aneN₂O complex must arise because cyclization of the linear analogue HEEN is occurring across an OH and an NH₂, and O donors do not appear to benefit as much electronically in changing from primary (alcoholic) to secondary (etheral). We are at present determining the structure of [Ni(9-aneN₂O)₂](ClO₄)₂ in order to see whether trigonal distortion contributes to the high *Dq* of this complex, as suggested⁷ for the 9-aneN₃ complex.

In conclusion, the complexes of the mixed nitrogen-oxygen donor 9-aneN₂O show all three characteristics of a strong macrocyclic effect, namely, increased stability, kinetic inertness, and

ligand field strength, compared with the linear analogues. A study of the chemistry of such ligands with a wider range of metal ions may reveal much about the macrocyclic effect, which we are now investigating with the synthesis of ligands such as 13-aneN₂O₂, 9-aneNO₂, and 13-aneN₃O.

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Photochemistry of *syn*- and *anti*-9,10-Epoxy-1,4-dihydro-1,4-dipropyl-1,4-ethano-naphthalene-2,3-dione

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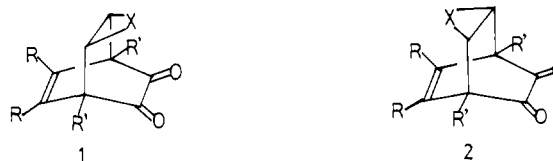
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Recently we have found the effect of number and nature of unsaturation on the photochemical behavior of bicyclic α -diketones.¹ It would be very interesting to examine the photochemistry of the compounds in which a double bond of bicyclo-[2.2.2]octadienedione is replaced by a three-membered ring such as **1** and **2**.² We report herein the photochemistry of the title compounds **3** and **4** which demonstrates the stereoelectronic effect of the epoxy ring on the photochemical behavior of unsaturated β,β' -epoxy- α -diketones.



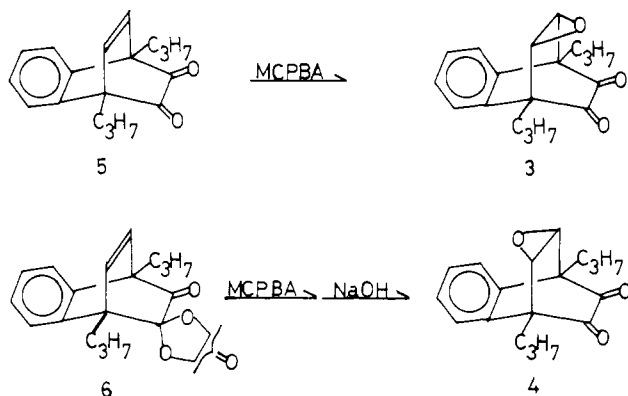
X = O, NR', CR'₂

The *syn*-isomer **3** was synthesized by direct epoxidation of compound **5**³ with *m*-chloroperbenzoic acid (MCPBA) while the *anti*-isomer **4** was prepared by epoxidation of **6**³ with MCPBA followed by alkaline hydrolysis. It is interesting to note that the former method gave only a *syn* isomer (**3**) (72%); however, the latter procedure afforded both **3** (5%) and **4** (69%). The stereoselective formations of **3** and **4** are presumably due to hydrogen

(1) (a) Ueng, Y. S. M.Sc. thesis, National Tsing Hua University, Hsinchu, Taiwan 300, 1980. (b) Lin, H. S. Ph.D. dissertation, National Tsing Hua University, Hsinchu, Taiwan 300, 1981.

(2) M. B. Rubin has recently studied the photochemistry of tricyclo-[3.2.2.0^{2,4}]non-6-ene-8,9-dione. We thank Professor Rubin for a preprint.

(3) Compounds **5** and **6** have been characterized by elementary analysis and spectroscopic data (IR, ¹H NMR, and mass spectra). The detailed procedure for their synthesis will be published in a full paper.



bonding between *m*-chloroperbenzoic acid and the carbonyl group in **5** and the steric hindrance caused by the spiro lactone ring in **6**, respectively. The gross structures of these two isomers were determined by microanalysis and spectroscopic data.⁴ Their stereochemistry was unambiguously established by X-ray diffraction method. Crystal structures of **3** and **4** were determined by single-crystal direct methods and refined to conventional *R* values of 0.066 and 0.065, respectively.⁵ The molecular structures of **3** and **4** are shown in Figure 1.

The irradiation conditions and yields of the products are given in Table I. Both direct and sensitized irradiations of **3** afforded 1,4-di-*n*-propylnaphthalene (**7**)⁶ in high yield. The gaseous products were found to be carbon monoxide and carbon dioxide as shown by mass spectroscopic analysis. The reaction was also followed by UV analysis in the cases of direct irradiation with an argon ion laser light of wavelength 457.9 nm and sensitized reaction. Only the disappearance of the $n \rightarrow \pi^*$ absorption at 429 nm was observed, and no new absorption band was detected in the visible region; thus no 1,3-acyl rearrangement as in the case of **5**¹ occurs. One of the plausible mechanisms to account for the formation of the products is given in Scheme I. Norrish type I cleavage followed by opening of the epoxide ring and subsequent extrusion of a molecule of carbon monoxide yields a diradical which recombines to give β -lactone **8**.⁷ The facile opening of the epoxide ring is presumably due to better overlap between the solely occupied orbital of the radical and the w_2 orbital of the epoxide ring.⁸ The loss of a molecule of carbon dioxide from β -lactone **8** to afford **7** is expected to occur rapidly.⁹

In contrast to **3**, irradiation of **4**, either by direct or sensitization method, yielded a complicated mixture, among which epoxy ketone **9**, oxepin **10**, and β -naphthol **11** were characterized.¹⁰ Again,

(4) Compound **3**: mp 147–148 °C; IR 1745 cm^{-1} ; ¹H NMR (CDCl_3) δ 1.16 (t, 6 H, $J = 7$ Hz), 1.40–2.62 (m, 8 H), 3.78 (s, 2 H), and 7.12–7.46 (m, 4 H); ¹³C NMR (CDCl_3) δ 14.85 (q), 17.44 (t), 29.30 (t), 55.25 (s), 59.83 (d), 124.53 (d), 129.22 (d), 138.79 (s), and 186.93 (s); mass spectrum, m/e (rel intensity) 284 (M^+ , 7), 228 (24), 212 (70), 186 (24), 185 (21), 183 (100), and 57 (22); UV $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ (ϵ) 439 (4.4×10^2), 287 (2.3×10^3), and 238 (3.8×10^3) nm. **4**: mp 164–164.5 °C; IR 1738 cm^{-1} ; ¹H NMR (CDCl_3) δ 1.17 (t, 6 H, $J = 7$ Hz), 1.40–2.33 (m, 8 H), 3.50 (s, 2 H), and 7.04–7.56 (m, 4 H); ¹³C NMR (CDCl_3) δ 14.79 (q), 17.14 (t), 28.18 (t), 49.90 (d), 124.88 (d), 129.69 (d), 133.09 (s), and 189.22 (s); mass spectrum m/e (rel intensity) 284 (M^+ , 5), 228 (100), 199 (22), 186 (37), 185 (28), and 157 (26); UV $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ (ϵ) 455 (2.9×10^2), 289 (1.9×10^3), and 234 (3.7×10^3) nm.

(5) Wang, J. L.; Tang, C. P.; Hseu, T. H.; Lin, H. S.; Liao, C. C., unpublished result. Full details of X-ray crystal structure determinations will be published separately.

(6) (a) Nemoto, F., *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1194–1198. (b) IR and NMR spectra are identical with those of the authentic sample obtained from photolysis of **5**.¹

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(8) For recent theoretical calculation of oxiranes, see: Rauk, A., *J. Am. Chem. Soc.* **1981**, *103*, 1023–2030 and references cited therein.

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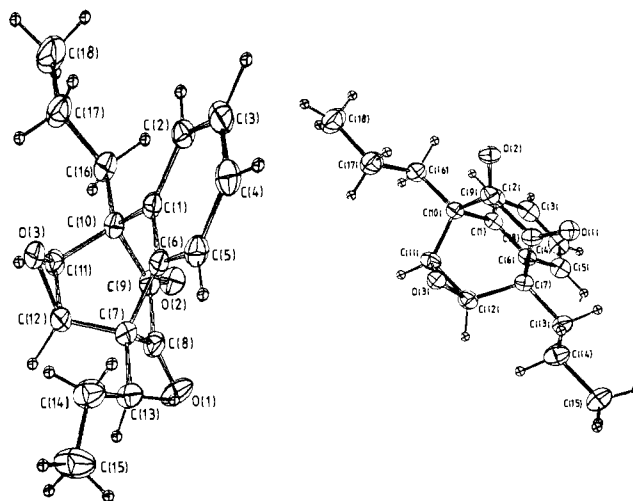
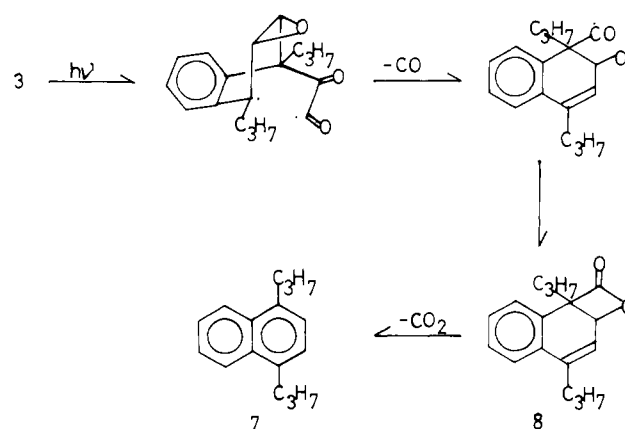


Figure 1. Perspective views of the molecular structures of **3** (right) and **4** (left).

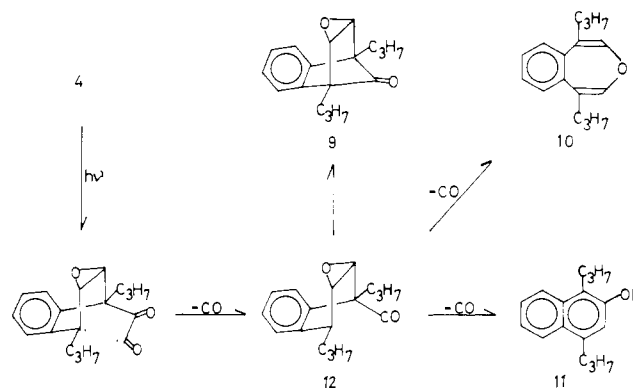
Table I. Irradiation Condition and Yield of Products

epoxy dike-tone	condition	product (yield, %)
3	Hg lamp, uranium glass filter	7 (92)
3	457.9 nm (Ar^+ laser)	7 (100)
3	Sensitized by benzophenone	7 (100)
4	Hg lamp, uranium glass filter	9 (18), 10 (27), 11 (12)
4	457.9 nm (Ar^+ laser)	9 (12), 10 (22), 11 (12)
4	Sensitized by benzophenone	9 (12), 10 (25), 11 (12)

Scheme I



Scheme II



no 1,3-acyl shift was observed as shown by UV analysis. A plausible mechanism for these transformations is depicted in

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.

(10) Compound **9**: IR 1775 cm^{-1} ; $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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} ; $^1\text{H NMR}$ (CDCl_3) δ 0.80 (t, 6 H, $J = 7.0$ Hz), 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); $^{13}\text{C NMR}$ (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 $\lambda_{\text{max}}^{\text{benzene}}$ (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} ; $^1\text{H NMR}$ (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).

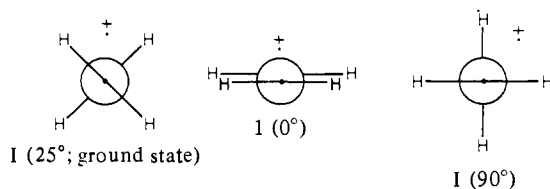
Twisting in Alkene Ion Radicals

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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

(1) Mulliken, R. S.; Roothan, C. C. *J. Chem. Rev.* **1947**, *41*, 219.
(2) Merer, A. J.; Schoonveld, L. *J. Chem. Phys.* **1968**, *48*, 522.

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	27.2 ^a
6-31G*	0 ^a	1.6 (30°) ^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.

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 presumably the cation radical (**2**) of tetrachloroethene.⁴ Somewhat surprisingly, planarity has also been ascribed to the cation radicals of tetraalkylethenes.⁵ Although several semi-empirical⁶⁻⁸ and ab initio⁹ 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.

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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