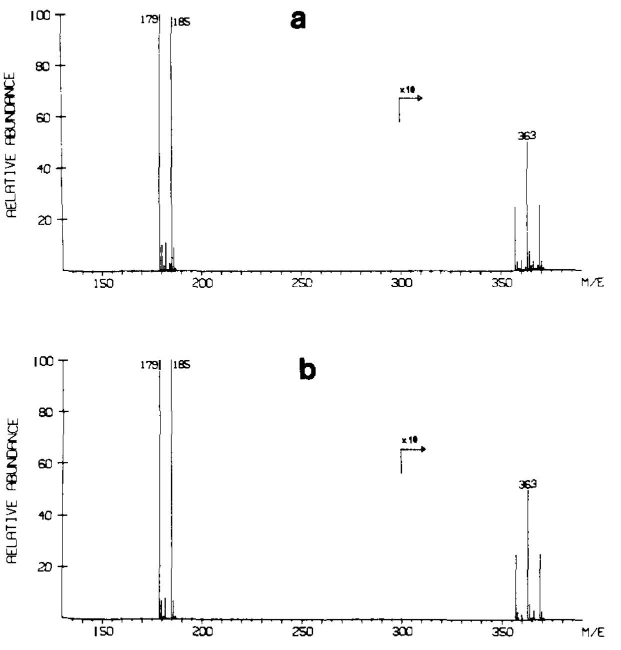


Figure 2. Dimethyl-d_0 D-tartrate (50%) and dimethyl-d_6 D-tartrate (50%) calculated (b) and found (a).

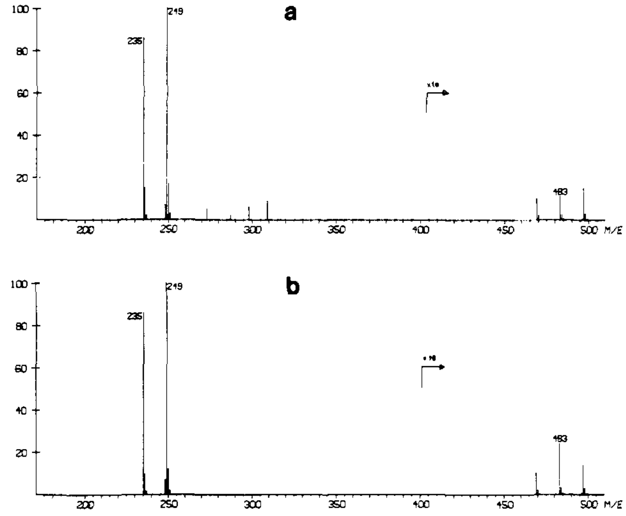


Figure 3. Diisopropyl-d_0 D-tartrate (50%) and diisopropyl-d_{16} L-tartrate (50%) calculated (b) and found (a).

mass spectrometry, as dimethyl tartrate[3] shows in a striking manner (Figure 1). With a mixture of 10% dimethyl-d_6 D-tartrate (MH$^+$ 185) and 90% dimethyl-d_0 L-tartrate (MH$^+$ 179) in the direct insertion probe, the excess optically active form preferentially evaporates, and the spectrum, corrected for incomplete deuteration, gradually approaches that expected for the pure racemate (Figure 1c).

However, inspection of the protonated dimer (2M + H$^+$) region reveals another effect due to chirality that is *independent* of the physical interactions between optical isomers in the liquid or solid state. Thus ratios of the intensities of the peaks in this region should obey the quadratic relation (d_0L + d_6D)^2, i.e., if D and L components are equally abundant as expected for a racemate, they should exhibit a 1:2:1 pattern of d_0L-d_0L, d_0L-d_6D, and d_6D-d_6D protonated dimer ions, respectively. However, close inspection of Figure 1c, where the ions reflect a nearly racemic composition of the sample, reveals a central peak due to the "meso"[4] ion that is only 78% of the value calculated from the ions at *m/e* 357 and 369. On the other hand, when equimolar mixtures of dimethyl-d_0D- and -d_6 D-tartrate are examined, the expected 1:2:1 pattern is indeed observed (Figure 2), ruling out isotope effects in the experiment.[5] This effect is even more dramatically exhibited by mixtures of diisopropyl-d_0 D-tartrate and its -d_{14} L isomer (Figure 3), where the central peak in the 2M + H$^+$ region is now only 46% of the calculated value. Since the effect only compares DD (or LL) with DL interactions, it is difficult to say whether it is caused by stronger bonding in the former (for example through multiple points of attachment) or steric hindrance in the latter. In any case, the interactions responsible must be quite unique since no similar effect was detected in the cases of D-camphor and L-camphor-*3,3*-d_2 and of *N*-acetyl-D-amphetamine and *N*-acetyl-d_3-L-amphetamine.

While the analytical utility of this effect would seem to be minimal, it does provide a tool to investigate certain structural features of these collision-stabilized 2M + H$^+$ ions in chemical ionization mass spectrometry. For example, it is clear that in such cases chirality must be preserved in at least a corresponding fraction of the 2M + H$^+$ ions. Furthermore, there seems to be no reason, a priori, that only relative *destabilization* of the "meso" ion should be found; indeed the opposite might have been predicted from the melting points of the dimethyl tartrates.[3] We are currently searching for further examples of this interesting effect, particularly outside of the tartrate class, in order to gain more insight into its structural requirements.

References and Notes

(1) A. Findlay and A. N. Campbell, "The Phase Rule and Its Applications", Dover, New York, N.Y., 1945, pp 136, 256.
(2) U.-I. Zahorsky and H. Musso, *Chem. Ber.*, **106**, 3608 (1973).
(3) We selected dimethyl tartrate because the unusually high congruent melting point of its racemate (90 °C) compared to its enantiomers (48, 50, or 61 °C, J. H. Adriani, *Z. Phys. Chem.*, **33**, 453 (1900).) suggested the presence of interactions in the racemic crystal that might result in a sublimation vapor pressure less than that of the crystalline enantiomers.
(4) We use the term "meso" ion without its usual implication of symmetry. All we know of these ions is that they are composed of one D and one L molecule combined with a proton. The actual structures present in an assemblage of such ions can be visualized as being either true meso (i.e., having a plane, center or alternating axis of symmetry), or mixtures of equal numbers of still asymmetric ions.
(5) One of our referees has pointed out that the difference in free energy between the dimers represented by Figure 1c and theory is only ca. −0.16 kcal/mol, about what might be expected for a hydrogen-deuterium isotope effect, so the d_0-D-d_6-D experiment in Figure 2 is especially important.

H. M. Fales*
National Heart, Lung, and Blood Institute
National Institutes of Health
Bethesda, Maryland 20014

G. J. Wright
Chemistry Department
University of Canterbury
Christchurch, New Zealand

Received August 31, 1976

Aza Analogy to Singlet Oxygen. The Simultaneous Stereospecific Functionalization of the Four Cyclopentadiene sp^2 Carbon Atoms by Reaction with Nitrosochloroethylenes

Sir:

Nitro[1] and nitroso[2] activated acetylenes and chloroethylenes **1** as their formal hydrochlorides[3,4] have been studied in our laboratories as versatile electron deficient synthons. The nitroso group is known to function as a dienophile,[5-7] and thus is analogous to singlet oxygen,[8-10] particularly when the nitroso function is attached to electronegative groups as in **1**. In fact

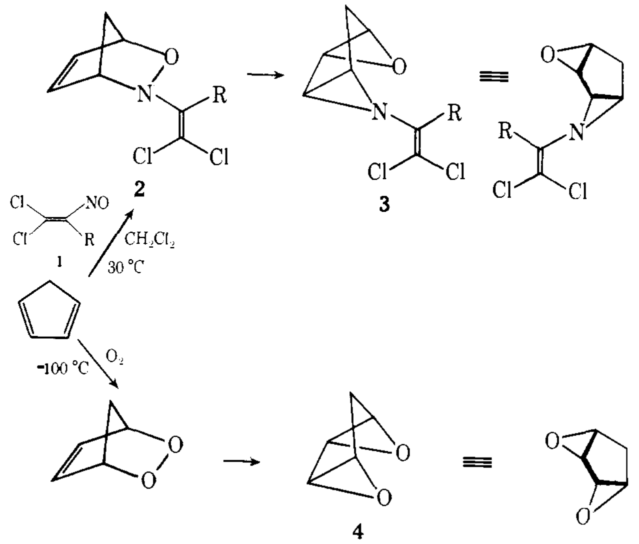
Table I. ^{13}C NMR and ^{1}H NMR Data of **3a** (in C_6D_6 solution)

Carbon or proton	^{13}C, δ ppm	$^{1}J_{CH}$, Hz	^{1}H,[a] δ ppm
1	53.7		
2	66.1	186.9	3.13
3	53.9		2.19
4	43.0	178.2	2.43
5a		127.5	1.10
b	28.4	133.1	1.72
6	137.3	183.4	5.98
7	110.5	—	—

[a] Proton-proton coupling constant (Hz): $J_{5a\text{-}5b} = 15.6$, $J_{5a\text{-}4} = 4.8$, $J_{5a\text{-}1} = 2.7$, $J_{3\text{-}4} = 5.0$, and $J_{2\text{-}3} = 1.6$.

we have found now that **1** mimics singlet oxygen in its reaction with cyclopentadiene.

Thus in complete analogy to the formation of the bis epoxide **4**,[11] the epoxy-epimine **3a** is obtained when 1,1-dichloronitrosoethylene (**1a**) is allowed to react with cyclopentadiene via intermediate **2a**.[12]

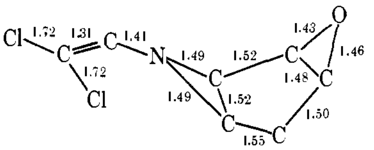


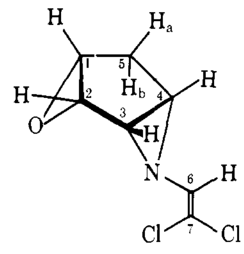
a, R = H
b, R = Cl
c, R = CH_3

Reaction of chloraloxime[13] in a two-phase system of CH_2Cl_2 and aqueous sodium bicarbonate gives the green nitroso compound **1a** which can be trapped with cyclopentadiene. Attempts to isolate the pure dichloronitrosoethylene **1a** were unsuccessful, but it has been characterized spectrally: IR ($CHCl_3$) 1580, 1430 cm^{-1} (NO); UV (C_5H_{12}) λ_{max} 279 and 800 nm; NMR ($CDCl_3$) δ 6.9 ppm; cf. ref 14-17. **1a** is thermally unstable at room temperature in dilute dichloromethane solution but can be kept for days in solution at −20 °C.

The tricyclic compound **3a** was purified by chromatography (silica gel, 43% yield, mp 52-53 °C) and submitted to x-ray analysis. Crystal data: $C_7H_7Cl_2NO$; orthorombic; space group P_{bca} with eight molecules per unit cell; a = 8.064 (2), b = 11.060 (3), c = 18.318 (4) Å. A total of 1016 independent reflections was collected with a semiautomatic Picker diffractometer working in ω-2θ scans and using filtered Cu Kα radiation. Structure was solved by direct methods (Multan) and refined by least-squares with the final atomic parameters. The conventional residual R is 0.06 for 483 observed reflections having $I2.5\gamma(I)$.

All the interatomic distances given (Å) are normal. NMR data are summarized in Table I. The attribution of the chemical shifts is based on selective proton decoupling when observing proton or carbon-13 spectra. The ^{1}H NMR spectrum of **3a** is analogous to the spectrum of **4**. In both cases the vicinal proton-proton coupling constants $J_{5b\text{-}4}$ and $J_{5b\text{-}1}$ are practically zero. As assumed for **4**,[11c] the planarity of the five-membered ring is proven for **3a** by our x-ray analysis. Models based on the x-ray data (which do not give the position of protons) show dihedral angles: $\angle_{5b\text{-}1} = 97 \pm 5°$ and $\angle_{5b\text{-}4} = 104 \pm 5°$. This may be the reason of the zero coupling and it supports the attribution of proton chemical shifts of **5a** and **5b**. In syntheses similar to that of **3a** we have obtained the analogous products **3b**, **3c** from the corresponding precursors **1b**[13] (also obtained from bis(trichlorovinyl)mercury and nitrosyl chloride[18]) and **1c**.

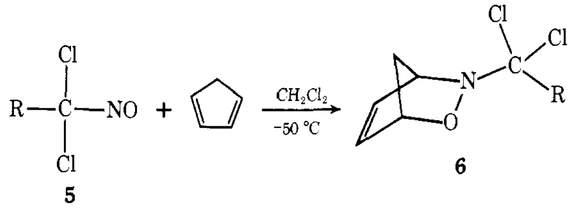




3a

Identification of these compounds is based on their spectral similarity (IR, NMR) to **3a** and their mass spectra (M^+ 225 and 205, respectively).

Our results with vinylic nitroso compounds contrast with the addition of other electron deficient nitroso groups[19,20] as **5** in which the primary adducts[21] **6** are stable to about 100 °C. This indicates the importance of the exocyclic double bond in **2** for its valence isomerization to **3**.



a, R = Cl
b, R = $CHCl_2$
c, R = CH_2Cl

The new compounds, **6**, with oxygen substituted sp^3 hybridized nitrogen are interestingly related to the trichloromethylamine-phosgene immonium salt chemistry[22] under study in our laboratories.

Thus the chlorines in **6a** are replaced by ethoxide, although **6a** does not show salt character and is distillable.

Note Added in Proof: After submission of this paper the addition α-nitrosostyrene to cyclopentadiene was reported to produce oxazine derivatives.[23]

References and Notes

(1) V. Jäger and H. G. Viehe, *Angew. Chem.*, **81**, 259 (1969).
(2) (a) J. C. Motte and H. G. Viehe, *Chimia*, **29**, 515 (1975); (b) V. Jäger, J. C. Motte, and H. G. Viehe, *ibid.*, **29**, 516 (1975).
(3) R. Verbruggen, E. Francotte, and H. G. Viehe, unpublished results.
(4) R. Verbruggen and H. G. Viehe, *Chimia*, **29**, 350 and 352 (1975).
(5) G. Kresze and J. Firl, *Fortschr. Chem. Forsch.*, 245-264 (1968).
(6) J. Hamer, M. Ahmad "1,4 Cycloaddition Reaction", J. Hamer, Ed., Academic Press, New York, N.Y., 1967, pp 419-452.
(7) (a) G. Kresze and G. Schulz, *Tetrahedron*, **12**, 7 (1961); (b) M. Ahmad and J. Hamer, *J. Org. Chem.*, **31**, 2831 (1966).
(8) W. Adam, *Chem. Zeit.*, **99**, 142 (1975).
(9) W. Adam, *Angew. Chem.*, **86**, 683 (1974).
(10) J. J. Basselier and J. P. Leroux, *Bull. Soc. Chim. Fr.*, 4448 (1971).

(11) (a) K. H. Schulte-Elte, B. Willhalm, and G. Ohloff, *Angew. Chem., Int. Ed. Engl.*, **8**, 985 (1969); (b) W. R. Adams and D. J. Trecher, *Tetrahedron*, **27**, 2631 (1971); (c) B. Tolbert, R. Steyn, J. A. Franks, and H. Z. Sable, *Carbohyd. Res.*, **5**, 62 (1967).
(12) At −60 °C the intermediate **2a** is evidenced by the following ^{1}H NMR spectrum: δ (CDCl$_3$) 6.23–6.33 (m, 2 H), 5.99 (s, 1 H), 5.03 (m, 1 H), 4.78 (m, 1 H), 2.00 (d ($J \approx$ 8.5 Hz) of m, 1 H) and 1.74 (d)$J \approx$ 8.5 Hz) of m, 1 H).
(13) H. Brintzinger and R. Titzmann, *Chem. Ber.*, **85**, 344 (1952).
(14) M. Angermann et al., *Wiss. Z. Tech. Hochsch. Chem. Leuna-Merseburg*, **8**, 187 (1966).
(15) W. Hobold, U. Prietz, and W. Pritzkow, *J. Prakt. Chem.*, **311**, 260) 1969).
(16) K. Wieser and A. Berndt, *Angew. Chem., Int. Ed. Engl.*, **14**, 70 (1975).
(17) P. Ciattoni and L. Rivolta, *Chim. Ind. (Milan)*, **49**, 1186 (1967).
(18) P. Skipper, H. G. Viehe, and E. Francotte, unpublished results.
(19) R. E. Banks, A. C. Harrisson, R. N. Hazeldine, and K.G. Orrel, *Chem. Commun.*, 41 (1965).
(20) G. Just and L. Cutrone, *Can. J. Chem.*, **54**, 867 (1976).
(21) ^{1}H NMR data for the compounds **6a**, **b**, and **c** in CDCl$_3$ solution: **6a**, δ 6.03–6.07 (m, 2 H), 5.42 (m, 1 H), 4.99 (m, 1 H), and 2.4–2.5 (m, 2 H); **6b**, δ 6.30 (s, 1 H), 6.0–6.1 (m, 2 H), 5.46 (m, 1 H), 5.00 (m, 1 H), and 2.35–2.45 (m, 2 H); **6c**, δ 6.1–6.2 (m, 2 H), 5.53 (m, 1 H), 5.06 (m, 1 H), 4.26 (s, 2 H), and 2.48–2.54 (m, 2 H).
(22) H. G. Viehe and Z. Janousek, *Adv. Org. Chem.*, in press.
(23) R. Faragher and T. L. Gilchrist, *J. Chem. Soc., Chem. Commun.*, 581 (1976).

H. G. Viehe,* R. Merényi, E. Francotte
Laboratoire de Chimie Organique, Université de Louvain
B-1348 Louvain-la-Neuve, Belgium

M. Van Meerssche,* G. Germain
J. P. Declercq, J. Bodart-Gilmont
Laboratoire de Chimie Physique, Université de Louvain
B-1348 Louvain-la-Neuve, Belgium

Received July 22, 1976

The Photochemistry of Vinylcyclopropenes; a New and General Cyclopentadiene Synthesis. Exploratory and Mechanistic Organic Photochemistry[1]

Sir:

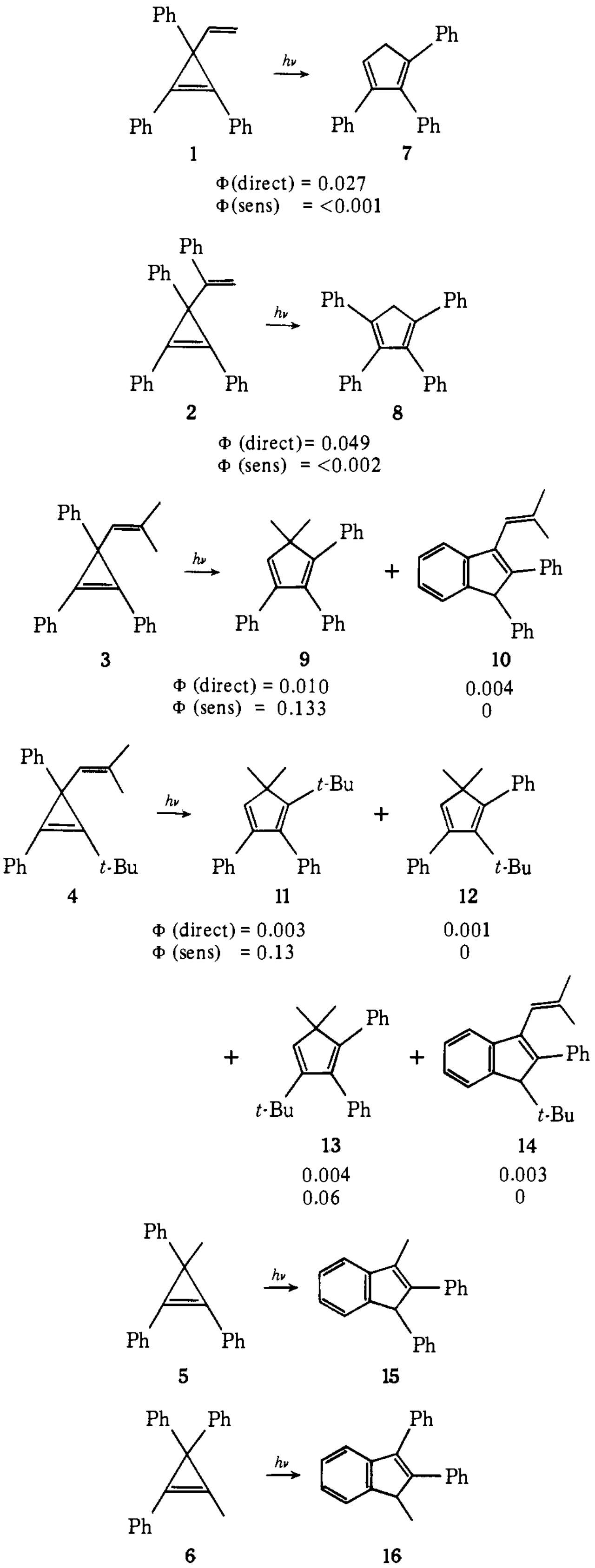
While 3-arylcyclopropenes have been photolyzed,[2] the photochemistry of 3-vinylcyclopropenes has remained uninvestigated. Presently we report: (a) the smooth formation of cyclopentadienes from the photolysis of these reactants, (b) competing with this, an unusual degenerate di-π-methane rearrangement, (c) a trend of quantum efficiencies as a function of structure, (d) a multiplicity dependence favoring singlet or triplet as a function of structure, (e) preliminary evidence indicating a diradical rather than a carbene mechanism, and (f) information suggesting that the rearrangement is mechanistically related to the previously known[2] formation of indenes from 3-arylcyclopropenes.

Thus we have irradiated[3] the four 3-vinylcyclopropenes, **1–4**, and the two 3-arylcyclopropenes **5** and **6** (note Chart I). Interestingly, although indenes are a priori products from the 3-vinyl-3-arylcyclopropenes **1–4**, cyclopentadienes were found exclusively in the cases of cyclopropenes **1** and **2** and as major products (note Chart I) from cyclopropenes **3** and **4**. The photolysis proved sufficiently facile and free of by-products such that the reaction is of considerable synthetic utility. For example, irradiation of 500 mg of vinylcyclopropene **1** for 3.25 h with a 450-W lamp afforded 436 mg (87%) of 1,2,3-triphenyl-1,3-cyclopentadiene (**7**).

Two mechanisms seem plausible. Path A (note Chart II) involves π–π bridging of the excited state to afford the housane diradical **17**. This, in turn, undergoes Grob fragmentation, typical[4] of 1,4-diradicals, to give cyclopentadiene product.

A second reasonable mechanism involves cyclopropene ring opening with formation of carbene **18** followed by electrocyclic closure affording cyclopentadiene product. This is depicted in Chart II as path B. There is, indeed, evidence for formation of carbenes from cyclopropenes both thermally[6] and photochemically.[7]

Chart I. Vinyl and Aryl Cyclopropene Reactions



Both mechanisms lead to the same skeletal change as can be seen from Chart II.

The formation of indenes from 3-arylcyclopropenes (note examples **5** and **6** in Chart I) can be formulated in exactly