Table I. Absorption Maxima for Olefin and Hydrazine Radical Cations

species	λ_m, nm (ϵ)
$1^{+\cdot}$ [a]	530 (>970)
$2^{+\cdot}$ [a]	450 (>750)
$4^{+\cdot}$ [b]	340 (4000), ca. 260 sh (1300)
$5^{+\cdot}$ [b]	338 (3200), ca. 250 (1300)
$6^{+\cdot}$ [b]	331 (5000), 236 (2500)

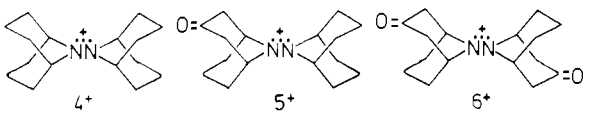
[a] CH_2Cl_2, −78 °C. [b] CH_3CN, room temperature; sh, shoulder.

absorption band for $1^{+\cdot}$ (λ(half-maximum absorption) = 635 nm) is even broader than that of the three-electron σ-bonded species 1,6-diazabicyclo[4.4.4]tetradecane radical cation, for which Alder and Sessions[8] report λ_m = 480, λ(half maximum absorption) = 575 nm. Assuming a 100% yield of $1^{+\cdot}$ and no decomposition, ϵ(530) is about 970; the true ϵ is doubtless somewhat larger than this. The short wavelength side of this very broad $1^{+\cdot}$ absorption is obscured by the tail of the neutral **3** absorption, which rises rapidly below about 380 nm, but there probably is shorter wavelength absorption maximum for $1^{+\cdot}$ as well.

The color of $1^{+\cdot}$ can only reasonably arise from σ,π^+ transitions. Large σ,π^+ interaction in $1^{+\cdot}$ is also indicated by the surprisingly facile oxidation of **1** ($E^{\circ\prime}$ for **1** is about the same as that of 1,2-benzanthracene, which as 18 π electrons), the unusually large long-range proton ESR splitting constants of $1^{+\cdot}$, and its anomalously large g factor for a hydrocarbon radical cation.[9]

2 behaves in a completely analogous fashion to **1**,[10] but $2^{+\cdot}$ is brownish peach color (λ_m = ca. 450 nm, see Table I). Although the 80-nm blue shift between $1^{+\cdot}$ and $2^{+\cdot}$ is initially surprising, perhaps it should not be considered so. The lack of the bridging CH_2 groups in **2** compared to **1** is known to cause flattening of the six-membered rings, and since the transition involves the upper σ orbitals of these rings, substantial differences in σ,π^+ interaction can occur. This is also borne out by the rather large differences in ^1H hyperfine coupling constants for $1^{+\cdot}$ and $2^{+\cdot}$ (principally a much larger $a(H_{\delta_{eq}})$ value for $1^{+\cdot}$, 6.05 vs. 3.20 G, but a smaller $a(H_{\gamma_{eq}})$ value, 3.27 vs. 3.70 G[9]).

We also suggest that "hyperconjugation transitions" are observed in the UV region for hydrazine radical cations $4^{+\cdot}$–$6^{+\cdot}$.



4^+ 5^+ 6^+

They show intense $\pi^* \leftarrow \pi$ absorption bands for the three-electron π bond and also a less intense, shorter wavelength band, which overlaps greatly with the $\pi^* \leftarrow \pi$ absorption and appears only as a shoulder for $4^{+\cdot}$ (see table). Because these cations are isolably stable and were crystallized to analytical purity, we believe it is unreasonable to contend the short-wavelength absorptions are caused by impurities. Neutral **5** and **6** show σ coupled charge-transfer bands due to nitrogen lone pair, carbonyl group overlap through the intervening σ bonds.[11] Although one might be tempted to try to attribute the 260–236 bands in their radical cations to such a phenomenon, this is not reasonable. The radical cations must have considerably stabilized nitrogen lone pairs (the nitrogens are formally half-positive), which would increase the lone pair, carbonyl π^* energy gap considerably and shift the band out of the near UV. More conclusively, $4^{+\cdot}$ shows a similar absorption but has no carbonyl groups. Although $4^{+\cdot}$ is expected to be nearly isostructural with $3^{+\cdot}$, it is not isoelectronic; the "hole" in $4^{+\cdot}$ is in the π_{NN}* antibonding orbital, while that in $2^{+\cdot}$ is in the π_{CC} bonding orbital. Despite the fact that the more electronegative nitrogens of $4^{+\cdot}$ will stabilize both its π and π^* orbitals relative to those of $2^{+\cdot}$, the large energy difference between the π and π^* orbitals ensures that the σ orbital, singly occupied π orbital energy gap of $4^{+\cdot}$ is larger than that for $2^{+\cdot}$, and we assign the 260-nm shoulder in the UV spectrum of $4^{+\cdot}$ to the "hyperconjugation transition". The blue shift observed upon successive carbonyl substitution in $5^{+\cdot}$ and $6^{+\cdot}$ is consistent with this assignment, as the electron-withdrawing C=O groups should stabilize the σ combination orbitals.[12]

Registry No. $1^{+\cdot}$, 70535-07-8; $2^{+\cdot}$, 79684-47-2; $3^{+\cdot}SbCl_6^-$, 58047-17-9; $4^{+\cdot}$, 62781-95-7; $5^{+\cdot}$, 74773-86-7; $6^{+\cdot}$, 74773-87-8.

Supplementary Material Available: Visible spectrum of $2^{+\cdot}$ in CH_2Cl_2 (−78 °C) and UV spectra of **4**, **5**, **6**, $4^{+\cdot}$, $5^{+\cdot}$, and $6^{+\cdot}$ (all in CH_3CN, room temperature) (7 pages). Ordering information is given on any current masthead page.

(12) We gratefully acknowledge the support of this work by the National Science Foundation, the National Institutes of Health, and the Wisconsin Alumni Research Foundation. We are also grateful to Prof. R. C. West of this department for the use of his low-temperature optical spectral equipment.

(8) (a) Alder, R. W.; Sessions, R. B. *J. Am. Chem. Soc.* **1979**, *101*, 3651. (b) We thank Dr. Alder for a reproduction of the spectrum from the Thesis of R. B. Sessions.

(9) Gerson, F.; Lopez, J.; Nelsen, S. F.; Akaba, R. *J. Am. Chem. Soc.* **1981**, *103*, 7045.

(10) Since $E^{\circ\prime}$ is higher for **2** than for **1**, the electron-transfer equilibrium with 3^+ is significantly less exothermic, only 0.5 kcal/mol at −78 °C in methylene chloride. Nevertheless, with a 10× excess of **2** over 3^+, the electron transfer is over 96% complete at −78 °C, allowing the experiment to be done.

(11) Nelsen, S. F.; Kessel, C. R.; Grezzo, L. A.; Steffek, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 5482.

Corner Bromination of Cyclopropane

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Electrophilic opening of cyclopropanes involves two points of attack, so that there are four stereospecific extremes (inversion/inversion, etc.), as well as a nonstereospecific continuum.[2] Possible intermediates include corner attack by X^+ (**1**), edge attack (**2**), and open carbocations (**3**). In most[3] but not all[2] cases open

1 2 3

carbocation intermediates are required by the observation of loss of stereochemistry, in contrast to analogous reactions of alkenes. All these examples involved substituted cyclopropanes, in which the open carbocation was secondary or tertiary. Apparently such carbocations normally are more stable than their bridged analogues when the electrophile is bromine. It is less likely that a primary carbocation (**3**) would be more stable than the bridged alternatives (**1** and **2**). Only unsubstituted cyclopropane forms primary carbocations as the sole open-chain possibility.

Deno and Lincoln[4] showed that cyclopropane reacts sluggishly with bromine in the dark, more facilely in the presence of $FeBr_3$ catalyst, to produce 1,3-dibromopropane, among other products. They suggested intermediates of the types **1**–**3** but made no mechanistic distinctions. Because unsubstituted cyclopropane seems an excellent candidate for bridged or pentavalent carbon intermediates in bromination,[5] we have carried out experiments

(1) This work was supported by the National Science Foundation (Grant CHE80-25601). We thank the Southern New England NMR Facility for a 500-MHz spectrum.

(2) DePuy, C. H. *Fortschr. Chem. Forsch.* **1973**, *40*, 73–101.

(3) Lambert, J. B.; Black, R. D. H.; Shaw, J. H.; Papay, J. J. *J. Org. Chem.*, **1970**, *35*, 3214–3216. Lambert, J. B.; Iwanetz, B. A. *Ibid.* **1972**, *37*, 4082–4086. LaLonde, R. T.; Debboli, A. D., Jr. *Ibid.* **1973**, *38*, 4228–4232. Day, J. C.; Shea, K. J.; Skell, P. S. *J. Am. Chem. Soc.* **1973**, *95*, 5089–5090. Skell, P. S.; Day, J. C.; Shea, K. J. *Ibid.* **1976**, *98*, 1195–1204.

(4) Deno, N. C.; Lincoln, D. N. *J. Am. Chem. Soc.* **1966**, *88*, 5357–5358.

(5) Such intermediates have been found in protonation reactions of cyclopropanes.[2,6]

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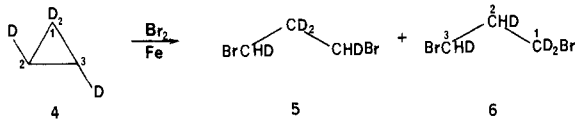
to establish the stereochemistry of the reaction.

In unsubstituted cyclopropane, stereochemistry must be ascertained by the use of isotopes. We have prepared *trans*-cyclopropane-*1,1,2,3-d*$_4$ (**4**), which in principle can distinguish each of the intermediates **1**–**3** for 1,3-bromination. Opening of the 2,3-bond produces **5**, and opening of the 1,2- or 1,3-bond produces



4 5 6

6, which exists in threo and erythro forms. The expected er-

erythro-6 threo-6

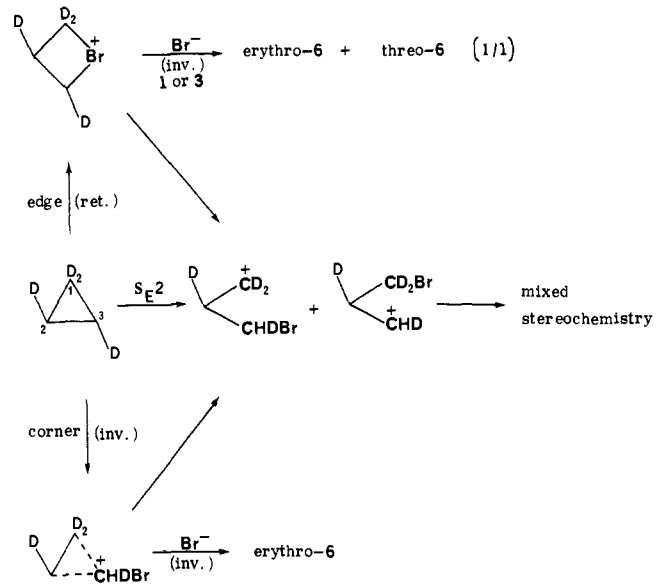
ythro/threo ratio for **6** is different for each mechanism. The stereoisomeric ratio for **6** may be determined from the ^{1}H resonance of the 2-proton. Although the two stereoisomers should give about the same chemical shift, they differ in their vicinal coupling constant with the 3-proton. The expected pair of doublets may be integrated to obtain the erythro/threo ratio. The proton resonances of **5** fall on those of the 3-proton of 6, but these resonances are not of interest. In using **6** as our probe, we ignore the stereochemical consequences of 2,3-opening (to give **5**) and use the chemically equivalent 1,2- and 1,3-bonds.

Our synthesis of **4** began with *trans*-β-bromostyrene and led in four steps to cyclopropanecarboxylic-*2,2,trans-3-d*$_3$ acid.[7] Reduction with B_2D_6 to the D_5 alcohol, oxidation with PCC to the D_4 aldehyde, and stereospecific decarbonylation with Rh(PPh$_3$)$_3$Cl gave **4**. The trans stereochemistry was confirmed by the value of the vicinal coupling constant, 4.1 Hz, from the carbon-13 satellite. The aldehyde was 85% trans and 15% cis; this ratio should carry over to the cyclopropane product.

Bromination was begun at −78 °C in the absence of solvent and light, with a catalytic amount (0.1 equiv compared with cyclopropane) of iron filings, and was completed at room temperature for 24 h. The absence of radical contributions was confirmed by the lack of effect on the reaction mixture by addition of 0.1 equiv of isoamyl nitrite or *N*-bromosuccinimide. Under these conditions, the desired 1,3-dibromopropane was a major product. The resonance of interest at δ 2.35, from the 2-proton of **6**, was present as one doublet with $J = 7 \pm 0.5$ Hz, confirmed at 90, 270, and 500 MHz.[1] The maximum height of any second doublet was estimated to be <15%, corresponding to the extent of nonstereospecific label in **4**. The large, 7-Hz coupling is consistent with the anti arrangement in the major conformer of *erythro*-**6**. Thus we conclude that the trans cyclopropane gave only the erythro product, within the accuracy of the experiment (probably >85%).

Scheme I shows possible stereochemical outcomes for 1,3 opening (1,2 opening would give equivalent results). The most likely stereochemistry for edge bromination is retention for the electrophilic step and inversion for the nucleophilic step.[2] The electrophilic step leaves the stereochemistry intact. Nucleophilic attack then gives *erythro*-**6** and *threo*-**6** in equal amounts, since bromide can attack with equal likelihood at the 1- and 3-positions. Any retention/inversion or inversion/retention mechanism in fact will give a 1/1 erythro/threo ratio. An open carbocation from a one-step S_E2 mechanism or from any of various multistep reactons could have a stereospecific electrophilic step but a nonstereoselective nucleophilic step. Although there are several stereochemical variants, they all give mixed stereochemistries. Thus the observation of >85% *erythro*-**6** excludes edge bromination and open carbocation formation. The only exception would

Scheme I



be the unlikely case that edge attack occurs with inversion.

Corner bromination is the only reasonable mechanism consistent with the observed result. Attack at the corner position with inversion[8] followed by nucleophilic attack with inversion on ion **1** leads exclusively to *erythro*-**6**. If **1** were simply the S_E2 transition state leading to an open carbocation, a mixed stereochemistry should have been observed. The observed stereospecificity of the reaction requires an intermediate of the type **1**, which contains a formally pentavalent carbon. With **4** now in hand, we are studying additional electrophilic reactions of cyclopropane, in hopes of uncovering other unusual intermediates.

(6) Collins, C. J. *Chem. Rev.* **1969**, *69*, 543–550.
(7) Berson, J. A.; Pederson, L. D.; Carpenter, B. K. *J. Am. Chem. Soc.* **1976**, *98*, 122–143.

(8) Corner electrophilic attack also could occur with retention but is contrary to our observation. This pathway would lead to 1/1 erythro/threo, if nucleophilic attack occurs with inversion. In general, any inversion/inversion mechanism gives only *erythro*-**6**. Similarly, any retention/retention mechanism gives only *threo*-**6**. The corner-brominated intermediate shown in Scheme I is a structural variant of **2** and is not intended to imply any difference.

Paramagnetic Phosphine Shift Reagents: New Probes for the Study of Structures of Transition-Metal Complexes in Solution

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Conventional paramagnetic shift reagents utilize the Lewis base affinity of metal ions for binding of substrates.[1] We report here the first of a complementary group of shift reagents that bind to Lewis acids and that have great potential for the elucidation of structure of metal complexes in solution. Owing to the ubiquitous presence of phosphines in organometallics and current interest in structural identification of catalytic intermediates by NMR, we have initially focussed attention on shift reagents containing a phosphorus donor.

When the donor lies along a 3-fold axis of the complex the dipolar shift equations accurately allow the comparison of shifts calculated from distances and angles based on model compounds.[2,3]

(1) "NMR of Paramagnetic Molecules"; LaMar, G. N., Horrocks, DeW., Jr., Holm, R. H. Eds.; Academic Press: New York, 1973.
(2) White, D. L.; Faller, J. W. *J. Am. Chem. Soc.* **1982**, *104*, 1548–1552; *Inorg. Chem.* **1982**, *21*, 3119–3122.

0002-7863/84/1506-0793$01.50/0