J. Am. Chem. Soc. **1990**, *112*, 2462–2464

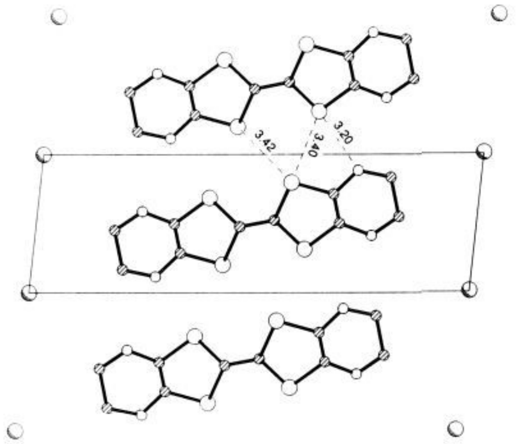
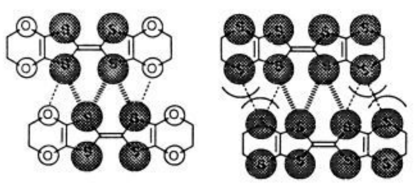


Figure 2. Projection of a unit cell of (BEDO)$_{2.4}$I$_3$ down the *b* axis. The triiodide counterions are at the corners of the unit cell. Two additional molecules in adjacent stacks are also shown to indicate the short interchalcogen contacts. Refer to footnote 11 for details.

different cation arrangement and I$^-$, rather than I$_3^-$.

The *b*-axis projection which coincides for the two lattices is shown in Figure 2. The shortest average[14] S–S contact (which is only of fulvenoid sulfurs) is 3.402 Å, *0.29 Å shorter than the corresponding distance* in α-(BEDT-TTF)$_2$I$_3$. The shortest interstack S–O contact is 3.206 Å, 0.12 Å shorter than the sum of O and S van der Waals radii.[15] In the refinement of the displacive modulations, the BEDO molecules were treated as rigid bodies. The displacements of the BEDO molecules have an amplitude of 0.033 Å, in the direction approximately along the long molecular axis. These displacements are smaller than those observed in β-(ET)$_2$I$_3$,[16] a difference that correlates with the strength of the S–S interactions.

Assuming, in analogy to the (TMTSF)$_2$X salts,[3] that the important intermolecular interactions responsible for the electronic properties of these solids are due to the fulvene chalcogens, we conclude that the stabilization of the metallic state in (BEDO)$_{2.4}$I$_3$, relative to BEDT-TTF salts, is due to the enhanced overlap between fulvene sulfur atoms facilitated by the decreased steric bulk of the ethylenedioxo relative to the ethylenedithio substituents, as shown schematically below, where the heavier dashed lines represent the fulvene sulfur interactions.



BEDO2.4I3   α (BEDT-TTF)2I3

The effect of oxygen in (BEDO)$_{2.4}$I$_3$ is therefore not only electronic but also, and perhaps more importantly, one of *steric enhancement of intermolecular interaction.*

Acknowledgment. We thank the National Science Foundation for support through Grant DMR-88-20933.

Supplementary Material Available: Results of magnetic measurements and thermopower and positional and thermal parameters of (BEDO)$_{2.4}$I$_3$ (4 pages). Ordering information is given on any current masthead page.

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[14] The average value does not take into account the displacive modulation which introduces a shortening in some and a lengthening in other unit cells.

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[16] Leung, P. C. W.; Emge, T. J.; Beno, M. A.; Wang, H. H.; Williams, J. M.; Petricek, V.; Coppens, P. *J. Am. Chem. Soc.* **1985**, *107*, 6184.

Nucleophilic Cleavage of One-Electron σ Bonds: Stereochemistry and Cleavage Rates

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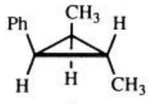
Received November 30, 1989

Nucleophilic addition reactions represent one of the most common reaction pathways available to organic cation radicals. These reactions have been the subject of current interest[1] and even some controversy.[2] It is interesting to note that, to date, efforts toward understanding these reactions have largely focused on the addition of nucleophiles to π cation radicals. In contrast, nucleophilic cleavages of cation radical σ bonds have received relatively little attention.[3] In this paper we describe experiments that define the stereochemistry of several nucleophilic one-electron C–C bond cleavages as well as provide rate constants for nucleophilic cleavage.

Arylcyclopropane cation radicals were chosen as substrates for determining the stereochemistry of nucleophilic one-electron σ bond cleavage based upon the work of Rao and Hixson.[4] These workers showed that the *p*-dicyanobenzene-photosensitized oxidation of phenylcyclopropane (**1**) and 1,1-diphenylcyclopropane (**2**) resulted in methanol addition products that were best rationalized as arising from nucleophilic capture of *ring-closed* cyclopropane cation radicals.[5] Ring-closed structures for $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ are also consistent with thermodynamic cycle calculations which place the cyclopropane one-electron bond energies of $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ at ca. 15 and 7 kcal mol^{-1}, respectively.[6]

If the arylcyclopropane cation radicals do indeed have ring-closed structures, they provide potential substrates for determining the stereochemistry of nucleophilic one-electron σ bond cleavages. Accordingly, cyclopropanes **3–5** were prepared for this purpose.[7]



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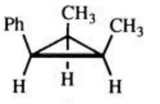

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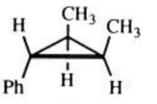

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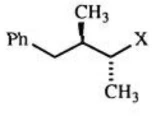
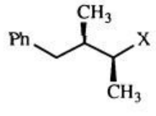
The 1-cyanonaphthalene (1-CN) photosensitized oxidations of **3–5** were performed in degassed acetonitrile/methanol (12:1 v/v) solution by irradiation using 300-nm Rayonet lamps. Reaction of **3** under these conditions produced erythro ether **6**[8] as the sole detectable product (96% yield). In contrast, the cleavage reactions of **4** and **5** produced only threo ether **7**[8] (83% yield). Product analysis by gas chromatography revealed that **6** and **7** were intercontaminated with each other by <0.1%. *These stereochemical results are consistent with the nucleophilic ring-opening of* $\mathbf{3}^{\bullet+}$*–*$\mathbf{5}^{\bullet+}$ *with essentially complete inversion of configuration at carbon.* Ring-opening of the cation radicals, during or after electron transfer, followed by rapid nucleophilic capture is excluded by the fact that the photolyses of **3–5** and 1-CN in the absence of methanol resulted in no detectable interconversion of the cyclopropanes.



6: X = OCH$_3$
8: X = OH
10: X = CN



7: X = OCH$_3$
9: X = OH
11: X = CN

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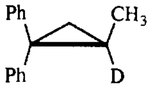
[‡] Fellow of the Alfred P. Sloan Foundation, 1988–1989.
[§] Eastman Kodak Company.

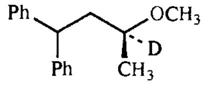
0002-7863/90/1512-2462$02.50/0

The photooxidative cleavages of **3**–**5** also proceeded with inversion of configuration with two other nucleophiles: water and cyanide ion. Thus photooxidation of **3** in acetonitrile/water (15:1 v/v) produced erythro alcohol **8**[8] as the sole product (82% yield, >99.8% pure). Cyclopropanes **4** and **5**, however, formed only threo alcohol **9**[8] (74% yield, >99.8% pure). Photolyses in the presence of cyanide were performed in acetonitrile/H_2O (6:1 v/v) containing 1.1 M KCN. Under these conditions, **3** formed **10**[8] (>99.8% pure), and **4**–**5** formed **11**[8] (>99.7% pure).[9]

Optically active (*R*)-(−)-1,1-diphenyl-2-deuterio-2-methylcyclopropane (**12**) was also used to probe the stereochemistry of nucleophilic one-electron bond cleavage. Photooxidation of **12**[10a] (22.8 (3)%[11] optically pure) in acetonitrile/methanol produced, regioselectively, *S* ether **13**[10b] (22.5 (7)% optically pure). This result requires addition of methanol with 99 (4)% inversion.



12



13

Why do these nucleophilic cleavage reactions proceed with inversion of configuration? Perhaps the simplest explanation is provided by the valence-bond configuration-mixing model for constructing state correlation diagrams.[12] This theoretical approach identifies the correlation that connects the electronic configurations of the reactants and products and the major orbital interactions involved in the correlations. The key interaction is identified as that between the nonbonding orbital of the nucleophile (n) and the σ^* orbital of the cation radical. At the intended surface crossing (transition state), the inversion geometry will have a positive orbital overlap between the n and σ^* orbitals while the retention transition state geometry should have ca. zero orbital overlap (by symmetry). Therefore the larger resonance interaction, and thus lower activation barrier, is achieved for the inversion transition state.[13]

Experimentally, we next sought to measure rate constants for the nucleophilic cleavage of the one-electron σ bond in the phenylcyclopropane cation radical (**1**$^{\bullet+}$) by using laser flash photolysis. Pulsed laser excitation (406 nm, 15 ns, 5 mJ) of an acetonitrile solution containing 9,10-dicyanoanthracene (ca. 10^{-5} M), **1** (0.25 M), and *p*-cyano-*N*-methylpyridinium tetrafluoroborate[14] (10^{-2} M) resulted in the rapid appearance of a transient species with a λ_{max} at 550 nm ($\tau \approx 1$ μs).[15] This species reacted rapidly with 1,2,4,5-tetramethoxybenzene (TMB) ($k_q = 1.9\ (5) \times 10^{10}$ M^{-1} s^{-1}) and also with tri-*p*-tolylamine to form the corresponding aminium ion ($\lambda_{max} = 670$ nm). The transient also reacted with methanol. The second-order rate constant for reaction with MeOH ($k_m = 9.5\ (4) \times 10^7$ M^{-1} s^{-1}) was obtained from the slope of a plot of the decay rates vs [MeOH]. On the basis of this data, we assign the transient species to **1**$^{\bullet+}$. This assignment is supported by γ-radiolysis studies, which have assigned a broad absorption at ≈550 nm to **1**$^{\bullet+}$.[16] It is further supported by the following steady-state quenching experiments. Addition of varying concentrations of TMB (10^{-3}–10^{-4} M) to an acetonitrile solution containing **1**, 1-CN, and MeOH (0.25 M) lowers the quantum yield for formation of $Ph(CH_2)_3OCH_3$. A plot of ϕ_0/ϕ vs [TMB] provided a Stern–Volmer slope (k_q/k_m[MeOH]) of 1.04 (9) × 10^3 M^{-1}. Multiplying the slope by the methanol concentration gives an estimate for k_q/k_m of 2.6 (2) × 10^2, which is in good agreement with the value obtained from flash photolysis, 2.0 (6) × 10^2. Finally, it is worth pointing out that the rate constant for reaction of methanol with **1**$^{\bullet+}$ (9.5 (4) × 10^7 M^{-1} s^{-1}) is comparable to that found for π cation radicals. For example, MeOH adds to the 1,1-dimethylindene cation radical with a rate constant of 9.6 × 10^6 M^{-1} s^{-1}.[17]

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(5) The photooxidative ring-opening reactions of other cyclopropane derivatives may also involve the nucleophilic cleavage of one-electron σ bonds. (a) Mizuno, K.; Ogawa, J.; Kagano, H.; Otsuji, Y. *Chem. Lett.* **1981**, 437. (b) Mizuno, K.; Ogawa, J.; Otsuji, Y. *Chem. Lett.* **1981**, 741. (c) Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977. (d) Gassman, P. G.; Olson, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 3740. (e) Mazzocchi, P. H.; Somich, C.; Edwards, M.; Morgan, T.; Ammon, H. L. *J. Am. Chem. Soc.* **1986**, *108*, 6828. (f) Mazzocchi, P. H.; Somich, C. *Tetrahedron Lett.* **1988**, *29*, 513.

(6) The C1–C2 one-electron bond energies in **1**$^{\bullet+}$ and **2**$^{\bullet+}$, BDE(CR), were calculated from the equation BDE(CR) = BDE(N) + E_{ox}(TB) − E_{ox}(N), where BDE(N) is the homolytic bond dissociation energy of the C1–C2 bond in **1** or **2**, E_{ox}(TB) is the oxidation potential of the trimethylene biradical produced by homolytic cleavage, and E_{ox}(N) is the oxidation potential of **1** or **2**. BDE(N)s for **1** and **2** were estimated to be 46 and 42 kcal/mol, respectively, based upon group additivity relationships. For **1**, BDE(N) was calculated by taking the C–C BDE for cyclopropane (59 kcal/mol)[6a] and correcting it for the effect of phenyl substitution by adding the difference between the C–H BDEs for PhCHMe–H (85 kcal/mol)[6b] and $MeCH_2$–H (98 kcal/mol).[6b] For **2**, BDE(N) was calculated by taking the C–C BDE for cyclopropane (59 kcal/mol)[6a] and correcting it for the effect of diphenyl substitution by adding the difference between the C–H BDEs for Ph_2CMe–H (81 kcal/mol)[6b] and $MeCH_2$–H (98 kcal/mol).[6b] E_{ox}(TB) values for **1** and **2** were approximated by the oxidation potentials of the 1-phenylethyl radical (0.37 V vs SCE)[6c] and the 1,1-diphenylethyl radical (0.23 V),[6c] respectively. E_{ox}(N) values for **1** (1.74 V) and **2** (1.75 V) were obtained by cyclic voltammetry (150 mV/s) at a platinum disk electrode in acetonitrile with ca. 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte and were irreversible. The potentials ($E_{p/2}$) were referenced to internal ferrocene (0.31 V vs SCE). (a) Doering, W. v. E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279. (b) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. (c) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

(7) Cyclopropanes **3**–**5** were prepared by cyclopropanation (Olofson, R. A.; Dougherty, C. M. *J. Am. Chem. Soc.* **1973**, *95*, 581) of *trans*- and *cis*-2-butene.

(8) Erythro ether **6** was independently prepared by ring-opening of *trans*-2,3-epoxybutane with benzyl magnesium bromide followed by methylation of the resulting erythro alcohol (**8**) with methyl iodide. Nitrile **11** was prepared from **8** in two steps by tosylation followed by reaction with potassium cyanide. Compounds **7**, **9**, and **10** were prepared by an analogous series of reactions starting with *cis*-2,3-epoxybutane.

(9) In addition to nitriles **10** and **11**, lesser amounts of the alcohols **8** and **9** were formed from **3** and **4**/**5**, respectively. The photochemical conditions for cyanation were modeled after literature procedures. (a) Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 535. (b) Reference 5b.

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(11) The standard deviation in the last digit is given in parentheses.

(12) For recent reviews, see: (a) Pross, A.; Shaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363. (b) Pross, A. *Adv. Phys. Org. Chem.* **1985**, *21*, 99. (c) Shaik, S. S. *Prog. Phys. Org. Chem.* **1985**, *15*, 197. (d) Shaik, S. S. In *New Theoretical Concepts for Understanding Organic Reactions*; Bertrân, J., Csizmadia, I. G., Eds.; Reidel: Dordrecht, 1989; NATO ASI Series, Vol. 267, p 165.

(13) A more detailed theoretical analysis of this and related problems will be provided elsewhere: Shaik, S. S.; Dinnocenzo, J. P., manuscript in preparation.

(14) The absorbance of the 9,10-dicyanoanthracene (DCA) anion radical partially overlaps with the phenylcyclopropane cation radical absorbance. We therefore added *p*-cyano-*N*-methylpyridinium tetrafluoroborate, which reacts with DCA$^{\bullet-}$ by electron transfer to form a radical, which is transparent at 550 nm. Similar but less effective results could be obtained by dioxygen saturation of the flash photolysis solutions.[3]

(15) In the absence of added quenchers or nucleophiles, the transient species decays by a first-order process. We have tentatively attributed this decay to a nucleophilic reaction with the solvent, acetonitrile. Consistent with this hypothesis, dilution of the solvent with large amounts of the nonnucleophilic alcohol $(CF_3)_2CHCOH$ (2–5 M) increases the lifetime of the transient.

(16) Andrews, L.; Harvey, J. A.; Kelsall, B. J.; Duffey, D. C. *J. Am. Chem. Soc.* **1981**, *103*, 6415.

The rate constants for the reaction of *i*-PrOH (k_i) and *t*-BuOH (k_t) with $1^{\bullet+}$ were also determined by flash photolysis: $k_i = 5.5$ (3) $\times 10^7$ and $k_t = 1.8$ (1) $\times 10^7$ M^{-1} s^{-1}. Interestingly, a comparison of the rate constants for MeOH, *i*-PrOH, and *t*-BuOH reveals a relative reactivity of ≈5:3:1, respectively. This shows that the *nucleophilic ring-opening of* $1^{\bullet+}$ *is remarkably insensitive to the steric environment of the nucleophile.* Some insight into this surprising observation may be provided by theory.

Molecular orbital calculations show that one-electron oxidation can be accompanied by large structural distortions.[18] For example, despite a one-electron bond energy of ≈50 kcal mol^{-1}, the ethane cation radical is calculated to have a C–C bond length of ca. 2 Å and a H–C–C bond angle of only 98°.[19] Similar structural changes have been calculated for cyclopropane cation radicals.[20] These structural changes are expected to lead to an "early" transition state for nucleophilic displacements on one-electron C–C bonds, which, in turn, should diminish steric effects on the reactions. The near equal reactivity of $1^{\bullet+}$ with MeOH, *i*-PrOH, and *t*-BuOH is consistent with this expectation.

In summary, arylcyclopropane cation radicals undergo nucleophilic substitution by a variety of nucleophiles with inversion of configuration at carbon. Furthermore, these substitution reactions have both diminished steric requirements and large reaction rate constants. Currently, we are investigating the reaction characteristics of other nucleophilic one-electron bond cleavages.

Acknowledgment. We thank Professor H. M. Walborsky (Florida State University) for sending us a generous sample of optically enriched **12** and Professor S. S. Shaik (Ben-Gurion University) for several enlightening discussions and for his encouragement. Research support was provided by the National Science Foundation (CHE86-10404) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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Stereochemistry of the Oxidative Addition of an Epoxide to Platinum(II): Relevance to Catalytic Reactions of Epoxides

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The activation of epoxides by transition-metal catalysts (A → B, Scheme I) is thought to occur by oxidative addition. Only a few examples of oxametallacyclobutane products have been isolated or fully characterized, and the mechanism for their preparation by oxidative addition has not been determined unambiguously.[1-3] The overall catalytic cycle shown in Scheme I may occur with overall retention of stereochemistry, as has been demonstrated by using the reagent *trans*-CHDCHDO with a copper(I) catalyst. It is not known whether this cycle occurs by double retention or double inversion of stereochemistry.[2,3] Other related reactions are complicated by hydrogen atom migration or exchange.[4,5]

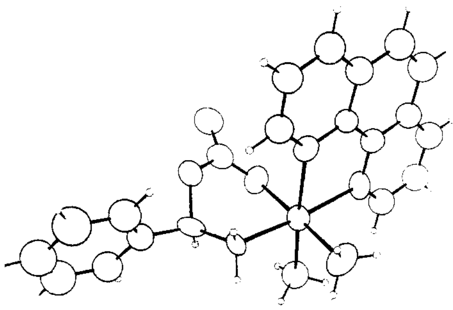
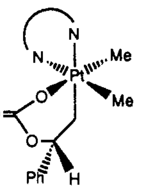
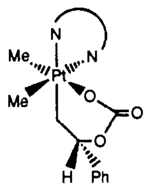


Figure 1. A view of the structure of complex **2**-RΔ.

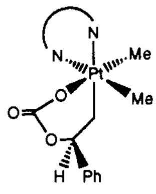
The recent discovery of the conversion A → C shown in Scheme I, L_nM = [PtMe$_2$(1,10-phenanthroline)] (**1**), in which the intermediate B is trapped by carbon dioxide to give the stable metallacarbonate C,[5,6] provides a reaction for which the stereochemistry of epoxide oxidative addition can be assessed.[7] The product of reaction of styrene oxide, carbon dioxide, and **1** can adopt two diastereomeric forms, each of which has two enantiomeric forms.[8] The isomers **2**-RΔ/**2**-SΛ and **2**-RΛ/**2**-SΔ are possible, in which R/S and Λ/Δ describe the chiralities at carbon and platinum, respectively.[8] NMR studies reveal that both diastereomers are present in a ratio of ≈5:1, but resonances cannot be assigned to a specific diastereomer.[7,8]



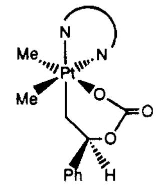
2-SΛ



2-RΔ



2-RΛ



2-SΔ

Reaction of (*R*)-styrene oxide and CO$_2$ with **1** gave crystals of **2** in two crystalline forms. Thin colorless platy crystals[9] were readily grown on many occasions from methylene chloride solutions layered with pentane. These crystals were not suitable for a Bijvoet study. From one recrystallization attempt, a single, pale yellow, prismatic crystal was obtained, which was cut into three pieces. The smallest fragment, of dimensions 0.45 × 0.45 × 0.45 mm, was used in the X-ray determination,[10] while the other two were used for NMR experiments, vide infra. The molecular structure was shown to be that of the **2**-RΔ isomer by the Bijvoet method, Figure 1. Thus retention of configuration at the chiral carbon center is observed on oxidative addition of the epoxide.[11] When either the single-crystal fragments or the platy crystals were

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(8) There are several other possible isomers; however, only those containing the stable *fac*-trialkylplatinum(IV) units are viable, and mer isomers need not be considered.

(9) Orthorhombic, space group $P2_12_12_1$, with cell dimensions $a = 9.757$ (6) Å, $b = 27.47$ (2) Å, $c = 7.122$ (4) Å, $V = 1909$ Å^3, $Z = 4$.

(10) $\overline{\mathrm{Pt(CH_3)_2\{CH_2CH(C_6H_5)OC(O)O}}\}$(phen), monoclinic, space group $P2_1$, $a = 11.185$ (2) Å, $b = 14.622$ (3) Å, $c = 6.350$ (2) Å, $\beta = 105.77$ (2)°, $V = 999.5$ (7) Å^3, $Z = 2$, λ (Mo Kα) = 0.71073 Å, Zr prefilter, $\mu = 711.6$ mm^{-1}, $R_1 = 0.0658$ and $R_2 = 0.0683$. The data were processed by using the Enraf-Nonius Structure Determination Package.

0002-7863/90/1512-2464$02.50/0