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- (5) (a) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2715–2724. (b) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *ibid.* **1976**, *98*, 6733–6735. (c) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333–340.
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- (10) The thorium compound, **1a**, displays infrared absorptions (Nujol mull) characteristic of an $\eta^5\text{-}(\text{C}_6\text{H}_5)_2\text{C}_5\text{H}_5$ ligand⁹ at 1019 and 799 cm^{-1} , as well as bands at 1655, 1252, and 1220 cm^{-1} . ¹H NMR signals (C_6D_6) are observed at δ 2.19 (30 H, s) and 2.03 (6 H, s). Anal. Calcd for $\text{C}_{48}\text{H}_{72}\text{Th}_2\text{O}_4$: C, 48.98; H, 6.17; mol wt, 1177 g/mol. Found: C, 49.84; H, 6.20; mol wt, 1210 \pm 10% g/mol (cryoscopic in benzene). The uranium derivative, **1b**, exhibits an identical infrared spectrum. Isotopically shifted singlets are observed in the ¹H NMR (C_6D_6) at δ 0.22 (30 H) and 1.08 (6 H). Anal. Calcd for $\text{C}_{48}\text{H}_{72}\text{U}_2\text{O}_4$: C, 48.48; H, 6.02; mol wt, 1189 g/mol. Found: C, 48.56; H, 6.13; mol wt, 1167 \pm 10% g/mol (cryoscopic in benzene).
- (11) Refinement is continuing with the more complete (2θ (Mo K α) < 63.7°) data set.
- (12) Petersen, J. L.; Lichtenberger, D. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6433–6441, and references therein.
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- (14) "Tables of Interatomic Distances and Configurations in Molecules and Ions; *Chem. Soc., Spec. Publ.* **1965**, No. 18, M665.
- (15) The bis(pentamethylcyclopentadienyl)uranium and -thorium bis(trimethylsilylmethyl) derivatives were prepared with trimethylsilylmethylolithium using the procedure employed for the dimethyls.³ The air-sensitive products were recrystallized from pentane. Anal. Calcd for $\text{C}_{28}\text{H}_{52}\text{USi}_2$: C, 49.25; H, 7.67; mol wt, 683 g/mol. Found: C, 48.96; H, 7.46; mol wt, 688 \pm 10% g/mol (cryoscopic in benzene). The infrared spectrum (Nujol mull) exhibits absorptions at 1252, 1241, 1018, 897, 820, 736, and 705 cm^{-1} . The ¹H NMR spectrum exhibits isotropically shifted singlets at δ 5.04 (30 H), –89 (4 H), and –6.14 (18 H). Anal. Calcd for $\text{C}_{28}\text{H}_{52}\text{ThSi}_2$: C, 49.68; H, 7.74; mol wt, 677 g/mol. Found: C, 49.57; H, 7.71; mol wt, 645 \pm 10% g/mol (cryoscopic in benzene). The infrared spectrum is identical with that of the uranium derivative. The ¹H NMR (C_6D_6) spectrum exhibits sharp singlets at δ 1.98 (30 H), –0.43 (4 H), and 0.31 (18 H).
- (16) For **2a**, the infrared spectrum (Nujol mull) displays bands at 1632, 1250, 1240, 1192, 1110, 1020, 956, 842, and 800 cm^{-1} ; the ¹H NMR spectrum (C_6D_6) exhibits singlets at δ 1.96 (30 H), 1.77 (4 H), and 0.31 (18 H). Anal. Calcd for $\text{C}_{30}\text{H}_{52}\text{ThO}_2\text{Si}_2$: C, 49.16; H, 7.15; mol wt, 733 g/mol. Found: C, 49.20; H, 7.19; mol wt, 781 \pm 10% g/mol (cryoscopic in benzene). The infrared spectrum of **2b** is identical with that of **2a**. The ¹H NMR (C_6D_6) exhibits isotropically shifted singlets at δ 1.89 (30 H), –8.72 (4 H), and –2.58 (18 H). Anal. Calcd for $\text{C}_{30}\text{H}_{52}\text{UO}_2\text{Si}_2$: C, 48.75; H, 7.09; mol wt, 739. Found: C, 48.67; H, 7.14; mol wt, 769 \pm 10% g/mol (cryoscopic in benzene).
- (17) Prepared from the corresponding dialkyls and dichlorides using the procedure of ref 3. Anal. Calcd for $\text{C}_{24}\text{H}_4\text{ThSiCl}$: C, 46.11; H, 6.61; Cl, 5.67 mol wt, 625 g/mol. Found: C, 46.16; H, 6.56; Cl, 6.40; mol wt, 660 \pm 10% g/mol (cryoscopic in benzene). The infrared spectrum (Nujol mull) exhibits absorptions at 1249, 1238, 1018, 892, 865, 850, 820, and 720 cm^{-1} . The ¹H NMR spectrum (C_6D_6) displays sharp singlets at δ 2.04 (30 H), 0.24 (2 H), and 0.45 (9 H). Anal. Calcd for $\text{C}_{24}\text{H}_4\text{USiCl}$: C, 45.67; H, 6.55; Cl, 5.62; mol wt, 631 g/mol. Found: C, 45.59; H, 6.59; Cl, 5.70; mol wt, 634 \pm 10% g/mol (cryoscopic in benzene). The infrared spectrum is identical with that of the thorium derivative; the ¹H NMR (C_6D_6) exhibits isotropically shifted singlets at δ 9.48 (30 H), –124 (2 H), and –11.52 (9 H).
- (18) The infrared spectrum of **3a** (Nujol mull) shows bands at 3075, $\nu_{\text{C}=\text{C}}$ 1576, 1253, 1243, ν_{CO} 1198, 1015, 1000, 842, 828, 752, and 685 cm^{-1} ; the ¹H NMR (C_6D_6) exhibits signals at δ 2.01 (30 H, s), 0.24 (9 H, s), 4.54 (1 H, s), and 4.88 (1 H, s). In the compound prepared from ¹³CO, $\nu_{\text{C}=\text{C}}$ and ν_{CO} shift to 1536 and 1168 cm^{-1} , respectively; the latter three ¹H NMR signals become doublets with $J_{\text{H}^{13}\text{C}} = 2.0, 9.6,$ and 6.6 Hz, respectively. Anal. Calcd for $\text{C}_{25}\text{H}_4\text{ThSiClO}$: C, 45.97; H, 6.33; Cl, 5.43; mol wt, 653 g/mol. Found: C, 45.89; H, 6.26; Cl, 5.39; mol wt, 690 \pm 10% g/mol (cryoscopic in benzene). The infrared spectral data of **3b** are identical with those of **3a**. The ¹H NMR (C_6D_6) displays isotropically shifted signals at δ 5.51 (30 H, s), –1.67 (9 H, s), 7.46 (1 H, s), and –11.08 (1 H, s). In the compound prepared from ¹³CO, the latter three signals become doublets with $J_{\text{H}^{13}\text{C}} = 2.0, 9.6,$ and 6.6 Hz, respectively. Anal. Calcd for $\text{C}_{25}\text{H}_4\text{USiClO}$: C,
- 45.55; H, 6.27; Cl, 5.38; mol wt, 659 g/mol. Found: C, 45.37; H, 6.27; Cl, 5.75; mol wt, 623 \pm 10% g/mol (cryoscopic in benzene).
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- (20) (a) In the case of $\text{Zr}(\text{C}_5\text{H}_5)_2(\text{OCCH}_3)(\text{CH}_3)^{\text{bb}}$ and $\text{Ti}(\text{C}_6\text{H}_5)_2(\text{OCCH}_3)(\text{Cl})^{\text{ea}}$ coordination of the oxygen atom allows the metal ion to achieve an 18-electron valence shell. This stabilization may explain the reluctance to incorporate a second CO molecule.^{20b} The rapidity of the second addition for the organoactinides reasonably reflects the expected relaxation of such electronic (and steric) constraints. (b) For the structure of a formally 20-electron bis(cyclopentadienyl)hafnium compound, see Johnson, P. L.; Cohen, S. A.; Marks, T. J.; Williams, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 2709–2716 ($\text{Hf}(\text{CH}_2\text{C}_5\text{H}_4)_2(\text{BH}_4)_2$).
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Novel Photochemical Addition Reactions of Iminium Salts. Electron Transfer Initiated Additions of Olefins to 2-Phenyl-1-pyrrolinium Perchlorate

Sir:

We recently described a novel photocyclization reaction involving the conversion of *N*-allyliminium salts to pyrrolidines.¹ In order to gain more information about the mechanistic details of this process and to probe its generality, we have initiated a more broadly targeted study of the photochemical behavior of iminium salt-olefin systems. We report here the results of our preliminary efforts using a simple iminium salt, 2-phenyl-1-pyrrolinium perchlorate (**1**), and a series of olefins of varying electron-donating ability.

Irradiations² of methanolic solutions of **1** (14 mM) containing isobutylene, cyclohexene, methyl β,β -dimethylacrylate, or 1,3-butadiene (1 M) gave after neutralization and chromatographic separation the pyrrolidine ethers and olefins shown in Chart 1. Triplet-sensitized irradiations of **1** in the presence of isobutylene using benzophenone, acetone, or xanthone failed to promote formation of the ether **2**. Triplet energy transfer from Ph_2CO to **1** is occurring under these conditions since **1** quenches both photoreduction and oxetane-forming processes. Structural assignments⁴ to the photoproducts were made using characteristic spectroscopic properties⁵ and, in selected cases, by independent synthesis. Interestingly, pyrrolizidine **11**,⁴ prepared by reduction (LiAlH_4) of the thermodynamic epimer of **6**, was derived

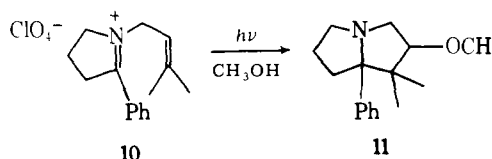
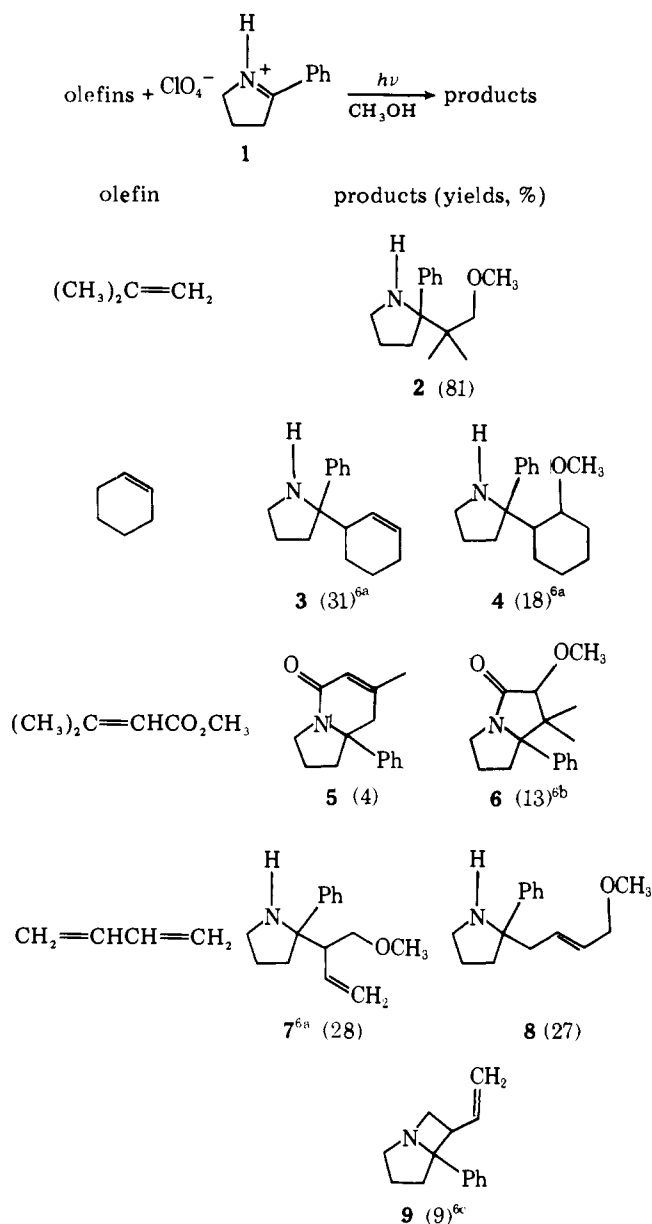


Chart I

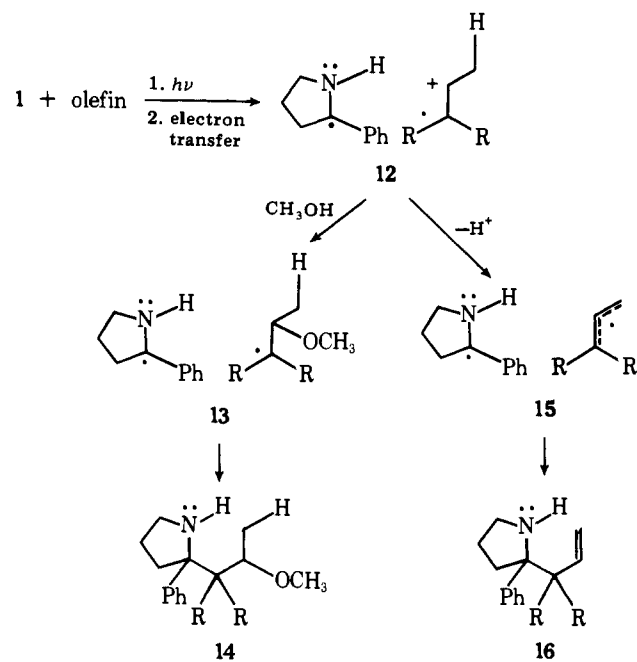


(50%) as a 1:1 epimeric mixture by irradiation of a methanolic solution of the isopentenyliminium perchlorate **10**.

Mechanisms for these interesting photoaddition reactions involving [2 + 2] cycloaddition of olefin to $\text{R}_2\text{C}=\text{N}^+\text{R}_2$ chromophore do not appear adequate in rationalizing the observed reaction regiochemistries⁷ nor would they account for the anticipated stability of the intermediate azetidinium salts.⁸ Indeed, the vinylazetidene **9** is not converted to ether **7** under the reaction conditions or the more rigorous refluxing methanolic HClO_4 .

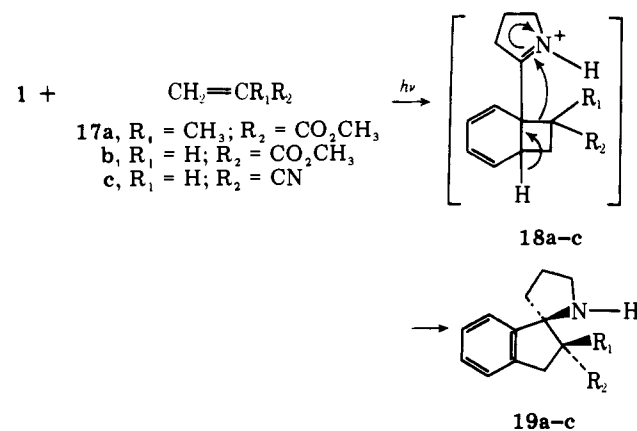
On the other hand, the structural and regiochemical features of these reactions appear nicely rationalized using the electron-transfer mechanisms presented in Chart II. The initial steps of these processes are analogous to those summoned by Arnold⁹ to explain the interesting anti-Markovnikoff additions of nucleophiles to olefins. Accordingly, methanol attack on the radical-cation fragment of the charged radical pair **12**, formed by electron transfer from the electron-rich olefin to singlet iminium salt, is expected⁹ to lead to the more stable radical pair **13**.¹⁰ Collapse of **13** would then generate the observed amino ether addition products **14**. Alternatively, deprotonation of **12** followed by radical coupling leads to the olefin adducts.¹¹ The

Chart II



fused bicyclic lactams from reactions with the dimethyl acrylate ester are a result of secondary lactamization of initially formed ether and olefin adducts.

Studies with electron-poor olefins have provided further support for this mechanistic rationale. The criteria for electron transfer based upon respective oxidation and reduction potentials and acceptor singlet energy have been outlined by Weller.¹² Indeed, the calculated rates of electron transfer (k_{et}) from the electron-rich olefinic substrates employed above to 1^{S_1} are calculated to be near the diffusion controlled limit ($\sim 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).¹³ Although methyl β,β -dimethylacrylate^{13g} is expected to transfer an electron to 1^{S_1} rapidly ($k_{\text{et}} \sim 7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), the less substituted olefins, methyl methacrylate, methyl acrylate, and acrylonitrile **17a-c**, should be poorer



donors ($k_{\text{et}} = 8 \times 10^2$, 7×10^{-6} , and $1 \times 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$, respectively).^{12,13} Importantly, irradiations⁴ of methanolic or acetonitrile solutions of **1** in the presence of olefins **17a-c** (1 M) do not produce pyrrolidine ether or olefin products. Instead, the spirocyclic amines **19a-c** are generated in reasonably high yields (45–50%).¹⁴ Structural assignments to these substances were made using spectroscopic data, and, for **19b-c**, by X-ray analysis of the HClO_4 salt of the syn epimer of **19c** ($\text{R}_1 = \text{CN}$; $\text{R}_2 = \text{H}$), interconversion of the nitriles **19c** (NaOCH_3 , CH_3OH), and independent conversions of the nitriles **19c** to esters **19b** (H_2SO_4 , CH_3OH).

Formation of the spirocyclic amines appears to involve initial

olefin-arene [2 + 2] cycloaddition¹⁵ followed by ring expansion and deprotonation. Thus, the nature of the photoaddition pathways followed by **1** appears to be critically dependent on the electron-donating ability of the olefin in a way strongly suggestive of electron-transfer mechanisms for pyrrolidine ether and olefin formation. Thus, competition between addition and cycloaddition might be regulated at an olefin-iminium salt exciplex stage by the relative magnitudes of k_{et} and k_{2+2} . Also, it is quite likely that the intramolecular version of this new photochemical reaction¹ observed for *N*-allyliminium salt systems also follows an electron-transfer mechanism. Further studies are underway to probe further the mechanistic details and synthetic potential of these reactions.

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References and Notes

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- A 450-W Hanovia, medium-pressure lamp, water-cooled immersion well, and Correx filter were used.
- (a) The iminium salt **1** is prepared in situ from 2-phenyl-1-pyrroline^{3b} and 1.34 equiv of HClO₄ or as a crystalline substance, mp 116–117 °C.⁴ Addition of HClO₄ to the pyrroline results in a decrease in the UV-absorption maximum at 243 nm and an increase at 264 nm (isosbestic 251 nm) which is reversible. (b) D. F. Starr, H. Bulbrook, and R. H. Hixon, *J. Am. Chem. Soc.*, **54**, 3971 (1932); S. J. Love and J. A. Moore, *J. Org. Chem.*, **33**, 2361 (1968).
- Spectroscopic and analytical data for all new compounds were in perfect accord with assigned structures.
- The mass spectra of **2**, **3**, **4**, **7**, and **8** all show a base peak at *m/e* 146 (C₁₀H₁₂N by high resolution) characteristic of the phenylpyrrolidine fragment.
- (a) Obtained as an ~1:1 separable mixture of diastereomers. (b) Obtained as a separable 1:1 mixture of diastereomers which can be interconverted by treatment with methanolic sodium methoxide giving the thermodynamic epimer (methoxy group exo) in a 5.9:1 excess. (c) Obtained as one diastereomer only of undetermined stereochemistry.
- (a) Cycloaddition of isobutylene to 6-azapyrimidines^{7b} resulting in azetidine products show a reversed regiochemistry than would be required to rationalize our results. (b) J. S. Swenton and J. A. Hyatt, *J. Am. Chem. Soc.*, **96**, 4879 (1974). (c) However, cycloadditions of isobutylene and other electron-rich olefins to 3-ethoxyisoindolone^{7d} follow regiochemical courses which are consistent with our results. (d) A. Howard and T. H. Koch, *ibid.*, **97**, 7288 (1975).
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- A. J. Marouli, Y. Shigemitsu, and D. R. Arnold, *J. Am. Chem. Soc.*, **100**, 535 (1978), and references cited therein.
- Internal capture of the radical cation derived from electron transfer from 1,3-butadiene to 1^{S1} by the pyrrolidine nitrogen would lead to the diradical precursor of **9**.
- (a) An alternative explanation for the formation of the olefin products, via hydrogen-atom-abstraction pathways,^{11b} is possible. (b) N. Toshima, S. Asao, K. Takada, and H. Hirai, *Tetrahedron Lett.*, 5123 (1970).
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- (a) Contributions to the free energy and, thus, rate of electron transfer due to electrostatic attraction between charged radical products were ignored since they apply only when donor and acceptor molecules are neutral. (b) Experimentally determined $E_{1/2}(-)$ of **1** is ~0.99 V vs. SCE as expected on the basis of previous measurements.^{13c} (c) C. P. Andrieux and J. M. Saveant, *J. Electroanal. Chem.*, **26**, 223 (1970). (d) $E_{1/2}(+)$ of olefins were calculated from known ionization potentials^{13a} using the relationship of Miller.^{13f} (e) K. N. Houk and L. L. Munchausen, *J. Am. Chem. Soc.*, **98**, 937 (1976). (f) L. L. Miller, G. D. Nordblom, and E. A. Mayeda, *J. Org. Chem.*, **37**, 916 (1972). (g) Ionization potential of this ester was estimated using a cumulative methyl substituent effect.
- The amines **19b-c** were formed as 1:1.5 mixtures of anti ($R_1 = H$; $R_2 = CN$ or CO_2CH_3) and syn epimers and **19a** as a 4:3 epimeric mixture of unassigned stereochemistry.
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Stereochemistry of Free-Radical Substitution on the Peroxide Bond

Sir:

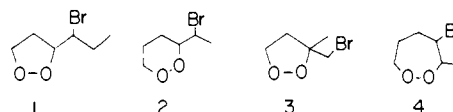
The stereochemical course of the S_H2 reaction has been the subject of intensive theoretical interest for some 40 years.^{1–3} Calculations suggest^{1,3} that homolytic substitution in simple three-atom systems occurs via a colinear geometry and scattering experiments support the linear arrangement for deuterium-halogen exchange.⁴ Examples of experiments designed to provide stereochemical information about the S_H2 reaction in more complicated organic systems are rare and studies have been limited to halogen atom substitution on cyclopropane carbon for the first row elements.^{5–7} Homolytic substitution on phosphorus⁸ and sulfur⁹ has been studied and inversion of configuration is generally observed, although the possibility of a metastable radical-addition intermediate may complicate the interpretation of these results.

Carbon radical attack on the peroxide bond represents an important pathway in the autoxidation of olefins. For example, intramolecular carbon radical substitution (S_{HI}) on the peroxide bond initiates the unzipping of styrene-oxygen copolymer.¹⁰ Because of the importance of this reaction in the ox-



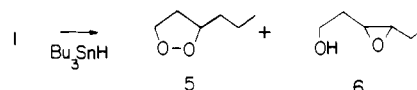
idation of polymers and natural products such as polyunsaturated lipids, we have initiated a study directed toward determining the stereochemical preference of carbon radical substitution on peroxide. We report here results of studies of the S_{HI} reaction in which the orientation of the attacking radical with respect to the peroxide bond is systematically varied. This approach gives information about the stereochemical preference of the substitution reaction and the results suggest that a "back-side attack" of the carbon radical on the peroxide bond is required.

The β-bromo peroxides **1–4** were prepared by reaction of



the corresponding mercuri bromides^{11,12} with molecular bromine.¹³ Compounds **1** and **2** are formed as threo and erythro diastereomers and **4** consists of a mixture of cis and trans isomers as prepared.¹² These diastereomers can all be separated by high pressure liquid chromatography (HPLC) on μ-Porasil with 5% ethyl acetate-hexane.

The bromo peroxides **1–4** were reacted with 1.0 equiv of tributyltin hydride in benzene at 25 °C with 2–5% *tert*-butyl hyponitrite initiator present.¹⁴ For example, reaction of **1** (threo or erythro) with 0.455 M tin hydride leads to a mixture of cyclic peroxide **5** and epoxy alcohol **6** in a **5:6** ratio of 82:18.



The epoxy alcohol **6** was formed as a 3:1 mixture of the trans and cis geometric isomers and this product distribution was independent of the stereochemistry (threo or erythro) of the starting β-bromo peroxide. The results of analogous reactions of **2**, **3**, and **4** with tributyltin hydride led to mixtures of the corresponding cyclic peroxides and epoxy alcohols.¹⁵ The epoxy alcohol **7** derived from **2** rearranges under the conditions of analysis to the furan and pyran products **8** and **9**. **7** was prepared independently from the corresponding olefin and was converted into **8** and **9** by traces of acid.