Table III. Comparison of Enantiomeric Ratios of
trans-2-Phenylcyclopropanecarboxylic Acid (4) to
Diastereomeric Ratios of Its Quinine Salt

recrystn no.	$[\alpha]^{22}{}_D$, deg, for acid[a]	ratio of acid enantiomers	ratio of diastereomeric salts
1	+113.9 (c 1.758, EtOH)	68.3/31.7	68.2/31.8
2	+156.8 (c 1.660, EtOH)	75.1/24.9	74.5/25.5
3	+168.8 (c 1.700, EtOH)	77.1/22.9	75.6/24.4

[a] The pure (+) acid has a specific rotation of +311.7° (c 1.776, EtOH).

from the peak heights of a pair of peaks representing the corresponding carbon atoms in each diastereomer. Since the specific rotations of the enantiomers of these two compounds were known, we could calculate the enantiomeric ratio from the specific rotation of the regenerated acid after each recrystallization. These diastereomeric and enantiomeric ratios were in good agreement (Tables II and III).

Weighing errors or the presence of impurities (water, solvents, other compounds, or particularly the amine enantiomer) affect the accuracy of the enantiomeric ratio determination but do not affect the diastereomeric ratio determination except for the unlikely superposition of a contaminent peak with one of the pair of peaks selected. Of course, as the peak height of one of the paired peaks approaches base line, the accuracy of the measurement of the peak height decreases. Approach to base line of one of the paired peaks provides direct indication of completion of the resolution.

Experimental Section

Partial Resolution of Compounds 3 and 4. The quinine salts of 2-phenylpropanoic acid (3) and trans-2-phenycyclopropanecarboxylic acid (4) were each recrystallized from a saturated solution of refluxing acetone. The salts were vacuum dried at room temperature. The partially resolved acids were regenerated from the salts by acidification with dilute sulfuric acid and extraction with ether. The ether solutions were washed and dried; the ether was evaporated, and the acids were vacuum dried at room temperature.
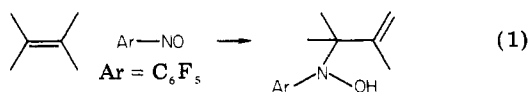
Communications

On the Reaction of the Nitroso Group with Olefins. Mechanisms of Ene Reactions[1]

Summary: Intra- and intermolecular isotope effects point to a two-step process for the reaction of pentafluoronitrosobenzene with tetramethylethylene to afford the ene product, 4—rate-determining formation of an intermediate (for which the aziridine N-oxide 5 is suggested) followed by C–H (or C–D) cleavage to the ene product.

Sir: Reaction of nitroso compounds with monoolefins has afforded a variety of results including the formation of paramagnetic species[2] and the formation of products of a simple ene reaction (eq 1).[3]

Recent studies have called attention to the importance of inadvertent photolysis of nitroso compounds as a source of some of the paramagnetic products;[4] and a study of the reaction of CF_3NO with a series of olefins[3c] has provided strong evidence for the (overall) ene reaction in this system. In these and some earlier studies the reasonable six-center mechanism (eq 2) was suggested. Some examples of olefin–carbonylnitroso[5a] reactions affording ene products of synthetic value also have been described.[5b]

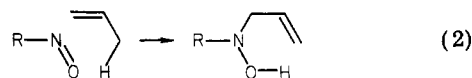Recently the ene reactions of singlet oxygen[6] and of triazolinediones[7] with some olefins have been shown to

(1) This work has been supported by the National Science Foundation (Grant CHE-8022783).

(2) Mulvey, D.; Waters, W. A. J. Chem. Soc., Perkin Trans. 2 1978, 1059. Waters, W. A. Ibid. 1979, 1078. Ginsburg, V. A.; Medvedev, A. N.; Lebedeva, M. F.; Martynova, L. L. Zh. Org. Khim. 1974, 10(7), 1416 and earlier papers in that series. See also ref 4.

(3) (a) Abramovitch, R. A.; Challand, S. R.; Yamada, Y. J. Org. Chem. 1975, 40, 1541. (b) Schenk, C.; deBoer, Th. J. Tetrahedron 1979, 35, 147. (c) Barlow, M. G.; Haszeldine, R. N.; Murray, K. W. J. Chem. Soc., Perkin Trans. 1 1980, 1960.

(4) Chatgilialoglu, C.; Ingold, K. U. J. Am. Chem. Soc. 1981, 103, 4833.

(5) (a) These are highly unstable species, generated in situ by oxidation of RCONHOH or by thermal transfer of RCONO from its Diels–Alder adduct with 9,10-dimethylanthracene. (b) Keck, G. E.; Webb, R. R.; Yates, J. B. Tetrahedron 1981, 37, 4007.

(6) (a) Grdina, B.; Orfanopoulos, M.; Stephenson, L. M. J. Am. Chem. Soc. 1979, 101, 3111. (b) Stephenson, L. M.; Grdina, M. J.; Orfanopoulos, M. Acc. Chem. Res. 1980, 13, 419. (c) Frimer, A. A.; Bartlett, P. D.; Boschung, A. F.; Jewett, J. G. J. Am. Chem. Soc. 1977, 99, 7977.
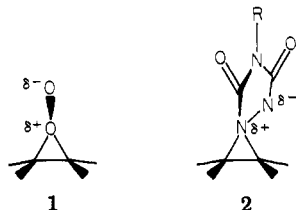
(7) Seymour, C. A.; Greene, F. D. J. Am. Chem. Soc. 1980, 102, 6384.

Table I. Isotope Effects in the Reaction of C_6F_5NO and Tetramethylethylene (3)

olefin	k_H/k_D
(Z)-3[a]	1.2 ± 0.2
(E)-3[a]	3.0 ± 0.2
gem-3[a]	4.5 ± 0.2
3-d_0, 3-d_{12}[b]	1.03 ± 0.05

[a] In $CDCl_3$, see footnote 11a.   [b] In Et_2O, see footnote 11b.

proceed through intermediates, most simply interpreted (in our opinion) as three-center species (e.g., 1 and 2).[8] It

is of interest to ascertain how broadly intermediates (and specifically, three-center species) may be involved in reactions of olefins with various reagents. We have applied the Stephenson isotope test[6a] [use of (Z)- and (E)-2,3-bis(trideuteriomethyl)-2-butene, 3] to the reaction of nitrosopentafluorobenzene,[9] and have also determined the intramolecular isotope effect with tetramethyl-*gem-d₆*-ethylene [$(CH_3)_2C=C(CD_3)_2$, *gem*-3][10] and the intermolecular isotope effect (by competition with tetramethylethylene-d_0 and -d_{12}).[11] The results are summarized in eq 3 and Table I.
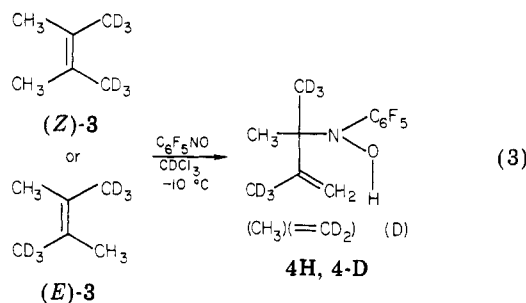
The lack of an intermolecular isotope effect compared with large isotope effects with (E)-3 and gem-3, and the substantial difference in isotope effects for (E)-3 compared to (Z)-3, are strong evidence against a mechanism (e.g., eq 2) involving cleavage of an allylic carbon–protium bond in the rate-determining step. The results are consistent with rate-determining formation of an intermediate, followed by cleavage of the "allylic" carbon–protium bond in a subsequent (and faster) step—with isotopic discrimination when "allylic" C–H is cis to C–D (i.e., in (E)-3 and in gem-3).[12] These results (eq 3 and Table I) are accom-

modated by an aziridine N-oxide, e.g., 5 (eq 4).

Aziridine N-oxides[13] are strongly implicated in the ozonolysis of aziridines; species considered to be aziridine N-oxides (considerably less hindered than 5 in eq 4) were observed directly by NMR at low temperatures and decomposed to unsaturated hydroxylamines (analogous to 4) and to nitrosoalkanes and olefins.[13a]

In summary, nitroso compounds, singlet oxygen, and triazolinediones appear to react with simple olefins via rate-determining formation of intermediates—5, 1, and 2 or species with these structural characteristics.
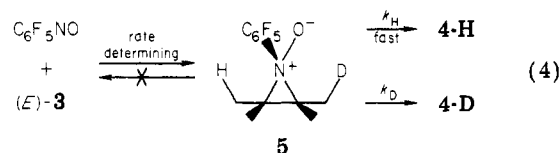
(8) For some evidence on mechanisms of ene reactions, including temperature dependence of isotope effects, see Munsterer, H.; Kresze, G.; Brechbiel, M.; Kwart, H. *J. Org. Chem.* 1982, 47, 2677, and Kwart, H.; Brechbiel, M. W. *Ibid.* 1982, 47, 3353.

(9) Compound 4, undeuterated, N-(1,1,2-trimethyl-2-propenylpentafluorophenyl)hydroxylamine (ref 3a), mp 78–79 °C; ¹H NMR ($CDCl_3$, 250 MHz) δ 1.25 (t, *J* = 1.6 Hz, 6 H), 1.92 (s, 3 H), 4.96 (s, 1 H), 5.02 (br s, 1 H), 5.20 (br, 1 H, OH).

(10) We thank Chen-Chih Cheng for the tetramethyl-*gem-d₆*-ethylene.

(11) (a) Intramolecular isotope effects were determined in $CDCl_3$ by ¹H NMR analysis of products (see footnote 9). (b) Intermolecular isotope effects were determined in diethyl ether by GC–mass spectral analysis for tetramethylethylene at time = 0 (before the addition of C_6F_5NO) and at time = ∞ (2 h) starting with a 1:1:1 ratio of TME-d_0, TME-d_{12}, and C_6F_5NO, initial concentrations 0.005 M.

(12) The larger isotope effect observed with *gem*-3 (4.5) compared with (E)-3 (3.0), also seen in the reactions of these olefins with singlet oxygen (ref 6b) and with N-phenyl- and N-methyltriazolinedione (unpublished results of these laboratories), probably arises from secondary β-D isotope effects on the developing double bonds in the transition states for H (and D) transfer.

(13) (a) Baldwin, J. E.; Bhatnagar, A. K.; Choi, S. C.; Shortridge, T. J. *J. Am. Chem. Soc.* 1971, 93, 4082. (b) Aziridine N-oxides also have been suggested as intermediates in the enzymatic oxidation of aziridines: Hata, Y.; Watanabe, M.; Matsubara, T.; Touchi, A. *J. Am. Chem. Soc.* 1976, 98, 6033. See also Hata, Y.; Watanabe, M. *Ibid.* 1979, 101, 1323.

Catherine A. Seymour, Frederick D. Greene*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received September 10, 1982

Conjugate Addition of RMgX to Mononitroarenes. Unequivocal Evidence for a Single-Electron-Transfer Mechanism

Summary: 1,6 conjugate addition of 5-hexenylmagnesium bromide to 2-methoxy-1-nitronaphthalene in THF at room temperature provides an unequivocal evidence for a single-electron-transfer pathway of the reaction, resulting in a 36% of cyclized vs. a 64% of uncyclized product.

Sir: Conjugate addition of RMgX to mononitroarenes[1] and its synthetic application[2] has been reported by us in recent years. So far it has not been strictly examined if this reaction proceeds exclusively through a polar mechanism or rather, as already well-recognized for related reaction of Grignard reagents with aromatic ketones,[3] a single-electron-transfer (SET) pathway could be involved as well.

Recently Savin,[4] using ESR and CIDNP techniques, observed the formation of nitrobenzene radical anion and

(1) (a) G. Bartoli, R. Leardini, A. Medici, and G. Rosini, *J. Chem. Soc., Perkin Trans. 2*, 692 (1978); (b) G. Bartoli, M. Bosco, A. Melandri, and A. C. Boicelli, *J. Org. Chem.*, 44, 2087 (1979).

(2) (a) G. Bartoli, A. Medici, G. Rosini, and D. Tavernari, *Synthesis*, 436 (1978); (b) G. Bartoli and M. Bosco, *Synthesis*, 616 (1980); (c) G. Bartoli, M. Bosco, and G. Baccolini, *J. Org. Chem.*, 45, 522 (1980).

(3) E. C. Ashby and J. R. Bowers, Jr., *J. Am. Chem. Soc.*, 103, 2242 (1981).

(4) V. I. Savin, *Zh. Org. Chim.*, 14, 2090 (1978); *Chem. Abstr.*, 90, 71443r (1979).