Catalytic Epoxidation of Hindered Olefins with Dioxygen. Fast Oxygen Atom Transfer to Olefin Cation Radicals from Nitrogen Oxides

Eric Bosch and Jay K. Kochi*

Contribution from the Chemistry Department, University of Houston, Houston, Texas 77204-5641

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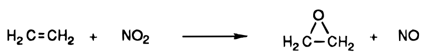
Abstract: Hindered olefins are efficiently converted to epoxides by dioxygen at 25 °C in dichloromethane containing catalytic amounts of nitrogen oxides (NO_2, NO^+, NO, etc.). Nitrogen dioxide also effects the direct (stoichiometric) epoxidation of the same hindered olefins. Olefin cation radicals are spectrally identified as the first observable intermediate, and separate experiments confirm the facile transfer of an oxygen atom from nitrogen dioxide to olefin cation radicals to produce epoxides. At low temperature (−78 °C), the epoxidation is rapidly initiated by added 1-electron oxidants such as tris(2,4-dibromophenyl)amine cation radical and nitrosonium (NO^+). Scheme 3 presents the complete sequence of redox changes that are mediated by the nitrogen oxides in the catalytic conversion of hindered olefins to epoxides *via* the cation radical. The deliberate irradiation of the charge-transfer absorption band of the corresponding olefin electron donor−acceptor complexes with tetranitromethane also establishes the formation of epoxides to occur *via* the same reactive pair, *i.e.*, the olefin cation radical and NO_2. The mechanistic implication of rapid oxygen atom transfer to olefin cation radicals is underscored in the general consideration of catalytic epoxidations with dioxygen.

Introduction

The direct oxidation of olefins by transfer of an oxygen atom from the common reagent nitrogen dioxide is potentially a straightforward transformation to epoxides. On the basis of the readily available thermodynamic data,[1] ethylene epoxidation by NO_2 shown in eq 1 is exothermic by 11.4 kcal mol^{-1} and the driving force is $-\Delta G = 11.0$ kcal mol^{-1} at 25 °C. Despite these favorable energetics, the thermal epoxidation of ethylene and various alkenes according to the stoichiometry in eq 1 is unknown at ambient temperature. Instead, the treatment of olefins with nitrogen dioxide generally results in a variety of nitrogen oxide adducts—including dinitro, nitro/nitrite, nitro/nitrate and nitroso/nitrate derivatives.[2,3] Allylic substitution products are detected in very dilute solutions.[4,5] The epoxidation represented by eq 1 has only been achieved by photochemical activation of the reactants. Thus, Jaffe[6] irradiated a gaseous mixture of nitrogen dioxide and ethylene diluted with dinitrogen and found traces of ethylene oxide (0.004%). Nojima and co-workers[7] subsequently irradiated mixtures of cyclohexene and NO_2 in air with a xenon lamp and isolated cyclohexene oxide in 50% yield. Frei and co-workers irradiated a mixture of NO_2 and ethylene in an argon matrix at 10 K and detected ethylene oxide by low-temperature infrared spectroscopy.[8,9]



(1)

We recently observed the facile reaction of nitrogen dioxide with the sterically hindered olefin adamantylideneadamantane in dichloromethane solution to afford a quantitative yield of adamantylideneadamantane oxide at 25 °C (in the dark).[10] We now report that catalytic amounts of nitrogen dioxide are sufficient to effect the epoxidation of related hindered olefins with dioxygen. These studies will demonstrate that at low temperatures the epoxidation is initiated by 1-electron oxidants, and that the olefin cation radical can be spectrally identified as the critical intermediate. In this regard, it should be noted that an electron-transfer mechanism has been proposed[11] for the epoxidation of olefins by cytochrome P-450 analogues, although no direct evidence for the electron-transfer process was presented. However, Bauld and Mirafzal[12] recently showed that tris(4-bromophenyl)amine cation radical was an effective initiator in olefin epoxidation with selenium dioxide or selenic anhydride as the oxygen atom donor.

Results

We reasoned that the epoxidation of olefins with NO_2 would predominate if the formation of nitrogen oxide adducts were restricted by the presence of bulky substituents. Accordingly, we prepared a series of adamantane-based olefins, **1**−**6**,[13] and a series of sterically crowded tetraarylethylenes, **7**−**9**.[14]

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

[1] Weast, R. C., Lide, D. R. Eds. *Handbook of Chemistry and Physics,* 70th ed.; CRC Press: Boca Raton, FL, 1989.

[2] (a) Chatterjee, J.; Coombes, R. G.; Barnes, J. R.; Fildes, M. J. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1031. (b) Shechter, H. *Rec. Chem. Prog.* **1964**, *25,* 55. (c) Reibsomer, J. L. *Chem. Rev.* **1945**, *36,* 157. (d) Bonetti, G. A.; de Savigny, C. B.; Michalski, G.; Rosenthal, R. *J. Org. Chem.* **1968**, *33,* 237. (e) Wilkes, J. B.; Wall, R. G. *J. Org. Chem.* **1980**, *45,* 247.

[3] Larson, H. O. In *The Chemistry of the Nitro and Nitroso Groups*; Feuer, H., Ed.; Interscience: New York, 1969; pp 319 ff.

[4] (a) Pryor, W. A.; Lightsey, J. W.; Church, D. F. *J. Am. Chem. Soc.* **1982**, *104,* 6685. (b) Giamalva, D. H.; Kenion, G. B.; Church, D. F.; Pryor, W. A. *J. Am. Chem. Soc.* **1987**, *109,* 7059.

[5] Brand, J. C. D.; Stevens, I. D. R. *J. Chem. Soc.* **1958**, 629.

[6] (a) Jaffe, S.; Keith, J. *J. Chem. Phys.* **1968**, *48,* 2805. (b) Jaffe, S.; Grant, R. C. S. *J. Chem. Phys.* **1969**, *50,* 3477.

[7] Nojima, K.; Ohya, T.; Kanno, S.; Hirobe, M. *Chem. Pharm. Bull.* **1982**, *30,* 4500.

[8] (a) Nakata, M.; Frei, H. *J. Am. Chem. Soc.* **1989**, *111,* 5240. (b) Nakata, M.; Frei, H. *J. Phys. Chem.* **1989**, *93,* 7670. (c) Fitzmaurice, D. J.; Frei, H. *J. Phys. Chem.* **1992**, *96,* 10308. (d) Blatter, F.; Frei, H. *J. Phys. Chem.* **1993**, *97,* 1178. (e) Frei, H. *Chimia* **1991**, *45,* 175.

[9] See also: (a) Loison, J. C.; Dedonder-Lardeux, C.; Jouvet, C.; Solgadi, D. *J. Phys. Chem.* **1991**, *95,* 9192. (b) Tanaka, N.; Kajii, Y.; Shibuya, K.; Nakata, M. *J. Phys. Chem.* **1993**, *97,* 7048.

[10] Bosch, E.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1993**, 667.

[11] (a) Traylor, T. G.; Miksztal, A. R. *J. Am. Chem. Soc.* **1987**, *109,* 2770. (b) Traylor, T. G.; Xu, F. *J. Am. Chem. Soc.* **1988**, *110,* 1953. (c) He, G.-X.; Arasasingham, R. D.; Zhang, G.-H.; Bruice, T. C. *J. Am. Chem. Soc.* **1991**, *113,* 9828. See also: Kim, T.; Mirafzal, G. A.; Liu, J.; Bauld, N. L. *J. Am. Chem. Soc.* **1993**, *115,* 7653.

[12] Bauld, N. L.; Mirafzal, G. A. *J. Am. Chem. Soc.* **1991**, *113,* 3613.

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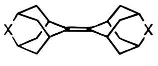
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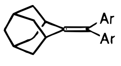
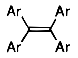
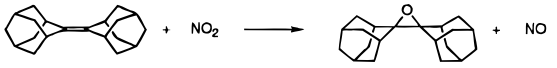
2. X = H,H


3. Ar = C$_6$H$_5$
4. Ar = *p*-MeC$_6$H$_4$
5. Ar = *p*-MeOC$_6$H$_4$
6. Ar = Me

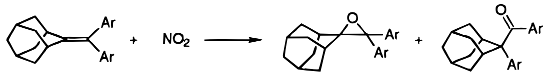

7. Ar = C$_6$H$_5$
8. Ar = *p*-MeC$_6$H$_4$
9. Ar = *p*-MeOC$_6$H$_4$

I. Stoichiometric Oxidation of Sterically Hindered Olefins with Nitrogen Dioxide. Adamantylideneadamantane **1** was treated with 1.1 equiv of nitrogen dioxide[15] in dichloromethane solution under an argon atmosphere for 1 h at 25 °C. The simple removal of the solvent and nitrogen oxides *in vacuo* led to quantitative yields of epoxide **12**, which upon spectral (NMR, IR, and GC−MS) analysis was found to be free of organic impurities (< 2%). UV−vis and IR analyses of the gaseous products confirmed the concomitant formation of nitric oxide by its characteristic spectral bands at $\lambda = 204$, 214, and 226 nm and $\nu = 1904$, 1876, and 1851 cm^{-1},[16] respectively, *i.e.*



1 **12** (2)

The oxidation of **1** was severely retarded in tetrachloromethane and cyclohexane solutions, and after 1 h, the epoxide **12** was isolated in only 13% and 9% yield, respectively. The oxidation of the series of hindered olefins **2**−**9** was thus uniformly performed in dichloromethane solutions containing 1.1−1.2 equiv of NO$_2$. Under these standard conditions, even the less rigid analogue **2** was quantitatively transformed to epoxide **13** in less than 2.5 h. The treatment of benzhydrylideneadamantane **3** with NO$_2$ yielded a mixture of epoxide **15** (55%) and the spiroketone **18** (45%), *i.e.*



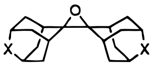
3 **15** **18** (3)

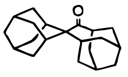
The combination of NO$_2$ with the related unsymmetrical olefins **4** (Ar = *p*-MeC$_6$H$_4$) and **5** (Ar = *p*-MeOC$_6$H$_4$) also yielded mixtures of the corresponding epoxides and rearranged ketones (see Table 1). The rates of oxidation of **3**, **4**, and **5** were directly correlated with the donor strength of the olefin, as assessed by the reversible 1-electron oxidation potentials recorded at a platinum electrode (see Table 1, column 2). For example, **3** ($E°_{1/2} = 1.56$ V vs SCE) required more than 24 h for 100% conversion, while **4** ($E° = 1.43$ V) afforded **22** after 12 h, and **5** ($E° = 1.16$ V) was completely consumed after only 30 min, under otherwise identical reaction conditions. Treatment of the less hindered isopropylideneadamantane **6** with NO$_2$ resulted in a complex mixture of products which was not fully characterized.

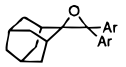
Table 1. Epoxidation of Olefins with NO$_2$^{a}

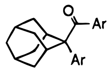
olefin (amt, mmol)	$E°_{1/2}$^{b} (V vs SCE)	NO$_2$ (amt, mmol)	time (h)	conv^{c} (%)	epoxide^{d} (%)
1 (0.26)	1.52	0.30	1	100	**12** (96)
1 (0.26)^{e}	1.52	0.30	1	13	**12** (95)
1 (0.26)^{f}	1.52	0.30	1	9	**12** (95)
1 (0.26)^{g}	1.52	0.30	1	9	**12** (95)
1 (0.26)^{h}	1.52	0.30	1	<5	**12** (90)
2 (0.06)	1.56	0.14	2	100	**13** (92)
3 (0.25)	1.56	0.30	24	100	**15** (55)^{i}
4 (0.20)	1.43	0.22	12	90	**16** (35)^{j}
5 (0.20)	1.16	0.22	0.3	100	**17** (28)^{k}
7 (0.20)	1.37	0.22	1	100	**21** (<3)^{l}
8 (0.09)	1.12	0.10	0.1	100	**22** (69)^{m}
8 (0.09)^{n}	1.12	0.10	4.0	5	**22** (2)^{o}

[a] All reactions with [NO$_2$] = 0.1 M in dichloromethane at 25 °C, unless stated otherwise. [b] Reversible oxidation potential in dichloromethane solution with 0.1 M (n-Bu)$_4$N$^+$PF$_6^-$ at $v = 0.1$ V s^{-1} and 25 °C. [c] Consumed olefin determined by quantitative GC. [d] Yields based on consumed olefin determined by quantitative GC (see the Experimental Section). [e] Reaction in carbon tetrachloride solvent. [f] Reaction in cyclohexane solvent. [g] Nitric oxide (0.3 mmol) added. [h] Bu$_4$N$^+$NO$_3^-$ (0.3 mmol) added. [i] **18** (45%) also formed. [j] **19** (55%) also formed. [k] **20** (62%) also formed. [l] 1-(4-Nitrophenyl)triphenylethylene (95%) formed. [m] **25** (16%) and a nitro product also formed (see the Experimental Section). [n] PPN$^+$NO$_3^-$ (0.2 mmol) added. [o] **26** (2%) also formed.

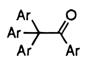

12. X = CH$_2$
13. X = H,H


14.

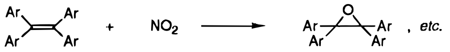

15. Ar = C$_6$H$_5$
16. Ar = *p*-MeC$_6$H$_4$
17. Ar = *p*-MeOC$_6$H$_4$


18. Ar = C$_6$H$_5$
19. Ar = *p*-MeC$_6$H$_4$
20. Ar = *p*-MeOC$_6$H$_4$


21. Ar = C$_6$H$_5$
22. Ar = *p*-MeC$_6$H$_4$
23. Ar = *p*-MeOC$_6$H$_4$


24. Ar = C$_6$H$_5$
25. Ar = *p*-MeC$_6$H$_4$
26. Ar = *p*-MeOC$_6$H$_4$

Tetraphenylethylene (**7**) was *nitrated* almost quantitatively by NO$_2$, and (*p*-nitrophenyl)triphenylethylene was isolated in 92% yield, but only traces of tetraphenylethylene oxide (**21**) (< 3%) were detected by GC−MS analysis of the crude reaction product.[17] By contrast, the reaction of tetra-*p*-tolylethylene (**8**) with NO$_2$ yielded tetra-*p*-tolylethylene oxide (**22**) as the major product in 69% yield, together with minor amounts of tri-*p*-tolyl-4-methylacetophenone (**25**) (16%) and an unidentified nitroarene (10%), *i.e.*



8 **22** (4)

where Ar = *p*-MeC$_6$H$_4$.

The reactivity of olefins with NO$_2$ was not amenable to a direct kinetics analysis owing to strong retardation by the gaseous product NO. For example, the reaction of adamantylideneadamantane with NO$_2$ in the presence of added nitric oxide (under anaerobic conditions) led to a sharply diminished conversion of adamantylideneadamantane oxide (see entry 4, Table 1). The epoxidation of **1** and **8** with NO$_2$ was also severely retarded by the presence of nitrate anion (see entries 5 and 12 in Table 1).

II. Spectral Observation of the Olefin Cation Radical as a Reactive Intermediate. The oxidations of all the olefins in Table 1 were characterized by the formation of highly colored solutions. For example, immediately upon mixing NO$_2$ and **8** in dichloromethane, a transient purple color was observed, and the solution then faded to pale yellow. Since the purple color

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(13) (a) Belluci, G.; Bianchini, R.; Chiappe, C.; Marioni, F.; Ambrosetti, R.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1989**, *111*, 2640. (b) Nugent, W. A. *J. Org. Chem.* **1980**, *45*, 453. (c) Garratt, D. G. *Tetrahedron Lett.* **1978**, 1915. (d) Olah, G. A.; Schilling, P.; Westerman, P. W.; Lin, H. C. *J. Am. Chem. Soc.* **1974**, *96*, 3581. (e) Wieringa, J. H.; Strating J.; Wynberg, H. *Tetrahedron Lett.* **1970**, 4579. (f) Strating, J.; Wieringa, J. H.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1969**, 907. Note that the allylic hydrogens in olefins **1**−**5** are coplanar with the olefin and are thus not susceptible to abstraction or deprotonation (see: Nelsen, S. F. *Acc. Chem. Res.* **1987**, *20*, 269).

(14) The aromatic rings are tilted with respect to the central double bond sufficient to cause tetraarylethylenes to be severely hindered. (a) Suzuki, H. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 389. (b) Suzuki, H.; Koyano, K.; Shida, T.; Kira, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2794. See also: Bock, H.; Nather, C.; Havlas, Z. *J. Chem. Soc., Chem. Commun.* **1995**, 1111.

(15) For brevity, we do not distinguish between the monomeric nitrogen dioxide (NO$_2$) and the dimeric dinitrogen tetraoxide (N$_2$O$_4$) which coexist in a highly mobile equilibrium.

(16) (a) Marmo, F. F. *J. Opt. Soc. Am.* **1953**, *43*, 1186. (b) Fateley, W. G.; Bent, H. A.; Crawford, B., Jr. *J. Chem. Phys.* **1959**, *31*, 204. (c) Keck, D. B.; Hause, C. D. *J. Mol. Spectrosc.* **1980**, *27*, 465.

(17) For aromatic nitrations with NO$_2$, see: Bosch, E.; Kochi, J. K. *J. Org. Chem.* **1994**, *59*, 3314.

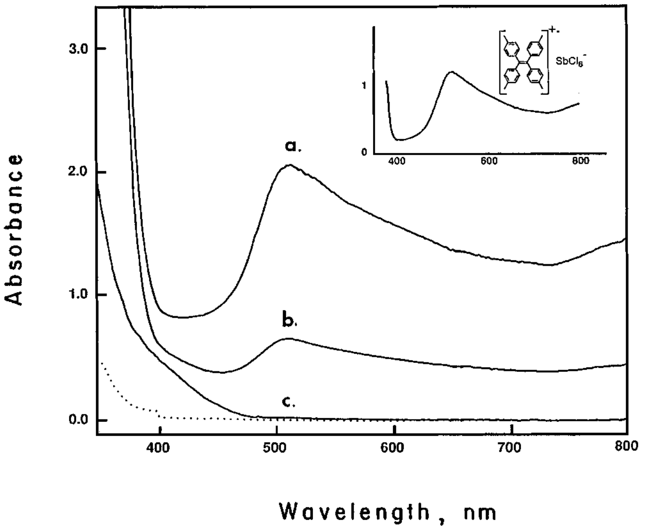
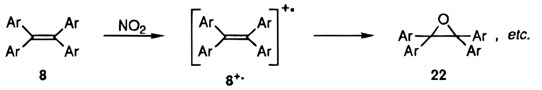


Figure 1. Spectral changes attendant upon the mixing of 0.003 M tetratolylethylene and 0.004 M NO_2 in dichloromethane at −5 °C: (a) immediately upon mixing, (b) after 2 min, and (c) prior to workup at 15 min. The dotted curve is the residual (low-energy) tail of the nitrogen dioxide absorption. Inset: Absorption spectrum of authentic tetratolylethylene cation radical hexachloroantimonate in dichloromethane solution.

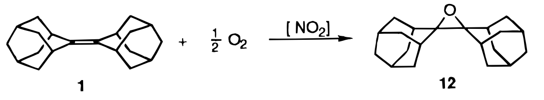
was more persistent at lower temperatures, the reaction profile could be readily examined by UV−vis absorption spectroscopy at −5 °C, as shown in Figure 1. The initial intense color was spectrally characterized as a broad absorption band centered at $\lambda_{max} = 516$ nm, which was identical with that obtained from an authentic crystalline sample of the hexachloroantimonate salt of tetra-*p*-tolylethylene cation radical[18] (*vide infra)*. We concluded therefore that the cation radical $8^{\cdot+}$ was the reactive intermediate in epoxide formation, *i.e.*



(5)

where Ar = *p*-MeC_6H_4.

III. Nitrogen Dioxide-Catalyzed Epoxidation of Hindered Olefins with Dioxygen. The well-known aerial oxidation of the nitric oxide[19] formed in the stoichiometric reaction of NO_2 with olefins (eq 2) provided the basis for the nitrogen dioxide-catalyzed oxidation of olefins with dioxygen. Thus, a dichloromethane solution of adamantylideneadamantane **1** (2 mmol) was saturated with dioxygen and cooled to 0 °C and the Schlenk flask connected to an O_2-filled gas buret. Nitrogen dioxide (0.1 mmol) was added and the consumption of dioxygen monitored volumetrically. The uptake of dioxygen ceased after 20 mL (0.89 mmol) of O_2 was consumed, and epoxide **12** was isolated in quantitative yield simply upon the removal of the nitrogen oxides and the solvent *in vacuo, i.e.*



(6)

Spectral analysis of the gaseous products indicated the presence of unchanged NO_2 ($\nu_{NO} = 1600$ and $1620\ cm^{-1}$).[20]

The epoxidation with dioxygen was also catalyzed by small amounts of other nitrogen oxides such as nitrosonium cation (NO^+) and nitric oxide (NO), as listed in Table 2, entries 3 and 2. The other olefins listed in Table 2 were also subjected to these catalytic conditions, and while **2** was quantitatively converted to epoxide **13** in high yield, the olefins **4**, **5**, and **8** yielded mixtures of epoxides and ketones. Although the reaction conditions were not optimized, catalytic turnovers of up to 40 were readily obtained under these mild conditions.

Table 2. Epoxidation of Olefins with Dioxygen Catalyzed by Nitrogen Oxides[a]

olefin	amt (mmol)	catalyst	amt (mmol)	epoxide	amt (mmol)
1	2.00	NO_2	0.10	**12**	1.94
1	0.26	NO	0.05	**12**	0.26
1	0.26	NO^+	0.10[b]	**12**	0.24
2	0.36	NO_2	0.04	**13**	0.34
4	0.50	NO_2	0.05	**16**	0.17[c]
5	0.50	NO_2	0.05	**17**	0.14[d]
8	1.50	NO_2	0.10	**22**	0.93[e]

[a] All reactions in dichloromethane at 25 °C for 14 h (see the Experimental Section). [b] Reaction at 25 °C for 40 min. [c] **19** (0.34 mmol) also formed. [d] **20** (0.32 mmol) also formed. [e] **25** (0.31 mmol) and a nitroarene (~0.010 mmol) also formed.

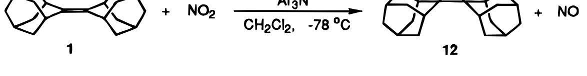
Table 3. Electron-Transfer Catalysis of Olefin Epoxidation with NO_2[a]

olefin (amt, mmol)	NO_2 (amt, mmol)	oxidant[b] (concn, mol %)	time (min)	product[c] (yield, %)
1 (0.24)	1.00	DB (1)	20	**12** (93)
1 (0.20)	1.00	NO^+ (5)	50	**12** (94)
2 (0.06)	0.14	DB (8)	40	**13** (97)
3 (0.15)	0.30	DB (3)	90	**15** (55)[d]
4 (0.20)	0.40	DB (4)	5	**16** (36)[e]

[a] All reactions in dichloromethane at −78 °C. [b] DB = *tris*(2,4-dibromophenyl)aminium hexachloroantimonate; $NO^+ = NO^+BF_4^-$. [c] Yields determined by GC−MS using internal standard; in each reaction, the olefin was totally consumed (see the Experimental Section). [d] **18** (40%) also formed. [e] **19** (58%) also formed.

In order to gain further understanding of both the stoichiometric and catalytic oxidations, we investigated the selective activation of the epoxidation at low temperature as follows.

IV. Electron-Transfer Catalysis of Olefin Epoxidation with Nitrogen Dioxide at −78 °C. Olefin epoxidation was severely retarded merely by lowering the reaction temperature, as readily indicated by a mixture of **1** and 2 equiv of NO_2, which was stable at −78 °C for extended periods. However, when a small amount (0.01 equiv) of tris(2,4-dibromophenyl)amine cation radical as the hexachloroantimonate salt ($E^\circ_{red} = 1.6$ V vs SCE)[21] was added to the stable colorless solution at −78 °C, a rapid series of color changes ensued. The green color due to the amine cation radical was immediately replaced by a purple-colored solution, which turned brown and then pale blue within 20 min.[22] After removal of the nitrogen oxides and solvent *in vacuo*, the epoxide **12** was isolated in 93% yield (see Table 3). IR spectral analysis of the head gas led to the identification of nitric oxide ($\nu_{NO} = 1876\ cm^{-1}$),[16] *i.e.*



(7)

Control experiments confirmed that the amine cation radical under these conditions quantitatively oxidized adamantylideneadamantane **1** to its purple radical cation $1^{\cdot+}$ which was readily identified by its diagnostic (broad) absorption band with

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[18] See also: Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: New York, 1988.

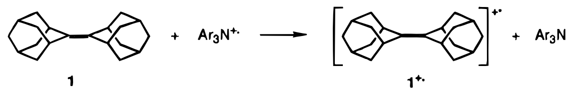
[19] Smith, J. H. *J. Am. Chem. Soc.* **1943**, *65*, 74.

[20] Laane, J.; Ohlsen, J. R. *Prog. Inorg. Chem.* **1980**, *27*, 465.

[21] Schmidt, W.; Steckhan, E. *Chem. Ber.* **1980**, *113*, 577. See also: Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Chem. Soc. C* **1969**, 2719.

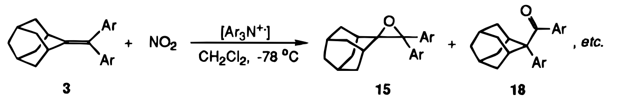
[22] The final blue color is characteristic of N_2O_3 ($\lambda_{max} = 690$ nm) formed by combination of NO with the excess NO_2. See: (a) Shaw, A. W.; Vosper, A. J. *J. Chem. Soc., Dalton Trans.* **1959**, *31*, 204. (b) Ashmore, P. G.; Tyler, B. *J. Chem. Soc.* **1961**, 1017.

λ_{max} = 530 nm,[23] *i.e.*



(8)

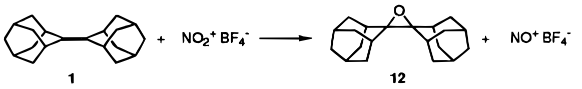
The low-temperature epoxidation of olefin **1** with NO_2 at −78 °C was also catalyzed by nitrosonium cation as the 1-electron oxidant. Thus, the addition of 5 mol % NO^+ (as the tetrafluoroborate salt) to a dichloromethane solution of **1** and NO_2 at −78 °C resulted in the quantitative formation of epoxide **12** within 50 min. The low-temperature oxidation of the olefins **2**, **3**, and **4** with NO_2 in dichloromethane solution was also catalyzed by the amine cation radical (see Table 3). In particular, the low-temperature (−78 °C) aminium-catalyzed oxidation of **3** with NO_2 resulted in the epoxide **15** and ketone **18** in excellent yield after only 90 min, *i.e.*



(9)

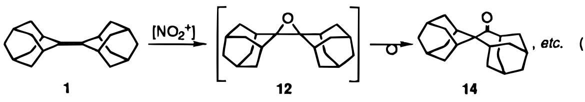
By comparison, the same transformation at 25 °C in the absence of the amine cation radical required more than 24 h to yield the same mixture of **15** and **18** (see Table 1, entry 7).

V. Stoichiometric Epoxidation of Adamantylideneadamantane with Nitryl Cation. When a cold (−40 °C) dichloromethane solution of **1** was added to a slurry of 1 equiv of nitryl tetrafluoroborate in acetonitrile at −40 °C, the olefin was rapidly consumed. After 5 min, the colorless slurry was diluted with ether and washed with water, and epoxide **12** was isolated in quantitative yield. In a separate experiment, the crystalline salt was verified as the nitrosonium salt $NO^+BF_4^-$ spectroscopically (see the Experimental Section), *i.e.*



(10)

In another experiment, the reaction mixture was allowed to stir at −30 °C for a prolonged period, and the products were monitored by periodic removal of aliquots and analysis by quantitative GC. The results showed that **1** was completely transformed to epoxide **12** within 5 min. However, the yield of **12** steadily decreased with the passage of time, and this change was accompanied by a corresponding increase in the yield of spiroketone **14**. After 1 h, the rearranged ketone **14** was the sole organic product,[24] *i.e.*



(11)

VI. Charge-Transfer Oxidation of Hindered Olefins with Tetranitromethane by Selective Activation of the EDA Complex. The critical role of olefin cation radicals and NO_2 in the formation of epoxides was probed by the selective photochemical generation of this reactive pair. Earlier flash photolysis studies[25] established the specific photoactivation ($h\nu_{CT}$) of the charge-transfer absorption bands of electron donor−acceptor (EDA) complexes between various electron donors (D) and tetranitromethane to yield a reactive triad that was comprised of the donor cation radical, NO_2, and trinitromethide, *i.e.*

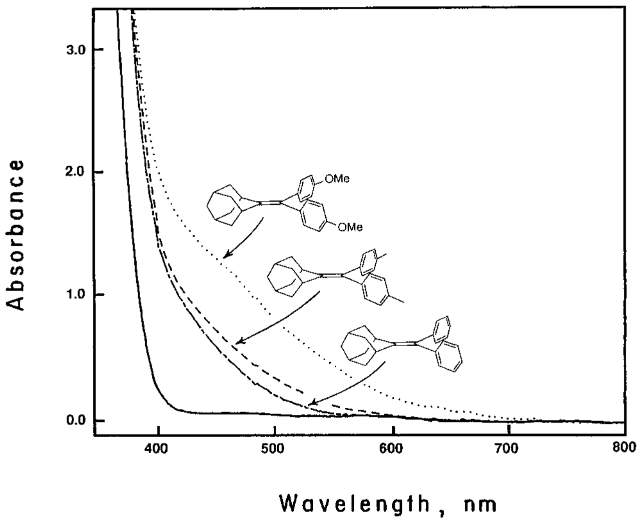


Figure 2. Bathochromic (and hyperchromic) shifts of the charge-transfer absorption bands of the 1:1 EDA complexes of 0.15 M tetranitromethane and 0.04 M **3** (- • -), 0.04 M **4** (- - -), and 0.04 M **5** (•••) in dichloromethane solution at 25 °C. The solid curve is the tail absorption of TNM (0.15 M) alone.

$$[D, C(NO_2)_4] \xrightarrow{h\nu_{CT}} [D^{+\bullet}, NO_2, C(NO_2)_3^-] \qquad (12)$$

Thus, the complementary means of generating the olefin cation radicals in the presence of NO_2 was the charge-transfer activation of analogous olefin donors (D), as follows.[26]

A. Formation of EDA Complexes of Hindered Olefins with Tetranitromethane. The observation of orange-brown solutions immediately upon mixing colorless solutions of olefins and tetranitromethane (TNM) was indicative of the formation of 1:1 electron donor−acceptor (EDA) complexes.[26]

$$>C=C< \; + \; C(NO_2)_4 \xrightarrow[CH_2Cl_2]{} [>C=C<, C(NO_2)_4] \qquad (13)$$

The colored solutions remained unchanged over a period of several hours at room temperature when protected from room light. UV−vis spectral analysis of the yellow-brown solutions formed on mixing each of the olefins in Table 1 with TNM revealed a broad tailing charge-transfer absorption band which precluded a precise determination of the spectral band energies ($h\nu_{CT}$). The variation of the spectral band energy with the donor strength of the olefin was however apparent in Figure 2 from the progressive bathochromic shift of the charge-transfer absorption bands formed between TNM and the structurally similar olefins **3**, **4**, and **5** with increasing donor strengths that were evaluated from the reversible oxidation potentials of $E_{1/2}$ = 1.56, 1.43, and 1.16 V vs SCE, respectively.

B. Selective Photochemical Activation of the Olefin EDA Complexes with Tetranitromethane. The EDA complexes formed from TNM and each of the olefins **1**, **3**, **4**, **5**, and **8** were selectively activated at 25 °C by the deliberate irradiation of charge-transfer absorption bands with actinic radiation from a 250-W mercury lamp. The lamp was fitted with a sharp cutoff filter so that only light with λ_{max} > 410 nm was transmitted. Under these controlled conditions (compare Figure 2), there could be no ambiguity about the adventitious excitation of either the uncomplexed olefin or TNM. The selective photoactivation

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[23] Nelsen, S. F.; Teasley, M. F.; Kapp, D. L.; Kessel, C. R.; Grezzo, L. A. *J. Am. Chem. Soc.* **1984**, *106*, 791.

[24] (a) Olah and co-workers[13d] reported the exclusive formation of ketone **14** on reaction of **1** with nitryl cation, but they did not detect epoxide **12**. (b) However, our control experiments showed that epoxide **12** readily rearranged to **14** in the presence of NO^+ (Compare Lopez *et al.* in ref 31).

[25] Masnovi, J. M.; Kochi, J. K.; Hilinski, E. R.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 1126.

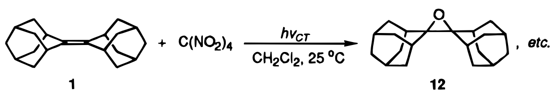
[26] (a) Masnovi, J. M.; Kochi, J. K. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 286. (b) Rathore, R.; Kochi, J. K. *J. Org. Chem.*, in press. (c) Bosch, E.; Kochi, J. K. *Res. Chem. Intermed.*, in press.

Table 4. Charge-Transfer Epoxidation of Olefins with Tetranitromethane[a]

olefin (amt, mmol)	TNM (amt, mmol)	time (h)	conv[b] (%)	epoxide[c] (yield, %)
1 (0.17)	0.41	0.5	45	**12** (87)[d]
3 (0.25)	0.33	4.0	70	**15** (45)[e]
4 (0.20)	0.25	0.2	17	**16** (35)[f]
4 (0.20)	0.25	1.0	35	**16** (34)[g]
4 (0.20)	0.25	2.2	65	**16** (32)[h]
5 (0.25)	0.28	0.2	37	**17** (27)[i]
5 (0.25)	0.28	0.5	78	**17** (23)[j]
8 (0.20)	0.30	0.7	70	**22** (59)[k]

[a] All oxidations performed in dichloromethane solution at 25 °C by irradiation with a medium pressure Hg lamp and a 410-nm cutoff filter (see the Experimental Section). [b] Based on recovered olefin, determined by quantitative GC. [c] Yield of epoxide based on consumed olefin. [d] Adamantanone (4%) also formed. [e] **18** (40%) also formed. [f] **19** (53%) also formed. [g] **19** (57%) also formed. [h] **19** (46%) and traces of 4,4′-dimethylbenzophenone (<5%) also formed. [i] **20** (71%) also formed. [j] **20** (70%) also formed. [k] **25** (35%) also formed.

of the EDA complex of **1** and TNM for 30 min at 25 °C resulted in the formation of epoxide **12** in 87% yield. UV−vis spectral analysis of the aqueous washing confirmed the formation of trinitromethide ($\lambda_{max} = 350$ nm; $\epsilon = 1.4 \times 10^4$ M^{-1} cm^{-1})[27] in 80% yield based on the amount of **1** converted, *i.e.*



(14)

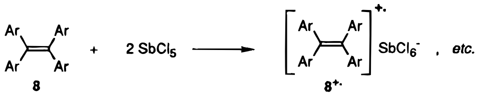
A control dark experiment with an identical solution (protected from light) showed no apparent (visible) change after 30 min, and quantitative GC−MS analysis confirmed the complete recovery of **1**. The charge-transfer oxidations of the related olefins **3**, **4**, **5**, and **8** with TNM resulted in good yields of the respective epoxides and ketones as shown in Table 4. In each case, there was no reaction in the dark control over the period of the irradiation. Furthermore, there was no change in the degree of conversion or the relative distribution of the products whether the reaction mixture was worked up immediately or left in the dark for 6 h prior to workup and analysis. These controls showed that the olefin oxidation did not proceed *via* a photochemically initiated chain reaction of the type previously observed with *N*-vinylcarbazole.[26]

The selective irradiation of the charge-transfer absorption band of the EDA complex formed between tetranitromethane and tetra-*p*-tolylethylene (**8**) at 25 °C resulted in the formation of a deep purple coloration which was persistent throughout the irradiation. However, the color faded rapidly when the solution was removed from the light, but it persisted when the irradiated solution was cooled to −78 °C. UV−vis spectral analysis of the purple solution revealed the characteristic absorption spectrum of the tetra-*p*-tolylethylene cation radical ($\mathbf{8}^{\cdot+}$) with $\lambda_{max} = 516$ nm (compare Figure 1). We thus concluded that the cation radical $\mathbf{8}^{\cdot+}$ was the direct intermediate in the charge-transfer oxidation of **8** with TNM, *i.e.*

(15)

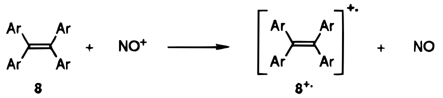
VII. Isolation of Crystalline Salts of Olefin Cation Radicals. The consistent observation of olefin cation radicals in each of the above oxidation procedures prompted us to prepare and isolate olefin cation radicals in order to directly assess their role in the epoxidation. Adamantylideneadamantane cation radical hexachloroantimonate was prepared *in situ* as stable dilute solutions (10^{-3} M) at −78 °C in dichloromethane. However, the solutions were not stable at higher temperatures, and the crystalline salt could not be isolated in pure form. Since the tetra-*p*-tolylethylene cation radical was more stable even at 25 °C, it was isolated as the hexachloroantimonate salt as follows.

Tetra-*p*-tolylethylene Cation Radical Hexachloroantimonate. The addition of antimony pentachloride (2 equiv) to a dichloromethane solution of tetratolylethylene (1 equiv, cooled in a dry ice/acetone bath) resulted in a deep purple solution. The addition of a cold mixture of ether and hexane led to a heavy purple precipitate. The microcrystalline solid was filtered, washed sequentially with cold ether and hexane, dried *in vacuo*, and stored under an argon atmosphere. The purity of the salt was established by elemental analysis, and by titrimetric oxidation of iodide and *N*-phenylphenothiazine (see the Experimental Section). The hexachloroantimonate salt of tetra-*p*-tolylethylene cation radical was readily soluble in dichloromethane to afford a deep purple solution with λ_{max} 516 nm ($\epsilon = 14\,000$ M^{-1} cm^{-1}).



(16)

Tetra-*p*-tolylethylene cation radical was also readily obtained by reaction with 1 equiv of nitrosonium cation according to eq 17.[28]

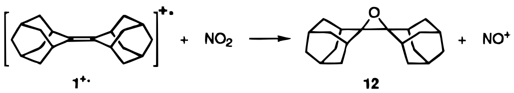


(17)

VIII. Reactivity of Olefin Cation Radicals toward Various Nitrogen Oxides. If cation radicals were intermediates in the oxidation of olefins, they must have been transformed to the oxidized products by another species extant in the reaction mixture. Accordingly, authentic samples of the cation radicals $\mathbf{1}^{+\cdot}$ and $\mathbf{8}^{+\cdot}$ were directly treated with various nitrogen oxides as follows.[29]

Nitric Oxide. Tetratolylethylene cation radical did not react with NO in dichloromethane solution at 25 °C in the absence of oxygen. Thus, a purple solution of the tetratolylethylene cation radical and NO in dichloromethane persisted indefinitely when protected from air.

Nitrogen Dioxide. A purple solution of $\mathbf{1}^{+\cdot}$SbCl$_6^-$ (10^{-3} M) was prepared in dichloromethane at −78 °C according to eq 8. When a dichloromethane solution of NO$_2$ (1 equiv) was added, the purple color bleached immediately. Quantitative GC−MS analysis of the colorless solution indicated that epoxide **12** was formed in 84% yield, and the concomitant production of the nitrosonium salt was confirmed spectroscopically (see the Experimental Section), *i.e.*



(18)

In a separate experiment, a dark purple dichloromethane solution of $\mathbf{8}^{+\cdot}$SbCl$_6^-$ was added dropwise into a stirred solution of nitrogen dioxide in dichloromethane at 25 °C. The purple color

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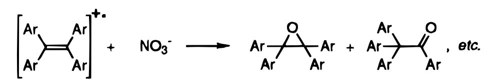
[27] Bielski, B. H. J.; Allen, A. O. *J. Phys. Chem.* **1967**, *71*, 4544.

[28] Our attempts to isolate $\mathbf{8}^{\cdot+}$ as the tetrafluoroborate salt have not been successful. Concentrated solutions of $\mathbf{8}^{\cdot+}$ decolorized, and 3,6-dimethyl-9,10-bis(4′-methylphenyl)phenanthrene was formed.

[29] Reactions with $\mathbf{1}^{\cdot+}$ were performed at −78 °C owing to the instability of the cation radical at higher temperatures. The reactions with $\mathbf{8}^{\cdot+}$ were performed at −5 to +10 °C since the cation radical was persistent in the presence of nitrogen oxides at −78 °C.

faded, and after 5 min, quantitative GC−MS analysis indicated that epoxide **22** and ketone **25** were the major products.

Nitrate. A solution containing 1 equiv of $PPN^+NO_3^-$ [30] was added dropwise to a dark purple dichloromethane solution of $\mathbf{8}^{+\cdot}SbCl_6^-$ at 10 °C. The color bleached within 5 min, and quantitative GC−MS analysis indicated that epoxide **22** and ketone **25** were the major products, *i.e.*

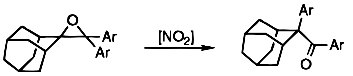


8+· 22 25 (19)

where Ar = p-MeC_6H_4. No reaction was apparent when the solutions were cooled to −78 °C prior to mixing. In a separate experiment, $PPN^+NO_3^-$ reacted with $\mathbf{1}^{+\cdot}SbCl_6^-$ at −78 °C to afford the epoxide **12** and ketone **14** in good yields.

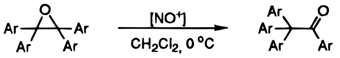
IX. Stability of the Epoxides under the Oxidation Conditions. In the oxidation of olefins under the various conditions described above, rearranged ketone was consistently isolated along with the epoxide. In order to determine whether the ketone was derived from the epoxide, we tested the stability of epoxides to nitrogen dioxide, nitrosonium cation, and the intermediate olefin cation radicals as follows.[31,32]

Nitrogen Dioxide. Epoxide **16** was slowly transformed into ketone **19** on treatment with 1 equiv of NO_2 in dichloromethane at 25 °C (see the Experimental Section), *i.e.*



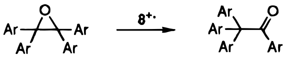
16 19 (20)

Nitrosonium Cation. Tetra-p-tolylethylene oxide (**22**) was rapidly and quantitatively transformed to ketone **25** on treatment with 2 mol % nitrosonium hexachloroantimonate in dichloromethane at 0 °C,[33] *i.e.*



22 25 (21)

Olefin Cation Radicals. Epoxide **22** was also quantitatively transformed to ketone **25** within 10 min by catalytic amounts of the olefin cation radical $\mathbf{8}^{+\cdot}SbCl_6^-$ (1 mol %) in dichloromethane at 0 °C.



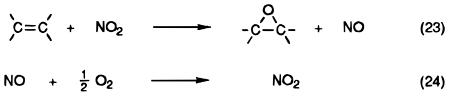
22 25 (22)

The efficacy of the rearrangement in eq 22 was further evaluated by varying both the 1-electron oxidant and the epoxide as detailed in the Experimental Section.[34]

Discussion

The novel catalysis of olefin epoxidation by nitrogen dioxide as described in eq 6 represents a rare example in which both oxygen atoms of dioxygen are utilized.[35] Such an autooxidation is however not general for all olefins since the less congested analogues yield little or no epoxide (but other products result from 1,2-addition or allylic hydrogen abstraction). We emphasize that the hindered nature of olefins **1**−**11** is designed to discourage multiple access to the double bond and to render hydrogen abstraction unfavorable.[36] Although the epoxidation of these hindered olefins is also promoted by nitric oxide and nitrosonium cation, nitrogen dioxide is unique in its ability to also be separately used as a *stoichiometric* reagent for the epoxidation. Indeed, the direct reduction of NO_2 by adamantylideneadamantane in eq 2, coupled with the facile aerial reoxidation of NO to nitrogen dioxide[19] provides the initial basis for the formulation of NO_2 catalysis (see Scheme 1). However, this simple scheme does not explain the catalysis by nitrosonium cation in Table 2, and it does not account for all the characteristics of the stoichiometric epoxidation with NO_2, such as (a) the retardation of the oxidation by the NO product (see entry 4, Table 1) and by added nitrate (entries 5 and 12) and (b) the spontaneous appearance of the olefin cation radical (see Figure 1). Clearly any mechanistic formulation must also take into account the effective initiation of the epoxidation at low temperatures by 1-electron oxidants (see eqs 7 and 9). In order to reconcile these diverse observations, let us first focus on how NO_2 in stoichiometric amounts effects the epoxidation of olefins—with particular regard to the transient formation of olefin cation radicals and their subsequent conversion to epoxides.

Scheme 1



I. Oxidative Transformation of Olefins to their Cation Radicals by Nitrogen Dioxide. The direct observation in Figure 1 of the cation radical, immediately on mixing tetra-p-tolylethylene and NO_2, provides definitive identification of the first observable intermediate in the epoxidation. Since NO_2 itself is a weak oxidant ($E° \approx 0.25$ V vs SCE),[37] the oxidation of the olefins listed in Table 1 is prohibitively endergonic with $\Delta G_{ET} > 20$ kcal mol^{-1}. Therefore, the effective oxidant must be another species (that is derived from NO_2). Indeed, NO_2 is known to exist in solution in equilibrium with its dimeric forms, namely, the predominant N−N bonded dimer $O_2N{-}NO_2$[38] and the N−O bonded minor isomer $O_2N{-}ONO$,[39] *i.e.*

$$O_2NNO_2 \rightleftarrows 2\,NO_2 \rightleftarrows ONONO_2 \qquad (25)$$

Significantly, the minor dimer has been independently shown to afford nitrosonium nitrate as the ion pair salt.[40] Although the heterolysis of the N−O bond in $O_2N{-}ONO$ is unlikely to be important in nonpolar media such as dichloromethane, we

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[30] Where PPN^+ = bis(triphenylphosphoranylidene)ammonium prepared according to Ruff, J. K.; Schlientz, W. J. *Inorg. Synth.* **1974**, *15*, 84.

[31] The cation radical catalyzed rearrangement of epoxides to ketones has been reported.[32]

[32] (a) Lopez, L.; Troisi, L. *Tetrahedron Lett.* **1989**, *30*, 3097. (b) Lopez, L.; Mele, G.; Finandanese, V.; Cardellicchio, C.; Nacci, A. *Tetrahedron* **1994**, *50*, 9097.

[33] The reaction was heterogeneous since nitrosonium salts are only sparingly soluble in dichloromethane.

[34] The epoxides were also rapidly isomerized to the corresponding ketones during cyclic voltammetric measurements as described in the Experimental Section. For the electron-transfer chain isomerization at the electrode during cyclic voltammetric studies, see: Lebouc, A.; Tallee, A.; Simonet, J. *J. Chem. Soc., Chem. Commun.* **1982**, 387. Uneyama, K.; Isimura, A.; Fujii, K.; Torri, S. *Tetrahedron Lett.* **1983**, *24*, 2857.

[35] (a) Compare: Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790. See also Groves, J. T.; Stern, M. K. *J. Am. Chem. Soc.* **1987**, *109*, 3812. (b) For a review, see: Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981.

[36] Indeed, the least hindered olefin in this study, isopropylideneadamantane **6**, yielded a complex mixture of products which did not include the epoxide. Note that the allylic hydrogen atoms of **6** are susceptible to abstraction/deprotonation. See: Nelsen, S. F.; Kapp, D. L.; Teasley, M. F. *J. Org. Chem.* **1984**, *49*, 579.

[37] Eberson, L.; Radner, F. *Acta Chem. Scand., Sect. B* **1985**, *39*, 343.

[38] (a) James, D. W.; Marshall, R. C. *J. Phys. Chem.* **1968**, *72*, 2963. (b) Redmond, T. F.; Wayland, B. B. *J. Phys. Chem.* **1968**, *72*, 1626. (c) Brunning, J.; Frost, M. J.; Smith, I. W. M. *Int. J. Chem. Kinet.* **1988**, *20*, 957. (d) Vosper, A. J. *J. Chem Soc. A* **1970**, 2191.

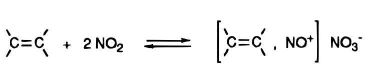
[39] Pinnick, D. A.; Agnew, S. F.; Swanson, B. I. *J. Phys. Chem.* **1992**, *96*, 7092.

[40] (a) Parts, L.; Miller, J. T., Jr. *J. Chem. Phys.* **1965**, *43*, 136. (b) Givan, A.; Loewenschuss, A. *J. Chem. Phys.* **1991**, *94*, 7562.

previously demonstrated that the strong complexation of the nitrosonium moiety by electron-rich aromatic hydrocarbons promotes ion pair formation,[41,42] *i.e.*

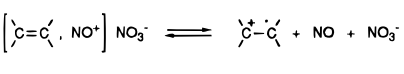
$$ONONO_2 \rightleftharpoons NO^+\,NO_3^- \xrightleftharpoons{ArH} [ArH, NO^+]\,NO_3^- \qquad (26)$$

Indeed, the extent of disproportionation of NO_2 according to eq 26 is correlated with the donor strength of the aromatic hydrocarbon. For example, hexamethylbenzene which is a strong donor (IP = 7.85 eV) promotes the ionization of NO_2 to an extent of 80%. On the other hand, the use of the weaker donor durene (IP = 8.05 eV) results in less than 25% ion pair formation. Since all the olefins in Table 1 are uniformly strong donors, as evidenced by the relatively low oxidation potentials ($E^\circ_{ox} < 1.6$ V vs SCE), they are also expected to promote an analogous ionic disproportionation of NO_2, *i.e.*[43]



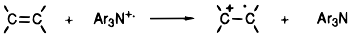
$$>C{=}C< + 2\,NO_2 \rightleftharpoons [>C{=}C<,\ NO^+]\ NO_3^- \qquad (27)$$

Furthermore, the reduction potential of nitrosonium in dichloromethane (E°_{red} 1.50 V vs SCE)[44] is sufficient to effect the rapid oxidation of the olefins in Table 1, since the redox reaction in eq 28 is predicted to be moderately exothermic (compare eq 17). The EDA complex is the putative (unobserved) precursor to the electron-transfer oxidation of the olefin,[26] *i.e.*



$$[>C{=}C<,\ NO^+]\ NO_3^- \rightleftharpoons >\overset{+}{C}-\overset{\cdot}{C}< + NO + NO_3^- \qquad (28)$$

Most importantly, the mechanistic formulation in eqs 27 and 28 accounts for (a) the immediate formation of the olefin cation radical and (b) the marked retardation of olefin epoxidation by added nitrate and by nitric oxide. Moreover, the facile (alternative) initiation of the epoxidation by added 1-electron oxidants circumvents the electron-transfer step in eq 28, and such oxidants can thus effectively generate higher steady-state concentrations of olefin cation radicals at low temperature *via* the alternative electron transfer, *i.e.*

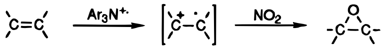


$$>C{=}C< + Ar_3N^{+\cdot} \longrightarrow >\overset{+}{C}-\overset{\cdot}{C}< + Ar_3N \qquad (29)$$

II. Olefin Cation Radical as the Critical Reactive Intermediate. There are four independent lines of evidence that identify the olefin cation radical as the critical reactive intermediate in epoxidation, namely (a) the strong correlation between the rate of epoxidation and the oxidation potential of the olefinic substrate, (b) the initiation of epoxidation at low temperatures by added 1-electron oxidants, (c) the ready transformation of the olefin cation radical to the epoxide by nitrogen dioxide, and (d) the alternative formation of epoxides *via* photoactivation of the olefin complex with tetranitromethane. Let us consider each of these separately in the following way.

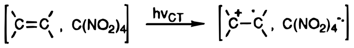
A. Structure/Activity Relationship. The effect of the donor strength on the reactivity of the olefins in Table 1 is best addressed with the structurally similar olefins **3**, **4**, and **5,** since they only differ in the remote *para*-substituent. For these olefins, the donor strength (as assessed by the oxidation potentials in Table 1) increases in the order **5** > **4** > **3**. Although no direct kinetics analysis was performed, the qualitative rate data in Table 1 show that **5** reacts very quickly (30 min), an intermediate rate is observed for **4** (12 h), and **3** reacts very slowly (24 h). Such a distinctive trend suggests that electron transfer is rate-limiting. This conclusion is also consistent with the equilibria in eqs 27 and 28, since the varied donor strength of the olefin will exert two synergistic effects on the overall rate of the electron-transfer oxidation with respect to (a) the degree of autoionization of NO_2, which will be greatest for **5** and least for **3** owing to a progressively enhanced complexation of NO^+ to stronger donors, and (b) the driving force for electron transfer, which is exergonic for **5**, moderately so for **4**, and almost thermoneutral for **3**, as given by $-\Delta G = F[E^\circ_{ox}(C{=}C) + E^\circ_{red}(NO^+)]$, where F is the Faraday constant and E° is the redox potential.

B. Electron-Transfer Initiation of the Epoxidation at Low Temperature. The rate of the epoxidation of olefins with NO_2 is subject to temperature control—merely lowering the temperature to −78 °C being sufficient to suppress the epoxidation. The addition of the strong 1-electron oxidant tris(2,4-dibromophenyl)amine cation radical (E°_{red} = 1.60 V vs SCE)[21] at this low temperature results in the rapid consumption of olefin and a quantitative yield of epoxide. It is independently known[45] that at −78 °C the aminium salt rapidly oxidizes each of the olefins in Table 3. Thus, the first-formed cation radical can be formulated as the critical intermediate in the reaction with NO_2, *i.e.*

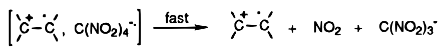


$$>C{=}C< \xrightarrow{Ar_3N^{+\cdot}} [>\overset{+}{C}-\overset{\cdot}{C}<] \xrightarrow{NO_2} -\overset{O}{C-C}- \qquad (30)$$

C. Photochemical Epoxidation *via* the Olefin Cation Radical in the Presence of NO_2. An independent verification of the reactivity of the olefin cation radical in eq 28 is provided in the charge-transfer irradiation of the EDA complexes of olefins and tetranitromethane. The latter is based on earlier studies[25,26] that demonstrated the direct irradiation of the charge-transfer (CT) absorption bands of the EDA complexes of tetranitromethane and olefins to generate the reactive triad in eq 32. The isolation of the trinitromethide salt (following the charge-transfer irradiation in Table 4) indicates that the triad in eq 32 leads directly to the epoxide *via* the collapse of the olefin cation radical with NO_2 according to eq 18.[46] Such an olefin cation radical paired with NO_2 must also be common to the thermal epoxidation and the aminium-catalyzed (low-temperature) epoxidation in eqs 2 and 7, respectively, since the product distributions in Table 4 are identical to those in Tables 1 and 3.



$$[>C{=}C<,\ C(NO_2)_4] \xrightarrow{h\nu_{CT}} [>\overset{+}{C}-\overset{\cdot}{C}<,\ C(NO_2)_4^{-\cdot}] \qquad (31)$$



$$[>\overset{+}{C}-\overset{\cdot}{C}<,\ C(NO_2)_4^{-\cdot}] \xrightarrow{fast} >\overset{+}{C}-\overset{\cdot}{C}< + NO_2 + C(NO_2)_3^- \qquad (32)$$

D. Direct Transformation of Olefin Cation Radicals to Epoxides with Nitrogen Oxides. Any formulation in which the olefin cation radical is the critical reactive intermediate in epoxidation with NO_2 requires that it be quantitatively converted to epoxide after it is formed according to the sequence of disproportionation/electron-transfer steps in eqs 27 and 28. Indeed, this requirement for the reactive triad is met by independent studies that establish the facile transfer of an oxygen

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[41] (a) Bontempelli, G.; Mazzochin, G.-A.; Magno, F. *Electroanal. Chem. Interfacial Electrochem.* **1974**, *55*, 91. (b) Wartel, A.; Boughriet, A.; Fischer, J. C. *Anal. Chim. Acta* **1979**, *19*, 811.

[42] Bosch, E.; Kochi, J. K. *Res. Chem. Intermed.* **1993**, *19*, 811.

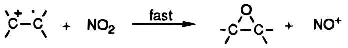
[43] The ionic disproportionation of NO_2 is, however, expected to be less favored in nonpolar solvents, and it will result in a slower reaction. Several authors have proposed that the reaction of NO_2 with olefins in nonpolar solvents such as carbon tetrachloride and cyclohexane proceeds *via* a radical (addition) mechanism. See Chatterjee *et al.* in ref 2a, Shechter in ref 2b, and Pryor in ref 4.

[44] Lee, K. Y.; Kuchynka, D. J.; Kochi, J. K. *Inorg. Chem.* **1990**, *29*, 4196.

[45] Nelsen, S. F.; Akaba, R. *J. Am. Chem. Soc.* **1981**, *103*, 2096. See also: Nelsen, S. F. *Acc. Chem. Res.* **1987**, *20*, 269.

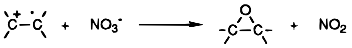
[46] Nitrosonium trinitromethide $(NO)C(NO_2)_3$ is presumably the other product of the photolysis, but the nature or subsequent reactivity of this ion pair is not known. However, any nitrosonium cation thus formed can intervene in the reaction pathway.

atom to the olefin cation radicals $\mathbf{1}^{\cdot+}$ and $\mathbf{8}^{\cdot+}$ from nitrogen dioxide in eq 18, *i.e.*



(33)

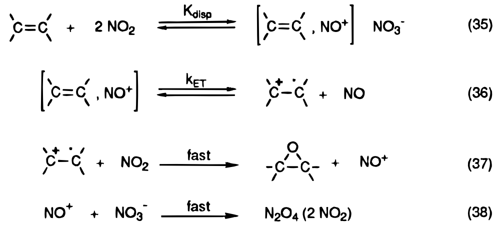
and nitrate in eq 19, *i.e.*



(34)

III. Electron Transfer in the Stoichiometric Epoxidation of Olefins with Nitrogen Dioxide. The formation and reaction of olefin cation radicals (as described in eqs 28 and 33) provide the mechanistic basis for the facile transfer of oxygen atom from NO_2 to olefin, as originally outlined in eq 23. The complete sequence of steps from olefin to epoxide, including the preequilibrium disproportionation of NO_2 in eq 27, is presented in Scheme 2.[47]

Scheme 2

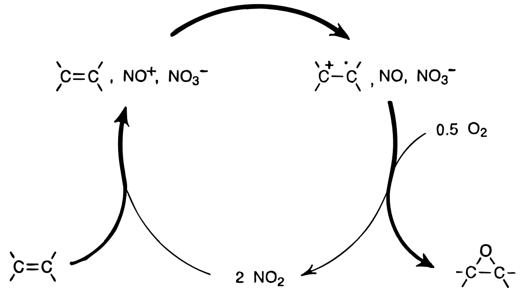


According to Scheme 2, the rate of olefin epoxidation is limited by electron transfer in eq 36, which occurs subsequent to the rapid disproportionation of NO_2. The marked suppression of epoxidation at low temperatures relates to electron-transfer reversibility in eq 36, which favors the free olefin at low temperatures (−78 °C), but the cation radical at 25 °C.[48] The addition of the aminium salt at low temperatures then increases the concentration of olefin cation radicals, and it results in a higher steady-state concentration of nitrosonium by virtue of eq 37.

We believe that the olefin cation radical is uniquely suited to effect rapid oxygen atom transfer from the paramagnetic NO_2 in eq 37, since the intermolecular interaction of $^{+}C{-}C^{\cdot}$ and $NO_2^{\cdot}$ is reminiscent of other radical/radical coupling processes with low activation barriers.[49] As such, it can occur in a single step by the direct transfer of oxygen anion radical ($O^{\cdot-}$) or in two successive steps via a cationic ($^{+}C{-}C{-}ONO$) adduct followed by oxirane ring closure and loss of NO^+.[50]

IV. Catalytic Mechanism for Olefin Epoxidation with Dioxygen. In order to gain insight into the nature of the catalytic epoxidations with dioxygen as the terminal oxidant, we note that nitrogen oxides in three different oxidation states, *viz.*, nitrogen(IV), -(III), and -(II) as NO_2, NO^+, and NO, respectively, can be employed with comparable catalytic efficiencies (see Table 2). Such an interchangeability of NO_x species is consistent with their ready interconversion during the course of the catalytic cycle. Accordingly, let us initially proceed from the combination of the simple catalytic process outlined in eqs 23 and 24 with the mechanistic details provided by eqs 35−38 (see Scheme 3). According to the catalytic mechanism in Scheme 3, olefin oxidation by nitrosonium (eq 36) is driven to completion by the efficient interception of nitric oxide (NO) by dioxygen,[19] and the accompanying olefin cation radical is rapidly converted to epoxide by oxygen atom transfer from nitrogen dioxide *via* eq 37.[47,51] Since the active species in NO_2 catalysis is the disproportionated nitrosonium nitrate, the separate initiation by nitrosonium salt $NO^+BF_4^-$ (see entry 3, Table 2) simply circumvents the initial disproportionation of NO_2 (compare eq 17).[52]

Scheme 3



The catalytic mechanism for olefin epoxidation as presented in Scheme 3 underscores the importance of electron transfer in the formation of paramagnetic intermediates. The role of nitrogen oxides in mediating the electron-transfer processes also extends to byproduct formation. Indeed, the appearance of rearranged ketones **18**−**20**, **24**, and **25** is common to both the stoichiometric epoxidation (Table 1) and the catalytic epoxidation (Table 2). Furthermore, its ubiquity extends to the aminium-induced (low-temperature) epoxidation in Table 3, as well as to the charge-transfer epoxidation with tetranitromethane in Table 4. Separate experiments confirm that the isolated epoxides are rapidly transformed into the corresponding ketones by catalytic amounts of strong 1-electron oxidants, including the triarylamine cation radical $\mathbf{8}^{\cdot+}$ and NO^+. [Note that NO_2 itself is somewhat less efficient.] On this basis, we conclude that an electron-transfer mechanism[31] for the rearrangement of the epoxides to ketones is compatible with the results in Table

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(47) An alternative formulation involves the reaction of the olefin cation radical with nitrate to generate the epoxide and NO_2 according to eq 34. However, the actual nitrogen oxide species (NO_2 or NO_3^-) which reacts with the olefin cation radical will depend on their relative concentrations and the relative rates of reaction in eqs 33 and 34. For the sake of clarity, we only present the formulation with NO_2, but we do not intend to exclude the direct involvement of nitrate.

(48) Such a temperature-dependent electron transfer is reminiscent of that previously observed during aromatic nitration with NO_2. We noted then that the electron transfer between NO^+ and dimethoxybenzene (DMB) is reversible. At ambient temperatures, the radical pair [$DMB^{\cdot+}$, NO] predominates, but at low temperatures the charge-transfer complex [DMB, NO^+] is favored. See: Rathore, R.; Bosch, E.; Kochi, J. K. *Tetrahedron* **1994**, *50*, 6722. Note that the temperature dependence of the preequilibrium disproportionation in eq 35 is expected to follow the reverse trend (compare Bosch, E.; Kochi, J. K. *J. Org. Chem.* **1994**, *59*, 3314).

(49) (a) Ingold, K. U. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York 1973; Vol. 1, pp 37 ff. (b) Note that the facile (paramagnetic) interactions of $NO_2^{\cdot}$ in bimolecular coupling to N_2O_4 and ionic disproportionation to $NO^+NO_3^-$ in eqs 25 and 26 also bear a strong parallel to the paramagnetic behavior of alkyl radicals ($R^{\cdot}$) in bimolecular coupling (R−R) and disproportionation [RH + R(−H)] with uniformly low activation barriers (see: Benson, S. W. *Adv. Photochem.* **1964**, *2*, 1).

(50) For examples of concerted and stepwise atom transfers in free radical chemistry, see: Ingold, K. U.; Roberts, B. P. *Free-Radical Substitution Reactions*; Wiley: New York 1971.

(51) Since the aerial oxidation of NO to NO_2 is likely to be a multistep process, the reviewer has suggested that an intermediate peroxynitrite radical ($^{\cdot}OONO$) may also enter separately into the catalytic chain process in Scheme 3 in indeterminant amounts. Compare the epoxidation of olefins by alkylperoxy radicals. Marnett, L. J. *Carcinogenesis* **1987**, *8*, 1365. See also: Mayo, F. R. *Acc. Chem. Res.* **1968**, *1*, 193.

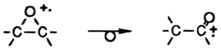
(52) The cation radical catalyzed chain oxygenation of adamantylideneadamantane with dioxygen has been reported by Nelsen et al. in ref 45 to yield adamantylideneadamantane−dioxetane. In oxygenations catalyzed by nitrosonium and nitryl salts, these authors found adamantylideneadamantane oxide to be the major (isolated) product. They suggested that epoxide was formed by a nitrosonium-catalyzed decomposition of the dioxetane. However, we believe that the epoxide formed during the oxygenations induced by nitrosonium can be ascribed to eq 37. We further note that the reaction of adamantylideneadamatane cation radical with dioxygen is generally competitive with its reaction with either nitrogen dioxide or nitrate. Since the competition (quantitatively) will be a function of the respective concentrations of reactants, the absolute rates of reactions and the reversibile nature of the reactions cannot be evaluated at this juncture.

Table 5. Electron-Transfer-Induced Rearrangement of Epoxides to Ketones[a]

epoxide	reagent[b]	ketone	conv (%)[c]
21	$TT^{\cdot +}SbCl_6^-$	**24**	20
22	$TT^{\cdot +}SbCl_6^-$	**25**	100
22	$TH^{\cdot +}BF_4^-$	**25**	100
22	$BA^{\cdot +}SbCl_6^-$	**25**	100
22	$MP^{\cdot +}SbCl_6^-$	**25**	2
22	$NO^+SbCl_6^-$	**25**	100

[a] All reactions with epoxide at 1.4×10^{-2} M and oxidant at 1.3×10^{-4} M in dichloromethane at 0 °C for 10 min. [b] TT = tetra-*p*-tolylethylene; TH = thianthrene; BA = tris(4-bromophenylamine; MP = *N*-methylphenothiazine; NO^+ = nitrosonium. [c] Based on recovered olefin. In all reactions, the ketone was formed in quantitative yield based on consumed olefin (see the Experimental Section).

5, *i.e.*



(39)

Thus, the best epoxide donors (*e.g.*, **17**) afford the highest yields of rearranged ketones. By the same token, the weakest epoxide donors (*e.g.*, **21**) are the least likely to produce rearranged ketones. Furthermore, weak 1-electron oxidants do not catalyze the rearrangement (see Table 5, entry 5). With the weakest epoxide donors (*i.e.*, **12** and **13** with $E° > 2$ V vs SCE), the amount of rearrangement is minor, and olefin oxidation leads only to epoxides in high yields.[53]

Summary and Conclusions

Oxygen atom transfer from nitrogen dioxide directly to olefins, according to the stoichiometry in eq 1, is (disappointingly) ineffective. In marked contrast, the corresponding oxygen transfer to the olefin cation radical is very fast and produces epoxides efficiently. Such a facile oxygen transfer (eq 33) forms the basis for the electron-transfer formulation of catalytic epoxidations with dioxygen as presented in Scheme 3. Thus, the olefin cation radical and NO are formed by an initial oxidation of the olefin by nitrogen dioxide (as the disproportionated ion pair $NO^+NO_3^-$) in eqs 35 and 36. The subsequent combination of the olefin cation radical with NO_2 generates the epoxide, together with the chain-transfer oxidant NO^+. The fast aerial oxidation of nitric oxide to NO_2 then completes the catalytic cycle. We predict that the facile oxygen atom transfer from nitrogen dioxide to olefin cation radicals in eq 33 will prove to be the prototypical example of a general case in which catalytic epoxidations are considerably facilitated by the electron-transfer generation of olefin cation radicals as the reactive intermediate by other types of (oxidizing) catalytic species.[11,12]

Experimental Section

Epoxidation of Olefins with Nitrogen Dioxide. General Procedure. A solution of nitrogen dioxide in dichloromethane (3 mL, 0.1 M) was prepared under an argon atmosphere in a Schlenk tube fitted with a Teflon stopcock. Adamantylideneadamantane **1** (70 mg, 0.26 mmol) was added, the flask sealed with the aid of a Teflon stopcock, and the solution stirred at 25 °C for 1 h. The solution was degassed, and the gases were transferred to an evacuated 5-cm gas IR cell. The IR spectrum thus recorded exhibited the characteristic absorbances at 1852, 1875, and 1904 cm^{-1} of nitric oxide.[16b] The gases from the IR cell were then transferred to an evacuated 1-cm quartz cuvette, and the UV absorption spectrum was recorded. The three sharp absorbances at $\lambda = 204$, 214, and 226 nm due to nitric oxide were observed.[16a] The solvent and remaining nitrogen oxides were removed *in vacuo*, and the solid residue was recrystallized from ethanol to yield adamantylideneadamantane oxide **12** as colorless crystals in 96% yield.

Effect of Solvent on the Rate of Epoxidation with NO_2. Reactions were carried out as described above, except the solvent was tetrachloromethane. The progress of the reaction was monitored by quantitative GC−MS: after 1 h there was 13% conversion to epoxide **12**, after 2.5 h there was 30% conversion to **12**, and after 24 h **12** was formed quantitatively. In cyclohexane solution, a 9% conversion of **1** to **12** was observed after 1 h, 27% after 2.5 h, and 100% conversion after 24 h.

Effect of Additives on the Rate of Epoxidation with NO_2. A. Nitric Oxide. A solution of nitrogen dioxide in dichloromethane (3 mL, 0.1 M) was prepared under an argon atmosphere in a Schlenk tube capped with a rubber septum. The solution was cooled to −10 °C, and NO (7 mL) was bubbled into the solution with the aid of a gas-tight syringe. Adamantylideneadamantane **1** (70 mg, 0.26 mmol) was added, the flask capped with a Teflon stopcock, and the solution stirred at 25 °C for 1 h. The solvent and nitrogen oxides were removed *in vacuo*, and the solid residue was analyzed by quantitative GC−MS. Unreacted **1** (91%) and **12** (8.5%) were the only organic products. The oxidation of **8** (0.09 mmol) with NO_2 (0.10 mmol) in dichloromethane (3 mL) was also severely retarded by added NO (0.10 mmol). After 2 h, there was only 11% conversion of **8** to a mixture of **22** and **25**.

B. Nitrate. A solution of nitrogen dioxide in dichloromethane (3 mL, 0.1 M) was prepared under an argon atmosphere in a Schlenk tube capped with a rubber septum. Tetrabutylammonium nitrate (0.3 mmol) and adamantylideneadamantane **1** (70 mg, 0.26 mmol) were added sequentially. The flask was capped with a Teflon stopcock and the solution stirred at 25 °C for 1 h. The solution was diluted with dichloromethane, washed with water, and dried with anhydrous $MgSO_4$. Quantitative GC−MS analysis indicated that **1** was largely recovered (95%) along with traces of **12** (∼4.5%).

The other olefins listed in Table 1 were treated according to the general procedure in dichloromethane solution. The oxidation products were isolated by TLC or flash chromatography, and the characteristic physical data are included in the supporting information.

Nitrogen Dioxide-Catalyzed Epoxidation of Olefins with Oxygen. General Procedure. A solution of adamantylideneadamantane **1** (536 mg, 2 mmol, 20 mL) in dichloromethane (20 mL) was prepared in a flask fitted with a side arm. The solution was cooled to 0 °C in an ice bath and saturated with oxygen and the flask sealed with a Teflon stopper. An O_2-filled gas buret was attached to the side arm, and a dichloromethane solution of nitrogen dioxide (1.0 mL, 0.1 mmol) was added with the aid of an all-glass syringe. The temperature of the solution was carefully controlled at 0 °C, and the uptake of oxygen was monitored. After 12 h, 20 mL (0.89 mmol) of oxygen was consumed, and the uptake of oxygen ceased. The head gas was transferred to an evacuated 5-cm IR gas cell and the presence of NO_2 confirmed by the characteristic absorptions at $\nu = 1629$ and 1604 cm^{-1}.[20] The reaction was worked up as described above and adamantylideneadamantane oxide **12** (556 mg, 97%) isolated as a colorless solid.

Electron-Transfer Catalyzed Oxidation of Olefins with Nitrogen Dioxide. General Procedure. A dichloromethane solution of adamantylideneadamantane **1** (180 mg, 0.67 mmol, 60 mL) was prepared, under an argon atmosphere, in a Schlenk flask and cooled to −78 °C in a dry ice/acetone bath. A green solution of tris(2,4-dibromophenyl)aminium hexachloroantimonate (7 mg, 0.006 mmol, 5 mL) in dichloromethane was prepared in a separate Schlenk flask and cooled to −78 °C under an argon atmosphere. The solution of the aminium cation radical was rapidly transferred by cannula into the cold solution of **1** which immediately became purple. A cold (−78 °C) dichloromethane solution of NO_2 (0.5 mmol, 10 mL) was then rapidly added with the aid of a cannula. The resultant mixture was stirred at −78 °C for 20 min, whereupon the solution turned blue [the absorbance at $\lambda_{max} = 690$ nm corresponded to the formation of N_2O_3 by combination of NO and NO_2].[22] The gaseous products were transferred to an evacuated 5-cm IR cell, and the characteristic absorbances of NO ($\nu_{NO} = 1876$ cm^{-1})[16b] and NO_2 ($\nu_{NO} = 1629$, 1601 cm^{-1})[20] were observed. After complete removal of the nitrogen oxides *in vacuo*, the solution was slowly warmed to 0 °C and the solvent evaporated *in vacuo*. The crude

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(53) However, we hasten to add the caveat that the mechanistic distinction been electron-transfer and electrophilic (acid) catalysis[54] is difficult to rigorously delineate. See: Rathore, R.; Kochi, J. K. *J. Org. Chem.* **1995**, *60*, 7479.

(54) The acid-catalyzed pinacol rearrangement of epoxides, in particular adamantylideneadamantane oxide, is well known (see: Wynberg, H.; Boelema, E.; Wieringa, J. H.; Strating, J. *Tetrahedron Lett.* **1970**, 3613).

residue was analyzed by quantitative GC−MS and found to contain adamantylideneadamantane oxide **12** (0.629 mmol, 94%), adamantylideneadamantane **1** (< 0.004 mmol), and adamantanone (∼0.003 mmol). A control ("uncatalyzed") reaction was performed as follows: An identical solution of **1** and NO_2 in dichloromethane was prepared in a separate Schlenk flask (but without the electron-transfer catalyst) and stirred at the same temperature for the same time and then worked up in the same way. The solution remained colorless throughout the reaction time, and there was no evidence for the formation of either NO or N_2O_3 [IR and UV−vis spectroscopic analysis]. The olefin **1** (0.636 mmol, 95%) was recovered, and less than 0.004 mmol of epoxide **12** was detected by quantitative GC−MS analysis. The other olefins listed in Table 3 were treated according to the above procedure at the concentrations and times listed. In all cases, the olefin was recovered intact (>95%) from the uncatalyzed (control) reaction.[55]

Epoxidation of Adamantylideneadamantane with Nitryl Tetrafluoroborate. A Schlenk flask was charged with nitryl tetrafluoroborate (130 mg, 1 mmol) in a drybox and the flask capped with a rubber septum. The flask was removed from the drybox and dry acetonitrile (5 mL) added under a flow of argon with the aid of a hypodermic syringe. A dichloromethane solution of adamantylideneadamantane **1** (268 mg, 1 mmol, 5 mL) was prepared under an argon atmosphere in a separate Schlenk flask, and both flasks were cooled to −40 °C in a dry ice/acetone bath. The dichloromethane solution of **1** was then rapidly transferred by cannula into the acetonitrile solution of $NO_2^+BF_4^-$ and the mixture stirred at this temperature for 5 min. A mixture of aqueous bicarbonate and ether was added and the mixture vigorously stirred as it warmed to room temperature. The organic layer was washed with water and dried and the solvent removed *in vacuo*. Adamantylideneadamantane oxide **12** was obtained as a colorless crystalline solid (264 mg, 93%). A second identical reaction was diluted with dichloromethane after 5 min, an excess of 18-crown-6 (5 mmol) was added, and the UV−vis absorption spectrum of the dilute solution was recorded. The characteristic absorption spectrum of the complex of nitrosonium with 18-crown-6 ($\lambda_{max} = 300$ nm)[56] confirmed the formation of NO^+ (0.9 mmol) by comparison with a standard solution of 18-crown-6 and $NO^+BF_4^-$.

A separate experiment was performed as described above at −40 °C with 134 mg (0.5 mmol) of **1** and 65 mg of $NO_2^+BF_4^-$ (0.5 mmol), but the reaction mixture was stirred at −30 °C for a prolonged period. During this time, a series of aliquots were extracted and analyzed by quantitative GC. The yield of epoxide **12** steadily decreased after 5 min, with a concomitant increase in the yield of a second product. After 1 h, there was no epoxide, and the spiroketone **14** was isolated in quantitative yield (147 mg, 0.49 mmol) as a white solid.

Photochemical Oxidation of Olefins with Tetranitromethane *via* the Selective Activation of the EDA Complex. General Procedure. Tetranitromethane (50 μL, 0.41 mmol) was added, under a flow of argon, to a dichloromethane solution of **1** (45 mg, 0.17 mmol, 5 mL) in a quartz cuvette. The cuvette was sealed with a Teflon stopcock and the solution irradiated at 25 °C with light from a medium-pressure 250-W Hg lamp passed through a water filter and a 410 nm ESCO sharp cutoff filter. This ensured that only the charge-transfer absorption band was irradiated. After 30 min, the solution was diluted with dichloromethane, washed with water, dried, and analyzed by quantitative GC−MS. The epoxide **12** (18.6 mg, 0.065 mmol), **1** (24.8 mg, 0.093 mmol), and adamantanone (2 mg, 0.013 mmol) were observed as the only organic products [the conversion of **1** was thus 45%]. The combined aqueous washings were diluted to 2500 mL, and the UV−vis absorption spectrum was measured. The concentration of trinitromethide was estimated to be 5.2×10^{-5} mol ($\lambda_{max} = 350$ nm, $\epsilon = 14\,000$ M^{-1} cm^{-1}),[27] and it corresponded to 80% of the conversion of **1**. A second identical solution of TNM and **1** was prepared, under an argon atmosphere, in a separate Schlenk tube and stored at 25 °C in the dark for the duration of the irradiation. This "dark" control was worked up simultaneously with the irradiated solution and the olefin **1** recovered quantitatively. Analysis of the aqueous washings indicated that less than <0.1% of trinitromethide was formed.

Reaction of the other olefins was similarly performed at the concentrations and times listed in Table 4. A dichloromethane solution of **5** and TNM (0.05 M) was irradiated for 25 min (see Table 4, entry 7) and the solution then divided into two portions. One portion was immediately worked up and analyzed. The second portion was stored in the dark for 5 h before analysis. There was no significant difference in the final analyses. During the irradiation of **8** and TNM (see Table 4, entry 8), an intense purple color developed which dissipated after the solution was stirred for a few minutes in the dark. On cooling the solution to −78 °C, the purple color persisted. The UV−vis absorption spectrum confirmed the formation of $\mathbf{8}^{\cdot+}$ ($\lambda_{max} = 516$ nm). Indeed, when the irradiation was performed at −78 °C, a dark purple colored solution was formed. However, the conversion was <5% even after 4 h.

Reaction of Tetra-*p*-tolylethylene Cation Radical Hexachloroantimonate with Nitrogen Oxides. Nitrate. A Schlenk flask was charged with tetratolylethylene cation radical hexachloroantimonate (110 mg, 0.152 mmol) in the drybox and the flask capped with a rubber septum. The flask was removed from the drybox and dichloromethane (60 mL) added with the aid of a syringe. The resultant dark purple solution was cooled to 0 °C in an ice bath. A cold (0 °C) solution of $PPN^+NO_3^-$ (91 mg, 0.152 mmol) in dichloromethane (5 mL) was added with the aid of a Teflon cannula under argon pressure. The purple color was quenched over the course of 5 min, the resultant pale yellow solution was washed with water (3 × 25 mL) and dried, and the solvent was removed *in vacuo*. Quantitative GC−MS and NMR analysis of the crude reaction product indicated that tetratolylethylene oxide was formed in 62% yield. In addition, the rearranged ketone (20%) was observed together with traces of the nitroarene (previously detected), three chlorinated products (M^+ *m/z* 433), and a product tentatively identified as 3,6-dimethyl-9,10-bis(4′-methylphenyl)phenanthrene which was >95% pure by ^1H and ^{13}C NMR analysis (see the supporting information). In a separate reaction, a dark purple solution of $\mathbf{8}^{\cdot+}$ $SbCl_6^-$ was cooled to −78 °C under an argon atmosphere, and a precooled (−78 °C) dichloromethane solution of PPN nitrate was added with the aid of a cannula. There was no apparent color change over the period of 1 h, but the color rapidly bleached upon warming to 0 °C.

Nitrogen Dioxide. A Schlenk flask was charged with $\mathbf{8}^{\cdot+}SbCl_6^-$ (72 mg, 0.10 mmol) in the drybox and the flask capped with a rubber septum. Dichloromethane (20 mL) was added, and the resultant purple solution was added dropwise, with the aid of a cannula, to a cool (5 °C) dichloromethane solution of nitrogen dioxide (0.15 mmol, 80 mL). The purple color completely faded after the addition was complete. The solution was washed with water and dried and the solvent removed *in vacuo*. The pale yellow residue, analyzed by quantitative GC−MS, contained epoxide **22** (19.6 mg, 0.048 mmol), acetophenone **25** (9.1 mg, 0.022 mmol), and 3,6-dimethyl-9,10-bis(4′-methylphenyl)phenanthrene. The relative yield of the phenanthrene increased when the reaction was performed at higher concentrations.

Reaction of Adamantylideneadamantane Cation Radical with Nitrogen Oxides. Nitrogen Dioxide. A dichloromethane solution of antimony pentachloride (0.6 mL, 0.5 M, 0.3 mmol) was added, under a flow of argon, to a vigorously stirred dichloromethane solution of tris(2,4-dibromophenyl)amine (85 mg, 0.11 mmol, 2 mL) in a Schlenk flask. The resultant deep green solution was stirred at 25 °C for 10 min. Hexane (10 mL) was added with the aid of a hypodermic syringe and the resultant green precipitate allowed to settle. The supernatant solution was carefully removed by cannula using argon pressure and the solid washed twice in this manner with hexane (2 × 10 mL). The dark green solid was dissolved in 20 mL of dichloromethane and cooled to −78 °C and the solution transferred dropwise by cannula into a cold (−78 °C) dichloromethane solution of adamantylideneadamantane **1** (27.2 mg, 0.10 mmol, 80 mL) under an atmosphere of argon. The mixture which immediately became purple was stirred at −78 °C for 10 min, and a cold (−78 °C) dichloromethane solution of nitrogen dioxide (1.1 mL, 0.11 mmol) was added by cannula under a flow of argon. The color bleached to pale green within 1 min. The solution was immediately diluted with ether and washed with water (2 × 25 mL). The organic layer was separated and dried and the solvent removed *in vacuo*. The residue was analyzed by quantitative GC−MS: Adamantylideneadamantane oxide **12** (23.3 mg, 0.08 mmol, 81%), adamantylideneadamantane **1** (0.5 mg, 2%), spiroketone **14** (0.6 mg, 2%), and an unidentified chlorinated product [GC−MS *m/z* 302 (M^+,^{35}Cl, 100), 304 (M^+,^{37}Cl, 34]. A second reaction was performed

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[55] The low conversions (<5%) observed in the control reactions may have occurred adventitiously during workup.

[56] Elsenbaumer, R. L. *J. Org. Chem.* **1988**, *53*, 437.

in the same manner, but the reaction was not worked up. The colorless solution obtained after addition of NO$_2$ was further diluted and 18-crown-6 (0.5 mmol) added. The UV–vis absorption spectrum confirmed the formation of nitrosonium (0.08 mmol) by the characteristic absorbance at $\lambda_{max} = 300$ nm.[56]

Nitrate. A dichloromethane solution of adamantylideneadamantane **1** radical cation (0.102 mmol, 80 mL) was prepared with tris(2,4-dibromophenyl)aminium hexachloroantimonate at −78 °C, as described above. A cold (−78 °C) solution of PPN$^+$NO$_3^-$ (65 mg, 0.11 mmol) in dichloromethane (20 mL) was rapidly added with the aid of a cannula, and the purple color bleached immediately. The colorless reaction mixture was worked up and analyzed as described above. Adamantylideneadamantane oxide **12** (13.1 mg, 0.05 mmol, 46%), adamantylideneadamantane **1** (5.9 mg, 21%), the spiroketone **14** (4.1 mg, 14%) and an unidentified chlorinated product [GC–MS *m/z* 302 (M$^+$, ^{35}Cl, 100), 304 (M$^+$, ^{37}Cl, 34] were formed.

Stability of Epoxides. Nitrogen Dioxide. A dichloromethane solution of epoxide **16** and 1 equiv of NO$_2$ was stirred at 25 °C, and aliquots were periodically removed for GC–MS analysis. Rearranged ketone **19** was detected in 15% conversion after 2 h. Under similar conditions, adamantylideneadamantane oxide **12** underwent <3% conversion to the rearranged ketone **14**.

Nitrosonium. A Schlenk flask was charged with nitrosonium hexachloroantimonate (3 mg, 0.008 mmol) in the drybox, and the flask was sealed with the aid of a rubber septum. The flask was removed from the glovebox and dichloromethane (8 mL) added to the flask under a flow of argon. A dichloromethane solution of tetratolylethylene oxide **22** (50 mg, 0.124 mmol, 3 mL) was prepared, under an argon atmosphere, in a separate Schlenk flask and transferred with the aid of a cannula into the stirred slurry of nitrosonium salt. After 10 min, the slurry was diluted with dichloromethane (25 mL). The dichloromethane extract was washed with aqueous sodium bicarbonate and water and dried over magnesium sulfate, and the solvent was removed *in vacuo* to yield the rearranged ketone **25** in 91% yield. Adamantylideneadamantane oxide **12** underwent a 20% conversion to ketone **14** when treated with 20 mol % NO$^+$BF$_4^-$ at 25 °C in dichloromethane for 2 h.

Cation Radicals. A dichloromethane solution of **22** (50 mg, 0.124 mmol, 5 mL) was prepared, under an argon atmosphere, in a Schlenk flask sealed with a rubber septum. A purple solution of **8**$^{\cdot+}$SbCl$_6^-$ (9.5 mg, 0.013 mmol) in dichloromethane (2 mL) was added by cannula and the resultant purple solution stirred at room temperature for 20 min. Since there was no visible color change, the reaction was quenched by addition of zinc dust (50 mg) into the vigorously stirred mixture. After the purple color bleached, the slurry was diluted with dichloromethane (25 mL), washed sequentially with saturated aqueous sodium bicarbonate, water, and brine, and dried over magnesium sulfate. The solvent was removed *in vacuo*. The residue consisted of rearranged ketone **25** (93%) and tetratolylethylene oxide **22** (7%), in addition to tetratolylethylene **8** (6%). Rearrangement of tetraphenylethylene oxide **21** yielded α,α,α-triphenylacetophenone (**24**), mp 179 °C (lit.[57] mp 179–180 °C).

The efficacy of the cation radical catalyzed rearrangement was further evaluated by varying both the 1-electron oxidant and the epoxide. For example, when tetraphenylethylene oxide **21** was treated with 1 mol % **8**$^{\cdot+}$SbCl$_6^-$ under otherwise identical conditions, there was only a 20% conversion of the epoxide to α,α,α-triphenylacetophenone after 10 min. [After 3 h, the rearranged ketone was formed in quantitative yield.] The rearrangement of epoxide **22** to ketone **25** was efficiently catalyzed by both thianthrene cation radical[58] ($E°_{red} = 1.20$ V vs SCE) and tris(4-bromophenyl)aminium[21] ($E°_{red} = 1.16$ V vs SCE). However, *N*-methylphenothiazine cation radical[58] ($E°_{red} = 0.70$ V vs SCE) was not effective, and only 2% rearrangement of **22** to ketone **25** was observed after 10 min (see Table 5). The thermodynamics were further evaluated by measuring the oxidation potential of some representative epoxides at a platinum electrode as 5×10^{-3} M solutions in dichloromethane containing 0.2 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. It was particularly noteworthy that significant amounts of the rearranged ketone were observed—even on simply recording the cyclic voltammograms at scan rates of 1 V s^{-1}. The cyclic voltammograms (CV) were comprised of two irreversible anodic waves, the more positive of which was unequivocally assigned to that of the rearranged ketone by CV comparison with that of the authentic ketone.[34] The first anodic wave was assigned to the epoxide. The ratio of the two anodic waves was dependent on the CV scan rate—epoxide predominanting at higher scan rates and the ketone predominanting at lower scan rates, as shown in Figure 3. The anodic peak potentials for the irreversible oxidation of epoxides ranged from 1.3 V vs SCE for epoxide **21** to more than 2.0 V for **12**. [Note the latter did not undergo rearrangement in either the stoichiometric or catalyzed oxidation described above.]

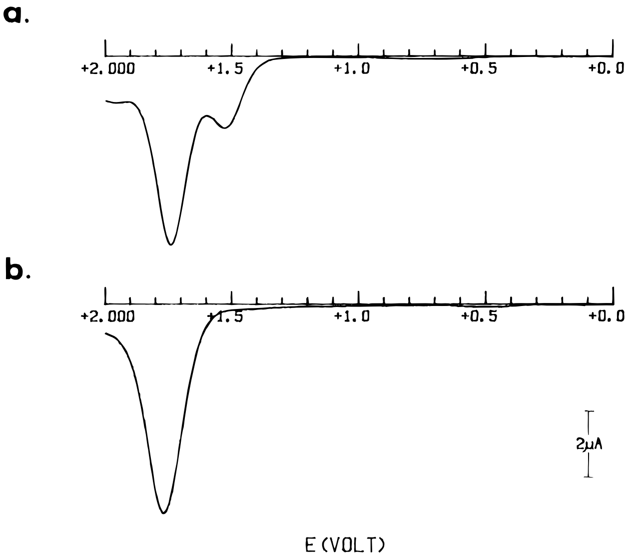

Figure 3. Square wave voltammograms of (a) epoxide **22** and (b) ketone **25** (both at 5×10^{-3} M) in dichloromethane containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte.

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Supporting Information Available: Text describing the materials and instrumentation used, the preparation and characterization of unsymmetrical adamantylidene analogues, tetraarylethylenes, and their oxidation products, the preparation of tetra-*p*-tolylethylene cation radical hexachloroantimonate, the spectral characterization of the precursor EDA complexes formed from olefins and tetranitromethane, and the cyclic voltammetry of olefins and epoxides and figures showing the ^{1}H and ^{13}C NMR spectra for 2-(4-methylphenyl)-2-(4-methylbenzoyl)adamantane (**19**) and 3,6-dimethyl-9,10-bis(4′-methylphenyl)phenanthrene (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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