

Electron-transfer Catalysis of Olefin Epoxidation with Nitrogen Dioxide (Dinitrogen Tetroxide)

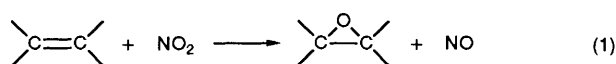
Eric Bosch and Jay K. Kochi

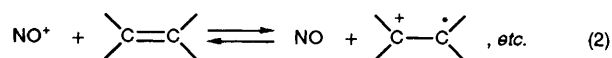
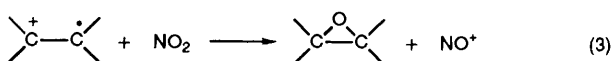
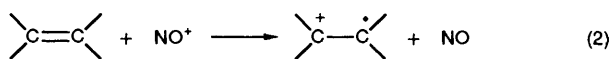
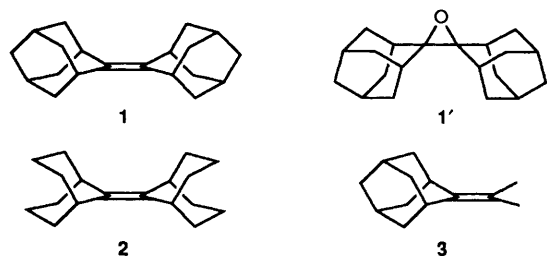
Chemistry Department, University of Houston, Houston, Texas 77204-5641, USA

The novel epoxidation of diadamantylidene **1** and related hindered olefins with NO₂ proceeds by way of the cation radical **1**^{•+} generated during the electron-transfer chain (ETC) catalysis initiated by nitrosonium.

Despite the generally favourable energetics, the thermal conversion of olefins to epoxides *via* the conceptually straightforward oxygen-atom transfer from nitrogen dioxide, *i.e.* reaction (1), is unknown¹ at ambient temperatures. [For example, based on the readily available thermodynamic data,² ethylene epoxidation in eqn. (1) is exothermic by 11.4 kcal mol⁻¹ and $\Delta G^\circ = -11.0$ kcal mol⁻¹ at 25 °C; 1 cal = 4.184 J]. More commonly, the combination of ethylene and various alkenes with nitrogen dioxide (in equilibrium with its dimer

N₂O₄) leads to complex mixtures containing a variety of olefin adducts including dinitro, nitronitrite, nitronitrate, nitronitroso and related derivatives³ as well as allylic substitution products.⁴ Our approach to the promotion of olefin epoxidation according to eqn. (1) was to identify diadamantylidene **1** as the olefinic substrate, since multiple access to its sterically





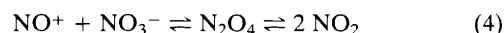
Scheme 1

hindered double bond is restricted.⁵ Thus the exposure of **1** (5.7 mmol dm⁻³) to excess of NO₂ (2 equiv.) in dichloromethane at 23°C under an inert (argon) atmosphere led within 2 h to an 87% (isolated) yield of the crystalline epoxide **1'** that was free of nitro and nitrito contaminants. Coupled with the IR analysis of nitric oxide (ν_{NO} 1876 cm⁻¹),⁷ we conclude that epoxidation of diadamantylidene with NO₂ indeed occurs with the stoichiometry given in eqn. (1). Moreover, the analogous olefin **2** with NO₂ also afforded excellent yields (> 95%) of its epoxide, but during ca. 4 h owing to its conformationally less rigid structure. By contrast, the unsymmetrical analogue **3** yielded a complex product mixture resulting from the facile allylic (methyl) attack, which is relatively unimportant in either **1** or **2**.⁸

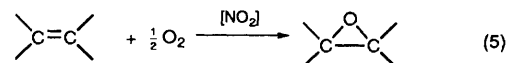
In order to ascertain how the oxygen atom is transferred in eqn. (1), the epoxidation of **1** (5.8 mmol dm⁻³) was reexamined with more NO₂ (4 equiv.) at low temperatures, at which the rate was markedly retarded [e.g. conversion was <5% (20 min) at -78°C]. Significantly, the addition of catalytic amounts (1%) of a one-electron oxidant (either the nitrosonium salt⁹ NO⁺ BF₄⁻ or the aminium salt¹⁰ Ar₃N⁺ SbCl₆⁻) at this low temperature to the solution of **1** and NO₂ led immediately to quantitative yields of diadamantylidene epoxide (*i.e.* complete epoxidation within 20 min at -78°C). Control experiments showed that both additives were capable of the rapid oxidation of diadamantylidene to its purple-coloured cation radical **1**^{•+}, *e.g.* reaction (2), which was readily identified by its diagnostic absorption spectrum (λ_{max} 530 nm¹¹). Since the cation radical **1**^{•+} was easily converted by NO₂ to epoxide **1'** on mixing, we propose the catalytic sequence for epoxidation to be that in Scheme 1.

Electron-transfer chain (ETC) catalysis¹² as presented in Scheme 1 relies on the production of the cation radical [eqn. (2)] as the reactive intermediate which is then rapidly converted in the unique epoxidation step with NO₂ [eqn. (3)]. As such, the severe retardation of NO⁺-induced catalysis that was observed in the presence of added NO gas is consistent with the reversibility of the electron-transfer step [eqn. (2)].⁹ Furthermore, the retardation that was also effected by added nitrate (as the tetrabutylammonium salt) provides an impor-

tant clue to the role of NO⁺ in the initiation step for eqn. (1), *i.e.* ¹³ reaction (4).



Olefin epoxidation by nitrogen dioxide [eqn. (1)] is a particularly appealing catalytic process since the instantaneous reoxidation of nitric oxide by dioxygen¹⁴ (*i.e.* NO + ½O₂ → NO₂), can accommodate the novel autoxidation in eqn. (5)¹⁵ that proceeds according to the mechanism in Scheme 1.



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