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PHOTOOXIDATION OF ADAMANTYLIDENEADAMANTANE IN THE PRESENCE OF TETRACYANOETHYLENE. A NEW PHOTOEPOXIDATION PROCESS

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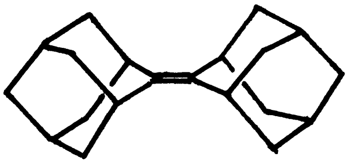
Irradiation of a dichloromethane solution of adamantylideneadamantane in the presence of tetracyanoethylene with bubbling oxygen through a pyrex filter by a 650-W tungsten-halogen lamp gave a high yield (84%) of the corresponding epoxide. A reasonable mechanism for the efficient epoxidation will be described.

We have previously shown that selective excitation of contact charge-transfer pairs of organic compounds with molecular oxygen exhibits various types of oxidation reactions depending on the substrates used.[1)] We now wish to report efficient photochemical epoxidation of adamantylideneadamantane 1 in the presence of tetracyanoethylene used as an electron acceptor. Although photo-induced electron-transfer oxidations have been extensively studied using cyanoaromatics as sensitizers,[2)] little systematic study has been made on the role of excited charge-transfer complexes in electron-transfer oxidations. Since excited charge-transfer complexes may give radical ion pairs,[3)] it can be generally expected that photoreactions of electron-donor-acceptor (EDA) systems in the presence of oxygen may lead to their interesting oxidation chemistry and will give important information on structure-reactivity relationships of the excited charge-transfer complexes using oxygen as a probe.

We selected 1 as an electron donor since 1) 1 has a low oxidation potential ($E^{\circ\prime}$ = 1.45 V/SCE in CH_3CN),[4)] 2) the radical cation, $1^{+\cdot}$, is long-lived at room temperature because it is Bredt's rule protected,[4)] and 3) $1^{+\cdot}$ is known to react with triplet oxygen.[5)] These characteristics of 1 and $1^{+\cdot}$ will lead to clean reactions of 1 under oxidative conditions and thus give mechanistic information for the reaction pathways.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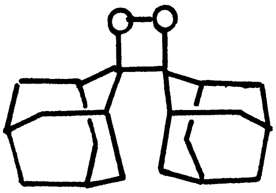
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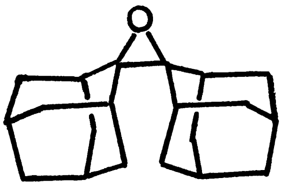
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When 1 (0.05 mol/dm^3) and tetracyanoethylene (TCNE, 0.05 mol/dm^3) were mixed in dichloromethane, the solution assumed a pale purple color, and exhibited a long wavelength absorption band (λ_{max} ~540 nm) not present in the spectrum of the individual components at the same concentrations. Photooxidations were carried out at the same concentrations of 1 and TCNE. The results are summarized in Table 1.

When a dichloromethane solution of 1 and TCNE were irradiated through a pyrex filter by a 650-W tungsten-halogen lamp with bubbling oxygen for 7 h (entry 3), a high yield (84%) of the epoxide 3 [6a] was obtained along with a small amount of the dioxetane 2[6b] and the recovered olefin (12%). Furthermore, selective excitation of the charge-transfer band with glass filters (>350 or >500 nm) under similar oxidative conditions (entries 4 and 5) caused fairly slow but selective reactions to give only 3 (11-14%). In a striking contrast, photooxidation of 1 in the absence of TCNE gave a very different product distribution, and 3 was found to be a minor product. Thus, irradiation of a dichloromethane solution of 1 through a pyrex filter with the 650-W tungsten-halogen lamp with bubbling oxygen for 15 h gave 3 and adamantanone 4 in 11 and 20% yields, respectively (entry 1). A similar reaction with a 1 kW high-pressure mercury lamp gave also 3 and 4 in 9 and 30% yields, respectively (entry 2). Since irradiation of 2 in the presence of TCNE (0.05 mol/dm^3) through a pyrex filter under oxygen gave only a trace amount of 3 (entry 6), 3 is not a secondary product from the decomposition of 2 in the presence of TCNE.

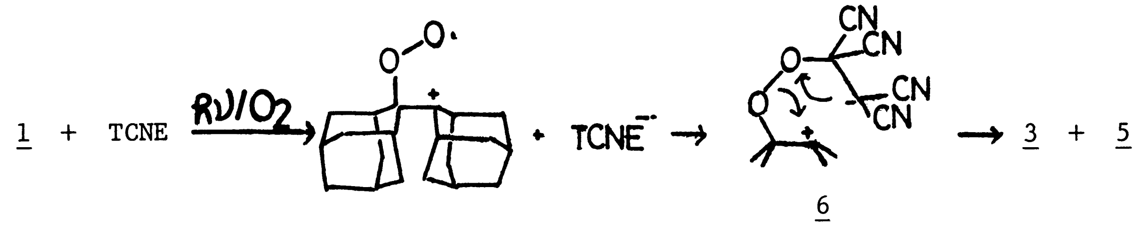
Table 1. Photooxidation of Adamantylideneadamantane in the Presence of Tetracyanoethylene under Oxygen in Dichloromethane [a]

No.	System	Light source	Wavelength / nm	Time / h	Product yield/%[b]			
					1	2	3	4
1[c]	1	650-W tungsten-halogen lamp	≳300	15	52	trace	11	20
2[c]	1	1 kW high-pressure mercury lamp	313	16	38	unobs	9	30
3	1/TCNE	650-W tungsten-halogen lamp	≳300	7	12	2	84	unobs
4	1/TCNE	650-W tungsten halogen lamp	≳350	15	69	unobs	14	unobs
5	1/TCNE	650-W tungsten halogen lamp	≳500	15	80	unobs	11	unobs
6	2/TCNE	650-W tungsten halogen lamp	≳300	1	unobs	31	1	54

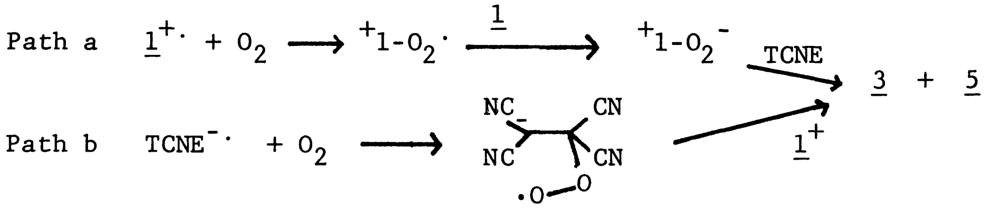
a) Reactions were usually followed and the products were isolated by TLC, and weighed yields are reported. b) The entry "unobs" means that none of these products were detected by TLC. c) Reactions in the absence of TCNE.

A ^{13}C-NMR spectrum of the reaction mixture (entry 3, for example) showed signals at 108.56 and 47.51 (ppm/TMS) in acetone-d_6. These signals can be assigned to tetracyanoethylene oxide 5 formed in the solution since authentic 5$^{7)}$ exhibited the signals at 108.51 and 47.40 ppm in the same solvent.

These results strongly suggest that oxygen-atom transfer occurs in the present epoxide-forming reaction with concomitant formation of 5. The following mechanism involving zwitterionic intermediate 6 may be considered for the efficient epoxide forming reaction.$^{8)}$ Thus, irradiation of the charge-transfer complex of 1 and TCNE will give a radical ion pair ($1^{+\cdot}$ + $TCNE^{-\cdot}$) which reacts with oxygen giving another radical ion pair ($^{+}1\text{-}O_2\cdot$ + $TCNE^{-\cdot}$). The resulting peroxy radical cation, $^{+}1\text{-}O_2\cdot$, will recombine with $TCNE^{-\cdot}$ to give 6 followed by elimination of 5 to give 3.



In order to get further insight into the reaction mechanism, we have undertaken electrochemical experiments. First, preparative electrochemical oxidation of 1 with bubbling oxygen in the presence of 10-fold excess of TCNE gave exclusively 2 but no detectable amount of 3.$^{10)}$ Since $1^{+\cdot}$ is known to react rapidly with oxygen in a chain fashion to give a high yield of 2,$^{5b)}$ TCNE could act as an oxygen acceptor to intercept the chain oxidation of the photochemically-generated 1^{+} (path a). However, the present result suggests that TCNE is not likely to be an oxygen acceptor.



Second, cyclic voltammetry of TCNE was examined in the presence and absence of oxygen to check the possibility of oxygenation of $TCNE^{-\cdot}$ followed by oxygen-atom transfer to $1^{+\cdot}$ (path b). TCNE exhibited completely reversible CV behavior in the absence of oxygen ($E^{o\prime}_{red}$ = + 0.23 V/SCE in CH_3CN), and the CV reversibility did not change significantly in the presence of oxygen. These results show that $TCNE^{-\cdot}$ is not reactive with oxygen,$^{11)}$ and that oxygen reacts much faster with $1^{+\cdot}$ than with $TCNE^{-\cdot}$ in the photochemically-generated radical ion pairs ($1^{+\cdot}$ + $TCNE^{-\cdot}$). Therefore, path b may also be excluded as a major pathway for the epoxidation in the presence of TCNE.

Although alternative mechanisms for the epoxide-forming reaction in the presence of TCNE might be possible,12) the present results clearly demonstrate that photooxidation involving EDA systems may offer new insight into mechanisms of olefin epoxidation reactions. Further studies are in progress.

References

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8) Bartlett mentioned that yields of the corresponding epoxide could be significantly increased in singlet oxygen oxidation of 7,7'-binorbornylidene in the presence of TCNE.9a) Recently, Schaap also reported an efficient epoxide formation in singlet oxygen oxidation of 1 in the presence of phenyl methyl sulfoxide.9b)
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10) The electrochemical oxidations were performed at 1.65 V/SCE in dichloromethane in a three-compartment cell with a platinum foil and a platinum gauze as a working and a counter electrode, respectively. Tetrabutylammonium perchlorate (TBAP) was used as a supporting electrolyte.
11) The CV's were measured in acetonitrile with TBAP as a supporting electrolyte. A usual three-compartment cell was used as mentioned in Ref. 10.
12) Since the energy (1.22 eV) of the radical ion pair ($1^{+\cdot}$ + $\text{TCNE}^{-\cdot}$) seems not enough to produce triplet state of 1 or TCNE upon back electron transfer, formation of singlet oxygen and thus its participation in the present epoxidation is not likely. Also electron transfer from $\text{TCNE}^{-\cdot}$ to oxygen is highly endothermic.

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