2.53 (br s, 2 H), 2.12–1.37 (m, 18 H); IR (KBr) 3060 (w), 2900 (s), 1650 (m), 1460 (w), 1445 (m), 875 (s) cm^{-1}; MS, m/z (relative intensity) (M^+, 100), 148 (5), 105 (15), 91 (30). Anal. Calcd for $C_{22}H_{28}$: C, 90.35; H, 9.65. Found: C, 90.24; H, 9.85.

The Minor Product: 10 mg; ^{13}C NMR ($CDCl_3$) δ 157.6 (s, 2 C), 133.3 (s, 2 C), 100.7 (t, 2 C), 43.0 (d, 2 C), 42.0 (t, 2 C), 40.5 (t, 2 C), 39.2 (2 t, 4 C), 38.9 (d, 2 C), 32.0 (d, 2 C), 28.5 (d, 2 C); ^1H NMR ($CDCl_3$) δ 4.49 (d, J = 2.2 Hz, 2 H), 4.45 (d, J = 2.2 Hz, 2 H), 3.57 (br s, 2 H), 2.89 (br s, 2 H), 2.51 (br s, 2 H), 2.09–1.46 (m, 18 H).

The ether fractions gave 25 mg of a mixture of, at least, four products (by gas chromatography on a FS-1265 column at 100 °C; the retention times were quite short at these conditions). The benzene fractions yielded 67 mg of a white polymeric material (by ^{13}C NMR and ^1H NMR) poorly soluble in pentane or ether.

Acknowledgment. We gratefully acknowledge support of this work by the Research Council of the Republic of Croatia and the U.S.–Yugoslav Cooperative Program PN-531, NSF.

Registry No. 1, 73586-31-9; **2a**, 102780-95-0; **2b**, 102918-62-7; 4-methylene-2-adamantanone tosylhydrazone, 102780-96-1; 4-methylene-2-adamantanone tosylhydrazone sodium salt, 102780-94-9.

Electron-Transfer Chain Oxidation of 4,5-Dimethylhomoadamant-4-ene

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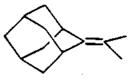
Received January 22, 1986

A dichotomy of products has been observed for oxygenation reactions of isopropylideneadamantane (1) with various reagents.[1] Both singlet oxygen[2] and the olefin cation, O_2^- pairs produced by use of 9,10-dicyanoanthracene as a photosensitizer[3] gave exclusively the ene product 2, but dioxetane 3 was produced by treatment of 1 in oxygen-saturated CH_2Cl_2 with a catalytic amount of 4^+ $SbCl_6^-$ at −78 °C. Because conversion of 1 to 3 by both the Kopecky method[4] and peroxymercuration[5] failed (the latter because debromination of brominated 3 could not be accomplished),[6] this result suggests that electron-transfer chain oxidation of hindered olefins having abstractable α-hydrogens might have practical importance for dioxetane preparation.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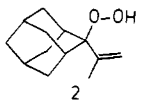

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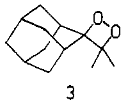
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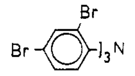
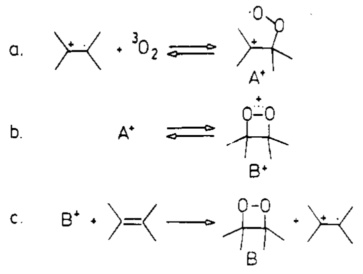
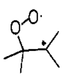


4

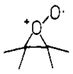
Scheme I



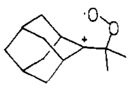
The three-step chain reaction shown in Scheme I has been suggested as the mechanism for conversion of tetraalkylolefins to dioxetanes catalyzed by one-electron oxidants. The two CO bonds of the dioxetane are apparently formed in separate steps as shown, because oxygenation of *anti*-8,8′-bis(bicyclo[3.2.1]octylidene) gives the *syn*- as well as the *anti*-dioxetane, and the CC bond rotation required has been shown not to occur in the absence of oxygen.[7] Much more rapid formation of one CO bond to give A^+ than two at once to give B^+ directly is also predicted by MNDO calculations for the reaction of ethylene cation radical with O_2.[8]

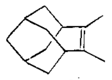

A^+

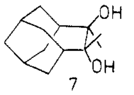

B^+


C^+

If A^+ is accepted as an intermediate in the addition of $^3O_2$ to 1^+, however, conversion of 1 to 3 does not provide a reasonable test of whether A^+ would undergo closure to B^+ in preference to internal hydrogen atom transfer to give ene products. On both steric and electronic grounds, the A^+ intermediate formed either from 1^+ and $^3O_2$ or by single CO bond cleavage of 3^+ should be 5^+, which is Bredt's rule protected against intramolecular hydrogen transfer from the bridgehead carbons α to the cation. We have therefore prepared the symmetrical isomer of 1, 4,5-dimethylhomoadamantene (6), which can only give a single A^+ intermediate having an unprotected methyl group attached to the formally cationic carbon atom to provide such a test.


5^+


6



7

Preparation of 6 without contamination by 1 (a serious problem in methods which involve carbocation intermediates) was achieved by addition of methyllithium to homoadamantane-4,5-dione[9] to give the *trans*-4,5-dimethylhomoadamantane-4,5-diol (7) in 97% yield and subsequent deoxygenation of 7 using low-valent titanium to give 6 in 68% yield. The ^{13}C NMR spectrum of 7 showed seven signals, establishing it as the trans isomer because the cis isomer would display eight signals. Use of HMPA had no effect on the addition and 7 was still the only product. Since most deoxygenation methods require *cis*-diols, low-valent titanium reagents were tried instead. McMurray's reagent[10] has Ti^0 stoichiometry but failed to

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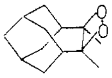
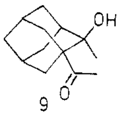
effect any reaction and only **7** was recovered after workup. Mukaiyama's reagent,[11] which has Ti^{2+} stoichiometry, gave **6**, although somewhat sluggishly.

Cyclic voltammetry on **6** under N_2 gave $E^{\circ\prime} = 1.70$ V vs. SCE at room temperature with $\Delta E_p = 0.10$ V at a 0.2 V/s scan rate, and at −78 °C, the couple moved to 1.68 V. When the solution was saturated with O_2, the chemistry shown in Scheme I became operative and at a 0.1 V/s scan rate the reversible couple for **6** was replaced by the characteristic ECbE wave seen for electron-transfer chain oxygenation of olefins.[12] By increasing the scan rate to 1 V/s, the oxidation current increased and the reduction wave began to return, indicating that the observed oxygen addition rate is slow enough that it can be frozen out on the CV timescale, although it is clearly faster than addition of oxygen to biadamantylidene cation.[12]

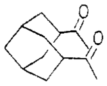
Treatment of **6** with 4% $4^+SbCl_6^-$ at −78 °C caused only a 19% conversion of **6** to oxidation products, for a chain length (which we will use to refer to the ratio of olefin oxidized to oxidant consumed) of only 5, an order of magnitude smaller than the ca. 60 observed for **1** under the same conditions. Addition of trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAA) to the solvent was found to increase the oxidation chain length about tenfold, presumably by removal of basic impurities which decompose 6^+ in competition with its overall reaction with $^3O_2$. The amount of acid added is not critical, and chain lengths of 53 ± 4 (which we estimate to be on the order of our error) were observed for CH_2Cl_2:TFA:TFAA ratios varying from 20:1:1 to 220:1:1. The products obtained are extremely sensitive to workup conditions, although the primary product appears to be the desired dioxetane **8**. Ether quench of excess $4^+SbCl_6^-$ at −78 °C in 20:1:1 solvent followed by rotary evaporation and chromatography on silica gel gave a 70% yield of 1-acetyl-2-methyl-2-adamantanol (**9**), which arises by cleavage of **8** to **10**, followed by acid-catalyzed aldol condensation. Even at room temperature 10% aqueous HCl extraction led to complete decomposition of **8**, although in this case the dione **10** was the isolated product. A basic workup incorporating only neutral washes provided a 67% yield of recrystallized **8** and neither **9** nor **10** was initially detected by NMR, although **8** does slowly decompose to **9** in $CDCl_3$ at room temperature, presumably catalyzed by acidic impurities.



8



9



10

Despite the unusual sensitivity of **8** to acid, **8** survives the brief treatment at −78 °C to the acidic solvent necessary to achieve usefully long chain lengths in the electron-transfer chain oxidation. Successful conversion of **6** to **8** proves that dioxetane formation according to Scheme I will tolerate abstractable α-hydrogens at the formally carbocationic carbon of the presumed intermediate A^+ in a tetraalkyl olefin. Abstractable α-hydrogens are strictly forbidden for obtaining dioxetanes from alkyl olefins and singlet oxygen, as their reaction gives ene products. There is a great deal of evidence that ene reactions of $^1O_2$[13] as well as nitrosoaromatics and triazolinediones[14] go through an intermediate with perepoxide-like geometry (this intermediate has been detected by NMR for the reaction of triazolinediones with the ene-reaction protected olefin biadamantylidene[14e]). Closure of A^+ to the perepoxide cation is unlikely to occur on thermodynamic grounds (the perepoxide cation is probably as strained as B^+ and lacks the stabilization of the 3e-π bond of B^+). The conditions reported here are limited to tetraalkyl olefins by the necessity for the initial electron transfer (step a of Scheme I) being reasonably favorable (oxidation by $4^+SbCl_6^-$ is 0.5 kcal/mol endothermic for **6**, and 2.5 kcal/mol endothermic for **1**). Not all tetraalkyl olefins give long oxidation chains and dioxetane products, but it is already clear from this work that the structural requirements for efficient dioxetane production by cation radical chain oxygenation are considerably different from those of the previously discussed methods.

Experimental Section

General. All experiments were performed in dry glassware under N_2 unless noted. THF was distilled from benzophenone ketyl anion and CH_2Cl_2 from CaH_2 and then P_2O_5. Cyclic voltammetry was performed in 0.1 M $TBABF_4/CH_2Cl_2$ with TFA and TFAA (20:1:1 by volume) with a Princeton Applied Research Model 132 and platinum disk electrode. ^1H NMR (200 MHz) and ^{13}C NMR (50.1 MHz) spectra were obtained in $CDCl_3$ using an IBM WP-200 and a JEOL FX-200 spectrometer, respectively. Mass spectra were obtained on an AEI MS-902, a KRATOS MS-80 RFA, or a KRATOS MS-25 spectrometer.

***trans*-4,5-Dimethylhomoadamantane-4,5-diol (7).** A solution of 7.0 mL of 1.57 M methyllithium in ether (11.0 mmol) was added to 710 mg (4.0 mmol) of homoadamantane-4,5-dione (**6**) in 30 mL of THF at −78 °C. After being stirred overnight at room temperature, the reaction was quenched with water, extracted with ether, dried with $MgSO_4$, filtered, evaporated, and sublimed (100 °C, 0.1 torr) to give 820 mg of **7** (97%): mp 172 °C dec; ^1H NMR δ 2.90 (2 H, s), 2.24 (2 H, d, $J = 13.6$ Hz), 1.95–1.75 (8 H, m), 1.65–1.50 (4 H, m), 1.31 (6 H, s); ^{13}C NMR δ 77.63 (s), 45.09 (d), 37.40 (t), 32.58 (t), 31.07 (t), 29.27 (q), 26.99 (d); MS, *m/e* 210.1622 (M^+, 210.1620 calcd for $C_{13}H_{22}O_2$), 192 ($M^+ - H_2O$), 174 ($M^+ - 2H_2O$).

4,5-Dimethylhomoadamantene (6). A total of 3.30 mL (30.0 mmol, 15 equiv) of $TiCl_4$ was carefully added to 30 mL THF at −78 °C, followed by 600 mg (15.9 mmol, 5.3 equiv) of LAH. The slurry was brought to reflux for 30 min, producing a fine black suspension, to which was added 420 mg (2.0 mmol, 1 equiv) diol **7** and 0.96 mL (4.0 mmol, 2 equiv) of n-Bu_3N in 10 mL of THF. After 4 days refluxing, the reaction was cooled and quenched with saturated Na_2CO_3. Cautious addition of 10% HCl gave a homogeneous solution, which was extracted with pentane. Extraction of the organic phase with saturated Na_2CO_3, drying with $MgSO_4$, filtration, and evaporation gave a quantitative crude yield of 360 mg of **6**. Filtration through alumina with pentane, evaporation, and bulb-to-bulb distillation (60 °C, 0.1 torr) gave 240 mg of **6** (68%) as an oil: ^1H NMR δ 2.03 (4 H, m), 1.71 (10 H, m), 1.63 (6 H, s); ^{13}C NMR δ 136.06 (s), 40.12 (d), 36.62 (t), 33.99 (t), 28.79 (d), 21.40 (q); MS, *m/e* 176.1555 (M^+, 176.1565 calcd for $C_{13}H_{20}$), 161.1329 ($M^+ - CH_3$).

4,5-Dimethylhomoadamantene Peroxide (8). To an O_2-saturated solution of 76 mg (0.43 mmol) of **6** in 10 mL of CH_2Cl_2 and 0.10 mL each of TFA and TFAA at −78 °C was added dropwise 0.93 mL of a 9.49 mM solution of $4^+SbCl_6^-$ (8.8 μmol) in CH_2Cl_2 to give a persistent green solution. The reaction was quenched with 0.5 mL of Et_3N and extracted with ether and brine, and the organic phase was dried with K_2CO_3, filtered, and evaporated to give 150 mg of oil. The oil was filtered through basic alumina with 5% EtOAc/hexane and recrystallized from

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pentane (−78 °C) to give 60 mg of yellow crystalline **8** (67%): mp 86–87 °C; ^{1}H NMR δ 2.63 (2 H, d, J = 13.4 Hz), 2.00–1.60 (10 H, m), 1.60 (6 H, s), 1.45 (2 H, d, J = 11.2 Hz); ^{13}C NMR δ 93.10 (s), 41.92 (d), 36.48 (t), 32.97 (t), 31.12 (t), 27.91 (d), 26.36 (d), 24.65 (q); MS, m/e 208.1463 (M^+, 208.1463 calcd for $C_{13}H_{20}O_2$).

1-Acetyl-2-methyl-2-adamantanol (9). To an O_2-saturated solution of 88 mg (0.50 mmol) of **6** in 10 mL of CH_2Cl_2 and 0.50 mL each of TFA and TFAA at −78 °C was added dropwise 1.20 mL of a 7.60 mM solution of $4^+SbCl_6^-$ (9.1 μmol) in CH_2Cl_2 to give a persistent green solution. The reaction was quenched with ether and warmed to room temperature, and the solvent was evaporated to give 110 mg of crude **9**. Column chromatography using 10% EtOAc/hexane gave 73 mg of **9** (70%): mp 94–95 °C; ^{1}H NMR δ 4.11 (1 H, s), 2.35 (2 H, m), 2.17 (3 H, s), 2.05–1.40 (11 H, m), 1.28 (3 H, s); ^{13}C NMR δ 217.68 (s), 74.02 (s), 52.47 (s), 39.57 (d), 37.23 (t), 36.53 (t), 35.71 (t), 33.67 (t), 32.09 (t), 27.95 (d), 27.30 (q), 27.19 (d), 24.56 (q); MS, m/e 208.1465 (M^+, 208.1463 calcd for $C_{13}H_{20}O_2$), 193.1229 ($M^+ - CH_3$), 190.1366 ($M^+ - H_2O$), 165.1308 ($M^+ - CH_3CO$); IR ($CHCl_3$) 3475, 1678.

Cleavage of 8 to Dione 10. To an O_2-saturated solution of 26.3 mg (0.15 mmol) of **6** in 5 mL of CH_2Cl_2 and 23 μL each of TFA and TFAA was added 1.1 mL of a 2.4 mM solution of $4^+SbCl_6^-$ (2.6 μmol) in CH_2Cl_2 to give a persistent green solution. The reaction was quenched with 0.5 mL of Et_3N, diluted with pentane, and extracted with saturated Na_2CO_3. The organic phase was extracted once with 10% HCl, and then saturated Na_2CO_3, dried with K_2CO_3, filtered, and evaporated to give 50 mg of oil. Immediate spectroscopic observation indicated the presence of **10**: ^{1}H NMR δ 2.53 (2 H, m), 2.15 (6 H, s), 2.00–1.50 (10 H, m), 1.43 (2 H, t, J = 3.5 Hz); IR ($CHCl_3$) 1707.

Acknowledgment. We thank the donors of Petroleum Research Fund, administered by the American Chemical Society, for partial financial support of this work, and Amoco Oil Company for a fellowship to M.F.T.

Registry No. 6, 103241-27-6; 7, 103241-28-7; 8, 103241-29-8; 9, 58773-73-2; 10, 103241-30-1; O_2, 7782-44-7; homoadamantane-4,5-dione, 26775-76-8.

Photochemical Isomerization and Dimerization of 1-(9-Anthryl)-2-nitroethylene

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Received February 10, 1986

Photoexcited nitroalkenes may undergo a variety of molecular transformations that are governed by the nature of the ethylene substituents. For example, *trans*-1-phenyl-2-nitroethylene in cyclohexane solution upon irradiation through Pyrex undergoes geometrical isomerization to give the cis compound in an apparently rather inefficient reaction, as is suggested by the long irradiation times reported for preparative conversions.[1,2] By contrast, *trans*-2-nitro-1-(9-phenanthryl)propene in dioxane solution undergoes photochemical geometric isomerization with a quantum yield of 0.50.[3] The cis isomer does not regenerate the trans isomer (Φ < 0.001) upon photoexcitation but yields both 2-methylphenanthro[9,10-*b*]furan and 9-phenanthraldehyde. Spectroscopically detectable transients are attributed to the formation of labile intramolecular cycloaddition products.[3,4] As for α-nitro-substituted arylethylenes, their photochemistry is characterized by far more complex reaction patterns involving both cyclization, rearrangement, and cleavage reactions.[5,6]

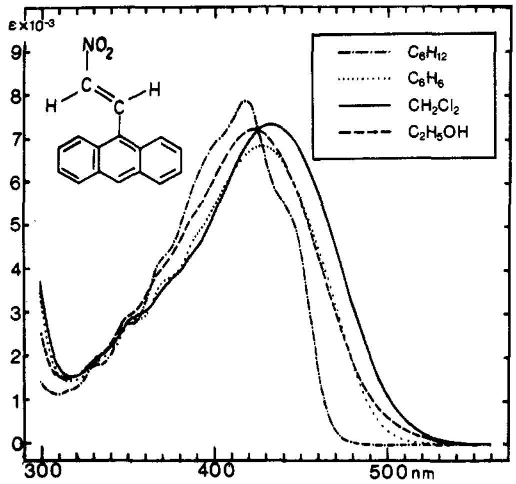

Figure 1. Electronic absorption spectra of 1 in cyclohexane, benzene, methylene chloride, and ethanol.

Within the scope of a study dealing with the effects of molecular geometry on the excited-state properties of 9-anthryl-substituted alkenes,[7] we have now investigated the photochemistry of *trans*-1-(9-anthryl)-2-nitroethylene (**1**). Commercially available "9-(2-nitrovinyl)anthracene" is of unspecified geometry, and it has been used as such in a previous photochemical investigation of light-induced viscosity changes of micellar solutions of substituted anthracenes.[8] The melting point of the commercial product suggests the material to consist mainly of the trans isomer. For the present study, we have prepared *trans*-1-(9-anthryl)-2-nitroethylene in excellent yield by piperidine-catalyzed condensation of 9-anthraldehyde with nitromethane in methylene chloride solution. The trans substitution of the ethylene bond in the product prepared this way is supported by its ^{1}H NMR spectrum in which the ethylene protons are characterized by a coupling constant of 14 Hz (see Experimental Section).

In accordance with earlier spectroscopic studies on nitro-substituted ethylenes,[9,10] the electronic absorption spectrum of **1** is characteristically affected by solvent polarity. Thus, the onset of absorption is shifted bathochromically in the solvent order cyclohexane, benzene, and ethanol, whose $E_T(30)$[11] values are 31.2, 34.5, and 51.9 kcal/mol, respectively. Remarkably, the largest bathochromic shift of the absorption maximum of **1** is observed in methylene chloride ($E_T(30)$ = 41.1 kcal/mol), suggesting unique solvent–solute interactions in this particular case (see Figure 1).

When dilute solutions of **1** in benzene are briefly exposed to ordinary laboratory light, drastic absorption spectral changes are noticeable. Upon irradiation in benzene so-

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