perylene. Similar mechanisms are proposed for the other condensation reactions.

Aryl migration occurs in parallel with condensation. In this reaction only the aryl groups move. Methyl and fluoro substituents do not migrate under our experimental conditions.

Dissociation is generally less sensitive to the nature and concentration of the donor than is condensation or isomerization. This, it is suggested, is due to significantly lower rates of selective H transfer to the position leading to dissociation (arylated positions) than to positions leading to the other reactions (unsubstituted positions). As a result, lower order, nonselective H-transfer process tend to play a more important role in dissociative processes.

These studies clearly distinguish three regimes of hydrogen transfer. In the presence of reactive, multiple H-atom-donating species, hydropyrolysis predominates. In this environment, addition of an H atom to an aromatic ring initiates ring hydrogenation. In the presence of less effective donors, conditions that might be attained after reactive hydroaromatic molecules have been oxidized, selective means of H transfer predominate, leading to both condensation and dissociation. Rates of H transfer under these conditions depend strongly on the thermodynamics of H-atom transfer (that is, on the R–H bond strength of the donor and the hydrogen atom affinity of the acceptor). In the absence of donors containing labile H atoms, H transfer via free H atoms predominates. In this regime, H transfer is unselective and rates depend little on the nature of the donor.

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Registry No. 1,1′-Binaphthyl, 604-53-5; 1,2′-binaphthyl, 4325-74-0; 1-phenylnaphthalene, 605-02-7; 9-phenylanthracene, 602-55-1; xanthene, 92-83-1.

Chemistry of Dioxiranes. 10. Oxidation of Quadricyclane and Norbornadiene by Dimethyldioxirane[1]

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Treatment of quadricyclane (**2**) with dimethyldioxirane (**1**) leads to the formation of *exo*-norborna-2,5-diene monoepoxide (**4**), *exo,exo*-norborna-2,5-diene diepoxide (**5**), bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (**6**), and *exo*-2,3-epoxybicyclo[3.1.0]hexane-6-*endo*-carboxaldehyde (**7**). The reaction is believed to involve prior catalyzed isomerization of **2** by **1** to norbornadiene (**3**) and subsequent conversion of **3** to the observed products. Under suitable conditions **1** reacts with **3** to give **4** and **6** in a 97:3 distribution, respectively.

Evidence for the intervention of dimethyldioxirane (**1**) in the reaction between monoperoxysulfuric acid and acetone has been reported by Edwards, Curci, and coworkers.[2] The case for the production of **1** in this reaction was made even more convincing by our demonstration[3] that **1** could be removed from the generation vessel and obtained as a solution in acetone. Indeed we have shown[3] that a number of methyldioxiranes can be prepared by a similar procedure. Acetone solutions of **1** have also been used to obtain a range of spectroscopic data on **1**.[3-5] The observation[4a] of a single peak in the ^{17}O NMR spectrum of **1** is particularly telling and clearly distinguishes **1** from the isomeric carbonyl oxide.

Dimethyldioxirane is a powerful O-atom donor. It has been shown to transfer an O atom rapidly and efficiently to olefins,[2,3] polycyclic aromatic hydrocarbons,[3,6,7] phosphines,[3] sulfides and sulfoxides,[1,3,5,8] imines,[9] and azo compounds.[9] In addition it inserts O atom into nitrogen–hydrogen[10] and carbon–hydrogen[11] bonds. In the latter case **1** demonstrates a unique chemistry that appears to resemble that of some monooxygenase enzymes.[12] In many respects the chemistry of **1** parallels that of some oxiziridines which Davis et al.[13] are studying, in part, because of their possible relationship to flavin-dependent monooxygenases.

Our continuing work on the chemistry of dioxiranes is proceeding along two lines. In one line of research we are carrying out physical organic studies designed to elucidate the details of the O atom transfer and insertion reactions. We are also attempting to demonstrate the synthetic

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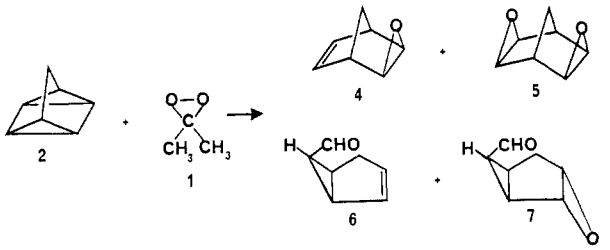
usefulness of 1 by oxidizing a series of selected substrates. We report here the results of the reaction of 1 with quadricyclane (2) and norbornadiene (3). The epoxidation of 3 by the dioxirane demonstrates the ability of 1 to epoxidize a sensitive system in a manner that is superior to that of other available epoxidizing reagents. The interaction of 1 with 2 brings about a surprising valence isomerization[14] which is apparently related to the unusual orbital occupation in 1.

Results

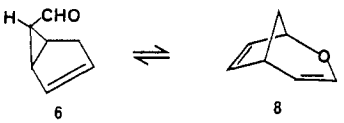
Treatment of quadricyclane (2) with dimethyldioxirane (1) in acetone or acetone:CH_2Cl_2 (1:1) solvent gave a number of products. The products formed were *exo*-



norborna-2,5-diene monoepoxide (4), *exo,exo*-norborna-2,5-diene diepoxide (5), bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (6), and *exo*-2,3-epoxybicyclo[3.1.0]hexane-6-*endo*-carboxaldehyde (7).

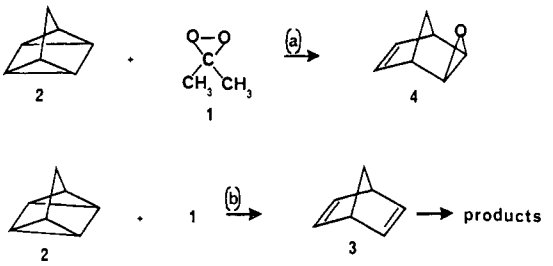
The yield and distribution of the products were found to be dependent on the solvent composition and the details of the preparation of the solution of 1 (Table II, Experimental Section). Attempts to separate and isolate the products by preparative GC or TLC were unsuccessful as all but the diepoxide, 5, were found to be unstable. The products were identified by a combination of techniques, including GC co-injection using authentic samples and for 4 and 6, a comparison of NMR data with the literature values.[15-17] Aldehyde 7 was separately prepared from 6 and identified by its NMR spectrum and a comparison of its spectrum with that of the known 6. The diepoxide 5 could be isolated for melting point determination, elemental analysis, and complete NMR analysis.

The exo configuration in 4 was previously demonstrated[15] by conversion to the saturated material. These workers[15] had also noted the ready conversion of 4 to 6 at room temperature. We also prepared an authentic sample of 4 by treating norbornadiene (3) with less than an equivalent amount of 1. The endo configuration in 6 had been demonstrated by Rey and Dreiding,[16] who observed the facile conversion of 6 to its valence isomer, 8.

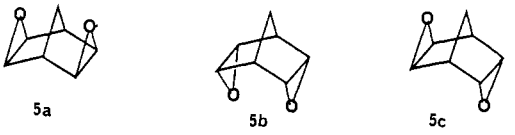


The anti configuration in 7 was arrived at by a comparison of the multiplicity of the oxirane protons in the NMR spectrum to those in a comparable system where syn–anti isomerism is possible. Thus, the oxirane protons in 7 occur as two doublets. The doublet for the H_2 proton at δ 3.56 confirms its trans disposition to H_1.[17] If the H_2 proton were cis to H_1, then a complex multiplet would be expected.

Scheme I



Diepoxide 5 is the major product when dioxirane 1 interacts with quadricyclane in 100% acetone as solvent. We have also separately shown that 5 can be produced by treating monoepoxide 4 with 1. The structure and stereochemistry in 5 were established as follows. The parent peak in the mass spectrum of 5 corresponds to the molecular weight of the structure shown. This material also gives a correct elemental analysis for structure 5, which is a new compound. There are three likely possibilities, **5a**, **5b**, and **5c**, that satisfy the molecular weight and elemental analysis data. The ^1H NMR spectrum of this compound has only three absorptions, thus ruling out structure **5c**, which would give five absorptions.



Since the exo stereochemistry in 4 had been established by Meinwald et al.[15] and 4 was converted to a single diepoxide by 1, then 5 must have the exo,exo stereochemistry, **5a**. This structural assignment was further confirmed by carrying out NMR decoupling experiments. Guided by the ^1H NMR assignments made[15] for 4, we assigned the three absorptions given by **5a** as follows: δ 0.99 (t, J = 1.7 Hz, H_7), 2.78 (t of t, J = 1.7, J = 0.7 Hz, H_1, H_4), and 3.32 (s, H_2, H_3, H_5, H_6). Irradiation of the absorption at δ 2.78 (H_1, H_4) leads to a singlet at δ 0.99 (H_7). Likewise, irradiation of the δ 3.32 peak converts the peak at δ 2.78 to a clean triplet ($J_{1,7}$ = 1.7 Hz). The dihedral angle between the bridgehead hydrogen (H_1) and the endo protons (e.g., H_2) is approximately 90°, thus giving an expected[19] low (J = 0.7 Hz) coupling constant.

Since epoxide 4 could be the result of a rare ($_\sigma 2_s + {}_\sigma 2_s + \omega 2_s$) reaction between 2 and the dioxirane (Scheme I), we carried out a number of experiments in order to determine whether the alternative valence isomerization of 2 to 3, followed by conversion of 3 to products, was operating.

Using a combination of GC and NMR techniques, we have been able to show[14] that extremely small amounts of 1 (e.g., 7.4×10^{-4} mmol) are able to catalyze the valence isomerization of 2 to 3. Turnover numbers as high as 60 have been measured. The ability to measure turnover number is limited by the high reactivity of 1 toward norbornadiene (3). Indeed, while we cannot totally exclude the direct cycloaddition route (path a, Scheme I), it seems most likely that the products observed in the reaction between quadricyclane (2) and 1 arise as a result of the prior isomerization route b. The previously noted solvent influence on product distribution appears to be the result

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Table I. Oxidation of 3 by Various Oxidants

expt no.	oxidant	product distribution, % epoxide 4	aldehyde 6
1	1 in acetone–CH_2Cl_2 (1:2)	97	3[a]
2	1 in acetone (wet)	77	23[a]
3	MCPBA in CH_2Cl_2	33	67[a]
4	peracetic acid in CH_2Cl_2	0	100[b]
5	peracetimidic acid in CH_3CN–CH_3OH	14[c]	86[d]

[a] Present work. [b] Reference 17. [c] *endo*-Norborna-2,5-diene monoepoxide. [d] Reference 20.

of a solvent effect on the isomerization reaction or oxidation of 3, or both.

Discussion

The use of 1 to prepare the monoepoxide, 4, of norbornadiene gives results that indicate that it is the reagent of choice. As observed by previous workers,[15,17,20] we have found that production of the epoxide is accompanied by rearrangement product, 6. However, use of the dioxirane method leads to a distribution of 97% epoxide 4, and 3% aldehyde 6 while other conventional methods using peracids lead exclusively or predominantly to 6 (Table I).

The use of 1 to prepare sensitive epoxides such as 4 has several advantages. First 1 is a very powerful O-atom donor so that reactions can be carried at low temperature (0 °C in the present case). Second 1, used as a solution in acetone[3] (or other solvent), avoids the use of acidic conditions. The product distribution is somewhat sensitive to reaction conditions. When the solution of 1 is carefully dried, 4 is the almost exclusive product. When the solution of 1 is used without drying, then the product distribution, while favoring 4, shifts to give more 6 (Table I). It seems likely that the conversion of 4 to 6 is catalyzed by acid, leading to lower epoxide content in experiments 3–5. Apparently when 1 is accompanied by a small amount of water, the conditions are sufficiently acidic to promote conversion to the aldehyde.

The catalyzed valence isomerization of 2 to 3 has received a large amount of attention,[21] particularly as a potential solar energy storage system. While the thermal conversion of 2 to 3 is forbidden by symmetry considerations,[22] a number of metal complexes have been used to bring about the isomerization. The latter presumably relax symmetry constraints by utilizing d-orbital interaction with 2. The observation[14] that an organic reagent, 1, could cause a similar catalytic isomerization is a remarkable one. On the other hand, dioxirane 1 is an unusual reagent. Furthermore, Allen[23] has carried out ab initio computations on the electronic structure of 1 and finds that the HOMO and LUMO have symmetry properties that are useful in understanding the reactivity of 1. In particular, the HOMO and LUMO of 1 could act analogously to the d orbitals of the transition metals, which have been observed to cause the isomerization of 2 to 3. Control reactions indicate that the isomerization is not catalyzed by peracetic or *m*-chloroperbenzoic acid under the reaction conditions. Likewise, carrying out the procedure for the preparation of 1 with any one of the components absent gives solutions that do not cause isomerization. When the solvent ($CDCl_3$) for 2 is saturated with HCl and the solution stirred overnight, NMR analysis indicates only a slight increase in the absorption due to 3.

As indicated earlier,[14] the details of the interaction between 1 and 2 are not clear. This interaction could lead to the formation of a short-lived complex or to complete electron transfer. While we have not found[14] any experimental evidence for the latter case, we plan to examine this possibility further by treating 1 with substrates that could encourage electron transfer.

Experimental Section

Instrumentation. Gas chromatography was performed on a Perkin-Elmer Sigma 2000 gas chromatograph interfaced with a Hewlett-Packard integrator, Model 3360-A. ^1H NMR and ^{13}C NMR spectra were recorded with a Varian XL-300 NMR spectrometer. Deuteriated chloroform (Aldrich) was used as solvent with TMS as internal standard. IR spectra were recorded with a Perkin-Elmer 337 instrument. Mass spectra were obtained with an Associated Electronics Industries Model MS-1201 B mass spectrometer at a 70-eV ionizing voltage.

Chromatography. Gas chromatography was performed with a 30 m × 0.311 mm DB 210 column. The GC conditions used were as follows. (A) FID: temperature 1, 45 °C; time 5 min; rate 5 °C/min; temperature 2, 100 °C; time 20 min, injection temperature 80 °C; detector temperature 150 °C; internal pressure 20 psi. (B) FID: temperature 1, 45 °C; time 5 min; rate 10 °C/min; temperature 2, 80 °C; time 5 min; injection temperature 80 °C; detector temperature 130 °C; internal pressure 5 psi. (C) FID: temperature 1, 45 °C; time 5 min; rate 20 °C/min; temperature 2, 100 °C; time 0; injection temperature 80 °C; detector temperature 150 °C; internal pressure 8 psi.

Materials. Oxone (DuPont), $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, was obtained from Aldrich Chemical Co. and used as such for the preparation of dimethyldioxirane. Dioxirane solutions were routinely assayed for dioxirane content using phenyl methyl sulfide by the GC method.[3] Reagent grade acetone (Aldrich) was distilled from dry potassium carbonate prior to use. Dry methylene chloride was made by distilling reagent grade material (Aldrich) from calcium hydride. Norborna-2,5-diene (Eastman Kodak Co.) and quadricyclane (Aldrich) were used as received after verifying their purity by GC and NMR. *m*-Chloroperbenzoic acid (Aldrich) and peracetic acid 40% (FMC Corp.) were used as such. The acetone diperoxide used was a pure sample from an earlier preparation in our laboratory. Anhydrous sodium sulfate (Aldrich) was used for drying. Freshly prepared dimethyldioxirane solutions were used in all experiments.

Preparation of Dimethyldioxirane Solution. In general, the previously published[3] procedure was followed. The slight vacuum described to increase the yield is provided by water aspirator (ca. 100 mm). Also it is important to note that the inert

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gas used (He, Ar, etc.) is bubbled through the reaction mixture so that dimethyldioxirane is carried away from the generation flask.

Oxidation of Norborna-2,5-diene by Dimethyldioxirane to *exo*-Norborna-2,5-diene Monoepoxide (4). Norborna-2,5-diene (3) (0.553 g, 6.01 mmol) was dissolved in methylene chloride (35 mL) and cooled to 0 °C in a three-necked flask. A freshly prepared solution of dimethyldioxirane in acetone was diluted with an equal volume of methylene chloride and again dried. Eighty milliliters of this solution (2.0 mmol of 1) was added dropwise to the cold solution of 3 with stirring during 45 min. The reaction mixture was stirred for an additional 3 h at 0 °C and at room temperature for 1 h. The solvent and excess of 3 were removed in a rotary evaporator. Capillary GC analysis (condition A) showed that the residue contained only one product with retention time of 8.00 min. However, the NMR spectrum indicated that it was contaminated with ~3% of aldehyde 6. The major product was identified as *exo*-norborna-2,5-diene monoepoxide (4): ^{1}H NMR (CCl_4) δ 1.19 (d, J = 8.3 Hz, 1 H), 1.59 (d, J = 8.3 Hz, 1 H), 2.85 (br s, 2 H), 3.29 (s, 2 H), 6.35 (t, J = 1.6 Hz, 2 H); ^{13}C NMR (CCl_4) δ 40.41 (methylene C), 43.30 (ring junction C), 49.50 (oxirane C), 140.70 (olefinic C); IR (neat) 850 cm^{-1} (strong epoxide absorption). These data agree with the literature values.[15] The combined yield (0.08 g) was 37% based on the amount of 1 used.

Oxidation of Norborna-2,5-diene by 1 in Acetone. The above experiment was repeated with acetone as the solvent. The NMR analysis of the crude product showed that it was a mixture of 4 and 6. The ratio of 4 and 6 was found to be 23:77 from the ratio of integrated areas of the aldehyde proton of 6 (1 H) and the oxirane proton of 4 (2 H) in the ^{1}H NMR spectrum.

Oxidation of Norborna-2,5-diene by Excess 1 to *exo,exo*-Norborna-2,5-diene Diepoxide (5). A solution of dimethyldioxirane (200 mL, 0.05 M) in acetone was diluted with dry methylene chloride (300 mL), dried with anhydrous sodium sulfate, placed in a three-necked flask with a thermometer and an addition funnel, and protected from light and moisture. A solution of 3 (0.4 g, 4.3 mmol) in methylene chloride (100 mL) was added dropwise to the above solution of 1 at 0 °C with stirring during 45 min. The reaction mixture was stirred for an additional 3 h during which time the temperature was allowed to rise to room temperature gradually. The solvent and excess of 1 were stripped off in a rotary evaporator, the residue was dissolved in methylene chloride (25 mL) and dried, and solvent was rotoevaporated to give a white solid. Capillary GC (condition A) showed that the product was a single compound (R_t = 23.5 min) and analytical TLC also confirmed this. Recrystallization from hexane gave the pure product, which was identified as *exo,exo*-norborna-2,5-diene diepoxide (5): yield 0.498 g (93%): mp 163–165 °C; ^{1}H NMR δ 0.99 (t, J = 1.7 Hz, H_7), 2.78 (a broad triplet of triplets, J = 1.7, J = 0.7 Hz, H_1, H_4), 3.32 (s, H_2, H_3, H_5, H_6); ^{13}C NMR δ 12.38 (methylene C), 38.48 (ring junction C), 52.65 (oxirane C); MS m/e 124, 95, 68 (base peak), 67, 57, 55, 41, 39, 32, 28; IR (KBr) 2980, 1345, 1185, 995, 900, 855, 820, 580 cm^{-1}.

Anal. Calcd for $C_7H_8O_2$: C, 67.73; H, 6.49. Found: C, 67.87; H, 6.54.

Oxidation of *exo*-Norborna-2,5-diene Monoepoxide to *exo,exo*-Norborna-2,5-diene Diepoxide by 1. A solution of 1 (20 mL, 0.08 M) was diluted with methylene chloride (50 mL), dried, and cooled to 0 °C in a three-necked flask with a thermometer and an addition funnel. The crude monoepoxide 4 (0.047 g, 0.438 mmol) was dissolved in methylene chloride (20 mL) and added dropwise to the cold solution of 1 in 30 min with stirring. The reaction mixture was stirred for an additional 3 h during which time the temperature was allowed to rise to room temperature. The solvent and the excess of 1 were rotoevaporated. TLC, GC, and NMR analyses showed that there was a single product, which was identical with the diepoxide 5 obtained directly from 3 with excess of 1. Yield was 0.044 g (80%).

Oxidation of Norborna-2,5-diene by *m*-Chloroperbenzoic Acid (MCPBA). To a solution of 3 (0.556 g, 6.05 mmol) in methylene chloride (20 mL) was added a solution of MCPBA (0.493 g, 2.87 mmol) dropwise at 0 °C with stirring in 45 min. The course of the reaction was monitored by capillary GC, and the product began to form during the addition. The reaction mixture was stirred for a further 2 h after the addition was complete. The white solid that separated out was filtered off. The filtrate was rapidly washed with ice-cold sodium bicarbonate solution (5%) and water and dried. The excess of 3 and the solvent were removed in a rotary evaporator. GC and NMR analyses showed a mixture of *exo*-norborna-2,5-diene monoepoxide (4) and bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (6). Aldehyde 6 has NMR absorptions at δ 9.08 (d, J = 6.6 Hz), 5.77 (s), 2.5–2.8 (br m), 2.25 (q, J = 7.0 Hz), and 1.6 (m). These are all comparable to the literature[14] values. The distribution of 6 to 4 in the product was determined from the ratio of integrated areas of the ^{1}H NMR peak of the formyl proton (δ 9.08) of the aldehyde (1 H) and the epoxide proton (δ 3.29) of the monoepoxide and was found to be 67:33. The total yield of products was 0.234 g (75% based on MCPBA).

Conversion of Bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde to *exo*-2,3-Epoxybicyclo[3.1.0]hexane-6-*endo*-carboxaldehyde. The crude product from the above preparation, which contained mainly the aldehyde 6 (0.152 g, 1.41 mmol), was dissolved in methylene chloride (10 mL) and cooled to 0 °C. A solution of dimethyldioxirane (20 mL, 0.035 M, 0.07 mmol) in acetone–methylene chloride (1:1) was added dropwise to this solution with stirring during 45 min. The stirring was continued for an additional 1.5 h at 0 °C. The solvent was removed after drying with anhydrous sodium sulfate. NMR analysis of the residue indicated the presence of aldehyde 7 by the appearance of the doublet peak of the aldehydic proton at δ 9.55 along with aldehyde 6 (aldehydic proton, δ 9.08). The ratio of 6 and 7 in the reaction product was found to be 4:1 from the integrated areas of the aldehydic protons.

Treatment of Quadricyclane with Dimethyldioxirane. Quadricyclane 2 (1.5–3 mmol) was treated with dimethyldioxirane in acetone or acetone–methylene chloride mixed solvent. In a typical experiment, a solution of 1 (30 mL, 0.07 M, 2.1 mmol), dried and distilled in a rotary evaporator (Büchi), was diluted with methylene chloride (30 mL) and added dropwise to a cold solution (0 °C) of 2 (0.571 g, 6.2 mmol) in methylene chloride (30 mL) with stirring in a three-necked flask in 45 min. The reaction mixture was stirred at 0–5 °C for 3 h and at room temperature for 1 h and the crude product was subjected to GC and spectral analyses. The components were identified, and the distribution of the products was determined, either by GC (condition A) or by the NMR method. The product mixture was found to contain *exo*-norborna-2,5-diene monoepoxide (4), *exo,exo*-norborna-2,5-diene diepoxide (5), bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (6), and *exo*-2,3-epoxybicyclo[3.1.0]hexane-6-*endo*-carboxaldehyde (7). The products were identified by their retention times (condition A; R_t values: 4, 8 min; 6, 10 min; 5, 21 min; 7, 27 min) and their individual NMR absorptions in the spectrum of the crude product. Attempts to separate the components either by preparative GC or by TLC led to the decomposition of products 4, 6, and 7. The diepoxide 5, separated by GC, was found to be identical with the diepoxide prepared from 3. This was confirmed by GC co-injection and TLC co-application analysis and by a comparison of NMR spectra. The ^{1}H NMR peaks for 7 were assigned from the spectrum of a mixture containing 5 and 7: δ 9.55 (d, J = 5.8 Hz, aldehydic proton), 3.56 (d, J = 2.9 Hz, H_2), 3.39 (d, J = 2.9 Hz, H_3), 2.43 (dd, J = 7.9, J = 5.7 Hz, H_1), 2.19 (d, J = 4.2 Hz, H_4, H_4), 1.83 (ddd, partially resolved, J = 7.9, J = 5.8 Hz, H_6), 1.78 (m, H_5). The distribution of the products was found to depend on the molar ratio of the reactants, history of the dimethyldioxirane solution, and the solvent composition. Some of the observed dependencies are presented in Table II.

Treatment of Quadricyclane with *m*-Chloroperbenzoic Acid. Quadricyclane (0.244 g, 2.7 mmol) was dissolved in methylene chloride (10 mL), and a solution of MCPBA (0.242 g, 1.4 mmol) in methylene chloride (15 mL) was added dropwise with cooling (0 °C) and stirring in 45 min. Stirring was continued for a further 3 h while the temperature was allowed to come to ambient condition. Capillary GC analysis of the reaction mixture at this time and after an additional 24 h showed that no norbornadiene had been formed. NMR analysis confirmed this observation.

Treatment of Quadricyclane with Peracetic Acid. Quadricyclane (0.833 g, 9.04 mmol) was dissolved in methylene chloride (20 mL), and a solution of peracetic acid (40%, 0.75 mL, 3.9 mmol) saturated with potassium acetate in methylene chloride (25 mL)

Table II. Product Distributions Observed When Quadricyclane (2) Is Treated with Dimethyldioxirane (1)

entry	molar ratio 1:2	[1]	solvent comp acetone:CH_2Cl_2	product distribution, % 4	6	5	7
1	1:2.5	0.075[a]	1:3	88.8	0.13	11.2	0
2	1:3	0.07[a]	1:2	78.9	3.4	17.8	0
3	1:3.5	0.06[b]	1:2	24.4	7.8	64.2	3.6
4	1:3	0.075[b]	4:1	0	14.1	37.5	48.4
5	1:3	0.06[a]	1:0	0	12.2	74.3	13.5
6	1:1.5	0.07[b]	1:2.6	8.7	1.9	89.4	0
7	1:1.5	0.05[b,c]	1:2	0.6	2.9	95.4	1.1
8	1:1.5	0.07[d]	1:2.6	1.7	9.1	89.2	0
9	1:1.5	0.07[e]	1:1.2	0.4	0	97.0	2.5
10	1:2	0.07[a]	1:1.5	0.9	9.4	63.2	26.5
11	1:1.3	0.075[b]	1:1.5	0	5.0	29.8	65.2

[a] Solution of 1 distilled in rotary evaporator before use. [b] Solution of 1 dried twice with anhydrous Na_2SO_4. [c] Not protected from light. In all other cases light protection was used. [d] Solution of 1 dried once with anhydrous Na_2SO_4. [e] Solution of 1 not dried.

was added dropwise with cooling (0 °C) and stirring in 45 min. Stirring was continued for a further 3 h while the temperature was allowed to reach room temperature. The course of the reaction was monitored by capillary GC. NMR and GC analyses on the material obtained after stripping off the solvent showed that no norbornadiene was present.

Repetition of the experiment under the above conditions with potassium carbonate (1.4 g) instead of potassium acetate also gave negative results.

Identification of Norborna-2,5-diene in the Treatment of Quadricyclane with Dimethyldioxirane. In an experiment in which quadricyclane (0.5 g, 5.4 mmol in 30 mL of methylene chloride) was treated with **1** (30 mL, 0.06 M, 1.8 mmol, diluted with an equal volume of methylene chloride) at 0 °C, aliquots of the reaction mixture drawn at various intervals of time were analyzed for the presence of **3** by capillary GC (condition C). Under GC condition C, **2** and **3** have retention time values of 6.22 and 4.89 min, respectively. The first aliquot was withdrawn and analyzed 10 min after starting the dropwise addition of **1** to the stirred solution of **2**. Aliquot I (10 min) and aliquot II (21 min) gave the peak (R_t = 4.89 min) for norbornadiene, whereas aliquots III (33 min), IV (48 min), V (63 min), and VI (165 min) did not give this peak. The peak due to **3** remained unaltered in aliquots I and II, at room temperature, for at least 1 week.

In a related experiment a solution of **1** (0.05 M, 20 mL) was diluted with methylene chloride (20 mL) and added dropwise to a cold (0 °C) solution of **2** (0.28 g, 3.0 mmol) in methylene chloride (15 mL) with stirring. Aliquots were withdrawn at 8, 18, and 30 min and analyzed by capillary GC (condition B). The first two aliquots were found to contain norborna-2,5-diene and monoepoxide (**4**), whereas the latter one contained monoepoxide only.

Isomerization of Quadricyclane by Dimethyldioxirane. (a) GC Calibration: Seven solutions of **3** of concentrations ranging from 0.002 to 0.02 M in acetone–methylene chloride (1:1) were prepared, and a calibration curve was generated by using peak areas and GC condition C. (b) Quadricyclane (0.099 g, 1.07 mmol) was dissolved in methylene chloride (10 mL) and cooled to 0 °C. A freshly prepared solution of **1** (0.056 M) was diluted with an equal volume of methylene chloride. This solution (0.5 mL, 0.014 mmol) was added to the solution of **2** with stirring. A sample was withdrawn quickly (45 s) and injected into the GC. A prominent peak for **3** was present. Subsequent analysis was done at 16-min and 30-min points. The peak area for **3** was corrected for the very small amount present in starting **2**. Using the calibration curve, the amount of **3** generated was found to be 0.09 mmol. The ratio of dimethyldioxirane added to norbornadiene generated was 1:6.6. Repeating the experiment with 0.2 mL of **1** (0.028 M, 0.00056 mmol) led to a ratio of added **1** to **3** generated 1:15. (c) Additional experiments were carried out in order to determine the maximum measurable turnover number. When **2** (0.129 g, 1.4 mmol) was treated with **1** (0.02 mL, 0.037 M, 7.4×10^{-4} mmol) at 0 °C and the resulting solution analyzed by GC as above, the ratio of **1** to **3** was found to be 1:20 after 1 min and reached 1:60 at 16 min. This latter ratio was also measured at 30 and 45 min. Duplication of this experiment gave the same results. (d) The isomerization of **1** was also studied in the presence of **4**. To a cold (0 °C) was added a solution of **1** (2 mL, 0.035 M, 0.07 mmol) in acetone–CH_2Cl_2 (1:1) dropwise in 4 min. An aliquot of the solution was analyzed immediately by capillary GC (condition C). A prominent peak for **3** was present. After 20 min an additional 2 mL of the solution of **1** was added and again a sample was analyzed by GC. The peak area for **3** had decreased to 60% of that first observed. The peak due to **4** decreased to 1% of its original area after the first addition of **1** and increased to 4% of its original area after the second addition of **1**. (e) **Control Experiments.** (1) GC analysis of a solution of **2** in acetone, CH_2Cl_2, or acetone –CH_2Cl_2 indicated that it contained only a trace of **3**. (2) The procedure for the preparation of **1** was carried (a) out in the absence of acetone and (b) in the absence of oxone. In both cases the solutions collected did not cause isomerization of **2**. (3) A solution of peracetic acid in CH_2Cl_2 (0.0058 mmol) did not cause isomerization of **2**. (4) A solution of *m*-chloroperbenzoic acid in CH_2Cl_2 (0.0058 mmol) did not cause isomerization of **2** in the same time period used for **1**. However, keeping the MCPBA solution overnight did lead to a slight increase in the peak for **3**. The ratio of MCPBA used to **3** formed was 1:1. (5) A solution of acetone diperoxide in CH_2Cl_2 (0.0087 mmol) did not cause isomerization of **2**. (6) To a solution of **2** (0.032 g, 0.35 mmol) in 3 mL of $CDCl_3$ was added 0.008 mL of $CDCl_3$ saturated with HCl. The resulting solution was stirred at −23 °C for 3.5 h, and an NMR spectrum was then recorded at the same temperature. There was no increase in the peak (δ 6.75) for **3** (over trace in blank). An additional 0.02 mL of $CDCl_3$ saturated with HCl was added, and the solution was stirred overnight at room temperature. NMR analysis indicated only a slight increase in the trace peak (δ 6.75) for **3**. These latter experiments were repeated using GC instead of NMR analysis with the same results.

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