J. Org. Chem. **1991**, *56*, 6043–6050

dried with Na_2SO_4, evaporated, and purified by layer chromatography on silica gel (CH_2Cl_2/2% MeOH) to afford oily 18 (1.99 g, 81%) as a crystalline mass: mp 40 °C, $[\alpha]^{20}_{D}$ 8.9° (*c* 0.58, CH_2Cl_2); IR (KBr) 3398, 2936, 2902, 1421, 1247, 1193, 1101, 1085, 998, 878, 877 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.82–2.02 (m, 3 H, 2 × 2-H and $SCH_2C\mathit{H_2}$), 2.09–2.18 (m, 1 H, $SCH_2C\mathit{H_2}$), 2.75 (d, *J* = 3.6 Hz, 1 H, OH), 2.80–2.96 (m, 4 H, SCH_2), 3.40 (s, 3 H, OCH_3), 3.44 (s, 3 H, OCH_3), 3.44 (d, *J* = 5.9 Hz, 2 H, 5-H), 3.50–3.56 (m, 1 H, 3-H), 3.85–3.92 (m, 1 H, 4-H), 4.21 (dd, *J* = 5.1 and 9.3 Hz, 1 H, 1-H); ^{13}C NMR ($CDCl_3$) δ 26.22 (t, $SCH_2\mathit{C}H_2$), 30.09 u, 30.54 (t, SCH_2), 36.51 (t, C-2), 43.92 (d, C-1), 58.62 and 59.38 (q, OCH_3), 71.27 and 78.43 (d, C-3/C-4), 73.60 (t, C-5); MS (EI, 70 eV) *m/z* 252 (16) (M)$^+$, 220 (14) (M – CH_4O)$^+$, 175 (6), 145 (76), 119 (100), 113 (16), 87 (18). Anal. Calcd for $C_{10}H_{20}O_3S_2$: C, 47.59; H, 7.99; S, 25.41. Found: C, 47.60; H, 8.04; S, 25.40.

2-Deoxy-3,5-di-*O*-methyl-4-*O*-[(4-methylphenyl)sulfonyl]-D-*erythro*-pentose Cyclic 1,3-Propanediyl Mercaptal (19). A solution of dithioacetal 18 (1.80, g 7.1 mmol) in anhydrous pyridine (20 mL) is treated with *p*-toluenesulfonyl chloride (1.49 g, 1.1 equiv) and stirred for 2 d at 20 °C. The mixture is poured into ice-cold 1 N HCl (20 mL) and extracted three times with CH_2Cl_2 (100 mL). The organic phase is washed with aqueous saturated sodium hydrogen carbonate solution, dried with Na_2SO_4, and evaporated at reduced pressure. The residue is separated by column chromatography on silica gel (CH_2Cl_2) to afford oily **19** (2.20 g, 76%): $[\alpha]^{20}_{D}$ –9.0° (*C* 1.35, CH_2Cl_2); IR (CH_2Cl_2) 3055, 2987, 2936, 1423, 1363, 1122, 1097, 1033, 1011, 910, 897, 816 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80–1.92 (m, 3 H, 2 × 2-H and $SCH_2C\mathit{H_2}$), 2.06–2.14 (m, 1 H, $SCH_2C\mathit{H_2}$), 2.44 (s, 3 H, Ar-CH_3), 2.78–2.91 (m, 4 H, SCH_2), 3.25 (s, 3 H, OCH_3), 3.31 (s, 3 H, OCH_3), 3.48–3.59 (m, 2 H, 5-H), 3.68–3.73 (m, 1 H, 3-H), 4.09 (t, *J* = 7.4 Hz, 1 H, 1-H), 4.64–4.69 (m, 1 H, 4-H), 7.33 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.81 (d, *J* = 8.1 Hz, 2 H, Ar-H); ^{13}C NMR ($CDCl_3$) δ 21.65 (q, Ar-$\mathit{C}H_3$), 25.90 (t, $SCH_2\mathit{S}CH_2$), 29.52 and 30.07 (t, SCH_2), 36.54 (t, C-2), 43.38 (d, C-1), 58.65 and 59.08 (q, OCH_3), 70.74 (t, C-5), 76.55 and 80.86 (d, C-3/C-4), 127.98 and 129.61 (d, C-Ar), 133.93 and 144.67 (s, C-Ar); MS (DCI, NH_3, pos) *m/z* 424 (100) (M + NH_4)$^+$, 407 (7) (M + H)$^+$, 373 (5), 270 (18), 203 (32), 178 (76), 162 (18). Anal. Calcd for $C_{17}H_{26}O_5S_3$: C, 50.22; H, 6.45; S, 23.66. Found: C, 50.23; H, 6.49; S, 23.55.

Cyclization of Tosylate 19. A solution of dithioacetal **19** (1.10 g, 2.7 mmol) in anhydrous THF (30 mL) is treated under nitrogen at –50 °C within 0.5 h with a solution of 1.6 N *n*-BuLi (1.7 mL) in *n*-hexane and stirred for 2 h at 20 °C. An aqueous ammonium chloride solution (3 mL) is added, and the THF is removed at reduced pressure. The residue is dissolved in diethyl ether, washed with water, dried with Na_2SO_4, evaporated, and separated by layer chromatography (ether:hexane (1:1)) to afford oily **20** (114 mg, 18%) from the less polar fraction $[\alpha]^{20}_{D}$ 43.7° (*c* 1.9, CH_2Cl_2)] and oily **21** (208 mg, 35%) from the polar fraction $[\alpha]^{20}_{D}$ –22.3° (*c* 1.5, CH_2Cl_2)].

(1*S*-*cis*)-2-Methoxy-1-(methoxymethyl)-5,9-dithiaspiro[3.5]nonane (20): IR (film) 2930, 2896, 2827, 1221, 1131, 1103, 1044 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.87–2.09 (m, 2 H, $SCH_2C\mathit{H_2}$), 2.21 (dd, J_{gem} = 12.7 Hz, $J_{2,3}$ = 7.1 Hz, 1 H, 3a-H), 2.58–2.67 (m, 2 H, 3b-H, 1-H), 2.75–2.82 and 2.84–2.92 (m, 2 H, SCH_2), 3.05–3.12 (m, 2 H, SCH_2), 3.26 (s, 3 H, OCH_3), 3.39 (s, 3 H, OCH_3), 3.66 (dd, J_{gem} = 10.0 Hz, $J_{1a',1}$ = 5.4 Hz, 1 H, 1a′-H), 3.72 (dd, J_{gem} = 10.0 Hz, $J_{1'b,1}$ = 8.6 Hz, 1 H, 1b′-H), 4.16 (q, *J* = 7.2 Hz, 1 H, 2-H); ^{13}C NMR ($CDCl_3$) δ 25.17 (t, $SCH_2\mathit{C}H_2$), 28.52 and 28.60 (t, SCH_2), 43.61 (t, C-3), 46.60 (s, C-4), 53.27 (d, C-1), 56.82 (q, OCH_3), 58.61 (q, OCH_3), 69.90 (t, C-1′), 72.36 (d, C-2); MS (70 eV) *m/z* 234 (5) (M)$^+$, 202 (2), 189 92), 176 (4), 161 (4), 145 (10), 132 (100), 101 (10), 85 (6), 71 (10). HRMS 234.0748, calcd for $C_{10}H_{18}O_2S_2$ 234.074826. Anal. Calcd for $C_{10}H_{18}O_2S_2$: C, 51.25; H, 7.74. Found: C, 51.02; H, 7.73.

(*S*)-4-(1,3-Dithian-2-yl)-3-methoxy-2-butanone (21): IR (film) 2985, 2934, 2902, 1715, 1422, 1355, 1119, 909 cm^{-1}, ^1H NMR ($CDCl_3$) δ 1.85–1.96 (m, 1 H, $SCH_2C\mathit{H_2}$), 2.04–2.15 (m, 3 H, 1 × $SCH_2C\mathit{H_2}$ and 2 × 4-H), 2.20 (s, 3 H, CCH_3), 2.78–2.92 (m, 4 H, SCH_2), 3.41 (s, 3 H, OCH_3), 3.88 (dd, *J* = 5.2 and 7.8 Hz, 1 H, 3-H), 4.16 (dd, *J* = 5.2 and 8.3 Hz, 1 H, 2′-H); ^{13}C NMR ($CDCl_3$) δ 25.54 (q, C-1), 25.83 (t, $SCH_2\mathit{C}H_2$), 29.23 and 29.62 (t, SCH_2), 37.30 (t, C-4), 42.50 (d, C-2′), 58.55 (q, OCH_3), 83.71 (d, C-3), 210.41 (s, C-2); MS (70 eV) *m/z* 220 (2) (M)$^+$, 177 (1.5), 145 (1.5), 133 (92), 119 (100), 103 (8), 88 (24); HRMS 220.0591 ±2 ppm (M^+) calcd for $C_9H_{16}O_2S_2$ 220.05917. Anal. Calcd for $C_9H_{16}O_2S_2$: C, 49.06; H, 7.32. Found: C, 49.22; H, 7.44.

Acknowledgment. We thank Dr. H. Rieger (Beilstein Institute, Frankfurt, FRG) for checking the CA nomenclature.

Registry No. **1**, 533-67-5; **2**, 50907-65-8; **3**, 135598-34-4; **4**, 135598-35-5; **5**, 135598-36-6; **6**, 135598-37-7; **7**, 135598-38-8; **8**, 135598-39-9; **9**, 135598-40-2; **10**, 135619-08-8; **11**, 135598-41-3; **12**, 135598-42-4; **13**, 135598-43-5; **14**, 135598-44-6; **15**, 135598-45-7; **16a**, 51255-17-5; **16b**, 51255-18-6; **17a**, 83149-37-5; **17b**, 83149-38-6; **18**, 135598-46-8; **19**, 135598-47-9; **20**, 135598-48-0; **21**, 135598-49-1; 1,3-propanedithiol, 109-80-8.

Spontaneous Oxygenation of Cyclic Olefins: Effects of Strain[1]

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Reactivity of strained olefins 1–3, 41, and 44 toward spontaneous oxygenation has been evaluated. Angle-strained olefins 1, 32, and 35 react spontaneously with ground-state triplet oxygen, at room temperature, to yield quantitatively, not copolymers or hydroperoxides, but epoxides and diketones in approximately a 2:1 ratio. The autoxidation of 1 is carried out with various solvents, inhibitors, initiators, and in the presence of 2 and 1,2-dimethylcyclohexene to determine the mechanistic details. Compared with 1, autoxidation of 2 and 3 follows a different route yielding mainly hydroperoxides along with other products. The mechanism of the spontaneous autoxidation is discussed in light of these results.

Introduction

The familiar examples of olefins becoming oxygenated under mild conditions follow a few well-defined models. One[2] is olefin autoxidation involving a chain reaction initiated by a free radical, generally from a thermally unstable peroxide or azo compound. Depending on the nature of the olefinic target, different chain steps at different points lead to allylic hydroperoxides, carbonyl-bearing cleavage products, epoxides, and other special products from oxygenated radicals. A second model[3] is the

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(2) Mayo, F. R.; *Acc. Chem. Res.* **1968**, *1*, 193.

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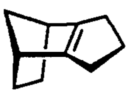
concerted reaction of singlet oxygen with an olefin yielding, where possible, an allylic hydroperoxide and otherwise a 1,2-dioxetane or its cleavage products. The conditions of singlet oxygen formation are so specialized that examples of spontaneous concerted oxygen addition to the double bond are understandably rare. In view of this, it has long been a problem why certain olefins react spontaneously with ground-state oxygen in the absence of any initiator. One starting point in understanding these reactions seems to be detailed studies of oxidations of olefins capable of spontaneous reaction with oxygen. In recent studies, we have become interested in a class of strained olefins, including 1 and 2, which react with ground-state triplet oxygen without the aid of an initiator.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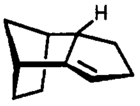

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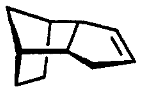
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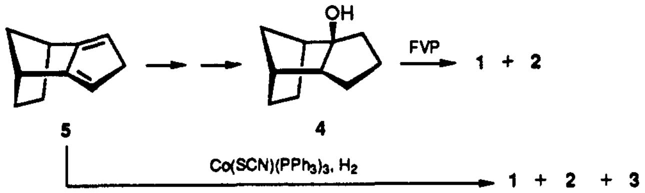
Results and Discussion

Although the synthesis of 1 and 2 was accomplished earlier in this laboratory[4] by the dehydration of alcohol 4, the multistep procedure used in the preparation starting with isodicyclopentadiene[5] 5 was considered lengthy and low yielding. Recourse was therefore had to a new method involving selective hydrogenation of diene 5 catalyzed by thiocyanotris(triphenylphosphine)cobalt[6] (Scheme I).

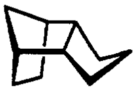
After 40 h of stirring under hydrogen in the presence of the catalyst, 85% conversion of diene 5 to the olefins 1 (46%), 2 (30%), and 3 (24%) was realized. However, special difficulties in separating and purifying the products led to the adoption of the new synthetic procedure of Takaishi and co-workers[7] which appeared while this work was in progress. 1 and 2 are most advantageously prepared by the dehydration of the alcohol 4, made by the *m*-chloroperbenzoic acid (MCPBA) oxidation[8] of 6, the saturation product of *endo*-dicyclopentadiene. Isomeric olefin 3 is conveniently prepared as the first hydrogenation product of *endo*-dicyclopentadiene.

The dehydration of 4 produces 1 and 2 in a ratio of 3:1, and the separation of this pair can be carried out by silver nitrate impregnated silica gel column chromatography. This method, however, works well only on a small scale. Therefore, large-scale separations were made by selective hydroboration of 2 with bulky 9-borabicyclo[3.3.1]nonane (9-BBN) to isolate 1 and selective epoxidation of 1 with MCPBA to isolate 2. The stabilities of the olefins follow the order 2 < 1 < 3. Warming of any mixture of 1 and 2 leads, over the course of several days, to increasing amounts of 3 and the eventual disappearance of the other two isomers. The relative amounts of 1 and 2 remain nearly unchanged during their slow conversion into 3. However, mixtures of 1 and 2 show very slow conversion of 2 to 1. When olefin 3 is heated under similar conditions, no conversion to 1 or 2 is observed. Also, when a methylene chloride solution of 1 and 2 is stirred with the strongly acidic ion-exchange resin Amberlyst XN-1010 at 0 °C, alcohol 4 is obtained in quantitative yield.

Scheme I



The olefins react with MCPBA in a reactivity order of 1 ≫ 2 ≫ 3 to produce corresponding epoxides 7–9. Epoxidation in all cases proceeded exclusively from the *exo* side. Thus, the reactivities of the olefins 1 and 2 differ by a much larger factor than their thermodynamic stabilities, and the more stable isomer is the more reactive one in this comparison. On the other hand, olefin 3, which slowly accumulates at equilibrium in the presence of 1 and 2, is by far the least reactive of the three toward MCPBA.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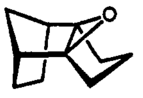

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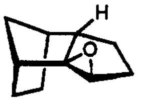

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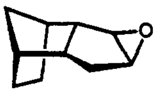

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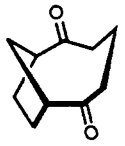
Olefin 1 also reacts rapidly with singlet oxygen, produced under both photochemical[3] and thermal[3,9] generation conditions, to give 10, in quantitative yield, through the dioxetane precursor. The intermediacy of the dioxetane could be confirmed by bluish green chemiluminescence observed when 9,10-dibromoanthracene[10] was present in the reaction mixture during the addition of singlet oxygen.

Autoxidation of 1. Olefin 1 is so reactive toward molecular oxygen that its samples are usually contaminated with oxidation products. (Rigorous exclusion of oxygen and low temperatures are needed to keep the olefin pure.) When allowed to stir under O_2 sparging, either neat or in solution, for 28 h (room temperature and protected from light), the reaction is completed and produces only two products. These products may be separated by preparative TLC to give the epoxide 7 (70–80%) and diketone 10 (20–30%).



10

The structures of 7 and 10 were confirmed by their spectral and molecular weight data as well as by comparison with authentic samples. Autoxidation of 1 is remarkably simple in that only two products are detected. All attempts to detect other products lead to the conclusion that 7 and 10 are formed in yields in excess of 97% at 98% olefin conversion. This low-temperature spontaneous autoxidation and simplicity of the products are quite noteworthy and led to further studies of this reaction.

Exploratory rate measurements and product distributions have been determined for a total of 15 different solvents (Table I). The rate studies show that aut-

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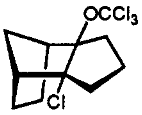
Table I. Autoxidation of 1 in Various Solvents

	solvent	half life (h)	% yield of 7 + 10	ratio of 7:10	other products (%)
1.	$CDCl_3$	3	98.7	70:30	1.3
2.	$CHCl_3$	3.5	91.5	75:25	8.5
3.	CD_3CN	3.5	100	72:28	
4.	CH_3CN	4	100	76:24	
5.	CD_2Cl_2	3	100	71:29	
6.	acetone	5.5	100	78:22	
7.	CH_2Cl_2	7	100	74:26	
8.	C_6D_6	12.5	100	70:30	
9.	CCl_4	13	80.7	55:45	19.3[a]
10.	CH_3OH	13	14	28:72	77[b]
11.	C_6H_6	14	100	75:25	
12.	hexanes[c]	18	100	78:22	
13.	THF	2.5	95	70:30	4–5
14.	DMSO[c]	8.5	100	76:24	
15.	DMF	110	25 after 4 days	72:28	

[a] Other product is 11. [b] Other product is 13. [c] Solubility problems with either 1 or its oxidation products.

oxidation is pseudo-first order in 1, and a good fit over 3 half-lives could be obtained. These half-life figures are used empirically in making comparisons of overall rates among different conditions. In the present experiments, autoxidation is clearly spontaneous as evidenced by lack of an induction period. By UV analysis, it may be confirmed that autoxidation products are detected after less than 1 min of exposure of 1 to oxygen. In most of the solvents studied, only 7 and 10 could be detected as products. The reaction rate seems to be about six times as rapid in $CDCl_3$ as in benzene. This difference is greatest among the solvents studied with the exceptions of tetrahydrofuran (THF), dimethylformamide (DMF), hexanes, and dimethyl sulfoxide (DMSO). In these solvents, special problems such as solubility and solvent impurities seem to alter the reaction rates. The rate differences among other solvents do not correlate with solvent polarity or Kosower z-values, thus excluding any strongly ionic character in the reaction. In addition to the rate differences, the range of solvents studied also shows differences in the ratio of the epoxide 7 to the diketone 10, being highest in acetone (78:22) and lowest in methanol (28:72). Interestingly, in the four pairs of deuterated–nondeuterated solvents studied, the rate of autoxidation always increased and the ratio of 7 to 10 decreased by changing to the deuterated solvent.

In addition to 7 and 10, a minor product (19.3%) can be observed in the autoxidation of 1 in carbon tetrachloride. The product was identified as the compound 11 based on the ^{13}C NMR data.



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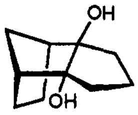

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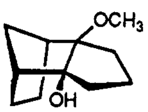
It is possible to isolate 11 by preparative TLC separation, but if not protected from water, it readily hydrolyzed to 12 during workup. The identity of 12 was established by its high-resolution mass spectral data. By capillary GC analysis, it may be seen that similar products are also formed in $CHCl_3$ and $CDCl_3$ solvents with yields of 8.5% and 1.3%, respectively. On the other hand, the major product (77%) obtained in the autoxidation of 1 in methanol is assigned the structure 13 on the basis of its spectral data.

A priori, one would predict that 13 results from the addition of CH_3OH to the primary autoxidation product 7. However, in a control experiment, epoxide 7 was quite stable under similar conditions. Thus, product 13 may well be the addition product of CH_3OH and the intermediate that goes on to become epoxide 7. Another possibility is that 13 arrives via addition of methanol to 7, catalyzed by a stray acid generated during the autoxidation. Similar reactions may be taking place in the halocarbon solvents (CCl_3X).



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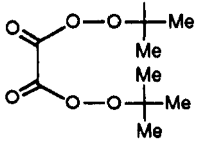
Autoxidation of 1 can be inhibited by a number of compounds. Addition of 2,6-di-*tert*-butyl-*p*-cresol (butylated hydroxytoluene or BHT), a well-known free radical quencher, at 0.24 equiv, inhibits oxidation for nearly 15 h during which the inhibitor itself undergoes chemical reaction. After destruction of BHT, the previously observed autoxidation process is resumed.

A similar effect can be seen with the commercial antioxidant *N*-phenyl-2-naphthylamine. With only 0.1 equiv of this inhibitor (0.009 M or 1000 ppm) present in the reaction mixture, an induction period of 10 h was observed. In the first 26 h, only 10% of the olefin is consumed. After this period the reaction is accelerated, and in the next 12 h half of the olefin is consumed.

Diazabicyclo[2.2.2]octane (DABCO) and triethylamine, which are not known as radical inhibitors, but singlet oxygen quenchers, also show powerful inhibitory effects. Only 2 mg of DABCO (0.025 equiv, 0.02 M) is sufficient to inhibit autoxidation for 20 h. By comparison with DABCO, triethylamine is a slightly weaker inhibitor. At 0.02 equiv amount of NEt_3 (0.0158 M) an induction period of 8 h is observed in autoxidation.

Addition of DABCO (0.1 M) to the reaction mixture of an autoxidation which is in progress and about 50% complete inhibits the reaction almost completely (only 5% additional reaction in next 42 h). The rate of autoxidation of 1 can be increased about 4-fold by irradiating the reaction mixture with high-intensity visible light. The products obtained are 7 and 10 in the same ratio as in the experiments carried out in darkness. It is of interest to note that addition of DABCO (0.09 equiv) to the light-catalyzed reaction mixture only slows the reaction (half-life 5 h) without any induction period.

How can we best determine whether the autoxidation of 1 originates in a direct reaction of $^3O_2$ with the olefin or in its reaction with trace initiators or catalysts? If autoxidation were initiated by some "foreign" radical, then a known, well-behaved added initiator should accelerate the reaction with the same results. Classical free-radical chain initiators azoisobutyronitrile (AIBN), benzoyl peroxide, and di-*tert*-butylperoxyoxalate 14[11] were tried for this reason, without success.



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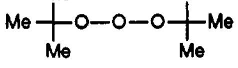

15

The problem here is that rates of decomposition of these initiators, to produce radicals, are much slower than the

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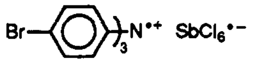
[11] Bartlett, P. D.; Benzing, E. P.; Pincock, R. E. *J. Am. Chem. Soc.* **1960**, *82*, 1762.

autoxidation rate of 1 at room temperature. If the solutions containing 1 and any of these initiators are heated under an oxygen atmosphere, essentially the same results are obtained as those for the pure solution of 1. Attention was then focused on di-*tert*-butyl trioxide (15),[12] which decomposes above −25 °C efficiently. Using 0.1 mol equiv or less of 15 produced many other products in addition to the usual 7 and 10. It appears that 15 produces *tert*-butoxy radicals that initiate different kinds of chain reactions. This result seems to fit with our initial observation that autoxidation of 1 appears to be spontaneous.

In order to shed some light on the possible intermediacy of radical cations in the autoxidation of 1, an experiment was performed in the presence of the one-electron oxidant, tris(*p*-bromophenyl)aminium hexachloroantimonate (16).



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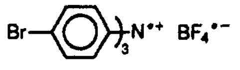
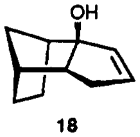


17

Such radical cations are reportedly[13] effective in catalyzing the 1,4-addition of triplet oxygen to certain 1,3-dienes at low temperature. It also has been shown[14] that radical cation 17 catalyzes the addition of $^3O_2$ to adamantylideneadamantane to give the corresponding dioxetane. However, the addition of 16 at −78 °C to a solution of 1, in dry methylene chloride in the presence of oxygen, did not result in any oxidation of 1. A similar reaction performed at room temperature did not show any significant differences compared to the normal autoxidation of 1.

To test the intermediacy of superoxide anion ($O_2^{\bullet -}$) in the autoxidation of 1, an experiment was performed where $^3O_2$ was replaced by $O_2^{\bullet -}$. When a solution of 1 in methylene chloride was stirred with KO_2 and 18-crown-6 ether under argon atmosphere for a 2-day period, no oxidation of 1 was observed. Although this experiment does not rule out the case of initiation by superoxide anion followed by a triplet oxygen chain process, it shows that the entire autoxidation is not carried out by superoxide anion.

Autoxidation of 2. Compared to 1, autoxidation of 2 seems to follow a different route. Under conditions identical with that used for the autoxidation of 1, no oxidation of 2 is seen for the first 12 h. After 20 h of O_2 bubbling, only 5% conversion is realized and 40 h of exposure results in 12% oxidation. However, after this time, the rate of oxidation is increased and the reaction is 95% complete at the end of a 100-h period. On the other hand, 2 reacts rapidly under singlet oxygen conditions to yield hydroperoxides as a mixture of at least four products. Bisulfite reduction and separation of the mixture yielded about 70% of the tertiary allylic alcohol 18, arising from the strongly preferred "ene" reaction which forms hydroperoxide 19.



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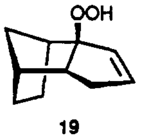
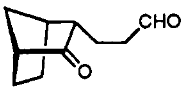


19

Capillary GC analysis of the autoxidation mixture shows three major products. Two of these were identified as epoxide 8 and the hydroperoxide 19. The third product appears to be due to olefin cleavage to give the keto aldehyde 20 and its further oxidation product 21. The ratio of 8:19:20 (and/or 21) is 40:25:35.



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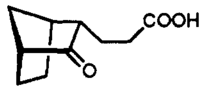


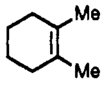
21

The oxidation product profile and the reaction kinetics (long induction period followed by autocatalysis) of 2 suggest that this autoxidation is not spontaneous, as in the case of 1, but is the result of socalled "initiated" autoxidation. Furthermore, autoxidation of 2 is inhibited by BHT but not by DABCO.

Addition of AIBN or dibenzoyl peroxide as a radical initiator (at 40–60 °C) to an oxygen-saturated solution of 2 produces mostly the allylic hydroperoxide 19 along with other minor products. Epoxide 8 is formed in minor amounts (4–5%).

There is a striking synergism between olefins 1 and 2 in the autoxidation reaction. The absorption of oxygen by 1 becomes three times slower in the presence of 2, but under these conditions 2 is autoxidized much faster than in the absence of 1, yielding nearly 60% of epoxide 8 along with 10–15% of the hydroperoxide 19 and three other minor products. It appears from this set of experiments that the spontaneous reaction is faster between oxygen and olefin 1, but that chain propagation of the intermediate species with 2 is favored, making 2 an effective retarder for 1 while its own oxidation rate is enhanced by the 1 initiation process. Similar behavior has been observed in the case of 1,2-dimethylcyclohexene 22. Literature reports[15] indicate that 22 is susceptible to autoxidation when heated or irradiated in the presence of oxygen. Although the reported product composition differs somewhat among different research groups, the products seem to be predominantly the corresponding allylic hydroperoxides.

When autoxidation of 22 is carried out at room temperature and in darkness over a period of 3 days, only trace amounts (2–3%) of oxidation products could be observed. In contrast, when autoxidation of 22 is carried out under similar conditions, but in the presence of 1 (40:60 ratio), 50% conversion of 22 is obtained in a 26-h period. During this period, olefin 1 is almost completely oxidized (same products as before). The products and their composition obtained in this case are quite different from simple radical autoxidation of 22, being the epoxide 23 (62.5%), the hydroperoxide 24 (20%), and the diketone 25 (17.5%) which were identified by comparison with authentic samples prepared by reported procedures.[15]



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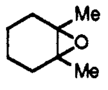

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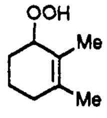

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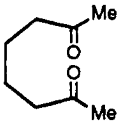

25

Autoxidation of 3. At room temperature, olefin 3 appears unreactive to triplet oxygen compared to 1 and 2. However, at 55–60 °C in methylene chloride, 3 undergoes 75% oxygenation in 35 h with oxygen bubbling. After workup with sodium bisulfite, the reduced products included epoxide 9 (5%), alcohol 18 (18.3%), ketone 26 (21.4%), and alcohol 27 (41.25%). The two allylic alcohols 18 and 27 were also observed as impurities in samples of

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[12] Bartlett, P. D.; Lahav, M. *Isr. J. Chem.* **1972**, *10*, 101.

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[14] Bartlett, P. D. *ACS Symp. Ser.* **1978**, *No. 69*, 15–32.

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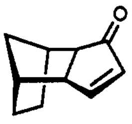

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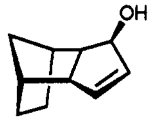
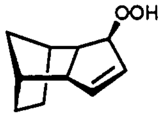


27

3 that had stood in the laboratory for a long time without protection from air and light. Olefin 3 also reacts with singlet oxygen, and the product is entirely allylic hydroperoxide 28.



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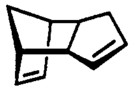
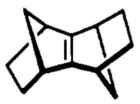


29

Olefin 3 is not particularly strained and behaves like a simple olefin toward autoxidation. The autoxidation proceeds at a significant rate only when heated, and the product mixture obtained is of the type found in typical radical-initiated autoxidation. In this regard, 3 compares well with its parent molecule *endo*-dicyclopentadiene 29, in its autoxidation behavior.[15a] When heated at 40–60 °C with bubbling of oxygen for a few hours, 29 produces a similar mixture of epoxides, allylic alcohols, and a ketone.

Autoxidation Behavior of Sesquinorbornenes. The interesting results obtained in the autoxidation of 1 prompted us to look into similar behavior in the sesquinorbornene series. Whereas the parent molecules *anti*-[16] and *syn*[17]-sesquinorbornenes (30 and 31, respectively) have been shown to be inert toward attack by both singlet and triplet oxygen, the corresponding anti derivatives with higher unsaturation are known[17] to be highly sensitive toward autoxidation. Earlier work from this laboratory[18] had demonstrated the susceptibility of benzo-*syn*-oxasesquinorbornene 32 toward autoxidation.



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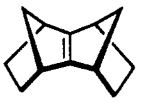

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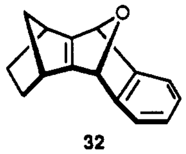
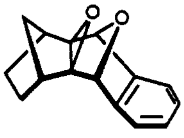


32

We have now studied the autoxidation of 32 in detail and noted its similarity with that seen in the case of 1. As with 1, autoxidation of 32 proceeds smoothly at room temperature (with oxygen bubbling) to give epoxide 33 and diketone 34 in a 60:40 ratio.



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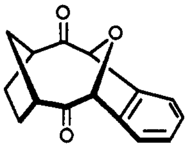
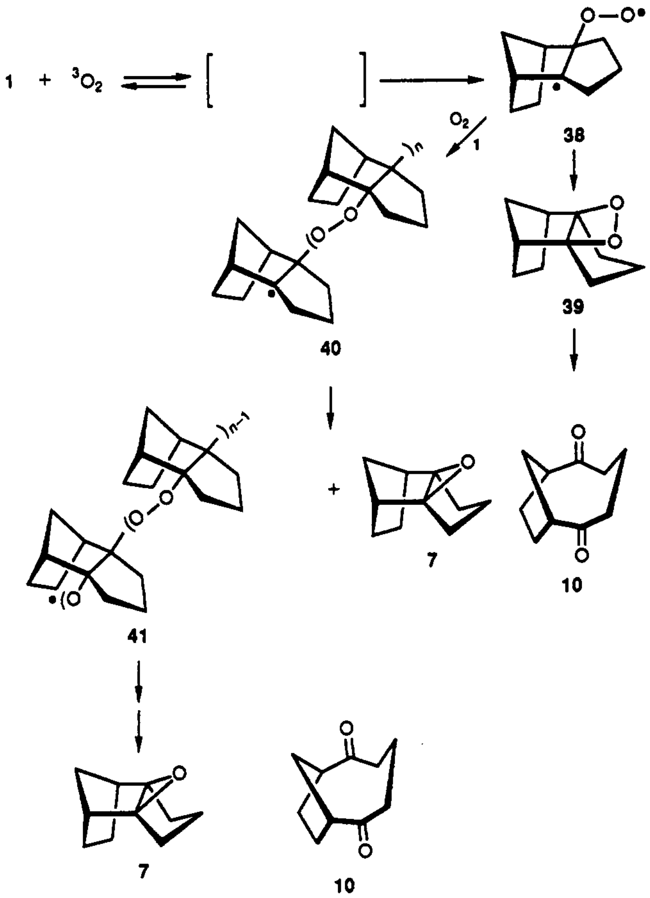


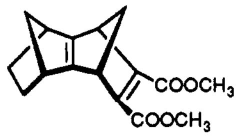
34

Identification of 33 and 34 was accomplished by comparison of the spectral data of both products, after preparative TLC separation, with authentic samples. Whereas epoxide 33 was prepared independently by the MCPBA oxidation, diketone 34 was obtained by periodic acid cleavage[19] of the strained epoxide itself. Similar results were obtained with 35, the dimethylacetylene dicarboxylate syn cycloadduct of diene 5.

Scheme II



Bubbling oxygen through a methylene chloride solution of 35 at room temperature for 2 days in darkness leads to its complete conversion to epoxide 36 (70%) and diketone 37 (30%). Both 36[20] and 37[21] have been characterized by spectral data and X-ray crystal structures.



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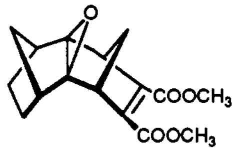

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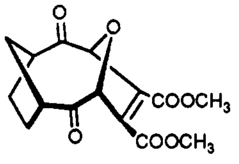

37

Some Features of the Autoxidation Mechanism. The observations discussed above illustrate several features of the autoxidation mechanism in operation. The results indicate that, as best we can tell, the autoxidation of 1 (also 31 and 35) is spontaneous in that it is initiated by direct reaction of triplet oxygen with the olefin. The ease with which initiation occurs is related to the angle strain in the double bond with four bond angles contracted to 108° or

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[16] Bartlett, P. D.; Blakeney, A. J.; Kimura, M.; Watson, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 1383.

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less which would prefer to be 120°. The exact nature of initiation, involving an overall triplet–singlet change, is only speculative at the moment. One highly attractive mechanism seems to be initial electron transfer from the strained olefinic bond to triplet oxygen to produce corresponding radical ions or a charge-transfer complex, respectively, in a reversible step. The ability of DABCO to interfere with this process can explain its inhibitory effect. The intermediate thus obtained can lead efficiently to the peroxy biradical **38** with several reaction channels available (Scheme II) to it, yielding the observed products. Since the reaction is initiated by ground-state triplet oxygen, the peroxy biradical **38** will originate as a triplet. The triplet **38** will require intersystem crossing in order to undergo ring-closure to yield the corresponding dioxetane **39** with rapid exothermic cleavage to diketone **10**. The most likely pathways for **38** are the various radical chain processes leading to the formation of **7** and **10**. A substrate most likely to enter into biradical chains is olefin **1** itself to yield a new triplet biradical **40**. The peroxide biradical prefers to add to the olefinic bond instead of removing allylic hydrogen atoms because of the obvious constraints involved. Intersystem crossing is also required for **40** to cleave to two molecules of **7**. However, a chain length of two to arrive at the final products is too short to show total inhibition by radical chain quenchers. In such a case, a polymeric radical chain can be envisioned where the polyperoxide radical ending in the olefin unit splits off an epoxide unit **7**, and the remaining alkoxy radical **41** continues the oxidation chain or possibility splits off another epoxide unit. In the ideal sequence, this alkoxy radical can be used repeatedly to oxidize relatively large amounts of **1** to produce **7** and **10**. Interception of **38** by **2** and **22** can explain the autoxidation synergism and predominance of epoxides observed when these olefins are autoxidized in the presence of **1**.

Experimental Section

The phrase "at reduced pressure" refers to the use of a rotary evaporator operating with a water aspirator (10–100 mmHg); the phrase "in vacuo" refers to the use of an oil pump (0.1–10 mmHg). Melting and boiling points are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer 197 instrument and were calibrated with a polystyrene film. Mass spectra (MS) were obtained on a Finnegan OWA-1020 GC-MS-DS operating in the electron impact mode with an ionizing energy of 70 eV. Only the most characteristic and/or the most intense fragments are reported. New compounds were characterized either by high-resolution mass spectral analyses performed by the Midwest Center of Mass Spectroscopy, University of Nebraska–Lincoln, NE, or by elemental analyses performed by Schwarzkopf Microanalytical Laboratory, NY. NMR spectra were obtained with JEOL-FX60, Varian XL-300, and Varian EM-390 NMR spectrometers with internal Me_4Si as reference and $CDCl_3$ as solvent. Gas chromatography was performed on a Perkin-Elmer Sigma 2000 gas chromatograph equipped with a flame ionization detector using helium as the carrier gas using a J & W fused silica capillary column (30 × 0.26 mm i.d.), coated with 0.25-μm film of carbowax 20 M obtained from Alltech Associates, Inc., Deerfield, IL. Ozonolyses were performed using a Welsbach Ozonator model T-23, which produces a steady stream of between 2 and 4% ozone in oxygen (0.2 mmol/min). Thin-layer chromatography was performed on Eastman No. 6060 silica gel sheets with fluorescent indicator obtained from Eastman Kodak Company, Rochester, NY. Preparative TLC was accomplished using glass plates (20 × 20 cm) precoated with 0.25- or 1.0-mm thickness silica gel with fluorescent indicator UV-254 purchased from Analtech, Newark, DE. Developing solvents are as indicated, and visualization was achieved using UV irradiation and/or concd H_2SO_4 charring. Capillary GC conditions: detector, 225 °C; injector, 225 °C; column, 70 °C/2 min, then 15 °C/min to 225 °C. All quantitative analyses by capillary GC are calculated from standardized analyses and GC integrations using Hewlett-Packard 3390 A integrator.

Purification of Solvents and Reagents.[22] Extreme precautions were taken to avoid contamination of solvents, olefins, and the reaction vessels from antioxidants, plasticizers, and trace metals. All solvents were purchased as "analytical grade" and were freshly distilled in glass over drying agents and stored under argon in the dark. Oxygen was delivered from oxygen tank of 99.9% purity by polyethylene tubing (free of plasticizers and antioxidants). Oxygen was dried on-line by passage through a column of anhydrous $CaCl_2$ and molecular sieves.

Although these oxidations are very sensitive to certain antioxidants, the rates do not vary significantly with other impurities, small changes in moisture content, or stray light intensity.

Hydrogenation of Diene 5.[5] To 200 mL of dry 1,2-dimethoxyethane (distilled over Na/benzophenone ketyl) were added $Co(CN)_2 (PPh)_2$ (4.5 g, 6.5 mmol), Zn (4.24 g, 65 mmol), $ZnBr_2$ (22 mmol, 4.88 g), and triphenylphosphine (6.5 mmol, 1.90 g) under argon. The solution, which was initially purple, turned brown after 3 h of stirring. Then diene **5** (40 mmol, 5.4 g) was added to this solution and argon was replaced by hydrogen. The hydrogenation was carried out at room temperature and under the atmospheric pressure of hydrogen and vigorous stirring. Progress of the reaction was monitored by GC. After 40 h of stirring, the reaction mixture was filtered. The solvent was removed under reduced pressure. The oily brown residue obtained was extracted with hexanes. The solvent was then evaporated to give a colorless oil (2.5 g). This oil was dissolved in methylene chloride and cooled to 0 °C. To this solution, maleic anhydride (300 mg, 3 mmol) was added and the solution stirred for 2 h to capture unreacted **5** as its Diels–Alder adduct. Then the solvent was evaporated at reduced pressure and the residue was quickly eluted through a silica gel column with hexanes to get 2 g of colorless oil. By capillary GC analysis it was found to be a mixture of **1**, **2**, and **3** (ratio 46:30:24), yield 36%.

Hydrogenation of Dicyclopentadiene 29. Dicyclopentadiene (66 g, 0.5 mole) was mixed with 15 mL of absolute ethanol in a Parr shaker bottle, and 400 mg of 5% Pd on activated charcoal was added. The bottle was agitated under pressurized hydrogen until 0.5 mol of H_2 was absorbed. The solution was filtered through Celite filter-aid and the solvent removed to give 60 g of **3**, *endo*-tricyclo[5.2.1.0^{2,6}]dec-3(4)-ene.

Hydroboration of 2 in Presence of 1. To a cooled mixture of **1** and **2** (3:1, 1.31 g) in anhydrous tetrahydrofuran (10 mL) was added dropwise a 0.5 M solution of 9-BBN in THF (9 mL, 4.5 mmol). The reaction mixture was stirred at room temperature for 2 h. The solvent was then evaporated at reduced pressure and the oil chromatographed with hexanes. The first fraction was collected to afford 0.9 g (90%) of unreacted **1**.

Competitive Epoxidation of 1–3 with MCPBA. To a cold (0 °C) solution of **1–3** (67 mg, 0.5 mmol each) in dichloromethane was added 85% MCPBA (100 mg, 0.5 mmol) at once. The solution was stirred for 5 min and analyzed by GC. The same procedure was repeated two more times at 5-min intervals.

The epoxidation of individual olefins was also carried out to isolate the respective epoxides for characterization. For **7**:[7] colorless crystals (mp 40–41 °C), sweet smell; high-resolution mol wt found 150.1044 (cald 150.1041); ^1H NMR δ 2.4 (s, 2 H), 1.9–1.6 (series of multiplets, 7 H), 1.54 (distorted doublet of doublet, 2 H), 1.39 (d of d, 2 H), 0.93 (d, 1 H); ^{13}C NMR δ 69.39 (s, C_2, C_9), 38.40 (d, C_1, C_7), 34.76 (t, C_4 or C_{10}), 27.81 (t, C_{10} or C_4), 24.75 (t, C_3, C_5), 22.93 (t, C_8, C_9); IR 2960, 2860, 1460, 1300, 1131, 950, 910, 820 cm^{-1}; MS 150 (30), 135 (13), 121 (56), 117 (21), 107 (37), 104 (34), 94 (51), 93 (40), 91 (47), 84 (31), 79 (100), 77 (39), 67 (27). For **8**: colorless liquid, high resolution mol wt found 150.1042 (cald 150.1044); ^1H NMR δ 3.43 (s, 1 H), 2.4 (m, 2 H), 0.98 (s, 1 H); ^{13}C NMR δ 85.28 (s, C_2), 61.65 (d, C_6 or C_3), 51.50 (d, C_3 or C_6), 43.20 (t, C_4), 39.48 (d, C_1 or C_7), 38.26 (d, C_7 or C_1), 32.01 (t, C_{10}), 28.67 (t, C_9), 26.81 (t, C_5), 20.88 (t, C_8). For **9**: colorless oil, camphor-like pleasant smell; ^1H NMR δ 3.55 (s, 1 H), 3.35 (s, 1 H), 2.4 (m, 2 H), 2.2 (m, 1 H), 1.8 (m, 2 H), 1.4 (m, 7 H); ^{13}C NMR δ 61.39 (d), 60.88 (d), 47.84 (d), 44.77 (d), 42.48 (t), 41.26 (d), 38.73 (d), 28.15 (t), 23.18 (t), 22.42 (t). Anal. Calcd for $C_{10}H_{14}O$: C, 80.01; H, 9.33. Found: C, 80.02, H, 9.31.

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Reaction of 1 and 2 with Amberlyst XN-1010. Olefins 1 and 2, either separately or as a mixture, were stirred in methylene chloride at room temperature. To this solution were added Amberlyst XN-1010 beads (0.2–1 equiv), and the solution was stirred for 1 h. The GC analysis showed complete disappearance of the olefins and appearance of 4. The beads were filtered and the solvent was evaporated at reduced pressure to give white precipitate of 4, and its structure was confirmed by comparison of mp and spectral data with those of the authentic material.[4]

General Procedure for Photosensitized Oxidations. A Pyrex vessel, fitted with a fritted gas inlet tube, was charged with the appropriate solution of olefin and sensitizer and placed in a cooling bath at the appropriate temperature. Dry O_2 was bubbled through the solutions. The solutions were externally irradiated by a GE DYH lamp (600 W, 120 V) contained in an immersion well which was cooled with circulating water. The lamp was additionally cooled by a direct flow of air. When polymer-bound Rose Bengal was used, the workup consisted only of filtration of the polymeric beads. On the other hand, all other sensitizers were removed by short silica gel column chromatography. The products were analyzed before and after the workup. For isolation, the reaction mixtures were first reduced with aqueous $NaHSO_3$ and then separated by preparative TLC when two or more products were formed. For olefins 1 and 3, when only one product was formed it could be isolated directly in a pure form without further separation. Diketone 10: colorless crystals (mp 62–64 °C); ^{13}C NMR δ 214.14 (s), 51.53 (d), 39.24 (t), 31.14 (t), 24.88 (t), 23.84 (t); IR: 2960, 2925, 2850, 1720, 1470, 1260 cm^{-1}; MS 166 (30), 138 (10), 125 (90), 97 (100), 79 (12), 67 (35), 55 (67); high-resolution mol wt found 166.0993 (calcd 166.0992).

Thermal Generation of Singlet Oxygen. (a) Triphenylphosphite ozonide decomposition.[3] Methylene chloride (5 mL) at −78 °C was continuously saturated with a stream of O_3/O_2. To this O_3/O_2 solution, triphenylphosphite (5 mmol, 1.55 g) in 5 mL of methylene chloride was added dropwise. Ozone was passed into the solution until the blue color of excess ozone was observed. The ozone stream was disconnected and replaced by a stream of dry argon. Argon purging was carried out well after the time the solution lost its blue color. After the purging, a solution of the appropriate olefin (1 mmol) in 5 mL of methylene chloride was slowly added to this solution. The −78 °C bath was replaced with a −25 °C bath. The solution was kept at −25 to −15 °C for 5 h and then warmed to room temperature. The solvent was removed at reduced pressure and the residue fractionated by preparative TLC (40% ethyl acetate in hexanes). The products obtained were analyzed and the structures proven by comparison with the authentic samples. (b) Triethylsilane hydrotrioxide decomposition[9] method. The above experiment was performed by substituting triethylsilane for triphenylphosphite.

Chemiluminescence in the Reaction of Singlet Oxygen with 1. Methylene chloride (5 mL) at −78 °C was continuously saturated with a stream of O_3/O_2. To this solution triphenylphosphite (5 mmol 1.55 g) in 5 mL of methylene chloride was added dropwise. Ozone was passed into the solution until the blue color of excess ozone was observed. The ozone stream was disconnected and replaced by a stream of dry argon. Argon purging was carried out well after the time the solution lost its blue color. After the purging, a solution of olefin (1 mmol) and 9,10-dibromoanthracene (50 mg, 0.13 mmol) in 5 mL of methylene chloride was slowly added to this solution. The −78 °C bath was replaced with a −25 °C bath. The solution was kept at −25 °C to −15 °C for 5 h and then warmed to room temperature. The solution was visually observed during this period in total darkness. A few minutes after the solution was warmed to −25 °C, a purple bluish chemiluminescence (CL) was observed. This CL persisted for at least 7 h.

Autoxidation General Procedure. All autoxidation experiments were carried out in 20-cm long graduated test tubes equipped with magnetic micro fleas for gentle stirring. All solvents and reagents used were freshly purified. The test tubes were capped with a rubber septum. Oxygen was gently bubbled into the solution through the rubber septum via a hypodermic needle connected to the end of the polyethylene tubing on the oxygen line. The reaction vessel was vented through a mineral oil bubbler via another short hypodermic needle. Contact of the rubber septa with the organic liquid was avoided at all times. The reaction vessel was protected from light by wrapping it in aluminum foil. In addition, all of these experiments were conducted in a dark fume hood. The solvent level was maintained at a predetermined level by periodic addition of the fresh solvent as needed. The quantitative analysis was performed by periodic sampling of the reaction mixture and immediate GC analysis.

Photosensitized Oxidation. The same general procedure was used as mentioned above, except the reaction vessel was irradiated by a GE DYH lamp (600 W, 120 V) contained in a Pyrex immersion well and was cooled with circulating ice-cold water. The lamp was additionally cooled by a direct flow of air. The reaction vessel was kept in a water bath at 10–25 °C.

All the products mentioned have been isolated by preparative TLC from the reaction mixtures and identified by their spectral data and/or by comparison with the authentic samples. Various experiments involving inhibitors, initiators, other olefins, superoxide anion, etc. were performed in a similar manner.

Isolation of 8, 19, and 21 from Autoxidation of 2. Preparative TLC fractionation after bisulfite reduction gave epoxide 8, alcohol 18, and 20. Compounds 8 and 18[23] were identified by comparison of their spectral data with those of the authentic samples. The band of R_f 0.6 was extracted to give a colorless oil which was identified at the keto aldehyde 20: ^1H NMR δ 9.8 (s, 1 H), 2.6 (m, 3 H), 1.9 (m, 3 H), 1.9–1.1 (m, 7 H); ^{13}C NMR δ 216 (s), 200.4 (s), 51.03 (d), 49.17 (d), 40.90 (d), 37.34 (t), 35.56 (t), 23.93 (t), 19.78 (t), 17.87 (t). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.3; H, 8.43; O, 19.26. Found: C, 72.1; H, 8.3; O, 19.6. Compound 20 was unstable in the presence of air and slowly oxidized to 21. Identity of 21 was established on the basis of its elemental analysis alone. Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.95; H, 7.7; O, 26.3 Found: C, 66.1; H, 7.8; O, 26.1.

Isolation of 11 from Autoxidation of 1 in CCl_4. The autoxidation mixture of 1 in CCl_4 was fractionated by a preparative TLC using ethyl acetate–hexanes (1:1). The band of R_f 0.6 was isolated to get 19% of yellow oil. The compound was characterized as *exo*-2-[(trichloromethyl)oxy]-6-chloro-*endo*-tricyclo[5.2.1.0^{2,6}]decane (11): ^1H NMR δ 2.70 (s, 1 H), 2.5–2.34 (m, 1 H), 2.28–2.09 (m, 4 H), 1.92–1.62 (m, 2 H), 1.55–1.2 (m, 7 H); ^{13}C NMR δ 88.7 (s), 88.24 (s), 52.49 (s), 49.79 (d), 46.6 (d), 39.79 (t), 38.78 (t), 35.77 (t), 24.66 (t), 24.34 (t), 23.57 (t). Anal. Calcd for $C_{11}H_{14}OCl_4$: C, 43.35; H, 4.6. Found: C, 43.5; 4.7.

The compound 11 is unstable and is converted into 12 during the workup. The identity of 12 was established on the basis of its high-resolution mol wt found 168.1148 (calcd 168.1149).

Isolation of 13 from Autoxidation of 1 in Methanol. When the above experiment was run in methanol, the major product isolated by preparative TLC (R_f 0.5) was characterized as 13: ^1H NMR δ 3.3 (s, 3 H), 2.4 (br s, 1 H), 2.2–1.1 (series of m, 14 H); ^{13}C NMR δ 90.9 (s), 86.97 (s), 51.56 (9), 48.84 (d), 41.50 (d), 38.36 (t), 36.2 (t), 31.32 (t), 24.48 (t), 23.50 (2t, superimposed); MS 182 (19), 150 (13), 127 (13), 121 (20), 115 (32), 113 (45), 94 (26), 84 (47), 83 (32), 79 (44), 67 (62), 57 (28), 55 (90), 53 (31), 43 (70), 41 (100), 29 (51), 28 (66), 27 (76). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.53; H, 9.9; O, 17.59. Found: C, 72.4; H, 9.9; O, 17.45.

Autoxidation of 32. Autoxidation of 32 was carried out as mentioned previously. At the end of the 24-h period, all of 32 had reacted and epoxide 33 (60%) and diketone 34 (40%) were isolated as the only products by preparative TLC (EtOAc–hexanes (1:1)). Epoxide 33 was identified by comparison of its spectral data with an authentic sample prepared by MCPBA epoxidation[18] of 32. Diketone 34 was also identified by comparison with an authentic sample prepared as described below.

Preparation of 34. A magnetically stirred solution of 33 (50 mg, 0.24 mmol) in 20% aqueous methanol (3 mL) was mixed with periodic acid (60 mg, 0.24 mmol) and heated to reflux, under argon atmosphere, for 7 h. The resulting mixture was added to water (5 mL) and extracted with methylene chloride. The combined organic layers were washed with 20% sodium bisulfite solution and brine prior to drying and evaporating to obtain 49 mg (90%) of 34 as a semisolid: ^1H NMR δ 7.25 (s, 4 H), 5.75 (s, 2 H), 3.60 (m, 2 H), 3.08 (m, 1 H), 1.75 (m, 3 H), 0.9 (d, 2 H); ^{13}C NMR δ 211.43 (s), 135.96 (s), 128.66 (d), 121.1 (d), 90.67 (d), 51.51 (d), 30.74 (t), 29.05 (t); IR 2950, 1690, 1460, 1260, 1060 cm^{-1}. Anal.

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(23) Bartlett, P. D.; Wu, C. *J. Org. Chem.* **1984**, *49*, 1880.

Calcd for $C_{15}H_{14}O_3$: C, 74.37; H, 5.8; O, 19.83. Found: C, 74.3; H, 5.8; O, 19.75.

Autoxidation of 35. A solution of **35** (1 M in methylene chloride) was stirred at room temperature in darkness. Dry oxygen was slowly bubbled through the solution for 2 days. The reaction progress was followed by capillary GC. At the end of the 48 h period, more than 98% of **35** was reacted. The mixture was separated by preparative TLC (EtOAc–hexanes (1:1)) to obtain two bands. The top band (R_f 0.6) was isolated and the product characterized as epoxide **36** by comparison of the spectral and mp data with those of the authentic material[20] (yield 67%).

The lower band (R_f 0.3) was isolated to obtain colorless crystals of **37** (29%). The structure of **37** was established by its spectral properties and X-ray crystal structure determination.[21]

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Registry No. **1**, 87238-75-3; **2**, 99872-98-7; **3**, 2825-86-7; **4**, 86594-77-6; **5**, 6675-72-5; **6**, 2825-83-4; **7**, 87238-74-2; **8**, 135561-80-7; **9**, 65437-13-0; **10**, 87625-85-2; **11**, 135561-81-8; **12**, 135637-11-5; **13**, 135561-82-9; **18**, 89689-39-4; **19**, 135561-83-0; **20**, 135561-84-1; **21**, 135561-85-2; **22**, 1674-10-8; **23**, 17612-36-1; **24**, 56201-42-4; **25**, 1626-09-1; **26**, 5019-96-5; **27**, 58616-86-7; **28**, 102935-93-3; **29**, 1755-01-7; **32**, 88230-07-3; **33**, 88230-09-5; **34**, 135583-80-1; **35**, 91048-24-7; **36**, 82918-67-0; **37**, 109636-11-5; $Co(SCN)(PPh_3)_3$, 53765-50-7.

Carbodications. 3.[1] The Two Dications Derived from Mesityl Oxide

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The hydronation of mesityl oxide (4) is best followed by measuring the difference between chemical shifts of signals for C(4) and C(3) ($\Delta\delta$), linearly extrapolated at infinite dilution. It was found that half-hydronation occurs near H_0-4. The acidity dependence of C(4) and $\Delta\delta^0$ indicates, however, that the amount of positive charge increases monotonically in stronger acids (100% H_2SO_4, CF_3SO_3H, 4:1 FSO_3H-SbF_5), far beyond the acidity level where hydronation should be complete. The existence of a fast second hydronation of 4 is proposed; the same conclusion comes from a study of acidity dependence of the slope of the $\Delta\delta$ vs concentration of 4 line. The fast second hydronation forms a dication with two hydrons attached to oxygen. The other dication, hydronated at C(3) and at oxygen, is the intermediate in conversions of 4 in superacid. Its rate of formation is estimated from the exchange of C(3)-H in FSO_3D–SbF_5 to an extent of 60% in 20 min at 30 °C. Even though the second hydronation at C(3) is slow, the rate-determining step for the conversion of 4 occurs after it.

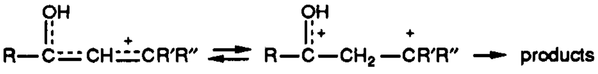
Introduction

Our group has been studying reactions of carbocations in superacids, involving dications as intermediates. Ionization of chloroacyl cations **1** to acylalkyl dications **2** (eq 1) was already reported.[1] For our work on calibration of

$$\underset{\mathbf{1}}{\text{R—CHCl—CHR}'\text{—CH}_2\text{—CO}^+} \rightarrow \underset{\mathbf{2}}{\text{R—}\overset{+}{\text{C}}\text{H—CHR}'\text{—CH}_2\text{—CO}^+} \rightarrow \text{products} \quad (1)$$

strength of superacids[2] it was interesting to find that the reactions of eq 1 are dependent upon acidity.

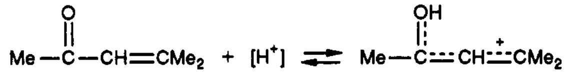
Earlier, Brouwer had discovered the same type of chemistry in the conversions of cations of unsaturated ketones **3** involving dications as intermediates (eq 2). The reaction rates were acidity-dependent and were used to rank superacids by strength.[3,4]



3

(2)

Recently, we also investigated the hydronation of an α,β-unsaturated ketone, mesityl oxide (**4**, eq 3), to the



4 **5**

(3)

monocation **5** (**3**, R = R′ = R″ = Me) as a means of acidity measurement by ^{13}C NMR spectroscopy in the range of 50–100% sulfuric acid. To remove the medium effects (other than hydron transfer) on chemical shifts the parameter correlated with acidity was the difference between chemical shifts of the signals for C(4) and C(3), $\Delta\delta$.[2d] We discovered that $\Delta\delta$ varies linearly with the total concentration of indicator base (**4** + **5**), at least between 0.04 and 1.25 M. Its extrapolation to zero concentration of base (infinite dilution), $\Delta\delta^0$, can be used, therefore, to generate a theoretically justified acidity function, like H_0.[2d] The $\Delta\delta^0$ vs H_0[5] plot was a typical sigmoid curve with the inflection point corresponding to half hydronation around H_0 −4.[2d] On the basis of this value observed for half-hydronation we expected that **4** should be fully converted to **5** around H_0-8. We found, however, that $\Delta\delta^0$ increased further with solvent acidity up to H_0 −12 (100% sulfuric

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