for 1 h and at ambient temperature for an additional hour before it was quenched with saturated aqueous ammonium chloride. The aqueous layer was extracted with ether and worked up in the usual way.

2-(Methylthio)-5-methyl-5-aza-1,3-dithiacyclohexane (1). The general procedure was followed, with 2 equiv of dimethyl disulfide as the electrophile. The product (clear oil, slightly yellow) was purified by flash chromatography[40] [hexane/ethyl acetate (9:1)] followed by distillation at reduced pressure; bp 105 °C/1.5 mmHg; yield 39%. ^1H and ^{13}C NMR spectra are in Tables I and II, respectively (supplementary material).

Anal. Calcd for $C_5H_{11}NS_3$: C, 33.12; H, 6.11; N, 7.72. Found: C, 33.30; H, 6.09; N, 7.73.

2-(Phenylthio)-5-methyl-5-aza-1,3-dithiacyclohexane (2). The general procedure was followed, with 2 equiv of diphenyl disulfide as the electrophile. The product was purified by flash chromatography[40] [hexane/ethyl acetate (70:30)] and recrystallized from methanol/acetone (70:30). The pure product (white crystals with mp 75–77 °C) was obtained in 50% yield. ^1H and ^{13}C NMR spectra are in Tables I and II, respectively (supplementary material).

Anal. Calcd for $C_{10}H_{13}NS_3$: C, 49.34; H, 5.38; N, 5.75. Found: C, 49.28; H, 5.33; N, 5.93.

2-Benzoyl-5-methyl-5-aza-1,3-dithiacyclohexane (3). The general procedure was carried out with 10 equiv of ethyl benzoate as the electrophile. The unreacted ethyl benzoate was removed by distillation (58 °C/1 mmHg), and the desired product was purified by flash chromatography[40] [hexane/ethyl acetate (30:70)] and subsequent recrystallization from hexane/chloroform (9:1) to afford **3** as white crystals, mp 109–111 °C, in 48% yield. ^1H and ^{13}C NMR spectra are in Tables I and II, respectively (supplementary material).

Anal. Calcd for $C_{11}H_{12}NOS_2$: C, 55.20; H, 5.47; N, 5.85. Found: C, 55.44; H, 5.31; N, 5.99.

2-Carboethoxy-5-methyl-5-aza-1,3-dithiacyclohexane (4). The general procedure was carried out with 10 equiv of diethyl carbonate. Excess carbonate was removed by distillation (50 °C/5 mmHg), and the desired product was purified by flash chromatography[40] [hexane/ethyl acetate (80:20)] and distillation in a Kugelrohr apparatus, bp 93 °C/0.2 mmHg, to afford pure **4** as a colorless oil in 30% yield. ^1H and ^{13}C NMR spectra are in Tables I and II, respectively (supplementary material).

Anal. Calcd for $C_7H_{13}NO_2S_2$: C, 40.56; H, 6.32; N, 6.76. Found: C, 40.57; H, 6.32; N, 6.77.

2-Carbophenoxy-5-methyl-5-aza-1,3-dithiacyclohexane (5). The general procedure was followed with 10 equiv of diphenyl carbonate. The product was purified by flash chromatography[40] (pure methylene chloride) followed by crystallization from hot petroleum ether and sublimation at 80 °C/0.1 mmHg. Pure **5** was obtained in 35% yield as white crystals, mp 84–85 °C. ^1H and ^{13}C NMR spectra are in Tables I and II, respectively (supplementary material).

Anal. Calcd for $C_{11}H_{13}NO_2S_2$: C, 51.74; H, 5.13; N, 5.48. Found: C, 51.93; H, 5.15; N, 5.44.

2,5-Dimethyl-5-aza-1,3-dithiacyclohexane (6). The general procedure was followed with 2 equiv of methyl iodide as the electrophile. The product was purified by flash chromatography[40] (pure CH_2Cl_2 eluent) and distillation (bp 70 °C/0.1 mmHg) to afford pure **6** as a colorless oil, in 83% yield. ^1H NMR (400 MHz, CD_2Cl_2) δ 1.43 (d, J = 6.9 Hz, 3 H), 2.53 (s, 3 H), 4.08 (d, J = 12.8 Hz, 2 H), 4.25 (q, J = 6.9 Hz, 1 H) 4.68 (d, J = 12.8 Hz, 2 H).

Anal. Calcd for $C_5H_{11}NS_2$: C, 40.23; H, 7.43; N, 9.38. Found: C, 40.51; H, 7.56; N, 9.46.

Acknowledgment. We are indebted to Dr. A. Flores-Parra for a generous gift of 5-methyl-5-aza-1,3-dithiacyclohexane, and for her advice on its preparation. We thank Prof. R. S. Glass for the PE spectrum and G. Uribe for recording the Jeol ^1H and ^{13}C NMR spectra. We are also grateful to the Natural Sciences and Engineering Research Council of Canada for financial support in the form of an operating grant (to B.M.P.) and an International Collaborative Research Grant (to E.J. and B.M.P.) and to the Consejo Nacional de Ciencia y Tecnología de México for a scholarship to E.A.G.

Supplementary Material Available: Tables I and II listing the ambient and low-temperature ^1H and ^{13}C NMR signal assignments in **1–5** and Tables V and VI listing the equilibrium data for the conformational equilibria of **2–5** (8 pages). Ordering information is given on any current masthead page.

Oxidations by Methyl(trifluoromethyl)dioxirane. 2.[1] Oxyfunctionalization of Saturated Hydrocarbons[†]

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Abstract: The reaction of methyl(trifluoromethyl)dioxirane (**1b**), a novel dioxirane species, with two open-chain, four cyclic, and five polycyclic saturated hydrocarbons and two aralkyl hydrocarbons in CH_2Cl_2/1,1,1-trifluoropropanone has been studied; under mild conditions (−22 to 0 °C), it gives alcohols and/or ketones (deriving from further oxidation of secondary alcohols) in high yields and within very short reaction times. Primary C–H bonds are not appreciably oxidized and high regioselectivities were determined for attack at tertiary over secondary C–H bonds, with the exception of norbornane, which showed opposite regioselectivity. The reaction is also highly stereoselective, since hydroxylations of *cis*- and *trans*-decalin and of *cis*- and *trans*-1,2-dimethylcyclohexane were found to be in each case stereospecific with retention. From kinetic data, E_a = 14.3 kcal mol^{-1} and log A = 9.9 were estimated for cyclohexane oxidation. Relative rates change in the order cyclohexane (0.78) < norbornane (1) < bicyclo[2.2.2]octane (9.2) < adamantane (146); *cis*-1,2-dimethylcyclohexane was observed to be 7-fold more reactive than its trans isomer, demonstrating remarkable discrimination for equatorial vs axial C–H attack (also noticed in the case of *cis*- and *trans*-decalin). The relative rate of oxidation of cumene vs ethylbenzene was found to be ca. 3.1 (after statistical correction), i.e., in sharp excess over values usually recorded in classical radical H-atom abstraction from benzylic position. Rate constants determined for the reactions of cumene and of ethylbenzene show the title dioxirane (**1b**) is more reactive than dimethyldioxirane (**1a**) by factors of ca. 600 and over 700, respectively. The whole of the observations is better accommodated by an "oxenoid" mechanism, involving concerted O-atom insertion by dioxirane into C–H bonds of hydrocarbons.

During the past 15 years, the achievement of selective conversions of alkanes into oxygenated compounds has continued to pose a challenge to the community of chemists.[2-4] Along with the older methods,[5] some more recent studies have regarded alkane oxidations by peroxy acids,[4-6] peroxides,[7] hydroxy radicals,[8] *N*-oxides,[9] ozone,[10,11] hydrogen peroxide, and ozone in superacids.[12] Homogeneous catalysis by transition-metal ions[31] has been em-

[†] Dedicated to the memory of Professor Angelo Mangini (University of Bologna, Italy), deceased in August 1988.

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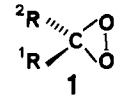
ployed to attain alkane oxidations by dioxygen,[13] as, e.g., in the Gif and Gif–Orsay systems.[14]

In most of the above alkane functionalizations, the energetic and mechanistic characteristics differ significantly from those of free-radical chain autoxidations that are more common with industrial processes;[3l,15] with all methods, the major problem seems to be not in the low reactivity of the alkane molecules themselves but rather in the difficulty of achieving selective oxidations. Indeed, oxidations of nonactivated alkane C–H bonds that are highly selective pertain to a few biological systems[2,3,16] that are hard to imitate. In nature, the biochemical activation of alkanes is accomplished by metal-containing monooxygenases, as exemplified by the cytochrome P-450 group of enzymes.[3a,b,17] Thus, studies on alkane oxygenation by metalloporphyrin and related complexes have now grown to constitute a major area of research.[18]

In recent times, a class of reactive organic peroxides became available that are powerful oxidants and appear to have great potential for synthetic purposes. This is the family of dioxiranes **1**, the smallest ring peroxide species containing carbon.[19]



1

a: $^1R = {}^2R = CH_3$; **b**: $^1R = CH_3$, $^2R = CF_3$

Starting in 1979, we have been reporting on kinetic, ^{18}O-labeling, reactivity, and stereochemical data that stringently indicate that dioxiranes are generated in the reaction of potassium peroxomonosulfate (caroate) with ketones.[20] In 1985, Murray and Jeyaraman showed that dimethyldioxirane (**1a**) and a few other low molecular weight dialkyldioxiranes can actually be isolated from buffered (pH 7) aqueous solutions containing caroate and the parent ketone by low-temperature distillation.[21] The dioxiranes are obtained as dilute solutions in the parent ketone.[21,22] Thus, authentic members of the elusive[19] dioxirane family became available in condensed phase for full spectroscopic characterization,[19,21-24] including ^{17}O NMR.[23,24]

At the same time, the feat[21] of isolating volatile dialkyldioxiranes from the ketone/caroate system precipitated an intensive research that led to confirmation of the reactivity of these species when generated in situ.[19,20,25,26] Indeed, by use of solutions of isolated dimethyldioxirane (**1a**), a number of very efficient and selective oxygen-atom transfers could be recorded to occur under quite mild conditions to a variety of substrates,[19] including olefins,[21,27,28] alkynes and ketenes,[20,29] allenes,[30] isocyanates,[31] and enol ethers.[1]

Murray and co-workers have also reported on the remarkable insertion of oxygen atoms into C–H bonds of saturated hydrocarbons by isolated dimethyldioxirane (**1a**).[32] Even simple alkanes and cycloalkanes could be oxidized to give directly alcohols, or ketones deriving from further oxidation of the alcohols, at ambient temperature.[32] Although it was noticed that these reactions require reaction times measured in hours (instead than in minutes as in the case of more reactive substrates),[19,21,22,27] this conversion

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conveniently demonstrated the remarkable efficiency of dioxiranes as oxidants. Indeed such transformations are rare for organic peroxides without the help of transition-metal catalysts.[3i] Murray et al. have also called attention to the high selectivity of hydrocarbon oxidation by isolated dimethyldioxirane, to the high retention of configuration of O-atom insertion, and—for mechanistic considerations—to the relatively large kinetic isotope effect, i.e., $(k_H/k_D) \sim 5$ measured for cyclododecane oxidation.[32]

We have recently reported on the isolation and full spectroscopic characterization of methyl(trifluoromethyl)dioxirane (**1b**) in solution.[24] During the preliminary screening tests, we noticed this new dioxirane presents a reactivity by far in excess of that already remarkably recorded for dimethyldioxirane (**1a**).[24] We believe the results presented herein suggest that this new powerful reagent is eminently suited for selective oxidation of alkanes in the condensed phase.

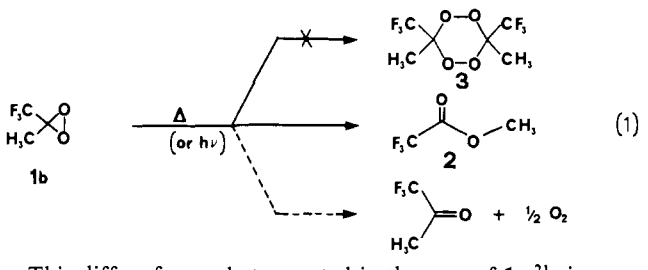
Results and Discussion

Methyl(trifluoromethyl)dioxirane. Solutions of this new dioxirane could be obtained by following closely the procedure described for dimethyldioxirane[20] starting with buffered (pH 7, $NaHCO_3$) aqueous potassium peroxomonosulfate ($KHSO_5$) and 1,1,1-trifluoro-2-propanone (CF_3COCH_3, hereafter TFP). Actually, the commercial product triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ was used as a source of potassium peroxomonosulfate.[33] Some of the dioxirane intermediate, which builds up in a stationary concentration[19a,20] during the early stages of the reaction, could be removed by distillation at modestly subambient temperatures (5–8 °C) in a gentle stream of inert gas (He or Ar). The dioxirane, along with other volatiles entrained, is collected by subsequent condensation at −60 to −75 °C. The simple apparatus to be employed for small[21,22] or larger scale[31] preparations of dioxirane solutions has been described in detail;[19b] it should be emphasized that apparatus, procedure, and precautions[19b,21,22,31] are just a trifle more complex than those routinely adopted to isolate other reactive species (e.g., diazomethane)[34] in the organic laboratories.

Thus, by following a general protocol, we were able to obtain yellow[19] solutions of the title dioxirane **1b** (Mello dioxirane)[24] in TFP. These can be collected within a few (5–10) minutes and have dioxirane concentrations ranging from 0.6 to 0.8 M **1b** (hence, over 6 times higher than the concentration of **1a** routinely attainable by the same procedure). Then, this new dioxirane was fully characterized spectroscopically.[24]

Solutions of **1b** can be stored at −20 °C with only minor loss (~6–8%, 48 h) of dioxirane content. Thus, the stability of **1b** appears to be comparable to that of **1a**.[24] However, impurities or trace metals can bring about the rapid deterioration of dioxirane content.

Also, solutions of **1b** have to be kept well protected from light, since we find that brief exposure to UV or even to 586-nm radiation causes the rapid (and exothermic) decomposition of the dioxirane. In all cases, we find the loss of dioxirane yields mainly methyl trifluoroacetate (**2**) and trifluoroacetic acid, the hydrolysis product of the latter (eq 1).[24]



(1)

This differs from what reported in the case of **1a**,[21] since no 1,2,4,5-tetraoxane (**3**, ketone diperoxide) could be detected to arise from loss of dioxirane **1b**.[24] Thus, in the absence of reaction partners, the observed rearrangement of **1b** into **2** agrees with the path of decay recorded for dioxirane species when generated in the gas phase[35] or at low temperatures in argon matrices.[36] For this transformation, evidence so far available suggests that a radical chain process does not apply.[35,36] Since production of oxygen gas is the major reaction course in the generation of dioxiranes in situ by the ketone–caroate systems,[19a,20] a pathway also open to dioxirane decomposition would appear to be release of dioxygen, presumably singlet (eq 1). However, our preliminary mass spectrometric analyses have shown that only small amounts (if any) of dioxygen are produced during the decay of **1b** in solution.[37]

To probe into the mechanism of dioxirane autodecomposition is in itself an interesting target.[19] However, with dioxirane **1b** this is of no practical concern, since it turns out that its decomposition is much slower than oxygen transfer to most substrates,[24] including representative alkanes. This is illustrated below.

Products. Methyl(trifluoromethyl)dioxirane (**1b**) was found to react with a variety of hydrocarbons in CH_2Cl_2/TFP ca. 9:1,[38] at temperatures ranging from −25 to +5 °C, giving excellent yields of functionalized products.

The procedure plainly involves mixing of standard solutions of the hydrocarbon and of the dioxirane; product isolation is attractively simple since CH_2Cl_2 and TFP (bp 22 °C), both the solvent and the reduction product of **1b**, are quite volatile and easily removed. Also, at variance with the dimethyldioxirane (**1a**) case,[31] in most instances reaction times are of the order of minutes, rather than hours. Typical yields and product distributions observed for representative alkanes and cycloalkanes, as well as for two aralkyl hydrocarbons, are shown in Chart I. Pertinent examples of product distributions, reaction times, and percent conversion at different hydrocarbon to dioxirane ratios are collected in Table I.

The expected[32] high selectivity of O-atom insertion at the tertiary over secondary and at secondary over primary "unactivated" C–H bonds of alkanes is illustrated by the second and third entries in Chart I. In fact, 2,3-dimethylbutane quickly yields tertiary alcohol **7** exclusively; with dioxirane in excess over stoichiometric ratio, sizeable amounts of pinacol but no ketones[39] or rearrangement products are observed (Table I). The ketones **5**, **5′**, and **5″** are generated, in almost statistical distribution, from *n*-heptane (**4**); no heptanal (or heptanoic acid) could be detected. Most likely the ketones derive from further oxidation of the alcohols initially formed. The same holds for cyclohexanone (**9**), the sole product of oxidation of cyclohexane (**8**) even at **8**/dioxirane initial concentration ratios close to unity. Indeed, we could verify that cyclohexanol is very rapidly converted into **9** under identical conditions (e.g., 87% conversion during 8 min, with cyclohexanol/**1b** ca. 1:1, at −22 °C). In these, as well as in all of the other reactions shown in Chart I, no appreciable amount of chlorinated products[11,40] (e.g., isomeric chloroheptanes, cy-

(33) This product is available in Europe as Curox (Interox Peroxid-Chemie GmbH) and in the U.S.A. as Oxone (Du Pont).

(34) (a) Hudickly, M. *J. Org. Chem.* **1980**, *45*, 5277. (b) Hopps, H. B. *Aldrichimica Acta* **1970**, *3*, 9, and references therein.

(35) (a) Suenram, R. D.; Lovas, F. J. *J. Am. Chem. Soc.* **1978**, *100*, 5117. (b) Gillies, J. Z.; Gillies, C. W.; Suenram, R. D.; Lovas, F. J. *J. Am. Chem. Soc.* **1988**, *110*, 7991, and references therein.

(36) (a) Sander, W. W. *J. Org. Chem.* **1988**, *53*, 121. (b) Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517, and references therein.

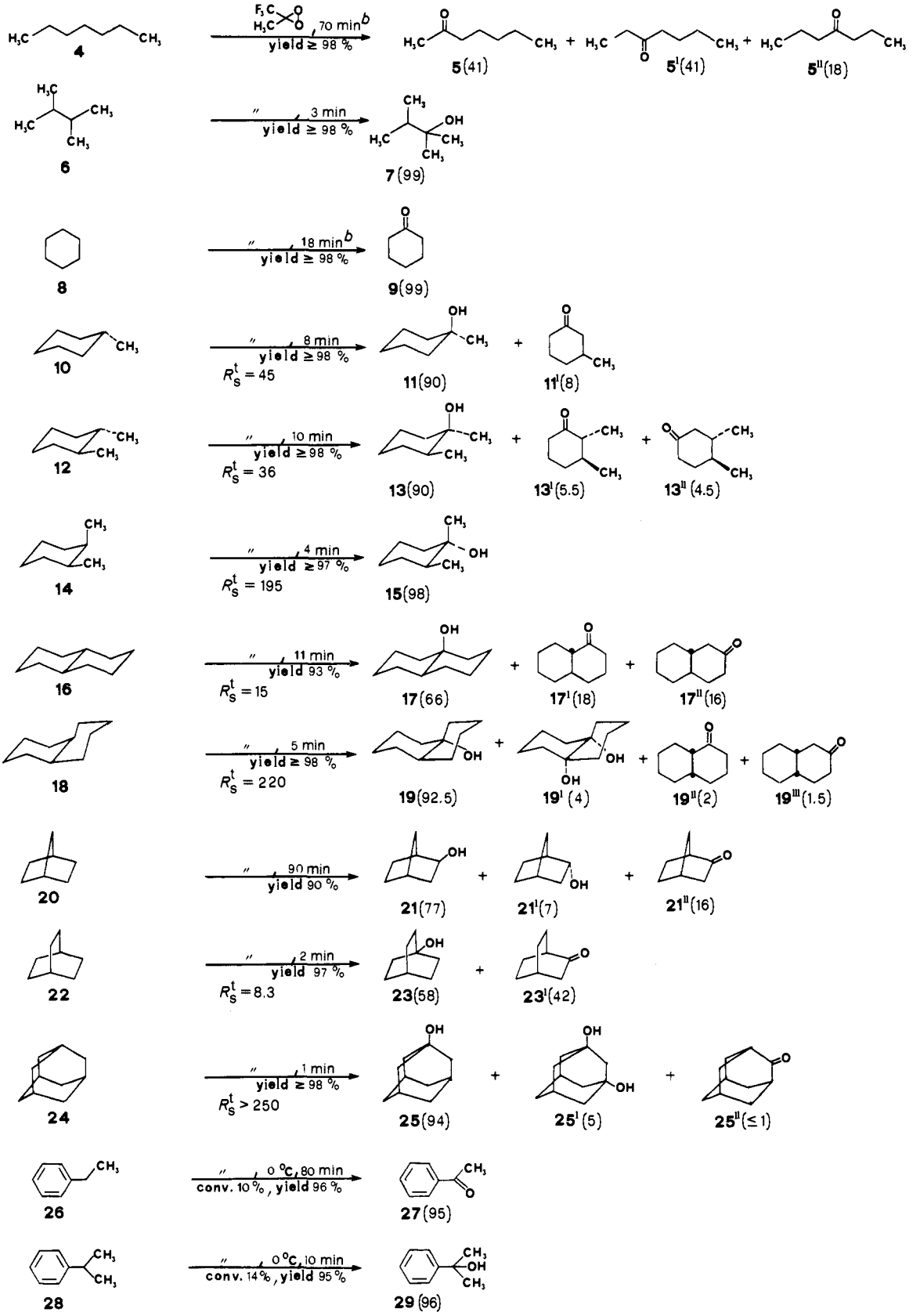
(37) We routinely adopt an apparatus and procedure that have been described into details [see, e.g.: Koubek, E.; Haggett, M. L.; Battaglia, C. J.; Ibne-Rasa, K. M.; Pyun, H.-Y.; Edwards, J. O. *J. Am. Chem. Soc.* **1963**, *85*, 2263. Ball, R. E. Ph.D. Thesis, Brown University, Providence, RI, 1967] to collect and analyze by MS samples of gas evolved during decomposition of peroxide species. During loss of **1b** in solution at 0 °C the oxygen gas detected was in only slight excess over that measured in a blank run. The major component of the gas was CO_2; this was also detected in solution of **1b** prior to decomposition by ^{13}C NMR: δ 125.6 (s), at −20 °C. Most likely this is produced from the reaction of caroate and/or $KHSO_4$ with the bicarbonate buffer during dioxirane synthesis; the CO_2 evolved is then entrained into the stream of the dioxirane and the ketone vapors to be condensed. Labeling experiments are now being performed to confirm that CO_2 comes uniquely from bicarbonate.

(38) Different proportions of CH_2Cl_2 and TFP solvents can also be used, and CH_2Cl_2 substituted with 1,2-dichloroethane with similar results.

(39) Tal, D.; Keinan, E.; Mazur, Y. *J. Am. Chem. Soc.* **1979**, *101*, 502.

(40) (a) Smegal, J. A.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3515, and references therein. (b) Brown, R. B., Jr.; Hill, C. L. *J. Org. Chem.* **1988**, *53*, 5762.

Chart I[a]



[a] In CH_2Cl_2/TFA (from 9:1 to 7:3) mixed solvent, at −22 °C; yields and product distributions (parenthetic values) determined with hydrocarbon to dioxirane ratios of initial concentration (ca. 0.1 M) close to unity (unless noted otherwise), at hydrocarbon conversion ≥50%. [b] Ratio of hydrocarbon to dioxirane initial concentration ca. 0.5.

clohexyl chloride, etc.) were detected.

With the *notable exception of norbornane* (**20**) the fourth to the eighth entries in Chart I indicate remarkable selectivity for oxygenation at tertiary over secondary C–H bonds by Mello dioxirane **1b**, *despite its high reactivity*. In fact, from the relative distribution of tertiary vs secondary alcohols (and or ketones) one can estimate, after statistical correction, the selectivity ratios[4] R_s^t which are shown in Chart I. It is seen that, akin to hydroxylation

Table I. Typical Product Analyses for the Reaction of Methyl(trifluoromethyl)dioxirane (**1b**) with Representative Saturated Hydrocarbons at −22 °C

substrate	ratio RH/**1b**	time, min	conv,[b] %	yield,[b,c] %	prod dist,[b,d] % ROH	R=O	R(OH)$_2$
2,3-dimethylbutane (**6**)	1	3	50	≥98	99		<1
	0.50	2	65[e]	≥98	99		≤1
	0.50	20	>98	≥98	90		10[f]
methylcyclohexane (**10**)	0.83	5	45	≥98	≥98		
	0.83	90	94	≥95	87	8[g]	
norbornane (**20**)	0.90	1	3	≥98	86 (exo), ≤1 (endo)	13	
	0.90	90	50	90	77 (exo), 7 (endo)	16	
	0.5	1	11	93	52 (exo), 9 (endo)	39	
	0.5	100	95	95	48 (exo), ≤1 (endo)	51	
bicyclo[2.2.2]octane (**22**)	0.9	2	50	97	54	46	
	0.48	1	50	≥98	52	48	
	0.48	60	≥98	97	49	51	
adamantane (**24**)	0.90	1	98	≥98	94	≤1	5
	0.88[h]	1	88	≥98	93	≤1	6
	0.50	1	≥98	≥98	38	3	59
	0.50	45	≥98	94	5	3	92

[a] In CH_2Cl_2/TFP (unless noted otherwise); dioxirane initial concentration ranged from 0.1 to 0.2 M. [b] As determined by GLC: percentages (±2%) were based on peak areas corrected for relative response; products were identified by GC/MS and/or isolation from reaction mixtures (column chromatography, silica gel). [c] Based on the amount of substrate reacted. [d] Abbreviations used: ROH, alcohol; R=O, ketone; R(OH)$_2$, diol; refer to Chart I for product structures. [e] 1,2-Dichloroethane cosolvent. [f] 2,3-Dimethylbutane-2,3-diol. [g] 2-Methylcyclohexanone and trace amounts of 3-methylcyclohexanone. [h] Reaction run under an argon gas blanket.

by moderately reactive peroxy acids[4] and to "dry" ozonization methods,[41] the regioselectivity is virtually total with adamantane. The same holds for *Z*-1,2-dimethylcyclohexane (**14**). For bicyclo[2.2.2]octane (BCO, **22**) we find $R_s^t = 8.3$; this is about the same ratio reported by Hamilton[10c] for oxidation of tertiary over secondary C–H bonds in (normal) ozonization of alkanes. Except for norbornane (**20**), for the remaining substrates regioselectivities are markedly larger (Chart I), the R_s^t values being of the same order of magnitude as those recorded in oxidation by peracids.[4]

The fifth through eighth entries in Chart I bear witness to the high stereoselectivity characterizing the reaction at hand. Indeed, for stereomeric 1,2-dimethylcyclohexanes and *cis*- and *trans*-decalin the reaction is completely stereospecific with retention. This is akin to what observed in oxidations by dimethyldioxirane (**1a**)[32] and by ozone.[10c,41]

Also similar to the ozonization[11a] is the finding that with norbornane (**20**) only products derived from reaction at C-2 are found (Chart I); no chloronorbornanes are formed however. Both at low and high conversion, *exo*-norborneol (**21**) is the major product (Table I).[11a] Nevertheless, it is unlikely that the exo/endo ratios of norborneols determined under different conditions (Table I) reflect accurately the initial ratios, because of further oxidation. Indeed, control experiments under identical conditions have revealed that *endo*-norborneol (**21′**) is converted by dioxirane **1b** into norcamphor (**21″**) over 40 times faster than its exo stereomer **21**.

Aralkyl hydrocarbons ethylbenzene (**26**) and cumene (**28**) gave the expected oxidation products, i.e., acetophenone (**27**) and 1-methyl-1-phenylethanol (**29**), respectively, in high yield; however, with substrate to dioxirane ratios 1:1, an increase of temperature from −22 to 0 °C was necessary to attain sizeable conversion within short times (cf. the last two entries in Chart I). In fact, the conversion of ethylbenzene was only 4% during 60 min at −22 °C. The oxidation of toluene by the title dioxirane at 0 °C is much slower than that of ethylbenzene; it does not afford appreciable amounts of products derived from oxidation at the methyl group, but rather attack at the phenyl ring seems to take place.[42] The reaction of toluene with dimethyldioxirane (**1a**) at 20 °C has been shown to result in oxidation at the methyl moiety;[32] however, Murray gives yields for benzaldehyde and benzoic acid produced that are quite low, i.e., 3.3 and 1.8%, respectively.[19b]

A few of the reactions shown in Chart I were monitored directly into a sample tube by ^1H and/or ^{13}C NMR to check whether any intermediate (e.g., hemiacetals $(CF_3)CH_3C(OH)OR$) builds up that is the precursor of the alcohol product. No evidence of this could be found. As an example, when the reaction of methylcyclohexane (**10**) with dioxirane **1b** was monitored at −30 °C, in the ^1H NMR spectra the methyl group resonance of **10** at δ 0.85 (a doublet, $J = 6.46$ Hz) was seen to disappear gradually, while the CH_3 resonance of the alcohol **11** (a singlet at δ 1.18)[43] grew in intensity; at the same time the methyl resonance of **1b** (a characteristic quartet centered at δ 1.92)[24] faded away, changing into the intense CH_3 signal of TFP (δ 2.39). At no time were signals seen that could be attributed to other products.

Rates. Rate data were gathered to gain insight into the mechanism of the insertion reaction at hand. In the majority of kinetic experiments the rate of disappearance of the hydrocarbon was monitored by GLC under pseudo-first-order conditions, i.e., with dioxirane initial concentration in large excess over the substrate. Competition experiments were also run in which a couple of hydrocarbon substrates, each of known initial concentration, were allowed to react with excess dioxirane; GLC analyses of aliquots over the first 15–30% reaction led to relative rate values (see Experimental Section). Rate data are summarized in Table II.

A kinetic isotope effect of $k_H/k_D = 2.2 \pm 0.2$ is measured at −23.9 °C, and data in Table II allow one to estimate $k_H/k_D \sim 1.9$ at 25.0 °C. Of course, since it was determined by using perdeuteriocyclohexane, the measured value is the algebraic sum of primary and (possibly weak) secondary effects. Nevertheless, this points out C–H bond breaking should occur in the slow step. Noteworthily, the isotope effect measured is less than half than that measured by Murray et al. in the dimethyldioxirane (**1a**) case by using cyclododecane-d_{12} [i.e., $k_H/k_D = 4.97$].[32] Instead, it is more similar to the value of $k_H/k_D = 2.2$ estimated for the hydroxylation of methylcyclohexane and perdeuteriomethylcyclohexane by *p*-nitroperoxybenzoic acid.[4] An "oxenoid"[2] mechanism involving a cyclic (Bartlett's "butterfly") transition state has been proposed for attack at alkane C–H bonds by peracids.[4]

The activation energy value estimated for cyclohexane oxidation by **1b** (Table II) is near to that measured by Pryor and co-workers ($E_a = 14.6$ kcal mol^{-1}) for the reaction of the same substrate with ozone;[11] however, the log *A* value is sensibly higher, i.e., 8.8 vs 7.7 per hydrogen atom.[11] Thus, the increased reactivity of dioxirane with respect to ozone toward cyclohexane might be largely attributed to an overall activation entropy value ($\Delta S^{\ddagger} \sim -15$ cal

(41) Cohen, Z.; Keinan, E.; Mazur, Y.; Varkony, T. H. *J. Org. Chem.* **1975**, *40*, 2141, and references therein.
(42) A detailed study on this interesting reaction is now in progress.
(43) In these experiments chemical shift were measured from CH_2Cl_2 internal standard and referred to Me_4Si, taking CH_2Cl_2 δ 5.30, at −20 °C.
(44) Bartlett, P. D. *Rec. Chem. Prog.* **1950**, *11*, 47.

Table II. Rates of Reaction of Methyl(trifluoromethyl)dioxirane (**1b**) with Saturated Hydrocarbons[a]

substrate	T, °C	10^2k_2,[b] M^{-1} s^{-1}	rel rates (k_r)	k_H/k_D	E_a, kcal mol^{-1}	log A
cyclohexane-h_{12} (**8**)	−23.9	0.215			14.3 ± 0.15[c]	9.9 ± 0.1[c] (8.8)[d]
	−22.0	0.270[e]	0.77 (0.70)[f]			
	−13.9	0.695				
	−8.2	1.230				
	−3.9	1.830[g]				
cyclohexane-d_{12}	−23.9	0.095		2.26 (2.16)[f]	15.2 ± 0.15[c]	10.3 ± 0.1
	−13.9	0.330		2.11		
	−8.2	0.596		2.07		
	−3.9	0.940		1.98 (2.06)[f]		
norbornane (**20**)	−22.0	0.350	1.0 (1.0)[f]			
bicyclo[2.2.2]octane (**22**)	−22.0	3.230	9.2 (8.6)[f]			
adamantane (**24**)	−22.0	51.2[h]	146.0			
ethylbenzene (**26**)	0.0	2.46[i] [0.0030][j]				
cumene (**28**)	0.0	3.84 [0.0064][j]				

[a] In CH_2Cl_2/TFP (see Experimental Section). [b] Unless noted otherwise, second-order rate constant values were calculated as (k_1/[dioxirane]$_0$); k_1 values (s^{-1}) were obtained from pseudo-first-order rate integrated plots with [substrate]$_0$ = 0.02–0.03 M; rate constant values obtained from two or more independent runs and agreeing within ±10% were averaged. [c] From Arrhenius plots, standard error shown. [d] log A per H (cf. ref 11a) given in parentheses. [e] Value interpolated on a log k_2 vs [$(1/T)$, K^{-1}] plot. [f] Relative rate values in parentheses were obtained directly from competition experiments (see Experimental Section). [g] Under argon gas. [h] Runs under second-order rate conditions; from log $[(a - x)/(b - x)]$ vs time plots. Estimated error is ±10%. [i] As estimated over the first 30–40% reaction. [j] Values in brackets refer to oxidation of the given substrate by dimethyldioxirane (**1a**) in CH_2Cl_2/acetone.

mol^{-1} K^{-1}, at 25.0 °C) that is some 5–5.5 cal mol^{-1} K^{-1} *less negative* than in ozonization.

On a track parallel to that followed to probe into the mechanism of ozonization of alkanes,[10,11] we then measured the rates of oxygenation of bicycloalkanes **20** and **22**, as well as that of adamantane (**24**), with the title dioxirane (Table II). Similar to ozonization,[11] norbornane was found to react with **1b**, yielding products deriving only from attack at the C-2 carbon (Chart I); however, its rate is just 1.3 higher than that of cyclohexane (Table II). If a hydride abstraction mechanism were operative, given the stability of the 2-norbornyl cation,[45] one would expect norbornane to be more reactive than either cyclohexane and BCO (**22**); BCO, in turn, should be less reactive than adamantane by a factor on the order of 10^3, based on bromides or tosylate solvolyses.[46]

Instead, inspection of data in Table II reveals that the order of relative rates is norbornane < BCO < adamantane; the trend is the same found by Pryor et al. for ozonization, i.e., **20** < **22** < **24** (with relative rates ca. 1:1.25:2.5),[11] but the magnitudes are different. For instance, the rate of oxygenation of adamantane by dioxirane **1b** is 16 times that of BCO. This difference in reactivity is more than twice that observed for the reaction of the same couple of substrate by peracid;[4] in fact, it is close to that estimated[47] for generation of 1-adamantyl vs 1-bicyclo[2.2.2]octyl radicals from *tert*-butyl perester decomposition.[48]

On the other hand, data in Table II allow one to estimate a relative reactivity *per H* of ca. 3.1:1 for cumene (**28**) over ethylbenzene (**26**). This indicates the O-atom insertion by dioxirane **1b** is more selective than H-atom abstraction in typical radical process (e.g., relative rate *per H* ca. 2:1 for **28** vs **26** with *t*-BuO•).[49] After statistical correction, the relative reactivity of cumene with respect to ethylbenzene is 3.9:1 in the reaction with dimethyldioxirane (**1a**).[32]

Furthermore, other data mirror more closely concerted insertion reactivities rather than free-radical processes. Indeed, in competition experiments we have determined that relative rate of *cis*- to *trans*-1,2-dimethylcyclohexane (**14**/**12**) is ca. 7:1 in the reaction with **1b**. This is identical with what found by Hamilton et al. for ozonization of the same couple of stereomers.[50] That alicyclic hydrocarbons carrying equatorial tertiary C–H bonds consistently react more readily than stereoisomers presenting axial C–H bonds can be also qualitatively appreciated by comparing reaction times for near total conversion of *trans*- and *cis*-decalin (**16** and **18**, respectively) reported in Chart I. This trend parallels that reported for O-atom insertions by dimethyldioxirane (**1a**) and by moderately reactive peracids.[4] However, dioxirane **1b** appears to be by far more reactive than both these reagents; for instance, the rate of reaction of **1b** with cumene is higher than that measured for **1a** (Table II) by a factor close to 6×10^2!

Reaction Mechanism. Along with information derived from product distributions, the dependency of rates from substrate structure provides useful hints as to the likely mechanisms of oxyfunctionalization of alkanes RH. These are (a) hydride abstraction by the dioxirane, producing carbenium ions R^+, (b) generation of radicals R•, by H-atom abstraction, and (c) a concerted O-atom insertion into the alkane R–H bond.

The main argument for carbocation vs radical character in the transition state (ts) would be the high tertiary to secondary to primary selectivities noted for attack at C–H, with the notable exception of norbornane (Chart I). However, the fact that norbornane is found to react only slightly faster than cyclohexane and the trend of relative rates recorded for polycyclic aliphatic hydrocarbons (i.e., **20** < **22** < **24**), militate against the intermediacy of carbocations and might suggest formation of R• (see previous paragraph). Also, in a radical process adamantane (**24**) should react primarily at C-1 (bridgehead), as observed; instead, the C-1 and C-2 position in **24** should have similar reactivity in a cationic pathway.[11] Furthermore, the relatively high log A value recorded in cyclohexane oxidation, i.e., 8.8 cal mol^{-1} K^{-1} *per H* (Table II), argues in favor of a marked radical character in the ts.[11,51]

Nonetheless, several facts stand against a classical H-atom abstraction. First, the kinetic isotope effect measured, i.e., $k_H/k_D \cong 2$ (Table II), is rather modest given that the ts clearly contains the alkane. Indeed, primary kinetic isotope effects observed in rate-determining radical abstraction from sp^3-hybridized C–H bonds are usually severalfold higher than the value above[52] and can be over 10.[18a] Second, as noted in the previous paragraph, the discrimination observed for attack at the benzyl position of aralkyl hydrocarbons seems in sharp excess to that of typical radical processes. Actually, the reaction of **1b** with toluene is sluggish and does not yield significant amounts of products deriving

(45) (a) Brown, H. C. *Acc. Chem. Res.* **1983**, *16*, 432. (b) Olah, G. A.; Surya Prakash, G. K.; Saunders, M. *Ibid.* **1983**, *16*, 440. (c) Walling, C. *Ibid.* **1983**, *16*, 448, and references therein.

(46) (a) Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426. (b) Gleicher, G. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 582.

(47) Breslow, D. S.; Edwards, E. I.; Leone, R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1968**, *90*, 7097.

(48) (a) Bartlett, P. D.; McBride, J. M. *J. Am. Chem. Soc.* **1965**, *87*, 1727. (b) Humphrey, L. B.; Hodgson, B.; Pincock, R. E. *Can. J. Chem.* **1968**, *46*, 3099.

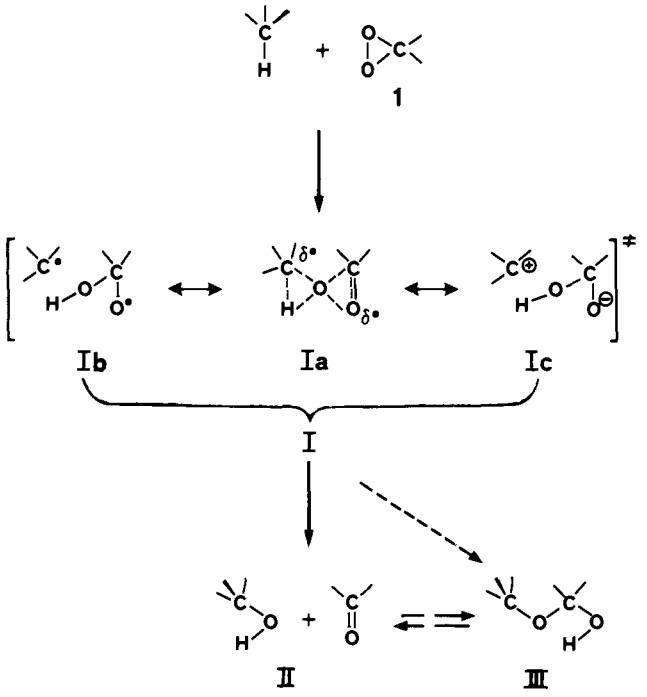
(49) Walling, C.; Thaller, W. *J. Am. Chem. Soc.* **1961**, *83*, 3877.

(50) Hamilton, G. A.; Ribmer, B. S.; Hellman, T. M. *Adv. Chem. Ser.* **1968**, *No. 77*, 15.

(51) Hendry, D. G.; Mill, T.; Piszkiewicz, L.; Howard, J. A.; Eigenmann, H. K. *J. Phys. Chem. Ref. Data* **1974**, *3*, 937.

(52) Russel, G. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, Chapter 7.

Scheme I



from oxidation of the CH_3 moiety. Third, in all of the oxygenations shown in Chart I, we could not detect appreciable formation alkyl chlorides side products. Instead, the latter would be seen if freely diffusing alkyl radicals were involved that can be intercepted by CH_2Cl_2 (a chlorinated solvent), as found in other recent alkane oxygenation systems.[3,7b,40] Even in alkane ozonizations, when carried out in CCl_4 solvent, chlorinated products may account for up to 40% of the products.[11] Also at odds with a mechanism involving radicals R• is the mentioned high stereospecificity that attains in hydroxylations of stereomeric 1,2-dimethylcyclohexanes (**12** and **14**) and stereomeric decalins (**16** and **18**); in no case was appreciable epimerization found to occur (Chart I).

Therefore, as noted by Murray et al. for **1a**,[32] it seems the characteristics of hydrocarbon oxygenation by dioxirane **1b** are mirrored more closely by ozone[11] (as well as nitrene and carbene)[47] insertion into alkane C–H bonds. In Scheme I a mechanism is sketched that bears resemblance to that advanced by Hamilton for ozonizations.[2,10c,11]

This is in its essence an "oxenoid" mechanism.[2] Isomerization of dioxirane **1** into "carbonyl oxide" $R_2C^+–O–O^-$ or $R_2C^•–O–O^•$ (isoelectronic with O_3) previous to the ts was excluded, since theoretical calculations[53] and experimental evidence[35,36] stringently indicate that this event is much unfavored energetically.[19] Also uphill by at least 10–15 kcal mol^{-1} should be the preliminary dioxirane ring opening to yield bis(oxymethylene) diradicals $^•O–CR_2–O^•$.[53c] Of course, alkane activation via electron transfer[19c] yielding $[RH^{•+}/R_2CO_2^{•-}]$ couples cannot be safely invoked (or ruled out) until reliable data concerning electron affinities of dioxiranes become available. Also, it should be noted that caged radical cations $RH^{•+}$ might yield R• upon deprotonation,[54] and in our system there is no indication of freely diffusing alkyl radicals. Furthermore, the observed kinetic isotope effect would then become hard to rationalize.

Clearly, to invoke a more or less concerted insertion process involving a "butterfly" ts such as Ia (Scheme I) is more conservative. In a parallel to ozonization,[11] the possibility of hemiacetal formation (analogous to hydrotrioxide ≡COOOH) is envisaged; however it would be required that hemiacetal (III) breakdown into alcohol and ketone be faster than its production, since no hemiacetals could be detected (see above). Then, it is more reasonable to assume that the alcohol originates from I directly. It should be mentioned that, on going to the ts I, the dioxirane OCO angle (~70°)[53] should widen significantly, approaching that of bis(oxymethylene) $^•O–CR_2–O^•$ (i.e., ~109°). This might serve to alleviate the entropy requirements of the (loose) "butterfly" ts I.

As in the mechanism invoked for the ozonization,[11] Ib and Ic need not be resonance forms but might be viewed as extremes in a spectrum of transition states of concerted insertion. It is unlikely, however, that they can be taken to represent actual caged pair intermediates. Indeed, if this were the case, one would need to introduce the additional assumption that collapse to alcohol of the pair occurs faster than loss of stereochemistry, to account for the high stereoselectivities observed.

Finally, the relative contributions to the transition state of the resonance forms Ib and Ic may vary depending on substrate nature and/or dioxirane structure. Thus, the remarkable enhancement of rates occurring on passing from dimethyl- to methyl(trifluoromethyl)dioxirane might be accommodated.[24,55] It should be mentioned, however, that the lower reactivity recorded for attack at benzylic hydrogens of ethylbenzene and of toluene with respect to simple hydrocarbons RH cannot be rationalized solely on the grounds of the simple mechanism outlined in Scheme I. Thus, further studies to unravel the reaction mechanism into details are warranted.

Conclusions

Dioxirane **1b** is an extremely powerful O-atom insertion agent, allowing efficient oxyfunctionalizations of saturated hydrocarbons under extremely mild conditions. Its outstanding reactivity exceeds many times that of dimethyldioxirane (**1a**) and permits the fast and selective conversion of alkanes into alcohols (or ketones) with high yields. Despite its exceptional reactivity, the high regio- and stereoselectivities noted in alkane oxidations using **1a** are not diminished with **1b** and in some cases seem even enhanced. The potential of alkane oxidations by this novel dioxirane species in synthesis should be apparent, since it allows the efficient oxyfunctionalization of certain hydrocarbons that would otherwise be difficult to derivatize. An example is the conversion of adamantane into adamantane-1,3-diol (Table I; see also Experimental Section).

Although mechanistic details are sketchy as yet, it appears that the efficiencies and selectivities displayed in hydrocarbon oxyfunctionalization by **1b** are matched only by few systems.[3] Actually, the sensitivity to substrate structure noted in oxygenations via dioxiranes seems to mimic that exhibited by certain microorganisms; their reactivity resembles that of certain monooxygenase enzymes.[3,56] With this in mind, it would now seem appropriate to address the question as to whether dioxirane intermediates may be involved in certain biochemical oxidations.

Experimental Section

Equipment. Melting points and boiling points were not corrected. The ^1H and ^{13}C NMR spectra were obtained by using a Varian Model XL 200 (200 MHz) spectrometer; a Varian Model EM 360 (60 MHz) instrument was also used for routine ^1H NMR spectra. The FT-IR spectra were recorded on a Perkin-Elmer Model 1710 instrument interfaced with a Perkin-Elmer Model 7300 data station. Mass spectra of organics were obtained by employing a Hewlett-Packard Model 5970 mass-selective detector connected to a Model 5890 gas chromatograph. A Balzer Model QMG 511 (40-eV ionizing energy) was employed to carry out MS gas analyses.[37] The GLC analyses were performed on a DANI Model 3800 (and Shimadzu Model C-R1A integrator) equipped with a SE 30 (or OV 101), 30 m × 0.25 μm i.d. capillary column; a Supelcowax wide bore

(53) For instance, see: (a) Cremer, D.; Schindler, M. *Chem. Phys. Lett.* **1987**, *133*, 293. (b) Cremer, D.; Schmidt, T.; Gauss, J.; Radhakrishnan, T. P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 427. (c) Harding, L. B.; Goddard, W. A. *J. Am. Chem. Soc.* **1978**, *100*, 7180.

(54) Becker, J. Y.; Miller, L. L.; Siegel, T. M. *J. Am. Chem. Soc.* **1975**, *97*, 849.

(55) Kobayashi, Y.; Kumadaki, I. *Acc. Chem. Res.* **1981**, *14*, 76, and references therein.

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capillary column (60 m × 0.75 mm i.d., 1.0-μm film thickness) was employed for analyses of volatile materials. A Fischer Spaltrohr microcolumn was used to perform fractional distillations.

Materials. All solvents, starting materials, and compounds used as reference in product analyses were of the highest purity commercially available; further purification, whenever appropriate, was achieved by following standard methods.[57] Purified methylene chloride, 1,2-dichloroethane, and 1,1,1-trifluoro-2-propanone (bp 22 °C) solvents were stored over 5-Å molecular sieves at 2–5 °C and routinely redistilled and flushed with dry inert gas (N_2 or Ar) immediately prior to use. Curox triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (a gift by Interox Peroxid-Chemie, Munich, FRG) was our source of potassium peroxomonosulfate;[33] it was used as received. Bicyclo[2.2.2]octane (**22**) was obtained (yield 97%) upon hydrogenation of commercial (Aldrich) bicyclo[2.2.2]octene in *n*-hexane over Pd/C at 20–22 °C; it was purified by sublimation at 30 °C in vacuo (4 mmHg): mp 172–174 °C (subl);[58] IR (KBr) 2933, 1453 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.51 (s); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 23.93, 25.98; MS (70 eV) *m/z* (rel abund) 110 (53, M^+), 96 (11), 95 (13), 82 (41), 81 (70), 67 (100), 55 (14), 54 (46), 53 (19), 41 (50).

Methyl(trifluoromethyl)dioxirane (1b). A 150-mL, five-necked round-bottomed vessel is equipped with a mechanical stirrer, an air-cooled straight condenser loosely packed with silanized glass wool, a solids addition funnel, a gas inlet tube extending into the reaction mixture, and a thermometer. The air condenser is connected laterally to the top entry of an efficient jacketed spiral condenser cooled at −75 °C (dry ice/acetone); the bottom exit of this condenser is fitted to a two-ways fraction-collector adapter carrying two 50 mL receiving flasks, also cooled at −75 °C. In succession to the adapter, two cold traps are placed, the first cooled at −75 °C, and the second at liquid nitrogen temperature. The main vessel is charged with $NaHCO_3$ (15 g) and Na_2H_2EDTA (0.5 g) dissolved in 15 mL of bidistilled water, and cooled at 2–5 °C. To this 20 g (0.179 mol) of 1,1,1-trifluoro-2-propanone (TFP) is added, and mechanical stirring is initiated. The solid potassium peroxomonosulfate (0.081 mol, 25 g of Curox triple salt) is quickly added (1–2 min) to the reaction vessel, while passing a gentle stream of He (or Ar) gas through the mixture. Just before starting the addition of the solid inorganic peroxide, a slight vacuum (650–700 mmHg) is applied to the last trap. Shortly after the addition is initiated, the end two-ways adaptor is switched to insert the main collection flask, and during 6–8 min ca. 12 mL of yellow solution of **1a** in TFP is collected, having dioxirane concentrations ranging from 0.5 to 0.8 M; ^1H NMR (CF_3COCH_3, Me_4Si, −20 °C) δ 1.97 (s);[23] ^{13}C, ^{19}F, and ^{17}O NMR, IR, and UV-vis spectral data for **1b** have been reported.[24] Cold solutions of **1b** can be dried briefly over $MgSO_4$ (Analar grade), quickly filtered, and stored over 5-Å molecular sieves at −20 °C (keep well protected from light). Provided that care is exercized in using extra clean glassware (before drying, for final wash we use 0.01% Na_2H_2EDTA in bidistilled water) and that trace metals and other impurities are carefully excluded, only minor loss of dioxirane content of solutions is observed (e.g., 5–6% during 48 h, at −20 °C).[24] The expensive TFP solvent can be recovered from decomposed dioxirane **1b** solutions by low-temperature fractional distillation (bp 22 °C) through an efficient column.

Reactions of Hydrocarbons with Methyl(trifluoromethyl)dioxirane (1b). These were carried out under conditions described in Chart I and Table I. The following procedure is representative: to a cold (−20 °C) and stirred 0.08 M hydrocarbon solution in 7 mL of CH_2Cl_2 (0.4 mmol), also containing 0.04 M 1,1,2,2-tetrachloro-1,2-difluoroethane (Freon A 112, an *inert* internal standard), 0.7 mL of a 0.63 M solution of **1b** in TFP is quickly added. The reaction flask is kept in a thermostatic bath at −20 °C, and GC (or GC/MS) monitoring is begun at once. Percent substrate conversion and product yields are estimated by GC analyses on calibration curves previously constructed by using standard solutions of the hydrocarbon starting material and of authentic samples of product(s). Upon completion of the reaction (a few minutes in most cases), the solvent is removed in vacuo (20 mmHg) at 15–20 °C; the residue is taken up in CH_2Cl_2 and the product alcohol (or ketone) separated from residual hydrocarbons and/or from byproducts (if any) by column flash chromatography (silica gel, *n*-hexane/Et_2O). Since the isolation procedure is quite straightforward, it is found that isolated yields are practically the same (or just slightly lower than) GC yields reported in Chart I and Table I.

(*Z*)-1,2-Dimethylcyclohexanol (13). After distillation, yield 82%: bp 63 °C (17 mmHg);[58] IR (neat) 3465 (O–H), 2965 (C–H), 1452, 1374 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.85 (d, ^2J = 8 Hz, 3 H, CH_3CH), 1.13 (s, 3 H, CH_3COH), 1.16–1.67 (m, 9 H), 3.10 (br s, 1 H, O*H*); MS (70 eV) *m/z* (rel abund) 128 (11, M^+), 113 (13), 110 (2), 99 (3), 95 (12), 85 (32), 72 (16), 71 (100), 68 (12), 43 (70).

(*E*)-1,2-Dimethylcyclohexanol (15). After distillation, yield 92%; bp 83 °C (25 mmHg);[58] mp 22.5–23.0 °C [lit.[32] mp 22.8 °C]; IR (KBr) 3393 (O–H), 2933 and 2861 (C–H), 1457, 1378, 1175 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.89 (d, ^2J = 6.5 Hz, 3 H, CH_3CH), 1.07 (s, 3 H, CH_3COH), 1.10–1.70 (m, 9 H), 3.15 (br s, O–*H*); MS (70 eV) *m/z* (rel abund) 128 (10, M^+), 113 (10), 110 (2), 99 (3), 95 (10), 85 (31), 72 (14), 71 (100), 68 (13), 58 (61), 57 (16), 43 (70).

(*E*)-9-Decalol (17). After distillation, yield 48%; white leaflets upon sublimation: bp 57–58 °C (1 mmHg) [lit.[59] bp 104–106 °C (20 mmHg)]; mp 50–51 °C;[60] IR (KBr) 3448 (O–H), 2927 (C–H), 1447, 1262, 1214, 1095, 799 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.30–1.38 (m, 10 H), 1.40–1.80 (m, 8 H including O*H*); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.62, 26.25, 28.62, 39.68, 44.12, 70.14 (^9C–OH);[61] MS (70 eV) *m/z* (rel abund) 154 (26, M^+), 136 (2), 125 (2), 112 (8), 111 (100), 98 (50), 97 (25), 83 (19), 70 (11), 67 (15), 57 (5), 56 (5), 55 (47), 43 (20).

(*E*)-1-Decalone (17′). Yield 18%: mp 32–33 °C;[62] IR (KBr) 2924 and 2855 (C–H), 1712 (C=O), 1448, 1313, 1208, 904 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.5–2.10 (m, 10 H), 2.20–2.40 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) 20.08, 25.42, 25.74, 26.49, 33.03, 34.36, 41.82, 44.94, 55.06, 212.91 (*C*=O); MS (70 eV) *m/z* (rel abund) 152 (51, M^+), 137 (5), 136 (5), 134 (16), 124 (13), 123 (26), 111 (10), 110 (63), 109 (100), 108 (28), 97 (40), 95 (20), 81 (85), 67 (95), 55 (52), 41 (80).

(*E*)-2-Decalone (17″). Yield 15%: mp 50–52 °C;[60] IR (KBr) 1708 (C=O) cm^{-1}, etc.; MS (70 eV) *m/z* (rel abund) 152 (60, M^+), 137 (9), 136 (6), 135 (2), 134 (12), 123 (18), 110 (43), 109 (28), 108 (96), 97 (26), 96 (38), 95 (50), 81 (98), 79 (43), 67 (88), 55 (96), 41 (100).

(*Z*)-9-Decalol (19). After recrystallization (petroleum ether), yield 88%: mp 64.5 °C;[60] IR (KBr) 3359 (O–H), 2926 and 2860 (C–H), 1447, 1158, 1137, 1028, 992, 932 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.15–2.0 (m, 16 H), 2.10 (br, 2 H, O*H* and ^{10}C–*H*); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 22.87, 27.98, 42.75, 71.86 (^9C–OH); MS (70 eV) *m/z* (rel abund) 154 (23, M^+), 136 (2), 125 (2), 112 (9), 111 (100), 98 (53), 97 (27), 95 (3), 83 (22), 81 (6), 79 (9), 77 (7), 70 (14), 69 (12), 67 (17), 55 (53), 43 (23).

Bicyclo[2.2.2]octan-1-ol (23). Upon reaction of **22** with **1b** and removal of solvent, the mixture was treated with Ac_2O/py at gentle reflux (0.5 h) and diluted with ice-cold water, and the solution extracted (Et_2O). The extracts were washed (10% aq HCl, then water) and dried ($MgSO_4$); removal of solvent in vacuo and column chromatography (silica gel, *n*-hexane/Et_2O 6:1) of the residue allow one to separate bicyclo[2.2.2]-octan-2-one (**23′**, mp 178–179 °C)[63] from pure **bicyclo[2.2.2]-oct-1-yl acetate (30)**, a clear liquid at 25 °C: IR (neat) 2927, 2869 (C–H), 1730 (C=O), 1461, 1368, 1245, 1048 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.50 (m, 1 H), 1.59–1.70 (m, 4 H), 1.91 (s, 3 H, CH_3), 1.82–2.00 (m, 8 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 22.52 (q, ^1J = 128.4 Hz, CH_3), 23.87 (d, ^1J = 135.1 Hz), 26.81 (t, ^1J = 135.1 Hz), 29.75 (t, ^1J = 135.1 Hz), 80.63 (s, ^1C), 170.33 (q, ^2J = 6.73 Hz, CH_3C=O); MS (70 eV) *m/z* (rel abund) 168 (4, M^+), 127 (4), 126 (50), 109 (4), 108 (17), 98 (6), 97 (70), 93 (15), 83 (7), 80 (13), 79 (28), 70 (91), 67 (16), 66 (28), 55 (25), 43 (100). Hydrolysis (10% aq KOH) of **30**, followed by extraction (Et_2O), drying of the extracts ($MgSO_4$), and removal of solvent in vacuo (20 mmHg), affords alcohol **23** (92% yield, 45% overall yield based on amount of hydrocarbon **22** starting material); after sublimation: mp 214–215 °C;[64] IR (KBr) 3270 (O–H), 2941, 2920 (C–H), 1456, 1103, 1093 cm^{-1}; MS (70 eV) *m/z* (rel abund) 126 (10, M^+), 111 (2), 108 (2), 98 (6), 97 (74), 83 (10), 71 (9), 70 (100), 67 (5), 55 (27), 43 (16).

Adamantane-1,3-diol (25′) was the main product when adamantane (**24**) was treated with **1b** in a 1:2 molar ratio (Table I); after recrystallization (MeOH/*n*-hexane), yield 86%: mp 256–258 °C; IR (KBr) 3275 (O–H), 2930 and 2851 (C–H), 1453, 1135, 1027, 968, 911, 801 cm^{-1}; ^1H NMR (CD_3OD, 200 MHz) δ 1.50 (m, 2 H), 1.62 (apparent d, 8 H), 1.65 (s, 2 H), 2.23 (m, 2 H), 4.88 (O*H*); ^{13}C NMR (CD_3OD, 50 MHz) δ 30.70 (d, ^1J = 133.4 Hz), 33.97 (t, ^1J = 126.5 Hz), 42.80 (t, ^1J = 128.3 Hz), 51.40 (t, ^1J = 126.8 Hz), 68.82 (s, ^1C and ^3C); MS (70 eV) *m/z* (rel abund) 168 (12, M^+), 150 (3), 135 (2), 125 (2), 112 (8), 111 (100), 109 (4), 105 (5), 107 (3), 95 (14), 83 (3), 82 (2), 81 (3), 77 (4), 69 (4), 67 (4), 65 (32), 58 (2), 55 (7), 53 (4), 43 (18), 41 (11).

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Other products listed in Chart I were identified upon comparison of their NMR and/or MS spectra with those of authentic samples; ^{13}C NMR chemical shifts agreed within ±0.1 ppm with literature data.[61,65]

Kinetic Measurements. In the majority of cases, absolute rates were determined under pseudo-first-order conditions, with the dioxirane in large excess over the hydrocarbon initial concentration. At zero time an aliquot (0.2 mL) of a thermostated solution of the given hydrocarbon (usually 0.15–0.20 M), also containing the calibration standard Freon A112 (see above), was added to 2 mL of a 0.3–0.4 M dioxirane **1b** solution (also thermostated). Aliquots (10 μL) of the reaction solution were withdrawn periodically, quenched with 0.1 mL of ca. 0.15 M n-Bu_2S or p-MeC_6H_4SMe in CH_2Cl_2, and the samples analyzed by GLC. Linear ln (C_0/C) vs time plots were obtained for hydrocarbon consumption to over 70% reaction, yielding k_1 (s^{-1}); from this, and the known dioxirane initial concentration (iodometric titre), k_2 (M^{-1} s^{-1}) values could be estimated (Table II). In competition kinetics essentially the same procedure was followed, but now two hydrocarbons (A and B) in the same solution, were allowed to react with excess dioxirane, making ($[A]_0$ + $[B]_0$) ≪ [dioxirane]$_0$). Aliquots were withdrawn (and quenched) within the first 15–30% of reaction; GLC analyses of these allowed to obtain relative rate (k_r) data as k_A/k_B = log ($[A]/[A]_0$)/(log ($[B]/[B]_0$). In each experiment, at least three values were measured and averaged (estimated error ≤±8%).

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Cyano--Halogen Interactions and Their Role in the Crystal Structures of the 4-Halobenzonitriles

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Abstract: A survey of 73 intermolecular cyano--halogen contacts retrieved from 124 crystal structures in the Cambridge Structural Database has revealed that short C≡N--X contacts are commonly found when X = Cl and Br, with the linearity of the C≡N--X angle being a particularly prominent feature when X = Br. These contacts arise due to halogen polarizability and are also found when X = I. The crystal packing of several simple halogen–cyano compounds may be rationalized on the basis of a linear secondary motif built up via these C≡N--X contacts. These structures may be nominally visualized in terms of parallel or antiparallel alignment of the linear motifs. However, a closer examination of some of the "model" structures evoked serious questions about their reliability, and thus the crystal structures of 4-chloro-, 4-bromo-, and 4-iodobenzonitrile were reinvestigated. 4-Chlorobenzonitrile exists as two polymorphs, the previously reported centrosymmetric form ($P2_1/c$, Z = 4) with antiparallel chains of molecules linked by linear C≡N--Cl contacts [N--Cl, 3.350 (2) Å] and a new noncentrosymmetric, polar form (Pc, Z = 2) with parallel, zigzag chains [N--Cl, 3.370 (4) Å; C≡N--Cl, 87.7 (3)°]. In the centrosymmetric form, the alignment of the linear chains is variable and often less than perfect, leading to unusual features in the diffraction pattern and to a crystal structure that is partially "disordered" (C≡N versus Cl). In contrast, the crystal structure of the noncentrosymmetric form is not disordered. The centrosymmetric form converts to the noncentrosymmetric form upon grinding; this interconversion has been followed by X-ray powder diffraction and Second Harmonic Generation techniques. 4-Bromobenzonitrile exists only as a noncentrosymmetric, polar form (Am, Z = 2) with parallel chains of molecules connected by short, linear C≡N--Br contacts of 3.249 (5) Å. Some disordering of the Br and C≡N groups was noted here, indicating again that the alignment of the chains is not perfect. In the structure of 4-iodobenzonitrile, the linear chains have very short C≡N--I contacts of 3.127 (4) Å and pack in an ordered, antiparallel fashion in a centrosymmetric space group ($I2/a$, Z = 4). However, there is no evidence of misalignment of linear motifs here. The crystallographic anomalies encountered in this study emphasize that the tertiary interactions that link secondary motifs in organic solids may be very subtle, rendering difficult the deliberate design or engineering of their crystal structures.

The stabilizing role of weak intermolecular interactions in the crystal structures of molecular solids has elicited much recent interest.[1-5] An appreciation of interactions such as C–H--O, C–H--N, C–H--halogen, halogen--halogen, halogen--O, halogen--S, N--S, and S--S may be quite useful in efforts at predicting and designing new crystal structures.[6-12] Although such heteroatom interactions are very weak, they are directional in nature and are therefore able to steer or direct molecules to predictable packing modes characterized by recurring geometrical patterns. Construction of such molecular patterns is accordingly a convenient first step in crystal engineering. Of course, the dissection of a three-dimensional crystal structure into modular units is a subjective exercise, but it is convenient to define these secondary units

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