Oxidations by Methyl(trifluoromethyl)dioxirane. 5.[1] Conversion of Alcohols into Carbonyl Compounds

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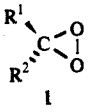
Abstract: The oxidation of a number of secondary alcohols (i.e., 2-propanol, 1-phenylethanol, 3-octanol, cyclobutanol, *exo*- and *endo*-2-norborneol) by methyl(trifluoromethyl)dioxirane (**1a**) affords the corresponding ketones in high yield (92–99%), under mild conditions and within short reaction times (2–20 min). Primary alcohols 1-butanol and benzyl alcohol are converted by **1a** into butyric acid and into $PhCHO/PhCO_2H$ mixtures, respectively, while 2-methyl-2-propanol is not oxidized. Functional group selectivity is illustrated by the clean conversion of two epoxy alcohols, namely 3,4-epoxy-2-butanol (**8**) and (+)-1,2-epoxy-3-pentanol (**9**), into the corresponding epoxy ketones, leaving the epoxy functionality untouched. The oxidation of cyclohexanol by **1a** follows a second-order rate law, and a kinetic isotope effect (k_H/k_D) = 1.6 ± 0.15 was measured by using cyclohexanol-d_{11}. Remarkable stereoselectivity was recorded in the oxidation of 2-norborneol, since the *endo*-alcohol was found to be ca. 40 times more reactive than its exo stereomer. The available evidence suggests that a radical-chain mechanism is unlikely for the title transformation.

Numerous oxidizing agents can affect the conversion of alcohols into carbonyl compounds.[2] For this transformation, in the development of nonmetal oxidants,[2a-b,3] a major break-through constituted the introduction of DMSO-based reagents,[3] which have been reported in a considerable number of variants.[2a,3] Nonetheless, the majority of synthetic methods still appear to utilize metal species,[2a] with chromium compounds being employed in the largest part.[4] As for metal-catalyzed H_2O_2 oxidations of alcohols,[5] Fenton and Fenton-like systems have been carefully investigated,[5,6] and catalysis by molybdenum or tungsten[7] and by ruthenium compounds[8] as well as by several other metal species has been amply illustrated.[5] However, in some instances the preparative value of these procedures is limited, especially when relatively high catalyst to substrate ratios are required or high H_2O_2 concentrations are to be employed. Concerning peroxide reagents in the *absence* of metal catalysts, studies on alcohol oxidations have proven fruitful during the past 30 years in terms of providing insight into the behavior of free-radical intermediates;[6,9] however, synthetic applications of these systems have received less attention.

In this context, an opportunity has arisen recently from the introduction of a new class of powerful peroxide oxidants, namely the family of dioxiranes **1**.[10] In fact, once it became established



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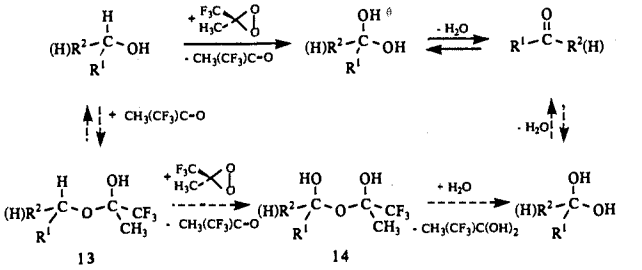
(**1a**: $R^1 = CF_3$, $R^2 = CH_3$; **1b**: $R^1 = R^2 = CH_3$)

that dioxiranes are generated in the reaction between their parent ketones and potassium peroxomonosulfate $K^+HSO_5^-$ (caroate, an inexpensive inorganic peroxide),[11] the actual isolation of a few volatile species, such as dimethyldioxirane (**1b**)[12-14] and the title dioxirane **1a**,[15] spurred an intensive utilization of these reagents in synthetic applications.[1,16] Among these, particularly valuable is the direct oxyfunctionalization of saturated hydrocarbons,[17,18] for which methyl(trifluoromethyl)dioxirane (**1a**) appears to be best suited.[16e,18] In this reaction, high selectivities were recorded for O-atom insertion at the tertiary > secondary ≫ primary "unactivated" C–H bonds; oxidation of tertiary C–H gives tertiary alcohols (with complete retention of configuration, whenever applicable), while oxidation at secondary carbon yields primarily ketones.[18] Control experiments[18] suggested that ketones derive from the rapid further oxidation of the alcohols initially formed in the reaction of the alkane with the dioxirane.[17,18]

Scheme I



We now report the results of a more systematic study, showing that methyl(trifluoromethyl)dioxirane (**1a**) can be fruitfully em-

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(1) Part 4: Mello, R.; Ciminale, F.; Fiorentino, M.; Fusco, C.; Prencipe, T.; Curci, R. *Tetrahedron Lett.* **1990**, *31*, 6097.

(2) (a) Haines, A. H. *Methods for the Oxidation of Organic Compounds, Alcohols, Alcohol Derivatives, etc.*; Academic: London, 1988; p 5 ff; a recent general overview, see references. (b) Anelli, P. L.; Biffi, C.; Montanari, F.; Quici, S. *J. Org. Chem.* **1987**, *52*, 2559. (c) Griffith, W. P.; Ley, S. V. *Aldrichimica Acta* **1990**, *23*, 13.

(3) For example, see: (a) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165, and references to previous articles. (b) Moffatt, J. G. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. V, p 242 ff. (c) Takano, S.; Ionomata, K.; Tomita, S.; Yanase, M.; Samizu, K.; Ogasawara, K. *Tetrahedron Lett.* **1988**, *29*, 6619. (d) Tidwell, T. J. *Org. React.* **1990**, *38*, and references cited therein.

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(6) For instance, see: (a) Walling, C. *Acc. Chem. Res.* **1975**, *8*, 125. (b) Huyser, E. S.; Hawkins, G. W. *J. Org. Chem.* **1983**, *48*, 1705. (c) Masarawa, M.; Cohen, H.; Meyerstein, D.; Hickman, D. L.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1988**, *110*, 4293, and references cited therein.

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(9) For instance, see: (a) Gallopo, A. R.; Edwards, J. O. *J. Org. Chem.* **1971**, *36*, 4089, and previous articles of the series. (b) Snook, M. E.; Hamilton, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 860. (c) Bida, G.; Curci, R.; Edwards, J. O. *Int. J. Chem. Kinet.* **1973**, *5*, 859. (d) Walling, C.; Camaioni, D. M. *J. Org. Chem.* **1978**, *43*, 3266. (e) Huyser, E. S.; Kahl, A. A. *J. Org. Chem.* **1970**, *35*, 3742.

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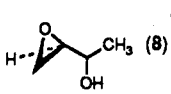
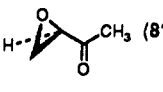
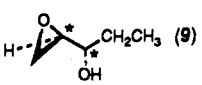
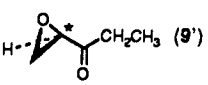
Table I. Oxidation of Alcohols to Carbonyls by Methyl(trifluoromethyl)dioxirane (**1a**)[a]

entry	alcohol	reactn time, min	conversion,[b] %	product	yield,[b] %
1	3-octanol (**2**)	2	37	3-octanone (**2'**)	99
		20	>98		99
2	cyclobutanol (**3**)	4	59	cyclobutanone (**3'**)	98
		20	97		99
3	cyclohexanol (**4**)	2	72	cyclohexanone (**4'**)	98
		9	98		99
4	*endo*-norborneol (**5a**)	2	99	norcamphor (**5'**)	99
					95 (i)
5	*exo*-norborneol (**5b**)	2	40	norcamphor (**5'**)	98
		5	60		98
		13	98		99
6	$PhCH(CH_3)OH$ (**6**)	3	60	$Ph\text{-}CO\text{-}CH_3$ (**6'**)	98
		20	98		99
7	$(CH_3)_2CHOH$ (**7**)	8	>95	$(CH_3)_2C{=}O$ (**7'**)	>92[c]
8	 (**8**)[d]	12	93	 (**8'**)	92 (i)
9	 (**9**)	15	96	 (**9'**)	94 (i)
10	$PhCH_2OH$ (**10**)	30	46	PhCHO (**10'**) (*95*), $PhCO_2H$ (**10''**) (*5*)[e]	98
		60	60	(*80*), (*20*)[e]	99
		30[f]	77	(*44*), (*56*)[e]	98
		90[f]	89	(*6*), (*94*)[e]	99
11	1-butanol (**11**)	10[f,g]	90	$CH_3CH_2CH_2CO_2H$ (**11'**)	90[h]
12	2-methyl-2-propanol (**12**)	3600		no reaction	

[a] In CH_2Cl_2/TFP mixed solvent: composition from 70:30 to 50:50; reactions routinely run at −20 °C, with dioxirane to substrate ratios 1.1–1.3 (unless noted otherwise). [b] As determined (±2%) by GC (unless noted otherwise); (i) denotes yield of isolated product. [c] As determined (±5%) by ^1H NMR analysis. [d] A 40:60 mixture of erythro/threo stereomers (ref 34). [e] Parenthetic italic figures refer to product distribution, as determined by GC. [f] Reaction run by adopting inverse addition, i.e., alcohol solution in CH_2Cl_2 added to dioxirane in TFP (see text). [g] Dioxirane to substrate ratio = 2.2. [h] The ^1H NMR spectra also reveal residual hemiacetal $CH_3(CF_3)C(OH)OCH_2CH_2CH_2CH_3$ (ca. 8%) (see text).

ployed to carry out the transformation of alcohols into carbonyls.

Results and Discussion

By use of a general protocol, solutions that were 0.6–0.9 M **1a** in its parent ketone (1,1,1-trifluoro-2-propanone, hereafter TFP) could be obtained.[18] Then, the reactions of **1a** with representative alcohols were examined; in most cases the procedure simply involved the quick addition of a standardized[18] cold solution of **1a** to the substrate, dissolved in CH_2Cl_2 or CH_2Cl_2/TFP.

Data concerning the oxidation of representative alcohols are shown in Table I. These indicate that the dioxirane **1a** is an efficient reagent allowing the fast and selective conversion of secondary and primary alcohols into carbonyl compounds; with few exceptions, yields are higher than 90%. With secondary alcohols (entries 1–9), high conversions are attained within quite short reaction times, even at temperatures well below 0 °C; on the other hand, 2-methyl-2-propanol—a simple aliphatic tertiary alcohol—is not appreciably oxidized under the conditions adopted (last entry, Table I).

That alcohol oxidations by dioxirane **1a** can be chemioselective is demonstrated by the clean conversion of epoxy alcohols **8** and **9** into the corresponding epoxy ketones, leaving the oxirane functionality untouched (entries 8 and 9); also, no configurational loss at an adjacent stereo center occurs during oxidation (entry 9, Table I). As expected, benzyl alcohol (a primary alcohol) gave mixtures of benzaldehyde and benzoic acid, depending on the extent of conversion and reaction time (entry 10); it should be mentioned, however, that in this case we did not investigate in detail the effect of dissolved oxygen[16b] on product distribution. With the appropriate stoichiometric 2:1 ratio of dioxirane to alcohol, 1-butanol could be converted into butyric acid in high yield (entry 11, Table I).

In general, with respect to primary alcohols, oxidation of secondary alcohols by **1a** is smoother and requires shorter reaction times (cf., e.g., entries 6 and 10, Table I). This might be related to the different ease of formation of hemiacetals and to their subsequent oxidation (Scheme I).

Some ^1H NMR experiments seem to support this view. In fact, we observe that, when ca. 0.1 M 2-propanol (**7**) is mixed with an 8-fold excess of dry TFP in $CDCl_3$ at 0 °C, the corresponding hemiacetal **13'** (in **13**: $R^1 = R^2 = CH_3$)[19] is formed only slowly,

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(15) Mello, R.; Fiorentino, M.; Sciacovelli, O.; Curci, R. *J. Org. Chem.* **1988**, *53*, 3890.

(16) For recent developments, see, e.g.: (a) Murray, R. W.; Rajadhyaksha, S. N.; Mohan, L. *J. Org. Chem.* **1989**, *54*, 5783. (b) Baumstark, A. L.; Beeson, M.; Vasquez, P. C. *Tetrahedron Lett.* **1989**, *30*, 5567. (c) Adam, W.; Hadjiarapoglou, L.; Jäger, V.; Seidel, B. *Tetrahedron Lett.* **1989**, *30*, 4223. (d) Eaton, P. E.; Wicks, G. E. *Tetrahedron Lett.* **1989**, *30*, 257. (e) Mello, R.; Cassidei, L.; Fiorentino, M.; Fusco, C.; Curci, R. *Tetrahedron Lett.* **1990**, *21*, 3067. (f) Wittman, M. D.; Halcomb, R. L.; Danishefsky, S. J. *J. Org. Chem.* **1990**, *55*, 1981. (g) Boyd, D. R.; Coulter, P. B.; McGuckin, M. R.; Sharma, N. D. *J. Chem. Soc., Perkin Trans. 1* **1990**, 304. (h) Baldwin, J. E.; O'Neil, L. A. *Tetrahedron Lett.* **1990**, *31*, 2047. (i) Adam, W.; Mello, R.; Curci, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 890.

(17) Murray, R. W.; Jeyaraman, R.; Mohan, L. *J. Am. Chem. Soc.* **1986**, *108*, 2470.

(18) Mello, R.; Fiorentino, M.; Fusco, C.; Curci, R. *J. Am. Chem. Soc.* **1989**, *111*, 6749.

(19) Hemiacetal **13'**: ^1H NMR ($CDCl_3$, 200 MHz) δ 1.17 (d, 6 H, $CHCH_3$, ^2J = 6.10 Hz), 1.50 (q, 3 H, CF_3CCH_3, $^3J_{HF}$ = 1.22 Hz, and 4.21 (septet, 1 H, $CHCH_3$, ^2J = 6.10 Hz). Cf., CH_3COCF_3 (TFP): ^1H NMR ($CDCl_3$, 200 MHz) δ 2.42 (q, $^3J_{HF}$ = 0.95 Hz). $(CF_3)(CH_3)C(OH)_2$: ^1H NMR ($CDCl_3$, 200 MHz) δ 1.54 (q, $^3J_{HF}$ = 1.18 Hz). Dioxirane **1a**: ^1H NMR ($CDCl_3$, 200 MHz) δ 1.96 (q, $^3J_{HF}$ = 1.12 Hz). $(CH_3)_2CHOH$: ^1H NMR ($CDCl_3$, 200 MHz) δ 1.19 (d, 6 H, ^2J = 6.15 Hz), and 4.02 (septet, 1 H, ^2J = 6.15 Hz). $(CH_3)_2C{=}O$: ^1H NMR ($CDCl_3$, 200 MHz) δ 2.18 (s). All spectral parameters above refer to $CDCl_3$ solutions containing 5–30% TFP, at 0 °C.

requiring about 60 min to reach an equilibrium composition of ca. 35:65 hemiacetal **13′**/alcohol. Under identical conditions, when 2-propanol (**7**) is added to 1.1 equiv of dioxirane **1a** in TFP/$CDCl_3$, ^1H NMR monitoring reveals that complete conversion of **7** into acetone is attained within 4 min only. After the complete disappearance of the resonances of **7**, inspection of the ^1H NMR spectrum revealed just a small amount (<3%) of hemiacetal **13′**.

On the other hand, with ca. 0.08 M initial concentration of ethanol, the ^1H NMR spectra of EtOH/TFP mixtures 1:8 in $CDCl_3$ at 0 °C showed that equilibrium formation of ca. 70% (over stoichiometric) hemiacetal **13″** (in **13**: $R^1 = CH_3$, $R^2 = H$) occurs within 5 min after mixing. When an aliquot of dioxirane **1a** solution (ca. 1.5 equiv with respect to $[EtOH]_0$) was added to the above equilibrium mixture of EtOH and hemiacetal **13″**, the NMR signals of ethanol disappeared quickly (ca. 8 min), giving rise to the characteristic CH_3 singlet (δ 2.06) of acetic acid. Then, fading of the CH_3 resonance (δ 1.97) due to residual dioxirane and of hemiacetal **13″** NMR signals ensued at a slower pace, requiring about 30 min for a 50% decrease in intensity.[21] In both of the cases above, no ^1H NMR signals were detected that could be attributed to hemialdals **14**; under the conditions adopted, their formation (if any) should be followed by rapid breakdown (Scheme I).

Whatever complications might be introduced by competitive hemiacetal formation, the synthetic outcome—i.e., the efficient conversion of alcohols into carbonyls by **1a**—is straightforward, and it can be quite useful especially in transformations involving secondary alcohols (Table I).

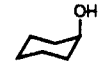
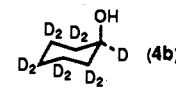
As for the reaction mechanism, worthy of note is the fact that cyclobutanol (**3**) is transformed into cyclobutanone (**3′**) only by **1a**. In fact, it is known[22,23] that cyclobutanol presents the unique property of reacting in basically different ways with one-electron and two-electron oxidants. Namely, with one-electron oxidants C–C bond cleavage occurs preferentially, leading to acyclic products such as γ-hydroxybutyraldehyde.[22,23] On the other hand, two-electron oxidants plainly convert cyclobutanol into cyclobutanone, with cleavage of the C–H bond α to the OH functionality occurring in the rate-determining step (rds).[22-24]

To gain further insight concerning the mechanism, the rates of oxidation of a few secondary alcohols by **1a** were measured. The oxidations were found to obey second-order kinetics (first order each in dioxirane and in substrate), yielding integrated second-order rate law plots that were linear to over 80% substrate conversion in most cases. Rate constant values are presented in Table II.

The observed clean second-order kinetics and the lack of significant interference by atmospheric oxygen (cf., e.g., entries 3 and 4 in Table II) suggest that a chain process involving free radicals[9] should not be operative. Also at odds with a purely radical process is the remarkable selectivity recorded in the oxidation of the two 2-norbornanols **5a** and **5b** with the *endo*-alcohol being ca. 40 times more reactive than its exo stereomer, as well as the outcome of the cyclobutanol probe mentioned above.

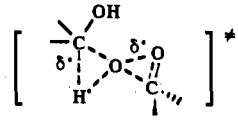
Furthermore, in a radical-chain mechanism involving rate-determining attack by $R_2C^{\bullet}$–OH at the peroxide O–O bond, a primary kinetic isotope effect is not expected[9] when R_2CHOH and R_2CDOH are used. Instead, in the reaction at hand an isotope effect of $k_H/k_D = 1.6$ was measured by using substrates **4a** and **4b** (Table II), indicating that the C–H bond in position α to the OH moiety is being broken in the rds. It should be recalled that, in the oxidation of secondary alcohols by metal oxo species, the reactions exhibit a range of kinetic isotope effects; this extends from $k_H/k_D = 1.9$ and 3.6 measured in the oxidation of cyclobutanol by Ce(IV) and by V(V) respectively, to $k_H/k_D \cong 7$ for the oxidation of 2-propanol by Cr(VI) to 18 in the oxidation of $(CH_3)_2CHOH/(CD_3)_2CDOD$ by Ru(IV).[22,25-27] In most of these cases, however, either direct spectroscopic evidence or kinetics suggests the formation of discrete, inner-sphere metal–alcoholate complexes which decompose via homolytic or heterolytic pathways; large and negative $\Delta S^{\ddagger}$ values are often recorded. Instead, from the log A value reported in Table II, one can estimate a $\Delta S^{\ddagger}$ value of ca. −15 cal mol^{-1} K^{-1} (at 25.0 °C) for cyclohexanol oxidation by **1a**, which is significantly less negative than in the case of metal oxide oxidations mentioned above.

Table II. Rates of Oxidation of Some Secondary Alcohols by Methyl(trifluoromethyl)dioxirane (**1a**) in CH_2Cl_2/TFP (50:50)

substrate	T, °C	$10^2 \times k_2$,[a] M^{-1} s^{-1}
 (**4a**)	−33.0	5.6[b]
	−22.5	13.6[b]
	−12.5	42.5[b]
	−12.5	46.2[c]
	−12.5	[0.22][d]
 (**4b**)	−12.5	26.2[e]
 (**5a**)	−22.0	85.6
 (**5b**)	−22.0	2.2

[a] Unless noted otherwise, k_2 values were obtained from log $[(a - x)/(b - x)]$ vs time plots in experiments run under second-order conditions, with initial concentrations of both reagents 0.05–0.075 M; data agreeing within ±5% were averaged. [b] $E_a = 12.2 \pm 0.2$ and log $A = 9.8 \pm 0.2$, estimated from log k_2 vs $[(1/T), K^{-1}]$ plot. [c] Run performed under inert gas (Ar) blanket. [d] Rate of oxidation of **4a** by dimethyldioxirane (**1b**); runs performed under pseudo-first-order conditions, with $[\mathbf{1b}]_0 = 0.03$–0.04 M and $[\mathbf{4a}]_0 = 0.80$–1.1 M, allowed to obtain k_1 (s^{-1}) values, and then k_2 values as $(k_1/[\mathbf{4a}]_0)$. [e] Kinetic isotope effect: $(k_H/k_D) = 1.6 \pm 0.15$.

On the grounds of evidence available so far, it seems that the simplest mechanism of alcohol oxidation by dioxiranes would be an "oxenoid"[28] O-atom insertion into the alcohol α C–H bond, perhaps involving a transition state (ts) like I. Here, some radical



I

character might develop. While the O–O bond is being broken, significant widening of the dioxirane O–C–O angle from 60° to nearly 107°[10] and ts asymmetry might serve to relax the energy requirements of the three-centered O-atom insertion, resulting in an increase of the log A term.

Borrowing from the current terminology of biomimetic oxidations, the overall transformation of alcohols R^1R^2CHOH into $R^1R^2C{=}O$, via the geminal diol $R^1R^2C(OH)_2$, amounts to "heteroatom release", as contrasted to simple "carbon

(20) Hemiacetal **13″**: ^1H NMR ($CDCl_3$, 200 MHz) δ 1.21 (t, CH_3CH_2, 3 H, $^2J = 7.07$ Hz), 1.55 (q, CF_3CCH_3, $^3J_{HF} = 1.22$ Hz), and 3.71 (q, 2 H, CH_3CH_2, $^2J = 7.07$ Hz). Cf., CH_3CH_2OH: ^1H NMR ($CDCl_3$, 200 MHz) δ 1.22 (t, 3 H, CH_3CH_2, $^2J = 7.02$ Hz), and 3.69 (q, 2 H, CH_3CH_2, $^2J = 7.02$ Hz). Spectral parameters above refer to $CDCl_3$ solutions containing 5–30% TFP, at 0 °C.

(21) This observation suggests that dioxirane **1a** is also capable of oxidizing hemiacetals; indeed, an investigation concerning oxidation of hemiacetals, acetals, and ethers is now underway in our laboratories.

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hydroxylation" of alkanes.[29] Pursuing the analogy between dioxirane oxidation and enzymatic oxygen transfers,[28-30] one might envisage that—after the ts of the slow step—the formation of the diol $R^1R^2C(OH)_2$ (Scheme I) be mediated by caged radical pairs $||R^1R^2C^{\bullet}-OH\ {}^{\bullet}O-C(CH_3)(CF_3)-OH||$ (II); eventually, even ion pairs $||R^1R^2C^{+}-OH\ {}^{-}O-C(CH_3)(CF_3)-OH||$ (III) might be formed, either from II by in-cage electron transfer or from ts I directly.[31] However, if radicl pairs were involved, one would have to postulate that during the oxidation of cyclobutanol the oxidation and/or recombination of the resulting α-hydroxycyclobutyl radical in the cage (II) occurs faster than ring opening to yield $^{\bullet}CH_2CH_2CH_2CH{=}O$.[22,23] Also, as mentioned above, in the oxidation at hand no hemialdal intermediate (Scheme I), the logical cage recombination product from II or III, could be detected.

Therefore, until discrete evidence is found concerning the intervention of radical pairs either before or prior to the ts of the slow step, Occam's razor demands that one stays with the simplest, one-step mechanism mentioned above.

Concluding Remarks

Formation of side products is a problem that is frequently encountered with oxidation of alcohols by common oxidants of broad scope, such as chromium- or DMSO-based reagents.[2a-4,32] Furthermore, chromium or other metal oxidants require careful handling and disposal, because of the toxicity of their residues. No such difficulties seem to arise in oxidations by dioxiranes, as results reported herein indicate that dioxirane **1a** allows the fast and selective oxidation of alcohols under mild conditions, unencumbered by side-product formation or residue disposal problems. Procedures and product isolation are quite straightforward, since TFP (the reduction product of **1a**) is quite volatile and easily removed. Also, methyl(trifluoromethyl)dioxirane is over 200-fold more effective than dimethyldioxirane (**1b**) in carrying out the title transformation (Table II). It appears, therefore, that the unique characteristics of this new dioxirane should encourage its adoption as a viable alternative to classic reagents[2a] at least in some special cases and applications.

Experimental Section

Equipment. The ^1H and ^{13}C NMR spectra of products and starting materials were obtained by using a Varian Model XL 200 spectrometer, except for the spectra of compounds **8**, **8′**, **9**, and **9′**, which were run by using a Bruker AC 250 instrument (at University of Würzburg). Specific rotations of optically active compounds were determined by using a Perkin-Elmer Model 241 MC spectropolarimeter. Other instrumentation and equipment employed have been described in a previous paper of this series.[18]

Materials. The procedure followed to obtain solutions of methyl(trifluoromethyl)dioxirane (**1a**) and its spectroscopic characterization have been reported.[15,18] Alcohols **2–7** and **10–12** (starting materials) and their products **2′–7′**, **10′**, and **11′** (Table I) as well as solvents were commercial (Aldrich or Fluka) chemicals of the highest available purity; whenever appropriate, they were further purified by standard methods. Cyclohexanol-d_{11} (**4b**) was obtained upon D/H exchange with H_2O. Epoxidation of 3-buten-2-ol (Aldrich) with *m*-chloroperoxybenzoic acid[33] afforded a mixture (60:40, by GC) of *erythro*- and *threo*-3,4-epoxy-2-butanol (**8**),[33,34] in 38% yield (after distillation): bp 34.5–36 °C (3 mmHg) [lit.[35] bp 76–80 °C (45 mmHg)]; $\{^1H\}$ ^{13}C NMR ($CDCl_3$, 50 MHz) δ 18.62 (*erythro*, CH_3), 19.58 (*threo*, CH_3), 43.55 (*erythro*, *C-4*), 45.09 (*threo*, *C-4*), 55.34 (*erythro*, *C-3*), 56.34 (*threo*, *C-3*), 64.79 (*erythro*, *C-2*), 68.10 (*threo*, *C-2*).

(+)-(2*R*,3*S*)-1,2-Epoxy-3-pentanol (**9**) was obtained upon catalytic hydrogenation with H_2 and Rh/Al_2O_3[36,37] of 1,2-epoxy-4-penten-3-ol,[38] in >90% yield: bp 100 °C (20 mmHg); ^1H NMR ($CDCl_3$, 250 MHz) δ 1.04 (t, 3 H, CH_3, J = 7.5 Hz), 1.45–1.76 (complex m, 2 H, *4-H*$_{A'}$, *4-H*$_{B'}$), 1.89 (br s, 1 H, O*H*) 2.75 (*A* of *ABX*, 1 H, *1-H*$_A$, J_{AX} = 4.0 Hz, J_{AB} = −5.1 Hz), 2.83 (*B* of *ABX*, 1 H, *1-H*$_B$, J_{BX} = 2.9 Hz, J_{AB} = −5.1 Hz), 3.03 (*X* of *ABX*, 1 H, *2-H*$_X$, dX ("dt"), J_{BX} = $J_{X,X'}$ = 2.9 Hz, J_{AX} = 4.0 Hz), 3.76 (m, 1 H, *3-H*$_{X'}$, $J_{X,X'}$ = 2.9 Hz, $J_{B'X'}$ = 4.8 Hz, $J_{A'X'}$ = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz)[37] δ 9.41 (q, *C-5*), 26.36 (*t*, *C-4*), 43.44 (t, *C-1*), 54.31 (d, *C-2*), 69.78 (d, *C-3*); IR (film) 3600–3200 (OH), 3050, 2960, 2920, 2870, 1460, 1245, 1060, 970, 875, 730 cm^{-1}; $[\alpha]^{22}_D$ = +19.6° (*c* 1.41, $CDCl_3$), >96% ee by ^1H NMR polarimetry[39] using (+)-Eu(hfc)$_3$ (Aldrich).

Oxidation of Alcohols 1–11. The following procedure is representative: To a stirred solution of epoxy alcohol **9** (0.50 g, 4.9 mmol) in dry CH_2Cl_2 (20 mL) kept at −20 °C is added quickly an aliquot of dioxirane **1a** (standardized solution in TFP;[18] 6.6 mL, 0.92 M, 6.3 mmol). Upon completion of the reaction (15 min, GC monitoring), the solvent mixture is removed at 100–150 mmHg (condensation at −10 °C allows one to recover TFP mixed with CH_2Cl_2);[18] distillation of the residue in vacuo gave (+)-(2*R*)-1,2-epoxy-3-pentanone (**9′**) (0.46 g, 4.5 mmol, yield 92%): bp 85 °C (20 mmHg); ^1H NMR ($CDCl_3$, 250 MHz) δ 0.99 (t, 3 H, CH_3, J = 7.3 Hz), 2.19–2.50 (complex m, 2 H, *4-H*$_{A'}$, *4-H*$_{B'}$), 2.80 (*B* of *ABX*, 1 H, *1-H*$_B$, J_{BX} = 2.5 Hz, J_{AB}, J_{AB} = −5.8 Hz), 2.93 (*A* of *ABX*, 1 H, *1-H*$_A$, J_{AX} = 4.7 Hz, J_{AB} = −5.8 Hz), 3.38 (*X* of *ABX*, 1 H, *2-H*$_X$, J_{AX} = 4.7 Hz, J_{BX} = 2.5 Hz); $\{^1H\}$ ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 6.98 (*C-5*), 30.02 (*C-4*), 46.24 (*C-1*), 53.25 (*C-2*), 208.25 (*C-3*); IR (neat, NaCl) 3450, 3000, 2960, 2895, 1720 (C=O), 1465, 1410, 1380, 1240, 1090, 1040, 970, 915, 875 cm^{-1}; $[\alpha]^{20}_D$ = +61.8° (*c* 5.3, $CDCl_3$), >96% ee by ^1H NMR polarimetry using (+)-Eu(hfc)$_3$. Other products listed in Table I were identified upon comparison of their NMR and MS spectra with those of authentic samples.

Kinetics. The kinetic techniques and procedures followed were identical with those described in detail in a previous paper[18] (see also footnotes, Table II).

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Registry No. 1a, 115464-59-0; **2**, 589-98-0; **2′**, 106-68-3; **3**, 2919-23-5; **3′**, 1191-95-3; **4**, 108-93-0; **4′**, 108-94-1; **4b**, 93131-17-0; **5a**, 497-36-9; **5b**, 497-37-0; **5′**, 497-38-1; **6**, 98-85-1; **6′**, 98-86-2; **7**, 67-63-0; **7′**, 67-64-1; **8** (isomer 1), 119070-12-1; **8** (isomer 2), 85316-62-7; **8′**, 85316-61-6; **9**, 104596-07-8; **9′**, 131792-60-4; **10**, 100-51-6; **10′**, 100-52-7; **10″**, 65-85-0; **11**, 71-36-3; **11′**, 107-92-6; **13** (R^1 = R^2 = Me), 131792-61-5; **13′** (R^1 = Me; R^2 = H), 131792-62-6; $H_3CC(OH)(CF_3)OBu$, 131792-59-1; EtOH, 64-17-5; H_3CCO_2H, 64-19-7; $H_3CCH(OH)CH{=}CH_2$, 598-32-3; 1,2-epoxy-4-penten-3-ol, 100017-22-9; **12**, 75-65-0.

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