Applications of the Peracid-Mediated Oxidation of Alcohols

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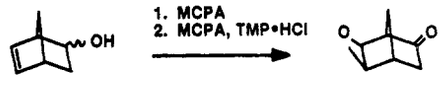
An efficient, general, one-pot procedure for the preparation of epoxy ketones from olefinic alcohols is described. Epoxidation of olefinic alcohols with *m*-chloroperbenzoic acid followed by oxidation of the alcohol with the same reagent in the presence of catalytic amounts of 2,2,6,6-tetramethylpiperidine hydrochloride affords epoxy ketones in excellent yield. Application of this procedure to allylic alcohols bearing bulky substituents in the β position followed by reduction of the resulting epoxy ketones with hydrazine yields the rearranged allylic isomer of the starting alcohol. Epoxy ketones of unhindered allylic alcohols yield diazoles on treatment with hydrazine. Oxidation of secondary alcohols using a large excess of *m*-chloroperbenzoic acid in the presence of 2,2,6,6-tetramethylpiperidine hydrochloride affords esters or lactones via a Baeyer–Villiger oxidation of initially generated ketones.

Alcohols are rapidly and efficiently oxidized to carbonyl compounds by *m*-chloroperbenzoic acid (MCPA) in the presence of catalytic amounts of nitroxide radicals and mineral acids.[2,3] The value of this convenient procedure is amplified when it is combined with the ability of peracids to effect epoxidations and Baeyer–Villiger reactions. This paper describes a number of these applications.

Preparation of Epoxy Ketones. The utility of epoxy ketones in preparative organic chemistry derives from the multitude of predictable transformations achievable when these compounds are manipulated under various conditions.[4] For example, the rearrangement of epoxy ketones can be induced thermally,[5] photochemically,[5,6] and by treatment with acids and bases.[7] Rearrangement products vary with the reaction conditions. Reaction of α,β-epoxy ketones with hydrazine yields allylic alcohols.[8] Fragmentation of the hydrazones from α,β-epoxy ketones and *N*-aminoaziridines affords carbonyl compounds and acetylenes.[9] The oximes of α,β-epoxy ketones are alkylated at the α position by dialkylcopper lithium reagents to yield α-alkylated β-hydroxy ketones.[10] Finally, epoxy ketones can be reduced to diols or β-hydroxy ketones.[11]

In spite of this versatility, no generally applicable method exists for the preparation of epoxy ketones. Direct epoxidation of olefinic ketones with peracids gives rise to complex mixtures of products due to competing Baeyer–Villiger and subsequent epoxidation and/or rearrangement reactions[12]. Epoxidation with basic hydrogen peroxide[13] or *tert*-butyl hydroperoxide[14] is applicable only to the preparation of α,β-epoxy ketones. Moreover, Baeyer–Villiger type cleavage can occur in these reactions in some cases[15] and the stereochemistry of the products is often less predictable than for peracid epoxidations. A third method which can, in principle, be used to prepare any epoxy ketone is epoxidation of an olefinic alcohol followed by oxidation of the resultant epoxy alcohol. A problem with this sequence is the instability of intermediate epoxy alcohols or epoxy ketone products to the conditions of oxidation. This problem is sometimes avoided by use of the chromium trioxide-pyridine complex to oxidize the epoxy alcohol,[16] although epoxide cleavage can occur even under these conditions and low yields have been reported in some cases.[17]

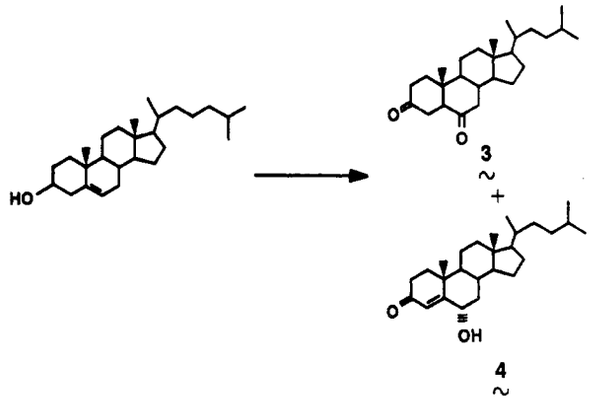
The nitroxide catalyzed oxidation of secondary alcohols by *m*-chloroperbenzoic acid offers a number of advantages for the preparation of epoxy ketones from olefinic alcohols. First, the conditions are mild enough so that epoxide cleavage should not occur. Second, since the peracid used in the oxidation can also be employed in the initial epoxidation, the entire sequence from an olefinic alcohol to an epoxy ketone can be accomplished in a single operation without isolation of the intermediate epoxy alcohol! The feasibility of this process was demonstrated by the one-pot conversion of olefinic alcohol, **1**, to epoxy ketone, **2**.[2] We now report that this method is generally applicable to the preparation of α,β-, β,γ-, and other epoxy ketones.



1 **2**

Experimentally, the epoxidation–oxidation sequence is conducted by addition of MCPA (1 equiv) to a cold solution of an olefinic alcohol in methylene chloride or tetrahydrofuran. When epoxidation is complete (usually 1–2 h), a catalytic amount (2–4 mol %) of 2,2,6,6-tetramethylpiperidine hydrochloride (TMP·HCl) is added followed by a second portion of MCPA (1.5–2.0 equiv). Oxidation is generally complete in 1–2 h at ambient temperature. An extractive workup removes *m*-chlorobenzoic acid and affords the epoxy ketone in excellent yield. Results of application of this sequence to a number of olefinic alcohols are given in Table I.

Application of the epoxidation–oxidation sequence to cholesterol afforded a mixture of diketone, **3**, and keto alcohol, **4**. Presumably, the epoxy ketone is formed, but undergoes acid-catalyzed rearrangement to **3** and **4**. Keto alcohol **4** rearranges to **3** on treatment with acid,[18] so that **3** is the principal product of the reaction if the mixture is allowed to stand for some time prior to workup.



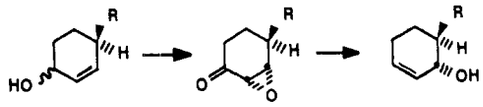
In general, this one-pot epoxidation–oxidation sequence is a convenient, efficient procedure for the preparation of epoxy ketones. The epoxidation–oxidation of allylic alcohols by this procedure affords α,β-epoxy ketones which can undergo reductive cleavage on treatment with hydrazine (Wharton reaction).[8] Since the allylic alcohol derived from this reaction is the isomer of the starting allylic alcohol, the two-step sequence of epoxidation–oxidation followed by the Wharton reaction constitutes a method for the rearrangement of allylic alcohols. Most methods for effecting this transfor-

Table I. Epoxidation–Oxidation of Olefinic Alcohols

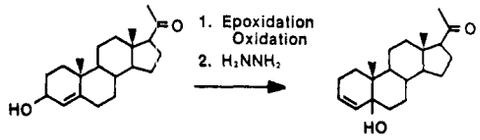
Olefinic alcohol	Epoxy ketone	% yield[a]
5-Norbornen-2-ol	5,6-Epoxy-2-norbornanone	86[b]
2-Cyclohexenol	2,3-Epoxycyclohexanone	61
4-Phenyl-3-buten-2-ol	3,4-Epoxy-4-phenyl-2-butanone	93
1,3-Diphenylpropenol	2,3-Epoxy-3-phenylpropiophenone	81
1-Hexen-3-ol	1,2-Epoxy-3-hexanone	90
2,6-Dimethyl-2-nonen-8-ol	2,3-Epoxy-2,6-dimethyl-8-nonanone	73
4-Pregnen-20-on-3-ol	(α- + β-)4,5-Epoxypregna-3,20-dione	50[c]
4-Methyl-3-penten-2-ol	3,4-Epoxy-4-methyl-2-pentanone	89

[a] Yields are of isolated products. No attempt was made to optimize individual yields. The physical and spectral properties of all products were in accord with their structures (see Experimental Section). [b] Taken from ref 2. [c] Yield determined gas chromatographically.

mation are less direct and rely on the thermodynamic or kinetic properties of the system to determine the predominant isomer.[19] The present method should yield the allylic isomer of the starting alcohol regiospecifically, regardless of the relative stabilities of the two isomers. In rigid systems, moreover, an additional feature of stereochemical control is introduced since the stereochemistry of the alcohol in the final product will be determined by the stereochemistry of the epoxide in the intermediate epoxy ketone.



The feasibility of this two-step sequence for the rearrangement of an allylic alcohol is demonstrated for the alcohol derived from the selective reduction of progesterone (pregn-4-en-20-on-3-ol)[20] (**5** → **6**). While in this case the allylic



5 **6**

transposition proceeded in reasonable yield, results with other systems were disappointing. In most cases, little or no allylic alcohol could be isolated from the reaction of various epoxy ketones with hydrazine.

The proposed mechanism for the Wharton reaction[8] involves hydrazone formation followed by a Wolff–Kishner type elimination of nitrogen with cleavage of the epoxide. An alternate pathway can be envisaged involving attack at the β carbon of the epoxy ketone by hydrazine itself (path A) or intramolecularly, via the hydrazone (path B). In either case, an intermediate, **7**, is produced which does not lose nitrogen,

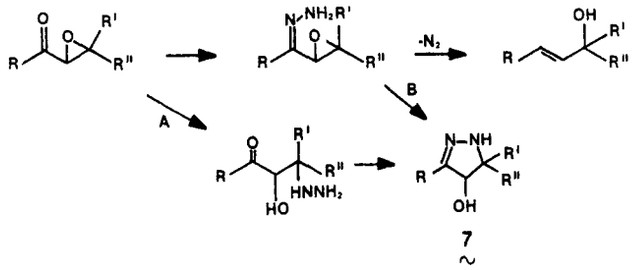


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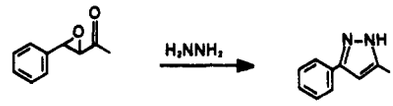
Table II. Hydrazine Reduction of Epoxy Ketones

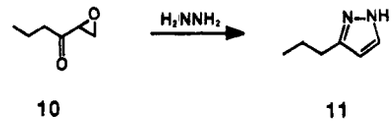
Epoxy ketone	Method[a]	Yield of N_2 evolved
Isophorone oxide	B[b]	89
4,5-Epoxypregna-3,20-dione	A	90
2,3-Epoxycyclohexanone	B[b]	75
4-Phenyl-3,4-epoxy-2-butanone	A	60
1,2-Epoxy-3-hexanone	A	50
2,3-Epoxy-3-phenylpropiophenone	A	27
Glycidaldehyde	B[b]	20

[a] See Experimental Section for details. In each case, the method reported is that which gave the best yield. [b] Taken from ref 8.

hence does not produce an allylic alcohol. Table II reveals the yield of nitrogen evolved when several epoxy ketones are subjected to the Wharton reaction. These results indicate that as the degree of substitution at the β carbon increases, the yield of gas evolved increases. This is consistent with the proposed formation of **7** as a competitive process in those cases where attack at the β carbon is unencumbered. This postulate is further substantiated by the isolation of diazoles **9** and **11** from the Wharton reaction of epoxy ketones **8** and **10**. These derivatives presumably arise via loss of water from intermediate **7**.



8 **9**



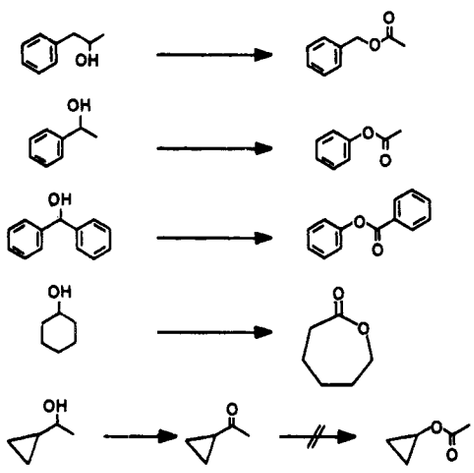
10 **11**

This two-step allylic transposition is thus limited to those allylic alcohols having a highly substituted β carbon.

Preparation of Esters and Lactones from Secondary Alcohols. The Baeyer–Villiger cleavage of ketones by peracids finds importance both as a preparative method and as a degradative reaction for the identification of unknowns.[21] While under ordinary conditions this reaction does not interfere with the nitroxide catalyzed oxidation of alcohols, more forcing conditions will enable both processes to occur.[2] This combination of alcohol oxidation followed by Baeyer–Villiger reaction constitutes a method for the degradation of secondary alcohols, since the net result of the process is cleavage of a carbon–carbon bond at the site of the initial alcohol function.[22] Moreover, since both reactions employ peracid as the oxidant, the overall cleavage can be effected as a one-pot operation.

Since the Baeyer–Villiger reaction requires more severe conditions than those employed in the alcohol oxidation, an attempt was made to optimize the two-step sequence by employing more reactive peracids such as trifluoroperacetic[23] and permaleic[24] acids, which are known for their efficacy in the Baeyer–Villiger reaction. Unfortunately, these peracids are rapidly decomposed by the nitroxide catalyst and are ineffective in the alcohol oxidation.[25] The sequence can be conducted using MCPA, provided that a large excess (3.5–4.0 equiv) is employed. Thus, treatment of phenyl-2-propanol with 4 equiv of MCPA and a catalytic amount (3 mol %) of TMP·HCl in methylene chloride for 5 h afforded benzyl acetate in 90% yield. In some cases these conditions were insuf-

ficient and longer reaction times, higher temperatures, or both were required to effect the oxidation. For example, the conversion of diphenylcarbinol to phenyl benzoate required heating the reactants at 90 °C for 18 h in a sealed bottle. Even under these forcing conditions, cyclopropylmethylcarbinol was oxidized only as far as the ketone.[26] Typical results for this process are given below. These results demonstrate the feasibility of this one-pot procedure for the degradation of secondary alcohols.



Experimental Section[27]

The starting alcohols used in this study were obtained as follows: 5-norbornen-2-ol, 2-cyclohexen-1-ol, hexen-3-ol, 4-methyl-3-penten-2-ol, and cholesterol were obtained commercially. Cyclohexanol, benzhydrol, 1-phenylethanol, and phenyl-2-propanol were obtained by lithium aluminum hydride reduction of the corresponding ketones. 4-Pregnen-20-on-3-ol was obtained by the selective reduction of progesterone with diborane.[20] 4-Phenyl-3-buten-2-ol was obtained from the reaction of methyllithium with *trans*-cinnamaldehyde. 1,4-Diphenyl-2-propen-1-ol was obtained from the reaction of phenylmagnesium bromide with *trans*-cinnamaldedyde. 2,6-Dimethyl-2-nonen-8-ol was prepared by the reaction of methyllithium with citronellal.

Representative Procedure for the Preparation of Epoxy Ketones. *exo*-5,6-Epoxy-2-norbornanone (2). To a stirred, ice-chilled solution of 2.20 g (20 mmol) of 5-norbornen-2-ol (1) in 5 mL of methylene chloride was added a solution of 4.3 g (21 mmol) of 85% *m*-chloroperbenzoic acid in 50 mL of methylene chloride. Analysis of the reaction mixture after 2 h revealed that all of the starting material had reacted. To the resultant mixture was added 1 mL (0.2 mmol) of a 0.2 M solution of TMP·HCl in methylene chloride, followed by an additional 5.3 g (26 mmol) of MCPA in 50 mL of methylene chloride. After 1.5 h the mixture was transferred to a separatory funnel and worked up as usual. The residue was sublimed to afford 2.1 g (86%) of pure **2** whose melting point and infrared spectrum correlate with those reported:[17b] mass spectrum *m/e* (rel intensity) 124 (M^+, 24.4), 106 (2.6), 96 (24.0), 95 (43.0), 82 (77.6), 81 (100), 68 (52.8), 67 (57.1), 41 (38.9), 39 (56.4).

The following epoxy ketones were prepared using the above procedure.

2,3-Epoxycyclohexanone was obtained as an oil, bp 87 °C (15 mm), IR 5.85 μ (ν C=O).

3,4-Epoxy-4-phenyl-2-butanone was obtained as an oil which crystallized on standing. Recrystallization from hexane afforded the pure epoxy ketone: mp 52–54 °C; NMR (CCl_4) δ 2.03 (s, 3, $COCH_3$), 3.28 (d, 1, J = 1 Hz, COCH), 3.90 (d, 1, J = 1 Hz, COCH), and 7.19 ppm (s, 5, ArH); mass spectrum *m/e* (rel intensity) 162 (M^+, 32.7), 120 (41.3), 91 (100), 90 (28.7), 89 (36.4).

2,3-Epoxy-3-phenylpropiophenone was obtained as an oil which crystallized on standing: NMR (CCl_4) δ 3.98 (d, 1, COCH), 4.10 (d, 1, CCH), 7.32 and 7.90 ppm (m, 10, ArH); mass spectrum *m/e* (rel intensity) 224 (M^+, 12.3), 208 (26.9), 207 (42.1), 131 (10.6), 105 (100), 89 (15.2), 77 (57.1).

1,2-Epoxy-3-hexanone was obtained as an oil: NMR (CCl_4) δ 0.92 (t, 3, CH_2CH_3), 1.55 and 2.31 (m, 4, CH_2CH_2), 2.90 (m, 2, $COCH_2$), and 3.35 ppm (m, 1, $RCHOCH_2$).

2,3-Epoxy-2,6-dimethyl-8-nonanone was obtained as an oil: NMR (CCl_4) δ 0.90 (d, 3, $CHCH_3$), 1.20 and 1.23 [s, 3, $COC(CH_3)_2$], and 2.08 ppm (s, 3, $COCH_3$), no vinyl Hs.

4,5-Epoxypregna-3,20-dione was obtained as a white solid after chromatography over silica gel, mp 120–123 °C. This material was identical with the epoxy ketone obtained from the reaction of progesterone with basic hydrogen peroxide.[28]

3,4-Epoxy-4-methyl-2-pentanone was obtained as a colorless liquid: bp 60–65 °C (20 mm); NMR (CCl_4) δ 1.27 (s, 3, $COCCH_3$), 1.40 (s, 3, $COCCH_3$), 2.14 (s, 3, $COCH_3$), and 3.22 ppm (s, 1, COCHOC).

Epoxidation–Oxidation of Cholesterol. To a stirred, ice-chilled mixture of 1.17 g (3 mmol) of cholesterol and 10 mL of methylene chloride was added a solution of 0.66 g (3.14 mmol) of MCPA in 6 mL of methylene chloride. After 2 h an additional 0.90 g (4.28 mmol) of MCPA in 9 mL of methylene chloride plus 0.3 mL of 0.1 M solution of TMP·HCl in methylene chloride were added. The resultant mixture was stirred for 18 h at room temperature, then worked up in the usual fashion to yield 1.0 g of a viscous residue which was chromatographed on 40 g of alumina (elution with chloroform) to afford 0.43 g of a white solid whose infrared spectrum exhibited two carbonyl absorptions. Fractional crystallization of this material (acetone–water) afforded pure **3** [mp (acetone–H_2O) 168–170 °C (lit.[18] mp 169–170 °C); IR 5.84 μ (ν C=O); mass spectrum *m/e* (rel intensity) 400 (M^+, 95.5), 385 (12.4), 287 (50.6), 245 (100), 231 (32.6)] and 4 [mp (CH_2Cl_2–ligroin) 154–155 °C (lit.[29] mp 156 °C); IR 2.98 (ν OH) and 6.00 (ν C=O); UV λ_{EtOH} (max) 237 nm; mass spectrum *m/e* (rel intensity) 400 (M^+, 80.4), 385 (17.1), 382 (13.7), 331 (100), 287 (18.0), 245 (32.7), 231 (11.5)].

Hydrazine Reduction of Epoxy Ketones. The epoxy ketones were allowed to react with hydrazine according to the procedures of Wharton et al.[8] Two techniques were employed. Method A. Hydrazine hydrate was added to a solution of the epoxy ketone, neat, and the mixture was heated (60–90 °C) until gas evolution ceased. Method B. Hydrazine hydrate was added to a solution of the epoxy ketone in ethanol containing 10–15% acetic acid by weight. The yield of gas evolved in each case is given in Table II.

Reduction of 4,5-Epoxypregna-3,20-dione. 4,5-Epoxypregna-3,20-dione (1.1 g, 3.3 mmol) was treated neat with 4 mL of 85% hydrazine hydrate at 90 °C. Gas evolution was 90% complete in 10 min. Following an extractive workup, the crude product was chromatographed on silica gel (hexane–ethyl acetate). The major component was crystallized from aqueous ethanol to yield pure **6**: mp 220–224 °C; mass spectrum *m/e* (rel intensity) 316 (M^+, 2.4), 298 (74.0), 254 (34.8).

Reduction of 3,4-Epoxy-4-phenyl-2-butanone. 3,4-Epoxy-4-phenyl-2-butanone (2.43 g, 15 mmol) in 20 mL of ethanol plus 0.12 mL of acetic acid was treated with 2.0 g of hydrazine hydrate (35 mmol). Gas evolution was complete in 5 min. Following an extractive workup, the crude residue (0.8 g) was purified by preparative thin layer chromatography (silica gel G, 4:2:1 C_6H_6–$CHCl_3$–EtOAc). The major component was identified as diazole **9**: NMR (CCl_4) δ 2.20 (s, 3, $ArCH_3$), 6.23 (s, 1, ArH), 7.30 and 7.60 (m, 5, PhH), and 10.33 ppm (s, 1, NH); mass spectrum *m/e* (rel intensity) 158 (M^+, 100), 157 (44.4), 130 (13.5), 128 (21.6), 77 (32.2).

Reduction of 1,2-Epoxy-3-hexanone. 1,2-Epoxy-3-hexanone (0.57 g, 5 mmol) in 0.5 mL of ethanol was treated with 2.0 mL of hydrazine hydrate at room temperature. Gas evolution was complete in 5 min and was not increased by further heating. The residue obtained after an extractive workup was a mixture of at least two major components (TLC). The gas chromatogram (10% Carbowax 1540 on 40/60 mesh Chromosorb T) of this mixture exhibited only one peak. This component was identified by its mass spectrum as the diazole **11**. The crude product is apparently a mixture of the diazole, **11**, and its hydrated analogue (**7**, R = C_3H_7; R′ = R″ = H). Loss of water from the hydrated analogue occurs in the injector port to produce **11** as the only eluted peak. The mass spectrum of the eluted peak exhibited a fragmentation pattern analogous to that of diazole **9**: mass spectrum *m/e* (rel intensity) 110 (M^+, 30.8), 95 ($M - CH_3$, 21.1), 82 (96.2), 81 (100), 68 (5.0).

Oxidation. Baeyer–Villiger Reactions. Method A. Preparation of Benzyl Acetate. A solution of 2.72 g (20 mmol) of phenyl-2-propanol, 16.0 g (80 mmol) of MCPA, and 4.0 mL of 0.1 M TMP·HCl in 150 mL of methylene chloride was stirred for 5 h at room temperature (the reaction was slightly exothermic at first). The usual workup afforded 2.7 g (90%) of pure benzyl acetate: NMR (CCl_4) δ 2.00 (s, 3, O_2CCH_3), 5.02 (s, 2, $ArCH_2O$), and 7.27 ppm (s, 5, ArH).

ϵ-Caprolactone was prepared similarly from cyclohexanol.

Method B. A solution of 0.92 g (5 mmol) of diphenylcarbinol, 4.2 g (20 mmol) of MCPA, and 1.0 mL of 0.1 M TMP·HCl in 40 mL of methylene chloride was stirred at room temperature for 1 h to oxidize the alcohol to the ketone. The vial was then sealed and immersed in

an oil bath at 100 °C. After 18 h the vial was removed from the bath and allowed to reach room temperature. The usual workup afforded, after chromatography (silica gel, 2:1 C_6H_6–hexane), 0.53 g (53.5%) of pheryl benzoate, crystals from hexane, mp 68–69 °C (lit.[29] mp 71 °C).

Phenyl acetate was prepared in a similar fashion from 1-phenylethanol.

Registry No.—**1**, 13080-90-5; **2**, 55044-07-0; **3**, 13492-22-3; **4**, 570-90-1; **5**, 566-66-5; 5β-**6**, 61990-52-1; 5α-**6**, 61990-53-2; **8**, 6249-79-2; **9**, 3347-62-4; **10**, 61990-54-3; **11**, 7231-31-4; 2,3-epoxycyclohexanone, 6705-49-3; 2,3-epoxy-3-phenylpropiophenone, 5411-12-1; 2,3-epoxy-2,6-dimethyl-8-nonanone, 61990-55-4; α-4,5-epoxy-3,20-dione, 17503-05-8; β-4,5-epoxy-3,20-dione, 17597-24-9; 3,4-epoxy-4-methyl-2-pentanone, 4478-63-1; cholesterol, 57-88-5; benzyl acetate, 140-11-4; phenyl-2-propanol, 698-87-3; diphenylcarbinol, 91-01-0; phenyl benzoate, 93-99-2; 2-cyclohexenol, 822-67-3; 4-phenyl-3-buten-2-ol, 17488-65-2; 1,3-diphenylpropenol, 4663-33-6; 1-hexen-3-ol, 4798-44-1; 2,6-dimethyl-2-nonen-8-ol, 40596-76-7; 4-methyl-3-penten-2-ol, 4325-82-0.

References and Notes

(1) Address to which correspondence should be sent: General Electric Co., Research & Development Center, P.O. Box 8, Bldg. K-1, Room 5A20, Schenectady, N.Y. 12301.
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(26) Cyclopropyl methyl ketone is particularly unreactive in the Baeyer–Villiger reaction, but can be oxidized by trifluoroperacetic acid (ref 23).
(27) Melting points were determined on a Thomas-Hoover melting point apparatus. Infrared spectra were recorded on a Beckman IR-5A spectrophotometer using sodium chloride disks or potassium chloride pellets. Mass spectra were determined on an LKB 9000 gas chromatograph–mass spectrometer system operated with an accelerating voltage of 3.5 kV, an ionizing current of 60 μA, an electron energy of 70 eV, and an ion source temperature of 250 °C or on a Hewlett-Packard 5982 A gas chromatograph–mass spectrometer system with an ion source temperature of 180 °C, ionizing current 0.15 μA, and an electron energy of 70 eV. Aliquots of crude reaction and isolated products were monitored using gas chromatographic columns described below. Gas chromatography was performed on a Varian 2700 gas chromatograph equipped with a FID detector using 6 ft × 0.25 in. glass columns: column A, 3% OV-1 on 80/100 mesh Supelcoport; column B, 5% Carbowax 1540 on 40/60 mesh Chromosorb T. The phrase "worked up in the usual fashion" means that the organic phase was washed successively with 1.0 M NaOH, water, and brine, then dried by passage through a cone of anhydrous sodium sulfate.
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Reevaluation of the Use of Peroxycamphoric Acid as an Asymmetric Oxidizing Agent

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The usual method for preparation of monopercamphoric acid for asymmetric synthesis is shown to afford significant quantities of two isomers giving opposite stereochemical senses of asymmetric induction. One of the isomers can be obtained crystalline and use of this single isomer for asymmetric induction leads to optical yields of chiral sulfoxides, epoxides, and oxaziridines 50–100% greater than previously reported to result from use of the mixed isomers. In one of the more favorable cases, 2-*tert*-butyl-3-(*p*-bromophenyl)oxaziridine (**4**) was obtained in 60% enantiomeric excess using the crystalline peracid.

In recent years, a monoperoxycamphoric acid (MPCA) ascribed structure **1** has found use as a chiral oxidant for the asymmetric syntheses of chiral sulfoxides,[1–3] epoxides,[3–6] and oxaziridines.[3,7–9] In most instances, the degree of asymmetric induction afforded by MPCA is rather low. In this paper, we report an experimental modification that substantially increases the optical yields of products afforded by oxidation with MPCA.

Ordinarily, MPCA is prepared by reaction of camphoric anhydride with hydroperoxide ion, as originally described by Milas and McAlevy.[10] So far as can be ascertained from most published procedures ,the MPCA used for asymmetric synthesis is isolated via an extractive workup and does not appear to be purified further (apart from drying and iodometric standardization) before use *even though Milas and McAlevy originally reported it to be a crystalline solid.* Use of the unpurified extract is tantamount to a general de facto assumption that MPCA **1** is the only significant peracid in the