m); IR (neat) 1720 cm^{-1}; exact mass calcd for $C_{20}H_{35}NO_4$ 353.2564, found 353.2551.

Synthesis of *tert*-Butyl 3-Oxooctanoate (6) from 1 and *N,N*-Dimethylhexanamide (5). The reaction was carried out as in the general procedure except that the reaction was quenched with triethylamine (1 mL) to give **6** (30% yield).

6: ^1H NMR δ 0.7–1.0 (3 H, m), 1.0–1.8 (6 H, m), 1.45 (9 H, s), 2.52 (2 H, t, J = 7 Hz), 3.32 (2 H, s); IR (neat) 1750–1710, 1640 cm^{-1}.

Acknowledgment. We thank Mr. Y. Nobayashi for his assistance.

Registry No. **2a**, 4783-65-7; **2b**, 28737-46-4; **2c**, 95936-18-8; **2d**, 872-50-4; **2e**, 5291-77-0; **2f**, 40296-20-6; **2g**, 95936-19-9; **2h**, 33241-96-2; **3a**, 95936-20-2; **3b**, 95936-21-3; **3c**, 95936-22-4; **3d**, 78167-70-1; **3e**, 95936-23-5; **3f**, 95936-24-6; **3g**, 95936-25-7; **3h**, 95936-26-8; **4b**, 95936-27-9; **5**, 5830-30-8; **6**, 66720-07-8; *tert*-butyl acetate, 540-88-5.

Catalytic Asymmetric Synthesis of Chiral 4-Substituted 2-Oxetanones

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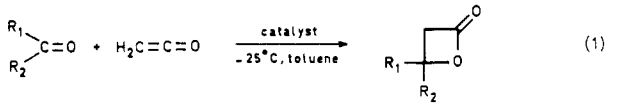
Although 2-oxetanones are generally regarded as useful starting materials in synthesis[1] and polymerization,[2] relatively few preparations of optically active 2-oxetanones have been described. The published procedures usually consist of the ring closure of optically active β-functionalized carboxylic acid derivatives,[3] the latter obtained by resolution.[4]

The high chemical and enantiomeric yields in the C–C bond-forming reaction of ketene and chloral,[5] catalyzed by chiral tertiary amines, to produce the chiral 4-(trichloromethyl)-2-oxetanone, prompted us to investigate the reaction of other carbonyl compounds with ketene.

Table I lists the results of the reaction of some chlorinated aldehydes and ketones with ketene. The reactions were run according to the general scheme in eq 1 by



(1)

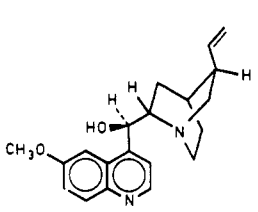
bubbling gaseous ketene through a toluene solution of the aldehyde or ketone and 1–2 mol % of the chiral catalyst at temperatures, depending on the substrate, between −25 °C and −50 °C.

Table I

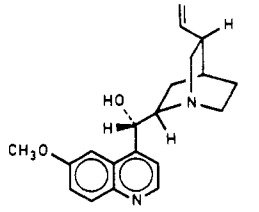
R_1	R_2	% ee *a*	% ee *b*	c.y., %
CCl_3	H	98	76	89
CCl_2H	H	45		67
CCl_2CH_3	H	91	76	95
$CCl_2CH_2CH_3$	H	89	70	87
$CCl_2C_6H_5$	H	90	68	89
CCl_3	CH_3	94	85	72
CCl_3	CH_2CH_3			1–2
CCl_3	C_6H_5			
CCl_3	C_6H_4Cl-*p*	90	65	68
CCl_3	$C_6H_4NO_2$-*p*	89	65	95

[a] Catalyst is quinidine. [b] Catalyst is quinine.

The cinchona alkaloids quinidine and quinine are used as standard catalysts. In all cases these two alkaloids give



quinine



quinidine

products with opposite signs of rotation and therefore opposite absolute configuration. Both chemical and enantiomeric yields are high in this reaction.

An important factor determining the rate of the reaction between the aldehydes and ketones seems to be the polarization of the carbonyl group. The effect of the polarization is shown nicely in the series of trichloroacetophenones. The parent compound α,α,α-trichloroacetophenone did not react with ketene to give a 2-oxetanone under a wide range of reaction conditions. If an electron-withdrawing substituent is introduced into the phenyl ring the reaction to form the 2-oxetanone does occur. Under more drastic conditions (high concentrations, excess ketene), the 2-oxetanone of *p*-chloro-α,α,α-trichloroacetophenone could be isolated in 68% chemical yield, along with some starting material. A more powerful electron-withdrawing substituent such as NO_2 leads to a quantitative conversion of the acetophenone, under standard conditions, to the 2-oxetanone. The enantiomeric purities of the two adducts are the same. No differences in the reaction rate could be observed for the chlorinated aldehydes. Monochlorinated aldehydes do not react with ketene. 1,1,1-Trichloroacetone reacts considerably slower with ketene than do the aldehydes. Excess ketene and higher concentrations are necessary to obtain satisfactory yields. The ketene adduct of 1,1,1-trichlorobutan-2-one could be isolated in trace amounts.

The absolute configuration of the 4-(trichloromethyl)-2-oxetanone, derived from ketene and chloral, was correlated to malic acid.[5] The original assignment of the *S* configuration to the 2-oxetanone yielding (*S*)-malic acid is erroneous.[6] During conversion to malic acid inversion takes place at the chiral center and the starting 2-oxetanone must therefore be of *R* configuration.[6]

To determine the absolute configuration of some of the other 2-oxetanones, their CD spectra were compared.

(1) Fujisawa, T.; Sato, T.; Kawara, T.; Noda, A.; Obinata, T. *Tetrahedron Lett.* **1980**, *21*, 2553. Sato, T.; Kawara, T.; Kawashima, M.; Fujisawa, T. *Chem. Lett.* **1980**, 571. Cannone, P.; Foscolos, G. B.; Bélanger, D. *J. Org. Chem.* **1980**, *45*, 1828. Mulzer, J.; Kerkmann, T. *J. Am. Chem. Soc.* **1980**, *102*, 3620. Normant, J. F.; Alexalis, A.; Cahiez, G. *Tetrahedron Lett.* **1980**, *21*, 935. Fujisawa, T.; Mori, T.; Kawara, T.; Sato, T. *Chem. Lett.* **1982**, 569. Sato, T.; Naruse, K.; Fujisawa, T. *Tetrahedron Lett.* **1982**, *23*, 3587.

(2) Teranishi, K.; Iida, M.; Araki, T.; Yamashita, S.; Tani, H. *Macromolecules* **1974**, *7*, 421. Iida, M.; Araki, T.; Teranishi, K.; Tani, H. *Macromolecules* **1977**, *10*, 275. Bigdeli, E.; Lenz, R. W. *Macromolecules* **1978**, *11*, 493. Chatani, Y.; Yokouchi, M.; Tadokoro, H. *Macromolecules* **1979**, *12*, 822. Grenier, D.; Prud'homme, R. E.; Leborgne, A.; Spassky, N. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1781.

(3) Blume, R. C. *Tetrahedron Lett.* **1969**, *13*, 1047. Mulzer, J.; Pointer, A.; Chucholowski, A.; Brüntrup, G. *J. Chem. Soc., Chem. Commun.* **1979**, 52. Adam, W.; Baeza, J.; Liu, J.-C. *J. Am. Chem. Soc.* **1972**, *94*, 2000. Merger, F. *Chem. Ber.* **1968**, *101*, 2413.

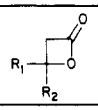
(4) Sato, T.; Kawara, T.; Nishizawa, A.; Fujisawa, T. *Tetrahedron Lett.* **1980**, *21*, 3377. Grenier, D.; Prud'homme, R. E.; Leborgne, A.; Spassky, N. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1781.

(5) Wynberg, H.; Staring E. G. J. *J. Am. Chem. Soc.* **1982**, *104*, 166.

(6) Wynberg, H.; Staring, E. G. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1181.

0022-3263/85/1950-1977$01.50/0

Table II



R_1	R_2	concn,[a] mol/L	UV, ϵ (λ_{max}, nm)	CD, [θ] (λ_{max}, nm)
CCl_3	H	9.25×10^{-3}	158 (206)	2260 (211)
CCl_2H	H	7.29×10^{-3}	107 (203)	1000 (209)[b]
CCl_2CH_3	H	11.24×10^{-3}	103 (201)	2300 (211)
$CCl_2CH_2CH_3$	H	8.27×10^{-3}	146 (201)	2270 (209)[c]
CCl_3	CH_3	6.90×10^{-3}	206 (205)	3260 (196)

[a] Solvent cyclohexane. [b] 45% ee. [c] 89% ee.

Table II lists the UV and CD data for these compounds. CD spectra were run on optically pure compounds from reactions using quinidine as a catalyst. Optically pure compounds can be obtained by crystallization from a suitable solvent. The CD and UV absorption stems from the n–π^* transitions of the carbonyl group, which is in the 200–220-nm region, characteristic for esters and lactones. The CD spectra of the 2-oxetanones containing an aromatic ring were useless for configurational assignment because of the strong absorption of the aromatic system in the 200–220-nm region.

As can be seen from Table II, all of the recorded CD spectra of the 2-oxetanones show the same positive CD effect. The conformational rigidity of the 2-oxetanone system justifies the conclusion that the positive CD effects in all cases are solely due to the fact that the 2-oxetanones have identical absolute configurations at the chiral center. Since the 4-(trichloromethyl)-2-oxetanone obtained from the quinidine-catalyzed reaction is shown to have the *R* configuration, the other 2-oxetanones from this reaction must also have *R* configurations. The 2-oxetanones obtained from reactions using quinine as a catalyst must therefore be of *S* configuration. To our knowledge this is the first example of assignment of absolute configuration of 2-oxetanones by CD measurement.

We would like to draw attention to the 2-oxetanone resulting from the addition of ketene to trichloroacetone. The hydrolysis product, namely, (*R*)- or (*S*)-2-hydroxy-2-methylsuccinic acid[12] (citramalic acid) is a valuable isoprenoid (C_5) chiral synthon.[13]

Experimental Section

General Methods. All solvents were dried and purified by distillation according to literature procedures. Ketene was produced using a ketene lamp as described by Williams and Hurd.[7] Residual acetone vapors were removed as thoroughly as possible by cooling the vapors to −40 °C. All ketene reactions were performed under an inert atmosphere of dried N_2. Chloral and dichloroacetaldehyde (as its diethyl acetal) were purchased from Aldrich. Trichloroacetone was prepared by a combination of the methods of Wyman[8] and of Bańkowska.[9]

α,α-Dichloro aldehydes were prepared by the method published by de Buyck.[10] Trichloroacetophenone and derivatives were prepared by direct chlorination according to the method by Gauthier.[11]

^{1}H NMR spectra were recorded on a Hitachi-Perkin-Elmer R-24B high Resolution NMR spectrometer using $CDCl_3$ as a solvent and Me_4Si as internal standard. Chemical shifts are in ppm relative to Me_4Si. IR spectra were recorded on a Perkin-Elmer 257 grating infrared spectrophotometer. Optical rotations were measured on a Perkin-Elmer 241 polarimeter.

Enantiomeric excesses were determined by integrating ^{13}C and/or ^{19}F NMR signals of diastereomers. For ^{13}C NMR determination diastereomeric amides were prepared by reaction of the 2-oxetanones with optically pure *l*-α-phenylethylamine in CH_3CN. ^{13}C NMR spectra were run on a Nicolet NT-200 spectrometer. For ^{19}F NMR determination diastereomers were prepared by reaction of the corresponding methyl esters of the 3-hydroxy carboxylic acids with (−)-α-methoxy-α-(trifluoromethyl)-phenylacetic acid chloride (Mosher's reagent). ^{19}F NMR spectra were recorded on a Varian XL-100 spectrometer. All CD spectra were recorded on a Jobin Ivon auto dichrograph Marc V, using cyclohexane (Merck, Uvasol quality) as a solvent.

Melting points were determined on a Mettler FP-2 melting point apparatus using a Mettler FP-21 microscope. Melting points are uncorrected.

General Procedure for 2-Oxetanones. For 4-(Trichloromethyl)-2-oxetanone, see ref 5.

4-(1,1-Dichloroethyl)-2-oxetanone. In a 250-mL three-necked flask, equipped with a thermometer and ketene inlet tube, was dissolved 389 mg of quinidine (1.2 mmol) in a mixture of 150 mL of toluene and 13.4 g (105 mmol) 2,2-dichloropropionaldehyde. At −25 °C about 1 equiv of ketene was bubbled through the solution (about 30 mmol/h). The reaction was stopped and after warming to room temperature, the catalyst was removed by acid washing (3 × 30 mL of 4 N HCl). After drying over $MgSO_4$ and removal of the solvent under reduced pressure, the crude product was purified by flash chromatography (SiO_2/CH_2Cl_2) and distillation (bulb-to-bulb, bp 90 °C (0.5 mmHg)): isolated yield 16.2 g (96%); $[\alpha]^{RT}_{578}$ +19.7° (*c* 1, cyclohexane), corresponding to an enantiomeric excess of 91%. Crystallization of 16.0 g from methylcyclohexane yielded 12.5 g (77%) of 2-oxetanone: $[\alpha]^{RT}_{578}$ +21.5° (*c* 1, cyclohexane), optically pure; mp 51.1–51.2 °C. Quinine, used as a catalyst, gave a product: $[\alpha]^{RT}_{578}$ −16.3° (*c* 1, cyclohexane), 76% ee; IR 1845 cm^{-1} (C=O) 2-oxetanone; ^{1}H NMR 2.2 (3 H, s, CH_3), 3.6 (2 H, d, CH_2), 4.6 (1 H, t, CH).

Anal. Calcd for $C_5H_6O_2Cl_2$: C, 35.53; Cl, 41.95; H, 3.58. Found: C, 35.36; Cl, 41.43; H, 3.57.

4-(1,1-Dichloropropyl)-2-oxetanone. From 15.1 g (107 mmol) of 1,1-dichlorobutyraldehyde in 150 mL of toluene, using quinidine at −25 °C, 17.0 g (93 mmol, 87%, bp 100 °C (0.5mmHg)) of 4-(1,1-dichloropropyl)-2-oxetanone could be isolated; $[\alpha]^{RT}_{578}$ +18.9° (*c* 1, cyclohexane) corresponding to an enantiomeric excess of 89%. When the reaction using quinine as a catalyst was run, the product shows $[\alpha]^{RT}_{578}$ −14.8 (*c* 1, cyclohexane), 69% ee: IR 1840 cm^{-1} (C=O), 2-oxetanone; ^{1}H NMR δ 1.2 (3 H, t, CH_3), 2.2 (2 H, m, CH_2), 3.6 (2 H, d, CH_2CO), 4.7 (1 H, t, CH).

4-(Dichloromethyl)-2-oxetanone. With use of the method as published for the addition of chloral, 913 mg (8.1 mmol) of dichloroacetaldehyde, using quinidine as a catalyst in 25 mL toluene at −50 °C, yielded 840 mg (5.4 mmol, 67%) of 4-(dichloromethyl)-2-oxetanone, $[\alpha]^{RT}_{578}$ −1.2° (*c* 3, toluene), corresponding to an enantiomeric excess of 45% (bp 100 °C (0.1 mmHg)): IR 1840 cm^{-1} (C=O) 2-oxetanone; ^{1}H NMR δ 3.5 (2 H, m, CH_2), 4.6 (1 H, m, CH), 5.9 (1 H, d, $CHCl_2$).

4-Methyl-4-(trichloromethyl)-2-oxetanone. Trichloroacetone (10 g, 62 mmol) was reacted with ketene in 10 mL of toluene. With excess ketene (3-fold) and 400 mg (1.2 mmol) of quinidine as a catalyst at −25 °C, 9.1 g (45 mmol) of 2-oxetanone

(7) Williams, J. W.; Hurd, C. D. *J. Org. Chem.* **1940**, *5*, 122.
(8) Wyman, D. P.; Kaufman, P. R. *J. Org. Chem.* **1964**, *29*, 1956.
(9) Bańkowska, Z.; *Rocz. Chem.* **1958**, *32*, 739; *Chem. Abstr.* **1959**, *53*, 4117.
(10) de Buyck, L.; Verhi, R.; De Kimpe, N.; Courtheyn, D.; Schamp, N. *Bull. Soc. Chem. Belg.* **1980**, *89*, 441.
(11) Gautier, H. *Justus Liebigs Ann. Chim.* **1888**, *14*, [6], 337.
(12) Conversion of the 2-oxetanones to optically pure β-hydroxy carboxylic acids and derivatives[5,6] will be the subject of a subsequent publication.
(13) Patent pending: Wynberg, H.; Staring, E. G. J. PCT/NL 83/00040.

could be isolated (72%, bp 120 °C (0.1 mmHg)): $[\alpha]^{RT}_{578}$ +6.20° (c 2, EtOH, 96%), corresponding to an enantiomeric excess of 94% (R enantiomer). Quinine as a catalyst gave the S enantiomer in 85% ee: IR 1840 cm^{-1} (C=O) 2-oxetanone; ^1H NMR δ 2.0 (3 H, s, CH_3), 3.5 (2 H, dd, CH_2). Recrystallization of reaction products from the quinidine and quinine reaction from a suitable quantity of methylcyclohexane, by cooling to 4 °C, gave both the R and the S enantiomer, enantiomerically pure, $[\alpha]^{RT}_{578}$ +6.57° (c 2, EtOH, 96%) (R enantiomer), mp 40–41 °C.

Anal. Calcd for $C_5H_5O_2Cl_3$: C, 29.52; Cl, 52.28; H, 2.48. Found: C, 29.20f Cl, 52.28; H, 2.43.

4-(Dichlorophenylmethyl)-2-oxetanone. In 50 mL of toluene, 3.1 g (16.5 mmol) of (dichlorophenyl)acetaldehyde was reacted with ketene, using 79 mg (0.2 mmol) of quinidine as a catalyst at −25 °C. After workup 3.4 g (14.7 mmol) of the 2-oxetanone could be isolated (89%, bp 100 °C (0.1 mmHg)), $[\alpha]^{RT}_{578}$ −35.7° (c 1, EtOH, 96%), corresponding to an enantiomeric excess of 90%. Quinine in the same reaction gave a product, $[\alpha]^{RT}_{578}$ +27.0° (c 1, EtOH, 96%), corresponding to an enantiomeric excess of 68%. Recrystallization of 3.1 g of a portion, $[\alpha]^{RT}_{578}$ −35.7°, from methylcyclohexane yielded 1.9 g of a crystalline product, $[\alpha]^{RT}_{578}$ −39.5° (c 1, EtOH, 96%), optically pure, mp 36–36.5 °C: IR 1845 cm^{-1} (C=O) 2-oxetanone; ^1H NMR δ 3.5 (2 H, d, CH_2), 4.9 (1 H, t, CH), 7.1–7.9 (5 H, m, C_6H_5).

Anal. Calcd for $C_{10}H_8Cl_2O_2$: C, 51.98; Cl, 30.68; H, 3.49. Found: C, 51.73; Cl, 30.73; H, 3.41.

4-(Trichloromethyl)-4-(4-chlorophenyl)-2-oxetanone. With approximately a 5-fold excess of ketene, starting with 1.05 g (4 mmol) of trichloro-4-chloroacetophenone, in 10 mL of toluene, using 90 mg (0.28 mmol) of quinidine as a catalyst, 810 mg (2.7 mmol, 68%) of the 2-oxetanone could be isolated, $[\alpha]^{RT}_{578}$ −51.5° (c, 1, toluene), corresponding to an enantiomeric excess of 90%. Quinine yielded a product, $[\alpha]^{RT}_{578}$ +37.9° (c 1, toluene), corresponding to 65% ee. Recrystallization of the product from the quinidine reaction from methylcyclohexane afforded a white crystalline material, $[\alpha]^{RT}_{578}$ −57.4° (c 1, toluene), enantiomerically pure, mp 148–149 °C: IR 1840 cm^{-1}, (C=O) 2-oxetanone; ^1H NMR δ 3.9 (2 H, dd, CH_2), 7.3 (4 H, dd, C_6H_4).

Anal. Calcd for $C_{10}H_6Cl_4O_2$: C, 40.04; Cl, 47.28; H, 2.02. Found: C, 40.03; Cl, 47.08; H, 2.07.

4-(Trichloromethyl)-4-(4-nitrophenyl)-2-oxetanone. From 3.1 g (11.5 mmol) of trichloro-p-nitroacetophenone, using 89 mg (0.27 mmol) of quinidine in 50 mL of toluene at −25 °C, 3.4 g (11 mmol) of adduct could be isolated (95%), $[\alpha]^{RT}_{578}$ −55.4° (c 1, toluene), corresponding to an enantiomeric excess of 89%. Quinine, used as catalyst, gave a product, $[\alpha]^{RT}_{578}$ +39.0° (c 1, toluene), 65% ee. Recrystallization of 3.3 g of a portion, $[\alpha]^{RT}_{578}$ −55.4° (c 1, toluene), from chloroform yielded 2.5 g of a white crystalline product, $[\alpha]^{RT}_{578}$ −62.5° (c 1, toluene), optically pure, mp 188 °C dec: IR 1840 cm^{-1} (C=O) 2-oxetanone; ^1H NMR δ 4.0 (2 H, dd, CH_2), 7.9 (4 H, dd, C_6H_4).

Anal. Calcd for $C_{10}H_6Cl_3NO_2$: C, 38.68; Cl, 34.25; N, 4.51; H, 1.95. Found: C, 38.49; Cl, 34.37; N, 4.48; H, 1.94.

Improved Procedure for the Tungstate-Catalyzed Epoxidation of α,β-Unsaturated Acids

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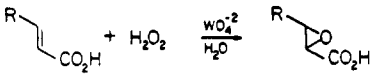
Since its discovery by Payne in 1959,[1] the aqueous, tungstate-catalyzed epoxidation of α,β-unsaturated acids by H_2O_2 has found limited application as an oxidative synthetic method.[2]

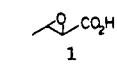
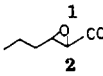
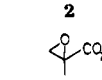
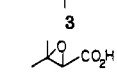
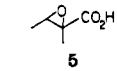


(1) Payne, G. B.; Williams, P. H. *J. Org. Chem.* **1959**, *24*, 54.

Table I. Modifications to the Original Payne Epoxidation Procedure for α,β-Unsaturated Acids

variable	original	modification: disubstituted	modification: trisubstituted
% catalyst	10	15	10
pH	4–5.5	5.8–6.8	5.8–6.8
T (°C)	60–65	60–65	r.t.

Table II. Products of the Modified Tungsten Epoxidation of α,β-Unsaturated Acids

entry	epoxy acid	time,[a] h	% crude product (purity)[b]	lit. % yield (ref)
1	 1	3	83.1 (86)	50[c] (1, 7)
2	 2	2	82.0 (88)	
3	 3	2	70.7 (91)	
4	 4	1.5	76 (>96)	46.7[d] (2b)
5	5	1.75	81.3 (100)	
6	 6	2	48.3 (100)[e]	

[a] Reaction followed by TLC. [b] Purity determined by ^1H NMR immediately following product isolation. [c] Yield is of purified product. [d] Yield listed is for the total crude material recovered only. No purity was given. [e] Isolated, purified (chromatography), and analyzed as the methyl ester.

We were attracted to this tungsten-catalyzed process because of the apparent substrate similarity between this reaction and the epoxidation of allylic alcohols with alkyl hydroperoxides catalyzed by titanium[3] and other early transition metal catalysts. In both cases the substrate possesses a functional group, proximate to the olefin undergoing epoxidation, which is capable of coordinating to the metal catalyst. Also intriguing are the apparent dissimilarities (i.e., electron-poor olefin as substrate, H_2O as solvent, H_2O_2 as oxidant). This process has been studied with an eye toward broadening the scope of its synthetic utility, as well as investigating its mechanism.[4]

Regarding the first of our objectives, a few simple modifications (Table I) of the original epoxidation procedure described by Payne[1] have been found to substantially improve yields of some epoxy acids. Thus, using the modifications in Table I, both di- and trisubstituted unsaturated acids can be epoxidized in high yield (Table II). While the reaction of disubstituted unsaturated acids does not go to completion, the yield of epoxycrotonic acid (1) in the crude reaction mixture, when using the modifications, is well above that provided by the literature. Entry

(2) In all, only four substrates have been epoxidized by using this procedure: (a) Aberhart, D. J.; Tann, C.-H. *Biorg. Chem.* **1981**, *10*, 375. (b) Chan, T. H.; Hill, R. K. *J. Org. Chem.* **1970**, *35*, 3519. (c) Creighton, S. M.; Mitchell, D. L. *Can. J. Chem.* **1967**, *45*, 1304. (d) Menger, F. M.; Vasquez, P. C. *J. Org. Chem.* **1982**, *47*, 5400. (e) For tungsten-catalyzed epoxidations under heterogeneous conditions, see: Allan, G. G. U.S. Patent 3 156 709; *Chem. Abstr.* **1965**, *62*, 2762g.

(3) (a) Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237. (b) Rossiter, B. E.; Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 464. (c) Kirshenbaum, K. S. *Nouv. J. Chim.* **1983**, *7*, 699.

(4) For other mechanistic studies, see: (a) Badasyan, G. V.; Gabrielyan, S. M.; Kamalov, G. L.; Treger, Y. A. *Arm. Khim. Zh.* **1980**, *33*, 794. (b) Saegebarth, K. A. *J. Org. Chem.* **1959**, *24*, 1212. (c) Khante, R. N.; Chandalia, S. B. *Indian J. Chem.* **1981**, *15*, 33. (d) Ahmad, I.; Beg, M. A. *Indian J. Chem.* **1978**, *16A*, 475.

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