sulting precipitate was collected to give 1.15 g (82%) of the quinone **5d**: mp 164–166° (lit.[15] mp 172°); ir (Nujol) 3475, 3275, 1685, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) 6.05 br (2), 7.25 br (5), 7.62–8.33 m (4).

2-Amino-5-azido-3,6-dimethyl-1,4-benzoquinone (1c). A solution of 1.1 g (5.0 mmol) of 2,5-diazido-3,6-dimethyl-1,4-benzoquinone[14] in 200 ml of ether was treated with 100 ml of a saturated aqueous solution of sodium dithionite, and the mixture was vigorously stirred for 60 min under an atmosphere of nitrogen. The organic layer was washed several times with water and dried and the solvent was then removed in vacuo (25°). The resulting 2,5-diazido-3,6-dimethylhydroquinone was dissolved in 75 ml of acetone and small amount of sodium azide was added. This caused the rapid disproportionation[16] of the hydroquinone and gave the crude product, **1c**, after approximately 1 hr. Chromotography of this crude product on 100 g of silica gel using chloroform as the eluent gave 0.72 g (74%) of **1c**, which turns from purple to white at 132–134° with gas evolution and the white solid then melts at 150–151°: ir (Nujol) 3310, 3220, 2100, 1630, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) 1.84 s (3), 1.89 s (3), 5.00 br (2).

Anal. Calcd for $C_8H_8N_4O_2$: C, 50.00; H, 4.17; N, 29.17. Found: C, 49.83; H, 4.29; N, 28.93.

2-Amino-3-methyl-1,4-naphthoquinone (2a), 2-Amino-3,6-dimethyl- (2b), 2-Amino-3,6-diphenyl- (2d), 2-Amino-3,6-di(1,1-dimethylethyl)- (3) and 2,5-Diamino-3,6-di(1,1-dimethylethyl)-1,4-benzoquinone. The above aminoquinones were prepared in good yields (>75%) by catalytic reduction (PtO_2, 30–40 psi) of ethanolic solutions of the respective azidoquinones.[12,14,17]

2-Amino-3-methyl-1,4-naphthoquinone (**1a**), mp 164–165° (lit.[18] mp 162–163°).

2-Amino-3,6-dimethyl-1,4-benzoquinone (**1b**): mp 194–196°; ir (Nujol) 3420, 3300, 1640, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.82 s (3), 1.98 d (3), J = 2 Hz, 4.79 br (2), 6.42 q (1), J = 2 Hz.

Anal. Calcd for $C_8H_9NO_2$: C, 63.57; H, 5.96; N, 9.27. Found: C, 63.71; H, 6.17; N, 9.12.

2-Amino-3,6-diphenyl-1,4-benzoquinone (**1d**): mp 244–246°; ir (Nujol) 3410, 3250, 1630, 1560 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 6.14 br (2), 6.65 s (1), 7.15–7.52 m (10).

Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.54; H, 4.72; N, 5.09. Found: C, 78.39; H, 4.71; N, 4.92.

2-Amino-3,6-di(1,1-dimethylethyl)-1,4-benzoquinone (**3**): mp 111–113°; ir (Nujol) 3450, 3320, 1675, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 s (9), 1.38 s (9), 5.49 br (2), 6.44 s (1).

Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.49; H, 8.94; N, 5.96. Found: C, 71.37; H, 9.10; N, 5.73.

2,5-Diamino-3,6-di(1,1-dimethylethyl)-1,4-benzoquinone: mp 192–193°; ir (Nujol) 3440, 3320, 1540 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 .

Anal. Calcd for $C_{14}H_{22}N_2O_2$: C, 67.20; H, 8.80; N, 11.20. Found: C, 67.15; H, 8.94; N, 11.12.

Acknowledgment. The authors gratefully acknowledge the financial support of the National Science Foundation (GP43712X) and the National Institutes of Health (CA 11890).

Registry No.—**1a**, 7427-09-0; **1b**, 31679-93-3; **1c**, 26351-46-2; **1d**, 56908-60-2; **2a**, 56908-61-3; **2b**, 56908-62-4; **2c**, 56908-63-5; **2d**, 56908-64-6; **3**, 35612-59-0; **4**, 56908-65-7; **5d**, 56908-66-8; **7**, 56908-67-9; **8**, 56908-68-0; **9**, 56908-69-1; **12**, 56908-70-4; **13**, 56908-71-5; **19**, 56908-72-6; **24**, 1133-72-8; **25**, 4056-72-8; **26**, 26138-64-7; **27**, 56908-73-7; **30**, 56908-74-8; 2,5-di-*tert*-butyl-3,6-diamino-1,4-benzoquinone, 56908-75-9; 2,5*H*-3-azido-4-methyl-6,7-benzoazepine-2,5-dione, 56908-76-0; 2,5*H*-4-methyl-6,7-benzoazepine-2,5-dione, 10315-37-4; sodium azide, 26628-22-8; 2-azido-1,4-naphthoquinone, 15707-29-6; 2,5-diazido-3,6-dimethyl-1,4-benzoquinone, 27977-29-3.

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Asymmetric Synthesis of Oxaziridines

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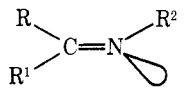
Oxidation of Schiff bases formed by the reaction of chiral (*R*)-(+)-α-phenylethylamine and carbonyl compound using *m*-chloroperbenzoic acid gives rise to the formation of nonracemic diastereomeric 3,3-disubstituted oxaziridines in a high optical yield. Oxidation of (*E*)-(*R*)-(−)-*N*-benzylidene-α-phenylethylamine yields a mixture of all four possible nonracemic diastereomers with predominance of *E* products.

The relatively small group of oxaziridines, containing the stable chiral N atom, is characterized by a high energy barrier for inversion, thus permitting the separation of enantiomers.[1-6]

Until now, optically active oxaziridines have been obtained by the oxidation of imines, using optically active peroxy acids.[2,3] Depending upon the substrate used, mixtures of compounds obtained represented nonracemic diastereomers or enantiomers with the presence of a small excess of one of them.[2,3] Such mixtures were usually separated by physical methods; in the case of a mixture of enantiomers, multiple recrystallizations afforded compounds which did not show a marked change of optical rotation after further recrystallizations.[4,6]

Two alternative mechanisms of imine oxidation have been postulated: (a) olefin type epoxidation (one step) involving nucleophilic reaction of π electrons of the C=N bond,[7,8] (b) Baeyer–Villiger (two step) type, through cleavage of π bonding followed by the elimination of one molecule of carboxylic acid used as peroxy acid.[9]

Chart I



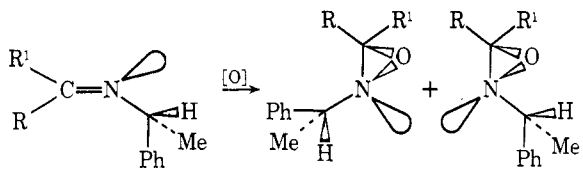
1

The next factor of influence in the course of reaction, is the kind and configuration of the imine used (Chart I).

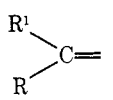
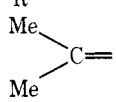
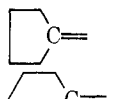
Using imines derived from symmetrical ketones (1, R = R^1) a mixture of N enantiomers is obtained regardless of the mechanism. When aldimines or imines derived from unsymmetrical ketones are employed (1, R ≠ R^1) one can expect (a) in the case of the one-step mechanism two enantiomers (assuming that there is no inversion of the N atom in the intermediate stage and that the imine used was one of the isomers *Z* or *E*), (b) in the case of the two-step mechanism a mixture of four compounds, two enantiomers each of *Z* and *E*.

In our asymmetric synthesis of oxaziridines Schiff bases were used as substrates. These were obtained from (*R*)-(+)-α-phenylethylamine and a series of carbonyl compounds. We have observed that the oxidation of this type of imine by *m*-chloroperbenzoic acid yields a mixture of diastereomers with an excess of one of them.[10] The results obtained using ketimines of type 1 (R = R^1) and (*R*)-(+)-α-phenylethylamine are summarized in Scheme I.

Scheme I



1 diastereomers (I and II)

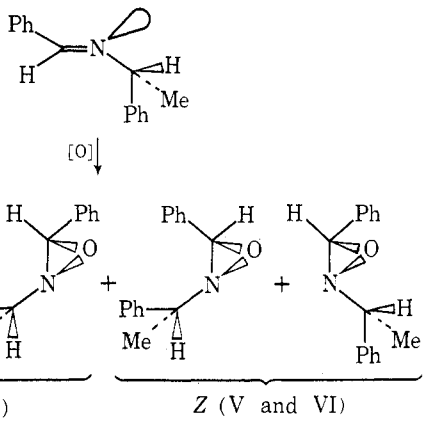
Starting 1	% diastereomers	
	I	II
	82	18
	87	13
	97	3

These results have been obtained by separation of nonracemic diastereomers through column chromatography (SiO_2) or HPLC (high performance liquid chromatography). The chemical yields have been determined by iodometric titration of the reaction mixture after removal of excess peroxy acid. The purity of the reaction products was determined by TLC and ^1H NMR spectroscopy.

In the case of the derivative of acetone (1, R = R^1 = Me), the ratio of I/II was also confirmed by integration of methyl signals in the ^1H NMR spectra. The signals from diastereotopic methyl groups originating from the presence of the acetone residue have the following value: I, 1.32 (s, 3, CH_3), 1.40 (s, 3, CH_3); II, 1.43 (s, 3, CH_3), 1.61 ppm (s, 3, CH_3). The signals from methyl group of residual amine are found: I, 1.47 (d, 3, CH_3), II, 1.32 ppm (d, 3, CH_3).

On the basis of our results one cannot assign configuration *RR* or *SR* to one of diastereomers I or II, since, so far as we could determine, no absolute configuration has as yet been determined for the N atom in oxaziridines. It has only been determined that the sign of the Cotton effect of the

Chart II



E (III and IV) *Z* (V and VI)

enantiomer product in excess agreed with the chiral peroxy acid used.[3,6]

In order to obtain more information in regard to the mechanism of imine oxidation we have used Schiff bases from benzaldehyde and (*R*)-(+)-α-phenylethylamine (1, R = H; R^1 = Ph). The resulting imine compound represent a pure *E* isomer (^1H NMR, TLC). This compound, oxidized as in former cases, gave a mixture of four nonracemic diastereomers, which were separated by column chromatography (Chart II).

The quantitative composition of the mixture was as follows.

Product (III, IV, V, VI)	*E* {*RRR*}	61.1%	(III)
	E {*SSR*}	22.2%	(IV)
	Z {*RSR*}	11.1%	(V)
	Z {*SRR*}	5.5%	(VI)

The composition of diastereomeric mixture *E* (III and IV) and *Z* (V and VI) could be confirmed by integration of signals produced by proton at C-3. The δ values (CCl_4, s) follow: III, 4.35, IV, 4.40 (*E*); V, 5.05, VI, 5.20 (*Z*).

The stability of the diastereomers was checked by heating their mixture in acetonitrile at 80° for ca. 60 hr. The samples of this solution investigated periodically did not show any quantitative change of the ^1H NMR signals of protons at C-3. We found only that after prolonged heating a thermal decomposition took place (titration of active oxygen).

The formation of four nonracemic stable diastereomers (III, IV, V, and VI) is not a convincing proof of a "two-step" mechanism.

We cannot exclude however, that in the cyclic intermediate postulated in the "one-step" mechanism[8] in which the free electron pair of nitrogen was engaged, an inversion of configuration on nitrogen takes place, which would lead to the additional formation of two diastereomers.

The "two-step" mechanism seems to be more probable. Its first step is the addition of peracid molecule to the C=N double bond with the formation of chiral center at C-3 (imine carbon atom). The preference of *R* or *S* attack depends on the chiral substituent (R) at nitrogen (Chart III).

Chart III

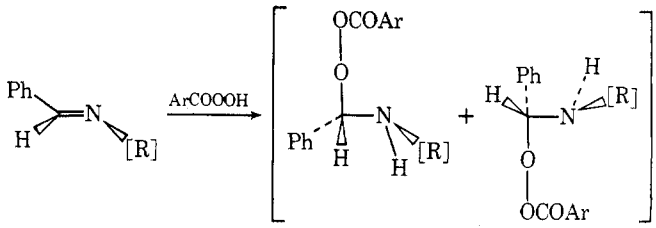
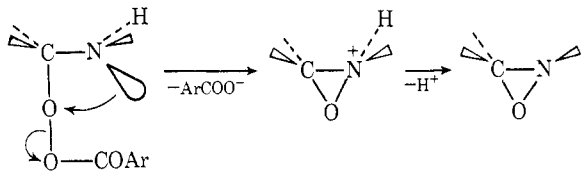


Chart IV



Thus formed two diastereomeric intermediates undergo elimination of the free acid, and this reaction requires an eclipsed configuration of the free electron pair at nitrogen with respect to oxygen atom in the peracid residue (Chart IV). Such an arrangement can occur in two ways: (a) rotation of the C–N bond or (b) inversion at nitrogen atom. The latter possibility leads consequently to the formation of two further diastereomers in the resulting reaction mixture.

In the case of an imine formed from a symmetric ketone, i.e., cyclohexanone, the addition of the peracid to the C=N double bond does not create a chiral center at C-3; however, the second reaction step involves a stereospecific intramolecular elimination of the acid and this particular reaction is responsible for the high stereospecificity observed in our experiments.

Experimental Section[13]

Schiff bases were prepared according to known procedures.[11,12] Active oxygen contents of oxaziridines were determined by iodometric titration with potassium iodide in a stirred mixture of dichloromethane, water, and glacial acetic acid.

Typical Preparation of Oxaziridine. A small excess of *m*-chloroperbenzoic acid (0.022 mol) in 40 ml of methylene chloride was added with stirring and cooling (0–5°C) to a solution of 0.02 mol of imine in 10 ml of methylene chloride. After the peroxy acid had been added, the reaction mixture was stirred for an additional 5 hr at 0–5°C. After that time the formed *m*-chlorobenzoic acid was removed by filtration. The filtrate was washed two times with a dilute solution of Na_2SO_3, then twice with a solution of Na_2CO_3, and finally with water. After drying over $MgSO_4$ (anhydrous), the solvent was evaporated and the residue was chromatographed over a column of SiO_2 using hexane–ethyl ether (9:1) as a solvent.

(*R*)-(+)-*N*-Isopropylidene-α-phenylethylamine (1, R = R¹ = Me): $[\alpha]_{436}^{22}$ +82.3° (*c* 1, $CHCl_3$); bp 60–62°C (0.9 mm); ir 1660 cm^{-1} (C=N); $n^{20}D$ 1.517; ^1H NMR 1.34 (d, 3, CH_3), 1.78 (s, 3, CH_3 at C=N), 1.97 (s, 3, CH_3 at C=N), 4.48 ppm (m, 1, CH).

(*R*)-(+)-*N*-Cyclopentylidene-α-phenylethylamine (1, R, R¹ = Tetramethylene): $[\alpha]_{436}^{22}$ +221.2° (*c* 1, $CHCl_3$); bp 93.5–94°C (0.7 mm); ir 1675 cm^{-1} (C=N); $n^{20}D$ 1.537; ^1H NMR 1.37 (d, 3, CH_3), 4.51 ppm (m, 1, CH at N).

(*R*)-(+)-*N*-Cyclohexylidene-α-phenylethylamine (1, R, R¹ = Pentamethylene): $[\alpha]_{436}^{22}$ +102.6° (*c* 1, $CHCl_3$); bp 102.5–104°C (0.8 mm); ir 1670 cm^{-1} (C=N); ^1H NMR 1.35 (d, 3, CH_3), 4.63 ppm (m, 1, CH at N).

(*R*)-(−)-*N*-Benzylidene-α-phenylethylamine (1, R = H; R¹ = Ph):[12] $[\alpha]^{20}D$ −83° (*c* 1.03, benzene); bp 115–116°C (0.5 mm); ir 1650 cm^{-1} (C=N); $n^{20}D$ 1.5881; ^1H NMR 1.48 (d, 3, CH_3), 4.38 (m, 1, CH at N), 8.15 ppm (s, 1, CH=N).

2-[(*R*)-α-Phenylethyl]-3,3-dimethyloxazirane. Diastereomer I: $[\alpha]_{436}^{22}$ +98.5° (*c* 1, $CHCl_3$); $n^{20}D$ 1.503; uv max (95% EtOH) 208 nm (ε 8675), 215 (5184), 242 (227), 248 (228), 252 (274.7), 258 (265), 264 (213.1), 268 (126.7); ^1H NMR 1.32 (s, 3, CH_3 at C-3), 1.40 (s, 3, CH_3 at C-3), 1.47 (d, 3, CH_3 at CHN), 3.43 ppm (m, 1, CH).

Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.89; H, 8.72; N, 7.95; *m/e* 177.

Diastereomer II: $[\alpha]_{436}^{22}$ +271.9° (*c* 1, $CHCl_3$); $n^{20}D$ 1.508; uv max (95% EtOH) 207 nm (ε 8287), 211 (7432), 215 (4183), 247 (249), 252 (262), 257 (272), 264 (214), 268 (155.1); ^1H NMR 1.43 (s, 3, CH_3 at C-3), 1.61 (s, 3, CH_3 at C-3), 1.32 (d, 3, CH_3 at CHN), 3.4 ppm (m, 1, CH at N); *m/e* 177.

Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.61; H, 8.69; N, 7.81.

2-[(*R*)-α-Phenylethyl]-3,3-tetramethyleneoxazirane. Diastereomer I: $[\alpha]_{436}^{22}$ +63.0° (*c* 1, $CHCl_3$); $n^{22}D$ 1.518; uv max (95% EtOH) 208 nm (ε 8063), 216 (4866), 242 (143.1), 248 (152), 253 (186), 259 (220.4), 264 (179.4), 268 (102); ^1H NMR 1.47 (d, 3, CH_3), 3.22 ppm (m, 1, CH at N); *m/e* 203.

Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.97; H, 8.45; N, 6.77.

Diastereomer II: $[\alpha]_{436}^{22}$ +295.4° (*c* 1, $CHCl_3$); $n^{22}D$ 1.522; uv max (95% EtOH) 208 nm (ε 8501), 211 (7911), 215 (4668), 247 (270), 251 (295), 258 (307), 264 (248.1), 268 (165.8); ^1H NMR 1.30 (d, 3, CH_3), 3.17 ppm (m, 1, CH at N); *m/e* 203.

Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.93; H, 8.72; N, 7.16.

2-[(*R*)-α-Phenylethyl]-3,3-pentamethyleneoxazirane. Diastereomer I: $[\alpha]_{436}^{22}$ +118.5° (*c* 1, $CHCl_3$); $n^{20}D$ 1.523; uv max (95% EtOH) 208 nm (ε 9000), 216 (5426.3), 241 (203.5), 248 (189), 252 (223), 258 (259), 264 (211), 268 (119); ^1H NMR 1.5 (d, 3, CH_3), 3.54 ppm (m, 1, CH at N); *m/e* 217.

Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.17; H, 9.07; N, 6.47.

Diastereomer II: $[\alpha]_{436}^{22}$ +205.4° (*c* 1, $CHCl_3$); $n^{20}D$ 1.529; uv max (95% EtOH) 208 nm (ε 10401), 210 (9929), 214 (6273), 247 (240.5), 252 (260), 258 (271), 264 (200), 268 (103); ^1H NMR 1.3 (d, 3, CH_3), 3.54 (m, 1, CH at N); *m/e* 217.

Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.68; H, 9.1; N, 6.64.

2-[(*R*)-α-Phenylethyl]-3-phenyloxazirane. Diastereomer III: $[\alpha]_{436}^{20}$ −238.2° (*c* 1.08, EtOH); oil; uv max (95% EtOH) 211 nm (ε 12400), 216 (11500), 247 (666), 253 (770), 258 (8. 45), 271 (535), 310 (230); ^1H NMR 1.58 (d, 3, CH_3), 3.14 (m, 1, CH at N), 4.35 ppm (s, 1, H-3); *m/e* 225.

Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 80.40; H, 7.07; N, 6.07.

Diastereomer IV: $[\alpha]_{436}^{20}$ +188.4° (*c* 1.42, EtOH); mp 52–53°C (from hexane); uv max (95% EtOH) 209 nm (ε 14000), 211 (13730), 216 (12150), 247 (300), 253 (400), 259 (500), 260 (473), 264 (482), 272 (304); ^1H NMR 1.45 (d, 3, CH_3) 3.25 (m, 1, CH at N), 4.40 ppm (s, 1, H-3); *m/e* 225.

Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 80.08; H, 6.90; N, 6.20.

Diastereomer V: $[\alpha]_{436}^{20}$ +350.9° (*c* 1.18, EtOH); oil; uv max (95% EtOH) 209 nm (ε 29000), 217 (21200), 247 (685), 252 (665), 259 (612), 264 (481), 271 (254); ^1H NMR 1.52 (d, 3, CH_3), 3.15 (m, 1, CH at N), 5.05 ppm (s, 1, H-3); *m/e* 225.

Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 80.21; H, 7.07; N, 6.75.

Diastereomer VI: $[\alpha]_{436}^{20}$ +630.0° (*c* 0.94, EtOH); mp 98° (from hexane); uv max (95% EtOH) 207 nm (ε 27550), 211 (26056), 215 (21410), 252 (647), 259 (732.4), 264 (642.2), 271 (293); ^1H NMR 1.02 (d, 3, CH_3), 3.17 (m, 1, CH at N), 5.20 ppm (s, 1, H-3); *m/e* 225.

Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.48; H, 6.68; N, 6.18.

Registry No.—1, R = R¹ = Me, 56424-40-9; 1, R, R¹ = tetramethylene, 56424-41-0; 1, R, R¹ = pentamethylene, 56424-42-1; 1, R = H, R¹ = Ph, 56941-77-6; I, R = R¹ = Me, 56907-09-6; II, R = R¹ = Me, 56424-43-2; I, R, R¹ = tetramethylene, 56907-10-9; II, R, R¹ = tetramethylene, 56424-44-3; I, R, R¹ = pentamethylene, 56907-11-0; II, R, R¹ = pentamethylene, 56424-45-4; III, 56830-31-0; IV, 56907-12-1; V, 56907-13-2; VI, 56907-14-3.

References and Notes

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(13) Melting points were measured on a micro hot plate and are not corrected. Ir spectra were determined in film with a Unicam SP-200 ir instrument, and ^1H NMR spectra were measured with a Jeol 100-MHz spectrometer in CCl_4 solution (accuracy ±0.5 Hz) and are given in δ values. Optical rotations were measured with a Perkin-Elmer automatic photoelectric polarimeter (Model 141). The microanalyses were performed in our microanalytical laboratory (head Z. Celler, M.S).