Olefin Epoxidation with α-Substituted Hydroperoxides

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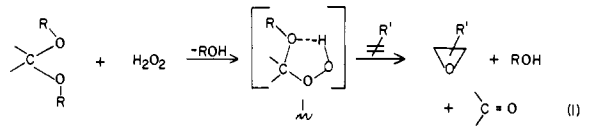
Abstract: A number of α-substituted hydroperoxides were examined for their ability to epoxidize olefins in a stereospecific manner. Hydroperoxy ethers, amines, carbonyl compounds, and nitriles showed this capability. Intramolecular epoxidation was demonstrated in cases where ortho esters of some olefinic alcohols were treated with H_2O_2, and methyl orthooleate–H_2O_2 mixtures also epoxidized the internal olefin in an intramolecular reaction. Attempts to generate chiral hydroperoxides for asymmetric epoxidation are described and structural features required for epoxidation reagents are discussed.

During our study[1] of the action of dehydrating agents on H_2O_2 we found that ortho esters act on H_2O_2 to produce intermediates capable of olefin epoxidation[2] (eq 1). Here we report further



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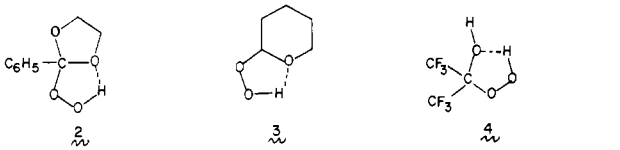


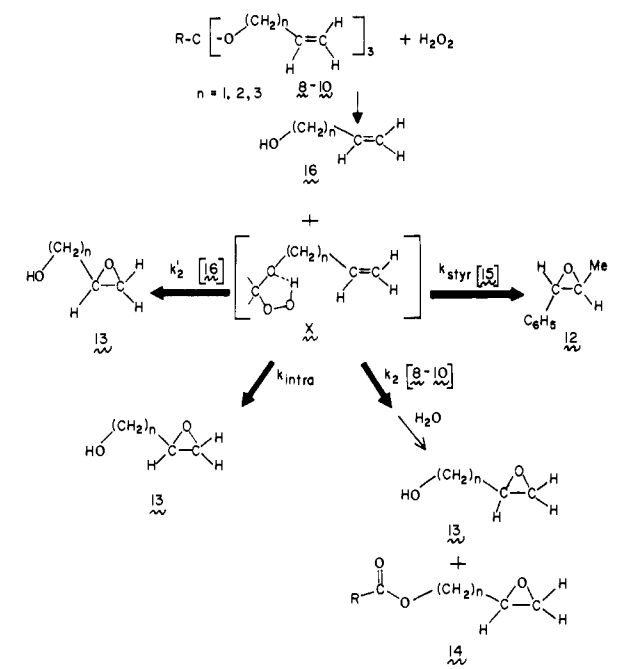
details on our experiences with these and related systems. Our direction in these studies has been toward the definition of structural features required for oxgyen atom transfer reagents rather than synthetic applications. Consequently, only the more promising reagents have been examined in preparative reactions.

The likely intermediates involved in the epoxidation of eq 1 are the α-hydroperoxy ethers **1**. A few members of this class of substances had been isolated and characterized: Rieche[3] obtained the crystalline **2** and Milas[4] distilled the THP derivative of H_2O_2, **3**. Epoxidations with **2** or **3** proved that **1** was a viable intermediate; moreover, Kim[5] had shown that the related **4** would also epoxidize olefins. Thus the nature of the epoxidant in eq 1 seems secure.

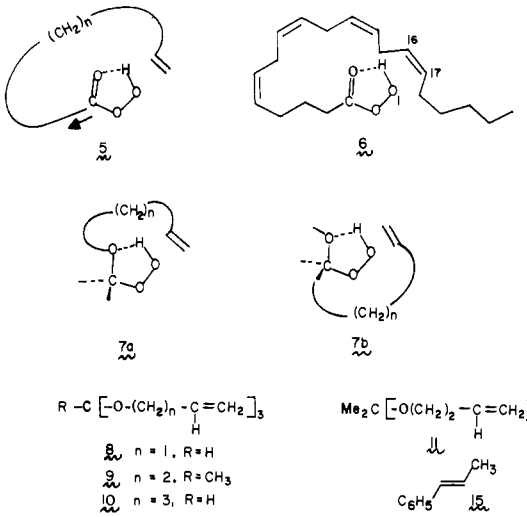
Intramolecular Epoxidation

The α-hydroperoxy ethers present unusual opportunities for the study of intramolecular epoxidation. For such epoxidation to occur with peroxy acids, a large number of connecting atoms between the peroxy function and the olefin are required; the first bond from the acyl carbon is directed *away* from the terminal oxygen and entropy renders an arrangement such as **5** unlikely if the connecting atoms are free to rotate. Indeed, the first clear case of intramolecular epoxidation, peroxyarachidonic acid (**6**), recently reported by Corey[6] involves a 16.5-membered transition state. Its remarkable success can be attributed, in part, to the restricted rotation provided by the three additional π-bonds. The corresponding situation with α-hydroperoxy ethers is considerably more favorable: the direction of the first bond away from the peroxy carbon (**7a** or **7b**) permits the geometry required for intramolecular

Scheme I



epoxidation to be achieved with fewer connective atoms. Just how few was tested as follows.



The ortho esters **8-10** derived from allyl, homoallyl, and bishomoallyl alcohols were prepared by standard exchange reactions from the ethyl ortho esters while the ketal **11** was prepared similarly from 2,2-dimethoxypropane. A competition experiment was designed as the test for intramolecular epoxidation using the more

(1) Rebek, J., Jr.; McCready, R.; Wolf, S.; Mossman, A. B. *J. Org. Chem.* **1979**, *44*, 1485-1493.
(2) Rebek, J., Jr.; McCready, R. *Tetrahedron Lett.* **1979**, 1001-1002.
(3) Rieche, A.; Schmitz, E.; Beyer, E. *Chem. Ber.* **1958**, *91*, 1942-1946.
(4) Milas, N. A.; Peeler, R. L.; Mageli, O. L. *J. Am. Chem. Soc.* **1954**, *76*, 2322-2325.
(5) Kim, L. U.S. Patent Appl. 181 734; *Chem. Abstr.* **1973**, *78*, 159400n. Preparative epoxidations with this reagent have also been recently described: Ganem, B.; Heggs, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 2484-2486.
(6) Corey, E. J.; Niwa, H.; Falck, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 1586-1587.

0002-7863/80/1502-5602$01.00/0

Table I

$$\underset{(1\ \text{mol})}{\text{8-11}} + \underset{(5\ \text{mol})}{15} \xrightarrow[\text{THF}]{H_2O_2} \xrightarrow{H_2O} 12 + 13 + 14$$

expt	[8-11], M	[15], M	epoxide ratios (13 + 14)/12 from 8	from 9	from 10	from 11
1	1	5	0.39	1.5	8.8	2.5
2	0.5	2.5	0.35	2.8	16	3.8
3	0.33	1.67	0.33	4.2	27	6.9
4	0.25	0.28	0.28	10	33	9.9
			(allylic, $n = 1$	(homoallylic, $n = 2$)	(bishomoallylic, $n = 3$)	(homoallylic ketal, $n = 2$)
	k_{intra}/k_{styr}		<1	~7 M	~40 M	~11 M

reactive (disubstituted vs. monosubstituted) olefin β-methylstyrene (**15**). As shown in the generalized Scheme I, the intermediate X, generated from the action of H_2O_2 on **8–10** in the presence of **15**, has a number of olefin sites with which to react. Bimolecular reaction with **15** gives the styrene oxide **12**, and at low conversions the principal sources of **13** involve k_2 and k_{intra}. The relative importance of inter- and intramolecular reactions of X was examined by determining the effect of dilution on the ratio (**13** + **14**)/**12**.

Each of the ortho esters **8–10** and the ketal **11** were placed in competition with **15** at four different dilutions in THF at ambient temperature. The initial molar ratios [**8–11**]/[**15**] were kept constant at 1/5 and low conversions (10%) were ensured by monitoring the epoxide formed by GLC. Ortho esters remaining at the end of the reaction were decomposed by the addition of H_2O and the epoxide products were determined by GLC against internal standards. In practice, the esters **14** represented only a small fraction of the epoxides obtained, yet all products were shown to be stable to the reaction and workup conditions. The results of these competition experiments are summarized in Table I.

The results show that for the allylic case ($n = 1$) no intramolecular component for epoxidation could be detected while the homo- and bishomoallylic cases show clear evidence for the intramolecular epoxidation pathway. At all concentrations used these latter cases gave more epoxide derived from the intrinsically less reactive olefin; the approximately linear increase in the epoxide ratio with dilution is best accommodated by the rate ratios given in the lowest row of the table. These were obtained from plots of (**13** + **14**)/**12** against 1/[**15**].

Of particular interest is the case of the ketal **11**, since its efficiency in intramolecular epoxidation implies that structure **7a** is sufficient to describe the nature of the intermediate involved in these reactions. A more refined picture of how the epoxidation occurs is postulated in structure **17**. The π bond can approach

17

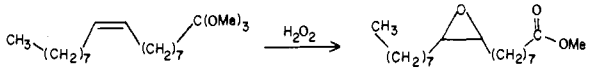
the backside of the terminal oxygen on a line defined by the O–O single bond of the peroxide.[7] With fewer connective atoms, i.e., the allylic case, this approach cannot be realized. Such geometries have been favored by calculations of peracid–olefin transition states;[8] in addition, this approach can place a lone pair of the terminal oxygen parallel with the approaching π bond as has recently been proposed for peracid epoxidations by Sharpless.[9] However, this degree of refinement must await further experimental verification.

Table II

$$18 + 20 \xrightarrow[\text{THF}]{H_2O_2} 19 + 21$$

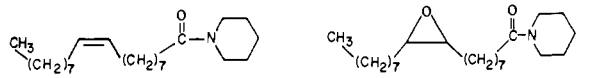
[18] = [20], M	[19]/[21]
1	7
0.5	12
0.25	27

In order to examine the possibility of epoxidation via structure **7b** we examined an ortho ester derived from an olefinic acid. Specifically, oleic acid was converted to the corresponding ortho ester **18**. On treatment with H_2O_2 in CH_2Cl_2 for 24 h, a 40% yield of the corresponding epoxide **19** was obtained.



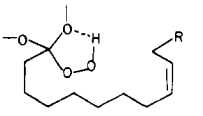
18 **19**

To establish that epoxidation was indeed intramolecular, a competition experiment was performed along the lines of those previously described. Here the competing olefin was the amide **20**. On successive dilutions of a THF solution containing equimolar amounts of **18** and **20** with H_2O_2, the yield of **19** increased at the expense of **21** (Table II).



20 **21**

Structures such as **22** are, consequently, likely candidates for



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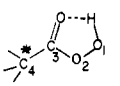
this epoxidation. Systematic studies are underway to determine the fewest number of connective atoms necessary for intramolecular oxygen transfer in these cases.

Asymmetric Epoxidations

These α-hydroperoxy ethers offer an opportunity for generating chiral epoxidizing agents in which the asymmetric center is nearer the oxygen-transfer site than is the case with peroxy acids (compare **23** with **24**). However, a number of cases examined gave disappointing results. Perhydrolysis of optically active ketals **25**[10] and **26**[11] in the presence of the test olefin **15** gave only 3–5% enantiomeric excess in the epoxide **12**. Similar results were obtained with **27** or **28**.



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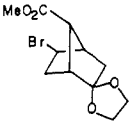

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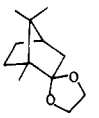

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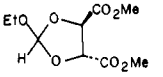

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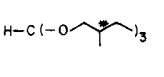

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(7) In the nomenclature suggested by Baldwin (*J. Chem. Soc., Chem. Commun.* **1976**, 734–736) **17** represents a "7 1/2 endo-tet" closure.

(8) Yonezawa, T.; Kato, H.; Yamamoto, O. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 307–311. Hanzlik, R. P.; Shearer, G. O. *J. Am. Chem. Soc.* **1975**, *97*, 5231–5233. Bach, R. D.; Willis, C. L.; Domagala, J. M. In "Applications of Molecular Orbital Theory in Organic Chemistry", Csimadia, I. G., Ed.; Elsevier: Amsterdam, 1977, pp 221–229. Plesnicar, B.; Taseuki, M.; Azman, A. *J. Am. Chem. Soc.* **1978**, *100*, 743–746. Reference 9.

(9) Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *12*, 63–74.

(10) Grieco, P. A.; Takigawa, T.; Moore, D. *J. Am. Chem. Soc.* **1979**, *101*, 4380–4381.

(11) Traylor, T. C.; Perrin, C. L. *J. Am. Chem. Soc.* **1966**, *88*, 4934–4942, have examined the exo/endo exchange rate in such ketals.

Scheme II

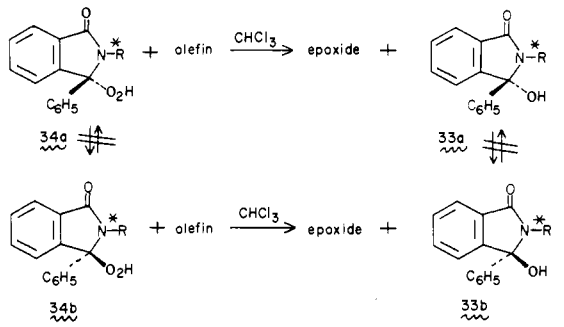
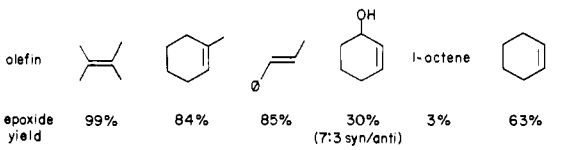
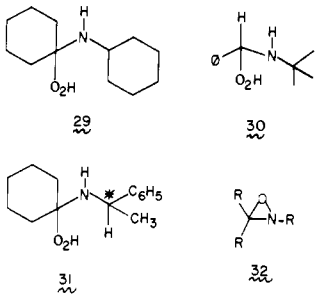


Table III. Olefin Epoxidation with 35 ($CHCl_3$, 24 h, 60 °C)

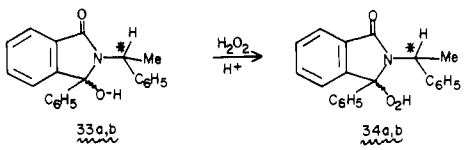


olefin					1-octene	
epoxide yield	99%	84%	85%	30% (7:3 syn/anti)	3%	63%

In addition, a few α-aminohydroperoxides were tested. These substances can be isolated[12] or generated in situ from Schiff's bases and H_2O_2. While epoxide yields with **29–31** were up to 45%, the asymmetric induction (with **31**) was <5% and the competing cyclization to the oxaziridines **32** placed great restrictions on the use of these reagents for synthetic purposes.



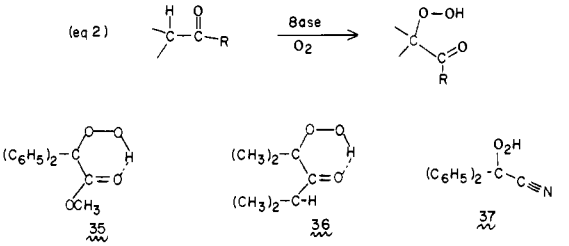
A somewhat cleaner system was found in the hydroperoxides **34a,b**, derived from the isoindolone **33**. These proved quite stable (<10% loss of active oxygen after 2 weeks) and the diastereomers of **34** were readily separated by LC.[13]



Exposure of either diastereomer to **15** gave epoxide and *each gave a single alcohol* **33**. Surprisingly, neither **33** nor **34** was found to isomerize under the conditions of epoxidation and we conclude that oxygen transfer occurs without opening of the five-membered ring (Scheme II). However, this reagent as well showed insufficient asymmetric induction to warrant further pursuit.

α-Hydroperoxy Carbonyl Compounds

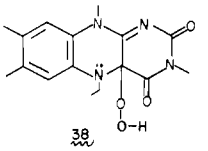
The base-catalyzed oxidation of carbonyl compounds (eq 2) has made α-hydroperoxy esters and ketones readily available.[14] Their decomposition under basic, acidic, and thermal conditions has been extensively explored,[15] yet no reports regarding their reactions with olefins are known to us. The curious instability of *olefinic* α-hydroperoxy esters vs. their saturated counterparts has, however, been noted.[14b] This instability is now explained by our finding that either the ester **35**, ketone **36**, or nitrile **37** are remarkably effective at olefin epoxidation.



Several olefins were examined in this reaction using **35** and results are given in Table III. Like peroxy acid reactions, a preference for syn epoxidation was observed with allylic alcohols and **35** and cyclopentanone gave a 35% yield of the Baeyer–Villiger oxidation product.

Conclusions

A number of α-substituted hydroperoxides have been shown capable of olefin epoxidations and all reagents examined were cleanly stereospecific. In this respect they resemble peroxy acids rather than, say, carbonyl oxides. Moreover, these reagents can all exist in intramolecularly hydrogen bonded form. Whether this feature is the minimum requirement for stereospecific oxygen atom transfer, or is merely a consequence of the electronegative substituent on the hydroperoxy-bearing carbon, has yet to be resolved. We do note, however, the resemblance borne by many of these reagents to flavin hydroperoxides[16] **38** and predict that these latter substances are likewise capable of olefin epoxidation.



Experimental Section

A. Analysis. Gas–liquid chromatography was performed on a Varian Model A-90 (15% OV-101 on Chromosorb W) and Hewlett-Packard 5710A (3% OV-17 on Chromosorb W) using a Varian Model 101 electronic integrator for peak area determinations. High-pressure liquid chromatography was accomplished by using a Waters Associates LC system on a 1-ft μ-Porasil column and Model R401 refractive index detection system. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., and high-resolution mass spectra were obtained on a Varian CH-5 instrument.

B. Materials. Literature preparations were followed for **19**,[17] **20**,[18] **26**,[19] **27**,[20] **28**,[23] **29**,[12] Schiff bases leading to **30**,[21] **31**,[22] and hydroperoxides **35**,[14a] **36**,[24] and **37**.[25] Hydrogen peroxide (90%) was obtained from FMC Corp. and was used as received. Triallyl orthoformate (**8**) was purchased from Pfaltz and Bauer.

(12) Rieche, A.; Hoft, E. *Angew. Chem., Int. Ed. Engl.* **1965**, **4**, 524–525. Hawkins, E. G. E. *J. Chem. Soc. C* **1971**, 160–166.

(13) The absolute stereochemistry at the hydroperoxy carbon is arbitrarily assigned; moreover, we assume that this stereochemistry is retained (as shown in Scheme II) rather than inverted on oxygen transfer.

(14) (a) Avramoff, M.; Sprinzak, Y. *J. Am. Chem. Soc.* **1963**, *85*, 1655–1657. (b) Konen, D. A.; Silbert, L. S.; Pfeffer, P. E. *J. Org. Chem.* **1975**, *40*, 3253–3258. (c) Sastry, Y.; Lakshminarayan, G. *Chem. Abstr.* **1972**, *76*, 4486g.

(15) For leading references see: Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1978**, *100*, 856–860.

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(18) Skau, E.; Mod, R.; Magne, F. U.S. Patent 3219659; *Chem. Abstr.* **1966**, *64* 3498c. The corresponding epoxide is also known: *Ibid.* **1966**, *64*, 3779*f*.

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(20) Crank, G.; Eastwood, F. W. *Aust. J. Chem.* **1969**, *17*, 1392–1398.

(21) Emmons, W. D.; Pagano, A. S. *Org. Synth.* **1957**, *49*, 13–15.

(22) Kitamoto, M.; Hiroi, K.; Terashima, S.; Yamada, S. *Chem. Pharm. Bull.* **1974**, *22*, 459–464.

(23) Piacenti, F. *Gazz. Chim. Ital.* **1962**, *92*, 225–243.

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(25) Selikson, S. J.; Watt, D. S. *J. Org. Chem.* **1975**, *40*, 267–268. Wasserman, H.; Lipshutz, B. *Tetrahedron Lett.* **1975**, 1731–1734, 4611–4614.

Preparation of Unsaturated Ortho Esters. Ortho esters **9** and **10** and ketal **11** were prepared by transesterification of the ethyl ortho esters or 2,2-dimethoxypropane under standard exchange conditions.[29]

(1) Tri-3-butene Orthoacetate (**9**): bp 132–136 °C (30 mm); NMR δ 1.47 (s, 3 H), 2.33 (m, 6 H), 3.52 (t, J = 6.0 Hz, 6 H), 5.12 (m, 6 H), 5.80 (m, 3 H); IR 1160, 1050 cm^{-1}; mass ($M^+ - CH_3$) 225.3071 (calcd ($M^+ - CH_3$), 225.3071).

(2) Tri-4-pentene Orthoformate (**10**): bp 178–180 °C (30 mm); NMR δ 1.68 (m, 6 H), 2.10 (m, 6 H), 3.42 (t, J = 8.0 Hz, 6 H), 4.72 (m, 6 H), 5.00 (s, 1 H), 5.63 (m, 3 H); IR 1420, 1120, 1250, 1050 cm^{-1}; mass ($M^+ - H$) 267.3871 (calcd ($M^+ - H$), 267.3875).

(3) 2,2-Di-3-butenoxypropane (**11**): bp 77–78 °C (25 mm); NMR δ 1.30 (s, 6 H), 2.23 (m, 4 H), 3.40 (t, J = 8.0 Hz, 4 H), 5.10 (m, 4 H), 5.80 (m, 2 H); IR 1630, 1040 cm^{-1}. Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.65; H, 10.90.

Competition Experiments for Intra- vs. Intermolecular Epoxidation of 8–11. The ortho ester (1 mmol) and *trans*-β-methylstyrene (5 mmol) in THF (appropriate amount depending on the concentration desired) were stirred at room temperature as H_2O_2 (90%, 100 μL/mmol of ortho ester) was added slowly. The solution was checked periodically by GLC until the reaction was approximately 10% complete, then water was added and the solution was stirred for 15–30 min. The solution was extracted several times with ether and the combined extracts were dried over Na_2SO_4. The crude reaction mixture was analyzed by GLC for epoxide ratios.

Preparation of Trimethyl Orthooleate (**18**). **18** was prepared by using the Pinner synthesis.[26]

(1) Preparation of Methyl Oleoimidate Hydrochloride. Dry HCl (4.02 g, 0.11 mol, through concentrated sulfuric acid) was bubbled into a mixture of commercial oleonitrile (26.35 g, 0.1 mol) in 4.46 mL (0.11 mol) of methanol cooled in an ice bath. The solution was placed in the freezer, when, after 24 h, 38 mL of dry ether was added and the solution was allowed to stand in the refrigerator for an additional 24 h. The suspension of the salt was filtered rapidly, washed with cold, dry ether, then immediately placed in a vacuum desiccator (the salt is extremely hygroscopic). This salt (10.0 g) in 18 mL of methanol was stirred until solution occurred, then ether (95 mL) was added and the solution was refluxed for 24 h. The solution was cooled in an ice bath and filtered through Celite to remove $NH_4^+Cl^-$. Sodium methoxide (0.54 g) was then added to the filtrate to neutralize acidic residues. Washing the filtrate twice with 10% Na_2CO_3 and once with saturated Na_2CO_3 and drying over K_2CO_3 provided, after evaporation, the ortho ester contaminated with amide and methyl ester. The crude product was triturated with hexane at −10 °C, then filtered free of the solid amine. Evaporation provided the ortho ester as a light yellow oil containing less than 5% methyl ester. Distillation in vacuo provided an analytical sample: 6.54 g (64%); bp 145 °C (0.057 mm); NMR δ 0.9–2.0 (m, 17 H), 3.27 (s, 3 H), 5.37 (m, 2 H); IR 1465, 1380, 1250, 1050 cm^{-1}; mass spectrum ($M^+ - CH_3O$) 311.2950 (calcd ($M^+ - CH_3O$), 311.2950).

Competition Experiment of 18 with 20. Intermolecular Oxidation. The ortho ester **18** and amide **20**[18] (1 mmol each) were stirred in THF (appropriate amount depending on concentration desired) as H_2O_2 (100 μL/mmol of ortho ester) was added slowly. After the solution was stirred for 24 h at room temperature, 5 mL of H_2O was added and the solution was stirred for 15 min. Ether was added and the layers were separated; the ether was dried over Na_2SO_4 and then evaporated. The residue was analyzed by LC (5:1 hexane/EtOAc) for epoxide ratios.

Preparative Epoxidation, 18 → 19. Ortho ester **18** (1 mmol) in 1 mL of CH_2Cl_2 was stirred and 100 μL of H_2O_2 was added slowly. The solution was stirred *vigorously* for 24 h, after which time H_2O was added and the solution was stirred for an additional 15 min. The organic phase was dried over Na_2SO_4 and the crude mixture was analyzed by LC (10:1 hexane/EtOAc) and NMR showing a 40% yield of methyl ester peroxide **19**, identical with an authentic sample.[17]

(26) For illustrative examples see: DeWolfe, R. H. "Carboxylic Ortho Acid Derivatives"; Academic Press: New York, 1970.

Preparation of 1-Oxo-2-[(+)-α-methylbenzyl]-3-hydroxy-3-phenylisoindole (33a,b). (+)-α-Methylbenzylamine (6.44 mL, 0.05 mol) was added slowly (dropwise) with cooling to a mixture of the crude pseudochloride (12.25 g, 0.05 mol, prepared by refluxing benzophenone-2-carboxylic acid with thionyl chloride) and 4.0 mL of dry pyridine in 30 mL of dry benzene. After the mixture was stirred at room temperature for 12–24 h, 100 mL of chloroform was added and the mixture was washed four times with 1.0 M HCl, twice with 1.0 M NaOH, and once with brine and dried over $MgSO_4$. The crude product was recrystallized once from CCl_4, giving mostly one isomer as white plates. Repeated recrystallization resulted in a 1:1 mixture of diastereomers which were separated by LC (20% EtOAc/hexane): 10.8 g (66%); mp 167–170 °C; NMR (isomer 1) δ 1.66 (d, J = 7.5 Hz, 3 H), 3.04 (s, 1 H), 4.47 (q, J = 7.5 Hz, 1 H), 7.40 (m, 14 H); (isomer 2) 1.87 (d, J = 6.0 Hz, 3 H), 3.23 (s, 1 H), 4.85 (q, J = 6.0 Hz, 1 H), 7.20 (m, 14 H); IR 3550, 3300 (br), 1690 cm^{-1}. Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.22, H, 5.81; N, 4.25. Found: C, 80.25; H, 5.89; N, 4.23.

Preparation of 1-Oxo-2-[(+)-α-methylbenzyl]-3-hydroperoxy-3-phenylisoindole (34a,b). H_2O_2 (0.340 g, 90%) was added slowly to a solution containing 1.645 g (5 mmol) of **46** (mixture of isomers) and 10 μL of H_2SO_4 (catalytic amount) in 5–10 mL of CH_2Cl_2 at 0 °C. The solution became homogeneous after 5 min and the cooling bath was removed. After being stirred for 24 h at room temperature the solution was washed with saturated sodium bicarbonate solution (thrice) and once with brine and dried over Na_2SO_4. Evaporation provided 1.54 g (89%) of the hydroperoxide as a mixture of isomers, mp 136–140 °C. Separation of the isomers by LC provided pure **34a,b** (25% EtOAc/hexane): NMR (isomer 1) δ 1.80 (d, J = 8.0 Hz, 3 H), 4.38 (q, J = 8.0 Hz, 1 H), 7.25 (m, 14 H), 10.20 (br s, 1 H); (isomer 2) 1.87 (d, J = 6.5 Hz, 3 H), 4.74 (q, J = 6.5 Hz, 1 H), 7.15 (m, 14 H), 10.10 (br s, 1 H). Anal. Calcd for $C_{22}H_{20}NO_3$: C, 76.50; H, 5.54; N, 4.06. Found: C, 73.25; H, 5.65; N, 3.89. Individual hydroperoxide isomers did not isomerize after 16 days at room temperature (determined by NMR) and active oxygen content was virtually unchanged (determined by titration[27]) over this time span.

Reaction of 34 with *trans*-β-Methylstyrene. After separation of the isomers **34a,b** by LC, 80.0 mg (0.23 mmol) of a single isomer was added to a solution containing 65 μL of *trans*-β-methylstyrene (0.5 mmol) in 1 mL of $CHCL_3$. After the solution was stirred at room temperature for 4 days, the epoxide was isolated by preparative GLC (28.2% yield), $[\alpha]^{22}_D$ −3.89° (*c* 1.52, EtOH), 5.5% ee (lit.[28] $[\alpha]^{20}_D$ −70.8° (*c* 4.44, EtOH)). NMR of the reaction mixture revealed that only isomer 1 of alcohol **35** was obtained from isomer 1 of **34** and only isomer 2 of **33** was obtained from isomer 2 of **34**.

Reaction of 35 with Olefins. The olefin (1 mmol) was added to a solution containing 1 mmol of **35**[14a] in 3 mL of $CHCl_3$ which was heated to 60 °C (bath temperature). After 24 h the reaction mixture was examined by GLC and NMR for epoxide. For Baeyer–Villiger oxidation, the ketone was added to the hydroperoxide solution containing a catalytic amount of *p*-toluenesulfonic acid. The same procedure was used to prepare epoxides with **36**[24] and **37**;[25] the latter was the most reactive of these reagents.

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(28) Audier, H. E.; Dupin, J. F.; Jullien, J. *Bull. Soc. Chim. Fr.* **1966**, 2811–2816.

(29) For examples see: Roberts, R. M.; Higgins, T. D.; Noyes, P. R. *J. Am. Chem. Soc.* **1955**, *77*, 3801–3805. Alexander, E. R.; Busch, H. M. *Ibid.* **1952**, *74*, 554–555.