flask, and the flask was evacuated and flushed with argon (five cycles). Then the stopcock was turned to connect the rubber septum and the mercury bubbler, and the bubbler was flushed with argon. The flask was charged with 8.2 mL (0.009 mol) of borane THF (1.1 M) through the three-way stopcock with a syringe. The stopcock was turned to connect only the flask and the mercury bubbler, and the reaction mixture was heated at 70–75 °C (bath temperature) with gentle stirring for 2 days. The solvent was removed under reduced pressure (exclusion of air) to give 1.21 g of colorless residue, which was dissolved in dry THF (6 mL total volume) to give a 0.5 M solution of catalyst **2**.

Oxazaborolidine 4. A solution of (*S*)-(−)-2-(diphenylhydroxymethyl)pyrrolidine (96 mg, 0.38 mmol) and methylboronic acid (23 mg, 0.38 mmol) in benzene (6 mL) was stirred at room temperature in the presence of powdered molecular sieves (4A type, 0.8 g) for 1.5 h. The reaction mixture was filtered and the residue was washed with benzene (2 mL). Concentration of the combined extracts under vacuum afforded B-methylated oxazaborolidine **4** (95 mg, 0.34 mmol, 94.5% yield).

(*S*)-(+)-α-(Chloromethyl)benzenemethanol. A dry 250-mL, two-necked, round-bottomed flask equipped with a rubber septum, a thermometer, and a magnetic stirrer was flushed with nitrogen and charged with 2 mL (0.001-mol scale) of the above solution of catalyst **3** (0.5 M). To this solution was added 9.1 mL (0.01 mol) of borane–THF (1.1 M) with stirring under nitrogen. A solution of 15.5 g (0.1 mol) of 2-chloroacetophenone in 45.5 mL of THF contained in a syringe and a solution of 45.5 mL (0.05 mol) of borane–THF (1.1 M) were added simultaneously to the THF solution of **3** with stirring at 20–30 °C under nitrogen (addition rate 1 mL/min). The reaction mixture was stirred for 10 min and decomposed by the addition of 14.6 mL (0.36 mol) of methanol with stirring and ice bath cooling over 10 min. To the resulting solution was added 2 mL of dry saturated hydrogen chloride in ether with stirring and ice bath cooling over 5 min. After 30 min at 20 °C the solvent was removed under reduced pressure to give an oily residue. The residue was dissolved in 50 mL of benzene, and the solvent was removed under reduced pressure (twice). To the residue was added 100 mL of ether and the mixture was cooled to 0 °C. Colorless crystals of ((*S*)-(−)-2-(diphenylhydroxymethyl)pyrrolidine hydrochloride) were collected by filtration and converted to amino alcohol **2** (recovery 218 mg, 86.5%). The ether solutions were combined, washed successively with brine, saturated sodium bicarbonate solution, and brine, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure to give after distillation (bp 112-114 °C/6 Torr) 15.2 g (0.0971 mol, 97.1% yield) of chloro alcohol **5** $[\alpha]_D^{24}$ +49.6° (cyclohexane, *c* 2.81), absolute configuration *S*, enantiomeric excess (ee) 96.5%.[1,7]

(*S*)-(−)-Phenyloxirane (1). A 250-mL, one-necked, round-bottomed flask equipped with a pressure-equalizing 10-mL dropping funnel and a magnetic stirrer was charged with 100 mL of a 2 M sodium hydroxide aqueous solution. To the aqueous solution was added dropwise 10 g (0.0647 mol) of (*S*)-(+)-α-(chloromethyl)benzenemethanol over 15 min at 22 °C with stirring. The dropping funnel was rinsed with 2 mL of ether, and the ether solution was added to the reaction mixture. The resulting mixture was stirred vigorously for 1 h at room temperature, saturated with sodium sulfate, and extracted with pentane (3 × 20 mL). The extracts were combined and dried over calcium chloride, and the solvent was removed at atmospheric pressure to give 8.64 g of colorless oil. This oil was distilled in a short-path still to give 7.48 g (0.0623 mol, 96.2% yield) of **1** as a colorless oil, bp 88–89 °C (19 Torr), α_D^{24} −34.9 (neat, *c* 1.0), $[\alpha]_D^{24}$ −33.2° (neat), $[\alpha]_D^{23}$ −44.9° (benzene *c* 1.02), absolute configuration *S*.[1,8–10]

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New Manganese Tetrakis(halogenoaryl)porphyrins Featuring Sterically Hindering Electronegative Substituents: Synthesis of Highly Stable Catalysts in Olefin Epoxidation

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Received September 28, 1987

Metal tetraarylporphyrins, especially Mn(III) and Fe(III) complexes, are very efficient catalysts in the oxidation of organic substrates carried out with a variety of oxidants.[1] Among these, the use of NaOCl under phase-transfer conditions aroused a special interest from the preparative point of view.[2] Unfortunately, metal tetraarylporphyrins are easily deactivated in the course of the reactions, mainly by the irreversible formation of μ-oxo dimers[3] and by autocatalytic oxidative demolition.[4] The latter becomes very fast in the oxidation of poorly reactive substrates, as in the epoxidation of α-olefins, or with a deficiency of substrate.[1] Porphyrin stability also depends on the nature of the oxidizing species.[5]

It has been reported that the chemical stability of tetraphenylporphyrin (**1**) is increased by the introduction of sterically hindering[4,6,7] and/or electron-withdrawing groups[4,8] on the phenyl rings. However, the relative importance of these two parameters has never been thoroughly studied and unambiguously established. Only the Mn(III) and Fe(III) complexes of tetrakis(2,6-dichlorophenyl)porphyrin (**2**),[4,5,9] tetrakis(pentafluorophenyl)-porphyrin (**6**),[8,10,11] and tetrakis(2,4,6-triphenylphenyl)-porphyrin[7] were found to be noticeably stable.[12] Furthermore, the claimed stability of some metalloporphyrins often relies upon very particular reaction conditions, such as large substrate/oxidant ratios.[9,11,13]

In order to get a deeper insight into the effects of substituents, we synthesized tetrakis(3,5-dimethyl-2,4,6-trichlorophenyl)- (**3**), tetrakis(3,5-dimethyl-2,4,6-tribromophenyl)- (**4**), and tetrakis(3,5-dichlorophenyl)porphyrin (**5**). These compounds were prepared in 7.4, 2.7, and 5.1% yield, respectively, from the corresponding aldehydes,

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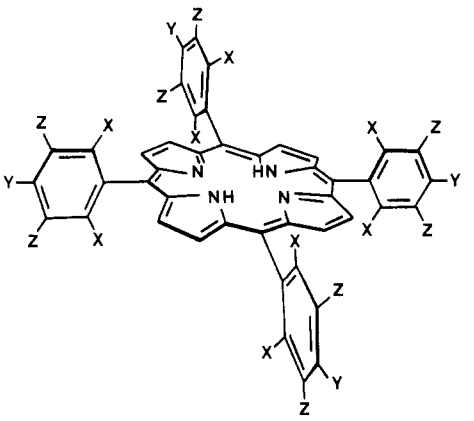


	X	Y	Z
1	H	H	H
2	Cl	H	H
3	Cl	Cl	Me
4	Br	Br	Me
5	H	H	Cl
6	F	F	F
7	Me	Me	H

1a–7a = Mn(III) complexes of 1–7

following the modified Rothemund–Alder synthesis recently described by Lindsey.[14] The same methodology allowed us to noticeably improve the synthesis of **2** (7.0% yield). These porphyrins were converted in quantitative yields into their manganese(III) acetate complexes **2a–5a** by reaction with $Mn(OAc)_2$ in refluxing DMF.[15]

Aldehydes **12** and **13** were prepared from trihalomesitylenes **8** and **9**, respectively (Scheme I). Benzylic bromination of **8** and **9** with 0.5 molar equiv of *N*-bromosuccinimide (NBS), followed by reaction with potassium acetate, separation from the unreacted trihalomesitylene, and final treatment with KOH, afforded alcohols **10** and **11** in 74% and 80% overall yield, respectively.[16] Alcohols **8** and **9** were oxidized to aldehydes **12** and **13** (83% and 85% yield, respectively) with NaOCl in CH_2Cl_2–H_2O at 0 °C and pH 8.5 and 2,2,6,6-tetramethyl-4-methoxypiperidine-1-oxyl and KBr as catalysts, following a general procedure previously described by us.[17]

The matter of catalytic activity and chemical stability of **2a–5a** was then addressed. For the sake of completeness, the Mn(III) complexes of tetraphenylporphyrin (**1a**), tetrakis(pentafluorophenyl)porphyrin (**6a**), and tetrakis(2,4,6-trimethylphenyl)porphyrin (**7a**) were also examined. The epoxidations of cyclooctene and 1-dodecene were studied as model reactions. Oxidations were carried out with 0.35 M NaOCl in an aqueous–organic two-phase system at a controlled pH (9.5) and at 0 °C in the presence of *N*-hexylimidazole as axial ligand.[18] The catalysts showed markedly different behaviors.

The oxidation of cyclooctene was completed in 40–50 min with **2a–4a** and in <15 min with **1a** and **5a–7a**, the epoxide being always obtained in ≥85% GC yield (Figure 1). The oxidation of 1-dodecene was over in <10 min, with catalysts **2a–4a** affording the epoxide in ≥90% GC yield,

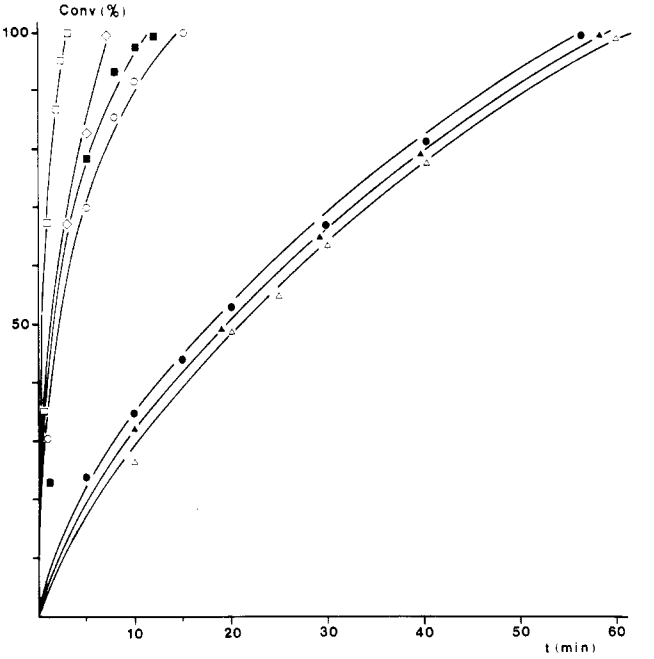
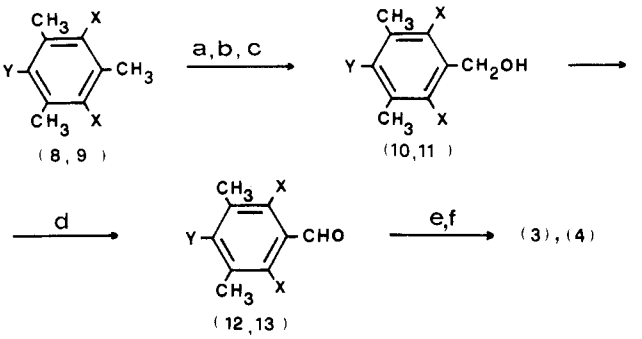


Figure 1. Time–conversion curve of the oxidation of cyclooctene catalyzed by manganese porphyrins **1a** (□), **2a** (●), **3a** (▲), **4a** (△), **5a** (○), **6a** (■), and **7a** (◇). Conditions: CH_2Cl_2–H_2O, 0.35 M NaOCl (3.5 molar equiv), pH 9.5, 0 °C, manganese porphyrin (0.005 molar equiv), *N*-hexylimidazole (0.125 molar equiv), methyltrioctylammonium chloride (0.05 molar equiv).[2c]

Scheme I[a]



3, 8, 10, 12 X = Y = Cl
4, 9, 11, 13 X = Y = Br

[a] (a) NBS; (b) CH_3COOK, $(C_8H_{17})_3N^+MeCl^-$ (cat.), MeCN, 70 °C; (c) KOH, EtOH, H_2O, reflux; (d) NaOCl, 2,2,6,6-tetramethyl-4-methoxypiperidine-1-oxyl (cat.), KBr (cat.), CH_2Cl_2–H_2O, 0–5 °C, pH 8.5; (e) pyrrole, CF_3COOH, CH_2Cl_2, 20 °D; (f) chloroanil, CH_2Cl_2, reflux.

whereas with **1a** and **5a–7a** the reaction stopped at about 20% conversion (65% with **6a**).

As shown in Figure 2, the oxidation of cyclooctene is accompanied, from the beginning, by the progressive deactivation of manganese porphyrins **1a** and **5a–7a**, **7a** being slightly more resistant than the other three catalysts.[19] Deactivation is much faster in the presence of 1-dodecene so that bleaching is complete before the end of the epoxidation. On the contrary, manganese porphyrins **2a–4a** turned out to be perfectly stable under the reaction conditions, as shown by the intensity of the Soret absorption bands, which were unchanged after 120 min with both olefins.

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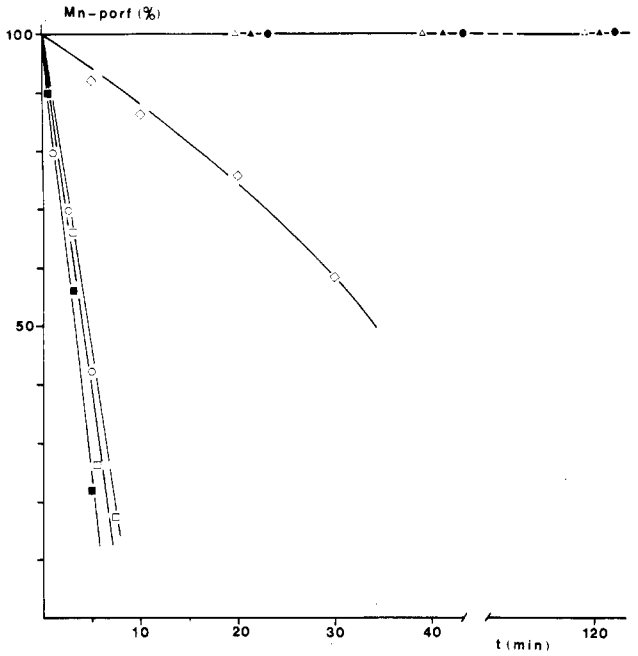

Figure 2. Time–conversion curve of the oxidative demolition of manganese porphyrins under the epoxidation conditions of cyclooctene.

A few main conclusions can be drawn from these results: (i) Manganese tetraarylporphyrins **2a–4a**, combining the presence of electron-withdrawing substituents with the steric protection of the metal center, are stable under the oxidation conditions reported here. (ii) The absence of either one of the features mentioned above largely decreases the chemical resistance of manganese porphyrins toward the oxidizing agents. Hypochlorous acid is one of the most powerful oxidizing agents known[20] and is particularly suited to discriminate the most robust porphyrins. (iii) Manganese tetrakis(3,5-dichlorophenyl)porphyrin (**5a**), which differs from **2a** in the position of the chlorine atoms, is totally unstable under the oxidation conditions. This umambiguously proves that both steric and electron-withdrawing effects of substituents must coexist to determine the chemical stability of metalloporphyrins.

Further investigations on the influence of oxidants, ligands, and phase-transfer catalysts on the chemical stability of metalloporphyrins and on the epoxidation rates are currently under way.

Experimental Section

Materials and Methods. ^{1}H NMR spectra were recorded on Bruker WP80SY and Varian XL300 spectrometers in $CDCl_3$ as solvent. UV–visible spectra were obtained with a Varian Cary 219 spectrophotometer. GC analyses were performed on a Varian Model 3700 gas chromatograph flame ionization instrument (20 × 0.125 in. OV-101 (5%) on CHP 100–125-mesh column) with a VISTA CDS 401 Varian chromatography data system. Melting points are uncorrected. 2,4,6-trichloromesitylene (**8**),[21] 2,4,6-tribromomesitylene (**9**),[22] and porphyrins **1**,[23] **6**,[23] and **7**[23] were prepared by literature procedures. ACS grade organic and inorganic reagents were used without further purification.

3,5-Dimethyl-2,4,6-tribromobenzyl Alcohol (11). 2,4,6-Tribromomesitylene (**9**) (8.57 g, 24.0 mmol) and NBS (2.14 g, 12.0 mmol) were refluxed in 150 mL of CCl_4, under irradiation with a 100-W lamp, for 3 h. The succinimide was filtered off from the hot solution, and the solvent was evaporated. The product was treated with 4.71 g (48 mmol) of CH_3COOK in 200 mL of CH_3CN in the presence of 0.16 g (0.4 mmol) of trioctylmethylammonium chloride (Aliquat 336) at 70 °C for 12 h. After this period the reaction mixture was cooled at 0 °C, and 4.0 g (11.2 mmol) of tribromomesitylene was collected by filtration. The solvent was evaporated, and the crude material containing the acetate was treated with 2.8 g (50 mmol) of KOH in an $EtOH/H_2O$ mixture at reflux for 4 h. At the end of the hydrolysis a clear solution was observed. The solid product obtained by evaporation of the solvents was thoroughly washed with H_2O and with a few milliliters of MeOH, giving 3.59 g (80.1%) of alcohol **11**: mp 214–215 °C; ^{1}H NMR ($CDCl_3$) δ 2.3 (t, 1 H), 2.7 (s, 6 H), 5.1 (d, 2 H). Anal. Calcd for $C_9H_9Br_3O$: C, 28.99; H, 2.43. Found: C, 29.18; H, 2.56.

3,5-Dimethyl-2,4,6-trichlorobenzyl alcohol (10) was obtained from 11.88 g (53.1 mmol) of trichloromesitylene and 7.12 g (40 mmol) of NBS, using the procedure described for **11**. Column chromatography (silica gel, 7:3 petroleum ether/Et_2O) was necessary in the last step of the sequence to recover the desired product **10**: 7.1 g (74%); mp 194–195 °C; ^{1}H NMR ($CDCl_3$) δ 2.1 (bs, 1 H), 2.5 (s, 6 H), 5.0 (bs, 2 H). Anal. Calcd for $C_9H_9Cl_3O$: C, 45.13; H, 3.79. Found: C, 45.48; H, 3.82.

3,5-Dimethyl-2,4,6-tribromobenzaldehyde (13). To a flask containing 150 mL of CH_2Cl_2 kept at 0 °C were added, in sequence, 9.5 g (25.47 mmol) of alcohol **11**, 0.095 g (0.51 mmol) of 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl,[24] and 0.3 g (2.5 mmol) of KBr. Then 71 mL of 0.43 M aqueous sodium hypochlorite, previously saturated with $NaHCO_3$ in order to adjust the pH to 8.6, was dropped in the reaction mixture over a period of 30 min. Stirring was maintained for a further 30 min, then the organic phase was separated, and the product was purified by column chromatography (silica gel, 7:3 petroleum ether/CH_2Cl_2) to give 8.0 g (85%) of compound **13**: mp 224–225 °C; ^{1}H NMR ($CDCl_3$) δ 2.7 (s, 6 H), 10.1 (s, 1 H). Anal. Calcd for $C_9H_7Br_3O$: C, 29.15; H, 1.90. Found: C, 29.34; H, 1.82.

3,5-Dimethyl-3,4,6-trichlorobenzaldehyde (12). The same procedure described for compound **13** was used, starting from 6.88 g (28.7 mmol) of alcohol **10**. Column chromatography (silica gel, 7:3 petroleum ether/CH_2Cl_2) afforded aldehyde **12**: 5.22 g (83.1%); mp 192–194 °C; ^{1}H NMR ($CDCl_3$) δ 2.5 (s, 6 H), 10.4 (s, 1 H). Anal. Calcd for $C_9H_7Cl_3O$: C, 45.51; H, 2.97. Found: C, 45.87; H, 2.94.

***meso*-Tetrakis(2,6-dichlorophenyl)porphyrin (2).** 2,6-Dichlorobenzaldehyde (1.75 g, 10 mmol), pyrrole (0.67 g, 10 mmol), and CF_3COOH (1.14 g, 10 mmol) were poured in order in 1 L of CH_2Cl_2 freshly distilled from P_2O_5 and stirred in the dark for 20 h. Then chloranil (2.5 g, 10 mmol) was added, and the mixture refluxed for 3 h. Column chromatography on neutral Al_2O_3 (7:3 petroleum ether/CH_2Cl_2) afforded porphyrin **2** as a violet powder: 0.155 g (7%) after being crushed with *n*-hexane; ^{1}H NMR ($CDCl_3$) δ −2.55 (s, 2 H), 7.7 (s, 12 H), 8.6 (s, 8 H).

***meso*-Tetrakis(3,5-dimethyl-2,4,6-trichlorophenyl)porphyrin (3)** was obtained from aldehyde **12** as described for **2**. Column chromatography (alumina, 1:1 petroleum ether/CH_2Cl_2) and crushing with *n*-hexane afforded **3** in 7.4% yield as purple shiny crystals: ^{1}H NMR ($CDCl_3$) δ −2.5 (bs, 2 H), 2.8 (s, 24 H), 8.7 (s, 8 H); λ_{max}/nm (ϵ/(mmol L^{-1})) (CH_2Cl_2) 418 (185).

***meso*-Tetrakis(3,5-dimethyl-2,4,6-tribromophenyl)porphyrin (4)** was obtained from aldehyde **13** as a brownish solid in 2.7% yield, following the same procedure as described for **2**: ^{1}H NMR ($CDCl_3$) δ −2.3 (bs, 2 H), 2.9 (s, 24 H), 8.6 (s, 8 H). λ_{max}/nm (ϵ/(mmol L^{-1})) (CH_2Cl_2) 425.5 (434).

***meso*-Tetrakis(3,5-dichlorophenyl)porphyrin (5)** was obtained from 3,5-dichlorobenzaldehyde as described for **2**. Column chromatography (Al_2O_3, 1:1 petroleum ether/CH_2Cl_2) afforded **5** in 5.1% yield as a dark red solid, which is practically insoluble in most common solvents. Electronic spectra were registered in highly diluted solutions of unknown concentration (ca. 10^{-5} M): λ_{max}/nm (*n*-hexane) 416; λ_{max}/nm (CH_2Cl_2) 450 (pale red and pale green solutions, respectively). Porphyrin **5** was characterized by mass spectroscopy of its Mn complex (see below) and by ^{1}H NMR

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spectroscopy of its Zn complex, prepared in quantitative yield by literature procedures:[15] ^{1}H NMR (4:1 (v/v) $CDCl_3$/DMSO-d_6) δ 7.3 (t, 4 H), 7.6 (d, 8 H), 8.4 (s, 8 H).

Manganese(III) acetate complexes of porphyrins 1-7 were prepared[15] and purified by column chromatography (silica gel, 1:1 $CHCl_3$/MeOH); the unknown complexes were characterized by their electronic and mass spectra.

3a: λ_{max}/nm (ϵ/(mmol L^{-1})) 480 (192); MS for $C_{52}H_{32}Cl_{12}N_4$Mn(OAc), cluster, m/z 1193 (100%).

4a: λ_{max}/nm (ϵ/(mmol L^{-1})) 482 (352); MS for $C_{52}H_{32}Br_{12}N_4$Mn(OAc), cluster, m/z 1726 (100%).

5a: λ_{max}/nm (ϵ/(mmol L^{-1})) 477.5 (151); MS for $C_{44}H_{20}Cl_8N_4$Mn(OAc) cluster, m/z 943 (100%).

General Procedure of Olefin Epoxidation. Oxidations were carried out in a 20-mL flask equipped with a Teflon-lined screw cap and magnetic stirrer, thermostated at 0 ± 0.2 °C with circulating ethanol by a Colora Misstechnik Gmbh Lorch/Württ cryostat. Stirring speed was maintained at 1300 ± 50 rpm. The flask was charged with (a) 1 mL of a CH_2Cl_2 solution containing 0.5 mmol of substrate, 0.25 mmol of decane as internal standard, and 0.025 mmol of Aliquat; (b) 1 mL of a 0.0025 M CH_2Cl_2 solution of manganese porphyrin; and (c) 5 mL of aqueous 0.35 M NaOCl, whose pH was adjusted to 9.5 by adding 10% aqueous HCl solution. The required amount (0.0625 mmol) of *N*-hexylimidazole[18] was added via syringe. The mixture was then stirred, and samples taken at different times were analyzed by GC.

Chemical Stability of Manganese Porphyrins 1a-7a. In the epoxidation experiments 50-μL samples of the organic phase, withdrawn at different times, were diluted in 10 mL of CH_2Cl_2 containing a large excess (50 mg) of triphenylphosphine, which ensured the fast reduction of manganese(V) oxoporphyrins to manganese(III) porphyrins. The manganese porphyrin decomposition was followed by UV-visible spectroscopy in the 350-750-nm range, measuring the percentage decrease of the absorbance at the λ_{max} referred to the sample taken at zero time of each reaction. The results are reported in Figure 2.

Acid-Catalyzed Migration of the Vinyl Substituent in the Dienone-Phenol Rearrangement

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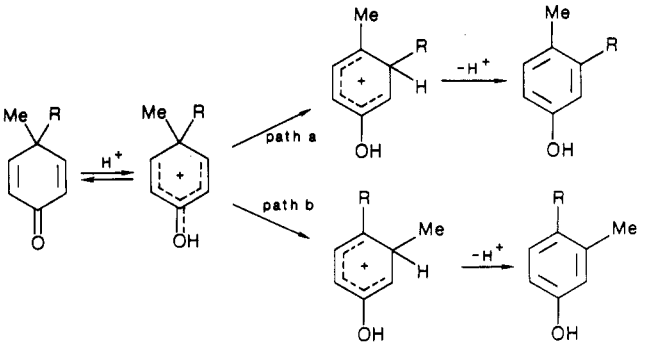
Received November 4, 1987

Introduction

The acid-catalyzed rearrangement of carbonium ions is an important process which has been studied extensively throughout the history of organic chemistry.[1-4] The group R undergoining the rearrangement is commonly alkyl, aryl, or hydrogen. The order of relative migratory aptitude of the group R is mainly related to the ability of the substituent to stabilize a positive charge in the transition state of the migration reaction.

The acid-catalyzed cyclohexadienone-phenol rearrangement has been studied extensively.[5-8] This system is attractive for the following reasons:[5,6] (a) there is a large driving force (aromatization), so each reactant gives stable and quantitative product(s); (b) the potential migrating groups are in the same steric environment, held conformationally rigid on either side of the planar dienone ring, so their steric effects in the rearrangement are minimized; (c) the reaction is initiated by protonation on oxygen, so no leaving groups are present; (d) the initial ion can be detected by UV or NMR spectroscopy and the charge density at the migration terminus before the rearrangement can be calculated;[5] (e) the migration is rate-determining and irreversible, so the migration tendency can be obtained directly from the rate constants and the product ratio.

The mechanism of the acid-catalyzed dienone-phenol rearrangement has been well established.[5-8]



When two possible migrating groups such as methyl and ethyl are in intramolecular competition in this dienone system, the ethyl group migrates much faster than the methyl group.[5-7] The product ratio reflects this greater ethyl group migration (ethyl migration, 98%; methyl migration).[5-7]

The migration tendency, MT, a term which was first introduced by Stiles and Mayer,[9] is defined as k_p^R/k_p^R, where k_p^R = the partial rate constant under the defined conditions for the migration of the group R. Migration tendencies allow intermolecular comparisons of rates. In highly conjugated systems, for which the migration is controlled primarily by electronic factors, the MT values appear to measure primarily differences within the migrating group itself.

The MT for the ethyl group in the dienone system has been reported as 51[5] or 49[7] in aqueous H_2SO_4 and 55 in trifluoroacetic acid.[6] This is the largest value reported to date for ethyl migration relative to methyl migration.[1] However, when the highly polar ethoxycarbonyl group migrates in this system, it also acts as a good migrating group (MT = 14), although it is polarized such that it should be poor in stabilizing positive charge density in the transition state. We have suggested[6] that back-donation of electron density from the π bond of the carbonyl group is primarily responsible for this high MT value.

In order to put this to an experimental test, we have prepared 4-methyl-4-vinylcyclohexadienone (1). The vinyl substituent, lacking the adverse polarity but containing the π bond, is predicted to have an MT value much greater than the ethoxycarbonyl group. Exclusive vinyl group migration is also expected.

Results and Discussion

4-Methyl-4-formylcyclohex-2-en-1-one (3) was prepared by a Diels-Alder reaction using 3-(trimethylsiloxy)-1-methoxy-1,3-butadiene (2) (Danishefsky's diene)[10] and methacrolein, followed by acidic hydrolysis. Direct

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