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_4Mn(OAc), cluster, m/z 1726 (100%).

5a: λ_{max}/nm (ϵ/(mmol L^{-1})) 477.5 (151); MS for $C_{44}H_{20}Cl_8$-N_4Mn(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 In the epoxidation experiments 50-μL samples of the organic phase, withdrawn at different times, were diluted in 10 mL of CH_2Cl_2 containing a large excess (50 mg) of triphenylphosphine, which ensured the fast reduction of manganese(V)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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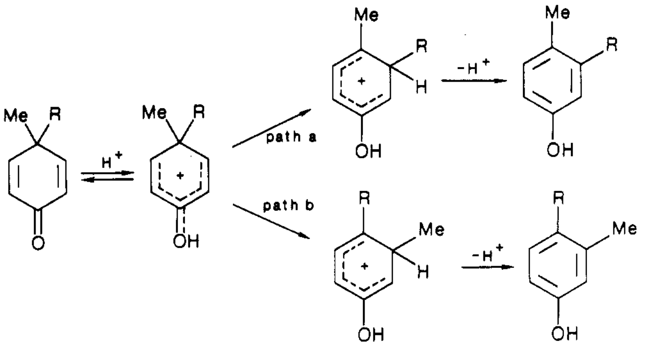
Introduction

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 undergoing 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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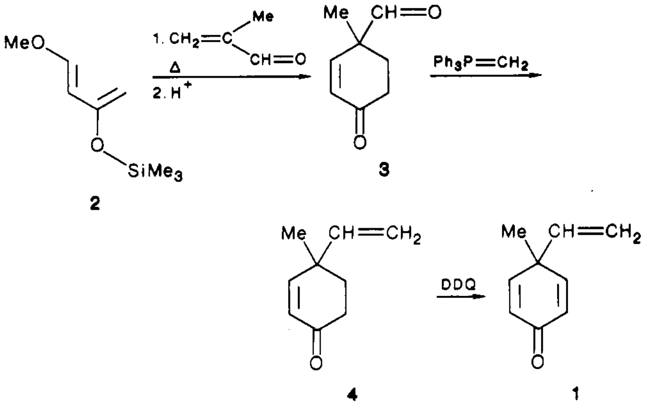
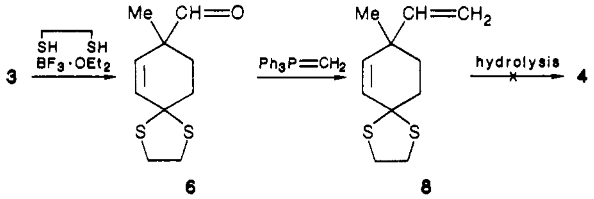
treatment of compound **3** with the methylene Wittig reagent[11,12] gave 29% of 4-methyl-4-vinylcyclohex-2-enone (**4**), along with 7% of the corresponding triene resulting from overreaction. Compound **4** was refluxed with DDQ in dioxane for 48 h to give vinyl dienone **1**.

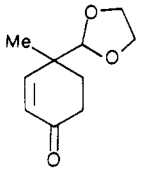


2 **3** **4** **1**

Several attempts were made to protect selectively the enone carbonyl group in **3**, to try to improve the yield of **4**. It was found that the reaction of keto aldehyde **3** with ethylene glycol gave exclusively the undesired compound **5**. However, reaction of keto aldehyde **3** with 1 equiv of ethanedithiol and boron trifluoride etherate catalyst gave very different results, depending on the solvent. On a small scale in dry ether, the product was almost exclusively thioketal **6**, with desired protection. However, in chloroform, the product was **7**. Further reactions in ether on a larger scale gave varying amounts of the two compounds.



6 **8**



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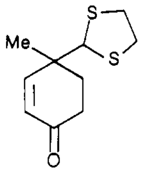

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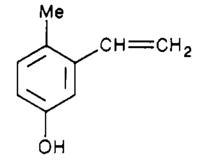

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These results are best explained as follows. Compound **6** is the result of kinetic control, but its formation is easily reversible, since it contains an allylic system. The product is fairly insoluble in ether and separates as it is formed. Compound **7** is the product of thermodynamic control and forms rapidly in chloroform, in which the compounds are very soluble.

A Wittig reaction on thioketal **6** gave compound **8**. However, attempted thioketal hydrolysis of **8** under a number of mild conditions gave no recognizable amount (or at best a trace amount) of the desired enone **4**.[13-17]

For the product study of the acid-catalyzed rearrangement, vinyl dienone **1** was completely rearranged by using 29.4% aqueous sulfuric acid at room temperature for 30 min. The exclusive product of the rearrangement was identified as 3-vinyl-4-methylphenol (**9**) by comparison of its hydrogenation product with authentic samples of both 3-ethyl-4-methylphenol and 4-ethyl-3-methylphenol.[5-7]

Dienone **1** showed excellent pseudo-first-order kinetics in aqueous acids in the range of 19–40% H_2SO_4 or $HClO_4$. The product had peaks at 299, 245, and 212 nm, and showed good isosbestic points through at least 10 half-lives. However, in 47.4% $HClO_4$, the rearrangement product of **1** underwent polymerization, as judged by the disappearance of the 299 and 245 nm peaks, and the appearance of a peak at 276 nm. Similar behavior was observed in trifluoroacetic acid.

Total rate constants, k_{obs}, for the rearrangement of **1** in various strengths of aqueous H_2SO_4 and $HClO_4$ at 25 °C were calculated. A plot of log k_{obs} against $-H_0$ showed a linear relationship; slope = 1.26 (r = 0.9995) in H_2SO_4 and slope = 1.32 (r = 0.9974) in $HClO_4$. The reactions in $HClO_4$ were about 1.5 times faster than the reactions in H_2SO_4 at the same H_0 value. Bunton et al.[18,19] reported that carbonium ion like transition states in A-1 reactions are stabilized by low charge density anions such as perchlorate and that the catalytic order in such reactions is $HClO_4 >$ HCl, H_2SO_4. Therefore, the kinetic results of faster reaction rates in $HClO_4$ than in H_2SO_4 at the same H_0 value is supported by this mechanistic criterion.

It proved to be impossible to determine kinetics for the vinyl dienone **1** and 4,4-dimethylcyclohexadienone, needed for calculating MT values, under the same acidic conditions. However, we have determined that the MT value for the ethyl compound remains essentially constant over a wide range of acidities.[5] The vinyl group migrates about 240 times faster than the ethyl group in aqueous sulfuric acid. Since ethyl migrates about 50 times faster than methyl in this system,[5-7] the migration tendency for the vinyl group relative to methyl in aqueous sulfuric acid is calculated to be 12 000.

This large value of the migration tendency of the vinyl group implies that the group is involved in substantial stabilization of the transition state during the migration step. This stabilization is due to back-donation of the π electron density in the transition state, which is substantially more efficient (MT = 12 000) than that for the ethoxycarbonyl group (MT = 14).

Unfortunately, it is not possible to make quantitative comparisons of this data with that for the ethoxycarbonyl group, since the effects of the ethoxy group are not taken into account, and the formyl group, which would provide a more direct comparison with the vinyl group, undergoes fragmentation[10] rather than migration in this system.

Experimental Section

Instrumental. NMR spectra were run in $CDCl_3$ on a Varian EM-360A spectrophotometer. Infrared spectra were obtained on a Nicolet MX-S FT-IR spectrophotometer. UV spectra were recorded on a Perkin-Elmer Lambda-5 UV–vis spectrophotometer. Melting points were taken in open capillaries on a Mel-Temp apparatus and are uncorrected. Analyses were performed by MicAnal, Tuscon, AZ.

Procedure for Kinetic Runs. A 3.0-mL aliquot of a solution of the desired strength of acid was placed in a 1-cm spectrophotometer cell in the thermostatted cell compartment of a Perkin-Elmer Lambda-5 UV/vis spectrophotometer. After the solution has come to 25 °C, the reaction was initiated by injecting 5 μL of a 0.1 M solution of dienone in 95% ethanol and mixing

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it thoroughly with the acidic media in the cell. The increase in the optical density of the solution at 299 nm with time was then followed. The rate of rearrangement was determined from the slope of a plot of ln $(A_\infty - A_t)/(A_\infty - A_0)$ vs time. The kinetics were cleanly pseudo first order over 10 half-lives unless otherwise stated.

Preparation of 4-Methyl-4-vinylcyclohex-2-enone (4). To a stirred slurry of 4.290 g (12.0 mmol) of triphenylmethylphosphonium bromide in 100 mL of dry THF was added 9.6 mL (12 mmol) of 1.25 M methyllithium in ether under a nitrogen atmosphere at room temperature. After 30 min of stirring, to the resulting methylene triphenylphosphorane (red solution) was added 2.76 g (20 mmol) of 4-methyl-4-formylcyclohex-2-enone (3), which was prepared by the method of Danishefsky and Kitahara,[10] in 10 mL of dry THF at 0 °C (immediate exothermic reaction). After 30 min, the reaction mixture was poured into 200 mL of ether and washed with 150-mL portions of water. The aqueous washings were extracted twice with 100-mL portions of ether. After being dried ($MgSO_4$), the combined organic layers were concentrated under reduced pressure. Chromatography of the residue on 25 g of silica gel with 1:99 ether/petroleum ether eluted first 0.175 g (7%) of undesired byproduct triene as a colorless oil (which decomposed on storage): NMR ($CDCl_3$) δ 1.10 (s, 3 H), 1.45–2.47 (m, 4 H), 4.70–6.25 (m, 7 H). Further elution with 10:90 ether/petroleum ether afforded 0.780 g (29%) of vinyl enone 4 as a colorless oil: R_f 0.35 (silica gel, 10:90 ether/petroleum ether); IR (CCl_4) 1720, 1685, 1635 cm^{-1}; NMR ($CDCl_3$) δ 1.21 (s, 3 H), 1.77–2.57 (m, 4 H), 5.00 (dd, 1 H, J = 18, 2 Hz), 5.08 (dd, 1 H, J = 10, 2 Hz), 5.82 (dd, 1 H, J = 18, 10 z), 5.96 (d, 1 H, J = 10 Hz), 6.63 (d, 1 H, J = 10 Hz).

Preparation of 4-Methyl-4-vinylcyclohexa-2,5-dienone (1). A solution of 272 mg (2 mmol) of vinyl enone 4, 0.681 g (3 mmol) of DDQ, and 10 mL of dioxane was refluxed for 48 h. After cooling, the hydroquinone was filtered off under reduced pressure. The reaction with poured into water and extracted with CH_2Cl_2 twice. The combined organic layers were dried and concentrated under reduced pressure. Chromatography of the residue on 10 g of silica gel with 10:90 ether/petroleum ether eluted first 67 mg (25%) of starting material and 45 mg (17%) of 4-methyl-3-vinylphenol (9): R_f 0.19 (silica gel, 10:90 ether/petroleum ether); NMR ($CDCl_3$) δ 2.25 (s, 3 H), 5.12–5.77 (m, 2 H), 6.55–7.17 (m, 4 H). There were then eluted 93 mg (35%) of vinyl dienone 1. After microdistillation using a micropipette under vacuum, a slightly yellow liquid of vinyl dienone 1 was obtained: R_f 0.11 (silica gel, 10:90 ether/petroleum ether); UV λ_{max} 238 nm (H_2O); IR (neat) 1662, 1620 cm^{-1}; NMR ($CDCl_3$) δ 1.33 (s, 3 H), 4.95–6.04 (m, 3 H), 6.27 (d, 2 H, J = 10 Hz), 6.87 (d, 2 H, J = 10 Hz). Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.10; H, 7.77.

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Registry No. 1, 114300-63-9; 3, 54125-08-5; 4, 114300-64-0; 5, 114300-65-1; 6, 114300-66-2; 7, 114300-67-3; 8, 114300-68-4; 9, 66164-30-5; triphenylmethylphosphonium bromide, 1779-49-3.

Reaction of α-Bromoisobutyronitrile with Nitroalkane Anions

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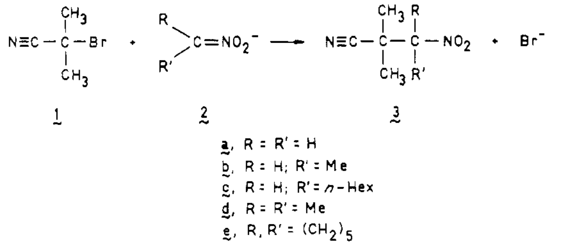
The ability of a nitro group in the substrate to bring about electron-transfer free-radical chain nucleophilic substitutions ($S_{RN}1$) at a saturated carbon atom is well documented.[1] Among other nitro derivatives,[2] the 2-halo-2-nitropropanes are substrates of $S_{RN}1$ reactions.[3] We have found that 2-bromo-2-cyanopropane (1) alkylates the anion of nitromethane and of primary and secondary nitroalkanes (2a–e) at the carbon atom (reaction 1), and a mechanistic examination shows that this is an electron-transfer chain nucleophilic substitution.[4]



$$N{\equiv}C{-}C(CH_3)_2{-}Br + RR'C{=}NO_2^- \longrightarrow N{\equiv}C{-}C(CH_3)_2{-}C(R)(R'){-}NO_2 + Br^- \qquad (1)$$

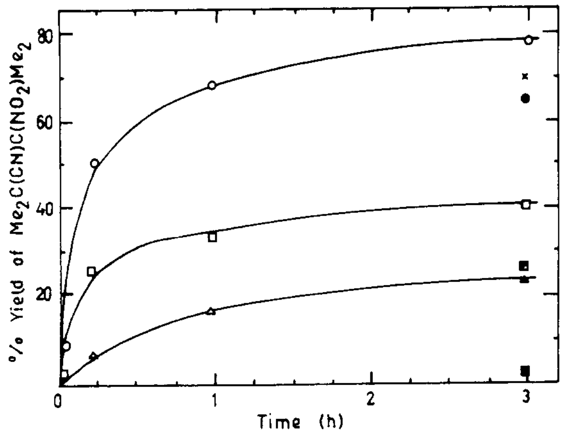


Figure 1. Formation of $Me_2C(CN)C(NO_2)Me_2$ by reaction of an equimolar mixture of $Me_2C(Br)CN$ and $Me_2C{=}NO_2K$ in HMPA at 20 °C under N_2 in ordinary laboratory light ($[Me_2C(Br)CN]_0$ = 0.3), as affected by inhibitors: ○, control reaction; ●, in the dark; ×, with 20 mol % of O_2 added; □, with 5 mol % of $(t\text{-}Bu)_2NO^\bullet$; ▨, with 10 mol % of $(t\text{-}Bu)_2NO^\bullet$; ■, with 25 mol % of $(t\text{-}Bu)_2NO^\bullet$; △, with 10 mol % of $m\text{-}(O_2N)_2C_6H_4$.

Table I. Alkylation of Nitroalkane Anions ($RR'C{=}NO_2^-$) by α-Bromoisobutyronitrile[a]

R, R'	% yield of $Me_2C(CN)C(NO_2)RR'$[b]
H, H	45, *36*, 42,[c] 44,[d] 37,[e] 27,[f] 8,[g] 8,[h]
H, Me	72, *57*
H, *n*-Hex	67, *61*
Me, Me	82, *68*, 58,[i] 81,[j] 79[d]
$(CH_2)_5$	*76*

[a] Reactions conducted under N_2 with a $RR'C{=}NO_2^-K^+/Me_2C(Br)CN$ molar ratio of 0.9 in HMPA at 20 °C for 6 h in ordinary laboratory light, unless otherwise noted. [b] Crude yields estimated by ^1H NMR with internal standard; yields of pure isolated products in italics. [c] In DMSO with K^+/18-crown-6 as counterion. [d] With 2 equiv of H_2O added. [e] In the dark. [f] With 20 mol % of O_2. [g] With 10 mol % of $(t\text{-}Bu)_2NO^\bullet$. [h] With 10 mol % of $m\text{-}(O_2N)_2C_6H_4$. [i] In DMSO. [j] With 1 equiv of H_2O.

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