addition of ammonium chloride. The ammonia was evaporated and ether/methanol was added to the residue. The mixture was separated into its components by column chromatography. Elution with petroleum ether (bp 60–80 °C)/chloroform (1:1) and chloroform gave the starting material 1 and 2-amino-4-phenylpyrimidine (2): mp 165–166 °C from petroleum ether (bp 60–80 °C); yield 60% (average of three experiments). Further elution with 4% methanol in chloroform gave 6-amino-4-phenylpyrimidine (4): mp 222–225 °C from benzene/ethanol (50/50); yield 15%.

Hydrolysis of the Amino Compounds. A 10-mg sample of 2- or 6-amino-4-phenylpyrimidine was heated with concentrated hydrochloric acid in a Carius tube (150 °C during 15 h). After neutralization the 4-phenylpyrimidones were purified by column chromatography using 3% methanol in chloroform as eluent.

Acknowledgment. We are indebted to Dr. C. A. Landheer and Mr. W. P. Combé for the mass spectrometric data and to Mr. A. van Veldhuizen for the NMR spectra of the adducts.

Registry No. 1, 3438-48-0; 1*, 71734-70-8; 2, 2305-87-5; 2*, 71734-71-9; 3, 38675-31-9; 3*, 71734-72-0; 4, 3435-29-8; 4*, 71734-73-1; 5, 4891-69-4; 5*, 40889-17-6; 6, 71734-74-2; 6*, 71734-75-3; 7, 71734-76-4; 7*, 71734-76-4; 6-deuterio-4-phenylpyrimidine, 71734-77-5; 2-deuterio-4-phenylpyrimidine, 71734-78-6; 4-hydrazino-6-phenylpyrimidine, 35594-08-2; 2-hydrazino-4-phenylpyrimidine, 71734-79-7.

Stereoselectivity in the Cycloaddition Reactions of 2-Ethoxy-3-methylisoquinolinium Salts[1]

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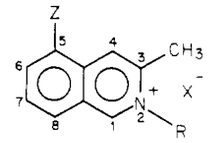
Received February 27, 1979

With styrenes, norbornenes, and cyclopentadiene, 2-ethoxy-3-methylisoquinolinium ion and its 5-nitro derivative undergo polar cycloaddition more readily than do their 2-methyl counterparts. Characteristic of these cycloadditions is a stereoselectivity which in many instances is 100% and which in nearly all instances is believed to have a polar origin.

The discovery[2-5] that 2,3-dimethylisoquinolinium salts (1) will undergo 1,4-addition both regioselectively and stereoselectively with alkyl vinyl ethers or cyclopentadiene was of theoretical interest but of limited synthetic value since less reactive alkenes (e.g., styrene) failed to react under any of the conditions tried. It was demonstrated that the reactivity of the isoquinolinium salt could be greatly enhanced if a nitro group was introduced at position 5 (cf. 2), permitting reaction with such relatively unactivated alkenes as β-pinene or norbornene.[6]

A promising alternate approach was suggested by earlier observations[7,8] that 2-alkoxyisoquinolinium salts show high reactivity toward the attack of nucleophiles. One of the implications of the electrophilic addition model[9-11] for cationic polar cycloaddition[12,13] is that enhanced electrophilicity of the cation should result in increased tendency toward cycloaddition.[14] The purpose of the present investigation was to determine whether cycloaddition was favored by replacing the *N*-alkyl group of quaternary isoquinolinium salts by *N*-ethoxyl and to learn whether the observed stereochemistry of addition was explicable in terms of the explanations presented earlier,[11] in particular with those parts dealing with stereoselectivity due to coulombic repulsion.

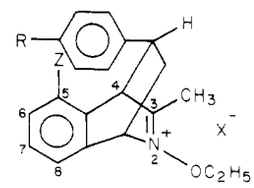
2-Ethoxy-3-methylisoquinolinium tetrafluoroborate (3, X = BF_4) can be prepared[15] conveniently by the action of triethyloxonium tetrafluoroborate on the *N*-oxide of 3-methylisoquinoline. With ethyl vinyl ether, 3 appeared



1, Z = H; R = CH_3
2, Z = NO_2; R = CH_3
3, Z = H; R = OC_2H_5
4, Z = NO_2; R = OC_2H_5

to induce immediate polymerization, and no pure cycloadduct was obtained. Similar results were obtained when the cation was 2-ethoxy-5-nitro-3-methylisoquinolinium tetrafluoroborate (4, X = BF_4).

The less reactive nucleophile *p*-methoxystyrene underwent simple cycloaddition, affording after 10 days a 96% yield of the expected adduct 5. From the ^1H NMR of the



5, R = OCH_3; Z = H
6, R = H; Z = NO_2
7, R = OCH_3; Z = NO_2

adduct 5 it is clear that only a single racemate is formed

(1) This research was supported by U.S. Public Health Service Research Grant No. HL02170 from the National Heart and Lung Institute of the National Institutes of Health.

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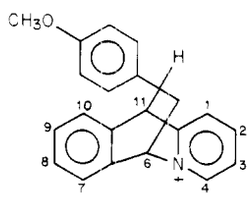
Table I. Adducts

no.	R	Z	X	mp,[a] °C	time, days	concn, M: cation	concn, M: olefin	yield, %	^{1}H NMR data,[b] δ: H_1	H_4	C-3 Me	OCH_2CH_3
						With Styrenes						
5	OCH_3	H	BF_4	122-122.5	10	0.36	1.25	96	6.13 (q)	4.73 (d)	2.87	4.61 (m), 1.50 (t)
6	H	NO_2	BF_4	158 dec	11	0.31	1.92	91	6.33 (q)	5.97 (d)	2.90	4.63 (m), 1.50 (t)
7	OCH_3	NO_2	BF_4	143-144	0.12	0.47	1.12	82	6.31 (q)	5.90 (d)	2.88	4.37 (m), 1.53 (t)
9	(indene)		PF_6	186.5 dec	3	0.25	2.15	85	6.47 (d)	6.07 (d)	2.93	4.53 (m), 1.53 (t)
						With Norbornenes						
10			PF_6	156.5 dec	7	1.0	7.44	76	6.12 (d)	6.03 (d)	2.81	4.53 (m), 1.43 (t)
11			PF_6	162-164	8	0.83	1.48	89	6.26 (d)	6.17 (s)	2.98	
12	(norbornadiene)		BF_4	174 dec	8	0.47	3.40	90	6.07 (d)	5.94 (d)	2.84 (syn) 2.87 (anti)	4.60 (m), 1.47 (t)
						With Cyclopentadiene						
13a	OC_2H_5	H	BF_4	131-132	0.2	0.15	3.5	90	5.87 (d)[c]	4.90 (d)	2.63	4.38 (m), 1.29 (t)
13	OC_2H_5	NO_2	PF_6	165 dec	0.08	0.32	4.04	71	6.41 (d)[d]	6.07 (d)	2.84 (anti) 2.91 (syn)	4.62 (m), 1.38 (t)

[a] Acceptable C, H, and N analyses were found for compounds listed in this table. [b] Except as noted all ^{1}H NMR data were obtained in CD_3COOH by using tetramethylsilane as an internal standard. [c] All NMR data with CD_3CN as solvent. [d] All NMR data with $(CD_3)_2CO$ as solvent.

(see Table I). This 100% stereoselectivity stands in contrast to the only 3:1 preference for the syn[16] compound (with respect to the phenylene ring, viz., 8) observed[11] when



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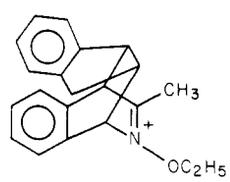

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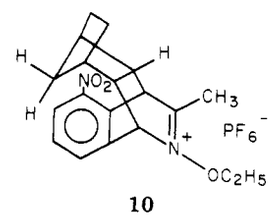
the acridizinium (benzo[*b*]quinolizinium) ion was the reactive cation. It was explained[11] that this stereochemical selectivity probably arose from the coulombic repulsion between the developing and receding positive charges in the charge-transfer complex at or near the transition state leading to the formation of 8 and its congeners. On the basis of the charge-repulsion theory[11] and the observations with respect to the addition of 2-phenyl-2-norbornene (vide infra), we feel confident in assigning to **5** the syn configuration. The adducts (**6** and **7**) obtained by the reaction of the 2-ethoxy-5-nitro-3-methylisoquinolinium ion (**4**) with styrene and *p*-methoxystyrene were each identified as a single racemate likewise assigned the syn configuration.

Indene, a congener of the styrenes, was shown earlier[11] to add to the 9-methylacridizinium ion to afford a mixture of stereoisomers in which the syn racemate predominated by a ratio of 4:1. With the 2-ethoxy-5-nitro-3-methylisoquinolinium hexafluorophosphate (**4**, X = PF_6), indene reacted in 3 days at room temperature to give an 85% yield of a single racemate, presumably the syn isomer (**9**).

An earlier study[17] of the polar cycloaddition of norbornene derivatives showed that in the addition to the acridizinium ion norbornene exhibits only a slight (60:40) preference for the syn isomer. The addition of norbornene to 5-nitro-2-ethoxy-3-methylisoquinolinium hexafluorophosphate (**4**, X = PF_6) afforded only a single racemate (**10**) easily identified by high-field protons which appear



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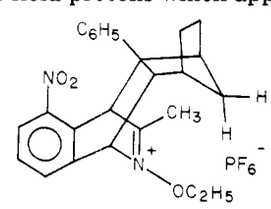

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as doublets at δ −0.68 and 0.67. The cause for the selectivity is not understood, but the forces involved must be fairly weak, for when 2-phenyl-2-norbornene is used as the addend, the phenyl group becomes stereocontrolling, taking the syn position (viz., **11**), while the norbornane ring must be anti, as judged by the lack of very high field signals.[18]

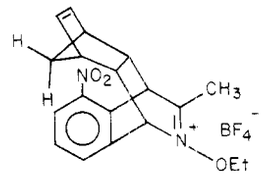
In its addition to the acridizinium ion, 2,5-norbornadiene is more stereoselective than is norbornene (73 vs. 60% syn). It is interesting that when the cation is 5-nitro-2-ethoxy-3-methylisoquinolinium tetrafluoroborate (**4**, X = BF_4), norbornadiene is *less* stereoselective, giving a mixture of stereosiomers in which the syn (**12a**) to anti (**12b**) ratio is

(16) The use of syn and anti to describe the spatial geometry with reference to the phenylene ring will be continued in this paper to permit easy comparison with the course of similar additions to the acridizinium nucleus. Clearly the expressions exo and endo are meaningless as applied to 8.

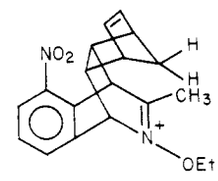
(17) Parham, M. E.; Frazer, M. G.; Bradsher, C. K. *J. Org. Chem.* **1972**, *37*, 358.

(18) A reviewer has suggested that those adducts (**11** and **12a**) of 2-phenyl-2-norbornene and norbornadiene which show no strongly shielded methylene groups may result from exo addition to the norbornadiene system. While such a violation of Alder's rule is not rigorously excluded, it is considered improbable since no such violation was seen in the addition of norbornene and norbornadiene to the acridizinium ion.[17]

only 60:40. It appears that in the anti isomer the 3-methyl



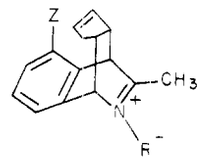
12a, syn, 60%



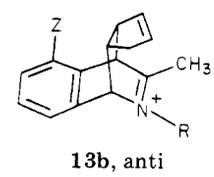
12b, anti, 40%

group is slightly deshielded, perhaps as a result of lying approximately in the plane of the ethylenic linkage and roughly at right angles to its principal axis.[19]

It was demonstrated earlier[5] by single-crystal X-ray crystallography that the only product obtained when cyclopentadiene reacts with 2,3-dimethylisoquinolinium ion is almost certainly **13a** (R = CH_3; Z = H), having the



13a, syn



13b, anti

cyclopenteno ring in the syn configuration.[20] The preference for syn (**13a**) over anti (**13b**) was explained[5,21] in terms of coulombic repulsion between developing and receding positive charges at or near the transition state. The same preference was shown[6] when the cationic substrate was further activated by introduction of a nitro group at position 5 (viz., **2**), only the syn racemate (**13a**, Z = NO_2; R = CH_3) being obtained.

When activation of the cationic substrate was carried out by replacing the 2-methyl group of **1** by an ethoxyl group (viz., **3**), cycloaddition occurred rapidly, a 90% yield being obtained in 5 h at room temperature as compared with the 2 weeks needed to produce a slightly smaller yield of **13a** (Z = H; R = CH_3) from **1**. The new adduct (**13a**, Z = H; R = OC_2H_5) appears to consist of only a single racemate, the syn form.

With **4**, in effect a double activated isoquinolinium salt, and cyclopentadiene a mixture of racemates is obtained (viz., **13a,b**, Z = NO_2; R = OC_2H_5), for the ^1H NMR of the product shows two separate signals for the 3-methyl group, one at δ 2.84 and the other at δ 2.91, in an integration ratio of 3:5. A model of the two adducts shows that in the anti isomer the plane of the double bond in the cyclopentene ring lies roughly at right angles to the 3-methyl group and should therefore[19] have a *shielding* effect. On this basis the less plentiful isomer (38%) with the resonance at δ 2.84 is assigned as the anti isomer so that the majority of the cycloadduct (62%) would have the syn configuration in accord with the coulombic repulsion rule.[5,11]

From the present work it appears that the stereoselectivity shown in the cycloadditions of isoquinolinium salts is in general greater than that found earlier[11] for acridizinium salts. It seems quite possible that the effectiveness of coulombic repulsion may be less in the three-ring acridizinium system simply because the positive charge, usually represented symbolically at the quaternary nitrogen, is further dissipated through resonance involving the additional ring. The failure of some of the isoquinolinium adducts (viz., **12** and **13**, Z = NO_2; R = OC_2H_5) to be formed with 100% selectivity is a reminder that steric factors (e.g., the NO_2 group) can be important, and in any case, the difference in energy of activation for the formation of syn vs. anti isomer must be quite small.

Experimental Section

The elemental analyses were carried out by M-H-W Laboratories. Melting points were determined in capillaries with a Thomas-Hoover melting point apparatus and are uncorrected. ^1H NMR spectra were obtained at 60 MHz on Varian A-60 and T-60 spectrometers.

2-Ethoxy-3-methylisoquinolinium Tetrafluoroborate (3, X = BF_4). To 12 g (75.4 mmol) of 3-methylisoquinoline *N*-oxide[22] dissolved in 100 mL of methylene chloride was added a solution containing 16 g (84.2 mmol) of triethyloxonium tetrafluoroborate in 80 mL of methylene chloride. After 3 days thin-layer chromatography showed that reaction was complete. Most of the solvent was removed under reduced pressure. Addition of 5 mL of methanol followed by addition of anhydrous ether gave a colorless crystalline material (18 g) which was recrystallized from methanol–ethyl acetate (80% yield): mp 93–95 °C (with previous softening at 83 °C); ^1H NMR ($CDCl_3$) δ 1.58 (t, 3, CH_3CH_2O), 2.87 (s, CH_3 at C-3), 4.71 (q, 2, CH_3CH_2O), 8.2 (m, 5, aromatic), 9.98 (s, 1, C-1).

Anal. Calcd for $C_{12}H_{14}BF_4NO$: C, 52.36; H, 5.09; N, 5.09. Found: C, 52.26; H, 5.08; N, 4.90.

3-Methyl-5-nitroisoquinoline *N*-Oxide. A solution of nitrosylsulfuric acid, prepared by dissolving 11.1 g (0.11 mol) of anhydrous potassium nitrate in 60 mL of concentrated sulfuric acid, was added dropwise, with stirring, over a period of 1 h to a solution prepared by addition of 15.9 g (0.1 mol) of 3-methylisoquinoline *N*-oxide to 80 mL of ice-cold concentrated sulfuric acid. The mixture was allowed to warm to room temperature and stirred for an additional 10 h before it was poured on ice and neutralized by addition of concentrated ammonium solution. The crude product (21 g) was collected, washed with water, and recrystallized from ethanol, affording 17 g (83%) of yellow crystals, mp 197–199 °C, suitable for further reaction. The analytical sample was recrystallized from ethanol: mp 201–202 °C; ^1H NMR (CF_3COOH) δ 3.11 (s, 3, Me), 8.20 (t, 1, C-7), 8.77 (d, 1, C-8), 9.11 (d, 1, C-6), 9.27 (s, 1, C-4), 9.91 (s, 1, C-1).

Anal. Calcd for $C_{10}H_8N_2O{\cdot}H_2O$: C, 54.05; H, 4.50; N, 12.61. Found: C, 54.03; H, 4.40; N, 12.61.

For comparison, a sample of 3-methyl-5-nitroisoquinoline *N*-oxide was prepared by action of hydrogen peroxide on the known[23] 3-methyl-5-nitroisoquinoline. The two preparations were shown to be identical by ^1H NMR and mixture melting point determination.

2-Ethoxy-3-methyl-5-nitroisoquinolinium Hexafluorophosphate (4, X = PF_6). To 16.3 g (73.7 mmol) of 3-methyl-5-nitroisoquinoline *N*-oxide monohydrate dissolved in 35 mL of methylene chloride was added 20.7 g (83.3 mmol) of triethyloxonium hexafluorophosphate in 40 mL of methylene chloride and the mixture allowed to stand for 3 days. The mixture was diluted with anhydrous ether and 28 g of crude salt collected. Recrystallization from methanol–acetonitrile afforded 25 g (90%) of colorless crystalline product: mp 188–189.5 °C; ^1H NMR (CF_3COOH) δ 1.73 (t, 3, CH_3CH_2), 3.10 (s, CH_3), 4.91 (q, 2, CH_3CH_2), 8.20 (t, 1, C-7), 9.11 (d, 1, C-6), 9.30 (s, 1, C-4), 10.02 (s, 1, C-1).

Anal. Calcd for $C_{12}H_{13}F_6N_2O_3P$: C, 38.10; H, 3.44; N, 7.41. Found: C, 37.96; H, 3.39; N, 7.15.

The tetrafluoroborate salt (4, X = BF_4) was prepared (91% yield) as described for the hexafluorophosphate salt (4, X = PF_6) except that triethyloxonium tetrafluoroborate was used as the

(19) Jackman, L. M.; Sternhell, S. "Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon: Oxford, 1969; pp 83–8.

(20) For convenience in making assignments the crystallographic study[5] was performed with the 2-ethyl rather than the 2-methyl cation (similar to **1** except R = C_2H_5); however, a detailed comparison of the ^1H NMR spectra showed that cyclopentadiene adducts from the two cations had similar configurations.

(21) A more considered view of the detailed mechanism involved in coulombic repulsion can be found in ref 9 and 11.

(22) Robison, M. M.; Robison, B. L. *J. Org. Chem.* **1956**, *21*, 1337.

(23) Elderfield, R. C.; Lagowski, J. M.; McCurdy, O. L.; Wythe, S. L. *J. Org. Chem.* **1958**, *23*, 435.

ethylating agent: mp 147–148 °C (presoftening at 136 °C); ^{1}H NMR (CF_3COOH) δ 1.73 (t, 3, CH_3CH_2), 3.11 (s, 3, CH_3), 4.91 (q, 2, CH_3CH_2), 8.25 (t, 1, C-7), 8.88 (d, 1, C-8), 9.15 (d, 1, C-6), 9.33 (s, 1, C-4), 10.09 (s, 1, C-1).

Anal. Calcd for $C_{12}H_{13}BF_4N_2O_3$: C, 45.00; H, 4.06; N, 8.75. Found: C, 44.93; H, 4.05; N, 8.81.

General Procedure for Cycloaddition Reactions. The appropriate quantity of the isoquinolinium salt (3 or 4) and the olefinic compound was dissolved in acetonitrile and (except as noted) the solution allowed to stand at room temperature until the ^{1}H NMR signal due to the H-1 proton of the isoquinolinium cation disappeared or until UV absorption at 236 nm disappeared. The solution was concentrated and anhydrous ether added to precipitate the adduct. The adduct was washed with ether to remove excess alkene and polymer and then recrystallized from methanol–acetonitrile.

Registry No. 3 (X = BF_4), 6220-89-9; **4** (X = BF_4), 71837-95-1; **4** (X = PF_6), 71837-96-2; (±)-**5**, 71837-98-4; (±)-**6**, 71838-00-1; (±)-**7**, 71838-02-3; (±)-**9**, 71886-79-8; (±)-**10**, 71838-04-5; (±)-**11**, 71886-81-2; (±)-**12a**, 71838-06-7; (±)-**12b**, 71883-68-6; (±)-**13a**, 71838-08-9; (±)-*syn*-**13**, 71927-79-2; (±)-*syn*-**13**, 71838-10-3; 3-methylisoquinoline *N*-oxide, 14548-00-6; nitrosylsulfuric acid, 7782-78-7; 3-methyl-5-nitroisoquinoline, 18222-17-8; *p*-methoxystyrene, 637-69-4; styrene, 100-42-5; indene, 95-13-6; 2-norbornene, 498-66-8; 2-phenyl-2-norbornene, 4237-08-5; cyclopentadiene, 542-92-7.

Mechanism of Allylic Hydroxylation by Selenium Dioxide

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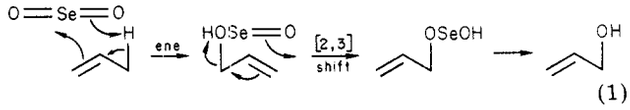
Received June 4, 1979

Both regiochemical and stereochemical aspects of the allylic hydroxylation reactions of selenium dioxide have been investigated. The principal findings are as follows. (1) In *tert*-butyl alcohol the mechanism is more complex than would be predicted by using the ene–[2,3]sigmatropic shift scheme proposed by Sharpless. (2) The stereochemical complexities appear to derive from ionic intermediates and can be suppressed in more basic media, e.g., *tert*-butyl alcohol/pyridine. (3) The strong preference for trans allylic alcohol products in the reaction is due to steric preferences in the [2,3]sigmatropic migration. The ene step is nonselective.

Allylic oxidation by selenium dioxide is one of a limited number of chemical reactions which introduce oxygen into a hydrocarbon molecule selectively and without structural rearrangement. Since its development by Guillemonat in the 1930's,[1] several mechanisms have been proposed for this transformation. Each of the early proposals had difficulty explaining the remarkable site selectivity of the reaction. A recent proposal by Sharpless and co-workers[2] has been able to overcome most of these difficulties. Their mechanism consists of a three-step sequence commencing with an ene reaction followed by a [2,3]sigmatropic rearrangement which generates an easily solvolyzed Se^{II} ester (reaction 1). In this mechanism the ene step can explain



(1)

the site selectivity of the reaction while the [2,3] shift explains the preference for *E* allylic alcohol products. Both key steps of this sequence can be formulated as a thermally allowed six-electron pericyclic process under the Woodward–Hoffmann formalism. This transformation could then be expected to proceed with clearly defined stereochemical constraints. We wish to report here the results of a study of the detailed stereochemistry of this reaction. These results are not entirely consistent with the rigid stereochemical pattern predicted by the ene–[2,3]-shift mechanism. The data are better accommodated by a mixture of mechanisms involving a stereospecific path such as that proposed and a stereochemically random path involving a stepwise ene reaction equivalent.

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Results and Discussion

This reaction has two important stereochemical aspects: (1) the relationship of the site attacked in the ene step to the final olefin geometry of the allylic alcohol and (2) the overall stereochemistry of the C–H → C–O transformation. Since the question of olefin geometry is crucial to the interpretation of the allylic stereochemistry, we will address this aspect of the problem first.

Olefin Geometry. Synthetic applications of the SeO_2 allylic oxidation have revealed that the reaction proceeds to give predominantly *E* olefin products.[3] These results parallel the geometric preference shown by [3,3] sigmatropic rearrangements of the Cope and Claisen variety.[4] The preference in the [3,3] cases apparently arises from the most favorable transition state geometry, generally a pseudochair cyclohexane with the largest groups in equatorial positions.[5] Similar geometric selectivity is evident in the selenium dioxide rearrangement studied by Sharpless and Lauer[2,6] (eq 2), indicating that an analogous steric effect might be operating in the pseudocyclopentane transition state.

Only one systematic study of this aspect of the SeO_2 reaction exists. Bahlerao and Rapoport[7] have examined a series of (*E*)- and (*Z*)-2-alkyl-2-heptenes. While this

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