Preparation of 28. A slurry of 0.204 g (1.07 mmol) of CuI in 5 mL of THF at −78 °C was treated with 1.10 mL of a 1.0 M solution of 3-pentyn-1-ylmagnesium bromide in THF. The resulting gray solution was treated with 0.132 mL (1.07 mmol) of $BF_3 \cdot Et_2O$ over a period of 30 min. The resulting orange solution at −78 °C was treated with 0.080 g (0.285 mmol) of enone **22** in 5 mL of THF in small protions over 6 h. The reaction was warmed slowly to 25 °C over 4 h. Normal workup gave 0.1281 (128%) of crude product. Chromatography on silica gel (6:1 hexane–ether) gave 0.055 g (55%, 76% based on recovered **22**) of **28** and 0.022 g (27%) of recovered **22**.

The data for **28** are: NMR ($CDCl_3$) δ 3.78 (dd, 1, J = 9, 9 Hz), 2.85–1.19 (m, 14), 1.77 (t, 3, J = 1 Hz), 0.88 (s, 9), 0.71 (s, 3), 0.05 (s, 6); IR (neat) 1710 cm^{-1}. An analytical sample was prepared by evaporative distillation (120 °C, 0.1 torr). Anal. Calcd for $C_{21}H_{36}O_2Si$: C, 72.35; H, 10.41. Found: C, 72.07; H, 10.35.

Oxidation of 28. Oxidation of **28** as described above for **31** gave 0.022 g (87%) of **29**: NMR ($CDCl_3$) 3.78 (dd, 1, J = 7, 7 Hz), 2.73 (m, 2), 2.58–1.15 (m, 12), 2.34 (s, 3), 0.88 (s, 9), 0.71 (s, 3), 0.04 (s, 6); IR (neat) 1715 cm^{-1}.

Cyclization of 29. A stirred solution of 0.022 g of diketone in 3 mL of EtOH was treated with 5 drops of 3 M aqueous NaOH. The solution was stirred for 20 min, diluted with water (20 mL), and acidified to pH 7 with dilute hydrochloric acid. The solution was extracted with three portions of CH_2Cl_2 which was dried (Na_2SO_4) and evaporated at reduced pressure to give 0.019 g of crude **30**. Chromatography on silica gel (4:1 hexane–ether) gave 0.012 g (59%) of **30** as white crystals: mp 94.0–95.5 °C; NMR ($CDCl_3$) 3.75 (m, 1), 2.75–1.15 (m, 12), 1.88 (d, 3, J = 2.3 Hz), 0.88 (s, 9), 0.81 (s, 3), 0.06 (s, 6); IR (CCl_4) 2960, 2930, 2860, 1685, 1470, 1460, 1255, 1140, 1110, 840 cm^{-1}; UV max (EtOH) 258 nm (ϵ 4880), 204. The data correspond closely to those of the corresponding *tert*-butyl ether.[22c]

Cyclization of Trione 34. Three drops of 10% aqueous potassium hydroxide solution was added to a solution of trione **34** (29 mg, 0.17 mmol) in MeOH (1 mL). The solution was stirred for 20 min and evaporated in vacuo. The residue was taken up in ether which was filtered through Na_2SO_4 and evaporated to give 16.4 mg of crude product which was ~50% **36**. Chromatography on silica gel (2:1 pentane–ether) gave 4.0 mg (14%) of a pure compound tentatively identified as **36**: NMR ($CDCl_3$) δ 1.60 (s, 3), 1.43 (s, 3); IR (CCl_4) 3600, 1765 cm^{-1}.

Acknowledgment. We wish to thank Keith McDaniel for carrying out the synthesis of **8** and its cyclization. We wish to thank Gary Phillips for carrying out the synthesis of **34** and its cyclization. We thank the National Institutes of Health for financial support of this research. Acknowledgment is made to the donors of the petroleum research Fund, administered by the American Chemical Society, for the partial support of this research.

Registry No. 8, 69245-96-1; **9**, 17428-83-0; **10**, 501-52-0; **11**, 85029-28-3; **12**, 85029-29-4; **13**, 85029-30-7; **15**, 85029-31-8; **18**, 85048-00-6; **19**, 85029-32-9; **20**, 85029-33-0; **21**, 85029-34-1; **22**, 85029-35-2; *cis*-**22**, 85029-48-7; **23**, 85081-51-2; **24**, 85029-36-3; **25**, 85029-37-4; **26**, 85029-38-5; **27**, 85081-52-3; **27** (aldehyde), 85029-49-8; **28**, 85029-39-6; **29**, 85029-40-9; **30**, 85029-41-0; **31**, 85029-42-1; **32**, 85029-43-2; **33**, 73922-20-0; **34**, 85029-44-3; **36**, 85029-45-4; 5-hexyn-1-ol, 928-90-5; 5-heptyn-1-yl tosylate, 70396-17-7; 5-heptyn-1-yl iodide, 70396-14-4; 1-ethoxyvinyllithium, 40207-59-8; 2-ethoxy-1-nonen-7-yne, 85029-46-5; 7-nonyn-2-one, 85029-47-6; 4-phenyl-2-butanone, 2550-26-7; 4-bromo-1-butene, 5162-44-7; 2-cyclohexenone, 930-68-7; 3-pentyn-1-yl bromide, 18719-27-2.

Chromyl Complexes in the Direct Epoxidation of Alkenes

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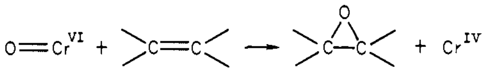
Received September 13, 1982

Abstract: Alkenes such as (*E*)- and (*Z*)-β-methylstyrene are converted stereospecifically by dinitratodioxochromium(VI), or chromyl nitrate, to the corresponding epoxide with high selectivities in aprotic media under rather mild conditions. The presence of the cosolvents, *N,N*-dimethylformamide (DMF), acetone, pyridine, etc., is critical for effective epoxidation with this reagent. In DMF and pyridine, the epoxide remains generally intact, but in acetone it is transformed to the corresponding alkene ketal which can also be isolated in high yields. The rates of oxidation are evaluated by the competition method, and the relative reactivities of various alkenes toward chromyl nitrate are found to generally parallel those previously determined for other chromyl reagents such as chromic acid, chromyl acetate, and chromyl chloride. Under optimum conditions for epoxidation, chromyl nitrate effects exclusive oxidation of 1,2-diphenylethanol to deoxybenzoin, which is uncontaminated by the usual cleavage products benzaldehyde and benzyl alcohol. Since the latter is known to derive from chromium(IV) intermediates, we conclude that the active species in chromyl epoxidation is oxochromium(V) formed in situ by the prior one-electron oxidation of solvent. The latter is in accord with the efficient transfer of the oxygen atom from macrocyclic oxochromium(V) species previously observed by Groves and co-workers. The ESR spectra of the transient chromium(V) intermediates derived from chromyl nitrate and chromyl acetate by reduction with cosolvent are reported.

Introduction

Chromium(VI) complexes have been extensively used as oxidants in a wide variety of both inorganic and organic systems.[1-4] The presence of at least one oxo–chromium bond, i.e., O═Cr, is the most common feature in such high-valent complexes.[5] Chemical reactivity is frequently centered around this functionality, and the possibility of effecting a direct transfer of the oxygen atom to a donor such as an olefin, e.g.,



represents a synthetically attractive goal and a theoretically challenging transformation.[6,7] Indeed, the oxidation of olefins by various chromium(VI) comlexes has a particularly long and interesting history revolving around the epoxide which has been suspected as the prime intermediate. Although there are some sporadic instances of the isolation of epoxides from the chromi-

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um(VI) oxidation of olefins, more generally they are putative intermediates by which formation of the ultimate products such as ketones, aldehydes, glycols, and their derivatives, etc., have been rationalized.

Chromic acid, $O_2Cr(OH)_2$, typically derived from the dissolution of chromium trioxide in aqueous acetic acid, is generally not a useful reagent for epoxidation, owing to the facile rearrangement (ring opening) and further oxidation of most epoxides under the acidic reaction conditions, the exception being the highly encumbered ones such as those derived from tetraarylethenes.[8] With the simpler olefins, epoxides are generally trapped as glycol monoacetates, although cyclohexene oxide has been successfully isolated once in 20% yields under controlled conditions.[9]

Chromic oxide complexes with bases such as Sarett's and Collin's reagent ($CrO_3{\cdot}2py$), are known to oxidize allylic alcohols to various epoxy derivatives.[10] However, epoxides are not reported to be major products from nonfunctionalized olefins.[11]

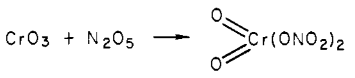
Chromyl acetate, $O_2Cr(OAc)_2$, is soluble in aprotic solvents such as acetic anhydride.[12] Compared to chromic acid, it does more generally afford epoxides in isolable amounts, especially from the highly substituted alkenes such as diphenyldimethylethylene, phenyltrimethylethylene, etc.[13-15] However, the yields of epoxides are generally poor, and none could be isolated from the oxidation of styrene.

Chromyl chloride, O_2CrCl_2, reacts readily with most olefins even in nonpolar solvents such as carbon tetrachloride, but a complex mixture of products is common. For example, from cyclohexene, less than 5% yield of cyclohexene oxide could be isolated only under carefully controlled conditions.[16] More often, the chlorohydrins and in some cases the *vic*-dichlorides are the important products.[17,18] However, stereochemical and deuterium-labeling studies have indicated that epoxides are actually formed in much larger amounts. Similar conclusions also probably apply to the related chromyl fluoride.[19]

We judge from the foregoing brief history that oxygen-atom transfer to alkenes is a common characteristic of chromyl oxidants despite the paucity of reports in which epoxides have been uniformly isolated. It is thus desirable to find another chromyl reagent which would be capable of the general epoxidation of various alkenes. Indeed the nitrate derivative has a number of physical and chemical properties[20] which make it an interesting chromyl reagent for the study of alkene oxidation.

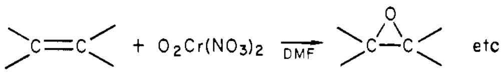
Results

Chromyl nitrate can be prepared readily from anhydrous chromium trioxide and dinitrogen pentoxide as a dark red, mobile liquid.[21,22] Since it is extremely hygroscopic and a powerful oxidizing agent, chromyl nitrate should be stored either in sealed ampoules or in glass-stoppered flasks (preferably with the aid of Teflon tape) in the dark, and care must be exercised to avoid direct contact with oxidizable compounds, including stopcock grease. However, chromyl nitrate dissolved in carbon tetrachloride is stable at ambient temperatures for up to several weeks, and is a useful form for all further manipulations of this reagent.



(1)

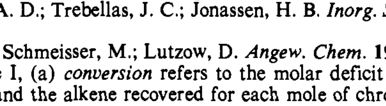
I. Formation of Epoxides from Alkenes with Chromyl Nitrate. Epoxidations were conveniently carried out by the dropwise addition of a solution of chromyl nitrate in carbon tetrachloride to an equimolar amount of the appropriate alkene dissolved in either a 1:1 v/v mixture of *N*,*N*-dimethylformamide (DMF) or pyridine and methylene chloride at −78 °C (eq 2). The various olefins in Table I afforded relatively large proportions of epoxides, with selectivities in the range from ~50% to more than 90%.[23] Although no systematic attempt was made to optimize the reaction conditions for each alkene, some important variations in the stoichiometry and the solvent are described separately in the Experimental Section (see Table X). Ketones and aldehydes as the principal byproducts (derived from the acid-catalyzed ring opening of the epoxides and/or carbon–carbon bond cleavages) were generally formed in less than 10% yield. With cyclohexene, however, small amounts of 2-cyclohexenol were observed under some conditions (vide infra).



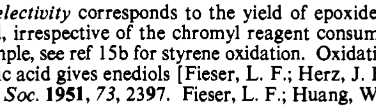
(2)

Conversions listed in Table I[23] were evaluated under a standard set of reaction conditions. As a result, the low conversions observed for alkenes, such as 1-octene and cyclohexene, are in direct contrast with the relatively high conversions of styrene and its analogues. The difference largely reflects the reactivity of the various double bonds to attack by chromyl nitrate since there always exists a concomitant oxidation of the medium, as described later.

Selectivity to epoxide formation[23] of styrene, norbornene, and 2,3-dimethyl-1,3-butadiene is unique insofar as there are no previous reports of the successful epoxidation of these olefins with other chromyl reagents.[24] i.e., eq 3 and 4. Although norbornene, 2,3-dimethyl-1,3-butadiene, and 2,3-dimethyl-2-butene are highly



(3)



(4)

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(8) (a) Mosher, W. A.; Steffgen, F. W.; Lansbury, P. T. *J. Org. Chem.* **1961**, *26*, 670. (b) Tetraarylethylenes are rather unreactive, and the epoxides were formed nonstereospecifically under rather drastic conditions in ~50% yields, together with benzpinacolones (~10%) and benzophenones (~40%). (c) Note that cyclized 9,10-diphenylphenanthrene is formed from chromyl chloride. See: (d) Gatzke, A. L.; Stairs, R. A.; Diaper, D. G. M. *Can. J. Chem.* **1968**, *46*, 3695. Gooden, R.; Brauman, J. I. *J. Am. Chem. Soc.* **1982**, *104*, 1483.

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(11) Usually a complex mixture resulting from allylic attack is obtained. See Dauben, W. G.; Lorber, M.; Fullerton, D. S. *J. Org. Chem.* **1969**, *34*, 3587. Marshall, C. W.; Ray, R. E.; Laos, I.; Riegel, B. *J. Am. Chem. Soc.* **1957**, *79*, 6308. Mailloux, M.; Weinman, J.; Weinman, S. *Bull. Soc. Chim. Fr.* **1970**, 3627. Rao, P. N.; Kurath, P. *J. Am. Chem. Soc.* **1956**, *78*, 5660.

(12) Chromyl acetate has been obtained as a low-melting red solid [Krauss, H. L. *Angew. Chem.* **1958**, *70*, 502]. More commonly it is generated in situ from chromium trioxide and acetic anhydride.

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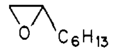
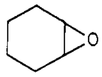
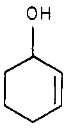
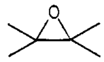
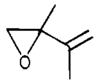
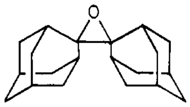
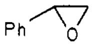
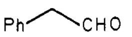
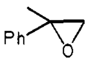
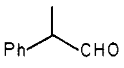
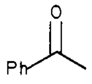
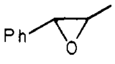
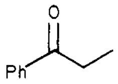
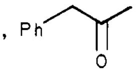
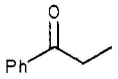
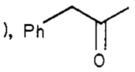
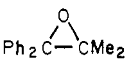
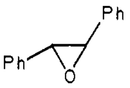
(22) See also Schmeisser, M.; Lutzow, D. *Angew. Chem.* **1954**, *66*, 230.

(23) In Table I, (a) *conversion* refers to the molar deficit between the alkene charged and the alkene recovered for each mole of chromyl reagent employed; (b) *selectivity* corresponds to the yield of epoxide based on the alkene converted, irrespective of the chromyl reagent consumed.

(24) For example, see ref 15b for styrene oxidation. Oxidation of steroidal dienes by chromic acid gives enediols [Fieser, L. F.; Herz, J. E.; Huang, W. Y. *J. Am. Chem. Soc.* **1951**, *73*, 2397. Fieser, L. F.; Huang, W. Y.; Babcock, J. E. *Ibid.* **1953**, *75*, 116. Fieser, L. F.; Herz, J. E. *Ibid.* **1953**, *75*, 121. Windaus, A. *Chem. Ber.* **1906**, *39*, 2249]. The formation of pinacolone has been reported from 2,3-dimethyl-2-butene [see ref 13 and Hickinbottom, W. J.; Wood, D. G. M. *J. Chem. Soc.* **1957**, 1600]. Norbornene with chromyl chloride affords chlorohydrins but no isolable epoxide [see Bachelor, F. W.; Cheriyan, U. O. *Tetrahedron Lett.* **1973**, 3291].

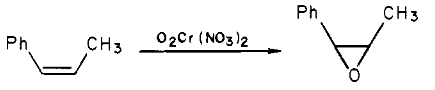
Table I. Formation of Epoxides from Alkenes with Chromyl Nitrate[a]

alkene	convn (%)	products (selectivity, %)
1-octene	14	 (43)
cyclohexene	38	 (45),(75)[b]  (<5)
norbornene	88	 (51)
2,3-dimethyl-2-butene		 (74)
2,3-dimethyl-1,3-butadiene	84	 (55)
diadamantilidene	71	 (92), adamantanone (3)
styrene	76	 (83),  (13), PhCHO (4)
α-methylstyrene	82	 (45),  (15),  (7)
(*E*)-β-methylstyrene[c]	70	 (94), [d]  (0),  (1), PhCHO (1)
(*Z*)-β-methylstyrene[e]	93	 (73), [f]  (3),  (1), PhCHO (3)
1,1-diphenylethene	87	no epoxide, Ph_2CHCHO (8), Ph_2CO (8)
2-methyl-1,1-diphenylpropene	43	 $Ph_2C\overset{O}{—}CMe_2$ (70), Ph_2CO (7)
(*E*)-stilbene	48	 (30), PhCHO (9)

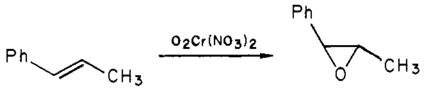
[a] Reactions carried out as described in the Experimental Section. [b] DMF (2 mL) replaced by pyridine (1 mL). [c] *E*/*Z* isomer ratio of 94/6. [d] Consists of 95% trans- and 5% cis isomers. [e] *E*/*Z* isomer ratio of 1/99. [f] Consists of 98% cis- and 2% trans isomers.

prone to afford rearranged products on treatment with various electrophiles (as a result of Wagner–Meerwein-type rearrangements of carbonium ion intermediates), no appreciable amounts of byproducts derived from such processes were observed with chromyl nitrate. However, the lowest selectivities were obtained with those alkenes, such as α-methylstyrene and 1,1-diphenylethene, which afford epoxides known to be among the most susceptible to acid-catalyzed ring opening.

Stereochemistry of epoxide formation is shown in Table I by the oxidation of (*E*)- and (*Z*)-β-methylstyrenes with chromyl nitrate to the corresponding trans and cis epoxides with a high degree of retention (>99%) (eq 5 and 6). The configuration is



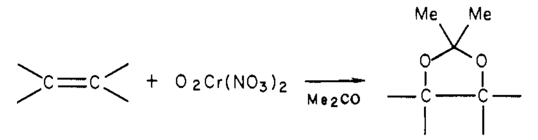
(5)



(6)

also known to be retained in previous studies of the chromyl acetate epoxidation of 2-butene,[25] the formation of chlorohydrins and epoxides (low yields) with chromyl chloride,[18] and the oxidation of (*Z*)-stilbene with tetraphenylporphinatochromium(V) oxide.[26]

II. Alkene Ketals from Chromyl Nitrate Oxidations in Acetone. When alkenes dissolved in acetone were treated with chromyl nitrate under the same conditions described above, the acetone ketals of the alkene diols, rather than the alkene oxides, were usually the major products (eq 7). The conversions of the alkenes



(7)

in acetone roughly parallel those obtained in DMF, the order of

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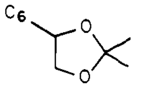
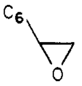
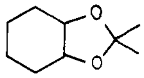
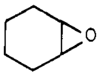
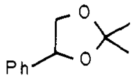
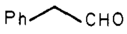
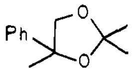
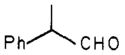
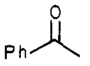
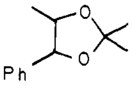
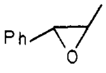
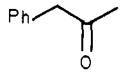
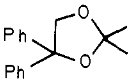
(25) Kruse, W. *J. Chem. Soc., Chem. Commun.* **1968**, *1610*.

(26) (a) Groves, J. T.; Kruper, W. J., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 7613. (b) Groves, J. T.; Kruper, W. J.; Nemo, T. E.; Myers, R. S. *J. Mol. Catal.* **1980**, *7*, 169. (c) For the oxochromium(IV) analogues, see Buchler, J. W.; Lay, K. L.; Castle, L.; Ullrich, V. *Inorg. Chem.* **1982**, *21*, 842.

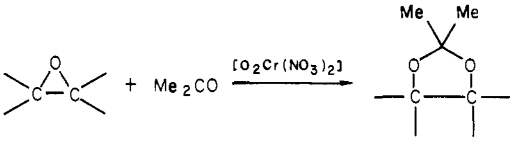
Table II. Formation of Alkene Ketals from Chromyl Nitrate in Acetone[a]

alkene	convn (%)	products (selectivity, %)
1-octene	40	 (5),  (45)
cyclohexene	52	 (29),  (6)
styrene	49	 (83),  (4), PhCHO (7)
α-methylstyrene	73	 (90),  (80),  (2)
β-methylstyrene[b]	63	 (16)[c],  (29)[d],  (1), PhCHO (8)
1,1-diphenylethene	75	 (80), Ph_2CHCHO (8), Ph_2CO (12)

[a] For the description of the reaction conditions, see Experimental Section. [b] Mixture of E/Z isomers used in the ratio of 94/6. [c] Mixture of cis/trans isomers formed in the ratio of 86/14. [d] Mixture of cis/trans isomers formed in the ratio of 91/9.

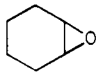
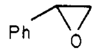
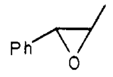
reactivity being: 1-octene < cyclohexene < substituted styrenes. With the exception of 1-octene, all of the olefins in Table II were generally converted with rather high selectivity to the alkene ketal (relative to the alkene oxide). The stereochemistry was indicated by the conversion of cyclohexene to the acetone ketal of *trans*-1,2-cyclohexanediol. However, the oxidation is not generally so stereospecific, since (*E*)-β-methylstyrene was converted to a cis/trans mixture of the corresponding alkene ketals. It is singularly noteworthy that 1,1-diphenylethene in acetone was oxidized to the corresponding ketal in excellent yields, especially if one considers that the oxidation of this olefin in DMF produced no isolable epoxide (see Table I).

The foregoing trends observed in acetone suggest that the alkene oxide is also the primary oxidation product, which under reaction conditions is subsequently converted to the alkene ketal, i.e., eq 8. In order to test this possibility, we subjected acetone solutions

 (8)

of several alkene oxides to a limited amount of chromyl nitrate at −78 °C for an hour under conditions which were equivalent to those employed for the alkene oxidations. The results in Table III show that epoxides were indeed converted to the acetone ketals in yields which more or less paralleled the selectivity listed in Table II. Thus cyclohexene oxide was only partially converted to the acetone ketal, whereas styrene oxide was completely converted to its ketal. β-Methylstyrene oxide showed intermediate sensitivity to ring opening. Importantly, the stereochemistry of the ring opening of epoxides under these conditions was such as to afford acetone ketals with the same configurations as those obtained directly from the chromyl nitrate oxidations of alkenes carried out in the presence of acetone. As shown in Table III, the stereochemistry is also the same as that obtained from epoxide ring openings catalyzed by the more conventional acid catalyst, boron trifluoride etherate.[27,28]

Table III. Conversions of Epoxides to Acetone Ketals under Reaction Conditions[a]

oxirane	catalyst	mol %	convn (%)	yield of ketal[b] (%)
	$O_2Cr(NO_3)_2$	40	28	43 (c/t = 5/95)
	$BF_3 \cdot OEt_2$	10	100	82 (c/t = 0/100)
	$O_2Cr(NO_3)_2$	20	97	88 + others[d]
	$O_2Cr(NO_3)_2$	20	58	27 (c/t = 84/16)[e]
		40	76	55 (c/t = 88/12)[e]
(*E*/*Z* = 95/5)		60	90	60 (c/t = 85/15)[e]
	$BF_3 \cdot OEt_2$	10	98	89 (c/t = 87/13)[e]
	HNO_3	10	68	16 (c/t = 33/67)[e]
	$O_2Cr(NO_3)_2$	20[c]	11	0[e]
	$ZnCl_2$	10	6	0

[a] In acetone at −78 °C for 1 h unless indicated otherwise. [b] Based on epoxide consumed. [c] In 50 vol % DMF-acetone. [d] PhCHO (2%) and $PhCH_2CHO$ (1%). [e] Other products detected: PhCHO (~1%), PhCOEt (trace), $PhCH_2COCH_3$ (~3%), and two unidentified components.

When either DMF or pyridine was used as a cosolvent with acetone, the rate of ring opening of the epoxide to ketal was retarded, probably as a result of ligand coordination to the catalytic chromium center (compare entries 4 and 9 in Table III). Since the acetone ketals are relatively stable to further oxidation, they provide a useful measure of the actual yields of epoxides formed during chromyl nitrate oxidations. Thus the low yields of epoxides derived from the oxidations of α-methylstyrene and 1,1-diphenylethene in DMF (see Table I) probably arose from the facile ring opening followed by further oxidation, since both olefins afforded excellent yields of the corresponding acetone ketal (see Table II).

III. Comparison of Chromyl Nitrate with Other Chromyl Complexes. The efficacy of chromyl nitrate as an epoxidizing agent for alkenes is illustrated in Table IV, in which it is compared to other chromyl complexes. We judge, from the conversion of styrene with high selectivity to styrene oxide in DMF and to the styrene ketal in acetone, that chromyl nitrate is significantly more effective in epoxidation than the chromyl reagents listed in Table IV.

IV. Solvent Effect on Epoxidations with Chromyl Nitrate. The choice of the solvent is critical to the successful formation of

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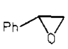
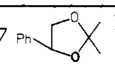
(27) Cf. Bersin, T.; Willfang, G. *Chem. Ber.* **1937**, *70B*, 2167. Willfang, G. *Ibid.* **1941**, *74B*, 145.

(28) In this regard, the formation of alkene ketals in acetone is similar to the ring-opened products usually observed in chromyl oxidations. It is also related to the cyclic carbonate formed in the chromic acid oxidation of tetraphenylethene[5a] from the bridged acetate intermediate (see discussion in ref 2, p 141).

Table IV. Various Chromyl Reagents for Styrene Oxidation in *N,N*-Dimethylformamide[a] and in Acetone[b]

			product (selectivity, %)			
chromyl reagent	solvent	conv (%)			$PhCH_2$-CHO	PhCHO
O_2CrCl_2	DMF	49	18		1	6[d]
O_2CrCl_2	py[c]	60	28		7	3[d]
$O_2Cr(OAc)_2$	DMF	44	18		2	7
$O_2Cr(O_2CCF_3)_2$	DMF	89	34		17	1
$O_2Cr(ONO_2)_2$	DMF	76	83		13	4
O_2CrCl_2	Me_2CO	63	tr[e]	16	tr[e]	14[d]
$O_2Cr(OAc)_2$	Me_2CO	70	13	7	6	23
$O_2Cr(O_2CCF_3)_2$	Me_2CO	79	1	51	1	6
$O_2Cr(ONO_2)_2$	Me_2CO	49	0	83	4	7

[a] Reactions carried out under conditions in Table I unless indicated otherwise. [b] Under conditions in Table II. [c] DMF–CH_2Cl_2 replaced by 25 vol % pyridine/CH_2Cl_2. [d] Small amounts of β-chloro-α-phenethyl alcohol and an unidentified minor product also found. [e] Trace detected.

Table V. Solvent Effects on the Epoxidation of Styrene with Chromyl Nitrate[a]

			product and yield (%)		
solvent	ε[b]	convn (%)	styrene oxide	$PhCH_2$-CHO	PhCHO
CH_3CN	36.2	100	30	9	4
CH_2Cl_2[c]	8.9	100	trace	12	9
CH_3NO_2	35.9	83	1	2	11
CH_3CO_2Et[d]	6.02	59	15	3	5
acetone[e]	20.7	49	83[f]	4	7
pyridine	12.3	64	67	9	trace
DMF	37.8	76	83	13	4
HMPA	~30	48	23	2	2

[a] Reactions carried out under conditions described in Table I, except the DMF was replaced by the solvent indicated. [b] Dielectric constant from Riddick, J. A.; Bunger, W. B. "Organic Solvents"; Weissberger, A., Ed.; Wiley: New York, 1970; Vol. II. [c] Under conditions of Table II. except acetone replaced by methylene chloride. [d] Same as footnote c, except acetone replaced by ethyl acetate. [e] See Table II, third entry. [f] Acetone ketal.

epoxide from chromyl nitrate. Thus Table V shows that styrene is converted to its epoxide with high selectivity in solvents such as *N,N*-dimethylformamide, acetone (ketal formation), acetonitrile, and pyridine. Ethyl acetate and hexamethylphosphoric triamide were less effective, and no significant amounts of styrene oxide were observed in either methylene chloride or nitromethane.

Several important features of epoxidation are qualitatively revealed by inspecting the solvent effects in Table V. First, there is no apparent correlation between the conversion of styrene and the selectivity to styrene oxide. Thus those factors involved in the attack on the double bond appear to be separate from the formation of epoxide. Second, the polarity of the solvent (as indicated by its dielectric constant) is less important than its ability to coordinate to a Lewis acid site on chromium.[29] Solvents such as DMF, pyridine, and acetone are particularly effective in this regard.

V. Reactivity of Alkenes in Chromyl Nitrate Oxidation. Owing to rates of chromyl nitrate oxidation which were too fast to follow conveniently, we chose the competition method to evaluate the reactivity of various alkenes. The various pairs of alkenes (X and Y) listed in Table VI were treated with chromyl nitrate under a standard set of conditions. Since a five-fold molar excess of alkene was generally employed, the relative reactivity can be readily approximated by the expression:[30]

$$k_x/k_y = (\Delta X/\Delta Y)(Y_0/X_0) \quad (9)$$

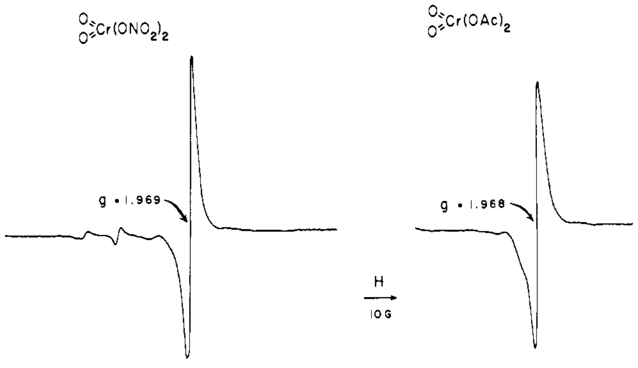


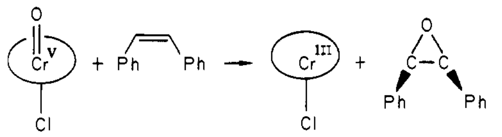
Figure 1. The X-band ESR spectrum obtained from the treatment of (left) chromyl nitrate and (right) chromyl acetate with acetone at −78 °C.

where ΔX and ΔY represent the consumption of the alkenes, and X_0 and Y_0 are their initial concentrations. As expected, the relative reactivity k_x/k_y evaluated by eq 9 is shown to be rather independent of the initial concentrations, X_0 and Y_0, of the styrene/α-methylstyrene pair in Table VI, entries 5–9. Furthermore as an additional check of the method, we also carried out competitive oxidations of other permuted pairs of alkenes, as presented in Table VI. For example, the direct competition indicated α-methylstyrene to be 2.2 times more reactive than styrene. The same relative reactivity was obtained when evaluated by an indirect competition by using either 1,1-diphenylethene or (*E*)-β-methylstyrene, as the common alkene (compare entries 10–11 and 14–15).

Discussion

Chromyl nitrate is particularly effective among other chromyl complexes in its ability to convert alkenes directly to epoxides. Although the alkene selectivity to epoxide can be high (see Table I), the yields based on the conversion of chromium(VI) to chromium(III) never exceeded ~60%, even in the most favorable cases (e.g., β-methylstyrene and diadamantilidene[31]). Accordingly, the chromyl epoxidation cannot be represented at this juncture by a simple stoichiometric relationship between reactants (chromyl nitrate, alkene) and products (epoxide, chromium(III), etc.). Indeed this ambiguity has permeated the extant literature concerning many oxidations with chromyl reagents.[32] Critical to this point is the uncertain role of chromium species with intermediate oxidation states such as Cr^V and Cr^{IV} in the step leading to epoxide formation.

In a particularly pertinent series of studies, Groves and coworkers[26] were able to generate a macrocyclic oxochromium(V) as a transient species capable of effectively converting alkenes to epoxides with high stereospecificity, e.g.,[33] eq 10. Since such



(10)

transformations are strikingly akin to epoxidations examined in this study, we might inquire whether analogous oxochromium(V) species can be generated from chromyl nitrate under reaction conditions. Indeed the ESR spectrum shown in Figure 1 (left) was obtained when acetone was added to a CCl_4 solution of chromyl nitrate frozen at −190 °C, and the mixture was allowed

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[29] For example, the ability of solvents to coordinate to a metal center such as $SbCl_5$ is in the order: HMPA > py > DMF > DMK > MeCN > $MeNO_2$ > CH_2Cl_2. See Gutman, V. "Coordination Chemistry in Nonaqueous Solutions"; Springer Verlag: New York, 1968.

[30] The relative reactivity determined by the competition method relates to the disappearance of alkene and is probably comparable to that usually measured spectroscopically by the disappearance of chromium(VI). Compare the methods employed in ref 49–51.

[31] Note that the epoxide of diadamantilidene was especially persistent since it is not susceptible to either electrophilic or nucleophilic ring opening: Wynberg, H.; Boelema, E.; Wieringa, J. H.; Strating, J. *Tetrahedron. Lett.* **1970**, 3613.

[32] See ref 2–4, 6, 8–10, 13–19 for examples of such ambiguities.

[33] The equatorial macrocyclic ligand is most commonly *meso*-tetraphenylporphyrin (TPP).

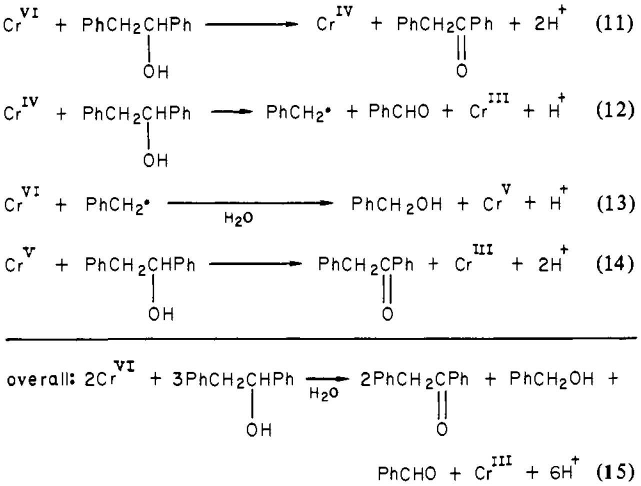
Table VI. Relative Reactivity of Various Alkenes toward Chromyl Nitrate[a]

alkene (X)	alkene (Y)	X (mmol)	Y (mmol)	ΔX^b (mmol)	ΔY^b (mmol)	$\frac{\Delta X + \Delta Y}{X + Y}$	rel rate[c] k_Y/k_X
cyclohexene	1-octene	0.486	0.503	0.107	0.0077	0.116	0.0695
styrene	cyclohexene	0.506	0.487	0.150	0.0353	0.187	0.244
styrene	norbornene	0.501	0.459	0.0533	0.149	0.210	3.05
α-methylstyrene	norbornene	0.521	0.503	0.0754	0.106		1.45
styrene	α-methylstyrene	0.500	0.493	0.0598	0.131	0.192	2.22
		0.755	0.489	0.109	0.157	0.214	2.22
		1.00	0.493	0.141	0.159	0.201	2.29
		1.26	0.491	0.184	0.170	0.202	2.38
		2.54	0.495	0.444	0.212	0.216	2.45
styrene	(*E*)-β-methylstyrene	0.508	0.493	0.0667	0.125	0.192	1.93
α-methylstyrene	(*E*)-β-methylstyrene	0.509	0.501	0.122	0.106	0.229	0.883
styrene	(*Z*)-β-methylstyrene	0.492	0.502	0.0934	0.127	0.221	1.33
(*E*)-β-methylstyrene	(*Z*)-β-methylstyrene	0.503	0.481	0.114	0.0832	0.200	0.763
styrene	1,1-diphenylethene	0.495	0.514	0.130	0.0545	0.183	2.29
α-methylstyrene	1,1-diphenylethene	0.487	0.529	0.101	0.114	0.211	1.04
styrene	(*E*)-stilbene	0.500	0.505	0.126	0.0379	0.163	0.299
styrene	(*Z*)-stilbene	0.493	0.513	0.120	0.0326	0.152	0.261
(*E*)-stilbene	(*Z*)-stilbene	0.490	0.573	0.0677	0.086	0.145	1.09
(*E*)-stilbene	(*Z*)-stilbene[d]	0.558	0.561	0.119	0.125	0.219	1.04

[a] Reactions carried out under the conditions of Table I using 20 mol % Cr(VI) to total alkene for 30 min. [b] Alkene converted. [c] Calculated according to eq 9. [d] 40 mol % Cr(VI) used.

to slowly warm up in the cavity of the spectrometer to −80 °C. The g value of 1.97 is in the range reported for a variety of other stable and transient oxochromium(V) complexes.[34-38] A similar ESR spectrum (g = 1.96) shown in Figure 1 (right) was obtained from the treatment of chromyl acetate with acetone under the same conditions. The extent of oxochromium(V) production under these conditions was estimated by double integration of the ESR signals using the stable tetrachlorooxochromate(V) as the reference.[39] (See Experimental Section for details.) The conversions of 10 and 20% measured for chromyl nitrate and acetate, respectively, no doubt represent the barest *minimum* yields which can be obtained for oxochromium(V), owing to the somewhat transient character of the ESR signals and the difficulty of completely mixing the components at the low temperatures. Thus these ESR experiments demonstrate that chromium(V) species are formed in important, not minor, amounts when either acetone or DMF is added to chromyl nitrate dissolved in CCl_4. Notably the amplitude of the ESR spectra in Figure 1 diminished rapidly upon the addition of styrene at −80 °C. Similar experiments have demonstrated that the facile reduction of chromyl nitrate to metastable oxochromium(V) species can also be effected by DMF and pyridine.

Scheme I



$$Cr^{VI} + PhCH_2\underset{OH}{\underset{|}{C}}HPh \longrightarrow Cr^{IV} + PhCH_2\underset{O}{\underset{\|}{C}}Ph + 2H^+ \tag{11}$$

$$Cr^{IV} + PhCH_2\underset{OH}{\underset{|}{C}}HPh \longrightarrow PhCH_2\cdot + PhCHO + Cr^{III} + H^+ \tag{12}$$

$$Cr^{VI} + PhCH_2\cdot \xrightarrow[H_2O]{} PhCH_2OH + Cr^{V} + H^+ \tag{13}$$

$$Cr^{V} + PhCH_2\underset{OH}{\underset{|}{C}}HPh \longrightarrow PhCH_2\underset{O}{\underset{\|}{C}}Ph + Cr^{III} + 2H^+ \tag{14}$$

$$\text{overall: } 2Cr^{VI} + 3PhCH_2\underset{OH}{\underset{|}{C}}HPh \xrightarrow[H_2O]{} 2PhCH_2\underset{O}{\underset{\|}{C}}Ph + PhCH_2OH + PhCHO + Cr^{III} + 6H^+ \tag{15}$$

Table VII. Oxidation of Diphenylethanol by Chromyl Nitrate in Several Solvents[a]

	product (mmol)				
solvent	PhCHO	$PhCH_2OH$	$PhCH_2$-COPh	$PhCH_2$-CH(OH)Ph	material balance[b]
CH_2Cl_2	0.400	0.090	0.450	0.252	0.947
CH_3CN[c]	0.156	0.009	0.437	0.412	0.932
acetone	0.087	0	0.463	0.465	1.02
DMF[d]	0	0	0.430	0.555	0.985
pyridine[e]	0	0	0.330	0.667	0.997
HMPA[f]	0	0	0.253	0.749	1.00
DMF[g] (after 1 h)	0	0	0.139	0.825	0.964

[a] Solution of 0.5 mmol of $O_2Cr(NO_3)_2$ in 0.66 mL of CCl_4 added dropwise to a solution of 1 mmol of 1,2-diphenylethanol in 4 mL of solvent at −78 °C. [b] Sum of ketone, recovered alcohol, and one-half sum of benzaldehyde and benzyl alcohol. [c] 25 vol % CH_3CN/CH_2Cl_2. [d] 50 vol % DMF/CH_2Cl_2. [e] 25 vol % py/CH_2Cl_2. [f] 25 vol % $HMPA/CH_2Cl_2$. [g] $O_2Cr(NO_3)_2$ dissolved in 4 mL of DMF/CH_2Cl_2 at −78 °C, solution stirred for 1 hr, and then a solution of the alcohol in 1 mL of CH_2Cl_2 added.

In order to *quantitatively* determine the role of solvent in the production of oxochromium(V) from chromyl nitrate, we utilized the oxidative cleavage of 1,2-diphenylethanol as a mechanistic probe. Thus extensive studies of alcohol oxidation with chromic acid by Roček,[40] Wiberg,[41] Trahanovsky,[42] and co-workers have led to the conclusion that Cr^{IV} species are responsible for the byproducts derived by carbon–carbon bond cleavage. The relative involvement of Cr^{V} and Cr^{IV} species in this mechanistic scheme, as applied to the chromium(VI) oxidation of 1,2-diphenylethanol, is presented in Scheme I. According to this scheme, the ketone (deoxybenzoin) can be formed by two concurrent pathways involving Cr^{VI} and Cr^{V} in eq 11 and 14, respectively. Moreover, the extent to which Cr^{VI} is involved in ketone formation is directly reflected in the concomitant production of the cleavage products, benzyl alcohol and benzaldehyde, according to eq 11–13. Thus the production of benzaldehyde and benzyl alcohol can be used as a diagnosis for the overall three-electron [$Cr^{VI} \rightarrow Cr^{III}$] conversion via a pathway involving successive two-electron and

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(34) Kon, H. *J. Inorg. Nucl. Chem.* **1963**, *25*, 933.

(35) Krumpolc, M.; DeBoer, B. G.; Roček, J. *J. Am. Chem. Soc.* **1978**, *100*, 145.

(36) Wiberg, K. B.; Schafer, H. *J. Am. Chem. Soc.* **1969**, *91*, 933.

(37) Freeman, F.; Armstead, C. R.; Essig, M. G.; Karchefski, E. M.; Kojima, C. J.; Manopoli, V. C.; Wickman, A. H. *J. Chem. Soc., Chem. Commun.* **1980**, 65.

(38) Jennette, K. W. *J. Am. Chem. Soc.* **19828** *104*, 874.

(39) Krauss, H. L.; Leder, M.; Munster, G. *Chem. Ber.* **1963**, *96*, 3008.

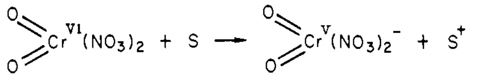
(40) (a) Roček, J.; Radkowsky, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 2986. (b) Roček, J.; Radkowsky, A. E. *Ibid.* **1973**, *95*, 7123.

(41) (a) Wiberg, K. B.; Mukherjee, S. K. *J. Am. Chem. Soc.* **1974**, *96*, 1884. (b) Wiberg, K. B.; Mukherjee, S. K. *Ibid.* **1974**, *96*. 6647.

(42) Nave, P. M.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1970**, *92*, 1120.

one-electron processes, such as that described by eq 11-13. Indeed the results corresponding to ~40% cleavage in Table VII show that chromyl nitrate oxidations in methylene chloride as the solvent do proceed in accord with Scheme I.[43] However, it is singularly noteworthy that the same oxidations carried out in either DMF or pyridine afford only deoxybenzoin, uncontaminated by either benzaldehyde or benzyl alcohol (see entries 4 and 5). Relatedly, the chromyl nitrate oxidations in acetone yield only minor amounts of benzaldehyde. It is interesting to note that essentially the same results were obtained when DMF was added to chromyl nitrate beforehand, and the resulting solution was allowed to stand an hour prior to the addition of 1,2-diphenylethanol (see entry 7, Table VII). We conclude from these observations that the overall three-electron [$Cr^{VI} \rightarrow Cr^{III}$] pathway is unimportant for chromyl nitrate oxidations in the presence of either acetone, DMF, or pyridine. Furthermore, in order to establish the intimate relationship between the rates of alcohol oxidation and alkene epoxidation, we carried out a direct competition between 1,2-diphenylethanol and styrene toward chromyl nitrate in acetone. The value of 0.31 determined for the reactivity of styrene relative to 1,2-diphenylethanol indicates that alcohol oxidation is indeed a reasonable measure of alkene epoxidation, insofar as the substrate reactivity is concerned.

The foregoing results are best accommodated by invoking oxochromium(V) as the predominant oxidant formed under those optimum conditions required for epoxidations with chromyl nitrate. If so, we speculatively suggest that it is derived from chromyl nitrate by one-electron oxidation of the solvent S by a process such as:[44]



$$O_2Cr^{VI}(NO_3)_2 + S \longrightarrow O_2Cr^{V}(NO_3)_2^- + S^+ \qquad (16)$$

Since chromyl nitrate is a potent oxidant, it may not be too surprising that even acetone, which is not commonly considered to be readily oxidized,[45] is easily attacked. Such a transformation must be effective even in competition with the oxidation of the alkene.[46] Barring the availability of further experimental evidence, let us proceed on the basis of oxochromium(V) as the active epoxidizing agent, in accord with the precedent established by Groves and co-workers[26,32] in eq 10. Following the postulation of eq 16, we would then formulate the epoxidation as:[47]

Table VIII. Reactivities of Various Alkenes Relative to Styrene during Chromyl Nitrate Oxidation. Ionization Potentials IP of Alkenes

alkene	rel rate $k/k_{styrene}$	($\log k/k_{styrene}$)	IP (eV)
1-octene	0.0154	−1.81	9.52[b]
cyclohexene	0.244	−0.613	8.95[c]
norbornene	3.14	0.497	8.95[d]
styrene	1	0	8.43[e]
α-methylstyrene	2.22	0.346	8.35[f]
(*E*)-β-methylstyrene	1.94	0.288	8.35[f]
(*Z*)-β-methylstyrene	1.41	0.149	
1,1-diphenylethene	2.30	0.362	8.00[g]
(*E*)-stilbene	0.225	−0.648	~7.70-7.76[g]
(*Z*)-stilbene	0.238	−0.623	7.80[g]

[a] From data in Table VI. [b] Honig, R. E. *J. Chem. Phys.* 1948, *16*, 105. [c] Watanabe, K. *Ibid.* 1957, *26*, 542. [d] Steele, W. C.; Jennings, B. H.; Botyos, G. L.; Dudek, G. O. *J. Org. Chem.* 1965, *30*, 2886. [e] Dewar, M. J. S.; Worley, S. D. *J. Chem. Phys.* 1969, *50*, 654. [f] Watanabe, K.; Nakayama, T.; Mottle, J. *J. Quant. Spectrosc. Radiat. Transfer* 1962, *2*, 369. [g] Rosenstock, H. M. "Ion Energetics Measurements"; U.S. Department of Commerce and National Bureau of Standards Publications: Washington, D.C., 1980.

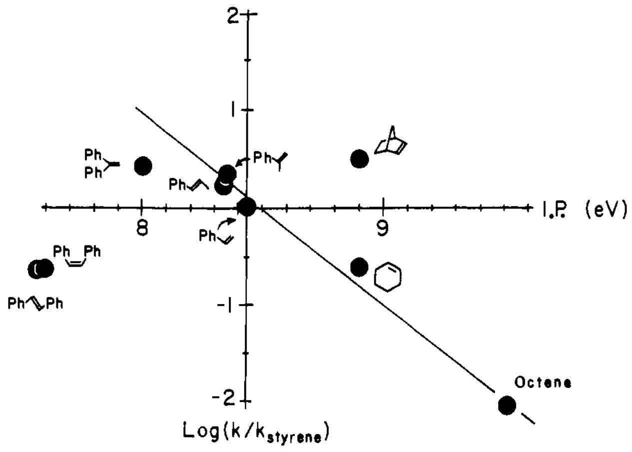
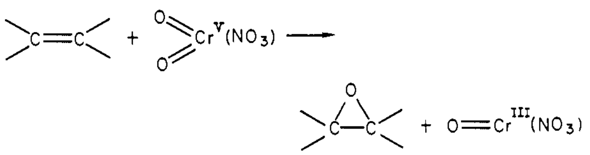


Figure 2. The relationship between the reactivity of an alkene to chromyl nitrate oxidation and the ionization potential IP of the alkene. The alkene reactivities are evaluated relative to that of styrene as log ($k/k_{styrene}$). See ref 48 for the significance of the line.



(17)

The sequence of steps in eq 16 and 17 readily accounts for the experimental observation that no more than two-thirds of chromium(VI) is available for epoxidation (see Table I). Let us now consider what the reactivity of the alkene reveals about the epoxidation step.

The relative reactivities of various alkenes to chromyl nitrate, as listed in Table VIII, can all be related to that of styrene as the common reference. The summary of the kinetics data in Table

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[43] The experimental stoichiometry is intermediate between (a) 4Cr(VI) + 5ROH → 3K + 3PhCHO + $PhCH_2OH$, and (b) 2Cr(VI) + 2ROH → K + 2PhCHO, where ROH is 1,2-diphenylethanol and K is deoxybenzoin.

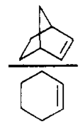
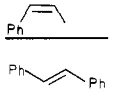
[44] (a) Chromyl nitrate even reacts with methylene chloride with foaming to afford a green solution [Cr(III) ?] at room temperature. (b) For a related example of the reduction of Cr(VI) to Cr(V), see Miteva, M.; Bonchev, P.; Kabasanov, K.; Petrov, G.; Natsokova, M. *Dokl. Bolg. Akad. Nauk.* **1978**, *31*, 1437. (c) A variety of other structures can be presented for the chromium(V) species in eq 16, such as the neutral $O_2Cr(NO_3)$. It is also possible that solvent reacts with $O_2Cr(NO_3)_2$ by hydrogen-atom transfer to afford species such as $OCr(OH)(NO_3)_2$. The experimental evidence thus points to chromyl nitrate as a rather indiscriminate oxidant. Since the cosolvent is present in excess, we believe that it is attacked preferentially over the alkene or alcohol substrate. The results in the last entry of Table VII indicate the chromium(V) species to be short-lived, but sufficiently persistent to be active for a short while at −78 °C. (d) A referee has suggested an alternative explanation of the effect of cosolvent, in which chromyl nitrate initially effects the epoxidation of alkene and affords a reactive, unstable chromium(IV) intermediate scavenged by the cosolvent. However, the ESR observation of chromium(V) in *substantial* amounts is not readily accommodated by this mechanism. [Note that the measurement of the instantaneous ESR signal for the metastable chromium(V) in this type of experiment allowed only a bare lower limit of 10-20% yield to be measured. The time-integrated conversion to chromium(V) formed in toto is no doubt much higher than this, and could have easily approached 100%.] A kinetic study measuring the effect of alkene on the rate of disappearance of chromium(VI) would clearly distinguish these mechanisms. Unfortunately, chromyl nitrate is too reactive (see note a above) to effectively carry out such experiments.

[45] However, compare studies of the electrochemical oxidation of ketones by Becker, J. Y.; Byrd, L. R.; Miller, L. L.; So, Y. H. *J. Am. Chem. Soc.* **1975**, *97*, 853. Becker, J. Y.; Miller, L. L.; Siegel, T. M. *Ibid.* **1975**, *97*, 849.

[46] Since the formation of oxochromium esters from alcohols is rapid,[41] it is possible that esterification occurs first, followed by one-electron oxidation of the chromium(VI) ester.

[47] (a) Since the extent of nitrate coordination to chromium(V) is unknown, it is presented as a neutral complex in eq 17. (b) The transfer of oxygen from the oxo-chromium bond is reasonable, but it will be established by oxygen-labeling studies at a later time. Note that oxygen atom transfer from a nitrate ligand is known. See, for example: Kuznetsova, N. I.; Likholobov, V. A.; Fedotov, M. A.; Yermakov, Y. I., *J. Chem. Soc., Chem. Commun.* **1982**, 973.

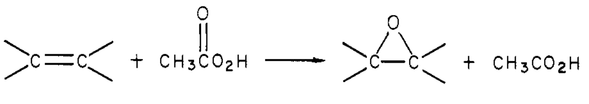
Table IX. Relative Reactivities of Alkenes toward Various Chromyl Reagents and Peroxides

electrophile	Hammett ρ	$\frac{\log (k/k_0)}{\text{IP}}$	$\frac{Ph_2C{=}CH_2}{\text{styrene}}$		
$O_2Cr(NO_3)_2$[a]		−1.95	2.30	12.9	1.1
$O_2Cr(OH)_2$[b]		−1.92	2.17	5.5	0.26
O_2CrCl_2[c]	−1.99[d]	−3.06	12.8	511	1.8
RCO_3H[e]	−1.30[d]	−3.23[f]	4.3[f]	1.2[g]	1.7[h]
MoO_5·HMPA[i]				1.94	

[a] This work. [b] Reference 49. [c] References 50 and 51. [d] Based on σ^+. [e] Various peracids as noted. [f] Peracetic acid from Swern, D. *J. Am. Chem. Soc.* **1947**, *69*, 1692. [g] Perlauric acid from Bingham, K. D.; Meakins, G. D.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1966**, 445. [h] Lynch, B. M.; Pausacker, K. H. *J. Chem. Soc.* **1955**, 1525. [i] Sharpless, K. B.; Townsend, J. M.; Williams, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 295.

VIII includes the gas-phase ionization potentials IP of the alkenes. Indeed, the plot of the ionization potential of the alkene, which is a measure of electron availability, against the relative reactivity (log k/k_{styrene}) is reasonably linear, as shown in Figure 2. Although most of the aliphatic and aromatic alkenes are included, (*E*)- and (*Z*)-stilbenes are significantly less reactive and norbornene is more reactive than expected from the linear correlation shown.[48]

The reactivity pattern for chromyl nitrate oxidations of alkenes bears a strong resemblance to the related chromic acid oxidations reported earlier by Awasthy and Roček.[49] Thus the slope of −1.9 for the plot of log (k/k_{styrene}) vs. IP in Figure 2 compares with a slope of −1.92 for the corresponding plot of chromic acid oxidations.[53] Chromyl chloride oxidations appear to be somewhat more sensitive to charge development, since the good linear correlation of log (k/k_{hexene}) vs. IP has a slope of −3.06.[50,53] The same effect is reflected in the chromyl chloride oxidation of substituted styrenes by Freeman and Yamachika,[51] who obtained a Hammett ρ value of −1.99. Such free-energy correlations for chromyl oxidations of alkenes are summarized in Table IX. Included are data relating to the peracid epoxidations of alkenes, e.g.,



(18)

for which there is ample discussion concerning the transition state for oxygen atom insertion into the carbon–carbon double bond.[52] In particular, the stereospecificity of epoxide formation has led to the consideration of the relative reactivities of various pairs of alkenes (such as cyclohexene/norbornene, (*E*)-/(*Z*)-stilbenes, styrene/1,1-diphenylethene, etc.) among others, as an indication of the ring size of the transition state for oxygen-atom transfer.[53] The summary of the extant data in Table IX provides no consistent clue on this point. However, taking into account some of the uncertainties relative to the experimental ambiguities,[54] we do not consider the activation process for these reactions to be strongly differentiated. Thus if the recent suggestion[18] of oxametallacyclobutane intermediates applies to chromyl chloride oxidations, it is reasonable to conclude from the data in Table IX that similar intermediates (or transition states) pertain to peracid epoxidations.

Summary and Conclusions

The oxidation of alkenes by chromyl nitrate bears a strong resemblance to other, widely used chromyl reagents such as chromic acid, chromyl chloride, and chromyl acetate. Thus the isolation of epoxides in high yields with chromyl nitrate supports the earlier, indirect evidence for epoxides as prime intermediates in the reactions of chromyl reagents with alkenes. However, studies based on the ESR observation of transient intermediates as well as the oxidative cleavage of 1,2-diphenylethanol indicate that oxochromium(V) species are the active agent for oxygen-atom transfer from the chromyl nitrate reagent. The extent to which analogous oxochromium(V) species are involved with other chromyl reagents bears direct relevance to theoretical formulations of chromyl oxidations.[55]

Experimental Section

Materials. Chromium trioxide from Matheson, Coleman and Bell was dried in vacuo for 6 h at 100 °C prior to use. 1-Octene, cyclohexene, norbornene, 2,3-dimethylbutadiene, styrene, α-methylstyrene, (*E*)-β-methylstyrene (containing 4% *Z* isomer), 1,1-diphenylethene were all commerical samples which were redistilled before use. (*E*)-Stilbene was used as received from Matheson, Coleman and Bell. (*Z*)-β-Methylstyrene was prepared from phenylpropyne by partial hydrogenation over 10% Pd on $BaSO_4$ in quinoline.[56] bp 54° (15 mm). 2-Methyl-1,1-diphenylpropene[57] and adamantylideneadamantane[58] were synthesized as described in the literature. (*Z*)-Stilbene was used as received from Aldrich Chemical Co.

Acetonitrile, nitromethane, ethyl acetate, acetone, pyridine, *N*,*N*-dimethylformamide, and methylene chloride were reagent-grade commercial solvents which were dried and repurified by standard methods described by Perrin et al.[59] and redistilled prior to use. Carbon tetrachloride (1 L of technical grade) was treated with 200 mL of concentrated H_2SO_4 for 2 days and then washed successively with water, 5% $NaHCO_3$ twice, and water several times before it was dried over anhydrous $CaCl_2$. The resulting CCl_4 was further purified by treatment with chromyl chloride (~4 g), as described by Freeman and Yamachika.[60]

Chromyl chloride was prepared by the reported procedure[61] and stored in a sealed ampoule. **Chromyl acetate** was prepared in situ from chromium trioxide and acetic anhydride, prior to use as described.[62] The

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(48) The line in Figure 2 was arbitrarily drawn to include 1-octene and styrene, since these alkenes have been commonly employed in studies of other chromyl oxidations (see ref 49–53). It is not intended to indicate whether there is, or there is not, a relationship between the reactivity and the ionization potential of the alkene. It does emphasize the enhanced reactivity of norbornene and the diminished reactivity of the stilbenes to chromyl nitrate.

(49) Awasthy, A. K.; Roček, J. *J. Am. Chem. Soc* **1969**, *91*, 991.

(50) Freeman, F.; Arledge, K. W. *J. Org. Chem.* **1972**, *37*, 2656.

(51) Freeman, F.; Yamachika, N. J. *J. Am. Chem. Soc.* **1972**, *94*, 1214.

(52) (a) For a discussion of the transition state, see Dryuk, V. G. *Tetrahedron* **1976**, *32*, 2855, and Plesničar, B.; Tasevski, M.; Ažman, A. *J. Am. Chem. Soc.* **1978**, *100*, 743. (b) See also ref 6 and 53 for discussions of the effects of the alkene structure on the stereospecific oxygen insertion.

(53) (a) Freeman, F. *Chem. Rev.* **1975**, *75*, 439. (b) This approach focuses exclusively on the structure of the alkene to reveal the nature of the transition state for oxygen atom transfer, more or less independent of the transferring reagent, whether it be a peracid, oxometal, peroxometal, etc.

(54) Chromyl oxidations of alkenes are notorious for producing mixtures of products. Although the stoichiometry with chromyl nitrate is better than most, the relative reactivities determined from the consumption of alkene are limited by this factor. Essentially the same ambiguities apply to alkene reactivities determined from the measurement of chromium(VI) disappearance. See ref 30.

(55) Note that the recent theoretical formulation[7] of chromyl oxidations proceeding via oxametallacyclobutane intermediates is based on an oxochromium(VI) model.

(56) Cram, D. J.; Allinger, N. L. *J. Am. Chem. Soc.* **1956**, *78*, 2518.

(57) See ref 14b.

(58) Geluk, H. W. *Synthesis* **1970**, 652.

(59) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: New York, 1980.

(60) Freeman, F.; Yamachika, N. J. *J. Am. Chem. Soc.* **1970**, *92*, 3730.

(61) Sisler, H. H. *Inorg. Syn.* **1946**, *2*, 205.

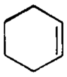
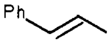
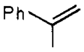
(62) Schildknecht, H.; Fottinger, W. *Justus Liebigs Ann. Chem.* **1962**, *659*, 20.

carbon tetrachloride solution was kept in the dark and the titer standardized iodometrically[63] (usually ~85–95%). **Chromyl trifluoroacetate** was prepared by a modification of Gard and Gerlach's[64] procedure as follows. Powdered chromium trioxide (2.75 g, 27.5 mmol) contained in a 50-mL flask stoppered with a Teflon stopcock was dried in vacuo (~10^{-2} mm) at 100 °C for 5 h. The flask was cooled to 0 °C, and 40 mL of dried CCl_4 and 25 mmol of trifluoroacetic anhydride were added. The mixture was stirred over nitrogen with the aid of a Teflon-coated magnetic stirbar for 16 h in the dark. The excess chromium trioxide was separated by filtration through a sintered glass filter, and the dark red solution standardized iodometrically was 0.54 M (92%). This solution of chromyl trifluoroacetate was more stable than a similar solution of chromyl acetate and could be kept in the dark in a sealed flask for several days. Chromyl trifluoroacetate is an active oxidant capable of readily reacting with most common solvents (including methylene chloride) and silicone vacuum grease under ambient conditions. Thus all manipulations must be carried out in wholly glass systems with no grease. Teflon tape is recommended for making the seals in all ground-glass joints. **Chromyl nitrate** was synthesized by the Jonassen method[21] from chromium trioxide and dinitrogen pentoxide. The dark red liquid was kept in the dark in a flask sealed with a Teflon stopcock. Chromyl nitrate is a more powerful oxidizing agent than chromyl trifluoroacetate, and due care must be exercised to avoid all contact with organic materials and metals. Teflon tape was a suitable sealant, and transfers were made with the aid of glass hypodermic syringes equipped with Teflon needles. All of the chromyl reagents share a common dark red color characteristic of the dioxochromium(VI) moiety. The visible–ultraviolet absorption spectrum of chromyl chloride shows a broad maximum centered at 298 nm (415 sh).[65] Similarly chromyl fluoride has λ_{max} 278 nm, 383 (sh),[64] chromyl acetate, λ_{max} 283 nm, 400 (sh);[66] chromyl trifluoroacetate, λ_{max} 286 nm, 410 (sh);[64] chromyl nitrate, λ_{max} 278 nm, 235 (sh), 254 (sh), 393 (sh).[67]

The epoxides used in this study were prepared from the epoxidation of the corresponding alkene with *m*-chloroperbenzoic acid by the conventional procedure:[68] 1-octene oxide, bp 59 °C (13 mm) [lit.[69] bp 61 °C (15 mm)]; 2,3-dimethyl-2-butene oxide, bp 91 °C; norbornene oxide, bp 155–6 °C, mp 118 °C [lit.[70] bp 155–8 °C, mp 125–7 °C]; 2,3-dimethyl-1,3-butadiene monoxide, bp 99–102 °C; diadamantilidene oxide, mp 181 °C [lit.[31] mp 181.5–183 °C]; α-methylstyrene oxide, bp 73° (14 mm) [lit.[71] bp 72–5 °C (11 mm)]; *trans*-β-methylstyrene oxide, bp 72–5 °C (13 mm) [lit.[72] bp 87–90 °C (13 mm)]; *cis*-β-methylstyrene oxide, 77 °C (16 mm); 1,1-diphenyl-2-methylpropene oxide, mp 63 °C [lit.[14b] mp 64 °C]; *trans*-stilbene oxide, mp 69 °C [lit.[73] mp 68 °C].

The acetone alkene ketals were prepared from standard procedures via the corresponding glycols, which were synthesized from the alkene and performic acid:[74,75] styrene glycol, bp 82 °C (1 mm) [lit.[76] bp 272–4 °C]; α-methylstyrene glycol, bp 105 °C (1 mm) [lit.[77] bp 160–2 °C (26 mm)]; 1-octene glycol, bp 87 °C (1 mm) [lit.[69] bp 135–6 °C (10 mm)]; 1,1-diphenylethylene glycol, mp 121 °C [lit.[78] mp 121 °C]; β-methylstyrene glycol, bp 99 °C (1 mm) for erythro/threo = 22/78. The alkene glycols were converted to the acetone ketals using *p*-toluenesulfonic acid as the catalyst and excess $CuSO_4$ as a dryer in anhydrous acetone: 1-octene glycol ketal, bp 81 °C (15 mm); styrene glycol ketal, bp 59 °C (0.5 mm); α-methylstyrene glycol ketal, bp 76 °C (1 mm); *trans*-, *cis*-β-methylstyrene glycol ketal (consisting of 20% cis and 80% trans isomers), bp 49 °C (0.2 mm); 1,1-diphenylethylene glycol ketal, bp 105–6 °C (0.5 mm); *trans*-cyclohexene glycol ketal, bp 72 °C (20 mm) [lit.[79] bp 182–4 °C].

Table X. Effects of Dimethylformamide and Tetramethylurea on Epoxidation Yields with Chromyl Nitrate[a]

alkene	solvent/ CH_2Cl_2 [b] (equiv with nitrate)	$O_2Cr(NO_3)_2$ (equiv with alkene)	convn (%) of alkene	yield (%) epoxide	selectivity (%)
	TMU (17)	1.0	18	16	89
	(3.3)	1.0	58	47	81
	(2.2)	1.0	52	44	85
	(1.1)	1.0	59	44	75
	(3.3)	1.5	64	57	89
	(2.2)	1.5	76	62	82
	py (25)	1.0	32	24	75
	(12)	1.0	54	37	69
	DMF (26)	1.0	38	17	45
	(13)	1.0	56	36	64
	(6)	1.0	65	45	69
	HMPA (12)	1.0	34	3	9
	TMU (6.0)	1.0	59	29	49
	(2.2)	1.0	52	25	48
	DMF (26)	1.0	76	66	93
		1.3	98	77	78
		1.5	99	75	76
	DMF (26)	1.0	82	45 (15)[c]	55
	py (25)	1.0	66	39 (13)[c]	59
	(25)	1.5	99	55 (18)[c]	55

[a] Under the conditions of the reactions in Table I using 0.5 mmol of $O_2Cr(NO_3)_2$ in 0.6 mL of CCl_4. [b] TMU = tetramethylurea. [c] Yield of α-phenylpropionaldehyde in parenthesis.

Epoxidation of Alkenes with Chromyl Nitrate. The chromyl nitrate oxidations of alkenes described in Table I were carried out under the following conditions. A dry 25-mL flask was charged with 0.5 mmol of the appropriate alkene and 2 mL each of DMF and methylene chloride under nitrogen. The flask was cooled to −78 °C, and a solution of 0.5 mmol of chromyl nitrate in ~0.7 mL of carbon tetrachloride was added dropwise from a hypodermic syringe over a period of 3 to 4 min. After the solution was stirred for 1 h at −78 °C, the dry ice bath was removed and 5 mL of 10% aqueous $NaHSO_3$ was added all at once. The mixture was stirred for 15–20 min and then extracted with CH_2Cl_2. The extract was washed with 5% aqueous $NaHCO_3$ and saturated aqueous NaCl and dried over anhydrous $MgSO_4$. Analysis was carried out by gas–liquid chromatography on a 15-m SB-1 glass capillary column mounted in a Varian 3700 gas chromatograph, using the internal standard method. Typically starting at 60 °C and a temperature program rate of 5 deg min^{-1} and 5 psi pressure, the retention times (min) were: ethylbenzene (internal standard), 4.11; 1-octene, 3.11; 1-octene oxide, 6.70; acetone ketal, 11.39. At 60 °C, 10 deg min^{-1}, retention times (min) were: cyclohexene, 2.20; cyclohexene oxide, 4.50; ethylbenzene (internal standard), 4.75; 2-cyclohexenol, 6.30. For β-methylstyrene: ethylbenzene (internal standard), 3.87; benzaldehyde, 5.25; (*Z*)-β-methylstyrene, 6.07; (*E*)-β-methylstyrene, 6.83; cis epoxide, 8.55; trans epoxide, 8.87; phenyl ethyl ketone, 8.99; phenylacetone, 9.84; *trans*-acetone ketal, 13.55; *cis*-acetone ketal, 14.18. The products from norbornene, 2,3-dimethyl-2-butene, diadamantilidene, 2,3-dimethyl-1,3-butadiene, styrene, α-methylstyrene, and 1,1-diphenylethylene were analyzed by a similar method. Owing to its high boiling point, stilbene was analyzed by its ^1H NMR spectrum [δ 7.05 (s, 2 H), using 1,1-diphenylethylene as the internal standard [δ 5.42, 2 H]. The epoxide showed a singlet resonance at δ 3.82.

Preparation of Epoxides with Chromyl Nitrate. The isolation of the epoxides formed by chromyl nitrate oxidation was carried out as follows. To a solution of 1.18 g (10 mmol) of (*E*)-β-methylstyrene in 20 mL of DMF and 20 mL of methylene chloride at −78 °C was added dropwise 12.9 mL of a 0.93 M solution of chromyl nitrate in CCl_4. After stirring for 30 min at −78 °C, the dry ice bath was removed and 75 mL of a 10% solution of $NaHSO_3$ was added all at once. The mixture was stirred vigorously for 15 min, and then extracted with 100 mL of CH_2Cl_2. The extract was washed twice with 50-mL portions of 5% aqueous $NaHCO_3$ and five times with water to remove DMF, and dried over $MgSO_4$. Removal of the solvent afforded a residue which was distilled in vacuo to afford 0.91 g of *trans*-β-methylstyrene oxide (68% based on the alkene charged), bp 96–8 °C (18 mm) [lit.[80] 90–5 °C (15 mm)].

A similar procedure using 1.05 g (5.05 mmol) of 2-methyl-1,1-diphenylpropene and 7.6 mmol of chromyl nitrate afforded 0.67 g (59%)

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of the epoxide as white needles after recrystallization from 80% ethanol–water at −15 °C, mp 63 °C [lit.[57] 64 °C].

Solvent Effects on the Chromyl Nitrate Epoxidation of Styrene. The effect of solvents generally on the epoxidation of chromyl nitrate was examined with styrene since it represents an alkene from which the epoxide is not effectively isolated with other chromyl reagents. The reactions were carried out by the general procedure outlined in the foregoing section, with the exception that the medium in which styrene is dissolved, i.e., 2 mL of DMF plus 2 mL of CH_2Cl_2, was replaced by the following: CH_3CN (2 mL) plus CH_2Cl_2 (2 mL), CH_2Cl_2 (4 mL), CH_3NO_2 (1 mL) plus CH_2Cl_2 (3 mL), pyridine (1 mL) plus CH_2Cl_2 (3 mL), ethyl acetate (4 mL) and hexamethylphosphoric triamide (1 mL) plus CH_2Cl_2 (3 mL). After the customary ($NaHSO_3$) workup, the methylene chloride extract was analyzed by gas chromatography using the internal standard method. The results are summarized in Table V.

Stemming from the favorable effect of DMF as the cosolvent for chromyl nitrate epoxidation of alkenes in Table V, we also examined the concentration dependence of DMF and the effect of tetramethylurea (TMU) on the yields. The procedure was essentially the same as that employed above. The results are summarized in Table X. The solvent in the first entry corresponds to 1 mL of TMU in 3 mL of CH_2Cl_2. Entries 2 through 6 correspond to 0.30, 0.20, 0.13, and 0.066 mL of TMU, respectively, in 4 mL of CH_2Cl_2.

Alkene Ketals from Chromyl Nitrate Oxidations in Acetone. The results summarized in Table II were all carried out under the following conditions. To a solution of 0.5 mmol of the appropriate alkene in 3 mL of acetone at −78 °C was added dropwise 0.62 mL of a 0.81 M solution of chromyl nitrate (0.5 mmol) in carbon tetrachloride over the course of 3–4 min. The reaction mixture was stirred for 1 h at −78 °C, the dry ice bath removed, and 5 mL of a 5% aqueous solution of $NaHSO_3$ added all at once. After stirring for ~15–20 min, the products were extracted with CH_2Cl_2, and the extract was washed successively with 5% aqueous $NaHCO_3$ and saturated aqueous NaCl. The methylene chloride solution was dried over $MgSO_4$ and analyzed by gas chromatography, as described above.

Direct Preparation from Styrene of the Isopropylidene Glycol. To a solution of 1.04 g (10 mmol) of styrene in 30 mL of acetone at −78 °C was added dropwise 14.3 mL of 0.91 M chromyl nitrate (13 mmol) in carbon tetrachloride over a course of 1 h. After the mixture was stirred, followed by the usual $NaHSO_3$ workup, the product was extracted with methylene chloride which was then washed with 5% aqueous $NaHCO_3$ and dried over $MgSO_4$. Removal of the solvent afforded a residue, which yielded 0.84 g (70%) of acetone styrene ketal upon distillation under reduced pressure, bp 49 °C (0.07 mm).

Conversion of Alkene Oxides to Acetone Ketals under Reaction Conditions. To a solution of 0.5 mmol of the epoxide (from cyclohexene, styrene, or β-methylstyrene) in 3 mL acetone was added calculated amounts of either chromyl nitrate (0.12, 0.24, 0.36 mL of an 0.84 M solution in CCl_4), boron trifluoride etherate (0.05 mmol), zinc chloride (0.05 mmol), or nitric acid (0.05 mmol) at −78 °C. The mixture was stirred at −78 °C for 1 h, after which the dry ice bath was removed and 5 mL of a 5% aqueous $NaHSO_3$ solution added. The mixture stirred for 15 min, and the products were extracted with CH_2Cl_2. The extract was washed with 5% $NaHCO_3$ and saturated NaCl and dried over $MgSO_4$. With $BF_3 \cdot Et_2O$, $ZnCl_2$, and HNO_3, a solution of 5% $NaHCO_3$ replaced the $NaHSO_3$ treatment. Analysis was carried out as described above.

Relative Reactivities of Alkenes toward Chromyl Nitrate. The rates of chromyl nitrate oxidation of alkenes were determined by the competition method as follows. Equimolar mixtures (0.5 mmol each) of two alkenes were dissolved in a medium consisting of 2 mL of DMF and 2 mL of CH_2Cl_2. After the solution was cooled to −78 °C, a solution of 0.2 mmol of chromyl nitrate in 0.7 mL of CCl_4 was added dropwise with vigorous stirring. After the usual workup (using $NaHSO_3$), the methylene chloride extract was analyzed quantitatively by gas chromatography using the internal standard method. The relative reactivities were evaluated with the aid of eq 9. The analyses were carried out in multiples of at least 5, from which the reproducibility was judged to be within 2%. In order to check the reliability of the method, various ratios (and amounts) of styrene and α-methylstyrene were examined (see entries 5–9 in Table VI). The minor deviations in the relative reactivities lend support to the validity of the method. Moreover, the other combinations of alkene pairs examined, as listed in Table VI, also support this conclusion. Thus despite the rapidity of the chromyl nitrate oxidations, the results indicate that limitations in the mixing and/or the possibility of encounter-controlled rates do not appear to limit the applicability of the method.

Oxidation of Styrene with Various Chromyl Reagents. A standard procedure consisted of treating 0.5 mmol of styrene in 2 mL of DMF and 2 mL of CH_2Cl_2 at −78 °C with a solution of the chromyl reagent made up as follows: chromyl chloride, 0.50 mL of a 1.0 M solution in CCl_4; chromyl acetate, 1.17 mL of a 0.43 M solution in CCl_4; chromyl trifluoroacetate, 0.83 mL of a 0.61 M solution in CCl_4. The oxidations were carried out by the same procedure used for chromyl nitrate (0.71 mL of a 0.70 M solution in CCl_4) described above.

Table **XI.** ESR Parameters of Oxochromium(V) Species

reagent	*g* value	ref
CrO_3 in HOAc	1.965	Kon[34]
$K_2Cr_2O_7 + (COOH)_2$	1.978	Kon[34]
$OCrCl_4^- R_3NH^+$	1.988	Kon[81]
$CrO_3 + (HOCH_2)_2$	1.975	Garifyanov[82]
$CrO_3 + (CH_3)_2CHOH/HOAc$	1.981	Wiberg[36]
$O_2Cr(OAc)_2 + RH$	1.971	Freeman[37]
$CrO_3 + \alpha$-HO acids	1.978	Rocek[35]
$OCrCl_5^{2-}H_2Bpy^{2+}$	1.988	this work

Chromyl Nitrate Oxidation of 1,2-Diphenylethanol. Solvent Effects. 1,2-Diphenylethanol (0.198 g, 1.00 mmol) was dissolved in a solvent consisting of either CH_2Cl_2 (4 mL), MeCN (1 mL) plus CH_2Cl_2 (3 mL), acetone (4 mL), DMF (2 mL) plus CH_2Cl_2 (2 mL), pyridine (1 mL) plus CH_2Cl_2 (3 mL), or HMPA (1 mL) plus CH_2Cl_2 (3 mL). After such a solution was cooled to −78 °C, chromyl nitrate (0.66 mL of a 0.758 M solution in CCl_4, or 0.5 mmol) was added dropwise over a course of 3–4 min. After the solution was stirred for 1 h, at −78 °C, it was allowed to warm up to room temperature, and then stirred for an additional hour. The mixture was hydrolyzed with 10 mL of water at room temperature for 1 h, and the products were extracted with methylene chloride. The methylene chloride solution was washed with 5% $NaHCO_3$, dried over $MgSO_4$ and analyzed by gas chromatography, as described above. Typically starting at 100 °C and a program rate of 15° min^{-1} and 5 psi pressure, the retention times (min) were: benzaldehyde, 2.49; benzyl alcohol, 2.87, diphenylmethane (internal standard), 6.89; 1,2-diphenylethanol, 10.05; phenyl benzyl ketone, 10.31. The results are summarized in Table VI.

The competition reaction between 1,2-diphenylethanol and styrene was carried out as follows. To a solution of 1 mmol each of 1,2-diphenylethanol and styrene in 4 mL of acetone at −78 °C was added dropwise a solution of 0.5 mmol of chromyl nitrate in 0.6 mL of CCl_4. After reaction and workup as described above, the gas chromatographic analysis indicated that 0.88 mmol of styrene and 0.62 mmol of 1,2-diphenylethanol remained unreacted. The relative reactivity of styrene to 1,2-diphenylethanol was 0.12/0.39 = 0.31.

Detection of Oxochromium(V) Intermediates by Electron Spin Resonance Spectroscopy. A solution of chromyl nitrate in carbon tetrachloride showed no ESR signal, even when frozen at −80 °C. Acetone was added and to promote mixing of the two-solid phase mixture, it was allowed to warm slightly until partial melting occurred and then refrozen. The procedure was repeated. Initially the ESR signal was very weak, but increased in intensity with each successive mixing procedure. The amplitude attained a maximum after five to six repetitions, and further mixing caused the signal to decay until none was observed after complete mixing. The oxochromium(V) species thus generated was stable at −80 °C (frozen in CCl_4 or as a glassy solution) over a period of several hours, but decayed at −60 °C. The ESR spectrum shown in Figure 1 (left) shows a rather narrow line width ($\Delta H_{pp} = 2$ G) and a *g* value of 1.96_9, characteristic of other oxochromium(V) species previously reported, as listed in Table XI.

In order to make a rough assessment of the maximum concentration of the oxochromium(V) species, the intensity of the ESR signal at its optimum was evaluated by double integration using an authentic sample of oxopentachlorochromate(V) as an external standard.[39] This procedure indicated that 10 ± 3% of the chromyl nitrate was converted to oxochromium(V) at *maximum* concentration. Owing to the transient character of oxochromium(V), the integrated concentration could not be determined. Using the same procedure, we found that the addition of either pyridine or DMF (instead of acetone) led to a similar ESR spectrum ($g = 1.96_8$–1.97_1), but the signal intensity was much diminished, probably owing to further facile reaction with solvent. The reduction of chromyl acetate by acetone under similar conditions afforded an intense ESR signal [$\Delta H_{pp} = 2.5$ G, $g = 1.96_8$] which reached a maximum concentration corresponding to 21 ± 6% of the chromyl acetate added.

These results clearly indicate that rather high yields of oxochromium(V) species can be produced when chromyl reagents are treated with either acetone or DMF, even at low temperatures. Such a reduction accords with the chemical results using the oxidative cleavage of 1,2-

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diphenylethanol as a probe for chromium species in intermediate oxidation states, as indicated by the results in Table VII. The formation of oxochromium(V) could result from two consecutive one-electron reductions,[44c]

$$\mathrm{Cr^{VI} + S \rightarrow Cr^{V} + S^{+\cdot}} \qquad (19)$$

$$\mathrm{Cr^{VI} + S^{+\cdot} \rightarrow Cr^{V} + P} \qquad (20)$$

or an initial two-electron reduction followed by disproportionation.

$$\mathrm{Cr^{VI} + S \rightarrow Cr^{IV} + P} \qquad (21)$$

$$\mathrm{Cr^{IV} + Cr^{VI} \rightarrow 2Cr^{V}} \qquad (22)$$

However, the absence of oxidative cleavage of 1,2-diphenylethanol to benzaldehyde and benzyl alcohol precludes the presence of Cr(IV) species. We thus favor the sequence in eq 19–20.

The indication of the viability of oxochromium(V) as an epoxidizing agent can also be obtained from ESR studies. To a frozen solution of oxochromium(V) prepared from chromyl nitrate and acetone was added a small amount of either styrene or tetramethylethylene at −80 °C. Immediately upon addition, the signal intensity was greatly diminished, followed by a slower decay over a period of 1 h. We surmise that the epoxidation of alkenes by oxochromium(V) must be very rapid at these temperatures since the ESR signal disappeared immediately when the mixture was mixed.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for the support of this research.

Registry No. $O_2Cr(ONO_2)_2$, 16017-38-2; $O_2Cr(OAc)_2$, 4112-22-5; O_2CrCl_2, 14977-61-8; $O_2Cr(O_2CCF_3)_2$, 27184-84-5; $OCrCl_5^{2-}H_2Bpy^{2+}$, 54170-73-9; 1-octene, 111-66-0; cyclohexene, 110-83-8; norbornene, 498-66-8; 2,3-dimethyl-2-butene, 563-79-1; 2,3-dimethyl-1,3-butadiene, 513-81-5; diadamantylidene, 30541-56-1; α-methylstyrene, 98-83-9; (*E*)-β-methylstyrene, 873-66-5; (*Z*)-β-methylstyrene, 766-90-5; 1,1-diphenylethene, 530-48-3; 2-methyl-1,1-diphenylpropene, 781-33-9; (*E*)-stilbene, 103-30-0; 1,2-diphenylethanol, 614-29-9; styrene, 100-42-5; dimethylformamide, 68-12-2; tetramethylurea, 632-22-4; 1-octene oxide, 2984-50-1; cyclohexene oxide, 286-20-4; *exo*-norbornene oxide, 3146-39-2; 2,3-dimethyl-2-butene oxide, 5076-20-0; 2,3-dimethyl-1,3-butadiene monoxide, 34485-82-0; diadamantylidene oxide, 29186-07-0; styrene oxide, 96-09-3; α-methylstyrene oxide, 2085-88-3; *trans*-β-methylstyrene oxide, 23355-97-7; *cis*-β-methylstyrene oxide, 4541-87-1; 1,1-diphenyl-2-methylpropene oxide, 60227-39-6; *trans*-stilbene oxide, 1439-07-2; 1-octene glycol ketal, 79413-15-3; styrene glycol ketal, 52129-03-0; α-methylstyrene glycol ketal, 84895-18-1; 1,1-diphenylethylene glycol ketal, 84895-19-2; *trans*-cyclohexene glycol ketal, 24148-95-6; *cis*-β-methylstyrene glycol ketal, 64216-06-4; *trans*-β-methylstyrene glycol ketal, 64216-05-3.

Theory of Cation-Radical Pericyclic Reactions

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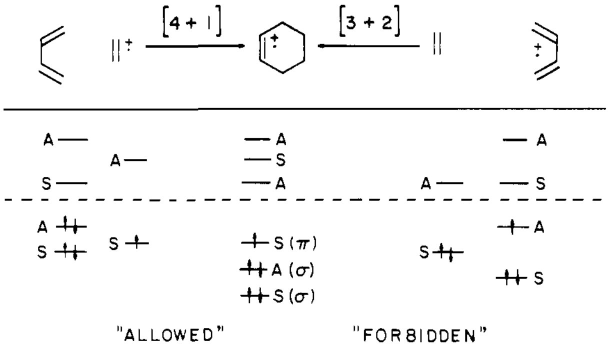
Received September 30, 1982

Abstract: Reaction paths are calculated for representative cation-radical pericyclic reactions, including the Diels–Alder, olefin cycloaddition, and the Cope reaction. Ionization to form cation radicals is found to lower the activation energy dramatically in each case, in agreement with experimental observations relative to cation-radical pericyclic reactions. The basis for this effect is analyzed theoretically and found to be consistent with a nonsynchronous, concerted mechanism for such reactions, but not with a synchronous mechanism. It is suggested that the sequence (i) ionization, (ii) pericyclic reaction, (iii) electron acceptance provides a powerful catalytic route for a wide variety of pericyclic reactions.

The recent discovery of the cation-radical catalyzed Diels–Alder reaction[1,2] naturally stimulates interest in the general concept of cation-radical pericyclic reactions. The observation that ionization of one of the components (specifically, the dienophile) in a Diels–Alder cycloaddition can engender enormous rate enhancements immediately evokes interest in the possibility that hole formation (ionization) may exert analogous effects on other pericyclic reactions. Using FMO, MINDO/3, MNDO, and optimized ab initio calculations, the effect of hole formation on activation energy has been studied for a variety of pericyclic reactions. The results suggest that a wealth of cation-radical pericyclic chemistry of minimal activation requirements may await discovery. The important question of the theoretical basis for the observed powerful kinetic effect has also been explored and answered, and the analysis yields valuable insights concerning the structure of the transition states of the cation-radical Diels–Alder and other cation-radical pericyclic processes.

The Cation-Radical Diels–Alder. Although not many pericyclic reactions of doublet (spin) species are symmetry allowed,[3] the cation-radical Diels–Alder is one such reaction. The orbital correlation diagrams presented in Scheme I reveal that cycloaddition of the ethene cation radical to *s-cis*-1,3-butadiene is indeed symmetry allowed. Interestingly, the role-reversed cycloaddition of neutral ethene to the butadiene cation radical is forbidden. This preference of the cation radical for the dienophilic role has been observed experimentally and termed role selectivity.[1,2] Although orbital correlation diagrams for the corresponding Diels–Alder dimerization of a conjugated diene, such as 1,3-butadiene, cannot rigorously be constructed because of insufficient symmetry, local symmetry considerations suggest a similarly favored status for this reaction. The experimentally observed stereospecificity of the cation-radical Diels–Alder is, in fact, in excellent accord with

Scheme I. Orbital Correlation Diagrams for the Cation-Radical Diels–Alder



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