Oxidation of Isopropylcyclopropane by Chromyl Chloride: Ring-Opened Products Support a Hydrogen Atom Abstraction Mechanism

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Chromyl chloride (CrO_2Cl_2) reacts with neat isopropylcyclopropane at 65 °C to give a dark precipitate along with at least 20 organic products. Both cyclopropyl products and ring-opened products are observed: 2-cyclopropyl-2-chloropropane (**1**, 0.4% yield based on chromium), 2-cyclopropyl-2-propanol (**2**, 0.2%), 5-chloro-2-methyl-2-pentene (**3**, 0.3%), and 4-methyl-3-penten-1-ol (**4**, 0.5%) as well as other ring-opened products. Authentic samples of **1**−**4** were synthesized, and their GC and GC/MS data were compared with the reaction mixture. Other organic products (**5**−**10**) were tentatively assigned by GC/MS on the basis of their *m*/*z* and fragmentation patterns. The ratio of (**1** + **2**) vs (**3** + **4**) increases by a factor of 2 when the initial concentration of CrO_2Cl_2 increases from 0.3 to 1.12 M. The reaction was also carried out in the gas phase, and essentially all the products from the liquid phase reaction were observed. The products are explained by a mechanism involving initial hydrogen atom abstraction from the substrate. The resulting dimethylcyclopropylcarbinyl radical can either be trapped by CrO_2Cl_2 (to form **1** and **2**) or ring-open to give 4-methyl-3-pentenyl radical, which reacts with CrO_2Cl_2 to form **3** and **4** as well as further oxidized products. The oxidation of isopropylcyclopropane by MnO_4^- in pyridine was also examined. Acetone, an expected ring-opened product, was the only product observed by our analytical techniques. $Me_2C^{18}O$ is produced from ^{18}O-labeled MnO_4^-. These results suggest that the reactions of CrO_2Cl_2 and MnO_4^- with isopropylcyclopropane proceed by hydrogen atom transfer to form organic radical intermediates.

Introduction

The development of selective hydrocarbon oxidation reactions will be aided by mechanistic understanding. Chromyl chloride (CrO_2Cl_2), permanganate (MnO_4^-), and other metal−oxo species are well known to oxidize C−H bonds.[1] Our recent studies of alkane and arylalkane oxidation by CrO_2Cl_2[2] and MnO_4^- [3] in nonpolar solvents indicate that the rate-limiting step in all cases is transfer of a hydrogen atom from the hydrocarbon to a metal oxo group. In other words, CrO_2Cl_2 and MnO_4^- behave like organic free radicals, abstracting $H^\bullet$ from the substrate RH, although they are both closed-shell species with no unpaired electrons.

The organic radical formed by hydrogen atom abstraction, $R^\bullet$, rapidly undergoes further oxidation by CrO_2Cl_2 or MnO_4^-.[2−5] In the oxidation of cyclohexane by CrO_2Cl_2, the intermediate cyclohexyl radicals are trapped by CrO_2Cl_2 ($k \cong 3 \times 10^9$ M^{-1} s^{-1} at 80 °C) in competition with trapping by $CBrCl_3$, which gives bromocyclohexane.[2b] MnO_4^- is similarly known to trap radicals at close to the diffusion limit.[5] In the oxidation of toluene by permanganate in organic solvents, the presence of O_2 was found to significantly affect the rate of disappearance of MnO_4^-, suggesting that O_2 is competing with MnO_4^- in the trapping of benzyl radical.[3]

Radical probes have been widely used in elucidating reaction mechanisms.[6] The probe is a precursor to a reactive intermediate that undergoes a characteristic reaction, usually a structural rearrangement or isomerization. Detection of rearranged products from the probe provides evidence that the intermediate is formed. We report here the reactions of isopropylcyclopropane with CrO_2Cl_2 and MnO_4^-. Abstraction of the most weakly bound hydrogen atom[7] would generate the dimethyl cyclopropylcarbinyl radical,[8] a "radical-clock" that undergoes ring-opening with a rate constant of 2.3×10^8 s^{-1} at 65 °C.[9] The observation of products derived from the ring-opened species provides further evidence for radical intermediates in these reactions.

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(7) Although the C−H bond strengths in isopropylcyclopropane are not known, presumably the weakest bond is the tertiary one in the isopropyl group. *Cf.* H-cyclopropyl, 106 kcal/mol; H-isopropyl, 98 kcal/mol. Colussi, A. J. In *Chemical Kinetics of Small Organic Radicals*; Alfassi, Z. B., Ed.; CRC Press: Boca Raton, FL, 1988; pp 25−43.

(8) Alternative names: dimethylcyclopropylmethyl radical, 2-cyclopropyl-2-propyl radical.

(9) Calculated from the Arrhenius parameters in ref 6c.

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Experimental Section

All reaction mixtures were prepared under an N_2 atmosphere either in a glovebox or by using vacuum-line techniques with Teflon-sealed Pyrex reaction vessels, and all were shielded from light. CrO_2Cl_2 (99.99%, Aldrich) was sealed in a greaseless, light-free glass vessel and was vacuum transferred prior to use in a vacuum-line greased with KRYTOX fluorinated grease (DuPont). *Caution: CrO_2Cl_2 is a corrosive and carcinogenic volatile liquid that should be handled with extreme caution*. Isopropylcyclopropane (99%, Wiley Organics) was dried over Na, vacuum transferred into a sealed vessel, and stored in a freezer in the glovebox. GC/MS analysis of the isopropylcyclopropane showed no unsaturated olefinic species. [PPN]MnO_4 (PPN = $(Ph_3PNPPh_3)^+$) was prepared according to a literature method[10] and recrystallized from CH_2Cl_2/Et_2O. $KMn^{18}O_4$ (ca 10% ^{18}O enriched) was prepared by exchange of $KMnO_4$ with $H_2{}^{18}O$.[3c] Pyridine was purified by standard procedures,[11] stored over CaH_2, and vacuum transferred prior to use. 4-Methyl-3-penten-1-ol (**4**, 97%, Aldrich) was used as received. Methyl cyclopropyl ketone (99%; Aldrich) was dried over Na_2SO_4 for use in the reaction with CrO_2Cl_2. Product analyses were performed on an HP5890 series GC equipped with a 30-m cross-linked PH ME silicone column and an FID detector; GC/MS were obtained on a Kratos mass spectrometer equipped with an HP5890 GC and a cooling unit for low-temperature analysis.

2-Cyclopropylpropene was prepared following a reported procedure[12] and was dried over sodium. NMR and IR data are consistent with literature values.[12] MS (70 eV) *m/z*: 83 (4), 82 (58), 67 (100), 41 (90). 2-Cyclopropyl-2-chloropropane (**1**) was prepared, following ref 13, by reacting 2-cyclopropylpropene with HCl in CH_2Cl_2. MS (70 eV) *m/z*: 121 (18), 119 (65), 103 (12), 83 (39), 79 (28), 78 (12), 77 (100), 76 (32), 69 (15), 67 (20), 56 (34), 43 (36), 41 (64). 2-Cyclopropyl-2-propanol (**2**) was synthesized from methylcyclopropyl ketone and MeMgBr by a literature method[14] and dried over 4 Å sieves. MS (70 eV) *m/z*: 85 (67), 83 (14), 72 (61), 67 (13), 59 (49), 57 (45), 55 (18), 43 (100), 41 (60); the fragmentation pattern matches that reported.[15]

The reported procedure[16] for 5-chloro-2-methyl-2-pentene (**3**), from 4-methyl-3-penten-ol and $SOCl_2$ in pyridine, gives a very low yield. Therefore, **3** was prepared from **2** plus HCl by a modification of the reported procedure.[17] Compound **2** (3.0 mL, 27 mmol assuming 100% purity) was dissolved in 20 mL of dry CH_2Cl_2 under N_2 in a 50 mL round-bottom flask and cooled to −10 °C. HCl gas (99%, Aldrich) was passed through the solution for 15 s, and the solution was allowed to slowly warm to room temperature while stirring was maintained for ca. 30 min. CH_2Cl_2 was removed *in vacuo*, and the residue was dried over K_2CO_3. A slightly yellow liquid (~2.5 mL) was obtained after vacuum transfer. In contrast to the prior report,[17] GC and GC/MS indicated the liquid was a mixture of **3** and **1** (ca. 3:1 by GC), suggesting a yield of **3** of 60%. Separation of the two by distillation was not successful (presumably due to their similar boiling points: **3**, 128 °C;[16] **1**, 105 °C[13]), so the mixture was used without purification. MS (70 eV) *m/z*: 120 (72), 118 (86), 69 (100), 103 (11), 83 (67), 79 (47), 77 (66), 75 (41), 69 (100), 65 (44), 56 (64), 55 (72), 53 (64), 51 (49), 43 (45), 42 (47).

Reaction of CrO_2Cl_2 with Isopropylcyclopropane. In the glovebox under a red "safe" light, 10 μL of CrO_2Cl_2 (0.12 mmol) was syringed into a 70 mL Pyrex bomb that was then sealed with a Teflon stopcock and wrapped in foil. Isopropylcyclopropane (0.4 mL; ca. 7.5 M) was later vacuum transferred into this bomb at −78 °C. (*Caution:* Direct addition of isopropylcyclopropane to CrO_2Cl_2 at ambient temperatures results in violent reaction and should be avoided.) The bomb was placed in a 65 °C water bath for ca. 30 min to ensure complete reaction of CrO_2Cl_2. The initial orange-red color of CrO_2Cl_2 turned brown, and a precipitate formed (the Étard complex[2]). The organic volatiles were then vacuum transferred out and analyzed by GC and low-temperature GC/MS. The Étard complex was hydrolyzed by treatment with 1.0 mL of 1 M aqueous solution of $Na_2S_2O_3$ and passage through a column of alumina (to remove chromium), and the aqueous solution was also analyzed by GC and GC/MS.

Other Reactions of CrO_2Cl_2. CrO_2Cl_2 (10 μL, 0.13 mmol) was vacuum transferred onto 50 μL of **2-cyclopropyl-2-propanol** (**2**, ca. 0.43 mmol) at −78 °C. The mixture was allowed to warm to room temperature and react overnight. Organic volatiles were vacuum transferred out, and the Étard complex was destroyed by treatment with an aqueous solution of $Na_2S_2O_3$. The aqueous solution was then extracted with Et_2O. Both the organic volatiles and the ether layer were analyzed by GC. Similar reaction and workup conditions were used for the reactions of CrO_2Cl_2 with **methyl cyclopropyl ketone** [2 M CrO_2Cl_2 in neat substrate (ca. 8.4 M)] and **2-cyclopropylpropene** [0.9 M CrO_2Cl_2 in neat substrate (ca. 8.4 M)].

Gas-Phase Reactions of CrO_2Cl_2. CrO_2Cl_2 (5.0 μL, 0.065 mmol) was placed in a 40-mL Pyrex bomb in the glovebox, and isopropylcyclopropane (20.0 μL, ca. 0.18 mmol) was placed in a 100 mL bomb. Both reactants were completely in the gas phase at room temperature. The bombs were then attached to the vacuum line through a short-path T-joint and freeze-pump-thawed. The contents in the bombs were allowed to diffuse to each other at room temperature. Instant reaction occurred with consumption of the orange CrO_2Cl_2 vapor and formation of a brown precipitate. After about 1 h, the bombs were detached from the vacuum line and the Étard complex destroyed by treatment with an aqueous solution of $Na_2S_2O_3$. The aqueous solution was then extracted with Et_2O and the ether layer collected and analyzed by GC. Reactions with 2-cyclopropylpropene and 2-cyclopropyl-2-propanol (**2**) were carried out similarly.

Reaction of [PPN]MnO_4 with Isopropylcyclopropane. In a glovebox, [PPN]MnO_4 (26 mg, 0.04 mmol) was dissolved in 0.6 mL of a 3.1 M solution of isopropylcyclopropane in pyridine in a Pyrex bomb wrapped in foil. A control reaction of [PPN]MnO_4 in pyridine without substrate was also prepared. The bombs were placed in a 65 °C water bath. After ca. 4 h, the solution turned from dark purple to rusty brown, while there was no observable color change in the control. The bombs were then taken out of the water bath, and the volatiles were vacuum transferred out. The residue was dissolved in an aqueous $Na_2S_2O_3$/HCl solution, with reduction of the solid MnO_2, and extracted with Et_2O. The volatiles, the ether layer, and the aqueous layer were all analyzed by GC and GC/MS. For the ^{18}O-labeling experiment, a solution of $KMn^{18}O_4$, 16 mM in 4:1 (v/v) pyridine/isopropylcyclopropane, was heated at 65 °C for 2.5 h, and product analysis was carried out as above.

Results and Discussion

Reaction of CrO_2Cl_2 with Isopropylcyclopropane. The reaction of CrO_2Cl_2 with isopropylcyclopropane was carried out in the neat substrate to avoid involvement of solvent in the reactions. Direct addition of neat substrate to CrO_2Cl_2 at ambient temperatures results in a violent reaction accompanied by a large release of heat. Therefore, reaction solutions were prepared by vacuum transfer of the hydrocarbon to a −78 °C sample of CrO_2Cl_2 in a Pyrex vessel with a Teflon stopcock. Reactions were

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(13) Shellhamer, D. F.; McKee, D. B.; Leach, C. T. *J. Org. Chem.* **1976**, *41*, 1972−1976.
(14) Julia, M.; Julia, S.; Guégan, R. *Bull. Soc. Chim. Fr.* **1960**, 1072−1079.
(15) Hamuise, J.; Puttemans, J. P.; Smolders, R. R. *Tetrahedron* **1969**, *25*, 1757−1769.
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(17) (a) Julia, S.; Julia, M.; Brasseur, L. *Bull. Soc. Chim. Fr.* **1962**, 1634−1638. (b) Corey, E. J.; Hartmann, R.; Vatakencherry, P. A. *J. Am. Chem. Soc.* **1962**, *84*, 2611−2614.

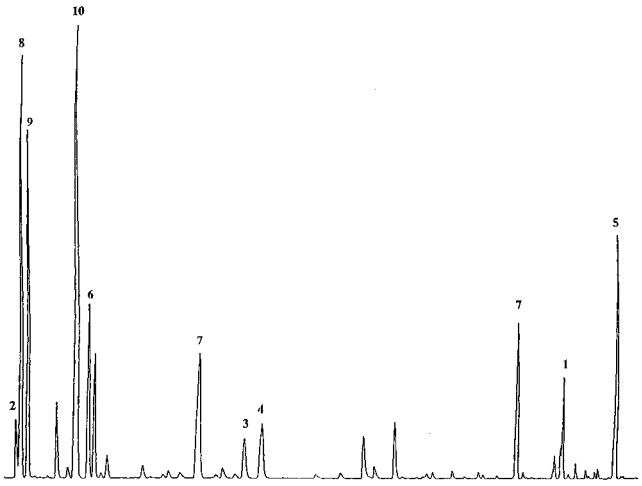


Figure 1. Typical chromatograph of the reaction mixture from isopropylcyclopropane and CrO_2Cl_2. GC oven temperatures: 35 °C (12 min) → 10 °C/min → 200 °C (20 min).

protected from light and were prepared using a red "safe" light. Reaction mixtures were heated to 65 °C to ensure complete consumption of CrO_2Cl_2. Reactions run in the gas phase indicate that a similar mix of products is formed at ambient temperatures (see below). The orange-red color of CrO_2Cl_2 is replaced by a colorless solution and a brown precipitate (the Étard complex). The organic products are present in solution and bound to chromium in the precipitate, as is characteristic of these reactions.[2] GC and GC/MS analysis of the solution and an aqueous workup of the precipitate showed a complex spectrum of at least 20 products (Figure 1). It should be emphasized that some of the reaction products, such as carboxylic acids, are not observed by this analytical procedure.[2]

A subset of the observed products have been identified by GC/MS on the basis of their *m*/*z* and fragmentation patterns (Table 1). Some of the assignments are tentative; for instance, stereoisomers cannot typically be distinguished on the basis of mass spectral data. Four of the compounds have been identified by comparison of their GC and GC/MS data with authentic samples: 2-cyclopropyl-2-chloropropane (**1**), 2-cyclopropyl-2-propanol (**2**), 5-chloro-2-methyl-2-pentene (**3**), and 4-methyl-3-penten-1-ol (**4**). The yields of these four products, per mole of CrO_2Cl_2, are given in Table 1. For the other products, approximate yields are given based on the yields for **1**−**4** and assuming that all of the compounds have roughly the same response factor in the GC (FID detection). While this assumption is not very accurate, the calculation provides a rough measure of the product distribution. The sum of these yields is not a measure of the reaction mass balance as multiple CrO_2Cl_2 molecules are consumed for many of the products. With further assumptions about the number of CrO_2Cl_2 molecules consumed per oxidized product, the compounds listed in Table 1 represent roughly a quarter of the CrO_2Cl_2 oxidizing equivalents expended in the reaction.[18] The remaining oxidative equivalents are likely expended in the formation of carboxylate products, which have proven very difficult to liberate from the chromium(III) products in this system.[2]

The observed products are readily explained by a mechanism involving initial hydrogen atom abstraction from the tertiary position (Scheme 1). The resulting *c*-$C_3H_5\dot{C}Me_2$ radical either is trapped by CrO_2Cl_2 or ring-opens to form the 4-methyl-3-pentenyl radical, and products are observed from both pathways. Reaction of *c*-$C_3H_5\dot{C}Me_2$ with CrO_2Cl_2 should be similar to the reaction of the *tert*-butyl radical, which occurs by (i) chlorine atom abstraction to give *t*-butyl chloride, (ii) C−O bond formation yielding *tert*-butoxide ligands that are observed as the alcohol on hydrolysis, and (iii) a second hydrogen atom transfer to give isobutylene.[2a] In the isopropylcyclopropane reaction, 2-cyclopropyl-2-chloropropane (**1**) is the product of Cl abstraction and 2-cyclopropyl-2-propanol (**2**) is the result of C−O bond formation.[19] Similar trapping of the 4-methyl-3-pentenyl radical gives the observed 5-chloro-2-methyl-2-pentene (**3**) and 4-methyl-3-penten-1-ol (**4**).

The reaction is much more complex than these four products because of the rapid and nonselective oxidation of alkenes by CrO_2Cl_2.[2,20,21] Isobutylene, for instance, reacts with CrO_2Cl_2 to give a variety of products including isobutyraldehyde, 2-chloroisobutyraldehyde, chlorohydrins, and acetone (by C=C bond cleavage).[2a] So **3** and **4** are predominantly oxidized further, as are the products resulting from hydrogen atom abstraction from the intermediate radicals 2-cyclopropylpropene (**11**) and 4-methyl-1,3-pentadiene. Reasonable pathways to the observed products are given in Scheme 2, but this is by no means an exhaustive description of products or pathways. Oxidation of the double bond in **3** gives chlorohydrins, chloro ketone, acetone, aldehydes, and likely carboxylic acids and CO_2. Independent oxidation of a mixture of **3** and **1** (0.3 mL; ~3:1 by GC) with limited CrO_2Cl_2 (40 μL, roughly 0.2 equiv) resulted in the formation of dichloro ketone **5** (0.4%), acetone, chloroaldehyde **6** (0.1%), and chlorohydrin **7** (4%). [These estimated yields, and those given below, are per mole of CrO_2Cl_2 and assume that all species have the same response factor in the GC. The other products, as noted above, were not observed.] CrO_2Cl_2 reacts preferentially with **3** over **1**, as expected, because the ratio of **3** to **1** decreased to 3:2 after reaction as revealed by GC. These data support **3** being on the route to other ring-opened products.

The reaction of CrO_2Cl_2 and 2-cyclopropyl-2-propanol (**2**) has been examined both in the neat liquid substrate and in the gas phase. GC analysis indicated quite similar product distributions from the two reaction conditions: **3** (77%), **6** (10%), **7** (1%), **5** (0.3%), **1** (0.2%), and **4** (trace; yields are from the solution reaction). The formation of these products likely occurs by initial dehydration of the alcohol, presumably via chromium−alkoxide formation,[2a] and subsequent reactions of 2-cyclopropylpropene (**11**). It should be noted that alcohol products such as **2** are present only as alkoxide ligands to reduced chromium during the alkane oxidation and are liberated as the alcohol only on protic workup. The reaction of **2** and

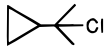
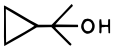
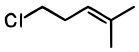
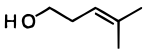
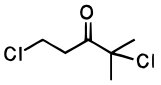
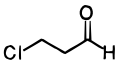
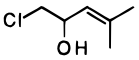
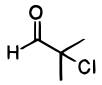
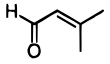
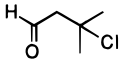
(18) A final chromium oxidation state of 3.5 is assumed, by analogy with the reaction of Me_3CH.[2a] This is likely a lower estimate because FID response factors are smaller for lower carbon-number products. The issue of mass balances in CrO_2Cl_2 reactions is discussed in more detail in ref 2a,b.

(19) The alcohol is not formed by autoxidation, as O_2 is rigorously excluded from these reactions and there is no formation of methylcyclopropyl ketone, the facile fragmentation product from the tertiary alkoxy radical.

(20) (a) Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 3120−3128. (b) Miyaura, N.; Kochi, J. K. *Ibid.* **1983**, *105*, 2368−2378.

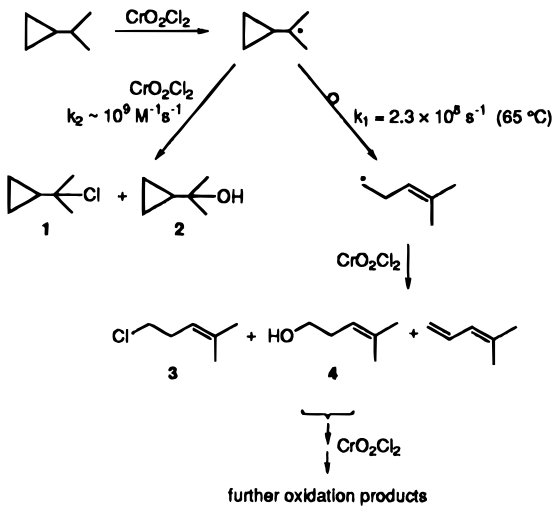
(21) (a) Wiberg, K. B. In ref 1b, pp 69−184. (b) Freeman, F. In ref 1f, pp 41−118.

Table 1. Products from the Reaction of CrO_2Cl_2 with Isopropylcyclopropane[a]

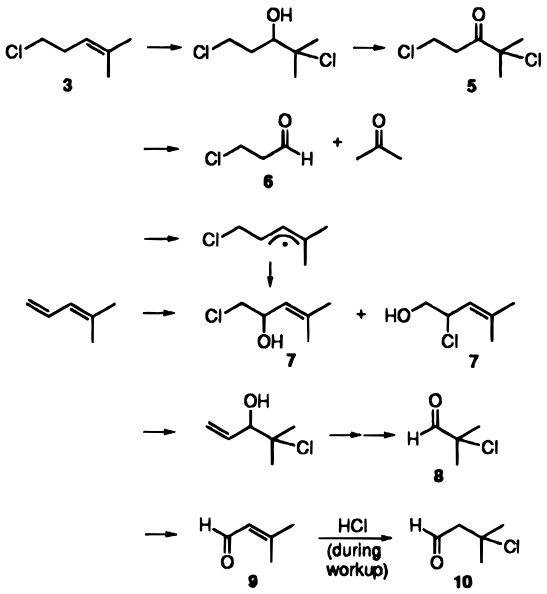
product		m/z(%)[b]	key fragments[c]	yield[d] (%)	relative yield[e] (%)
	(**1**)	120(18), 118(65), 103(12), 83(38), 79(27), 77(100), 67(20), 43(36), 41(64)	M^+ - cyclopropyl	0.4	4
	(**2**)[f]	85(67), 83(14), 72(61), 67(13), 59(49), 57(45), 55(18), 43(100), 41(60)[f]	M^+ - OH	0.2	3
	(**3**)	120(30), 118(86), 103(8), 83(60), 79(21), 77(62), 69(100), 55(72), 43(38)	M^+ - CH_2Cl	0.3	3
	(**4**)	100(80), 83(63), 69(100), 55(72), 43(76)	M^+ - CH_2OH	0.5	5
	(**5**)	172(2), 170(12), 168(20), 135(1), 133(3), 91(100), 77(63), 65(25), 63(73)	M^+ - CMe_2Cl	-	11
	(**6**)	91(3), 65(2), 63(6), 57(100)	M^+ - CHO	-	8
	(**7**)	136(5), 134(16), 99(3), 79(7), 77(21), 71(26), 57(100)	M^+ - $CCMe_2$	-	18
	(**8**)	105(6), 91(4), 79(32), 77(100), 56(87)	M^+ - CHO	-	18
	(**9**)	84(90), 69(100), 55(12)	M^+ - CHO	-	14
	(**10**)	120(3), 105(1), 91(3), 84(100), 78(9), 76(28), 55(50)	M^+ - CHO	-	30

[a] Reaction conditions: 3.1 M of CrO_2Cl_2 in neat isopropylcyclopropane at 65 °C for 30 min. [b] From GC/MS. [c] Fragments most useful in structure elucidation, not the strongest MS peaks. [d] Absolute yields, from GC data, per mole of CrO_2Cl_2 using authentic samples as calibration. [e] Approximate relative yields, from GC data, assuming equal response factors for all products and that all products were observed (see text). [f] Identified by spiking the reaction mixture with an authentic sample; MS data is for the authentic sample.

Scheme 1



Scheme 2



CrO_2Cl_2 is an approximation to the behavior of these alkoxides during alkane oxidation.

2-Cyclopropylpropene (**11**) is not observed in the oxidation of isopropylcyclopropane, but as noted above, it is a likely intermediate, both from dehydration of the alcohol **2** and by hydrogen atom abstraction from *c*-$C_3H_5\dot{C}Me_2$. Reaction of CrO_2Cl_2 (0.9 M) in neat **11** yields **3** (6%), **6** (2%), methylcyclopropyl ketone (0.3%), and trace amounts of **7** (0.05%), **1** (0.07%), and **5** (0.03%). Methylcyclopropyl ketone, the product derived from C=C bond cleavage in **11**, is formed in low yield apparently because it reacts

further with CrO_2Cl_2, as confirmed by an independent reaction. In sum, **2** and **11** are precursors to some of the ring-opened products observed on oxidation of isopropylcyclopropane. But the product distributions—for instance, the lack of formation of **8** or **9**—indicate that these are not the major pathway to ring-opened products. The data are most consistent with formation of ring-opened products via the dimethylcyclopropylcarbinyl radical "clock" (Scheme 1).

A prediction of Scheme 1 is that the partitioning between cyclopropyl products and ring-opened products depends on the relative rates of trapping vs ring-opening of *c*-$C_3H_5\dot{C}Me_2$. Ring-opening occurs with a rate constant of 2.3×10^8 s^{-1} at 65 °C.[9] Reaction of CrO_2Cl_2 with the tertiary radical likely occurs at ca. 10^9 M^{-1} s^{-1}, assumed to be a little slower than the reaction with cyclohexyl radical (3×10^9 M^{-1} s^{-1} [2b]) for steric reasons. With an initial CrO_2Cl_2 concentration of 0.15 M, it is predicted that the trapping of the radical by CrO_2Cl_2 should be competitive with ring opening. This is consistent with the observation of significant products from both pathways. The prediction cannot be quantitatively tested, however, because not all of the products were detected or identified and because of the complexity of the kinetic scheme, with further oxidation of many of the products.

This analysis implies that increasing the initial concentration of CrO_2Cl_2 should give a corresponding increase in the trapped, cyclopropyl-containing products. Using the four products for which standards are available, it is found that the ratio of (**1** + **2**) vs (**3** + **4**) increases from 0.6 to 1.0 when $[CrO_2Cl_2]_{initial}$ increases from 0.3 to 1.12 M in neat isopropylcyclopropane. This is qualitatively consistent with the proposed mechanism (Scheme 1) that a second-order trapping reaction is competing with first-order ring-opening. As above, quantitative agreement should not be expected.

The reaction of CrO_2Cl_2 and isopropylcyclopropane was also run in the gas phase by allowing the vapor of CrO_2Cl_2 and isopropylcyclopropane to diffuse to each other in a vacuum manifold. Although the relative yields vary, the same products were observed in the gas phase as found in solution. This strongly argues against the involvement of charged species in the reaction, as the formation of ions from neutral species in the absence of a dielectric medium is a high energy process. Therefore, the ring-opened products are not formed via a carbocation rearrangement, for instance in *c*-$C_3H_5C^+Me_2$. Similarly, charged species are not likely to be involved in the oxidation of **2** by CrO_2Cl_2 on the basis of the similarity of the gas- and solution-phase reactions.

Reaction of MnO_4^- with Isopropylcyclopropane. Reactions of permanganate with isopropylcyclopropane cannot be done in the neat substrate as the CrO_2Cl_2 oxidations were, due to the insolubility of the ionic reagent in the hydrocarbon. $[PPN]MnO_4$[10] has been used as the permanganate salt because of its relative stability and solubility. According to control experiments, pyridine is a good solvent for $[PPN]MnO_4$ since there is limited decay of permanganate: about 10% decomposition was observed by UV/vis spectroscopy after 5 h at 65 °C. Reactions were performed in mixed pyridine/isopropylcyclopropane solvent (2/1 by volume, 3.1 M in the substrate). Reactions were run at 67 mM $[PPN]MnO_4$, close to the saturation point. Other solvents such as acetonitrile and *o*-dichlorobenzene also provide solubility but are too reactive with permanganate. The reaction of MnO_4^- with isopropylcyclopropane does not occur as readily as that of CrO_2Cl_2, requiring heating at 65 °C for 4 h.

Product analyses are problematic for this reaction because of the small concentrations involved and because the ring-opened products, if any, are likely to be predominantly carboxylic acids that have been difficult to detect.[22] Quenching a reaction mixture of 67 mM MnO_4^- and 3.1 M isopropylcyclopropane with aqueous $NaHSO_3$/HCl and analysis by GC/MS revealed only the formation of acetone. The possibility that acetone was introduced inadvertently was ruled out after carefully scrutinizing the control sample. In addition, reaction of partially isotopically enriched $Mn^{18}O_4^-$ (ca. 10% ^{18}O enriched)[3c] gave $Me_2C^{18}O$ (ca. 10%). In a control experiment, no exchange was observed between Me_2CO and $Mn^{18}O_4^-$ under these conditions. Neither [^{18}O]methyl cyclopropyl ketone nor [^{18}O]-2-cyclopropyl-2-propanol were detected.[23] Acetone is one of the expected products if ring-opening occurs, as permanganate is known to cleave C=C double bonds to the corresponding aldehydes and ketones.[1] Aldehydes and primary or secondary alcohols would most likely be oxidized further by permanganate under these conditions.

Conclusion

The reaction of chromyl chloride with isopropylcyclopropane gives a large number of products, including both compounds that retain the cyclopropane ring and ring-opened compounds. The nature and yields of the products are consistent with formation of the dimethylcyclopropylcarbinyl radical clock, which is trapped by CrO_2Cl_2 in competition with ring opening. The only material observed from permanganate oxidation of this substrate is acetone, which is a logical product of vigorous oxidation of the ring-opened radical. These observations support the contention that alkane oxidation by chromyl chloride and permanganate proceeds by initial hydrogen atom abstraction to give an organic radical intermediate.

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(22) The carboxylate products are bound to the MnO_2 colloid. They are liberated on acidic reduction. Direct detection by GC has been unsuccessful, as were attempts to esterify carboxylic acid products by diazomethane treatment,[3c] possibly because of manganese ion interference of CH_2N_2 reactions.

(23) Addition of 2-cyclopropyl-2-propanol (**2**) to the reaction mixture showed that this compound is stable to the reaction conditions and would have been detected if formed. (Tertiary alcohols are known to be stable to high valent manganese complexes: Müller, P. In *The Chemistry of the Functional Groups: Ethers, Crown Ethers and Hydroxyl Groups*; Patai, S., Ed.: Wiley: New York, 1980; Vol. 1, p 469). However, trapping of the 2-cyclopropyl-2-propyl radical by MnO_4^- would give the manganese(VI) alkoxide, $[O_3Mn\{OCMe_2(C_3H_5)\}^-]$, which is less likely to be stable.