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(25) The lifetime of triplet adamantanone in fluid solution at room temperature is estimated to be ca. 0.1 nsec.

Directive Effects in Free Radical Oxidation by Fe(III). Reductive Decarboxylation of Peroxy Acids[1]

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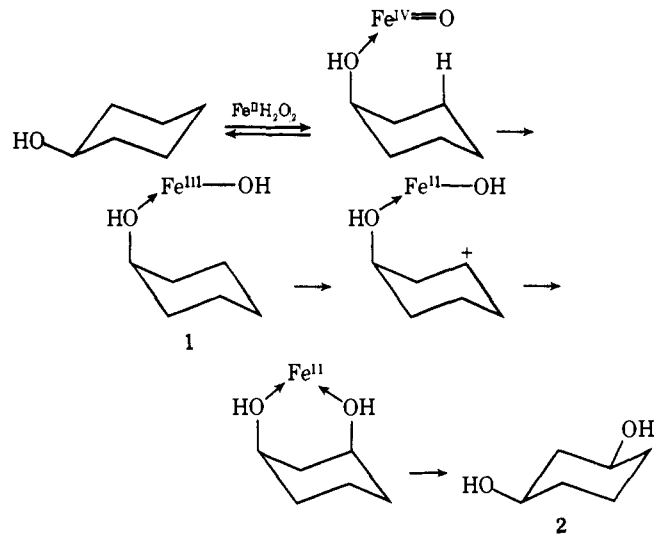
Abstract: Treatment of peroxycyclohexanecarboxylic acid with ferrous perchlorate in acetonitrile has been found to afford a 25% yield of cyclohexanol. Similar treatment of *cis*- or *trans*-3-hydroxyperoxycyclohexanecarboxylic acid yields largely *cis*-1,3-cyclohexanediol, revealing a directive effect for free radical oxidation by iron(III) analogous to that observed for the stereospecific cis-1,3 hydroxylation of cyclohexanol by ferrous ion–hydrogen peroxide. Preference for cis diol formation is also observed for *cis*-4-hydroxyperoxycyclohexanecarboxylic acid, but the cis- and trans-1,2 isomers give a cis/trans diol ratio near unity. Analysis of the stereoisomeric mixture of 1,2-cyclohexanediols from the reaction of cyclohexene with ferrous ion–hydrogen peroxide leads to the conclusion that, in acetonitrile, the predominant mode of olefin hydroxylation does not proceed via addition of hydroxyl radical to the double bond.

Transition metal ions are known to catalyze the decomposition of peroxides by reductive cleavage of the peroxy linkage.[2] Thus, reductive decomposition of peroxy esters[3] leads predominantly to metal carboalkoxides and alkoxy radicals. Similarly, the reaction of diacyl peroxides with cuprous ion is known to afford carboalkoxy radicals.[4] Much less is known of the fate of peroxy acids upon reductive decomposition by variable valence metals.[5] The observed formation of carbon dioxide upon treatment of peracetic acid with ferrous ion in acetic acid is not definitive since substantial amounts of the decarboxylation results from reactions of the solvent. These results have been interpreted as the consequence of competing modes of one-electron cleavage of the peroxy bond leading either to acyloxy radicals or hydroxyl radicals.[6]

We have been interested in site-specific aliphatic hydroxylation mediated by metal–peroxide species both from the view of developing new stereospecific remote functionalization procedures and elaborating possible parallels between iron–peroxide chemistry in solution and intermediates involved in aliphatic hydroxylation by mixed function oxidases. Toward these ends we reported[7] recently the cis-1,3 hydroxylation of cyclohexanol with net retention at the oxidized carbon together with the proposal that this process proceeds by directed oxidation by a bound iron species, formally equivalent to a ferryl ion, and leading to discreet radical and carbonium ion intermediates (Scheme I). An important consequence of this conclusion is that aliphatic hydroxylation with retention of configuration, common among the steroid hydroxylases,[8] need not necessarily require an

Scheme I



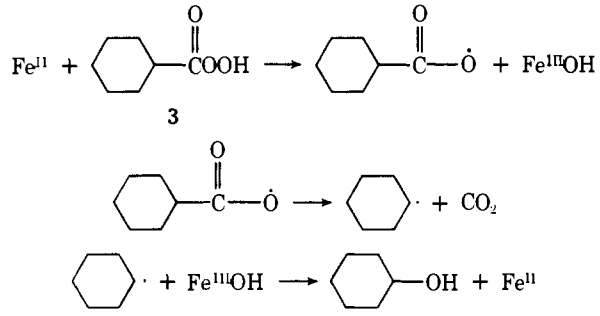
"oxene insertion" mechanism. Indeed, it is our view that a stepwise process through well precedented intermediates is a preferable route.

A requisite consequence of this mechanism is that properly substituted carbon free radicals, generated independently in the presence of iron(III), should reflect the same strong substituent-derived directive effects. Accordingly, 3-hydroxycyclohexyl radicals (**1**) are expected to be oxidized by ferric ion to give *cis*-1,3-cyclohexanediol (**2**). The possible reductive decarboxylation of 3-hydroxyperoxycyclohexanecarboxylic acid (**3**) as a route to **1** independent of hydrogen peroxide has prompted us to study the reaction of the family of isomeric hydroxyperoxycyclohexanecarboxylic acids with ferrous ion. We report herein the first evidence of stereoselective peroxy acid *reductive* decarboxylation.[9]

Results and Discussion

Peroxycyclohexanecarboxylic Acid. The treatment of peroxycyclohexanecarboxylic acid (**3**) with ferrous perchlorate in acetonitrile at 0° afforded a 25% yield of cyclohexanol and a 75% yield of cyclohexanecarboxylic acid. Significantly, no cyclohexanone or other oxidation products were observed. Taken together, these results indicate decomposition of the peroxy acid via a carboalkoxy radical (Scheme II) and subsequent decarboxylation.

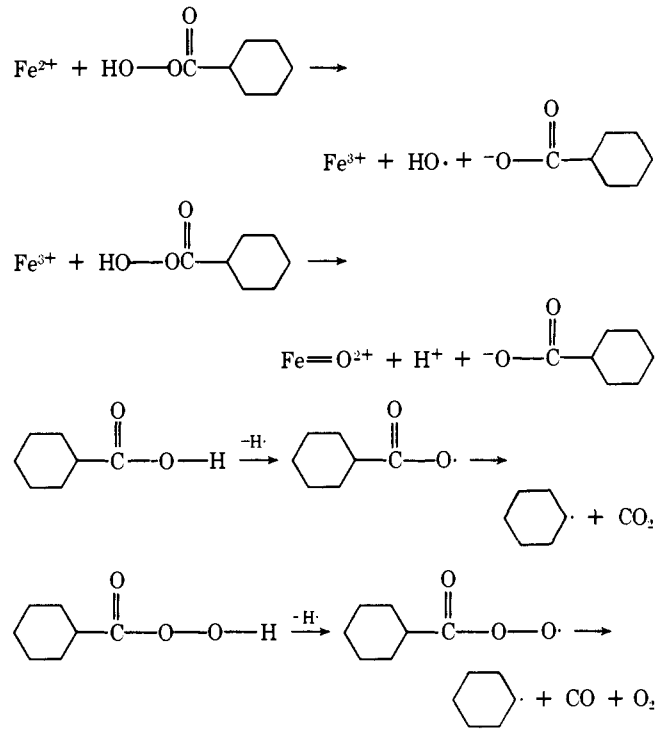
Scheme II



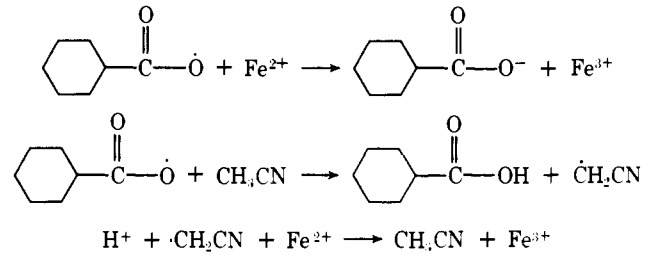
Reductive cleavage in the opposite sense, producing either a hydroxyl radical or a kinetically equivalent ferryl ion (FeO^{2+}),[10] could conceivably lead to cyclohexyl radicals by subsequent hydrogen abstraction from either cyclohexanecarboxylic acid or peroxycyclohexanecarboxylic acid (Scheme III). These possibilities can be ruled out with some confidence, however, on several bases: (1) the cyclohexanol produced is not oxidized further under the reaction conditions; (2) treatment of cyclohexanecarboxylic acid with ferrous perchlorate–hydrogen peroxide in acetonitrile produced no detectable cyclohexanol or cyclohexanone;[11] and (3) all reactions were carried out by slow addition of peroxy acid to the reaction medium and, accordingly, ambient concentrations of unreacted peroxy acid were always low. Thus the reactive intermediates formed from the ferrous ion induced decomposition of peroxycyclohexanecarboxylic acid are distinct from those derived from ferrous ion–hydrogen peroxide in acetonitrile, and the major one-electron reductive path for peroxy acid decomposition is to form carboalkoxy radicals and not hydroxyl radicals.

A corollary conclusion is that the formation of cyclohexanecarboxylic acid, the major reduction product, is not the result of competing paths of peroxy bond cleavage either. Since high concentrations of ferrous ion are present during the addition of peroxy acid, the most reasonable explanation for acid formation is reduction of the carboalkoxy radical by ferrous ion *prior* to decarboxylation. A closely related alternative is hydrogen abstraction from the solvent followed by the anticipated[12] reduction of the incipient cyanomethyl radical by ferrous ion (Scheme IV).

Scheme III



Scheme IV



The formation of carboalkoxy radicals by reductive cleavage of the peroxy bond contrasts markedly with the behavior of peroxy esters which decompose to give alkoxy radicals.[3] The sources of this difference are under continued study.

***cis*- and *trans*-3-Hydroxyperoxycyclohexanecarboxylic Acid (4 and 5).** Pure *cis*-3-hydroxyperoxycyclohexanecarboxylic acid (**4**) and *trans*-3-hydroxyperoxycyclohexanecarboxylic acid (**5**) were prepared by the treatment of the corresponding carboxylic acids with 70% hydrogen peroxide in methanesulfonic acid. The ferrous ion induced reductive decarboxylation of **4** and **5** in acetonitrile afforded nearly identical mixtures (83:17 and 85:15, respectively) of *cis*- and *trans*-1,3-cyclohexanediol (Table I).

These results are in accord with the formation of a common intermediate from the ferrous ion induced decomposition of **4** and **5**. If, as seems likely, the initial steps of the reaction of **4** and **5** with ferrous ion parallel the reductive decomposition of peroxycyclohexanecarboxylic acid (Scheme II), the formation of the same 3-hydroxycyclohexyl radical (**10**) is expected from both stereoisomers. This radical must then undergo stereoselective oxidation to give the observed preference for *cis*-1,3-cyclohexanediol (Scheme V).

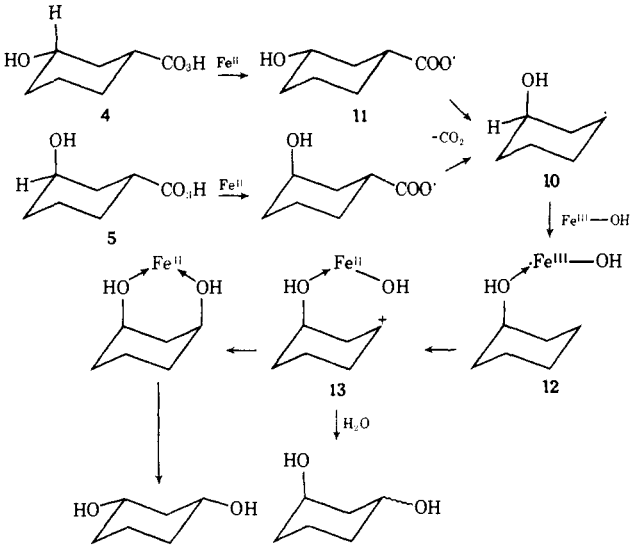
Stereoselective reduction of **10** to give cis diol is required if Scheme I is an accurate description of the aliphatic hydroxylation mechanism observed with ferrous ion hydrogen peroxide.[7] Thus, the results reported here confirm this requirement and support hydrogen abstraction to give **10** as the initial step.

Table I. Decomposition of Hydroxyperoxycyclohexanecarboxylic Acids

	Compd[a]	Conditions[b]	% cis diol	% trans diol
A)	4	80°	50.0[c]	50.0
B)	4	Fe^{2+}	82.8[c]	17.2
C)	4	50% CH_3CN-H_2O,Fe^{2+}	57.7	42.3
D)	4	$Fe,^{2+}$ O_2	85.5	14.5
E)	5	Fe^{2+}	85.2	14.8
F)	6	Fe^{2+}	72.0	28.0
G)	8	Fe^{2+}	54.5	45.5
H)	9	Fe^{2+}	47.2	52.8

[a] 4, *cis*-3-Hydroxy peroxy acid; 5, *trans*-3-Hydroxy peroxy acid; 6, *cis*-4-hydroxy; 8, *cis*-2-hydroxy; 9, *trans*-2-hydroxy. [b] Except for *a*, all are at 0° and contain $HClO_4$; B, E, F, G, H in CH_3CN under N_2; C under N_2. [c] Average of two runs, ±3%. No diols were present in any of the runs which represented interconversion of isomers; e.g., no 1,4- or 1,2-diols were found in the decompositions of 4 or 5.

Scheme V



The stereospecificity for diol formation upon decomposition of **4** has been found to be a sensitive function of the medium. Thus, the preference for *cis*-1,3-cyclohexanediol formation is substantially reduced in 1:1 acetonitrile–water and is completely lost upon thermal[13] decomposition of **4** in the absence of metal ions. The effect of added water observed here also parallels the behavior of 3-hydroxycyclohexyl radicals derived from cyclohexanol by hydrogen abstraction and can be regarded most simply as providing a competing, nondirected nucleophile (H_2O) from the solvent. Attack by water on the intermediate carbonium ion **13** may then occur from either side giving a stereoisomeric mixture. Alternatively, water may compete with the alcohol as a ligand on iron leading to nondirected radical oxidation by ferric ion. It is interesting that, even in 50% water, the efficiency with which ferric ions oxidize these secondary radicals remains high. Aquo iron(III) is known to oxidize radicals only slowly,[12a] leading instead to dimeric products. Careful scrutiny of reaction mixtures has not revealed any dimeric products (e.g., dihydroxydicyclohexyl). Apparently acetonitrile plays a crucial role in accelerating the rate of radical oxidation by iron(III).[14] The extent of this acceleration is punctuated by the *insensitivity* of the product diol ratio to added oxygen. Ordinarily oxygen is an extremely efficient radical trap,[15] and it is unlikely such a radical recombination process would lead similarly to predominant formation of *cis*-1,3-cyclohexanediol. Accordingly, ferric ion in acetonitrile must oxidize secondary carbon radicals faster than trapping by oxygen. This very rapid time scale

Table II

	Starting material	Reaction conditions	1,2-Cyclohexanediol cis:trans
(a)	Cyclohexanol	Fe^{2+}–H_2O_2–CH_3CN	1:1
(b)	Cyclohexanol	Cu^{2+}–H_2O_2–CH_3CN	1:16
(c)	Cyclohexene	Fe^{2+}–H_2O_2–CH_3CN	1:10
(d)	Cyclohexene oxide	$HClO_4$–CH_3CN	1:10
(e)	8	Fe^{2+}–CH_3CN	54.5:45.5
(f)	9	Fe^{2+}–CH_3CN	47.2:52.8

puts severe limitations on the events which transpire between intermediates **11** and **13**. Since ligand substitution rates for iron are known to be rather slow ($\sim 10^3$),[16] it seems likely that the iron(III) produced by reduction of the starting peroxy acid is still in the solvent cage when radical oxidation occurs.

The extremely rapid rate of carbon radical oxidation by cupric ion has been attributed by Kochi[14] to rate-limiting formation of a copper alkyl. It is consistent with the arguments and results presented here that the accelerating effect of acetonitrile in promoting radical oxidation by ferric ion results from a change in mechanisms for radical oxidation from an outer sphere electron transfer process to an inner sphere process made possible by changes in the solvation state of the metal. Ligation of iron by the neighboring hydroxyl group in **10** is by itself insufficient to explain facile radical oxidation by ferric ion in acetonitrile since no such effect is possible in the observed oxidation of cyclohexyl radicals (Scheme II).

The lifetime of **13** must also be very short since no alkylation of solvent or 1,2-hydride shifts are observed. Indeed, careful scrutiny of product mixtures from all the peroxy acids studied did not reveal any rearranged diols. The observed integrity of the diol substitution patterns thus contrast with results obtained for cyclohexyl tosylate solvolyses which lead to significant rearrangement.[17]

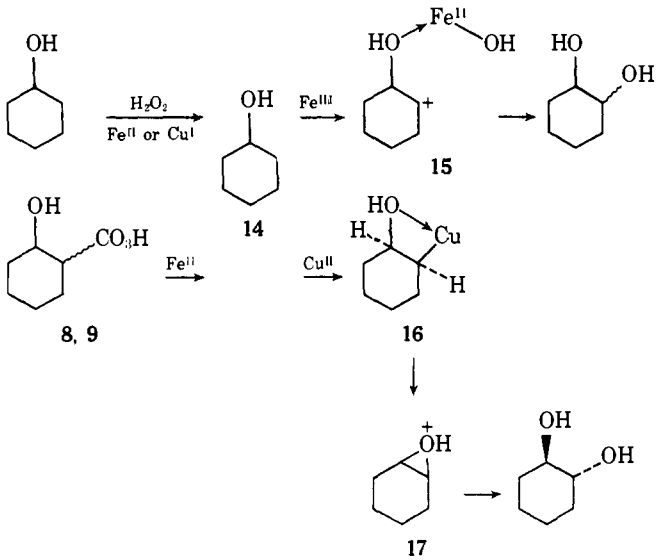
The ferrous ion induced decomposition of *cis*-4-hydroxyperoxycyclohexanecarboxylic acid gave a 72:28 mixture of *cis*- and *trans*-1,4-cyclohexanediol. Significantly, the preference here is for the *less* stable of the two isomers. We conclude, therefore, that the directed nature of the radical oxidation process persists over a span of four carbon atoms even though such a process requires a boat-like transition state.

***cis*- and *trans*-2-Hydroxyperoxycyclohexanecarboxylic Acid.** In striking contrast to the 3 and 4 isomers, the reduction of *cis*- and *trans*-2-hydroxyperoxycyclohexanecarboxylic acid (**8** and **9**) does not exhibit marked stereoselectivities. Instead there is observed a near 1:1 mixture with a small but significant *retention* of configuration. Models indicate that octahedral iron complexed to a 2-hydroxycyclohexyl radical should be able to approach the radical or subsequent carbonium ion from either side with equal ease. Interestingly, this 1:1 ratio of isomers is similar to that obtained from the fraction of 1,2-diol derived from the Fe^{2+}/H_2O_2 hydroxylation of cyclohexanol under otherwise similar conditions.[7] In contrast, the Cu^{2+}/H_2O_2 hydroxylation of cyclohexanol, the Fe^{2+}/H_2O_2 oxidation of cyclohexene, and acid catalyzed ring-opening of cyclohexene oxide all afford predominantly *trans*-1,2-cyclohexanediol (Table II). The preference for trans diol formation from cyclohexene oxide is well studied and is attributable to nucleophilic displacement on a protonated epoxide intermediate. It is tempting to ascribe a common intermediate, the protonated epoxide (**17**), to each of the routes that favors *trans*-1,2-cyclohexanediol.

This assumption leads to revealing secondary conclusions. The contrasting stereochemical results of the iron and

copper catalyzed hydroxylation of cyclohexanol seem to require a divergent fate of the incipient 2-hydroxycyclohexyl radical (**14**) in the two cases (Scheme VI).

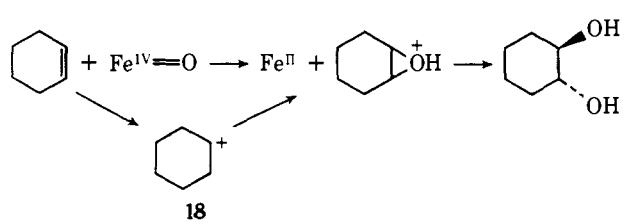
Scheme VI



The observed facile oxidation of even primary carbon radicals by cupric ion[14] seems to indicate that discrete carbonium ions are not necessarily formed in those processes. In this light, oxidative substitution of the alkyl copper species **16** to afford the protonated epoxide **17**, a formal ligand insertion process,[18] would seem to be an attractive route to trans diol.

In contrast we view the oxidation of **14** by ferric ion as proceeding to **15** irrespective of the exact mode of electron transfer. Nucleophilic attack by iron-bound water can in this case approach either side of the molecule to give the observed 1:1 mixture of cis and trans diols. The distinct amount of *retention* observed contrasts sharply with the complete convergence of results observed for *cis*- and *trans*-3-hydroxycyclohexanecarboxylic acid.

Another important conclusion from these results is that the Fenton's reagent oxidation of cyclohexene cannot involve addition of hydroxyl radical to the double bond to afford **14**, as has generally been proposed.[19] As was reported above, ferric ion oxidation of **14** generated either by hydrogen abstraction or reductive decarboxylation produces nearly a 1:1 ratio of cis and trans diol. The observed strong preference for trans diol formation upon Fe^{2+}/H_2O_2 oxidation of cyclohexene requires another path. One explanation consistent with our proposal for the formation of an iron(IV) species from iron(II)-hydrogen peroxide in acetonitrile is that **17** is produced directly by a two-electron oxidation of cyclohexene by ferryl ion.



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Alternatively, olefin hydroxylation by Fenton's reagent may in this case involve electron transfer from the π bond to the metal forming a radical cation (**18**).[22] Such details of the mechanism of peroxy compound decomposition in nonaqueous environments remain to be more fully elaborated.

Experimental Section

Peroxycyclohexanecarboxylic Acid. The peroxy acid was prepared by the method of Swern:[20] ir (neat) 3260, 2915, 2840, 1745, 1450, 1070, 975 cm^{-1}. Recrystallization of the product was not attempted, and titration with thiosulfate of the iodine produced by the reaction with KI gave an apparent mol wt of 167.6 (calcd, 144.17). Decomposition by ferrous perchlorate, as described below, gave approximately 0.026 g (25%) cyclohexanol from 0.140 g of the crude peroxy acid.

***cis*-3-Hydroxycyclohexanecarboxylic Acid.** 3-Hydroxybenzoic acid (8.62 g, 0.0625 mol) (recrystallized from H_2O) was hydrogenated in 50 ml of ethanol with 1 g of 5% Rh on alumina (Engelhard) at 45 psi. After 20 hr, the catalyst was removed by filtration through a Celite pad and the solvent removed under vacuum. The product (5.0 g, 55.6% theory), after recrystallization from $CHCl_3$-CH_2Cl_2, is mainly the cis isomer:[21] mp 130–131°; NMR (D_2O) δ 3.55 (broad s, 1 H), 2.80–0.80 (9 H).

***cis*-3-Hydroxyperoxycyclohexanecarboxylic Acid.** The synthesis of this material was modeled after the procedure of Swern.[20] Pure *cis*-3-hydroxycyclohexanecarboxylic acid, prepared above (2.49 g), was dissolved in 7.5 ml of CH_3SO_3H with ice-bath cooling. Three milliliters of 70% H_2O_2 was added dropwise at such a rate as to maintain the temperature near 5°. After stirring at ice-bath temperature for 2 hr, the mixture was slowly added to 15–20 ml of crushed ice. The aqueous mixture was then extracted with five 80-ml portions of cold ether, which were combined and washed with 10 ml of saturated ammonium sulfate. After drying ($MgSO_4$) and removing the solvent, the crude oil was placed under vacuum (0.2–0.1 mm) for 1 hr. Crystals (1.73 g) formed upon standing at room temperature. The iodine produced by reaction of the peroxy acid with an acidic solution of KI was titrated with standard thiosulfate to determine the content of active oxygen and was within 5% of the calculated value: ir (neat film) 1740 cm^{-1} (C=O); NMR (CD_3CN) δ 3.55 (s, 1 H), 1.0–2.65 (11 H).

***cis*- and *trans*-3-Hydroxyperoxycyclohexanecarboxylic Acids.** 3-Hydroxybenzoic acid was hydrogenated as above and, after removing solvent and catalyst, the crude product was esterified with methanol and a small amount of *p*-toluenesulfonic acid. An aqueous work-up gave a mixture of methyl esters which was purified by distillation. The first fraction, bp 28° (0.2 mm), was methyl cyclohexanecarboxylate, while the second fraction (4.7 g), bp 70–80° (0.1 mm), a clear colorless liquid, consisted of a 50:50 mixture of *cis*- and *trans*-methyl-3-hydroxycyclohexanecarboxylate: glc retention time (10 ft DEGS, 80–160° at 6°/min): trans 29.3 min, cis 32 min; mixture ir (CCl_4) 3630, 3460, 2940, 2865, 1740, 1454, 1438, 1375, 1200, 1165, 1060 cm^{-1}; trans NMR ($CDCl_3$), δ 4.3–3.8 (broad s, 1 H), 3.66 (s, 3 H), 3.1–2.5 (broad, 1–2 H), 2.1–1.3 (~9 H); cis NMR δ 3.66 (s, 3 H), 3.70–3.25 (broad s), 2.65 (2, 1 H), 2.60–1.0 (9 H). Preparation of the corresponding peroxy acids was as described above using the mixture of methyl esters.

Thermolysis of *cis*-3-Hydroxyperoxycyclohexanecarboxylic Acid. The peroxy acid described above (0.156 g) was dissolved in 50 ml of benzene and brought to reflux under nitrogen. After 2 days, the solution gave a negative KI test for peroxy acid, and the product mixture was acetylated (pyridine–acetic anhydride) and analyzed by GLC (3% OV-225, 120°) after a standard aqueous work-up.

Decomposition of *cis*-3-Hydroxyperoxycyclohexanecarboxylic Acid with Ferrous Ion. A solution of 0.507 g of $Fe(ClO_4)_2 \cdot 6\,H_2O$ and 0.25 ml of $HClO_4$ (70%) in 50 ml of CH_3CN was cooled to 0° under a nitrogen atmosphere. A solution of the peroxy acid (0.1759 g) in 10 ml of CH_3CN was added to the former with rapid stirring over a period of 40 min. After neutralizing wth strong NaOH, K_2CO_3 was added until saturation. The mixture was then filtered, and the filtrate was concentrated, acetylated, and analyzed as below. For the decomposition in the presence of oxygen, dry air was passed through the ferrous perchlorate solution for 15 min before the addition of the peroxy acid and also throughout the addition period.

***cis*-4-Hydroxyperoxycyclohexanecarboxylic Acid.** Synthesis of this material from the corresponding hydroxy acid (contaminated with lactone) as well as the decomposition with ferrous ion was as described for the 3-hydroxyperoxy acid. Infrared analysis of the decomposition products showed that none of the 1,3 isomer was present.

***cis*- and *trans*-2-Hydroxycyclohexanecarboxylic Acids.** The preparation of these isomers, from ethyl-2-oxocyclohexanecarboxylate, followed the procedure described by Kilpatrick and Morse.[21] Complete separation of the trans isomer was not affected, but the cis isomer was obtained essentially pure (~95% cis, 5% trans). Preparation of the corresponding peroxy acids was accomplished as described above using the methyl esters, which were readily separated by GLC (5 ft 20% DEGS, 80–160° at 4°/min; retention time *cis*-methyl ester, 11.9 min; *trans*-methyl ester, 14.1 min). Isolation of the hydroxy acids from the decomposition (as above) of the peroxy acids indicated that stereochemical integrity is maintained under the conditions employed. Analysis of the decomposition products was by GLC (10 ft 20% DEGS, 80–160° at 6°/min).

Analysis of Cyclohexanediols. Iron salts were precipitated from the crude reaction mixture by the addition of concentrated sodium hydroxide. Two phases were present at this time. Potassium carbonate was added until the lower aqueous phase was saturated, resulting in a thick sludge. The acetonitrile layer was filtered through Whatman No. 3 filter paper, and the sludge was washed several times with CH_3CN. The combined acetonitrile portions were clear and were dried over K_2CO_3–Na_2SO_4. GLC analysis for cyclohexanol and cyclohexanone was reliable at this point, and a quantitative analysis of the alcohol and ketone was performed on this dilute solution. For analysis of the diol products, the above dilute solution was concentrated under vacuum and filtered again if necessary. The concentrated solution was then acetylated, using approximately 8 mol equiv of a 5:1 acetic anhydride–pyridine mixture for each mole of starting material used in the reaction. The mixture was refluxed 1 hr before pouring onto ice and water and subsequently removing pyridine and acetic acid by an aqueous work-up which involved extraction with three portions of ether, followed by washing the combined ether extracts with dilute HCl, dilute bicarbonate, and saturated NaCl.

The amounts of cyclohexanol and cyclohexanone were determined by GLC analysis on a 10 ft 20% DEGS column at 100°, adding 1-phenylethanol as the internal standard after the reaction mixture was neutralized with NaOH. For the cyclohexyl diacetates, the conditions were 80–160° at 6°/min on the same column, retention times: cis-1,2 (24 min), trans-1,2 (25.6 min), trans-1,3 (29.5), trans-1,4 (32), cis-1,3 and cis-1,4 (34.3). The yields of diols were determined prior to acetylation on an OV-225 at 100°.

Separation and Identification of Isomeric Cyclohexanediacetates. A mixture of *cis*- and *trans*-1,4-cyclohexanediol was acetylated (2 g of diol, 10 ml of acetic anhydride, and 10 ml of pyridine were refluxed 0.5 hr) and the mixture poured into 75 ml ice–water after cooling to room temperature. The solid was filtered and recrystallized from ethanol–water (mp 96–100°, lit. mp cis 41°, trans 102–103°) to give largely the trans isomer. Both isomers were obtained in roughly equal amounts by extraction of the aqueous solution with ether and subsequent work-up. The 1,2-cyclohexanediacetates were prepared as the 1,4 isomers. Authentic *trans*-1,2-cyclohexanediol was obtained from commercial sources. After acetylation of *cis*- and *trans*-1,3-cyclohexanediol, distillation gave a clear, colorless liquid, bp 130–134° (15 mm) (mixture of isomers, about 60:40). Repeated recrystallization of a mixture of *cis*- and *trans*-1,3-cyclohexanediols with ethyl acetate gave crystals, mp 82–83° (about 95% one isomer by GLC; lit. cis 86°, trans 117°). Acetylation of this material allowed the assignments of the GLC peaks to be completed.

Acknowledgment. Financial support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and The University of Michigan is gratefully acknowledged.

References and Notes

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