Oxidation by Transition Metal Complexes. VI.[1] Oxidation of Cyclohexenes Catalyzed by Rhodium Complexes

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Rhodium complexes can cause the catalytic oxidation of cyclohexene to give ketone, alcohol, and epoxide. The product distribution is dissimilar to that of the metal-catalyzed decomposition of cyclohexene hydroperoxide(V). Ketone and alcohol are derived from the decomposition of the intermediate hydroperoxide (V) but epoxide is not formed by the oxygen transfer reaction from V. Oxidation of methylcyclohexenes was also studied and discussed in relation to the effect of methyl substituent.

X-Ray analysis of oxygen complexes indicated that the coordinated oxygen is in an electronically excited state, that is, the anionic species of O_2^-, O_2^{--} formed by charge transfer from the metal.[2] Recently, the application of the coordinated oxygen to oxidation reaction has been studied extensively, particularly using rhodium complexes.[3] It is generally said that rhodium complexes act as the catalyst for hydrogen abstraction from substrates by the coordinated oxygen and as a catalyst inducing the decomposition of hydroperoxide formed by oxygen and olefin (Haber-Weiss mechanism).

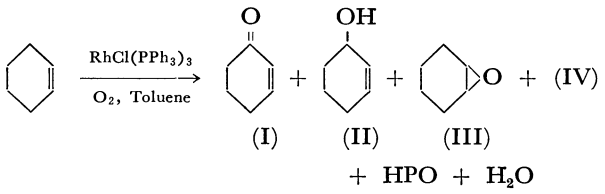
In previous papers, we reported on the oxidation of styrene and its derivatives catalyzed by rhodium complexes and proposed that the oxidation might proceed *via* a four-center intermediate in which both oxygen molecule and olefin are coordinated to the rhodium complex.[1,4]

In connection with this work, we have studied the oxidation of cyclohexene and methylcyclohexene catalyzed by $RhCl(PPh_3)_3$. Although the oxidation of cyclohexene having active hydrogens at the allylic position of olefin has been investigated by many workers,[5] in the cyclohexene oxidation using rhodium complexes, the reaction products have not yet been examined in detail.

In this paper we will discuss the development of the reaction products, *i.e.*, ketones, alcohols, and epoxides.

Results and Discussion

Oxidation of Cyclohexene. Cyclohexene was oxidized under a constant bubbling of oxygen with $RhCl(PPh_3)_3$ catalyst in toluene at 80 °C for 8 hr. It gave 2-cyclohexen-1-one (I, 1530% based on catalyst), 2-cyclohexen-1-ol (II, 852%), cyclohexene oxide (III, 351%), benzaldehyde (IV, 524%), hydroperoxides, and water.



The formation of aldehyde IV is considered to arise from the oxidation of toluene solvent.[6]

The relation between yields of the products and reaction time in the cyclohexene oxidation is given in Fig. 1. The yields of I and II increased with reaction time. I was the main product for 8 hr. The content of hydroperoxides determined by the iodometric method showed a maximum value at 3 hr, suggesting that they could be intermediate species for I and II.[7] The hydroperoxides should be composed of mostly cyclohexene hydroperoxide (V).

The decomposition of V by $RhCl(PPh_3)_3$ under argon atmosphere was then carried out under the same reaction conditions as above. The starting hydroperoxide (V) was perpared by treatment of cyclohexene

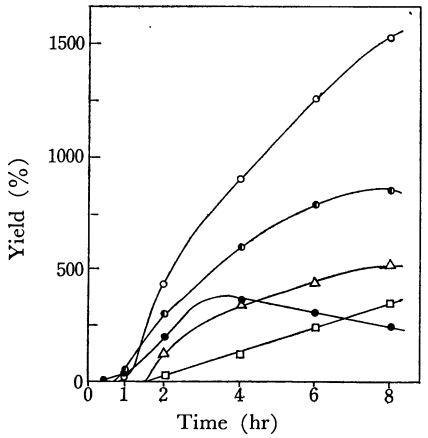


Fig. 1. Oxidation of cyclohexene with $RhCl(PPh_3)_3$.
○: 2-Cyclohexen-1-one, ◐: 2-Cyclohexen-1-ol,
●: Hydroperoxides, △: Benzaldehyde,
□: Cyclohexene oxide.

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1) Part V of this series: K. Takao, H. Azuma, Y. Fujiwara, T. Imanaka, and S. Teranishi, This Bulletin, **45**, 2003 (1972).

2) a) R. Mason, *Nature*, **217**, 543 (1968). b) R. McWeeny, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, **47**, 20 (1969). c) S. J. Laplaca and J. A. Ibers, *J. Amer. Chem. Soc.*, **87**, 2581 (1965). d) J. A. Mcginnety, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6** 2243 (1967).

3) E. W. Stern "Transition Metals in Homogeneous Catalysis", ed. by G. N. Schrauzer, Marcel Dekker, Inc., New York (1971), p. 137.

4) K. Takao, M. Wayaku, Y. Fujiwara, T. Imanaka, and S. Teranishi, This Bulletin, **43**, 3898 (1970).

5) a) V. P. Kurkov, J. Z. Pasky, and J. B. Lavigen, *J. Amer. Chem. Soc.*, **90**, 4743 (1968). b) A. Fusi, R. Ugo, A. Pasini, and S. Cenini, *J. Organometal. Chem.*, **26**, 417 (1971). c) C. Dudley and G. Read, *Tetrahedron Lett.*, **1972**, 5273.

6) It is of noteworthy that toluene could not be directly oxidized to IV by $RhCl(PPh_3)_3$ under oxygen atmosphere.

7) In the case of styrene, hydroperoxides were scarcely detected at all and the oxidation was not remarkably affected by a free radical inhibitor. On the other hand, oxidation of cyclohexene was perfectly inhibited by the inhibitor.

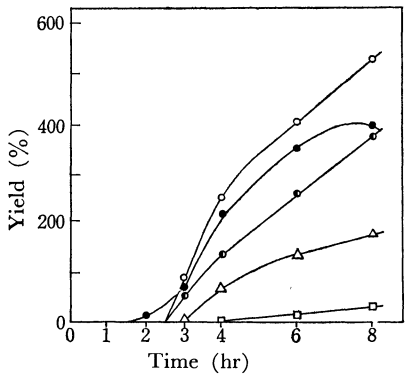


Fig. 2. Oxidation of cyclohexene with $RhCl(PPh_3)_3$ in the presence of pyridine.
Cyclohexene: 50 mmol, $RhCl(PPh_3)_3$: 0.50 mmol, Pyridine: 5 mmol, Toluene: 75 ml.
○: 2-Cyclohexen-1-one, ◐: 2-Cyclohexen-1-ol, ●: Hydroperoxides, △: Benzaldehyde, □: Cyclohexene oxide.

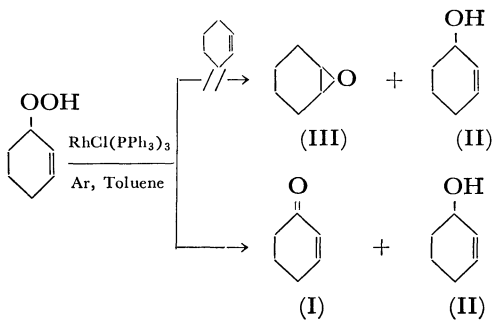
with azobis(2-methylpropionitrile), (ABN) under oxygen atmosphere. It decomposed within 2 hr to give ketone (I, 53% based on V), alcohol (II, 47%), IV (trace), and water, whereas the thermal decomposition of V without $RhCl(PPh_3)_3$ did not occur at 80°C for 8 hr. Thus the formation of ketone (I) and alcohol (II) can be explained by the decomposition of intermediate V according to the Haber-Weiss mechanism.

Addition of pyridine or $O=PPh_3$ to the reaction system depressed the oxidation reaction (Fig. 2). This suggests that the coordination of oxygen to the rhodium complex is prevented by the high coordination ability of these compounds.[8]

It should be noted that the decomposition of V did not result in the formation of epoxide III, while the yield of III increased with reaction time and reached 351% after 8 hr, the oxidation of 1-methylcyclohexene giving 1-methylcyclohexene oxide as the main product (1340%).

Two types of reactions are known in catalytic epoxidation, *i.e.*, double bond reacting with (a) hydroperoxide and (b) organic peracid (cooxidation).

In order to examine the possibility of mechanism (a) in this reaction system, autoxidation of cyclohexene or 1-methylcyclohexene with ABN was carried out in the presence of oxygen. It gave mainly ketones and alcohols accompanied by a small amount of epoxide. The reaction of V and cyclohexene with $RhCl(PPh_3)_3$ under argon atmosphere gave rise to only the decomposition products, I and II. None of III could be detected, the same result being also obtained with *t*-butyl hydroperoxide.

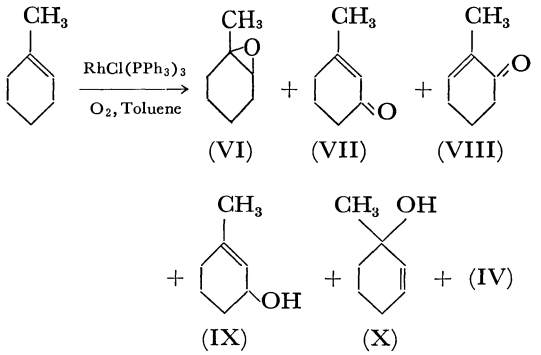


Thus the formation of epoxide (III) might be expected by cooxidation of aldehyde (IV), possibly derived from toluene solvent, and cyclohexene (mechanism b). Oxidation of cyclohexene was then carried out by adding about 5-fold excess of benzaldehyde to the catalyst. However, no remarkable accelerating effect of epoxidation was observed.

Thus the epoxidation could be explained by neither oxygen transfer reaction from V (mechanism a), nor cooxidation with IV (mechanism b). Details of the epoxidation are not clear at present, but it seems that the coordinated oxygen molecule would directly attack the olefin double bond to give epoxides.[10]

Oxidation of Methylcyclohexene. The oxidation of methylcyclohexenes with $RhCl(PPh_3)_3$ was studied in order to determine whether the methyl substituent has any steric factor or directive influence on the site of the oxidation and, hence, the isomer composition.

1-Methylcyclohexene was oxidized under the same conditions as for cyclohexene. The gas chromatogram of the reaction mixture showed eight major compounds, six of which have been isolated by preparative gas chromatography and was identified by NMR and IR in comparison with those of authentic samples. Two unidentified products were obtained in less than 50% yield. The identified products were 1-methylcyclohexene oxide (VI, 1340%), 3-methyl-2-cyclohexen-1-one (VII, 1052%), 2-methyl-2-cyclohexen-1-one (VIII, 366%), 3-methyl-2-cyclohexen-1-ol (IX 90%), 1-methyl-2-cyclohexen-1-ol (X, 83%) and IV (799%).



This indicates that all possible allylic positions except for the methyl group were oxidized in the reaction.

The reaction paths for the formation of ketones and alcohols might be as presented in Scheme I, allylic hydrogen of olefin being abstracted by oxygen. The attack of oxygen at the less hindered site of allyl radical (1) results in the formation of major product VII through hydroperoxide.

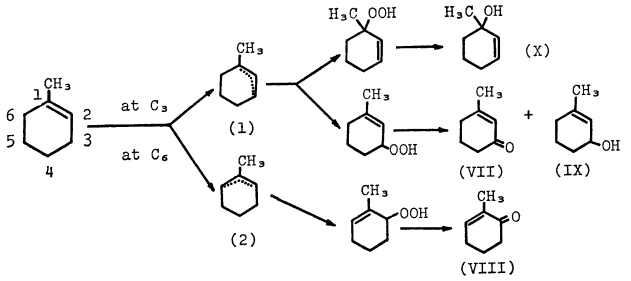
The total sum of yields of VII, IX, and X arising

8) James and Ochiai studied the oxidation of cyclooctene with a rhodium complex by infrared spectroscopy and reported on the mechanism in which both oxygen and olefin coordinated to rhodium.[9]

9) B. R. James and E. Ochiai, *Can. J. Chem.*, **49**, 975 (1971).

10) Recently, Minoun and his coworkers reported that expoxidation with molybdenum peroxy complex might proceed *via* the coordination of olefin to metal complex containing an aprotic 1,3-dipole mechanism.[11]

11) H. Mimoun, I. Seree de Roch, and L. Sajus, *Tetrahedron*, **26**, 37 (1970).

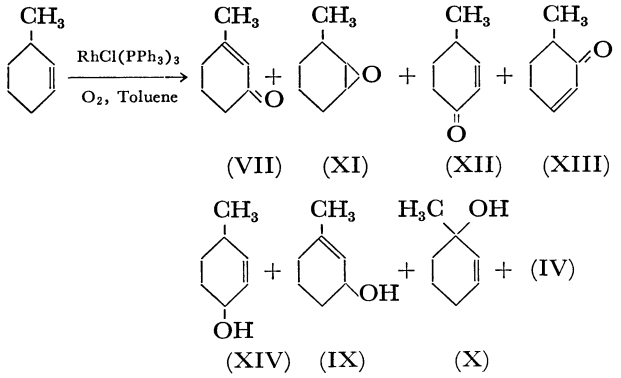


Scheme 1.

from hydrogen abstraction at C–3 was 1225%, whereas the yield of VIII from that at C–6 was 366%. Namely, hydrogen at C–3 is favorably abstracted over that at C–6 by a ratio of 3 : 1. This might be explained by the stabilization energy of the intermediate radical. The same tendency has been reported in the oxidation of methylcyclohexene using chromium trioxide in acetic acid and chromium trioxide–pyridine complex in methylene chloride (10 : 1 and 4 : 1 respectively).[12]

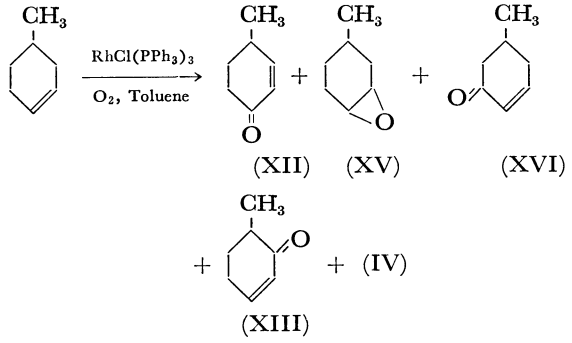
3-Methylcyclohexene and 4-methylcyclohexene were also oxidized with $RhCl(PPh_3)_3$ under the same reaction conditions as above. The product distribution of each reaction could be explained in a similar way to that for 1-methylcyclohexene.

Thus, 3-methylcyclohexene was oxidized to give VII (1372%), 3-methylcyclohexene oxide (XI, 391 %), 4-methyl-2-cyclohexen-1-one (XII, 384%), 6-methyl-2-cyclohexen-1-one (XIII, 232%), 4-methyl-2-cyclohexen-1-ol (XIV, 168%), IX (124%), X (98%), and IV (684%). These products were identified by comparison with authentic samples.

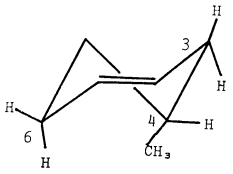


The main product VII could arise by oxygen attack at a less hindered site of the intermediate allyl radical.

Similarly, 4-methylcyclohexene was oxidized to give five products, XII (846%), 4-methylcyclohexene oxide (XV, 360%), 5-methyl-2-cyclohexen-1-one (XVI, 232%), XIII (115%), and IV (660%).



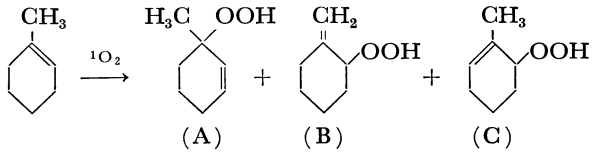
Hydrogen abstraction at C-3 yielding XII and XIII in 961% exceeds that at C-6 yielding XVI in 232% by a ratio of 4 : 1.



In all cases, ketones are formed in higher yields than the corresponding alcohol, though the decomposition of methylcyclohexene hydroperoxide by $RhCl(PPh_3)_3$ gave ketones and alcohols in nearly equivalent yields. Oxidation of alcohol IX did not afford the corresponding ketone XII in a good yield (6% yield based on the alcohol).

The yield of methylcyclohexene oxide increased as follows: 4-methyl < 3-methyl < 1-methylcyclohexene. This is in line with the increase of the electron density on carbon-carbon double bond.

It is known that singlet oxygen reacts with olefins bearing the allylic hydrogen to give hydroperoxides. The oxidation of 1-methylcyclohexene with singlet oxygen has been reported to give the following hydroperoxides.[13]



From the present result of 1-methylcyclohexene catalyzed by a rhodium complex, alcohol X and ketone VIII would be derived from the hydroperoxide of type A and type C, respectively. However, no ketone and alcohol arising from type B hydroperoxide could be observed. The formation of ketone VII, the major product of the present reaction, has not been detected among the products of oxidation reaction using singlet oxygen. This seems to be due to the fact that in cyclohexene oxidation, the oxygen molecule coordinated to a rhodium complex has few of the singlet oxygen character, if any.

Experimental

Materials and Analysis. All temperatures were uncorrected. The IR spectra were recorded on a JASCO IR-E spectrometer. The NMR spectra were measured on a Japan Electron Optics JNM-4H-100 spectrometer. Chemical shifts are given in τ units together with splitting patterns and relative integrated area. Vpc analysis was carried out with a Yanagimoto G-8 gas chromatograph using Chro-

12) a) F. C. Whitemore and G. W. Pedlow, Jr., *J. Amer. Chem. Soc.*, **63**, 758 (1941). b) W. G. Dauben, M. Lorber, and D. S. Fullerton, *J. Org. Chem.*, **34**, 3587 (1969).

13) K. Gollnick "Oxidation of Organic Compounds," Vol. III, ed. by F. R. Mayo, Amer. Chem. Soc., Washington, D. C. (1968), p. 91.

mosorb-W and Carbowax-20M columns. The gas chromatographic method was employed for both qualitative and quantitative determination of the reaction products. Cyclohexene hydroperoxide was decomposed in vpc to give nearly equal quantities of ketones and alcohols but no epoxides. The yields of ketones and alcohols should therefore be corrected according to the decomposition of hydroperoxides. However, no such correction was carried out since the content of hydroperoxide was low after 8 hr. The active oxygen in the reaction mixture was determined by the iodometric method.[14] Cyclohexene was prepared by the dehydration of cyclohexanol with phosphoric acid. Bp 82.7 °C (lit,[15] 82.7 °C). 1-Methylcyclohexene was prepared by treatment of cyclohexanone with methylmagnesium iodide followed by dehydration with anhydrous aluminum sulfate. bp 34.3 °C/38 mmHg (lit,[16] 110 °C/760 mmHg). 3-Methylcyclohexene was prepared by treatment of bromocyclohexene with methyl iodide. Bp 42.0 °C/97 mmHg (lit,[17] 104 °C/760 mmHg). 4-Methylcyclohexene was of commercial grade. All cyclohexenes used were subjected to repeated washing with ferrous sulfate solution containing sulfuric acid to eliminate the peroxides, separation and drying of the organic phase over anhydrous magnesium sulfate and distillation under nitrogen atmosphere before use. Absence of peroxides after the treatment was verified by vpc analysis. Cyclohexene hydroperoxide was prepared by treatment of cyclohexene with ABN under an oxygen atmosphere; bp 53—56 °C/0.6 mm Hg (lit,[18] 42—45 °C/0.5 mmHg). The peroxide content was 85%.

1-Methylcyclohexene 3-hydroperoxide was prepared from 1-methylcyclohexene in a manner similar to that for cyclohexene hydroperoxide; bp 42.5—46.2 °C/0.008 mmHg (lit,[19] 64—67 C°/0.2 mmHg). The peroxide content was 87%. Analysis by NMR indicated a mixture of 1-methylcyclohexene 3-hydroperoxide, 1-methylcyclohexene 6-hydroperoxide, and 3-methylcyclohexene 1-hydropreoxide. *t*-Butyl hydroperoxide was prepared by treatment of *t*-butanol with hydrogen peroxide in sulfuric acid solution; bp 34.5—36.0 °C/17 mmHg (lit,[20] 4.5—5.0 °C/2 mmHg). The peroxide content was 92%. Toluene was purified as mentioned previously.[4] $RhCl(PPh_3)_3$ was prepared by the method of Osborn *et al.*[21]

Oxidation of Cyclohexene. In a flask similar to that described previously[4] was charged a mixture of 0.463 g (0.500 mmol) of $RhCl(PPh_3)_3$ and 4.11 g (50 mmol) of cyclohexene and 75 ml of toluene as solvent under nitrogen atmosphere. The oxidation reaction was carried out at 80 °C with a constant bubbling of oxygen for 8 hr. A portion of the reaction solution was analyzed at an appropriate interval by the iodometric method and vpc. After work-up, brown solids deposited at the bottom of the flask. The resulting mixture was filtered to remove the brown precipitates (120 mg). In a separative experiment, the purified complex was not the active catalyst for oxidation of cyclohexene. The properties of the complex were as follows: mp 260—270 °C (decomp.), IR(nujol): 3360—3280, 1000, 762, 730, and 705 cm^{-1}. Found: C, 45.38; H, 3.95; Cl, 7.67%. Calcd for $RhCl_{0.7}(PPh_3)_{0.7}(H_2O)_{1.5}$: C, 44.66; H, 4.00; Cl, 7.64%. The filtrate was concentrated and the liquid phase was isolated and analyzed by vpc to give 738 mg (1530%) of I, 418 mg (852 %) of II, 173 mg (351%) of III, 277 mg (524%) of IV, and water. These compounds were identified by comparison with authentic samples. Compound I: IR(neat): 2940—2860, 1675—1650, 1458, 1430, 1397, 1243, 1210, 1128, 947, 888, 770, and 740 cm^{-1}; NMR (CCl_4): 3.10 (m, 1H, olefinic), 4.13 (m, 1H, olefinic), and 7.4—8.1 τ (m, 6H methylene). Compound II: IR(neat): 3400—3280, 2940—2860, 1650, 1440, 1275, 1182, 1068, 1048, 1007, 962, and 735 cm^{-1}; NMR(CCl_4): 4.35 (m, olefinic), 5.98 (m, 1H, methine), 8.10 (s, 1H, hydroxyl), and 7.9—8.5 τ (m, 6H, methylene). Compound III: IR (neat): 3000—2870, 1444, 1260, 972, 900, 885, 850, and 790 cm^{-1}; NMR(CCl_4): 7.06 (m, 2H, methine), 8.0—8.3 (m, 4H, methylene), and 8.5—8.9 (m, 4H, methylene). Compound IV: IR (neat): 3040, 1703, 1603, 1313, 1210, 1170, 840, 757, and 700 cm^{-1}; NMR(C_6D_6): −0.02 (s, 1H, formyl) and 2.3—3.1 τ (m, 5H, phenyl) The solid material was chromatographed on a silica gel column (50 g). Elution of ether (300 ml) gave triphenylphosphine oxide (235 mg).

Oxidation of 1-Methylcyclohexene. The same procedure as for cyclohexene was used. A solution of 0.463 g (0.500 mmol) of $RhCl(PPh_3)_3$, 4.81 g (50 mmol) of 1-methylcyclohexene and 75 ml of toluene was heated at 80 °C for 8 hr with a constant bubbling of oxygen. Reaction products were 750 mg (1340%) of VI, 579 mg (1052%) of VII, 202 mg (366%) of VIII, 50 mg (90%) of IX, 46 mg (83%) of X, and 413 mg (779%) of IV. These compounds were identified by comparison with authentic samples. Compound VI: IR(neat): 2960—2870, 1440, 1385, 1220, 1188, 1124, 1032, 918, 845, and 770 cm^{-1}; NMR(CCl_4): 7.24 (t, 1H, methine), 8.1—8.4 (m, 4H, methylene), 8.6—8.8 (m, 4H, methylene), and 8.77 τ (s, 3H, methyl). Compound VII: IR(neat): 2940—2880, 1670—1655, 1438, 1250, 1200, 970, 890, and 768 cm^{-1}; NMR(CCl_4): 4.27 (m, 1H, olefinic), 7.6—8.1 (m, 6H, methylene), and 8.02 τ (s, 3H, methyl). Compound VIII: IR(neat): 2940—2880, 1676—1657, 1456, 1364, 1178, 1108, 1020, 904, 885, and 809 cm^{-1}; NMR(CCl_4): 3.37 (m, 1H, olefinic), 7.5—8.1 (m, 6H, methylene), and 8.28 τ (s, 3H, methyl). Compound IX: IR(neat): 3360—3280, 2950—2880, 1677—1653, 1443, 1280, 1171, 1080, 1063, 1039, 964, 911, 827, 784, and 716 cm^{-1}; NMR(CCl_4): 4.58 (m, 1H, olefinic), 6.14 (m, 1H, methine), 8.49 (s, 1H, hydroxyl), 8.1—8.4 (m, 6H, methylene), and 8.28 τ (s, 3H, methyl). Compound X: IR(neat): 3400—3000, 2940—2880, 1702, 1650, 1460, 1180, 1130, 1020, 910, and 740 cm^{-1}; NMR(CCl_4): 4.45 (m, 2H, olefinic), 8.0—8.5 (m, 6H, methylene), 8.83 (s, 3H, methyl), and 8.95 τ (s, 1H, hydroxyl).

Oxidation of 3-Methylcyclohexene. The same procedure as above was used. A solution of 0.463 g (0.500 mmol) of $RhCl(PPh_3)_3$, 4.81 g (50 mmol) of 3-methylcyclohexene and 75 ml of toluene was heated at 80 °C for 8 hr with a constant bubbling of oxygen. Reaction products were 755 mg (1372%) of VII, 220 mg (391%) of XI, 212 mg (384%) of XII, 128 mg (232%) of XIII, 94 mg (168%) of XIV, 70 mg (124%) of IX, 55 mg (98%) of X, and 363 mg (684%) of IV. These compounds were identified by comparison with authentic samples. Compound XI: IR (neat): 3000—2880, 1455, 1386, 1255, 1004, 920, 879, 830, and 771

14) L. W. Fine, M. Grayson, and V. H. Suggs, *J. Organometal Chem.*, **22**, 219 (1970).
15) E. P. Carr, and H. Stücklen, *J. Amer. Chem. Soc.*, **59**, 2138 (1937).
16) F. K. Signaigo and P. L. Cramer, *ibid.*, **55**, 3326 (1933).
17) A. Berlande, *C. R. Acad. Sci., Paris*, **213**, 437 (1941).
18) L. H. Gale, D. C. Olson, and J. Vasilevskis, *J. Catal.*, **24**, 549 (1972).
19) E. H. Former and A. Sundralingam, *J. Chem. Soc.*, **1942**, 121.
20) N. A. Milas and D. M. Surgenor, *J. Amer. Chem. Soc.*, **68** 205 (1946).
21) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson *J. Chem. Soc., A*, **1966**, 1711.

cm^{-1}; NMR (CCl_4): 7.05 (m, 1H, methine), 7.38 (d, 1H, methine), 8.0—8.8 (m, 7H, methylene), and 8.98 τ (d, 3H, methyl). Compound XII: IR(neat): 2940—2860, 1685—1652, 1458, 1250, 1200, 1095, 835, 811, and 759 cm^{-1}; NMR (CCl_4): 3.36 (m, 1H, olefinic), 4.20 (m, 1H, olefinic), 7.5—8.1 (m, 5H, methylene and methine), and 8.84 τ (d, 3H, methyl). Compound XIII: IR(neat): 2930—2860, 1675—1650, 1457, 1134, 892, 810, and 711 cm^{-1}; NMR(CCl_4): 3.20 (m, 1H, olefinic), 4.12 (m, 1H, olefinic), 7.5—8.2 (m, 5H, methine and methylene), and 8.91 τ (d, 3H, methyl). Compound XIV: IR(neat): 3360—3280, 2940—2880, 1700, 1650, 1457, 1280, 1110, 1060, 1029, 855, and 743 cm^{-1}; NMR (CCl_4): 4.48 (s, 2H, olefinic), 5.93 (m, 1H, methine), 7.27 (s, 1H, hydroxyl), 7.8—8.9 (m, 5H, methine and methylene), and 9.03 τ (d, 3H, methyl).

Oxidation of 4-Methylcyclohexene. The same procedure as above was used. A solution of 0.463 g (0.500 mol) of $RhCl(PPh_3)_3$, 4.81 g (50 mmol) of 4-methylcyclohexene and 75 ml of toluene was heated at 80 °C for 8 hr with a constant bubbling of oxygen. Reaction products were 476 mg (846%) of XII, 202 mg (360%) of XV, 128 mg (232%) of XVI, 64 mg (115%) of XIII, 350 mg (660%) of IV. These compounds were identified by comparison with authentic samples. Compound XV: IR(neat): 2960—2870, 1440, 1259, 1153, 1010, 970, 818, 792, and 770 cm^{-1}; NMR(CCl_4): 7.05 (m, 2H, methine), 7.8—8.9 (m, 7H, methylene and methine), and 9.14 τ (d, 3H, methyl). Compound XVI: IR(neat): 2950—2880, 1684—1652, 1458, 1393, 1273, 1240, 1187, 884, and 742 cm^{-1}; NMR (CCl_4): 3.17 (m, 1H, olefinic), 4.10 (m, 1H, olefinic), 7.6—8.1 (m, 5H, methylene and methine), and 8.91 τ (d, 3H, methyl).

Autoxidation of 1-Methylcyclohexene with ABN as Initiator. A mixture of 4.81 g (50 mmol) of 1-methylcyclohexene, 0.041 g (0.250 mmol) of ABN, and 75 ml of toluene was heated at 80 °C for 8 hr under a constant bubbling of oxygen. The reaction solution was analyzed by vpc to give 263 mg of VII, 129 mg of 2-methyl-2-cyclohexen-1-ol (XVII), 127 mg of IX, 109 mg of VI, 100 mg of VIII, 32 mg of X, and trace of IV. Compound XVII: IR (neat): 3400—3300, 2950—2880, 1660, 1445, 1275, 1160, 1057, 990, 952, 919, 868, and 816 cm^{-1}; NMR(CCl_4): 4.60 (m, 1H, olefinic), 6.15 (m, 1H, methine), 6.80 (m, 1H, hydroxyl), 7.9—8.4 (m, 6H, methylene), and 8.30 τ (s, 3H, methyl).

Oxidation of 3-Methyl-2-cylcohexen-1-ol (IX). A solution of 0.463 g (0.500 mmol) of $RhCl(PPh_3)_3$, 2.80 g (25 mmol) of IX, and 75 ml of toluene was treated in a manner similar to that for cyclohexene oxidation. After 8 hr, the reaction product was 0.174 g (1.58 mmol) of VII.

Decomposition of V catalyzed by $RhCl(PPh_3)_3$. A mixture of 0.463 g (0.500 mmol) of $RhCl(PPh_3)_3$, 1.00 g of V and 75 ml of toluene was heated at 80 °C with a constant bubbling of argon. A portion of the reaction solution was analyzed at an appropriate interval, by the iodometric method. Decomposition of V was complete in 2 hr. After 2 hr, the solution was analyzed by vpc to give 462 mg of I and 399 mg of II. Decomposition of the mixture of three isomers of methylcyclohexene hydroperoxides (1.33 g) was complete in 1 hr to give 269 mg of IX, 214 mg of VII, 186 mg of XV, 140 mg of X, and 138 mg of VIII.

Oxygen Transfer Reaction of Cyclohexene Hydroperoxide and Cyclohexene. A mixture containing 0.463 g (0.500 mmol) of $RhCl(PPh_3)_3$, 1.34 g of V, 0.821 g (10 mmol) of cyclohexene, and 75 ml of toluene was heated at 80 °C with a constant bubbling of argon. A portion of the reaction solution was analyzed at an appropriate interval by the iodometric method. Decomposition of V was complete in 2 hr. After 8 hr, the solution was analyzed by vpc to give 475 mg of I and 504 mg of II. Oxygen transfer reaction of *t*-butyl hydroperoxide and cyclohexene gave only the hydroperoxide decomposition products.