1.9 g of trityl chloride for 12 hr. The trityl ether **22** (2.1 g, 84%), which was isolated in the manner previously described[1] for **20**, crystallized from ethanol as colorless prisms: mp 104–105°; pmr δ 4.66 (m, 1, exocyclic olefinic proton), 4.49 (m, 1, exocyclic olefinic proton), 3.10 (m, 2, C_{11} methylene), 0.94 (s, 3, C_1 methyl), 0.73 (d, $J = 6.5$ Hz, 3, C_9 methyl). *Anal.* Calcd for $C_{33}H_{38}O$: C, 87.95; H, 8.50. Found: C, 88.09; H, 8.50.

Preparation of Ketone 25.—To a solution of 4.9 g of the trityl ether **22** in 450 ml of purified dioxane and 150 ml of water was added 0.19 g of osmium tetroxide; the solution rapidly became dark brown. Finely powdered sodium metaperiodate (26 g) was added to the stirred solution over a period of 30 min and a flocculent precipitate of sodium iodate soon appeared. The mixture was stirred at 20° for an additional 22.5 hr, after which time the dark brown color of the solution had faded to a light yellow. The reaction mixture was poured into water and extracted with ether. The extract was washed with water and dried over anhydrous sodium sulfate, and the solvent was evaporated. The crude product was purified by chromatography on 240 g of neutral activity I alumina. Elution with benzene yielded 3.45 g (75%) of the ketone **25**, which crystallized from ethyl acetate as colorless prisms: mp 176°; ir 1720 cm^{-1} (ketone); pmr δ 3.11 (m, 2, C_{11} methylene), 1.06 (s, 3, C_1 methyl), 0.73 (d, $J = 6.5$ Hz, 3, C_9 methyl). *Anal.* Calcd for $C_{32}H_{36}O_2$: C, 84.91; H, 8.02. Found: C, 84.72; H, 7.80.

Preparation of Alcohol 26a.—A solution of 0.89 g of the ketone **25** in 30 ml of 1,2-dimethoxyethane was alkylated using potassium triphenylmethide[19] and methyl iodide (4 ml) in the manner described[1] for the ketone **6**. The trityl ether **26b** was not isolated, but the crude product was dissolved in 250 ml of ethanol and hydrogenated (2.5 atm) with 0.5 g of 5% palladium on charcoal at 20° for 14 hr. After removal of the catalyst by filtration and evaporation of ethanol, the product was purified by chromatography on 150 g of neutral activity I alumina. Elution with hexane and hexane–ether (9:1) yielded triphenylmethane, while 0.35 g (80%) of the alcohol **26a** was eluted with hexane–ether (1:1). Vpc analysis showed a single peak on 3% SE-30 at 160°: ir 3630 and 3450 (OH), 1715 cm^{-1} (ketone); pmr δ 3.56 (m, 2, C_{11} methylene), 3.37 (br s, 1, OH), 2.46 (br q, $J = 7$ Hz, 1, H_2), 0.99 (d, $J = 7$ Hz, 3, C_2 methyl), 0.98 (s, 3, C_1 methyl), 0.93 (d, $J = 6.5$ Hz, 3, C_9 methyl). The analytical sample was obtained by microdistillation, bp 114° (0.04 mm). *Anal.* Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.30; H, 10.99.

Preparation of Chloride 26d.—A mixture of 0.14 g of the alcohol **26a** and 0.17 g of *p*-toluenesulfonyl chloride in 5 ml of pyridine was left at 20° for 42 hr. Water (0.15 ml) was then added and the mixture was left for a further 6 hr at 20°, after which it was poured into excess dilute hydrochloric acid at 0° and extracted with hexane. The hexane extract was washed with dilute aqueous sodium carbonate and water, and then dried over anhydrous sodium sulfate. Evaporation of solvent yielded 0.11 g of a colorless oil, identified as the chloride **26d**: pmr δ 3.55 (m, 2, C_{11} methylene), 1.00 (d, $J = 7$ Hz, 3, C_2 methyl), 0.99 (s, 3, C_1 methyl), 0.97 (d, $J = 6.5$ Hz, 3, C_9 methyl). The ir spectrum showed no hydroxyl absorption.

Preparation of Tosylate 26c.—A mixture of 0.10 g of the alcohol **26a** and 0.23 g of *p*-toluenesulfonyl chloride in 3 ml of cold pyridine was left at −15° for 12 hr, and water (0.15 ml) was then added. The reaction mixture was left for a further 45 min at −15°, after which it was poured into excess dilute hydrochloric acid at 0° and extracted with hexane. The extract was washed with dilute aqueous sodium carbonate and water and dried over anhydrous sodium sulfate, and the solvent was evaporated to yield 0.16 g (93%) of the crude tosylate **26c** which crystallized from benzene–hexane as colorless prisms: mp 91–93°; ir 1715 cm^{-1} (ketone); pmr δ 4.02 (m, 2, C_{11} methylene), 2.46 (s, 3, aromatic methyl), 0.93 (d, $J = 7$ Hz, 3, C_2 methyl), 0.89 (s, 3, C_1 methyl), 0.85 (d, $J = 6.5$ Hz, 3, C_9 methyl). *Anal.* Calcd for $C_{21}H_{30}O_4S$: C, 66.64 H, 7.99 S, 8.46. Found: C, 66.98; H, 8.12; S, 8.20.

Cyclization of Tosylate 26c.—Potassium triphenylmethide solution[19] was added dropwise with a syringe to 80 mg of the tosylate in 3 ml of 1,2-dimethoxyethane. An immediate white precipitate of potassium tosylate was observed at 20°. The base was added until the red color of the triphenylmethide ion just persisted. The reaction mixture was left at 20° for 1.5 hr and then poured into water. Extraction with hexane followed by evaporation of the dried extracts yielded a crude product which was purified by chromatography on a small column of 10 g of neutral activity I alumina. Elution with hexane and hexane–benzene (9:1) gave triphenylmethane, while 35 mg (80%) of norseychellanone **5** was eluted with hexane–benzene (1:1). Vpc analysis (5% Ucon) showed the product to be homogeneous. The pmr, ir, and mass spectra of this compound were identical with the spectra[20] of authentic norseychellanone: ir (liquid film) 1715 cm^{-1} (ketone); pmr ($CDCl_3$) δ 0.97 (s, 3, tertiary methyl), 0.94 (s, 3, tertiary methyl), 0.79 (d, $J = 6.5$ Hz,[21] 3, secondary methyl).

Cyclization of Chloride 26d.—Potassium triphenylmethide solution was added with a syringe to 50 mg of the chloride in 2 ml of 1,2-dimethoxyethane until the red color of the triphenylmethide ion just persisted. The sealed flask was heated at 80–90° for 1.5 hr and by this time precipitation of potassium chloride was complete. The reaction mixture was then poured into water and the cyclic ketone norseychellanone (30 mg, 70%) was isolated as above.

Registry No.—(±)-**1**, 24568-69-2; (±)-**2**, 29450-72-4; (±)-**5**, 24461-21-0; **8**, 34993-78-7; **9**, 34993-79-8; **12**, 34996-50-4; (±)-**13**, 29448-19-9; **14**, 34996-52-6; **18**, 34996-53-7; (±)-**21**, 34996-54-8; (±)-**22**, 29448-16-6; (±)-**25**, 29448-15-5; (±)-**26a**, 29448-22-4; (±)-**26c**, 29448-23-5; (±)-**26d**, 34996-59-3.

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(19) H. O. House and V. Kramar, *J. Org. Chem.*, **27**, 4146 (1962).

(20) Copies of spectra were very kindly forwarded by Professor Ourisson.

(21) This coupling constant was incorrectly reported[4] as 5.5 Hz.

The Oxidation of Tetramethylethylene in the Presence of Rhodium(I) and Iridium(I) Complexes

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The oxidation of tetramethylethylene (TME) was studied in the presence of the oxygen-carrying complexes *trans*-MCl(CO)(Ph_3P)$_2$ (M = Rh, Ir). The oxidation was found to be rapid and quite selective under mild conditions, yielding 2,3-dimethyl-2,3-epoxybutane and 2,3-dimethyl-3-hydroxybutene-1 as the major oxidation products. The reactions are inhibited by hydroquinone, which is consistent with a free radical initiated autoxidation. The reaction of TME with oxygen was far more rapid than was oxidation of less substituted olefins in the presence of the Rh(I) and Ir(I) complexes, suggesting that initial coordinative interaction between the olefin and the metal center is not an important factor. A mechanistic pathway involving an allylic hydroperoxide intermediate is proposed.

Current interest in the oxidation of olefins in the presence of hydrocarbon-soluble, oxygen-carrying transition metal complexes has been stimulated by the possibility of novel oxidation pathways in these systems. The results of recent studies concerning the role of transition metal complexes in the oxidation of olefinic

TABLE I

THE OXIDATION OF TETRAMETHYLETHYLENE[a] IN THE PRESENCE OF $MCl(CO)(Ph_3P)_2$ (M = Rh, Ir)

Metal complex	Radical inhibitor	Yield of products, %[b] I	II	III	Acetone	Unreacted TME, %[c]
None[d]	None	2	0.5	2		92
$RhCl(CO)(Ph_3P)_2$	None	25	22	11	4	34
$RhCl(CO)(Ph_3P)_2$	HQ[e]	3	5	2	0.5	88
$IrCl(CO)(Ph_3P)_2$	None	19	15	11	3	47
$IrCl(CO)(Ph_3P)_2$	HQ[e]	3	3	1	0.3	92

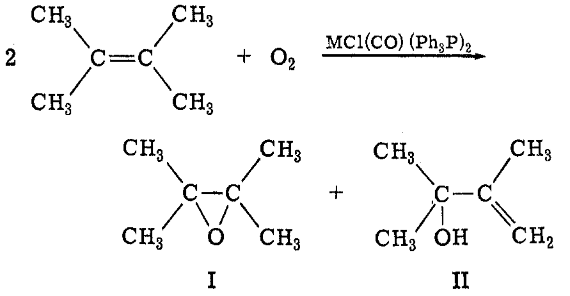
[a] Oxygen bubbled through 12 ml of TME containing 8×10^{-5} mol metal complex for 4 hr at 50°. [b] Conversions, mol %, of TME to the indicated products. [c] Unidentified high-boiling by-products were also formed in 2–5% yield. [d] Reaction run in the presence of 4×10^{-4} mol of azobisisobutyronitrile. [e] Hydroquinone present in 3.3 mol %.

hydrocarbons have been interpreted in two different ways. There is evidence which suggests[1,2] that the oxidation of cyclohexene using iridium(I) and rhodium(I) phosphine complexes, first reported by Collman,[3] proceeds *via* a radical pathway similar to autoxidation in the presence of metal salts.[4] Takao, *et al.*,[5,6] have investigated the oxidation of styrene in the presence of iridium(I) and rhodium(I), but these authors suggest that the observed catalytic activity is due to coordination of molecular oxygen by the metal center causing an increased oxygen–oxygen bond length and enhanced reactivity with olefin in the coordination sphere of the metal. James and Ochiai[7] have proposed a mechanism for the oxidation of a cyclooctene–rhodium(I) complex which involves oxygen activation and transfer to the olefin. These authors suggest that this mechanism may be operative in the oxidation of cyclohexene in the presence of Rh(I) and Ir(I).

We have studied the oxidation of tetramethylethylene in the presence of the metal complexes *trans*-$MCl(CO)(Ph_3P)_2$ (M = Rh,[8] Ir[9]) and have compared the results with autoxidation using a free-radical initiator. Tetramethylethylene was found to be an excellent model compound for study since it was rapidly and selectively oxidized at low temperatures in the presence of these metal complexes. In contrast to the oxidation of cyclohexene,[2] little polymerization occurred during the oxidation of TME in the presence of the rhodium(I) and iridium(I) complexes.

Results and Discussion

The oxidation of tetramethylethylene (TME) in the presence of $MCl(CO)(Ph_3P)_2$ (M = Rh, Ir) at 50° gives two major reaction products: 2,3-dimethyl-2,3-epoxybutane (I) and 2,3-dimethyl-3-hydroxybutene-1 (II) (eq 1). Acetone and small amounts of high molecular weight by-products are also formed. The reaction mixtures are completely homogeneous throughout with no observable deposits of insoluble materials. Little oxidation of TME occurs under the same conditions in the absence of the metal complexes, but low yields of I and II are obtained in the presence of a radical source.[10] Reactions are severely inhibited by hydroquinone (3.3 mol %). The results are summarized in Table I.



(1)

In an attempt to explain the formation of II, we have shown that the epoxide I does not rearrange to form II under reaction conditions in the presence of the metal complexes. Furthermore, II is not formed from 2,3-dimethylbutene-1 in detectable amounts under the reaction conditions, thus eliminating the possibility of isomerization of TME to 2,3-dimethylbutene-1 followed by allylic oxidation. Despite the fact that the rhodium(I) and iridium(I) complexes are catalysts for olefin isomerization when used in an inert atmosphere,[11,12] little or no isomerization occurs under oxidation conditions.

We were able to observe the formation of 2,3-dimethyl-3-hydroperoxybutene-1 (III) in as much as 10% yield during the course of the oxidation of TME in the presence of $RhCl(CO)(Ph_3P)_2$ and $IrCl(CO)(Ph_3P)_2$. We have also shown that these complexes are capable of catalytically decomposing *tert*-butyl hydroperoxide in toluene solution with liberation of oxygen and formation of *tert*-butyl alcohol at room temperature (Table II). However, when the $MCl(CO)(Ph_3P)_2$-catalyzed reaction of *tert*-butyl hydroperoxide was carried out in TME rather than in toluene, little or no oxygen was liberated and the products were I and *tert*-butyl alcohol (eq 2, Table II). No observable epoxidation of TME occurred under similar conditions in the absence of the catalyst. Therefore, it is reasonable to suggest that the allylic hydroperoxide III formed during the reaction of TME with oxygen reacts with TME to give I and II in the presence of the metal complexes (eq 3).

James and Ochiai have cited spectral evidence for hydroperoxide intermediates, and Fusi, *et al.*,[2] invoked the intermediacy of an allylic hydroperoxide in explaining the oxidation of cyclohexene in the presence of

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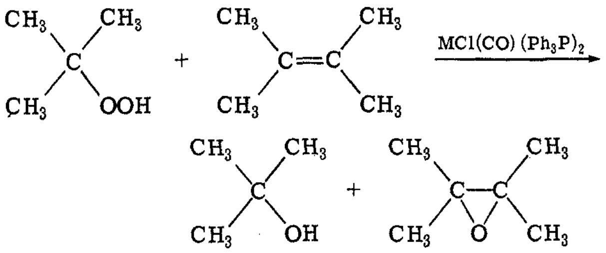


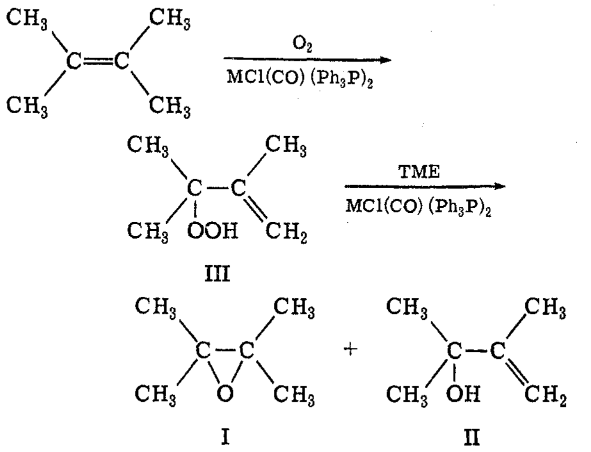
(2)

TABLE II

REACTIONS OF *tert*-BUTYL HYDROPEROXIDE IN THE PRESENCE OF $MCl(CO)(Ph_3P)_2$[a] (M = Rh, Ir)

		Yield of products, %[b]		Unreacted *tert*-butyl hydroperoxide, %
Metal complex	Medium	*tert*-Butyl alcohol	I	
$RhCl(CO)(Ph_3P)_2$	Toluene	14		85
$RhCl(CO)(Ph_3P)_2$	TME	25	26	71
$IrCl(CO)(Ph_3P)_2$	Toluene	46		53
$IrCl(CO)(Ph_3P)_2$	TME	59	42	34

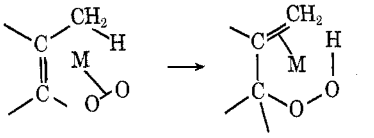
[a] *tert*-Butyl hydroperoxide (1 g) was added dropwise over 5 min to 0.08 mmol of the complex in 10 g of TME or toluene at 25° and the mixture was stirred for a total of 1 hr. [b] Conversions, mol %, based on *tert*-butyl hydroperoxide.



(3)

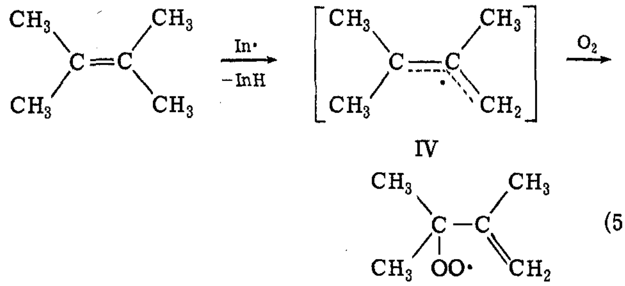
metal complexes, although hydroperoxides were not isolated from their reaction mixtures. Fusi, *et al.*,[2] showed further that such a hydroperoxide was decomposed in the presence of several metal complexes. Our results show that the metal-catalyzed reactions of *tert*-butyl hydroperoxide in the presence of TME follow a different course than in the absence of the olefin. When $RhCl(CO)(Ph_3P)_2$ is used, reaction occurs according to eq 2, although, with the iridium analog, some decomposition to oxygen and alcohol occurs simultaneously (Table II). Thus, *the Rh(I) and Ir(I) complexes are efficient catalysts for epoxidation of TME with an alkyl hydroperoxide.*[13]

Since the product of the reaction of TME with singlet oxygen is III,[14] we considered the possibility that we had generated singlet oxygen *in situ* during the course of this reaction. Fusi, *et al.*, however, failed to find evidence of singlet oxygen during the oxidation of cyclohexene in the presence of iridium(I) and rhodium(I) complexes. Similar experiments in our laboratories have also failed to detect singlet oxygen[15] when O_2 is liberated from the metal complex. Since the adducts formed from reaction of d^8 and d^{10} group VIII metal complexes with molecular oxygen are generally diamagnetic,[16] formation of III by an "ene" reaction[17] between coordinated oxygen and olefin (eq 4) cannot be



(4)

disregarded. If a metal-catalyzed "ene" reaction (eq 4) were the pathway for the formation of III, the rate of reaction would be expected to parallel the coordinative ability of the olefin, as is found in many other metal-catalyzed reactions (hydrogenation,[18] hydroformylation,[19] isomerization,[12] etc.). Contrary to what would be expected of a coordinative mechanism, we have found that the relative rates of olefin oxidation using $MCl(CO)(Ph_3P)_2$ are just the reverse of this. The ease of the olefin oxidations *increases* with the degree of substitution: TME > 2-methyl-2-pentene > *cis*-2-hexene ≫ hexene-1. This holds true for *both* the hydroperoxide formation *and* the epoxidation steps. When TME is oxidized at 50° in the presence of $RhCl(CO)(Ph_3P)_2$, the total hydroperoxide content as determined titrimetrically was nearly 11% after 4 hr, while less than 1% hydroperoxide was detected in hexene-1 oxidation under the same conditions. Similarly, we have found that TME is epoxidized much faster than hexene-1 in the presence of the rhodium(I) and iridium(I) complexes. Furthermore, the tertiary allylic hydroperoxide III has been shown to be the product of radical-initiated oxidation due to the greater electron density at the tertiary carbon of the initial intermediate IV of a radical pathway (eq 5).[20] The observation



(5)

that hydroquinone inhibits oxidation of TME by the Rh(I) and Ir(I) complexes (Table I) supports the existence of a radical chain mechanism for the formation of the allylic hydroperoxide. Our data do not enable us to distinguish between initiation by the metal center and initiation by radical species present due to metal-catalyzed decomposition of trace impurities.[21] Our results, however, are consistent with the existence of a mechanistic pathway in which the initial step is ini-

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[13] It has been shown that several group Vb and VIb complexes catalyze the epoxidation of olefins by hydroperoxides: (a) N. Indictor and W. F. Brill, *J. Org. Chem.*, **30**, 2074 (1965); (b) N. N. Sheng and J. G. Zajacek, *Advan. Chem. Ser.*, **76**, 418 (1968).

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tiated autoxidation of the olefin to form an allylic hydroperoxide and a subsequent epoxidation step which is catalyzed by the metal complexes.

Experimental Section

Infrared spectra were determined using Perkin-Elmer infrared spectrophotometers Models 137-B and 21. Nmr spectra were run using Varian T-60 and A-60 spectrometers. Gas chromatographic analyses were carried out on a Hewlett-Packard Model 5750B instrument. Fractional distillations were performed on a Nester-Faust 18-in. semimicro spinning band column equipped with a stainless steel band.

Materials.—Olefinic hydrocarbons of at least 99% purity were obtained from Chemical Samples Co., distilled under nitrogen, and then passed through freshly activated silica gel under nitrogen prior to use. The complexes $RhCl(CO)(Ph_3P)_2$ and $IrCl(CO)(Ph_3P)_2$ were obtained from Strem Chemical Co. *tert*-Butyl hydroperoxide (92% by titration) was purchased from Lucidol. Oxygen cylinders were obtained from Linde Air Products Co.

Oxidation of TME Using $MCl(CO)(Ph_3P)_2$ (M = Rh, Ir) as Catalyst.—Oxygen was bubbled (1.5 l./hr) through 12.0 ml of TME containing 8×10^{-5} mol of metal complex for 4 hr at 50°. The Rh(I) complex slowly dissolved to give a bright yellow solution, whereas the Ir(I) gave a clear green solution. Liquid was returned to the reaction flask by an efficient micro Dry Ice condenser. A small amount of liquid (~0.5 ml) was carried by the gas stream into a −78° trap, and was returned to the reaction flask at the conclusion of the run. After 4 hr the volatile reaction products were immediately flash evaporated away from the catalyst and 0.3–0.5 g of a viscous liquid which did not distil by gentle warming at 0.01 mm. The vacuum-transferred reaction mixture was then analyzed by glpc using a 6 ft × 0.125 in. column packed with 10% silicone UC-W98 on 80–100 mesh Chromosorb W (Hewlett-Packard) and an injection port temperature under 200°. It was established using pure standards that little or no decomposition of reaction products occurred during glpc analysis of product mixtures. I and II were unaffected by column conditions while a small amount of decomposition of III occurred in the injection port. For this reason III was also analyzed titrimetrically (iodometric method[22]) and results agreed to within ±1% of the glpc value. Compounds I, bp 90.5°, n^{20}_D 1.4014 (lit.[23] n^{20}_D 1.4010), >99.5% glpc purity, and II, bp 117°, n^{20}_D 1.4316 (lit.[23] n^{20}_D 1.4312), >99% glpc purity, were obtained by spinning band distillation of a run ten times the size of those reported above and were identified by comparison of their ir, nmr, and mass spectra with those of authentic samples. Pure III, n^{20}_D 1.4432 (lit.[14] n^{20}_D 1.4428), was obtained by preparative glpc and identified by comparison of ir and nmr spectra with those of an authentic sample. Spectral data for I, II, and III were identical with that reported in the literature.[23,24] When the reaction was run under conditions identical with those given above in the *absence* of a metal complex or an initiator, less than a 2% yield of oxidation products was observed (glpc) after 4 hr.

Inhibition by Hydroquinone.—Reactions were carried out under conditions identical with the above in TME which contained 3.3 mol % hydroquinone.

Effect of the Catalyst and Reaction Conditions on Isomerization of TME, I, and II during Oxidation.—Less than 0.5% isomerization of TME to 2,3-dimethylbutene 1 occurred during oxidation (glpc analysis).

When O_2 was bubbled through 12 ml of I at 50° for 4 hr in the presence of 8×10^{-5} mol of either $RhCl(CO)(Ph_3P)_2$ or $IrCl(CO)(Ph_3P)_2$ no change was noted (glpc) and I was recovered in 98% yield.

When O_2 was bubbled through a solution of 1 g of II in 5 ml of benzene for 3 hr at 50° in the presence of 8×10^{-5} mol of $RhCl(CO)(Ph_3P)_2$, then vacuum transferred at 0.01 mm, a 1.5% yield (by weight) of a nonvolatile gummy residue was left behind and II was recovered unchanged in 98% yield.

Decomposition of *tert*-Butyl Hydroperoxide in the Presence of $MCl(CO)(Ph_3P)_2$ (M = Rh, Ir).—*t*-Butyl hydroperoxide (1.0 g) was added dropwise over a 15-min period to 0.08 mmol of the complex in 10 g of toluene at 25° and the mixture was stirred for a total of 1 hr. The volatiles were immediately vacuum transferred from the catalyst and analyzed by glpc (Table II). No organic residue remained.

Reaction of *tert*-Butyl Hydroperoxide with TME in the Presence of $MCl(CO)(Ph_3P)_2$.—*tert*-Butyl hydroperoxide (1.0 g) was added dropwise over 15 min to 0.08 mmol of the complex in 10 g of TME at 25° and the mixture was stirred for a total of 1 hr. The volatiles were immediately vacuum transferred from the catalyst and analyzed by glpc (Table II). No organic residue remained.

Relative Ease of Olefin Oxidation Using $MCl(CO)(Ph_3P)_2$.—Using conditions identical with those for the oxidations above, the per cent conversions of TME, 2 methyl-2-pentene, *cis*-2-hexene, and hexene-1 to oxidation products were 66, 33, 3, and <1%, respectively, with the Rh(I) complex and 53, 8, 1, and <1%, respectively, with the Ir(I) complex. Titration of reaction mixtures by the standard iodometric method[22] showed that, in the case of TME, a buildup of 11% hydroperoxide had occurred after 4 hr at 50° using either the Rh(I) or the Ir(I) complex, whereas with either complex less than 1% hydroperoxide had formed from hexene-1. When TME was epoxidized using *tert*-butyl hydroperoxide at room temperature as described above, a 26% yield of I was obtained after 1 hr with the Rh(I) complex and a 42% yield of I was obtained using Ir(I). When hexene-1 was treated with *tert*-butyl hydroperoxide under the same conditions using the Rh(I) complex, *tert*-butyl alcohol was formed in 25% yield but less than 1% hexene oxide was detected (glpc). With the iridium(I) complex no epoxide could be detected under identical conditions.

Registry No.—I, 5076-20-0; II, 10473-13-9; tetramethylethylene, 563-79-1; $RhCl(CO)(Ph_3P)_2$, 13938-94-8; $IrCl(CO)(Ph_3P)_2$, 14871-41-1; *tert*-butyl hydroperoxide, 75-91-2; *tert*-butyl alcohol, 75-65-0.

Acknowledgment.—The authors with to express their thanks to Miss Caroline Link and Mr. Arthur Brown for their experimental assistance in this work.

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