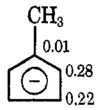
charge.[21] Thus we conclude that methyl substitution has left the charge distribution in the cyclopentadienide ring almost unchanged. This conclusion contrasts with the charge densities predicted by simple HMO theory shown below.[22] We believe that the ^{13}C chemical shifts provide a more reliable guide.



The sum of downfield chemical shifts of ring carbons in cyclopentadienide due to trimethylsilyl substitution is −30.0 ppm (see Table I) compared to −18.9 ppm for trimethylsilyl substitution on benzene.[23] This is evidence for withdrawal of electron density from cyclopentadienide by silicon.

Qualitative low-temperature ^{13}C nmr spectra of "C_5H_5MgCl" and "$CH_3C_5H_4MgCl$" were similar to each other and to the pmr spectra of "C_5H_5MgCl." At −67° a proton-decoupled spectrum of C_5H_5MgCl prepared from commercial Grignard reagent showed two peaks separated by 21 Hz with relative areas of 4:1. These peaks must be "C_5H_5MgCl" and an impurity (probably a cyclopentadienylmagnesium alkoxide), because the proton spectra indicate that $(C_5H_5)_2Mg$ should not be detectable at the sensitivity limits available in the ^{13}C experiment. Spectra of "$CH_3C_5H_4MgCl$" prepared from commercial Grignard reagent showed sharp proton-decoupled peaks at 50°. The peaks due to C_2 and C_3 were examined as a function of temperature. On cooling each peak broadened and then separated into two sharp peaks at −38°. The intensity ratio of each pair of peaks was 4:1 and this ratio remained unchanged down to −65°. Peak separations were 10 and 33 Hz for C_2 and C_3, respectively. Only sharp singlets could be seen in a spectrum of "$CH_3C_5H_4MgCl$" prepared from $(CH_3C_5H_4)_2Mg$ and anhydrous $MgCl_2$ even at −67°. All of the Grignard solutions prepared from commercial Grignards showed similar exchange phenomena in their ^{13}C spectra. These observations show that cyclopentadienylmagnesium chlorides are in rapid equilibria with the impurities (presumably alkoxides) in commercial Grignard solutions.[24] Precautions should be taken to prevent this complication in kinetic studies. The high solute concentrations required without the aid of Fourier transform spectroscopy prevented observation of the Schlenk equilibrium by carbon magnetic resonance.

Registry No.—$MgCl_2$, 7786-30-3; $MgBr_2$, 7789-48-2; $(C_5H_5)_2Mg$, 1284-72-6; cyclopentadienylmagnesium chloride, 11112-17-7; methylcyclopentadienylmagnesium chloride, 11112-18-8; 1,3-dimethylcyclopentadienyl chloride, 11112-19-9; trimethylsilylcyclopentadienylmagnesium chloride, 11112-20-2.

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(24) The impurities affect only slightly the chemical shifts in Table II. For example, in the contaminated sample of "$CH_3C_5H_4MgCl$" the 33-Hz separation between the two C_3 peaks at −38° corresponds to a chemical shift difference of only 0.26 ppm between $CH_3C_5H_5MgCl$ and the weighted average of $CH_3C_5H_5MgCl$ and impurity. Since all other peak separations in all the compounds in Table II at low temperature were smaller than 33 Hz, the errors in chemical shifts due to impurities are <0.3 ppm.

Oxidation by Metal Salts

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Oxidation of *p*-cymene with cobalt(III) acetate gives *p*-isopropylbenzyl acetate and *p*-isopropylbenzaldehyde as predominant products. With manganese(III) acetate, however, a mixture of cymene dimers is formed predominantly. In the presence of oxygen, with the cobalt salt, *p*-isopropylbenzoic acid is formed, and with the manganese salt, a mixture of *p*-toluic acid and *p*-methylacetophenone. The different nature of the products suggests two mechanisms, electron transfer with cobalt and a free-radical pathway with manganese.

The catalytic effect of transition metal ions in the autooxidation of hydrocarbons is well established. Metal ions take part in the initiation step by decomposing hydroperoxides into radicals which propagate the chain mechanism.[1-3] Recently, direct interactions of metal ions with hydrocarbons have been stressed. Such interactions appear to be important when rather large, as opposed to catalytic, concentrations of metal ions are used. Two of the ions, Co(III)[4-10] and Mn(III),[11-13] have been studied in detail. Initially, both were thought to operate in an analogous manner. Now, it is believed that Co(III) functions primarily

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TABLE I

REACTION OF *p*-CYMENE WITH OXYGEN

Catalyst[a]	$C_{10}H_{14}$,[b] *M*	Conditions	$C_{10}H_{14}$, % Conversion	Products (% molar selectivity)
0.2 *M* $Co(OAc)_2 \cdot 4H_2O$/HOAc	1.0	100°, 22 atm O_2,[c] 1.5 hr	100	*p*-Isopropylbenzoic acid (90) *p*-Acetobenzoic acid (10)
0.2 *M* $Mn(OAc)_2 \cdot 4H_2O$/HOAc	1.2	100°, 22 atm O_2,[c] 2.0 hr	~29	*p*-Toluic acid (68) *p*-Methylacetophenone (16) *p*-Isopropylbenzoic acid (16)

[a] Each experiment was initiated with MEK. [b] *Ca.* 2 mol of *n*-butane was added for promotion. [c] Total pressure, partial pressures of C_4H_{10} and O_2.

TABLE II

REACTION OF *p*-CYMENE WITH Co(III) AND Mn(III) ACETATES

Catalyst	$C_{10}H_{14}$	Conditions	Products (mmol, % molar selectivity)
98 mmol of Co(III)	100 mmol, and 40 mmol of NaOAc/100 cc of HOAc	65°, 1.5 days	*p*-Isopropylbenzyl acetate (35.4, 81.2) *p*-Isopropylbenzaldehyde (6.6, 15.1) *p*-Isopropylbenzaldehyde diacetate (1.0, 2.3) Dimers (0.6, 1.4) *p*-Methylacetophenone (trace, 0.1)
Cymene converted: 32%			
167 mmol of Mn(III)	245 mmol/540 cc of HOAc[a]	95°, 4 days	Dimers (*m/e* 266, 280)[b] (6.4, 80.0) Methyl isopropyl benzyl acetates (*m/e* 206) (0.7, 8.7) *p*-Methylacetophenone (0.4, 5.0) Assorted products (?, ~7.0)
Cymene converted: ~7%			

[a] With added NaOAc, oxidation of intermediate radicals is rapid (120°, 2 hr) so that $-CH_2OAc$ and $-CH_2COOH$ adducts are formed predominantly. [b] Analysis showed ~38% of bicymyls, $C_{20}H_{26}$, and ~62% of $C_{21}H_{28}$. The latter can be formed by a series of radical reactions involving (a) cross-coupling of cymyl and carboxymethyl radicals[11] to give $p\text{-MePhC(Me)}_2CH_2COOH$, (b) reaction of this acid with $Mn(OAc)_3$ followed by thermolysis to give $C_{11}H_{15}\cdot$, and (c) coupling of $C_{11}H_{15}\cdot$ with another cymyl radical. This reaction is therefore dominated by the coupling of cymyl radicals. The precise structure of dimers at this time is not known.

via electron transfer, while Mn(III) is effective by both electron transfer and a free-radical pathway, depending on experimental conditions and the reactivity of the substrate. Mechanisms were proposed mostly on the basis of kinetic evidence, trapping of intermediates, and spectroscopic data. We noticed, however, that these studies, with or without oxygen, were mostly limited to toluene. Compounds such as ethyltoluenes and cymenes, in which competition between alkyl groups is possible, were not examined, probably because of the ease with which they are oxidized by a free-radical mechanism, and due to the complexity of the products formed. Russell, *et al.*,[14] reported difficulty in oxidizing alkoxycumenes in acetic acid because of apparent decomposition of the hydroperoxide into phenolic materials. In the only reference available,[5] *p*-cymene was oxidized in acetic acid with cobaltic acetate to determine its reactivity, but products of this reaction have not been cited. We have reported results on the Co(III) ion catalyzed oxidation of *p*-cymene with oxygen to form *p*-isopropylbenzoic acid.[15,16] Now, we comment on the Mn(III) ion catalyzed oxidation of *p*-cymene with oxygen, as well as the reaction of cymene with Co(III) and Mn(III) acetates.

Results and Discussion

Experiments with oxygen are summarized in Table I. Under comparable conditions, oxidation of *p*-cymene with oxygen proceeds more readily with the cobalt than with the manganese catalyst. This may be attributed, in part, to the difference in the redox potentials of the two systems. More striking, however, is the different nature of the products formed. Whereas *p*-isopropylbenzoic acid is the major product in the cobalt system, *p*-toluic acid and its precursor *p*-methylacetophenone are predominant when mangenese is used. These results suggest that different mechanisms are operative. Selectivities with manganese-catalyzed oxidations are analogous to those from noncatalytic air oxidation of *p*-cymene reported by Serif, *et al.*[17]

Results of cymene oxidation by Co(III) and Mn(III) acetates are summarized in Table II. Major products with Co(III) salt are *p*-isopropylbenzyl acetate and *p*-isopropylbenzaldehyde. Both were isolated and characterized by vpc, nmr, ir, and derivatives. Identification of minor products was based primarily on vpc behavior. It is surprising that essentially no attack on the isopropyl group occurred. This suggests that the 10% of *p*-acetobenzoic acid formed in the presence of oxygen may have come by a competitive free-radical pathway.

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Oxidation of cymene with Mn(III) salt was carried out in the absence of sodium acetate and without removal of water, conditions favoring an electron transfer mechanism.[11] Even under such conditions, coupling of cymene radicals was the dominant course of the reaction. Some dimers could also be formed by gradual addition of diacetyl peroxide to boiling cymene.[18] Minor products consisted of 15 components (vpc), mostly esters and some acids. Only a trace or *p*-isopropylbenzaldehyde, its diacetate, and *p*-isopropylbenzyl acetate was detected. Analysis of the total product by nmr after removal of unreacted cymene by column chromatography showed that virtually all of the isopropyl groups had reacted.

Conclusion

Products formed in the oxidation of *p*-cymene using cobaltic or manganic salts alone or in conjunction with oxygen indicate operation of different mechanisms in the two cases studied. Electron transfer with cobalt and a free-radical path with manganese are in accord with our results as well as published data.

Experimental Section

Reactions with oxygen at elevated pressure were carried out as previously reported.[16] Experiments with metal salts alone were done in sealed tubes under nitrogen atmosphere. Concentrations of metal ions were determined by iodometric titration. After termination of the reaction, the mixture was taken up in ether and repeatedly extracted with cold water. The organic layer was dried ($MgSO_4$) and filtered, and the ether was removed. After addition of methyl palmitate as internal standard, the residue was analyzed by vpc (6 ft × 0.25 in., OV-1 column, programmed from 50 to 275° at 10°/min). Unreacted cymene was removed from the product by column chromatography over silica gel. Standard analytical procedures were then used for the characterization of the residual product mixture. Cobaltic acetate and manganic acetate were prepared by published procedures.[10,13]

Registry No.—*p*-Cymene, 99-87-6; Co(III) acetate, 917-69-1; Mn(III) acetate, 993-02-2.

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The Formation of 1,4 Diketones, Monoketones, and β-Epoxy Ketones by Reaction of Iron Pentacarbonyl with α-Halo Ketones. A Possible Mechanism for Iron Pentacarbonyl–Halide Reactions

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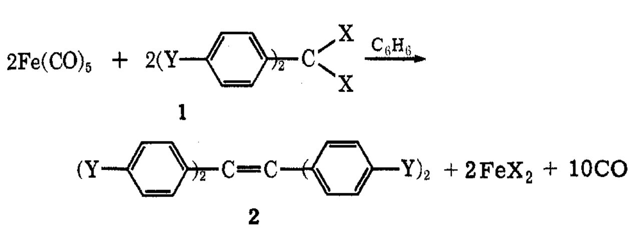
Iron pentacarbonyl reacts with a variety of primary, secondary, and tertiary aryl and alkyl α-halo ketones in refluxing 1,2-dimethoxyethane, followed by treatment with water, to generally give the coupled 1,4 diketones and the reduced monoketones. Use of deuterium oxide instead of water results in α-deuterio ketone formation. β-Epoxy ketones were produced in several instances. The reaction apparently occurs *via* organoiron tetracarbonyl halide and organoiron halide complexes. Some support is presented for the intermediacy of such complexes. The reactions of $Fe(CO)_5$ with sulfonyl chlorides and *gem*-dihalides likely proceed *via* similar intermediates.

A number of papers have appeared in the literature concerning the reaction of iron pentacarbonyl with halides. A simple preparation of tetraarylethylenes (2) was reported by Coffey,[2a] in 1961, by treatment of certain *gem*-dihalides (1) with $Fe(CO)_5$ in refluxing benzene. Activating groups such as aryl, halo, cyano, and carbalkoxy must be attached to the halogen-bearing carbon in order for this thermal reaction to occur, but substituted ethylenes are not produced in all instances; *e.g.*, (i) although bisfluorenylidene was obtained by reaction of 9,9-dibromofluorene with the metal carbonyl in hot benzene, the alkene and 9,9′-dibromobisfluorenyl are formed by using dioxane as the solvent; (ii) diethyl dibromomalonate and dibromomalonitrile react with $Fe(CO)_5$ in benzene giving iron-containing materials of no apparent synthetic utility; (iii) some hexachloroethane, along with substantial amounts of tar, resulted when carbon tetrachloride was the starting halide.[2] Some *gem*-dihalides with other activating groups failed to react with the metal carbonyl (*e.g.*, dichloromethyl phenyl sulfone).[3] Vicinal dihalides are dehalogenated by $Fe(CO)_5$.[1,3]



X = Cl; Y = H, CH_3, $C(CH_3)_3$, CH_3, Cl
X = Br; Y = NO_2

Coffey observed no reaction between $Fe(CO)_5$ and any monohalide. Recently, Pankowski and Bigorgne reported that no reaction occurred when methyl iodide and $Fe(CO)_5$ were mixed at room temperature.[4] However, Bruce[5] showed that decafluorobenzhydryl bromide (3) reacts with $Fe(CO)_5$ in hot petroleum ether (bp 100–120°) to give the expected coupling product 4, in 37% yield, and small amounts of bis(pentafluorophenyl)methane (5), the formation of the latter attrib-

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