THF (20 ml). The mixture was refluxed for 5 hr. The excess of hydride was destroyed by the addition of an aqueous concentrated solution of Na_2SO_4 and the purification procedure followed was identical with that described for compound **6**. The yield of product after ether trituration was 0.9 g (51%), mp 159–160°. The compound recrystallized from acetone as white prisms: mp 161–162°; ir 3450, 3200, 1680, 1675 (shoulder), 1300, 1070, 1030, 860, 850, 790, 765, 745, and 710 cm^{-1}; nmr δ 3.48 (t, 2), 3.53 (q, 2), 4.04 (s, 2), 4.70 (t, 1), 7.32 (m, 10), and 7.92 (s, 1); mass spectrum m/e (rel intensity) 282 (33) (parent), 252 (34), 251 (76), 209 (15), 208 (69), 205 (24), 178 (34), 108 (40), 105 (56), 91 (55), 77 (45), 74 (54), 72 (42), 58 (64), and 43 (100).

Anal. Calcd for $C_{17}H_{18}N_2O_2$: C, 72.31; H, 6.42; N, 9.92. Found: C, 72.17; H, 6.60; N, 9.87.

1-(2-Hydroxyethyl)-4,4-diphenyl-2-imidazolidinone Methanesulfonate Ester (2b).—Following the procedure for the preparation of **2a**, compound **5** (0.58 g, 2.07 mmol) was treated with methanesulfonyl chloride (0.19 ml, 2.17 mmol) in 5 ml of pyridine. After the addition of concentrated HCl, the solution was extracted with $CHCl_3$. The chloroform layer was washed with water and dried (Na_2SO_4). The oil recovered after removal of the solvent was triturated with ether and the solid formed was recrystallized from benzene to yield 0.40 g (54%) of **2b**: mp 124–125°; ir 3200, 1680, 1370, 1340, 1180, 1000, 990, 900, 805, 750, 715, and 705 cm^{-1}; nmr δ 3.02 (s, 3), 3.42 (t, 2), 4.00 (s, 2), 4.27 (t, 2), 7.28 (m, 10), and 8.10 (s, 1).

Anal. Calcd for $C_{18}H_{20}N_2O_4S$: C, 59.98; H, 5.59; N, 7.77; S, 8.89. Found: C, 59.83; H, 5.71; N, 7.65; S, 8.92.

2,3,5,6-Tetrahydro-6,6-diphenylimidazo[2,1-*b*]oxazole (1b).—Following a similar procedure for the synthesis of **1a**, compound **2b** (0.40 g, 1.15 mmol) was treated with 0.2 g of NaH (57% oil suspension) in toluene. The reaction was completed in 1.5 hr according to tlc analysis [one spot, R_f 0.33, silica gel, $CHCl_3$–EtOAc (1:1)]. The starting material in the same system had an R_f value of 0.18. After work-up, 0.25 g (85%) of **1b** was obtained. One recrystallization from toluene afforded an analytical sample: mp 197–198°; ir 1670, 1260, 1210, 980, 780, 755, 732, 710, and 700 cm^{-1}; nmr δ 3.22 (t, 2), 3.80 (s, 2), 4.64 (t, 2), and 7.26 (m, 10); mass spectrum m/e (rel intensity) 264 (100) (parent), 208 (96), 187 (60), 180 (30), 165 (38), 160 (100), 132 (22), 105 (31), 91 (33), and 77 (83).

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.24; H, 6.10; N, 10.60. Found: C, 77.40; H, 6.15; N, 10.70.

Registry No.—**1a**, 34806-22-9; **1b**, 34792-37-5; **2a**, 34806-23-0; **2b**, 34792-38-6; **5**, 34806-24-1; **6**, 34806-21-8.

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^1H and ^{13}C Nuclear Magnetic Resonance Spectra of Cyclopentadienylmagnesium Compounds in Tetrahydrofuran

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Low-temperature pmr spectra of mixtures of magnesium cyclopentadienide and magnesium chloride and of magnesium cyclopentadienide and magnesium bromide, 0.05–0.56 *M* in tetrahydrofuran, indicate that the cyclopentadienylmagnesium halides consist of Schlenk equilibrium mixtures, $(C_5H_5)_2Mg + MgX_2 \rightleftarrows 2C_5H_5MgX$, in which the C_5H_5MgX predominates. A rapid exchange between cyclopentadienylmagnesium chlorides and cyclopentadienyl impurities (presumedly alkoxides) has been detected. ^{13}C nmr chemical shifts of cyclopentadienyl-, methylcyclopentadienyl-, 1,3-dimethylcyclopentadienyl-, and trimethylsilylcyclopentadienylmagnesium chlorides are reported and discussed in terms of the charge distributions in substituted cyclopentadienides.

The observation that benzyne adds to cyclopentadienylmagnesium bromide ("C_5H_5MgBr")[2] to give benzonorbornadien-9-ylmagnesium bromide[3] has stimulated investigation of the structure of cyclopentadienylmagnesium compounds. Ir and uv spectra of "C_5H_5MgBr" and "C_5H_5MgCl" and magnesium cyclopentadienide [$(C_5H_5)_2Mg$] in tetrahydrofuran (THF) indicated that the principal components of these compounds in solution all have magnesium atoms located on or near the C_5 axes of the cyclopentadienide ions.[4] They do not have carbon–magnesium σ bonds. X-Ray analysis proved that a solvated C_5H_5MgBr crystal had a similar structure,[5] and the crystallographic unit cell parameters of $(C_5H_5)_2Mg$ suggested that it was isostructural with ferrocene.[6] This spectroscopic and X-ray data, however, provide no clue as to the nature of aggregation of cyclopentadienylmagnesium compounds in solution.

In 1929 Schlenk[7] suggested that Grignard reagents were equilibrium mixtures as shown in eq 1, because

$$R_2Mg + MgX_2 \rightleftarrows 2RMgX \qquad (1)$$

addition of dioxane to "RMgX" precipitated MgX_2. In spite of numerous attempts to detect Schlenk equilibria,[8] only recently has direct identification of RMgX and R_2Mg in solution by nmr established positions of equilibrium quantitatively.[9,10] Evans and Fazakerley[9] reported ^{19}F and ^1H spectra of RMgX and R_2Mg for over 20 different Grignard reagents and found the position of equilibrium to be highly dependent on the alkyl or aryl group and the solvent. Temperatures of −68° and below were needed to observe slow exchange pmr spectra of CH_3MgBr and $(CH_3)_2Mg$ in THF. A similar study of "C_5H_5MgCl" and "C_5H_5MgBr" in THF is reported here.

In an extension of our cycloaddition research benzyne was generated in solutions of several substituted "cyclo-

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[2] In this paper "C_5H_5MgBr" denotes cyclopentadienyl Grignard reagent without specification of its composition, and C_5H_5MgBr denotes cyclopentadienylmagnesium bromide, a specific component of the Schlenk equilibrium mixture.

[3] (a) G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958); (b) W. T. Ford, R. Radue, and J. A. Walker, *Chem. Commun.*, 966 (1970).

[4] W. T. Ford, *J. Organometal. Chem.*, **32**, 27 (1971).

[5] G. D. Stucky, personal communication.

[6] E. Weiss and E. O. Fischer, *Z. Anorg. Allg. Chem.*, **278**, 219 (1955).

[7] W. Schlenk and W. Schlenk, *Ber.*, **62**, 920 (1929).

[8] For a review of earlier literature on Schlenk equilibria see E. C. Ashby, *Quart. Rev., Chem. Soc.*, **21**, 259 (1967).

[9] D. F. Evans and G. V. Fazakerley, *J. Chem. Soc. A*, 184 (1971).

[10] (a) G. E. Parris and E. C. Ashby, *J. Amer. Chem. Soc.*, **93**, 1206 (1971); (b) J. A. Magnuson and J. D. Roberts, *J. Org. Chem.*, **37**, 133 (1972).

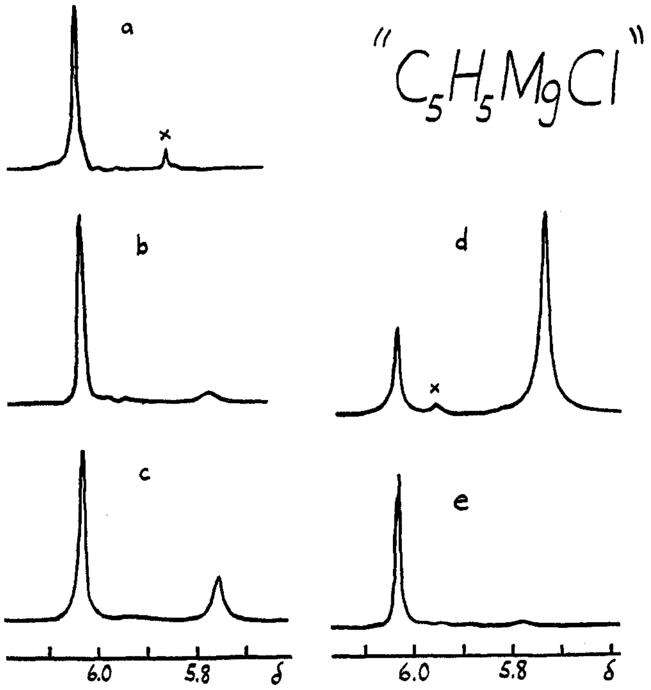

Figure 1.—Low-temperature pmr spectra of "C_5H_5MgCl" in THF: (a) 0.185 *M* "C_5H_5MgCl", 0°; (b) 0.093 *M* "C_5H_5MgCl", −60°; (c) 0.093 *M* "C_5H_5MgCl", −85°; (d) 0.267 *M* $C_5H_5^-$, 0.175 *M* Mg^{2+}, 0.084 *M* Cl^-, −95°; (e) 0.077 *M* $C_5H_5^-$, 0.144 *M* Mg^{2+}, 0.211 *M* Cl^-, −75°. Peaks marked × are spinning side bands.

pentadienylmagnesium chlorides."[11] The resulting isomeric substituted benzonorbornadienes were formed neither randomly nor highly selectively. In order to determine whether charge distributions in the substituted cyclopentadienylmagnesium compounds affected their courses of addition to benzyne, ^{13}C chemical shifts of their ring carbons were measured.

Experimental Section

Preparations of substituted cyclopentadienes, cyclopentadienylmagnesium chlorides, and $(C_5H_5)_2Mg$ were described earlier.[4,11] Magnesium methylcyclopentadienide $[(CH_3C_5H_4)_2Mg]$ was prepared by a procedure identical with that for $(C_5H_5)_2Mg$.[4] Tetrahydrofuran was freshly distilled from potassium fluorenide.

Anhydrous magnesium chloride was prepared from mercuric chloride and magnesium turnings in THF.[12] Analyses[13] of white powder after drying for 3 hr at 120° *in vacuo* follow. *Anal.* Calcd for $MgCl_2$: Mg, 25.53; Cl, 74.47. Found: Mg, 11.79; Cl, 33.81. This corresponds to an atom ratio Cl/Mg of 1.966. A pmr spectrum in THF revealed no water peak. A pmr spectrum in D_2O revealed a large amount of THF in the sample. We suspect that the literature preparation[12] of anhydrous $MgCl_2$ also contained THF, although the authors did not report it. Since all our spectra were recorded in THF, the solvent in the solid sample did not matter as long as the composition of the solid was known.

Anhydrous magnesium bromide was prepared from 1,2-dibromoethane and magnesium turnings in THF. Analyses[13] of the white powder which remained after evaporation of solvent and drying 12 hr at 130° *in vacuo* follow. *Anal.* Calcd for $MgBr_2 \cdot C_4H_8O$: Mg, 9.48; Br, 62.37. Found: Mg, 9.67; Br, 61.52. This corresponds to an atom ratio Br/Mg of 1.941. A pmr spectrum of the sample in D_2O revealed THF signals.

Preparation of Cyclopentadienide Solutions.—All of the ^{13}C chemical shifts and some preliminary low-temperature pmr spectra were obtained with solutions prepared as described earlier[4,11] from Alfa 3.0 *M* ethylmagnesium chloride in THF and Alfa 2.95 *M* methylmagnesium bromide in diethyl ether. When low-temperature pmr showed an extraneous cyclopentadienide peak in solutions prepared from these commercial Grignard reagents, their use was discontinued and all subsequent solutions for pmr study were prepared from $(C_5H_5)_2Mg$ and anhydrous magnesium halides. (See Results and Discussion for explanation.) All ^{13}C samples were 1.0 *M* in cyclopentadienide, magnesium, and chloride. Pmr samples of "C_5H_5MgCl" were prepared from analyzed[13] stock solutions of 0.40 *M* $MgCl_2$ in THF and 1.01 *M* $(C_5H_5)_2Mg$ in THF. Pmr samples of "C_5H_5MgBr" were prepared from weighed amounts of $MgBr_2 \cdot C_4H_8O$ and the stock solution of 1.01 *M* $(C_5H_5)_2Mg$ in THF. All nmr samples were prepared in an argon-filled drybox. The capped tubes were sealed immediately after removal from the drybox. No changes were observed when selected spectra were repeated after periods of 60 days or more.

Spectra.—Proton spectra were obtained with a Varian HA-100 instrument. Proton chemical shifts were measured relative to the β-CH_2 of THF (1.767 ppm) with a Varian V-4315 frequency counter. Temperatures were determined to ±1° with a calibrated methanol sample.

Carbon spectra were obtained at 25.2 MHz with a Varian XL-100 spectrometer. Deuterioacetone, contained in a concentric tube, provided the lock signal. Proton noise or off-resonance decoupling techniques were used in all cases. Carbon chemical shifts were determined relative to internal tetrahydrofuran and are reported relative to TMS. Tetrahydrofuran shifts $C_\alpha = 65.8$, $C_\beta = 22.7$ were determined relative to internal benzene and converted to TMS scale using the relationship $\delta_{TMS} = \delta_{benzene} + 128.5$. The addition of $MgCl_2$ to THF did not change the shifts by more than 1 Hz. Temperatures were measured with a 5-mm Wilmad long-stem thermometer placed in a 12-mm tube containing methanol. We have noted that simple replacement of the 12-mm sample tube by the 5-mm thermometer leads to errors as large as 20°. This discrepancy can be traced to the change in gas flow in the probe with change in tube size.

Results and Discussion

At probe temperature (28°) the pmr spectra of "C_5H_5MgBr" and "C_5H_5MgCl" in THF were sharp singlets. Upon cooling either Grignard reagent the signal broadened and at about −60° a second signal appeared at higher field. Further cooling to −90° sharpened the higher field signal and increased its relative area. Sample spectra of "C_5H_5MgCl" are shown in Figure 1. A sample of "C_5H_5MgCl" prepared with excess $(C_5H_5)_2Mg$ showed the same two peaks at $< -60°$, but the relative area of the higher field peak was markedly increased (Figure 1d). A sample of "C_5H_5MgCl" prepared with excess $MgCl_2$ showed the lower field peak at $\leq -60°$ but only a trace of the higher field peak (Figure 1e). Similar experiments with C_5H_5MgBr, $(C_5H_5)_2Mg$, and $MgBr_2$ gave similar results. The relative areas of the two signals in low temperature pmr spectra of "C_5H_5MgCl" were independent of concentration over a 0.056–0.56 *M* range. The relative peak areas in low temperature spectra of "C_5H_5MgBr" also were independent of concentration over a 0.050–0.40 M range.

This spectral behavior is the same as that observed with other Grignard reagents[9,10] and is consistent with the Schlenk equilibrium (eq 1) in which the lower and higher field pmr signals are due to C_5H_5MgX and $(C_5H_5)_2Mg$, respectively. Moreover, the chemical shifts of the two signals are the same as those of separate solutions of "C_5H_5MgX" and $(C_5H_5)_2Mg$ at 27°.[4] Actually these and the previous[9,10] nmr results are also consistent with a host of other equilibria similar to eq 1 but involving higher states of aggregation.

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[11] W. T. Ford, *J. Org. Chem.*, **36**, 3979 (1971).

[12] E. C. Ashby and R. C. Arnott, *J. Organometal. Chem.*, **14**, 1 (1968).

[13] Analyses for magnesium by EDTA titration and for halides by mercuric thiocyanate titration were performed by J. Nemeth.

The independence of position of equilibrium on Grignard reagent concentration rules out equilibria involving different states of aggregation, such as 2 monomer ⇄ dimer. We presume, however, that "C_5H_5MgX" and "C_5H_5MgBr" are monomeric in THF because several other Grignard reagents have been found previously to be monomeric in THF by ebulliometry.[14]

In a preliminary investigation of low-temperature pmr spectra of "C_5H_5MgCl" and "C_5H_5MgBr" prepared from commercial Grignard reagents not two, but three well-resolved peaks appeared. The third peak was located between those assigned to C_5H_5MgX and $(C_5H_5)_2Mg$. Since the third peak did not appear in samples prepared from $(C_5H_5)_2Mg$ and anhydrous magnesium halides, it apparently was an impurity derived from the commercial Grignard reagents. We suspect the impurity was a cyclopentadienylmagnesium alkoxide because low-temperature spectra of a "C_5H_5MgBr" sample to which a drop of methanol was added also contained a third peak at approximately the same position.

The Schlenk equilibrium constants for "C_5H_5MgBr" and "C_5H_5MgCl" were temperature dependent (see Table I). Extrapolation of the −65 to −90° data indicates that "C_5H_5MgBr" contains 0.5 mol % $(C_5H_5)_2Mg$ and "C_5H_5MgCl" contains 1.3 mol % $(C_5H_5)_2Mg$ at 25°.

TABLE I

EQUILIBRIUM CONSTANTS IN THF FOR

$$(C_5H_5)_2Mg + MgX_2 \overset{K}{\rightleftharpoons} 2C_5H_5MgX$$

	K^a	
Temp, °C[b]	X = Br[c]	X = Cl[d]
−65	233	106
−70	114	75
−75	74	54
−80	46	39
−85	26	29
−90	13.6	19.0
$\Delta H°$, kcal mol^{-1} [e]	7.3 ± 1.3	5.1 ± 1.8
$\Delta S°$, cal deg^{-1} mol^{-1} (−75°)[e]	45 ± 7	34 ± 9

[a] At most temperatures only one measurement was made. Values at −75° were reproducible to ±5% in duplicate experiments. [b] ±1°. [c] 0.20 *M* "C_5H_5MgBr." [d] 0.093 *M* "C_5H_5MgCl." [e] Errors estimated from maximum deviations of points from lines in log *K* vs. 1/*T* plots.

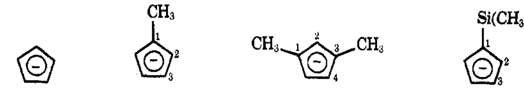
Although the relative areas of peaks in low-temperature "C_5H_5MgBr" and "C_5H_5MgCl" pmr spectra were independent of concentration, the linewidths of the C_5H_5MgX peaks at −60 and −75° increased as the concentration of "C_5H_5MgX" increased. This implies that exchange of C_5H_5MgX is of kinetic order greater than one in C_5H_5MgX, or that impurities are catalyzing the exchange process. Second-order kinetics for inversion of primary alkyl groups and exchanges of alkyl groups in Grignard reagents have been noted before.[15] No attempt was made to obtain better kinetic data because the Grignard solutions in this investigation were prepared from common "Grignard" grade magnesium turnings and may contain impurities which catalyze alkyl group exchange.[16] Although minor impurities may affect greatly the kinetic processes in Grignard reagents, they should not affect the position of the Schlenk equilibrium much.

The proton chemical shifts of substituted "cyclopentadienylmagnesium chlorides" provided little indication of charge distribution in the cyclopentadienide ions.[11] However, ^{13}C chemical shifts are more closely related and more sensitive to charge density than are proton chemical shifts. There is theoretical justification for an approximately linear ^{13}C chemical shift *vs.* charge density relationship in cyclic aromatic systems.[17]

Carbon chemical shifts of the "cyclopentadienylmagnesium chlorides" appear in Table II. Assignments were made from proton-coupled and off-resonance-decoupled spectra when possible. The tentative C_2 and C_3 assignments of methylcyclopentadienide were made by analogy to 1,3-dimethylcyclopentadienide.

TABLE II

^{13}C CHEMICAL SHIFTS[a] OF "CYCLOPENTADIENYLMAGNESIUM CHLORIDES"[b]



C 103.8	C_1 116.1	C_1 114.4	C_1 112.6
	C_2 104.1	C_2 105.2	C_2, C_3 112.5, 105.7
	C_3 101.6	C_4 101.4	
	CH_3 11.1	CH_3 11.2	CH_3 −3.8

[a] In parts per million downfield from TMS; values are accurate to ±0.3 ppm (see footnote 24). [b] 1.0 *M* in THF at 35°.

Methyl substitution for hydrogen in cyclopentadienide shifts the ^{13}C signal of the methyl-bound ring carbon downfield 12.3 and 10.6 ppm, respectively, in the methyl and 1,3-dimethyl compounds, but has little effect on the unsubstituted ring carbons. Comparisons of ^{13}C chemical shifts of methylbenzenes to benzene give very similar results,[18] although the changes of chemical shifts in the cyclopentadienides are slightly greater than in the benzenes, as expected for nonalternant systems.[19] If we take toluene as a model for methyl group effects on ring carbon chemical shifts, then all other structural factors influencing chemical shifts change the methyl- and 1,3-dimethylcyclopentadienide ring carbons by ≤3.2 ppm compared to unsubstituted cyclopentadienide.[20] A linear correlation between ^{13}C chemical shift and charge density has been established for a series of ionic and neutral monocyclic aromatic systems with a slope of 167.8 ppm per unit

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[14] F. W. Walker and E. C. Ashby, *J. Amer. Chem. Soc.*, **91**, 3845 (1969), and references therein.

[15] (a) G. M. Whitesides and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 4878 (1965); (b) G. Fraenkel and D. T. Dix, *ibid.*, **88**, 979 (1966); (c) H. O. House, R. A. Latham, and G. M. Whitesides, *J. Org. Chem.*, **32**, 2481 (1967); (d) G. Fraenkel, C. E. Cottrell, and D. T. Dix, *J. Amer. Chem. Soc.*, **93**, 1704 (1971).

[16] For a discussion of the nature of impurities in common magnesium turnings which attributes line broadening to the presence of Mn(II) see ref 15c, p 2483. The $(C_5H_5)_2Mg$ stock solution in this work was pink, also suggestive of Mn(II) impurities.

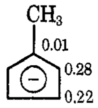
[17] (a) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963); (b) T. Tokuhiro and G. Fraenkel, *J. Amer. Chem. Soc.*, **91**, 5005 (1969).

[18] (a) P. C. Lauterbur, *ibid.*, **83**, 1838 (1961); (b) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

[19] A. J. Jones, T. D. Alger, D. M. Grant, and W. M. Litchman, *J. Amer. Chem. Soc.*, **92**, 2386 (1970).

[20] [$\Delta\delta$ for CCH_3 in $CH_3C_5H_4^-$ (−12.3 ppm)] − [$\Delta\delta$ for CCH_3 in $CH_3C_6H_5$ (−9.1 ppm)^{18b}] = −3.2 ppm.

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.

Acknowledgments.—We thank R. L. Thrift and S. Silber for running the low-temperature pmr spectra and R. E. Santini and R. L. Spaeth for assistance with the ^{13}C spectra. W. T. F. thanks the Merck Company Foundation and E. I. du Pont de Nemours and Company and J. B. G. thanks Eli Lilly and Company for financial support.

[21] (a) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961); (b) E. A. LaLancette and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 1941 (1965).

[22] S. McLean and P. Haynes, *Tetrahedron*, **21**, 2313 (1965).

[23] G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, **42**, 2427 (1965).

[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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[3] Y. Kamiya, S. Beaton, A. Lafortune, and K. U. Ingold, *Can. J. Chem.*, **41**, 2020, 2034 (1963).

[4] W. F. Brill, *Ind. Eng. Chem.*, **52**, 837 (1960).

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