of 5% sodium bicarbonate and twice with 10-ml portions of water. The chloroform solution was dried over anhydrous sodium sulfate, filtered, and the filtrate was concentrated to dryness *in vacuo* on a water bath. The residue was recrystallized from methanol to yield 0.170 g (15.1%) of pure **15**: mp 211–212°; infrared band at 5.76 μ (C=O); nmr ($CDCl_3$) δ 3.82, 4.07, and 4.12 (three singlets, 18 H, CH_3) and 7.80 and 8.78 (two singlets, 4 H, aromatic).

Anal. Calcd for $C_{24}H_{22}O_{12}$: C, 57.37; H, 4.41. Found: C, 57.44; H, 4.56.

(b) **From 14.**—A solution of 0.209 g (0.5 mmole) of **14** in 100 ml of ether containing 3.5 ml of absolute ethanol and 100 ml of ether containing 0.336 g (8.0 mmoles) of diazomethane was allowed to stand at room temperature for 18 hr. The solvent was then allowed to evaporate slowly and the residue dissolved in hot methanol and decolorized with charcoal. On cooling the methanol filtrate, 0.180 g of crude **15** was obtained. This solid was filtered and washed with 25 ml of 5% sodium bicarbonate solution, 50 ml of water, and a small volume of cold methanol. Three additional recrystallizations from methanol yielded 0.170 g (70.0%) of **15**, mp 211–212°, identical by all the usual criteria with the Ullman coupling product of 5-bromo-1,2,4-tricarbomethoxybenzene.

Registry No.—**1**, 222-93-5; **2**, 189-55-9; **3**, 3302-52-1; **4**, 2202-80-4; **5**, 13124-76-0; **6**, 13124-77-1; **7**, 13124-78-2; **9**, 2178-03-2; **12**, 13124-80-6; **13**, 13124-81-7; **14**, 13124-82-8; **15**, 13124-83-9; **17**, 13124-84-0; **18**, 13124-85-1; **19**, 4859-19-2; **20**, 13124-86-2; acetonate of **20**, 13124-87-3; **21**, 13124-88-4.

Kinetics of Hydrogenation of Benzhydrol and Related Compounds under Hydroformylation Conditions

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The hydrogenation of benzhydrol, nuclear-substituted benzhydrols, triphenylcarbinol, and phenylmethylcarbinol under hydroformylation conditions with dicobalt octacarbonyl catalyst appears to proceed *via* an acid–base reaction between cobalt hydrocarbonyl and aromatic carbinol to give an oxonium salt (I), followed by loss of water to form a complex (II), *e.g.*, $Ph_2CHCo(CO)_4$ for benzhydrol. The formation of complex II is the rate-determining step. Complex II hydrogenates to give an aromatic hydrocarbon as the product. The rate of the over-all reaction is dependent on the aromatic carbinol concentration, hydrogen pressure, and dicobalt octacarbonyl concentration and is also affected by the structure of the carbinol. Unlike the hydrogenation of aldehydes or the hydroformylation of olefins, the hydrogenation of these aromatic carbinols is not inhibited by excess carbon monoxide.

Both the Fischer–Tropsch reaction for making liquid fuels from coal and the oxo reaction for synthesizing alcohols from olefins involve intermediates with carbon-transition metal bonds. In the present investigation, the nature of the reaction of benzhydrol with synthesis gas in the presence of $Co_2(CO)_8$ has been elucidated. Although we are concerned with hydrogenation rather than chain lengthening, the intermediates in the reduction of benzhydrol to diphenylmethane resemble those involved in both the synthesis of liquid fuels *via* the Fischer–Tropsch and of alcohols *via* the oxo reaction. This study can therefore furnish a better understanding of both processes.

It is well known that the hydroformylation (oxo reaction) of olefins is accompanied by some hydrogenation of the double bond; this hydrogenation increases with branching at the double bond.[2] Hydrogenation under oxo conditions is often the major reaction with many compounds, including aldehydes[3] and ketones,[4] benzyl alcohols,[5] polynuclear hydrocarbons,[6] thiophenes,[7] azobenzenes,[8] etc. In spite of the importance of these homogeneously catalyzed hydrogenation reactions, very few kinetic studies are available.

The hydrogenation of aldehydes in the hydroformylation mixture has been studied by Marko[9] and Aldridge and Jonassen[10] and the indications are that the first steps of the reaction are analogous to that of hydroformylation,[11]. although details of the interpretation differ considerably between the two groups of investigators. Marko[2] also studied the hydrogenation of olefins under oxo conditions and suggested that the relative rates of hydroformylation and hydrogenation of carbon–carbon double bonds depend on the carbon skeleton of R in the intermediate complex, $RCo(CO)_4$, formed from an olefin and cobalt hydrocarbonyl.

The present study is concerned with the hydrogenation of benzhydrol and related aromatic carbinols under hydroformylation conditions. The interesting finding that the reaction rate is independent of carbon monoxide partial pressure has enabled us to simplify the rate equation in order to estimate a composite rate constant which is independent of hydrogen pressure and carbon monoxide pressure. It demonstrates that the kinetic data conform to a mechanism which involves, as the rate-determining step, the formation of benzhydrylcobalt tetracarbonyl *via* the loss of water from an intermediate oxonium salt and that the structure of the incipient carbonium ion probably plays an important role in determining the rate of the transformation.

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Experimental Section

The reactions were carried out in a 200-ml stainless steel rocking autoclave. In each experiment, 167 mmoles of aromatic carbinol and 2.6 g of dicobalt octacarbonyl in 50 ml of benzene (151 mmoles/l.) were placed in the autoclave. Carbon monoxide and hydrogen mixtures of 0.33:1 to 3:1 ratios were used at varying total pressures of 125–385 atm at reaction temperatures. When the autoclave reached the desired temperature, the reaction progress was followed by observing the pressure change on a gage mounted inside the stall. The temperature could be controlled to ±1°. Time corrections for the reaction that occurred during heating to reaction temperatures could be determined by extrapolating first-order plots to zero conversion; however, in the actual data treatment, the moment the first pressure reading was taken after the operating temperature was reached was used as zero time. Since our kinetic analysis is based on the disappearance of reactants and is thus virtually irreversible, an arbitrary assignment of zero time would not affect the slope—and hence the rate constant—of a linear rate plot.

Results

Hydrogenation of Benzhydrol.—It was found earlier[5] that the reaction of benzhydrol with CO and H_2 in the presence of dicobalt octacarbonyl forms only the reduced product, diphenylmethane, but no homologous alcohol, 2,2-diphenylethanol. This is in contrast to the reaction of benzyl alcohol[4,5] under similar conditions to form a mixture of toluene and 2-phenylethanol. The conversion of the carbinol to the corresponding hydrocarbon requires the absorption of 1 mole of hydrogen/mole of carbinol.

The oxo reaction is first order with respect to olefin[11,12] and the hydrogenation of aldehydes under hydroformylation conditions is first order with respect to aldehyde;[9,10] similarly, the reduction of benzhydrol to diphenylmethane is first order with respect to benzhydrol. The plot of ln $(P_0 - P_f)/(P_t - P_f)$ *vs.* time is linear with slight curvature after about 75% of the reaction has been completed (P_0 is the initial pressure at reaction temperature, P_f is the final pressure at reaction temperature after the completion of the reaction, and P_t is the pressure at time t, during the reaction). In our autoclave system, 167 mmoles of carbinol would correspond to a pressure drop of 42.5 atm of hydrogen at the completion of the reaction at 135°. The apparent first-order reaction rate constant obtained from the slope is found to be independent of carbon monoxide partial pressure in the range of 70–260 atm, but increases with hydrogen partial pressure and amount of dicobalt octacarbonyl charged. Although the partial pressure of carbon monoxide has no effect on the reaction, the dependence of the rate of conversion of benzhydrol to diphenylmethane on the hydrogen partial pressure and on the catalyst concentration is quite analogous to that shown in earlier studies for conversions of olefins to aldehydes[11,12] and aldehydes to alcohols.[9,10]

It is generally accepted that cobalt hydrocarbonyl is the catalyst for both the hydroformylation and hydrogenation reactions. The cobalt hydrocarbonyl is a strong acid[13] and it may readily react with the aromatic carbinol to form an intermediate oxonium salt. Thus, the most probable mechanistic scheme for the hydrogenation of benzhydrol arrived at is given by

$$H_2 + Co_2(CO)_8 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2HCo(CO)_4 \tag{1}$$

$$HCo(CO)_4 + Ph_2CHOH \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \underset{\mathrm{I}}{[Ph_2\overset{H}{C}OH_2{}^+Co(CO)_4{}^-]} \tag{2}$$

$$\mathrm{I} \xrightarrow{k_5} \underset{\mathrm{II}}{Ph_2CHCo(CO)_4} + H_2O \tag{3}$$

$$\mathrm{II} \xrightarrow[k_6]{+H_2} Ph_2CH_2 + HCo(CO)_4 \tag{4a}$$

$$\mathrm{II} \xrightarrow[k_6']{+HCo(CO)_4} Ph_2CH_2 + Co_2(CO)_8 \tag{4b}$$

eq 1–4b. We consider it likely that k_5, *i.e.*, the formation of II from I by loss of water, is the rate-determining step. It would explain our later observation that the rate of hydrogenation is affected by the structure of the carbinol (see following). At this stage, we are unable to decide whether complex II is reduced by cobalt hydrocarbonyl or by hydrogen. As a matter of fact, we believe that the route of this type of reduction is still an unsettled subject.[9-11] Whether the mechanism includes reaction 4a or reaction 4b, however, the rate equation for both cases can be written as eq 5. The

$$\frac{d[Ph_2CH_2]}{dt} = \frac{k_3k_5}{k_4 + k_5}[HCo(CO)_4][Ph_2CHOH] \tag{5}$$

constant k_5 in the denominator may be eliminated when k_5 is far smaller than k_4.

Assuming that catalyst equilibrium is maintained, then

$$\frac{[HCo(CO)_4]^2}{[H_2][Co_2(CO)_8]} = \frac{k_1}{k_2} = K_1 \tag{6}$$

and therefore eq 5 becomes

$$\frac{d[Ph_2CH_2]}{dt} = k_5K_1{}^{1/2}K_2[Co_2(CO)_8]^{1/2}[H_2]^{1/2}[Ph_2CHOH] \tag{7}$$

where $K_2 = k_3/k_4$.

Assuming that the catalyst concentration is constant for the moment, eq 7 may be rewritten

$$\frac{dx}{dt} = k_\alpha(A - x)\sqrt{B - x} \tag{8}$$

where x = concentration of benzhydrol which has reacted, A = initial concentration of benzhydrol, B = initial concentration of H_2, and $k_\alpha = k_5K_1{}^{1/2}K_2[Co_2(Co)_8]^{1/2}$. The integrated equation for $B > A$ is

$$\ln\frac{-\sqrt{B - x} - \sqrt{B - A}}{-\sqrt{B - x} + \sqrt{B - A}} = \sqrt{(B - A)}\,k_\alpha t + \ln\frac{-\sqrt{B} - \sqrt{B - A}}{-\sqrt{B} + \sqrt{B - A}}$$

and for $B < A$ is

$$\tan^{-1}\frac{-\sqrt{B - x}}{\sqrt{A - B}} = \frac{\sqrt{A - B}}{2}k_\alpha t + \tan^{-1}\frac{-\sqrt{B}}{\sqrt{A - B}}$$

Substituting in pressure terms, $A = P_0 - P_f$, $A - x = P_t - P_f$, $B = P_H$, and $B - x = P_H + P_t - P_0$, where P_0, P_f, and P_t are defined earlier and P_H is the

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initial partial pressure of hydrogen. The equations then become

$$\ln \frac{-\sqrt{P_H + P_t - P_0} - \sqrt{P_H + P_f - P_0}}{-\sqrt{P_H + P_t - P_0} + \sqrt{P_H + P_f - P_0}} =$$

$$\sqrt{P_H + P_f - P_0}\, k_\alpha t + \ln \frac{-\sqrt{P_H} - \sqrt{P_H + P_f - P_0}}{-\sqrt{P_H} + \sqrt{P_H + P_f - P_0}} \qquad (9)$$

or

$$\tan^{-1} \frac{-\sqrt{P_H + P_t - P_0}}{\sqrt{P_0 - P_f - P_H}} =$$

$$\frac{\sqrt{P_0 - P_f - P_H}}{2}\, k_\alpha t + \tan^{-1} \frac{-\sqrt{P_H}}{\sqrt{P_0 - P_f - P_H}} \qquad (10)$$

A plot of the left-hand side of eq 9 *vs.* t yields a straight line of slope $\sqrt{P_H + P_f - P_0}\, k_\alpha$ with an intercept of $\ln (-\sqrt{P_H} - \sqrt{P_H + P_f - P_0})/(-\sqrt{P_H} + \sqrt{P_H + P_f - P_0})$. If the concentration of benzhydrol is greater than that of hydrogen, a plot of the left-hand side of eq 10 *vs.* t yields a straight line of slope $\sqrt{P_0 - P_f - P_H}\, k_\alpha/2$ with an intercept of $\tan^{-1} -\sqrt{P_H}/(P_0 - P_f - P_H)$.

The slope of the linear equations and the k_α value were obtained with a computer using the least-squares method. The consistency of the k_α values, independent of the total pressure, and the good linearity of the typical pressure–time plots shown in Figure 1 clearly demonstrate the validity of the proposed mechanism. The k_α values are dependent on the one-half power of the catalyst concentration, as shown in Figure 2. Table I summarizes the results of benzhydrol hydrogenation at a dicobalt octacarbonyl concentration of 151 mmoles/l. of solvent. The Arrhenius parameters obtained from the k_α values are

$$\log k_\alpha = 6.53 - \frac{21{,}500}{4.576T} \qquad (11)$$

Table I

Rates of Hydrogenation of Benzhydrol[a]

Temp, °C	Partial pressure,[b] atm H_2	CO	CO/H_2 ratio	Time,[c] min	Reaction at end, %	$k\alpha \times 10^6$ atm$^{-1/2}$ sec^{-1}
135	42.2	84.4	2	260	48	9.2
	89.8	29.9[d]	0.33	330	72	7.1
	92.0	46.0[d]	0.5	360	78	7.0
	88.1	88.1	1	340	82	9.6
	90.5	90.5	1	325	81	8.6
	88.2	176.4	2	280	79	10.0
	90.5	181.0	2	285	80	9.0
	91.2	273.5	3	230	73	9.3
	107.8	107.8	1	340	82	8.8
	128.4	128.4	1	365	88	8.8
	156.3	156.3	1	275	83	9.5
	188.5	188.5	1	290	88	9.7
	192.2	192.2	1	325	90	8.9
	264.8	88.3	0.33	310	96	10.9
125	147.8	147.8	1	345	72	5.4
	158.8	158.8	1	315	80	5.8
130	148.4	148.4	1	365	85	7.7
	151.1	151.1	1	365	85	7.3
140	149.6	149.6	1	300	93	13.5
	152.2	152.2	1	205	89	14.7
145	152.9	152.9	1	240	97	20.1
	152.9	152.9	1	260	98	20.2
	157.9	157.9	1	220	96	19.6

[a] Benzhydrol = 167 mmoles, equivalent to 42.5 atm of H_2 pressure drop at 135°; $Co_2(CO)_8$ = 151 mmoles/l. of solvent. [b] Pressure at indicated temperature. [c] Time required to reach the desired temperature (usually about 1 hr) is not included. [d] CO partial pressure is in the vicinity of the dicobalt octacarbonyl stability limit (see text).

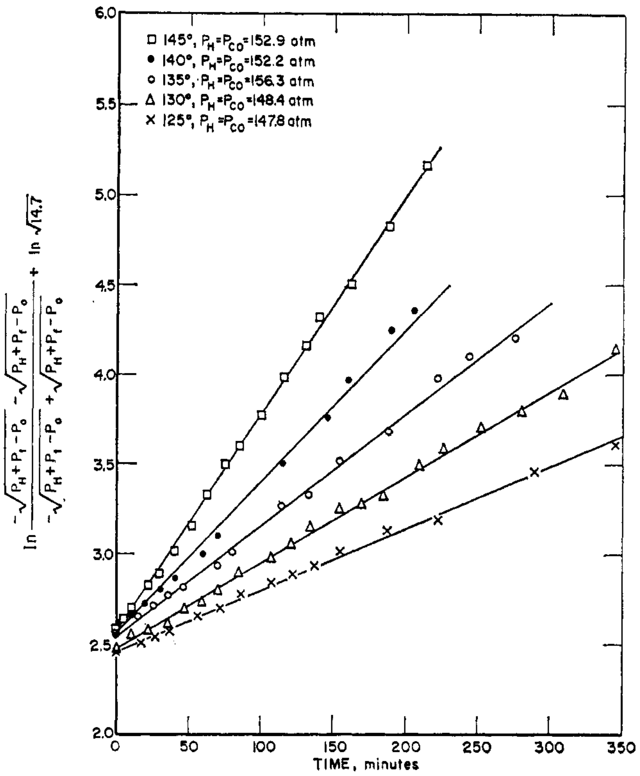


Figure 1.—Representative rate curves for hydrogenation of benzhydrol.

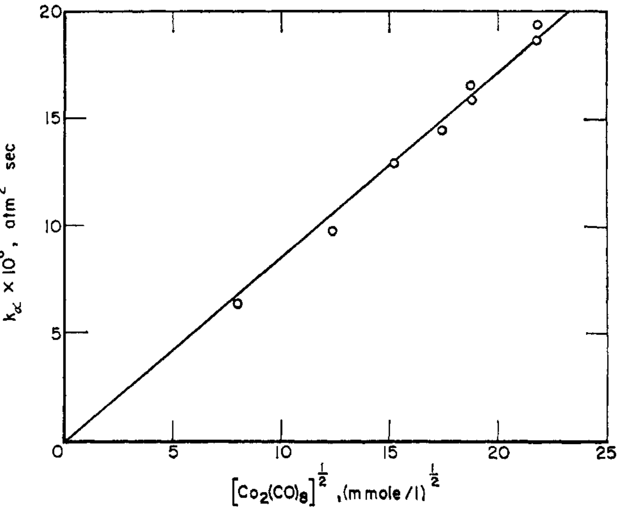


Figure 2.—Effect of catalyst concentration on the rate of hydrogenation of benzhydrol.

Hydrogenation of Substituted Benzhydrols.—The hydrogenation of triphenylcarbinol, phenylmethylcarbinol, and nuclear-substituted benzhydrols under similar conditions also produces substituted hydrocarbons exclusively. As expected, the pressure–time plots of eq 9 are linear and hence the same rate law applies. The results are shown in Table II. Triphenylcarbinol hydrogenates most rapidly. Electron-releasing substituents in the *para* position of benzhydrol also

TABLE II

RATES OF HYDROGENATION FOR VARIOUS AROMATIC CARBINOLS[a]

Aromatic alcohol	Temp, °C	Total pressure,[b] atm	Time,[c] min	Reaction at end, %	$k_\alpha \times 10^6$ atm$^{-1/2}$ sec^{-1}	ΔH, kcal mole^{-1}
p-Methyl-benzhydrol	115	295.2	220	84	12.2	19.9
	120	302.7	260	95	17.1	
	125	302.7	215	97	21.8	
	130	309.5	140	95	32.7	
p-Methoxy-benzhydrol	100	286.7	350	76	5.6	28.3
	105	288.4	270	82	9.3	
	110	285.7	250	93	16.5	
	115	283.8	195	96	23.7	
p-Chloro-benzhydrol	160	319.3	280	88	10.9	20.8
	165	322.8	285	94	14.3	
	170	324.5	230	93	18.1	
	175	326.2	180	96	24.8	
p,p'-Dichloro-benzhydrol	177	334.4	330	93	11.3	
Phenylmeth-ylcarbinol	150	303.7	320	55	3.2	
	160	315.1	335	79	5.4	
Triphenyl-carbinol	125	297.7	70	97	77.3	

[a] Benzhydrol = 167 mmoles, equivalent to 42.5 atm of H_2 pressure drop at 135°; $Co_2(CO)_8$ = 151 mmoles/l. [b] Total pressure of 1:1 H_2 and CO mixture at indicated temperature. [c] Time required to reach the desired temperature is not included.

markedly enhance the rate. A similar effect was observed for the over-all rate of reaction of benzyl alcohol.[5]

Effect of Solvent on Hydrogenation of Benzhydrol.—The effect of solvent on the rate of hydrogenation of benzhydrol is illustrated in Table III. Each experiment was run with 167 mmoles of benzhydrol, 2.6 g of dicobalt octacarbonyl, 50 ml of solvent, and 1:1 synthesis gas at an initial pressure of 220 atm at room temperature. The rate increases with increasing polarity of the solvent. In contrast, the effect of solvents on the rate of the hydroformylation reaction on olefins is small, indicating that highly polar intermediates are not involved.[12]

TABLE III

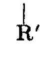
EFFECT OF SOLVENT ON RATE OF HYDROGENATION OF BENZHYDROL

Solvent	Temp, °C	$k_\alpha \times 10^6$, atm$^{-1/2}$ sec^{-1}
Butyl ether	135	6.7
Ethyl ether	135	8.6
Benzene	135	9.4
Isopropyl ether	135	11.9
Benzene–diphenylmethane[a]	135	12.8
Diphenylmethane	135	13.6
Chlorobenzene	135	15.8
Ethanol	105	40.7
Methanol	95	65.7
Acetone	110	102

[a] 1:1 by volume.

Discussion

It has been demonstrated that the kinetic data for the hydrogenation of benzhydrol and aromatic carbinols of formula



$$\mathrm{Ph{-}C(R)(R'){-}OH}$$

where R and R′ are alkyl or phenyl groups, under the hydroformylation conditions, are consistent with a mechanism involving the transformation of a carbinol-cobalt hydrocarbonyl oxonium salt (I) to a PhC(RR′)-$Co(CO)_4$ complex (II) by loss of water as the rate-determining step. The rate of the over-all reaction is dependent on the first power of the carbinol concentration and the one-half power of hydrogen pressure and dicobalt octacarbonyl concentration. Actually, the dicobalt octacarbonyl concentration varies slightly during the reaction, but a steady state is reached during the period of experimental measurements. The hydrogenation apparently is independent of the carbon monoxide pressure as long as that pressure is above the stability limit of dicobalt octacarbonyl.[14]

Comparison of eq 7 and 8 reveals that $k_\alpha = k_5K_1^{1/2}\cdot K_2[Co_2(CO)_8]^{1/2}$. The average k_α of our data at 135° is 9.4×10^{-6} atm$^{-1/2}$ sec^{-1}. Thus it can be calculated approximately that a catalyst concentration independent composite rate constant $k_5K_1^{1/2}K_2$ is 2.5×10^{-5} l.$^{1/2}$ mole$^{-1/2}$ atm$^{-1/2}$ sec^{-1}. Although the equilibrium data for $H_2 + Co_2(CO)_8 \rightleftarrows 2HCo(CO)_4$ are available in the literature,[10,15] no means can be found presently to resolve this composite rate constant into its components. The implied activation energy of 21.5 kcal in eq 11 would then represent the sum of ΔH for the rate-determining step (k_5), the square root of ΔH for the catalyst equilibrium (K_1), and ΔH of eq 2 (K_2).

Whether complex II is reduced by hydrogen (eq 4a) or by cobalt hydrocarbonyl (eq 4b) is rather difficult to determine on the basis of the available kinetic data. It is interesting, however, to note that the change of the concentration of cobalt hydrocarbonyl at the steady state for each case can be expressed, respectively, as

$$\frac{\mathrm{d}[HCo(CO)_4]}{\mathrm{d}t} = k_1[H_2][Co_2(CO)_8] - k_2[HCo(CO)_4]^2 = 0 \quad (12)$$

and

$$\frac{\mathrm{d}[HCo(CO)_4]}{\mathrm{d}t} = k_1[H_2][Co_2(CO)_8] - k_2[HCo(CO_4]^2 - k_5K_2[HCo(CO)_4][Ph_2CHOH] = 0 \quad (13)$$

Equation 12 simply satisfies the catalyst equilibrium condition, that there should be an equilibrium amount of cobalt hydrocarbonyl present during the reaction. On the other hand, eq 13 indicates that the maintenance of the catalyst equilibrium is somewhat affected by a quick removal of $HCo(CO)_4$ by reaction 4b to regenerate dicobalt octacarbonyl. From the kinetic viewpoint, however, one may argue that the concentration of $HCo(CO)_4$ is nearly equal to $K_1^{1/2}[H_2]^{1/2}[Co_2(CO)_8]^{1/2}$ if one assumes that $k_2[HCo(CO)_4] >> k_5K_2[Ph_2CHOH]$. Thus, both mechanisms including reactions 4a and 4b seem to satisfy the rate expression of eq 7.

The transformation of I to $Ph_2CHCo(CO)_4$ may proceed *via* a carbonium ion as suggested earlier.[5] It would then be expected that triphenylcarbinol and benzhydrols with electron-releasing substituents in the aromatic ring favor the formation of carbonium ions and accelerate the water-removing process from the corresponding oxonium salts. The polar solvents would also be capable of promoting the formation of the

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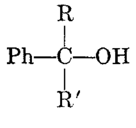
oxonium salt and the resultant carbonium ion by solvation. Thus the hydrogenation of benzhydrol may be explained as a process involving cleavage of the C–O bond of the benzhydrol in the presence of an acid catalyst, the rate of which is enhanced by solvation of the carbonium ion. It appears that the mechanism of the hydrogenation of benzhydrol or aromatic carbinols of formula



$$\mathrm{Ph{-}\overset{R}{\underset{R'}{C}}{-}OH}$$

does not involve an intermediate cobalt tricarbonyl, unlike the hydrogenation of aldehydes[9,10] or the hydroformylation of olefins,[11] which are inhibited by CO.

An interesting fact is that benzyl alcohol reacts under oxo conditions to give both toluene and 2-phenylethanol.[4,5] When R and R′ are H as for benzyl alcohol, it is possible that carbon monoxide may insert between the carbon and cobalt of the corresponding complex II, probably owing to less steric hindrance. Benzhydrol, in contrast to benzyl alcohol, gives no homologated product, perhaps owing to steric hindrance in complex II.

Registry No.—Benzhydrol, 91-01-0; *p*-methylbenzhydrol, 1517-63-1; *p*-methoxybenzhydrol, 720-44-5; *p*-chlorobenzhydrol, 119-56-2; *p,p*′-dichlorobenzhydrol, 90-97-1; phenylmethylcarbinol, 98-85-1; triphenylcarbinol, 76-84-6.

Acknowledgement.—We are indebted to Dr. M. Orchin for his interest and aid in carrying out this work.

Methyl(2-thienyl)- and Methyl(2-furyl)cyclopolysiloxanes

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The trimeric, tetrameric, and pentameric methyl(2-thienyl)- and methyl(2-furyl)cyclosiloxanes were prepared and characterized by nmr spectroscopy. All of the possible stereoisomers were detected in the mixtures. In both the 2-thienyl and 2-furyl series, the 2,4,6′-trimethyl-2′,4′,6-triarylcyclotrisiloxane and the 2,4′,6,8′-tetramethyl-2′,4,6′,8-tetraarylcyclotetrasiloxane stereoisomers were isolated and identified by nmr spectroscopic techniques. 2-Thienyl-substituted cyclosiloxanes were found to undergo facile acid-catalyzed cleavage under mild hydrolysis conditions. Base-catalyzed redistribution of thienyl–silicon and oxygen–silicon bonds also was observed.

The synthesis[1,2] and characterization[2–6] of methylphenylcyclopolysiloxanes have been the subject of numerous papers, but relatively little attention has been paid to cyclosiloxanes containing aromatic heterocyclic groups. Mixtures of methyl(2-thienyl)cyclosiloxanes have been reported,[7] but the cyclic trimer, tetramer, and pentamer fractions were not described. Poly(2-thienylsilsesquioxanes) have been prepared.[8] Furyl-substituted siloxanes have not been reported. In this paper we report the synthesis of the methyl(2-thienyl)- and methyl(2-furyl)cyclotrisiloxanes, -cyclotetrasiloxanes, and -cyclopentasiloxanes and the isolation and nmr characterization of some of the individual stereoisomeric trimers, **1** and **2**, and tetramers, **3**–**6** (Chart I).

Results

Hydrolysis of methyl(2-thienyl)- and methyl(2-furyl)dichlorosilane in aqueous potassium carbonate or potassium bicarbonate solution produced a crude hydrolysate from which the corresponding cyclosiloxanes could be distilled in 46–49% yield. The distillation residue consisted of a brittle resin typical of a cross-linked silicone polymer. Fractional distillation of the cyclosiloxane mixtures afforded the cyclic trimers, tetramers, and pentamer, listed in Table I, together with their physical and analytical data. In the absence of an acid acceptor, hydrolysis of methyl(2-thienyl)dichlorosilane gave hydrolysate which polymerized to a rubbery polymer upon attempted distillation; thiophene was the only volatile product isolated. In an effort to equilibrate siloxane linkages, distillation of the rubbery polymer over potassium hydroxide was attempted. The only volatile product which could be isolated was methyltris(2-thienyl)silane, identified by elemental, infrared, and nmr analyses. Hydrolysis of methyl(2-thienyl)dichlorosilane in the presence of excess potassium carbonate, followed by distillation of the hydrolysate without prior neutralization, gave a 25% yield of volatiles, the remainder of the product being an intractable polymer. The distillate consisted predominantly of methyltris(2-thienyl)silane and a product tentatively identified as 1,3-dimethyl-1,1,3,3-tetrakis(2-thienyl)disiloxane.

The nmr spectra of the cyclic trimers, tetramers, and pentamer listed in Table I were in agreement with theory, giving a ratio of methyl to ring protons of 1:1. The structures also were confirmed by the infrared spectra, with characteristic[3] Si–O–Si stretching bands noted at 1020 cm^{-1} for the trimers and 1075 cm^{-1} for the tetramers and pentamer.

The cyclotrisiloxane fraction in both the methyl(2-thienyl)- and methyl(2-furyl) series exhibited three methyl proton singlets, see Table II, expected for a mixture of isomers **1** and **2** having the *cis* and *trans*

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