[CONTRIBUTION OF THE SYNTHETIC LIQUID FUELS BRANCH, BUREAU OF MINES]

Chemistry of the Oxo and Related Reactions. IV. Reductions in the Aromatic Series[1]

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Previous work has shown that certain aliphatic alcohols react with hydrogen and carbon monoxide in the presence of a cobalt catalyst to give an homologous alcohol; only in the case of methanol is any of the alcohol reduced to a hydrocarbon. The present study is concerned with the reaction of alcohols and ketones in the aromatic series under the same conditions and shows that, in all cases, hydrocarbons are the principal products. Benzyl alcohol gives both 2-phenylethanol and toluene, but substituted benzyl alcohols of the type $C_6H_5CR_1R_2OH$ where R_1 and R_2 may be hydrogen, alkyl or aryl groups react to give hydrocarbons in excellent yields. The mechanism of hydrocarbon formation is discussed. A simple, convenient procedure for the preparation of dicobalt octacarbonyl is given.

The hydrogenation reactions that proceed in the presence of carbon monoxide and hydrogen and a cobalt catalyst under appropriate (oxo) conditions constitute a unique example of homogeneous catalysis.[2] The reduction of aliphatic aldehydes and ketones under these conditions gives the corresponding alcohols in good yields.[3] Although the alcohols may, in turn, further react under identical conditions to give homologous alcohols,[4] the primary and secondary alcohols, with the exception of methanol,[5] react so sluggishly that they may be isolated directly from the reduction of their aldehydic and ketonic precursors. The active catalyst in all cases is either dicobalt octacarbonyl or cobalt hydrocarbonyl. Not only does the carbon monoxide fail to poison the hydrogenation, but its presence in sufficient concentration is essential to the success of the reaction.

The present paper presents the results of reactions of aromatic ketones and alcohols with a cobalt catalyst in the presence of synthesis gas. The experimental data are summarized in Table I.

Experimental

Apparatus.—The autoclave and compressor employed in these experiments have been described in an earlier paper.[3] The autoclave had a maximum free space, when empty, of 468 ml.; when a glass liner was used (for small amounts of material), the free space was 306 ml. Air at 25 p.s.i., applied externally, was used to cool the reaction apparatus at the end of a reaction. The synthesis gas used was manufactured and compressed at the Bureau of Mines.

Preparation of Dicobalt Octacarbonyl.—Metallic cobalt and cobalt salts of aliphatic and naphthenic acids react very slowly with pure carbon monoxide at 140–160°. In the presence of carbon monoxide and hydrogen, however, the cobalt salts of these acids react rapidly.[6] The dicobalt octacarbonyl prepared in the presence of hydrogen contains some cobalt hydrocarbonyl, $HCo(CO)_4$; the benzene solution of these carbonyls slowly evolves both hydrogen and carbon monoxide. Although the carbonate, acetate, octoate, naphthenate, and stearate react completely in less than one hour at 140–160°, cobalt formate, for some reason, reacts much more slowly.

In a typical preparation of dicobalt octacarbonyl, a slurry of 30 g. (0.25 mole) of cobalt(II) carbonate in 100 ml. of benzene was placed in the autoclave and 3.2 moles of synthesis gas ($1H_2$:1CO) added (3200 p.s.i.). The autoclave was heated, with rocking, to 160° within 68 minutes. The maximum pressure recorded was 4230 p.s.i. at 127°. After heating at 160° for 1 hour, the vessel was cooled to 22° (2280 p.s.i.) and the gases discharged. The pressure drop corresponded to approximately 0.9 mole or 3.6 moles of gas absorbed per mole of cobalt carbonate. The clear, dark benzene solution of dicobalt octacarbonyl was pipetted from the bomb and centrifuged. This solution was usually stored at −30° in a pressure bottle and used as a stock solution of catalyst; it contained about 0.25 g. of dicobalt octacarbonyl per ml. If pure, crystalline dicobalt octacarbonyl is desired, the benzene may be evaporated at the water pump. The temperature of the heating-bath should not exceed 30°. Most of the benzene can be removed by pressing the solid carbonyl between filter papers. This operation should be done quickly since the filter paper may catch fire due to the decomposition of the carbonyl to pyrophoric metallic cobalt. In one experiment the yield of dicobalt octacarbonyl, orange crystals, m.p. 51°,[7] was 23 g. (54%).

The crystalline carbonyl can be stored in a closed glass vessel. Some decomposition occurs with the liberation of carbon monoxide, but equilibrium is soon reached and no further decomposition takes place. The crystalline material is preferably stored in the cold under an atmosphere of carbon monoxide

Reduction and Decarbonylation Experiments.—The results of the experiments are summarized in Tables I and II. When the quantity permitted, the products were separated by distillation. When less than 0.1 mole was used, the products were separated by chromatographic adsorption. Most of the reactions were run only once, and the yield reported for a product is not to be considered as the maximum that may be secured. The experiment with fluorenone will be described in detail since it illustrates many of the techniques employed.

Reduction of Fluorenone.—A solution of 10.37 g. (0.058 mole) of fluorenone in 60 ml. of benzene and 7 g. (0.028 mole) of cobalt(II) acetate tetrahydrate were placed in a glass liner which was lowered into the autoclave. Synthesis gas ($2H_2$:1CO) was added until the pressure reached 3000 p.s.i.; this corresponded to approximately 2 moles of gas. The autoclave was heated with rocking to 185° within 65 minutes and held at this temperature for 4 hours. The maximum pressure reached was 3980 p.s.i. at 185°. The autoclave was allowed to cool to room temperature overnight, and the gases were then discharged.

A solution of the products in benzene–petroleum ether (60–68°) was chromatographed on a column of alumina-supercel (1:1). The column was eluted with petroleum ether giving 9.15 g. (94.8%) of fluorene, m.p. 114.2–115.4°; a mixed melting point with an authentic sample of fluorene exhibited no depression. The identity of this fraction was verified by comparison of its ultraviolet spectrum with that of a known sample of fluorene.

Further elution with benzene–petroleum ether gave traces of materials not further investigated. The most strongly adsorbed fraction was eluted with a 50-50 mixture of benzene and ethyl alcohol. Recrystallization of this fraction from petroleum ether (90–100°) yielded 220 mg. (2%) of 9-fluorenol, m.p. 154.0–154.8°, not depressed when mixed with an authentic sample prepared by reducing fluorenone with lithium aluminum hydride.

Discussion of Results

Although the reduction of aliphatic compounds

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[1] Presented before the Division of Organic Chemistry at the 118th Meeting of the American Chemical Society, Chicago, Ill., September, 1950. Not copyrighted.

[2] I. Wender, M. Orchin and H. H. Storch, THIS JOURNAL, **72**, 4842 (1950).

[3] I. Wender, R. Levine and M. Orchin, *ibid.*, **72**, 4375 (1950).

[4] I. Wender, R. Levine and M. Orchin, *ibid.*, **71**, 4160 (1949).

[5] I. Wender, R. A. Friedel and M. Orchin, *Science*, **113**, 206 (1951).

[6] W. F. Gresham and J. V. E. Hardy, U. S. Patent 2,473,993.

[7] L. Mond, H. Hirtz and M. D. Cowap, *J. Chem. Soc.*, **97**, 798 (1910).

TABLE I

REACTION OF AROMATIC ALCOHOLS AND KETONES WITH SYNTHESIS GAS[a] AND COBALT CATALYST[b] AT 180–185°

Starting compound	Mole	Benzene Ml.	Synthesis gas, H_2:CO	Time, hr.	Products			
					Composition	Yield, %	Boiling and/or melting point, °C.[c]	Mm.
Benzyl alcohol	0.78	0	1:1	3	Toluene[d]	49	109–110	
					2-Phenylethanol[e]	26	74–76	3
					Water	99		
Benzyl alcohol	.60	50	2:1	5	Toluene	63	109–110	
					2-Phenylethanol	32	109–110	8
					Water	100		
1-Naphthalenemethanol	.45	65	2:1	3	1-Methylnaphthalene[f,p]	72	123–127	23–24
1-Phenylethanol	.75	0	2:1	3	Ethylbenzene[d]	70	135–136	
Benzhydrol	.05	70	1:1	3	Diphenylmethane[d]	95	105–108	4–5
Triphenylcarbinol	.04	94	1:1	3	Triphenylmethane	94	92.3–93.4 (alc.)	
Benzopinacol	.03	93	1:1	3	Diphenylmethane[d]	89	25.0–26.3	
					Benzophenone[h]	5		
Acetophenone	1.0	0	1:1	1	Ethylbenzene[d]	53	135–136	
					Acetophenone[i]	14	80–82	9–10
Acetophenone	.69	0	2:1	3	Ethylbenzene	67	135–136	
					Acetophenone	9	91–92	20
Methyl 2-thienyl ketone	1.0	0	2:1	1	2-Ethylthiophene[d]	66	133–134	
					Methyl 2-thienyl ketone[j]	25	98–99	18
p-Methoxyacetophenone	.70	20	2:1	4	*p*-Ethylanisole[k]	91	193–194	
					2-(*p*-Methoxyphenyl)-propanol-1[l]	6		
Benzophenone	.60	90	1:1	2	Diphenylmethane[d]	86	25.5–26.5	
					Benzophenone[m]	8		
Fluorenone	.06	60	2:1	4	Fluorene[g]	95	114.2–115.4	
					9-Fluorenol	2	154.0–154.8	
Benzanthrone	.07	50	1:1	3	1,10-Trimethylenephenanthrene[n]	59	80.0–80.8[o]	

[a] The total initial pressure, measured at room temperature, was always between 3000 and 3500 p.s.i. [b] In each experiment, 1.5–2.5 g. of cobalt was added as either cobalt(II) carbonate, cobalt(II) acetate tetrahydrate or dicobalt octacarbonyl. [c] All melting points are corrected. Unless otherwise indicated, the melting points of all crystalline compounds were compared with authentic samples by the mixed melting point technique and gave no depressions. [d] Infrared absorption spectrum identical with that of an authentic sample. [e] α-Naphthylurethan, m.p. 117.5–118.5°. Distillation of a 10-g. sample of this alcohol from molten KOH gave an 86% yield of styrene, identified by means of the dibromide, m.p. 70.5–71.5°. [f] Picrate, m.p. 141.2–142.6°. [g] Ultraviolet absorption spectrum identical with that of an authentic sample. [h] 2,4-Dinitrophenylhydrazone (2,4-DNP), m.p. 236.0–237.6°. [i] 2,4-DNP, m.p. 246.0–248.5°. [j] 2,4-DNP, m.p. 242.5–244.5°. [k] *Anal.* Calcd. for $C_9H_{12}O$: C, 79.37; H, 8.89. Found: C, 79.22; H, 9.16. [l] An authentic sample of this alcohol was prepared by lithium aluminum hydride reduction of the corresponding aldehyde; α-naphthylurethan, m.p. 109.1–110.0°, identical with that prepared from the isolated alcohol. *Anal.* Calcd. for $C_{21}H_{21}NO_2$: C, 75.20; H, 6.31. Found: C, 75.28; H, 6.41. [m] 2,4-DNP, m.p. 236.5–238.2°. [n] Picrate, m.p. 126.7–128.0°; see E. Clar, "Aromatische Kohlenwasserstoffe," Edward Bros., Inc., Ann Arbor, Mich., 1941, p. 299. [o] Ultraviolet absorption spectrum and melting point correspond to those given by E. Clar (see ref. "*n*"). [p] Some 1-methyl and 5-methyl-1,2,3,4-tetrahydronaphthalene also present.

TABLE II

DECARBONYLATION EXPERIMENTS (185° FOR THREE HOURS)

Starting compound	Mole	Benzene, ml.	Synthesis gas, H_2:CO	Initial pressure, p.s.i.	Products			
					Composition	Yield, %	Boiling and/or melting point, °C.	Mm.
2-Phenylpropionaldehyde[a]	0.75	0	1:4	2000	Ethylbenzene[b]	3	134–136	
					2-Phenylpropanol-1[c]	38	120–145	33–34[d]
					2-Phenylpropionaldehyde	18		
Diphenylacetaldehyde[e]	.03	100	1:8	1800	Diphenylmethane[b]	7		
					2,2-Diphenylethanol[f]	87	187–191	19
Diphenylacetaldehyde[e]	.05	100	1:1	2500	Diphenylmethane	8		
					2,2-Diphenylethanol	88	162–164	7

[a] Seven grams cobalt(II) acetate tetrahydrate used as catalyst. [b] Infrared absorption spectrum identical with that of an authentic sample. [c] α-Naphthylurethan, m.p. 100.0–100.8°. C. Golumbic and D. L. Cottle, THIS JOURNAL, **61**, 996 (1939). [d] Boiling range of a mixture of 2-phenylpropionaldehyde and 2-phenylpropanol-1. Amount of 2-phenylpropionaldehyde determined by hydroxylamine hydrochloride titration. [e] Five grams cobalt(II) carbonate used as catalyst. [f] 3,5-Dinitrobenzoate, m.p. 134.4–136.0°. M. S. Kharasch and H. A. Clapp, *J. Org. Chem.*, **3**, 359 (1939).

with synthesis gas leads to alcohols, the data in Table I show that similar treatment of aromatic compounds yields hydrocarbons in all cases; in some cases the hydrocarbon was isolated in over 90% yield. The hydrogenation of the aromatic ketones (acetophenone, methyl 2-thienyl ketone, benzophenone and fluorenone) very likely proceeds *via* the carbinol since the alcohol was isolated occasionally as a minor constituent and in other cases (benzhydrol, triphenylcarbinol) the carbinol was employed as the starting material. The conversion of benzopinacol, $Ph_2C(OH)C(OH)Ph_2$, to diphenylmethane may be explained by the fact that the pinacol decomposes on heating to benzophenone and benzhydrol,[8] both of which are readily reduced to diphenylmethane under oxo conditions.

We have previously suggested the possibility of a free radical mechanism for the hydrogenation of aliphatic aldehydes and ketones to alcohols.[3] Essentially the same mechanism may be applied to the reduction of aromatic alcohols. The stability of the substituted benzyl radical may account for the fact that hydrocarbons are the chief product of the hydrogenation in the aromatic series. Using triphenylcarbinol as an example, the mechanism may be detailed as

$$2Co + 8CO \rightleftarrows [Co(CO)_4]_2 \qquad (1)$$

$$[Co(CO)_4]_2 \rightleftarrows 2\ \cdot Co(CO)_4 \qquad (2)$$

$$\cdot Co(CO)_4 + H_2 \rightleftarrows H\cdot + HCo(CO)_4 \qquad (3)$$

$$H\cdot + Ph_3COH \longrightarrow Ph_3C\cdot + H_2O \qquad (4)$$

$$Ph_3C\cdot + HCoCO_4 \longrightarrow Ph_3CH + \cdot Co(CO)_4 \qquad (5)$$

Although the production of hydrocarbons from aromatic alcohols and ketones is most easily explained by the hydrogenolysis mechanism given above, an alternate possibility should be considered. This second possibility involves the formation of an aldehyde and its subsequent decarbonylation under reaction conditions. When benzyl alcohol is used, a mixture of toluene and the homologous alcohol, 2-phenylethanol, is obtained. Both products may be explained as having been derived from the intermediate formation and reaction of phenylacetaldehyde

$$C_6H_5CH_2OH \longrightarrow C_6H_5CH_2CHO \begin{cases} \xrightarrow{H_2} C_6H_5CH_2CH_2OH \\ \longrightarrow C_6H_5CH_3 + CO \end{cases}$$

The question arises as to whether the toluene results from the direct hydrogenolysis of benzyl alcohol or from the decarbonylation of phenylacetaldehyde; analogous decarbonylations have been well-established as proceeding through a free radical mechanism.[9] In an attempt to establish the validity of the decarbonylation explanation, phenylacetaldehyde was treated under conditions similar to those that result in the conversion of benzyl alcohol to toluene and 2-phenylethanol; the phenylacetaldehyde, however, polymerized very readily, and no identifiable reaction products were secured. The attempted decarbonylation was repeated using diphenylacetaldehyde (Table II) which is less readily polymerized than phenylacetaldehyde. A small yield of the hydrocarbon, diphenylmethane, was indeed secured but the major product of the reaction was 2,2-diphenylethanol. Since the reduction of benzhydrol under similar conditions gives diphenylmethane exclusively, it is unlikely that this hydrocarbon is formed to any great extent *via* diphenylacetaldehyde according to the scheme $Ph_2CHOH \rightarrow Ph_2CHCHO \rightarrow Ph_2CH_2$. An attempted decarbonylation using 2-phenylpropionaldehyde (Table II) was also performed; a small yield of ethylbenzene was secured but the principal reaction was the hydrogenation of the aldehyde to 2-phenylpropanol-1. The evidence at hand indicates that the hydrocarbons listed as products in Table I probably result from direct hydrogenolysis of the aromatic alcohol.

The conversion of benzanthrone to 1,10-trimethylenephenanthrene under oxo conditions is an interesting example of nuclear hydrogenation. Attempts[10] to prepare this hydrocarbon from benzanthrone by the Wolff-Kishner method or its modifications, by Raney nickel reduction, by the Clemmensen procedure and by zinc dust distillation were either unsuccessful or gave the desired hydrocarbon in poor yield.

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(8) W. E. Bachmann, THIS JOURNAL, **55**, 391 (1933).

(9) S. Winstein and F. H. Seubold, *ibid.*, **69**, 2916 (1947).

(10) M. Orchin and L. Reggel, unpublished work.