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Studies of Organic Catalytic Reactions. IV.[1] A Redox Reaction between Unsaturated Organic Compounds and Primary Alcohols in the Presence of Nickel Catalysts

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Styrene, mesityl oxide, benzonitrile and nitrobenzene are reduced when heated with primary alcohols, such as methanol, ethanol, 1-butanol and benzyl alcohol, in the presence of nickel catalysts. On the other hand, aldehydes are obtained by the dehydrogenation of the primary alcohols. The relative reactivity of the functional groups for the reduction is as follows: $C=C > C\equiv N > NO_2 > C=O$. The carbonyl group and the benzene nucleus can not be reduced under these reaction conditions. A selective reduction occurs in the reaction with mesityl oxide. The lower limit of the reaction temperature depends on the combination of the two species of the hydrogen donor (primary alcohol) and the acceptor compounds. The use of a large excess of alcohols for the reduction is effective in this redox reaction. In the reaction between styrene and benzyl alcohol, the ratio of the decreased amount of styrene to the increased amount of ethylbenzene is always 1 : 1, as determined by gas chromatographic analysis.

It has been found that a redox reaction occurs between some kinds of unsaturated organic compounds and primary alcohols when they are heated in the presence of nickel catalysts. The ethylenic bond is reduced to the saturated bond, while nitrile and nitro groups are reduced to the corresponding amino groups. The carbonyl group and the benzene nucleus can not be reduced under these reaction conditions. A trace of benzyl alcohol was obtained in the reaction with benzaldehyde. On the other hand, primary alcohols afford the corresponding aldehydes by dehydrogenation. When primary alcohols alone are refluxed with the catalysts, the velocity of dehydrogenation is extremely slow. Of course, this redox reaction does not proceed without catalysts.[*1]

It is well-known that secondary alcohols are excellent hydrogen donors in the reaction with metallic catalysts. Some studies of the redox reaction with metallic catalysts have been reported in which 2-propanol,[2] cholesterol[3] and benzhydrol[3] are employed. Borneol is also useful.[*2] Newham and Burwell[2] reported that, in the presence of large amounts of hydrogen at temperatures of 115—150°C, the reaction 2-propanol + 2-butanone = acetone + 2-butanol occurs as a coupled surface reaction on metallic copper at about 2.5 times the rate of the net hydrogenation. The redox reaction between cholesterol and cyclohexanone with Raney nickel affords cholestenone in 80% yield.[3]

In the present paper, it may be concluded that primary alcohols may generally be used for the reduction of some types of organic compounds, though the reactivity is lower than when secondary alcohols are used. On the other hand, this redox reaction is specifically useful for the preparation of aldehydes from primary alcohols under mild reaction conditions.

Styrene, mesityl oxide, benzonitrile, nitrobenzene, acetophenone and benzaldehyde were used as the hydrogen acceptors, while methanol, 1-butanol and benzyl alcohol were used as the hydrogen donors. Ethanol could also be used. In order to investigate the reaction process, the use of benzyl alcohol was advantageous. The catalysts used were Raney nickel W-7 (R-Ni), Urushibara nickel-B

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[1] Paper III: "The Hydration Mechanism of Nitriles to Amides with Nickel Catalysts," K. Watanabe and K. Sakai, This Bulletin, **39**, 8 (1966).

[*1] Braude and Linstead established that high-potential quinones are hydrogen acceptors for unsaturated primary alcohols or secondary alcohols without metallic catalysts. E. A. Braude and R. P. Linstead, *J. Chem. Soc.*, **1956**, 3070.

[2] J. Newham and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **86**, 1179 (1964); K. Tarama, S. Teranishi, T. Kubomatsu and S. Kishida, *Catalyst* (*Shokubai*), *Japan*, **7**, 289 (1965).

[3] E. C. Kleiderer and E. C. Kornfeld, *J. Org. Chem.*, **13**, 455 (1948).

[*2] Unpublished: The redox reaction between borneol and carbonyl compounds has been studied in our laboratory with regard to the studies of the dehydrogenation and dehydration of exo- and endo-borneol on metallic catalysts. When borneol and cyclohexanone are heated in xylene (140°C) in the presence of nickel catalysts, the redox reaction occurs predominantly.

(U-Ni-B)[*3] and a stabilized nickel (S-Ni)[*4], all can also be used for the catalytic hydrogenation. The use of a large excess of alcohols for the reaction seems to be useful for the effective reduction of the organic compounds.

Results and Discussion

The results of the experiments are shown in Table I. As is shown in Exp. Nos. 5, 11 and 12, the reduction of carbonyl groups hardly ever proceeds under these reaction conditions. This may be due to the oxidation-reduction potentials of the correlating compounds (donor-acceptor) in the reactions. A study of oxidation-reduction potentials in the catalytic reactions was presented by Adkins and his co-workers.4) With regard to the reaction temperatures, their lower limits depend on the combination of the two species. When the reaction temperature is lower than the limit for the reaction, only a little reduction takes place with the adsorbed hydrogen on the catalysts used.

According to Table I, it may be concluded that the relative reactivity of the functional groups for the reduction is as follows: $C{=}C > C{\equiv}N > NO_2 > C{=}O$. The selective reduction can be applied

TABLE I. THE REDOX REACTION BETWEEN ORGANIC COMPOUNDS AND PRIMARY ALCOHOLS IN THE PRESENCE OF NICKEL CATALYSTS

Exp. No.	Catalysts	Nickel content g.	Compound (sample)	g.	Solvent (alcohol)	ml.	Reaction time hr.	Reaction temp. °C
1	U-Ni-B	4	Styrene	25	Benzyl alcohol	50	5	100
2	R-Ni	4	Styrene	25	Benzyl alcohol	50	6	100
3	R-Ni	10	Styrene	10	Benzyl alcohol	100	11	100
4	R-Ni	4	Styrene	10	Methanol	100	20	Reflux
5	R-Ni	4	Mesityl oxide	25	Benzyl alcohol	50	15	100
6	U-Ni-B	4	Benzonitrile	25	Benzyl alcohol	50	10	160
7	U-Ni-B	4	Benzonitrile	20	1-Butanol	80	14	Reflux
8	S-Ni	12.5	Benzonitrile	20	Benzyl alcohol	100	12	160
9	U-Ni-B	4	Nitrobenzene	20	Benzyl alcohol	80	15	180
10	R-Ni	4	Nitrobenzene	10	1-Butanol	100	20	Reflux
11	U-Ni-B	4	Acetophenone	20	Benzyl alcohol	80	8	100
12	R-Ni	4	Benzaldehyde	20	1-Butanol	80	8	Reflux

Exp. No.	Main product	g.	(%)	Recovered* sample %	Aldehyde* produced	g.	By-products
1	Ethylbenzene*	14	(55)	45	Benzaldehyde	9	Toluene* (trace)
2	Ethylbenzene*	17.5	(68.5)	31	Benzaldehyde	15	Toluene* (trace)
3	Ethylbenzene*	9.8	(95)	trace	Benzaldehyde	10	Toluene* (trace)
4	Ethylbenzene*	14	(55)	45	Formaldehyde	+	
5	Isobutyl methyl ketone*	17	(66.5)	32	Benzaldehyde	17.5	Toluene* (trace)
6	Amines-HCl	10		13	Benzaldehyde	5.2	Toluene* (trace), Benzamide 3 g.
7	Amines-HCl	15		37	*n*-Butyraldehyde	+	Toluene* (trace), Benzamide 0.4 g.
8	Amines-HCl	19.5		trace	Benzaldehyde	20	Benzene*, Toluene,* Benzylidenebenzylamine
9	Aniline	3.5	(23.2)	30	Benzaldehyde	10	Toluene* (trace), Benzylideneaniline
10	Aniline	1.2	(7.9)	48	*n*-Butyraldehyde	+	
11	—			100	Benzaldehyde	6.8	Toluene* (trace)
12	Benzyl alcohol*	(trace)		95	*n*-Butyraldehyde	+	

* Approximate value calculated from the gas chromatographic analysis.

[*3] The nickel precipitated on the zinc dust from a nickel chloride solution, treated with a sodium hydroxide solution and water, is as active as Raney nickel. K. Watanabe, This Bulletin, **37**, 1325 (1964); Y. Urushibara and S. Nishimura, ibid., **27**, 480 (1954); **28**, 446 (1955).

[*4] Obtained from the Nikko Scientific & Chemical Co., Ltd., Tokyo, this is kind of nickel-kieselguhr catalyst (50%) prepared from nickel formate, stabilized with inert gas. It is used directly for the reaction without any treatment.

4) H. Adkins, R. M. Elofson, A. G. Rossow and C. C. Robinson, *J. Am. Chem. Soc.*, **71**, 3622 (1949).

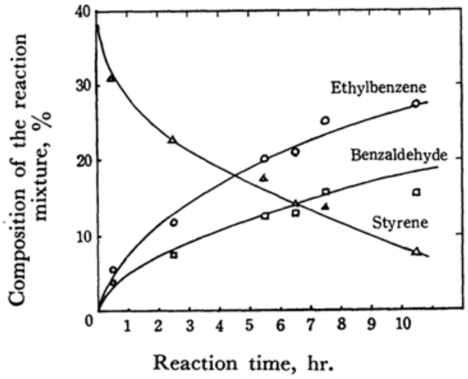

Fig. 1. The redox reaction between styrene and benzyl alcohol in the presence of U-Ni-B.
Sample: Styrene 25 g. and benzyl alcohol 50 ml.
Catalyst: U-Ni-B containing 4 g. Ni
Reaction temperature: 100°C

to compounds that have both C=C and C=O groups together.

The Reduction of Styrene and Mesityl Oxide.—With a combination of styrene and benzyl alcohol, the reaction occurred preferably at 100°C, no reaction took place below 80°C, and the polymerization of styrene occurred at 120°C. When the mole ratio of styrene to benzyl alcohol was ca. 1 : 2 (Exp. Nos. 1 and 2, Table I, Fig. 1), unreacted styrene was recovered even after twelve hours' reaction. When about ten times as much alcohol as styrene was used (Exp. No. 3), almost all the styrene was reduced in eleven hours in the presence of much more of the catalyst than in other cases. Methanol was not a suitable hydrogen donor for styrene (Exp. No. 4). The formaldehyde formed by the dehydrogenation of methanol was expelled out of the reaction system during the refluxing. Isobutyl methyl ketone was mainly obtained by the selective reduction of mesityl oxide (Exp. No. 5).

The Reduction of Benzonitrile and Nitrobenzene.—The reaction with the combination of benzonitrile and benzyl alcohol took place above 160°C, but with 1-butanol instead of benzyl alcohol, the reaction proceeded at the reflux temperature (ca. 120°C). A mixture of primary and secondary amines was obtained by the reduction of benzonitrile. The activity of S-Ni is relatively low, so much more of it should be used than when other catalysts are used (Exp. No. 8). It may be presumed that a part of the benzylamine reacts with aldehydes to form the corresponding Schiff base during the reaction. However, the formation and existence of the aldehyde as the free form were confirmed by gas chromatographic analysis, and also by the formation of 2, 4-dinitrophenylhydrazone from the reaction mixture. In Exp. Nos. 6 and 7, benzamide was obtained in varying amount. The U-Ni-B used in these reactions may have contained some water that remained after the preparation process, even though the catalyst was washed with alcohols. It has been reported[1,5] that nitriles are hydrated to the corresponding amides when refluxed in water with catalysts for hydrogenation (the nickel catalysts are the best), in which case no acid or base is necessary. Therefore, water should be excluded from the reaction system as far as possible. The reduction of nitrobenzene seemed to proceed slowly. Even after a twenty-hour reaction with an excess of alcohol, the yield of aniline was low (Exp. No. 9). Amines formed by the reduction of benzonitrile and nitrobenzene may be adsorbed on the catalysts and may interfere with the adsorption of the alcohols. This may be one of the reasons for their low reactivity.

The Combination of Hydrogen Donor and Acceptor.—On the whole, it may be concluded that a suitable combination of the two species of hydrogen donor and acceptor compounds in the reaction is essential if we are to expect successful redox reactions to occur. Further, this combination may determine the preferable temperature in the individual reaction. Actually, the effect of the reaction temperature on the reactions is delicate; its lower limit depends on the combination of species employed.

The Investigation of the Reaction Process.—During the reaction between styrene and benzyl alcohol, the diminution of styrene and the formation of ethylbenzene and benzaldehyde were investigated by gas chromatographic analysis (Fig. 1). In Fig. 1, the quantity percentage of styrene indicates ca. 37 when the reaction starts, which means that ca. 63 per cent of the reaction mixture is benzyl alcohol. After the reaction has proceeded for four hours, about a half of the styrene remains (ca. 18 per cent as determined by gas chromatographic analysis, Fig. 1), while about an equal percentage of ethylbenzene is formed. According to the graphic curves of styrene and ethylbenzene, the ratio of the decreased amount of styrene to the increased amount of ethylbenzene throughout the reaction is always ca. 1 : 1. This fact indicates that the reduction proceeds almost quantitatively. On the other hand, benzaldehyde is formed by the dehydrogenation of benzyl alcohol, and the proportion of the benzaldehyde formed to the ethylbenzene should be 1 : 1 if no other reaction occurs. However, some hydrogen adsorbed on the catalysts works for the formation of ethylbenzene. The shapes of the graphic curves show this.

Experimental

The Reduction of Styrene (Exp. No. 2).—In a 200-ml. three-necked, round flask equipped with a reflux

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[5] K. Watanabe, This Bulletin, **32**, 1280 (1959); **37**, 1325 (1964).

condenser, a stirrer and a thermometer, were placed 25 g. of styrene, 50 ml. of benzyl alcohol and 4 g. of Raney nickel. The contents were then stirred for 6 hr. at 100°C. After the reaction had been completed, the catalyst was separated by filtration. A part of the filtrate was analyzed by gas chromatography. The yield of ethylbenzene was 68.6%; unreacted styrene, benzaldehyde, and a trace of toluene were detected. When the filtrate was distilled, ca. 17.5 g. of the crude ethylbenzene fraction was obtained, b. p. 129—131°C. The ethylbenzene was also identified by infrared spectrum analysis. Benzaldehyde was identified as 2, 4-dinitrophenylhydrazone, m. p. 237°C, from an aliquot of the filtrate. The latter was recrystallized from ethanol and identified by infrared spectrum analysis, too. Gas chromatography: column, 30% Carbo-wax 1500 on Celite 30—40 mesh; length, 2 m.; temp., ca. 180°C; flow rate, 14—20 cm./sec.; carrier gas, H_2; relative retention times of the components: ethylbenzene 1, styrene 1.33, benzaldehyde 2.83, benzyl alcohol 7.29, and (toluene 0.9). Gas chromatograph apparatus: Yanagimoto-GCG 220 Type, Yanagimoto Mfg. Co., Ltd., Kyoto, Japan.

The Reduction of Mesityl Oxide (Exp. No. 5). —The reaction procedure was almost the same as in Exp. No. 2. After fifteen hours' reaction at 100°C, the reaction mixture was analyzed by gas chromatography as follows: the column and the conditions of analysis were the same as in Exp. No. 2; relative retention times of the components: isobutyl methyl ketone 1, mesityl oxide 1.27, benzaldehyde 3.42, and benzyl alcohol 8.79. The yeild of the reduction product, isobutyl methyl ketone, was 66.5%.

The Reduction of Benzonitrile (Exp. No. 6).— The reaction procedure was almost the same as in Exp. No. 2. After ten hours' reaction at 160°C, the catalyst was separated by filtration. A part of the filtrate was then analyzed by gas chromatography. The column and the conditions of analysis were the same as in Exp. No. 2; relative retention times of the components: benzaldehyde 1, benzonitrile 1.26, benzyl alcohol 2.54, and (toluene 0.29). The filtrate was acidified with concentrated hydrochloric acid, and then extracted with ether. From the ether extract, 3 g. of benzamide were obtained, m. p. 127—128°C. When the acidic solution was carefully evaporated to dryness, 10 g. of amine salt were obtained. The amine salt was decomposed with an alkaline solution, benzylamine was obtained as an acetyl derivative, 6.5 g.; m. p. 58.3—59.8°C. Dibenzylamine was detected by Hinsberg's method.[6] The quantity of the primary amine in the amine product obtained was ca. 60%. When 1-butanol was used instead of benzyl alcohol (Exp. No. 7), *n*-butyraldehyde was obtained as 2, 4-dinitrophenylhydrazone, recrystallized from ethanol, m. p. 119—120°C; it was also identified by infrared spectrum analysis.

The Reduction of Nitrobenzene (Exp. No. 9).— The reaction procedure was also the same as in Exp. No. 2. After fifteen hours' reaction at 180°C, the catalyst was separated by filtration. A part of the filtrate was then analyzed by gas chromatography. The column and the conditions of analysis were the same as in Exp. No. 2; relative retention times: benzaldehyde 1, nitrobenzene 1.26, benzyl alcohol 2.6, and (toluene 0.27). A very small quantity of a precipitate was obtained from the filtrate. It was washed with water and then identified as benzylideneaniline by infrared spectrum analysis. The filtrate was acidified with concentrated hydrochloric acid, and then extracted with ether to take off the unreacted nitrobenzene, benzyl alcohol, and benzaldehyde. When the water part (acidic) was evaporated to dryness, amine salt was obtained. It was decomposed with an alkaline solution and extracted with ether. From the ether solution, 3.5 g. of aniline were obtained by distillation, b. p. 182—184°C.

The authors wish to express their hearty thanks to Professor Kazuo Hata for his kind advice.

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6) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," Asian Edition, Maruzen Co., Tokyo (1956), p. 103.