Reduction of Organic Compounds with Urushibara Catalysts under High Pressure. IX[1]. *Reduction of Some Carbonyl Compounds with Urushibara Catalysts Prepared by Various Modified Methods*

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In the preceding paper[1] of this series, catalytic reduction of acetophenone with various Urushibara nickel catalysts, especially with the catalyst prepared from preserved precipitated nickel and with the regenerated catalyst, was reported. The procedure for preparing the Urushibara catalysts has been successively modified and some varieties of the catalysts, namely, U-Ni-B[2-7], U-Ni-BA[5,6,8], U-Ni-NH$_3$[9], U-Ni-CB[7], U-Ni-A[3-7,10], U-Ni-AA[11], U-Ni-CA[7], U-Co-B[7,9,12,13], U-Co-CB[7], U-Co-A[7,13], U-Co-CA[7], U-Cu[7] and U-Cu-C[7], were developed. Each of them has intrinsic characteristics and can be used properly in accordance with the substance to be reduced. The preparation of the Urushibara catalysts is divided into two steps, that is, the preparation of precipitated metals and the digestion of them with acid or alkali. Therefore the

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[1] Part VIII: S. Taira, This Bulletin, **34**, 1072 (1961).

[2] Y. Urushibara and S. Nishimura, ibid., **27**, 480 (1954).

[3] Chem. Soc. Japan, ed., "Jikken Kagaku Kōza", Vol. 17, Part 2, Maruzen, Tokyo (1956), p. 311.

[4] Y. Urushibara and K. Hata, *Kagaku Kōgyō*, **7**, 15 (1956).

[5] K. Hata and S. Taira, *Kagaku Gijutsu*, **2**, 42 (1958).

[6] K. Hata and S. Taira, *J. Soc. Org. Synth. Chem. Japan* (*Yūki Gōseikagaku Kyōkai-shi*), **16**, 596 (1958).

[7] S. Taira, This Bulletin, **34**, 261 (1961).

[8] K. Hata, S. Taira and I. Motoyama, ibid., **31**, 776 (1958).

[9] S. Nishimura and A. Sugimori, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 314 (1960).

[10] Y. Urushibara, S. Nishimura and H. Uehara. This Bulletin, **28**, 446 (1955).

[11] K. Hata, K. Watanabe and H. Watanabe, ibid., **32**, 6 (1959).

[12] S. Saito, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **76**, 351 (1956).

[13] Chem. Soc. Japan, ed., "Jikken Kagaku Kōza", Vol. 17, Part 2, Maruzen, Tokyo (1956), p. 334.

nature of an Urushibara catalyst is decided by the method of preparation and digestion of precipitated metal.

In the present paper, reductions of deoxybenzoin, benzoin, benzil and furil with the Urushibara catalysts prepared by various methods are studied, and the further modifications of the preparation of the catalyst are presented.

Experimental

Apparatus.—Reductions were carried out in an electro-magnetically stirring type autoclave having a capacity of 100 ml. (the Sakashita SE-10 type). For the reduction of furil, SE-20 (200 ml. capacity) was used.

Materials.—Deoxybenzoin was prepared from phenylacetyl chloride and benzene by the Friedel-Crafts reaction[14]. The crude material was purified by distillation under reduced pressure and then recrystallized from methanol, b. p. 159.5∼160.5°C/6 mmHg, m. p. 55∼56°C.

Benzoin was prepared from benzaldehyde[15]. The crude product was recrystallized three times from ethanol, m. p. 133∼134°C.

Benzil was prepared by catalytic oxidation of the benzoin with ammonium nitrate[16]. The raw product was recrystallized from methanol, m. p. 96.5∼97°C.

Furil was obtained by the same manner from furoin prepared from furfural[17], m. p. 165°C.

General Procedure for Reduction.—Catalyst was carefully transferred with ethanol into the autoclave. Then the air present in the autoclave was replaced by hydrogen gas four times. Most operations were carried out under the following conditions: (1) Catalyst was prepared so as to contain 0.5 g. of nickel metal. (2) Sample; 0.05 mol. (deoxybenzoin 9.8 g., benzoin 10.6 g., benzil 10.5 g., furil 9.5 g.). (3) Solvent; ethanol (99%) 50 ml. (4) pH; 9∼11. When U-Ni-A, U-Ni-CA or U-Cu-C was used, 0.5 ml. of 5% sodium hydroxide solution was added. (5) Agitation; 40∼45 strokes per minute. (6) Reaction temperature; 60∼68°C. Agitation was started when the temperature in the autoclave reached 60°C. The heating of the autoclave was regulated so as to get to 60°C within 30∼35 min., and then the temperature was kept between 60 and 68°C throughout the operation. (7) Initial pressure; 50∼100 kg./cm^2. As it has been recognized[7] that initial pressure affected only slightly the velocity of reduction of the carbonyl group under 100 kg./cm^2, the effect of initial pressure was ignored. Depression of pressure was observed at intervals of 5 min. When U-Cu-C was used, reduction was carried out with the catalyst prepared so as to contain 1 g. of copper and at about 130°C.

Reduction Products.—*Phenylbenzylcarbinol.*—After the reduction of deoxybenzoin was finished, the catalyst was filtered off and washed with ethanol. The major part of ethanol was distilled off and the hot residue was poured into hot water with stirring and the mixture was cooled in an ice-bath. The precipitate was filtered off and dried. It was recrystallized from petroleum benzin into colorless needles, m. p. 66∼67°C. Yield, 91∼94% of the theoretical.

Hydrobenzoin. — After the reduction of benzoin was finished, the catalyst, mixed with some crystals separated out, was filtered off and washed with hot ethanol to dissolve the crystals. From the combined filtrate, the major part of ethanol was removed by distillation. The hot residue was poured into hot water with stirring. After cooling, the crude hydrobenzoin was filtered off and dried. It was recrystallized from aqueous ethanol into colorless scales, m. p. 139∼140°C. Yield, 90∼93% of the theoretical.

Benzoin.—After the partial reduction of benzil was finished, the contents were filtered off and washed throughly with hot ethanol. After removal of the major part of ethanol from the combined filtrate, benzoin crystallized in prisms, m. p. 132∼134°C. Yield, 76∼80% of the theoretical.

Furoin.—After the reduction of furil, the product was treated by the same procedure as is described above. Pale yellow prisms, m. p. 137∼138°C. Yield, 79∼81% of the theoretical.

Preparation of Catalysts.—The U-Ni-B[2-6], U-Ni-A[3-6,10], U-Ni-CB[7] and U-Ni-CA[7] were prepared by the methods described in the references cited. The others were prepared by the methods described below.

Precipitated Nickel Prepared by a Simplified Method.—To the well mixed zinc dust (10 g.) and water (4 ml.) placed in a 50 ml. beaker 4.04 g. of the crystals of commercially available nickel chloride ($NiCl_2 \cdot 6H_2O$) is added at once and the mixture is stirred with a glass rod. Soon reaction begins and a vigorous reaction takes place suddenly within a few minutes. The reaction mixture swells up into a slushy mass. It is washed with 200 ml. of cold water, and then the washing is filtered or removed by decantation. Thus about 13.5 g. of precipitated nickel, containing about 1 g. of nickel contaminated with a quantity of zinc, zinc oxide and basic zinc chloride, was obtained.

U-Ni-B was prepared from the above described precipitated nickel (containing 0.5 g. of nickel) by digesting with 80 g. of 10% sodium hydroxide solution at about 50°C for 15 min. The upper liquor was decanted and the residue was washed with two 50 ml. portions of water and then with the same amount of ethanol. The obtained catalyst was less bulky than the usual U-Ni-B and carried a black color (the usual U-Ni-B has rather grayish appearance). Every washing was removed by decantation.

U-Ni-A was prepared from the same precipitated nickel (containing 0.5 g. of nickel) by treatment with 75 ml. of 20% acetic acid at ordinary temperature until the generation of hydrogen gas subsided and a solid came up to the surface of the green solution. The solid was collected on a glass filter and washed with each 100 ml. portions of water and ethanol.

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[14] C. F. H. Allen and W. E. Barker, "Organic Syntheses", Coll, Vol. II (1948), p. 156.

[15] R. Adams and C. S. Marvel, ibid., Coll. Vol. I, p. 94.

[16] M. Weiss and M. Appel, *J. Am. Chem. Soc.*, **70**, 3666 (1948).

[17] W. W. Hartman and J. B. Dickey, ibid., **55**, 1228 (1933).

U-Ni-A Obtained by Treatment of the Precipitated Nickel with Hydrochloric Acid, Abbreviated as U-Ni-A(HCl).—The precipitated nickel (containing 0.5 g. of nickel), prepared by normal or simplified method, was digested with 240 ml. of 0.75 N hydrochloric acid at ordinary temperature for about one minute until a solid came up to the surface of the green solution. The solid was collected on a glass filter and washed with 200 ml. of water and then with 100 ml. of ethanol.

U-Cu-C.—The precipitated copper was prepared by the same way as was reported in the previous paper[7]. It was treated with 200 ml. of 20% acetic acid on a boiling water bath at 80∼90°C for about 20 min. At the end of the digestion a solid, adsorbing hydrogen gas, came up to the surface of the solution likely in case of preparing the U-Ni-A. The solid was collected on a glass filter and washed with 200 ml. of water and then with 150 ml. of ethanol. About 2.3∼2.5 g. of bulky catalyst, containing copper (about 1 g.) and zinc, was obtained.

In all procedures, distilled water was used for washing except for the preparations of precipitated metals. The solid should be protected from contact with air as far as possible after the treatment of precipitated metals with acid or alkali.

Results and Discussion

In the reduction of benzophenone[7] and acetophenone[1] to the corresponding alcohols with various Urushibara catalysts, the U-Ni-A was found to be the most useful catalyst. The same conclusion was confirmed also in the reduction of deoxybenzoin, benzoin and benzil. The U-Ni-CB was also found to be highly active (Tables I, II and III).

Modification of the Preparation of the Catalyst.—As was reported in the preceding paper[1], the preparation of the Urushibara nickel catalyst was fairly simplified. The

TABLE I. REDUCTION OF DEOXYBENZOIN

Deoxybenzoin 9.8 g. (0.05 mol.); solvent: ethanol (99%, about 50 ml.)

Exp. No.	Catalyst[a]	Total weight of catalyst, g.[b]	Initial press. kg./cm²	Initial temp. °C	Reaction temp. °C	Time[c] min.
11	U-Ni-B	3.2	56	22	60∼62	30
12	U-Ni-CB	4.3	58	27	62∼65	18
13	U-Ni-A[d]	0.7	56	18	60∼61	17
14	U-Ni-CA[d]	0.4	60	20	60∼63	22

a) Each catalyst was prepared so as to contain 0.5 g. of nickel.

b) The figures were obtained by weighing the dried catalyts after use for reduction.

c) The figures show the time required from the start of agitation (when the temperature reached to 60°C) till the cease of pressure depression, which had been observed every minute.

d) 0.5 ml. of 5% sodium hydroxide solution was added.

TABLE II. REDUCTION OF BENZOIN WITH VARIOUS URUSHIBARA NICKEL AND URUSHIBARA COPPER CATALYSTS

Benzoin 10.6 g. (0.05 mol.); solvent: enhanol (99%, about 50 ml.)

Exp. No.	Catalyst[a]	Total weight of catalyst, g.[b]	Initial press. kg./cm²	Initial temp. °C	Reaction temp. °C	Time min.
21	U-Ni-B	3.5	59	22	60∼61	100
22	U-Ni-B	3.3	55	16	60∼65	50
23	U-Ni-B[c]	2.8	64	30	60∼66	60
24	U-Ni-B[c]	2.6	54	20	60∼64	50
25	U-Ni-CB	5.5	60	30	60∼61	50
26	U-Ni-CB	4.6	60	26	61∼63	17
27	U-Ni-A[d]	0.7	55	21	65∼67	10
28	U-Ni-A[d]	0.6	60	23	60∼64	20
29	U-Ni-A[c,d]	0.4	67	26	62∼64	35
210	U-Ni-A[c,d]	0.5	57	23	61∼64	25
211	U-Ni-A(HCl)[d]	0.25	53	28	60∼66	115
212	U-Ni-A(HCl)[c,d]	0.3	56	26	62∼64	85
213	U-Cu-C[d]	2.3	38	23	130∼132	30

a) Each U-Ni catalyst was prepared so as to contain 0.5 g. of nickel. The U-Cu catalyst was prepared so as to contain 1 g. of copper.

b) The figures were obtained by weighing the dried catalysts after use for reduction.

c) The catalyst was prepared from the newly developed precipitated nickel (cf. Experimental part).

d) 0.5 ml. of 5% sodium hydroxide solution was added.

TABLE III. REDUCTION OF BENZIL WITH VARIOUS URUSHIBARA NICKEL AND URUSHIBARA COPPER CATALYSTS

Benzil 10.5 g. (0.05 mol.); solvent: ethanol (99%, about 50 ml.)

Exp. No.	Catalyst[a]	Total weight of catalyst, g.[b]	Initial press. kg./cm^2	Initial temp. °C	Reaction temp. °C	Time[c] min.
31	U-Ni-B	3.4	93	22	60∼64	120(45, 75)
32	U-Ni-B	4.9	96	26	60∼68	165(60, 105)
33	U-Ni-B[d]	—	80.5	30	60∼66	75(20, 55)
34	U-Ni-B[d]	2.8	90	23	60∼65	100(35, 65)
35	U-Ni-CB	5.6	97.5	25	63∼66	35(10, 25)
36	U-Ni-CB	4.2	101	26	59∼66	95(20, 75)
37	U-Ni-A[e]	0.65	95	20	60∼66	25(10, 15)
38	U-Ni-A[e]	0.7	84	20	58∼61	110(40, 70)
39	U-Ni-A[d,e]	0.35	42.5[f]	23	60∼68	55(20, 35)
310	U-Ni-A[d,e]	0.35	42[f]	22	60∼66	90(30, 60)
311	U-Cu-C[e]	2.3	80	24	128∼138	55(20, 35)

[a] Each U-Ni catalyst was prepared so as to contain 0.5 g. of nickel. The U-Cu catalyst was prepared so as to contain 1 g. of copper

[b] The figures were obtained by weighing the dried catalysts after use for reduction.

[c] The figures in the parentheses are the time required for reducing each carbonyl group, the first figures being for the first carbonyl group.

[d] The catalyst was prepared from the newly developed precipitated nickel (c. f. Experimental part).

[e] 0.5 ml. of 5% sodium hydroxide solution was added.

[f] Supplementary hydrogen gas was charged three times when the pressure dropped to 30 kg./cm^2.

activity of U-Ni-A or U-Ni-B, prepared from the preserved precipitated nickel, being the same as that of the catalyst obtained from the freshly prepared precipitated nickel, time can be saved to prepare the catalyst if a large quantity of the precipitated nickel is previously reserved. On the other hand, the recovered Urushibara nickel catalysts can be repeatedly used by a simple process of regeneration, especially in form of the U-Ni-A.

As the process for the preparation of the Urushibara nickel catalyst is divided into the preparation of the precipitated nickel and the treatment of it with acid or alkali, the modification of preparing a catalyst can be devised in each of both procedures. Already many modifications have been accomplished, and varieties of the catalyst were reported. The precipitated nickel prepared at low temperature gives a highly active Urushibara nickel C. But the preparation of it requires so much time, that a favorable feature of the Urushibara catalysts to be prepared in a short time is lost. In case of preparing the precipitated nickel from hot aqueous nickel chloride solution and zinc dust on a boiling water bath, a vigorous exothermic reaction is observed. If the heat of the reaction is utilized, the time for preparing the precipitated nickel will be shortend and the procedure may be simplified. For the purpose of attaining this request, it may be suitable to use the concentrated solution of nickel chloride in place of the diluted solution used in the usual preparation. Thus, the first attempt was the addition of a very concentrated nickel chloride solution onto a dry zinc dust, but this method was unsuccessful as the reaction was so vigorous that an uniform agitation was impossible and an uniform deposition of nickel metal on the particles of zinc could not be expected. After several trials, it was found that the most profitable method consists in adding crystals of nickel chloride to the mixture of zinc dust and a little water, and a good precipitated nickel could be prepared in a few minutes.

In the preparation of the U-Ni-A by digesting the precipitated nickel with acid, acetic or propionic acid has been used and formic, butyric and hydrochloric acids had been regarded as unprofitable[3,4,10]. Supposing the action of the acid is to activate the precipitated nickel by generating hydrogen gas, removing the deactivating substances and eroding the surfaces of nickel particles[1], there is no reason that hydrochloric acid cannot be applicable except for some special poisonous action to a nickel catalyst. Therefore the nickel catalyst obtained from the precipitated nickel by treatment with hydrochloric acid is expected to have ability of hydrogenation though it may be lower than those of the other Urushibara nickel catalysts.

Comparison of the Activities of Various Catalysts.—The results of reduction of benzoin and benzil with the usual Urushibara nickel

TABLE IV. PARTIAL REDUCTION OF α-DIKETONES

Exp. No.	α-Diketone	Solvent	Catalyst[a]	Initial press. kg./cm^2	Reaction temp. °C	Time min.	Reduction product	Yield %
41	Benzil 10.5 g. (0.05 mol.)	Ethanol (50 ml.)	U-Ni-A	80	20	100	Benzoin	76
42	Benzil 10.5 g. (0.05 mol.)	Ethanol (50 ml.)	U-Ni-A[b]	85	22	115	Benzoin	80
43	Furil 9.5 g. (0.05 mol.)	Ethanol (100 ml.)	U-Ni-A	56	60～63	90	Furoin	81
44	Furil 9.5 g. (0.05 mol.)	Ethanol (100 ml.)	U-Ni-A[b]	60	60～62	100	Furoin	79

a) Each catalyst was prepared so as to contain 0.5 g. of nickel, and in each operation 0.5 ml. of 5% sodium hydroxide solution was added.

b) The catalyst was prepared from the newly developed precipitated nickel (cf. Experimental part).

catalysts and with the newly developed ones are tabulated in Tables II and III. In consideration of the condition of preparing the newly developed precipitated nickel, it is expected that it possesses both natures of the precipitated nickels prepared in hot and in cold conditions. Accordingly the nature of the catalyst obtained from it may be situated between those of the usual Urushibara nickel and the Urushibara nickel C. When the Urushibara nickel catalysts of B type (prepared by digestion with alkali) are used for the reduction in an autoclave, the rates of reduction are influenced by the factors such as the fineness and dispersability of the catalyst, the bulk and the kind of carrier (e. g. zinc, zinc oxide) etc. On the other hand, as the Urushibara nickel catalysts of the A type (prepared by digestion with acid) contain only small quantities of zinc and zinc compounds, if any, and are less bulky than the B type, the inherent activities of the catalysts may dominate the velocities of reduction. In consideration of these facts, the time required for the completion of reduction with various Urushibara nickel catalysts is compared with each other. The activity of each catalyst is not always constant, but it can be approximately estimated by repeated experiments. Both for the reduction of benzoin and benzil, the usual U-Ni-A gives the best results. The U-Ni-A prepared from the newly developed precipitated nickel is somewhat inferior to the usual U-Ni-A, but has enough activity for practical use. The activity of the Urushibara nickel catalysts has been studied[3,18], in connection with the size of their crystallites, which was estimated by X-ray diffraction method. According to the authors, the more vigorous the reaction to prepare the precipitated nickel takes place, the smaller the crystallites of the obtained catalyst become, and the activity of the catalyst is lowered with the growth of the size of crystallites. The size of crystallites of the highly active Urushibara nickel catalysts was reported to be about 40 Å and the same as that of the Raney nickel catalyst. The values obtained by the present author were 39～45 Å for the usual U-Ni-A, and 33～41 Å for the modified U-Ni-A obtained from the newly developed precipitated nickel. On the whole the size of crystallites of the modified U-Ni-A was found to be smaller than that of the usual U-Ni-A. Therefore, the activities of the freshly prepared catalysts may not be discussed only from a standpoint of the size of crystallites, although the catalyst used in Exp. No. 39 gave a smaller value (33 Å) than that (37 Å) of the catalyst used in Exp. No. 310.

The U-Ni-A prepared by digesting the precipitated nickel with hydrochloric acid was proved to be still active though it was inferior to the other U-Ni-A. The cause may be partly due to the small contents of nickel metal and partly to the adsorption of some chlorine compound on the surface of the catalyst. As it has been previously reported[7], the Urushibara copper catalyst has an activity for reduction of a carbonyl group and the U-Cu-C is superior. But the treatment of the precipitated copper with acetic acid at room temperature requires much time. If the temperature of digesting the precipitated metal with acid affects the activity only slightly, it is advantageous to operate the digestion at high temperature. The results obtained with such catalyst are given as Exp. Nos. 213 and 311 in Tables II and III.

Partial Reduction of α-Diketones.—In every experiment on the reduction of benzil, a sudden fall of hydrogen uptake was observed after a certain quantity of hydrogen had been absorbed. It is conceivable that the reduction of one carbonyl group of the two has been finished at this point. Then, the partial reduction of α-diketones to α-ketols is expected to be possible under suitable condition. It was realized in the reduction of benzil and furil,

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18) Y. Urushibara, M. Kobayashi, S. Nishimura and H. Uehara, *Shokubai*, **12**, 107 (1956).

and the results of the partial reduction are shown in Table IV. In case of reducing a carbonyl group to the corresponding alcohol, it has been noticed that the velocity of hydrogen uptake increases at about 60°C and that the reduction is promoted by a trace of an alkali. The reduction in neutral solution being presumed to require a long time for the completion⁷⁾, the reduction of benzil to benzoin was carried out with the U-Ni-A added with a little quantity of alkali at room temperature. On the other hand, the partial reduction of furil was practised at about 60°C and in a large quantity of ethanol, as furil dissolves only slightly in ethanol at room temperature.

Summary

The catalytic reduction of deoxybenzoin, benzoin, benzil and furil with various Urushibara catalysts under high pressure were studied. It was found that benzil and furil was converted into the corresponding α-ketols by the partial reduction under proper condition.

Some modifications for the preparation of the Urushibara catalyst were attained. The newly developed precipitated nickel prepared by a very simple way proved to give a catalyst as active as the usual Urushibara nickel catalyst for practical use. Hydrochloric acid was found to be applicable for the digestion of the precipitated nickel in place of acetic acid.

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