Studies on Organic Catalytic Reactions. I

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It is interesting to study the application of metallic catalysts to new organic reactions beyond the customary catalytic reactions. Various reactions of organic compounds may be accelerated with the aid of catalysts and subsequently some new catalytic reactions are expected to be found. In this paper, general aspects of hydrolysis of aromatic nitriles and esters with nickel catalysts—mainly the Urushibara nickel catalyst[1]— are reported, and reactions of aromatic halogen compounds with the catalyst are also described.

When aromatic nitriles were refluxed with water in the presence of the catalyst, they were found to be hydrolyzed to the

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[1] Y. Urushibara and S. Nishimura, This Bulletin, 27, 480 (1954).

TABLE I. HYDROLYSIS OF BENZONITRILE WITH URUSHIBARA NICKEL CATALYST

Benzonitrile g.	U-Ni-B g.	Solvent	cc.	Time hr.	Products, g. Amide	Amine	acid	Remarks
5	4	Water	80	11	4.2 (73%)	0.4	+	
5	4	Ethanol	60	9	0.6 (11%)	4.0	+	
10	8	Ethanol	100	8	3.6 (19%)	3.6	+	Recovered 0.1 g.
10	8	Dioxane	100	12	4.0 (34%)	1.5	−	Recovered 0.4 g. White crystals m.p. 220°C

corresponding acid amides in fairly good yields even though the reaction medium was neutral to litmus. The hydrolysis was generally stopped at the amide stage and very small amounts of acids were obtained. Further hydrolysis of amides to acids could not be observed even when the amides were treated again with a newly prepared catalyst. Small quantities of nitriles were hydrogenated to amines by hydrogen absorbed on the nickel catalyst. Some factors, effective for the reaction, were examined in regard to the kind of catalyst, promoter or poison, solvent and duration of refluxing. In most of the reactions, the Urushibara nickel was used as the catalyst, and representative results of the experiments with benzonitrile are shown in Table I. Stabilized nickel catalysts (K. S. Y. Catalysts)[2] were also used in some experiments, and similar results could be observed.

Among the varieties of the Urushibara catalyst, U-Ni-B was the most advantageous for the hydrolysis; U-Ni-A[3], BA[4], AA[5] and U-Cu-B were not so admirable because some undesirable side reactions were induced. When precipitated nickel prepared from nickel chloride and zinc dust was used in place of the Urushibara catalyst, the product was found to be a complex of a primary amine and zinc, which can be decomposed to the amine by treating with alkali. Zinc powder by itself did not show any catalytic activity for hydrolysis.

As for the reaction solvents, water, ethanol, dioxane and *n*-butanol were used, and water was proved to be the most excellent of all as shown in Table I. A small quantity of thiophene or pyridine was added to the U-Ni-B catalyst in order to examine specific behavior as a promoter for the catalyst. However, they were of no use but rather gave an unfavorable effect.

The hydrolysis of the nitrile group was also observed in *p*-tolunitrile, *o*-nitrobenzonitrile and benzyl cyanide, yielding the appreciable amounts of the corresponding amides. On the contrary, hydrolysis of ethyl benzoate hardly proceeded with the same method, and benzoic acid could scarcely be obtained.

On the other hand, some aromatic halogen compounds were treated with the nickel catalyst in the same procedure mentioned above. Chlorobenzene, bromobenzene and iodobenzene were mainly dehalogenated to bezene along with a small quantity of biphenyl, although the reaction velocity of chlorobenzene was very slow compared with those of the others. When a small quantity of thiophene was added to the catalyst in the reaction of bromobenzene, alternative obscure reaction occurred yielding an unidentifiable oily product of a high boiling point. Reactions of nitro or amino derivatives of halogenobenzenes were more complicated. Among the reactions of this series, remarkable result was obtained with benzyl chloride. When benzyl chloride was refluxed with U-Ni-B in ethanol, a Wurtz type reaction was observed and bibenzyl was obtained in a good yield (above 70%). However, when the mixture was refluxed for a long time, the production of bibenzyl was accompanied with the formation of a highly boiling oil.

As the results of the studies on these catalytic reactions, it was found that amides are obtained from nitriles without acidic or alkaline hydrolysis, and that bibenzyl is obtained from benzyl chloride without sodium metal. These reactions are simple in procedure, and the yields of products are fairly good when the reactions are carried out under suitable conditions. The details of these experiments and discussion will be published in a following paper.

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[2] T. Yamanaka et al., *J. Sci. Res. Inst.*, **51**, 168 (1957); **52**, 143, 224 (1958).

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

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

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

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