A Novel Reduction with Water as the Hydrogen Donor

Koji SAKAI and Ken-ichi WATANABE

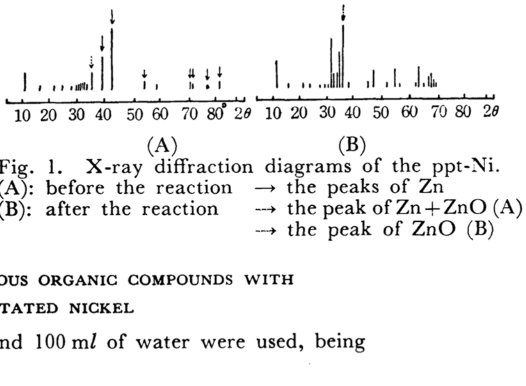
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo

(Received February 7, 1967)

It has been found that various organic compounds are reduced by refluxing them with water in the presence of precipitated nickel (ppt-Ni).[1] ppt-Ni is easily prepared by adding a hot solution of nickel chloride to zinc dust. For example, to 40 g of commercial zinc dust in a 1-*l* Erlenmeyer flask, a small quantity of water is added, and the mixture is heated to boiling. In another vessel, 40 m*l* of a nickel chloride solution containing 16 g of $NiCl_2 \cdot 6H_2O$ is heated to 60°C and then added to the former under vigorous shaking. A violent exchange reaction takes place, depositing nickel. The precipitates are washed with water three times by decantation, and then filtered. The ppt-Ni[2] thus obtained contains about 4 g of nickel, plus Zn, ZnO, Zn(OH)Cl, $Zn(OH)_2$, and $Ni(OH)_2$. The activity of the ppt-Ni dried under reduced pressure did not decrease even if it was exposed to air for a long time.

This reaction is simply performed without hydrogen gas or an activated catalyst, and the yields are remarkably high. Thus, C=C, NO_2, C≡N, and C=O groups can be reduced, but the benzene nucleus and the C=O group in camphor can not be reduced (Table 1). The C=C bond of mesityl oxide is reduced preferentially.

It is of interest that benzonitrile gives benzylamine-HCl and that no secondary amine is formed. As the hydrogen donor, water is the best. With methanol, the results were unsatisfactory as compared with those with a water solvent (see Table 1). The reduction of mesityl oxide did not occur when ethyl ether or *n*-hexane was used instead of water (refluxed for 16 hr). Further, the introduction of hydrogen gas into the reaction mixture had no effect, and no catalytic hydrogenation took place under high pressure, either. Zn, ZnO, $Zn(OH)_2$, Zn(OH)Cl, or $Ni(OH)_2$ could not effect any reduction. From the results of the X-ray diffraction analysis of ppt-Ni, the peak of Zn disappeared after the reaction, but that of ZnO and Zn(OH)Cl did not (Fig. 1). Consequently, the behavior of ppt-Ni in this reaction might be complicated.



(A) (B)

Fig. 1. X-ray diffraction diagrams of the ppt-Ni.
(A): before the reaction → the peaks of Zn
(B): after the reaction ⇢ the peak of Zn+ZnO (A)
⇢ the peak of ZnO (B)

TABLE 1. THE REDUCTION OF VARIOUS ORGANIC COMPOUNDS WITH WATER AND PRECIPITATED NICKEL

10 g of sample, 4 g of nickel (contented), and 100 m*l* of water were used, being refluxed for 16 hr in each run.

Exp. No.	Compound	Product[1]	(%)	Recovered (%)
1	Styrene	Ethylbenzene	81.4 (53.5)	19.6
2	Nitrobenzene	Aniline	98 (34)	–
3[2]	Benzonitrile	Benzylamine-HCl Benzamide	90 (11.8) Trace	+
4	Methyl ethyl ketone	2-Butanol	87	13
5	Cyclohexanone	Cyclohexanol	90 (62.5)	+
6	Benzaldehyde	Benzyl alcohol	>90 (49)	–
7	Mesityl oxide	Isobutyl methyl ketone	95[3] (*ca.* 90)	–

1) Calculated from the results of gas chromatographic analyses. The values in parentheses show the yields when methanol was used.
2) The reaction time was 20 hr. The products were obtained by evaporation.
3) More than 90% in 5 hr.

---

[1] K. Watanabe, This Bulletin, **37**, 1325 (1964); Y. Urushibara and S. Nishimura, *ibid.*, **27**, 480 (1954); **28**, 446 (1955).

[2] Y. Urushibara, M. Kobayashi, S. Nishimura and H. Uehara, *Catalyst* (*Shokubai*), *Japan*, **12**, 111 (1956).