Drynap Reduction. II.* The Reduction of Nitrobenzene with a Commercial Sodium-Lead Alloy

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(Received November 29, 1965)

Recently the commercial sodium-lead alloy, "Drynap," was introduced and recommended by one of the present authors as a mild reducing agent in place of sodium amalgam.[1] Nitrobenzene was submitted to Drynap reduction under various conditions.

Acetic acid or hydrochloric acid was chosen as the neutralizing agent, while ethanol or water was used as the reaction solvent. The reduction products were separated through an alumina column and checked by thin-layer chromatography. The product in each experiment was identified by mixed-melting-point determination.

As expected, aniline (over 70% yield; m. p. 114°C; as acetanilide) was the main product of the reduction of nitrobenzene in an aqueous suspension with the alloy and hydrochloric acid. The yield was rather poor (about 20%) with an ethanol solvent, and a large amount of nitrobenzene (about 70%) was recovered. The above-mentioned decrease in the yield may be due to the production of insoluble lead chloride, which covers the surface of the alloy. A small amount of azobenzene (m. p. 68°C; below 3% yield) and hydrazobenzene (m. p. 125—126°C; below 1% yield) was detected as a by-product in the above two experiments.

By using acetic acid as the neutralizing agent, however, nitrobenzene was reduced to azobenzene in a yield greater than 45%, while the yield of aniline decreased (about 25%) either in ethanol or in a water solvent. Efficient stirring, a higher temperature, and a longer reaction time seemed to raise the yield of aniline. Azoxybenzene (m. p. 36°C; yield 3—10%) and hydrazobenzene (below 1% yield) were obtained as by-products.

Without using an acid, nitrobenzene was also reduced to azobenzene in 60—80% yields by vigorously stirring Drynap into an ethanolic solution or an aqueous suspension. In this experiment, small amounts of hydrazobenzene and azoxybenzene were obtained as by-products.

From the above results, it may be concluded that the Drynap reduction of nitrobenzene in a hydrochloric acid solution gives the same product as in an ordinary reduction with mineral acid and such metals as zinc, iron, and tin, and that, in acetic acid or a neutral solution, the reaction gives the same results as in the case of sodium amalgam or sodium ethoxide.[2,3]

Experimental

Materials.—Nitrobenzene and aniline of G. R. grade were used after distillation. Azobenzene, hydrazobenzene, azoxybenzene, and phenylhydroxylamine were derived from nitrobenzene by the usual method[4] and were purified.

Reduction Procedure.—Five grams (0.04 mol.) of nitrobenzene dissolved in 80 ml. of ethanol or suspended in 80 ml. of water was reduced by the addition of 50 g. (corresponding to 0.2 atom of sodium metal) of Drynap (in small portions) at 35—40°C. In acidic reduction, 0.5 mol. of an acid was also added.

After one hour, the ethanol was removed with an

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* A previous report, Ref. 1, represents Part I of the series.

[1] K. Tabei, H. Hiranuma and N. Amemiya, This Bulletin, **39**, 1085 (1966).

[2] V. O. Lukashevich, *Ann.*, **521**, 198 (1936).

[3] H. S. Fry and J. J. Cameron, *J. Am. Chem. Soc.*, **49**, 864 (1927).

[4] L. Gattermann, "Die Praxis des Organischen Chemikers," 36. Aufl., 161, 163 (1954); H. Gilman, "Organic Syntheses", Coll. Vol. I, 445 (1956).

Table I. Drynap reduction of nitrobenzene

Expt. No.	Solvent	Acid	Product	Yield, %	By-product*
1	Water	HCl	Aniline	70—80	AB, HAB
2	Ethanol	HCl	Aniline	20—25	AB, HAB
3	Water	AcOH	Azobenzene Aniline Azoxybenzene	45—65 10—25 ~10	HAB
4	Ethanol	AcOH	Azobenzene Aniline	45—65 ~25	AOB
5	Water	—	Azobenzene	~70	HAB, AOB
6	Ethanol	—	Azobenzene	60—70	HAB, AOB

* AB represents azobenzene, HAB: hydrazobenzene, AOB: azoxybenzene.

ethanol solvent, and the reduction mixture was extracted with ether. The ether extract was washed with water (and a 5% sodium hydrogen carbonate solution) and dried over sodium sulfate.

After the evaporation of the ether, the extract was dissolved in benzene, and a small portion of the benzene solution was subjected to thin-layer chromatography in order to check the reduction product. Most of the benzene solution was passed through an alumina column, and each reduction product was collected as a fraction.

In the case of an aqueous suspension, the reaction mixture was extracted with ether and the extract was treated in the way described above.

Each product was purified by recrystallization or by distillation, and was identified by means of mixed-melting-point determination and by thin-layer chromatography. The results are tabulated in Table I.

Thin-layer Chromatography. — The thin-layer chromatoplate (0.5 mm.) used for the check of the product was made with Wako Gel B-10 (silica gel). The spot of the sample was developed with benzene at 18—20°C. The spot of each component developed was detected either by exposing the plate to iodine vapor or by letting the plate stand under ultraviolet light after spraying sulfuric acid on it and heating it at 105°C for 15 min. The R_s values (the ratio of the R_f value to that of azobenzene) were compared with those of the authentic compounds: azobenzene: 1.00; nitrobenzene: 0.97; *p*-hydroxyazobenzene: 0.95; azoxybenzene: 0.89; hydrazobenzene: 0.79; aniline: 0.35; phenylhydroxylamine: 0.15.

The authors wish to thank the Wako Pure Chemical Co., Ltd., for its gift of Drynap.