

cedure a small amount of solid separated. This later proved to be II. It was more convenient to prepare II from the normal and more soluble product, 1-methyl-3-hydroxypyridinium iodide (I). For this purpose there was added dropwise to an acetone solution of I, m.p. 114–116°, triethylamine until precipitation on addition ceased. The solid was collected, washed with acetone, and recrystallized from methanol-ether. The sample for analysis⁶ had m.p. 179–181°.

Anal.: Calcd. for $C_{12}H_{15}IN_2O_2$: C, 41.63; H, 4.37; N, 8.09; I, 36.66. Found: C, 41.95; H, 4.36; N, 7.99; I, 36.50.

The compound gave a dark red color with ferric chloride solution. It was soluble in polar solvents, but insoluble in ether, acetone, and ethyl acetate. It gave a precipitate with silver nitrate solution. When a solution of 1.00 g. of I in 20 ml. of acetone was treated dropwise with 2.0 g. of triethylamine, 0.63 g. of precipitate was formed, m.p. 179–181°, no depression when mixed with II. Evaporation to dryness of the mother liquor gave 0.57 g. of residue, which on extraction with acetone and evaporation of the solvent, gave 0.26 of a white powder, m.p. 179–180°, no depression when mixed with authentic triethylamine hydroiodide, but m.p. 140–160°, when mixed with II.

Titration of II. Potentiometric titration of an aqueous solution of II with 0.05N NaOH gave a sharp break (0.02 ml.) between pH 7.8 and 8.4. The neutral equivalent calculated from this consumption of alkali was 344.4 ± 2.0 . Calcd. for $C_{12}H_{15}IN_2O_2$: 346.2.

Ultraviolet spectra of II. The spectra determinations were made with a Beckman DU quartz spectrophotometer using water as a solvent. At pH 2.1, a solution of II gave maxima at 288 $m\mu$, $\epsilon = 11,800$ and 225 $m\mu$, $\epsilon = 21,300$. At pH 9.7 maxima were at 320 $m\mu$, $\epsilon = 10,500$ and 248 $m\mu$, $\epsilon = 16,000$. From the literature curves,¹ the comparable figures secured with I were, at pH 2.1, 288 $m\mu$, $\epsilon = 5700$ and at pH 10.2, 320 $m\mu$, $\epsilon = 5,200$.

Attempted preparation of III. To 1.0 g. of II in methanol there was added freshly prepared silver carbonate until no further precipitation of silver iodide occurred. The mixture was heated to boiling and filtered. Ether was added to the filtrate until it became turbid. Cooling in an ice-salt bath gave a silvery crystalline mass melting at 10–20° to a clear oil. The oil gave a negative test with silver nitrate solution. Attempted distillation of the oil at 1 mm. gave extensive decomposition. On standing in air, the oil turned brown. The spectrum of the freshly prepared oil in water (pH 7.6) showed maxima at 319 and 248 $m\mu$. Heating II with triethanolamine at 150° gave triethanolamine hydroiodide, m.p. 173–174, no depression with a sample prepared from triethanolamine and hydrogen iodide. No product could be isolated from the mother liquor.

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Hydrogenolysis of 1-Nitronaphthalene by Complex Metal Hydrides

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A number of reports have appeared in recent years on hydrogenolysis by complex metal hy-

drides.² Most of these have concerned the hydrogenolysis of carbon-oxygen bonds, such as in alcohols, ketones, esters, and amides. The hydrogenolysis of halogen compounds has been reported also,^{2,3} while two reports on the hydrogenolysis of an aliphatic nitro group have appeared.^{4,5}

We are now able to add to these examples of the reactions of complex metal hydrides the hydrogenolysis of an aromatic nitro group. This occurred during attempts to convert 1-nitronaphthalene to the azonaphthalene. Although some nitrobenzenes are reduced to the azobenzenes by lithium aluminum hydride⁶ and nitrobenzene to azoxybenzene by sodium borohydride,⁷ 1-nitronaphthalene behaves quite differently. Numerous attempts to prepare 1,1'-azonaphthalene from 1-nitronaphthalene by the action of lithium aluminum hydride, sodium-, potassium-, and lithium borohydride have proved, for the most part, unsuccessful. A small amount of the azocompound was obtained from some experiments with lithium aluminum hydride, while in other experiments with this hydride no azocompound could be isolated. No azonaphthalene was found in experiments with the other hydrides even though the red color of the solutions during reduction suggested the presence of azocompound. In all of the reductions some naphthylamine was formed along with large amounts of tars. In all experiments with sodium- and potassium borohydride small amounts of naphthalene were also obtained. Although there was usually a faint smell of naphthalene during the working-up of the products from lithium aluminum hydride reductions, it was possible to isolate the naphthalene in only one experiment with this hydride; this was in the case of reduction by reverse addition. There is no doubt that the naphthalene was formed as a result of reaction during these experiments; the nitronaphthalene used was well purified.

The course of the hydrogenolysis is not clear. There is some indication that the tarry products obtained in the reductions lead partly to naphthalene on treatment with dilute hydrochloric acid. Thus, we suspect that naphthalene may arise

(1) From the M. S. thesis of Miss Meiling Tsai, Texas Technological College, 1958.

(2) N. G. Gaylord, *Reduction with Complex Metal Hydrides*, Interscience Publishers, Inc., New York, N. Y., 1956, pp. 979–91.

(3) W. E. Rosen, V. P. Toohey, and A. C. Shabica, *J. Am. Chem. Soc.*, **80**, 935 (1958).

(4) H. J. Backer, *Rec. trav. chim.*, **64**, 844 (1949), obtained a small amount of $CH_2(SO_2CH_3)_2$ from the action of lithium aluminum hydride on $O_2NCH(SO_2CH_3)_2$.

(5) R. Adams and W. Moje, *J. Am. Chem. Soc.*, **74**, 5557 (1952), obtained a 60% yield of bis-2-(1,4-naphthalenedibenzene-sulfonamido)methane by the action of lithium aluminum hydride on bis-2-(1,4-naphthalenedibenzene-sulfonamido)nitromethanol.

(6) Reference 2, p. 773.

(7) C. E. Weill and G. S. Panson, *J. Org. Chem.*, **21**, 803 (1956).

partly from the decomposition of metal hydride-organano complex. The naphthalene cannot have been formed from first-formed naphthylamine, since experiments with 1-naphthylamine led only to the recovery of the naphthylamine. Also, 1,1'-azonaphthalene was recovered quantitatively from attempted reduction with the same reducing agents under the same conditions. The ease with which naphthalene is formed appears to be greater with the borohydrides than with lithium aluminum hydride.

It is possible to account for the naphthalene by an extension of the scheme⁸ for the hydrogenolysis of ketones, in the present case attack occurring at the polar C—N bond. We have no direct evidence for this, however.

Attempts to hydrogenolyze nitrobenzene were unsuccessful. Further work is being carried out in the naphthalene series and with dinitrobenzenes.

EXPERIMENTAL

Sodium borohydride. A solution was made by dissolving 10.35 g. of sodium borohydride in 200 ml. of diglyme (diethylene glycol methyl ether), which had been previously distilled over solid sodium hydroxide. The solution was filtered and stored in a protected vessel. The concentration of the solution was determined by the method of Lyttle, Jensen, and Struck.⁹

Reduction with sodium borohydride. To 80 ml. of solution (0.09 mole sodium borohydride) was added slowly a solution of 10 g. (0.058 mole) of 1-nitronaphthalene in 35 ml. of diglyme. The temperature during addition was kept below 0°. After addition the solution was allowed to come to room temperature and stirred for 18 hr. To the orange solution was added 150 ml. of water followed by 50 ml. of dilute hydrochloric acid. The color changed to dark brown.

Steam distillation gave 0.54 g. (7.3% yield) of naphthalene. Crystallization from ethanol gave m. p. 81°. The mixture remaining from steam distillation was made alkaline and steam distilled. Extraction of the distillate with ether and addition of hydrogen chloride to the dried ether solution gave 3.06 g. (29% yield) of 1-naphthylamine hydrochloride. Customary treatment with base gave 1-naphthylamine, m.p. 48°.

The tarry residue from the steam distillations was extracted with benzene. Evaporation of the benzene left a brown tar. Vacuum sublimation gave only a small amount of an unidentified oil.

In a second experiment water was added to the deep red reduction solution obtained after standing overnight at

room temperature. The aqueous solution was then stripped of solvent at room temperature by vacuum distillation. The residue was triturated several times with water to give 7 g. of a light brown odorless solid. This burned completely only on strong heating. Warming the solid with dilute hydrochloric acid gave the distinct smell of naphthalene.

Reduction with lithium aluminum hydride (direct addition). To an ether solution containing 0.2 mole of lithium aluminum hydride was added dropwise an ether solution of 17.3 g. (0.1 mole) of 1-nitronaphthalene. The addition was carried out at room temperature. The solution became light orange at the beginning of addition and was dark brown at the end. Ice water was added and after separation the aqueous tarry slurry was extracted with benzene. The combined benzene and ether layers were washed with dilute acid, dried, and evaporated to give 2.9 g. of brown solid. Vacuum sublimation gave 0.75 g. (5.3% yield) of 1,1'-azonaphthalene, melting point, after crystallization from acetic acid, 189–190°. No naphthalene could be detected. The combined aqueous portions were made alkaline and steam distilled to give 1-naphthylamine. This was extracted into ether solution and precipitated as the hydrochloride. Treating the hydrochloride with base gave 2.2 g. (15.3% yield) of 1-naphthylamine; crystallization from aqueous ethanol gave m.p. 48°.

In two other experiments carried out as described above there was a faint smell of naphthalene in the steam distillate. Attempts to isolate the naphthalene were unsuccessful. In these experiments, also, no azonaphthalene was obtained.

*Reduction with lithium aluminum hydride (reverse addition).*¹⁰ A solution of 10.38 g. (0.06 mole) of 1-nitronaphthalene in 150 ml. of dry ether was used. To this was added dropwise 100 ml. of an ether solution of the hydride (0.053 mole). After stirring an additional 45 min. cold water was added cautiously followed by hydrochloric acid. The ether was distilled off at reduced pressure and replaced with benzene. Subsequent treatment as described above gave 0.165 g. (1.95% yield) of azonaphthalene. Steam distillation of the aqueous solutions, after addition of sodium hydroxide, gave a mixture of naphthylamine and naphthalene. These were separated by dissolving in ether and extracting the amine with hydrochloric acid. The brown residue remaining after evaporation of the ether gave, by sublimation, 0.04 g. (0.5% yield) naphthalene, m.p. 79–81°. The naphthylamine was recovered as the hydrochloride; 1.2 g. (11.2% yield), and was identified as the acetyl derivative, m.p. 156–158°.

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(8) Reference 2, p. 981.

(9) D. A. Lyttle, E. H. Jensen, and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).

(10) These data were included in the revised copy of this paper, received in the Editor's office June 26, 1958.