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# Studies on Catalytic Action, I : Catalytic Reduction of $\alpha$ -Naphthol and $\alpha$ -Naphthylamine

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# Studies on Catalytic Action, I. Catalytic Reduction of $\alpha$ -Naphthol and $\alpha$ -Naphthylamine.

By

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Ar-Tetrahydro- $\alpha$ -naphthol and ar-tetrahydro- $\alpha$ -naphthylamine were prepared by Bamberger and his collaborators<sup>1</sup> by the action of sodium and boiling amylalcohol on  $\alpha$ -naphthol and  $\alpha$ -naphthylamine respectively. H. Lerowx,<sup>2</sup> however, has reported that decahydro- $\alpha$ -naphthol and decahydro- $\alpha$ -naphthylamine were formed when  $\alpha$ -naphthol and  $\alpha$ -naphthylamine were reduced with hydrogen and reduced nickel at 200°. On the other hand, Professor P. Sabatier<sup>3</sup> succeeded in preparing tetrahydro-naphthalene by reducing naphthalene with hydrogen in the presence of nickel.

Authors, therefore, expected that ar-tetrahydro- $\alpha$ -naphthol would be obtained from  $\alpha$ -naphthol by catalytic reduction, when the favorable conditions had been discovered for effecting the partial reduction of the compound.

15 gm. pure  $\alpha$ -naphthol (m. p. 95–96°) prepared by the potash-fusion of  $\alpha$ -naphthalenesulphonic acid and then purified by steam distillation, were passed with pure hydrogen over reduced nickel heated to 100–110°, and 11.7 gm. of the reaction product were obtained. The product, proved free from naphthol by the conc. sulphuric acid-nitrous acid test, was extracted with 10% caustic potash solution. The caustic alkaline solution after washing with ether to remove

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<sup>1</sup> Ber. D. Chem. Ges., **23**, 215 (1800); **21**, 1786 (1886).

<sup>2</sup> C. R., **141**, 953 (1905); Ann. chim. phys., (8) **21**, 483 (1910).

<sup>3</sup> C. R., **132**, 1254 (1901).

neutral substances completely, was acidified with diluted hydrochloric acid, whereupon 4.9 gm. of crude hydrogenated naphthol separated which was then purified by distillation under 750 mm. and collected fraction boiling at 262–266°. The yield was 2 gm.

It was soluble in dilute caustic alkaline solution and organic solvents but scarcely in ammonia water. It melted at 68.5°, and yielded azo-compound with diazobenzene chloride. The physical and chemical properties so far studied agree with those of ar-tetrahydro- $\alpha$ -naphthol prepared first by Bamberger.<sup>1</sup> For confirmation, the substance was oxidized with potassium permanganate, and oxalic and adipic acids were isolated from the oxidation product. The latter compound was identified by its melting point (m. p. 148.5–149°) and the preparation of a characteristic copper salt of the acid. On analysis of the hydrated naphthol, it gave the following results:

0.1370 gm. substance gave 0.4043 gm. CO<sub>2</sub> and 0.1019 gm. H<sub>2</sub>O.

	Calc. for C <sub>10</sub> H <sub>12</sub> O.	Found.
C	81.03	80.49
H	8.17	8.32
O	10.80	—

The oily substance, insoluble in caustic potash solution, was extracted with ether; the ether being distilled off from the solution, the residual oil amounted to 6 gm. It was subjected to fractional distillation under 22 mm., and 3.5 gm. A fraction, B. p. 100–130°, and 1.5 gm. B fraction, B. p. 130–155°, were separated. The B fraction was confirmed to consist of  $\alpha$ -ketotetrahydronaphthalene by converting into its semicarbazone in the manner described by F. S. Kipping and Hill.<sup>2</sup> The melting point and solubility of the semicarbazone agree with those of Kipping's compound. On analysis of the semicarbazone, it gave the following results:

0.1005 gm. substance gave 0.2356 gm. CO<sub>2</sub> and 0.0611 gm. H<sub>2</sub>O.

	Calc. for C <sub>11</sub> H <sub>13</sub> ON <sub>3</sub> .	Found.
C	65.00	63.91
H	6.48	6.80

<sup>1</sup> Loc. cit.; P. Jacobson and A. Turnbull: Ber. D. chem. Ges., **31**, 897 (1898).

<sup>2</sup> J. Chem. Soc., **75**, 144 (1899).

A fraction was also studied and was found to consist of tetrahydronaphthalene by the analysis and determination of density and index of refraction of the purified substance (B. p. 202-4°, 753 mm.), distilled under ordinary pressure and then on metallic sodium.

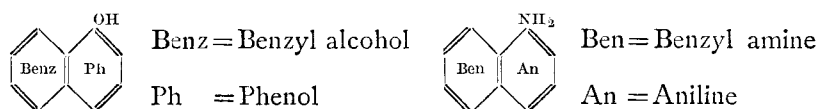
0.1258 grm. sub. gave 0.4161 grm. CO<sub>2</sub> and 0.1102 grm. H<sub>2</sub>O.

	Calc. for C <sub>10</sub> H <sub>12</sub> .	Found.
C	90.84	90.22
H	9.16	9.80
	n <sub>D</sub> <sup>25°</sup> = 1.5327	d <sub>4</sub> <sup>25°</sup> = 0.9629

In another experiment, 11 grm. of the product were obtained from 15 grm. *α*-naphthol by reducing at 135-145°, from which 1 grm. pure ar-tetrahydro-*α*-naphthol, and 10 grm. of a mixture of keto-tetrahydronaphthalene and tetrahydronaphthalene, were isolated.

The formation of both tetrahydronaphthalene and *α*-keto-tetrahydronaphthalene from *α*-naphthol was easily explained by assuming the intermediate formation of ac-tetrahydro-*α*-naphthol, since naphthol could be presumed to behave analogously as phenol did toward the reducing agent. We were, therefore, led to the conclusion that *α*-naphthol upon reduction with hydrogen in the presence of reduced nickel at 100-110° simultaneously 41% crude ar-tetrahydro-*α*-naphthol (20% pure comp.) and 51% ac-tetrahydro-*α*-naphthol, but at 135-145°, 10% pure ar-compound and 90% ac-compound.

*α*-Naphthol may be regarded as a phenol derivative in consideration of the substitution of the benzene nucleus by the hydroxyl group and on the other hand as a benzyl alcohol derivative, in respect of the non-substituted nucleus:



The difference in the yield of the reducing substances from *α*-naphthol as above mentioned can be viewed as that which prevails between benzylalcohol and phenol derivatives towards the reducing agent.<sup>1</sup> In the same way, when *α*-naphthylamine is regarded as a condensed com-

<sup>1</sup> P. Sabatier and Senderens: C.R., 137, 1025 (1903).

pound of benzylamine and aniline, a fruitful result in the yield of ar-tetrahydro- $\alpha$ -naphthylamine from  $\alpha$ -naphthylamine by catalytic reduction can easily be anticipated by referring to the results of aniline and benzylamine.<sup>1</sup> 20 gm.  $\alpha$ -naphthylamine (B. p. 174–6°, 20 mm.) obtained from a commercial substance by fractional distillation at reduced pressure, was reduced with hydrogen in the presence of reduced nickel at 135–145°, and 16 gm. of the product were obtained. The product was treated with dilute hydrochloric acid and the acid solution separated from the insoluble oil was alkalinized with caustic potash solution after washing with ether to expel a hydrocarbon formed simultaneously during the catalytic reduction. The basic substance thus isolated after drying with anhydrous sodium sulphate was fractionated 3 times at ordinary pressure.

20 gm.  $\alpha$ -naphthylamine :

16 gm. reaction product.

1.2 gm. crude hydrocarbon.

10 gm. crude hydrogenated base, B. p. 260–278° 752 mm.

4 gm. crude  $\alpha$ -naphthylamine, B. p. above 278°, 752 mm.

The crude hydrogenated base was purified by distillation at ordinary pressure and also under reduced pressure, of the fraction boiling at 156–160°, 22 mm., the density and the index of refraction were determined:  $d_4^{25} = 1.0500$  and  $n_D^{25} = 1.5829$ .

It yielded a diazonium chloride and azo-compound. As far as could be judged, the main portion of the fraction, B. p. 260–278°, consisted of ar-tetrahydro- $\alpha$ -naphthylamine which was formerly obtained by Bamberger<sup>2</sup> by a different method. In order to confirm the idea, the substance was analysed :

0.1350 gm. sub. gave 0.4052 gm. CO<sub>2</sub> and 0.1094 gm. H<sub>2</sub>O.

0.1390 gm. sub. gave 0.01285 gm. N by Kjeldahl's method.

	Calc. for C <sub>10</sub> H <sub>13</sub> N	Found.
C	81.57	81.86
H	8.90	9.06
N	9.52	9.25

<sup>1</sup> P. Sabatier and Senderens : C. R., 138, 457 (1904); P. Sabatier and Mailhe : Ibid., 153, 160 (1911); P. Sabatier : La Catalyse en Chimie Organique. 1920, p. 177.

<sup>2</sup> Loc. cit.

On the other hand the base was converted into naphthol with nitrous acid and the resulting ar-tetrahydro- $\alpha$ -naphthol<sup>1</sup> was confirmed by its elementary analysis:

0.068 grm. sub. gave 0.2015 grm. CO<sub>2</sub> and 0.0523 grm. H<sub>2</sub>O.

	Calc. for C <sub>10</sub> H <sub>12</sub> O	Found.
C	81.03	80.82
H	8.17	8.60

A mixture of the hydrogenated naphthol thus obtained and that from  $\alpha$ -naphthol by direct reduction showed no lowering in the melting point (m. p. 68.5°).

The hydrocarbon separated from the basic portion of the reaction product was found to boil at 204-6°, and was confirmed to be tetrahydronaphthalene<sup>2</sup> by its analysis:

0.0958 grm. sub. gave 0.0760 grm. H<sub>2</sub>O and 0.3190 grm. CO<sub>2</sub>.

	Calc. for C <sub>10</sub> H <sub>12</sub> .	Found.
C	90.84	90.81
H	9.16	8.88

Of the reaction product from  $\alpha$ -naphthylamine by catalytic reduction at 135-145°, obtained 90% ar-tetrahydro- $\alpha$ -naphthylamine and 10% ac-tetrahydro- $\alpha$ -naphthylamine and the latter transformed into tetrahydronaphthalene and thus our hypothesis was proved.

Reduction temp.		Percentage of reduction product	
		ar-tetrahydro-comp.	ac-tetrahydro-comp.
Naphthol	100-110°	20 (41 as crude sub.)	(51 as crude sub.)
	135-145°	10	90
Naphthylamine	135-145°	90	10

(July, 1922. Laboratory of Organic & Bio-chemistry.)

<sup>1</sup> A. G. Green & F. M. Rowe: J. Chem. Soc., **113**, 965 (1918); E. Bamberger & M. Althaus: Ber. D. Chem. Ges., **21**, 1893 (1888).

<sup>2</sup> C. Graebe and P. A. Guye: Ber. D. chem. Ges., **16**, 3028 (1883).