

# Studies on Catalytic Action, V. Catalytic Reduction of $\alpha$ and $\beta$ -Naphthyl Methyl Ethers.

By

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In the first communication on the subject<sup>1</sup>, a brief account was given on the investigation of the catalytic reduction of  $\alpha$ -naphthol and  $\alpha$ -naphthylamine, yielding 10% ar-compounds and 90% ac-compounds in the former, and 90% ar-compounds and 10% ac-compounds in the latter respectively. The cause of the difference in the yield of the ar- and ac-compounds in both  $\alpha$ -derivatives of naphthalene, which was explained by regarding  $\alpha$ -naphthol as a condensed compound of phenol and benzylalcohol, and  $\alpha$ -naphthylamine analogously as a united one of aniline and benzylamine. It may also be attributed to the difference of the electronic nature of the groups substituting H <sub>$\alpha$</sub>  atom of the naphthalene molecule; the NH<sub>2</sub> group having a strong basic character compared with the OH group, exerted a certain amount of influence on the naphthalene molecule to prevent the hydrogenation of the substituted nucleus, accordingly in  $\alpha$ -naphthylamine the ar-compounds predominate in the reduced compounds compared with the case of naphthol as shown in the experiment.

When  $\alpha$ -naphthol was transformed into the methyl ether, the basic character of the oxygen atom in the compound by replacing the hydrogen atom combined with the oxygen atom with the methyl group<sup>2</sup>

<sup>1</sup> These Memoirs. **6**, 177 (1923).

<sup>2</sup> A. Wurtz : Atomic theory, 7th Ed., 250 ; J. H. vant Hoff : Ansichten ü. Org. Chem., **63**. (1877), N. Collie and Tickle : J. Chem. Soc., **75**, 710 (1897), A. Baeyer und Villiger : Ber. D. Chem. Ges., **34**, 2679, 3612 (1901); **35**, 120 (1902); J. Schmidt : u. d. Basischen Eigenschaft. d. Sauerstoffs u. Kohlenstoffs, 1904.

was evidently strengthened and consequently the  $\text{OCH}_3$  group should naturally be expected to exert an influence similar to that observed on the  $\text{NH}_2$  group in naphthylamine, on the hydrogenation of the naphthyl ether, with a greater yield of ar-compounds than the ac-one.

$\text{NH}_3$	$\text{OH}_2$
base	neutral.
$\text{N}(\text{CH}_3)_3$	$\text{O}(\text{CH}_3)_2$
strong base	weak base.

$\alpha$ -Naphthyl methyl ether<sup>1</sup> used in this experiment, was prepared by the interaction of 270 gm.  $\alpha$ -naphthol purified by steam distillation, and 450 gm. dimethyl sulphate in 500 c.c. 15% caustic soda solution at ordinary temperature, the reaction product alkalined with 600 c.c. 30% caustic soda solution, was then subjected to steam distillation to isolate the ether, and the oily layer in the distillate, separated from the aqueous part, was purified by distillation after drying with sodium sulphate and then with fused caustic soda. It boiled at  $67-9^\circ$ , and the yield was 229 gm. which corresponds to 77% of the theory.

175 gm. of the ether were passed with the purified hydrogen gas on the reduced nickel heated at  $200^\circ$ , and 150 gm. of the reaction product obtained.

It was subjected to the fractional distillation under ordinary pressure as usual for about 20 times, and was separated into the following ten portions :

Fractions.	Yield.	
	in gm.	in mol.
1. 204--206°	0.8	0.006
2. 210--214°	3.5	0.030
3. 216--220°	1.0	0.008
4. 230--240°	1.6	0.012
5. 240--243°	2.7	0.016
6. 245--250°	4.2	0.044
7. 250--253°	7.0	0.088
8. 254--258°	14.0	0.099
9. 258--260°	15.8	
10. above 260°	58.1	
	<u>108.7</u>	

<sup>1</sup> V. Meyer and P. Jacobson : *Lehrbuch d. Organ. Chem.*, II, 2, 365.

The chemical analysis and the determination of the physical constants were made of each fraction and the results were as follows :

**1. The fraction, B. p. 204--206°, Tetrahydronaphthalene<sup>1</sup>.**

It was found to consist of tetrahydronaphthalene<sup>1</sup>, by analysis and determination of density and the index of refraction.

C=90.55 ; H=8.93 (theory requires C=90.84 ; H=9.16 for C<sub>10</sub>H<sub>12</sub>) and  $n_D^{25} = 1.5494$  ;  $d_4^{25} = 0.9767$ .

**2. The fraction, B. p. 210--214°, Dihydronaphthalene.**

The results of the analysis, C=92.49 ; H=8.93, and the determination of the physical constants,  $n_D^{25} = 1.5499$  ;  $d_4^{25} = 0.9878$ , agree fairly well with those of dihydronaphthalene obtained by other chemists<sup>2</sup>.

**3. The fraction, B. p. 216--220°, Naphthalene.**

Expecting that the fraction consisted of naphthalene and some other hydrocarbons, it was treated with the alcoholic solution of picric acid to isolate naphthalene, whereas yellow needle crystals separated, which, after being purified by recrystallisation, were confirmed to be naphthalene picrate by determination of melting point<sup>3</sup>(149°).

The formation of naphthalene and its hydrogenated hydrocarbons in the course of the catalytic reduction of the ether, was explained by assuming the formation of dihydronaphthalene by the decomposition of ac-tetrahydronaphthyl methyl ether which was regarded to be formed simultaneously with ar-tetrahydronaphthyl ether by the catalytic reduction of the naphthyl ether ; dihydronaphthalene partially transformed catalytically into naphthalene and tetrahydronaphthalene, as H. Wieland<sup>4</sup> has already observed on dihydronaphthalene, which by shaking with palladium black dissolved in benzene, yields naphthalene and tetrahydronaphthalene, and the remainder evidently reduced by the catalytic action of hydrogen and nickel to tetrahydronaphthalene :

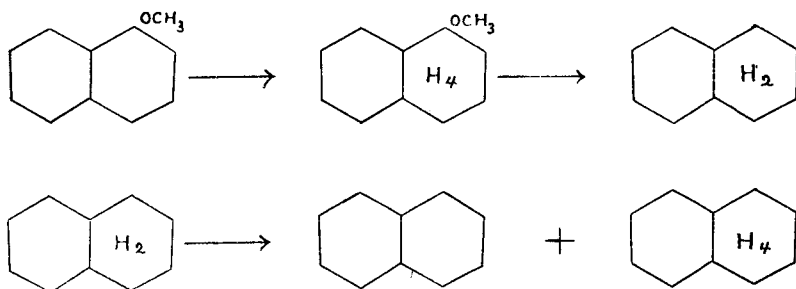
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<sup>1</sup> Beilsteins Handbuch d. Org. Chem., 4 Auf., V, 491 (1922).

<sup>2</sup> Ibid., 518.

<sup>3</sup> V. Meyer and P. Jacobson : Lehrbuch d. Organ. Chem., II, 2, 323.

<sup>4</sup> Ber. D. Chem. Ges., 45, 486 (1912) ; and also refer A. Mailhe and M. Murat : Bull. soc. chim., (4), 11, 122 (1912).



#### 4. The fraction, B. p. 229—231°,

The analytical results indicate that the fraction consists of a mixture of hydrocarbon and ether : C=87.07 ; H=8.45.

#### 5. The fraction, B. p. 245—248°, $\alpha$ -ar-Tetrahydronaphthyl Methyl Ether.

Its theoretical value for the elementary composition and methoxyl value agrees with the experimental results of the fraction : C=80.93 ; H=8.70 ; OCH<sub>3</sub>=18.28.  $n_D^{25}$ =1.5700 ;  $d_4^{25}$ =1.0413.

#### 6. $\alpha$ -ar-Dihydronaphthyl Methyl Ether. ( $\Delta^6$ and $\Delta^7$ ).

The analytical results and methoxyl determination indicate the fractions B. p. 254—256° and B. p. 250—252°, consist of pure ar-dihydronaphthyl ether though the methoxyl value of the fractions showed a slight difference compared with the theoretical one for the ether.

The fraction, B. P. 250—252° : C=82.51 ; H=7.83 :

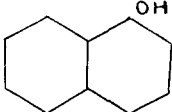
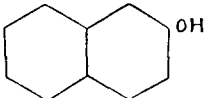
The fraction, B. p. 254—256° : C=82.38 ; H=7.74 ;

OCH<sub>3</sub>=18.33,  $d_4^{25}$ =1.5768 ;  $n_D^{25}$ =1.5768 ; theory requires C=82.50 ; H=7.50 ; OCH<sub>3</sub>=19.38. for C<sub>10</sub>H<sub>9</sub>OCH<sub>3</sub>.

Two structural formulae ( $\mathcal{J}^6$  and  $\mathcal{J}^7$ ) for  $\alpha$ -ar-dihydronaphthyl ether are theoretically possible but their decision was remained.

When  $\alpha$ -naphthyl methyl ether was reduced catalytically with hydrogen and nickel at a temperature of 200°, it yielded 19% ar-compounds and 81%  $\alpha$ -ar-compounds calculated on the molecular weight basis, and thus our expectation was realised.

The authors<sup>1</sup> attention was directed to the examination of the relative yield of ac- and ar-compounds in the reduction of the naphthols and the results compiled from many experiments were summarised in the following table :

	Temp.	Ac-comp. %	Ar-comp. %
	{ 150 <sup>o1</sup>	85	15
	{ 135 <sup>2</sup>	89	11
	{ 110 <sup>2</sup>	56	44
	{ 135 <sup>4</sup>	—	100
	{ 150 <sup>o1</sup>	75	25
	{ 135 <sup>3</sup>	60	40
	{ 135 <sup>4</sup>	79	21

When we examine the above figures in detail, the following conclusions were drawn : 1. the rate of formation of the ac-compounds increase with rise of temperature, 2. the velocity of the formation of ac-compounds in the case of  $\beta$ -naphthol is much more retarded than in  $\alpha$ -isomer, so that under the same experimental conditions, it yielded 75% ac-compounds in the former but 85% in the latter. The second conclusion may be explained, if we adopt the hypothesis of steric hindrance ; the spatial disposition of the OH group to the non-substituted nucleus— the neighbouring benzene nucleus of the naphthalenemolecule, effects the chemical character of the molecule as a whole, in the catalytic reduction of the naphthols, to result as described above in details.

The catalytic reduction of  $\beta$ -naphthyl methyl ether was undertaken to study whether a steric hindrance which could be encountered in the reduction of the ethers, resembled that observed in naphthols.

The sample used in the experiment was obtained from the

<sup>1</sup> A. Brchet and R. Cornubert : Bull. soc. chim., (4), **31**, 1280 (1922).

<sup>2</sup> S. Komatsu and R. Nodzu : These Memoirs, **6**, 177 (1923).

<sup>3</sup> S. Komatsu and I. Nishimatsu : Unpublished work.

<sup>4</sup> E. Bamberger & W. Lodter : Ber. D. Chem. Ges., **23**, 197 (1890) ; E. Bamberger & M. Kitschelt : Ibid., **23** 885 (1890) ; E. Bamberger and F. Lengfeld : Ibid., **23**, 1124 (1890)

market and was purified by steam distillation in an alkaline solution, and distillate collected, and this was found to melt at 72°.

155 gm. of the sample were reduced catalytically with reduced nickel at 200° and the product amounting to 123 gm., after repeated distillation under ordinary pressure for about 20 times, was separated into the following 7 portions :

Fractions.	Yield.	
	in gm.	in mol.
1. 203--205°	20	0.152
2. 211--213°	1	0.008
3. 215--225°		0.008
4. 238--250°	3	0.020
5. 252--255°	40	0.244
6. 256--258°	3	0.020
7. above 258°	13	
	81	

The results of the analysis and of the determination of the physical constants of each fraction, were as follows :

**1. The fraction, B. p. 203--205°, Tetrahydronaphthalene.**

It gave on analysis C=91.07 ; H=8.50, (theory requires C=90.84 ; H=9.16 for  $C_{10}H_{12}$ ),  $n_D^{25} = 1.5490$  ;  $d_4^{25} = 0.984$  .

**2. The fraction, B. p. 211--213°, Dihydronaphthalene.**

It gave on analysis C=91.62 ; H=8.08 (theory requires C=92.31 ; H=7.69 for  $C_{10}H_{10}$ ).

**3. The fraction, B. p. 215--225°, Naphthalene.**

It was supposed that this portion consisted partly of naphthalene which was confirmed by transforming it into picrate as usual.

**4. The fraction, B. p. 238--250°,  $\beta$ -ar-Hexahydronaphthyl Methyl Ether.**

The analytical results of this fraction giving C=80.84 ; 81.02 ; H=8.38 ; 8.34, agree fairly well with those of hexahydronaphthyl methyl ether which require C=80.49 ; H=9.76, however, confirmation was lacking due to the small quantity.

**5. The fraction, B. p. 252--255°,  $\beta$ -ar-Tetrahydronaphthyl Methyl Ether.**

It gave on analysis C=81.38 ; H=8.49 ;  $CH_3O=18.45$ , a

result which agrees with the theoretical values  $C=81.48$ ;  $H=8.64$ ;  $CH_3O=19.14$  for tetrahydronaphthyl methyl ether, and also gave the physical constants  $n_D^{25} = 1.5437$ ;  $d_4^{25} = 1.0344$ .

#### 6. The fraction, B. p. 256--258°, $\beta$ -ar-Dihydronaphthyl Methyl Ether.

It gave on analysis  $C=82.13$ ;  $H=7.97$ ;  $CH_3O=18.80$ , and the constants  $n_D^{25} = 1.5800$ ;  $d_4^{25} = 1.0605$ , the theory requiring  $C=82.50$ ;  $H=7.50$ ;  $CH_3O=19.38$  for  $C_{10}H_9OCH_3$ .

Of the reaction products from  $\beta$ -naphthyl ether, by the catalytic reduction at 200°, we obtained 37% ac-compounds and 63% ar-compounds, and the former calculated from the yield of the hydrocarbons, since they were regarded as formed from the ac-hydronaphthyl ether by catalytic action of reduced nickel at high temperature and ordinary pressure, as explained in the case of  $\alpha$ -isomer.

It is the intention of one of the authors (S. Komatsu) of this paper to discuss in the next article how finely divided reduced nickel acts to promote dehydration, under certain condition, as reduced copper does<sup>1</sup>.

It was noteworthy fact that  $\alpha$ -naphthyl methyl ether by reduction with metallic sodium and boiling amyl alcohol, instead of hydrogen and finely divided nickel yields only ar-tetrahydronaphthyl methyl ether, B. p. 245--248°, givin on analysis  $C=80.72$ ;  $H=8.83$ .

$\beta$ -Isomer, analogously, was resulted by the same treatment to form ar-tetrahydronaphthyl methyl ether,  $C=81.31$ ;  $H=8.28$ . When, however,  $\beta$ -ether reduced with metallic sodium and ethyl alcohol, it yields a new hydrogenated ether boiled at 256--258°, which was confirmed to be  $\beta$ -ar-dihydronaphthyl methyl ether by analysis  $C=82.49$ ;  $H=7.44$ .

As a matter of fact, the atomic groups possessing a basic character such as  $NH_2$  or  $OCH_3$ , when combined with  $\alpha$  or  $\beta$  carbon atom of the naphthalene molecule, facilitate the formation of ar-compounds in the catalytic reduction of naphthalene derivatives, while

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<sup>1</sup> S. Komatsu: These Memoirs, 7. 85 (1923).

the methoxyl group replaced by the hydroxyl group of non-basic nature in the naphthalene molecule, retards their formation. We, however, must confess that we are still ignorant of the reasons why the atomic group of basic character retards the formation of ac-compounds, and why the spatial disposition of the methoxyl group in naphthalene, exerts an influence on the formation of ac-compounds— the only term, so far as we know, to call such phenomena is “steric hindrance”.

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