L.—*Studies in the Naphthalene Series. Part III. The Preparation of 3-Amino-2-naphthyl Methyl Ether.*

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THE importance of the 3-substituted derivatives of β-naphthol, *e.g.*, 2-hydroxy-3-naphthoic acid and its arylamides, makes it of interest to examine the hitherto unknown or little known compounds, such as the 3-halogeno-derivatives and the 3-sulphonic acid.

The most convenient intermediate for the latter is 3-amino-2-naphthol or its methyl ether. This compound was first prepared by Friedländer and Zakrewski (*Ber.*, 1894, **27**, 763) by the following route : β-naphthol ⟶ β-naphthol-3 : 6-disulphonic acid ⟶ 2 : 3-dihydroxynaphthalene-6-sulphonic acid ⟶ 2 : 3-dihydroxynaphthalene ⟶ 3-amino-2-naphthol. The process is, however, long and the yields are unsatisfactory, and the substitution of ammonium sulphite for ammonia in the last step (D.R.-P. 117471) does not greatly improve the over-all yield.

It seemed, therefore, desirable to work out an alternative method, starting from the readily accessible 2-hydroxy-3-naphthoic acid.

(1) *The Hofmann method*: 2-Hydroxy-3-naphthoic acid ⟶ methyl ether ⟶ acid chloride ⟶ amide ⟶ 3-amino-2-naphthyl methyl ether ⟶ 3-amino-2-naphthol.

The first three stages were carried out by means of methyl sulphate, thionyl chloride, and dry ammonium carbonate respectively. 2-Methoxy-3-naphthoic acid coupled readily with various diazotised aromatic amines in aqueous solution to form azo-dyes, in most cases with total or partial demethylation (see *J. Soc. Dyers and Colourists*, 1930, **46**, 339).

For the conversion of the amide into 3-amino-2-naphthyl methyl ether the Hofmann reaction was tried in many ways (with hypochlorite; hypobromite; and bromine in alkaline aqueous, alcoholic, and aqueous-alcoholic solutions), but with uniformly unsatisfactory results, the yield under the best conditions varying from 5% to 20% of the theoretical. The methoxy-base was converted into 3-*chloro*-2-*naphthyl methyl ether* by the Sandmeyer–Gattermann method, and was hydrolysed by hydriodic acid to 3-chloro-2-naphthol, which coupled in the usual manner with amines to give ice colours of rather brighter shades than those obtained from β-naphthol itself.*

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* After this investigation was completed the preparation of 3-amino-2-naphthyl methyl ether (2-methoxy-3-naphthylamine) by the Hofmann method was described by Clemo and Spence (J., 1928, 2818), but as few experimental details were given it has been thought desirable to publish the results of the present extended investigation.

(2) *The Curtius method* : 2-Hydroxy-3-naphthoic acid ⟶ methyl ether ⟶ ethyl ester ⟶ hydrazide ⟶ azide ⟶ carbamate ⟶ 3-amino-2-naphthyl methyl ether ⟶ 3-amino-2-naphthol.

2 - *Methoxy* - 3 - *naphthhydrazide*, obtained from 2 - hydroxy - 3 - naphthoic acid through the stages indicated above, formed characteristic *hydrazides* on condensation with aldehydes; *di*-(2-*methoxy*-3-*naphth*)*hydrazide* was also obtained.

The hydrazide was converted into ethyl 2-methoxy-3-naphthylcarbamate by means of ethyl nitrite by the method of Jackson and Kenner (J., 1928, 1657).

In the conversion of the carbamate into the amine the normal method of heating with slaked lime was at first employed, but later it was found that more than 90% of the theoretical yield could be obtained by heating the carbamate with concentrated aqueous sodium hydroxide. This modification does not appear to have been employed before and may be useful in other cases.

3-Amino-2-naphthol was obtained in very good yield by method (2).

EXPERIMENTAL.

(1) *The Hofmann Method* [With G. W. B. JAMBUSERWALA].—2-*Methoxy*-3-*naphthoic acid*. 2-Hydroxy-3-naphthoic acid (48 g.), dissolved in 20% sodium hydroxide solution (100 c.c.), was gradually treated at 15° with methyl sulphate (64 g.), a little more sodium hydroxide being added if necessary to ensure alkalinity. The solution was acidified with hydrochloric acid and the precipitated methoxy-acid was dried and recrystallised from glacial acetic acid or alcohol, forming slightly yellow crystals (49·6 g.), m. p. 133—135° (yield, 96%) (Found : C, 71·1 ; H, 5·2. Calc. for $C_{12}H_{10}O_3$: C, 71·3 ; H, 4·9%). The use of too great an excess of alkali diminishes the yield of the desired product, and if a larger amount of methyl sulphate is used the product is contaminated with the methyl ester.

This method avoids the circuitous procedure of Lesser, Kranepuhl, and Sad (*Ber.*, 1925, **58**, 2116; compare also von Auwers and Frühling, *Annalen*, 1921, **422**, 197).

2-*Methoxy*-3-*naphthoyl chloride*. A mixture of the well-dried acid (19·2 g.) and ether (50 c.c.) was treated with thionyl chloride (38 g.; 18 c.c.) and heated on the water-bath until evolution of hydrogen chloride ceased. The ether and the excess of thionyl chloride were then removed under diminished pressure, the chloride being left as a transparent yellow gum, which fumed strongly in moist air; m. p. about 59° (decomp.). It could be distilled with difficulty under reduced pressure, readily decomposing (compare Fries and Schimmelschmidt, *Ber.*, 1925, **58**, 2839).

2-*Methoxy*-3-*naphthoamide*. The acid chloride (22 g.), dissolved in dry benzene (25 c.c.), was treated gradually with dried ammonium carbonate (20 g.) with good stirring; the mixture was finally heated on the water-bath to remove benzene and the excess of ammonium carbonate. (The use of ammonia in a neutral solvent gave much resinous product which could be removed only with difficulty.) After being washed with water, the amide crystallised from benzene as a yellowish-white granular substance (15·5 g.), m. p. 172—173° (yield, 77%) (Found: C, 71·6; H, 5·5; N, 6·9. Calc. for $C_{12}H_{11}O_2N$: C, 71·6; H, 5·5; N, 7·0%).

3-*Amino*-2-*naphthyl methyl ether*. A solution of the amide (15 g.) in warm alcohol (500 c.c.) was cooled, and treated with a hypobromite solution (prepared from 16 g. of bromine and 220 c.c. of 10% potassium hydroxide solution), the colour becoming brownish-red. After removal of the alcohol the semi-solid tarry residue was boiled with dilute hydrochloric acid, and from the acid extract the base was precipitated by dilute aqueous ammonia. After recrystallisation from benzene it melted at 109—110° (yield, not exceeding 3·0 g.) (Found: C, 76·2; H, 6·5; N, 8·0. Calc. for $C_{11}H_{11}ON$: C, 76·3; H, 6·4; N, 8·1%).

3-*Chloro*-2-*naphthyl methyl ether*. The amino-base (2·5 g.) was dissolved in 20% hydrochloric acid (25 c.c.) and diazotised with a concentrated solution of sodium nitrite (2 g.). The product was added gradually to a solution of cuprous chloride (2·6 g.) in concentrated hydrochloric acid (100 c.c.), and the temperature raised slowly to 50°. 3-*Chloro*-2-*naphthyl methyl ether*, which separated as a gum, crystallised, after steam-distillation, from methyl alcohol in leaflets, m. p. 78·5° (yield, 82%) (Found: C, 68·7; H, 4·6; Cl, 18·1. $C_{11}H_9OCl$ requires C, 68·7; H, 4·7; Cl, 18·2%).

3-*Chloro*-2-*naphthol*. A portion of the methyl ether was refluxed with " Zeisel " hydriodic acid for $\frac{3}{4}$ hour, and the residual 3-chloro-2-naphthol steam-distilled and crystallised from alcohol; m. p. 63—64·5° (Found: C, 67·6; H, 3·7; Cl, 19·0. Calc. for $C_{10}H_7OCl$: C, 67·7; H, 3·9; Cl, 19·9%). It had a peculiar characteristic odour, more pungent than that of β-naphthol, was easily soluble in benzene, ether, and alcohol, and gave a green coloration with ferric chloride (compare Marschall, *Bull. Soc. chim.*, 1928, **43**, 1363; D.R.-P. 431165).

(2) *The Curtius Method* [With S. HOLT].—*Ethyl* 2-*methoxy*-3-*naphthoate*. A solution of 2-methoxy-3-naphthoic acid (72 g.) in absolute alcohol (540 c.c.) was saturated with dry hydrogen chloride, boiled under reflux for 2 hours, and poured on ice. The resulting ester, isolated, washed, and dried in benzene, had b. p. 198°/18 mm. (yield, 60 g.; 73·2%). Von Auwers and Frühling (*Annalen*, 1921, **422**, 197) give b. p. 208°/18 mm.

2-*Methoxy*-3-*naphthhydrazide*. The above ester (72 g.) was added dropwise during 45 minutes to hydrazine hydrate (38 g.) refluxing under an air condenser the top of which was maintained at about 90° in order that the alcohol should distil off as formed. After the mixture had boiled for a further hour, the *hydrazide* crystallised, on cooling, in colourless plates (63·5 g.; 94% of the theoretical yield), m. p. 121—124° after recrystallisation from benzene (Found: C, 66·7; H, 5·4; N, 13·2. $C_{12}H_{12}O_2N_2$ requires C, 66·7; H, 5·6; N, 13·0%). The hydrazide was soluble in the common organic solvents except petrol. It melted slowly when heated on the water-bath and then resolidified; thereafter the m. p. was 137—138° (corr.). The same melting point was shown by a recrystallised specimen which had been kept for a year.

An attempt to replace hydrazine hydrate by a mixture of hydrazine sulphate and magnesium oxide was unsuccessful.

Di-(2-*methoxy*-3-*naphth*)*hydrazide*. The monohydrazide (2·2 g.) was dissolved in dry benzene (100 c.c.), 2-methoxy-3-naphthoyl chloride (from 2·3 g. of the acid and 1·2 g. of thionyl chloride) in 50 c.c. of benzene was added dropwise with stirring, and the mixture heated to ebullition and cooled. The residue, after being washed with aqueous sodium carbonate, crystallised from alcohol in needles (3·2 g.; 80%), m. p. 248—250° (corr.), sparingly soluble in most organic solvents, but readily soluble in acetone (Found: N, 7·1. $C_{24}H_{20}O_4N_2$ requires N, 7·0%).

Benzylidene-2-*methoxy*-3-*naphthhydrazide* (from benzaldehyde and the hydrazide in absolute alcohol) formed microscopic needles, m. p. 222·5° (corr.), from acetone, sparingly soluble in alcohol and benzene (Found: N, 9·4. $C_{19}H_{16}O_2N_2$ requires N, 9·2%). The m-*nitrobenzylidene* derivative formed canary-yellow platelets from benzene, m. p. 223—224° (corr.), soluble in most organic solvents (Found: N, 12·2. $C_{19}H_{15}O_4N_3$ requires N, 12·0%), and the o-*nitrobenzylidene* derivative canary-yellow crystals from acetone, m. p. 185—186° (corr.), soluble in most organic solvents except ether and petrol (Found: N, 12·1%).

4′-*Hydroxy*-2 : 2′-*dimethoxybenzylidene*-3-*naphthhydrazide* (from vanillin and the hydrazide) crystallised from acetone in colourless prismatic needles, m. p. 211—212° (corr.), soluble in most organic solvents (Found: N, 7·7. $C_{20}H_{18}O_4N_2$ requires N, 8·2%).

Ethyl 2-*methoxy*-3-*naphthylcarbamate*. 2-Methoxy-3-naphthhydrazide (86·4 g.; 2/5 g.-mol.) was dissolved in warm absolute alcohol (1200 c.c.), and dry hydrogen chloride (22 g.; 3/5 g.-mol.) in 150 c.c. of absolute alcohol added. To the well-cooled, vigorously agitated suspension, freshly prepared ethyl nitrite (58 g.; ½ g.-mol.) was added, and after 12 hours the clear solution was refluxed until nitrogen evolution ceased and then reduced in volume to about 200 c.c. by distillation. The *carbamate*, which crystallised on cooling (70·5 g.; 72%), was obtained by recrystallisation from alcohol in colourless plates, m. p. 104—105° (corr.) (Found: C, 68·5; H, 6·5; N, 5·9. $C_{14}H_{15}O_3N$ requires C, 68·9; H, 6·1; N, 5·7%).

Hydrolysis. (i) With hydrochloric acid. The carbamate (2·5 g.) was heated in a sealed tube for 3 hours at 120° with concentrated hydrochloric acid (10 c.c.) and the cooled diluted product was basified with ammonia. A practically quantitative yield of 3-amino-2-naphthol (1·6 g.) was obtained, demethylation having occurred simultaneously.

When 10% sulphuric acid was used in place of the hydrochloric acid, the product obtained consisted chiefly of the demethylated base, accompanied by some 3-amino-2-naphthyl methyl ether and a trace of β-naphthol.

(ii) With lime. An intimate mixture of the carbamate (25 g.) and slaked lime (125 g.) was heated for 3 hours at 200°. After cooling, the product was extracted with benzene and purified (yield, 14·5 g. or 85%).

(iii) With sodium hydroxide. A mixture of the carbamate (24·5 g.), 40% aqueous sodium hydroxide (100 c.c.), and alcohol (10 c.c.) was refluxed for 1 hour with vigorous stirring and, after cooling, treated with ice and excess of dilute hydrochloric acid. The filtered liquid, basified with ammonia or 40% sodium hydroxide solution, gave 16·0 g. of 3-amino-2-naphthyl methyl ether, m. p. 109—110° (corr.). The yield was 92·5% of the theoretical; in general it varied from 78% to 92%.

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