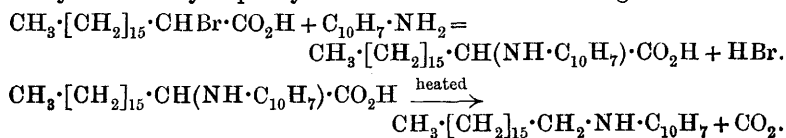


LXXXVII.—*Preparation of Secondary Amines from Carboxylic Acids. Part II. Preparation of the Heptadecyl and Pentadecyl Derivatives of  $\alpha$ - and  $\beta$ -Naphthylamine.*

By HENRY RONDEL LE SUEUR.

THE first part of this investigation (Trans., 1910, **97**, 2433) dealt with the preparation of the higher alkyl derivatives of aniline from the corresponding  $\alpha$ -anilino-acids, and in the present communication the preparation of the heptadecyl and pentadecyl derivatives of  $\alpha$ - and  $\beta$ -naphthylamine is described. When the acid resulting from the replacement of an  $\alpha$ -hydrogen atom in stearic or palmitic acid by either the  $\alpha$ - or  $\beta$ -naphthylamino-group is heated above its melting point, it readily loses carbon dioxide, and the corresponding alkyl-naphthylamine results.

The naphthylamino-acids themselves are quite readily obtained by the interaction of the  $\alpha$ -bromo-acid and the naphthylamine; also, the yield of alkyl-naphthylamine from the acid is a good one:



EXPERIMENTAL.

*Preparation of  $\alpha$ -2-Naphthylaminostearic Acid,*  
 $\text{C}_{16}\text{H}_{33} \cdot \text{CH}(\text{NH} \cdot \text{C}_{10}\text{H}_7) \cdot \text{CO}_2\text{H}.$

Eleven grams of  $\alpha$ -bromostearic acid (1 mol.) and 16 grams of  $\beta$ -naphthylamine ( $3\frac{1}{2}$  mols.) were finely powdered, well mixed, and heated together in a flask immersed in boiling water for nine and a-half hours. The resulting product consisted of a hard cake, from

which the excess of  $\beta$ -naphthylamine was removed by digesting it with hot dilute hydrochloric acid, filtering, and washing with hot water. The residue of crude acid was crystallised first from ethyl acetate, and finally from alcohol, until its melting point was constant, when 9 grams of the pure acid were obtained:

0.2278 gave 6.5 c.c.  $N_2$  (moist) at  $18^\circ$  and 770 mm.  $N=3.34$ .

$C_{28}H_{43}O_2N$  requires  $N=3.29$  per cent.

$\alpha$ -2-Naphthylaminostearic acid is insoluble in ether, chloroform, benzene, alcohol, or ethyl acetate in the cold, is moderately soluble in boiling alcohol or ethyl acetate, and separates from the former in crystalline nodules, melting at  $151$ – $152^\circ$ .

*Heptadecyl- $\beta$ -naphthylamine*,  $C_{17}H_{35}\cdot NH\cdot C_{10}H_7$ .

The pure  $\alpha$ -2-naphthylaminostearic acid was heated in quantities of 6 grams at a time in a small flask immersed in a metal-bath, and containing a thermometer the bulb of which dipped into the substance. As soon as the substance was completely melted, its temperature was raised rapidly to about  $190^\circ$ , at which point the evolution of carbon dioxide commenced. The temperature was then raised more slowly to  $295$ – $300^\circ$ , and the heating stopped when the evolution of carbon dioxide had ceased. This took place after about twelve minutes from the time the temperature was  $190^\circ$ . The resulting product was dissolved in ether, the ethereal solution washed with aqueous potassium hydroxide, dried with solid potassium hydroxide, evaporated, and the residue crystallised from alcohol. The yield of amine corresponded with 70 per cent. of the theoretical:

0.1526 gave 0.4754  $CO_2$  and 0.1536  $H_2O$ .  $C=84.96$ ;  $H=11.18$ .

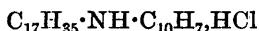
0.2554 „ 8.2 c.c.  $N_2$  (moist) at  $16^\circ$  and 758 mm.  $N=3.73$ .

$C_{27}H_{43}N$  requires  $C=85.04$ ;  $H=11.28$ ;  $N=3.67$  per cent.

*Heptadecyl- $\beta$ -naphthylamine* is readily soluble in cold ether, benzene, or chloroform, sparingly so in cold light petroleum, acetone, or alcohol, and dissolves readily in boiling alcohol, from which it crystallises, on cooling, in colourless, thin plates, melting at  $59$ – $61^\circ$ . It is insoluble in water or hydrochloric acid, but dissolves readily in concentrated sulphuric acid. The product obtained on treating the amine with nitrous acid gives Liebermann's reaction for nitrosoamines.

The *hydrochloride*,  $C_{17}H_{35}\cdot NH\cdot C_{10}H_7\cdot HCl$ , was prepared by dissolving 1.3 grams of the base in 30 c.c. of ether, and saturating the resulting solution with dry hydrogen chloride. The precipitated hydrochloride was filtered and crystallised from a mixture of chloroform and light petroleum, when it was obtained in glistening,

flat needles, melting at 170—171°. It is insoluble in alcohol, ether, acetone, or light petroleum in the cold, and dissolves readily in boiling chloroform. When heated with water, it melts, but does not dissolve, and the aqueous liquid acquires a strongly acid reaction. Its purity was determined by warming it with a slight excess of *N*/10-sodium hydroxide, filtering the liberated amine, and determining the excess of sodium hydroxide in the filtrate, using methyl-orange as indicator. 0.2474 required 5.7 c.c. *N*/10-NaOH for neutralisation, whereas the same amount of



requires 5.9 c.c. *N*/10-NaOH. The free base obtained in the above titration was dried, and after crystallisation from alcohol melted at 60—61°.

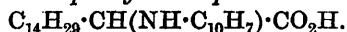
The *benzenesulphonyl* derivative,  $\text{C}_{17}\text{H}_{35}\cdot\text{N}(\text{SO}_2\text{Ph})\cdot\text{C}_{10}\text{H}_7$ , was prepared by heating in boiling water for two and a-quarter hours a mixture of 1 gram of the base and an equal weight of benzenesulphonyl chloride dissolved in 10 grams of dry pyridine. The resulting solution was poured on crushed ice, and when all the ice had melted, the benzenesulphonyl derivative was collected, washed, dried, and crystallised from a mixture of methyl and ethyl alcohols:

0.2336 gave 5.7 c.c.  $\text{N}_2$  (moist) at 16° and 780 mm.  $\text{N}=2.92$ .

$\text{C}_{33}\text{H}_{47}\text{O}_2\text{NS}$  requires  $\text{N}=2.69$  per cent.

*Heptadecyl-β-naphthylbenzenesulphonamide* is readily soluble in ether, chloroform, light petroleum, or benzene in the cold, and also in warm alcohol, from which it separates, on cooling, in stellar groups of long needles, melting at 51—52°.

*Preparation of α-2-Naphthylaminopalmitic Acid,*



Thirty grams of α-bromopalmitic acid (1 mol.) and 45 grams of β-naphthylamine ( $3\frac{1}{2}$  mols.) were heated together in a flask immersed in boiling water for twenty-nine hours, and the product was worked up exactly as described for the preparation of the corresponding naphthylaminostearic acid (p. 827). The acid was purified by crystallisation from alcohol, and was obtained in nodules of small needles, melting at 154—155°. It is insoluble in ether, light petroleum, chloroform, benzene, or acetone in the cold, and moderately soluble in boiling alcohol. The weight of pure acid obtained corresponded with a 74 per cent. yield of the theoretical:

0.2272 gave 7.3 c.c.  $\text{N}_2$  (moist) at 20° and 746 mm.  $\text{N}=3.61$ .

$\text{C}_{26}\text{H}_{39}\text{O}_2\text{N}$  requires  $\text{N}=3.53$  per cent.

*Pentadecyl-β-naphthylamine*,  $C_{15}H_{31} \cdot NH \cdot C_{10}H_7$ .

The α-2-naphthylaminopalmitic acid was heated in quantities of 6 grams, as described for the preparation of heptadecyl-β-naphthylamine. The duration of the heating and the course of the decomposition were similar in the two cases. The crude amine was dissolved in ether, the ethereal solution washed with aqueous potassium hydroxide, dried with solid potassium hydroxide, and the residue left after evaporation of the ether crystallised from alcohol:

0.1712 gave 0.5342  $CO_2$  and 0.1700  $H_2O$ .  $C = 85.09$ ;  $H = 11.03$ .

0.2226 „ 7.4 c.c.  $N_2$  (moist) at  $17^\circ$  and 770 mm.  $N = 3.91$ .

$C_{25}H_{30}N$  requires  $C = 84.99$ ;  $H = 11.05$ ;  $N = 3.96$  per cent.

*Pentadecyl-β-naphthylamine* is readily soluble in ether, acetone, light petroleum, chloroform, or benzene in the cold, sparingly soluble in cold alcohol, but dissolves readily on heating, and crystallises from this solvent in colourless, glistening plates, melting at  $53-54^\circ$ . It is insoluble in water or hydrochloric acid, but dissolves readily in concentrated sulphuric acid. The product obtained by treating the amine with nitrous acid gives Liebermann's reaction for nitrosoamines.

The *hydrochloride*,  $C_{15}H_{31} \cdot NH \cdot C_{10}H_7, HCl$ , was obtained by passing dry hydrogen chloride into an ethereal solution of the amine, and crystallising the precipitated hydrochloride from a mixture of chloroform and light petroleum. It forms glistening, flat needles, melting at  $176-177^\circ$ . It is insoluble in alcohol, ether, light petroleum, or acetone in the cold, and dissolves readily in hot chloroform. When heated with water, it melts, but does not dissolve, and the aqueous liquid acquires a strongly acid reaction. The hydrochloride was titrated as described for the hydrochloride of heptadecyl-β-naphthylamine, when it was found that 0.3100 required 7.6 c.c.  $N/10-NaOH$  for neutralisation, using methyl-orange as indicator, whereas the same weight of  $C_{15}H_{31} \cdot NH \cdot C_{10}H_7, HCl$  requires 7.9 c.c.  $N/10-NaOH$ .

The *benzenesulphonyl* derivative,  $C_{15}H_{31} \cdot N(SO_2Ph) \cdot C_{10}H_7$ , was obtained by heating in a flask immersed in boiling water a solution of 1 gram of the amine and 1.5 grams of benzenesulphonyl chloride in 10 c.c. of dry pyridine for three hours. The product was worked up as described for the preparation of the benzenesulphonyl derivative of heptadecyl-β-naphthylamine. The substance is readily soluble in ether, chloroform, light petroleum, or benzene in the cold, is sparingly soluble in cold alcohol, but dissolves readily on heating, and crystallises from this solvent in small needles, melting at  $50.5-51.5^\circ$ :

0.2544 gave 6.4 c.c.  $N_2$  (moist) at  $16^\circ$  and 768 mm.  $N=2.96$ .  
 $C_{31}H_{43}O_2NS$  requires  $N=2.84$  per cent.

*Preparation of  $\alpha$ -1-Naphthylaminostearic Acid,*  
 $C_{16}H_{33}\cdot CH(NH\cdot C_{10}H_7)\cdot CO_2H$ .

Thirty grams of  $\alpha$ -bromostearic acid (1 mol.) and 45 grams of  $\alpha$ -naphthylamine ( $3\frac{1}{2}$  mols.) were heated in a flask immersed in boiling water for twelve hours. The resulting product was digested with hot dilute hydrochloric acid to remove excess of naphthylamine, and the aqueous liquid filtered from the crude acid. The acid was dissolved in ether, the ethereal solution washed first with dilute hydrochloric acid, then with water, dried, evaporated, and the residue crystallised from light petroleum (b. p.  $100-120^\circ$ ), when it was obtained in small, glistening, lenticular plates, melting at  $69-70^\circ$ . It is readily soluble in alcohol, ether, chloroform, benzene, or acetone in the cold, and is sparingly soluble in cold light petroleum. The yield obtained was 56 per cent. of the theoretical:

0.2340 gave 6.9 c.c.  $N_2$  (moist) at  $16.5^\circ$  and 770 mm.  $N=3.47$ .  
 $C_{28}H_{43}O_2N$  requires  $N=3.29$  per cent.

*Heptadecyl- $\alpha$ -naphthylamine,  $C_{17}H_{35}\cdot NH\cdot C_{10}H_7$ .*

This amine was prepared by heating  $\alpha$ -1-naphthylaminostearic acid, as described for the preparation of the other amines, and was purified by crystallisation from alcohol:

0.1632 gave 0.5086  $CO_2$  and 0.1652  $H_2O$ .  $C=84.99$ ;  $H=11.24$ .  
 0.2274 „ 7.6 c.c.  $N_2$  (moist) at  $18^\circ$  and 752 mm.  $N=3.82$ .  
 $C_{27}H_{43}N$  requires  $C=85.04$ ;  $H=11.28$ ;  $N=3.67$  per cent.

*Heptadecyl- $\alpha$ -naphthylamine* is readily soluble in ether, light petroleum, chloroform, or benzene in the cold, is moderately soluble in boiling alcohol, and crystallises from this solvent in white nodules, melting at  $53-55^\circ$ . It is insoluble in water and hydrochloric acid, but dissolves readily in concentrated sulphuric acid. The substance obtained by treating the amine with nitrous acid gives Liebermann's reaction for nitrosoamines.

The *hydrochloride*,  $C_{17}H_{35}\cdot NH\cdot C_{10}H_7\cdot HCl$ , was prepared by saturating with dry hydrogen chloride a solution of 1 gram of the amine in 30 c.c. of ether. Light petroleum (15 c.c.) was then added, and the ether evaporated, when, on cooling, the hydrochloride separated out in lenticular plates, which, after crystallisation from light petroleum, melted at  $96-97^\circ$ . The substance is insoluble in ether, light petroleum, or acetone in the cold, but readily dissolves in cold chloroform. It melts, but does not dissolve, in hot

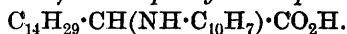
water, and the liquid becomes strongly acid. Its purity was determined as described for the other hydrochlorides. 0.3222 required 7.5 c.c. *N*/10-NaOH for neutralisation, using methyl-orange as indicator, whereas the same weight of the compound  $C_{17}H_{35}\cdot NH\cdot C_{10}H_7, HCl$  requires 7.7 c.c. *N*/10-NaOH.

The *benzenesulphonyl* derivative,  $C_{17}H_{35}\cdot N(SO_2Ph)\cdot C_{10}H_7$ , was prepared from the amine and benzenesulphonyl chloride, as described for the preparation of the other benzenesulphonyl derivatives. It is readily soluble in ether, chloroform, benzene, or acetone in the cold, is sparingly soluble in cold alcohol, and crystallises from this solvent in nodular aggregates of needles, melting at 66—68°:

0.2626 gave 6.5 c.c.  $N_2$  (moist) at 14.5° and 764 mm.  $N=2.92$ .

$C_{33}H_{47}O_2NS$  requires  $N=2.69$  per cent.

*Preparation of  $\alpha$ -1-Naphthylaminopalmitic Acid,*



This acid was prepared by the interaction of  $\alpha$ -bromopalmitic acid and  $\alpha$ -naphthylamine, the method being in every way similar to that used for the preparation of  $\alpha$ -1-naphthylaminostearic acid. It is readily soluble in alcohol, ether, chloroform, benzene, or acetone in the cold, is sparingly soluble in cold light petroleum, and crystallises from this solvent in glistening, slender needles, melting at 72—73°:

0.1684 gave 0.4846  $CO_2$  and 0.1482  $H_2O$ .  $C=78.48$ ;  $H=9.78$ .

0.2354 „ 7.5 c.c.  $N_2$  (moist) at 17° and 758 mm.  $N=3.69$ .

$C_{26}H_{39}O_2N$  requires  $C=78.59$ ;  $H=9.82$ ;  $N=3.53$  per cent.

*Pentadecyl- $\alpha$ -naphthylamine,  $C_{15}H_{31}\cdot NH\cdot C_{10}H_7$ .*

This amine was obtained by heating  $\alpha$ -1-naphthylaminopalmitic acid, and working up the product as described for the preparation of the other amines. It was purified by crystallisation from alcohol:

0.1478 gave 0.4600  $CO_2$  and 0.1446  $H_2O$ .  $C=84.88$ ;  $H=10.87$ .

0.2148 „ 7.3 c.c.  $N_2$  (moist) at 17.5° and 752 mm.  $N=3.89$ .

$C_{25}H_{39}N$  requires  $C=84.99$ ;  $H=11.05$ ;  $N=3.96$  per cent.

*Pentadecyl- $\alpha$ -naphthylamine* is readily soluble in ether, benzene, chloroform, or acetone in the cold, is only sparingly so in cold alcohol, and crystallises from this solvent in nodular aggregates of flat needles, melting at 47—48°. The product obtained by treating the amine with nitrous acid gives Liebermann's reaction for nitrosoamines.

The *hydrochloride*,  $C_{15}H_{31}\cdot NH\cdot C_{10}H_7, HCl$ , was obtained from

pentadecyl- $\alpha$ -naphthylamine by the method used for the preparation of the hydrochloride of heptadecyl- $\alpha$ -naphthylamine, and was purified by crystallisation from light petroleum. It dissolves readily in cold chloroform, is sparingly soluble in ether or light petroleum in the cold, and crystallises from the latter solvent in flat needles, melting at 92—94°. 0.3354 required 8.34 c.c.  $N/10$ -NaOH for neutralisation, using methyl-orange as indicator, whereas the same amount of the compound  $C_{15}H_{31}\cdot NH\cdot C_{10}H_7\cdot HCl$  requires 8.61 c.c.  $N/10$ -NaOH.

The *benzenesulphonyl* derivative was prepared by the interaction of the amine and benzenesulphonyl chloride in pyridine solution, and was purified by crystallisation from alcohol, when it was obtained in flat needles, melting at 68—69°. It dissolves readily in ether, chloroform, benzene, or acetone in the cold, and is sparingly soluble in cold alcohol:

0.2550 gave 6.1 c.c.  $N_2$  (moist) at 10° and 752 mm.  $N = 2.83$ .

$C_{31}H_{43}O_2NS$  requires  $N = 2.84$  per cent.

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