VI.—*The Inversion of the Optically Active ac-Tetrahydro- β -naphthylamines prepared by the aid of d- and l-Bromocamphorsulphonic Acids.*

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IN order to further investigate the possibilities of the methods devised during recent years for the resolution of externally compensated basic substances (Pope and Peachey, *Trans.*, 1898, **73**, 893 ; 1899, **75**, 1066, 1127 ; 1900, **77**, 1072 ; Pope and Rich, *Trans.*, 1899, **75**, 1093), the

study of Bamberger and Müller's *ac*-tetrahydro- β -naphthylamine (*Ber.*, 1888, 21, 847) was undertaken; this substance, according to the constitution assigned to it by these authors, contains an asymmetric carbon atom.

Resolution of Externally Compensated ac-Tetrahydro- β -naphthylamine,

$$\begin{array}{c} \text{CH} \cdot \text{CH} : \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ | \qquad \qquad | \\ \text{CH} \cdot \text{CH} : \text{C} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{NH}_2 \end{array}$$

Crude racemic *ac*-tetrahydro- β -naphthylamine hydrochloride is purified by precipitating the carbonate of the base from ether as described by Bamberger and Müller and subsequently evaporating to dryness with hydrochloric acid, or by the simpler but equally efficient method of crystallising it several times from moist boiling acetone; it melts at 242—243° (Noyes and Ballard, *Ber.*, 1894, 27, 1450). In accordance with the method devised by Pope and Rich (*loc. cit.*), hot concentrated aqueous solutions of one molecular proportion of ammonium *d*-bromocamphorsulphonate and of two molecular proportions of racemic tetrahydro- β -naphthylamine hydrochloride are mixed. An immediate separation of the least soluble salt possible in the system takes place in accordance with the equation:

and, by the time that the solution has cooled to the ordinary temperature, a practically quantitative separation of the *d*-tetrahydro- β -naphthylamine *d*-bromocamphorsulphonate as a mass of colourless needles has been effected. After filtering and washing with cold water, the salt is crystallised from boiling spirit and then from hot absolute alcohol, ethyl acetate being added to the latter solution before cooling.

It may be remarked that this resolution partakes more of the nature of a separation by precipitation than of a separation by fractional crystallisation.

d-ac-Tetrahydro- β -naphthylamine d-Bromocamphorsulphonate,

$$\text{C}_{10}\text{H}_{11} \cdot \text{NH}_2, \text{C}_{10}\text{H}_{14}\text{BrO} \cdot \text{SO}_3\text{H}.$$

The salt crystallises in long, colourless needles melting with decomposition at 185—188°, and a solution of 0.4471 gram made up to 25.1 c.c. with absolute alcohol gave $\alpha_D + 3.08$ at 12° in a 200 mm. tube; whence the specific rotatory power $[\alpha]_D + 86.5$. It is very soluble in hot alcohol, but less so in ethyl acetate and very sparingly soluble in boiling water. The following analytical results were obtained:

0.1642 gave 0.3146 CO_2 and 0.0949 H_2O . $\text{C} = 52.25$; $\text{H} = 6.42$.

0.1719 „ 0.3285 CO_2 „ 0.0989 H_2O . $\text{C} = 52.12$; $\text{H} = 6.39$.

0.4006 „ 0.1679 AgBr . $\text{Br} = 17.86$.

$\text{C}_{20}\text{H}_{28}\text{O}_4\text{NBrS}$ requires $\text{C} = 52.40$; $\text{H} = 6.11$; $\text{Br} = 17.47$ per cent.

Ammonium l-Bromocamphorsulphonate.—The *l*-camphor required for the preparation of the hitherto unknown *l*-bromocamphorsulphonic acid is conveniently obtained by treating Schimmel and Co.'s *l*-borneol with successive quantities of nitric acid of sp. gr. 1.42 until no further evolution of red fumes takes place; the product is then poured into water and the precipitated camphor collected, well washed with cold water, and dried. The *l*-camphor thus obtained is brominated by Armstrong and Matthews' method (*Chem. News*, 1878, 37, 4), and after crystallisation from boiling spirit, *l*- α -bromocamphor is obtained in long, colourless needles melting at 76° (compare Haller, *Compt. rend.*, 1887, 105, 66). The rotatory power was determined in benzene solution, and compared with that of the enantiomorphously related *d*- α -bromocamphor, with the following results:

0.4195 gram of *d*-bromocamphor, made up to 25.0 c.c. with benzene, gave $\alpha_D + 3.93^\circ$ at 19° in a 200 mm. tube: whence $[\alpha]_D + 117.1^\circ$.

0.4172 gram of *l*-bromocamphor, made up to 25.1 c.c. with benzene, gave $\alpha_D - 3.93^\circ$ at 19° in a 200 mm. tube: whence $[\alpha]_D - 118.2^\circ$.

The *l*-bromocamphor, on sulphonation and subsequent treatment by Kipping and Pope's method (*Trans.*, 1895, 67, 356), yields ammonium *l*-bromocamphorsulphonate having properties similar to those of its stereoisomeride, as is shown by the following determinations of rotatory power:

0.4531 gram of ammonium *d*-bromocamphorsulphonate, made up to 25 c.c. with water, gave $\alpha_D + 3.06^\circ$ in a 200 mm. tube at 18.5° : whence $[\alpha]_D + 84.4^\circ$ and $[M]_D + 277^\circ$.

0.4559 gram of ammonium *l*-bromocamphorsulphonate, made up to 25.1 c.c. with water, gave $\alpha_D - 3.06^\circ$ in a 200 mm. tube at 18.5° : whence $[\alpha]_D - 84.2^\circ$ and $[M]_D - 276^\circ$.

The description of derivatives of *l*- α - and of externally compensated bromocamphorsulphonic acids will form the subject of a future paper.

l-ac-Tetrahydro- β -naphthylamine *l*-Bromocamphorsulphonate,

The mother liquors remaining after separation of the *d*-bromocamphorsulphonate of the *d*-base are treated with a trifle more than the requisite amount of soda to liberate the base, which is then exhaus-

tively extracted with ether; after washing the ethereal solution with water, the base is precipitated as carbonate, and the latter, dissolved in just the requisite amount of hydrochloric acid, is then treated with a hot aqueous solution of one equivalent of ammonium *l*-bromocamphorsulphonate. A crystalline precipitate of *l*-tetrahydro- β -naphthylamine *l*-bromocamphorsulphonate at once falls, and is purified in the same way as its enantiomorphously related isomeride.

The salt crystallises in colourless needles melting at 185—188° with decomposition, and, after drying at 100°, was analysed with the following results:

0.1527 gave 0.2922 CO₂ and 0.0891 H₂O. C = 52.19; H = 6.48.

0.1668 „ 0.3206 CO₂ „ 0.0965 H₂O. C = 52.42; H = 6.43.

0.4219 „ 0.1747 AgBr. Br = 17.65.

C₂₀H₂₈O₄NBrS requires C = 52.40; H = 6.11; Br = 17.47 per cent.

A solution of 0.4206 gram, made up to 25.1 c.c. with absolute alcohol, gave α_D -2.89° at 16° in a 200 mm. tube: whence $[\alpha]_D$ -86.2°, a result numerically identical with that obtained for the antipodal isomeride.

It may be remarked that, by the successive application to an externally compensated base of the enantiomorphously related *d*- and *l*-bromocamphorsulphonic acids, the practically quantitative resolution of the inactive base into its optically active components becomes possible.

d-ac-Tetrahydro- β -naphthylamine Hydrochloride,
C₁₀H₁₁·NH₂·HCl.

On suspending *d*-tetrahydro- β -naphthylamine *d*-bromocamphorsulphonate, having the specific rotatory power $[\alpha]_D$ +86.5°, in a little water, adding rather more than sufficient soda to liberate the base, extracting with ether, washing the ethereal solution with water, and distilling off the ether after addition of hydrochloric acid, a crystalline residue of the hydrochloride is obtained. This salt, however, proves to be a mixture of the dextro- and racemic hydrochlorides; on crystallisation from hot water, a deposit of salt was obtained which melted at 239—241°, and had a specific rotatory power of $[\alpha]_D$ +32.9° in a 2 per cent. aqueous solution, corresponding to a molecular rotatory power of $[M]_D$ +59°, which, as shown later, is an impossibly low value for *d*-tetrahydro- β -naphthylamine hydrochloride. Further, on dealing with a large quantity of carefully purified *d*-bromocamphorsulphonate and systematically crystallising the mixture of hydrochlorides from water and dilute acetone, a specimen of the pure racemic hydrochloride was isolated which melted at 242—243°, did not depress the melting point of an undoubted sample of the salt, and

was optically inactive. The racemic salt was isolated as the most sparingly soluble component of the mixture, and from the mother liquors, pure *d*-tetrahydro- β -naphthylamine hydrochloride was separated as the most soluble constituent by repeated crystallisation. *d*-Tetrahydro- β -naphthylamine hydrochloride crystallises from boiling moist acetone in colourless needles melting at 243—245° and separates in long, flattened needles of glassy lustre during the spontaneous evaporation of its cold aqueous solution. It is practically insoluble in dry organic solvents, but readily dissolves in water. The following analytical results were obtained with the salt dried at 100°:

0.1426 gave 0.3415 CO₂ and 0.1007 H₂O. C = 65.31; H = 7.85.

0.1308 „ 0.3136 CO₂ „ 0.0916 H₂O. C = 65.39; H = 7.78.

0.2160 „ 0.1699 AgCl. Cl = 19.46.

C₁₀H₁₄NCl requires C = 65.43; H = 7.63; Cl = 19.30 per cent.

A solution of 0.3645 gram, made up to 25.2 c.c. with water, gave $\alpha_D + 2.08^\circ$ at 12° in a 200 mm. tube; whence $[\alpha]_D + 71.9^\circ$ and $[M]_D + 131.9^\circ$.

In moist acetone solution, the salt has about twice as high a rotatory power as in water; since, however, the values vary with the amount of moisture present in the acetone, they need not be quoted.

l-ac-Tetrahydro- β -naphthylamine Hydrochloride,

In just the same way, it was found that optical inversion takes place during the preparation of *l*-tetrahydro- β -naphthylamine hydrochloride from its *l*-bromocamphorsulphonate; the racemic hydrochloride is first isolated as the least soluble constituent, whilst the mother liquors contain the hydrochloride of the *l*-base which is ultimately purified by repeated crystallisation from moist acetone. The salt melts at 243—245°, and was analysed with the following result:

0.2238 gave 0.1765 AgCl. Cl = 19.51. Calculated Cl = 19.30 per cent.

A solution of 0.1206 gram, made up to 25.1 c.c. with water, gave $\alpha_D - 0.67$ at 16° in a 200 mm. tube: whence $[\alpha]_D - 69.7^\circ$ and $[M]_D - 128^\circ$.

d-ac-Tetrahydro- β -naphthylamine *d*-Camphorsulphonate,

The preceding results indicate that both *d*- and *l*-tetrahydro- β -naphthylamine undergo a partial racemisation during the conversion of their bromocamphorsulphonates into the corresponding hydrochlorides; it is, in consequence, very difficult to isolate the optically active hydrochlorides in a state of sufficient purity to allow of their proper

characterisation. It seemed probable that the active bases would be most conveniently characterised by means of their more soluble salts with optically active acids, and to this end the salts with Reychler's *d*-camphorsulphonic acid were prepared.

The base was separated from the *d*-bromocamphorsulphonate of $[\alpha] + 86.5^\circ$ as described above, and the ethereal solution evaporated to dryness with the corresponding weight of pure *d*-camphorsulphonic acid, the solid residue being subsequently crystallised from hot water. The greater part of the product consists of *d*-tetrahydro- β -naphthylamine *d*-camphorsulphonate, which was easily obtained in a state of purity. It crystallises in long, colourless needles from hot water, and in stout prisms several centimetres in length by spontaneous evaporation of its cold aqueous solution; the crystals contain $\frac{1}{2}\text{H}_2\text{O}$ and melt at $210-211^\circ$. The following analytical results were obtained:

0.3338 air-dried salt lost 0.0078 H_2O at 100° . $\text{H}_2\text{O} = 2.33$.

0.1225 dried salt gave 0.2817 CO_2 and 0.0858 H_2O . $\text{C} = 62.71$; $\text{H} = 7.78$.

0.1168 " " 0.2689 CO_2 " 0.0816 H_2O . $\text{C} = 62.79$; $\text{H} = 7.77$.

0.2530 " " 0.1623 BaSO_4 . $\text{S} = 8.81$.

$\text{C}_{20}\text{H}_{29}\text{O}_4\text{NS}$ requires $\text{C} = 63.32$; $\text{H} = 7.65$; $\text{S} = 8.44$; $\frac{1}{2}\text{H}_2\text{O} = 2.32$ percent.

A solution of 0.3156 gram of the dried salt, made up to 25.1 c.c. with water, gave $\alpha_D + 1.20^\circ$ in a 200 mm. tube at 12.5° ; whence $[\alpha]_D + 47.7^\circ$ and $[\text{M}]_D + 180.9^\circ$. Since Pope and Peachey have shown (Trans., 1899, 75, 1085) that the *d*-camphorsulphonic ion has $[\text{M}]_D + 51.7^\circ$, that of the *d*-tetrahydro- β -naphthylammonium ion should be $[\text{M}]_D + 129.2^\circ$; this value agrees well with that obtained above for the molecular rotatory power of *d*-tetrahydro- β -naphthylamine hydrochloride, namely, $[\text{M}]_D + 131.9^\circ$.

After the major portion of this salt has separated, the solution begins to deposit *l*-tetrahydro- β -naphthylamine *d*-camphorsulphonate in the characteristic form of colourless scales; this salt owes its formation to the partial optical inversion of the *d*-tetrahydro- β -naphthylamine.

This salt cannot be conveniently isolated from the mother liquors containing the inversion product of the *d*-base, but was prepared by extracting the base from *l*-tetrahydro- β -naphthylamine *l*-bromocamphorsulphonate with soda and ether, and subsequently evaporating the ethereal solution with the requisite quantity of *d*-camphorsulphonic acid. It crystallises from water in small, colourless scales containing $\frac{1}{2}\text{H}_2\text{O}$, and on heating melts first in its water of crystallisation at

83°, and for the second time at 207—208°. The following analytical results were obtained :

1.2016 air-dried salt lost 0.0555 H₂O at 100. H₂O = 4.61.

0.1195 dried salt gave 0.2768 CO₂ and 0.0814 H₂O. C = 63.17; H = 7.57.

0.1264 „ „ 0.2920 CO₂ „ 0.0890 H₂O. C = 63.00; H = 7.82.

0.2205 „ „ 0.1403 BaSO₄. S = 8.74.

C₂₀H₂₉O₄NS requires C = 63.32; H = 7.65; S = 8.44; 1 H₂O = 4.53 percent.

A solution of 0.1429 gram of the dried salt, made up to 25.2 c.c. with water at 16°, gave α_D - 0.11° in a 200 mm. tube, whence $[\alpha]_D$ - 9.7° and $[M]_D$ - 36.8°. Since it has already been shown that the molecular rotatory powers of the tetrahydro- β -naphthylammonium and camphorsulphonic ions are 130° and 51.7° respectively, *l*-tetrahydro- β -naphthylamine *d*-camphorsulphonate should have the molecular rotatory power $[M]_D$ - 68°; the salt was evidently still contaminated with a little of the racemisation product of the *l*-base, its purification from which is very difficult.

l-Camphorsulphonic Acid and its Salts with the Optically Active Tetrahydro- β -naphthylamines.

l-Camphorsulphonic acid was prepared from *l*-camphor by the method which Reychler used for the preparation of *d*-camphorsulphonic acid (*Bull. Soc. Chim.*, 1898, [iii], 19, 120), and was purified by crystallisation from acetic acid and ethyl acetate; on converting a portion of the product into ammonium salt, the following determination of the rotatory power of the latter showed it to be enantiomorphously related to ammonium *d*-camphorsulphonate, which has $[M]_D$ + 51.7° (Pope and Peachey, *Trans.*, 1899, 75, 1086). A solution of 0.4965 gram, made up to 25.1 c.c. with water at 17°, gave α_D - 0.82° in a 200 mm. tube; whence $[\alpha]_D$ - 20.7° and $[M]_D$ - 51.6°.

The following two salts were prepared from *d*- and *l*-tetrahydro- β -naphthylamine *d*- and *l*-bromocamphorsulphonates respectively, with the aid of *l*-camphorsulphonic acid, for purposes of comparison with their enantiomorphously related isomerides.

l-ac-Tetrahydro- β -naphthylamine *l*-Camphorsulphonate,

This salt crystallises from water in long, transparent prisms containing $\frac{1}{2}$ H₂O, which is lost at 100°; it melts at 210—211°, and was analysed with the following results :

0.8662 lost 0.0205 H₂O at 100°. H₂O = 2.36.

0.1137 dried salt gave 0.2627 CO₂ and 0.0792 H₂O. C = 63.01; H = 7.74.

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0.1109 dried salt gave 0.2569 CO_2 and 0.0791 H_2O . $\text{C} = 63.18$;
 $\text{H} = 7.92$.

$\text{C}_{20}\text{H}_{29}\text{O}_4\text{NS}$ requires $\text{C} = 63.32$; $\text{H} = 7.65$; $\frac{1}{2}\text{H}_2\text{O} = 2.32$ per cent.

A solution of 0.3284 gram of the dried salt, made up to 25.1 c.c. with water, gave $\alpha_D - 1.24^\circ$ at 17° in a 200 mm. tube : whence $[\alpha]_D - 47.4^\circ$ and $[\text{M}]_D - 179.6^\circ$, values in close numerical agreement with those given for the antipodal isomeride.

d-ac-Tetrahydro- β -naphthylamine 1-Camphorsulphonate,
 $\text{C}_{10}\text{H}_{11}\text{NH}_2 \cdot \text{C}_{10}\text{H}_{15}\text{O} \cdot \text{SO}_3\text{H} \cdot \text{H}_2\text{O}$.

This salt crystallises from water in glistening scales containing H_2O , and, after drying, melts at $207-208^\circ$.

0.3268 air-dried salt lost 0.0144 H_2O at 100° . $\text{H}_2\text{O} = 4.41$.

0.1185 dried salt gave 0.2753 CO_2 and 0.0833 H_2O . $\text{C} = 63.36$;
 $\text{H} = 7.81$.

$\text{C}_{20}\text{H}_{29}\text{O}_4\text{NS}$ requires $\text{C} = 63.32$; $\text{H} = 7.65$; $\text{H}_2\text{O} = 4.53$ per cent.

A solution of 0.1320 gram of the dried salt, made up to 25.1 c.c. with water, gave $\alpha_D + 0.14^\circ$ at 16° in a 200 mm. tube : whence $[\alpha]_D + 13.3^\circ$ and $[\text{M}]_D + 50.4^\circ$.

d-ac-Tetrahydro- β -naphthylamine platinichloride,
 $2\text{C}_{10}\text{H}_{11} \cdot \text{NH}_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$.

On adding the requisite amount of platinic chloride to an aqueous solution of *d*-tetrahydro- β -naphthylamine *d*-camphorsulphonate acidified with hydrochloric acid, a crystalline precipitate of the platinichloride is obtained ; it crystallises from hot, dilute hydrochloric acid in golden-yellow scales which blacken at 235° and melt, with decomposition, at 240° . The salt is practically insoluble in water, and its rotatory power could not be determined.

0.7007 lost 0.0333 H_2O at 100° . $\text{H}_2\text{O} = 4.75$.

0.2941 gave 0.0776 Pt. $\text{Pt} = 26.38$.

$\text{C}_{20}\text{H}_{28}\text{N}_2\text{Cl}_6\text{Pt}$ requires $\text{Pt} = 26.33$; $2\text{H}_2\text{O} = 4.84$ per cent.

The Racemisation of d- and l-Tetrahydro- β -naphthylamines.

It has been proved above that, on preparing the hydrochloride or the camphorsulphonate from *d*-tetrahydro- β -naphthylamine *d*-bromocamphorsulphonate, a certain proportion of the optically active base is inverted ; the only alternative to this view is that the original bromocamphorsulphonate is a kind of partially racemic compound containing several equivalents of the *d*-base to one of the *l*-base. That this cannot

be accepted we have proved by treating a pure sample of *d*-tetrahydro- β -naphthylamine *d*-camphorsulphonate with soda, extracting with ether, and once more preparing the *d*-camphorsulphonate from the ethereal extract. The salt obtained proved to be a mixture of *d*- and *l*-tetrahydro- β -naphthylamine *d*-camphorsulphonates. It follows that, in general, the optically active tetrahydro- β -naphthylamines undergo partial racemisation when liberated from their salts by soda and converted into other salts. During which of these two distinct operations the racemisation takes place is not decided; but it is at least probable that it is connected with the liberation of the base, rather than with its recombination, because on preparing a solution of the hydrochloride of known rotatory power, evaporating it to dryness with somewhat less than an equivalent of sulphuric acid, dissolving in water and making up to the original volume, the rotatory power is found to be unchanged. Some kind of momentary tautomerism seems to exist during the liberation of the base from its salts; this tautomerism, however, does not persist after the new salt is formed because no alteration in rotatory power attends the heating of the optically active salts in solution. In the hope that the facility with which racemisation occurs might be applied to the conversion of the externally compensated base into one enantiomorphous component as was done with the compounds containing an asymmetric tin atom (Pope and Peachey, Proc., 1900, 16, 42, 116), the following experiment was performed. The base was liberated from 20 grams of pure racemic tetrahydro- β -naphthylamine hydrochloride by soda and extracted with ether; the ethereal solution was then treated with sufficient *d*-bromocamphorsulphonic acid solution to combine with all the base, and the solution slowly evaporated to dryness. The base was then liberated from the whole by addition of soda and extracted with ether, the ethereal solution being then evaporated and the residual base distilled under about 15 mm. pressure. The pure product thus obtained had the rotatory power $\alpha_D +0.05^\circ$ in a 100 mm. tube. It was once more treated with *d*-bromocamphorsulphonic acid in a sealed tube and the whole heated at 100° for three days, after which the base was liberated, extracted with ether, and distilled under reduced pressure as before. The distillate now had the rotatory power $\alpha_D +0.18^\circ$ in a 100 mm. tube. These results indicated that the externally compensated base was slowly becoming optically active under this treatment, but this might well be because the *l*-base, which remained always dissolved, was more liable to undergo slight oxidation than its *d*-isomeride which was mainly present as solid salt.

d-ac-Tetrahydro- β -naphthylamine.

d-Tetrahydro- β -naphthylamine was prepared by treating *d*-tetrahydro- β -naphthylamine *d*-bromocamphorsulphonate of $[\alpha]_D + 86.5^\circ$ with a slight excess of soda solution, extracting with ether, drying the ethereal solution with potash, and distilling the base under about 15 mm. pressure. It is a colourless oil which is very viscous and does not fume in the air. One preparation had the rotatory power $\alpha_D + 30.5^\circ$ in a 100 mm. tube at 16° , whilst another had the value $\alpha_D + 37.24^\circ$ in a 100 mm. tube at 15° . The difference between the rotatory powers of these two preparations indicates that racemisation had taken place to a certain extent.

0.2632 gram of the base of $\alpha_D + 37.24^\circ$ was made up to 25.1 c.c. with water containing the calculated quantity of hydrochloric acid; the solution had $\alpha_D + 0.71^\circ$ at 15.5° in a 200 mm. tube: whence $[\alpha]_D + 33.8^\circ$ and $[M]_D + 49.8^\circ$.

Since we have shown that the *d*-tetrahydro- β -naphthylammonium ion has the molecular rotatory power $[M]_D + 130^\circ$, it follows that, if no racemisation attends the formation of the hydrochloride from the free base, pure *d*-tetrahydro- β -naphthylamine should have a rotatory power of about $\alpha_D + 96^\circ$ in a 100 mm. tube, and our best specimen of $\alpha_D + 37.24^\circ$ consisted of 70 per cent. of *d*- and 30 per cent. of *l*-base.

Benzylidene-d-ac-tetrahydro- β -naphthylamine,
 $C_{10}H_{11} \cdot N : CH \cdot C_6H_5$.

d-Tetrahydro- β -naphthylamine carbonate was precipitated from an ethereal solution of the base obtained by treating the *d*-bromocamphorsulphonate of $[\alpha]_D + 86.5^\circ$ with a little more than the equivalent proportion of soda. On heating this carbonate with 1 molecular proportion of benzaldehyde on the water-bath, reaction occurs readily with formation of the benzylidene derivative of the base. On crystallisation from spirit, the product is found to consist of two substances; the less soluble constituent is present in the larger quantity and is the racemic benzylidenetetrahydro- β -naphthylamine prepared from the inactive base by Bamberger and Kitschelt (*Ber.*, 1890, 23, 876). It crystallises readily in anorthic plates of rhomboidal habit and melts at $51-52^\circ$; its identity was established by comparison with the benzylidene derivative prepared from inactive tetrahydro- β -naphthylamine carbonate as described by Bamberger and Kitschelt. It is accompanied by 5 or 10 per cent. of a dextrorotatory isomeride which separates from the mother liquors in spherical aggregates of colourless needles and may be obtained in an apparently pure state by mechanical separation during fractional crystallisation from alcohol.

The purest sample which we succeeded in obtaining melted at 58—60°; it was analysed with the following results:

0.1046 gave 0.3322 CO₂ and 0.0700 H₂O. C = 86.61; H = 7.44.

0.1119 „ 0.3553 CO₂ „ 0.0745 H₂O. C = 86.59; H = 7.40.

C₁₇H₁₇N requires C = 86.81; H = 7.23 per cent.

A solution of 0.3657 gram made up to 25.0 c.c. with absolute alcohol at 18.5°, gave $\alpha_D + 0.81^\circ$ in a 200 mm. tube: whence $[\alpha]_D + 27.6^\circ$.

On treating powdered *d*-tetrahydro-β-naphthylamine *d*-bromocamphor-sulphonate of $[\alpha]_D + 86.5^\circ$ suspended in water, with benzoyl chloride and soda by the Schotten-Baumann method, benzoylation readily occurs with separation of an oil which immediately solidifies. The product, after preliminary purification in the usual way, is found to be very slightly optically active in alcoholic solution, the specific rotatory power of different preparations varying from 1° to 3°; it consists almost entirely of the inactive benzoyltetrahydro-β-naphthylamine prepared by Bamberger and Müller (*Ber.*, 1888, 21, 850), and contains but a small proportion of the dextrorotatory benzoyl derivative. A product containing more of the latter compound is obtained by adding benzoyl chloride to an ethereal solution of the base cooled to 0°; after extracting the ethereal solution with water, the tetrahydro-β-naphthylamine hydrochloride recovered from the aqueous solution was found to be still highly dextrorotatory, so that the base unacted upon by the benzoyl chloride does not undergo extensive racemisation. After evaporating the ethereal solution to dryness and fractionally crystallising the residue from dilute acetone, a considerable proportion of it is found to consist of the racemic benzoyl derivative melting at 150—151°, whilst some 5 per cent. or so consists of benzoyl-*d*-tetrahydro-β-naphthylamine. The latter is much more readily soluble than its racemic isomeride, and is ultimately obtained from the acetone solution in felted needles of a woolly appearance; the purest sample obtained melted at 155—157°, and was analysed with the following results:

0.1007 gave 0.2994 CO₂ and 0.0624 H₂O. C = 81.07; H = 6.89.

0.1053 „ 0.3134 CO₂ „ 0.0657 H₂O. C = 81.16; H = 6.93.

C₁₇H₁₇ON requires C = 81.27; H = 6.77 per cent.

A solution of 0.0238 gram, made up to 25.1 c.c. with acetone at 19°, gave $\alpha_D + 0.11^\circ$ in a 200 mm. tube; whence $[\alpha]_D + 58^\circ$.

Acetyl-d-ac-tetrahydro- β -naphthylamine,
 $C_{10}H_{11} \cdot NH \cdot CO \cdot CH_3$.

On adding one-half a molecular proportion of acetyl chloride dissolved in benzene at 0° to a benzene solution of *d*-tetrahydro- β -naphthylamine prepared from the *d*-bromocamphorsulphonate of $[\alpha]_D + 86.5^\circ$, a mixture of the racemic tetrahydro- β -acetonephthalide melting at $107-108^\circ$, which was prepared by Bamberger and Müller (*Ber.*, 1888, 21, 850), with some 5 per cent. of its dextrorotatory isomeride is obtained. The latter is much more soluble than the racemic compound, and may be separated by continued fractional crystallisation from benzene. It crystallises from the latter solvent in long, colourless needles melting at $104-106^\circ$, and on rubbing the crystals with a glass rod they exhibit vivid triboluminescence resembling that of orthobenzoisulphinide (Pope, *Trans.*, 1895, 67, 985); this property is lost when the crystals are kept and the racemic compound does not show it at all. The purest sample of the active compound obtained was analysed with the following results:

0.1062 gave 0.2960 CO_2 and 0.0777 H_2O . $C = 76.02$; $H = 8.13$.

0.1085 „ 0.3026 CO_2 „ 0.0790 H_2O . $C = 76.07$; $H = 8.09$.

$C_{12}H_{15}ON$ requires $C = 76.19$; $H = 7.94$ per cent.

A solution of 0.1122 gram, made up to 25.1 c.c. with benzene, gave $\alpha_D + 0.33^\circ$ at 16.5° in a 200 mm. tube: whence $[\alpha]_D + 36.9^\circ$.

The Optical Inversion of Amino-compounds.

Although the present investigation was undertaken with a view to further extending the methods available for resolving externally compensated bases, it has led to the observation of a previously unrecorded property which may be exhibited by certain optically active substances, that, namely, of a partial optical inversion attending the liberation of a base from its salts by means of alkali; it has further been found that on preparing the benzyldiene, benzoyl, and acetyl derivatives from an active base racemisation may occur, and to a much greater extent than on simply liberating the base from its salts. Two cases of the latter kind are already known: Emil Fischer has shown (*Ber.*, 1900, 33, 2370) that partial racemisation occurs on benzoylating leucine, $CHMe_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$, in presence of soda and also on hydrolysing optically active benzoylleucine; Fischer has also shown, (*Ber.*, 1899, 32, 2466) that considerable inversion takes place on benzoylating optically active glutaminic acid,

Tetrahydro- β -naphthylamine is more liable to undergo inversion than

either leucine or glutaminic acid, because racemisation attends the liberation of the former base from its salts, whilst this is not observed with the other two substances.

Fischer's observations, together with our own, allow of some conclusions respecting a branch of knowledge in which stereochemical methods will doubtless ultimately prove of the greatest importance, that, namely, which concerns the mechanism of chemical change. The three bases just mentioned all contain the group $\begin{smallmatrix} R' \\ R'' \end{smallmatrix} > C < \begin{smallmatrix} H \\ NH_2 \end{smallmatrix}$; further, salt decomposition and the formation and hydrolysis of acidic derivatives are operations involving the conversion of triad into pentad nitrogen and *vice versa*. The probable cause of the optical inversion is as follows: The salts of tetrahydro- β -naphthylamine contain pentad nitrogen, and consequently also the group $\begin{smallmatrix} R' \\ R'' \end{smallmatrix} > C < \begin{smallmatrix} H \\ NH_3X \end{smallmatrix}$; when treated with soda, they decompose, with separation of HX , in two ways. The two atomic groups, H and X , may both come from the nitrogen atom, so as to lead to the immediate formation of the stable base, or X may come from the nitrogen and H from the asymmetric carbon atom, leading to the momentary liberation of the transition product, $\begin{smallmatrix} R' \\ R'' \end{smallmatrix} > C:NH_3$, which immediately becomes converted into the stable base by isomeric change. That part of the material which passes through this intermediate stage is necessarily obtained as an externally compensated end-product. This explanation of the partial optical inversion of the base itself is directly applicable, *mutatis mutandis*, to the formation of the much more nearly compensated acidic and benzylidene tetrahydro- β -naphthylamines. A view similar to this has been advanced by Armstrong (Trans., 1900, 77, 1049) to explain the conversion of phenylacetylchloramine into *p*-chloracetanilide and the optical inversion of glutaminic acid.

Further, the environment of the asymmetric carbon atom is certainly tetrahedral, whilst that of the pentad nitrogen atom is probably either that of a pyramid upon a square base or of a double pyramid upon a triangular base, the group X occupying the apex of a pyramid; it would follow that, in the molecule, the distance between H and X attached to the nitrogen atom is of the same order of magnitude as one of the distances between X on the nitrogen atom and the three groups H , R' and R'' , attached to the carbon atom. In the case when H and X attached to carbon and nitrogen respectively are at a distance similar to that separating H and X attached to nitrogen alone, the acid HX would be expected to leave the molecule in both of the two ways indicated above. This case apparently fits that of tetrahydro- β -naphthylamine, leucine, and glutaminic acid;

other substances containing the group $\begin{smallmatrix} R' \\ R'' \end{smallmatrix} > C < \begin{smallmatrix} H \\ NH_2 \end{smallmatrix}$, such as alanine, do not undergo optical inversion, probably because in their additive compounds, R' or R'', but not H, on the carbon atom, and X on the nitrogen atom, are at a distance apart comparable with that separating H and X attached to the nitrogen atom alone.

The incompatibility of the environments of the tetrad carbon atom and the pentad nitrogen atom may well be responsible for the peculiar course taken by many reactions involving the conversion of triad into pentad nitrogen, and *vice versa*, reactions such as those concerned, for instance, in the interconversions of isomeric oximes.

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