

XCI.—*Influence of Substitution on Specific Rotation in the Bornylamine Series.*

By MARTIN ONSLOW FORSTER, Ph.D., D.Sc.

ALTHOUGH recent years have witnessed the rapid multiplication of optically active substances, much remains to be learned respecting the influence of substitution on specific rotation before the guiding principles of the subject can be properly established. The theory propounded in 1890 almost simultaneously by Guye and Crum Brown, attracted considerable attention at the time, and has exerted a marked influence on the character of subsequent investigations. Some among the latter have seemed to afford confirmation of the theory, and more particularly of that deduction from it which predicts the occurrence of a point of maximum rotation in a homologous series (compare Frankland and MacGregor, *Trans.*, 1893, 63, 1417, and 1894, 65, 756; Guye and Chavanne, *Compt. rend.*, 1893, 116, 1454; 1894, 119, 906, and 1895, 120, 452). The general tendency of recent work, however, has been unfavourable to the original conception. Numerous cases of disagreement between results predicted and those found by experiment have led inevitably to a fuller recognition of influences exerted by the qualitative nature of substituent groups, influences foreshadowed by Crum Brown, and latterly

verified experimentally by other workers (compare Frankland and MacGregor, *Trans.*, 1896, 69, 119, and Frankland, *this vol.*, 347).

In the hope of gaining some information on this subject, I have prepared several alkyl derivatives of bornylamine, and determined their rotatory power in the liquid and dissolved states. Bornylamine was chosen because, in the first place, although numerous homologous series of optically active ethereal salts and alkyl oxides have been examined, the effect of replacing the amine hydrogen of an optically active base by alkyl groups does not appear to have been studied. Secondly, it was recognised that a primary base, in which the amino-group is attached to asymmetric carbon, offers two points of attack in one of the four groups causing asymmetry, instead of the one occurring in hydroxylic and carboxylic groups. An additional advantage which bornylamine offers may be found in the fact that it should give rise to one series of derivatives in which asymmetric nitrogen occurs in the trivalent condition, and a second containing quinequivalent asymmetric nitrogen.

Two objections to the choice of this substance, however, present themselves. In the first place, it contains two asymmetric carbon atoms besides that to which the amino-group is directly attached, and, secondly, this carbon atom forms part of a ring system, and consequently the "product of asymmetry" cannot be calculated by Guye's formula. On the other hand, active primary bases are not very numerous, and, in general, are not very readily obtained, whereas bornylamine can now be prepared without much difficulty (*Forster, Trans.*, 1898, 73, 390).

At the outset of this investigation, much time was occupied in attempting to prepare methylbornylamine, and a suitable process for obtaining the compound was not discovered until the study of the other derivatives enumerated in this paper had been concluded. The cause of the difficulty lies in the fact that the action which methylic iodide exerts on the primary base is sufficiently vigorous to give rise to the dimethyl derivative in a cold ethereal solution, a large proportion of bornylamine being precipitated from the liquid in the form of hydriodide. Even when the more usual method of heating the base with methylic iodide and alcoholic potash in a reflux apparatus is adopted, it is found that the methyl and dimethyl derivatives are produced in approximately equal quantities, along with a considerable amount of trimethylbornylammonium iodide. A fresh obstacle is encountered on isolating methylbornylamine from the basic mixture by conversion into the nitrosamine, inasmuch as this method cannot be relied upon to yield a base having the maximum rotation. So misleading, in fact, is the result of using this process, that at one

time I regarded ethylbornylamine as having greater specific rotatory power than the lower homologue (Proc., 1899, 15, 71).

By having recourse to a method which avoids both direct methylation and treatment with nitrous acid, it is possible to obtain highly purified methylbornylamine without much loss of material. The procedure is as follows. Bornylamine is first condensed with benzaldehyde, yielding benzylidenebornylamine, which melts at 57°; this compound is then heated with methylic iodide, which converts it into an unstable methiodide, melting at 215°. On attempting to recrystallise this derivative from a solvent containing water, it is resolved almost quantitatively into benzaldehyde and methylbornylamine hydriodide, from which the base may be liberated in the usual way.

The remaining alkyl derivatives of bornylamine are readily obtained. The nitrosamine method of separating the secondary from the tertiary bases may be applied in the case of ethylbornylamine without impairing the specific rotatory power of the product. At this point the action of alkyl iodides sustains a sharp check; mono-alkyl bases are still obtained without difficulty, but no production of the corresponding dialkyl derivative occurs under ordinary conditions.

The following table summarises the information which has been gained respecting the rotatory power of bornylamine and its alkyl derivatives.

	$[\alpha]_D$.	$[M]_D$.	$[\alpha]_D$ in benzene.	$[M]_D$ in benzene.	$[\alpha]_D$ in alcohol.	$[M]_D$ in alcohol.
Bornylamine	—	—	+ 57·1°	+ 87·3	+ 46·2°	+ 70·7
Methylbornylamine	+ 96·8°	+ 161·6	95·9	160·1	81·0	135·3
Ethylbornylamine.....	93·0	163·3	90·3	163·4	75·4	136·4
<i>n</i> -Propylbornylamine ...	89·0	173·5	87·1	169·8	72·0	140·4
<i>iso</i> -Propylbornylamine...	84·0	163·8	81·1	158·1	63·3	123·4
Butylbornylamine.....	81·7	170·7	80·3	167·8	64·8	135·4
Dimethylbornylamine ...	62·5	113·1	59·6	107·8	48·7	88·1
Diethylbornylamine.....	—	—	62·6	130·8	50·5	105·5

From this it appears that the introduction of a single methyl group produces a striking increase of rotatory power. The second column of figures will show that a maximum in the molecular rotation occurs at the third term of the homologous alkylbornylamines, which form a series in this respect quite similar to those examined by Guye and Chavanne, Frankland and MacGregor, Tschügäeff, and others. The first column indicates, however, that the specific rotatory power of these compounds undergoes a regular decline from the first member of the series; groups such as this, in which the maximum occurs at the first term, are not common, but the phenomenon has been observed

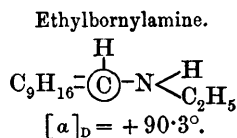
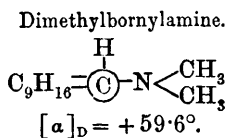
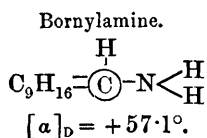
by Guye and Chavanne in the valeric series (*Compt. rend.*, 1893, 116, 1454), by Purdie and Williamson in studying the ethereal salts of methoxy- and ethoxy-succinic acids (*Trans.*, 1895, 67, 957), and by Frankland and MacGregor among the dibenzoylglycerates (*Trans.*, 1896, 69, 118).

In view of the suggestion that the true optical behaviour of initial members of such series may be possibly masked by molecular association (Frankland, this vol., 347), the molecular volumes of the secondary bases, experimentally determined, are compared in the following table with the values calculated by Traube's method (*Ber.*, 1895, 28, 2724).

	Density.	Mol. vol. calculated.	Mol. vol. experimental.
Methylbornylamine, $C_{11}H_{21}N$	0.9075 (21°)	185.7	183.7
Ethylbornylamine, $C_{12}H_{23}N$	0.8947 (21°)	201.8	201.9
Propylbornylamine, $C_{13}H_{25}N$	0.8919 (18°)	217.6	218.2
Butylbornylamine, $C_{14}H_{27}N$	0.8902 (15°)	233.4	234.3

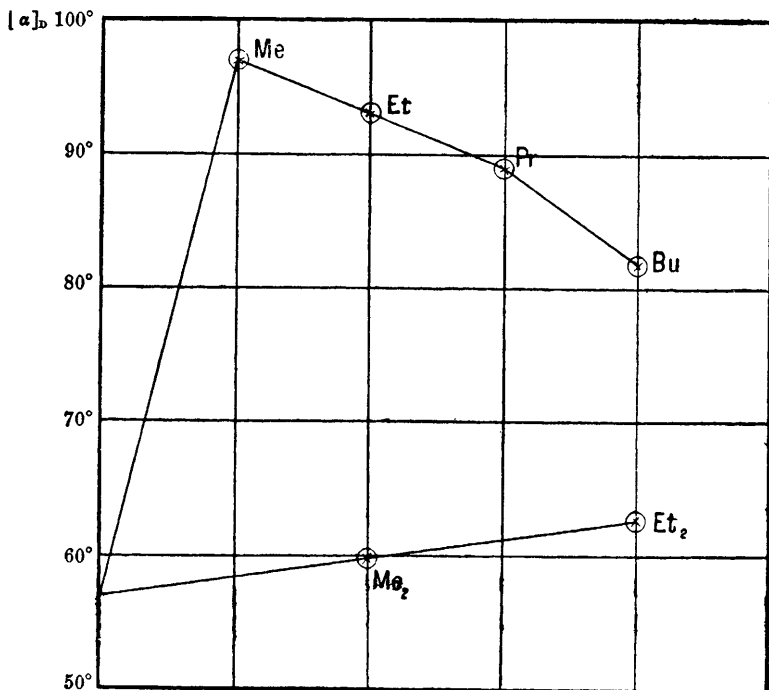
Although the higher homologues are not associated, these data suggest the possibility that molecular association may occur to a slight extent in the case of the methyl derivative.

A more novel point presents itself on comparing the specific rotatory power of bornylamine and its monalkyl derivatives with that of the corresponding tertiary bases. Reverting to the table on p. 936, it will be noticed that the effect produced on the rotation of bornylamine by introducing a single alkyl radicle into the amino-group, compared with the result of replacing both atoms of hydrogen, is very considerable. If it can be shown that other groups of alkylated amines exhibit the same characteristic, the phenomenon should have some bearing on a discussion of the influence exerted by substitution upon rotatory power. For it will be recognised that, in the series under consideration, it is destruction of molecular symmetry, and not increase of mass, which produces the more marked effects on the optical activity. Thus, on comparing the specific rotatory power of ethylbornylamine and dimethylbornylamine with that of the primary base in benzene, it is found that although the radicle attached to asymmetric carbon undergoes in each instance a change in mass from 16 units to 44, the specific rotatory power is raised through only 2.5° in the one case, and through 33.2° in the other.



Similarly, the change in mass from 16 units to 72, associated with the conversion of bornylamine into diethylbornylamine and butylbornylamine, is attended by an increase in specific rotatory power of 5.5° and 23.2° in the respective cases; the difference in this

Influence of Substitution on Specific Rotation in the Bornylamine Series.



The specific rotation of each monalkyl derivative in the liquid state is plotted on the upper curve; the values obtained with a dilute solution of the dialkyl derivatives in benzene are those represented in the lower.

instance, although considerable, is less striking, owing to the lower position in the curve occupied by butylbornylamine.

The fact that such a difference exists may not be due solely to molecular distortion occasioned by the unsymmetrical disposition of the single alkyl group; it is possible that an asymmetric atom of nitrogen, even in the trivalent condition, may be inherently capable of at least modifying optical activity. With the object of studying this question, an attempt will be made to prepare unsymmetrical dialkylbornylamines, in order to compare their specific rotatory power with that of the bases under discussion.

It has become usual to represent the affinities of trivalent nitrogen

as if symmetrically disposed in one plane. From this point of view, it will be readily understood that the disposition of the nitrogen atom, relatively to asymmetric carbon, is seriously disturbed by replacement of a single hydrogen atom, whilst undergoing but slight modification when substitution of both occurs. It therefore became of interest to

compare the rotation of the derivatives, $C_{10}H_{17} \cdot NH \cdot CH_2 \begin{array}{c} X \\ \diagup \quad \diagdown \\ \text{Cyclohexane ring} \end{array}$ and $C_{10}H_{17} \cdot NH \cdot CH_2 \begin{array}{c} \diagdown \quad \diagup \\ \text{Cyclohexane ring} \end{array} X$, in order to ascertain which differed the more widely from that of the compound $C_{10}H_{17} \cdot NH \cdot CH_2 \begin{array}{c} \diagdown \quad \diagup \\ \text{Cyclohexane ring} \end{array}$.

In the case of the nitrobenzylbornylamines, the specific rotation of the ortho-derivative shows the greater divergence, which is even more striking among the hydrochlorides.

	$[\alpha]_D$ in benzene.	$[M]_D$ in benzene.	$[\alpha]_D$ in alcohol.	$[M]_D$ in alcohol.
Benzylbornylamine	+84.1°	+204.3	+75.7°	+183.9
Orthonitrobenzylbornylamine.....	74.0	213.1	61.2	176.2
Paranitrobenzylbornylamine	77.9	224.3	66.6	191.8
Benzylbornylamine hydrochloride	—	—	35.8	100.0
Orthonitrobenzylbornylamine hydrochloride..	—	—	113.2	366.7
Paranitrobenzylbornylamine hydrochloride ...	—	—	20.3	65.7

Such investigations are of less value than those which deal with replacement of hydrogen atoms in closer proximity to asymmetric carbon. Considerable attention has been recently paid, however, to the relationship between optical activity and position isomerism (compare Frankland and Wharton, *Trans.*, 1896, **69**, 1309; Frankland and McCrae, *Trans.*, 1898, **73**, 307, and Tschúgaeff, *Ber.*, 1898, **31**, 1775). It has been shown that, in the case of methylic and ethylic tartrates, the greatest influence is exerted on rotation by the introduction of two paratolyl groups, and the least by two orthotolyl groups (Frankland and Wharton), but, as pointed out by Frankland and McCrae (*loc. cit.*), this relationship does not appear to be a general one; in fact, of the ten series quoted by these authors, six exhibit a relationship similar to that subsisting between benzylbornylamine and its nitro-derivatives, namely, closer approximation to the specific rotatory power of the original compound on the part of a para- than of an ortho-derivative. This is also true of the series comprising diethylic monobenzoyltartrate, diethylic monoparatoluyltartrate, and diethylic monorthotoluyltartrate, examined by Frankland and McCrae

(*loc. cit.*), and of two series not mentioned by these investigators, namely, the hydroxybenzylidenefenchylamines and the methoxybenzylidenefenchylamines, described by Wallach and Binz (*Annalen*, 1893, 276, 315). The regularity is again noticeable in the series of menthylic ethers studied by Tschügäeff (*Ber.*, 1898, 31, 1778), but the converse holds among the methylic and ethylic salts of benzoylmalic and toluylmalic acids, as shown quite recently by Frankland and Wharton (this vol., 337), and also among the methylic and ethylic salts of dibenzoylglyceric and ditoluylglyceric acids (Frankland and Aston, this vol., 493). It follows that in twelve of the twenty-one cases which have been hitherto examined, the effect produced on specific rotatory power by substitution is greater in the ortho- than in the para-position, a result from which it is scarcely possible to draw any definite conclusion.

The following table of benzoyl derivatives reveals the marked influence exerted on rotatory power by the qualitative nature of a substituent (compare Frankland and MacGregor, *Trans.*, 1896, 69, 119).

	$[\alpha]_D$.	$[M]_D$.
Benzoylbornylamine.....	-21·8°	-55·9
Benzoylmethylbornylamine.....	65·5	177·5
Benzoylethylbornylamine	65·2	185·7
Benzoylpropylbornylamine	60·4	180·5

Whereas the benzyl group increases the specific rotation of bornylamine, in alcohol, by 29·5°, introduction of the benzoyl radicle changes a dextrorotation of 46·2° into a lævorotation of 21·8°. The ethyl group increases the dextrorotation of the alcoholic base by 29·2°, whilst the formyl radicle, although of equal mass, converts it into a lævorotation of 42·1°; the propyl and acetyl groups exhibit a similar relationship. Moreover, the entrance of a single alkyl group into bornylamine and benzoylbornylamine is attended in each case by intensification of rotatory power.

In this connection, the series of bornylammonium iodides deserves notice. The hydriodides of the alkylbornylamines have higher specific rotation than the salt of the primary base, in other words, replacement of hydrogen in bornylamine hydriodide by a single alkyl group produces an increase in rotatory power; but the following table would seem to indicate that when an alkyl group replaces hydrogen of the ammonium group in members of this series, the optical activity, instead of increasing in the positive sense, actually becomes reduced to feeble lævorotation.

	$[\alpha]_D$.	$[M]_D$.
Bornylamine hydriodide	+ 16·0°	+ 44·9
Trimethylbornylammonium iodide	- 3·9	- 12·6
Dimethylethylbornylammonium iodide	- 3·3	- 11·1
Dimethylpropylbornylammonium iodide	- 4·1	- 14·4
Dimethylbutylbornylammonium iodide	- 3·1	- 11·3

Numerous reasons already exist for regarding the two affinities satisfied by nitrogen on becoming quinquevalent as differing in character from the three which it exerts in the trivalent form. If the above relation extends to other groups of active ammonium compounds, it will afford another illustration of this principle.

EXPERIMENTAL.

Methylbornylamine, $C_{10}H_{17}\cdot NH\cdot CH_3$.

When an ethereal solution of methylic iodide is added to bornylamine dissolved in ice-cold, dry ether, a bulky precipitate of white needles quickly separates, and if removed after an interval of only a few minutes, is found to consist chiefly of bornylamine hydriodide. During the succeeding hours precipitation continues, but the appearance of the product changes, until leaflets separate in place of needles; if the liquid is filtered after six or seven days and then evaporated, dimethylbornylamine hydriodide is obtained. Intermediate fractions consist of bornylamine and methylbornylamine hydriodides in varying proportions.

From this it appears that methylic iodide acts very readily on bornylamine. The preparation of methylbornylamine in quantity is consequently a matter of some difficulty, because even in presence of alcoholic potash, methylic iodide yields the methyl and dimethyl bases in almost equal proportion, leaving a considerable quantity of the primary base unattacked. The following method was therefore adopted for the direct methylation of bornylamine.

Eighty grams of bornylamine hydrochloride, dissolved in 500 c.c. of alcohol, were treated with 45 grams of caustic soda dissolved in the minimum quantity of water; methylic iodide (30 grams) was added to the cold liquid, which, after an interval of 12 hours, was heated in a reflux apparatus and treated from time to time with small quantities of the iodide until altogether 80 grams had been employed. The product was then acidified with hydrochloric acid, freed from alcohol by means of a current of steam, then rendered strongly alkaline with caustic soda, and again distilled in an atmosphere of steam. The distillate was just dissolved in dilute hydrochloric

acid, heated with 30 grams of sodium nitrite on the water-bath until action ceased, and when cold, extracted with ether. The ethereal solution was dried with calcium chloride, evaporated, and the residue digested with three parts of concentrated hydrochloric acid at about 70°. In a few minutes, vigorous action took place, and when this had ceased, the liquid was diluted with 300 c.c. of water, cooled, and extracted with ether in order to remove products of the action of nitrous acid on the bornylamine which had escaped the influence of methylic iodide; the aqueous portion was made alkaline with caustic soda and distilled in a current of steam, yielding methylbornylamine as a limpid, colourless oil.

The base has a faint odour of piperidine, and is readily volatile in steam; it boils at 205° under 759 mm. pressure.

0.1607 gave 0.4618 CO₂ and 0.1834 H₂O. C = 78.37; H = 12.68.

C₁₁H₂₁N requires C = 79.00; H = 12.57 per cent.

A solution containing 0.4787 gram diluted with benzene to 25 c.c. at 15°, gave $\alpha_D = 3^\circ 12' 25''$ as the mean of six readings in a 2 dm. tube, whence $[\alpha]_D = +83.7^\circ$; a solution in absolute alcohol, prepared in a similar manner, gave $[\alpha]_D = +69.5^\circ$. As stated in the introductory portion of this paper, however, the values here recorded are too low.

The most satisfactory method of preparing methylbornylamine consists in treating the methiodide of benzylidenebornylamine with boiling ethylic acetate (undried), when benzaldehyde is eliminated, and the liquid deposits methylbornylamine hydriodide as it cools. The salt is recrystallised from boiling water until the specific rotatory power remains constant at $[\alpha]_D = +26.6^\circ$ for a 1 per cent. solution in absolute alcohol; it is then dissolved in hot water, made alkaline with caustic soda, and extracted with ether. The ethereal solution is afterwards dried with solid potash and evaporated.

Methylbornylamine is strongly dextrorotatory, giving $\alpha_D = 175^\circ 50'$ in a 2 dm. tube at 21°; the sp. gr. is 0.9075 at the same temperature, whence $[\alpha]_D = +96.8^\circ$.

A solution containing 0.5172 gram diluted to 25 c.c. with benzene at 19° gave $\alpha_D = 3^\circ 58'$ in a 2 dm. tube, whence $[\alpha]_D = +95.9^\circ$; a solution in absolute alcohol containing 0.5064 gram diluted to 25 c.c. at 23° gave $\alpha_D = 3^\circ 17'$ in a 2 dm. tube, whence $[\alpha]_D = +81.0^\circ$.

The *hydrochloride* is not very soluble in cold alcohol, and separates slowly in transparent, prismatic needles infusible below 250°. A 2.4 per cent. solution in absolute alcohol gave $[\alpha]_D = +31.0^\circ$.

The *hydriodide* is freely soluble in boiling water, and crystallises in lustrous needles; it also separates from ethylic acetate in transparent needles.

0·1510 gave 0·1210 AgI. $I = 43\cdot30$.

$C_{11}H_{21}N, HI$ requires $I = 43\cdot05$ per cent.

The salt has a definite melting point and fuses to a colourless liquid at 251° . A one per cent. solution in absolute alcohol has $[\alpha]_D = +26\cdot6^\circ$.

The *platinochloride* is immediately precipitated on adding alcoholic platinum chloride to a solution of the hydrochloride in dilute alcohol. It dissolves very sparingly in boiling alcohol, but is freely soluble on addition of hydrochloric acid, and crystallises in felted masses of long, silky, pale red needles; the salt melts and decomposes at 254° .

0·2101 (dried in desiccator) gave 0·0541 Pt. Pt = $25\cdot75$.

0·1835 " " " 0·0473 Pt. Pt = $25\cdot77$.

$(C_{11}H_{21}N)_2, H_2PtCl_6$ requires Pt = $26\cdot14$ per cent.

$(C_{11}H_{21}N)_2, H_2PtCl_6 + \frac{1}{2}H_2O$ requires Pt = $25\cdot83$ per cent.

The *benzoyl* derivative dissolves freely in hot alcohol, and crystallises in large, transparent, hemimorphic pyramids of monosymmetric habit; it melts at 127° .

0·1479 gave 0·4338 CO_2 and 0·1238 H_2O . C = $80\cdot00$; H = $9\cdot30$.

$C_{18}H_{25}NO$ requires C = $79\cdot70$; H = $9\cdot22$ per cent.

A solution containing 0·4429 gram in 25 c.c. of absolute alcohol at 24° gave $\alpha_D = -2^\circ 20'$ as the mean of six readings in a 2 cm. tube, whence $[\alpha]_D = -65\cdot5^\circ$.

Methylbornylhydrazine, $C_{10}H_{17}\cdot N(CH_3)\cdot NH_2$, is obtained by reducing nitrosomethylbornylamine with zinc dust and glacial acetic acid. It is a colourless oil, having an ammoniacal, camphor-like odour, and boils at 190 — 195° under 752 mm. pressure. The base reduces an ammoniacal solution of silver nitrate almost immediately when warmed, and is also oxidised by boiling Fehling's solution. Methylbornylhydrazine causes an immediate precipitation of mercury in a cold, aqueous solution of mercury acetamide (compare Forster, *Trans.*, 1898, 73, 783).

Although there can be little doubt that methylbornylhydrazine is really produced by the method indicated, crystalline derivatives of the base have not yet been obtained. When mixed with benzaldehyde, water quickly separates, and a viscous oil is produced which does not reduce ammoniacal silver nitrate; similarly, acetaldehyde acts vigorously on the hydrazine, but the product is of an uninviting character. Furthermore, an attempt to prepare the benzoyl derivative by the Schotten-Baumann method gave a semi-solid substance from which nothing could be isolated besides benzoylmethylbornylamine (m. p. 128 — 129° ; $[\alpha]_D = -64\cdot5^\circ$; N = $5\cdot60$ per cent.).

Dimethylbornylamine, $C_{10}H_{17}\cdot N(CH_3)_2$.

The mixture of bases obtained on heating 100 grams of bornylamine hydrochloride dissolved in 400 c.c. of alcohol with 50 grams of caustic soda and 80 grams of methylic iodide, was dissolved in dilute hydrochloric acid and heated with sodium nitrite in a reflux apparatus on the water-bath during half an hour. The nitroso-derivative of methylbornylamine, along with the products of the action of nitrous acid on the unmethylated base, was removed by distillation in a current of steam; the aqueous residue was then made alkaline with caustic soda, and once more distilled in steam.

Dimethylbornylamine is a limpid, colourless oil, having an odour which is distinctly basic, but less pronounced than that of the mon-alkyl base; it boils at 210—212° under 763 mm. pressure.

0.1330 gave 0.3903 CO_2 and 0.1524 H_2O . C = 80.03; H = 12.73.

$C_{12}H_{23}N$ requires C = 79.55; H = 12.70 per cent.

The base is dextrorotatory, giving $\alpha_D = 114^\circ 12'$ in a 2 dcm. tube at 16°; its specific gravity is 0.9123 at the same temperature, whence $[\alpha]_D = +62.5^\circ$.

A solution containing 0.3895 gram diluted to 25 c.c. with benzene at 10° gave $\alpha_D = 1^\circ 51.5'$ as the mean of ten readings in a 2 dcm. tube, whence $[\alpha]_D = +59.6^\circ$; a similarly prepared solution in absolute alcohol containing 0.6514 gram, gave $[\alpha]_D = +48.7^\circ$ at 23°.

Employing benzene as the solvent, a cryoscopic determination of the molecular weight of dimethylbornylamine was made. An examination of bornylamine was first carried out, in order to test the apparatus, and as a mean of four determinations the molecular weight was found to be 153.6 (calculated 153).

Molecular weight of dimethylbornylamine = 181.

Grams of benzene.	Grams of base.	Grams of base in 100 grams of solvent.	Depression of freezing point.	Molecular weight deduced.
13.12	0.1043	0.795	0.262°	148.7
„	0.2608	1.988	0.614	158.6
„	0.3701	2.821	0.860	160.7

The *hydrochloride* crystallises from alcohol in small, white needles, and does not melt below 300°; a 1.7 per cent. solution in absolute alcohol has $[\alpha]_D = +37.2^\circ$.

The *platinochloride* crystallises from alcohol in two forms, (I) long, dark red needles, and (II) smaller, orange needles.

I. 0·1318 gave 0·0330 Pt. Pt = 25·04.

II. 0·2040 „ 0·0515 Pt. Pt = 25·24.

(C₁₂H₂₃N)₂·H₂PtCl₆ requires Pt = 25·19 per cent.

Both forms melt and decompose at 230—231°.

Trimethylbornylammonium Iodide, C₁₀H₁₇·N(CH₃)₃I, prepared by heating bornylamine with methylic iodide (3½ mols.) and alcoholic soda, is sparingly soluble in cold water, and crystallises from the hot solution in magnificent, rectangular, transparent plates, infusible below 250°; a 2·9 per cent. solution in absolute alcohol has [α]_D = -3·9°.

0·1477 gave 0·1071 AgI. I = 39·18.

C₁₃H₂₆NI requires I = 39·32 per cent.

The *chloride* is highly deliquescent, and dissolves very readily in water, from which it crystallises in lustrous, white leaflets; a 4·1 per cent. solution in water has [α]_D = -4·4°.

The *platinochloride* crystallises from alcohol in highly lustrous, flat needles.

0·2243 gave 0·0548 Pt. Pt = 24·43.

(C₁₃H₂₆N)₂·H₂PtCl₆ requires Pt = 24·25 per cent.

The crystals are transparent in the mother liquor, becoming opaque on exposure to air; they melt and decompose at 242°.

Ethylbornylamine, C₁₀H₁₇·NH·C₂H₅.

One hundred and twenty grams of bornylamine hydrochloride were dissolved in 750 c.c. of alcohol and treated with 75 grams of caustic potash dissolved in the minimum quantity of water; 75 grams of ethylic bromide were then added in small quantities at a time to the liquid, which was heated in a reflux apparatus on the water-bath during 8 hours. The basic product, which weighed 100 grams, was converted into the hydrochloride, which is not very readily soluble in water, particularly in presence of hydrochloric acid; a definite salt was therefore secured by recrystallising the mixture from dilute hydrochloric acid, and then from water, until a product of constant specific rotatory power was obtained. The base is a colourless oil, with a faint, fragrant odour; it boils at 215—216° under 758 mm. pressure.

0·1885 gave 0·5490 CO₂ and 0·2148 H₂O. C = 79·43; H = 12·66.

C₁₂H₂₃N requires C = 79·55; H = 12·70 per cent.

Ethylbornylamine is strongly dextrorotatory, giving α_D = 166° 23' in a 2 dm. tube at 21°; the sp. gr. is 0·8947 at the same temperature, whence [α]_D = +93·0°.

A solution containing 0·5077 gram diluted to 25 c.c. with benzene

946 FORSTER: INFLUENCE OF SUBSTITUTION ON

at 15° , gave $\alpha_D = 3^\circ 40'$ as the mean of five readings in a 2 dcm. tube, whence $[\alpha]_D = +90.3^\circ$; a similarly prepared solution in absolute alcohol containing 0.6682 gram gave $\alpha_D = 4^\circ 2'$, corresponding to $[\alpha]_D = +75.4^\circ$. The molecular weight, as determined in benzene, was found to be abnormal in almost the same degree as that of dimethyl bornylamine.

Molecular weight of ethylbornylamine = 181.

Grams of benzene.	Grams of base.	Grams of base in 100 grams of solvent.	Depression of freezing point.	Molecular weight deduced.
16.65	0.1088	0.6534	0.205°	156.1
„	0.2219	1.3327	0.405	161.2
„	0.3300	1.9820	0.603	161.0

The *hydrochloride* crystallises from water in white, lustrous leaflets, infusible below 250° ; a 1.3 per cent. solution in water has $[\alpha]_D = +35.6$

The *hydriodide* crystallises from water in thin, transparent plates a 2 per cent. solution in absolute alcohol has $[\alpha]_D = +26.6^\circ$.

The *nitrite* is sparingly soluble in water and crystallises from boiling ethylic acetate in minute, lustrous needles, decomposing at 194° .

0.1410 gave 14.7 c.c. of moist nitrogen at 17° and 740 mm. $N = 11.77$.

$C_{12}H_{23}N, HNO_2$ requires $N = 12.28$ per cent.

The *platinochloride* crystallises from alcohol in long, red, transparent prisms; it blackens at $220-230^\circ$, and melts and decomposes at 238° .

0.1514 gave 0.0384 Pt. Pt = 25.36. 0.2484 gave 0.0622 Pt. Pt = 25.04.

$(C_{12}H_{23}N)_2, H_2PtCl_6$ requires Pt = 25.19 per cent.

The *nitrosamine* is a yellow oil, having a fragrant, camphor-like odour; it gives Liebermann's reaction, and decomposes when distilled under atmospheric pressure. Concentrated hydrochloric acid regenerates the secondary base when heated with the nitroso-derivative at the temperature of the water-bath; the base prepared in this way has the same specific rotatory power as a specimen derived from the recrystallised hydrochloride.

The *acetyl* derivative is a pale yellow oil which boils at $285-290^\circ$ under a pressure of 765 mm.; it is slightly volatile in an atmosphere of steam, and is almost without odour. It is extremely difficult to regenerate the secondary base by the agency of hydrolytic agents (compare Wallach, *Annalen*, 1898, 300, 278).

The *benzoyl* derivative crystallises slowly from absolute alcohol in well-formed, transparent prisms and melts at $93-94^\circ$.

SPECIFIC ROTATION IN THE BORNYLAMINE SERIES. 947

0.1756 gave 8.5 c.c. of moist nitrogen at 20° and 764 mm. $N = 5.56$.

$C_{19}H_{27}NO$ requires $N = 4.91$ per cent.

A solution containing 0.6903 gram in 25 c.c. of absolute alcohol at 21° gave $\alpha_D = -3^\circ 36'$ as the mean of seven readings in a 2 dcm. tube, whence $[\alpha]_D = -65.2^\circ$.

Dimethylethylbornylammonium Iodide, $C_{10}H_{17} \cdot N(CH_3)_2(C_2H_5)I$, prepared by heating ethylbornylamine with methylic iodide ($2\frac{1}{2}$ mols.) and alcoholic soda in a reflux apparatus, crystallises from water in minute, white needles and melts at 270°, when it decomposes.

0.2100 gave 0.1454 AgI. $I = 37.41$.

$C_{14}H_{28}NI$ requires $I = 37.69$ per cent.

A 2 per cent. solution in absolute alcohol gave $[\alpha]_D = -3.3^\circ$ at 18°.

Diethylbornylamine, $C_{10}H_{17} \cdot N(C_2H_5)_2$.

The action of ethylic iodide differs from that of methylic iodide on bornylamine. Whereas the latter, even in cold ether, produces a certain amount of dimethylbornylamine, diethylbornylamine is obtained with some difficulty even under the influence of boiling alcoholic potash, whilst the iodide of the ammonium type, produced in large quantities when bornylamine is heated with methylic iodide and alcoholic soda, has not been hitherto obtained in the case of the higher homologue.

Fifty grams of bornylamine hydrochloride, dissolved in 300 c.c. of alcohol, were heated with 30 grams of caustic potash and 90 grams of ethylic iodide during several hours in a reflux apparatus. The mixture of bases obtained in this way was dissolved in excess of dilute sulphuric acid, and heated with 50 grams of sodium nitrite on the water-bath during one hour; after removing the nitrosamine with ether, the aqueous solution of diethylbornylamine sulphate was reduced to a small bulk on the water-bath and again extracted with ether in order to free it from a small quantity of nitrosamine which had separated during evaporation. The liquid was then treated with excess of caustic soda and distilled in steam. The base is a colourless oil with a faint, fragrant odour; it boils at 232—234° under a pressure of 750 mm.

0.1910 gave 0.5646 CO_2 and 0.2251 H_2O . $C = 80.62$; $H = 13.10$.

$C_{14}H_{27}N$ requires $C = 80.38$; $H = 12.92$ per cent.

A solution containing 0.3991 gram, diluted to 25 c.c. with benzene at 15°, gave $\alpha_D = 2^\circ 0'$ as the mean of five readings in a 2 dcm. tube, whence $[\alpha]_D = +62.6^\circ$; a similarly prepared solution in absolute

alcohol containing 0.4952 gram gave $\alpha_D = 2^\circ 0'$ as the mean of six readings at 22° , corresponding to $[\alpha]_D = +50.5^\circ$.

The *platinochloride* crystallises slowly from cold alcohol in bright red, transparent prisms.

0.1958 gave 0.0465 Pt. Pt = 23.75. 0.2340 gave 0.0558 Pt. Pt = 23.84.

$(C_{14}H_{27}N)_2 \cdot H_2PtCl_6$ requires Pt = 23.48 per cent.

The salt melts and intumesces at 203° .

Propylbornylamine, $C_{10}H_{17} \cdot NH \cdot C_3H_7^a$.

Sixty grams of bornylamine hydrochloride dissolved in 400 c.c. of alcohol were heated with 60 grams of normal propylic iodide and the calculated amount of caustic soda in a reflux apparatus on the water-bath. On acidifying the product with hydrochloric acid and removing alcohol by distillation, a considerable precipitate of propylbornylamine hydriodide was obtained; this was recrystallised from boiling water and decomposed with alkali, the resulting base being then converted into the nitrosamine. The latter was hydrolysed by the action of three parts of concentrated hydrochloric acid at the temperature of the water-bath, and the salt, after being once washed with ether, was dissolved in water and rendered alkaline with soda. Propylbornylamine is a colourless, limpid oil having a faint basic odour; it boils at 234° under 769 mm. pressure.

0.1770 gave 0.5194 CO_2 and 0.2066 H_2O . C = 80.03; H = 12.97.

$C_{13}H_{25}N$ requires C = 80.00; H = 12.82 per cent.

The base is strongly dextrorotatory, giving $\alpha_D = 158^\circ 44'$ in a 2 dm. tube at 18° ; its sp. gr. is 0.8919 at the same temperature, whence $[\alpha]_D = +89.0^\circ$.

A solution containing 0.6051 gram diluted to 25 c.c. with benzene at 15° , gave $\alpha_D = 4^\circ 13'$ as the mean of seven readings in a 2 dm. tube, whence $[\alpha]_D = +87.1^\circ$; a similarly prepared solution in absolute alcohol containing 0.5210 gram gave $\alpha_D = 3^\circ 0'$ as the mean of six readings at 16° , corresponding to $[\alpha]_D = +72.0^\circ$.

The *hydrochloride* forms snow-white scales; a 2 per cent. solution in absolute alcohol gave $[\alpha]_D = +34.4^\circ$.

The *hydriodide* dissolves sparingly in cold water and crystallises in pale yellow, transparent prisms; a 1.7 per cent. solution in absolute alcohol gave $[\alpha]_D = +25.0^\circ$.

The *platinochloride* crystallises from alcohol containing hydrochloric acid in lustrous, red, prismatic needles; it blackens and intumesces at 231° .

0.2322 gave 0.0566 Pt. Pt = 24.37.

$(C_{13}H_{25}N)_2 \cdot H_2PtCl_6$ requires Pt = 24.31 per cent.

SPECIFIC ROTATION IN THE BORNYLAMINE SERIES. 949

The *benzoyl* derivative crystallises from dilute alcohol in white needles and melts at 85—86°.

0.1586 gave 0.4706 CO₂ and 0.1402 H₂O. C = 80.92 ; H = 9.82.

C₂₀H₂₉NO requires C = 80.27 ; H = 9.70 per cent.

A solution containing 0.4902 gram in 25 c.c. of absolute alcohol at 14° gave $\alpha_D = -2^\circ 22'$ as the mean of eight readings in a 2 dm. tube, whence $[\alpha]_D = -60.3^\circ$.

Dimethylpropylammonium Iodide, C₁₀H₁₇·N(CH₃)₂(C₃H₇)I, was the result of an attempt to prepare methylpropylbornylamine, consequent on a complete failure to obtain dipropylbornylamine. Thirty grams of propylbornylamine were dissolved in alcohol and heated with 45 grams of methylic iodide and 12 grams of caustic soda in a reflux apparatus during several hours. On applying the nitrosamine method of separation, about one-third of the propylbornylamine employed was recovered unchanged, whilst the remainder had been converted into dimethylpropylbornylammonium iodide. This crystallises from water in aggregates of lustrous leaflets, melts with effervescence at 204—205°, and displays a marked tendency to form supersaturated solutions. It is sparingly soluble in aqueous caustic soda.

0.2143 gave 0.1432 AgI. I = 36.11.

C₁₅H₃₀NI requires I = 36.18 per cent.

A solution containing 0.5086 gram in 25 c.c. of absolute alcohol at 16° gave $\alpha_D = -10'$ as the mean of six readings in a 2 dm. tube, whence $[\alpha]_D = -4.1^\circ$.

Isopropylbornylamine, C₁₀H₁₇·NH·C₃H₇^β.

The conditions observed in preparing this substance were the same as those followed for the production of the isomeride, but it was found that a considerable proportion of bornylamine remained unchanged, as if isopropylic iodide were less vigorous in its action than the normal compound. The base is a colourless, limpid oil, having an odour which is fainter than that of the normal base ; it boils at 223° under 769 mm. pressure.

0.1646 gave 0.4826 CO₂ and 0.1946 H₂O. C = 79.96 ; H = 13.14.

C₁₃H₂₅N requires C = 80.00 ; H = 12.82 per cent.

Examined in a 2 dm. tube, isopropylbornylamine gave $\alpha_D = 148^\circ 50'$ at 14° ; the sp. gr. is 0.8861 at the same temperature, whence $[\alpha]_D = +84.0^\circ$.

A solution containing 0.5008 gram diluted to 25 c.c. with benzene at 16° gave $\alpha_D = 3^\circ 15'$ in a 2 dm. tube, whence $[\alpha]_D = +81.1^\circ$; a

similarly prepared solution in absolute alcohol containing 0.5035 gram gave $\alpha_D = 2^\circ 33'$ at 16° , whence $[\alpha]_D = +63.3^\circ$.

The *platinochloride* dissolves very readily in alcohol, and separates slowly in red, transparent crystals.

0.2340 gave 0.0564 Pt. Pt = 24.10.

$(C_{13}H_{25}N)_2, H_2PtCl_6$ requires Pt = 24.31 per cent.

When heated in a capillary tube, the salt blackens at $210-220^\circ$ and intumesces at about 240° .

Normal Butylbornylamine, $C_{10}H_{17} \cdot NH \cdot C_4H_9$.

Forty grams of bornylamine hydrochloride were dissolved in 300 c.c. of alcohol and heated with normal butylic iodide and the calculated quantity of caustic soda during several hours in a reflux apparatus. The usual operations of acidification, removal of alcohol, liberation of the base, and distillation in steam were then carried out, and the oily product, which appeared to be free from unchanged bornylamine, was dissolved in dilute sulphuric acid. On adding a concentrated, aqueous solution of sodium nitrite, a voluminous precipitate of white needles separated, changing to a pale yellow oil when heated on the water-bath; this product, the nitrosamine of butylbornylamine, solidified on cooling, and the crystals were therefore freed from oily products and heated with three parts of concentrated hydrochloric acid on the water-bath. This treatment rapidly converted the nitroso-derivative into the hydrochloride of the amine, which was then dissolved in water and made alkaline with caustic soda.

Butylbornylamine is a colourless, somewhat viscous oil with a marked basic odour; it boils at $249-251^\circ$ under 760 mm. pressure.

0.1559 gave 0.4590 CO_2 and 0.1891 H_2O . C = 80.30; H = 13.47.

$C_{14}H_{27}N$ requires C = 80.38; H = 12.92 per cent.

The base is strongly dextrorotatory, giving $\alpha_D = 145^\circ 30'$ in a 2 dem. tube at 15° ; the sp. gr. is 0.8902 at the same temperature, whence $[\alpha]_D = +81.7^\circ$.

A solution containing 0.4867 gram diluted to 25 c.c. with benzene at 16° gave $\alpha_D = 3^\circ 7.5'$ as the mean of eight concordant readings in a 2 dem. tube, whence $[\alpha]_D = +80.3^\circ$; a similarly prepared solution in absolute alcohol containing 0.4983 gram gave $\alpha_D = 2^\circ 35'$ at 16° ; whence $[\alpha]_D = +64.8^\circ$.

The *hydrochloride* separates from hot, aqueous solutions in the form of long, lustrous needles; a 2 per cent. solution in absolute alcohol gave $[\alpha]_D = +32.7^\circ$.

The *hydriodide* is very sparingly soluble in water; a 2 per cent. solution in absolute alcohol gave $[\alpha]_D = +23.8^\circ$.

SPECIFIC ROTATION IN THE BORNYLAMINE SERIES. 951

The *platinochloride*, which separates slowly from an alcoholic solution in lustrous, red leaflets, melts and decomposes at 227°.

0·2102 gave 0·0496 Pt. Pt = 23·59.

$(C_{14}H_{27}N)_3, H_3PtCl_0$ requires Pt = 23·48 per cent.

The *nitrite* is scarcely soluble in cold water, and becomes dissociated when gently warmed with it; boiling ethylic acetate deposits it on cooling in highly lustrous, silky needles, which soften at about 195°, but have no definite melting point. The rotatory power of its solution in absolute alcohol indicates complete dissociation.

Dimethylbutylbornylammonium Iodide, $C_{10}H_{17} \cdot N(CH_3)_2(C_4H_9)I$, prepared by heating butylbornylamine with methylic iodide ($2\frac{1}{2}$ mols.) and alcoholic potash in a reflux apparatus, crystallises from water in long, silky, white needles and melts at 178°.

0·1980 gave 0·1262 AgI. I = 34·44.

$C_{16}H_{33}NI$ requires I = 34·79 per cent.

A 2 per cent. solution in absolute alcohol gave $[\alpha]_D = -3\cdot1^\circ$.

Benzylbornylamine, $C_{10}H_{17} \cdot NH \cdot CH_2 \cdot C_6H_5$,

Fifty grams of bornylamine hydrochloride were dissolved in 300 c.c of alcohol and heated with 50 grams of benzylic chloride and the calculated quantity of caustic soda in a reflux apparatus during 12 hours; the product was acidified with 100 c.c. of concentrated hydrochloric acid and evaporated on the water-bath to remove alcohol. The benzylbornylamine hydrochloride obtained in this manner was crystallised from a large volume of boiling water and redissolved in sufficient water to yield a clear solution when cold; the salt was then precipitated by hydrochloric acid in two separate fractions, of which the first represented about three-quarters of the total amount. This fraction, having a somewhat higher specific rotatory power than the second, was then triturated with concentrated alkali and extracted with ether; the ethereal solution was dried with solid potash and evaporated. The base is a colourless, highly refractive, somewhat viscous oil having a scarcely perceptible odour, and a slightly astringent taste; it boils at 313—315° under a pressure of 740 mm., and is not readily volatile in an atmosphere of steam.

0·1746 gave 0·5422 CO_2 and 0·1662 H_2O . C = 84·68; H = 10·57.

$C_{17}H_{25}N$ requires C = 83·95; H = 10·28 per cent.

Benzylbornylamine resembles the alkylic bases in its high dextro-rotation, giving $\alpha_D = 161^\circ 30'$ in a 2 cm. tube at 17°; the sp. gr. is 0·9818 at the same temperature, whence $[\alpha]_D = +82\cdot2^\circ$.

A solution containing 0.5025 gram, diluted to 25 c.c. with benzene at 14°, gave $\alpha_D = 3^\circ 23'$ as the mean of six readings in a 2 dm. tube, whence $[\alpha]_D = +84.1^\circ$; a similarly prepared solution, containing 0.5571 gram in absolute alcohol at 20°, gave $\alpha_D = 3^\circ 22.5'$ as the mean of six readings in a 2 dm. tube, whence $[\alpha]_D = +75.7^\circ$.

The *hydrochloride* is sparingly soluble in cold water, and crystallises from hot solutions in lustrous needles, remaining unfused at 250°; a 1.7 per cent. solution in absolute alcohol gave $[\alpha]_D = +35.8^\circ$.

The *platinochloride* is sparingly soluble in hot alcohol, but dissolves more readily when hydrochloric acid is added to the liquid, from which it crystallises on cooling in beautiful, bright red, transparent needles.

0.2432 gave 0.0518 Pt, Pt = 21.30.

$(C_{17}H_{25}N)_2 \cdot H_2PtCl_6$ requires Pt = 21.70 per cent.

The salt blackens and intumesces at 242°.

Orthonitrobenzylbornylamine, $C_{10}H_{17} \cdot NH \cdot CH_2 \cdot C_6H_4 \cdot NO_2$.

Forty grams of bornylamine hydrochloride, dissolved in 300 c.c. of alcohol, were heated with 46 grams of orthonitrobenzyl chloride and the calculated quantity of caustic soda in a reflux apparatus during 8 hours; on filtering the cold solution from sodium chloride and removing alcohol by evaporation, a dark red, syrupy residue was obtained which immediately solidified when treated with dilute hydrochloric acid. The crude salt had a penetrating benzylic odour, which it retained after being recrystallised twice from water, but on recrystallising the substance once more from boiling water and washing the product with ether on porous earthenware, highly lustrous, colourless, odourless scales were obtained. This treatment raised the specific rotatory power from 109.0° to 113.2°, at which point it remained constant; the salt was therefore dissolved in hot water and treated with excess of caustic soda, which precipitated the base as a pale yellow oil, rapidly solidifying in hard crystals as the liquid cooled. The product was boiled with a small quantity of hot alcohol and rapidly cooled; on recrystallisation from hot, dilute alcohol, orthonitrobenzylbornylamine was obtained in minute, pale yellow, transparent prisms, slowly becoming dark brown on exposure to light.

0.1757 gave 0.4601 CO₂ and 0.1356 H₂O. C = 71.42; H = 8.57.

$C_{17}H_{24}N_2O_2$ requires C = 70.83; H = 8.33 per cent.

The base melts at 39–40°, and although so easily fusible, solidifies with great readiness; from dilute solutions, it separates slowly in long, flat needles. It dissolves readily in benzene, forming a canary-yellow

liquid, an equally concentrated (2 per cent.) solution of $\frac{1}{2}$ paranitrobenzylbornylamine being practically colourless.

A solution containing 0.5082 gram in 25 c.c. of benzene at 15° gave $[\alpha]_D = 3^\circ 0'5''$ as the mean of ten readings in a 2 dcm. tube, whence $[\alpha]_D = +74.0^\circ$; a solution of 0.5068 gram in 25 c.c. of absolute alcohol at 22° gave $\alpha_D = 2^\circ 29'$, corresponding to $[\alpha]_D = +61.2^\circ$.

The *hydrochloride* forms highly lustrous, colourless scales, and has an intensely bitter taste; a 2 per cent. solution gave $[\alpha]_D = +113.2^\circ$.

The *platinochloride* crystallises from alcohol containing hydrochloric acid in slender, highly lustrous, pale red needles.

0.1910 gave 0.0371 Pt. Pt = 19.42.

$(C_{17}H_{24}N_2O_2)_2 \cdot H_2PtCl_6$ requires Pt = 19.71 per cent.

The salt blackens and intumescs at 235°.

Paranitrobenzylbornylamine, $C_{10}H_{17} \cdot NH \cdot CH_2 \cdot C_6H_4 \cdot NO_2$.

The paranitrobenzyl derivative was prepared by the same method as that used for producing the ortho-compound, paranitrobenzyl chloride being substituted for the ortho-derivative. The dark brown residue obtained on evaporating the filtered alcoholic liquid was treated with dilute hydrochloric acid, the product being recrystallised twice from boiling water, and finally washed with ether on porous earthenware. On adding caustic soda to a boiling, aqueous solution of the salt, paranitrobenzylbornylamine was precipitated as a heavy, pale yellow, viscous oil which solidified on agitation in cold water; it was boiled with a quantity of alcohol insufficient to completely dissolve the fused base, then rapidly cooled, and recrystallised from hot alcohol, in which it is less readily soluble than the ortho-compound. It forms long, slender, lustrous needles which change into transparent, sulphur-yellow prisms; the substance melts at 60—61°.

0.1583 gave 0.4129 CO₂ and 0.1245 H₂O. C = 71.13; H = 8.73.

$C_{17}H_{24}N_2O_2$ requires C = 70.83; H = 8.33 per cent.

A solution containing 0.5082 gram in 25 c.c. of benzene at 15° gave $\alpha_D = 3^\circ 10'$ as the mean of six readings in a 2 dcm. tube, whence $[\alpha]_D = +77.9^\circ$; a solution of 0.5037 gram in 25 c.c. of absolute alcohol at 22° gave $\alpha_D = 2^\circ 41'$, corresponding to $[\alpha]_D = +66.6^\circ$.

The *hydrochloride* forms highly lustrous, colourless leaflets and does not melt below 250°; a 2 per cent. solution in absolute alcohol gave $[\alpha]_D = +20.3^\circ$.

The *platinochloride* crystallises from alcohol containing a large proportion of hydrochloric acid, in lustrous, red, transparent prisms.

954 RUHEMANN AND CUNNINGTON: STUDIES OF THE

0.1829 gave 0.0356 Pt. Pt = 19.46.

$(C_{17}H_{24}N_2O_2)_2 \cdot H_2PtCl_6$ requires Pt = 19.71 per cent.

The salt blackens and intumescens at 234°.

A subsequent communication will deal with the condensation products of bornylamine with aromatic aldehydes.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S. W.
