XLV.—*Attempted Resolution of Racemic Aldehydes.*

By WILLIAM ORD WOOTTON.

DURING recent years numerous investigations have been undertaken with a view to elucidating the relationship between the chemical composition and rotatory power of optically active substances. Although considerable progress has been made in this direction by the study of homologous series of ethereal salts and alkyl oxides, it can scarcely be claimed that any generalisations of wide application have yet been established. This is no doubt to be explained partly by the uncertainty attaching to the conventional method of expressing optical rotatory power, and partly by the fact that with few exceptions the compounds chosen for examination have been of too complex a character to admit of great emphasis being laid on the conclusions drawn from them. Owing chiefly to

the difficulty in preparing them, we are acquainted with but few structurally simple substances which could be utilised in such work. The ideal substance from this point of view would be an easily accessible compound, of low molecular weight, having only one asymmetric carbon atom, and containing no cyclic grouping; it would be an additional advantage if it contained a chemically reactive group or radicle directly attached to the asymmetric carbon atom, through the agency of which the effect of substitution, addition, or of the introduction of double linkings could be studied. The value of a substance containing a single asymmetric carbon atom in connexion with the application of Guye's modified equation has been pointed out by Bose (*Physikal. Zeitsch.*, 1908, **9**, 860).

The series of aldehydes of the type $\text{CHRR}'\cdot\text{CHO}$ fulfils the foregoing conditions, and since they are easily obtained by the general method of Darzens (*Compt. rend.*, 1904, **139**, 1214), it appeared to be of interest to ascertain whether these presumably racemic substances are capable of resolution into optical antipodes, or whether by other processes they could be obtained in active forms. The direct resolution of racemic aldehydes has been accomplished by Neuberg and Federer (*Ber.*, 1905, **38**, 868), who employed *d*-phenylamylhydrazine, a substance not easy to prepare in the pure state, and which, like most amyl compounds, might be expected to form oily derivatives. In a previous communication (*Trans.*, 1907, **91**, 1890) I have described the preparation of an optically active amine, namely, 4-bromo-3-aminophenyl- α -camphoramic acid, which it was hoped might be applied to the same purpose. The action of this base on hydratropaldehyde, $\text{CHMePh}\cdot\text{CHO}$, has now been examined, but the results obtained did not seem to warrant the extension of its use.

Attention has been drawn (*loc. cit.*) to the difficulty with which camphoric anhydride unites with the nitroanilines to form the nitrophenyl- α -camphoramic acids. This combination has now been effected in the case of *m*-nitroaniline. The nitro-acid obtained has been reduced to the amino-compound, and the behaviour of the product towards a racemic aldehyde studied. For this purpose butylchloral, $\text{CCl}_2\text{Me}\cdot\text{CHCl}\cdot\text{CHO}$, was selected, since Wheeler (*J. Amer. Chem. Soc.*, 1908, **30**, 136) has found that chloral readily condenses with primary aromatic amines, forming well-defined compounds. In the present instance, however, although condensation between one molecule of the aldehyde and two molecules of the base presented no difficulty, it was not found possible to resolve the product by fractional crystallisation into its optically active components.

A more promising method that suggests itself would be to resolve

a $\beta\beta$ -substituted glycidic acid by the aid of an alkaloid, and then to decompose the active salts by a mineral acid, when carbon dioxide is eliminated and the aldehyde produced. Experiments have been carried out in this direction, but although a sodium salt of β -phenyl- β -methylglycidic acid has been obtained having $[\alpha]_D + 16.6^\circ$ in aqueous solution, yet the corresponding aldehyde appears to be optically inactive. This, however, may be due to the fact that the acid itself contains two asymmetric carbon atoms, and it is possible that resolution has only been effected in the case of the carbon atom which ceases to be asymmetric on conversion of the acid into the aldehyde:

In the expectation of obtaining optically active bases by the reduction of nitro-derivatives of benzylidenecamphor, I have examined the action of *o*-, *m*-, and *p*-nitrobenzaldehyde on sodium camphor. Although this line of inquiry has been abandoned on account of the very poor yields obtained, the results of the experiments are recorded in the sequel.

A point of some interest has been noticed in connexion with the optical properties of the derivatives of α -camphoramic acid. It has usually been found that the rotatory power of a cyclic compound is considerably greater than that of the corresponding open-chain derivative. Thus the rotatory powers of esters of 1-methyl-3-cyclopentanone-4-carboxylic acid are about thirty times as great as those of the corresponding esters of methyladipic acid (Haller, *Compt. rend.*, 1905, **140**, 1205). The hexahydrophthalic acids have much lower specific rotations than their anhydrides (Werner, *Ber.*, 1899, **32**, 3046). Many other instances might be quoted. Camphoric acid and its anhydride, however, form an exception to the rule, the acid having $[\alpha]_D + 46^\circ$ in alcohol, whilst the anhydride has $[\alpha]_D - 7.7^\circ$. Similarly, α -camphoramic acid has $[\alpha]_D + 45^\circ$ in acetone, whilst camphorimide has $[\alpha]_D - 10.1^\circ$. In order to ascertain whether this peculiarity was exhibited by the *N*-substituted amides and imides of camphoric acid, I have prepared several new members of this series, and determined their rotatory power in acetone solution at a temperature between 19° and 21° . Variations in the concentration of the solution between 1.5 and 3 parts per 100 have very little effect on the rotatory power.

The results are summarised on p. 408.

It will be noticed that the molecular rotatory power of the acid is always greater than that of its corresponding imide, except in the case of the α -naphthyl and *o*-bromophenyl derivatives. The difference between the molecular rotatory powers of the acid and

Derivative.	Camphoramic acid.		Camphorimide.	
	[α] _D .	[M] _D .	[α] _D .	[M] _D .
Methyl	33·24°	70·6°	7·26°	14·1°
Ethyl	17·1	38·8	8·87	18·5
<i>n</i> -Propyl	18·45	44·5	10·9	24·3
<i>n</i> -Butyl	15·8	40·3	12·8	30·3
<i>n</i> -Amyl	18·9	50·8	7·7	19·3
<i>n</i> -Hexyl	16·9	47·8	10·8	28·6
Allyl	13·54	32·4	7·95	17·6
<i>o</i> -Tolyl	33·9	98·0	15·7	43·0
<i>m</i> -Tolyl	31·0	89·0	17·6	47·0
<i>p</i> -Tolyl	37·0	107·0	12·7	34·0
α -Naphthyl	7·46	24·2	26·34	80·7
β -Naphthyl	64·9	210·9	18·0	55·2
4-Hydroxyphenyl	49·2	143·1	—	—
4-Ethoxyphenyl	39·5	130·0	18·5	55·0
2-Chlorophenyl	-16·4	-50·8	14·1	41·2
3-Chlorophenyl	37·0	114·0	16·2	47·0
4-Chlorophenyl	40·5	125·5	16·2	47·0
2-Bromophenyl	-11·8	-41·8	13·3	44·7
3-Bromophenyl	33·2	117·0	15·4	51·0
4-Bromophenyl	37·8	134·0	15·7	52·0
3-Nitrophenyl	32·0	102·4	1·7	5·1
3-Aminophenyl	39·9	116·5	—	—
4-Bromo-3-nitrophenyl ..	-48·4	-193·2 *	—	—
4-Bromo-3-aminophenyl ..	40·7	109·5 *	(feebly dextrorotatory)	—
4-Benzeneazophenyl	87·7	332·5 *	—	—

* In alcoholic solution.

imide in the case of *o*-, *m*-, and *p*-isomerides is always greatest in the *p*-compounds. The homologous series of alkyl derivatives show no marked regularity; it is noteworthy, however, that the two allyl compounds show distinctly lower rotatory power than the corresponding *n*-propyl derivatives, in this respect resembling the allylamides in the malic and tartaric series, which show abnormally low rotatory powers when compared with the propylamides (Frankland and Done, *Trans.*, 1906, **89**, 1861).

EXPERIMENTAL.

Attempted Preparation of Optically Active Hydratropaldehyde.

Hydratropaldehyde and 4-bromo-3-amino- α -camphoramic acid did not interact in alcoholic solution, either in the cold or on warming, and attempts to obtain a condensation product with benzaldehyde were equally unsuccessful.

Resolution of Sodium β -Phenyl- β -methylglycidate.

Preliminary experiments with the quinine salt of β -phenyl- β -methylglycidic acid having shown that this substance was unsuitable for the purpose, the brucine salt was prepared by adding

brucine hydrochloride (1 mol.), dissolved in the minimum amount of warm water, to a warm aqueous solution of sodium β -phenyl- β -methylglycidate (2 mols.). On allowing the solution to evaporate spontaneously over potassium hydroxide in a vacuum, clusters of radiating, irregular prisms separated, which were crystallised repeatedly from absolute alcohol until optically constant, care being taken to avoid prolonged heating with the solvent:

0.2402 gave 10.4 c.c. N_2 at 23° and 760 mm. $N=4.89$.

$C_{33}H_{36}O_7N_2$ requires $N=4.89$ per cent.

0.6475, in 20 c.c. water, gave, in a 2-dcm. tube, $\alpha - 1.14^\circ$, whence $[\alpha]_D - 17.7^\circ$.

0.6800, in 20 c.c. absolute alcohol, gave, in a 2-dcm. tube, $\alpha - 0.60^\circ$, whence $[\alpha]_D - 8.82^\circ$.

When rapidly heated, the salt melts and decomposes at $141-142^\circ$. It decomposes on boiling with water or when heated a few degrees above its melting point, giving brucine and hydratropaldehyde. A good yield of the latter was obtained when the salt was slowly heated under diminished pressure; the product was collected in three separate fractions, but each of these proved to be optically inactive when examined in ethereal or alcoholic solution. The mother liquor remaining from the preparation of the salt was pale brown in colour, and when kept in a vacuum deposited a small quantity of the crystalline brucine salt, together with a resinous substance which appeared to contain hydratropaldehyde together with the free alkaloid. Dilution of the liquid with water caused a further precipitation of brucine. The hydratropaldehyde was found to be inactive.

Sodium d- β -Phenyl- β -methylglycidate, $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}_6\text{H}_5 \end{array} \text{C} \begin{array}{c} \diagdown \\ \text{O} \end{array} \begin{array}{c} \text{CH} \cdot \text{CO}_2\text{Na} \\ \diagup \end{array}$, was

obtained by grinding the foregoing brucine salt with water containing the calculated amount of sodium hydroxide. The alkaloid was removed by repeated extraction with chloroform, and the solution allowed to evaporate in a vacuum. The sodium salt was finally obtained in colourless leaflets after three crystallisations from dilute alcohol:

0.3002 gave 0.1097 Na_2SO_4 . $\text{Na}=11.88$.

$C_{10}H_9O_3\text{Na}$ requires $\text{Na}=12.10$ per cent.

0.6000, in 20 c.c. water, gave, in a 2-dcm. tube, $\alpha + 1.00^\circ$, whence $[\alpha]_D + 16.6^\circ$.

When dissolved in water and treated with slightly less than the calculated amount of sulphuric acid, carbon dioxide was evolved, and the solution became turbid through the separation of hydratropaldehyde. In one experiment this was removed by steam dis-

tillation, and in another by extraction with ether; both specimens, however, appeared to be optically inactive when examined in 5 per cent. solutions of alcohol, chloroform, or ether. The aldehyde, moreover, gave a semicarbazone identical with that obtained from the racemic sodium salt.

Attempted Resolution of Butylchloral.—Condensation occurs readily when an aqueous solution of *m*-aminophenyl- α -camphoramic acid (see below) is shaken with butylchloral. It is advisable, however, to add the butylchloral (1 mol.) to a solution of the sodium salt of the acid (2 mols.). The aldehyde dissolves immediately with considerable development of heat.

Trichlorobutylidenebis-3-aminophenyl- α -camphoramic Acid,
 $\text{CMeCl}_2 \cdot \text{CHCl} \cdot \text{CH}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_8\text{H}_{14} \cdot \text{CO}_2\text{H})_2,$

separates as a bulky mass of colourless needles when the solution of its sodium salt is acidified with acetic acid. After crystallisation from dilute alcohol, it melts and decomposes at 126–130° when heated moderately rapidly. Attempts to resolve it by fractional crystallisation from this solvent and also from acetone were not successful, successive fractions showing practically the same rotatory power. Prolonged heating with solvents brings about decomposition:

0.0081 gave 0.0510 AgCl. $\text{Cl} = 13.89$.

$\text{C}_{36}\text{H}_{47}\text{O}_6\text{N}_4\text{Cl}_3$ requires $\text{Cl} = 14.38$ per cent.

0.5110, in 20 c.c. acetone, gave, in a 2-dcm. tube, $\alpha_D + 1.40^\circ$, whence $[\alpha]_D + 27.4^\circ$.

Nitro-derivatives of Benzylidenecamphor.

The only nitro-derivative of benzylidenecamphor hitherto known has been described by Haller (*Compt. rend.*, 1895, **121**, 36). By the action of fuming nitric acid on benzylidenecamphor, a colourless compound was obtained, to which he ascribed the constitution:

The nitro-groups do not appear to be attached to the benzene nucleus, since the substance furnishes benzylidenecamphor on reduction.

Action of p-Nitrobenzaldehyde on Sodium Camphor.—The sodium camphor required in these experiments was prepared by the action of sodium or finely divided sodamide on camphor dissolved in dry ether, benzene, or toluene. The reactions appeared to follow the same course whichever method was adopted, the use of sodamide with ether, however, was preferred as giving cleaner products and

a better yield. On adding two-thirds of the calculated quantity of *p*-nitrobenzaldehyde to a well-cooled suspension of sodium camphor, a vigorous action ensued, accompanied by development of heat. The mixture was kept below 5° for an hour, and then heated for a short time on the water-bath. The reddish-brown, pasty mass was extracted with water, the layer of organic solvent separated, dried, and finally heated on the water-bath until the solvent and the greater part of unaltered camphor had been removed. The aqueous extract on the addition of an acid gave a voluminous yellow precipitate consisting chiefly of *p*-nitrobenzoic acid. The residue left after evaporation of the organic solvent appeared as a viscous, red oil, which slowly deposited yellow crystals. The oily matter was removed by extraction with cold alcohol and examined separately. The crystalline residue contained the following two substances.

I. A compound, $C_{34}H_{38}O_4N_2$.—This product is sparingly soluble in alcohol, ether, or benzene, and readily so in pyridine or carbon tetrachloride, from which it separates in small, orange-red prisms, melting at 280—281°. The compound is distinguished by its remarkably high rotatory power; it does not give Liebermann's reaction, and develops no coloration with alcoholic potash. Two determinations of the molecular weight in chloroform solution by the ebullioscopic method gave 422 and 446 respectively, the above formula requiring 538:

0.0913 gave 0.2529 CO_2 and 0.0597 H_2O . $C=75.52$; $H=7.25$.

0.3559 „ 12.8 c.c. N_2 at 18° and 744 mm. $N=5.65$.

$C_{34}H_{38}O_4N_2$ requires $C=75.82$; $H=7.06$; $N=5.20$ per cent.

0.0939, in 25 c.c. chloroform, gave, in a 2-dcm. tube, $\alpha_D + 4.55^\circ$, whence $[\alpha]_D + 605^\circ$, and $[M]_D + 3255^\circ$.

II.—4-Nitrobenzylidenecamphor, $C_8H_{14} \begin{matrix} \diagup C:CH \cdot C_6H_4 \cdot NO_2 \\ \diagdown CO \end{matrix}$.—This

compound separates from alcohol in bright yellow, glistening leaflets, melting at 156—157°; it is sparingly soluble in alcoholic potassium hydroxide, giving a yellow solution. Concentrated sulphuric acid develops an orange-red coloration:

0.1012 gave 0.3148 CO_2 and 0.0592 H_2O . $C=71.71$; $H=6.38$.

0.1780 „ 7.6 c.c. N_2 at 16° and 754 mm. $N=4.82$.

$C_{17}H_{19}O_3N$ requires $C=71.59$; $H=6.66$; $N=4.88$ per cent.

0.3102, in 20 c.c. chloroform, gave, in a 2-dcm. tube, $\alpha_D + 3.55^\circ$, whence $[\alpha]_D + 437^\circ$, and $[M]_D + 1345^\circ$.

Examination of the Alcoholic Extract.—A deep red oil, having a slight odour of camphor, remained after removal of the alcohol by evaporation. The oil is insoluble in water, but freely soluble in the usual organic media; on adding alkali hydroxide to its alcoholic solution, an intense purple coloration is developed, which, on

dilution with water, changes to red. The colour is destroyed by acids, but restored by alkalis. It is possible that this product contains an enolic form of 4-nitrobenzylidenecamphor:

A chromophoric oil having similar properties has been described by Forster, who obtained it by the action of *p*-nitrobenzyl chloride on isonitrosocamphor in presence of sodium ethoxide (Trans., 1908, **93**, 249). Decomposition occurs when the oil is distilled under diminished pressure, and all attempts to isolate a pure compound or prepare a crystalline derivative have failed.

No chromophoric substance is formed if the temperature of reaction is allowed to rise during the preparation; under these conditions, the main product is the compound $\text{C}_{34}\text{H}_{38}\text{O}_4\text{N}_2$, together with a very insoluble brown substance which has not yet been obtained in a state of purity. To ascertain whether the presence of the camphor nucleus is essential for its formation, experiments have been carried out on the action of *p*-nitrobenzaldehyde on the sodium derivatives of ethyl acetoacetate, carvone, and pulegone; no chromophoric product was recognised, however, and this would appear to exclude the possibility of the colour having arisen from the action of the alkali on any derivative of dinitrostilbene. It may be mentioned that the sodium derivative of pulegone is very readily prepared by the action of sodamide on an ethereal solution of pulegone. The action proceeds briskly without warming, and a good yield is obtained.

Action of o- and m-Nitrobenzaldehyde on Sodium Camphor.

2-Nitrobenzylidenecamphor, $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$, prepared in the same way as the 4-nitro-compound, occurs as well-formed, light brown prisms, melting at 116–117°. A solution in chloroform gave $[\alpha]_D +50^\circ$ approximately; owing to the absorption of light, the rotatory power could not be accurately determined. The compound itself gives no coloration with alcoholic potassium hydroxide, but the oily material from which it is separated develops an intense purple coloration with this reagent:

0.2633 gave 11.9 c.c. N_2 at 28° and 766 mm. $\text{N}=4.99$.

$\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$ requires $\text{N}=4.88$ per cent.

3-Nitrobenzylidenecamphor, $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$.—This compound and *m*-nitrobenzoic acid are the only products of the action of *m*-nitrobenzaldehyde on sodium camphor. It was obtained as a yellow oil, which, on addition of alcohol, rapidly solidified. When

crystallised from hot alcohol, it forms very pale yellow needles, melting at 110—111°:

0.2024 gave 9.4 c.c. N_2 at 19° and 748 mm. $N = 5.13$.

$C_{17}H_{19}O_3N$ requires $N = 4.88$ per cent.

0.0934, in 15 c.c. chloroform, gave, in a 2-dcm. tube, $\alpha_D + 3.92^\circ$, whence $[\alpha]_D + 311^\circ$, and $[M]_D + 783^\circ$.

Alkyl Derivatives of α -Camphoramic Acid, $CO_2H \cdot C_8H_{14} \cdot CO \cdot NHR$.

The following new members of the series were prepared by the interaction of camphoric anhydride (1 mol.) with an alcoholic solution of the amine (2 mols.). After purification by conversion into the sodium salt, the free acid was regenerated by the addition of hydrochloric acid and crystallised from dilute acetone:

Derivative.	Empirical formula.	Crystalline form.	M. p.	Analysis.	
				Found.	Theory, per cent.
Ethyl	$C_{12}H_{21}O_3N$	Hexagonal leaflets	173—175°	$N = 6.08$	6.17
<i>n</i> -Propyl... ..	$C_{13}H_{23}O_3N$	Hexagonal leaflets	187—188	$N = 5.79$	5.81
<i>n</i> -Butyl	$C_{14}H_{25}O_3N$	Hexagonal leaflets	124—125	$C = 65.71$ $H = 9.48$	65.89 9.80
<i>n</i> -Amyl	$C_{15}H_{27}O_3N$	Crystalline mass	—	$C = 66.58$ $H = 10.25$	66.91 10.03
<i>n</i> -Hexyl	$C_{16}H_{29}O_3N$	Hexagonal leaflets	123—124	$N = 5.21$	4.95
Allyl	$C_{13}H_{21}O_3N$	Leaflets	157—158	$N = 5.66$	5.87

Aryl Derivatives of α -Camphoramic Acid,

In most cases these compounds are readily obtained by heating an intimate mixture of camphoric anhydride and the substituted amine for a few minutes at 150—180°. In the case of *m*-nitroaniline, α -naphthylamine, and ortho-substituted amines, it is necessary to heat for a longer period in sealed tubes.

3-Nitrophenyl- α -camphoramic Acid,

is prepared by heating 13 grams of camphoric anhydride with 10 grams of *m*-nitroaniline at 150° for one hour in a sealed tube. The crystalline mass is dissolved in dilute ammonia, the solution filtered after twenty-four hours, and then acidified. The first few drops of acid precipitate a brown, resinous product, but further addition of acid yields the required compound in a state of purity. It is crystallised from acetic acid containing a little stannous chloride, and finally from alcohol, from which it separates in large,

colourless, hexagonal leaflets, which darken at about 200° , and melt and decompose at $212-213^{\circ}$:

0.3052 gave 18.6 c.c. N_2 at 20° and 754 mm. $N=8.71$.

$C_{16}H_{20}O_3N_2$ requires $N=8.75$ per cent.

0.6178, in 20 c.c. acetone, gave, in a 2-dcm. tube, $\alpha_D + 1.97^{\circ}$, whence $[\alpha] + 32.0^{\circ}$.

3-Aminophenyl- α -camphoramic Acid,

prepared from the foregoing compound by reduction with ferrous sulphate in ammoniacal solution, forms small, colourless needles, melting at $196-197^{\circ}$:

0.2000 gave 16.6 c.c. N_2 at 21° and 766 mm. $N=9.53$.

$C_{16}H_{22}O_3N$ requires $N=9.65$ per cent.

0.3908, in 20 c.c. acetone, gave, in a 2-dcm. tube, $\alpha_D + 1.56^{\circ}$, whence $[\alpha]_D + 39.9^{\circ}$.

The *acetyl* derivative crystallises in silky needles, melting at $220-221^{\circ}$. The *hydrochloride* of the base is easily soluble in water, and on diazotisation yields a clear solution which, on the addition of alkaline β -naphthol, furnishes a bright red azo-compound. A solution of the base in dilute alcohol gives an immediate precipitate on the addition of an aldehyde; this arises from condensation of two molecules of the base with one of the aldehyde.

4-Hydroxyphenyl- α -camphoramic Acid,

A brisk reaction occurs when camphoric anhydride and *p*-aminophenol are heated together. The dark-coloured product contains small quantities of a substance characterised by the intense purple coloration developed with aqueous alkali hydroxides; it was crystallised from alcohol until the mother liquor no longer showed this reaction. Recrystallisation from acetic acid, after treatment with animal charcoal, gave small, pale brown prisms. The melting point was somewhat indefinite, the compound sintering at 236° and decomposing at 250° . The product after fusion dissolved in aqueous alkalis, giving deep purple solutions, probably owing to the formation of a phthalein:

0.0986 gave 0.2385 CO_2 and 0.0648 H_2O . $C=65.80$; $H=7.30$.

$C_{16}H_{21}O_4N$ requires $C=65.98$; $H=7.22$ per cent.

0.3641, in 20 c.c. acetone, gave, in a 2-dcm. tube, $\alpha_D + 1.80^{\circ}$, whence $[\alpha]_D + 49.16^{\circ}$.

The following aryl derivatives of α -camphoramic acid were also prepared:

Derivative.	Empirical formula.	Crystalline form.	M. p.	Analysis.	
				Found.	Theory, per cent.
<i>o</i> -Tolyl.....	C ₁₇ H ₂₃ O ₃ N	Long needles	194—196°	N = 4·72	4·84
<i>m</i> -Tolyl	C ₁₇ H ₂₃ O ₃ N	Needles	208—209	N = 4·76	4·84
<i>p</i> -Tolyl *	C ₁₇ H ₂₃ O ₃ N	Leaflets	212—214	N = 4·96	4·84
α -Naphthyl.....	C ₂₀ H ₂₃ O ₃ N	Needles	233—235	N = 4·31	4·31
β -Naphthyl.....	C ₂₀ H ₂₃ O ₃ N	Lustrous leaflets	210—212	N = 4·68	4·31
4-Ethoxyphenyl...	C ₁₈ H ₂₅ O ₄ N	Long needles	195—197	N = 4·35	4·39
2-Chlorophenyl ...	C ₁₆ H ₂₀ O ₃ NCI	Minute crystals	139—140	Cl = 11·22	11·47
3-Chlorophenyl ...	C ₁₆ H ₂₀ O ₃ NCI	Leaflets	207—209	Cl = 11·35	11·47
4-Chlorophenyl ...	C ₁₆ H ₂₀ O ₃ NCI	Prisms	192—194	Cl = 11·38	11·47
2-Bromophenyl ...	C ₁₆ H ₂₀ O ₃ NBr	Vitreous mass	about 78	Br = 22·42	22·60
3-Bromophenyl ...	C ₁₆ H ₂₀ O ₃ NBr	Small tablets	215—217	Br = 22·54	22·60

* This compound, together with the corresponding imide, has recently been described by Abati and Notaris (*Gazzetta*, 1909, **39**, ii, 219). These authors give the melting point 201—209° for the acid and 131° for the imide.

N-Alkyl and Aryl Derivatives of Camphorimide,

By boiling a solution of a *N*-substituted α -camphoramic acid in glacial acetic acid with acetyl chloride for two hours, and pouring the liquid into excess of dilute ammonia, the corresponding imide is obtained in almost theoretical yield. The following were prepared:

Derivative.	Empirical formula.	Crystalline form.	M. p.	Analysis.	
				Found.	Theory, per cent.
<i>n</i> -Propyl	C ₁₃ H ₂₁ O ₂ N	Prisms	40—41°	C = 69·92 H = 9·37	69·95 9·42
<i>n</i> -Butyl	C ₁₄ H ₂₃ O ₂ N	Lath-like crystals	61—62	N = 6·13	5·91
<i>n</i> -Amyl	C ₁₅ H ₂₅ O ₂ N	Oil	—	N = 5·50	5·58
<i>n</i> -Hexyl	C ₁₆ H ₂₇ O ₂ N	Oil	—	N = 6·31	5·28
<i>o</i> -Tolyl	C ₁₇ H ₂₁ O ₂ N	Long needles	195—196	N = 5·21	5·16
<i>m</i> -Tolyl	C ₁₇ H ₂₁ O ₂ N	Glistening leaflets	117—118	N = 5·27	5·16
<i>p</i> -Tolyl	C ₁₇ H ₂₁ O ₂ N	Flat prisms	127—128	C = 74·98 H = 7·61	75·26 7·75
α -Naphthyl.....	C ₂₀ H ₂₁ O ₂ N	Stout prisms	211—212	N = 4·68	4·56
β -Naphthyl.....	C ₂₀ H ₂₁ O ₂ N	Small needles	167—168	N = 4·57	4·56
2-Chlorophenyl ...	C ₁₆ H ₁₈ O ₂ NCI	Flat prisms	125—126	Cl = 11·97	12·18
3-Chlorophenyl ...	C ₁₆ H ₁₈ O ₂ NCI	Needles	172—173	Cl = 12·03	12·18
4-Chlorophenyl ...	C ₁₆ H ₁₈ O ₂ NCI	Prisms	162—163	N = 4·89	4·80
2-Bromophenyl ...	C ₁₆ H ₁₈ O ₂ NBr	Small prisms	139—140	Br = 23·57	23·80
3-Bromophenyl ...	C ₁₆ H ₁₈ O ₂ NBr	Needles	184—185	Br = 23·68	23·80
3-Nitrophenyl.....	C ₁₆ H ₁₈ O ₄ N ₂	Rhombic prisms	146—147	N = 8·97	9·27

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