CXXXVII.—*A Study of the Isomerism and Optical Activity of Quinquevalent Nitrogen Compounds.*

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THE experiments described in this paper were undertaken with the object of investigating more fully the extent and nature of the isomerism among quinquevalent nitrogen compounds, and particularly that isomerism which might theoretically be expected to exist in substituted ammonium salts of the general type $\text{NR}'\text{R}''\text{R}_2'\text{X}$. Difficulties were met with both on account of the extremely slow rate at which some of the compounds are formed, and also owing to the fact that it was found impossible to effect some of the desired combinations. It has not been found possible to prepare compounds exhibiting the expected isomerism, but since most of the compounds prepared during the course of the investigation have not hitherto been described,* and as the non-existence of the isomerism has an important theoretical bearing, the following account of the work is presented to the Society.

The isomerism of quinquevalent nitrogen compounds has already

* A note was published by the author, in which a few of the compounds first prepared were described (*Proc. Camb. Phil. Soc.*, 1901, 11, 111).

been the subject of a large number of investigations. Le Bel (*Compt. rend.*, 1891, 112, 724) found that *Penicillium glaucum* caused a dilute solution of methylethylpropylisobutylammonium chloride to acquire a small but fugitive rotatory power, and also observed certain differences in crystalline form in some compounds in which three of the radicles were identical. The latter phenomenon must be attributed to dimorphism.

Schryver and Collie (*Chem. News*, 1891, 63, 174) prepared diethyl-isoamylamine platinichloride in the three possible ways, and obtained two compounds differing in crystalline form; this difference, which readily disappeared on recrystallisation, is also probably due to dimorphism.

Wedekind (*Ber.*, 1899, 32, 517, 3561) prepared two stable isomerides of phenylbenzylmethylallylammonium iodide, and afterwards described two isomeric methyl benzylallylisobutylammonium-*N*-acetate bromides and two sets of isomeric tetrahydroquinoline derivatives. The existence of the last three pairs of isomerides has since been contradicted by Wedekind himself (*Ber.*, 1902, 35, 3580; 1903, 36, 1158), and hence the first pair stands alone as the only known case of isomerism among quinquivalent nitrogen compounds in which all the five radicles are different. The α -modification of Wedekind's salt has been resolved into optically active forms by Pope and Peachey (*Trans.*, 1899, 75, 1127), thus conclusively proving the atomic nature of the compound and the stability of its spatial configuration.

Two of the configurations proposed for the nitrogen atom, namely, the "double tetrahedron" structure proposed by Willgerodt and the "pyramid" configuration proposed by Bischoff, explain the above-mentioned results satisfactorily, but the former usually requires the larger number of isomerides and does not explain the phenomena observed by Kipping (see p. 1403), so that the latter will be used throughout the present paper.

It is readily seen that with this configuration two isomerides of the compound $\text{NR}'\text{R}''\text{R}_2'''\text{X}$ should exist, which would be represented as follows:

The first of these is planisymmetric and might be expected to exist in one optically inactive form only, the second is asymmetric

and should therefore exist in two enantiomorphous optically active forms, represented thus :

and

With Willgerodt's configuration, there should be three isomerides and one of these should exist in enantiomorphous forms.

A number of substituted ammonium iodides of this type, produced, with one exception, in two ways, have been examined for optical activity by fractional crystallisation from non-hydroxylic solvents of the *d*-camphorsulphonates (salts of Reychler's acid) and the *d*-bromocamphorsulphonates (Pope and Peachey's method).

In all cases, the compounds produced in different ways were found to be the same, as shown by taking the melting point of a mixture of the two preparations, which themselves had the same melting points, and were also identical in solubility, crystalline appearance, and optical properties. In many cases, when the velocity of reaction between the tertiary amine and the alkyl iodide was sufficiently great, the combination was effected at 0°, and the crystallisation was carried out in an ice-chest at as low a temperature as possible. All the compounds examined were found to be optically inactive; the salts with the above-mentioned optically active acids, on examination in aqueous solution, all showed the molecular rotatory power of salts of the respective acids combined with an inactive base, and the values were not changed by recrystallisation.

In many of the compounds prepared, it is clear that the limit of the so-called "space filling" ("Raum-erfüllung") has nearly been reached, as shown by the extremely small velocity of formation of the compounds. In some cases, the amine and alkyl iodide only combined to a small extent after several months. Also in the case of phenyldibenzylmethylammonium iodide, the compound could not be produced by the union of methyl iodide and dibenzylaniline (Proc., 1901, 17, 205). The absence of isomerism cannot, therefore, be attributed to this cause. Again, unless all the compounds examined are partially racemic, which is very unlikely, the compound formed in all cases is inactive, and therefore has the planisymmetric configuration, which would naturally be the more stable of the two possible configurations. It might be supposed that the absence of activity is due to spontaneous racemisation caused by the greater mobility of the groups used and to the limit of "space

filling " not having been approached to the same extent as in the compound resolved by Pope and Peachey. That this is not so is shown by the fact that two compounds examined by the author, namely, phenylbenzylmethylethylammonium iodide and phenylmethylethylallylammonium iodide, neither of which has been shown to exist in inactive isomerides, can be obtained in optically active forms.

Some explanation of the absence of this isomerism, the existence of which was to be expected from theoretical considerations, must therefore be sought. The author has delayed publication until the results of Kipping's investigations on the isomerism of the compounds of the type NRH_3X , in which R and X both contain an asymmetric carbon atom (Trans., 1900, 77, 861, and 1901, 79, 430, this vol., p. 918, 937), had been brought to a definite conclusion, as it was clear that these experiments had a direct bearing on those described in this paper, and must be considered before any definite theoretical conclusion can be reached.

It may fairly be assumed, until direct evidence to the contrary is forthcoming, that the three radicles in a trivalent nitrogen compound lie in one plane, there being as yet no direct evidence either against this assumption or in favour of the suggestion made by Pope and Harvey (Trans., 1901, 79, 838) as applied to the case of nitrogen, that during the change from tri- to quinque-valency a change of valency-direction takes place, and that therefore the three valencies need not be in one plane. This assumption and the Hantzsch-Werner theory of the isomerism of the oximes, &c., are not necessarily incompatible, since it is quite conceivable that the formation of a double union may cause a change in valency-direction giving rise to the isomerides in question, or the isomerism might arise as suggested by Pickering (Trans., 1893, 63, 1072).

The negative result of these experiments was most simply explained by assuming that the three valencies of the trivalent nitrogen atom were in a plane, and that, in becoming quinquevalent, the alkyl haloid, RX , was added on symmetrically at right angles to this plane so as to give rise to a molecule having practically the double tetrahedral configuration, rearrangement then took place leading to a change in the valency-direction with the formation of a molecule having the pyramidal configuration. This rearrangement would cause the radicle R to come between two of those already existing in the molecule, and in so doing it would take up a position giving rise to the most symmetrical (and therefore the most stable) configuration, namely, the planisymmetric (I). This hypothesis, however, although it affords a satisfactory explanation of the author's experiments, will not explain the existence of the isomerides observed by Kipping unless it is assumed that in the one case the rearrangement has occurred with the production of one isomeride, whereas in the other it has not taken place at all.

Kipping (this vol., 949) has suggested two hypotheses which explain the formation of two isomeric *d*-hydrindamine *d*-camphorsulphonates; the first assumes that the new radicles, H and X, are added to the trivalent nitrogen, in which the three existing groups are in one plane, in such a way that a pyramidal configuration arises. In this case, it is necessary to make the further assumption that the addition can take place in any one of the three planes of the original triangular configuration, or else this kind of isomerism would not arise, since it vanishes if the asymmetric carbon atom be made to occupy the apex of the pyramid. This hypothesis demands that, in the addition of $R'''X$ to $NR'R''R'''$, the compound which arises should correspond with one of the types:

or

both of which should exist in optical antipodes. None of the compounds produced in this way could be resolved into optically active forms: hence this hypothesis does not explain the results of the author's experiments.

The second hypothesis is that, addition having taken place as above, a molecular transformation occurs during which the acidic radicle changes positions with one of the hydrogen atoms of the original amine, thus giving rise to one isomeride, the other being the untransformed additive product. This hypothesis will explain the formation of the planisymmetric compound by the addition of $R'''X$ to $NR'R''R'''$ and $R''X$ to $NR'R_2'''$, if, as above, it is assumed that the addition can take place in any one of the three possible planes. It is clear, however, that in this case also, the untransformed product should be an isomeric substance of the existence of which there is no evidence. The slight difference observed by Kipping between the two hydrindamine hydrochlorides derived from the α - and β -camphorsulphonates, which could only be shown by reconvertng them into the camphorsulphonates (this vol., 943) does not exist in the present instance. The camphorsulphonates prepared from two specimens of phenylbenzylidimethylammonium iodide, produced in one case by the addition of methyl iodide and in the other by the addition of benzyl iodide, are identical in every respect, as are also the camphorsulphonates and the bromocamphorsulphonates obtained from two

specimens of phenyldimethylisobutylammonium iodide prepared in the two possible ways.

The existence of the untransformed product as a stable isomeride is probably due to some special circumstance, as, for instance, the presence of two asymmetric carbon atoms in the case of the hydrindamine camphorsulphonates. In the light of the abnormal behaviour of Kipping's β -isomeride, it was considered advisable to obtain the camphorsulphonate of Wedekind's β -compound and to see if it behaved in a similarly anomalous manner. This was unfortunately not found practicable on account of the extremely small yield of the β -iodide which was obtained.

The question of the existence of optical activity in cyclic ammonium compounds of the pyridine and tetrahydroquinoline series has also been investigated. Theoretically, α - and β -substituted pyridinium compounds and tetrahydroquinoline derivatives, $C_9H_{10}NR'R''X$, should exist as optical antipodes, since the molecules of these compounds have no plane of symmetry. Piperidinium compounds, on the other hand, can take up a planisymmetric configuration, and hence would not be expected to exist in optically active forms.*

The author has submitted the camphorsulphonates and bromo-camphorsulphonates of several of these salts to a long series of crystallisations from non-hydroxylic solvents, but in all cases the molecular rotatory powers of the salts were practically identical with those of salts of the respective acids and inactive bases. It is possible, although not likely, either that all the salts examined are partially racemic or that there is some other hitherto unsuspected reason for the unsuccessful attempts to resolve these compounds. The absence of activity in these compounds is inexplicable on the current views as

* Since the above was written, Barrowcliff and Kipping (this vol., p. 1141) have published an account of an unsuccessful attempt to resolve three piperidinium compounds. It may therefore be concluded that these compounds are symmetrical.

Wedekind has also recently (*Zeit. physikal. Chem.*, 1903, **45**, 235) given an account of his unsuccessful attempts to resolve *p*-tolylbenzylmethylallylammonium iodide into active forms by the fractional crystallisation of the *d*-camphorsulphonate. This salt is very similar in structure to that resolved by Pope and Peachey, and might certainly be expected to undergo resolution in a similar manner, whereas it behaves quite differently. It may therefore be of interest to record a similar unsuccessful attempt to resolve phenylmethylethylallylammonium camphorsulphonate, a salt which crystallised readily in lustrous prisms melting at 148–150°. After several crystallisations, two successive fractions gave $[M]_D = 49.1^\circ$ and 50.7° respectively; then, after three more crystallisations, the value of $[M]_D$ was 51.2° , a value very close to that of the acidic ion, 51.7° . The base was, however, apparently resolved by the crystallisation of the *d*-bromocamphorsulphonate. The fact that unexpected difficulties thus arise in the resolution of nitrogen compounds is of considerable interest, and may, as suggested, account for the non-resolution of the cyclic compounds.

to their constitution, and there is no evidence in support of any one of the possible explanations which might be suggested to account for this unexpected phenomenon.

EXPERIMENTAL.

Phenyldimethylallylammonium iodide was prepared by mixing molecular quantities of dimethylaniline and allyl iodide in the cold; the mass, which solidified in about twenty-four hours, was pressed out on a porous plate, and, when crystallised several times from a mixture of absolute alcohol and ether, separated in colourless, prismatic crystals melting at 86—87°. It was found to be identical in every respect with that obtained by the union of methyl iodide with methylallylaniline, even when both combinations were allowed to take place at 0° and recrystallisation carried out at a comparatively low temperature.

- I. 0.143 gave 0.241 CO₂ and 0.074 H₂O. C = 46.0; H = 5.73.
 - II. 0.3857 on titration required 13.3 c.c. N/10 AgNO₃. I = 43.8.
- C₁₁H₁₆NI requires C = 45.83; H = 5.55; I = 43.9 per cent.

Phenyldimethylallylammonium d-camphorsulphonate was prepared by mixing together molecular quantities of the iodide (18 grams) and Reychler's silver *d*-camphorsulphonate (20 grams) with ethyl acetate and a few drops of alcohol and heating for about one hour on the water-bath, after filtering and evaporating. The gummy residue, which readily becomes crystalline on rubbing, is very sparingly soluble in ether, but readily soluble in ethyl acetate, chloroform, and fairly so in benzene; it crystallises in monoclinic, colourless plates, which melt sharply at 156°.

- I. 0.3774 gave 12.9 c.c. moist nitrogen at 21° and 756 mm. N = 3.89.
 - II. 0.1668 gave 0.1231 PbSO₄. S = 7.8.
- C₂₁H₃₁O₄NS requires N = 3.56; S = 8.14 per cent.

The rotatory powers for sodium light of two specimens, repeatedly crystallised respectively from ethyl acetate and from a mixture of benzene and chloroform, were determined in aqueous solution by means of a half shadow polarimeter by Schmidt and Haensch, for the use of which the author is indebted to Mr. F. G. Hopkins.

- 0.779 in 25 c.c. gave $\alpha_D = 0.81^\circ$ in a 200 mm. tube; $[\alpha]_D = 13.0^\circ$ and $[M]_D = 51.1^\circ$.
- 1.1856 in 35 c.c. gave $\alpha_D = 1.78^\circ$ in a 400 mm. tube; $[\alpha]_D = 13.15^\circ$ and $[M]_D = 51.66^\circ$.

$[M]_D$ for compounds of the acid with an inactive base is 51.7° according to Pope and Peachey (Trans., 1899, 75, 1086), so that the radicle, $NPhMe_2 \cdot C_3H_5$, is inactive.

Phenyldimethylpropylammonium Iodide.

(1) Methylpropylaniline, prepared according to Claus and Hirzel's method (*Ber.*, 1886, 19, 2786), was found to boil at $215-217^\circ$. A mixture of molecular quantities of the amine and methyl iodide gradually set to a transparent, gummy mass, which was with difficulty induced to crystallise by repeatedly dissolving in alcohol and adding ether until the substance was partially precipitated as an oil, and then allowing the turbid solution to remain until the precipitated oil became crystalline, after which more ether was added. Colourless prisms soluble in acetone, ethyl acetate, and alcohol were obtained which, when recrystallised either from ethyl acetate or from a mixture of alcohol and ether, melted at 68.5° .

(2) Combination of dimethylaniline and propyl iodide took place slowly, a gummy mass being gradually formed which, when dissolved in cold alcohol and treated with ether until a turbidity was produced, crystallised out in large, white crystals melting at $65-66^\circ$. After repeated crystallisations the crystals melted at 68.5° , and did not depress the melting point of the preceding preparation.

0.155 gave 0.2572 CO_2 and 0.0845 H_2O . $C = 45.26$; $H = 6.06$.

$C_{11}H_{18}NI$ requires $C = 45.36$; $H = 6.17$ per cent.

The corresponding *d*-camphorsulphonate is crystalline.

Phenylmethyldipropylammonium Iodide.

(1) Dipropylaniline was prepared by Lippmann and Fleissner's method (*Monatsh.*, 1871, 3, 711); its boiling point was 238° under 750 mm. pressure.

Molecular quantities of the base and methyl iodide were mixed and allowed to remain for about 2 days, when colourless crystals began to separate; these were very soluble in alcohol, somewhat less so in ethyl acetate, very sparingly so in ether and light petroleum. The crude salt melted at $135-137^\circ$, but after repeated crystallisation from ethyl acetate and a mixture of alcohol and ether the melting point was 156° .

(2) A mixture of molecular quantities of methylpropylaniline and propyl iodide soon deposited a viscid mass, containing some crystals, and finally set to a crystalline solid which was repeatedly crystallised from alcohol and ether, when leaf-like crystals separated melting at

154—155°. A mixture of this with the foregoing preparation also melted at this temperature.

0.1455 gave 0.2588 CO₂ and 0.0897 H₂O. C=48.51; H=6.85.

C₁₃H₂₂NI requires C=48.8; H=6.86 per cent.

Phenyldimethylisobutylammonium iodide.

(1) A mixture of dimethylaniline and isobutyl iodide in molecular quantities very slowly deposited a small quantity of needle-like crystals, which melted at 154—155°, and when crystallised from dilute alcohol melted at 155—156°; by repeated crystallisation, the melting point may be raised a little higher, and in one case it reached 160°. The melting points of this and certain other compounds of this class were found to become slightly lowered by keeping the compound in an ordinary stoppered bottle for a few weeks or longer.

(2) Methylisobutylaniline was found to be very difficult to produce in a state approaching purity. On mixing methylaniline with isobutyl iodide or isobutylaniline with methyl iodide, treating the solid product with caustic potash, separating, drying, and distilling the liquid obtained, the boiling point varied continuously, and after repeated fractionation the greater part finally distilled between 220° and 230°. This liquid rapidly combined with methyl iodide and formed a solid crystalline substance which was found to be phenyltrimethylammonium iodide. Therefore, in each case, the main product was dimethylaniline. This change is of interest, since it shows that the methyl group can behave like the benzyl group in the transformations of benzylaniline and dibenzylamine observed by Wedekind and the author respectively; further, in the case of the action of methyl iodide on isobutylaniline, the reaction is somewhat analogous to the replacement of benzyl by methyl observed in certain ammonium salts (Proc., *loc. cit.*).

By heating together two molecular proportions of methylaniline and one of isobutyl bromide on a water-bath, filtering off the solid methylaniline hydrobromide, and repeatedly fractionating the oil, a liquid was obtained having a constant boiling point of 227—228°. This product, when mixed with a gram-molecule of methyl iodide and left for about a week, yielded an almost solid mass of crystals which were repeatedly crystallised from alcohol and ether, and finally from ethyl acetate. A small quantity of phenyltrimethylammonium iodide was obtained from the first fractions, but the more soluble part was found to reach a constant melting point of 155—156°, which was not changed by the presence of an equal quantity of the substance produced by the first method (1). The two compounds are therefore identical.

0.1820 gave 0.3145 CO₂ and 0.1120 H₂O. C=47.12; H=6.77.

C₁₂H₂₀NI requires C=47.21; H=6.55 per cent.

Phenyldimethylisobutylammonium d-camphorsulphonate, prepared in the same way as the other camphorsulphonates, crystallises readily, and is sparingly soluble in ethyl acetate and acetone, but very readily so in methylene diethyl ether. When crystallised repeatedly from a warm mixture of ethyl acetate and methylene ether, it was obtained in colourless needles melting at 190—192°.

After four recrystallisations, its rotatory power was determined in aqueous solution.

0.4325 in 25 c.c. gave $\alpha_D = 0.41^\circ$ in a 200 mm. tube. $[\alpha]_D = 11.86^\circ$ and $[M]_D = 48.6^\circ$.

The radicle $NPhMe_2 \cdot C_4H_9$ is therefore inactive.

Phenylbenzyltrimethylammonium Iodide.

(1) Dimethylaniline and benzyl iodide, when mixed in molecular proportion, rapidly set to a solid mass, which, after washing with ether, was crystallised repeatedly from alcohol. The salt then melted sharply at 165°, after becoming brown at 158°.

(2) Benzylmethylaniline was prepared by the action of benzyl chloride on methylaniline, as described by Wedekind. Molecular proportions of the amine and methyl iodide began to deposit solid almost immediately, and after 36 hours, about 30 per cent. had combined. The solid was crystallised several times from absolute alcohol; the melting point after one crystallisation was 157°, rising to 164.5° after four crystallisations. The compound, prepared at 0° and crystallised at the same temperature, also melted at 164—165°. The compound prepared by method (1) was shown to be identical with this by melting a mixture of the two.

0.1262 gave 0.2456 CO_2 and 0.0604 H_2O . C = 53.06; H = 5.32.

$C_{15}H_{18}NI$ requires C = 53.09; H = 5.32 per cent.

Phenylbenzyltrimethylammonium d-camphorsulphonate was prepared both from the iodide and also in larger quantity from phenylbenzyltrimethylammonium chloride, $NPhMe_2(C_7H_7) \cdot Cl, H_2O$ (Michler and Gradmann, *Ber.*, 1877, 10, 2079).

The chloride used was repeatedly crystallised from water and found to contain 14.2 per cent. of chlorine, whereas theory requires 14.3. The chloride or iodide, when boiled with the theoretical quantity of silver *d*-camphorsulphonate and some moist chloroform, filtered, and evaporated to dryness, yielded a product which crystallised readily, and was found to be very sparingly soluble in ethyl acetate, acetone, and light petroleum, although dissolving fairly readily in chloroform. The salt, when crystallised several times from a mixture of chloroform and light petroleum, formed colourless needles which melted at 189°.

0.1223 gave 0.3022 CO_2 and 0.0791 H_2O . $\text{C} = 67.38$; $\text{H} = 7.2$.

$\text{C}_{25}\text{H}_{35}\text{O}_4\text{NS}$ requires $\text{C} = 67.71$; $\text{H} = 7.4$ per cent.

The rotatory power was determined in aqueous solution in the manner already described.

1.224 in 35 c.c. gave $\alpha_D = 1.63^\circ$ in a 400 mm. tube. $[\alpha]_D = 11.65^\circ$, and $[\text{M}]_D = 51.62^\circ$.

This value had not been appreciably altered by repeated crystallisation. The radicle $\text{NPhMe}_2 \cdot \text{C}_7\text{H}_7$ is therefore inactive.

Phenyldibenzylmethylammonium Iodide.

Benzyl iodide and benzylmethylaniline combined readily; a mixture of the two substances in molecular proportion rapidly became cold, and in a few hours had set to a pale yellow gum, which subsequently crystallised, about 89 per cent. of the reagents having combined. The product was fairly pure, as shown by the following nitrogen determination:

0.312 gave 10.3 c.c. nitrogen at 19° and 770 mm. $\text{N} = 3.85$.

$\text{C}_{21}\text{H}_{22}\text{NI}$ requires $\text{N} = 3.38$ per cent.

The salt, when purified by repeated crystallisation from hot absolute alcohol, was obtained in colourless prisms melting at $134\text{--}135^\circ$; it was very soluble in chloroform and very sparingly so in water.

0.1220 gave 0.2710 CO_2 and 0.0610 H_2O . $\text{C} = 60.60$; $\text{H} = 5.53$.

$\text{C}_{21}\text{H}_{22}\text{NI}$ requires $\text{C} = 60.7$; $\text{H} = 5.30$ per cent.

As the camphorsulphonate was found to crystallise with a molecule of chloroform of crystallisation, it was expected that the iodide would behave similarly. A specimen crystallised from a mixture of chloroform and ether melted slowly at about 130° ; the following analytical result shows that the specimen does not contain chloroform:

0.1264 gave 0.2821 CO_2 and 0.0635 H_2O . $\text{C} = 60.8$; $\text{H} = 5.58$ per cent.

Phenyldibenzylmethylammonium Chloride.

Benzylmethylaniline and benzyl chloride do not combine, even when left for months in the cold or after heating for several hours. The chloride, which was accordingly produced by the action of silver chloride on a warm alcoholic solution of the iodide and purified by crystallisation from alcohol and ether, separated in colourless needles melting at $159\text{--}161^\circ$; it appears to be much more stable than the iodide, since the latter, when heated in alcoholic solution, evolves a strong odour of benzyl iodide, whereas no benzyl chloride can be detected when the former is similarly treated.

The analysis of a specimen, dried in a vacuum, gave the following result :

0.1095 gave 0.3126 CO_2 and 0.0668 H_2O . $\text{C} = 77.8$; $\text{H} = 6.7$.

$\text{C}_{21}\text{H}_{22}\text{NCl}$ requires $\text{C} = 78.2$; $\text{H} = 6.80$ per cent.

All attempts to cause dibenzylaniline to combine with methyl iodide were abortive ; there was practically no reaction either in the cold after several months or on gently warming. When the mixture was heated at 100° in a sealed tube, benzyl iodide was formed and a crystalline solid was produced which was found to be phenyltrimethylammonium iodide, the two benzyl groups having been removed as benzyl iodide and replaced by methyl groups, whilst the dimethylaniline thus produced combined with a molecule of methyl iodide (Proc., 1901, 17, 205).

Phenyldibenzylmethylammonium d-camphorsulphonate was prepared in the same way as the other camphorsulphonates, a mixture of moist ethyl acetate and acetone being used as solvent ; the viscid residue solidified when left in a desiccator and stirred at intervals. The salt was found to be very sparingly soluble in dry ethyl acetate and acetone but much more so in these solvents when slightly moist ; it dissolved fairly readily in chloroform, alcohol, and methylene diethyl ether. A specimen crystallised repeatedly from chloroform, and then from a mixture of chloroform and benzene, separated in fine needles which had a great tendency to aggregate into sheaves ; it melted slowly at 130 — 137° and gave the following analytical result after drying in a vacuum desiccator :

0.1135 gave 0.2490 CO_2 and 0.0630 H_2O . $\text{C} = 59.83$; $\text{H} = 6.17$.

$\text{C}_{31}\text{H}_{37}\text{O}_4\text{NS}$ requires $\text{C} = 71.7$; $\text{H} = 7.12$; and $\text{C}_{31}\text{H}_{37}\text{O}_4\text{NS} \cdot \text{CHCl}_3$ requires $\text{C} = 60.1$; $\text{H} = 5.95$ per cent.

The salt therefore crystallises with a molecule of chloroform of crystallisation, which accounts for its indefinite melting point. On account of the slight solubility of the salt in water, its rotatory power was determined in 10 per cent. alcohol.

0.6944 in 50 c.c. gave $\alpha_D = 0.464^\circ$ in a 400 mm. tube. $[\alpha]_D = 8.35^\circ$ and $[M]_D = 53.33^\circ$ (for $\text{C}_{31}\text{H}_{37}\text{O}_4\text{NS} + \text{CHCl}_3$), and 43.34° (for $\text{C}_{31}\text{H}_{37}\text{O}_4\text{NS}$).

The radicle $\text{NPhMe}(\text{C}_7\text{H}_7)_2$ therefore appears to be inactive.

Since the salt separated with a molecule of chloroform, it was thought advisable to crystallise the substance from some other solvent and redetermine its rotatory power. A mixture of methylene diethyl ether and benzene was found to be a suitable solvent, and after several

crystallisations, the salt melted sharply at 139—141°, and when dried at 100° gave the following result on analysis :

0.1197 gave 0.3140 CO₂ and 0.0768 H₂O. C=71.5 ; H=7.12.

C₃₁H₃₇O₄NS requires C=71.7 ; H=7.12 per cent.

Determinations of the rotatory power were made by dissolving the salt in as little absolute alcohol as possible, and then making the solution up to a definite volume with water or dilute alcohol.

The sparing solubility of the salt makes the determinations difficult; the solutions, although dilute, being in many cases nearly saturated.

(I) 0.7735 in 50 c.c. gave $\alpha_D = 0.561^\circ$ in a 400 mm. tube. $[\alpha]_D = 9.06^\circ$; $[M]_D = 47.0^\circ$.

(II) 0.5536 in 50 c.c. gave $\alpha_D = 0.457^\circ$ in a 400 mm. tube, $[\alpha]_D = 10.3^\circ$; $[M]_D = 53.5^\circ$.

(IV) 0.3464 in 25 c.c. gave $\alpha_D = 0.27^\circ$ in a 200 mm. tube (with a Landolt-Lippich three field polarimeter). $[\alpha]_D = 9.75^\circ$, and $[M]_D = 50.6^\circ$.

(V) 17.5 c.c. of the solution (IV) made up to 25 c.c. gave $\alpha_D = 0.18^\circ$ hence $[\alpha]_D = 9.28^\circ$ and $[M]_D = 48.2^\circ$.

These values are in sufficiently close agreement (allowing for the large experimental error) with the expected value 51.7° to show that the effect of the alcohol is not large, and that the radicle

is inactive. The iodide was precipitated from a dilute alcoholic solution of the camphorsulphonate by the addition of concentrated potassium iodide solution. After one crystallisation from alcohol, it melted at 134—135°, and, when examined in alcoholic solution, was quite inactive.

Dibenzylmethylisobutylammonium Iodide.

(1) Benzylisobutylamine, prepared as described by Wedekind, and methyl iodide in molecular proportion reacted rapidly and set to a solid mass, which was heated on the water-bath for some time, decomposed with caustic potash, the solution extracted with ether, and the ethereal extract dried over fused sodium sulphate. After evaporating off the ether, the oil was fractionated [under reduced pressure, when a very good yield of benzylmethylisobutylamine was obtained with a constant boiling point of 115—118° under 30 mm. pressure.

The base, when mixed with the theoretical quantity of benzyl iodide and allowed to remain in the cold for three weeks, yielded a red oil, which was twice dissolved in alcohol and precipitated by the

addition of ether, after which it crystallised when rubbed with a little alcohol. The salt, after repeated crystallisation from a mixture of alcohol and ethyl acetate, was obtained in colourless prisms melting sharply at 174—175°.

(2) Considerable difficulty was experienced in the preparation of dibenzylisobutylamine. When dibenzylamine (2 mols. and *isobutyl* bromide (1 mol.) were heated for about two hours on the water-bath, crystals separated, which, on filtering and washing with ether, were found to melt at 250°, and were therefore dibenzylamine hydrobromide (Carrara gives m. p. 250°). The liquid portion, when distilled under reduced pressure, yielded a first fraction distilling at 198—210° under 20 mm. pressure, which was found to be unchanged dibenzylamine (its hydrochloride was prepared, m. p. 256°). A very small quantity of oil then distilled over and partially solidified; the residue in the flask solidified completely. Both distillate and residue were pressed on a porous plate, and, when crystallised several times from light petroleum, yielded white needles melting at 92—93°.

(I) 0.1146 gave 0.3685 CO₂ and 0.0737 H₂O. C = 87.6; H = 7.06.

(II) 0.1930 „ 8.3 c.c. moist nitrogen at 14.5° and 765 mm. N = 5.0.
(C₇H₇)₃N requires C = 87.8; H = 6.9; N = 7.3 per cent.

The substance is therefore tribenzylamine, the melting point of which was given by Cannizzaro as 91.3°. This transformation is of interest from its similarity to the well known change which results from the action of methyl iodide on benzyaniline, in which dibenzylaniline is the chief product. A similar result was obtained when *isobutyl* iodide was used.

In order to avoid possible molecular transformation by the action of heat, a mixture of equivalent quantities of dibenzylamine and *isobutyl* iodide was left in the cold for several months. Crystals separated, which were undoubtedly dibenzylamine hydriodide, the oil was filtered off and mixed with methyl iodide. The crystalline product was drained and submitted to fractional crystallisation in the hope of separating any of the desired compound which might be present. The only substance which could be isolated was recrystallised from alcohol and ethyl acetate and then melted at 186—187.5°.

(I) 0.1444 gave 0.2867 CO₂ and 0.0744 H₂O. C = 54.15; H = 5.72.

(II) 0.1598 „ 0.3179 CO₂ „ 0.0807 H₂O. C = 54.31; H = 5.61.
N(C₇H₇)₂(CH₃)₂·I requires C = 54.5; H = 5.67. NMe(C₄H₉)(C₇H₇)₂·I requires C = 57.9; H = 6.6 per cent.

The product was therefore *dibenzylidimethylammonium iodide*. The corresponding chloride has been obtained by Jackson and Wing (*Amer. Chem. J.*, 1887, 9, 80).

The action of benzyl chloride on benzylisobutylamine was then studied. On heating together either one molecule of each or one molecule of the chloride and two molecules of the base, some benzylisobutylamine hydrochloride separated; but the reaction was very incomplete, even after heating for several hours. On filtering and distilling the filtrate under reduced pressure, the liquid boiled over a very wide range, and obviously consisted of a mixture from which it was found impossible to separate any pure compound.

The desired result was finally attained by the action of benzyl iodide on isobutylamine. A mixture of two molecular proportions of the base and one of the iodide rapidly became very hot and a solid separated. After cooling, the odour of benzyl iodide could still be detected, so that to complete the reaction the mixture was heated for about an hour on the water-bath. The solid, after washing with ether several times, formed colourless, glistening plates, very soluble in alcohol and fairly so in ethyl acetate and water; it was readily decomposed by caustic potash.

After crystallisation from hot ethyl acetate, the compound melted at 165—166° and gave the following numbers:

0.6950 required 23.8 c.c. $N/10$ $AgNO_3$. $I = 43.5$.

$NH(C_4H_9) \cdot C_7H_7, HI$ requires 43.6 per cent.

The solid is therefore benzylisobutylamine hydriodide and the liquid should be the required tertiary amine.

After distilling off the ether from the filtrate, the residual oil was fractionated three times under reduced pressure, after which the greater part boiled constantly at 170—173° under 10 mm. pressure.

The base, when mixed with one molecular proportion of methyl iodide, slowly deposited a red gum, which was purified and induced to crystallise in the foregoing manner. Small, colourless prisms were thus obtained, which were identical in appearance, melting point, and optical properties with those obtained by the first method. After drying in a vacuum desiccator, the following results were obtained:

(I) 0.1433 gave 0.3036 CO_2 and 0.0829 H_2O . $C = 57.8$; $H = 6.43$.

(II) 0.1378 „ 0.2926 CO_2 „ 0.0795 H_2O . $C = 57.9$; $H = 6.41$.
 $C_{19}H_{26}NI$ requires $C = 57.87$; $H = 6.6$.

(3) The same quaternary compound might also be produced by the union of dibenzylmethylamine and isobutyl iodide, but unfortunately it has not been found possible to produce the tertiary amine, since when dibenzylamine and methyl iodide are mixed in any proportion, even at low temperatures, a violent reaction takes place almost immediately with the production of the foregoing dibenzyltrimethylammonium iodide.

Dibenzylmethylisobutylammonium *d*-camphorsulphonate, prepared in the usual way, formed a colourless viscid mass, which, when kept in a desiccator, slowly became crystalline; the solid, however, crystallises badly from solvents, and is unsuitable for a long series of fractional crystallisations. All attempts to cause the *d*-bromocamphorsulphonate to crystallise have hitherto been unsuccessful, so that it has unfortunately not been possible to decide as to the activity of the radicle $\text{NMe}(\text{C}_7\text{H}_7)_2\cdot\text{C}_4\text{H}_9$, but there is no reason to believe that it would behave differently to the others which have been examined.

Cyclic Compounds.

1-Methyl- α -picolinium *d*-camphorsulphonate was prepared by heating together molecular proportions of the corresponding iodide (m. p. 224—224.5°) and silver *d*-camphorsulphonate with ethyl acetate and a small quantity of alcohol. The salt, which crystallised readily in a vacuum desiccator, is sparingly soluble in ethyl acetate, slightly more so in acetone, and dissolves very readily in methylene diethyl ether; it was repeatedly crystallised from a mixture of acetone and ethyl acetate, and then from acetone, being obtained in long, colourless needles which melted constantly, but not very sharply, at 162—164°. The rotatory power of the salt, determined after successive crystallisations, was constant, but the values of $[\text{M}]_D$ differed slightly from 51.7°, the discrepancy being very probably due to hydrolytic dissociation.

0.585 in 25 c.c. gave $\alpha_D = 0.685^\circ$ in a 200 mm. tube; $[\alpha]_D = 14.64^\circ$ and $[\text{M}]_D = 49.6^\circ$.

0.3450 gave 0.7550 CO_2 and 0.2290 H_2O . C = 59.0; H = 7.37.

$\text{C}_{17}\text{H}_{25}\text{O}_4\text{NS}$ requires C = 60.1; H = 7.37 per cent.

1-Methyl- α -picolinium *d*-bromocamphorsulphonate, prepared in the same way as the camphorsulphonate, was found to crystallise readily; it is very sparingly soluble in acetone and ethyl acetate, but dissolves more freely in methylene ether. After repeated crystallisation from a mixture of ethyl acetate with a small amount of methylene ether, it was obtained in colourless needles melting at 186—187°.

The following determinations were made on a specimen dried in a vacuum desiccator.

0.527 in 25 c.c. gave $\alpha_D = 2.72^\circ$; $[\alpha]_D = 64.52^\circ$ and $[\text{M}]_D = 270^\circ$.

0.3337 gave 0.5900 CO_2 and 0.1745 H_2O . C = 48.5; H = 5.81.

$\text{C}_{17}\text{H}_{24}\text{O}_4\text{NBrS}$ requires C = 48.8; H = 5.74 per cent.

The platinichloride, when precipitated from a solution of the camphorsulphonate or bromocamphorsulphonate, formed bright orange

plates melting at 225—226°; it is extremely sparingly soluble in alcohol, ethyl acetate, acetone, methylene ether and epichlorohydrin. A solution of the hydrochloride prepared by the action of hydrogen sulphide on this salt suspended in warm water was inactive.

The radicle $\text{NMe}:\text{C}_5\text{H}_4\text{Me}$, although apparently devoid of a plane of symmetry, still seems unable to give rise to optical activity.

Methyl kairolinium-1-acetate d-camphorsulphonate,

was prepared by heating together molecular proportions of silver *d*-camphorsulphonate and Wedekind's methyl kairolinium-1-acetate iodide (*Annalen*, 1861, 118, 114). The salt, which crystallised in long prisms, was found to be rather sparingly soluble in ethyl acetate, but slightly more so in acetone; it was crystallised from ethyl acetate several times and then from a mixture of ethyl acetate and acetone, and the rotatory powers of several of the fractions were taken in aqueous solution with the Landolt-Lippich three-field polarimeter, using sodium light. The value of $[\text{M}]_D$ gradually became constant at about 49.6° and did not attain the value for the acidic ion, 51.7°. The melting point of the salt was found to be 146.5—147°.

After the fourth crystallisation, 1.0380 in 35 c.c. gave $\alpha_D = 0.65^\circ$ in a 200 mm. tube; $[\alpha]_D = 10.96^\circ$ and $[\text{M}]_D = 49.4^\circ$.

After the eighth crystallisation, 0.9975 in 25 c.c. gave $\alpha_D = 0.87^\circ$ in a 200 mm. tube; $[\alpha]_D = 10.9^\circ$ and $[\text{M}]_D = 49.2^\circ$.

After the tenth crystallisation, 0.884 gave in 25 c.c. $\alpha_D = 0.78^\circ$ in a 200 mm. tube; $[\alpha]_D = 11.03^\circ$ and $[\text{M}]_D = 49.7^\circ$.

A specimen dried in a vacuum desiccator gave the following numbers:

0.1374 gave 0.3078 CO_2 and 0.0906 H_2O . $\text{C} = 61.09$; $\text{H} = 7.32$.

$\text{C}_{23}\text{H}_{33}\text{O}_6\text{NS}$ requires $\text{C} = 61.19$; $\text{H} = 7.31$ per cent.

Methyl kairolinium-1-acetate d-bromocamphorsulphonate, which was prepared in the usual way, gradually solidified when left in a desiccator, and triturated with ether; when crystallised repeatedly from hot acetone, it formed stellate needles melting at 134—136°. The values obtained for $[\text{M}]_D$ gradually rose to 263°, a value fairly near to that of 271°, calculated for the acidic ion.

After the fifth crystallisation, 0.477 in 25 c.c. gave $\alpha_D = 1.87^\circ$ in a 200 mm. tube; $[\alpha]_D = 49.0^\circ$ and $[\text{M}]_D = 259.7^\circ$.

After the eighth crystallisation, 0.597 in 25 c.c. gave $\alpha_D = 2.37^\circ$ in a 200 mm. tube: $[\alpha]_D = 49.6^\circ$ and $[\text{M}]_D = 263^\circ$.

A specimen gave the following result after drying in a vacuum desiccator:

0.1089 gave 0.2057 CO_2 and 0.0612 H_2O . $\text{C} = 51.5$; $\text{H} = 6.23$.

$\text{C}_{23}\text{H}_{32}\text{O}_6\text{NBrS}$ requires 6.04; $\text{C} = 52.0$; $4 = 6.04$ per cent.

The platinichloride, precipitated by the addition of an aqueous solution of chloroplatinic acid to an aqueous solution of the salt, was obtained as a dull yellow, crystalline powder melting at $182\text{--}183^\circ$ with decomposition; it was very sparingly soluble in all ordinary solvents and also in methylene ether and epichlorohydrin. A solution of the hydrochloride prepared by the action of hydrogen sulphide on a suspension of the platinichloride in warm water was found to be inactive. It therefore appears that the radicle $\text{C}_9\text{H}_{10}\text{:NMe}\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{Me}$ is inactive.

The results obtained with the above tetrahydroquinoline derivative are not very conclusive on account of the discrepancies between the observed values of $[\text{M}]_D$ and those of the acidic ion, the deviations being greater than could be accounted for by experimental error. The examination of other derivatives, however, gave more satisfactory numbers.

1-Methyl-1-ethyltetrahydroquinolinium d-bromocamphorsulphonate, prepared from the corresponding iodide already described by Claus and Stegelitz (*Ber.*, 1884, 17, 1331), crystallised readily, and, after repeated crystallisation from acetone, was obtained in stellate aggregates of leaf-like crystals melting at $161\text{--}161.5^\circ$.

After the sixth crystallisation, 0.448 in 25 c.c. gave $\alpha_D = 2.00^\circ$ in a 200 mm. tube; $[\alpha]_D = 55.8^\circ$ and $[\text{M}]_D = 271^\circ$.

After the eighth crystallisation, 0.3844 in 25 c.c. gave $\alpha_D = 1.71^\circ$; $[\alpha]_D = 55.6^\circ$ and $[\text{M}]_D = 270.2^\circ$.

0.1268 gave 0.2513 CO_2 and 0.0726 H_2O . $\text{C} = 54.1$; $\text{H} = 6.36$.

$\text{C}_{22}\text{H}_{32}\text{O}_4\text{NBrS}$ requires $\text{C} = 54.3$; $\text{H} = 6.57$ per cent.

The camphorsulphonate of the base was obtained in a crystalline state, but the crystals were very apt to become gummy, and as the substance was not very suitable for a long series of fractional crystallisations it was not further examined.

The platinichloride separated in small, bright yellow prisms, which melted at $192\text{--}193^\circ$ with decomposition; it was extremely sparingly soluble in all the ordinary solvents. A solution of the hydrochloride, prepared by the action of hydrogen sulphide on the platinichloride suspended in warm water, was found to be inactive. The radicle $\text{C}_9\text{H}_{10}\text{:NMeEt}$ therefore appears to be inactive.

1-Benzyl-1-ethyltetrahydroquinolinium iodide was very readily formed from a mixture in molecular proportion of ethyltetrahydroquinoline and benzyl iodide, the mixture becoming solid after 24 hours; it was repeatedly dissolved in alcohol, ether added until a permanent turbidity

was produced, and the solution then left until crystals were deposited. The salt was thus obtained in stellate aggregates of almost colourless needles melting at 105–106°.

0.5682 gave 18.7 c.c. moist N at 16° and 768 mm. $N = 3.89$.

$C_{18}H_{22}NI$ requires $N = 3.7$ per cent.

1-Benzyl-1-ethyltetrahydroquinolinium d-camphorsulphonate, prepared from the iodide, slowly became crystalline in the desiccator; it is very sparingly soluble in ethyl acetate, slightly more so in acetone, and dissolves very readily in methylene ether. When crystallised repeatedly from a hot mixture of acetone (10 vols.) and methylene ether (1 vol.), the salt was obtained in short, colourless prisms melting at 164–165°. The value of $[M]_D$ gradually rose towards the number for the acidic ion, namely, 51.7°.

After four crystallisations, 0.606 in 25 c.c. gave $\alpha_D = 0.47^\circ$ in a 200 mm. tube; $[\alpha]_D = 9.7^\circ$ and $[M]_D = 46.8^\circ$.

After ten crystallisations, 1.047 in 25 c.c. gave $\alpha_D = 0.87^\circ$ in a 200 mm. tube; $[\alpha]_D = 10.4^\circ$ and $[M]_D = 50.2^\circ$.

0.1042 gave 0.2670 CO_2 and 0.0730 H_2O . $C = 69.89$; $H = 7.78$.

$C_{28}H_{30}O_4NS$ requires $C = 69.6$; $H = 7.66$ per cent.

The corresponding d-bromocamphorsulphonate formed a gummy mass, which could not be induced to crystallise. The iodide recovered from an aqueous solution of the camphorsulphonate by the addition of concentrated potassium iodide solution was found to be quite inactive in solution in dilute alcohol. After recrystallisation from dilute alcohol, it was colourless and melted at 106°. The radicle $C_9H_{10}:NEt \cdot C_7H_7$ therefore appears to be inactive.

The Optical Activity of Asymmetric Ammonium Compounds.

The existence of optically active compounds, the activity of which is due entirely to the presence of an asymmetric nitrogen atom, was firmly established by Pope and Peachey (Trans., 1899, 75, 1127), and up to the present the d- and l- α -phenylbenzylmethylallylammonium salts isolated by them are the only optically active nitrogen compounds known. The author's object in examining these compounds was to determine: (1) whether compounds containing other radicles could also show this activity; (2) whether the phenomenon was in any way connected with the existence of inactive isomerides of the same compound or not, and hence to show that the absence of activity in compounds of the type $NR'R''R'''_2X$ was not due to the mobility of the groups or the absence of inactive isomerides. The examination has been pursued with this object alone, so that the values

of the rotatory powers given in this paper must be regarded as being only approximate; a further account of these compounds will shortly be laid before the Society.

Phenylbenzylmethylethylammonium iodide, readily obtained by mixing molecular quantities of methylethylaniline and benzyl iodide, was crystallised repeatedly from warm alcohol and thus obtained in colourless needles melting at about 145–146° when quickly heated.

Phenylbenzylmethylethylammonium d-camphorsulphonate was obtained from the iodide in the usual manner; it was rather sparingly soluble in ethyl acetate and acetone, much more so in methylene ether, and was crystallised repeatedly from a mixture of about one volume of the latter solvent to four or five volumes of the former.

A few polarimetric determinations made on successive fractions after drying in a vacuum desiccator showed that the salt was being gradually resolved into two fractions of different rotatory powers, the salt of the dextrorotatory base being the less soluble.

After the third crystallisation (m. p. 178–180°), $[\alpha]_D = 13.8^\circ$, $[M]_D = 63.2^\circ$; sixth crystallisation, $[\alpha]_D = 14.9^\circ$, $[M]_D = 68.1^\circ$; eighth crystallisation (m. p. 181°), $[\alpha]_D = 15.1^\circ$, $[M]_D = 69.0^\circ$.

0.2260 gave 0.565 CO₂ and 0.1585 H₂O. C = 68.2; H = 7.78.

C₂₈H₃₅O₄NS requires C = 68.2; H = 7.66 per cent.

d-Phenylbenzylmethylethylammonium iodide was precipitated in small, colourless prisms on mixing strong solutions of potassium iodide and the camphorsulphonate. After recrystallisation from rectified spirit in the dark, the salt melted at 146–147°, and in alcoholic solution gave $[\alpha]_D = 5.24^\circ$ and $[M]_D = 18.5^\circ$.

Another preparation obtained from the camphorsulphonate after eight crystallisations gave the following result:

0.562 in 25 c.c. alcohol gave $\alpha_D = 0.35^\circ$ in a 200 mm. tube, $[\alpha]_D = 7.8^\circ$; $[M]_D = 27.5^\circ$.

0.1334 gave 0.2650 CO₂ and 0.0700 H₂O. C = 54.2; H = 5.80.

C₁₆H₂₀NI requires C = 54.4; H = 5.66 per cent.

The great difference between the value of $[M]_D$ for this salt and that for the compound resolved by Pope and Peachey, owing to the replacement of the allyl radicle by ethyl, is very striking.

The more soluble portion of the camphorsulphonate could not be obtained pure, and it will be necessary to use *l*-camphorsulphonic acid for the isolation of the *l*-rotatory isomeride.

Phenylmethylethylallylammonium d-bromocamphorsulphonate, when prepared from the corresponding iodide [NMeEtPh(C₃H₅)·I + CHCl₃], described by Wedekind, crystallised readily from ethyl acetate in colourless prisms melting at 134–135°; it was repeatedly crystallised

from ethyl acetate and then from acetone. Successive fractions were used for determinations of rotatory power and the values obtained gradually increased until the value $[M]_D = 293^\circ$ was reached.

The corresponding platinichloride was precipitated as a dull yellow, crystalline powder on adding chloroplatinic acid to an aqueous solution of the bromocamphorsulphonate. It is extremely sparingly soluble in all the ordinary organic solvents, and even in epichlorohydrin, so that a determination of its rotatory power was impossible; a weak solution of the hydrochloride obtained by suspending the double salt in warm water and treating with hydrogen sulphide had a decided, although slight, dextrorotation. The platinichloride decomposed at $159-160^\circ$.

0.5296 gave 0.134 Pt. $Pt = 25.3$.

$(C_{12}H_{18}N)_2PtCl_6$ requires $Pt = 25.5$ per cent.

The isomerides of the quinquivalent nitrogen compounds, $NR'R''R'''X$, which were to be expected, on the basis of any possible configuration for the nitrogen atom (compare p. 1401), do not appear to be capable of existence, and the one compound which is always formed has the planisymmetric configuration (VII), since it cannot be resolved into optically active forms. The formation of the same compound from $NR'R''R'''$ and $R'''X$ and from $NR'R''R'''$ and $R''X$ is explained by assuming an intramolecular transformation of the initial additive product.

VII.

The non-existence of optical activity is not due to the mobility of the groups, since the salts of phenylbenzylmethylethylammonium hydroxide and phenylmethylethylallylammonium hydroxide are optically active, although the groups in the latter case have the lowest molecular weight possible in compounds of this class.

Derivatives of pyridine and tetrahydroquinoline which apparently contain an asymmetric nitrogen atom do not seem to be capable of resolution into optically active forms.

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