shaken with an aqueous suspension of freshly precipitated silver chloride. After filtering off the insoluble silver salts, the filtrate was evaporated. With much difficulty a crystalline product was obtained, 1.5 g. of gray-white crystals melting at 192°. The melting point of this compound has been previously reported as 190–192°.[2] The product is readily soluble in water and alcohol. The water solution gives a green coloration with a ferric chloride solution and a blue coloration with Folin phosphotungstic reagent after making alkaline.

Anal. Subs., 0.010: 0.68 mg. of N as NH_3 by micro-Kjeldahl analysis. Calcd. for $C_9H_{14}O_2NCl$: N, 6.87. Found: N, 6.8.

Summary

1. A new synthetic method for preparing *dl*-β-phenylisopropylamine and certain of its derivatives has been developed.

2. 4-Hydroxy- and 3,4-dihydroxyphenylisopropylamines have been prepared by this method for physiological studies.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE FURMAN CHEMICAL LABORATORY, VANDERBILT UNIVERSITY]

SOLUBILITY RELATIONSHIPS AMONG OPTICALLY ISOMERIC SALTS.

I. THE MALATES OF ALPHA-PARA-XENYLETHYLAMINE[1]

BY A. W. INGERSOLL AND E. G. WHITE

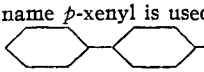
RECEIVED AUGUST 10, 1931 PUBLISHED JANUARY 7, 1932

In previous papers a method has been described by which it is possible,[2] in certain instances, to obtain both active forms of an externally compensated base or acid in an optically pure condition. For example, in the resolution of a base (*dl*B), as much as possible of one active form, for instance, *l*B, is obtained in the usual way by Pasteur's third method. The residual, partially active base (*dl*B + *d*B) is then recovered from the mother liquors, combined with any suitable inactive (externally compensated) acid (*dl*A) and the salts fractionally crystallized. In this step either of two mixtures of salts may be obtained, depending on whether the inactive acid is resolved by the active base present in excess (Equation 1) or forms a stable, partially racemic salt with it (Equation 2).

$$(dl\text{B} + d\text{B}) + dl\text{A} \longrightarrow dl\text{B}dl\text{A} + d\text{B}d\text{A} + d\text{B}l\text{A} \quad (1)$$

$$(dl\text{B} + d\text{B}) + dl\text{A} \longrightarrow dl\text{B}dl\text{A} + d\text{B}dl\text{A} \quad (2)$$

According to the usual results of fractional crystallization it may be expected that when any of the salts containing only the active base (here *d*B) is the least soluble, it can be purified and a complete resolution of the base results. On the other hand, should the totally racemic salt be the least

[1] The radical name *p*-xenyl is used in this paper as a brief designation of the *p*-diphenylyl radical,  .

[2] Ingersoll, THIS JOURNAL, **47**, 1168 (1925); **50**, 2264 (1928).

soluble, the salt containing the desired active base usually cannot be purified and the completion of the resolution fails.

In the earlier papers the possible scope and limitations of the method were briefly discussed, but it was pointed out that more experimental data and a closer analysis of the underlying theory were desirable. The success of the method obviously depends upon a favorable order of solubility of the salts concerned. The solubility order, however, is known only for the few instances previously reported and thus far no basis for predicting it in individual instances is apparent. It was decided, therefore, to continue the study experimentally by examining as many instances as possible of the use of the method with a view to determine its convenience, and to provide materials for the study of solubilities. Also, on the theoretical side, it was decided to study more fully the fundamental question of solubility relationships among optically isomeric salts.

In this paper there is presented an analysis of the possible systems and solubility relationships of the salts that may be involved when the method for complete resolution is applied in its usual form as outlined above, and in a modified form. Also a general consideration of solubility relationships is briefly introduced. In the experimental part an additional instance of the use of the method is described. Other instances in which the method is being used or in which solubility relationships are being studied will be described, it is hoped, in later papers.

Systems Resulting from the Usual Procedure.—In the absence of some natural regularity in the order of solubility, the salts resulting from the combination of an externally compensated acid with a partially active base may be arranged, so far as their solubilities are concerned, into eight possible cases, representing five experimentally different situations, as follows

$$\begin{cases} (1) & (d\mathrm{B}d\mathrm{A} \text{ or } l\mathrm{B}l\mathrm{A}) < (d\mathrm{B}l\mathrm{A} \text{ or } l\mathrm{B}d\mathrm{A}) < dl\mathrm{B}dl\mathrm{A} \\ (2) & (d\mathrm{B}l\mathrm{A} \text{ or } l\mathrm{B}d\mathrm{A}) < (d\mathrm{B}d\mathrm{A} \text{ or } l\mathrm{B}l\mathrm{A}) < dl\mathrm{B}dl\mathrm{A} \end{cases}$$

$$\begin{cases} (3) & (d\mathrm{B}d\mathrm{A} \text{ or } l\mathrm{B}l\mathrm{A}) < dl\mathrm{B}dl\mathrm{A} < (d\mathrm{B}l\mathrm{A} \text{ or } l\mathrm{B}d\mathrm{A}) \\ (4) & (d\mathrm{B}l\mathrm{A} \text{ or } l\mathrm{B}d\mathrm{A}) < dl\mathrm{B}dl\mathrm{A} < (d\mathrm{B}d\mathrm{A} \text{ or } l\mathrm{B}l\mathrm{A}) \end{cases}$$

$$\begin{cases} (5) & dl\mathrm{B}dl\mathrm{A} < (d\mathrm{B}d\mathrm{A} \text{ or } l\mathrm{B}l\mathrm{A}) < (d\mathrm{B}l\mathrm{A} \text{ or } l\mathrm{B}d\mathrm{A}) \\ (6) & dl\mathrm{B}dl\mathrm{A} < (d\mathrm{B}l\mathrm{A} \text{ or } l\mathrm{B}d\mathrm{A}) < (d\mathrm{B}d\mathrm{A} \text{ or } l\mathrm{B}l\mathrm{A}) \end{cases}$$

$$(7) \quad (d\mathrm{B}dl\mathrm{A} \text{ or } l\mathrm{B}dl\mathrm{A}) < dl\mathrm{B}dl\mathrm{A}$$

$$(8) \quad dl\mathrm{B}dl\mathrm{A} < (d\mathrm{B}dl\mathrm{A} \text{ or } l\mathrm{B}dl\mathrm{A})$$

When an externally compensated base is combined with a partially active acid, exactly the same cases are possible except that in (7) and (8) the partially racemic salts are the *dl*B*d*A or *dl*B*l*A types.

If it may be assumed that the order of separation in fractional crystallization is determined mainly by solubility, then in Cases 1,2,3,4 and 7 a successful completion of the resolution is possible. In Cases 5,6 and 8, while the proportion of the salts containing active components may be increased by the removal of a portion of the inactive salt in the head fractions, the complete purification of the desired active salts can succeed only in excep-

tional instances. If it may be expected that Cases 1–6, which depend on mutual resolvability of the acid and base, will be encountered equally often, then the method should be successful in two-thirds of these instances. Should Cases 7 and 8 occur more often than Cases 1–6, as seems probable from the prevalence of stable partially racemic salts, there is then an even chance that the solubility order will be favorable. An important object of the work now in progress is to determine how often each case occurs.

Systems Resulting from a Modified Procedure.—In the foregoing discussion there has been considered only that procedure for possible complete resolution which employs a completely inactive acid (or base) in the second step. It may, however, occasionally be convenient to combine a partially active base with an equivalent amount of a partially active acid, either for the purpose of completing a resolution or of obtaining some one of the resulting salts pure. For illustration, equivalent amounts of the partially active mixtures (*dl*B + *d*B) and (*dl*A + *d*A) may be combined, with the results shown in the following equations.

$$(dl\text{B} + d\text{B}) + (dl\text{A} + d\text{A}) \longrightarrow dl\text{B}dl\text{A} + (d\text{B}dl\text{A} \text{ or } dl\text{B}d\text{A}) + d\text{B}d\text{A} \quad (3)$$

$$(dl\text{B} + d\text{B}) + (dl\text{A} + dA) \longrightarrow dl\text{B}dl\text{A} + (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A}) + d\text{B}d\text{A} \quad (4)$$

The nature of the first or second alternative salt in the second term on the right side of the equations depends upon whether the inactive acid or the inactive base, respectively, is present in greater proportion, and upon whether the partially racemic salt corresponding to this is stable (Equation 3) or unstable (Equation 4). In the event that the inactive acid and base are present in the same proportion, the second term disappears (Equation 5).

$$(dl\text{B} + d\text{B}) + (dl\text{A} + d\text{A}) \longrightarrow dl\text{B}dl\text{A} + d\text{B}d\text{A} \quad (5)$$

When the possible orders of solubility are considered for the combination of any partially active acid and partially active base, it is clear that the salt mixtures resulting from Equations 4 and 5 constitute cases identical with or simpler than Cases 1–6 described above, and involve no new solubility relationships. The mixtures resulting from Equation 3, however, involve twelve new solubility relationships, grouped into six experimentally similar pairs. When the inactive acid is in greater proportion, the cases are as follows

$$\left\{\begin{array}{ll} (9) & (d\text{B}d\text{A} \text{ or } l\text{B}l\text{A}) < (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) < dl\text{B}dl\text{A} \\ (10) & (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A}) < (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) < dl\text{B}dl\text{A} \end{array}\right.$$

$$\left\{\begin{array}{ll} (11) & (d\text{B}d\text{A} \text{ or } l\text{B}l\text{A}) < dl\text{B}dl\text{A} < (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) \\ (12) & (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A}) < dl\text{B}dl\text{A} < (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) \end{array}\right.$$

$$\left\{\begin{array}{ll} (13) & (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) < (d\text{B}d\text{A} \text{ or } l\text{B}l\text{A}) < dl\text{B}dl\text{A} \\ (14) & (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) < (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A}) < dl\text{B}dl\text{A} \end{array}\right.$$

$$\left\{\begin{array}{ll} (15) & (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) < dl\text{B}dl\text{A} < (d\text{B}d\text{A} \text{ or } l\text{B}l\text{A}) \\ (16) & (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) < dl\text{B}dl\text{A} < (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A}) \end{array}\right.$$

$$\left\{\begin{array}{ll} (17) & dl\text{B}dl\text{A} < (d\text{B}d\text{A} \text{ or } l\text{B}l\text{A}) < (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) \\ (18) & dl\text{B}dl\text{A} < (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A} < (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) \end{array}\right.$$

$$\left\{\begin{array}{ll} (19) & dl\text{B}dl\text{A} < (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) < (d\text{B}d\text{A} \text{ or } l\text{B}l\text{A}) \\ (20) & dl\text{B}dl\text{A} < (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) < (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A}) \end{array}\right.$$

When the inactive base is in greater proportion twelve parallel cases are possible in which the partially racemic salts are the *dl*B*d*A or *dl*B*l*A types.

When fractional crystallization is applied it appears that Cases 9–12 favor the purification of salts containing both active acid and active base and may result in complete resolution. Cases 13–16 yield pure partially racemic salts containing one active component, though this may not be the one desired for complete resolution and may be present in small amount. Instances that fall in these cases in the modified procedure would, however, fall in the favorable Case 7 in the usual procedure. Cases 17–20 are unfavorable for complete resolution, but permit the recovery of the pure inactive components and the concentration of the active components from materials otherwise of little value. The modified procedure is being used in this Laboratory mainly as a supplement to the usual procedure in instances in which the solubility order is known to be favorable, but it may be seen that instances falling in the favorable cases (11) and (12) in the modified procedure would fall in the unfavorable Case 8 in the usual procedure.

It should be noted that either procedure is subject to the usual limitation of fractional crystallization, so that theoretically possible separations may be too tedious in practice. On the other hand, some or all of the salts may separate with solvent of crystallization and the degree of solvation or even the order of solubility may differ in different solvents or at different temperatures. These possibilities do not in any way invalidate the foregoing analysis, but instead are as likely as not to convert an unfavorable into a favorable case. A further element of flexibility in the method lies in the fact that the inactive or partially active acid or base used in the second step may be selected from those available after preliminary trials have indicated a favorable result. In Cases 1–4 and 9–12 the inactive or partially active resolving agent is itself resolved.

In previous papers there were described two instances that are now recognized as illustrating Case 4, and one illustrating Case 7. These resulted in complete resolution. The present paper contains a description of an instance in which an attempt to complete the resolution by the usual procedure failed (Case 8) but in which the resolution was ultimately completed by the modified procedure (Case 12). Thus inactive α-*p*-xenylethylamine ($C_6H_5C_6H_4CH(NH_2)CH_3$) was first partially resolved with *l*-malic acid. The less soluble *d*B*l*A salt and the component *d*-base were obtained pure. The solubility of this salt was 1.95 g. per 100 g. of water at 25°. The base recovered from the mother liquors (*dl*B + *l*B) was then combined with *dl*-malic acid and the salts were crystallized. The *dl*B*dl*A salt separated first and was purified. Its solubility was 2.42 g. per 100 g. of water at 25°. Though a part of the inactive base was in this way re-

moved from the mixture, the *l*B*dl*A salt remaining in the foot fractions could not be purified. The modified procedure was then employed. Another sample of the partially active base (as hydrochloride) was combined with a sample of partially active malic acid (as acid ammonium salt) which contained a considerable excess of the *d*-form. From the solubilities recorded above it was predicted that the *l*B*d*A salt should be the first to crystallize. This was verified by the experiment and this salt and the component *l*-base were obtained pure.

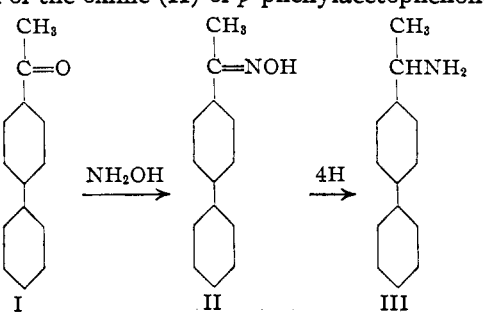
Extension of the Solubility Problem.—When the question of solubility relationships is considered from a general viewpoint it will be recalled that the active and inactive forms of a base and an acid may form a maximum of five differently soluble types (including nine varieties) of salts, as follows

(*d*B*d*A or *l*B*l*A); (*d*B*l*A or *l*B*d*A); *dl*B*dl*A; (*d*B*dl*A or *l*B*dl*A); (*dl*B*d*A or *dl*B*l*A)

The first three types are always capable of existence; the partially racemic types only when they happen to be stable in solution. Since a mixture of any two or more of the five types, if put into solution in any proportions, could not constitute or change into a system more complicated than those described in the preceding sections, the relative solubilities of as many as four or five of these types will never be concerned in any process based upon fractional crystallization. Nevertheless, it would appear that a knowledge of the solubility relationships of all of the stable types should have considerable theoretical interest.

In the absence of any extensive experimental data, it does not seem appropriate to set forth the obviously large number of possible solubility orders, but it is intended to record the solubilities for particular instances whenever the necessary salts can be prepared. In a previous paper the order for the camphor-10-sulfonates of isodiphenylhydroxyethylamine was reported as (*d*B*d*A or *l*B*l*A) < (*d*B*dl*A or *l*B*dl*A) < (*d*B*l*A or *l*B*d*A) < *dl*B*dl*A. The *dl*B*d*A or *dl*B*l*A salt is unstable. In the present work the malates of α-*p*-xenylethylamine are found to be in the order (*d*B*l*A or *l*B*d*A) < *dl*B*dl*A < *d*B*dl*A or *l*B*dl*A < (*d*B*d*A or *l*B*l*A). The *dl*B*d*A or *dl*B*l*A salt is unstable.

The α-*p*-xenylethylamine (III) used in these experiments was obtained by the reduction of the oxime (II) of *p*-phenylacetophenone (I).



I II III

This new base is one of a group of analogs of α-phenylethylamine now being studied. It was prepared in the hope that it might possess the advantages of α-phenylethylamine as a resolving agent, but would be a water-insoluble solid more convenient to handle than the parent base. It proved to be a sparingly soluble liquid which solidified only in an ice-bath. It is best purified and handled in the form of its sparingly soluble hydrochloride. Its use as a resolving agent is being further studied.

Experimental Part

***p*-Phenylacetophenone** was prepared by a method similar to that of Drake and Bronitsky.[3] Material melting at 117–119° was used to prepare the oxime. A specimen regenerated from the oxime melted at 120° (corr.).

***p*-Phenylacetophenone Oxime.**—The ketone (98 g., 0.5 mole) was dissolved in 500 cc. of 95% ethanol and hydroxylamine hydrochloride (45 g., 0.65 mole) and 100 cc. of 30% sodium hydroxide was added. The mixture was refluxed for five hours on a water-bath. A part of the oxime, together with sodium chloride, separated from the hot solution; most of the remainder separated on cooling. The solid was filtered by suction, washed with warm water to remove salt and when dry was crystallized from about ten parts of 95% ethanol. It separates as pale yellow irregular plates, m. p. 186° (corr.). The yield was 80–82%.

Anal. Calcd. for $C_{14}H_{13}ON$: N, 6.64. Found: N, 6.73.

α-*p*-Xenylethylamine.—An attempt to reduce the oxime with sodium and absolute alcohol failed because of the precipitation of the insoluble sodium salt. The reduction was readily accomplished with sodium amalgam. Twenty grams of the crude oxime was dissolved in 350 cc. of 95% ethanol on a water-bath and 700 g. of 3% sodium amalgam was added during an hour, with sufficient glacial acetic acid to keep the mixture always faintly acid. When the reaction had ceased most of the alcohol was distilled with steam and the amine was liberated with excess alkali and extracted with benzene. After drying and removing the solvent, the crude amine remained as a brown oil which set to a solid mass in a freezing mixture but liquefied on coming to room temperature. It partially decomposed on attempted distillation at 10 mm. pressure, could not be crystallized from any of the common solvents and gradually formed a carbonate in contact with air. It is most conveniently purified and kept in the form of its sparingly soluble hydrochloride, from which it is regenerated as a colorless water-insoluble liquid. The yield calculated from the hydrochloride was 80–87% in several preparations.

Hydrochloride.—The crude amine was dissolved in an excess of hot 5% hydrochloric acid and the solution filtered. The hydrochloride was recrystallized from water with decolorizing carbon. For analysis a sample was recrystallized from 95% ethanol and again from water. The salt forms glistening white needles, m. p. 221° (corr.). A sample placed on the lip induces slight numbness and irritation.

Anal. Calcd. for $C_{14}H_{16}NCl$: Cl, 15.18. Found: Cl, 15.27.

Benzoyl Derivative.—A sample of the pure hydrochloride was shaken with dilute sodium hydroxide and benzoyl chloride. The amide crystallized from 95% ethanol in small prisms, m. p. 179° (corr.).

Anal. Calcd. for $C_{21}H_{19}ON$: N, 4.65. Found: N, 4.55.

Partial Resolution of the *dl*-Base.—In preliminary experiments the base was combined with various active acids and the salts examined to determine the most suitable

[3] Drake and Bronitsky, THIS JOURNAL, **52**, 3715 (1930).

resolving agent. The salt formed with *d*-bromocamphor-π-sulfonic acid separated from water as an oil and could not be satisfactorily crystallized from any of the usual solvents. The acid *d*-tartrate crystallized readily from water or from 95% ethanol. The hydrochloride of the base from the head fractions had a small dextro rotation but the separation was too slow to be useful. The *d*-camphor-10-sulfonate separated from water or dilute ethanol partly as hair-like needles, partly as an oil which later solidified. Systematic fractionation gave results similar to those with the tartrate. The base was readily resolved through the acid *l*-malate.

The base (calcd. 42.2 g.) was recovered from 50 g. of the pure hydrochloride and combined with 28.5 g. of *l*-malic acid in 600 cc. of hot water. The solution deposited a dense crust of faintly colored crystals and smaller crops of similar crystals were obtained by concentrating the mother liquor. When this was reduced to about 100 cc. it slowly set to a semi-solid mass on cooling, but the more soluble *l*B*l*A salt could not be purified. By systematic crystallization of the less soluble fractions there was finally obtained 30.3 g. of pale yellow crystals of the nearly pure *d*B*l*A salt. Recrystallization from 95% ethanol, in which the salt is less soluble than in water, removed the color and a trace of insoluble solid. The pure salt weighed 28 g. (calcd. 35.4 g.).

d-α-*p*-**Xenylethylamine-*l*-malate** crystallizes from ethanol or water in glistening plates, m. p. 183° (corr.), and is anhydrous. Its faint dextro rotation could not be measured accurately. An aqueous solution (11.133 g.) saturated at 25° contained 0.2125 g. of salt, from which the solubility is 1.95 g. per 100 g. of water.

d-α-*p*-**Xenylethylamine.**—A sample of the pure *l*-malate was dissolved in hot water and decomposed with ammonium hydroxide. The base closely resembles the inactive variety described above. It was purified as the hydrochloride in nearly quantitative yield, calculated from the acid malate. A sample of the base was regenerated from the hydrochloride, washed several times by decantation with warm water and dried to constant weight in the absence of carbon dioxide.

Rotation. Subs. 2.2302 g. made up to 25 cc. in 95% ethanol gave α_D^{25} +2.21° in a 1-dm. tube, hence $[\alpha]_D^{25}$ +24.8°.

Hydrochloride.—This was prepared as described for the inactive form, which it closely resembles. It melts at 230° (corr.) and is slightly less soluble in water than the inactive form.

Anal. Calcd. for $C_{14}H_{16}NCl$: Cl, 15.18. Found: Cl, 15.06.

Rotation. Subs. 1.0105 g. made up to 50 cc. in water gave α_D^{25} +0.52° in a 2-dm. tube, hence $[\alpha]_D^{25}$ +12.8; M_D +30°.

In another experiment the resolution was repeated with minor variations in the details of the fractionation, but with similar results. The hydrochloride of the base finally obtained had $[\alpha]_D^{25}$ +12.7°.

Attempted Completion of the Resolution with *dl*-Malic Acid.—The mother liquors from the partial resolutions described above were combined and the base was liberated and converted to hydrochloride in the usual way. The specific rotation of the latter was −9.4°, from which it was calculated that about 76% excess of the *l*-form was present. A sample of this salt (23.4 g.) was converted to the base (calcd. 19.7 g.) and this was combined with 13.5 g. of *dl*-malic acid in 225 cc. of hot water. The solution on cooling deposited a crust of small crystals. The decanted solution on further standing deposited a loose mass of small spherules. The material obtained by concentrating the mother liquor was similar to the second crop. When the first fraction was crystallized twice from water and once from 95% ethanol there was obtained 6.6 g. of small anhydrous prisms, m. p. 170° (corr.). The salt was optically inactive. The hydrochloride of the base obtained from a sample of the salt melted at 221° and was optically inactive. The salt is therefore the *dl*B*dl*A type. A specimen prepared from the pure inactive hydro-

chloride and an equivalent amount of *dl*-ammonium acid malate had identical properties. An aqueous solution (9.666 g.) saturated at 25° contained 0.2331 g. of salt, from which the solubility is 2.42 g. per 100 g. of water.

The more soluble fractions of the malate upon further crystallization gave a small additional amount of the inactive salt but the main portion, presumably the *l*B*dl*A salt, could not be purified. The hydrochloride of the base obtained from the combined foot fractions had $[\alpha]_D^{25}$ −11.2°. For comparison the enantiomorphous *d*B*dl*A salt was prepared from the pure *d*-base and *dl*-malic acid. It crystallizes from water or ethanol in nodules or as a microcrystalline mass, m. p. 173°, and is anhydrous. An aqueous solution (10.1805 g.) saturated at 25° contained 0.2820 g. of salt, from which the solubility is 2.84 g. per 100 g. of water.

Completion of the Resolution with Partially Active Malic Acid.—A sample of the base hydrochloride (6.6 g.) containing about 68% excess of the *l*-form was dissolved in 100 cc. of water and there was added 4.3 g. of ammonium acid malate containing about 80% excess of the *d*-form. The latter had been previously obtained by a partial resolution of *dl*-malic acid with cinchonine.[4] A powdery solid separated on standing. When this was crystallized four times from water and once from 95% ethanol, it weighed 3.4 g. The salt was identified as the *l*B*d*A type. It melted at 182–183° (corr.) and closely resembled the *d*B*l*A salt described above. The material contained in the mother liquors was not further examined.

1-α-*p*-Xenylethylamine Hydrochloride.—The pure *l*B*d*A salt was decomposed with ammonium hydroxide solution and the base converted to hydrochloride. This melted at 230° (corr.) in exact agreement with the corresponding *d*-form.

Rotation. Subs. 1.2343 g. made up to 50 cc. in water gave $[\alpha]_D^{25}$ −0.60° in a 2-dm. tube, hence $[\alpha]_D^{25}$ −12.2°.

The authors are indebted to Dr. R. L. Jenkins of the Swann Corporation for a generous supply of pure diphenyl.

Summary

1. An analysis of the solubility relationships among the salts resulting from the combination of inactive and partially active acids and bases is presented, with particular reference to the problem of complete optical resolution.

2. The preparation of α-*p*-xenylethylamine and the appropriate intermediates and derivatives and the complete resolution of the base through its salts with active and inactive malic acids are described.

NASHVILLE, TENNESSEE

[4] Dakin, *J. Biol. Chem.*, **59**, 7 (1924).