4. Six of the resulting olefins have been identified by their ozonolysis products. These are 3-methyloctene-2, 5-methyldecene-4, 6-methyl undecene-5, 3-ethyloctene-2, 4-propylnonene-3 and 6-ethylundecene-5. In addition a mixture of 4-methylnonene-3 and -4 was identified.

5. Alcohols of the type, $R(CH_3)(n\text{-}C_5H_{11})COH$, were dehydrated chiefly through the R group.

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Solubility Relationships among Optically Isomeric Salts. III. The Mandelates and Alpha-Bromocamphor-Pi-Sulfonates of Alpha-Phenylethylamine and Alpha-Para-Tolylethylamine

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The following five types of optically isomeric salts represent all the possible combinations of active and inactive acid and base ions.

(*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 stabilities and relative solubilities of these types of salts determine which of them can exist in solution, and the order in which the stable salts can be separated from a mixture by fractional crystallization It has been shown in previous papers[1] that these factors are of primary importance for a method of complete optical resolution in which mixtures containing several varieties of isomeric salts may be encountered. It was shown that not more than three of the nine varieties of salts represented above can result from the evaporation of a solution, no matter what proportions of active and inactive acid and base ions may have been introduced originally. Nevertheless, it was pointed out that there are some twenty[2] different orders in which these coexistent salts may separate during fractional crystallization. At present it seems impossible to predict the stabilities and relative solubilities of the salts of a particular acid and base. Hence numerous groups of isomeric salts are being studied for the purpose of gaining a comprehensive knowledge of these factors. Five such groups of salts have already been described and classified. This paper describes a similar study of the four additional groups of salts named in the title.

The salts previously described illustrated two instances each of Cases 4[1a] and 7[1b,1d] and one of Case 8.[1c] The salts described in this paper were found to illustrate the previously unobserved cases (1) and (6), another instance of Case 8, and an instance of either Case 4 or 7, depending on the

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(1) (a) Ingersoll, THIS JOURNAL, **47**, 1168 (1925); (b) **50**, 2264 (1928); (c) Ingersoll and White, *ibid.*, **54**, 274 (1932); (d) Ingersoll and Burns, *ibid.*, **54**, 4712 (1932).

(2) Only eight orders (Cases 1–8) are possible in the mixtures resulting from the usual procedure for complete resolution. All of the cases were described and numbered in Part I.[1c]

procedure. Thus the mandelates of α-phenylethylamine were found to include four stable types of salts in the solubility order

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

When the partially active base (*dl*B + *l*B) was combined with the *dl*-acid the system *l*B*d*A < *dl*B*dl*A < *l*B*l*A (Case 4) resulted; when partially active acid (*dl*A + *d*A) was combined with the *dl*-base the system *dl*B*d*A < *dl*B*dl*A (Case 7) resulted. Both procedures permitted the purification of active acid and active base. Cases 4 and 7 have been observed previously, but the order of solubility for the four salts is new. It may be noted that the modified procedure for complete resolution would place the resulting salts in the favorable cases (10) or (15) depending on the proportions of active and inactive acid and base.

The mandelates of the closely related base, α-*p*-tolylethylamine, were then studied and the order of solubility was found to be

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

Thus, while the acid and base were reciprocally resolvable, only the inactive forms could be obtained pure from partially active specimens by either the usual or the modified procedure. This is the first example of an authentic Case 6. Perkin and Robinson[3] found a similar order of solubility in ethyl acetate for the corresponding α-bromocamphor-π-sulfonates of narcotine, but did not examine the (*d*B*dl*A or *l*B*dl*A) type of salt. Hence their salts cannot be definitely classified as Case 6.

The α-bromocamphor-π-sulfonates of α-phenylethylamine were found to exhibit the solubility order

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

Thus the *dl*-base can be resolved by the active forms of the acid,[4] but the *dl*-acid was found to form stable partially racemic salts with the active forms of the base. The order of solubility corresponded to Case 8 in the usual procedure and would have given cases (19) or (20) in the modified procedure. All of these cases are unfavorable for the purification of salts containing active ions. A similar solubility order for four salts has not previously been encountered.

It was shown in a recent paper[5] that *dl*-α-bromocamphor-π-sulfonic acid was resolved by the active forms of α-*p*-tolylethylamine. It has now been found that the *dl*-base can also be resolved, though not so readily, by the active forms of the acid. The stable salts were in the solubility order

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

This is the first observed instance of Case 1.

The above results show that even two bases as closely related as α-phenylethylamine and α-*p*-tolylethylamine form entirely different systems

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[3] Perkin and Robinson, *J. Chem. Soc.*, **99**, 788 (1911).

[4] Hunter and Kipping, *ibid.*, **83**, 1147 (1903).

[5] Ingersoll and Babcock, THIS JOURNAL, **55**, 341 (1933).

of salts with mandelic acid, and that these systems are again quite different from those formed from the same bases and α-bromocamphor-π-sulfonic acid. Hence it would not be safe to predict that the isomeric salts of structurally similar bases or acids should be similar in their stabilities and relative solubilities. It may be noted also that the order of solubility among all of the stable salts in each group has been found to be different in eight of the nine groups thus far described. In six of these the solubilities were favorable for the application of the method for complete resolution in its usual form. More groups of salts must be studied before the relative frequency of occurrence of the various cases can be estimated, though thus far Cases 4 and 7 have appeared rather often.

Experimental

α-Phenylethylamine Mandelates.—The resolution of *dl*-mandelic acid with *d*- and *l*-α-phenylethylamine has been briefly described by L. Smith.[6] The intermediate salts were not described. Since this method appears to be more satisfactory than any other given in the literature, it is briefly described here. *dl*-Mandelic acid (38 g.) was combined with 30 g. of *d*-α-phenylethylamine in 350 cc. of hot water and the solution cooled. The first fraction, when recrystallized three times from about four parts of water, was practically pure *d*B*l*A salt. By systematically working the mother liquors 29.5 g. (86%) of this salt was obtained. For analysis the salt was recrystallized from 95% ethanol.

***d*-α-Phenylethylamine-*l*-mandelate** formed elongated hexagonal plates or flattened prisms, m. p. 177° (corr.), and was anhydrous. The solubility was 4.91 g. per 100 g. of water at 30°.

Rotation. Subs. 1.7486 g. made up to 50 cc. in water gave α_D^{25} −4.23° in 2 dm.; $[\alpha]_D^{25}$ −60.4°, $[M]_D$ −165° $(10)^2$.

A sample of the salt was decomposed with a small excess of concentrated hydrochloric acid and the mandelic acid extracted with ether. After one crystallization from water with decolorizing carbon it melted at 133° and had $[\alpha]_D^{25}$ −154.8 (5% in water) in close agreement with published values. The active base was recovered by making the hydrochloric acid solution alkaline and distilling with steam. The distillate thus obtained was used directly in the next run.

***d*-α-Phenylethylamine-*d*-mandelate.**—The mother liquors from the separation of the *d*B*l*A salt became sirupy and discolored on concentration and slowly set to a mass from which the *d*B*d*A salt could not be obtained pure. This salt was therefore prepared from its pure components, but remained somewhat sticky and discolored slightly on drying. The solubility was about 18 g. per 100 g. of water at 30° and the molecular rotation was about +180° $(10)^2$. These values are slightly inaccurate but the salt is certainly the most soluble one of the group.

***dl*-α-Phenylethylamine-*d*-mandelate.**—The partially resolved mandelic acid (*dl*A + *d*A) was recovered from the mother liquors of the resolution and crystallized once from the least possible amount of water. The crystalline fraction (principally *d*-mandelic acid) was reserved and the mother liquor, which then contained about 17 g. of mandelic acid, $[\alpha]_D$ +48.5, was neutralized with *dl*-α-phenylethylamine. The resulting salts formed the system *dl*B*d*A < *dl*B*dl*A and the partially racemic salt (5.2 g.) was obtained by systematic crystallization from water. After crystallization from 95% ethanol and again from water it formed large, transparent plates, m. p. 176° (corr.), and was anhydrous. The solubility was 5.81 g. per 100 g. of water at 30°.

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(6) Smith, *J. prakt. Chem.*, [2] **84**, 743 (1911).

Rotation. Subs., 1.3904 g. made up 50 cc. in water gave α^{25}_{D} +3.53 in 2 dm.; $[\alpha]^{25}_{\mathrm{D}}$ +63.5°, $[M]_{\mathrm{D}}$ +174° (10)[2].

The mandelic acid was recovered from this salt with ether as described for the *d*B*l*A salt, washed with a little water and dried. It then melted at 131° and had $[\alpha]^{25}_{\mathrm{D}}$ +152.5° (3% in water). The recovered base was inactive.

***dl*-α-Phenylethylamine-*dl*-mandelate.**—The mother liquors from the separation of the *dl*B*d*A salt deposited a mass of small crystals consisting largely of the *dl*B*dl*A salt. A sample melted at 133° and was faintly dextrorotatory. The pure salt was therefore made from its components. It formed small plates, m. p. 138° (corr.), and was anhydrous. The solubility was 12.29 g. per 100 g. of water at 30°.

***l*-α-Phenylethylamine-*d*-mandelate.**—In a separate experiment 30 g. of the partially active amine (*dl*B 80% + *l*B 20%) was combined with 38 g. of *dl*-mandelic acid and the salts fractionated. The system *l*B*d*A < *dl*B*dl*A < *l*B*l*A resulted. After prolonged fractionation 3.2 g. of pure *l*B*d*A salt (calcd. 6.8 g.) was obtained. This had $[\alpha]^{25}_{\mathrm{D}}$ +58.9° and otherwise closely resembled the *d*B*l*A salt described above. The intermediate fractions were faintly dextrorotatory and the final mother liquors strongly levorotatory.

α-*p*-Tolylethylamine Mandelates.—The base used in the following experiments was prepared and resolved by a recently described modification[1d] of the method of Stenberg.[7]

***dl*-α-*p*-Tolylethylamine-*dl*-mandelate.**—A quantity (13.5 g.) of partially active base (*dl*B + *d*B, $[\alpha]_{\mathrm{D}}$ +19°) was combined with *dl*-mandelic acid (15.2 g.) in 100 cc. of hot water and the salts fractionally crystallized. After six recrystallizations the head fraction, which at first was levorotatory, became inactive. The salt (8.2 g.) formed transparent prisms or rhomboidal plates, m. p. 136° (corr.), and was anhydrous. It was identical with the salt prepared from equivalent amounts of the *dl*-base and *dl*-acid. The solubility was 4.89 g. per 100 g. of water at 25°.

***d*-α-*p*-Tolylethylamine-*l*-mandelate.**—The intermediate fractions from the crystallization described above contained a salt only slightly more soluble than the *dl*B*dl*A salt. From the maximum rotation observed (−41°) this appeared to be the impure *d*B*l*A salt. In a separate experiment this salt was prepared from the pure components. It formed slender prisms, m. p. 146° (corr.) and was anhydrous. The solubility was 5.18 g. per 100 g. of water at 25°.

Rotation. Subs., 1.3963 g. made up to 25 cc. in water gave $[\alpha]^{25}_{\mathrm{D}}$ −6.42° in 2 dm.; $[\alpha]^{25}_{\mathrm{D}}$ −57.5°, $[M]_{\mathrm{D}}$ −165° (10)[2].

***d*-α-*p*-Tolylethylamine-*d*-mandelate.**—The foot fractions from the crystallization described above yielded crops of dextrorotatory needles (maximum rotation +24°) but the *d*B*d*A salt could not be obtained pure from the mixture. It was therefore prepared from its components. It formed small needles, m. p. 140° (corr.), and was anhydrous. The solubility was 7.12 g. per 100 g. of water at 25°.

Rotation. Subs., 1.2345 g. made up to 25 cc. in water gave $[\alpha]^{25}_{\mathrm{D}}$ +6.45° in 2 dm.; $[\alpha]^{25}_{\mathrm{D}}$ +65.3°, $[M]_{\mathrm{D}}$ +188°(10)[2].

***l*-α-*p*-Tolylethylamine-*l*-mandelate.**—This salt was made from the pure components. It melted at 140° (corr.), had $[\alpha]^{25}_{\mathrm{D}}$ −65.0°, and was otherwise closely similar to the *d*B*d*A salt.

Instability of *dl*B*d*A or *dl*B*l*A Type.—A small-scale experiment was made to determine whether the *dl*-base could be resolved with *l*-acid. The salt formed from these was fractionated and finally gave three successive fractions having rotations −61.3, −62.3 and −64.8°, respectively. The base liberated from the head fraction was dextrorotatory, that from the foot fraction levorotatory. The resolution therefore occurred, but appeared too tedious for practical use and was not further studied.

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(7) Stenberg, *Z. physik. Chem.*, 70, 534 (1910).

α-Phenylethylamine-α-bromocamphor-π-sulfonates.—The pure *l*B*d*A salt and the impure *d*B*d*A salt of this series have been prepared by Hunter and Kipping[4] by the partial resolution of the *dl*-base with the *d*-acid. This work was repeated. The *dl*-α-bromocamphor-π-sulfonic acid required for the study of the other types of salts has been described in a recent paper.[5]

***l*-α-Phenylethylamine-*d*-α-bromocamphor-π-sulfonate.**—This salt formed large, transparent prisms, m. p. 205° (corr.), and is anhydrous. These properties and the rotation, $[\alpha]^{25}_D$ +62.6°, $[M]_D$ +270°(10)^2, agreed with the data of Hunter and Kipping. The solubility was found to be 5.40 g. per 100 g. of water at 25°.

***d*-α-Phenylethylamine-*d*-α-bromocamphor-π-sulfonate.**—This salt was not obtained completely pure during the resolution referred to above. Also an attempt to prepare it from its components gave a dense mass of needles that could not be entirely freed from the sirupy mother liquor. The salt after drying at 100° melted at 183–186° and had $[\alpha]^{25}_D$ +63.3°. It was by far the most soluble type of salt in the group.

***dl*-α-Phenylethylamine-*dl*-α-bromocamphor-π-sulfonate.**—This salt was prepared from the ammonium salt of the *dl*-acid and an acetic acid solution of the *dl*-base. It separated from water as coarse needles which melted at 155° (corr.) after drying at 110°. It was probably the monohydrate, but a sample kept for several weeks became anhydrous. The solubility of the hydrated salt was 2.05 g. per 100 g. of water at 25°.

Anal. Calcd. for $C_{18}H_{26}O_4NSBr \cdot H_2O$: H_2O, 4.00. Found: H_2O, 3.47 (air-dry salt).

***d*-α-Phenylethylamine-*dl*-α-bromocamphor-π-sulfonate.**—This salt was formed in an attempt to resolve the *dl*-acid with *d*-base. The resulting salt was crystallized from water, 95% ethanol, moist ethyl acetate, and chloroform under various conditions but was not thereby resolved. It formed massive prisms from water or ethanol and was probably the monohydrate. The solubility of this was 3.11 g. per 100 g. of water at 25°. The anhydrous salt melted at 170° (corr.).

Anal. Calcd. for monohydrate: H_2O, 4.00. Found: H_2O, 3.64.

Rotation. Subs., 1.4505 g. (anhydrous) made up to 50 cc. in water gave $[\alpha]^{25}_D$ +0.07° in 2 dm.; $[\alpha]^{25}_D$ +1.20, $[M]_D$ +5.2°(10)^2.

α-*p*-Tolylethylamine-α-bromocamphor-π-sulfonates.—The resolution of the *dl*-acid with the *l*-base and the pure *l*B*l*A and *l*B*d*A salts were described in a recent paper.[5] For convenience in comparison these salts are briefly described here.

*l*B*l*A·H_2O formed coarse prisms, $[\alpha]^{25}_D$ −62.7°, $[M]_D$ −291°(10)^2. Solubility 2.10 g. Anhydrous salt m. p. 165° (corr.).

*l*B*d*A·H_2O formed needles; after drying these had $[\alpha]^{25}_D$ +59.4°, $[M]_D$ +265°(10)^2. Solubility (hydrated salt) 2.96 g. Anhydrous salt m. p. 232° (corr.).

Resolution of *dl*-Base with *d*-Acid.—The base (67.5 g.) in dilute acetic acid was combined with ammonium *d*-α-bromocamphor-π-sulfonate (130 g.) in 1 liter of hot water and the salts fractionated. Although the salts (*d*B*d*A and *l*B*d*A) are the same *types* as those described above, they could not be separated with equal ease. Apparently the partially racemic salt, which in this case would be *dl*B*d*A, was considerably more stable than the *l*B*dl*A type from which the salts *l*B*l*A and *l*B*d*A were formed. Fractionation was conducted, as previously described, by allowing the first fraction to separate from about seven parts of water at 80 to 50° and the remaining material from 50° to room temperature. Similar fractions were then combined and recrystallized similarly. In this way an apparently homogeneous head fraction (80 g.) and a fraction consisting of the pure *l*B*d*A salt (52 g.) were obtained. The *l*B*d*A salt was practically identical in properties with the salt described above, but the head fraction melted at 162°, had $[\alpha]^{25}_D$ +63.4° and solubility 2.67 g. at 25°. The base obtained from it had $[\alpha]^{25}_D$ +28.2° instead of the value +34.6° previously obtained. When the salt was recrystallized repeatedly at 80 to 55° there was finally obtained 54 g. of pure *d*B*d*A salt. The intermediate crops were not further fractionated since this base can be much more easily resolved by means of *d*-camphoric acid.[1d]

***d*-α-*p*-Tolylethylamine-*d*-α-bromocamphor-π-sulfonate.**—This salt crystallized as monohydrate in transparent prisms; solubility 2.12 g. per 100 g. of water at 25°; m. p. (anhydrous) 165° (corr.).

Anal. Calcd. for $C_{19}H_{28}O_4NSBr \cdot H_2O$; H_2O, 3.87. Found: H_2O, 3.89.

Rotation. Subs., 0.9280 g. (hydrated) made up to 50 cc. in water gave $[\alpha]^{25}_{D}$ +2.32° in 2 dm.; $[\alpha]^{25}_{D}$ +62.5°, $[M]_D$ +290°(10)^2.

***dl*-α-*p*-Tolylethylamine-*dl*-α-bromocamphor-π-sulfonate.**—This salt was prepared from the inactive components. It first separated as an oil, which solidified. It crystallized from water in anhydrous needles, m. p. 161° (corr.). The solubility was 3.38 g. per 100 g. of water at 25°.

Summary

1. The resolution of *dl*-mandelic acid by an improvement of the method of Smith[6] has been described.
2. All of the stable isomeric mandelates and α-bromocamphor-π-sulfonates of α-phenylethylamine and α-*p*-tolylethylamine have been described and classified according to their stabilities and relative solubilities.
3. The significance of these factors for the separation of mixtures of optically isomeric salts has been discussed.

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The Acetoacetic Ester Condensation. IV. The Reaction Product of Certain Aliphatic Esters and Sodium Ethoxide

BY JOHN M. SNELL AND S. M. MCELVAIN

During the course of a study of the reaction of metallic sodium on various aliphatic esters[1] a product, which from its boiling point and method of isolation was thought at first to be ketene acetal,[2] was obtained in a small yield from the reaction of sodium and ethyl acetate in absolute ether. Further investigation of this product, however, showed it to be merely a mixture of alcohol and xylene. The latter compound had been used to powder the sodium for the reaction and, presumably, had not been completely removed from the metal by ether washing, for in subsequent experiments when the powdered sodium, after decantation of the xylene, was washed more thoroughly with ether no product was obtained at the point

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(1) Snell and McElvain, THIS JOURNAL, **53**, 750 (1931); John M. Snell, Ph.D., Thesis, University of Wisconsin, 1932.

(2) (a) Scheibler and Zeigner, *Ber.*, **55**, 801 (1922); (b) Scheibler and Marhenkel, *Ann.*, **458**, 15 (1927).