80%) was recrystallized from benzene and then acetone, m.p. 162–171°. Recrystallization from various solvents did not improve the melting point. On admixture with the dibromo sulfone prepared with N-bromosuccinimide no depression in melting point was observed.

3-Bromo-2,3-dihydrobenzo[*b*]thiophene 1,1-Dioxide.—Benzo[*b*]thiophene in glacial acetic acid was oxidized to the sulfone with 30% hydrogen peroxide[12] and then reduced to 2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide with zinc and sodium hydroxide.[13]

A mixture of 5.0 g. (0.030 mole) of 2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide, 0.58 g. of benzoyl peroxide, 5.5 g. (0.031 mole) of N-bromosuccinimide, and 300 ml. of carbon tetrachloride was refluxed for 5 hr. The carbon tetrachloride was evaporated and the residue was taken up in diethyl ether and washed with aqueous sodium thiosulfate and water. Evaporation of the ether yielded a liquid which was taken up in benzene and chromatographed over aluminum oxide using benzene as an eluting solvent. The initial fractions were collected, evaporated to dryness, taken up in methanol, and refrigerated. The resulting crystals (2 g., 27%) melted at 91–92° (lit.[14] m.p. 91–92°). Treatment of this material with triethylamine in hot benzene yielded benzo[*b*]thiophene 1,1-dioxide.

Thiochroman-4-ol 1,1-Dioxide.—3-Phenylmercaptopropanoic acid, prepared from thiophenol and 3-chloropropanoic acid,[15] was converted by means of concentrated sulfuric acid to thiochroman-4-one.[15] The cyclic keto sulfide was oxidized to thiochroman-4-one 1,1-dioxide with 30% hydrogen peroxide.[16]

To 10 g. (0.051 mole) of thiochroman-3-one 1,1-dioxide dissolved in 100 ml. of warm dioxane was slowly added 1.17 g. (0.0310 mole) of sodium borohydride dissolved in 40 ml. of 50% aqueous dioxane. The solution was kept at room temperature for 1 hr. and heated at 90° for an additional 0.5 hour. The dioxane was evaporated and the residue was treated with ice and 5% hydrochloric acid. The resulting solid (7.4 g., 73%) was recrystallized from boiling water, m.p. 95–97°.

Anal. Calcd. for $C_9H_{10}O_3S$: C, 54.53; H, 5.09. Found: C, 54.62; H, 5.23.

4-Bromothiochroman 1,1-Dioxide.—The thiochroman-4-one was converted by means of the Wolff–Kishner reduction to thiochroman which was then oxidized with 30% hydrogen peroxide to thiochroman 1,1-dioxide.[17]

Thiochroman 1,1-dioxide (2.7 g., 0.015 mole), 2.6 g. (0.015 mole) of N-bromosuccinimide, 0.5 g. of benzoyl peroxide, and 300 ml. of carbon tetrachloride were refluxed for 8 hr. The carbon tetrachloride was evaporated and the residue (3.5 g.) was treated with aqueous sodium thiosulfate and recrystallized from methanol and then benzene. The 4-bromothiochroman 1,1-dioxide (2 g., 51%) melted at 138–139°.

Anal. Calcd. for $C_9H_9BrO_2S$: C, 41.39; H, 3.47. Found: C, 41.64; H, 3.57.

A mixture of 5.0 g. (0.025 mole) of thiochroman-4-ol 1,1-dioxide and 9.5 g. (0.35 mole) of phosphorus tribromide was allowed to stand for 14 hr. at room temperature and was then heated on a steam bath for 10 min. The mixture was treated with ice–water and washed with cold, dilute sodium bicarbonate. The resulting 4-bromothiochroman 1,1-dioxide (4.2 g., 64%) was recrystallized from methanol and then benzene, m.p. 138–139°. Admixture of this material with the 4-bromo-1-thiochroman 1,1-dioxide prepared with N-bromosuccinimide gave no depression in melting point.

1,2-Dihydro-3-benzothiepine 3,3-Dioxide.—A solution of 10.0 g. (0.0364 mole) of 1-bromo-1,2,4,5-tetrahydro-3-benzothiepine 3,3-dioxide,[18] 4.00 g. (0.0396 mole) of triethylamine, and 200 ml. of benzene was heated at 80° for 0.5 hr., cooled, and filtered. Evaporation of the benzene afforded 6 g. (85%) of crystals, m.p. 135–137° [from methanol and petroleum ether (b.p. 35–37°)].

Anal. Calcd. for $C_{10}H_{10}O_2S$: C, 61.87; H, 5.18. Found: C, 62.07; H, 5.30.

The Reaction of 1,2-Dihydro-3-benzothiepine 3,3-Dioxide with N-Bromosuccinimide.—A solution of 300 ml. of carbon tetrachloride, 2.00 g. (0.0103 mole) of 1,2-dihydro-3-benzothiepine 3,3-dioxide, 1.79 g. (0.0101 mole) of N-bromosuccinimide, and 0.50 g. of benzoyl peroxide was heated at 70° for 9 hr. and refluxed for an additional 2 hr. Evaporation of the carbon tetrachloride and treatment of the resulting material with diethyl ether left a solid which after being washed with aqueous sodium thiosulfate and recrystallized from methanol proved to be starting material (1 g.). The ether-soluble red oil could not be crystallized.

In a second experiment the quantities remained the same but the reaction mixture was heated at 60–65° for 24 hr. The carbon tetrachloride was evaporated and the remaining material was extracted with diethyl ether. The undissolved solid was washed with aqueous sodium thiosulfate, water, and recrystallized from methyl alcohol. One gram of 1,2-dihydro-3-benzothiepine 3,3-dioxide was recovered. The volume of the ether was reduced and the crystalline material which separated was collected. The crystalline solid (0.3 g., 8.2%) after repeated crystallization from methanol melted at 195–199° and gave a positive test for halogen. This product was shown by mixture melting points and infrared spectra to be identical with 1,2-dibromo-4,5-dihydro-3-benzothiepine 3,3-dioxide.

Anal. Calcd. for $C_{10}H_{10}Br_2O_2S$: C, 33.92; H, 2.85. Found: C, 33.52; H, 2.75.

In a third experiment the reaction mixture was refluxed for 6 hr. The reaction mixture was worked up as described above. Starting material and some red oil were recovered.

1,2-Dibromo-4,5-dihydro-3-benzothiepine 3,3-Dioxide.—A solution of bromine (5.0 g., 0.031 mole) and 1,2-dihydro-3-benzothiepine 3,3-dioxide (6.1 g., 0.031 mole) in 50 ml. of chloroform was decolorized in the dark. The crystalline precipitate (7.7 g., 70%) which formed was collected and crystallized from methanol, m.p. 195–199°.

Anal. Calcd. for $C_{10}H_{10}Br_2O_2S$: C, 33.92; H, 2.85. Found: C, 33.61; H, 2.79.

(12) F. G. Bordwell, B. B. Lampert, and W. H. McKellin, *J. Am. Chem. Soc.*, **71**, 1702 (1949).
(13) F. Challenger and P. H. Clapham, *J. Chem. Soc.*, 1615 (1948).
(14) F. G. Bordwell and W. H. McKellin, *J. Am. Chem. Soc.*, **72**, 1985 (1950).
(15) F. Krollpfeiffer and H. Shultze, *Ber.*, **56**, 1819 (1923).
(16) F. Arndt, *ibid.*, **58**, 1612 (1925).
(17) W. E. Truce and J. P. Milionis, *J. Am. Chem. Soc.*, **74**, 974 (1952).
(18) W. E. Truce and F. J. Lotspeich, *ibid.*, **78**, 848 (1956).

The Structure of Secondary Amine–Sulfur Dioxide Salts

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Staudinger and co-workers found that amines and alcohols reacted with diazoalkanes at low temperatures in the presence of sulfur dioxide.[1] The intermediate was postulated as $Ph_2C{=}SO_2$. Reinvestigation of the amine reaction in 1952 substantiated these results.[2] However, Hesse and Majmudar[3] found that sulfite esters were formed in the alcohol reaction. In the mechanism proposed sulfur dioxide is in equilibrium with the alcohol forming a hydrogen alkyl sulfite which then reacts with the diazoalkane as a carboxylic acid.

$$R'OH + SO_2 \rightleftharpoons R'OSOH \quad (1)$$

$$R'OSOH + R_2CN_2 \longrightarrow R'OSOCHR_2 + N_2 \quad (2)$$

Investigations of the structure of amine–sulfur dioxide salts are limited; substituted anilines,[4] pyri-

(1) H. Staudinger and F. Pfenninger, *Ber.*, **49**, 1941 (1916).
(2) H. Kloosterziel, M. H. Dienema, and H. J. Backer, *Rec. trav. chim.*, **71**, 1228 (1952).
(3) G. Hesse and S. Majmudar, *Chem. Ber.*, **93**, 1129 (1960).
(4) W. E. Byrd, *Inorg. Chem.*, **1**, 762 (1962).

dines,[5] and tertiary amines[6] are among the few that have been studied. Piperidine[7] and diethylamine[8] are the only secondary amines that have been investigated.

We have found that various amine salts, including trimethylamine hydrochloride and piperidine picrate, do not react with diazoalkanes at room temperature. The piperidine–sulfur dioxide salt, $(piperidine)_2 \cdot SO_2$, does not react with diphenyldiazomethane; it does react with diazobutane, but produces neither amidosulfite nor sulfonamide. Furthermore, the 1:1 piperidine salt reacts with diphenyldiazomethane. We also observed the extremely rapid decomposition of diazo compounds by sulfur dioxide, as previously noted by Standinger and Pfenninger.[1]

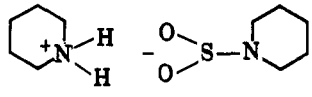
These results prompt us to suggest that diazoalkanes are attacked by sulfur dioxide and that the intermediate, $R_2C{=}SO_2$ or $R_2C(-N_2^+)-SO_2^-$, reacts with

$$R_2CN_2 + SO_2 \longrightarrow \left[\begin{matrix} R_2C{=}SO_2 \\ + N_2 \end{matrix}\right] \text{ or}$$

$$\left[\begin{matrix} R_2C-SO_2^- \\ | \\ N_2^+ \end{matrix}\right] \xrightarrow{R_2'NH} R_2CH-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-NR_2' + N_2 \quad (3)$$

amines more rapidly than it decomposes. The attack of sulfur dioxide must be slower than the equilibrium between alcohols and SO_2 (eq. 1). If this were not the case, sulfonates rather than sulfites would be products of the alcohol–sulfur dioxide–diazoalkane reaction.

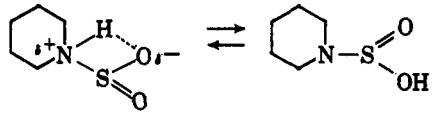
We propose structure I for $(piperidine)_2 \cdot SO_2$. Since neither sodium sulfite nor piperidine hydrochloride reacts with diphenyldiazomethane, neither ion would be expected to react with it. The n.m.r. spectrum is in agreement with this formulation. The amino



I

protons show a singlet at τ 1.44 in methylene chloride compared with the broad singlet at τ *ca.* 2.0 for the amino protons of piperidine picrate in acetonitrile.

The 1:1 salt must be represented as II, in analogy with tertiary amine–sulfur dioxide salts.[6] The equi-



II III

librium, II $\rightleftarrows$ III, must either be extremely slow or nonexistent as amidosulfites would be formed in the reaction of III with diazoalkanes (compare eq. 2). Sodium hydrogen sulfite reacts slowly with diphenyldiazomethane; owing to the negative charge on the ion, it might be expected to react even more slowly than III.

(5) H. A. Hoffman and C. A. VanderWerf, *J. Am. Chem. Soc.*, **70**, 262 (1948).

(6) J. A. Moede and C. Curran, *ibid.*, **71**, 852 (1949).

(7) K. Sharada and A. R. Vasudeva Murthy, *Current Sci.* (India), **29**, 130 (1960); *Chem. Abstr.*, **54**, 24715*b* (1960).

(8) J. Makranczy and B. Mohai, *Veszpremi Vegyip. Egyet. Kozlemen.*, **6**, 183 (1962); *Chem. Abstr.*, **58**, 6252*c* (1963).

Experimental[9,10]

Diazoalkanes.—Diphenyldiazomethane,[11] m.p. 29–31° (lit.[11] m.p. 29–32°), and diazobutane[12] were prepared according to previously published procedures. The latter was used in the ether solution in which it was prepared.

Piperidine–Sulfur Dioxide Salts.—The salt, $(piperidine)_2 \cdot SO_2$, was prepared by bubbling SO_2, generated by the dropwise addition of 6 *M* HCl onto $NaHSO_3$, through piperidine (0.10 mole, 10 ml.) in dry ether, 50% v./v. The white solid which separated from the solution melted at 70–80°. After being dried for 24 hr. in a desiccator, 0.0106 g. was added to a standard iodine solution; the sample required 19.84 ml. and the blank 20.70 ml. of 0.0493 *N* $Na_2S_2O_3$. The salt reduced 0.0424 mequiv. of I_2: calcd. for the 2:1 salt, 0.0452 mequiv.; for the 1:1 salt, 0.0710 mequiv. The n.m.r. spectrum taken in methylene chloride revealed a singlet at τ 1.44, a multiplet at 6.84, and a broad unresolved peak at 8.26.

A second salt was prepared by bubbling SO_2 through pure piperidine. During addition the solution became hot and a reddish brown solid resulted, probably the 1:1 adduct by analogy with diethylamine.[8] The salt was not particularly stable, and, in the presence of piperidine and ether, the 2:1 salt was formed.

1-Butanesulfonyl Piperidide.—To 5.68 g. of piperidine (0.060 mole) in 25 ml. of dry benzene was added dropwise with stirring 5.22 g. of 1-butanesulfonyl chloride (0.030 mole) in 25 ml. of benzene. After addition was complete, the mixture was cooled for 5 min., and 2.80 g. of piperidine hydrochloride (77%) was removed by filtration. The solvent was evaporated from the remaining solution and 4.02 g. (65%) of a solid was obtained. After recrystallization from aqueous ethanol, white crystals, m.p. 42–43°, were obtained; these did not decolorize iodine: n.m.r. in acetone, τ 6.7 (4 protons), 7.1 (2 protons), 8.4 (10 protons), and 9.0 τ (3 protons). Although the protons at τ 7.1 were a triplet, the other peaks were complex multiplets.

Anal.[13] Calcd. for $C_9H_{19}NO_2S$: C, 52.65; H, 9.33; N, 6.82; S, 15.61. Found: C, 52.63; H, 9.17; N, 6.71; S, 15.45.

Diazoalkanes, Piperidine, and SO_2.—Diazobutane (*ca.* 0.1 mole) in 100 ml. of ether was decanted into 30 ml. of piperidine (0.30 mole). Sulfur dioxide was bubbled slowly through the solution which was cooled in an ice bath; decolorization was complete after 0.5 hr. The small amount of piperidine salt that was formed was removed from the solution, and then ether and excess piperidine were evaporated. Attempted distillation resulted in recovery of 0.8 g. of a white solid, b.p. 50° (3.5 mm.), tentatively identified as a piperidine–sulfur dioxide salt from its n.m.r. spectrum. Nothing else distilled below 155° (1.5 mm.) and the solution began to darken. *n*-Butyl piperididosulfite, prepared by a standard procedure,[14,15] is a colorless liquid, b.p. 106–107° (3 mm.), $n^{27}D$ 1.4708.

Anal.[16] Calcd. for $C_9H_{19}NO_2S$: C, 52.65; H, 9.33; N, 6.82; S, 15.61. Found: C, 52.62; H, 9.12; N, 6.83; S, 15.51.

The residue. 12 g. (*ca.* 60%), was recrystallized from dilute ethanol after treatment with Norit, m.p. 41–42°, m.m.p. 41–42°.

With diphenyldiazomethane, the experiment of Kloosterziel and co-workers[2] was repeated. The white solid, m.p. 165–167° (lit.[2] m.p. 167–168°), did not decolorize iodine.

Diazoalkanes and Amine Salts.—No decolorization of diphenyldiazomethane occurred over 24 hr. in the presence of excess trimethylamine hydrochloride, piperidine hydrochloride, or piperidine picrate. Solid $(piperidine)_2 \cdot SO_2$ (*ca.* 0.2 g.) was added to 5 ml. of methylene chloride containing approximately 0.01 g. of diphenyldiazomethane; no decolorization occurred in 24 hr. Diphenyldiazomethane in ethanol solution was decolorized slowly after several hours by excess sodium hydrogen sulfite. No decolorization of sodium sulfite occurred during more than 10 days.

Trimethylamine hydrochloride did not decolorize diazobutane. When diazobutane (*ca.* 0.05 mole) in 50 ml. of ether was added

(9) The n.m.r. spectra were taken on a Varian A-60 spectrometer with tetramethylsilane present as internal standard.

(10) Melting and boiling points are uncorrected.

(11) J. B. Miller, *J. Org. Chem.*, **24**, 560 (1959).

(12) F. Arndt, *Org. Syn.*, **15**, 48 (1943); "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 165.

(13) Galbraith Laboratories, Inc., Knoxville, Tenn.

(14) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 379 (1952).

(15) G. Zinner, *Chem. Ber.*, **91**, 966 (1958).

(16) Triangle Chemical Laboratories, Chapel Hill, N. C.

to solid (piperidine)$_2 \cdot SO_2$, no reaction ensued. However, on addition of methylene chloride, gas evolution commenced and decomposition was complete after about 30 min. The products, though as yet not wholly identified, contained neither 1-butanesulfonyl piperidide nor *n*-butyl piperidosulfite.

The reddish brown piperidine salt gave a yellow solution in methylene chloride. When *ca.* 0.5 g. of the salt was added to *ca.* 0.01 *M* diphenyldiazomethane in methylene chloride, decomposition of the diazo compound ensued. Although decolorization was complete in about 30 min., no gas evolution was noted.

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Dehydroabietylamine. A New Resolving Agent[1]

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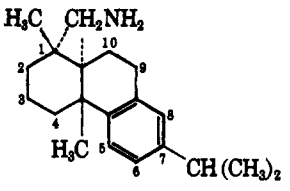
Dehydroabietylamine[2] (I) has been isolated in high yield from commercial Amine D.[3] It is an optically active base, inexpensive, relatively nontoxic, and forms



I

highly crystalline salts with many organic acids. These desirable characteristics led us to try dehydroabietylamine as a resolving agent for carboxylic acids. Results were notably favorable. For example, dehydroabietylamine was used advantageously to separate the (+)-enantiomorph[4] of racemic α-phenoxypropionic acid and the D-(−)-enantiomorph of racemic α-benzyloxycarbonylaminophenylacetic acid, when both were required in quantity for the synthesis of the corresponding penicillins.[5-7]

Although racemic α-phenoxypropionic acid has been resolved previously for Fourneau and Sandulesco[8] using yohimbine, we found that dehydroabietylamine afforded higher yields of resolved acid, required smaller volumes of solvents, and obviated the cumbersome task of recovering the resolving agent. The resolution of racemic α-benzyloxycarbonylaminophenylacetic acid gave the desired D-(−)-enantiomorph[6,7] previously prepared by N-acylation of D-(−)-phenylglycine with benzyl chloroformate. The ease in the separation of these enantiomorphs suggests the high potential of dehydroabietylamine for effecting the resolution of other racemic acids and for obtaining the optical isomers of amino acids through their N-benzyloxycarbonyl or N-formyl derivatives.

Experimental[9]

Dehydroabietylamine Acetate.—To a solution of 2.85 kg. of Amine D dissolved in 4.74 l. of toluene was added a solution of 654 g. (10.8 moles) of glacial acetic acid in 1.56 l. of toluene. The solution was stored at 10° for 2 hr. The crystalline salt was collected, washed with cold toluene, and recrystallized from 4.23 l. of boiling toluene. The colorless crystals were collected, washed several times with *n*-pentane, and air dried to obtain 1.365 kg. (78.5%) with m.p. 141–143.5°, $[\alpha]^{25}D$ +30.2° (*c* 5, methanol).

Anal. Calcd. for $C_{22}H_{35}NO_2$: C, 76.48; H, 10.21. Found: C, 76.70; H, 10.25.

Dehydroabietylamine (I).—A mixture of 540 g. (1.57 moles) of dehydroabietylamine acetate was stirred with 2 l. of water on the steam bath until the salt had dissolved. A total of 700 ml. of 10% sodium hydroxide was added, the mixture was chilled, and the amine was extracted with 2.5 l. of ether. The ether solution was washed with water and dried over anhydrous potassium carbonate. After evaporation of the ether, 440 g. (98%) of a pale yellow viscous oil remained which had a refractive index of $n^{33}D$ 1.5480 and crystallized after storage at room temperature for several days: m.p. 44–45°; lit.[10] $n^{30}D$ 1.5498, m.p. 41°.

Dehydroabietylammonium (+)-α-Phenoxypropionate.—To a solution of 914 g. (3.2 moles) of dehydroabietylamine dissolved in 7 l. of methanol was added 537 g. (3.2 moles) of racemic α-phenoxypropionic acid. The stirred solution was slowly diluted with 5.5 l. of water and stored at 10° for 5 hr. The crystals were collected and air dried to obtain 850 g., m.p. 168–170°. Recrystallization from a mixture of 8 l. of methanol and 3.5 l. of water during storage at 10° for 7 hr. gave 650 g. of salt, m.p. 173–177°. A final recrystallization was made from a mixture of 6 l. of methanol and 1.5 l. of water to yield 287 g. of colorless crystals, m.p. 188–189.5°, $[\alpha]^{23}D$ +27.7° (*c* 1, alcohol). Further recrystallization did not raise the melting point or change the rotation.

Anal. Calcd. for $C_{29}H_{41}NO_3$: C, 77.12; H, 9.15. Found: C, 77.03; H, 9.36.

(+)-α-Phenoxypropionic Acid.—To 1 l. of a saturated solution of sodium carbonate were added 287 g. (0.635 mole) of finely ground dehydroabietylammonium (+)-α-phenoxypropionate and 1 l. of ether. The mixture was shaken vigorously until all of the solid had dissolved. The ether layer was separated and the aqueous solution was washed twice with ether and acidified to pH 2 with concentrated hydrochloric acid. The mixture was cooled to 10° for 2 hr., and the white crystals were collected to obtain 76 g. of acid with m.p. 88–89°, $[\alpha]^{23}D$ +40.0° (*c* 1, absolute alcohol), lit.[8] $[\alpha]^{20}D$ +39.3°. A second crop of 22 g. was obtained from the mother liquor on further storage at 10° which had m.p. 88–89°, $[\alpha]^{23}D$ +39.1° (*c* 1, absolute alcohol).

Dehydroabietylammonium D-(−)-α-Benzyloxycarbonylaminophenylacetate.—To a solution of 163 g. (0.57 mole) of racemic α-benzyloxycarbonylaminophenylacetic acid dissolved in 3.7 l. of methanol was added 163 g. (0.57 mole) of dehydroabietylamine. The solution was diluted with 550 ml. of water and stored at 10° for 3 hr. The salt was collected and dried to obtain 203 g., m.p. 170–190°. Recrystallization from a mixture of 6 l. of methanol and 1.5 l. of water gave 103 g. of dry salt. A final recrystallization from a mixture of 4 l. of methanol and 700 ml. of water

(1) After the completion of this manuscript our attention was drawn to the recent report of B. Sjöberg and S. Sjöberg [*Arkiv Kemi*, **22**, 447 (1964)], wherein the use of this resolving base is described.

(2) L. C. Cheney, U. S. Patent 2,787,637 (1957); *Chem. Abstr.*, **51**, 13926*a* (1957).

(3) Amine D, formerly Rosin Amine D, is a trade-name of the Hercules Powder Co. It is composed of an average of 50% dehydroabietylamine (1,2,3,4,4a,9,10,10a-octahydro-7-isopropyl-1,4a-dimethyl-1-phenanthrenemethylamine), 20% dihydroabietylamine (the docecahydro analog of dehydroabietylamine with a double bond in either the 8a–9 or 7–8 position), 20% tetrahydroabietylamine (tetradecahydro analog of dehydroabietylamine), and 10% inert rosin [J. N. Borglin, *Soap Sanit. Chemicals*, **23**, 147 (1947); *Chem. Abstr.*, **43**, 9397*a* (1949)].

(4) A. Fredga and M. Matell [*Arkiv Kemi*, **4**, 325 (1952)] have presented inconclusive evidence that (+)-α-phenoxypropionic acid is related to D-(−)-lactic acid.

(5) Y. G. Perron, *et al.*, *J. Am. Chem. Soc.*, **82**, 3934 (1960).

(6) F. P. Doyle, *et al.*, *J. Chem. Soc.*, 1440 (1962).

(7) F. P. Doyle, J. H. C. Nayler, and H. Smith, U. S. Patent 2,985,641 (1961); *Chem. Abstr.*, **55**, 21472*e* (1961).

(8) E. Fourneau and G. Sandulesco, *Bull. soc. chim. France*, [4] **31**, 988 (1922).

(9) Melting points are uncorrected and were obtained on a Fisher-Johns apparatus. Optical rotations were measured on a Rudolph polarimeter. The authors wish to thank R. M. Downing for the microanalyses.

(10) A. Zvejnieks, *Svensk Kem. Tidskr.*, **66**, 316 (1954); *Chem. Abstr.*, **49**, 15809*e* (1955).