Methods and Results.—Dehydrogenation activity was determined by passing normal butane (Pure Grade) through a portion of catalyst supported vertically in an electrically heated tube furnace, under the following conditions: hydrocarbon space velocity of 500 volumes (STP) per volume of catalyst per hour, pressure of one atmosphere (absolute), average internal catalyst temperature of 1100° F., and on-stream period of sixty minutes. The catalyst was flushed for two minutes before and after each dehydrogenation period with nitrogen, and was revivified for fifty-six minutes with air at a space velocity of 1000 volumes per volume of catalyst per hour. The single-pass conversion to normal butenes plus butadiene during each of 5 to 8 cycles was determined with a hydrogen-sensitive, thermal-conductivity gas analyzer and these values were averaged. The gas analyzer was calibrated by data from low-temperature fractional analyses of total dehydrogenation effluent.

Surface area of each catalyst was determined after the dehydrogenation test by the low-temperature nitrogen-adsorption method developed by Brunauer and Emmett,[2] in an apparatus similar to that described by Krieger.[3] The area was calculated by a two-point substitution in the BET equation. The data obtained are in Fig. 1; they show that there is a definite correlation between surface area and dehydrogenation activity for the chromia–alumina catalyst.

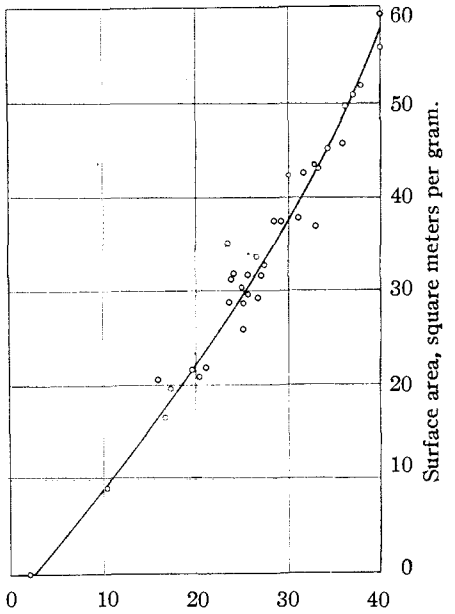

Fig. 1.—Correlation of surface area and dehydrogenation activity for chromia–alumina catalyst A.

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(2) S. Brunauer and P. H. Emmett, THIS JOURNAL, **57**, 1754 (1935); *et seq.*

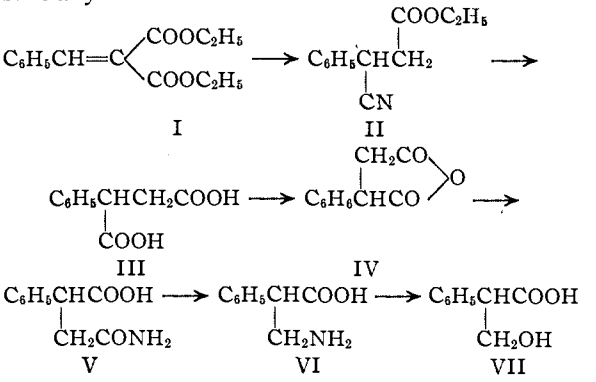
(3) K. A. Krieger, *Ind. Eng. Chem., Anal. Ed.*, **16**, 398 (1944).

A New Synthesis of *dl*-Tropic Acid

BY M. R. NATARAJAN AND S. SWAMINATHAN[1]

Tropic acid (VII) is formed through hydrolysis of atropine and related alkaloids. The earliest synthesis of this acid was by Ladenburg and Rügheimer[2] and this preparation was later improved by McKenzie and Wood.[3] In addition, syntheses have been reported by Müller[4] and by Chambon.[5]

The scheme of synthesis herein reported is essentially as follows:



β-Amino-α-phenylpropionic acid (VI) was obtained by McKenzie and Strathern[6] by interaction of atropic acid and hydroxylamine in alcoholic solution, and, more recently, by Craig and Henze[7] through reduction of β-amino-α-hydroxy-α-phenylpropionic acid. The conversion of VI to tropic acid was achieved by adopting the method outlined by McKenzie and Strathern.[6]

Experimental

Phenylsuccinic acid was prepared from benzalmalonic ester,[8] and the anhydride obtained therefrom either by distilling under reduced pressure,[8] or by treating with three equivalents of acetyl chloride at 110° for three hours and subsequently distilling after removal of acetic acid, acetic anhydride and acetyl chloride at reduced pressure. The pure product distilled at 191–192° (12 mm.). The ammonium salt of α-phenylsuccinamic acid was obtained by interaction of dry ammonia and an ether solution of phenylsuccinic anhydride; the amido acid was precipitated in almost quantitative yield by addition of hydrochloric acid;[9] it melted at 145–146°.

β-Amino-α-phenylpropionic Acid.—To a cooled solution of 11.6 g. of potassium hydroxide in 105 cc. of water, 4 g. of bromine was added gradually with thorough stirring, the temperature being maintained at 0–5°. Four and one-half grams of α-phenylsuccinamic acid was added portionwise, and the mixture was warmed at 70° for four hours. After neutralization with hydrochloric acid, the solution was evaporated, the residue shaken with 60 cc. of water, and separated by filtration. The undissolved portion was

(1) Lady Tata Research Scholar, Indian Institute of Science.

(2) Ladenburg and Rügheimer, *Ber.*, **13**, 2041 (1880); **22**, 2590 (1889).

(3) McKenzie and Wood, *J. Chem. Soc.*, **115**, 830 (1919).

(4) Müller, *Ber.*, **51**, 252 (1918); Wislicenus and Bilhuber, *ibid.*, **51**, 1237 (1918).

(5) Chambon, *Compt. rend.*, **186**, 1630 (1928).

(6) McKenzie and Strathern, *J. Chem. Soc.*, **127**, 85 (1925).

(7) Craig and Henze, *J. Org. Chem.*, **10**, 19 (1945).

(8) Bredt and Kallen, *Ann.*, **293**, 344–349 (1896); Wegscheider and Hecht, *Monatsh.*, **24**, 418 (1903).

(9) Hahn and Walter, *Ann.*, **354**, 132 (1907).

crystallized from hot water with aid of norite; m. p. 222–223°; yield 2.5 g.

Anal. Calcd. for $C_9H_{11}NO_2$: N, 8.48. Found: N, 8.35.

Tropic Acid.—The procedure adopted for conversion of VI to tropic acid was essentially that described by McKenzie and Strathern.[6] A concentrated aqueous solution of potassium nitrite (3 g.) was added gradually to 3 g. of β-amino-α-phenylpropionic acid dissolved in 55 cc. of normal hydrochloric acid. The reaction mixture was warmed on the water-bath for fifteen minutes; the oil which settled was separated. The aqueous solution was extracted with ether; the solvent was removed, and the residue was twice recrystallized from benzene; m. p. 116–117°; yield 0.2 g.

Anal. Calcd. for $C_9H_{10}O$: C, 65.06; H, 6.02. Found: C, 65.9; H, 6.1.

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Derivatives of Taurine and β-Alanine[1]

BY M. M. RAPPORT, J. F. MEAD, J. T. MAYNARD, A. E. SENEAR AND J. B. KOEPFLI

During an investigation of derivatives of pantoyltaurine as potential antimalarials,[2] a number of somewhat related compounds, derivatives of either taurine or β-alanine, were prepared and tested for antimalarial activity.[3]

Experimental[4]

Sodium γ-Hydroxybutyryltaurate[5] (I).—The sodium salt of taurine was heated with an excess of γ-butyrolactone for five hours at 115°. The product was extracted with boiling ethanol and treated with Norite and the solvent removed *in vacuo*. The residue after washing with acetone to remove unreacted lactone was crystallized from ethanol from which it separated as deliquescent plates, m. p. 204–210°.

Anal. Calcd. for $C_6H_{12}O_5NSNa$: N, 6.0; Na, 9.8. Found: N, 5.8; Na, 9.8.

γ-Hydroxybutyryltaurinamide (II).—The taurinamide obtained from 25 g. of taurinamide hydrochloride[2] was heated with 14 g. of γ-butyrolactone for twelve hours at 120°. The resulting oil crystallized after standing at 4° under acetone–ether solution and was recrystallized from absolute ethanol to give colorless rosets of prisms, m. p. 66–69°.

Anal. Calcd. for $C_6H_{14}O_4N_2S$: C, 34.3; H, 6.7. Found: C, 34.2; H, 6.7.

Analytical results, etc., when not given for a compound in the running text, are recorded in Table I.

p-Nitrobenzoyltaurinamide (III).—To 10 g. of taurinamide hydrochloride dissolved in 150 ml. of water containing 78 g. of sodium carbonate was added 11 g. of *p*-nitrobenzoyl chloride. The mixture was shaken and warmed on the steam-bath for two hours and then filtered. The product was washed with dilute sodium carbonate solution and water and dried *in vacuo* to give 10.5 g.

p-Aminobenzoyltaurinamide (IV).—Twelve grams of III was reduced with hydrogen at 2000 pounds pressure in dioxane over Raney nickel catalyst at 80°. After removal of the catalyst and evaporation of the solvent 8 g. of a light colored oil was obtained which crystallized on standing.

p-Nitrobenzenesulfonyltaurinamide (V).—Treatment of 4.1 g. of taurinamide hydrochloride with 6.8 g. of *p*-nitrobenzenesulfonyl chloride in a similar manner to that described for the preparation of III, yielded 8 g. of V.

p-Aminobenzenesulfonyltaurinamide (VI).—Eleven and one-half grams of V, reduced under the conditions employed to obtain IV, yielded 8.6 g. of VI.

O-Acetylmandeloyltaurinamide (VII).—To a solution of 10 g. of taurinamide hydrochloride and 13 g. of sodium bicarbonate in 100 ml. of water there was added 14.5 g. of acetylmandeloyl chloride.[6] The mixture was stirred for one hour after the evolution of gas had ceased and the precipitate filtered off, washed with sodium bicarbonate solution and water and dried *in vacuo*. The 18 g. of material thus obtained was pure enough for the next reaction, but was crystallized for analysis.

Mandeloyltaurinamide (VIII).—To 10.7 g. of VII dissolved in the minimum amount of methanol at 4° there was added 10 ml. of 2.2 *N* barium methylate[7] and the solution allowed to stand at 4° for two days. The solution was then treated with the required amount of 2 *N* sulfuric acid and centrifuged to remove the barium sulfate. The resulting solution was taken to dryness, dissolved in a little ethanol and poured into mixture of equal parts of ether and petroleum ether (30–60°). A crystalline solid was thus obtained which was recrystallized in the same way to give 8 g. of product.

N-Carbobenzoxy-β-amino-β-phenylpropionyl Chloride (IX).—To 5 g. of N-carbobenzoxy-β-phenyl-β-alanine[8] suspended in 50 ml. of dry ether there was added 3.9 g. of phosphorus pentachloride and the mixture shaken with cooling for twenty minutes. The reactants went into solution and the acid chloride began to crystallize out in long colorless needles. Two hundred milliliters of petroleum ether (30–60°) was added to complete the separation, and the mixture allowed to stand at 4° for one-half hour. The product was filtered off and washed with petroleum ether to give 4.9 g. of colorless needles, m. p. 89–91°.

Anal. Calcd. for $C_{17}H_{16}O_3NCl$: Cl, 11.2. Found: Cl, 11.8.

N-Carbobenzoxy-β-amino-β-phenylpropionyltaurinamide (X).—To 22.9 g. of IX there was added a solution of 13 g. of taurinamide hydrochloride and 18 g. of sodium bicarbonate dissolved in one liter of water. The mixture was stirred for one hour and then allowed to stand at 4° overnight. The precipitate was collected and washed with water to give 25.6 g. of product.

β-Amino-β-phenylpropionyltaurinamide (XI).—A suspension of 12 g. of X in anhydrous methanol was reduced over palladium black catalyst with hydrogen at 2500 pounds pressure for twenty-three hours. Filtration and evaporation yielded 4.5 g. of a colorless oil which crystallized on scratching.

N-Carbobenzoxy-β-amino-β-(4-nitrophenyl)-propionic Acid (XII).—A solution of β-amino-β-(4-nitrophenyl)-propionic acid[9] (14 g.) and sodium hydroxide (2.7 g.) in 400 ml. of water was chilled in an ice–salt-bath and 17.5 ml. of carbobenzoxy chloride (sp. gr. 1.16) added with continuous shaking over a period of one hour. During the reaction the solution was kept alkaline to phenol-

(1) This work was done under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and the California Institute of Technology.

(2) Mead, Rapport, Senear and Koepfli, *J. Biol. Chem.*, **163**, 465 (1946).

(3) The survey number, designated SN, identifies a drug in the records of the Survey of Antimalarial Drugs. The antimalarial activity is tabulated in a monograph entitled "A Survey of Antimalarial Drugs, 1941–1945," F. Y. Wiselogle, Editor, J. W. Edwards, Ann Arbor, Michigan, 1946.

(4) All melting points have been corrected for exposed stem. The microanalyses reported have been carried out by Dr. Gertrud Oppenheimer and Mr. G. A. Swinehart.

(5) Compare Winterbottom, Clapp, Miller, English and Roblin, THIS JOURNAL, **69**, 1393 (1947).

(6) Thayer, "Organic Syntheses," Coll. Vol. I, p. 12,

(7) Weltzien and Singer, *Ann.*, **443**, 104 (1925).

(8) Dyer, THIS JOURNAL, **63**, 265 (1941).

(9) Posner, *Ann.*, **389**, 40 (1912).