the case of 3-aminopyridine was any ethoxy compound formed (12.3% yield). In the case of *p*-nitrobenzenediazonium fluoborate the presence of zinc reduced the yield of nitrobenzene to 58% and increased the amount of tarry residue; the yield without zinc was 80%.

The reaction was carried out by adding the pure diazonium fluoborate to a flask containing absolute ethanol and powdered zinc; the addition of the salt was carried out slowly enough so that the solution is refluxing gently. The solution was then filtered from the zinc, the alcohol distilled off, and the alcoholic distillate diluted with several times its volume of water or brine; the hydrocarbon separating out was then removed in a separatory funnel. The residue from the alcoholic distillate was made slightly alkaline and subjected to steam distillation; the organic material from the two distillations was purified in the usual manner.

Experimental

Preparation of Diazonium Fluoborates.—The diazonium fluoborates were prepared in the usual manner[6]; the yields are reported in Table I. It was found that better results were obtained with diazonium fluoborates prepared by diazotization in fluoboric acid than with those prepared by diazotization in hydrochloric acid followed by addition of sodium fluoborate. The yields of diazonium fluoborate were increased some if the solutions were further cooled by the addition of Dry Ice directly to the diazotized solution before filtration. All the diazonium fluoborates were washed as indicated in reference 6 to remove impurities, and were dried by spreading thinly on absorbent paper suspended on a wire rack. The preparation of the quinolinediazonium fluoborates[8] and 3-pyridinediazonium fluoborates[9] required slightly different conditions as noted in the references given; 3-pyridinediazonium fluoborate decomposes at room temperature unless kept moist with petroleum ether. Of the other diazonium fluoborates reported, *o*-toluenediazonium fluoborate was fairly unstable, decomposing in a desiccator in 24 hours; *m*-toluenediazonium fluoborate decomposed within 48 hours.

Decomposition of Diazonium Fluoborates.—The diazonium salts were all decomposed in the same manner, as follows: One-tenth of a mole of the diazonium fluoborate was added slowly to 300 ml. of absolute ethanol and 15 g. of zinc dust contained in a one-necked 500-ml. round-bottomed flask fitted with an addition tube, to the top of which was attached a reflux condenser. The addition of the salt was slow enough to prevent violent reaction, but rapid enough to maintain a gentle reflux of the solution; a deep red color appeared as the salt was added. When all the salt had been added, the solution was refluxed gently for an hour, during which time the solution turned light straw in color. The solution was cooled, filtered from the zinc residue into a distillation flask, and the ethanol distilled off through an efficient fractionating column. The ethanol distillate was treated with six times its volume of saturated salt solution (except in experiments with the chloroanilines, when water was used); any organic product separating was removed in a separatory funnel. The residue from the distillation was made slightly alkaline and steam distilled. Any organic matter from the steam distillation was combined with that from the alcoholic distillation and purified by distillation or recrystallization. In every case, the residue in the distillation flask was then acidified and further distilled with steam; in no case did any organic matter distil from the acid solution. (The residue from the steam distillation was then extracted with ether to extract any organic material remaining; none was obtained in any case.)

In the case of benzenediazonium fluoborate, distillation of the organic fraction from the alcohol distillation gave in addition to benzene 9.1 g. of liquid, b.p. 102°, n^{28}D 1.3780; this proved to be diethyl acetal. From the basic steam distillation, 0.4 g. of biphenyl (m.p. 70°) was the only product isolated.

Variations in the decomposition procedure were tried, but found to be unsatisfactory. The addition of zinc dust to a suspension of the diazonium salt in alcohol produced greater amounts of tarry material and very low yields. Addition of an intimate mixture of zinc dust and the diazonium fluoborate to ethanol resulted in a more vigorous reaction; in the case of benzenediazonium fluoborate some fluorobenzene was isolated from the reaction mixture using this procedure.

The reaction products were in all cases known and were identified by melting point or boiling point and refractive index.

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[8] A. Roe and F. H. Hawkins, THIS JOURNAL, **71**, 1785 (1949).

[9] A. Roe and F. H. Hawkins, *ibid.*, **69**, 2443 (1947).

Some α-Arylsulfonamido Acids and Amides

BY RICHARD H. WILEY, NEWTON R. SMITH AND JOSEPH P. JOHANSEN

RECEIVED JUNE 9, 1952

This note will serve to record data on the preparation and properties of some previously undescribed benzene-, toluene- and *p*-ethylbenzenesulfonyl derivatives of alanine, sarcosine, α-aminoisobutyric acid and leucine. Techniques previously used[1,2] were adapted to the preparation of the arylsulfonyl chloride; the acyl chloride from the arylsulfonamido acid and thionyl chloride; and the sulfonamido acid amides from the acid chlorides and ammonia. The reactions for the preparation of the leucine derivatives from *p*-ethylbenzenesulfonyl chloride are given in detail as typical. Properties

TABLE I

α-ARYLSULFONAMIDO ACIDS AND AMIDES

Compound	Yield, %	M.p., (°C., cor.)	Analyses[a] Calcd.	Found
α-Benzenesulfonamido-				
isocaproic acid	59	116–117[b]	272.3 NE	272.1 NE
isobutyric acid	67.3	142–143[c]	243.3 NE	241.4 NE
isocapramide	61.2	208–209	10.4 N	10.4 N
isobutyramide	55.4	195–196	11.6 N	11.6 N
propionamide	..	179	12.3 N	12.3 N
α-(N-Methylbenzenesulfonamido-)				
acetamide	..	174	12.3 N	12.3 N
α-Toluenesulfonamido-				
isocaproic acid	55	118–119[d]	285.3 NE	286.5 NE
isobutyric acid	51.4	143–144[c]	257.3 NE	256.3 NE
isocapramide	54.7	233–234	9.5 N	9.7 N
isobutyramide	69.5	221–222	10.9 N	10.6 N
α-(*p*-Ethylbenzenesulfonamido)-				
isocaproic acid	48	117–118	299.4 NE 4.7 N	299.9 NE 4.8 N
isobutyric acid	60.5	131–132	271.3 NE 5.16 N	269.3 NE 5.03 N
isocapramide	65.5	202–203	9.1 N	9.1 N
isobutyramide	66	198–199	10.4 N	10.2 N
acetic acid	..	128–129	5.45 N	5.53 N
acetamide	..	190–191	10.9 N	10.9 N

[a] NE, neutral equivalent; N, nitrogen (Micro Tech Laboratory, Skokie, Illinois). [b] E. Fischer, *Ber.*, **33**, 2380 (1900). Reported m. p. 146°. We have no explanation for this discrepancy. [c] F. Fichter and M. Schmid, *Helv. Chim. Acta.*, **3**, 711 (1920). Reported m.ps. 144° (benzene); 147° (toluene). [d] E. Fischer and N. Lipschitz, *Ber.*, **48**, 365 (1915). Reported m. p. 124°.

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[1] R. H. Wiley and H. L. Davis, THIS JOURNAL, **73**, 494 (1951).

[2] R. H. Wiley, H. L. Davis, D. E. Gensheimer and N. R. Smith, *ibid.*, **74**, 936 (1952).

of the compounds prepared are stated in Table I. Previously reported compounds are noted therein.

Experimental

α-(*p*-Ethylbenzenesulfonamido)-isocaproic Acid.—A solution of 7.72 g. (0.038 mole) of *p*-ethylbenzenesulfonyl chloride, prepared as described elsewhere,[3] in 25 ml. of acetone was added slowly from a separatory funnel to a mechanically stirred solution of 5.0 g. (0.038 mole) of L-leucine in 55 ml. of 2 *N* sodium hydroxide and 25 ml. of acetone. During the addition the mixture was cooled in an ice-bath. Water was added to dissolve the precipitated sodium chloride. The acetone was removed under vacuum at 60° and the cooled solution was acidified to thymol blue with concd. hydrochloric acid. The precipitated crystals were collected and dried. The yield of crude material was 5.48 g. or 48% of the theoretical amount. Recrystallization from hot water gave crystals, m.p. 117–118°, used in the analyses.

α-(*p*-Ethylbenzenesulfonamido)-isocapramide.—Three grams (0.01 mole) of the acid as prepared above was dissolved in 10 ml. of purified thionyl chloride and heated on a steam-bath to solution. The gaseous products and excess thionyl chloride were removed under vacuum leaving a viscous liquid. Excess concd. ammonium hydroxide was added to this liquid. The crude reaction mixture was treated with 200 ml. of water. The crystals were collected and dried. The yield was 1.96 g. or 65% of the theoretical amount. Recrystallization from 95% ethanol gave crystals, m.p. 202–203°, used in the analysis.

Acknowledgment.—The authors are indebted to the Research Committee of the College of Arts and Sciences of the University of Louisville for a grant in support of this work.

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[3] R. H. Wiley and R. P. Davis, THIS JOURNAL, **74**, 6142 (1952).

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Improved Preparation of Stachyose

BY M. L. WOLFROM, R. C. BURRELL, A. THOMPSON[1] AND S. S. FURST

RECEIVED AUGUST 8, 1952

The tetrasaccharide stachyose was first isolated by von Planta and Schulze[2] from the root sap of *Stachys tuberifera*. Although stachyose has been found in a number of other plants, the tuber of *Stachys tuberifera* is still one of the better sources of this sugar. The method of isolation has been modified by Tanret.[3]

We wish to report herein a simple procedure for obtaining stachyose from the tuber of *Stachys tuberifera* wherein the organic solids in the extract of the tuber were adsorbed on a column of carbon and removed selectively by washing with increasing strengths of ethanol, according to the general adaptation of Whistler and Durso.[4] From the eluates the sugar could readily be crystallized.

Experimental

Fresh tubers of *Stachys tuberifera* (1 kg.) were ground in a food chopper and were refluxed on a water-bath with 1750 ml. of 85% ethanol for 80 min. in the presence of 2.5 g. of precipitated calcium carbonate. The liquid was removed by filtration and the extraction was repeated with 500 ml. of 75% ethanol for 60 min. The extract was filtered and combined with the first filtrate to produce a clear brownish solution which was concentrated under reduced pressure to a sirup; yield 80 g. The sirup was dissolved in 1000 ml. of water and placed on a 290 × 105 mm. (i.d.) column of Darco G-60[5]:Celite[6] (1:1 by wt.) and washed with 10 l. of water. This solution was evaporated under reduced pressure to a sirup which failed to crystallize; yield 17 g. The column was then washed with 10 l. of 5% ethanol. Upon evaporation under reduced pressure, this solution yielded a sirup (13 g.) which was crystallized by dissolving in the minimum amount of warm water, cooling to room temperature, adding ethanol (95%) to incipient crystallization and allowing to stand at room temperature. The column was again washed with 10 l. of 10% ethanol. Upon evaporation this solution yielded 35 g. of sirup which crystallized from water–ethanol as described above. A further yield of sirupy material was obtained by washing the column with 10 l. of 20% ethanol. The sirup from this fraction showed only a slight tendency to crystallize. This residue was combined with the mother liquors from the 5 and 10% ethanol washings and evaporated to a sirup which was extracted with 500 ml. of boiling 85% ethanol to yield a further amount of 6 g. of crystals. The combined crystalline material was recrystallized from water by the addition of ethanol; yield of recrystallized material 39 g., m.p. 101–105° (sealed tube), $[\alpha]^{25}\mathrm{D}$ +131.3° (*c* 4.5, water). These constants are in good agreement with those given in the literature for stachyose tetrahydrate.[3]

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[1] Corn Industries Research Foundation Associate.

[2] A. von Planta and E. Schulze, *Ber.*, **23**, 1692 (1890).

[3] G. Tanret, *Bull. soc. chim.*, [4] **13**, 176 (1913).

[4] R. L. Whistler and D. F. Durso, THIS JOURNAL, **72**, 677 (1950).

[5] Decolorizing carbon; a product of Darco Department, Atlas Powder Co., New York, N. Y.

[6] No. 535, a siliceous filter-aid produced by Johns-Manville Co. New York, N. Y.

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The Reaction of Phosphorus Pentachloride with Epimeric 2-Aminocycloalkanol Hydrochlorides

BY EUGENE E. VAN TAMELEN AND RICHARD S. WILSON[1]

RECEIVED AUGUST 7, 1952

During the course of work being carried out in this Laboratory, it became desirable to investigate the synthesis of diastereoisomeric 2-chlorocycloalkylamines through the reaction of phosphorus pentachloride with *cis*- and *trans*-2-aminocycloalkanol hydrochlorides. The results of these studies, together with evidence for the stereochemistry of the products, are presented below.

The synthesis of a 2-chlorocyclohexylamine hydrochloride (IIa) from *trans*-2-aminocyclohexanol hydrochloride (Ia) by this route was first reported by Osterberg and Kendall.[2] Direct evidence for the *cis* configuration (and therefore displacement by phosphorus pentachloride with inversion) has been presented by Carter, *et al.*,[3] and, more recently, by Paris and Fanta.[4] The isomeric 2-chlorocyclohexylamine and derivatives have been obtained by several methods.[4–7] Attempts to obtain this *trans* isomer through the action of phosphorus pentachloride on the hydrochloride of *cis*-2-aminocyclohexa-

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[1] Abstracted from a research report submitted by Richard S. Wilson in partial fulfillment of the requirements for the Master of Science degree, University of Wisconsin, February, 1952.

[2] A. E. Osterberg and E. C. Kendall, THIS JOURNAL, **42**, 2616 (1920).

[3] G. E. McCasland, R. K. Clark, Jr., and H. E. Carter, *ibid.*, **71**, 637 (1949).

[4] O. E. Paris and P. E. Fanta, *ibid.*, **74**, 3007 (1952).

[5] G. E. McCasland and D. A. Smith, *ibid.*, **72**, 2190 (1950); **71**, 637 (1949).

[6] W. S. Johnson and E. N. Schubert, *ibid.*, **72**, 2187 (1950).

[7] T. L. Cairns, P. J. Graham, P. L. Barrick and R. S. Schreiber, *J. Org. Chem.*, **17**, 751 (1952).