have been mentioned[2] but have not been described. The data for the derivatives are given in Table I. The method used in the preparation of these compounds is essentially that of Walther and v. Pulawski.[3]

TABLE I

o-Phenylenediamine condensed with, acid	Yield, %	M. p., °C.[a]	Formula	Analyses, % Nitrogen Calcd.	Nitrogen Found	Halide Calcd.	Halide Found
o-Chlorobenzoic	41	234	$C_{13}H_9N_2Cl$	12.25	12.32	15.5	14.9
m-Chlorobenzoic	44	238			12.20		14.8
p-Chlorobenzoic	49	303			12.58		15.0
o-Bromobenzoic	22	246	$C_{13}H_9N_2Br$	10.26	10.52	29.3	28.7
m-Bromobenzoic	35	252			10.30		29.4
p-Bromobenzoic	31	299			10.24		29.5
o-Iodobenzoic	26	258	$C_{13}H_9N_2I$	8.75	8.97	39.7	40.1
m-Iodobenzoic	23	262			8.86		39.4
p-Iodobenzoic	22	308			8.82		39.4

[a] All melting points were determined by means of a Fischer–Johns hot-stage melting point block.

Experimental

o-Phenylenediamine (0.1 mole) and the appropriate halobenzoic acid (0.11 mole) were heated in a tall beaker covered by a watch glass to about 180° (210° for the *p*-haloacids) in an oil-bath. The mixture was stirred occasionally and sublimed crystals of the acid were returned to the reaction mixture by means of a stirring-rod. After 45 minutes of heating the mass was allowed to cool then ground in a mortar with saturated sodium carbonate solution to remove excess acid. After filtration the residue was repeatedly crystallized (charcoal) from aqueous alcohol. All the pure compounds were white crystalline substances.

(2) C. Wiegand and E. Merkel, *Ann.*, **557**, 242 (1947).

(3) R. Walther and v. Pulawski, *J. prakt. Chem.*, [2] **59**, 249 (1899).

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Hydrogenation of Esters of L-Alanine and L-Leucine over Copper–Chromium Oxide Catalyst

BY EDWARD SEGEL

The hydrogenation of optically active α-amino esters at 175° using copper–chromium oxide catalyst has been reported to yield a racemized product.[1] It was concluded that a lower operating temperature is necessary to retain optical configuration and Raney nickel was turned to as being an effective catalyst at lower temperatures.[2,3,4]

The fundamental assumption of these researches, that copper–chromium oxide catalyst is not suitable for the hydrogenation of optically active amino esters, is unjustified. The results described in this paper demonstrate that copper–chromium oxide is in fact the catalyst of choice, giving excellent yields of optically active amino alcohols, without the necessity of using large amounts of catalyst.

The two esters hydrogenated, L-alanine butyl ester and L-leucine ethyl ester, were prepared from the commercial amino acids. The specific rotations of the amino alcohols prepared from these two esters, +18.2° and +3.8°, compare favorably with the values of +20.1° and +4.2° previously obtained[5] by reduction of the amino esters with lithium aluminum hydride.

(1) C. C. Christman and P. A. Levene, *J. Biol. Chem.*, **124**, 453 (1938).

(2) G. Ovakimian, C. C. Christman, M. Kuna and P. A. Levene, *ibid.*, **134**, 151 (1940).

(3) H. Adkins and A. A. Pavlic, THIS JOURNAL, **69**, 3039 (1947).

(4) H. Adkins and H. R. Billica, *ibid.*, **70**, 3121 (1948).

Experimental

Dioxane used as reaction medium was purified according to the method of Fieser.[6] L-Leucine ethyl ester was synthesized from L-leucine (from the Nutritional Biochemicals Corporation), by refluxing a solution containing 1-mole proportion of the amino acid, 10-mole proportions of absolute ethanol, and 1.5-mole proportions of sulfuric acid for 24 hours. The solvent was stripped off *in vacuo*, the residue brought to *p*H 10, and the free ester extracted with benzene. The extract was distilled through a 6″ Vigreux column, and L-leucine ethyl ester collected from 64.0–64.5° (4.0 mm.); rotation $[\alpha]^{24}D$ +9.6° (pure liquid); $[\alpha]^{24}D$ +20.8° (*c* 2, methanol).

L-Alanine butyl ester was prepared by the esterification of L-alanine (from the Bios Laboratories). Boiling point of the product after fractionation was 72–73° (10 mm.); neutral equivalent: found, 146; theory, 145.

Hydrogenations were effected in a 480-ml. stainless steel bomb fitted with a thermocouple well in the base. The bomb was rocked through a 45° arc 36 times per minute. It was charged with 0.2 mole of ester, 170 ml. of dioxane and 30% as much copper–chromium oxide catalyst as ester; the contents were then equilibrated to approximately 2000 p.s.i. hydrogen pressure. The vessel was heated, and maintained at temperature until the pressure remained constant for one hour. The bomb was quenched with cold water. After centrifuging out the catalyst, the reaction mixture was distilled *in vacuo*.

Hydrogenation of L-Leucine Ethyl Ester.—L-Leucine ethyl ester was hydrogenated for 3 hours at 150°. The reaction mixture was distilled from a Claisen flask *in vacuo*, air being bubbled in through a tube containing Ascarite absorbent. Product was collected from 74–77° (1.4 mm.); yield, 85%, neutral equivalent, 120 (theory for L-leucinol, 117); rotation $[\alpha]^{25}D$ +3.3° (*c* 3.5, methanol).

L-Leucinol was redistilled through a 6″ Vigreux column; the middle cut boiled from 73–74° (1.4 mm.); neutral equivalent, 119; rotation $[\alpha]^{23}D$ +3.8° (*c* 3.5, methanol).

Anal. Calcd. for $C_6H_{15}NO$: C, 61.5; H, 12.9; N, 11.9. Found: C, 61.0; H, 13.2; N, 12.4.

Hydrogenation of L-Alanine Butyl Ester.—This compound was hydrogenated under the same conditions as was L-leucine ethyl ester. Reaction temperature was maintained for 4.5 hours. L-Alaninol distilled from 56–60° (0.5 mm.), yield 55%; neutral equivalent, 77, theory, 75. Redistillation through a 3″ Vigreux column gave a product boiling from 50–52° (1.5 mm.), neutral equivalent 76; rotation $[\alpha]^{25}D$ +18.2° (*c* 2, methanol).

Anal. Calcd. for C_3H_9NO: N, 11.5. Found: N, 11.1.

(5) P. Karrer, P. Portmann and M. Suter, *Helv. Chim. Acta*, **31**, 1617 (1948).

(6) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 369.

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Some Syntheses of Compounds Related to Julolidine[1]

BY PETER A. S. SMITH AND TUNG-YIN YU

Incidental to a study of 9-substituted julolidines,[2] some attempts were made to find alternative general synthetic procedures for the julolidine ring system. Our limited success in this direction is reported here.

The successful cyclization of anilides of β-chloropropionic acid by fusion with aluminum chloride

(1) From part of the doctoral dissertation of Tung-yin Yu, 1951.

(2) Forthcoming communication; *cf.* Abstracts of Papers of the Chemistry Section, Meeting of The Australian and New Zealand Association for the Advancement of Science, Brisbane, Qld., May, 1951.