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 1

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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RECEIVED AUGUST 13, 1951

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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RECEIVED JULY 13, 1951

Some Syntheses of Compounds Related to Julolidine[1]

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

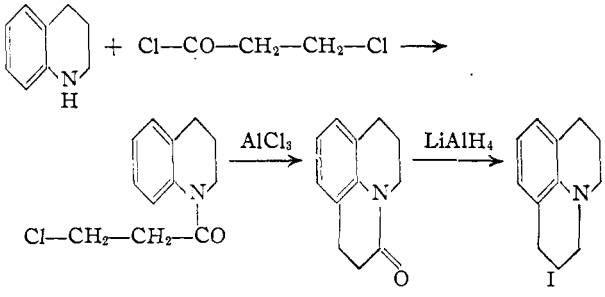
Incidental to a study of 9-substituted julolidines,[2] some attempts were made to find alternative general synthetic procedures for the julolidine ring system. Our limited success in this direction is reported here.

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.

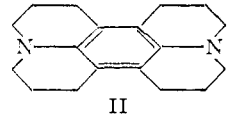
(2) Forthcoming communication; *cf.* Abstracts of Papers of the Chemistry Section, Meeting of The Australian and New Zealand Association for the Advancement of Science, Brisbane, Qld., May, 1951.

has been recorded.[3,4] The products are lactams, which we have been able to reduce with lithium aluminum hydride to tetrahydroquinoline derivatives. By coupling these steps and applying them to tetrahydroquinoline as starting material, we have obtained julolidine (I) in an over-all yield of about 50%. By the same procedures, tetrahydroquinoline was synthesized from aniline, and 1,2,3,4,5,6,7,8-octahydro-*p*-phenanthroline[5] was synthesized from *p*-phenylenediamine. Cyclization of the bis-β-chloropropionyl derivative of benzidine failed, however. Indoline was obtained from aniline by way of oxindole in 55% over-all yield, using chloroacetyl chloride in place of β-chloropropionyl chloride.



3-Oxojulolidine, obtained as an intermediate in the above procedure, undergoes mononitration, presumably in the 9-position, and also reacts with bromine. The chemistry of these products will be reported in detail upon the completion of contemplated further work.

Octahydro-*p*-phenanthroline obtained as described was smoothly converted into the new ring-system 1,2,3,3a,4,5,6,7,8,9,9a,10,11,12-tetradecahydro-3a,9a-diazaperylene (II) by heating with trimethylene chlorobromide. It appeared to be



II

readily oxidized by air to a highly colored substance presumably of the semiquinone type.

The chain of three carbon atoms required to build the julolidine skeleton from tetrahydroquinoline can in principle be obtained from acrylonitrile, as well as from β-chloropropionyl chloride or trimethylene halides, by N-cyanoethylation followed by cyclization.

Attempts were made to cyclize N-β-cyanoethyltetrahydroquinoline[6] by the Hoesch reaction, using the procedure of Clemo and Ramage,[7] and by fusion with aluminum chloride. The only result was the recovery of most of the starting material unchanged. N,N-Bis-β-cyanoethylaniline was similarly resistant to cyclization. However, these cyclizations have now been carried out successfully by altered procedures by Mann and Smith.[8] An attempt to cyanoethylate 9,10-dihydrophenanthridine resulted only in dehydrogenation to phenanthridine, which also resulted from heating with trimethylene chlorobromide. The cyanoethylation of carbazole was successful as reported in the patent literature,[9] but attempts to duplicate the cyclization claimed in the patent were unsuccessful.

(3) F. Mayer, L. van Zuetphen and H. Phillips, *Ber.*, **60**, 858 (1927).

(4) R. Stollé, R. Bergdoll, M. Luther, A. Auerhahn and W. Wacker, *J. prakt. Chem.*, **128**, 1 (1930).

(5) The name *p*-peryloline is suggested for this ring system in the interest of conciseness.

(6) F. C. Whitmore, H. S. Mosher, R. R. Adams, R. B. Taylor, E. C. Chapin, C. Weisel and W. Yanko, THIS JOURNAL, **66**, 725 (1944).

(7) G. R. Clemo and G. R. Ramage, *J. Chem. Soc.*, 49 (1931).

(8) F. G. Mann and B. B. Smith, *ibid.*, 1899 (1951).

(9) I. G. Farben, French Patent 806,715 (1936); *C. A.*, **31**, 4991 (1937).

Experimental

Julolidine.—Ten grams of tetrahydroquinoline (E. K. Co.) in 40 ml. of anhydrous acetone was refluxed for one hour with 10 g. of β-chloropropionyl chloride.[3] The oily product which separated when the resulting mixture was poured into dilute hydrochloric acid decomposed on attempted distillation, and would not crystallize; wt., 10 g. The crude product was heated over a small flame with 20 g. of powdered aluminum chloride until no more hydrogen chloride was evolved (about one hour). The product was obtained by treating the cooled mixture with chilled, dilute hydrochloric acid and extracting with ether. The extracts were dried over sodium sulfate and distilled; the fraction collected at 126–127.5° (0.6 mm.) crystallized after three days in a Dry Ice–acetone-bath to colorless needles, m.p. 55°, wt. 6.1 g. (51%).

Anal. Calcd. for $C_{12}H_{13}ON$: C, 76.97; H, 7.00. Found: C, 76.87; H, 7.18.

One gram of the 3-oxojulolidine so obtained was refluxed with 0.4 g. of lithium aluminum hydride in 50 ml. of anhydrous ether for 10 hr. After addition of water, filtering, and drying of the ethereal layer over sodium hydroxide pellets, the julolidine was obtained by distillation, wt. 0.9 g. (97%), and was identified as its picrate, m.p. 174°, undepressed when mixed with a known sample.

The preparation of tetrahydroquinoline from aniline was accomplished in like fashion with substantially similar results.

Indoline.—Oxindole was obtained from aniline and chloroacetyl chloride in a similar manner to the foregoing preparation in an over-all yield of 55%; m.p. 126–127°.[4] Reduction with lithium aluminium hydride gave indoline, b.p. 150–152° (30 mm.), in 61% yield; its picrate melted at 174°.[4]

Octahydro-*p*-phenanthroline.—The bis-β-chloropropionyl derivative of *p*-phenylenediamine was cyclized to 2,7-dioxo-1,2,3,4,5,6,7,8-octahydro-*p*-phenanthroline by fusion with aluminium chloride as described by Mayer, *et al.*[3,4] A solution of 5.0 g. of the dioxo compound and 2.0 g. of lithium aluminum hydride in 100 ml. of dry ether was refluxed overnight, decomposed with water, and filtered. Concentration of the ethereal filtrate gave 4.0 g. (90%) of 1,2,3,4,5,6,7,8-octahydro-*p*-phenanthroline, m.p. 161–162°, in two crops.

Anal. Calcd. for $C_{12}H_{16}N_2$: C, 76.55; H, 8.77. Found: C, 76.78; H, 8.66.

Tetradecahydrodiazaperylene.—A mixture of 0.7 g. of octahydro-*p*-phenanthroline and 30 ml. of trimethylene chlorobromide was refluxed for 24 hr., treated with 3 ml. of concd. hydrochloric acid, and steam distilled to remove excess alkyl halide. The residue was alkalized with sodium hydroxide solution and extracted with ether; concentration of the extracts after drying over solid sodium hydroxide yielded 0.8 g. (82%) of 1,2,3,3a,4,5,6,7,8,9,9a,10,11,12-tetradecahydro-3a,9a-diazaperylene, colorless platelets, m.p. 190–191°, in two crops. An alcoholic solution turned purple on standing, and became blue on dilution with water.

Anal. Calcd. for $C_{18}H_{24}N_2$: C, 80.55; H, 9.01. Found: C, 80.55; H, 8.98.

The picrate, prepared in ethereal solution, first separated as a yellow, crystalline solid, m.p. 125°. Upon recrystallization from ether or ethanol, it turned to shining, black needles, m.p. 205–210°.

Anal. Calcd. for $C_{24}H_{27}O_7N_5$: C, 57.94; H, 5.47. Calcd. for $C_{24}H_{25}O_7N_5$: C, 58.03; H, 5.28. Found: C, 58.06; H, 5.24.

9-Nitro-3-oxojulolidine.—To a solution of 4.0 g. of 3-oxojulolidine in 20 ml. of glacial acetic acid was added 5 ml. of nitric acid (sp. gr. 1.42). After 20 min. at room temperature the product was precipitated by dilution with 200 ml. of water, and recrystallized from hot water; wt. 3.6 g. (73%), m.p. 155–156.5°.

Anal. Calcd. for $C_{12}H_{12}O_3N$: C, 62.06; H, 5.21. Found: C, 62.31; H, 5.21.

Bromination of 3-Oxojulolidine.—Solutions of 3-oxojulolidine in glacial acetic acid reacted with bromine to produce, after dilution with water, a light yellow, amorphous, bromine-containing solid which did not have a definite melting point, and could not be successfully crystallized.

Carbazole-N-β-propionic Acid.—A mixture of 3.0 g. of carbazole-N-β-propionitrile[9] and 20 ml. of concd. hydrochloric acid was refluxed for 14 hr. The solid which separated on cooling was filtered off, dissolved in 10% sodium hydroxide solution, and reprecipitated with hydrochloric acid; wt. 2.8 g. (86%), m.p. 169–170°.

Anal. Calcd. for $C_{15}H_{13}O_2N$: C, 75.28; H, 5.48. Found: C, 75.61; H, 5.44.

N,N-Bis-(β-cyanoethyl)-aniline.—A mixture of 18 g. of aniline, 21 g. of acrylonitrile, 10 ml. of glacial acetic acid and 2.0 g. of cuprous chloride was refluxed for 12 hours. The viscous product was repeatedly extracted with warm ether, from which there separated on cooling 29 g. (75%) of N,N-bis-(β-cyanoethyl)-aniline, m.p. 85°. Details of the preparation and properties of this substance are not available from the original report of it in the literature,[10] but Cookson and Mann[11] report m.p. 80–82° for the compound as prepared in lower yield (23%) by a more drastic procedure.

Anal. Calcd. for $C_{12}H_{13}N_3$: C, 72.34; H, 6.58. Found: C, 72.17; H, 6.58.

This nitrile was recovered unchanged after treatment with dry hydrogen chloride and zinc chloride in anhydrous ether, and after fusion with anhydrous aluminum chloride. The recovered starting material was accompanied by a red lake, which was not further investigated, after the aluminum chloride fusion. We were not successful in obtaining crystalline aniline-N,N-β-propionic acid by alkaline hydrolysis of the nitrile, as were Cookson and Mann.[11]

(10) I. G. Farbenind., British Patent 404,744 [*C. A.*, **28**, 4068 (1934)]; British Patent 457,621 [*C. A.*, **31**, 3068 (1937)].

(11) R. C. Cookson and F. G. Mann, *J. Chem. Soc.*, 67 (1949).

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RECEIVED OCTOBER 5, 1951

The Oxidation of Indium Trisulfide

BY M. F. STUBBS

According to Dupuis and Duval[1] precipitated In_2S_3 loses water up to 94° and then may be weighed without loss from this temperature to 221°. When the sulfide is heated in air between 221–320°, an irregular loss of weight is said to take place with the formation of InS, the reaction being given by the equation

$$In_2S_3 + O_2 \rightleftarrows 2InS + SO_2$$

The InS is said to be stable in air between 320–544°. On raising the temperature, a second oxidation is said to take place according to the equation

$$2InS + 7/2O_2 \rightleftarrows In_2O_3 + 2SO_2$$

In view of the fact that no analytical data are given to support the postulates presented, a further study has been made of the effects of heating In_2S_3 in air.

We have found it necessary to heat small quantities of In_2S_3 (approximately 0.2 g.) for several hours at 140–150° to remove moisture, while complete purification requires heating in a vacuum or atmosphere of H_2S for at least an hour at approximately 300°. Such purified samples give a negative test for sulfate ion after digestion with hot water for one hour.

(1) P. Dupuis and C. Duval, *Anal. Chim. Acta*, **3**, 331 (1949).

Three samples of In_2S_3, purified as described above, were heated in air in the temperature range 220–280°, with results as shown in Table I. There was no visible change in the color of the sulfides after heating.

TABLE I

EFFECT OF HEATING In_2S_3 IN AIR 220–280°

No.	Wt. of sulfide, g.	Temp. range, °C.	Duration of heating, hrs.	Change in mass, g.	Change in mass theory for InS, g.	Sulfate present after heating
1	0.7869	220–275	12	−0.0027	−0.0775	None
2	.5943	278 ± 5	25	− .0022	− .0585	None
3	.6352	275 ± 2	63	− .0010	− .0626	Trace

Sample No. 1 was next heated for an additional 3.5 hours at 310 ± 5°, gaining 0.40 mg. There was still no visible change in the appearance of the sulfide. The sample was then heated for 89.5 hours between 310–400°, the temperature being raised gradually. During this period the sulfide gained 0.0937 g. A slight odor of SO_2 was detected above 325°. The surface of the product had changed to the light yellow color of In_2O_3. There was no evidence of the dark red brown color of InS.

The results obtained suggested the possibility that the loss of mass reported by Dupuis and Duval to take place when In_2S_3 is heated between 220–320° might possibly be accounted for by loss of small amounts of water or sulfur, due to incomplete purification of the sulfide used. Our results indicate that only a very slight loss of mass occurs on prolonged heating of purified In_2S_3 in air up to 280°. The small gain in mass, odor of SO_2, and the partial change to a light yellow color observed after prolonged heating between 310–400°, suggested the possibility that the apparent stability observed by Dupuis and Duval between 320–540° might possibly be due to a balance between sulfate and oxide formation.

Accordingly three additional samples of purified In_2S_3 were heated in air between 325–460° and the products analyzed for the presence of sulfate ion. The results are given in Table II.

TABLE II

EFFECT OF HEATING In_2S_3 IN AIR 320–460°

No.	Wt. of sulfide, g.	Temp. range, °C.	Duration of heating, hr.	Change in mass, g.	Sulfate analyses $BaSO_4$, g.	Conversion to sulfate, %
4	0.8321	325–380	138	+0.1782	0.6520	36.44
5	.7191	380 ± 10	135	+ .1210	.5061	32.74
6	.5743	455 ± 5	48	− .0484	.0464	3.76

In each case nearly all of the product changed to the light yellow color of In_2O_3. The odor of SO_2 was detected during the heating.

Three additional samples of purified In_2S_3 were spread out in boats to a very shallow depth, heated in air, and analyzed as shown in Table III.

TABLE III

CONVERSION OF In_2S_3 TO $In_2(SO_4)_3$ AND In_2O_3

No.	Wt. of sulfide, g.	Temp. range, °C.	Duration of heating, hrs.	Change in mass, g.	Sulfate analyses $BaSO_4$, g.
7	0.5651	380 ± 10	110	+0.0502	0.0901
8	.6158	380 ± 10	68	− .0516	.0909
9	.6375	210–380	168	− .0341	.0830

No.	Conversion to sulfate, %	Sulfide analyses $BaSO_4$, g.	Sulfide remaining, %	Conversion to oxide (difference), %
7	7.42	0.0586	4.83	87.75
8	6.86	.0516	3.90	89.24
9	6.24	.2455	18.46	75.30