

values for Folin color per 10 μg . N are given in Table I. Within experimental error antipneumococcal antibodies and human gamma globulin give identical results.

TABLE I
COLOR EQUIVALENTS OF HUMAN ANTIBODY AND NORMAL HUMAN GAMMA GLOBULIN

	Hexosamine ^{a,b} / Total N	Methylpentose ^b / Total N	Folin-Ciocalteu color D 7500 10 μg . N
Anti-C		0.032 ^e	
Anti-SII	0.07 ^c		0.155
Anti-SIII	.07 ^d	.030 ^f	.150
Gamma globulin			
Fraction II-1, 2 ¹³	.07		.149
Fraction II-3 ¹³	.07	.034	.146
Sample B ¹³		.032	
Sample S ¹³		.026	

^a Hexosamine was determined after hydrolysis with 2 N HCl at 100° for 2 hours. ^b The color values, while reproducible, are not assumed to be specific for either hexosamine or methylpentose.^{15,16} ^c Correction for hexosamine color value of SII-14%. ^d Correction for hexosamine color value of SIII-7%. ^e Correction for methylpentose color value of "C" substance-8%. ^f Correction for methylpentose color value of SIII-14%.

(15) E. Vasseur and J. Immers, *Arkiv Kemi*, **1**, 253 (1949).

(16) H. N. Horowitz, M. Ikawa and M. Fling, *Arch. Biochem.*, **25**, 226 (1950).

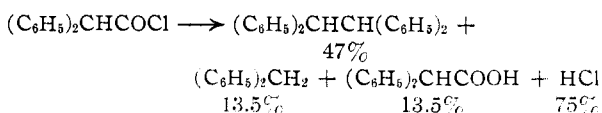
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The Attempted Rosenmund Reduction of Diphenylacetyl Chloride¹

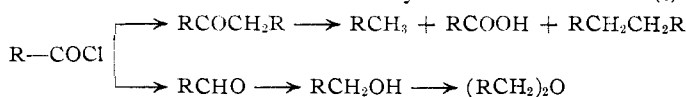
By JOHN G. BURR, JR.

Recently a supply of diphenylacetaldehyde was desired in this Laboratory, and since diphenylacetyl chloride was available, the Rosenmund reduction of this compound was investigated. The products which were obtained are



The occurrence of a product of the nature of tetraphenylethane as a product of a Rosenmund reduction has not been previously reported. Triphenylacetyl chloride also loses carbon monoxide and hydrogen chloride under Rosenmund conditions; the product in this case is triphenylmethane.²

The more usual products and by-products of this reaction were accounted for by Rosenmund³ as



This scheme does not predict products of the nature of tetraphenylethane or triphenylmethane.

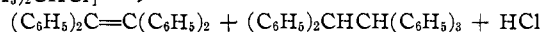
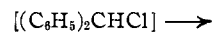
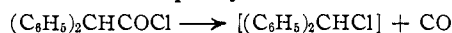
A possible explanation of these two products may be found in the temperature at which these

(1) This document is based upon work performed under Contract Number W-7405, eng. 26 for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) S. Daniloff and E. Venus-Danilova, *Ber.*, **59**, 377 (1926).

(3) K. W. Rosenmund and F. Zetzche, *ibid.*, **54**, 642, 2038 (1921).

reactions were carried out. It is known, for example, that diphenylacetyl chloride decomposes at temperatures of around 200–250° into carbon monoxide, hydrogen chloride, tetraphenylethylene and diphenylketene.^{4,5} Staudinger⁴ explains the formation of tetraphenylethylene through an intermediate diphenylchloromethane which is known to decompose upon heating to tetraphenylethylene^{6,7} and tetraphenylethane.⁷ The moderate



temperature of the reaction observed here (boiling xylene solution) with its long duration might well be sufficient for a smooth production of diphenylchloromethane (but little diphenylketene), and the thermal conversion of this to tetraphenylethylene and tetraphenylethane. The tetraphenylethylene, in the reductive atmosphere, might be converted to tetraphenylethane.

Similarly, triphenylacetyl chloride is known⁵ to be converted at 170–180° quantitatively to triphenylchloromethane and carbon monoxide. Under the conditions of the Rosenmund reduction, the triphenylchloromethane would probably be converted to triphenylmethane.

Experimental⁸

Attempted Rosenmund Reduction of Diphenylacetyl Chloride.—A suspension of 4 g. of 5% palladium-barium sulfate catalyst, poisoned with 0.6 ml. of quinoline-S solution, in 200 ml. of toluene was prepared, heated to boiling, and a small amount of solvent distilled to dry the remainder. To the cooled solution was added 44.6 g. of diphenylacetyl chloride. A moderately fast stream of hydrogen was passed through the stirred, refluxing mixture. The effluent gases were passed into water, and the absorbed hydrogen chloride titrated with 5 N sodium hydroxide. After overnight reaction, 28 ml. of NaOH had been consumed (75% of theory). The cooled solution was filtered from the catalyst, and the solvent was removed under vacuum. The residual pasty solid was heated with aqueous sodium bicarbonate. The undissolved material was filtered off, and the filtrate, after extraction with ether, acidified to give 5.5 g. (13.5%) of diphenylacetic acid (m.p. 145°). The neutral organic substances were stirred with ether. The ether-soluble material was obtained by filtration. It was evaporated, and the residue distilled at high vacuum. The distillate, 4.4 g. (13.5%), b.p. 87–89° (0.1 mm.), n_D^{20} 1.5788, was diphenylmethane. The residue was about 5 g. of a semisolid.

The ether-insoluble material weighed 15 g. (47% yield), and after several crystallizations from benzene formed a white microcrystalline powder melting at 211–212°. This material conforms in analysis, melting point, and general solubilities to tetraphenylethane. A mixture melting point with authentic tetraphenylethane (prepared from diphenylchloromethane and zinc, and melting at 211–212°) showed no depression.

(4) H. Staudinger, *ibid.*, **44**, 1619 (1911).

(5) A. Bistrzycki and A. Landtwing, *ibid.*, **41**, 686 (1908).

(6) R. Anschütz, *Ann.*, **235**, 220 (1886).

(7) C. Engler and H. Bethge, *Ber.*, **7**, 1128 (1886).

(8) All melting points were taken on a Fisher-Johns block and are uncorrected. Microanalyses are by Dr. H. W. Galbraith, Knoxville, Tenn.

OAK RIDGE NATIONAL LABORATORY

OAK RIDGE, TENN.

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Phenylalanine Analogs

By J. H. BURCKHALTER AND VERLIN C. STEPHENS

The following new compounds related to phenyl-

alanine were prepared in addition to the group already published.¹

Ethyl (2,4-Dichlorobenzyl)-acetamidomalonate (I).—By the process previously reported,¹ 39.2 g. (0.2 mole) of 2,4-dichlorobenzyl chloride² and the sodium salt of 43.4 g. (0.2 mole) of ethyl acetamidomalonate, gave 60 g. of product (80%), m.p. 159–160°. Subsequent recrystallizations from aqueous alcohol did not significantly alter the melting point.

*Anal.*³ Calcd. for $C_{18}H_{19}Cl_2NO_5$: C, 51.08; H, 5.09. Found: C, 51.40; H, 5.02.

β -(2,4-Dichlorophenyl)-alanine.—Hydrolysis of 37.6 g. (0.1 mole) of I by refluxing for 14 hours in 150 ml. of 48% hydrobromic acid, gave 24 g. (theoretical yield) of product, m.p. 237–239° dec. Two recrystallizations from water raised the melting point to 238–240° dec.

Anal. Calcd. for $C_9H_9Cl_2NO_2$: C, 46.18; H, 3.88. Found: C, 45.92; H, 4.22.

β -(3-Nitro-*p*-tolyl)-alanine.—3-Nitro-*p*-xylyl chloride was prepared by the method of Stephen, Short and Gladding.⁴ By treatment of 25 g. (0.13 mole) of this material with 23 g. (0.13 mole) of ethyl acetamidocyanacetate in the usual manner,¹ there was obtained a brown oil which could not be crystallized. The oil was hydrolyzed by heating at reflux temperature for four and a half hours in hydrochloric acid as described previously.¹ A solid formed in the neutralized solution after it had stood for several days; weight 17 g., m.p. 219° dec. (bath preheated to 210°). Recrystallization from aqueous alcohol gave 10 g. (34%) of product, m.p. 230° dec.

Anal. Calcd. for $C_{10}H_{12}N_2O_4$: C, 53.56; H, 5.40. Found: C, 53.77; H, 5.60.

(1) Burckhalter and Stephens, *THIS JOURNAL*, **73**, 56 (1951).

(2) Supplied by Heyden Chemical Corp., Garfield, N. J.

(3) Analyses by Mr. C. W. Beazley, Skokie, Illinois.

(4) Stephen, Short and Gladding, *J. Chem. Soc.*, **117**, 510 (1920).

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UNIVERSITY OF KANSAS SCHOOL OF PHARMACY
LAWRENCE, KANSAS RECEIVED MARCH 26, 1951

The Synthesis of 2,3-Bis-(*p*-carbethoxyphenyl)-2,3-butanediol by Electrolytic Reduction

BY MILTON J. ALLEN

It recently became necessary to prepare large quantities of 2,3-bis-(*p*-carbethoxyphenyl)-2,3-butanediol. A survey of the electrochemical literature¹ indicated that in acid medium an ester of an aromatic acid is readily reduced to an ether and aromatic acid reduced to an alcohol.

In view of the possibility of saponification of the *p*-carbethoxyacetophenone during reduction in alkaline medium, the free acid was reduced in alkaline medium at a constant reference potential with the resultant excellent yield of the pinacol. Treatment of the pinacol with ethanol and sulfuric acid yielded 2,3-bis-(*p*-carbethoxyphenyl)-2,3-butanediol.

Figure 1 illustrates the cell used in the electrolytic reduction. The instrument used for maintaining a constant reference potential has been previously described.²

Experimental³

2,3-Bis-(*p*-carbethoxyphenyl)-2,3-butanediol.—The catholyte consisted of 300 g. of *p*-carboxyacetophenone dissolved in 2500 ml. of distilled water containing 280.5 g. of potassium hydroxide (Baker reagent). The anolyte contained 56.1 g. of potassium hydroxide in 500 ml. of aqueous solution. At a reference potential of -2.0 volts the initial current was 4.2

(1) "Organische Elektrochemie," Fr. Fichter, Verlag von Theodor Steinkopf, Dresden, 1942, pp. 251–263.

(2) M. J. Allen, *Anal. Chem.*, **22**, 804 (1950).

(3) All melting points reported were done on a Kofler hot-stage and are corrected.

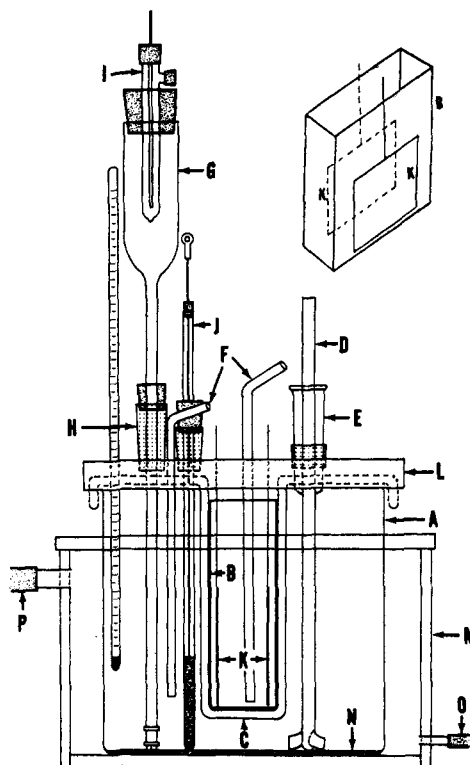


Fig. 1.—Electrolysis cell: A, glass electrolysis cell 8¹/₄" i.d. × 8³/₄" high; B, aluminum membrane 2" wide × 6" long × 6" deep, 1/8" wall mix RA 1143 (Norton Company); C, membrane support 1/4" diameter rod; D, paddle stirrer 16" long × 3/8" diameter; E, mercury seal type bearing with 29/42 joint; F, nitrogen inlet tubes to cathode and anode chambers; G, salt bridge, top portion 2" diam. × 4" high narrowing to 1/16" × 12" long at end of which is sealed a 14/35 male joint, 3/8" up from the bottom on one side of joint is a 1/64" hole, over the male end of the joint is a female collar 5/8" in length; H, support for salt bridge 24/40 joint extended 1.5 inches; I, standard Beckman calomel electrode; J, contact to mercury cathode consisting of tube 1/16" o.d. × 14" long at bottom of which is sealed a piece of platinum wire. The tube is filled part way with mercury and copper wire inserted for connection to cathode lead. The entire tube passes through a rubber stoppered 24/40 joint; K, platinum anode 4" × 4" × 1/64"; L, Plexiglas cover; M, cooling chamber 11" × 11" × 7 1/4" high o.d. 1/4" thick Plexiglas; N, mercury cathode; O, one water inlet to cooling chamber, 1/4" i.d. P; two water outlet from cooling chamber, 1/4" i.d.

amperes. After 937 minutes a current plateau of 0.9 ampere was reached. The catholyte was filtered, acidified with hydrochloric acid, refrigerated overnight and filtered. The residue was washed with water and dried in a vacuum oven; yield 290 g. (96.2%), m.p. 268–278°. Recrystallization from water gave platelets m.p. 272–273.5°. *Anal.* Calcd. for $C_{18}H_{18}O_8$: C, 65.45; H, 5.49. Found: C, 65.09; H, 5.85.

2,3-Bis-(*p*-carbethoxyphenyl)-2,3-butanediol.—Fifty grams of the pinacol was mixed with 1000 ml. of absolute ethanol and 200 ml. of sulfuric acid. The solution was refluxed for eight hours and diluted with an equal volume of water. After neutralization with aqueous sodium carbonate, most of the alcohol was evaporated on a steam-bath. The cooled solution was extracted a number of times with ether. The combined ether extracts were evaporated to a small volume and refrigerated; yield 48 g. (82%), m.p. 167–168°. Recrystallization from 61.5% methanol gave a crystalline compound m.p. 169.5–170.5°.