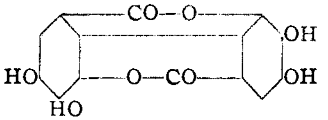
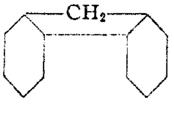
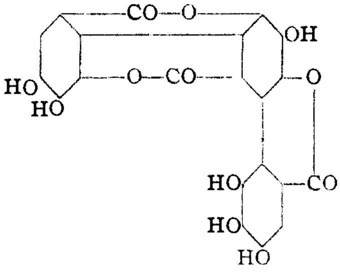
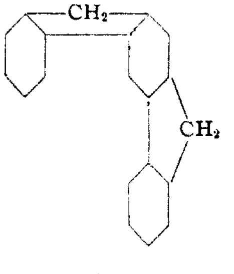
contains a trinuclear by-product which probably has the constitution shown in Formula III since on zinc dust distillation a new hydrocarbon is produced, for which we suggest the name *ellagene* (IV)


(I)


(II)


(III)


(IV)

For comparison we tabulate the melting points of these two hydrocarbons and their derivatives

	M. p., °C.	
	Ellagene	Fluorene
	197	113
Picrate	117	81
Benzylidene der.	107	76

Fifty grams of synthetic ellagic acid was exhaustively extracted with pyridine and the insoluble residue collected. Attempts to crystallize the latter or to prepare crystallizing derivatives gave only amorphous substances so that finally the remaining residue was distilled with zinc dust. *Ellagene* crystallizes from benzene in small flat plates.

Anal. Calcd. for $C_{20}H_{14}$: C, 94.44; H, 5.55; mol. wt., 254. Found: C, 94.37, 94.43; H, 5.61, 5.59; mol. wt., 261, 257 (in benzene).

Whereas fluorene easily forms a picrate, ellagene does so with difficulty, so that no analysis of the picrate was possible. The *benzylidene derivative* crystallizes from dilute alcohol in fawn-colored cubes.

Anal. Calcd. for $C_{34}H_{26}$: C, 94.00; H, 5.99. Found: C, 94.11; H, 6.07.

THE UNIVERSITY
BRISTOL 8, ENGLAND

RECEIVED NOVEMBER 16, 1944

Methyl Esterification of an Easily Lactonized Hydroxy Acid

BY MILTON D. SOFFER AND MILDRED C. HUNT[1]

In the course of some recent synthetic work in this Laboratory, it became necessary to prepare the methyl ester of γ-hydroxy-γ-(*p*-methoxyphenyl)-butyric acid. The usual methods of intermolecular esterification[2] are not readily applicable to hydroxy acids of this type because of favorable competition by the intramolecular reaction. In this case, after treatment with gaseous hydrogen chloride in absolute methanol failed to give any appreciable quantity of the methyl hydroxy ester from the corresponding γ-lactone,[3] the desired product was readily prepared by methylation of the free hydroxy acid with diazomethane.

Experimental

γ-Hydroxy-γ-(*p*-methoxyphenyl)-butyric Acid.—β-(*p*-Methoxybenzoyl)-propionic acid was prepared by the procedure of Fieser and Hershberg,[4] from 84 g. of succinic anhydride and 86 g. of anisole in a solution of 800 ml. of tetrachloroethane and 200 ml. of nitrobenzene. The recrystallized product (131 g., m. p.[5] 145–147°) was obtained in, 79% yield. The yield was only 55% when the reaction was carried out under the same conditions in a solvent mixture of 4:1 carbon bisulfide–nitrobenzene.

The methyl ester,[6] recrystallized from ether (m. p. 47.5–49.5°, 85% yield), was obtained by treatment with methanol and sulfuric acid in the usual way; 5% of unchanged keto acid was recovered by acidification of the alkaline washings.

The Meerwein–Ponndorf–Verley reaction was carried out[7] on 0.09 mole (20 g.) of the keto ester using 0.2 mole of aluminum isopropoxide and 220 ml. of anhydrous isopropyl alcohol. After twelve hours an additional 50 ml. of isopropyl alcohol was added. The reaction was completed in a total period of twenty-four hours. After treatment with excess dilute sulfuric acid, extraction with ether, and removal of solvent, the non-volatile fraction was refluxed with aqueous alkali. Following removal of a small amount of non-saponifiable matter by washing with ether, the clear solution was acidified with hydrochloric acid, and the product, γ-(*p*-methoxyphenyl)-butyrolactone, was isolated (16 g., 85%, m. p. 48–52°) by extraction with ether. One recrystallization from ether–petroleum ether afforded pure material, m. p. 55–57°.

The same lactone was obtained less advantageously by hydrogenation of 10 g. of the keto-acid in 250 ml. of absolute methanol at 1.6 atm. pressure. Only about half of the theoretical amount of hydrogen was taken up during forty-three hours of shaking with 50 mg. of Adams catalyst. After the addition, at this point, of 300 mg. of fresh catalyst, the reaction was carried to completion by thirty-seven hours of continued shaking. The residue, left on removal of solvent at reduced pressure, m. p. 75–87°, was assumed to be a mixture of lactone and hydroxy acid. Distillation at reduced pressure gave 5.2 g. (52% yield) of crude lactone, m. p. 38–42°, b. p. 160° (2 mm.). Recrystallization from aqueous methanol gave the pure product described above.[8]

The hydroxy acid was obtained in almost quantitative yield by careful acidification, at 0°, of a well-stirred alkaline solution of the lactone. Traces of lactone were removed from the product by recrystallization to constant melting point, 99–101°, from toluene or ether–petroleum ether. The hydroxy acid is moderately soluble in warm water and readily reverts to lactone at temperatures near its melting point.

Methyl γ-Hydroxy-γ-(*p*-methoxyphenyl)-butyrate.—After an ethereal solution of 5 g. of the pure hydroxy acid and a large excess of diazomethane had remained at room temperature for twenty-four hours, the solution was con-

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[1] Present address: E. I. du Pont de Nemours, Inc., Parlin, New Jersey.

[2] An alternative route, through the thionyl chloride adduct of the lactone, is described by Barbier and Locquin, *Bull. soc. chim.*, [4] **13**, 223 (1913).

[3] Findlay and Hickmans, *J. Chem. Soc.*, **95**, 1009 (1909), reported the conversion of γ-phenylbutyrolactone to the corresponding ethyl hydroxy ester, in unspecified yield, by similar treatment in ethanol.

[4] Fieser and Hershberg, THIS JOURNAL, **58**, 2314 (1936).

[5] All melting points are corrected.

[6] Hahn, THIS JOURNAL, **38**, 1517 (1916); Bagellini and Giua, *Gazz. chim. ital.*, **42**, I, 197 (1912).

[7] Baker and Adkins, THIS JOURNAL, **62**, 3305 (1940); "Organic Reactions," 1944, Vol. II, Ch. 5.

[8] This lactone has been prepared before by reduction of the keto acid with sodium amalgam, and by hydrogenation over Pd-$BaSO_4$ (Rosenmund and Shapiro, *Arch. Pharm.*, **272**, 313 (1934)). The melting points reported were about 45° and 53–55°, respectively.

centrated at reduced pressure and washed with aqueous sodium bicarbonate and with water, and dried over anhydrous magnesium sulfate. The residue (4.4 g., 82% yield) left by complete removal of solvent was relatively pure ester, m. p. 40–45°. Three recrystallizations from ether–petroleum ether gave 3.0 g. of pure material of constant melting point (41–43°).

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.51, 64.18; H, 7.32, 7.17.

A trial distillation at 2 mm. of a small sample of the pure hydroxy ester resulted in elimination of methanol, identified in the Dry Ice trap, and partial conversion to lactone.

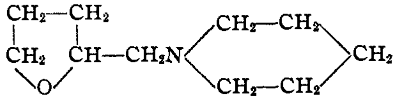
CHEMICAL LABORATORY
SMITH COLLEGE
NORTHAMPTON, MASSACHUSETTS

RECEIVED FEBRUARY 6, 1945

Pyridine from Furfural

BY CHRISTOPHER L. WILSON

The following observations with furfurylamine confirm and extend the recent findings of Kline and Turkevich.[1] Passage over typical dehydrating catalysts at elevated temperatures failed to give pyridine[2] but catalytic reduction in the liquid phase led first to tetrahydrofurfurylamine and then, under more drastic conditions, to piperidine (9%) and N-tetrahydrofurfurylpiperidine (formula inset, 43%). These experiments could be the basis of a satisfactory synthetic method for pyridine.



Hydrogenation of Furfurylamine.—Furfurylamine (193 g.), Raney nickel catalyst (30 g.) and hydrogen (137 atm. (20°)) were introduced into a 2-l. rotating autoclave. Two moles of hydrogen were rapidly absorbed at 140° and a third slowly at 200–215°. The product on fractionation consisted of (a) b. p. below 110°, which after drying over potassium carbonate gave piperidine (15 g.) identified as picrate, and (b) N-tetrahydrofurfurylpiperidine (new, 73 g.), b. p. 102–104° (11 mm.).

Anal. Calcd. for $C_{10}H_{19}ON$: C, 71.0; H, 11.35; N, 8.3; mol. wt., 169. Found: C, 70.7; H, 10.9; N, 8.9; equiv. by titr., 171.

The **picrate** had m. p. 140–141°.

Anal. Calcd. for $C_{16}H_{22}O_8H_4$: N, 14.1. Found: N, 13.8.

An authentic specimen was prepared by heating tetrahydrofurfuryl bromide and excess piperidine together at 100° for one hour.

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[1] Kline and Turkevich, THIS JOURNAL, **66**, 1710 (1944).

[2] Such a reaction was first envisaged by Ciamician and Dennstedt, *Ber.*, **14**, 1059, 1475 (1881).

UNIVERSITY COLLEGE, LONDON

RECEIVED JANUARY 29, 1945

NEW COMPOUNDS

Propylene Glycol *p*-Nitrobenzoate

Propylene glycol was converted to the *p*-nitrobenzoate by treatment with *p*-nitrobenzoyl chloride in pyridine according to the general procedure outlined by Shriner and Fuson.[1] After three recrystallizations from alcohol the product melted at 126–127°.

Anal: Calcd. for $C_{17}H_{14}N_2O_8$: C, 54.55; H, 3.77; N, 7.48. Found: C, 54.75; H, 3.99; N, 7.60.

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[1] Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., second edition, p. 137.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
HENNING EKLUND
CHARLES C. PRICE

RECEIVED FEBRUARY 5, 1945

Di-(*p,p'*-dichlorobenzohydryl) Ether

Three grams (12 millimoles) of *p,p'*-dichlorobenzohydrol (prepared by the reduction of *p,p'*-dichlorobenzophenone with zinc and sodium hydroxide[1]) was dissolved in 15 cc. of dry chloroform and 5 cc. of concentrated sulfuric acid was added slowly dropwise with vigorous stirring. After standing at room temperature for ten minutes the brown mixture was poured onto 50–60 g. of ice. The chloroform layer was separated, washed with 5% sodium carbonate solution and water until neutral, and then dried over anhydrous potassium carbonate. After filtering and removal of the chloroform on the steam-bath with reduced pressure, a viscous oil remained which was dissolved in 5 cc. of petroleum ether (60–70°) and the solution cooled in an ice-bath until crystals formed. These were collected by suction filtration and then crystallized twice from absolute ethanol, using a small amount of Norit each time. The yield of colorless crystals was 1.5 g., 51% of the theoretical, melting 126–127°.

Anal. Calcd. for $C_{26}H_{18}Cl_4O$: Cl, 29.1; mol. wt., 488. Found: Cl, 28.8; mol. wt., 490.

The ether was further characterized by cleavage with 3,5-dinitrobenzoyl chloride to form *p,p'*-dichlorobenzohydryl 3,5-dinitrobenzoate: 1.0 g. of the ether, 0.5 g. of 3,5-dinitrobenzoyl chloride and 0.15 g. of anhydrous zinc chloride were heated on the steam-bath for one hour and in an oil-bath at 150° for one-half hour. The oily product was poured into 50 cc. of ice water with stirring and the mixture allowed to stand forty-eight hours. The crude product slowly solidified and after washing with warm 2% sodium carbonate solution and crystallization from 2:1 benzene–alcohol there was obtained 0.2 g. of *p,p'*-dichlorobenzohydryl 3,5-dinitrobenzoate, m. p. 174–176°. A mixed melting point with the authentic ester[2] gave 174–176°. Attempts to cleave the ether with acetic acid–sulfuric acid, as Nef had done on benzohydryl ether,[3] gave only the unreacted ether. The ether was not appreciably hydrolyzed by heating with 5% sulfuric acid in a sealed tube at 150° for two hours.

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[1] Montagne, *Rec. trav. chim.*, **24**, 115 (1905).

[2] Grummitt, Buck and Joseph, THIS JOURNAL, **67**, 693 (1945).

[3] Nef, *Ann.*, **298**, 234 (1897).

SHERWIN-WILLIAMS LABORATORY
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OLIVER GRUMMITT
ALLEN BUCK

RECEIVED JANUARY 20, 1945

p,p'-Dichlorobenzohydryl 3,5-Dinitrobenzoate

A mixture of 2.0 g. (8 millimoles) of *p,p'*-dichlorobenzohydrol (prepared by the reduction of *p,p'*-dichlorobenzophenone with zinc and sodium hydroxide[1]), 1.5 g. (6 millimoles) of 3,5-dinitrobenzoyl chloride and 5–6 cc. of dry pyridine was heated on the steam-bath for one hour. It was then poured with stirring into 100 cc. of cold water and allowed to stand until the oil layer solidified. The water was decanted, the solid was pulverized and then thoroughly washed with several portions of warm 2% sodium carbonate solution. The solid was collected by

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[1] Montagne, *Rec. trav. chim.*, **24**, 115 (1905).