α-Chloroisobutyronitrile[5] fails to give any appreciable quantity of the iminoester hydrochloride when treated with phenol and hydrogen chloride in ether solution even after several months of standing. This nitrile, however, does give an iminoester hydrochloride slowly with ethyl alcohol and hydrogen chloride, but this salt on further treatment with alcohol is completely converted to the amide (reaction 1).

Experimental

Preparation of Nitriles.—Acetonitrile, chloroacetonitrile and bromoacetonitrile were prepared by dehydration of the corresponding amides with phosphorus pentoxide.

α-Chloroisobutyronitrile was prepared by the following procedure for which the authors are indebted to Mr. Stanley B. Mirviss.[5] To a solution of 250 g. (3 moles) of acetone cyanohydrin[6] in 250 ml. of benzene, contained in a 3-neck 2-liter flask, was added portion-wise, and with stirring, 500 g. (2.4 moles) of phosphorus pentachloride from an erlenmeyer flask attached to one of the side-necks of the reaction flask by rubber tubing. After the phosphorus pentachloride had been added, the benzene solution was heated to 50° until the evolution of hydrogen chloride ceased (about six hours). The reaction mixture then was poured slowly and with stirring into twice its volume of ice water. If the solutions became too warm more ice was added. The benzene and aqueous layers were shaken together vigorously in a separatory funnel in order to decompose all of the phosphorus chlorides. Then the benzene layer was separated and the aqueous layer extracted with ether. The combined ether and benzene layers, after drying over anhydrous sodium sulfate, was fractionated. The yield of α-chloroisobutyronitrile, boiling at 93–100° (60 mm.), n^{20}_{D} 1.4310, amounted to 95 g. (38%).

Anal. Calcd. for C_4H_6NCl: Cl, 34.26. Found: Cl, 34.16.

Phenyl Chloroacetiminoester Hydrochloride.—In a 500-ml. erlenmeyer flask, provided with a stopper carrying a gas inlet tube and a calcium chloride tube, was placed 76 g. (1 mole) of chloroacetonitrile and 94 g. (1 mole) of phenol. The resulting mixture was dissolved in 100 ml. of anhydrous ether and a slight excess over the required 36.5 g. (1 mole) of dry hydrogen chloride was passed into the ethereal solution. Then another 200 ml. of ether was added and the flask tightly stoppered and left overnight in a refrigerator. Before filtration of the precipitated salt the contents of the flask were cooled to −30° in a Dry Ice–ether mixture. The precipitated salt then was filtered off and dried in a vacuum desiccator, after which it was triturated under sufficient cold (−40°) anhydrous ether to cover it, and again filtered and dried in a desiccator. Another crop of crystals was obtained by allowing the mother liquor to stand for two more days in the refrigerator. The total amount of phenyl chloroacetiminoester hydrochloride, m. p. 95–97° dec., obtained was 144 g. (79%).

Anal. Calcd. for $C_8H_9ONCl_2$: Cl (ionized), 17.2. Found: Cl, 17.2.

This salt dissolved exothermically in water and from this solution phenyl chloroacetate[7] began immediately to separate as an oil which solidified on cooling. After recrystallization from an alcohol–water mixture this ester melted at 43–44°.

Phenyl Bromoacetiminoester Hydrochloride.—This salt was prepared from bromoacetonitrile in a manner similar to the chloro compound described above. The yield of product melting at 100–102° d. was 42% of the theoretical.

Anal. Calcd. for $C_8H_9ONClBr$: Cl, 14.2. Found: Cl, 14.1.

Hydrolysis of this salt yielded phenyl bromoacetate,[8] m. p. 32°.

Phenyl Acetiminoester Hydrochloride.—When acetonitrile was used instead of the halogenoacetonitriles in the above preparations, standing in the refrigerator for fifteen days was required to produce a 27% yield of the iminoester hydrochloride. This salt melted at 110–113° dec.

Anal. Calcd. for $C_8H_{10}ONCl$: Cl, 20.6. Found: Cl, 20.1.

Phenyl Diethyl Orthochloroacetate.—In a 500-ml. 3-neck flask, fitted with a stirrer, a reflux condenser protected with a calcium chloride tube, and a 250-ml. erlenmeyer flask that contained 100 g. (0.49 ml.) of phenyl chloroacetiminoester hydrochloride and was attached with a rubber tube to one of the necks of the flask was placed 49 g. (1.5 moles) of absolute ethyl alcohol. The iminoester hydrochloride was added slowly to the stirred alcohol from the erlenmeyer flask. When about half of the salt had been added, a fine precipitate of ammonium chloride began to settle out of the alcohol. After the addition of all the salt the mixture was warmed gently with a free flame to keep the alcohol boiling for about ten minutes. Stirring was continued while the reaction mixture was allowed to come to room temperature. It then was cooled to 0° and the precipitated ammonium chloride filtered off and washed with three 25-ml. portions of absolute alcohol. The dried ammonium chloride weighed 28 g. (93%).

The filtrate was fractionated in a modified Claisen flask. After the material boiling below 50° (45 mm.) was removed, it was found advisable to cool the liquid in the distilling flask in a Dry Ice–ether mixture and filter off the small amount of ammonium chloride and chloroacetamide (3–5%) that had precipitated.

The distillation of the filtrate then was resumed and the fraction boiling at 72–120° (10 mm.) was collected. On refractionation 82 g. (69%) of the colorless phenyl diethyl orthochloroacetate, b. p. 78–80° (10 mm.); d^{20}_{4} 1.1498; n^{20}_{D} 1.4988.

Anal. Calcd. for $C_{12}H_{17}O_3Cl$: Cl, 14.5. Found: Cl, 14.8.

This ortho ester also was obtained by the addition of phenol to chloroketene diethylacetal.[9]

Phenyl diethyl orthobromoacetate, prepared from the corresponding iminoester salt in the manner described above, boiled at 84–86° (2 mm.); n^{20}_{D} 1.5048; d^{20}_{4} 1.3192, and was obtained in 54% yield.

Anal. Calcd. for $C_{12}H_{17}O_3Br$: Br, 27.7. Found: Br, 27.6.

This orthoester also was prepared from phenol and bromoketene diethylacetal.[10]

Phenyl diethyl orthoacetate was obtained in 35% yield by the alcoholysis of phenyl acetiminoester hydrochloride. It had the same properties as the orthoester obtained from the reaction of phenol with ketene diethylacetal.[11]

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[5] Sobieranski and Chrzaszczewski, *Chem. Abs.*, **22**, 2146 (1928); Mirviss, B.S. Thesis, University of Wisconsin, 1944.

[6] "Organic Syntheses," Coll. Vol. II, 1943, p. 7.

[7] Kunckel and Johansen, *Ber.*, **30**, 1714 (1897).

[8] Kunckel and Schenen, *Ber.*, **31**, 172 (1898).

[9] Magnani and McElvain, THIS JOURNAL, **60**, 2210 (1938).

[10] Beyerstedt and McElvain, *ibid.*, **59**, 2266 (1937).

[11] McElvain and Kundiger, *ibid.*, **64**, 254 (1942).

DEPARTMENT OF CHEMISTRY
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MADISON, WISCONSIN

RECEIVED FEBRUARY 12, 1945

A New Hydrocarbon

BY M. NIERENSTEIN AND C. W. WEBSTER

Ellagic acid (I) yields on zinc dust distillation[1] fluorene (II) and we find that ellagic acid prepared according to Perkin and Nierenstein[2]

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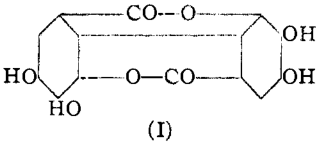
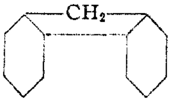
[1] M. Nierenstein, "The Natural Organic Tannins," J. & A. Churchill, London, 1934, p. 135.

[2] A. G. Perkin and M. Nierenstein, *J. Chem. Soc.*, **87**, 1412 (1905).

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)



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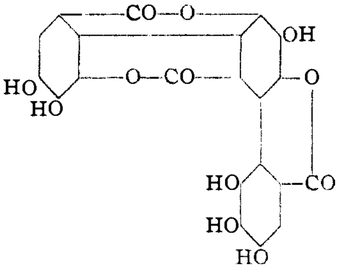
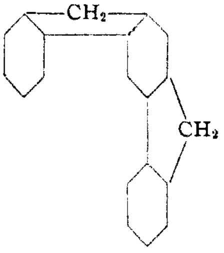


(III)



(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
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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.