graphic microscope, and are presented in Table II. The refractive indices were determined by the immersion method, with the interference figures being used as a means of determining the optical orientation of the crystals. The light source was that from the northern sky. The extinction angle on these compounds was the most commonly observed angle between the elongation of the crystal and an extinction direction. The most usual orientations are noted in order to facilitate the use of the optical properties in the detection of the barbiturates. The temperature at which the indices were taken was 25 ± 1°.

The optical properties of the derivatives of the three compounds differ sufficiently from each other to allow the use of the optical data in the identification of the original barbituric acid derivatives. No previous optical crystallographic data have been reported for the derivatives of these barbiturates.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF COLORADO
BOULDER, COLORADO

RECEIVED JANUARY 8, 1945

The Storing of Hydrocyanic Acid

BY VERNON K. KRIEBLE AND ROBERT SMELLIE, JR.

During the last few years it has been difficult to obtain liquid hydrocyanic acid promptly. Laboratories using this chemical have apparently retained the metal cylinders in which it was shipped until the acid was used up.

We have found that hydrocyanic acid mixed with an equal volume of glacial acetic acid makes a solution which can be kept indefinitely. Such solutions have been kept on our shelves for as long as two years with the temperature in the laboratory above 90° F. during the summer with no loss or deterioration of hydrocyanic acid. The containers never exhibit any pressure when opened. Whenever hydrocyanic acid is wanted it is distilled out of the acetic acid through any ordinary fractionating column and the acetic acid used over again. As the acid in the cylinders needs to be distilled anyway, if a pure sample is desired, there is little more trouble in distilling it out of the acetic acid than distilling it directly.

There is no difficulty in mixing hydrocyanic acid and acetic acid. The hydrocyanic acid can be poured into a container holding an equal quantity of acetic acid and the container rotated until the solution is uniform. If glass bottles are used they should be insulated against breakage preferably with an outside container filled with some absorbent material. This hydrocyanic acid–acetic acid solution should be poured and distilled in a well-ventilated hood only. In fact, this solution should be treated with the same care as pure hydrocyanic acid.

DEPARTMENT OF CHEMISTRY
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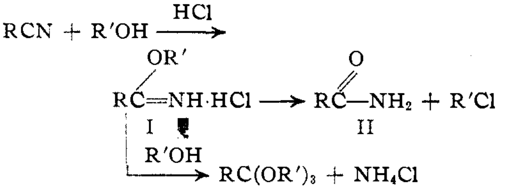
RECEIVED DECEMBER 11, 1944

The Preparation and Alcoholysis of Phenyl Iminoester Hydrochlorides

BY S. M. MCELVAIN AND BERNARDO FAJARDO-PINZÓN

The chief difficulty encountered in the conversion of a nitrile to an orthoester by the Pinner method[1] is the decomposition of the intermediate iminoester hydrochloride (I) into an amide (II) and an alkyl chloride (reaction 1) during the alcoholysis to the orthoester (reaction 2).



$$\mathrm{RCN} + \mathrm{R'OH} \xrightarrow{\mathrm{HCl}} \underset{\mathrm{I}}{\mathrm{R}\overset{\mathrm{OR'}}{\mathrm{C}}{=}\mathrm{NH{\cdot}HCl}} \longrightarrow \underset{\mathrm{II}}{\mathrm{R}\overset{\mathrm{O}}{\mathrm{C}}{-}\mathrm{NH_2}} + \mathrm{R'Cl} \qquad (1)$$

$$\mathrm{I} \xrightarrow{\mathrm{R'OH}} \mathrm{RC(OR')_3} + \mathrm{NH_4Cl} \qquad (2)$$

Some of the competitive reaction (1) always occurs, but it may be minimized in those cases in which the R of I is an unsubstituted methyl group or one that is monosubstituted with alkyl, halogen or ethoxy[2] by keeping the temperature of the alcoholysis below 40°. However, when the α-carbon of R carries two or more of these substituents, experience[3] in this Laboratory has shown that the yield of the orthoester drops sharply and that the amide is the major if not the sole reaction product when such an iminoester hydrochloride is merely dissolved in an alcohol.

It seemed that this undesirable decomposition of the iminoester salt could be avoided if R′ in I were phenyl, since the strength of the $O{-}C_6H_5$ linkage would prevent its facile rupture to produce the amide (II) and chlorobenzene. This has proved to be the case with phenyl chloro- and bromoacetiminoester hydrochlorides. These salts —which are formed in 70% and 41% yields, respectively, from the corresponding nitriles, phenol and hydrogen chloride—may be heated in boiling absolute alcohol solution without excessive amide formation.

The structures of the halogeno-orthoesters (III) resulting from this alcoholysis are shown by the fact that they are identical with those obtained from the addition of phenol to the halogenoketene diethylacetals.

$$XCH{=}C(OC_2H_5)_2 + C_6H_5OH \longrightarrow \underset{\mathrm{III}}{XCH_2C(OC_2H_5)_2OC_6H_5}$$

In contrast to the halogenacetonitriles, acetonitrile reacts very slowly and incompletely with phenol and hydrogen chloride in ether solution; only 27% of the iminoester hydrochloride is formed after 15 days. Alcoholysis converts this salt to the orthoester (III, X = H) which also may be formed from the reaction of phenol with ketene diethylacetal.[4]

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[1] Pinner, *Ber.*, **16**, 356, 1644 (1883).

[2] McElvain, *et al.*, THIS JOURNAL, **64**, 1825, 1963, 1966 (1942).

[3] Unpublished work of R. L. Clarke, R. E. Kent and Bryce Tate.

[4] McElvain and Kundiger, THIS JOURNAL, **64**, 259 (1942).

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]

DEPARTMENT OF CHEMISTRY
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RECEIVED FEBRUARY 12, 1945

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[5] Sobieranski and Chrzaszezewski, *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).

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).