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
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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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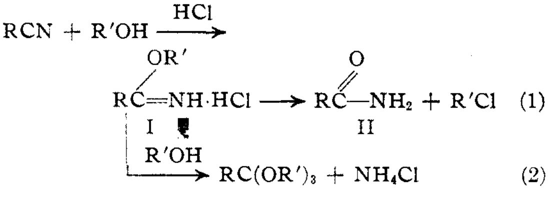
The Preparation and Alcoholysis of Phenyl Iminoester Hydrochlorides

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).



$$RCN + R'OH \xrightarrow{HCl} RC(OR'){=}NH\cdot HCl \;(I) \longrightarrow RC({=}O)NH_2 \;(II) + R'Cl \quad (1)$$

$$RC(OR'){=}NH\cdot HCl \;(I) \xrightarrow{R'OH} RC(OR')_3 + NH_4Cl \quad (2)$$

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.

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

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).