

cation. Although the analytical figures obtained with this derivative were satisfactory, its melting point (152°) proved to be higher than that recorded in the literature ($128^{\circ 2}$ and $143^{\circ 3}$). In order to clear up this discrepancy, we have since prepared the phenylhydrazone* of synthetic isobutyrylformic acid. The latter melts at 152° , thus confirming our observation on the substance obtained from ergotinine. A mixed melting point showed no depression.

The method of synthesis was essentially that reported by Tschelinzeff⁴ with a slight variation in the method of hydrolysis of the intermediate isobutyryl cyanide. It was found necessary to heat

(2) D. Tschtschenke, *Bull. soc. chim.*, [4] **37**, 623 (1925).

(3) E. Abderhalden and E. Rossner, *Z. physiol. Chem.*, **163**, 261 (1926).

(4) W. Tschelinzeff and W. Schmidt, *Ber.*, **62**, 2210 (1929).

the cyanide on the steam-bath for two hours in 1:1 hydrochloric acid in order to effect hydrolysis. The hydrolysis mixture was extracted with ether, the ether extract dried with sodium sulfate and evaporated to a sirup. If this sirup is used to prepare the hydrazone it does not crystallize. However, if the sirup is shaken with a little water, in which it is not completely soluble, and the aqueous layer used to prepare the hydrazone, the product crystallizes nicely. Repeated recrystallizations from dilute alcohol failed to raise the melting point above 152° .

Anal. Calcd. for $C_{11}H_{14}O_2N_2$: C, 64.08; H, 6.84; N, 13.59. Found: C, 64.15; H, 6.74; N, 13.66.

FROM THE LABORATORIES OF
THE ROCKEFELLER INSTITUTE
FOR MEDICAL RESEARCH
NEW YORK, N. Y.

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COMMUNICATIONS TO THE EDITOR

ORGANIC REACTIONS WITH LIQUEFIED HYDROGEN CHLORIDE

Sir:

Information is accumulating in our laboratories relative to the reaction of liquefied hydrogen chloride with various types of organic compounds. In the majority of cases the reactions proceed rapidly indeed, partly because of the fact that the liquefied hydrohalides, in particular hydrogen chloride, are excellent solvents for a wide range of compounds. Many of the resulting solutions are good conductors of electricity.

The reactions observed so far are additions to multiple bonds, dehydration, or both; acidolysis appears not to be as frequent as might be anticipated. Reactions of hydrohalides as exemplified by our experiments are interesting in view of theoretical considerations concerned with addition to multiple bonds. As example of these reactions the following are typical: (1) vinyl acetate reacts with liquid hydrogen chloride at atmospheric pressure forming α -chloroethyl acetate in 50 to 70% yields. The literature contains two boiling points for this compound, 119 – 121° (740 mm.¹) and 113 – 116° (740 mm.²); different preparations resulted in products which boiled at either one or the other

(1) Descade, *Ann. chim.*, [7] **29**, 488 (1903).

(2) Ulich and Adams, *THIS JOURNAL*, **43**, 660 (1921).

of the two points. This is being investigated. (2) Allyl alcohol (b. p. 96.5 – 97.5°) is converted to allyl ether (b. p. 91 – 93°) with a high yield. (3) Acetaldehyde yields α, α' -dichloroethyl ether boiling at 112.5 – 114° in yields of 70%, n_D^{25} 1.4186, d_4^{25} 1.106. This compound was identified by hydrolysis to acetaldehyde in the presence of *p*-nitrophenylhydrazine and isolation of the hydrazone. (4) Good yields of ethylene chlorohydrin are obtained from the reaction of ethylene oxide with liquefied hydrogen chloride.

A mixture of one mole of isopropyl acetate and one mole of *n*-butyl alcohol was treated with liquid hydrogen chloride at atmospheric pressure, from which was isolated some isopropyl alcohol and butyl acetate. This is being investigated on a series of such compounds with the purpose of obtaining data relative to negativity of the groups tested.

A number of cases have been found in which no action takes place. Cinnamic acid is a typical example. This work is being extended. A complete report will be made later.

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