

The acid amide was boiled under reflux with thirty parts of a 20% alcoholic solution of potassium hydroxide for three hours. The alcohol was replaced by water and evaporated, and the 4-methoxydibenzofuran-1-acetic acid was precipitated from the filtered solution. It was recrystallized from ethanol and appeared as colorless needles, m. p. 223–224°. The yield was 90%.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.28; H, 4.73. Found: C, 70.31; H, 4.43.

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The Preparation of Acetyl Bromide*

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Acetyl bromide was prepared as early as 1863 by distilling it as formed from a mixture of glacial acetic acid, bromine and phosphorus.¹

Investigations have shown, however, that acetyl bromide undergoes substitution with bromine to form bromo-acetyl bromides with decrease in the yield of acetyl bromide. Further improvements designed to increase the yield of acetyl bromide have also resulted in increased bromination in the nucleus.²

By the elimination of free bromine it was thought possible to increase the yield of acetyl bromide according to the reaction



Phosphorus tribromide (b. p. 169–170° at 740 mm.) can be prepared readily in 99.5% yield by slowly adding dried bromine from a dropping funnel into a slight excess of freshly washed and dried red phosphorus placed in a round-bottomed flask equipped with a mechanical stirrer and a reflux condenser.

The acetyl bromide was prepared by adding slowly through the dropping funnel, with stirring, a slight excess of 99.5% glacial acetic acid (3.075 moles of CH_3COOH per mole of phosphorus tribromide) to the cold phosphorus tribromide. The mixture separated into two layers which were distilled separately into a common receiver packed in ice. The crude acetyl bromide was rectified in a modified Podbielniak column to produce a water-white fraction boiling from 73–76° at 740 mm. The yield varied from 71.4 to 73.4% of the theoretical.

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(1) H. Gal, *Ann.*, **129**, 53 (1863); M. Hanriot, *Ann. chim. phys.*, [5] **17**, 83 (1879).

(2) H. Gal, *Compt. rend.*, **56**, 1258 (1863); F. Urech, *Ber.*, **13**, 1687 (1880); J. Volhard, *Ann.*, **242**, 144 (1887); C. Hell, *Ber.*, **21**, 1726 (1888); C. F. Ward, *J. Chem. Soc.*, **123**, 2207–2213 (1923); H. B. Watson, *ibid.*, **127**, 2067–2082 (1925); Bernard Gwynn and Ed. F. Degering, *Proc. Indiana Acad. Sci.*, **87** (1939).

In other experiments the phosphorus tribromide was purified before use, but yields were increased only by a slight amount to 74.9% of the theoretical. In an effort to test the effect of temperature, the acetyl bromide was distilled from the reaction mixture at room temperature under reduced pressure. The product was collected in a gas bottle immersed in a bath cooled with solid carbon dioxide. No change, however, was observed in the yield. In all cases large amounts of hydrogen bromide were liberated so that the reaction probably does not proceed as indicated in the above equation.

It was found possible to prepare acetyl bromide without the formation of hydrogen bromide by adding phosphorus tribromide slowly, with stirring, to an excess of boiling acetic anhydride. The boiling point dropped as acetyl bromide was formed and when the addition of phosphorus tribromide was completed, the acetyl bromide was distilled from the mixture and rectified as before. The yield was 81.7% of the theoretical.

By using the readily prepared phosphorus tribromide, instead of free bromine with glacial acetic acid, substitution reactions are avoided and the yield of acetyl bromide can be increased to about 80% of the theoretical.

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Hydrogen Bonds Involving the C–H Link. IX.¹ Nitriles and Dinitriles as Solvents for Hydrogen Containing Halogenated Methanes

BY M. J. COPLEY, G. F. ZELHOFER AND C. S. MARVEL

Nitriles should be capable of bonding with hydrogen in halogenated methanes of the CH_2X_2 and CHX_3 types and hence should be good solvents for these products. Work reported earlier¹ shows that valeronitrile and benzonitrile do dissolve methylene chloride and monochlorodifluoromethane in excess of the amount calculated from Raoult's law. It is interesting to find that the aliphatic dinitriles, succinonitrile and glutaronitrile, dissolve less than the calculated amounts of these two halogenated methanes. Adiponitrile dissolves almost the exact calculated amount and sebaconitrile takes up more than the calculated amount. These results are interesting when considered with the boiling points of the dinitriles.

(1) For the eighth communication in this series see THIS JOURNAL, **61**, 3550 (1939).