

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE]

## Hydrogen Fluoride as a Condensing Agent. VII.<sup>1</sup> The Acylation of Aromatic Compounds

By J. H. SIMONS, D. I. RANDALL AND S. ARCHER

The acylation of aromatic compounds is usually accomplished by the use of metallic halides such as aluminum chloride with acid anhydrides or acid halides as the reagents. The carboxylic acids themselves are not generally useful as the reagents and acidic condensing agents such as sulfuric acid can be used for these reactions only in special cases.<sup>2</sup> In our first experiments using hydrogen fluoride as the condensing agent for acylation reactions we attempted reactions between acetyl chloride and also benzoyl chloride and benzene at both ice temperature and the boiling point of hydrogen fluoride. In these reactions hydrogen chloride is immediately and copiously evolved and the acid fluoride formed, but no detectable amounts of ketones could be isolated.

As our previous work had shown reactions between alcohols and aromatic compounds with the elimination of water, it was believed that the carboxylic acids would react similarly to hydroxyl containing compounds. It has been shown<sup>3</sup> that the carboxylic acids in liquid hydrogen fluoride are analogous to the alcohols in that they both add hydrogen ions, *i. e.*, act as basic substances, to form conducting solutions. This hypothesis is substantiated as it has been found that acetic acid, benzoic acid, and valeric acid produced ketones when mixed with toluene or phenol and hydrogen fluoride, and when the reaction mixture was sealed in a copper bomb and heated at 80 to 100°.

Under similar conditions and at the same temperature it was found that acetyl chloride and benzoyl chloride would react with benzene or toluene to produce the expected ketones. In order to prevent a high pressure from developing in the bomb, at least the major portion of the hydrogen chloride, produced by the reaction between the chlorides and hydrogen fluoride, was allowed to escape before the bomb was sealed and while it was below the boiling point of hydrogen fluoride.

Acetic anhydride has been shown by Fredenhagen<sup>4</sup> to react with hydrogen fluoride to produce

a mixture of acetic acid and acetyl fluoride. It would, therefore, be expected to react in a similar manner to acetic acid or acetyl chloride. In a reaction with toluene *p*-methylacetophenone was formed.

It is observed in the two experiments using acetic acid but with different amounts of hydrogen fluoride that larger amounts of the latter result in higher yields of the product. This is to be expected as water is a reaction product which would reduce the activity of the hydrogen fluoride. As hydrogen fluoride forms additional compounds with oxygen containing organic substances, greater amounts are required than in reactions of olefins, or alkyl halides.

The yields reported are calculated on the basis of the amount of acylating reagent added to the original mixture. No attempts were made to recover any unreacted reagents but these were washed out with the hydrogen fluoride. As relatively small amounts of residues were obtained upon distillation of the reaction products, the amounts of side reactions occurring were small. Yields calculated on the difference between the amounts of reagents added and remaining after stopping the reaction would be much higher than those reported.

### Experimental

These reactions were all carried out in copper bombs which were made of three-inch (7.6-cm.) copper tubing with one-eighth-inch (3.2-mm.) copper plates silver soldered onto the ends. In one end a three-eighth-inch (9.5-mm.) copper tube was silver soldered. This was capped with a compression fitting which carried a sealed-off piece of tubing. The bombs were about twelve inches (31 cm.) long.

The hydrogen fluoride was run directly into the bomb containing the reaction mixture from the copper condenser which in turn connected to the storage cylinder. The bomb was then sealed, placed in a steam-bath, and heated. Eighteen to twenty-four hours later it was cooled, placed in ice, opened, and the contents poured into iced water. The acid was neutralized with sodium carbonate and the organic materials removed,

(1) For the previous paper of this series see Simons and Archer, *THIS JOURNAL*, **61**, 1521 (1939).

(2) For a recent reaction using sulfuric acid see Crawford, *ibid.*, **61**, 608 (1939).

(3) Simons, *Chem. Rev.*, **8**, 213 (1931).

(4) Fredenhagen, *Z. physik. Chem.*, **A164**, 176 (1933).

TABLE I

Acylating reagent	Amount used, g.	Aromatic compound	Amount used, g.	Hydrogen fluoride used, g.	Time, hrs.	Product formed	Yield, %
Acetic acid	40	Toluene	345	200	20	<i>p</i> -Methylacetophenone	31.7
Acetic acid	40	Toluene	345	67	17	<i>p</i> -Methylacetophenone	4
Acetic acid	40	Phenol	225	104	17	<i>p</i> -Hydroxyacetophenone	40
Valeric acid	66	Toluene	345	250	20	<i>p</i> -Tolyl <i>n</i> -butyl ketone	35.6
Benzoic acid	81.3	Toluene	345	335	20	<i>p</i> -Tolyl phenyl ketone	55
Acetic anhydride	33.6	Toluene	345	352	24	<i>p</i> -Methylacetophenone 2,4-Diacetyltoluene	27.3 9
Acetyl chloride	19.6	Benzene	150	150	30	Acetophenone	13
Benzoyl chloride	30.3	Toluene	265	160	17	<i>p</i> -Tolyl phenyl ketone	45

TABLE II

Compound	M. p., °C.	B. p., °C.	$n_D^{20}$	Derivative
<i>p</i> -Methylacetophenone		104–104.5 at 15 mm.	1.5335	Semicarb., m. p. 205°
<i>p</i> -Tolyl <i>n</i> -butyl ketone		144.5 at 15 mm.	1.5287	Semicarb., m. p. 199–201°, mixed m. p. with known sample 199–200°
<i>p</i> -Hydroxyacetophenone	109–110			Semicarb., m. p. 199–200°
<i>p</i> -Tolyl phenyl ketone	53–55			4,4'-Dimethylbenzpinacol, m. p. 170–171.5°
2,4-Diacetyltoluene		110 at 3 mm.		Benzene 1,2,4-tricarboxylic acid, m. p. 320–325°

separated, and purified. In Table I the results of the experiments are recorded and in Table II are the properties of the derivatives made for identification.

### Conclusions

The results of these experiments demonstrate the effectiveness of hydrogen fluoride to promote acylation reactions. The ability to use the carboxylic acids for such reactions should be of considerable value. It has not been found necessary to subject the reagents to extensive purification. Commercial grades of all substances including

(5) Bachman, *THIS JOURNAL*, **49**, 236 (1927).

hydrogen fluoride were entirely satisfactory.

### Summary

Hydrogen fluoride has been found effective in the synthesis of ketones from aromatic compounds and carboxylic acids, acid anhydrides, and acyl halides. The reactions proceed at 80 to 100° in copper bombs, and the yields are increased with increasing amounts of hydrogen fluoride. Acetic acid, valeric acid, benzoic acid, acetic anhydride, acetyl chloride, and benzoyl chloride were caused to react with benzene, toluene and phenol to form the expected ketones.

STATE COLLEGE, PENNA.

RECEIVED MAY 10, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

## Diphenylmethane as a Thermometric Standard at 25°

BY THOMAS DE VRIES AND HENRY A. STROW<sup>1</sup>

Because a need exists to have a convenient thermometric standard near 25°, it was decided to investigate the melting point of diphenylmethane which has been reported at various times at temperatures ranging from 25 to 27°. The best value seems to be 25.15° which was reported by Smith and Andrews<sup>3</sup> on a sample purified by re-

(1) Present address: The Udylyte Co., Detroit, Mich. This paper is an abstract of a thesis submitted by H. A. Strow in partial fulfillment of the requirements for the degree of Master of Science in Chemistry. (Original manuscript received December 12, 1938.)

(2) Huffman, Parks and Daniels, *THIS JOURNAL*, **52**, 1547 (1930); Krahl, *ibid.*, **54**, 1256 (1932).

(3) Smith and Andrews, *ibid.*, **53**, 3644 (1931).

peated distillation at reduced pressure. In this investigation we found the value 25.09°.

**Experimental.**—Two seven-junction copper-constantan thermels were constructed from No. 30 B. and S. gage wire using all the precautions recommended by White.<sup>4</sup> In order to show that the deviations from the thermocouple reference table were nearly linear over the range from 0 to 100°, it was necessary to use a Leeds and Northrup type K potentiometer. Below 10,000 microvolts a White potentiometer was used, namely, for the calibration of the thermels at the transition point of sodium sulfate and for the determination of the melting point of diphenylmethane.

(4) White, *ibid.*, **36**, 2292 (1914).