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	*p*-Methylacetophenone	31.7
Acetic acid	40	Toluene	345	67	17	*p*-Methylacetophenone	4
Acetic acid	40	Phenol	225	104	17	*p*-Hydroxyacetophenone	40
Valeric acid	66	Toluene	345	250	20	*p*-Tolyl *n*-butyl ketone	35.6
Benzoic acid	81.3	Toluene	345	335	20	*p*-Tolyl phenyl ketone	55
Acetic anhydride	33.6	Toluene	345	352	24	*p*-Methylacetophenone	27.3
						2,4-Diacetyltoluene	9
Acetyl chloride	19.6	Benzene	150	150	30	Acetophenone	13
Benzoyl chloride	30.3	Toluene	265	160	17	*p*-Tolyl phenyl ketone	45

TABLE II

Compound	M. p., °C.	B. p., °C.	n^{20}	Derivative
p-Methylacetophenone		104–104.5 at 15 mm.	1.5335	Semicarb., m. p. 205°
p-Tolyl *n*-butyl ketone		144.5 at 15 mm.	1.5287	Semicarb., m. p. 199–201°, mixed m. p. with known sample 199–200°
p-Hydroxyacetophenone	109–110			Semicarb., m. p. 199–200°
p-Tolyl phenyl ketone	53–55			4,4′-Dimethylbenzpinacol, m. p. 170–171.5°[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 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

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

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Diphenylmethane as a Thermometric Standard at 25°

BY THOMAS DE VRIES AND HENRY A. STROW[1]

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°.[2] The best value seems to be 25.15° which was reported by Smith and Andrews[3] on a sample purified by repeated 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.[4] 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.

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[1] Present address: The Udylite Co., Detroit, Mich. This paper is an abstract of a thesis submitted by H. A. Strow in partial fulfilment 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).

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

The cold junctions of the thermels were maintained at 0° by a "cold cell" of the type first described by White.[5] The thermels were calibrated at the boiling point of water in an hypsometer with copper double walls. The two thermels gave identical electromotive forces. One value of 161 and four values of 162 were obtained as the deviation in microvolts from the reference table,[6] with the boiling point of the water known to 0.01° from the corrected barometric pressure. The barometric readings are known to be accurate to 0.1 mm. by comparison with a Gaertner cathetometer. For the calibration of the thermels at the transition temperature of sodium sulfate decahydrate, the procedure of Dickinson and Mueller[7] was used. The hydrate was prepared from Mallinckrodt Analytical Reagent grade anhydrous sodium sulfate. It was further purified by six recrystallizations. Conductivity water was used throughout. A sharp transition point was obtained. Eight different measurements were made, five giving 60.5 as the deviation from the reference table, and one value each of 60.4, 60.6 and 60.7, the average being 60.5. The two thermels gave identical electromotive forces.

Purification of Diphenylmethane and Results.—The melting point of the diphenylmethane as obtained from the Eastman Kodak Co., was 24.5°. Several methods of purification were tried. Crystallization was decided upon as most likely to give a pure product. First recrystallization from absolute alcohol was attempted, but the alcohol was too difficult to separate from the diphenylmethane. After several other attempts the following method was found to be satisfactory and requiring little attention. The diphenylmethane was frozen slowly over a period of eight to twelve hours until between 5 to 10 cc. was left unfrozen. This was poured off and discarded. For the initial purification about 300 cc. (300 g.) was used. At the end of twenty such recrystallizations about 150 cc. of pure diphenylmethane was obtained. To obtain a uniform cooling rate an apparatus was constructed which gave uniform results regardless of the room temperature. Tap water in the laboratory has a temperature of about 16° and varies only slightly. A metal container was built of two cans so placed as to form a double-walled container. The inside can was of sufficient size to hold a 400-cc. beaker with a clearance of about half an inch (1.25 cm.) on each side. The bottom was covered with an asbestos pad. Tap water was circulated in the space between the two walls and a cover was placed on top. Diphenylmethane was recrystallized daily until a constant melting point was obtained. Seventeen recrystallizations were sufficient, there was less than a 0.001° change for an additional sixteen recrystallizations. Twelve recrystallizations raised the melting point to 25.082°; 5 more to 25.091°; 2 more raised it to 25.092°, and 14 additional recrystallizations produced no further change.

The melting point was determined with the thermel immersed 8 cm. into the diphenylmethane, about one-third of which was liquid. The mixture was stirred in a glass tube, 33 mm. in diameter and 150 mm. deep. Generally the room temperature was such that the diphenylmethane was melting slowly while the measurements were made. The melting point as calculated from the electromotive force was 25.092°. The values relative to each other are not in error exceeding 0.001°, but since the reference tables are consistent to only 0.01°, we report 25.09 ± 0.01° as the melting point of pure diphenylmethane.

Change of Melting Point.—Early in the work it was observed that a sample of diphenylmethane which had been kept in a clear glass bottle in the presence of diffused sunlight showed a marked lowering of the melting point. As a result of long exposure to light a brown color developed in the diphenylmethane and the melting point dropped to 24.1°. The effect of light on the change in the melting point was determined by measuring the melting point of a sample in a clear glass bottle exposed to diffused sunlight and another sample in a brown bottle kept away from light. Melting points were taken over a period of four weeks. The results are given in Table I.

TABLE I

CHANGE OF MELTING POINT UPON STANDING

Time	Melting points, °C. Brown bottle	Clear bottle
0	25.092	25.092
4 days	25.091	25.078
1 week	25.091	25.065
2 weeks	25.091	25.040
3 weeks	25.091	25.013
4 weeks	25.090	24.982

Four recrystallizations were needed to bring the sample in the brown bottle back to its correct melting point.

A more extended test was made by sealing a sample under its own vapor pressure in a tube containing a thermometer well, so that melting points could be taken without admitting air. This tube was kept in the dark over a period of five months except when melting points were determined. A similar sample was kept in an unsealed tube. The readings given in Fig. 1 were taken on these samples. Seven recrystallizations were necessary to bring each sample back to its original melting point.

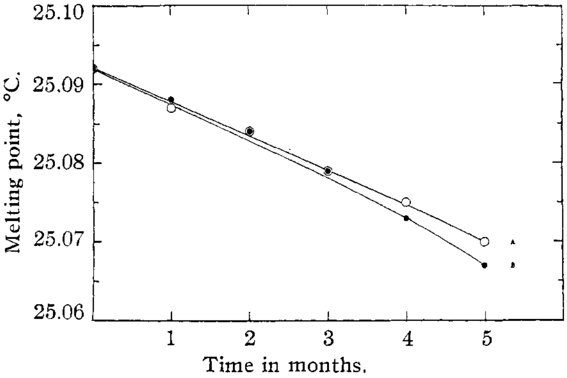

Fig. 1.—Decomposition of diphenylmethane kept in the dark: A, sealed tube, no air present; B, open tube.

Samples of pure diphenylmethane were dried over calcium chloride and over concentrated sulfuric acid in a desiccator without changing the melting point.

Summary

1. The use of diphenylmethane as a thermo-

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[5] White, THIS JOURNAL, **56**, 20 (1934).

[6] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1926, Vol. I, p. 58.

[7] Dickinson and Mueller, *ibid.*, **29**, 1381 (1907).

metric standard in the neighborhood of 25° was investigated.

2. The melting point of purified diphenylmethane was determined to be 25.09 ± 0.01°. Seven junction thermels were used.

3. A spontaneous decomposition occurs, which is accelerated by the presence of light, and which causes lowering of the melting point over a period of time.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

The Reaction of Zinc with Copper Sulfate in Aqueous Solution

BY F. W. VAN STRATEN[1] AND W. F. EHRET

Although it has long been known[2] that the reaction of zinc with copper sulfate solution is not one of simple displacement, many authors in modern scientific literature still retain the idea that only metallic copper is produced along with zinc sulfate. At the outset of this investigation, sufficient work had been done by others to permit the generalization that in displacement reactions the deposit of the more noble metal is rich in base metal if these metals show a tendency to form compounds when cooled from the melt.[3] That the deposits formed by the action of zinc on copper sulfate were heterogeneous had been noted, particularly by Galecki and Tomaszewski,[4] who studied the variation in their coherence, color, and composition with change in concentration and acidity of the copper ion solution.

In the present work it was hoped that a systematic study of the variation in composition of such deposits with the conditions prevailing during their formation would permit postulating a mechanism for the reactions—particularly since this study involved, in addition to the determination of the over-all chemical composition, an X-ray investigation of the solid phases formed.

Experimental

Materials and Apparatus.—The copper sulfate used was Kahlbaum "pro analyse"; the zinc sulfate, Merck reagent.

The zinc was Baker zinc metal, for standardization. The zinc strips were first washed, rinsed, and then rubbed dry with towels. Next, they were annealed by placing in a glass tube which was evacuated and heated to 200°. The cooling was fairly rapid and vacuum was maintained until the strips reached room temperature. The thickness of each strip was approximately 0.3 mm., which was sufficient to lend rigidity to the metal without introducing end effects by reaction along the sides. In order to prevent reaction on both sides of the strip, one side was covered with spar varnish. Immediately before a run was made, the four strips of zinc necessary to make the run were immersed for thirty seconds in an etching reagent made by mixing 144 ml. of hydrogen peroxide (3%), 24 ml. of concd. ammonium hydroxide, and 144 ml. of distilled water. After rinsing a few times with water, the strips were ready for the run.

A brass stirrer was constructed as shown in Fig. 1a. It was hollow and able to pump liquid from the bottom of the vessel as well as provide efficient turbulent stirring. Cavitation was prevented by insertion of two copper baffles in the solution studied. Both the stirrer and baffles were varnished to prevent reaction with the solution. The latter always had a volume of 1 liter and was contained in a 1-liter beaker immersed in a thermostat. The temperature regulation was to ±0.01° at 25° and to ±0.02° at the higher temperatures. The stirring speed was controlled to ±3 r. p. m.

The zinc strips (four) were attached to a glass cage (Fig. 1b) by cutting them slightly longer than required and folding the extra length, top and bottom, around the horizontal supports of the cage. The effective area of the exposed surface of each zinc strip was 9.6 by 1.25 cm. The long arms of the cage could be inserted in appropriate slots along the bearing of the rotor so that the cage was coaxial with the rotor and could be raised out of the solution being stirred until the latter acquired the proper temperature and until the stirrer was rotating at the required speed. At such time as everything was ready for the run, the cage with the zinc strips could be lowered rapidly into the solution. A stop at the top of one of the long arms of the cage enabled the experimenter, in one operation, to raise, swing, and lower the shaft of the rotor supporting the cage into a beaker of water, permitting the reaction to be stopped almost instantaneously and providing also for the rinsing of the deposit. The strips were placed on the cage with the varnished sides away from the rotor and so that the reacting surfaces were equidistant from the center of the shaft. The duration of all reactions, unless otherwise noted, was one minute at 25°, one-half minute at 50°, and one-fourth minute at 75°.

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(1) From a thesis submitted by F. W. van Straten in partial fulfilment of the requirements for the degree of Doctor of Philosophy at New York University.

(2) Wetzlar, *Schweigger's J.*, **50**, 98 (1827); Fischer, "Verhältnis der chemischen Verwandschaft zur galvanischen Elektrizität," Berlin, 1830; Odling, *J. Chem. Soc.*, **9**, 289 (1857); Raoult, *Compt. rend.*, **76**, 156 (1873); Mylius and Fromm, *Ber.*, **27**, 630 (1894); Kutzelnigg, *Z. Elektrochem.*, **38, 154** (1932).

(3) Tammann, *Nachr. Ges. Wiss. Göttingen*, 332 (1918).

(4) Galecki and Tomaszewski, *Roczniki Chem.*, **10**, 601 (1930).