the best results in the papers above cited, pressures ranging from 11 to 200 atmospheres have been employed. F. ALEX. MCDERMOTT.

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[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

BENZOYLPHENYLACETAMIDE.

BY TREAT B. JOHNSON AND LEWIS H. CHERNOFF.

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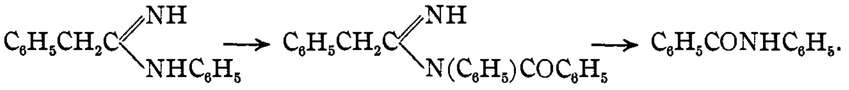
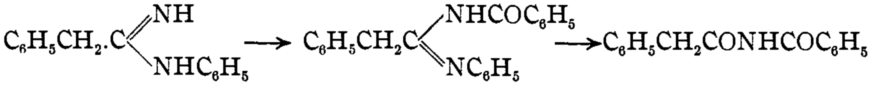
In a paper entitled "The Molecular Rearrangement of Unsymmetrical Acylamidines into Isomeric Symmetrical Derivatives", Wheeler, Johnson and McFarland[1] described the behavior of benzoylchloride towards phenylacetophenylamidine, I. They observed that they reacted in anhydrous ether, at ordinary temperature, giving an unsymmetrical benzoyl derivative, II, melting at 110–111°. The structure of this compound was established by the fact that it smoothly underwent hydrolysis with hydrochloric acid, giving benzanilide, III.



$$C_6H_5CH_2C\begin{array}{l}\diagup NH\\ \diagdown NHC_6H_5\end{array} \longrightarrow C_6H_5CH_2C\begin{array}{l}\diagup NH\\ \diagdown N(C_6H_5)COC_6H_5\end{array} \longrightarrow C_6H_5CONHC_6H_5.$$

I. II. III.

In one experiment, however, in which chloroform was used as the solvent instead of ether, the reaction was less smooth and the primary products of the reaction—acylamidines—were not isolated. Under these conditions a mixture of benzanilide and a compound, to which they assigned the structure of benzoylphenylacetamide, V, was obtained. The latter contained 6.1 per cent. nitrogen and it was soluble in cold alkali and melted at 129–130°. An amide of this structure would result by the hydrolysis of a symmetrical benzoyl derivative, IV.



$$C_6H_5CH_2.C\begin{array}{l}\diagup NH\\ \diagdown NHC_6H_5\end{array} \longrightarrow C_6H_5CH_2C\begin{array}{l}\diagup NHCOC_6H_5\\ \diagdown NC_6H_5\end{array} \longrightarrow C_6H_5CH_2CONHCOC_6H_5$$

IV. V.

Our attention has recently been called, by the revisers of Beilstein's Handbuch, to the fact that this diacidamide, V, had previously been described by Colby and Dodge,[2] who assigned to it the much higher melting point of 171°. They obtained it by heating benzonitrile, VI, and phenylacetonitrile, VIII, with phenylacetic, VII, and benzoic acids, IX, respectively at a high temperature. They state that the same compound, melting at 171°, was obtained in both reactions, and that it underwent hydrolysis with alkali, giving phenylacetic and benzoic acids. Their syntheses are expressed by the following equations:

[1] THIS JOURNAL, **25**, 787.

[2] *Am. Chem. J.*, 13, 6.

$$\begin{array}{l} \underset{\text{VI.}}{C_6H_5CN} + \underset{\text{VII.}}{C_6H_5CH_2COOH} \searrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \underset{\text{V.}}{C_6H_5CH_2CONHCOC_6H_5} \\ \underset{\text{VIII.}}{C_6H_5CH_2CN} + \underset{\text{IX.}}{C_6H_5COOH} \nearrow \end{array}$$

The writers have now reexamined the action of benzoyl chloride on phenylacetophenylamidine and find that the original conclusions were correct. Working under the same conditions, we obtained again the same diacidamide, melting at 129–130°, and it underwent hydrolysis giving benzoic and phenylacetic acids. Furthermore, we have prepared this same diacidamide, V, by a new method. We find that it is formed almost quantitatively by the action of benzoylisocyanate,[1] X, on phenylacetic acid at ordinary temperature.

$$\underset{\text{X.}}{C_6H_5CO.NCO} + C_6H_5CH_2COOH = \underset{\text{V.}}{C_6H_5CH_2CONHCOC_6H_5} + CO_2.$$

An attempt to prepare the amide by the action of benzoylisothiocyanate on phenylacetic acid was unsuccessful. The only product isolated in a pure condition was diphenyldiacetamide, XI, melting at 192°.

$$C_6H_5CO.NCS + C_6H_5CH_2COOH \longrightarrow \underset{\text{XI.}}{(C_6H_5CH_2CO)_2NH.}$$

These interesting results naturally led us to repeat the experiments of Colby and Dodge.[2] Following carefully their directions, we heated benzonitrile with phenylacetic acid and also phenylacetonitrile with benzoic acid, but obtained in neither case a diacidamide, melting at 171°. We obtained a crystallin substance which melted, after one crystallization from alcohol, at about 170°, but it was at once apparent, by examination under the microscope, that this was not a definit compound but a mixture. It was identified as a mixture of dibenzamide and diphenyldiacetamide, which were easily separated from each other by fractional crystallization from alcohol. Diphenyldiacetamide was the chief product of the reaction in both cases and melted sharply at 192°. These results explain satisfactorily why Colby and Dodge obtained benzoic and phenylacetic acids by hydrolysis of their supposed amide with alkali. A mixture of the two above amides would give the same acids on hydrolysis as pure benzoylphenylacetamide. Therefore, *benzoylphenylacetamide melts at 129–130° and not at 171°.*

Experimental Part.

Action of Benzoylisocyanate on Phenylacetic Acid. Formation of Benzoylphenylacetamide, $C_6H_5CONHCOCH_2C_6H_5$.—The benzoylisocyanate used for this preparation was prepared according to Billeter's directions,[2] by the action of benzoylchloride on silver cyanate.

Five grams of the freshly distilled isocyanate were poured upon 5 grams

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[1] Billeter, *Ber.*, 36, 3218.

[2] *Loc. cit.*

of dry phenylacetic acid, in a dry flask. They reacted immediately with violence and with evolution of carbon dioxide giving a clear liquid, which solidified in a few minutes. After heating on the steam bath for about 1 hour, to complete the reaction, the reaction product was treated with alcohol, when we obtained two substances differing decidedly in solubility in this solvent.

The chief amount was very soluble in hot alcohol and separated, on cooling, in colorless needles. After recrystallization from absolute alcohol, it melted sharply at 129–130° to a clear oil, and was identified as benzoylphenylacetamide. The compound was absolutely identical with the diacidamide obtained by the action of benzoylchloride on phenylacetophenylamidine.[1] A mixture of the two melted at the same temperature. A mixture of the diacidamide and benzamide melted at 105–115°. The compound was decomposed by alkali giving a mixture of benzoic and phenylacetic acids. Analysis (Kjeldahl):

Calculated for $C_{15}H_{13}O_2N$: N, 5.8 ; C_7H_7ON, 11.5.
Found: N, 6.00; 6.1

The product difficultly soluble in alcohol was identified as dibenzoylurea and melted at 208–211°. A nitrogen determination gave (Kjeldahl):

Calculated for $C_{15}H_{12}O_3N_2$: N, 10.4; Found, 10.0 per cent.

Action of Benzoylisothiocyanate on Phenylacetic Acid. Formation of Diphenyldiacetamide, $(C_6H_5CH_2CO)_2NH$.—This isothiocyanate reacts less energetically with phenylacetic acid than the corresponding benzoylisocyanate. Five grams of phenylacetic acid were dissolved in 5 grams of benzoylisothiocyanate and the solution heated in an oil bath at 104–110°. Carbonoxysulfide was slowly evolved and after heating about 17 hours the oil finally solidified. This product behaved in every respect like a mixture. After two crystallizations from 95 per cent. alcohol it separated in uniform crystals and melted at 170–175° but the melt was turbid in appearance and did not become transparent until heated to 185°. After several recrystallizations of this apparently homogeneous substance, a constant melting point of 191–192° was obtained and the compound identified as diphenyldiacetamide. A mixture of the compound and some pure diphenyldiacetamide melted at the same temperature. Analysis (Kjeldahl):

Calculated for $C_{16}H_{15}O_2N$: N, 5.53. Found, 5.7.

Action of Benzonitrile on Phenylacetic Acid.—Ten grams of the nitrile, 13.6 grams of phenylacetic acid and 3 drops of acetic anhydride were heated in a sealed tube for 5 hours at 200°, then 5.5 hours at 240° and finally for 2 hours at 260°. When the tube was opened, we obtained a colorless, crystallin substance suspended in some oil having the charac-

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[1] Wheeler, Johnson and McFarland, *Loc. cit.*

teristic odor of benzonitrile. The solid was purified by crystallization from 95 per cent. alcohol and melted, after the third crystallization, constant at 192°. It was identified as diphenyldiacetamide. Analysis (Kjeldahl):

Calculated for $C_{16}H_{15}O_2N$: N, 5.53; Found, 5.59.

Action of Phenylacetonitrile on Benzoic Acid.—Ten grams of the nitrile and 10.4 grams of benzoic acid were heated for 5 hours at 240° and finally for 2 hours at 260°. On opening the tube we obtained a crystallin substance and an oil having the odor of benzonitrile. The solid was triturated with a little cold 95 per cent. alcohol to remove the oil, and melted without further purification at about 166–172° to a turbid liquid. It behaved in every way like a mixture, and after two recrystallizations from alcohol the melting point was raised to 192° indicating the presence of diphenyldiacetamide. A mixture of the compound and some diphenyldiacetamide from the previous experiment melted at exactly the same temperature. The alcoholic filtrates, after crystallization of the diacidamide, were combined and concentrated. On cooling, colorless prisms finally separated, which melted, not sharply, at 145–147°. Not enough of this material was obtained sufficiently pure for analyses, but its melting point, and the fact that it was decomposed by alkali giving only benzoic acid, indicated that it was dibenzamide.

Action of Benzoylisocyanate on β-Phenylpropionic Acid. Formation of β-Phenylpropionylbenzamide,[1] $C_6H_5CONH.CO.CH_2CH_2C_6H_5$.—Benzoylisocyanate and the above acid reacted almost immediately, on mixing, with evolution of heat and carbon dioxide. After heating at 100° for a few minutes the reaction was complete and the diacidamide was obtained in a crystallin condition. The yield was practically quantitative. It crystallized from alcohol and melted at 104–105° to a clear oil. Analysis (Kjeldahl):

Calculated for $C_{16}H_{15}O_2N$: N, 5.35; Found, 5.14.

NEW HAVEN, CONN.,
January 21, 1911.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

2,3-DIMETHYLHEXANE.

BY LATHAM CLARKE.

Received February 8, 1911.

This paper contains first an account of the preparation and properties of 2,3-dimethylhexane, $CH_3CH(CH_3)CH(CH_3)CH_2CH_2CH_3$, the study of which has been taken up in continuation of a research on the octanes begun some time ago in the laboratory;[2] and second, a comparison of eight octanes, *viz.*, normal octane, the three methylheptanes, and the

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[1] Colby and Dodge, *Loc. cit.*

[2] Preliminary Notice, *Ber.*, 40, 352.