2. The specific volumes of these proteins are identical and independent of *P*H and, within the limits of error, also identical with the specific volumes of all other proteins studied in this Laboratory, except the hemocyanins. This fact is in line with the result of the molecular weight determinations, according to which all the proteins in question are loosely built up of units of approximately the same mass, *viz.*, 34,500. It is also probable that they have the same general constitution.

3. The light absorption of the phycoerythrins from *Porphyra* and *Ceramium* are identical and the same is the case for the corresponding phycocyans. The light absorption of phycocyan from *Aphanizomenon* is different from that of the *Rhodophyceae* proteins.

4. Near the isoelectric points the molecular weights of these three proteins are identical and approximately 208,000 ± 5000. With increasing *P*H decomposition of the molecules takes place. The phycoerythrin is the most stable one. At *P*H 6.8 it is still undecomposed but at *P*H 11.0 it consists of a mixture of 75% 208,000 and 25% $^1/_6 \times 208{,}000$. Phycocyan from *Porphyra* shows indications of decomposition at *P*H 6.8 but the bulk of it consists of $^1/_2 \times 208{,}000$ at that *P*H; at *P*H 11.0 it is decomposed into small units of varying size. Phycocyan from *Aphanizomenon* is decomposed into a mixture of 65% of 208,000 and 35% of 100,000 at *P*H 6.8 and is completely decomposed into the protein unit $^1/_6 \times 208{,}000$ at *P*H 12.0.

UPSALA, SWEDEN

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

THE PYROCHEMICAL DECOMPOSITION OF AZIBENZIL

BY JOHN J. RITTER AND GEORGE M. WIEDEMAN

RECEIVED JUNE 20, 1929 PUBLISHED DECEMBER 11, 1929

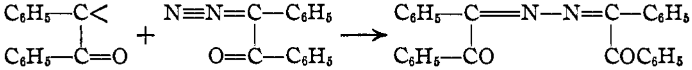
Introduction

Schroeter's[1] method for the preparation of diphenylketene has been recommended by Staudinger[2] in a slightly modified form as the most convenient source of that substance. The operations involved are (1) the preparation of benzil monohydrazone, (2) oxidation of this in benzene with mercuric oxide to azibenzil and (3) decomposition of azibenzil at 110–120° to nitrogen and diphenylketene in an atmosphere of carbon dioxide. During the preparation of diphenylketene in this Laboratory by this procedure certain hitherto unreported observations were made. The purpose of the present communication is to report on these, and also to describe a convenient and somewhat modified procedure used successfully by us in the synthesis of diphenylketene.

[1] Schroeter, *Ber.*, **42**, 2336 (1909).

[2] Staudinger, *ibid.*, **44**, 1619 (1911).

The decomposition of azibenzil into nitrogen and diphenylketene according to the procedure described by Staudinger yields, in addition, a viscous difficultly volatile nitrogen-containing residue. Staudinger[3] isolated from this residue a yellow crystalline solid melting at 201°, and assumed it to be a product of the addition of diphenylketene to azibenzil. We have noted that the residue yields, on distillation at ordinary pressure, benzonitrile and benzoic acid. The clue as to the source of these latter products was furnished by our further observation that *bis*-benzilketazine is also one of the products of the decomposition of azibenzil by heat. Its formation is apparently due to the addition of the desylene residue, formed by the loss of nitrogen from azibenzil, to a molecule of unchanged azibenzil



$$\begin{array}{l} C_6H_5-C< \\ \qquad | \\ C_6H_5-C=O \end{array} + \begin{array}{l} N\equiv N=C-C_6H_5 \\ \qquad\qquad | \\ \quad O=C-C_6H_5 \end{array} \longrightarrow \begin{array}{l} C_6H_5-C=N-N=C-C_6H_5 \\ \qquad | \qquad\qquad\quad | \\ C_6H_5-CO \qquad\quad COC_6H_5 \end{array}$$

The formation of azines from aliphatic diazo compounds has been reported by Staudinger and Kupfer[4] and by Hellerman, Cohn and Hoen,[5] and has been explained by these investigators in an analogous manner. It seemed probable, furthermore, that the production of benzonitrile on distillation of the viscous residue from the heat decomposition of azibenzil was due to the presence of *bis*-benzilketazine. Meisenheimer and Heim[6] obtained, among other products, benzonitrile and stilbene on the distillation of benzaldazine; *bis*-benzilketazine would be expected to yield benzonitrile and dibenzoylstilbene, if it were to behave in a similar fashion. Curtius and Blumer,[7] who first prepared *bis*-benzilketazine, reported that it may be distilled without decomposition; Staudinger and Kupfer[4] state that it may be heated for two hours at 180–200° without alteration. We have observed that it yields, on distillation at ordinary pressure, benzonitrile and benzoic acid. It is therefore quite evident that the yellow solid isolated by Staudinger (m. p. 201°) is *bis*-benzilketazine (m. p. 202°, corr.).

Further study of the decomposition of azibenzil by heat showed that it may be converted to diphenylketene with a yield of 45% by suspending crystalline azibenzil in ligroin and refluxing the mixture for several hours.

Experimental Part

Benzil Monohydrazone.—The best method for the preparation of this compound was found to be the following modification of the procedure of Curtius and Thun:[8] 88 g. of benzil was dissolved in 220 cc. of boiling 95% alcohol in a 500-cc. three-necked flask fitted with a reflux condenser, mechanical stirrer and dropping funnel. The solution was stirred and refluxed while 50 g. of 42% hydrazine hydrate solution was

---

[3] Staudinger, *Ber.*, **44**, 16 (1911).

[4] Staudinger and Kupfer, *ibid.*, **44**, 2201 (1911).

[5] Hellerman, Cohn and Hoen, THIS JOURNAL, **50**, 1716 (1928).

[6] Meisenheimer and Heim, *Ann.*, **355**, 274 (1907).

[7] Curtius and Blumer, *J. prakt. Chem.*, [2] **52**, 117, 137 (1895).

[8] Curtius and Thun, *ibid.*, [2] **44**, 168 (1891).

slowly added during half an hour. After the hydrazine hydrate had been all added the mixture was refluxed for an additional two hours. During the heating a part of the sparingly soluble monohydrazone separated in crystalline form. After cooling of the mixture, 83 g. of crude monohydrazone was filtered off. The melting point of the crude product was 148–154°, corr. It was crystallized once from boiling 95% alcohol (0.06 g. per cc.), and the recrystallized product was found to melt at 151–152° (corr.). Curtius and Thun[8] report the melting point as 151°.

Oxidation of Benzil Monohydrazone.—Twenty-five grams of recrystallized finely divided benzil-monohydrazone was suspended in 200 cc. of ether in a 500-cc. flask and 25.5 g. of yellow mercuric oxide added. The mixture was stirred mechanically for four hours. The time required for complete oxidation was found to vary considerably with the character of the mercuric oxide used. Uniformly good results were obtained with mercuric oxide prepared in the following manner: 500 cc. of cold 0.3 *M* mercuric acetate solution was added to 200 cc. of cold 2.5 *M* sodium hydroxide solution. The mercuric oxide which was precipitated was washed repeatedly by decantation with cold water until free from alkali. It was then filtered with suction and air-dried. The most rapid oxidation of the hydrazone occurred when freshly prepared mercuric oxide was used; on standing for a short time in diffused daylight the latter decomposed partly with liberation of mercury, and in this condition was not suitable for use.

After completion of the oxidation the ethereal solution of azibenzil was filtered and dried over calcium chloride. It was then placed in a vacuum desiccator and the latter evacuated. After removal of the ether in this way, 17.7 g. of azibenzil, m. p. 79° corr., was obtained in good crystalline form. This method is substantially the same as that of Forster and Cardwell.[9]

Decomposition of Azibenzil by Heat. A.—Twenty-five grams of benzil monohydrazone was oxidized with mercuric oxide in dry benzene and the resulting solution of azibenzil dried over calcium chloride. This solution was then allowed to drop into a small distilling flask at 110–120° while nitrogen was passed continuously through the flask. These operations were carried out according to Staudinger's directions.[2]

Diphenyl ketene was formed and removed from the reaction products by vacuum distillation in an atmosphere of nitrogen. A difficultly volatile viscous residue remained in the distilling flask. On distillation at ordinary pressure it yielded an oily distillate with the odor of benzonitrile, boiling from 167 to 189°. On cooling the distillate a portion of it solidified to a colorless crystalline mass.

B.—Seventeen and seven-tenths grams of crystalline azibenzil was suspended in 107 cc. of 60–90° ligroin which had been previously refluxed with potassium permanganate solution, washed and dried. The mixture was refluxed for eight hours on the water-bath, during which time the azibenzil slowly decomposed, the greater part of the decomposition products dissolving in the ligroin. After the azibenzil had disappeared, the solution was allowed to cool and was decanted from a small amount of *bis*-benzalketazine which was deposited on the walls of the flask during the reaction. The diphenyl ketene content of the ligroin solution was determined by precipitation with aniline and weighing of the diphenylacetanilide formed. Forty cc. of the solution gave 3.5 g. of diphenylacetanilide corresponding to a yield of 45% based on the azibenzil. The *bis*-benzilketazine melted at 202° (corr.) and its identity was established further by comparison with an authentic sample of the pure material, prepared as described in the following section.

Preparation of *Bis*-benzilketazine.—*Bis*-benzilketazine has been obtained by Curtius and Blumer[10] together with other products, by heating benzoin hydrazone alone

---

[9] Forster and Cardwell, *J. Chem. Soc.*, **103**, 868 (1913).

[10] Curtius and Blumer, *J. prakt. Chem.*, [2] **52**, 132 (1895).

in alcoholic solution, or by passing hydrogen chloride into a suspension of benzoin hydrazone in ether. Curtius and Kastner[11] obtained it by dissolving benzil monohydrazone in sulfuric acid and pouring the solution into water at zero, or by heating benzil monohydrazone with benzil at 200°. Staudinger and Kupfer[4] heated benzil monohydrazone for two hours at 240° and also got *bis*-benzilketazine. We were unable to find any mention in the literature of the following simple method used in this work for its preparation.

Fifty grams of benzil was dissolved in 135 cc. of 95% alcohol, 14 g. of hydrazine hydrochloride dissolved in 30 cc. of boiling water was added and the solution boiled on the steam-bath for five minutes. The ketazine separates rapidly from the boiling solution as a voluminous yellow mass. It was filtered from the hot solution, washed with hot alcohol and recrystallized from boiling glacial acetic acid (0.25 g. per cc.). The yield is quantitative. The recrystallized product melted at 202° (corr.). Staudinger and Kupfer report 195–196°; Curtius and Blumer, 202°. Our product, like that of Curtius and Blumer, yielded benzil on hydrolysis with aqueous sulfuric acid.

Distillation of *Bis*-benzilketazine.—Twelve grams of recrystallized material was placed in a distilling flask with a low side-arm, and distilled from a metal-bath through an air condenser. When the temperature of the bath reached 250°, a yellow oil began to distil over. Distillation was continued until the temperature of the bath reached 360°. A thermometer placed in the vapor during the distillation read 167° at the beginning and 169° at the end of the distillation. A portion of the oily distillate solidified on cooling and was removed mechanically from the air condenser. The oil was found to boil at 189°. This fraction was identified as benzonitrile by converting a portion of it to benzoic acid by hydrolysis. The solid which separated from the oil on cooling was identified as benzoic acid.

Summary

1. A modified procedure for the synthesis of diphenyl ketene by Schroeter's reaction has been described.

2. The decomposition of azibenzil by heat has been shown to yield *bis*-benzilketazine.

3. Distillation of *bis*-benzilketazine yields benzonitrile and benzoic acid.

NEW YORK, N. Y.

---

[11] Curtius and Kastner, *J. prakt. Chem.*, **83**, 215–232 (1911).