

increase for a saturated solution is 27.28 cc. per gram atom of potassium. It is found to increase at lower concentrations to a maximum value of 29.80 cc. and then to decrease in solutions containing a smaller amount of dissolved metal.

In order to point out the abnormal behavior of solutions of metals in liquid ammonia, the density of solutions of sodium bromide has been measured at  $-33.2^{\circ}$  over a considerable concentration range. The density of these solutions is found to decrease with decreasing concentration of sodium bromide in a normal manner.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN INVESTIGATIONS  
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## THE THERMAL DECOMPOSITION OF AZINES

BY LOUIS B. HOWARD AND GUIDO E. HILBERT

### A NOTE ON THE THERMAL DECOMPOSITION OF BENZALDAZINE UNDER 1000 ATMOSPHERES PRESSURE OF NITROGEN, HYDROGEN AND AMMONIA

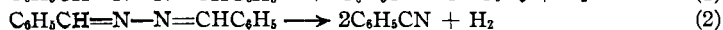
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## THE THERMAL DECOMPOSITION OF AZINES

Curtius and Jay<sup>1</sup> observed that aldazines, notably benzaldazine, decompose upon distillation into stilbenes and nitrogen. Later Meisenheimer<sup>2</sup> pointed out that benzonitrile was also one of the thermal decomposition products of benzaldazine and postulated two simultaneous reactions.



The most comprehensive study was that of Pascal and Normand,<sup>3</sup> who demonstrated in the case of benzaldazine that in addition to stilbene and nitrogen, some ammonia, a small amount of phenanthrene and a stable compound containing nuclear nitrogen were also produced. Azines in which the ortho position of the benzene ring was substituted yielded none of the phenanthrene derivatives. They suggested that the stable nuclear nitrogen compound (yield 15%) had the empirical formula of  $\text{C}_{23}\text{H}_{29}\text{N}_3$  (melting point  $261^{\circ}$  and boiling point  $460^{\circ}$ ) and probably was identical with the unknown product obtained by Curtius and Blumer<sup>4</sup> in the pyrolysis of benzoinhydrazone. The purposes of the present investigation were to

<sup>1</sup> Curtius and Jay, *J. prakt. Chem.*, [2] 39, 45 (1889).

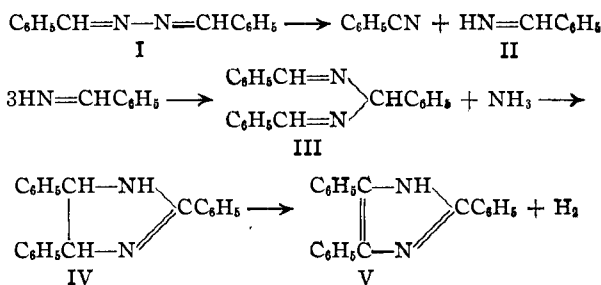
<sup>2</sup> Meisenheimer and Heim, *Ann.*, 355, 274 (1907).

<sup>3</sup> Pascal and Normand, *Bull. soc. chim.*, [4] 9, 1029 (1911); [4] 9, 1059 (1911); [4] 11, 21 (1912).

<sup>4</sup> Curtius and Blumer, *J. prakt. Chem.*, [2] 52, 126 (1895).

identify the extremely stable nitrogen compound of Pascal and Normand, to determine if analogous substances are formed in the decomposition of other aldazines, and to develop a satisfactory mechanism to explain the formation of the various products. In addition, a semi-quantitative study of the decomposition products of benzaldazine was made in order to ascertain whether the pyrolysis was appreciably affected by the application of 1000 atmospheres pressure of nitrogen, hydrogen, and ammonia.

The findings of the French investigators on the formation of the nuclear nitrogen compound have been confirmed. The product (17% yield) on purification, however, melted somewhat higher (m. p. 275°) and the analytical value for nitrogen was considerably lower than previously reported. It emitted visible light on oxidation, which is a property characteristic of lophine (V) with which it was subsequently shown to be identical. Since lophine is readily obtained by the pyrolysis of hydrobenzamide (III) under similar conditions<sup>5</sup> the following mechanism immediately suggests itself. It is known that benzalimine (II) is easily converted with



the elimination of ammonia<sup>6</sup> to hydrobenzamide and that the latter probably passes through amarine (IV) to form lophine (V). This mechanism in which all of the steps, with the exception of the first (I-II), have been well established, offers a simple and reasonable explanation for the formation of the ammonia and benzonitrile as well as the lophine. The azine must simultaneously decompose in another manner to yield stilbene and nitrogen as expressed in equation (1).

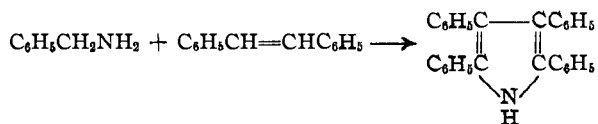
A number of other mechanisms for the formation of lophine are theoretically possible. One of these consists of the interaction of two moles of benzonitrile with an intermediate benzal radical. This was readily shown to be improbable since the pyrolysis of the azine in the presence of a large excess of the nitrile did not lead to any increase in the yield of lophine.

<sup>5</sup> Hurd, "Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1928, p. 247.

<sup>6</sup> Busch, *Ber.*, 29, 2143 (1896); Escourrou, *Bull. soc. chim.*, [4] 45, 742 (1929), found that benzalimine was considerably more stable than reported by Busch, but was broken down to ammonia and hydrobenzamide upon boiling below 175° at 10 mm. pressure.

Moreover, when the pyrolysis was carried out in the presence of copper powder, which in this case appeared to be a dehydrogenating catalyst, the yields of both lophine (12.3 to 1.4%) and stilbene (41 to 9.6%) diminished considerably, whereas that of benzonitrile was greatly increased (8.6 to 38.4%). Virtually the same result was obtained by raising the temperature of decomposition. This was effected by placing the azine in a steel bomb which was plunged into a metal bath already heated to the desired temperature. Under these conditions it seems probable that equation (2) represents the main course of the reaction and that the toluene observed arose as a result of the liberated hydrogen.

A further possibility for the formation of lophine was the reduction of part of the benzaldazine to benzyl or dibenzylamine<sup>7</sup> and the subsequent interaction of either of these with stilbene, or pyrolysis *per se*. Accordingly, both benzylamine and dibenzylamine were heated alone at 300° for forty hours and found to produce a mixture of lophine and tetraphenylpyrrole. Since it was felt that the low yield of lophine was due, possibly, to an insufficient amount of stilbene formed in the pyrolysis of the amines, the thermal decomposition was carried out in the presence of stilbene. The yield of tetraphenylpyrrole was increased markedly (9 to 22%) and lophine, instead of being augmented, was found to be absent except in experiments which had been subjected to rapid heating. The presence of the small amounts of lophine in such cases was evidently due to a pyrolysis of benzylamine *per se*. The insignificant amount of lophine formed, coupled with the fact that the pyrolysis of benzaldazine only occasionally gave a detectable amount of tetraphenylpyrrole, seemingly eliminated the possibility of lophine formation by such a mechanism. The formation of tetraphenylpyrrole from benzylamine and stilbene is very interesting al-



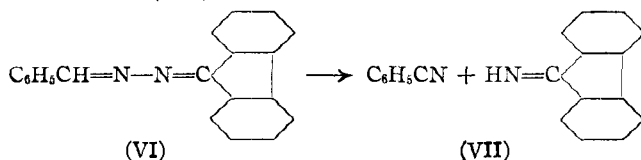
though the mechanism of its formation is not entirely obvious. It apparently arises from the interaction of some intermediate decomposition product of benzylamine, other than benzalimine, and stilbene.

It has been pointed out to us by Dr. P. H. Emmett of this Laboratory that any possible reaction between benzalimine (II) and some other molecular species of the system to give lophine (V) would be favored tremendously from the kinetic standpoint over the trimolecular reaction proposed ( $3\text{II} \longrightarrow \text{III} + \text{NH}_3$ ). The only reaction that appears to have any possibility of taking place is that occurring between benzalimine and

<sup>7</sup> There is little doubt that reducing conditions are present since both toluene and dibenzyl derivatives were obtained in the pyrolysis of anisaldazine and the dibenzyl derivative from tolualdazine (see experimental).

benzaldazine. The pyrolysis of benzaldazine in the presence of either benzalimine or benzaldehyde, however, did not lead to any increase in the yield of lophine above the normal amount expected from the individual reactants.

An effort to capture the intermediate benzalimine as N-phenylbenzalimine by pyrolysis in the presence of a large excess of aniline was unsuccessful. Since a direct method of proof of the intermediate imine formation in the case of benzaldazine was not available, it was necessary to study the thermal decomposition of an azine, the expected imine of which would be stable and isolable as such. Such an example happened to be benzalfluoreneazine (VI), which upon decomposition produced benzonitrile and 9-iminofluorene (VII). This affords excellent evidence supporting



the postulated mechanism of lophine formation.

A determination of the yields of lophine, benzonitrile and stilbene resulting from the pyrolysis of benzaldazine at 300° indicated that the reaction proceeded according to equation (1) to the extent of fifty mole per cent., and according to equation (3) to the extent of about twenty-five mole per cent. Unidentifiable residues in the form of tars constituted the balance. The yield of benzonitrile was somewhat less than that equivalent to the lophine, but this discrepancy may well have been due to the difficulty of complete separation and to possible partial polymerization.<sup>8</sup>

In order to determine whether or not other aldazines also produced analogous lophines, anisaldazine, di-*o*-chlorobenzaldazine and *p*-tolualdazine were prepared and pyrolyzed. In none of these cases was the lophine derivative isolated in the pure condition. There can, however, be little doubt that trimethyllophine was formed from *p*-tolualdazine since certain fractions, when tested with warm alcoholic potassium hydroxide and oxygen, gave the strong characteristic emission of light. In addition, *p*-tolualdazine yielded the stilbene, dibenzyl, nitrile and polymeric nitrile derivatives and a product which probably was *p*-xylene. From anisaldazine the corresponding stilbene, dibenzyl, toluene and nitrile derivatives were isolated. Di-*o*-chlorobenzaldazine formed the stilbene and nitrile derivatives and an unidentified base in small yield. Considerable hydrogen chloride and ammonium chloride were formed, indicating a rather complete degradation of much of the azine, which may well have accounted for the absence of the analogous lophine.

<sup>8</sup> In the pyrolysis of *p*-tolualdazine, a product that apparently is the polymeric toluic nitrile, was actually isolated.

The possibility that the unknown trimethoxylophine and tri-*o*-chloro-lophine could not be prepared from the corresponding benzhydramides was suggested by the failure to obtain either from the azines. Accordingly, hydroanisamide was pyrolyzed and found to yield no compound which corresponded in composition to trimethoxylophine. Only a buff-colored powder which could neither be crystallized nor rigorously purified was obtained. On the other hand tri-*o*-chlorohydrobenzamide gave a small yield of tri-*o*-chloro-lophine hydrochloride along with much hydrogen chloride and ammonium chloride. Trimethyllophine<sup>9</sup> may be obtained in fairly good yield from hydrotoluamide but its properties are such as to make its separation from the pyrolysis products of *p*-tolualdazine much more difficult than that encountered with lophine.

It has actually been found, as Pascal and Normand<sup>8</sup> suggested, that the nuclear nitrogen compound (lophine), obtained in the pyrolysis of benzaldazine, is identical with the previously unidentified product of similar properties, isolated by Curtius and Blumer<sup>4</sup> in the thermal decomposition of benzoinhydrazone. In addition to the other products obtained by Curtius and Blumer the presence of a small amount of a substance resembling tetraphenylfuran was observed.

Ketazines, in general, may be characterized as being considerably more stable (thermally) than aldazines and as being particularly reluctant to evolve free nitrogen with the formation of ethylenes. That this stability is not due to symmetry alone, as might be suggested in the case of benzophenoneketazine, is shown by the results obtained from the pyrolysis of acetophenoneketazine and the mixed ketazine of benzophenone and fluorenone. All three of these ketazines require higher temperatures to bring about decomposition than the aldazines studied and tend to eliminate benzonitrile instead of nitrogen. However, if one of the groups has a thermal lability approaching or exceeding that of hydrogen, such as the benzoyl group in bis-benzilketazine, the stability decreases as is shown by the fact that decomposition of this compound occurs at 250–270° to yield benzonitrile and benzoic acid.<sup>10</sup>

One is prone to question the usefulness of electronic interpretations as applied to thermal decompositions, especially those occurring at relatively high temperatures, such as the pyrolysis of the azines. Nevertheless, it is of interest to note several rather significant relationships. If the influence which the group R has upon the linkage between the carbon and hydrogen



<sup>9</sup> Gattermann, *Ann.*, **347**, 367 (1906); Fürth, *Monatsh.*, **27**, 843 (1906).

<sup>10</sup> Ritter and Wiedeman, *THIS JOURNAL*, **51**, 3586 (1929).

atoms (A) is considered, one should expect that an increase in the "electronegativity" of this radical<sup>11</sup> will tend to increase the instability (thermal dissociability) of the C—H linkage. The increasing ease in the elimination of hydrogen, according to equation (2) will be accompanied simultaneously by an increase in the amount of reduction products. The results are in accord with this point of view as in the pyrolysis of di-*o*-chlorobenzaldazine, benzaldazine, *p*-tolualdazine and anisaldazine, the first two compounds form negligible amounts, the third isolable amounts, and the last good yields of the toluene and dibenzyl derivatives. As might be expected, there is an accompanying increase in nitrile and decrease in lophine derivatives.<sup>12</sup>

A second implication of the concept is encountered in the case of the ketazines, in which group R<sub>1</sub> is substituted for the hydrogen atom (B) and may be of greater or weaker "electronegativity" than the substituted hydrogen atom. The ease of elimination of this group will also depend upon its own relative "negativity;" a decrease in the "negativity" tends to increase the ease of removal. It is not surprising then to find benzophenoneketazine exhibiting a markedly greater stability than benzaldazine. Acetophenoneketazine, as expected, occupies an intermediate position and yields benzonitrile. If the tendency had been toward the elimination of the more negative group, we should have obtained acetonitrile, of which not a trace was observed. Bis-benzilketazine is even more readily broken down than benzaldazine and again with the elimination of the weakly "negative" benzoyl group. Furthermore, as the radical (R<sub>1</sub>RC=) becomes relatively more "positive" by virtue of the attachment of the more "electronegative" groups R and R<sub>1</sub>, the ketazines become more polar with a decreasing tendency to decompose thermally with the ejection of molecular nitrogen.

We are greatly indebted to Dr. Reid T. Milner and Mrs. Mildred S. Sherman for carrying out the microanalyses recorded.

### Experimental

**Pyrolysis of Benzaldazine by Distillation.**—One hundred grams of benzaldazine (m. p. 93°)<sup>13</sup> was heated gradually in a short-necked distilling flask until a fairly rapid evolution of gas containing much ammonia took place. The flask was maintained at this temperature (290–310°) for ten hours during which time 6.8 g. of pale yellow oil distilled over. The residue (82.0 g.), which upon cooling solidified to a hard brown resin, was extracted and washed with a total of 500 cc. of ether. A pale gray, crystalline residue (17.0 g.) was obtained; m. p. 255–265°. Recrystallization from pyridine yielded fine colorless needles which melted at 276°. A dilute solution in alcoholic

<sup>11</sup> The radicals, methyl, *o*-chlorophenyl, phenyl, *p*-tolyl and *p*-anisyl are placed in the order of increasing "electronegativity;" see Kharasch and Flenner, *THIS JOURNAL*, **54**, 674 (1932).

<sup>12</sup> The failure to isolate the lophine derivative from *o*-chlorobenzaldazine is believed to be due to a more complete degradation as a result of chlorine elimination.

<sup>13</sup> Kuhn and Winterstein, *Helv. Chim. Acta*, **11**, 103 (1928).

potassium hydroxide emitted visible light when saturated with oxygen at 60°. When mixed with lophine prepared from hydrobenzamide<sup>14</sup> there was no depression of the melting point.

*Anal.* Calcd. for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>: N, 9.46. Found: N, 9.32.

From alcoholic hydrogen chloride the known salt was obtained which melted at 159–161° with evolution of gas.

The ether extract was evaporated to dryness and the residue distilled until no more stilbene passed over. The solidified distillate was crystallized from alcohol to yield the characteristic glistening plates which melted at 123°; yield 40 g. When mixed with an authentic specimen there was no depression of the melting point.

The oil (b. p. 190°) which distilled over during the pyrolysis had the characteristic odor of benzonitrile, and was hydrolyzed by alcoholic potassium hydroxide to benzoic acid.

**Pyrolysis of Benzaldazine in Sealed Tubes.**—The general procedure in these experiments was to seal the azine in evacuated glass tubes and to heat in an electric furnace for a given length of time at the designated temperature. In every case a considerable pressure of nitrogen and ammonia developed. The tube was made part of a three-legged system which was evacuated and then by proper manipulation of heating and cooling baths the benzonitrile was distilled into one leg and the stilbene into the other. The residues were extracted with ether to obtain the lophine in a reasonably pure condition.

TABLE I

	Azine, g.	Temp., °C.	Time, hours	Lophine, g.	Benzonitrile, g.	Stilbene, g.
I	2.08	300	18	0.255	0.180	0.850
II	2.08	300	5	.260	n. d.	n. d.
III <sup>a</sup>	2.08	300	18	.245	n. d.	n. d.
IV <sup>b</sup>	2.08	300	5	.030	0.800	0.200
V	10.4	325	5	.80 <sup>c</sup>	1.50 <sup>d</sup>	3.80
VI <sup>e</sup>	6.24	300	5	1.25	n. d.	n. d.
VII <sup>f</sup>	1.04	300	5	0.48	n. d.	n. d.

<sup>a</sup> The azine was heated with 4.0 g. of benzonitrile. <sup>b</sup> The azine was heated with 1.0 g. of copper-bronze powder. Lophine that was heated with copper powder, under the same conditions, was recovered quantitatively. <sup>c</sup> Partial evaporation of the ether extract of the lophine deposited some crystalline material which after trituration with benzene and crystallization from alcohol melted at 208–209°; yield 0.29. When mixed with tetraphenylpyrrole there was no depression of the melting point. <sup>d</sup> An odor of toluene was noted in the benzonitrile but none was separated. <sup>e</sup> The azine was heated with 6.36 g. (2 mols) of benzaldehyde. No odor of ammonia was detectable and the yield of lophine corresponded very closely to the normal amount from the azine (*ca.* 0.78 g.) in addition to that (*ca.* 0.39 g.) which was expected to form by the interaction of the benzaldehyde and ammonia. <sup>f</sup> The azine was added to a liquid ammonia solution of benzalimine prepared from 0.5 g. of hydrobenzamide [Strain, *THIS JOURNAL*, **49**, 1561 (1927)] and allowed to stand for four days. Since no interaction occurred at room temperature the tube was opened to boil off the ammonia, sealed, and plunged into the furnace at 300°. Here again the yield of lophine was remarkably close to the normal individual yields of the azine (*ca.* 0.13 g.) and the hydrobenzamide (*ca.* 0.35 g.).

**Pyrolysis of Benzaldazine in a Steel Bomb.**—A sample of 20.8 g. of benzaldazine contained in a glass bulb with a capillary opening was sealed in a steel bomb which

<sup>14</sup> Pinner, *Ber.*, **35**, 4140 (1902).

was plunged into a metal bath of large capacity previously heated to 325° and allowed to remain there for five hours. The reaction mixture was a thin, dark brown paste and the products were worked up in the usual manner. The yield of lophine was 0.51 g., of stilbene 8.25 g., of benzonitrile 3.04 g. and of toluene 0.26 g. (b. p. 111° and yielded the characteristic dinitro derivative melting at 70°).

**Preparation of Aldazines.**—The aldazines used in this work were most conveniently prepared by the following typical procedure. A cold solution of one mole of anisaldehyde in 400 cc. of 95% alcohol was treated by slow addition and stirring with one mole of 90% hydrazine hydrate. The precipitated azine was filtered from the cold solution and crystallized from a mixture of alcohol and benzene to give a yield of 125 g. (93%), m. p. 167–179° (liquid crystal).

**Pyrolysis of Anisaldazine.**—Fifty grams of the azine was heated in a short-necked distilling flask until an evolution of gas rich in ammonia began. The heat was removed but the reaction gained speed and an oil began to distil over. After the initial vigorous action had abated, heat was again applied until no further distillate passed. A considerable amount of charred residue remained which was not amenable to the isolation of a pure product. The material collected was redistilled to give 5 g. of a clear oil between 170 and 220°, 5 g. of a pale yellow oily solid between 220–270°, and finally a much higher melting solid between 270–330°. An intractable tarry residue remained.

The oil was thrice fractionated to give a portion of 1.7 g. which distilled between 174–178°. Its strong anise-like odor and boiling point suggested that it was the methyl ether of *p*-cresol (b. p. 175°). This was confirmed by oxidation with neutral permanganate to anisic acid.

The oily solid was extracted with boiling water (in which it was largely soluble), filtered and cooled. Beautiful white needles were obtained which, when dry, melted at 60°. Their identity with anisonitrile was confirmed by hydrolysis in potassium hydroxide solution to anisic acid.

The higher melting solid was crystallized from benzene to give brilliant glistening plates which melted at 205–207°. Recrystallization from a mixture of alcohol and benzene gave pure di-*p*-methoxystilbene; m. p. 215°. A portion was reduced with hydrogen and platinum oxide catalyst to the corresponding di-*p*-methoxydibenzyl; m. p. 126°. Concentration of the original benzene filtrate gave a crop of crystals which melted at 120–135°. They were treated with a sufficient quantity of boiling alcohol to dissolve about three-fourths of the material, filtered and chilled. About 1 g. of white plate-like crystals melting at 124–125° was obtained. Two recrystallizations from alcohol gave a product melting at 126–126.5°. Its identity with di-*p*-methoxydibenzyl was confirmed by the undepressed melting point when mixed with an authentic specimen.

**Pyrolysis of Di-*o*-chlorobenzaldazine.**—Twenty grams of the azine (m. p. 141°) was distilled from a short-necked flask. Hydrogen chloride was first evolved, then an oily somewhat yellowish distillate and finally a portion which solidified to a white solid in the side tube of the flask. Further heating gave only complete charring. The whole distillate was decolorized with charcoal and crystallized from alcohol to yield white needles of pure di-*o*-chlorostilbene; m. p. 97–98°. An attempt to separate pure *o*-chlorobenzonitrile from the filtrate of the first stilbene crystallization was unsuccessful. The impure material, which had a strong nitrile odor, was hydrolyzed directly with alcoholic potassium hydroxide and yielded an appreciable amount of *o*-chlorobenzoic acid; m. p. 137–139°.

In a second experiment 2.77 g. of the azine was heated in a sealed evacuated tube at 300° for eighteen hours. Upon opening the tube considerable gas containing hydrogen chloride escaped. The residue was extracted with 10 cc. of acetone which left a pale



buff colored product which melted at 250–255° (dec.). It was found to be insoluble in acetone, benzene, ether and water, but very soluble in alcohol. It gave a Beilstein test for halogen. An alcoholic solution on treatment with ammonium hydroxide yielded a white precipitate. The mixture was warmed to dissolve the precipitate and then cooled, depositing minute crystals which melted at 163–164°. When mixed with a sample of tri-*o*-chlorolophine (m. p. 167°) it melted at about 140°. There was an insufficient amount for further study. Since tri-*o*-chlorolophine hydrochloride, in which we were mainly interested, was insoluble in acetone, the original filtrate from the buff colored product was discarded.

**Pyrolysis of *p*-Tolualdazine.**—Ten grams of the azine (m. p. 153°) was heated in a sealed, evacuated tube at 325° for two hours. When cold, the material remained as a dark colored semi-solid mass and upon opening the tube a pressure of ammonia and nitrogen was released. The material was transferred to a vacuum sublimation apparatus and finally heated to 240°. An oil passed over (ca. 0.5 g.) which solidified upon cooling to 0°. It was taken up in 4–5 volumes of alcohol and chilled to deposit plate-like crystals which were worked on clay plate with a little solvent and dried. The product was very soluble in ether, melted at about 80° and was probably *p,p'*-dimethyldibenzyl (m. p. 82–86°). The filtrate from these crystals was evaporated and the residue distilled. A small fraction passed over at 140° (perhaps some *p*-xylene). The main portion, however, boiled constantly at 215°. Its identity as *p*-toluic nitrile was confirmed by hydrolysis with 60% sulfuric acid to *p*-toluic acid which after recrystallization from water melted at 175°.

After the removal of the oily products, a white solid sublimed into the receiver. It was crystallized from alcohol to give the pure 4,4'-dimethylstilbene melting at 177–178°. Greenish-yellow crystals collected on a hotter section of the vessel and were removed, extracted with hot alcohol, filtered and worked on clay plate with a little ether. A pale yellow crystalline material remained which melted at 250–260°; its properties were similar to those of polymeric toluic nitrile.<sup>15</sup> Concentration of the filtrate and the washings of this product yielded a small amount of the crude stilbene (m. p. 170°). Further concentration yielded only resins from which tri-*p*-methyllophine could not be isolated. The filtrates and resins gave the characteristic light emission when warmed with alcoholic potassium hydroxide, thus strongly indicating the presence of the lophine. Neither the polymeric nitrile nor the crude stilbene gave any visible emission.

**Pyrolysis of Benzal Fluorenone Azine.**—This mixed azine was prepared by the method of Staudinger and Kupfer,<sup>16</sup> who reported a melting point of 82–84° after crystallization from alcohol. Since our compound melted at 91–92° after one crystallization from alcohol, it was analyzed.

*Anal.* Calcd. for C<sub>20</sub>H<sub>14</sub>N<sub>2</sub>: N, 9.93. Found: N, 10.05, 9.81.

Five grams of the azine was heated in a nitrogen-filled sealed tube at 275° for about two hours. Considerable pressure of ammonia and nitrogen was released upon opening. The contents of the tube were fractionally distilled and the maximum temperature that the bath finally attained was 250°. The first fraction (0.39 g.) was identified as benzonitrile. The higher boiling portion of the distillate was a yellow solid which crystallized from ligroin in tufts of dense yellow crystals, melting at 121–122°. A mixed melting point with an authentic specimen of 9-iminofluorene was not depressed. Its identity was further confirmed by hydrolysis with dilute hydrochloric acid to fluorenone. The residue of 3.5 g. of a black brittle solid was extracted and washed with 35 cc. of

<sup>15</sup> Gattermann, *Ann.*, **347**, 367 (1906).

<sup>16</sup> Staudinger and Kupfer, *Ber.*, **44**, 2207 (1911).

acetone to leave 0.54 g. of an olive brown solid which melted between 280–300° and which could not be further purified.

#### Preparation of Some Hydrobenzamide and Lophine Analogs

**Preparation of Hydroanisamide.**—Hydroanisamide has been previously reported by Délépine<sup>17</sup> and Fischer and Prause.<sup>18</sup> It was more rapidly prepared by the following modification. A solution of 50 g. of anisaldehyde in 150 cc. of alcohol and 50 cc. of concentrated aqueous ammonia was allowed to stand in the cold for two days. Shaking induced crystallization and the beautiful white product so obtained was collected, washed with alcohol and desiccated; m. p. 126–127°; yield 92% of the theoretical.

**Attempt to Prepare Trimethoxylophine.**—Twenty grams of hydroanisamide heated in an open flask to 275° underwent an exothermic reaction with the evolution of much ammonia. The temperature was raised to and maintained at 310° for a few minutes until the reaction subsided. Trituration of the cooled dark brown product with ether yielded only a buff colored powder (m. p. 150–160°) which could neither be crystallized from any ordinary solvents nor further purified. Oxidation with permanganate in acetone gave some anisic acid.

*Anal.* Calcd. for  $C_{22}H_{22}O_4N_2$ :<sup>19</sup> C, 72.50; H, 5.36; N, 6.77. Found: C, 73.31, 72.99; H, 5.62, 5.24; N, 6.76, 6.78.

The original ether extracts yielded an intractable tar.

**Preparation of Tri-*o*-chlorohydrobenzamide.**—A solution of 62 g. of *o*-chlorobenzaldehyde in 150 cc. of 95% alcohol was treated in the cold with 50 cc. of concentrated aqueous ammonia. Within an hour a layer of oily appearance began to form at the bottom of the stoppered flask and after two days had solidified to a hard cake which was finely divided and crystallized from alcohol to a light buff colored product which melted at 98–100°. One recrystallization from acetone gave a pure white product which melted at 101–102°.

*Anal.* Calcd. for  $C_{21}H_{15}Cl_3N_2$ : N, 6.98. Found: N, 6.98 (Kjeldahl).

**Tri-*o*-chlorolophine.**—Ten grams of tri-*o*-chlorohydrobenzamide was heated on an oil-bath in a long-necked round-bottomed flask. At 240° some hydrogen chloride began to escape and a small amount of liquid distilled up into the neck of the flask. The temperature was raised to and maintained at 305° for one-half hour. A small amount of white solid which had sublimed up into the neck was found to be ammonium chloride. The dark brown residue was extracted in the cold with 50 cc. of acetone, which left 2 g. of a light buff colored product. This product which was found to contain both halogen (Beilstein) and nitrogen (sodium fusion) was insoluble in water, acetone and ether, but readily soluble in methyl, ethyl and butyl alcohols from which solution it was precipitated by the addition of ether as a white microcrystalline product which melted at 330° to a brown liquid. It analyzed well for tri-*o*-chlorolophine hydrochloride.

*Anal.* Calcd. for  $C_{21}H_{14}N_2Cl_4$ : N, 6.42. Found: N, 6.49, 6.39 (Kjeldahl).

The hydrochloride did not separate from a hot saturated solution upon chilling or diluting with as much as five parts of water but the addition of a drop of hydrochloric acid or a little ammonium chloride solution induced crystallization at once. A portion of the hydrochloride dissolved in a little alcohol was diluted with much water and made ammoniacal. The white precipitate which immediately formed was dried on a clay plate and crystallized from dilute methyl alcohol in clumps of small colorless needles

<sup>17</sup> Délépine, *Compt. rend.*, **126**, 343 (1898); m. p. 125–127°.

<sup>18</sup> Fischer and Prause, *J. prakt. Chem.*, [2] **77**, 129 (1908); m. p. 130°.

<sup>19</sup> Trimethoxylophine would have the composition  $C_{24}H_{22}O_3N_2$ .

which melted at 169–170°, and were found to be very soluble in all ordinary organic solvents.

*Anal.* Calcd. for  $C_{21}H_{13}N_2Cl_3$ : C, 63.08; H, 3.28. Found: C, 63.46, 63.46; H, 3.38, 3.31.

A solution in warm alcoholic potassium hydroxide did not emit visible light upon saturating with oxygen.

**The Pyrolysis of Benzoin Hydrazone.**—Benzoin hydrazone was prepared and pyrolyzed by the method of Curtius and Blumer.<sup>20</sup> Besides the tetraphenylpyrazine (m. p. 246°) and the bis-benzilketazine (m. p. 202°) we obtained a small amount of white crystalline material which deposited from the alcoholic solution of the pyrolysis product upon standing for a day or two after the pyrazine and ketazine had been removed. It was triturated with a little ether and recrystallized from alcohol to a pure white crystalline product which melted at 173°. It was possibly tetraphenylfuran. A portion of the filtrate, after the isolation of each of the various products, was tested for light emission in alcoholic potassium hydroxide. In every case a strong emission was observed which persisted after the product of m. p. 173° was removed. This filtrate after standing for three weeks deposited some yellowish material which after trituration with ether sintered at 200° but was not completely melted up to 260°. As it was impossible to purify it satisfactorily by crystallization,<sup>21</sup> it was sublimed in a small test-tube. The color was removed from the dark product obtained by washing with ether, m. p. 271–273°. When mixed with known lophine the melting point was 272–274°. Both this product and the one melting at 200–260° gave excellent chemiluminescence.

#### The Formation of Lophine and Tetraphenylpyrrole in the Thermal Decomposition of Benzylamine

**Pyrolysis of Benzylamine.**—A bomb tube containing 5 g. of benzylamine was gradually heated over a period of four hours to 300° and allowed to remain at this temperature for forty-four hours. A considerable pressure of ammonia developed and the reaction mixture was a yellowish brown, semi-solid, crystalline mass. It was thoroughly triturated with 30 cc. of ether and the insoluble colorless needles collected and identified as lophine; wt. 0.43 g., m. p. 270°. The ether was removed from the filtrate and the residue treated with 25 cc. of boiling alcohol and cooled. The crystals that separated were removed by filtration. The alcohol filtrate on evaporation yielded an additional amount of the same product. The total precipitate (0.40 g., m. p. 206°) was recrystallized several times from boiling alcohol in which it was slightly soluble and from which it separated as stout needles melting at 215° (corr.). It was insoluble in water, soluble to the extent of 1 g. in 100 cc. of ether and did not form a hydrochloride. The properties and analysis agreed well for those of tetraphenylpyrrole.

*Anal.* Calcd. for  $C_{23}H_{21}N$ : C, 90.52; H, 3.77; N, 5.70. Found: C, 90.19, 90.45; H, 3.75, 3.91; N, 5.73, 5.65.

Toluene, benzonitrile, stilbene and dibenzyl were also formed. These received only a superficial examination as we were mainly interested in the nuclear nitrogenous products.

**Pyrolysis of Benzylamine in the Presence of Stilbene.**—Five cubic centimeters of benzylamine and two grams of stilbene were heated under the same conditions as described above. Much ammonia was formed and the reaction product was a pale

<sup>20</sup> Curtius and Blumer, *J. prakt. Chem.*, [2] 52, 124 (1895).

<sup>21</sup> Curtius and Blumer<sup>20</sup> were unable to purify their product above a melting point of 261° by crystallization although they were unquestionably dealing with this impure lophine.

yellow solid. It was treated with 30 cc. of ether and filtered. The insoluble matter was shown to be tetraphenylpyrrole. The filtrate was worked up in the usual manner and the combined pyrrole weighed 1.10 g. The various fractions did not exhibit chemiluminescence, indicating the absence of lophine. In one experiment, however, 0.07 g. of lophine was isolated.

Experiments in which the ratio of benzylamine to stilbene was increased tended to decrease the yield of tetraphenylpyrrole. A typical example was an experiment involving 5 g. of benzylamine and 1 g. of stilbene; the yield of the pyrrole was 0.70 g. and lophine was found to be absent. The reaction was appreciably affected by increasing the rate of heating and resulted in the formation of a marked amount of lophine. One experiment, in which the bomb tube containing 5 g. of benzylamine and 1 g. of stilbene was introduced into the furnace heated to 300°, yielded 0.20 g. of lophine and 0.66 g. of tetraphenylpyrrole.

A solution of benzaldehyde, or benzyl alcohol, or benzyl ether with stilbene heated to 300° for forty hours did not yield any tetraphenylfuran.

**Pyrolysis of Dibenzylamine in the Presence of Stilbene.**—Five grams of dibenzylamine and 3 g. of stilbene were heated under the same conditions as given above. The results of the experiment in general were quite similar. The yield of tetraphenylpyrrole was 1.0 g. and lophine was absent.

#### Pyrolysis of the Ketazines

**Benzophenoneketazine.**—This ketazine (m. p. 163–164°) was heated in a sealed evacuated tube at 300° for eighteen hours. Upon opening, the tube was still partially evacuated and although a distinct odor of benzonitrile was present the ketazine was recovered almost quantitatively.

In another experiment, a container with 5 g. of ketazine *in vacuo* was heated at 350° for one hour. It was cooled and the pressure found to be less than atmospheric. The brown oil had a faint odor of ammonia and on distillation yielded 0.7 g. of benzonitrile. Further distillation under diminished pressure gave fractions of 1.3 g. between 160–175° at 4 mm. of a colorless oil and 0.7 g. between 190–225° at 6 mm. of a yellow viscous oil. These products were not identified. A tarry residue remained.

**Acetophenoneketazine.**—A portion of 50 g. (m. p. 121–122°) heated in a long-necked distilling flask began to decompose at a temperature of 296–340° and a fraction weighing 8.0 g. of a pale yellow oil boiling at 185–210° was collected. The oil smelled strongly of ammonia and benzonitrile. A second fraction of 2.8 g. of a pale yellow oil passed as the temperature of the residue increased to 370°. The combined distillate was fractionated and after repeated distillation a portion of 1.3 g. of pure ethylbenzene (b. p. 135.5°) was obtained which was confirmed by oxidation with aqueous permanganate to benzoic acid. Most of the remaining distillate was benzonitrile (b. p. 186°) which was hydrolyzed by alcoholic potassium hydroxide to benzoic acid. The residues were discarded because of their tarry nature.

**Mixed Ketazine of Fluorenone and Benzophenone.**—This compound was prepared by warming for one-half hour on the water-bath a solution of 18.0 g. of fluorenone and 19.6 g. of benzophenonehydrazone in 100 cc. of glacial acetic acid. The solution became deep red orange in color and after standing overnight deposited 33.7 g. of orange colored crystals; m. p. 105–107°; yield 94% of the theoretical. Recrystallization from glacial acetic acid gave two crystalline forms. The one form separated on rapid cooling as feathery tufts and the other on slow cooling as prismatic blocks. The ketazine was extremely soluble in cold ether, benzene, acetone and dioxane and quite soluble in hot ligroin, alcohol and acetic acid; m. p. 109–110°.

*Anal.* Calcd. for  $C_{24}H_{18}N_2$ : C, 87.11; H, 5.06; N, 7.83. Found: C, 87.07, 87.01; H, 4.77, 5.18; N, 7.97, 7.92.

Ten grams of the ketazine was heated gradually in a small distilling flask to 340° before any decomposition was noticeable. Between 350–360° a slow decomposition took place with the elimination of a small amount of ammonia and the distillation of about 1 g. of oil in one and one-half hours. On standing the oil deposited pale yellow needles which were identified as 9-iminofluorene (hydrolyzed by dilute acid to fluorenone), m. p. 123°.

*Anal.* Calcd. for  $C_{13}H_9N$ : C, 87.15; H, 5.03. Found: C, 87.23, 86.98; H, 5.19, 5.44.

The oil from the needles was purified by distillation and identified as benzonitrile. The residue solidified to a brittle tar on cooling.

### A NOTE ON THE THERMAL DECOMPOSITION OF BENZALDAZINE AT 1000 ATMOSPHERES PRESSURE OF NITROGEN, HYDROGEN AND AMMONIA

Benzaldazine was selected from the azines studied since its decomposition products were the most convenient to isolate. In each experiment 20.8 g. of benzaldazine was placed in a glass container inserted in a Rezial bomb, which was then charged with 1000 atmospheres of the desired gas. The bomb was then placed in a controlled temperature metal bath for five hours. Some representative results are given in the following table.

TABLE II

	333 atm. $H_2$ 300°, g.	1000 atm. $H_2$ 275°, g.	1000 atm. $H_2$ 300–315°, g.	1000 atm. $N_2$ 280°, g.	1000 atm. $NH_3$ 282°, g.	1000 atm. $NH_3$ 245°, g.
Lophine	2.46 <sup>a</sup>	2.31 <sup>b</sup>	0.30	2.1 <sup>c</sup>	3.05 <sup>b,d</sup>	3.46 <sup>b,d</sup>
Benzonitrile	1.57	2.20	4.00	0.90	0.53	0.8 <sup>e</sup>
Stilbene	8.00	5.00	4.57	4.08	.93	.46
Toluene	n. d.	Odor	0.60	n. d.	.42	n. d.

<sup>a</sup> Tetraphenylpyrrole (0.89 g.) was isolated. <sup>b</sup> A trace of cyaphenine was detected. <sup>c</sup> Unchanged azine (1.85 g.) was recovered. <sup>d</sup> A compound in the form of fine colorless needles which was quite soluble in benzene and ligroin, less soluble in ether and difficultly soluble in methyl and ethyl alcohols was isolated; yield 0.2–0.3 g. It was exceedingly difficult to purify either by crystallization or vacuum sublimation and in the purest form obtained melted at 185–187°. It does not form a hydrochloride with hydrochloric acid in benzene or ether solution. It distils without decomposition. *Anal.* Found: C, 87.29, 87.02; H, 5.40, 5.42; N, 7.30, 7.68. <sup>e</sup> Not too much significance must be placed upon the benzonitrile determinations in this case.

Very little if any change was effected by the application of high pressures of nitrogen and hydrogen. The thermal decomposition in the presence of ammonia, however, proved to be quite complex. This was possibly due to a partial ammonolysis of the azine. It is interesting to note that the decomposition temperature in this case was considerably lower.

#### Summary

The thermal decomposition of benzaldazine has been studied. In addition to the well-known breakdown to form stilbene and nitrogen an appreciable side reaction takes place in which benzonitrile and benzal-

imine, that is subsequently converted to lophine, are simultaneously formed. As evidence in favor of this mechanism it has been shown that the degradation of benzalfluorenoneazine yields benzonitrile and 9-imino-fluorene.

A number of other aldazines and ketazines have been pyrolyzed and the decomposition products isolated and identified. In general, when the lophine analog is difficult or impossible to make by the usual method, it is also absent in the pyrolysis of the azine.

Lophine and tetraphenylpyrrole are products of the decomposition of benzyl and dibenzylamine. The pyrolysis in the presence of stilbene leads solely to tetraphenylpyrrole.

High pressures of nitrogen and hydrogen did not appreciably affect the course of the decomposition of benzaldazine.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION OF THE U. S. BUREAU OF MINES]

## ENERGY EXCHANGES BETWEEN UNLIKE MOLECULES. THE DECOMPOSITION OF METHYL ETHER, ETHYL ETHER, ACETONE AND THEIR BINARY MIXTURES<sup>1</sup>

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Steacie<sup>3</sup> has recently reported that in mixtures of methyl ether and ethyl ether, each substance decomposes at the rate to be expected from its partial pressure. The decomposition of each of these substances is a homogeneous unimolecular reaction the rate of which, in the usual pressure range, has fallen considerably below the limiting high-pressure value. The conclusion to be drawn from Steacie's report, therefore, is that collisional transfer of energy takes place much more readily when two molecules of ethyl or of methyl ether collide, than when a molecule of ethyl ether collides with one of methyl ether. Such a conclusion is somewhat surprising, since it is a rather more extreme example of specificity than has yet been reported for energy transfers of this character. No directly comparable experiments have been made, but it is known, for example, that ethane is very effective in activating azomethane,<sup>4</sup> the only inert gases which have previously

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<sup>3</sup> Steacie, *THIS JOURNAL*, **54**, 1695 (1932); *J. Phys. Chem.*, **36**, 1652 (1932). I am indebted to Dr Steacie for permitting me to see his complete paper in advance of its publication.

<sup>4</sup> Ramsperger, *J. Phys. Chem.*, **34**, 669 (1930).