The intermediate, I, has been previously postulated as the initial product of the reaction of mercuric oxide with a hydrazone.[17,18]

Yellow mercuric oxide is more effective than red mercuric oxide in this reaction and this is generally thought to be due to the smaller particle size[19] of the yellow form. However, since red mercuric oxide is usually prepared by igniting the nitrate whereas the yellow form is usually prepared by adding a base to a soluble mercuric salt, we feel that contamination of the yellow mercuric oxide by base may be more important than the particle size in explaining the long standing preference for the yellow form. This may also explain the preference for freshly precipitated material[20] and the observed variations with different samples of mercuric oxide.[8] In agreement with this we find that by using slightly more catalyst red mercuric oxide performs as well as the yellow form (see Table I).

TABLE I

PREPARATION OF DIPHENYLDIAZOMETHANE[a]

Mercuric Oxide, g.	Time, min.	Yield, %	M.P., °C.
35 (yellow)	75	12[b,c]	...
28.7 (yellow)	60	54.5	26.5–28.5
35 (yellow)	75	88, 95	30.1–31.1, 29–33
36.5 (yellow)	75	89	30–31
44 (yellow)	70	83	29–30.5
44 (yellow)	90	79	30–32
35 (red)	75	4, 9[b,c]	...
35 (red)	75	20.5, 30, 46, 55, 81, 88	26–28.5 to 29–31
35 (red)	75	81[d]	28–31.5
35 (red)	75	95[d]	29–33
35 (red)	75	86[d]	27–29

[a] From 13 g. of benzophenone hydrazone, 15 g. of anhydrous sodium sulfate, 200 ml. of ether, and 5 ml. of ethanol saturated with potassium hydroxide (except where noted). [b] Based on recovered hydrazone. [c] No basic catalyst. [d] Ten ml. of basic catalyst.

This method of oxidation is, however, not always applicable. Thus, although the mercuric oxide oxidation of the 2-hydrazone of 4,7-dimethyl-1,2-indanedione showed definite basic catalysis, the yield was very low[4] and the base catalyzed mercuric oxide oxidation of *p*-chlorobenzophenone hydrazone gave erratic results.[10] Similarly, we find that contrary to some reports[17,18,21] and in agreement with Vollmann[22] the base catalyzed mercuric oxide oxidation of camphor hydrazone yields diazocamphane but in only trace amounts.

EXPERIMENTAL

Diphenyldiazomethane. A mixture of 13 g. (0.066 mole) of benzophenone hydrazone, 15 g. of anhydrous sodium sulfate, 200 ml. of ether, 5 ml. (10 ml. if red mercuric oxide is used) of ethanol saturated with potassium hydroxide, and 35 g. (0.16 mole) of yellow (or red) mercuric oxide was shaken for 75 min. in a pressure bottle wrapped in a wet towel. The reaction mixture was filtered and the solvent removed from the filtrate under reduced pressure at room temperature. The dark red oil thus obtained was dissolved in petroleum ether (b.p. 30–60°) and again filtered. Removal of the solvent from the filtrate under reduced pressure at room temperature gave an oil. Freezing this oil in a stoppered flask with Dry Ice and then allowing the flask to warm spontaneously to room temperature gave dark red crystals which, after drying on a porous plate, had m.p. 29–32° (reported[13] 29–30°), average yield 89% (see Table I). Reaction of this product with benzoic acid[2] gave benzhydryl benzoate, m.p. 88–91° (reported[2] 87°).

Diazocamphane. A potassium-sodium *tert*-butoxide solution was prepared by dissolving 2.05 g. of potassium-sodium eutectic alloy[23] in 100 ml. of *tert*-butyl alcohol. A mixture of 5 ml. of the above solution, 35 g. of mercuric oxide (yellow), 15 g. of sodium sulfate, 150 ml. of ether, and 10.6 g. of camphor hydrazone[24] (m.p. 52–57°, b.p. 130–133° [22 mm.]) was stirred for 3 hr. and then filtered. This filtrate was bright red in agreement with Vollmann[22] and Heubaum[25] and effervesced on acidification. The presence of the diazo group was shown by infrared absorption at 4.82 microns[26] which disappeared on acidification or treatment with anhydrous copper sulfate. Ethanolic potassium hydroxide solution worked less well than the *tert*-butoxide solution but in neither case was sufficient diazo compound formed to allow its isolation as bornyl or isobornyl chloride.

EXPLOSIVES DEPARTMENT
EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS & CO., INC.
WILMINGTON, DEL.

---

(17) H. Meerwein and K. Emster, *Ber.* **53**, 1815 (1920).

(18) German Patent 353,933 (1922).

(19) A. B. Garrett and A. E. Hirschler, *J. Am. Chem. Soc.*, **60**, 299 (1938).

(20) M. Busch and R. Knoll, *Ber.*, **60**, 2243 (1927); P. C. Guha and D. K. Sankaran, *Ber.* **70**, 1688 (1937).

(21) H. Staudinger and S. Schotz, *Ber.*, **53**, 1105 (1920).

(22) H. Meerwein and K. Emster, *Ber.*, **53**, 1816, footnote 2 (1920).

(23) A product of the MSA Research Corporation, Callery, Pa.

(24) L. Wolff, *Ann.*, **394**, 86 (1912).

(25) U. Heubaum and A. Noyes, *J. Am. Chem. Soc.*, **52**, 5070 (1930).

(26) P. Yates and B. L. Shapiro with N. Yoda and J. Fugger, *J. Am. Chem. Soc.*, **79**, 5756 (1957).

Acid Catalyzed Reactions between Carbonyl Compounds and Organic Azides. II. Aromatic Aldehydes[1]

J. H. BOYER AND L. R. MORGAN, JR.

Received October 10, 1958

An acid-catalyzed reaction between aromatic aldehydes and alkyl azides leading to the formation of amides (II) was recently reported.[2] It was suggested that elimination of a proton at an intermediate stage such as I followed by or accom-

---

(1) Financial assistance under a National Institutes of Health Grant No. H-2295 and Contract No. DA-01-009-ORD-428 with the Office of Ordnance Research, U. S. Army, is gratefully acknowledged.

(2) J. H. Boyer and J. Hamer, *J. Am. Chem. Soc.*, **77**, 951 (1955). Part I.

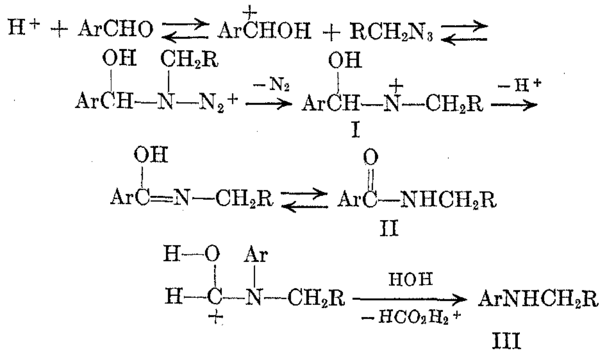
TABLE I

N-Substituted Anilines from Benzaldehyde and Azides

Azide	Aniline Derivative	B.P. or M.P., °C	Refractive Index	Yield, %	Derivative	M.P. °C
n-Butyl	*N*-*n*-Butyl	120 (5 mm.)	n_D^{20} 1.5381	21.9	Hydrochloride	114–115
n-Hexyl	*N*-*n*-Hexyl	158 (28 mm.)[a]	n_D^{20} 1.4235[a]	25	*p*-toluenesulfonamide	67–68[a]
n-Octyl	*N*-*n*-Octyl	118 (25 mm.)[b]	n_D^{25} 1.6381	18	*p*-toluenesulfonamide	42–43[b]
Phenyl	*N*-Phenyl	53–54.5[c]		10	*p*-toluenesulfonamide	64[d]

[a] W. J. Hickinbottom, *J. Chem. Soc.*, 1119 (1937) reported b.p. 165° (35 mm.), n_D^{20} 1.4240, *p*-toluenesulfonamide, m.p. 69°. [b] W. J. Hickinbottom, *J. Chem. Soc.*, 1119 (1937), reported b.p. 119–120° (20 mm.), *p*-toluenesulfonamide, m.p. 41–42°. [c] P. P. Karpuklien, *J. Chem. Ind. (Moscow)*, **23,** 1627 (1929). [d] I. Goldberg, *Ber.*, **40,** 4543 (1907) reported m.p. 65°.

panied with tautomerization accounted for amide formation. The expected migration of an aryl group from carbon to nitrogen with subsequent formation of formanilides or their hydrolysis products, secondary amines (III), was not detected.



$$H^+ + ArCHO \rightleftharpoons Ar\overset{+}{C}HOH + RCH_2N_3 \rightleftharpoons$$

$$Ar\overset{OH}{\overset{|}{C}}H-\overset{CH_2R}{\overset{|}{N}}-N_2^+ \xrightarrow{-N_2} \underset{I}{Ar\overset{OH}{\overset{|}{C}}H-\overset{+}{N}-CH_2R} \xrightarrow{-H^+}$$

$$Ar\overset{OH}{\overset{|}{C}}=N-CH_2R \rightleftharpoons \underset{II}{Ar\overset{O}{\overset{\|}{C}}-NHCH_2R}$$

$$H-\underset{+}{\overset{H-O}{\overset{|}{C}}}-\overset{Ar}{\overset{|}{N}}-CH_2R \xrightarrow[-HCO_2H_2^+]{HOH} \underset{III}{ArNHCH_2R}$$

In the present work this migration is detected insofar as the predicted amines (III) are isolated. From each of three different primary alkyl azides and benzaldehyde the corresponding *N*-alkylaniline is isolated in 18–25% yields; diphenylamine is obtained from phenyl azide and benzaldehyde in 10% yield. Each reaction is carried out in benzene which contains equimolar quantities of azide and aldehyde together with sulfuric acid is catalyst.

Curiously amides (II) are not found. In contrast amides (II) (requiring no rearrangement) but not amines (III) were products of those reactions which used an excess of aldehyde as solvent in place of benzene.[2] Apparently aldehyde solvation of intermediates represses migration.

The presence of strong electron releasing groups in positions *ortho* or *para* to the carbonyl carbon atom inhibits a reaction between aldehydes and azides probably as a result of a decrease in the acidity of the corresponding aldehyde conjugate acids.[2] In the present work *p*-anisaldehyde is nearly quantitatively recovered from attempted reactions with alkyl azides in benzene or nitrobenzene containing sulfuric acid at temperatures ranging from 75–190°. On the other hand *p*-tolualdehyde was successfully transformed into *N*-*n*-butyl-*p*-toluidine using *n*-butyl azide.

Electron attracting ring substituents in the aromatic aldehyde had no apparent effect upon the efficiency of its transformation, using ethylene azidohydrin, into an oxazoline.[2] Unexpectedly *m*- and *p*-nitrobenzaldehyde have now been nearly quantitatively recovered from attempted reactions with *n*-butyl azide in benzene or nitrobenzene containing sulfuric acid at temperatures from 75–190°.

EXPERIMENTAL

Preparation of n-butylaniline. A mixture of 3.18 g. (0.03 mole) of benzaldehyde in 50 ml. of benzene and 5 ml. of concentrated sulfuric acid was warmed to 75°. At a rate which maintained gentle reflux, 2.97 g. (0.03 mole) of *n*-butyl azide was added dropwise with efficient stirring. Gas evolution was complete about 5 min. after the last drop of azide was added. The reaction mixture was then treated with 50 ml. of ice and water, the layers were separated, and the water layer was neutralized with sodium carbonate and extracted with ether. Distillation of the combined dried ether extracts gave 0.9 g. (21.9%) of *N*-*n*-butylaniline, b.p. 120° (2 mm.), n_D^{20} 1.5381, hydrochloride m.p. 114–115°.[3] Trace amounts of benzaldehyde were recovered from the benzene layer which also contained a large amount of tar.

In a similar manner *N*-substituted anilines were obtained from other azides and benzaldehyde; results are summarized in Table I.

In a similar reaction with 6.00 g. (0.05 mole) of *p*-tolualdehyde and 4.95 g. (0.05 mole) of *n*-butyl azide in benzene containing concentrated sulfuric acid there was obtained 1.6 g. (21%) of *p*-methyl-*N*-*n*-butylaniline, b.p. 105–106° (3 mm.)[4] hydrochloride, m.p. 150–151°,[4] picrate m.p. 90°.[4]

Department of Chemistry
Tulane University
New Orleans, La.

---

(3) J. Reilly and W. J. Hickinbottom, *J. Chem. Soc.*, **113,** 99 (1918).

(4) J. Reilly and W. J. Hickinbottom, *J. Chem. Soc.*, **117,** 103 (1920); **113,** 974 (1918).

Theophylline in the Mannich Reaction[1]

J. H. Burckhalter and Dale R. Dill

Received October 13, 1958

As a continuation of studies employing the Mannich reaction, we wished to determine if theo-

---

(1) This investigation was supported by Research Grant H-1756 from the National Heart Institute, U.S. Public Health Service.