

## A Novel Synthesis of Azophenines

J. R. MERCHANT,\* Gail MARTYRES, and N. M. SHINDE

Organic Chemistry Department Institute of Science, Bombay-400 032 India

<sup>†</sup>D. G. Reparel College, Bombay-400016, India

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Arylamines react with polyhaloalkanes in the presence of copper bronze to yield azophenines.

In the course of our work on the reactions of arylamines with polyhaloalkanes we investigated the reaction of aniline and some substituted anilines with 1,1,2,2-tetrachloroethane and hexachloroethane in the presence of copper bronze. Heating the arylamines with the alkyl halide in the presence of a catalytic quantity of copper bronze for 2–4 h afforded bright red compounds, isolated as single substances (TLC, chloroform–methanol) in 25–35% yield. The latter dissolved in concentrated sulfuric acid, giving a deep violet solution, which on dilution gave back the red colour. The sulfuric acid solution on heating at about 300°C turned blue and when alkali was added to it a red coloration was observed. This property as well as the spectral and analytical data indicated that these compounds were probably *N,N'*-diphenyl-2,5-dianilino-*p*-benzoquinone diimines or azophenines.<sup>1)</sup> This assumption was confirmed since azophenine (**1a**)<sup>1)</sup> on heating with zinc and hydrochloric acid gave back aniline and *p*-phenylenediamine. The known azophenines were synthesized by previously reported methods and were found to be identical with our compounds. The literature methods reported so far are tedious, involve separation of mixtures and afford extremely low yields of the azophenines. These include the condensation of quinone with *N*-ethylideneaniline or *N*-benzylideneaniline in dry toluene<sup>2)</sup> under anhydrous conditions to yield azophenine along with a dark red amorphous residue which does not melt up to 360°C. Azophenines have also been obtained (in about 1% yield) by the peroxidase oxidation of a mixture of amines<sup>3)</sup> as well as by the periodic acid oxidation of aniline.<sup>4)</sup>  $\gamma$ -Irradiation of a mixture of aniline and bromobenzene afforded azophenine in a mixture of other products.<sup>5)</sup> Benzofurazan-1-oxide, not an easily accessible starting material, on heating with aniline hydrochloride in aniline is reported to furnish azophenine.<sup>6)</sup>

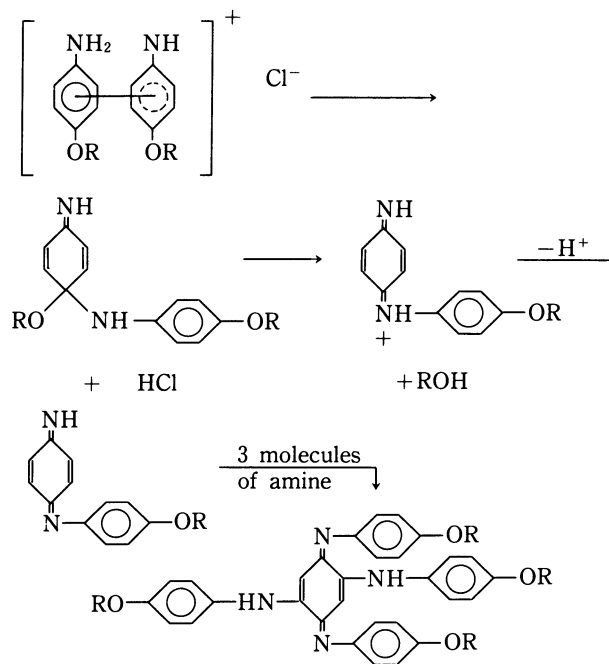
Azophenine (**1a**) has been prepared<sup>3)</sup> by oxidizing *N,N'*-diphenyl-*p*-phenylenediamine with mercury(II) oxide to *p*-benzoquinone dianil and heating the latter with aniline.

Most of the above methods cannot be used to prepare substituted azophenines. The method described by us constitutes a simple and novel synthesis of azophenines (especially the *p*-substituted compounds) which are reported to be important intermediates in the synthesis of dyes,<sup>7)</sup> such as Induline 3B and 6B and Nigrosine CF New. Indulines are blue basic dyes which could be prepared by heating azophenines with the arylamine concerned.

Mechanistically, it is indicated that polyhaloalkanes and copper bronze react to generate a sufficient amount of copper(II) chloride *in situ* which acts as an oxidising

agent in the presence of the amine to yield an *N*-phenyl-*p*-benzoquinone diimine as an intermediate. The latter reacts with an excess of the amine to give the azophenine. The intermediacy of *N*-phenyl-*p*-benzoquinone diimine was established by preparing it as described by Goldschmidt<sup>8)</sup> by oxidation of an ethereal solution of aniline with lead oxide. In the case of *p*-alkoxy substituted anilines the corresponding diimines were obtained by the method of Willstätter and Kubli<sup>9)</sup> involving the silver oxide oxidation of *N*-phenyl-*p*-alkoxy-*p*-phenylenediamines. The diimines so obtained were allowed to react with excess of the corresponding amines to afford the expected azophenines. To confirm our assumptions, *p*-phenetidine (6.85 g) was heated with dry copper(II) chloride (0.135 g) on a steam bath for 4 h when the corresponding azophenine (**1c**) was isolated in about 1.8 g yield.

It is pertinent to mention here that the oxidation of *p*-anisidine with peroxidase in presence of acetic acid has been reported<sup>10)</sup> to yield the corresponding azophenine in about 5% yield. The mechanism for the formation of azophenines in our reaction can be depicted as follows.



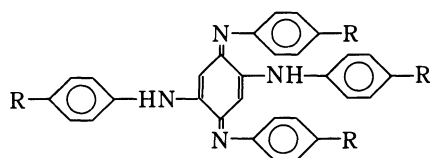
The formation of free radicals during the reaction could be ruled out since no 4-alkoxyazobenzene could be isolated during the reaction. Also *p*-benzoquinone, a known product of the oxidation of amines, is not an intermediate since its reaction with amines under mild conditions affords only 2,5-dianilino-*p*-benzoquinones.<sup>11)</sup> Further, it is well known that quinones do not

TABLE I. AZOPHENINES

Compound	Formula	Mp $\theta_m/^\circ\text{C}$	Found (Calcd) (%)		
			C	H	N
<b>1a</b>	$\text{C}_{30}\text{H}_{24}\text{N}_4$	242—244	82.0 (81.8)	5.6 5.4	12.5 12.7
<b>1b</b>	$\text{C}_{34}\text{H}_{32}\text{N}_4\text{O}_4$	230—232	72.6 (72.8)	5.4 5.7	10.4 10.2
<b>1c</b>	$\text{C}_{38}\text{H}_{40}\text{N}_4\text{O}_4$	237—239	74.3 (74.0)	6.8 6.5	9.2 9.0
<b>1d</b>	$\text{C}_{46}\text{H}_{56}\text{N}_4\text{O}_4$	220—222	75.0 (75.1)	7.4 7.3	8.3 8.3
<b>1e</b>	$\text{C}_{50}\text{H}_{64}\text{N}_4\text{O}_4$	155—157	75.8 (75.6)	7.6 7.5	7.6 7.7

easily form anils with amines.

Amines with strongly electron-donating groups like the alkoxyl in the *p*-position were found to take part in the reaction while amines with electron-withdrawing groups like a nitro group or a halogen atom in this position failed to yield the azophenine. The above reaction with *N,N*-dimethyl-*p*-phenylenediamine was also unsuccessful. When amines substituted at the *o*- or *m*-positions were employed, the reaction failed to occur probably due to steric hindrance.



**1:** **a**,  $\text{R}=\text{H}$ ; **b**,  $\text{R}=-\text{OCH}_3$ ; **c**,  $\text{R}=-\text{OC}_2\text{H}_5$ ;  
**d**,  $\text{R}=-\text{OC}_3\text{H}_7$ ; **e**,  $\text{R}=-\text{OC}_4\text{H}_9$

### Experimental

**General Procedure.** For Azophenine (**1a**), Tetra-*p*-methoxyazophenine (**1b**),<sup>10</sup> and Tetra-*p*-ethoxyazophenine (**1c**): The amine (10 g), (aniline, *p*-anisidine or *p*-phenetidine) hexachloroethane or 1,1,2,2-tetrachloroethane (6 g) and copper bronze (40 mg) were heated on a boiling water bath for 2 h to give a black mass which was decomposed and washed with dilute hydrochloric acid and the residue refluxed with ethanol and filtered to afford a reddish brown solid. The latter was crystallized from pyridine and then

from dioxane in dark red needles.

The spectral data of **1b** are as follows: UV  $\lambda_{\text{max}}^{\text{dioxane}}$ : nm (log  $\epsilon$ ): 305 (4.37), 420 (4.25); IR (KBr): 3350 (N-H), 1600, 1580, 1540, 1490, and 1450 (aromatic), 1050 (C-O-C)  $\text{cm}^{-1}$ ; MS:  $m/z$  560 ( $\text{M}^+$ ). The NMR spectrum of **1b** could not be taken due to its insolubility in the usual solvents.

The IR and mass spectral data of **1c** are as follows: IR (KBr): 3360 (N-H), 1600, 1580, 1540, 1490, 1450 (aromatic), 1040 (C-O-C)  $\text{cm}^{-1}$ ; MS:  $m/z$  616 ( $\text{M}^+$ ).

**Tetra-*p*-propoxyazophenine (1d):** The reaction was carried out as above with *p*-propoxyaniline. The black mass obtained was repeatedly recrystallized from ethanol to afford a reddish-violet solid. IR (KBr): 3360 (N-H), 1600, 1580, 1540, 1480, 1450 (aromatic), 1050 (C-O-C)  $\text{cm}^{-1}$ .

**Tetra-*p*-butoxyazophenine (1e):** The procedure used was similar to the general procedure. The black mass obtained was chromatographed over a silica-gel column. Elution with hexane-acetone (70:30) afforded a deep reddish-violet solid which was crystallized from ethanol. The NMR spectrum of compound **1e** is as follows: NMR ( $\text{CDCl}_3$ )  $\delta=0.8-1.2$  (12H, m, four  $-\text{CH}_3$ ), 1.26—2.0 (16H, m, eight  $-\text{CH}_2$ ), 3.76—4.19 (8H, q, four  $-\text{OCH}_2$ ), 5.63 (2H, s, two  $=\text{CH}-$ ), 6.66—7.76 (16H, m, aromatic protons).

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