

This alcohol (11.1 g., 0.079 mole) was dissolved in 60 ml. of pyridine, cooled to  $-15^{\circ}$ , and treated with 30 g. of *p*-toluenesulfonyl chloride. After 48 hr. at  $-8^{\circ}$ , the mixture was poured into cold diluted sulfuric acid and extracted with chloroform. Solvent was removed from the washed and dried extract by vacuum evaporation and the residue was crystallized twice from hexane yielding 15.6 g. (67%) of white crystals, m.p. 56.5–57.0°.

Anal.<sup>11</sup> Calcd. for  $C_{13}H_{17}N_3O_3S$ : C, 52.9; H, 5.8; N, 14.3; S, 10.9. Found: C, 52.7; H, 5.6; N, 14.3; S, 10.7.

**trans-2-Azidocyclohexyl Acetate.**—A solution of 6.6 g. (0.047 mole) of *trans*-2-azidocyclohexanol in 12 ml. of pyridine and 30 ml. of pentane was treated with 5.5 g. of acetyl chloride. After stirring for several hours, the washed and dried organic solution was distilled, yielding 3.4 g. of product, b.p. 65–69° (0.9–1.0 mm.),  $n_D^{20}$  1.4688.

Anal.<sup>11</sup> Calcd. for  $C_8H_{13}N_3O_2$ : C, 52.4; H, 7.1; N, 23.0. Found: C, 52.5; H, 7.3; N, 23.1.

**Kinetics.**—Glacial acetic acid was refluxed with acetic anhydride and a trace of toluenesulfonic acid and distilled. The material used for kinetics contained 0.06 mg./ml. of water by Karl Fischer titration.<sup>11</sup> A weighed amount of substrate was dissolved at room temperature and aliquots were sealed in am-

poules. Potentiometric titrations of kinetic points were made with a Metrohm potentiograph. Experimental infinity points agreed with the calculated infinities within 4%.

**Acetolysis Products.**—A solution of 13.6 g. (0.046 mole) of I and 3.8 g. (0.046 mole) of sodium acetate in 100 ml. of acetic acid was maintained at 120° for 120 hr. The cooled solution was made alkaline with aqueous sodium hydroxide and ice and extracted with pentane. Distillation of the washed and dried extract gave 3.5 ml. of a residue which was evaporatively distilled and maintained under vacuum to remove traces of pentane. The product in 37% yield,  $n_D^{20}$  1.4706, had an infrared spectrum identical with that of *trans*-2-azidocyclohexyl acetate.

Two grams of this product was reduced with 1.1 g. of lithium aluminum hydride in ether. The reaction mixture was decomposed with a small amount of saturated aqueous ammonium chloride and the dried ether layer was distilled. The residue was dissolved in 6 *M* hydrochloric acid, evaporated, and crystallized three times from benzene–ethanol to afford white crystals, m.p. 174–175° (reported<sup>12</sup> for the hydrochlorides of 2-aminocyclohexanol: *trans*, m.p. 176–177°; *cis*, m.p. 189–190°).

Dinitrophenylhydrazine reagent added to aliquots of acetolysis solutions after addition of water gave no precipitates on standing.

(11) Analysis by the Microanalytical Laboratory of the University of California.

(12) G. E. McCasland, R. K. Clark, Jr., and H. E. Carter, *J. Am. Chem. Soc.*, **71**, 637 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CASE INSTITUTE OF TECHNOLOGY, CLEVELAND, OHIO]

## Aromatic Amination with Hydrazoic Acid Catalyzed by Lewis Acids. Orientation, Activity, and Relative Rates<sup>1</sup>

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Amination of toluene and chlorobenzene by hydrazoic acid in the presence of aluminum chloride or sulfuric acid yielded toluidines and chloroanilines. The predominant *ortho*-*para* orientation and relatively high amount of *meta* isomer suggest an electrophilic substitution mechanism involving an attacking species of high activity. Competitive amination gave values for the relative rate,  $k_{\text{toluene}}/k_{\text{benzene}}$ , which are in good agreement with those calculated from the selectivity relationship. The reaction of methyl azide with toluene–aluminum chloride produced *N*-methyltoluidines and a considerable amount of higher boiling basic material.

### Introduction

Azides have been used for the direct amination of aromatic compounds under various conditions, such as Lewis acid catalysis, thermal initiation, and photolysis. The acid-catalyzed reactions are of most pertinence in relation to this investigation.

The literature contains several reports concerning amination with hydrazoic acid under Friedel–Crafts conditions. From Schmidt's laboratory came the disclosure that amines are formed from aromatic hydrocarbons and hydrazoic acid with sulfuric acid or aluminum chloride catalyst.<sup>2</sup> This lead was subsequently developed by other investigators.<sup>3,4</sup> Aromatic azides have also been used in this type of transformation.<sup>5,6</sup> For example, with benzene and aluminum chloride, phenyl azide was converted to diphenylamine.<sup>5</sup> Intramolecular amination has been realized in the acid-catalyzed rearrangement of 9-azidofluorene to phenanthridine.<sup>7</sup>

There are numerous examples of aromatic amination by thermal decomposition of azides. The reagent list includes hydrazoic acid or ammonium azide,<sup>8</sup> *o*-azidobiphenyls,<sup>9</sup> benzenesulfonyl azide,<sup>10–13</sup> and carbonyl azide.<sup>14</sup>

Photolysis of hydrazoic acid and alkyl azides in benzene, toluene, or nitrobenzene gave low yields of aromatic amines.<sup>3,15</sup> Hydrazoic acid has also been decomposed by active nitrogen in the presence of benzene with formation of traces of aromatic amines.<sup>16</sup>

In addition to azides, compounds in the hydroxylamine class are known to function as aminating agents. Acid-catalyzed substitutions have been performed with hydroxylamine,<sup>17</sup> hydroxylamine-*O*-sulfonic acid,<sup>3,18</sup> alkyhydroxylamines,<sup>17</sup> hydroxylammonium salts,<sup>19</sup> and *N*-benzoyloxypiperidine.<sup>20</sup>

(8) A. Bertho, *Ber.*, **59**, 589 (1926).

(9) P. A. S. Smith and J. H. Hall, *J. Am. Chem. Soc.*, **84**, 480 (1962); G. Smolinsky, *ibid.*, **83**, 2489 (1961).

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(15) D. H. R. Barton and L. R. Morgan, Jr., *J. Chem. Soc.*, 622 (1962).

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(19) P. Kovacic, R. P. Bennett, and J. L. Foote, *ibid.*, **84**, 759 (1962).

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(2) K. F. Schmidt, *Ber.*, **57**, 704 (1924); *Acta Acad. Aboensis, Math. Phys.*, **2**, No. 7, 1 (1924); U. S. Patent 1,564,631 (1925); K. F. Schmidt and P. Zutavaru, U. S. Patent 1,637,661 (1927).

(3) R. N. Keller and P. A. S. Smith, *J. Am. Chem. Soc.*, **66**, 1122 (1944).

(4) G. M. Hoop and J. M. Tedder, *J. Chem. Soc.*, 4685 (1961).

(5) W. Borsche and H. Hahn, *Ber.*, **82**, 260 (1949).

(6) E. Bamberger, *Ann.*, **424**, 233 (1921); E. Bamberger and J. Brun, *Helv. Chim. Acta*, **6**, 935 (1923).

(7) C. L. Arcus and J. V. Evans, *J. Chem. Soc.*, 789 (1958).

TABLE I  
 HYDRAZOIC ACID AND TOLUENE

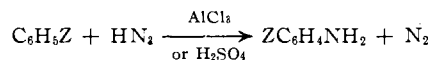
Pro- cedure	NaN <sub>3</sub> , mole	Toluene, moles	Catalyst <sup>a</sup>	Temp., °C.	Time, hr.	Yield, <sup>b</sup> %	Toluidines			S <sub>f</sub> <sup>c</sup>
							o	m	p	
A	0.077	2.4	AlCl <sub>3</sub>	5-85	0.5 <sup>d</sup>	65	49	14	37	0.72
A	.120	2.4	AlCl <sub>3</sub>	5-85	2.3	33 <sup>e</sup>	48	14	38	.74
A	.077	2.4	H <sub>2</sub> SO <sub>4</sub>	5-70	1 <sup>f</sup>	11 <sup>g</sup>	51	9	40	.95
A	.154	4.7	H <sub>2</sub> SO <sub>4</sub> <sup>h</sup>	<20-70	5 <sup>i</sup>	6 <sup>g</sup>	52	11	37	.83
A	.154	3	H <sub>2</sub> SO <sub>4</sub>	15-85	3	15	55	9	36	.90
B	.154 <sup>j</sup>	5.7	AlCl <sub>3</sub>	111	1.5	37 <sup>k</sup>	48	16	36	.65
B	.154	3.5	H <sub>2</sub> SO <sub>4</sub>	75-85	3	8	56	8	36	.95
C	.154	3	AlCl <sub>3</sub>	26-28	21	27 <sup>g</sup>	49	13	38	.77
C	.154 <sup>j</sup>	3	AlCl <sub>3</sub> <sup>l</sup>	26-28	2	24 <sup>m</sup>	48	13	39	.78

<sup>a</sup> Molar ratio of catalyst/sodium azide = 2/1 unless otherwise indicated. <sup>b</sup> Based on sodium azide. <sup>c</sup> Calculated from isomer distributions. <sup>d</sup> Reaction time at 80-85°. <sup>e</sup> B.p. 88-90° (16 mm.). *Anal.* Calcd. for C<sub>7</sub>H<sub>9</sub>N: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.36; H, 8.49; N, 13.29. <sup>f</sup> Reaction time at 60-70°. <sup>g</sup> Product not distilled. <sup>h</sup> 0.154 mole. <sup>i</sup> Reaction time at 65-70°. <sup>j</sup> 0.114 mole (74%) of the hydrazoic acid was extracted. <sup>k</sup> 54% based on hydrazoic acid present. <sup>l</sup> 0.22 mole. <sup>m</sup> 34% based on hydrazoic acid present.

### Discussion

Although the reactions of azides with various aromatic hydrocarbons have been studied previously, little information is available concerning the mechanism of Friedel-Crafts aminations in this category. The objective of the present investigation was to elucidate the mechanism of acid-catalyzed amination involving hydrazoic acid by determination of orientation, selectivity factors, and relative rates. Toluene and chlorobenzene were chosen for study with the catalysts aluminum chloride and sulfuric acid.

**Aminations with Hydrazoic Acid.**—A solution of hydrazoic acid in the aromatic compound to be aminated was prepared by extraction of an aqueous mixture containing sulfuric acid and sodium azide. In order to minimize diamination, a molar ratio of aromatic compound to sodium azide of at least 20/1 was employed. A 2/1 molar ratio of catalyst to azide was used, since this ratio gave best results in aminations with hydroxylamine-O-sulfonic acid.<sup>3,18</sup> After the hydrazoic acid extract and the catalyst were combined by one of several procedures, the reaction mixture was heated until nitrogen evolution was negligible. The reaction is represented by the equation



Z = CH<sub>3</sub> or Cl

Three systems were investigated: hydrazoic acid-toluene-aluminum chloride, hydrazoic acid-toluene-concentrated sulfuric acid, and hydrazoic acid-chlorobenzene-aluminum chloride. The basic products were characterized by elemental analyses, boiling points, and infrared spectra. Isomer distributions were determined by infrared spectroscopy.

The yield of toluidines from the aluminum chloride catalyzed reactions varied from 24 to 65% based on sodium azide (34 to 88% based on the hydrazoic acid present). Chlorobenzene gave a 19% yield of chloroanilines. The lower yield of toluidines from the sulfuric acid catalyzed reactions (6 to 15%) might be attributed to a side reaction resulting in the conversion of hydrazoic acid to hydrazine. Schmidt<sup>2</sup> reported mainly hydrazine formation in the hydrazoic acid-benzene-concentrated sulfuric acid reaction at room temperature. At 60-70° aniline was the main product, with only small amounts of hydrazine by-product.<sup>2</sup> In order to minimize hydrazine formation, we investi-

gated inverse addition of the hydrazoic acid. However, the yield of toluidines was not increased.

In all cases, there were no major changes in isomer distribution when the reaction procedure, temperature, and time were varied as shown in Tables I and II. The isomer distribution (49% *ortho*, 13% *meta*, 38% *para*) of the toluidines from the hydrazoic acid-toluene-aluminum chloride reaction is in disagreement with that (approximately 78% *para* and 22% *ortho-meta*) reported by Keller and Smith.<sup>3</sup> The chemical method (fractional crystallization of the oxalate salts) used in the earlier work is undoubtedly less reliable<sup>18</sup> than present-day instrumental techniques.

 TABLE II  
 HYDRAZOIC ACID AND CHLOROBENZENE

NaN <sub>3</sub> , mole	Chloro- ben- zene, moles	Cata- lyst <sup>a</sup>	Pro- cedure	Temp., °C.	Time, hr.	Yield, <sup>b</sup> %	Chloroanilines		
							o	m	p
0.154	3	AlCl <sub>3</sub>	A	5-80	2.3	19 <sup>c,d</sup>	36	16	48
0.154	5.3	AlCl <sub>3</sub>	B	132	1.8	18 <sup>d</sup>	38	19	43

<sup>a</sup> Molar ratio, catalyst/sodium azide = 2/1. <sup>b</sup> Based on sodium azide. <sup>c</sup> *Anal.* Calcd. for C<sub>6</sub>H<sub>6</sub>NCl: C, 56.49; H, 4.74; N, 10.98. Found: C, 56.68; H, 4.75; N, 10.79. <sup>d</sup> B.p. 96-113° (16 mm.).

In order to establish the validity of our isomer distributions, the individual toluidine and chloroaniline isomers were subjected to simulated reaction conditions. In no case was any isomerism indicated, in keeping with analogous, earlier studies.<sup>18,19</sup>

The predominant *ortho-para* orientation with toluene and chlorobenzene suggests an electrophilic substitution mechanism. The relatively large amount of *m*-isomer indicates that the attacking species possesses high activity<sup>21</sup> and therefore low selectivity. Brown and associates<sup>22,23</sup> have used the selectivity factor, S<sub>f</sub>, as a measure of activity. By definition,<sup>22</sup> S<sub>f</sub> = log p<sub>f</sub>/m<sub>f</sub>, where p<sub>f</sub> and m<sub>f</sub> are partial rate factors for *p*- and *m*-substitution in toluene. The selectivity factor can also be calculated from the isomer distribution by use of the equation<sup>22</sup> S<sub>f</sub> = log (2 × % *para*)/% *meta*.

Brown and Smoot<sup>22</sup> postulated a change in mechanism, based upon the change in S<sub>f</sub> values, for the Friedel-Crafts alkylation of toluene in the series:

- (21) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953).  
 (22) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).  
 (23) L. M. Stock and H. C. Brown, *ibid.*, **81**, 3323 (1959).

TABLE III  
 SELECTIVITY FACTORS

Reaction	Reagent	Conditions	$S_f$
Amination	$\text{HN}_3$	$\text{AlCl}_3$ , 26–28°	0.78
Methylation <sup>22</sup>	$\text{CH}_3\text{Br}$	$\text{GaBr}_3$ , 25°	.84
Ethylation <sup>22</sup>	$\text{C}_2\text{H}_5\text{Br}$	$\text{GaBr}_3$ , 25°	.59
Isopropylation <sup>22</sup>	<i>i</i> -PrBr	$\text{GaBr}_3$ , 25°	.55
<i>t</i> -Butylation <sup>22</sup>	<i>t</i> -BuBr	$\text{GaBr}_3$ , 25°	.62

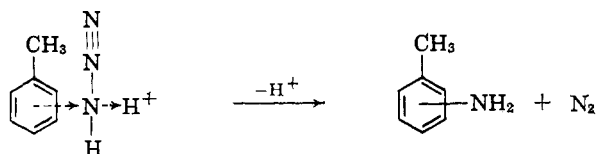
 TABLE IV  
 COMPETITIVE AMINATIONS WITH HYDRAZOIC ACID

NaNs, mole	Benzene, moles	Toluene, moles	$\text{AlCl}_3$ , mole	Temp., °C.	Time, hr.	Basic product			$S_f^a$	
						Aniline + toluidine, g.	Toluidines, %			
0.080	0.58	0.58	0.082	79–81	0.5	1.5 <sup>b</sup>	47	15	38	0.70
0.154	1.2	1.2	0.18	26–28	2	2.7	48	12	40	0.82

<sup>a</sup> Calculated from isomer distributions. <sup>b</sup> In a similar preliminary experiment, the aniline–toluidine was distilled, b.p. 84–92° (15 mm.) (negligible residue).

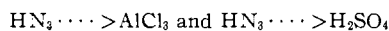
methylation, ethylation, isopropylation, and *t*-butylation (Table III).

*t*-Butylation and isopropylation probably proceed by an ionization mechanism, whereas methylation<sup>24,25</sup> is considered to involve a concerted displacement reaction. Since the selectivity factor (0.78) for the hydrazoic acid–toluene–aluminum chloride reaction is similar to that (0.84) for the gallium bromide-catalyzed methylation of toluene, a concerted displacement mechanism for the amination appears reasonable.<sup>4</sup> If a

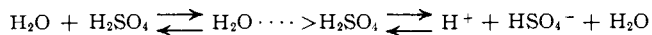
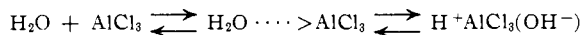


free  $\text{NH}_2^+$  fragment<sup>3</sup> were the actual electrophile, one would expect a lower  $S_f$  value (*cf.*  $S_f$  0.55 for isopropylation, Table III).

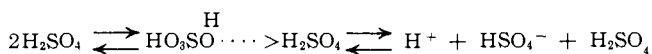
The crucial role of the catalyst is indicated by the failure of amination to occur when aluminum chloride was omitted. Apparently the catalyst coordinates with the hydrazoic acid, thereby providing an attacking entity of appropriate electrophilic character. Although the actual catalyst is not known, designation of aluminum chloride and sulfuric acid first comes to mind.



Partly for simplicity's sake, we have illustrated the reaction sequence using the proton (or hydrogen of enhanced acidity) as the catalytic agent. This approach assumes participation by a cocatalyst, such as water.



Support is provided by previous investigations which point to cocatalysis by Brønsted acids in the Friedel–Crafts alkylation of benzene with alkyl halides and ethers in the presence of boron trifluoride catalyst.<sup>26</sup> In the sulfuric acid aminations, autoprotolysis may be involved.

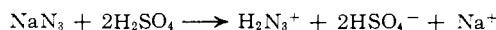


(24) H. Jungk, C. R. Smoot, and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 2185 (1956).

(25) H. C. Brown and H. Jungk, *ibid.*, **77**, 5584 (1955).

(26) G. F. Hennion and R. A. Kurtz, *ibid.*, **65**, 1001 (1943); R. L. Burwell, Jr., and L. M. Elkin, *ibid.*, **73**, 502 (1951).

It is quite significant that cryoscopic examination<sup>4</sup> of sodium azide in 99.8% sulfuric acid revealed an *i*-factor of  $\sim 4$ , thereby indicating the presence of  $\text{H}_2\text{N}_3^+$ .



The lower amounts of *m*-isomer and higher  $S_f$  values in the sulfuric acid catalyzed aminations of toluene suggest an attacking species of lower activity, as

compared with the aluminum chloride catalyzed reactions. Conceivably, the decreased activity may result from more effective solvation of electrophilic entities by sulfuric acid.

One should also consider metathesis between aluminum chloride and hydrazoic acid leading to  $\text{Cl}_2\text{AlN}_3$ . There is evidence for an analogous preliminary reaction in the aminations with hydroxylamine-*O*-sulfonic acid.<sup>18,27</sup>

In order to obtain more information on the activity of the attacking species in aminations with hydrazoic acid, competitive reactions were performed with equimolar quantities of toluene and benzene in the presence of aluminum chloride (Table IV). The relative rate  $k_{\text{toluene}}/k_{\text{benzene}}$  was calculated<sup>28</sup> from the amounts of toluidine and aniline formed (Table V). The isomer distribution of the toluidine fraction was essentially the same as that from the reaction of toluene alone.

 TABLE V  
 COMPETITIVE AMINATION OF BENZENE–TOLUENE

Aminating agent	Relative rate, $k_{\text{toluene}}/k_{\text{benzene}}$	
	Exptl.	Calcd. <sup>a</sup>
$\text{HN}_3^b$	3.9	3.6
$\text{HN}_3^c$	5.1	4.9
$\text{H}_2\text{NOSO}_3\text{H}^d$	3.7	4.3
$\text{H}_2\text{NOH}\cdot\text{HCl}^e$	2.9	3.2

<sup>a</sup> Calculated from the selectivity relationship. <sup>b</sup> Reaction temperature, 79–81°. <sup>c</sup> Reaction temperature, 26–28°. <sup>d</sup> Ref. 18. <sup>e</sup> Ref. 19.

Brown<sup>22,23</sup> has shown that for electrophilic substitution in toluene there exists a linear relationship (the selectivity relationship) between  $\log p_f$  and  $S_f$ . Furthermore, orientation data can be used to calculate<sup>22</sup> the relative rate  $k_{\text{toluene}}/k_{\text{benzene}}$  provided the selectivity relationship is obeyed. The values of the relative rate obtained from competitive aminations (Table V) agree favorably with those calculated from the selectivity relationship. A plot of  $\log p_f$  calculated<sup>22</sup> from the orientation and relative rate *vs.*  $S_f$  for amination afforded a good fit to Brown's linear relationship. The higher value of the relative rate obtained at the lower reaction temperature probably reflects a decrease in activity of the attacking species. Support for this interpretation is provided by the decrease in  $S_f$  values with increase in reaction temperature (Tables I and IV).

(27) R. N. Keller and P. A. S. Smith, *ibid.*, **68**, 899 (1946).

(28) S. U. Choi and H. C. Brown, *ibid.*, **81**, 3315 (1959).

In the toluene reaction, the results with hydrazoic acid were very similar to those observed with hydroxylamine-O-sulfonic acid<sup>18</sup> in regard to  $k_{\text{toluene}}/k_{\text{benzene}}$ , selectivity factors, and isomer distributions. The relative rates are in the same range as the values (2-6) reported for those reactions (*e.g.*, alkylations)<sup>22, 28, 29</sup> entailing electrophiles of high activity. Close similarities were also evident in the chlorobenzene aminations.

Whereas hydrazoic acid and hydroxylammonium chloride<sup>19</sup> gave comparable values for the relative rates and selectivity factors, there were pronounced differences in orientation. More specifically, there was a notable difference in the *ortho/para* ratios for the aminations of toluene and chlorobenzene. With hydrazoic acid, toluene gave higher *ortho/para* ratios than did chlorobenzene, whereas with hydroxylammonium chloride the opposite result was obtained. The relatively high amount of *o*-isomer from hydroxylammonium chloride-chlorobenzene has been rationalized in terms of an *ortho* coordination effect.<sup>19</sup>

Other mechanisms for aromatic aminations performed under various conditions have been advanced by previous investigators. Attention has been focused upon NH (imidogen, nitrene, azene, or imine) as the labile intermediate in azide reactions. Both Schmidt<sup>2</sup> and Bertho<sup>8</sup> postulated the NH route in hydrazoic acid aminations. Imidogen involvement has been proposed for thermal decomposition of aryl azides.<sup>9</sup> In addition, there are reports concerning the reaction of amino radicals with aromatics.<sup>30, 31</sup> For example, the requisite radical, which can be generated from hydroxylamine-titanous ion, combined with benzene to give a mixture of amines which lacked conjugative character. Thermal decomposition of the basic products yielded ammonia, biphenyl, and aniline.<sup>30</sup>

**Aminations with Methyl Azide.**—The amination procedure with methyl azide was very similar to one of those used for hydrazoic acid. Distillation of the basic product gave an initial fraction which corresponded to N-methyltoluidines on the basis of elemental analysis, boiling point, and infrared spectrum (Table VI). Qualitative infrared spectroscopy indi-

TABLE VI  
METHYL AZIDE AND TOLUENE

CH <sub>3</sub> N <sub>3</sub> , moles	Toluene, moles	AlCl <sub>3</sub> , moles	Temp., °C.	Time, hr.	N-Methyltoluidines, yield, % <sup>a</sup>
0.55	5.5	1.1	<0-84	1.8	9 <sup>b, c, d</sup>
0.30	3.1	0.62	<0-111	2.2	4 <sup>d, e</sup>

<sup>a</sup> Based on methyl azide. <sup>b</sup> *Anal.* Calcd. for C<sub>8</sub>H<sub>11</sub>N: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.00; H, 9.22; N, 11.72. <sup>c</sup> Distillation residue, 9.3 g. <sup>d</sup> B.p. 90-92° (10 mm.). <sup>e</sup> Distillation residue, 5.1 g.

cated predominant *ortho-para* orientation. Unfortunately, a large amount of distillation residue was obtained. The exact isomer distribution was not determined since the large amount of higher boiling basic product seriously decreases the usefulness of orientation data.

(29) F. E. Condon, *J. Am. Chem. Soc.*, **70**, 2265 (1948).

(30) H. Seaman, P. J. Taylor, and W. A. Waters, *J. Chem. Soc.*, 4690 (1954); C. J. Albisetti, D. D. Coffman, F. W. Hoover, E. L. Jenner, and W. E. Mochel, *J. Am. Chem. Soc.*, **81**, 1489 (1959).

(31) Z. Yoshida, T. Matsumoto, and R. Oda, *Kogyo Kagaku Zasshi*, **65**, 46 (1962); *Chem. Abstr.*, **57**, 16,446 (1962).

## Experimental<sup>32</sup>

**Materials.**—Toluene, benzene, chlorobenzene, aluminum chloride (anhydrous powder), sodium azide, and dimethyl sulfate were used without further purification. The standards for analysis by infrared spectroscopy and gas chromatography were purified by distillation under vacuum.

**Hydrazoic Acid Solutions.**<sup>2</sup>—A solution of sodium azide (10 g., 0.154 mole) in 27 ml. of water was covered with the aromatic compound to be aminated and the mixture was cooled in an ice bath. After 33 ml. of 50% sulfuric acid was added in small portions, the mixture was shaken and the nonaqueous layer was separated and dried in the cold over anhydrous sodium sulfate for 2 hr.

The amount of hydrazoic acid extracted was estimated in several preparations by addition of a portion to water and titration with 0.1 *N* sodium hydroxide (phenolphthalein indicator). The analysis, which indicated the presence of 74% of the hydrazoic acid,<sup>33</sup> should be considered approximate since there may have been traces of sulfuric acid in the extract. In the preparations for the competitive amination experiments, the use of a lower molar ratio (10:1) of toluene to sodium azide resulted in a reduction in the amount of hydrazoic acid extracted (60%).

**Amination with Hydrazoic Acid. General Procedures. A.**—The solution of hydrazoic acid was placed in a reaction flask fitted with a stirrer, thermometer, and reflux condenser. After the solution was cooled in an ice bath, the catalyst was added and the mixture was heated to the reaction temperature.

**B.**—A portion of the aromatic compound was used to prepare the extract of hydrazoic acid, whereas the remainder plus the catalyst were placed in the reaction flask and heated to the reaction temperature. The hydrazoic acid extract was then added to the reaction mixture.

**C.**—After the solution of hydrazoic acid was heated to the reaction temperature, aluminum chloride was added.

In representative experiments, the extent of reaction was estimated by collecting the evolved nitrogen over water. For isolation of the product, the reaction mixture was cooled and poured into a mixture of hydrochloric acid and ice. After the layers were separated, the nonaqueous portion was extracted several times with dilute hydrochloric acid. The combined acid extracts were washed several times with ether, and then the ether solution was added to the nonaqueous fraction.

The acid solution was made basic in the cold with enough concentrated sodium hydroxide solution to dissolve the aluminum hydroxide precipitate. Extraction with ether, followed by solvent removal through fractionation, gave the basic product which was distilled under vacuum (Ace Minilab apparatus). The amount of tarry residue from the distillation was less than 12%, usually less than 8%, of the weight of aromatic amine. The aminations with hydrazoic acid are summarized in Tables I and II.

In several cases the nonaqueous fraction was washed with water, dried, and distilled. Only the recovered aromatic compound and a negligible amount of residue were obtained.

**Hydrazoic Acid and Toluene.**—A solution of hydrazoic acid, prepared from 10 g. (0.154 mole) of sodium azide, in 320 ml. (3 moles) of toluene was heated at 79° for 3 hr. Processing in the usual manner yielded no basic product.

**Competitive Amination of Benzene-Toluene.**—The benzene-toluene solutions of hydrazoic acid were prepared by extracting the hydrazoic acid from aqueous solution with toluene, determining the hydrazoic acid content of the extract by titration, and adding benzene equivalent to the amount of toluene in the extract. After the hydrazoic acid solutions were heated to the desired temperature in a constant temperature bath, the aluminum chloride was added in portions during 7-8 min. in order to minimize the rise in temperature. The aniline-toluidine product was then isolated, but not distilled.

The toluidine/aniline molar ratios were obtained by gas chromatography. A standard curve was prepared by plotting the ratio of peak areas *vs.* molar ratios for mixtures of known composition. Essentially the same results were observed from a plot of the ratio of peak heights *vs.* the molar ratios. The isomer distribution of the toluidine used for the standards was 48% *ortho*, 12% *meta*, and 40% *para*. Isomer distributions for the competitive amination products were determined by infrared analysis of

(32) Boiling points are uncorrected. Microanalyses were performed by Drs. Weiler and Strauss, Oxford, England.

(33) A 90% yield is reported with benzene (*ref.* 2).

the toluidine fractions collected by gas chromatography. Results from the competitive aminations are summarized in Table IV.

**Isomerization Studies.**—The catalyst (0.2 mole) was added to a cold solution of the amine (0.1 mole) in the aromatic compound (1 mole). The mixture was heated under nitrogen to the highest temperature for the corresponding amination reaction and maintained at that temperature for at least the longest heating period of the amination reaction. After the mixture was cooled and poured into hydrochloric acid-ice, the amine was isolated by the usual method (88–95% recovery). In no case was any isomerization indicated by infrared analysis.

**Preparation of Methyl Azide.**—The method was adapted from the procedure of Dimroth and Wislicenus.<sup>34</sup> Dimethyl sulfate (170 ml., 1.8 moles) was added to an aqueous solution of sodium azide (39 g., 0.6 mole) at 70–80° with intermittent addition of 3 *N* sodium hydroxide in order to keep the reaction mixture slightly alkaline. The methyl azide was passed in the gas phase through a tube packed with soda-lime and sodium hydroxide pellets (to remove any hydrazoic acid contaminant) and was collected in a trap cooled with Dry Ice-acetone. The product (31 g., 91%) was used without further purification.

In a modified procedure, the sodium azide was dissolved in a buffer solution containing sodium bicarbonate and sodium carbonate in a 1:1 molar ratio. Dimethyl sulfate was added to the solution at 70–80°, and the product was collected as described. Although better control of the pH of the reaction mixture was

(34) O. Dimroth and W. Wislicenus, *Ber.*, **38**, 1573 (1905); O. Dimroth, *ibid.*, **39**, 3905 (1906).

maintained by this procedure, the yield of product was lower (51–64%). On the basis of qualitative tests<sup>35</sup> with aqueous ferric chloride and ethanolic silver nitrate, the product did not appear to be contaminated with hydrazoic acid.

**Methyl Azide-Toluene-Aluminum Chloride.**—After the addition of methyl azide, and then aluminum chloride, to toluene at –5°, the mixture was heated to the reaction temperature. The basic product was isolated by the standard method. Table VI summarizes the results.

**Analytical Procedures.**—The isomer distributions of the toluidines and chloroanilines were determined in cyclohexane by a modified base line procedure<sup>36</sup> with a Beckman IR-7 or IR-8 infrared spectrophotometer. The absorbance was measured at the following characteristic wave lengths ( $\mu$ ): *ortho* (toluidine, 13.42; chloroaniline, 13.50); *meta* (toluidine, 13.02; chloroaniline, 13.07); *para* (toluidine, 12.36; chloroaniline, 12.23).

Analyses of the aniline-toluidine mixtures were performed with an F and M Model 500 gas chromatograph: 12 ft. by 0.25 in. column, 14% Apiezon L on Chromosorb P-5% sodium hydroxide<sup>37</sup>; helium flow rate, 55 ml./min.; column temp., 175°.

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(35) P. A. S. Smith, *J. Am. Chem. Soc.*, **70**, 320 (1948).

(36) R. L. Bohon, R. Isaac, H. Hoftiezer, and R. J. Zellner, *Anal. Chem.*, **30**, 245 (1958).

(37) The caustic was used in order to minimize tailing of the peaks; see J. J. Cincotta and R. Feinland, *ibid.*, **34**, 774 (1962).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO, ILL.]

## Organometallic Semiconductors. I. Derivatives of Oximes of 1,5-Diacyl-2,6-dihydroxynaphthalenes<sup>1</sup>

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The problem of preparing semiconducting polymers is discussed. It is pointed out that the best hope of obtaining technically useful materials of this kind lies in the field of coordination polymers. A series of new polymers of this type are described which show interesting electrical properties; these are metal derivatives of the dioximes of 1,5-diformyl- and 1,5-diacetyl-2,6-dihydroxynaphthalene.

### Introduction

Electronic engineering has been revolutionized in the past 15 years by the introduction of a host of new devices based on semiconductors. The further development of this field has, however, been hampered by the limited number of suitable materials. All those in current use are metalloids (*e.g.*, germanium), alloys (*e.g.*, indium antimonide), or simple inorganic compounds (*e.g.*, cadmium oxide); the number of possible combinations of this kind is very limited. The situation could be transformed if suitable organic semiconductors could be found; it would then be possible to prepare ranges of materials with controlled properties, since organic molecules by their nature offer wide scope for structural variation.

Attempts to develop suitable organic semiconductors have, however, proved disappointing.<sup>3,4</sup> A number of

materials have been prepared which act as semiconductors and in which the energy gaps between the filled and conduction bands lie in the required range; however, the carrier mobilities in them have been much too small—orders of magnitude less than in typical inorganic semiconductors such as germanium or silicon.

The reasons for this are well understood. In the first place organic compounds form molecular crystals, the forces between adjacent molecules being relatively weak; there is consequently little electronic coupling between adjacent molecules and electrons find it difficult to jump from one molecule to another. Secondly, many of these materials have been amorphous polymers; the lack of ordered structure in such a material has the effect of scattering electrons when they try to flow through it and so lowers the conductivity.

The first difficulty can be minimized by using very large molecules, so as to reduce the number of gaps between one molecule and another. It is of course essential that electrons be able to migrate freely about each individual molecule; this can be achieved if the molecule is completely conjugated, the  $\pi$ -electrons occupying  $\pi$ -MO's that cover the whole system.

Completely conjugated organic polymers are known: for example, the poly-*p*-phenyls. However, such compounds are not easy to prepare, and their physical

(1) This work was supported by the Air Force Office of Scientific Research through Grant No. AF 62-104. A preliminary account of part of it has appeared: M. J. S. Dewar and A. M. Talati, *J. Am. Chem. Soc.*, **85**, 1874 (1963).

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(3) For reviews see D. D. Eley and M. R. Willis, and H. Akamatu and H. Inokuchi in "Symposium on Electrical Conductivity in Organic Solids," H. Kallmann and M. Silver, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, pp. 257, 277.

(4) H. A. Pohl and H. A. Pohl, J. A. Bornmann, and W. Itoh in "Organic Semiconductors," J. J. Brophy and J. W. Buttrey, Ed., The Macmillan Co., New York, N. Y., 1962, pp. 134, 142.