

2-Diphenylmethyl-6-methylphenol (14) was prepared from the sodium salt of cresol and benzhydryl chloride in the same manner as for 2. The crude product was recrystallized from methyl alcohol-water: mp 76–77.5° (lit.<sup>23</sup> mp 76–78°).

**The Rearrangement of 2,6-Dimethylphenyl Phenyl Ether (1).**—2,6-Dimethylphenyl phenyl ether (1, 1.0 g, 0.005 mol) was placed in a heavy-wall Pyrex tube and the tube was sealed under vacuum. The tube was heated in a furnace at 370° for 3.5 hr, cooled, and opened. Vpc indicated the presence of unreacted starting material and a more polar product in a 2:1 ratio. One half of the crude product was taken up in hexane and extracted with 25% aqueous potassium hydroxide solution. The basic extracts were combined and acidified with hydrochloric acid. The acidified solution was extracted with ether and the ether was stripped to give 125 mg of material. All of this was placed on two preparative tlc silica gel plates and developed in benzene. The major uv absorbing zone was cut out and the product was recovered by elution with acetone. 2-Benzyl-6-methylphenol (2), yield 110 mg (22%), was obtained. This product had the same nmr and ir spectra as authentic material.

When this reaction was run for a longer time, the yield increased and 4-methylxanthene (3) was detected as a minor product.

**The Rearrangement of Compounds 4, 5, 6, 7, and 8.**—These reactions were carried out in a similar manner as for 1 at the temperatures listed in Table I. The products were isolated either by chemical means, as for 1, or by trapping from vpc. They were identified by comparison with authentic compounds.

**Rate Measurements.**—A thick-wall nmr tube containing 2,6-dimethylphenyl phenyl ether (1, 100 mg) was degassed and sealed under vacuum. An nmr spectrum of the molten sample was measured after heating the tube to ca. 70°. The tube was placed in an electric furnace at 370 ± 2° and removed at intervals of 2–4 hr. The sample was cooled, the nmr spectrum was measured, and the composition of the sample was determined from the areas of the methyl and methylene peaks in compounds 1, 2, and 3. Percentage composition with time results are recorded in Table III.

In another determination, an internal standard, 1,1-diphenylpropane, which was stable at 370°, was also present in the nmr tube (30 mg with 100 mg of 1). Similar conversions into 2 and 3 were found.

(23) H. A. Iddles, D. H. Chadwick, J. W. Clapp, and R. T. Hart, *J. Amer. Chem. Soc.*, **64**, 2154 (1942).

TABLE III

Time at 370° hr	Mol %		
	1	2	3
2	98	2	
4	95	5	
6	93	7	
8	93	7	
10.5	89	11	
13	81	19	
15.5	74	25	1
17.5	70	29	1
21	59	38	3
24	38	59	3
41	18	75	8

At the end of the heating period, the tubes were opened and the mixture was analyzed quantitatively by vpc. The yields were in agreement with the nmr values.

Rearrangements were also carried out on small samples of 1 in evacuated ampoules which were heated at 370° for varying intervals, then opened and analyzed quantitatively by vpc. Naphthalene (50 mg per 100 mg of 1) was included as an internal standard in some cases.

When samples were analyzed on a 2-ft silicone rubber column, it was found convenient to convert the phenolic product, 2, into the trimethylsilylether derivative, which no longer overlapped the methylxanthene peak. Quantitative silylation was accomplished in several minutes by adding 2 drops of bistrimethylsilylacacetamide to 1 drop of the reaction mixture.

Rearrangements were also run in an identical manner on samples of 1 which contained sulfur (2 mg per 100 mg of 1) and on a sample of 1 which had been recrystallized two additional times. The rate curves are given in Figure 2.

**Registry No.**—1, 22040-02-4; 6, 22040-03-5; 7, 22040-04-6; 8, 4731-34-4; 9, 22040-06-8; 11, 22040-07-9; 13, 22040-08-0.

**Acknowledgment.**—The authors are indebted to Mrs. A. M. Toothaker and Mr. H. J. Klopfer for their technical assistance.

## Arylation by Aromatic Nitro Compounds at High Temperatures. VI. Reactions of Nitrobenzene and Nitrobenzene-*d*<sub>5</sub> with Pyridine

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Nitrobenzene reacts with pyridine at 600° to give phenylpyridines and bipyridines as major products. Isomer distribution of phenylpyridines is about the same as from phenyl radical sources in the liquid phase; however, product distribution from pyridine differs sharply between nitrobenzene at 600° and benzenediazonium chloride at 100°. Product yields increase considerably with increasing mole ratios of pyridine to nitrobenzene. Deuterated reagents give higher ratios of "normal" to "intramolecularly scrambled" arylation products than in the reactions of nitrobenzene with benzene or toluene. Evidently, the heteroatom in pyridine constitutes an appreciable barrier to intramolecular movement of protium and deuterium.

Earlier papers in this series have described the reactions at high temperatures of nitrobenzene, alone and with benzene and benzene-*d*<sub>6</sub>,<sup>1a</sup> with aromatic fluorine derivatives,<sup>1b</sup> and with toluene and toluene-*α-d*<sub>3</sub>.<sup>1c</sup> This paper concerns the reactions of nitro-

benzene and nitrobenzene-*d*<sub>5</sub> with pyridine; a few details were mentioned in a preliminary communication.<sup>1d</sup>

### Experimental Section

**Equipment and procedures** are fully described in ref 1c.

**Materials.**—With the exception of labeled compounds and analytical standards, all chemicals were reagent grade.

Nitrobenzene-*d*<sub>5</sub> was prepared in 50 mol % yield by nitrating benzene-*d*<sub>6</sub> with nitrogen pentoxide in carbon tetrachloride ac-

(1) (a) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **89**, 3224 (1967); (b) *J. Org. Chem.*, **32**, 3114 (1967); (c) *ibid.*, **33**, 2315 (1968); (d) *J. Amer. Chem. Soc.*, **89**, 724 (1967).

cording to Haines and Adkins.<sup>2</sup> Its isotopic composition was 96.9%  $d_3$  and 3.1%  $d_4$ .

**Analyses.**—Mass spectra were measured on a modified Consolidated Model 21-103 instrument at 70 eV, operating in the nonfocused mode, with the sample-introduction system and ionization chamber both at 250°. Isotopic compositions were derived from low-voltage measurements, in which possible isotope effects on sensitivity were ignored. Spectra were measured at the conventional 70 eV and at low voltage—7.5 eV, uncorrected. For the low-voltage measurements, the repellers were maintained at an average potential of 3 V, the exact values being selected to give maximum sensitivity.

Analyses were also performed with a directly coupled gas chromatograph-mass spectrometer combination<sup>3</sup> employing a 21-103 instrument with an electron multiplier in place of the Faraday-cup detector and by gas chromatography, usually on a column of polyethylene glycol sebacate on Chromosorb W. Other types of columns were used in special analyses.

Relative intensities in the low-voltage mass spectra of product mixtures were taken as a first approximation to relative concentration.<sup>1a-c</sup> To assess the validity of this approximation in the present context, the same sample was analyzed by both low-voltage mass spectrometry and gas chromatography. The ratios of peak intensities and areas, respectively, of a series of compounds of interest in the present work were almost identical (Table I). In any case, the use of relative intensities is perfectly valid for intercomparison of concentration ratios of identical components in separate samples<sup>4</sup> within the limits of reproducibility of the low-voltage data.

TABLE I

Compounds	Ratio	
	Low-voltage mass spectrometry	Gas chromatography
Pyridine and phenol	2.7	2.9
Phenylpyridines and bipyridines	1.1	1.2
Phenylthiophenes and bithiophenes <sup>a</sup>	2.8	3.0
Bithiophenes and naphthalene <sup>a</sup>	17.5	18.0

<sup>a</sup> Reference 17.

## Results and Discussion

The major products from the reaction of nitrobenzene with pyridine at five mole ratios are listed in Table II. For reference, 5 mol of pyridine alone,

TABLE II  
PRODUCTS FROM THE REACTION OF  
NITROBENZENE WITH PYRIDINE<sup>a</sup>

Product	Rel intensity <sup>b</sup>				
	Mol ratio of nitrobenzene/pyridine (product wt, g)				
	1:1 (36.5)	1:2 (45)	1:5 (80)	1:10 (96)	1:02 (13)
Phenol	125	54	32	7	12
Hydroxypyridine	20	11	22	17	11
Biphenyl	58	23	12	6	3
Phenylpyridine	100	100	100	100	100
Bipyridine	17	31	62	92	118
Diphenylpyridine	25	22	13	9	6
Phenylbipyridine	10	16	8	18	15
Terpyridine	1	3	9	10	9

<sup>a</sup> Conditions: 0.5 mol of nitrobenzene; 600°; N<sub>2</sub> at 20 cc/min; contact time, 10.9 sec. <sup>b</sup> Relative intensities in the low-voltage mass spectrum are normalized to phenylpyridine = 100.

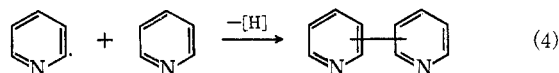
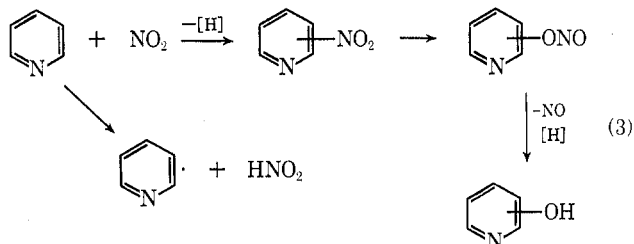
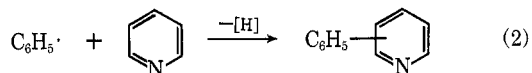
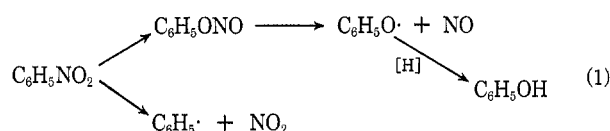
under the same conditions as in Table II, gave 4.6 g of products comprising 97% bipyridine, 3% terpyridine, and traces of quinoline and naphthyridine.

(2) L. B. Haines and H. Adkins, *J. Amer. Chem. Soc.*, **47**, 1419 (1925).

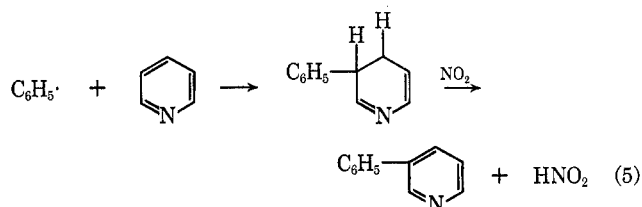
(3) R. S. Gohlke, *Anal. Chem.*, **31**, 535 (1959); L. P. Lindeman and J. L. Annis, *ibid.*, **32**, 1742 (1960); J. T. Watson and K. Biemann, *ibid.*, **36**, 1133 (1964).

(4) S. Meyerson and E. K. Fields, *Chem. Commun.*, 275 (1966).

In light of our previous work with nitrobenzene reactions at high temperatures,<sup>1</sup> formation of the products in Table II may be rationalized by the following reactions (eq 1-4).



Nitrobenzene dissociates at 600° to phenyl radical and NO<sub>2</sub>, itself a free radical. The phenyl radical phenylates pyridine to give a mixture of phenylpyridines after abstraction of hydrogen to rearomatize the initial adduct; abstraction most likely is by NO<sub>2</sub><sup>1a,b</sup> (eq 5).



The distribution of phenylpyridine isomers, determined by gas chromatography, was apparently independent of the mole ratio of nitrobenzene to pyridine. Moreover, as shown in Table III, it is strikingly simi-

TABLE III  
DISTRIBUTION OF PHENYLPYRIDINE ISOMERS

Radical source	Isomer distribution, %		
	2	3	4
Nitrobenzene	53-64	23-30	10-17
Benzoyl peroxide <sup>a,b</sup>	58-64	26-28	10-14
Benzoyl peroxide <sup>c</sup>	54	32	14
Phenyl iodosobenzoate <sup>c</sup>	58	28	14
Nitrosoacetanilide <sup>c</sup>	46	43	11
Triphenylmethylazobenzene <sup>c</sup>	53	31	16

<sup>a</sup> Reference 5. <sup>b</sup> Reference 6. <sup>c</sup> Reference 7.

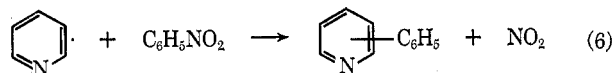
lar to those derived from reactions with phenyl radicals from a wide variety of sources.<sup>5-7</sup> Phenylation of toluene by benzoyl peroxide involves induced decom-

(5) D. H. Hey and G. H. Williams, *Discussions Faraday Soc.*, **14**, 216 (1953).

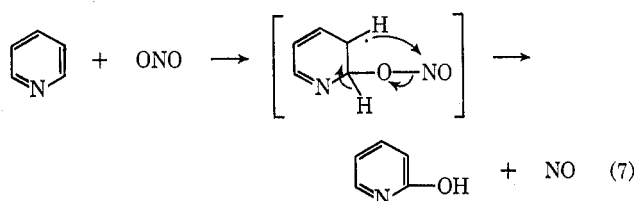
(6) R. L. Dannley, E. C. Gregg, Jr., R. E. Phelps, and C. B. Coleman, *J. Amer. Chem. Soc.*, **76**, 445 (1954); R. L. Dannley and E. C. Gregg, Jr., *ibid.*, **76**, 2997 (1954).

(7) D. H. Hey, C. J. M. Stirling, and G. H. Williams, *J. Chem. Soc.*, 3963 (1955).

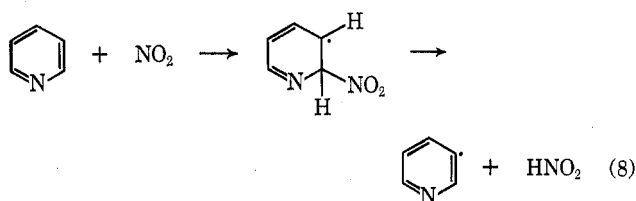
position,<sup>8,9</sup> and the rate of benzoyl peroxide decomposition also is greatly accelerated in pyridine.<sup>10</sup> So unless the similarity noted in Table III is fortuitous, our reactions at 600° may also involve induced decomposition of nitrobenzene by pyridine or pyridyl radical (eq 6).



Hydroxypyridine is pictured as formed by the same nitro-nitrite rearrangement that gives phenol from nitrobenzene. Alternatively, hydroxypyridine could arise more directly from NO<sub>2</sub> and pyridine (eq 7). Ab-



straction of hydrogen from pyridine to give pyridyl radicals is probably by addition of NO<sub>2</sub> to pyridine, followed by loss of HNO<sub>2</sub> (eq 8). This process becomes



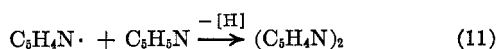
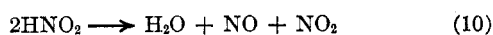
more efficient as the nitrobenzene/pyridine mole ratio decreases, as shown in Table IV. If all the NO<sub>2</sub>

TABLE IV  
YIELDS OF PHENYLPYRIDINES AND BIPYRIDINES  
FROM DIFFERENT RATIOS OF NITROBENZENE TO PYRIDINE<sup>a</sup>

Products	Yield, mol % <sup>b,c</sup>				
	Mol ratio of nitrobenzene/pyridine				
	1	0.5	0.2	0.1	0.05
Phenylpyridines	8.3	17.1	34.5	45.8	56.7
Bipyridines	1.4	5.3	21.2	40.8	65.8

<sup>a</sup> Conditions: 0.5 mol of nitrobenzene; 600°; N<sub>2</sub> at 20 cc/min; contact time, 10.9 sec. <sup>b</sup> On the basis of 0.5 mol of nitrobenzene giving a theoretical yield of 0.5 mol of phenylpyridines and 0.5 mol of bipyridines. <sup>c</sup> Determined by gas chromatography.

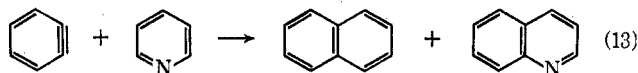
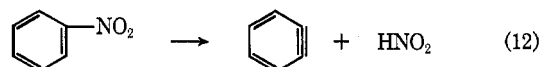
from fragmentation of nitrobenzene were to produce pyridyl radicals, all of which reacted with pyridine to form bipyridine, the theoretical yield of bipyridine at infinite dilution would be 200 mol %, based on the fate of NO<sub>2</sub><sup>1d</sup> (eq 9-11). Although some NO<sub>2</sub>



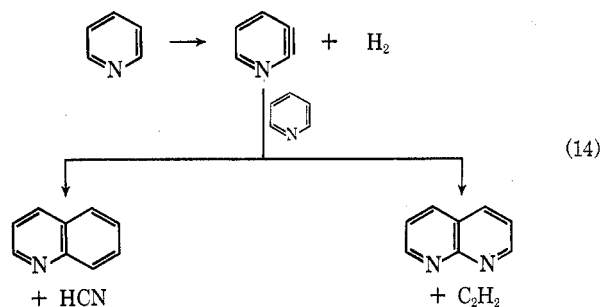
goes to NO in the nitro-nitrite rearrangement that gives phenol and hydroxypyridine, the data in Table

II show that yields of the two major products, phenylpyridines and bipyridines, are quite high at practical ratios of reactants.<sup>11</sup>

Naphthalene, quinoline, and naphthyridine were formed in small amounts (mol % estimated by low-voltage mass spectrometry and by gas chromatography, respectively): 0.7, 0.7; 0.7, 0.6; 0.2, 0.2. Formation of naphthalene and quinoline is most readily explained by intramolecular loss of HNO<sub>2</sub> from nitrobenzene<sup>1e</sup> (eq 12 and 13). Naphthyridine and/or its iso-



mers demand pyridyne as an intermediate. Indeed, quinoline and naphthyridine or isomers were found in the pyrolysis of pyridine alone at 600°. Their relative abundances (low-voltage mass spectrometry) were 0.2 and 0.1%, respectively, that of bipyridine. Pyridyne can form by intramolecular loss of hydrogen at 600° as well as at 700°, as previously found,<sup>12</sup> though to a much lesser extent (eq 14).



To determine whether bipyridines formed to any extent in other phenylations of pyridine, pyridine was allowed to react with benzenediazonium chloride according to the method of Haworth, Heilbron, and Hey.<sup>13</sup> The product distribution is shown in Table V, where those from nitrobenzene and pyridine at the same mole ratios are included for comparison.

Almost no bipyridine was formed in the benzenediazonium chloride reaction. The distribution of phenylpyridine isomers, as determined in the earlier work by isolation of picrates<sup>13</sup> and in this study by gas chromatography, follow (isomer, %): 2, 54.6, 57.9; 3, 22.7, 18.9; 4, 22.7, 23.2. These values are also quite similar to those obtained in the nitrobenzene reaction. By contrast, the isomer distribution of methylbiphenyls from phenylation of toluene with nitrobenzene at 600° differed sharply from that obtained in the liquid phase at 100°.<sup>3</sup> The nitrogen atom of pyridine evidently influences strongly the position of free-radical attack in both liquid and vapor phases. Isomer distributions from vapor-phase nitrobenzene phenylations of a wide variety of reagents are currently being studied.

(11) The yield of 72 mol % phenylpyridine reported earlier<sup>1d</sup> was in error because of overlapping of retention times of some phenylpyridine and bipyridine isomers on the gas chromatographic columns used originally.

(12) E. K. Fields and S. Meyerson, *Advan. Phys. Org. Chem.*, **6**, 1 (1968).

(13) J. W. Haworth, I. M. Heilbron, and D. H. Hey, *J. Chem. Soc.*, 349 (1940).

(8) R. L. Dannley and B. Zaremsky, *J. Amer. Chem. Soc.*, **77**, 1588 (1955).

(9) K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1680 (1946).

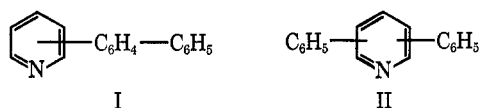
(10) L. Horner and H. Junkermann, *Ann.*, **591**, 53 (1955).

TABLE V  
 PRODUCTS FROM PHENYL RADICALS WITH PYRIDINE

	Rel intensity <sup>a</sup>	
	Reagents, mol (product <sup>b</sup> wt, g)	
	Nitrobenzene, 0.5, and pyridine, 5, at 600° (96)	Benzenediazonium chloride, 0.5, and pyridine, 5, at 100° (45.8)
Phenol	7	
Hydroxypyridine	17	
Naphthalene	1	
Quinoline	2	
Naphthyridine	0.5	
Biphenyl	6	0.5
Phenylpyridine	100	100
Bipyridine	92	0.3
Phenylaniline		25.5
Terphenyl	1	11.8
Diphenylpyridine	9	150
Phenylbipyridine	18	3
Terpyridine	10	
Diphenylaniline		11.3
Triphenylpyridine	0.6	33

<sup>a</sup> Relative intensities in the low-voltage mass spectrum, normalized to phenylpyridine = 100. <sup>b</sup> Boiling above 150°.

Diphenylpyridine, a minor product in the nitrobenzene reaction, exceeded phenylpyridine by 1.5 times in the benzenediazonium chloride reaction. Although the products were not isolated and characterized, most likely they are represented by isomer structures I rather than II. It seems unlikely on a



statistical basis that a second phenyl radical would attack phenylpyridine in preference to the pyridine available in much greater amount. There must, therefore, be a strong preference for the second phenyl radical to add to a benzene rather than to a pyridine ring. Phenyl radical from nitrobenzene, by contrast, prefers to add to the pyridine ring, judging by the relative amounts of phenylbipyridine and diphenylpyridine, 18:9, although phenylpyridine and bipyridine were present in nearly equal concentrations.

To gain further insight as to the mode of formation of the products listed in Table II, we pyrolyzed nitrobenzene-*d*<sub>5</sub> with unlabeled pyridine, and unlabeled nitrobenzene with pyridine-*d*<sub>5</sub>. The products are listed in Table VI, along with the products from solely unlabeled reactants at the same mole ratio for comparison.

There was much overlapping of chemical species containing varying numbers of deuterium atoms, but valid conclusions may be drawn by reference to the relative amounts of products in the reaction of unlabeled nitrobenzene with pyridine. Thus, hydroxypyridine comprises about 40% of the combined concentrations of phenol and hydroxypyridine. Hence, most of the products of masses 95, 96, and 97 from the reaction of nitrobenzene-*d*<sub>5</sub> with pyridine were hydroxypyridine-*d*<sub>0</sub>, -*d*<sub>1</sub>, and -*d*<sub>2</sub>; and some part of the heavier species listed under phenol were also most likely more highly deuterated hydroxypyridines. Similarly, the products of masses 98, 99, and 100 from nitrobenzene with

 TABLE VI  
 REACTION PRODUCTS FROM NITROBENZENE AND  
 NITROBENZENE-*d*<sub>5</sub> WITH PYRIDINE, AND FROM  
 NITROBENZENE WITH PYRIDINE-*d*<sub>5</sub><sup>a</sup>

Product	Mass of parent ion	Rel intensity <sup>b</sup>		
		Nitroben- zene + pyridine <sup>c</sup>	Nitroben- zene- <i>d</i> <sub>5</sub> + pyridine	Nitroben- zene + pyridine- <i>d</i> <sub>5</sub>
Phenol- <i>d</i> <sub>0</sub>	94	32	2	13
Phenol- <i>d</i> <sub>1</sub>	95	...	3 <sup>d</sup>	22
Phenol- <i>d</i> <sub>2</sub>	96	...	2 <sup>d</sup>	15
Phenol- <i>d</i> <sub>3</sub>	97	...	3 <sup>d</sup>	5
Phenol- <i>d</i> <sub>4</sub>	98	...	14	3 <sup>e</sup>
Phenol- <i>d</i> <sub>5</sub>	99	...	15	4 <sup>e</sup>
Phenol- <i>d</i> <sub>6</sub>	100	...	7	2 <sup>e</sup>
Hydroxypyridine	95	22	<i>f</i>	<i>f</i>
Biphenyl- <i>d</i> <sub>0</sub>	154	12	...	4
Biphenyl- <i>d</i> <sub>10</sub>	164	...	3	...
Phenylpyridine- <i>d</i> <sub>0</sub>	155	100	...	...
Phenylpyridine- <i>d</i> <sub>1</sub>	156	...	...	...
Phenylpyridine- <i>d</i> <sub>2</sub>	157	...	...	...
Phenylpyridine- <i>d</i> <sub>3</sub>	158	...	4	9
Phenylpyridine- <i>d</i> <sub>4</sub>	159	...	21	60
Phenylpyridine- <i>d</i> <sub>5</sub>	160	...	75	25
Phenylpyridine- <i>d</i> <sub>6</sub>	161	...	...	6
Bipyridine- <i>d</i> <sub>0</sub>	156	62	45	...
Bipyridine- <i>d</i> <sub>5</sub>	164	...	...	25

<sup>a</sup> Conditions: 600°; contact time, 8 sec; mol ratio of nitrobenzene to pyridine, 1:5. <sup>b</sup> Relative intensities in the low-voltage mass spectrum normalized to phenylpyridine = 100. <sup>c</sup> At 10.9-sec contact time. <sup>d</sup> Probably mostly hydroxypyridine-*d*<sub>0</sub>, -*d*<sub>1</sub>, and -*d*<sub>2</sub>, respectively. <sup>e</sup> Probably mostly hydroxypyridine-*d*<sub>3</sub>, -*d*<sub>4</sub>, and -*d*<sub>5</sub>, respectively. <sup>f</sup> Lumped with isobaric phenols.

pyridine-*d*<sub>5</sub> were doubtless mainly hydroxypyridine-*d*<sub>3</sub>, -*d*<sub>4</sub>, and -*d*<sub>5</sub>. This compound presumably arises by way of a nitro-nitrite rearrangement from nitropyridine. From the isotopic analyses, we inferred that only a minor amount of thermal scrambling of protium and deuterium<sup>14</sup> occurred at 600° and 8-sec contact time. Recovered pyridine from pyridine-*d*<sub>5</sub> (99% *d*<sub>5</sub>) was 86% *d*<sub>5</sub>, 13.4% *d*<sub>4</sub>, and 0.6% *d*<sub>3</sub>; benzene from nitrobenzene-*d*<sub>5</sub> (96.9% *d*<sub>5</sub>, 3.1% *d*<sub>4</sub>) was 83.3% *d*<sub>5</sub> and 16.7% *d*<sub>4</sub>. The extent of isotopic contamination by thermal exchange was nearly the same in the two reactions.

The 0.59 ratio of phenol-*d*<sub>0</sub>/phenol-*d*<sub>1</sub> from nitrobenzene and pyridine-*d*<sub>5</sub> differs but little from the 0.47 ratio of phenol-*d*<sub>6</sub>/phenol-*d*<sub>5</sub> from nitrobenzene-*d*<sub>5</sub> and pyridine; the difference may reflect simply the greater difficulty of abstracting deuterium than protium. In both cases the excess of available deuterium or protium, respectively, is 5:1; yet a considerable portion of the phenoxy radicals pull protium or deuterium from the scarcer source. This finding implies that nitrobenzene is more reactive than pyridine toward phenoxy radicals. Reported relative reactivities to phenyl radicals derived from benzoyl peroxide are 4 for nitrobenzene<sup>15</sup> and 1.04<sup>8</sup> and 1.5<sup>15,16</sup> for pyridine, relative to 1 for benzene. Of these two reported values for the reactivity to phenyl radicals of pyridine relative to benzene, the higher seems more probable, both from the present work and from the reaction of nitrobenzene with benzene-*d*<sub>6</sub> at a 1:5 mol ratio

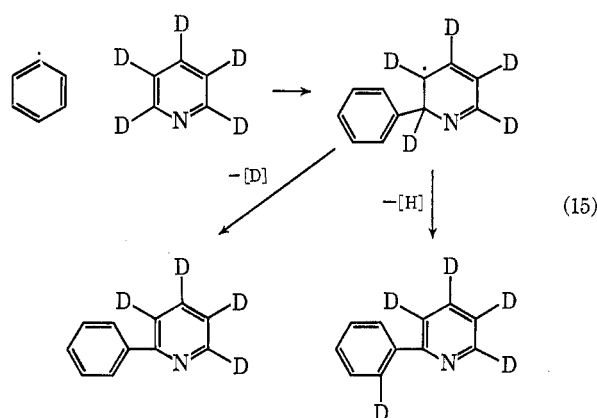
(14) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **88**, 21 (1966).

(15) D. R. Augood, D. H. Hey, and G. H. Williams, *ibid.*, **74**, 2094 (1952).

(16) D. R. Augood, D. H. Hey, A. Nechvatal, T. S. Robinson, and G. H. Williams, *Research*, **4**, 386 (1951).

previously described.<sup>1a</sup> In the latter study, the ratio of phenol-*d*<sub>0</sub> to phenol-*d*<sub>1</sub> was 1.5. This clearly shows a much higher reactivity ratio for nitrobenzene to benzene than to pyridine.

In the reaction of nitrobenzene-*d*<sub>5</sub> with pyridine, the ratio of phenylpyridine-*d*<sub>5</sub> (the anticipated product) to -*d*<sub>4</sub> is 3.6. In the reaction of nitrobenzene with pyridine-*d*<sub>5</sub>, the ratio of phenylpyridine-*d*<sub>4</sub> (the normal arylation product) to -*d*<sub>5</sub> is 2.3. These results contrast strongly with the 1.11 ratio of "normal" to "intramolecularly scrambled" biphenyl from the reaction of nitrobenzene with benzene-*d*<sub>6</sub>;<sup>1a</sup> from nitrobenzene-*d*<sub>5</sub> with toluene, the ratio was only 0.3.<sup>1c</sup> The inference here is that intramolecular movement of protium and deuterium between two unlike aromatic rings (eq 15) has a higher energy of activation than movement between two benzene rings.



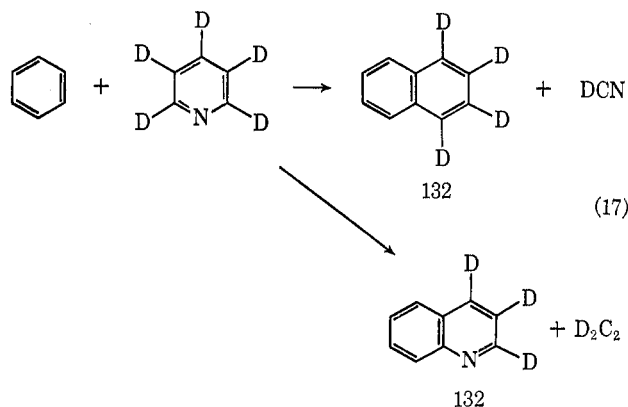
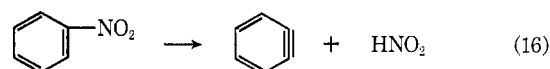
The naphthalene-quinoline-naphthyridine region, masses 128–136, was relatively clear of overlapping species in the reaction of nitrobenzene with pyridine-*d*<sub>5</sub>, as shown in Table VII.

TABLE VII  
RELATIVE AMOUNTS OF PRODUCTS IN THE MOLECULAR  
WEIGHT RANGE OF 128–136 FROM NITROBENZENE  
AND PYRIDINE-*d*<sub>5</sub>

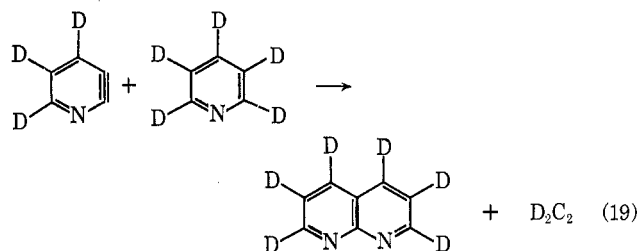
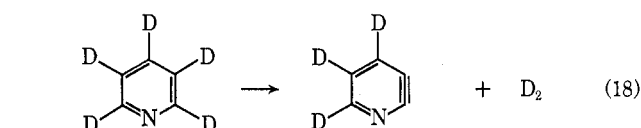
Mol wt	Rel intensity <sup>a</sup>
128	..
129	..
130	..
131	21
132	42
133	16
134	..
135	..
136	21

<sup>a</sup> Relative intensities in the low-voltage mass spectrum. The corresponding intensities follow: 131, 1.3; 132, 2.6; 133, 1.0; 136, 1.3, on the scale used in Table VI.

Benzyne from nitrobenzene, formed by intramolecular loss of HNO<sub>2</sub>, should react with pyridine-*d*<sub>5</sub> to give naphthalene-*d*<sub>4</sub> and quinoline-*d*<sub>3</sub>, both of mol wt 132 (eq 16 and 17). As shown in Table VII, the highest intensity occurs at this mass. The species of mol wt 131, constituting 21% of the total, is naphthalene-*d*<sub>3</sub> and/or quinoline-*d*<sub>2</sub>; the 16% yield at mol wt 133 is naphthalene-*d*<sub>5</sub> and/or quinoline-*d*<sub>4</sub>. Occurrence of these products implies some thermal scrambling of deuterium and protium. Formation of 21% of the product with mol wt 136 and the absence of products



of mol wt 128–130 and 134–135 strongly suggest that the material of mol wt 136 is naphthyridine-*d*<sub>6</sub> and isomers, formed from pyridine-*d*<sub>5</sub> (eq 18 and 19).



Another uncluttered region in the low-voltage mass spectrum of products formed in significant amounts from unlabeled nitrobenzene with pyridine at 600° is at mol wt 230–233, with no products of mol wt 221–229 and 234–244. These are shown in Table VIII, along with the distribution of deuterated species in the same region from nitrobenzene and pyridine-*d*<sub>5</sub>.

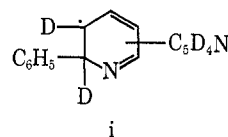
TABLE VIII  
RELATIVE AMOUNTS OF PRODUCTS IN THE MOLECULAR  
WEIGHT RANGE OF 230–244 FROM NITROBENZENE  
WITH PYRIDINE AND PYRIDINE-*d*<sub>5</sub>

Mol wt	Rel intensity <sup>a</sup>	
	Pyridine- <i>d</i> <sub>0</sub>	Pyridine- <i>d</i> <sub>5</sub>
230	6	3
231	41	4
232	25	3
233	28	1
234	...	6
235	...	16
236	...	14
237	...	6
238	...	3
239	...	14
240	...	15
241	...	5
242	...	2
243	...	2
244	...	6

<sup>a</sup> Relative intensities in the low-voltage mass spectrum.

In the reaction of nitrobenzene with unlabeled pyridine, the mol wt 230, 231, 232, and 233 correspond to terphenyl, diphenylpyridine, phenylbipyridine, and terpyridine, respectively. Of these, diphenylpyridine is formed in greatest amount. Therefore, in the reaction with pyridine- $d_5$ , we would expect a major proportion of species of mol wt 234, 235, and 236, corresponding to tri-, tetra-, and pentadeuterated diphenylpyridine and pyridylbiphenyl, the latter being derived from phenylpyridine by phenyl-radical attack at the benzene ring. This is indeed the case, as shown by the data in Table VIII. The  $d_5$  material, of mol wt 237, must of necessity involve intermolecular hydrogen exchange.

Phenylbipyridine from pyridine- $d_5$  should contain seven deuterium atoms, and indeed a significant amount of such product, of mol wt 239, appears in Table VIII. The formation of as much phenylbipyridine- $d_8$  indicates again the tendency for the radical intermediate<sup>1a</sup>



i to aromatize as readily by loss of protium as of deuterium. Terpyridine from pyridine- $d_6$  should have mol wt 244, and this is so shown in Table VIII.

We have studied the reactions of nitrobenzene and nitrobenzene- $d_5$  with thiophene. These, as well as the relative reactivities of phenyl radicals in the gas phase at 600° to benzene, pyridine, and thiophene, is described in the following publication.<sup>17</sup>

**Registry No.**—Nitrobenzene, 98-95-3; nitrobenzene- $d_5$ , 4165-60-0; pyridine, 110-86-1; pyridine- $d_5$ , 7291-22-7.

**Acknowledgment.**—We acknowledge with thanks the assistance of D. K. Albert of the American Oil Co. in gas chromatographic analyses.

(17) E. K. Fields and S. Meyerson, *J. Org. Chem.*, **35**, 67 (1970).

## Arylation by Aromatic Nitro Compounds at High Temperatures. VII. Reactions of Nitrobenzene and Nitrobenzene- $d_5$ with Thiophene

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Nitrobenzene with thiophene at 600° gives 2- and 3-phenylthiophenes, ca. 3:1, and bithiophenes. The reaction is relatively clean, and, at a 1:20 mole ratio of nitrobenzene to thiophene, results in high product yields. It has been used to prepare phenyl- $d_5$ -thiophenes easily and efficiently. Isomer distributions of phenylthiophenes and phenylpyridines are almost identical in the reaction of thiophene and pyridine with phenyl radical from nitrobenzene and benzyne from phthalic anhydride. In competitive arylations, at 600°, the relative reactivity to phenyl radicals has been determined as follows: benzene, 1; pyridine, 2.3; thiophene, 5.

Earlier papers in this series have described the reactions at high temperatures of nitrobenzene, alone and with benzene and benzene- $d_6$ ,<sup>1a</sup> with aromatic fluorine derivatives;<sup>1b</sup> with toluene and toluene- $d_3$ ;<sup>1c</sup> and with pyridine.<sup>1d</sup> This paper concerns the reactions of nitrobenzene and nitrobenzene- $d_5$  with thiophene; a few details were mentioned in a preliminary communication.<sup>1e</sup>

### Experimental Section

**Equipment and procedures** are fully described in ref 1c.

**Materials.**—With the exception of labeled compounds and analytical standards, all chemicals were reagent grade.

Nitrobenzene- $d_5$  was prepared in 50 mol % yield by nitrating benzene- $d_6$  with nitrogen pentoxide in carbon tetrachloride according to Haines and Adkins.<sup>2</sup> Its isotopic composition was 96.9%  $d_6$  and 3.1%  $d_4$ .

Authentic 2- and 3-phenylthiophenes for gas chromatographic standards were synthesized by the method of Melles and Backer.<sup>3</sup> The preparation of 2- and 3-phenyl- $d_5$ -thiophenes has been described elsewhere<sup>4</sup>—both isomers by reaction of nitrobenzene- $d_5$  with thiophene, and the 2 isomer also by reaction of

2-nitrothiophene with benzene- $d_6$  and by the photochemical reaction of 2-iodothiophene with benzene- $d_6$ .<sup>5a,b</sup> The nmr spectra of all the labeled products agreed closely enough with the appropriate published spectra<sup>5b</sup> to establish that the principal component in every case is the phenyl- $d_5$ -thiophene. In view of our isotopic analysis, however, the literature report<sup>5b</sup> of the photochemical preparation and nmr spectra of the two phenyl- $d_5$ -thiophenes is in error in that it failed to recognize  $d_6$  components in the products. The authors of that report have since found other isotopic components.<sup>5c</sup>

**Analyses.**—Mass spectra were measured on a modified Consolidated Model 21-103 instrument at 70 eV, operating in the nonfocused mode, with the sample-introduction system and ionization chamber both at 250°. Isotopic compositions were derived from low-voltage measurements, in which possible isotope effects on sensitivity were ignored. Spectra were measured at the conventional 70 eV and at low voltage—7.5 eV, uncorrected. For the low-voltage measurements, the repellers were maintained at an average potential of 3 V, the exact values being selected to give maximum sensitivity. Relative intensities in the low-voltage (7.5 eV, uncorrected) mass spectra of product mixtures were taken as a first approximation to relative concentrations.<sup>1a-c</sup> In any case, the use of relative intensities is perfectly valid for intercomparison of concentration ratios of identical components in separate samples<sup>6</sup> within the limits of reproducibility of the low-voltage data.

(1) (a) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **89**, 3224 (1967); (b) *J. Org. Chem.*, **32**, 3114 (1967); (c) *ibid.*, **33**, 2315 (1968); (d) *ibid.*, **35**, 62 (1970); (e) *J. Amer. Chem. Soc.*, **89**, 724 (1967).

(2) L. B. Haines and H. Adkins, *J. Amer. Chem. Soc.*, **47**, 1419 (1925).

(3) J. L. Melles and H. S. Backer, *Rec. Trav. Chim. Pays-Bas*, **72**, 325, 491 (1953).

(4) S. Meyerson and E. K. Fields, *Org. Mass Spectrom.*, **1**, 263 (1968).

(5) (a) N. Wolf and N. Kharasch, *J. Org. Chem.*, **26**, 283 (1961); (b) R. M. Kellogg and H. Wynberg, *J. Amer. Chem. Soc.*, **89**, 3495 (1967); (c) R. M. Kellogg, personal communication.

(6) S. Meyerson and E. K. Fields, *Chem. Commun.*, 275 (1966).