20 hr, and the solvent was evaporated. The residue had spectra essentially identical with those of **16a**, obtained by crystallization first from methanol–acetone, then from benzene–pentane, as pale yellow prisms (72%): mp 191.5–192.5°; ν (Nujol) 1730, 1683, 1652 cm^{-1} (enone, aroyl CO, C=N); λ_{max} (EtOH) 247, 281, 335 nm (ϵ 17,000, 23,200, 10,900); nmr ($CDCl_3$) τ 1.6–3.0 (m, 18, aromatic H), 7.85 (s, vinyl Me), 8.77 ppm (*tert*-Me).

Anal. Calcd for $C_{33}H_{24}N_4O_7$: C, 67.11; H, 4.44; N, 9.49. Found: C, 67.40; H, 4.56; N, 9.41.

B. 16b.—The reaction of the dimer of **3** (2.60 g, 5 mmol) with azodibenzoyl (2.38 g, 10 mmol) in refluxing benzene (50 ml) was monitored at 30-min intervals. After 10 hr the four methyl singlets of the dimer had been completely replaced by the two methyl singlets of **16b**, which was obtained as a glass, in high purity, on evaporation. An analytical sample was prepared by slowly adding hexane with stirring to a solution in benzene. The solvents were decanted and the residue on standing *in vacuo* became brittle; ν (CCl_4) 1732, 1665 cm^{-1} (enone and benzoyl C=O, C=N); λ_{max} (EtOH) 280 nm (ϵ 25,100); nmr (CCl_4) τ 2.0–3.2 (20, aromatic H), 7.85 (s, vinyl Me), 8.20 ppm (s, *tert*-Me).

Anal. Calcd for $C_{38}H_{26}N_2O_8$: C, 79.55; H, 5.26; N, 5.62. Found: C, 79.50; H, 5.40; N, 5.50.

A solution of the dimer of **3** and azodibenzoyl in benzene at the same concentration as above was kept at room temperature and the reaction was monitored by nmr analysis. As well as the two singlets at τ 7.90 and 8.57 due to the oxadiazine **16b**, a singlet was also evident at 8.00, attributable to **15b**, in the early stages of the reaction. It reached a maximum of about 10% of the total methyl absorption in 3 days.

Both **16a** and **16b** were stable to prolonged refluxing in bromobenzene.

Registry No.—**3** dimer, 38883-84-0; **3** *p*-bromophenyl dimer, 38883-85-1; **4a**, 2446-84-6; **4b**, 1972-28-7; **4c**, 38857-88-4; **4d**, 2449-14-1; **4e**, 870-50-8; **5a**, 38857-91-9; **5b**, 38857-92-0; **5c**, 38857-93-1; **5d**, 38857-94-2; **5e**, 38857-95-3; **6a**, 38864-11-8; **6b**, 38864-12-9; **6c**, 38864-13-0; **6d**, 38864-14-1; **7a**, 38857-96-4; **7b**, 38857-97-5; **7c**, 38857-98-6; **7d**, 38857-99-7; **9**, 38789-27-4; **10c**, 38858-01-4; **16a**, 38864-15-2; **16b**, 38864-16-3; di-2,2,2-trichloroethyl hydrazodicarboxylate, 38858-02-5; 1,4-dimethyl-5,6-di-*p*-bromophenyl-2,3-dicarbomethoxy-2,3-diazobicyclo[2.2.1]hept-5-en-7-one, 38858-03-6; azodi-*p*-nitrobenzoyl, 35630-50-3; azodibenzoyl, 959-31-9.

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Studies in the Imidazo[1,5-*a*]pyrazine System[1]

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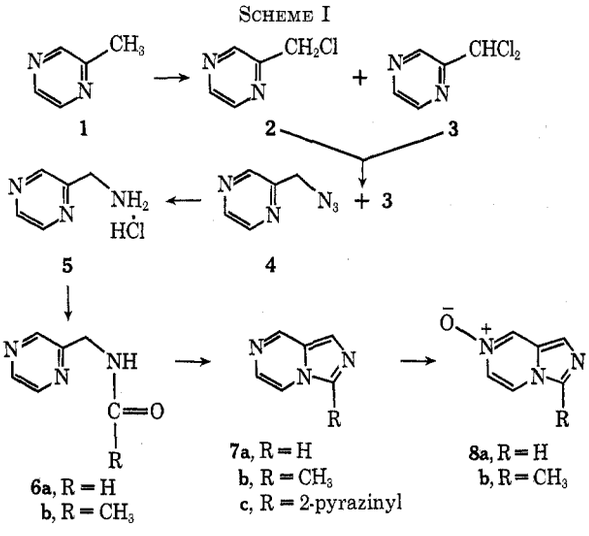
A general synthesis of imidazo[1,5-*a*]pyrazines as well as nmr studies on some derivatives is reported.

The first synthesis of an imidazo[1,5-*a*]pyrazine was reported recently using a novel reaction between pyrazine carboxaldehyde and ammonium chloride to give the 3-(2-pyrazinyl) derivative **7c**.[2] This method, however, cannot be used to prepare the parent heterocycle **7a** or alkyl-substituted derivatives such as **7b**, compounds in which we were interested as sources of imidazo[1,5-*a*]pyrazines that contained a variety of functional groups. This paper describes a general approach to such compounds and nmr studies that permit the identification of each of the protons in the heterocyclic system, an important consideration in assigning the structures of electrophilic substitution products of these heterocycles.

A key intermediate in our synthetic approach (Scheme I) was 2-aminomethylpyrazine. This rather unstable material has been reported previously derived from chloromethylpyrazine (**2**) using potassium phthalimide[3] but with very low yields, and this agrees with our observations of this method. We modified this procedure by utilizing the hydrolysis of the hexamine salt[4] prepared from **2** and hexamethylenetetramine, but again the yields were low and erratic. A practical route to **5** was available, however, by catalytic reduction of azidomethylpyrazine (**4**), which could be prepared,

SCHEME I



in good yield, from the reaction of **2** and sodium azide. Chloromethylpyrazine (**2**), prepared by the reaction of *N*-chlorosuccinimide with methylpyrazine (**1**),[5] was contaminated with dichloromethylpyrazine (**3**), which carries over as a contaminant in the formation of azide **4**. Pure **4** was obtained only after three distillations, in poor and impractical overall yield. Hydrogenation of the pure azide **4** furnished the amine, which was isolated as a hydrochloride salt (**5**) in 75% yield, but this repre-

(1) This work was carried out under the auspices of the Division of Cancer Treatment, National Cancer Institute, National Institutes of Health, Public Health Service Contract No. NIH-71-2312.

(2) E. Abushanab, *Tetrahedron Lett.*, 1441 (1971).

(3) A. Hirschberg and P. G. Mattner, *J. Med. Chem.*, **11**, 911 (1968).

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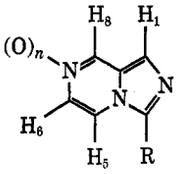
(5) A. Hirschberg and P. E. Spoerri, *J. Org. Chem.*, **26**, 2356 (1961).

TABLE I



	δ, ppm			δ, ppm		
	7a, R = H; n = 0	8a, R = H; n = 1	Δδ	7b, R = CH_3; n = 0	8b, R = CH_3; n = 1	Δδ
H_1	7.83 (s)	7.63 (s)	−0.20	7.64 (s)	7.40 (s)	−0.24
H_3	8.28 (s)	8.25 (s)	−0.03	2.61 (s, CH_3)	2.61 (s, CH_3)	0
H_5	7.58 (d), $J_{5,6}$ = 5 Hz	7.97 (m)	+0.41	7.45 (m), $J_{5,6}$ = 5 Hz	7.73 (d), $J_{5,6}$ = 6 Hz	+0.28
H_6	7.91 (m)	7.38 (q), $J_{5,6}$ = 5, $J_{6,8}$ = 1 Hz	−0.53	7.58 (m), $J_{5,6}$ = 5, $J_{1,6}$ = 1, $J_{6,8}$ = 1.6 Hz	7.23 (q), $J_{5,6}$ = 6, $J_{6,8}$ = 1.8 Hz	−0.35
H_8	9.03 (s)	8.56 (m)	−0.47	8.86 (d), $J_{6,8}$ = 1.6 Hz	8.41 (d), $J_{6,8}$ = 1.8 Hz	−0.45

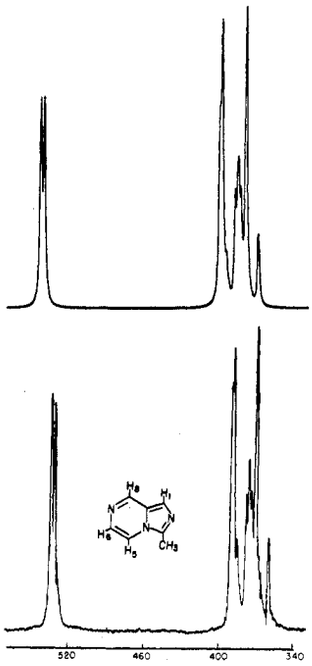


Figure 1.—Nmr spectrum of **7b**: relative δ 171.3 (H_1), 183 (H_5), 176.5 (H_6), and 100 Hz (H_8); theoretical $J_{1,6}$ = 1.0, $J_{6,8}$ = 1.6, $J_{5,6}$ = 5 Hz; T_2 = 0.37 sec.

sents an overall yield of **5** from **2** of 1.6%. Fortunately, a reproducible and more practical procedure was discovered which involves the hydrogenation of a mixture of **4** and **3**. Hydrogenolysis of **3** provided hydrogen chloride, at apparently the proper rate, that trapped the generated amine as the hydrochloride **5** in an overall yield from **2** of 63%. Under our synthetic conditions there was no tendency for hydrogenation of the pyrazine ring, a problem that we had anticipated might plague this approach. It is interesting that attempts to substitute chloroform[6] as the hydrogen chloride precursor or to deliberately add hydrogen chloride in the hydrogenation of distilled **4** that contained very small amounts of **3** were not successful and led to an unpurified product.

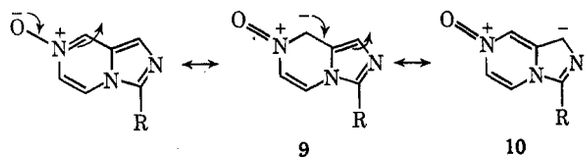
Reaction of the free base prepared from **5** with formic acid gave the formamide **6a**, while reaction with acetic anhydride yielded the acetamide **6b**. Cyclodehydration of the amides with neat phosphoryl chloride afforded the heterocycles **7a** and **7b**, respectively. When these imidazo[1,5-*a*]pyrazines were treated with *m*-chloroperbenzoic acid, the 7-*N*-oxides (**8a** and **8b**, respectively) resulted. The nmr spectra (discussed below) of **7a**, **7b**, **8a**, and **8b** permitted the assignment of the position of oxidation as N-7.

Nmr Spectra.—Chemical shifts and coupling constants for **7a**, **7b**, **8a**, and **8b** are listed in Table I.

The position of the oxygen in **8b** was based on the lack of changes of the chemical shift of the methyl group. A downfield shift would have been observed had oxidation taken place at N-2 or N-4.[7] Further, it is known from literature data[8] that N-oxidation results in an upfield shift of the protons on carbons adjacent to the *N*-oxide function with a downfield shift for protons on carbons which are once removed from the *N*-oxide. These considerations permitted unambiguous assignment in the spectrum of **8b** to H-5. Protons H-5, H-6, and H-8 formed an ABX system in **7b** and irradiation at the low-field doublet (δ 8.86) simplified the spectra such that assignments for H-6 and H-8 could be made. These decoupling studies revealed an unusual long-range coupling over six bonds between H-6 and H-1; in structurally related systems similar five-bond long-range couplings have been observed.[9] Further confirmation of these assignments was obtained by a calculation of the nmr spectrum of **7b** using computer program No. 140, DNMR (Quantum Chemistry Program Exchange). The results are shown in Figure 1.

The nmr studies on **7a** and its *N*-oxide **8a** (Table I) were completely analogous; the essential identity of the chemical shift of H-3 in both compounds is noteworthy.

It is interesting in both **8a** and **8b** that H-1 experiences a shielding effect by the *N*-oxide similar to its effect on H-8. It seems likely that the oxygen can furnish electrons to either position by the electronic shifts depicted in structures **9** and **10**.



9 **10**

(6) While our work was in progress, J. A. Secrist, III, and M. W. Logue, *J. Org. Chem.*, **37**, 335 (1972), reported that hydrogenation of amine precursors in the presence of chloroforom permitted the trapping of certain unstable amines as their hydrochloride salts.

(7) W. H. Grumprecht, T. E. Benkelman, and R. Poju, *J. Org. Chem.*, **29**, 2477 (1964).

(8) L. M. Jackman and S. S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Elmsford, N. Y., 1969, pp 209–212.

(9) W. W. Paudler, "Nuclear Magnetic Resonance," Allyn and Bacon, Boston, Mass., 1971, pp 144, 145.

Investigations of electrophilic subsitution reactions of **7a** and **7b** are in progress and will be reported at a later date.

Experimental Section

Melting points (uncorrected) were determined with a Thomas-Hoover capillary apparatus. Nmr spectra were determined on a Varian A-60 apparatus or on a JEOLCO C-60-HL instrument. Ultraviolet spectral measurements were obtained in 95% ethanol using a Spectronic 505 instrument. Mass spectral molecular weights were obtained from either a Perkin-Elmer RMV-6E or a CEC 24-104 spectrometer. All evaporations were conducted *in vacuo* using either a water aspirator or a vacuum pump.

Chloromethylpyrazine (2).—The procedure followed was essentially that of Hirschberg and Spoerri[5] with some changes in the ratio of reagents that were found to improve the conversion to **2**. A mixture of 50.0 g (0.51 mol) of methylpyrazine (1), 90.0 g (0.68 mol) of *N*-chlorosuccinimide, 0.8 g of benzoyl peroxide, and 1500 ml of carbon tetrachloride was refluxed, with stirring, for 16 hr, then cooled to 0°, and the succinimide separated by filtration, using 250 ml of carbon tetrachloride for washing. The residual oil weighed 59.2 g and was shown by nmr analysis to contain **1**, **2**, and dichloromethylpyrazine (**3**) in a weight ratio of 1:4.16:1, indicating a yield of **2** of 40 g (58.7%) with no allowance for unchanged **1**.

Azidomethylpyrazine (4).—The above-described sample of **2** was dissolved in 700 ml of acetonitrile, a solution of 29.5 g (0.50 mol) of sodium azide in 150 ml of water was added, and the mixture was heated at reflux, with stirring, for 12 hr, concentrated to *ca.* 200 ml, diluted with 200 ml of water, and extracted with four 300-ml portions of ether. The combined extracts were washed with two 150-ml portions of water, dried over sodium sulfate, and evaporated to leave a residue that was vacuum distilled, collecting 50 g of distillate at 55–62° (0.6 mm). Analysis by nmr indicated the weight ratios of **4** to **3** to be 4:1, giving a yield of **4** of 40.3 g (95%). Repeated fractional distillation of a mixture of **4** and **3** (3:1, 70 g) using a 6-in. Vigreux column furnished 1.1 g of the pure azide **4**, bp 65° (1.0 mm), for an overall recovery of 2.2% of the available azide.

Anal. Calcd for $C_5H_5N_5$: C, 44.44; H, 3.73; N, 51.83. Found: C, 44.45; H, 3.98; N, 51.62.

Aminomethylpyrazine Hydrochloride (5). **A.**—A 10-g portion of the above mixture containing **4** and **3** in a ratio of 4:1, dissolved in 200 ml of 95% ethanol, was hydrogenated at 3–4 atm over Adams catalyst (150 mg) with flushing of the system with hydrogen to sweep out the nitrogen formed at 0.5-hr intervals. About 5.5 hr was required to complete the reduction. Then 15 ml of ethanolic hydrogen chloride (12% v/v) was added and the catalyst was removed by filtration. The solvent was evaporated and the solid residue was crystallized twice from methanol–chloroform to yield 5.2 g (65%) of colorless plates, mp 183–184°. The mass spectrum exhibited a molecular ion at *m/e* 109, corresponding to that of the free amine.

Anal. Calcd for $C_5H_7N_3 \cdot HCl$: C, 41.28; H, 5.54; N, 28.88; Cl, 24.36; mol wt, 145.5. Found: C, 41.38; H, 5.54; N, 28.67; Cl, 24.32.

B.—Following the above procedure, azidomethylpyrazine (**4**, 1.0 g) was dissolved in 95% ethanol (50 ml) and hydrogenated over platinum oxide (15 mg) for 2 hr. Filtration followed by the addition of ethanolic hydrogen chloride (2.7 ml, 10% v/v) and evaporation of the solvent gave a solid residue of **5**, 0.84 g (75.6%), mp 174–175°. One recrystallization from methanol–chloroform furnished the pure hydrochloride **5**, mp 183–184, identical in all respects (mixture melting point, ir, tlc) with the analytical sample.

***N*-Formylaminomethylpyrazine** (6a).—A solution of 14.5 g (0.10 mol) of **5** in 15 ml of methanol was treated with a solution of 6.6 g (0.10 mol) of 85% potassium hydroxide in 15 ml of methanol. The mixture was evaporated and the residue was extracted with three 200-ml portions of dichloromethane. The combined extracts were dried over sodium sulfate and evaporated, leaving 10.9 g of liquid which was mixed with 30 ml of 97% formic acid, and the resulting solution was heated for 2 hr on the steam bath, then diluted with 15 ml of benzene and heated under reflux for 16 hr more. The solution was evaporated and the residue was vacuum distilled to give 12 g (87%) of a pale yellow oil at 113–114° (0.06 mm). On standing the distillate changed to a solid, mp 39–40°.

Anal. Calcd for $C_6H_7N_3O$: C, 52.55; H, 5.10; N, 30.69; mol wt, 137. Found: C, 52.65; H, 5.35; N, 30.36; mol wt, 137.

***N*-Acetylaminomethylpyrazine** (6b).—The hydrochloride **5** (14.5 g, 0.10 mol) dissolved in 15 ml of methanol was converted to its free base with potassium hydroxide as described for the preparation of **6a** but without evaporation of the methanolic solution. To the ice-cold methanolic solution of the amine was added, slowly, 15.5 g (0.15 mol) of acetic anhydride over a period of 10 min. Then a solution of 6.6 g (0.10 mol) of 85% potassium hydroxide in 15 ml of methanol was added over a 15-min period and this was followed by the addition of a further quantity (15.5 g) of acetic anhydride. After the reaction mixture had stood at room temperature for about 16 hr, it was concentrated to about 30 ml. Water (30 ml) was added and the solution was extracted with three 150-ml portions of dichloromethane. The combined extracts were dried over potassium carbonate, filtered, and evaporated to leave 15 g (quantitative yield) of solid residue that was homogeneous according to thin layer chromatography (tlc). Crystallization from ether furnished **6b** as colorless needles, mp 64°.

Anal. Calcd for $C_7H_9N_3O$: C, 55.63; H, 6.00; N, 27.81; mol wt, 151. Found: C, 55.40; H, 6.17; N, 27.80; mol wt, 151.

Imidazo[1,5-*a*]pyrazine (7a).—The formamide **6a** (1.0 g) was slowly added to phosphoryl chloride (5 ml) using cooling with an ice–methanol bath. The reaction mixture was then heated on a steam bath for 30 min and evaporated. The residue was washed with 50 ml of hexane, then dissolved in 5 ml of water. The pH was adjusted to 9 with 20% aqueous sodium hydroxide and the solution was extracted with four 150-ml portions of chloroform. The combined extracts were washed with 20 ml of water, dried over sodium sulfate, and evaporated to leave 0.87 g of residue which was crystallized three times from ether–hexane to afford 0.30 g (35%) of **7a** as pale yellow needles: mp 103–104°; uv max 269 nm (log ϵ 3.523), 280 (3.502), and 331 (3.331) with shoulders at 260 (3.414) and 263 (3.431).

Anal. Calcd for $C_6H_5N_3$: C, 60.50; H, 4.20; N, 35.29; mol wt, 119. Found: C, 60.16; H, 4.42; N, 35.02; mol wt, 119.

3-Methylimidazo[1,5-*a*]pyrazine (7b).—The procedure followed was essentially that for preparation of **7a** except that the phosphoryl chloride solution was heated for 1 hr. The crude product (0.80 g, 90% yield) was homogeneous according to tlc and was crystallized from ether–hexane to afford 0.60 g (67%) of **7b** as pale yellow needles: mp 142–143°; uv max 270 nm (log ϵ 3.647), 281 (3.611), and 340 (3.425) with shoulders at 260 (3.550) and 265 (3.571).

Anal. Calcd for $C_7H_7N_3$: C, 63.16; H, 5.26; N, 31.58; mol wt, 133. Found: C, 62.84; H, 5.38; N, 31.31; mol wt, 133.

Imidazo[1,5-*a*]pyrazine 7-Oxide (8a).[10]—To a solution of 5.0 g (42 mmol) of **7a** in 150 ml of chloroform was added 12.5 g (72 mmol) of *m*-chloroperbenzoic acid in 150 ml of chloroform. The mixture was stirred at room temperature for 30 min and then heated at reflux for 15 min. The solution was cooled to room temperature and filtered, and the filtrate was evaporated. The residue separated using dry-column chromatography on a 3.8 × 80 cm column of neutral alumina (30 g to which 3 g of water was added) using chloroform–methanol (94:6 v/v) for elution. The starting material, 0.5 g, was obtained from the initial fractions and this was followed by 0.40 g (9.8% yield based on consumed starting material) of the *N*-oxide **8a**, mp 170°, ir ($CHCl_3$), 1305 cm^{-1} (strong, characteristic of *N*-oxides). The mass spectrum showed a molecular ion at *m/e* 135 followed by a fragment indicating the loss of oxygen at *m/e* 119 ($M^+ - 16$).

3-Methylimidazo[1,5-*a*]pyrazine 7-Oxide (8b).[10]—The procedure used was identical with that described for the preparation of **8a**. The heterocycle **7b**, 4.0 g (30 mmol), was treated with 19.5 g (120 mmol) of *m*-chloroperbenzoic acid in 300 ml of chloroform. The solution was cooled to room temperature, filtered, and evaporated. The residue was adsorbed on neutral alumina (30 g + 3 ml of water) using methylene chloride, and was chromatographed on a dry column (3 × 40 cm) eluting with chloroform–methanol (98:2 v/v). The starting material, 0.9 g, was obtained from the initial fractions (1 l.) followed by **8b** (2.0 g, 58% based on consumed starting material). Crystallization from chloroform–ether gave the *N*-oxide **8b** as pale yellow needles,

(10) Although these two compounds were homogeneous by tlc and had sharp melting points, no acceptable elemental analyses for them could be obtained. Repeated crystallization resulted in progressively larger deviation from the calculated values, suggesting the instability of these compounds.

mp 165–166°. The mass spectrum similarly showed a molecular ion at m/e 149 followed by m/e 133 ($M^+ - 16$).

Registry No.—**1**, 1632-76-4; **2**, 39204-47-2; **4**, 39204-48-3; **5**, 39204-49-4; **6a**, 39204-50-7; **6b**, 39204-51-8; **7a**, 274-49-7; **7b**, 39204-53-0; **8a**, 39204-54-1; **8b**, 39204-55-2.

Acknowledgments.—The authors wish to thank Dr. Yuzuru Shimizu for the mass spectral determinations, and Mr. David Dauplaise for the nmr analyses. Many of the nmr spectra were determined on an instrument for which the National Science Foundation GP-28408 furnished partial financial support.

Acid-Promoted Aromatic Substitution Processes in Photochemical and Thermal Decompositions of Aryl Azides

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Photolysis of aryl azides in 50:4 mesitylene–trifluoroacetic acid (TFA) gives substantial amounts of diphenylamines derived from electrophilic substitution of the mesitylene. Products derived from ring expansion of an aryl nitrene intermediate are also observed. Thermal decomposition of aryl azides at about 85° in the same medium leads to increased yields of diphenylamines. The substitution reaction is not limited to mesitylene but also is observed in *p*-xylene, anisole, and toluene. No substitution product could be isolated in the case of benzene. Mechanistic interpretation of these results is offered.

We have observed that the course of deoxygenation of aromatic nitro and nitroso compounds is profoundly affected by the presence of carboxylic acids in the reaction medium. This was first noted[1] when it was observed that the presence of 5% acetic acid in the triethyl phosphite medium used for photochemical deoxygenation of aromatic nitro compounds substantially diverted the reaction from the normal product, triethyl *N*-arylphosphorimidates, to aromatic nucleophilic substitution products including *o*-hydroxyacetanilides and *o*- and *p*-aminophenylphosphonates. The chemical deoxygenation of aromatic nitroso compounds showed a similar response to the presence of acetic acid in the reaction medium.[1] Later, the deoxygenation of nitrosobenzenes in alcoholic solvents was shown to be very sensitive to solvent acidity. For example, although deoxygenation of nitrosobenzene in pure ethanol resulted in neglible yield of *o*- and *p*-phenetidines, identical reaction mixtures containing 0.02 mol % acetic acid in the ethanol gave rise to >60% yield of the phenetidines.[2]

In order to further define the role that proton donors might play in determining the fate of phenylnitrene and related intermediates on the C_6H_5N energy surface[3] we have studied the photochemical decomposition of several aryl azides in aromatic solvents containing trifluoroacetic acid (~7.5% by volume). We observe aromatic substitution under these conditions and we consider the substitution process to be mechanistically distinct both from the aryl nitrenium[1,2,4] and aryl nitrene[5] pathways for aromatic substitution.

Results

A. Photochemical Reactions.—The present study was concentrated largely on the system mesitylene–TFA. There are significant differences in the distribution of minor products from the individual azides. However, some unifying reactivity patterns emerge. Most important is the formation of diarylamines from each of the azides, usually in substantial yield. Scheme I and Table I summarize the yield data.

SCHEME I[a]

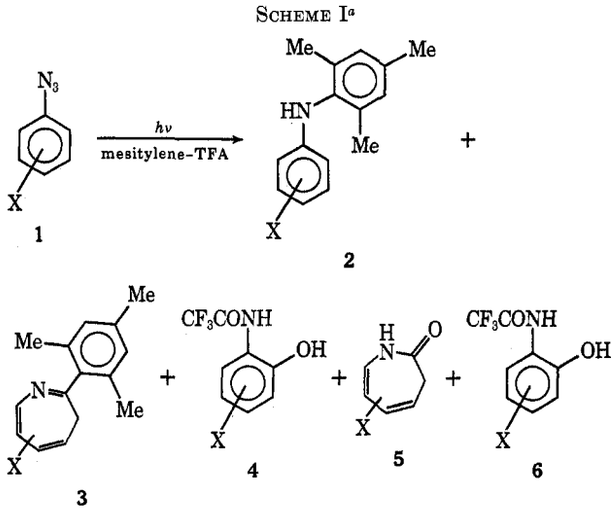

TABLE I
PRODUCT YIELD[a]

		Photochemical reactions					Thermal reactions	
Azide	Substituent	2	3	4	5	6	2	4
1a	None	13	10	3	2		55	1
1b	*p*-Me	40		11		2	84	
1c	*o*-Me	39				3	59	
1d	*o*-CF_3	6	6		15		*b*	
1e	*o*-F	36					*b*	
1f	*p*-CO_2Me	48	9	6			*b*	
1g	*o*-MeO	*b*					79	

[a] The yields of products 3–6 varied from run to run presumably because of variable efficiency chromatographic separation. [b] This reaction was not investigated.

Photolysis of phenyl azide in mesitylene containing 7.5% by volume TFA gave two major and two minor

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