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.

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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]

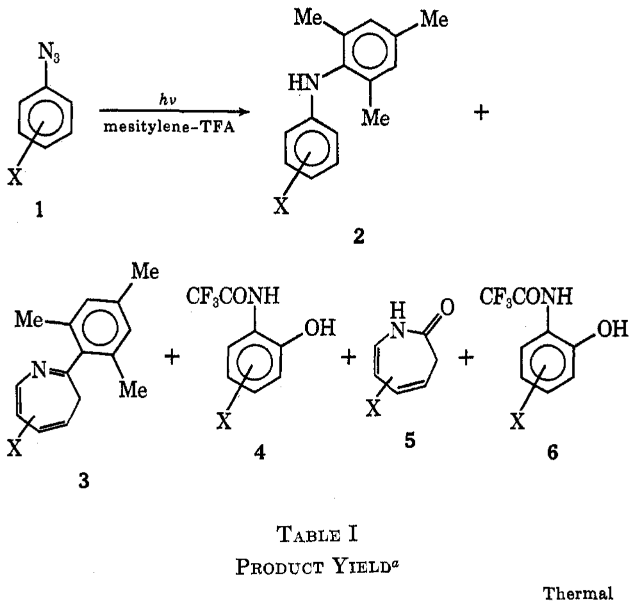

TABLE I

PRODUCT YIELD[a]

Azide	Substituent	Photochemical reactions 2	3	4	5	6	Thermal reactions 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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[1] R. J. Sundberg, R. H. Smith, Jr., and J. E. Bloor, *J. Amer. Chem. Soc.*, **91**, 3392 (1969).

[2] R. J. Sundberg and R. H. Smith, Jr., *J. Org. Chem.*, **36**, 295 (1971).

[3] W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 6149 (1968).

[4] P. G. Gassman, G. A. Campbell, and R. C. Frederick, *J. Amer. Chem.*, **94**, 3884 (1972).

[5] R. A. Abramovitch, S. R. Challand, and E. F. V. Scriven, *J. Org. Chem.*, **37**, 2705 (1972).

products isolated by chromatography. The major products were 2,4,6-trimethyldiphenylamine (**2a** 13%) and 2-(2,4,6-trimethylphenyl)-3*H*-azepine (**3a**, 10%). The minor products were 2-hydroxytrifluoroacetanilide (**4a**, 3%) and 1,3-dihydro-2*H*-azepin-2-one (**5a**, 2%). Nmr, ir, and mass spectral data permitted assignment of structures to **2a** and **4a**, and the melting points were in agreement with literature values. Compound **3a** was a somewhat unstable oil, but a satisfactory analysis was obtained and the elemental composition was also indicated by mass spectral data. The structure was assigned on the basis of the nmr spectrum. The presence of a mesityl group is indicated by methyl resonances in a 1:2 intensity ratio at δ 2.25 and 2.05 and by a singlet at δ 6.82. The remaining signals are a two-proton doublet, $J = 7$ Hz, at δ 2.72, a quartet, $J = 7$ Hz, at 5.13, a two-proton multiplet centered at 6.24 consisting of five principal lines and a doublet at 7.55. The saturated protons at 2.7 require that the phenyl ring has been rearranged. The spin–spin coupling pattern is consistent with the proposed 3*H*-azepine structure. The 2*H*-azepinone **5a** was identified on the basis of elemental analysis, mass spectrum, and consonance of the nmr with a literature report.[6]

Photolysis of *p*-tolyl azide in 50:4 mesitylene–TFA followed by chromatography provided three identifiable products. 2,4,4′,6-Tetramethyldiphenylamine (**2b**) was formed in 40% yield and identified by spectral data and elemental analysis. 4-Methyl-2-hydroxytrifluoroacetanilide was formed in 11% yield and a trace of 4-methyltrifluoroacetanilide was isolated. In comparison with the case of phenyl azide the azepines which are the product of ring expansion have disappeared with a significant increase in the amount of the substitution product **2b**. When methanol was included in the reaction medium, the yield of **2b** dropped to about 10%, **4b** was formed in 4% yield, and 5-methyl-1,3-dihydro-2*H*-azepin-2-one was formed in 8% yield on the basis of quantitative gas chromatographic analysis. The nmr spectrum shows a singlet for the methyl group at δ 1.89 and there is a two-proton doublet at δ 2.80 which was shown by decoupling to be coupled to a triplet at 5.31. There is a doublet at δ 5.70 which is coupled to a doublet of doublets at 6.18. The latter signal also is coupled to the NH proton as it collapses to a doublet on addition of D_2O.

When *p*-tolyl azide is photolyzed in 50:4 benzene–TFA, only **4b** (2%) and **6b** (2%) could be identified. The absence of 4-methyldiphenylamine indicates that benzene is too unreactive a substrate to undergo the substitution process.

Photolysis of *o*-tolyl azide in mesitylene–TFA (50:4) followed by chromatographic work-up gave 2,2′,4,6-tetramethyldiphenylamine (**2c**) (39%). The only other identifiable product, which was isolated only occasionally, was 2-methyltrifluoroacetanilide (**6c**). The formation of the diphenylamine was shown to be dependent on the presence of TFA. When TFA was replaced with ethyl trifluoroacetate, the only photolysis product was 2,2′-dimethylazobenzene (29%). The azo compound was also the only identifiable product when the solvent medium was pure mesitylene.

o-Trifluoromethylphenyl azide was also photolyzed in mesitylene–TFA (50:4). The yield of the diphenylamine **2d** was 6%. 3-Trifluoromethyl-1,3-dihydro-2*H*-azepin-2-one (**5d**) was formed in 15% yield. Spectral data for the formation of the 3*H*-azepine **3d**, which is analogous to **3a**, were obtained, but the instability of this compound prevented final characterization by analysis.

Photolysis of *o*-fluorophenyl azide under similar conditions gave the diphenylamine **2e** (42%). There was also formed a series of minor products. Although the structural assignments cannot be considered conclusive, the spectral data suggest that the minor products include 2-(2,4,6-trimethylphenyl)-5-hydroxytrifluoroacetanilide (1–3%), 2-hydroxytrifluoroacetanilide (1.5%), and an oxidative dimer of 2-hydroxytrifluoroacetanilide. All of the latter three products appear to have lost the ring fluorine by processes which are obscure at this time.

Photolysis of *p*-carbomethoxyphenyl azide gave the diphenylamine **2f** in 48% yield. Also formed were **3f** (9% yield) and **4f** (6%). Identification of **2f** and **4f** followed from elemental composition and comparison of spectral properties with those of the analogous compounds previously described. The composition of **3f** was deduced from the precise mass determination of the parent ion in the high-resolution mass spectrum. The ambient temperature nmr was suggestive of the 3*H*-azepine structure since a triplet at 6.35 and a doublet at 7.80 could be assigned to the C-4 and C-7 protons, respectively. However, the signal which could be assigned to the C-3 methylene group was broad and partially overlapped the aromatic methyl groups. The nmr is temperature dependent. The three methyl groups of the mesityl group are all nonequivalent below −30°. This proves that the mesityl is a substituent on a nonplanar ring in agreement with the assigned azepine structure. At 60° the broad signal due to the methylene group appeared as a doublet as expected for the assigned structure.

o-Methoxyphenyl azide decomposed under the reaction conditions at an appreciable rate in the absence of light. Control experiments demonstrated that the other azides did not decompose at rates competitive with photolysis in the absence of irradiation.

Photolyses of phenyl azide and *p*-tolyl azide were also conducted in anisole. In the former case 2-methoxydiphenylamine (**7**, 8%), 4-methoxydiphenylamine (**8**, 18%), and *o*-hydroxytrifluoroacetanilide (4%) were isolated. In the latter case 2-methoxy-4′-methyldiphenylamine (**9**, 4%), 4-methoxy-4′-methyldiphenylamine (**10**, 43%), and 2-hydroxy-4-methyltrifluoroacetanilide (15%) were formed.

B. Thermal Reactions.—Several of the azides were subjected to thermal decomposition at 85 ± 5° in the same 50:4 mesitylene–TFA medium employed in the photolyses. Under these conditions the yields of diphenylamines increased appreciably and products derived from apparent ring expansion of a nitrene intermediate were not observed. The reactions are considered individually in the succeeding paragraphs.

Phenyl azide gave the diphenylamine **1a** in 55% yield. Small amounts of 2-hydroxytrifluoroacetanilide (1%) and the 4-hydroxy isomer (4%) were isolated. The only other product which could be characterized after chromatographic work-up was a compound as-

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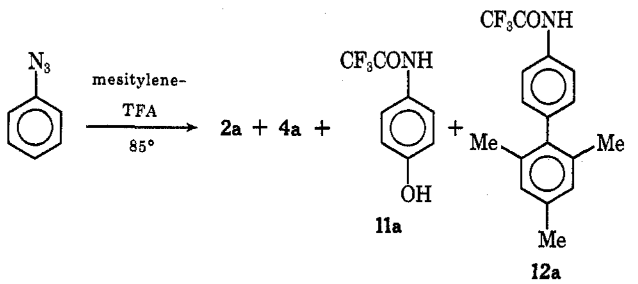
[6] E. Vogel, R. Erb, G. Lenz, and A. A. Bothner-By, *Justus Liebigs Ann. Chem.*, **682**, 1 (1965).

signed the biphenyl structure **12a** (5%) as shown in Scheme II. The elemental composition was deduced

SCHEME II



from the low-resolution mass spectrum and analysis. The nmr spectrum strongly indicated a para-substituted aromatic ring and a mesityl group.

The thermal decomposition of *p*-tolyl azide in mesitylene–TFA was quite clean. The only product isolated was the diphenylamine **2b** (84%). The reaction of *o*-tolyl azide gave **2c** in 59% yield along with the 2-methyl compound **12c** (2%) analogous to **12a**. *p*-Carbomethoxyphenyl azide remained largely unreacted (>85% recovery) after 24 hr at 85° in 50:4 mesitylene–TFA. A small amount of diphenylamine **2f** was the only reaction product detected. *o*-Methoxyphenyl azide evolved nitrogen at room temperature in 50:4 mesitylene–TFA with evolution of 57% of the theoretical amount of nitrogen after 3.5 hr. Product isolation after 48 hr gave the diphenylamine **2g** (79%) and a small amount of what is apparently a dehydro dimer (2%).

The scope of these acid-catalyzed thermal reactions with respect to the aromatic solvent–substrate was investigated using *p*-tolyl azide. In addition to the case of mesitylene, the expected diphenylamines were isolated from reactions in *p*-xylene [2,4′,5-trimethyldiphenylamine (**13**, 66%)], anisole [2-methoxy-4′-methyldiphenylamine (**9**, 4%), 4-methoxy-4′-methyldiphenylamine (**10**, 62%)], and toluene [2,4′-dimethyldiphenylamine (**14**, 5%), 4,4′-dimethyldiphenylamine (**15**, 26%)]. No tractable products were found after reaction in 50:4 benzene–TFA for 24 hr at reflux, although azide decomposition was complete.

The rate of decomposition of *p*-tolyl azide measured by gas evolution at 80° in a 25:4 mixture of aromatic solvent and TFA was strongly dependent on the aromatic solvent. Pseudo-first-order rate constants of 1.5×10^{-1} and 7.6×10^{-3} min^{-1} were measured for mesitylene and anisole, respectively. In acetophenone nitrogen evolution was <15% complete in 10 hr, making estimation of a rate unreliable but demonstrating that the reaction is very slow in this case.

Discussion

The common pattern of reactivity which is found in both the photochemical and thermal reactions is the formation of diarylamines. This reaction exhibits features which distinguish it from two other general mechanisms which operate in the decomposition of aryl azides. Unimolecular thermal decomposition to the nitrene gives diphenylamines, probably by an addition–ring opening sequence,[7,8] but only when the azide is substituted by electron-withdrawing groups.[5] This limitation has been attributed to the reduced electrophilicity of the nitrene intermediate in the absence of such substituents.[5] From the point of view of scope, then, the present acid-catalyzed thermal decomposition is complementary with respect to the azides to which it can be applied. As in the nitrene process, the aromatic substrate must be more reactive than benzene to give significant yields of diphenylamines.

Decomposition of the azide under the present conditions might *a priori* have been expected to occur *via* a nitrenium ion as is proposed, for example, for certain decompositions of azides in strong acids.[9,10] Two features of our results argue against this reaction being dominant under our conditions. The strong dependence of the rate on the identity of the solvent is inconsistent with rate-determining unimolecular decomposition of the conjugate acid of the azide, as required for a mechanism involving a discrete nitrenium ion. Furthermore, the site of electrophilic attack is at nitrogen, not the ortho and para positions of the ring. It is these sites which are the primary points of nucleophilic attack in reactions which are believed to involve aryl nitrenium ions.[2,4]

The general mechanistic features of the thermal reactions can be summarized as follows. The reaction is acid catalyzed and, since the rate is strongly influenced by the solvent–substrate, the aromatic substrate is apparently involved in the rate-determining step. The reaction is facilitated by electron-releasing substituents and retarded by electron-withdrawing groups on the aryl azide as illustrated in particular by the *p*-methoxy and *p*-carbomethoxy cases. The structures of the products demonstrate that the primary electrophilic site is at the nitrogen atom of the aryl azide. Only relatively reactive aromatic rings are suitable substrates for substitution. We propose the mechanism of Scheme III to account for these features of the reaction.

The mechanism of Scheme III is analogous to that proposed by Smith and Brown[11] for decomposition of biphenyl azides in HBr–acetic acid. In that case evidence was obtained for formation of *N*-bromoanilines as intermediates resulting from nucleophilic attack of bromide on the conjugate acid of the azide. The reaction is probably also related mechanistically to the aluminum trichloride catalyzed decomposition of aryl azides which also gives diphenylamines when conduced in aromatic solvents.[12] It may also be related to formation of cyclopropanes from the TFA-catalyzed decomposition of phenyldiazomethane in olefins.[13] A hydrogen-bonded complex of TFA and phenyldiazomethane was proposed as the reactive species in that reaction.

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(7) R. J. Sundberg and R. H. Smith, Jr., *Tetrahedron Lett.*, 267 (1971).

(8) R. A. Abramovitch, S. R. Challand, and E. F. V. Scriven, *J. Amer. Chem. Soc.*, **94**, 1374 (1972).

(9) R. A. Abramovitch and E. P. Kyba in "The Chemistry of the Azido Group," S. Patai, Ed., Interscience, New York, N. Y., 1971, pp 234–241.

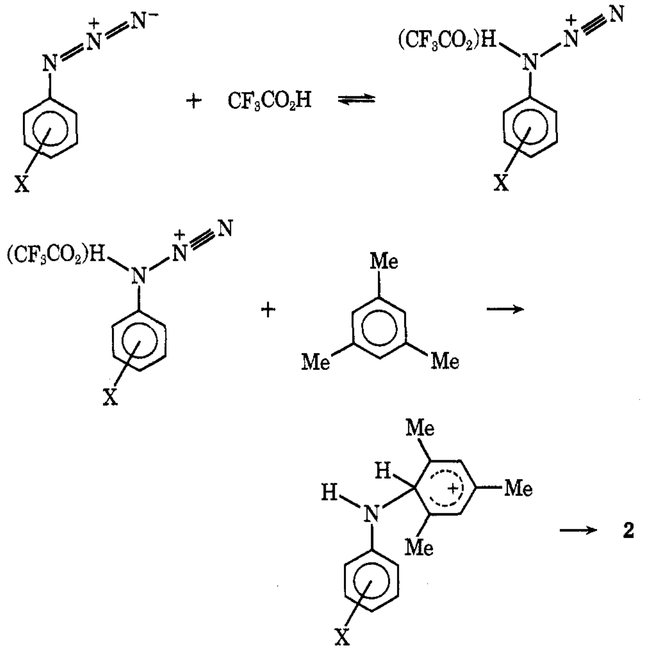
(10) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," W. A. Benjamin, Inc., New York, N. Y., 1966, pp 225, 226; J. H. Boyer and F. C. Canter, *Chem. Rev.*, **54**, 1 (1954).

(11) P. A. S. Smith and B. B. Brown, *J. Amer. Chem. Soc.*, **73**, 2438 (1951).

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

(13) G. L. Closs, R. A. Moss, and S. H. Goh, *J. Amer. Chem. Soc.*, **88**, 364 (1966).

SCHEME III

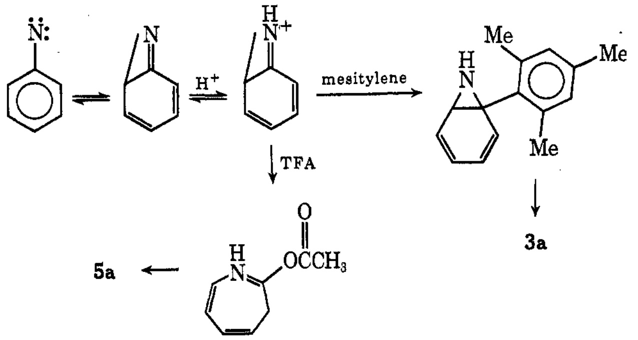


The mechanism of Scheme III is intended to convey primarily the conclusion that the observed electrophilic substitution does not involve a nitrene intermediate. The data indicating that the aromatic substrate is involved in the rate-determining step also argue against a discrete nitrenium ion. The electrophile would, therefore, appear to be a protonated (or hydrogen bonded) aryl azide molecule which is capable of attacking reactive aromatic substrates at a rate exceeding unimolecular elimination of nitrogen.

The case of phenyl azide indicates that the nitrenium ion pathway may be a competitive process. The production of the hydroxyacetanilides **4a** and **11a** is suggestive of a nitrenium ion intermediate. The formation of the biphenyl **12a** can also be accounted for in this way. The isolation of **12c** from thermal decomposition of *o*-tolyl azide also suggests a small amount of the nitrenium ion pathway in this case. No evidence of formation of nitrenium ion products was found for either *p*-tolyl or *o*-methoxy azide.

The photolytic processes appear to involve at least two competitive reaction systems. Products having rearranged aromatic skeletons as found in products **3** and **5** are highly suggestive of aryl nitrene intermediates.[7] The diphenylamines which are formed, however, cannot be reasonably accounted for in terms of a nitrene intermediate. Nucleophilic trapping of unrearranged aryl nitrenes has been observed only rarely and only when the aryl nitrene bears electron-withdrawing substituents.[14] Under the present conditions electron-donating methyl groups clearly do not prevent diphenylamine formation. An aryl nitrenium ion formed by protonation of an aryl nitrene is not a satisfactory intermediate. Substantial amounts of ortho and para substitution products, for example **12**, or formation of methoxy derivatives in the presence of methanol would be expected if aryl nitrenium ions were involved. Instead the most satisfactory explanation would seem to view the photochemical decompositions as involving competition between the nitrene rearrangement pathway and the mechanism of Scheme III. Since control experiments have indicated that the reaction is too rapid to be a purely thermal process, there must exist a photochemical mechanism for generating protonated azide molecules having sufficient energy for the substitution process to occur. Photoexcited azide molecules may be intercepted by protonation prior to complete thermal equilibration, or protonation of excited azides followed by rapid reaction with the aromatic substrates may be involved.

The formation of azepine **3a** represents a new type of reactivity for phenylnitrene. Formally, the product is analogous to the 2-diethylamino-3*H*-azepines formed when phenylnitrene is generated in the presence of secondary amines.[15] However, the effective trapping of phenylnitrene is restricted to good nucleophiles such as amines and hydrogen sulfide.[15b] Furthermore **3a** is not formed in the absence of trifluoroacetic acid so a proton donor is apparently required. We have no evidence for the mechanism of formation of **3a** beyond the analogy with nucleophilic trapping and the dependence on a proton source. A process such as shown below can be written to account for the product structure but, of course, has no significance beyond this at the present time. The azepinone **5a** can be accounted for by the reaction of trifluoroacetate ion with rearranged phenylnitrene, followed by deacylation. Only **4a** is suggestive of the involvement of an aryl nitrenium ion and the absence of the 4 isomer argues against the presence of a free aryl nitrenium ion capable of attack by nucleophiles at both the ortho and para position. This surmise is strengthened by results of a photolysis of phenyl azide in 40:10:4 mesitylene–methanol–TFA. No *o*- or *p*-anisidine was detected. The products were **5a** (14%) and **4a** (trace). The increased amounts of azepinones found in the presence of methanol suggest that some of the azepinone might arise *via* a methoxyazepine.



The electrophilic substitution process described in this work considerably expands the possibilities for synthesis of unsymmetrical diphenylamines *via* aryl azides relative to prior procedures.[5] Although the mechanism by which this reaction occurs is not established in detail, there is considerable evidence that protonated aryl azide or a hydrogen-bonded complex of the azide with TFA can act as the electrophilic species by a process which bypasses a free nitrene or nitrenium ion intermediate.

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[14] R. A. Odum and A. M. Aaronson, *J. Amer. Chem. Soc.*, **91**, 5680 (1969); R. Huisgen and K. V. Fraunberg, *Tetrahedron Lett.*, 2595 (1969).

[15] (a) R. J. Sundberg, S. R. Suter, and M. Brenner, *J. Amer. Chem. Soc.*, **94**, 513 (1972), and references therein; (b) W. von E. Doering and R. A. Odum, *Tetrahedron*, **22**, 81 (1966).

Experimental Section[16]

Photolytic Reactions.—A weighed amount of the azide (~10 mmol) was dissolved in mesitylene (50 ml) and trifluoroacetic acid (4 ml) was added. The resulting solution was purged with nitrogen for 0.5 hr and then irradiated for 3.0 hr by a 450-W Hanovia mercury lamp using a Pyrex filter and a water-cooled Vycor immersion well. The temperature in the reaction solution did not exceed 30° under these conditions. At the completion of photolysis the reaction mixture was diluted with ether (100 ml) and washed thoroughly with sodium bicarbonate solution to remove trifluoroacetic acid. The residue from evaporation of the ether and mesitylene was chromatographed on a column of silica gel (70–230 mesh). The products from the individual azides are described below in order of their elution from the column.

Phenyl Azide.—Hexane–ether (95:5) readily eluted 2,4,6-trimethyldiphenylamine (**2a**) (13%, glpc 16%): mp 56.5–57° (lit.[17] mp 54°), after recrystallization from hexane; nmr (CCl_4) δ 2.16 (s, 6), 2.30 (s, 3), 5.1 (broad s, 1), 6.4–7.4 (m, 7); mass spectrum 212 (25), 211 (100), 210 (46), 196 (45), 194 (27), 181 (19), 180 (17), 167 (6), 134 (21), 91 (21), 77 (17), 65 (6). Hexane–ether (90:10) eluted 2-(2,4,6-trimethylphenyl)-3*H*-azepine (**3a**) (10%, glpc yield 11.5%) as an oil: nmr (CCl_4) δ 2.05 (s, 6), 2.25 (s, 3), 2.9–2.6 (broad d, $J = 7$ Hz, 2), 5.15 (q, 1), 6.65–6.1 (m, 2), 6.82 (s, 2), 7.55 (d, 1, $J = 7$ Hz); mass spectrum 212 (23), 211 (100), 210 (46), 196 (58), 181 (25), 167 (8), 146 (19), 134 (135), 130 (16), 92 (21), 76 (17), 65 (29). Hexane–ether (50:50) eluted 2-hydroxytrifluoroacetanilide (**4a**): 3%; mp 164.5–165° (lit.[18] mp 167–169°), after recrystallization from carbon tetrachloride; mass spectrum 206 (9), 205 (79), 187 (10), 137 (15), 136 (100), (58), 80 (71). Ether eluted 1,3-dihydro-2*H*-azepin-2-one (**5a**) (2% by glpc) (purification was effected by preparative glpc using an SE-30 column at 180°, and the nmr spectrum was in accord with a reported spectrum):[6] mass spectrum 110 (7.5), 109 (83), 81 (32), 80 (100), 66 (23), 53 (28).

When the photolysis was carried out in 40:10:4 mesitylene–methanol–TFA, the only products isolated by a similar work-up procedure were **5a** (14%) and **4a** (trace).

When the photolysis was carried out in 50:4 anisole–TFA, the products isolated were 2-methoxydiphenylamine (**7**, 8%), 4-methoxydiphenylamine (**8**, 18%), and *o*-hydroxytrifluoroacetanilide (4%), each of which was identified by spectral comparison with purified samples from other reactions.

***p*-Tolyl Azide.**—The products isolated by the standard work-up and chromatographic separation are listed in order of elution. Hexane–ether (95:5) eluted 2,4,4′,6-tetramethyldiphenylamine (40%): mp 66–67°, after recrystallization from hexane; nmr (CCl_4) δ 2.08 (s, 6), 2.16 (s, 3), 2.22 (s, 3), 4.8 (broad s, 1), 6.3 (d, 2, $J = 7$ Hz), 6.8 (s overlapping d, $J = 7$ Hz, 4); mass spectrum 226 (19), 225 (100), 224 (25), 210 (24), 209 (9), 208 (16), 195 (10.5), 194 (9), 193 (6), 134 (7.5). Hexane–ether (90:10) eluted 4-methyltrifluoroacetanilide, 2%, mp 109–110, after recrystallization from hexane (lit.[19] mp 112–113°), having expected spectral properties. Hexane–ether (80:20) eluted 2-hydroxy-4-methyltrifluoroacetanilide (11%): mp 193–194°, after recrystallization from chloroform; nmr (acetone-d_6) δ 2.27 (s, 3), 6.6–6.8 (s at 6.8 overlapping d, $J = 8$ Hz at 6.7, 2), 7.7 (d, 1, $J = 8$ Hz), 8.9 (broad, 2); mass spectrum 220 (14), 219 (90), 201 (14), 200 (14), 151 (14), 150 (100), 123 (14), 122 (65), 94 (60), 78 (28), 77 (34).

When the photolysis was carried out in 40:10:4 mesitylene–methanol–TFA, **2b** was isolated in 10% yield and **4b** in 4% yield. Acetone eluted a crude fraction containing azepinone **5b** in 8% yield based on glpc. The analytical sample was collected as an oil by preparative glpc using an SE-30 column at 175°: nmr ($CDCl_3$) 1.89 (s, 3), 2.80 (d, 2, $J = 7$ Hz), 5.33 (broad t, 1, $J = 7$ Hz), 5.80 (d, $J = 9$ Hz), 6.18 (d of d, $J = 9, 4$ Hz), 8.8 (very broad, 1). Spin decoupling established that the signals at 2.80 and 5.33 were coupled. Deuterium exchange established that the 4-Hz coupling present in the signal at 6.18 is with N–H. Mass spectrum 124: (14.5), 123 (100), 108 (16), 95 (25), 94 (100), 70 (67), 44 (98).

When the photolysis was carried out in 50:4 benzene–TFA, 4-methyltrifluoroacetanilide (2%) and **4b** (3%) were the only products isolated.

When the photolysis was carried out in 50:4 anisole–TFA, the products were 2-methoxy-4′-methyldiphenylamine (**9**, 4% by glpc), 4-methoxy-4′-methyldiphenylamine (**10**, 43%, isolated), and 2-hydroxy-4-methyltrifluoroacetanilide (15%).

***o*-Tolyl Azide.**—Hexane–ether (95:5) eluted 2,2′,4,6-tetramethyldiphenylamine (39%): mp 78.5–79.5° after recrystallization from petroleum ether; nmr (CCl_4) δ 2.12 (s, 6), 2.28 (s, 6), 4.7 (broad s, 1), 6.02 (d, 1, $J = 8$ Hz), 6.80 (s, 2), 6.4–7.0 (m, 3); mass spectrum 226 (21), 225 (100), 224 (11), 210 (25), 209 (10), 208 (20), 195 (15), 194 (13), 134 (10), 121 (18).

In some runs a small amount (~3%) of 2-methyltrifluoroacetanilide, mp 79–80° (lit.[19] mp 81–82°), was isolated and identified by spectral properties.

When the photolysis was conducted in 50:4 mesitylene–ethyl trifluoroacetate, no **2c** was formed. The only product isolated was 2,2′-dimethylazobenzene (29%), mp 53–55° (lit.[20] mp 55°), identified by spectral properties.

***o*-Trifluoromethylphenyl Azide.**—Hexane–ether (98:2) eluted 2,4,6-trimethyl-2′-trifluoromethyldiphenylamine **2d** (6%): mp 66–69°, after preparative glpc on a 5% SE-30 column at 160°; nmr (CCl_4) δ 2.17 (s, 6), 2.33 (s, 3), 5.65 (broad s, 1) 6.21 (d, 1, $J = 8$ Hz), 6.4–7.2 (m, with s at 6.94, 4), 7.45 (d, 1, $J = 7$ Hz); mass spectrum 279 (100), 265 (9.5), 244 (62), 230 (9.5), 225 (14), 211 (12), 209 (14), 195 (9.5), 182 (7), 170 (7), 134 (20), 132 (12), 120 (12), 92 (28), 70 (57). Hexane–ether (90:10) eluted an oil with spectral properties suggesting that it was mainly 2-mesityl-3-trifluoromethyl-3*H*-azepine (**3d**): nmr ($CDCl_3$) 4.2 (d, $J = 5$ Hz), 5.38 (d of d, $J = 5, 9$ Hz), 6.2–7.0 (m), 7.62 (d, $J = 8$ Hz). Completely pure samples that would permit conclusive identification or analysis were not obtained. Ether eluted 3-trifluoromethyl-1,3-dihydro-2*H*-azepin-2-one (**5d**): 15% yield; mp 138–138.5°, after recrystallization from carbon tetrachloride; nmr (acetone-d_6) δ 3.4 (d of d, 1, $J = 6, 1$ Hz), 5.55 (d of d, 1, $J = 9, 4$ Hz), 5.90 (d of d, $J = 9, 4$ Hz), 6.65 (m, 2); mass spectrum 178 (13), 177 (100), 158 (46), 149 (17), 148 (15), 129 (25), 128 (25), 121 (19), 119 (60), 117 (69), 108 (81), 102 (25), 101 (23), 84 (33), 82 (92), 80 (100), 53 (42), 39 (23).

2-Fluorophenyl Azide.—Hexane–ether (95:5) eluted **2e**: 36% yield; mp 80–81°, after recrystallization from hexane; nmr (CCl_4) δ 2.17 (s, 6), 2.29 (s, 3), 5.1 (broad s, 1), 6.0–7.0 (m, 6–7); mass spectrum 230 (31), 229 (100), 228 (23), 114 (29), 112 (17), 108 (33), 194 (17), 134 (19), 121 (15), 120 (8). Hexane–ether (80:20) eluted a fraction containing 2-(mesityl)-5-hydroxytrifluoroacetanilide. The pure compound[16] (1% yield) was obtained by recrystallization from carbon tetrachloride: mp 192–192.5°; nmr (acetone-d_6) δ 2.05 (s, 6), 2.30 (s, 3) 3.2 (s, 1, OH?) 6.7–7.0 (m, 3), 7.1 (d, 1, $J = 8$ Hz), 7.70 (d, 1, $J = 1.5$ Hz), 9.3 (broad s, 1, NH); mass spectrum 324 (20), 323 (100), 322 (5), 290 (5), 254 (17), 226 (25), 210 (15), 195 (10).

Hexane–ether (50:50) eluted a fraction containing 2-hydroxytrifluoroacetanilide (1%), mp 163–164°, identified by spectral comparison with an authentic sample.

The photolyzed solution in this case contained a substantial amount of insoluble precipitate. The only substance which could be isolated in pure form[16] (2% yield) from this solid appeared to be a dehydro dimer of 2-hydroxytrifluoroacetanilide: mp >290°; nmr (DMSO-d_6) δ 7.0 (d, $J = 7$ Hz), 7.38 (d, $J = 7$ Hz), 7.52 (s), 10.0 (broad s), 10.5 (broad s); mass spectrum 409 (21), 408 (100), 390 (14), 372 (14), 339 (25), 321 (12), 311 (62), 293 (19), 171 (43), 149 (71).

***p*-Carbomethoxyphenyl Azide.**—Benzene–ether (90:10) eluted a mixture which was primarily the diphenylamine **2f** but also contained two other components according to tlc. The mixture was dissolved in hexane and refrigerated giving crystalline **2f**: 40% yield; mp 116–118°, after repeated recrystallization from hexane; nmr ($CDCl_3$) δ 2.18 (s, 6), 2.32 (s, 3), 3.84 (s, 3), 5.60 (broad s, 1), 6.41 (d, $J = 9$ Hz, 2) 6.93 (s, 2), 7.80 (d, $J = 9$ Hz, 2). The mother liquors from this crystallization contained additional **2f** (8%, total yield 48%) and two other materials. One was separated by preparative tlc on alumina (5:4:1 hexane–benzene–ether) and identified as unreacted **1f** (~15% recovery). The third material was extracted by 8% hydrochloric acid and isolated by basification and extraction to give **3f** (9% yield) (final purification was accomplished by preparative layer chromatog-

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[16] Satisfactory analytical values (±0.4% for C, H, and N) were reported for compound **2b–2g**, **3a**, **4b**, **4f**, **5b**, **5d**, **9**, **10**, **12a**, and **12c**, and other compounds as noted: Ed.

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[19] K. G. Rutherford, S. Y.-S. Ing, and R. J. Thibert, *Can. J. Chem.*, **43**, 541 (1965).

[20] I. Heibron, "Dictionary of Organic Compounds," 4th ed, Oxford University Press, London, 1965, p 1145.

raphy on alumina: nmr peaks (CDCl$_3$) δ 2.05 (s, 6; resolved at −50° to two s at 1.7 and 2.5), 2.18 (s, 3), 2.80 (very broad, 2, sharpened to doublet at 60°), 3.81 (s, 3), 6.19 (t, 1), 6.7–7.0 (m, 3), 7.65 (d, 1); mass spectrum 269 (100), 255 (22), 254 (52), 238 (15), 211 (52), 210 (89), 196 (18), 195 (26), 194 (18), 146 (30), 145 (18), 130 (26), 124 (48), 109 (40), 91 (30), 79 (26), 78 (26), 77 (22); accurate mass determination P$^+$ 269.1398 (calcd 269.1416). Benzene–ether (80:20) eluted **4f** (6%): mp 217–218°, after recrystallization from chloroform–hexane; nmr (acetone-d_6) δ 3.45 (s, 3), 7.0–7.3 (s overlapping d, 2), 7.68 (d, J = 8 Hz, 1); mass spectrum 263 (60), 233 (60), 214 (10), 194 (100), 176 (22), 166 (31), 162 (20), 148 (18), 147 (4), 146 (2), 145 (5), 144 (5), 110 (7), 109 (2), 108 (4), 107 (8), 106 (13), 79 (22), 78 (21), 69 (23), 54 (17), 53 (26), 52 (22), 51 (10).

Thermal Reactions.—A weighed amount of the azide (~10 mmol) was dissolved in the appropriate aromatic substrate (50 ml) and trifluoroacetic acid (4 ml) was added. The reaction flask was equipped with a condenser, and a nitrogen atmosphere was established. The flask was wrapped to prevent any competing photochemical reactions and heated at steam bath temperature (85 ± 5°) for 12–24 hr. Rate measurements subsequently established that the heating period could be shortened for azides with electron-donor substituents. The reaction mixture was then cooled and diluted with 100 ml of ether, washed thoroughly with sodium bicarbonate solution, dried, and concentrated to remove ether and the aromatic solvent. The residue was then subjected to column chromatography using silica gel.

Phenyl Azide.—Reaction was carried out in 50:4 mesitylene–TFA for 16 hr. A crystalline compound separated on removal of the mesitylene from the reaction mixture. This was identified by spectral data as 4-hydroxytrifluoroacetanilide (4%), mp 173–174° (lit.[18] mp 172–173°). On chromatography of the remainder of the product, hexane–ether (95:5) eluted **2a** (55%), identified by spectral comparison with the compound isolated from the photochemical reaction. This was followed by 2,4,6-trimethyl-4′-trifluoroacetamidobiphenyl (**12a**, 5%): mp 113–115°, after recrystallization from hexane; nmr (CDCl$_3$) δ 2.12 (s, 6), 2.29 (s, 3), 5.85 (broad s, 1) 6.42 (d, J = 9 Hz, 2), 6.90 (s, 2), 7.80 (d, J = 9 Hz, 2); mass spectrum 307 (45), 238 (90), 210 (5), 209 (5), 208 (8), 195 (20), 119 (12), 91 (4). Benzene–hexane–ether (2:2:1) eluted *o*-hydroxytrifluoroacetanilide (1%), identified by spectral comparison with a previously prepared sample.

Reaction in 50:4 anisole–TFA gave, on elution of the column with 95:5 hexane–ether, first 2-methoxydiphenylamine (4%) identified by spectral data and then 4-methoxydiphenylamine (6%), mp 104–106° (lit.[21] mp 105°).

***p*-Tolyl Azide.**—Reaction in 50:4 mesitylene-TFA for 12 hr followed by chromatography gave 2,4,4′,6-tetramethyldiphenylamine (84%) having spectral properties identical with the sample prepared in the photochemical reaction.

Reaction in 50:4 *p*-xylene-TFA for 12 hr gave 2,4′,5-trimethyldiphenylamine (**9**): 66% yield; mp 49.5–50.5° (lit.[17] mp 51°), after recrystallization from hexane; nmr (CDCl$_3$) δ 2.18, 2.22, 2.28 (closely spaced singlets, 9), 5.18 (broad s, 1), 6.65 (d, J = 8, 2), 6.8–7.2 (m, 5).

Reaction in 50:4 toluene–TFA for 24 hr followed by chromatography gave a mixture of 2,4′-dimethyldiphenylamine (**14**) and 4,4′-dimethyldiphenylamine (**15**). Crystallization from hexane gave **15** (19%), mp 79° (lit.[22] mp 78–79°). The mother liquors contained **14** (5%) and additional **15** (7%), as determined by glpc.

Reaction in 50:4 benzene–TFA gave a large amount of intractable tarry precipitate, and no 4-methyldiphenylamine was found.

Reaction in 50:4 anisole–TFA for 12 hr followed by chromatography gave, on elution with 95:5 hexane–ether, 2-methoxy-4′-methylbiphenylamine (**12**, 6%), an oil purified by bulb-to-bulb distillation: nmr (CDCl$_3$) δ 2.28 (s, 3), 3.83 (s, 3), 5.9 (very broad s, 1), 6.8–7.3 (m, 8); mass spectrum 213 (100), 198 (45), 197 (33), 196 (17), 183 (90), 155 (11), 154 (8), 91 (14), 77 (14), 65 (17). There was also obtained 4-methoxy-4′-methyldiphenylamine (**13**): 62% yield; mp 82–83°,[23] after recrystallization from hexane; nmr (CDCl$_3$) δ 2.25 (s, 3), 3.75 (s, 3), 5.35 (broad s, 1), 6.6–7.1 (m, 8); mass spectrum 213 (91), 198 (100) 155 (10), 154 (14), 128 (9), 91 (15), 65 (19).

***o*-Tolyl Azide.**—Reaction in 50:4 mesitylene–TFA for 2 hr gave **2c** (59% yield), identified by spectral comparison with the sample prepared photolytically. Hexane–ether (90:10) eluted 4′-trifluoroacetamido-2,3′,4,6-tetramethylbiphenyl (**12c**): 2% yield; mp 135–137°, after recrystallization from hexane; nmr (CDCl$_3$) δ 2.15 (s, 6), 2.35 (overlapping s, 6), 5.60 (broad s, 1), 6.1 (d, J = 8 Hz, 1), 6.95 (s, 2), 7.6–7.9 (m, 2); mass spectrum 321 (63), 252 (100), 222 (5), 209 (16), 208 (16), 111 (7), 104 (7), 104 (7).

***p*-Carbomethoxyphenyl Azide.**—After 24 hr at 85° in 50:4 mesitylene–TFA, 85% of the azide was recovered unreacted. The only product isolated by chromatography was 4′-carbomethoxy-2,4,6-trimethyldiphenylamine (**2f**, 20% yield based on unrecovered azide).

***o*-Methoxyphenyl Azide.**—The reaction in 50:4 mesitylene–TFA was carried out at room temperatures for 48 hr. Hexane–ether (90:10) eluted the diphenylamine **2g**: 79% yield; mp 100–100.5, after recrystallization from hexane; nmr (CCl$_4$) δ 2.14 (s, 6), 2.26 (s, 3), 3.87 (s, 3), 5.35 (broad s, 1), 6.0 (m, 1), 6.5–6.8 (m, 3), 6.82 (s, 3), 6.82 (s, 2); mass spectrum 242 (30), 241 (100), 226 (28), 211 (23), 210 (79), 209 (37), 208 (15), 207 (32). There was also obtained a compound which is apparently the dehydro dimer *N*,*N*′-bis(2,4,6-trimethylphenyl)-2,2′-dimethoxybenzidine:[16] 2% yield; mp 255–257°, after recrystallization from acetone; nmr (CDCl$_3$) δ 2.20 (s, 12), 2.13 (s, 6), 4.00 (s, 6), 5.60 (broad s, 2), 6.18 (d, J = 8 Hz, 2), 6.8–7.1 (m, 8); mass spectrum 481 (38), 480 (100).

Rates of Decomposition of *p*-Tolyl Azide.—A solution of containing about 1.5 mmol of *p*-tolyl azide in 25 ml of the appropriate solvent was thermostated at 80° in a reaction vessel equipped with a sealed magnetically driven high speed stirrer. The reaction was initiated by addition of TFA (4.0 ml). The rate of the reaction was measured by following nitrogen evolution. The following values were obtained: mesitylene, $k = 1.5 \times 10^{-1}$ min^{-1}, $t_{1/2} = 4.6$ min; anisole, $k = 7.6 \times 10^{-3}$ min^{-1}, $t_{1/2} = 91$ min; acetophenone, <15% theoretical N$_2$ evolution in 10 hr, too slow to measure with accuracy.

Registry No.—**1a**, 622-37-7; **1b**, 2101-86-2; **1c**, 18523-45-0; **1d**, 1548-68-1; **1e**, 3296-04-6; **1f**, 20442-96-0; **1g**, 20442-97-1; **2a**, 23592-67-8; **2b**, 39267-44-2; **2c**, 39267-45-3; **2d**, 39267-46-4; **2e**, 39267-47-5; **2f**, 39267-48-6; **2g**, 39267-49-7; **3a**, 39514-14-2; **3d**, 39267-50-0; **3f**, 39267-51-1; **4a**, 10595-66-1; **4f**, 39267-53-3; **5a**, 2183-86-0; **5b**, 39267-55-5; **5d**, 39267-56-6; **9**, 34160-15-1; **12a**, 39267-58-8; **12b**, 39267-59-9; **12c**, 39267-60-2; **13**, 39253-43-5; 2-hydroxy-4-methyltrifluoroacetanilide, 39267-61-3; 2-hydroxytrifluoroacetanilide, 10595-66-1; *N*,*N*′-bis(2,4,6-trimethylphenyl)-2,2′-dimethoxybenzidine, 39267-63-5.

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(23) This value is not in agreement with a recorded value of 55°: A. B. Sen and A. K. Sen Gupta, *J. Indian Chem. Soc.*, **34**, 413 (1957). However, these authors also record mp 79° for 4-methoxydiphenylamine while other sources agree on mp 105° for 4-methoxydiphenylamine.[21,24,25]

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