Table IV. Experimental Data for a Typical Kinetic Run: Reaction between 1-Phenylpropyne and $Hg(OAc)_2$ in MeOH at 25.0 °C[a]

A_t	*t*, min	A_t	*t*, min
0.1195	0	0.8052	24
0.2950	3	0.8427	27
0.4193	6	0.8762	30
0.5145	9	0.9058	33
0.5919	12	0.9321	36
0.6568	15	0.9556	39
0.7134	18	0.9769	42
0.7620	21	0.9964	45

[a] [alkyne] = 3.12×10^{-4} M; $[Hg(OAc)_2] = 2.85 \times 10^{-2}$ M; $A_\infty = 1.084$; $k_{obs} = 8.8 \times 10^{-2}\ s^{-1}$; correlation coefficient = 0.999; reaction % followed = 91%; $k_2 = 2.9 \times 10^{-2}\ s^{-1}\ M^{-1}$.

The data are reported in Table I, as overall second-order rate constants. They are mean values of several runs, carried out under the conditions specified as follows (wavelengths are given in parentheses).

4-Octyne ($C_3H_7C\equiv CC_3H_7$): 2.11×10^{-3} to 4.97×10^{-3} M; $Hg(OAc)_2$, 3.28×10^{-2} to 0.155 M (262, 266, 268, 270, 296, 300, 304, 306 nm).

2-Heptyne ($CH_3C\equiv C(CH_2)_3CH_3$): 2.60×10^{-3} to 4.66×10^{-3} M; $Hg(OAc)_2$, 2.67×10^{-2} to 5.22×10^{-2} M (258, 262, 266, 268, 290, 296, 300, 306, 310 nm).

2-Nonyne ($CH_3C\equiv C(CH_2)_5CH_3$): 2.31×10^{-3} to 3.76×10^{-3} M, $Hg(OAc)_2$, 2.67×10^{-2} to 5.22×10^{-2} M (290, 296, 300, 310, 316 nm).

1,4-Dimethoxy-2-butyne ($MeOCH_2C\equiv CCH_2OMe$): 1.75×10^{-3} M; $Hg(OAc)_2$, 2.86×10^{-2} to 4.60×10^{-2} M (290 nm).

1,4-Diacetoxy-2-butyne ($AcOCH_2C\equiv CCH_2OAc$): 1.75×10^{-3} to 4.10×10^{-3} M; $Hg(OAc)_2$, 2.1×10^{-2} to 4.6×10^{-2} M (290 nm).

Methyl 2-octynoate ($CH_3(CH_2)_4C\equiv CCO_2CH_3$): 8.08×10^{-4} to 4.81×10^{-3} M; $Hg(OAc)_2$, 4.35×10^{-2} to 0.145 M (310, 325 nm).

Methyl 3-phenylpropynoate ($PhC\equiv CCO_2CH_3$): 7.89×10^{-4} M; $Hg(OAc)_2$, 5.03×10^{-3} to 2.51×10^{-2} M (300, 310 nm).

1-Phenylpropyne ($PhC\equiv CCH_3$): 2.50×10^{-5} to 8.50×10^{-2} M; $Hg(OAc)_2$, 1.15×10^{-2} to 0.115 M (300, 310 nm).

1-Phenyl-1-pentyne ($PhC\equiv CC_3H_7$): 4.70×10^{-4} to 4.70×10^{-3} M; $Hg(OAc)_2$, 1.15×10^{-2} to 0.115 M (289, 310 nm).

Diphenylethyne ($PhC\equiv CPh$): 7.29×10^{-5} to 7.29×10^{-3} M; $Hg(OAc)_2$, 2.55×10^{-3} to 0.128 M (310, 316 mn).

Values for a typical run are given in Table IV.

Activation Parameters. The kinetic experiments at different temperatures were duplicated. The related data are as follows (temperatures given in parentheses).

1-Phenylpropyne ($PhC\equiv CCH_3$): 1.29×10^{-3} M; $Hg(OAc)_2$, 2.21×10^{-2} to 0.135 M; k_2 ($M^{-1}\ s^{-1}$) = 3.17×10^{-2} (30.0 °C), 3.95×10^{-2} (35.0 °C), 5.00×10^{-2} (40.0 °C), 5.72×10^{-2} (44.9 °C), 5.82×10^{-2} (45.1 °C).

1-Phenyl-1-pentyne ($PhC\equiv CC_3H_7$): 1.70×10^{-3} M; $Hg(OAc)_2$, 2.67×10^{-2} M; k_2 ($M^{-1}s^{-1}$) = 4.71×10^{-2} (35.0 °C), 5.94×10^{-2} (40.0 °C), 6.53×10^{-2} (44.9 °C), 7.17×10^{-2} (45.1 °C).

Diphenylethyne ($PhC\equiv CPh$): 1.59×10^{-2} M; $Hg(OAc)_2$, 4.98×10^{-2} to 9.97×10^{-2} M; k_2 ($M^{-1}s^{-1}$) = 3.00×10^{-2} (20.0 °C), 4.09×10^{-2} (30.0 °C), 4.55×10^{-2} (34.8 °C), 5.49×10^{-2} (40.0 °C), 6.45×10^{-2} (44.9 °C), 7.32×10^{-2} (49.9 °C).

The second-order rate coefficients, together with the values at 25 °C (Table I), yielded good Arrhenius plots. Activation parameters are in Table III.

Acknowledgment. Partial financing support from the Ministero della Pubblica Istruzione is acknowledged. We thank Dr. Giorgio Cerichelli for NMR spectra.

Registry No. $[Hg(OAc)_2]$, 1600-27-7; $CH_3(CH_2)_2C\equiv C(CH_2)_2CH_3$, 1942-45-6; $CH_3C\equiv C(CH_2)_3CH_3$, 1119-65-9; $CH_3C\equiv C(CH_2)_5CH_3$, 19447-29-1; $CH_3OCH_2C\equiv CCH_2OCH_3$, 16356-02-8; $AcOOCH_2C\equiv CCH_2OAc$, 1573-17-7; $CH_3OC(O)C\equiv C(CH_2)_5CH_3$, 111-12-6; $CH_3OC(O)C\equiv CPh$, 4891-38-7; $PhC\equiv CCH_3$, 673-32-5; $PhC\equiv C(CH_2)_2CH_3$, 4250-81-1; $PhC\equiv CPh$, 501-65-5; $CH_3(CH_2)_2C(O)CH(HgOAc)(CH_2)_2CH_3$, 122948-91-8; $CH_3CH(HgOAc)C(O)(CH_2)_3CH_3$, 122948-92-9; $CH_3C(O)CH(HgOAc)(CH_2)_3CH_3$, 122948-93-0; $CH_3CH(HgOAc)C(O)(CH_2)_5CH_3$, 122948-94-1; $CH_3C(O)CH(HgOAc)(CH_2)_5CH_3$, 122948-95-2; $AcOCH{=}C(HgOAc)CH(OCH_3)CH_2OAc$, 122948-96-3; $CH_3OC(O)C(HgOAc){=}C(OCH_3)(CH_2)_4CH_3$, 122948-97-4; $CH_3OC(O)C(HgOAc){=}C(OCH_3)Ph$, 122948-98-5; (*E*)-$CH_3C(HgOAc){=}C(OCH_3)Ph$, 122948-99-6; (*Z*)-$CH_3C(HgOAc){=}C(OCH_3)Ph$, 122949-00-2; (*E*)-$PhC(HgOAc){=}C(OCH_3)Ph$, 122949-02-4; (*Z*)-$PhC(HgOAc){=}C(OCH_3)Ph$, 122949-01-3; $CH_3(CH_2)_2C(O)(CH_2)_3CH_3$, 589-63-9; $CH_3(CH_2)_2CH(OH)(CH_2)_3CH_3$, 589-62-8; $CH_3(CH_2)_2C(O)CH(I)(CH_2)_2CH_3$, 122949-03-5; $CH_3C(O)(CH_2)_4CH_3$, 110-43-0; $CH_3CH_2C(O)(CH_2)_3CH_3$, 106-35-4; $CH_3CH_2C(O)(CH_2)_5CH_3$, 925-78-0; $CH_3C(O)(CH_2)_6CH_3$, 821-55-6; $CH_3OCH_2CH{=}C(OCH_3)CH_2OCH_3$, 122949-04-6; $CH_3O(CH_2)_2C(O)CH_2OCH_3$, 25680-86-8; (*Z*)-$AcOCH_2C(OCH_3){=}CHCH_2OAc$, 122949-05-7; (*E*)-$AcOCH_2C(OCH_3){=}CHCH_2OAc$, 122949-06-8; $CH_3OC(O)CH_2C(O)(CH_2)_4CH_3$, 22348-95-4; (*E*)-$CH_3OC(O)CH{=}C(OCH_3)Ph$, 60456-20-4; (*Z*)-$CH_3OC(I)CH{=}C(OCH_3)Ph$, 40203-51-8; $PhC(O)CH_2CH_3$, 93-55-0; (*E*)-$PhC(OCH_3){=}CHCH_3$, 4541-69-9; (*Z*)-$PhC(OCH_3){=}CHCH_3$, 4518-65-4; $PhC(OCH_3){=}C(HgOAc)(CH_2)_2CH_3$, 122949-07-9; $PhC(O)(CH_2)_3CH_3$, 1009-14-9; $PhCH(I)CH(OCH_3)Ph$, 122949-08-0; $PhC(OCH_3){=}CHPh$, 79341-79-0; $CH_3OC(I)CH_2C(O)Ph$, 614-27-7.

Photochemistry of Fluorinated Aryl Azides in Toluene Solution and in Frozen Polycrystals

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Several fluorinated triplet aryl nitrenes have been generated in low-temperature polycrystals by photolysis of the corresponding azides. Upon extended photolysis at −196 °C the nitrenes abstract hydrogen from frozen toluene to give anilino–benzyl radical pairs, which subsequently combine to give CH insertion products. The radical pairs and the triplet nitrenes have been detected by EPR. In toluene solution, the major reaction products are tar, the corresponding fluorinated anilines, and azo compounds.

The photochemical reactions of aryl azides have been studied for several years. These reactions have gained considerable attention due to their utility in heterocyclic synthesis,[1] in the production of photoimaging devices,[2] and in the biochemical method of photoaffinity labeling (PAL).[3] In a PAL experiment, an analogue of a natural

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[1] Wentrup, C. *Heterocyclic Chemistry*; Katritsky, A. R., Boultin, A. J., Eds.; Academic: New York, 1981; Vol. 28.

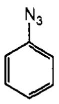
[2] Breslow, D. S. *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic: San Diego, CA, 1984.

[3] Bayley, H. Photogenerated Reagent In *Biochemistry and Molecular Biology*; Elsevier: New York, 1983.

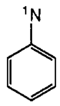
0022-3263/89/1954-5938$01.50/0

ligand bearing a photosensitive group is complexed with a biological macromolecular receptor. Upon photolysis of the receptor–ligand complex, a reactive intermediate is generated which in a successful experiment will react with a component of the receptor site and form a new covalent bond.

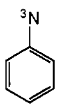
Aryl azides have been the most frequently utilized photoaffinity labels since they are relatively easy to synthesize and handle. However, photolysis of simple aryl azides can give a variety of products, the nature of which are affected by the temperature, the medium, and the placement of substituents on the aromatic ring.[4] It is well appreciated that phenyl azide will cleave upon photolysis to form molecular nitrogen and a "C_6H_5N" fragment. At least four reactive intermediates have at some time been associated with this fragment: singlet phenylnitrene **2S**, triplet phenylnitrene **2T**, 1,2-azacycloheptatetraene **3**, and benzazirine **4**. The nature of the intermediate produced upon photolysis of a given aryl azide may vary depending upon substitution patterns and temperature.[4,5] Thus, it would seem that a more complete understanding of the photochemistry of a given aryl azide is a basic prerequisite for its use in photoaffinity labeling.



1



2S



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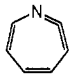

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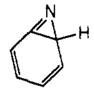
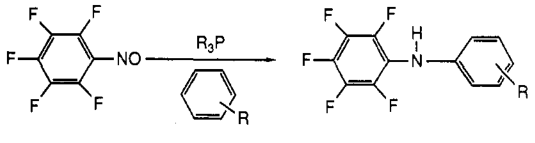


4

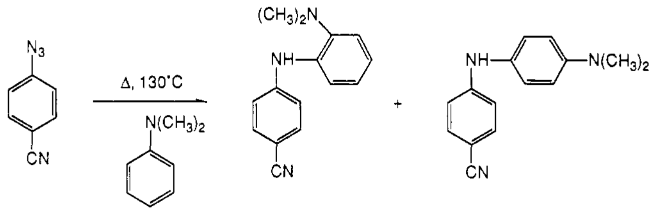
Recent work from several research groups has demonstrated that the principal reactive intermediate generated in solution upon photolysis of phenyl azide is the ketenimine **3**.[6] Triplet phenylnitrene can be generated in solution by triplet-sensitized photolysis of **1** or by direct photolysis of highly dilute solutions of phenyl azide in alkanes. Triplet phenylnitrene can also be generated by photolysis of phenyl azide at −196 °C.[4-6] Photolysis of phenyl azide **1** in hydrocarbons at 25 °C leads mainly to polymeric tar and to only a small amount of aniline and azobenzene. The formation of formal CH insertion adducts between singlet phenylnitrene and an external trapping reagent, the desired reaction in PAL, is not observed. The poor yields of volatile products obtained when phenyl azide is decomposed in hydrocarbons reflects the ease with which ketenimine **3** polymerizes in the absence of nucleophiles.[6] However, **3** reacts rapidly with amines to produce stable 3*H*-azepine adducts.[7] The use of simple aryl azides as photoaffinity labeling reagents has been somewhat limited by the poor reactivity of the photogenerated ketenimine intermediates toward nonnucleophilic substrates and their consequent inability to produce adducts with hydrocarbon traps. Obviously this type of ketenimine will work well in a PAL experiment only when a nucleophile is present in the binding pocket of the biomolecule.

The presence of electron-withdrawing substituents in an aryl azide is expected to have a dramatic effect on the nature and reactivity of the intermediate produced on photolysis. In fact, Reiser and Leyshon observed that electron-withdrawing substituents enhance the rate of hydrogen atom abstraction reactions of arylnitrenes immobilized in a polymer matrix.[8] Schuster and co-workers have shown that upon *p*-nitro substitution of phenyl azide the corresponding ketenimine is not generated by photolysis and that in this system triplet (*p*-nitrophenyl)nitrene is now the principal reactive intermediate in solution.[9] Unfortunately the atom-transfer reactions of triplet (*p*-nitrophenyl)nitrene produce (*p*-nitrophenyl)aniline rather than formal insertion products.

Only a few examples of formal nitrene insertion into CH bonds have been reported. Abramovitch, Challand, and Scriven[10] showed that the (pentafluorophenyl)nitrene intermediate generated from treatment of nitroso compound **5** with triethyl phosphite was very electrophilic. This nitrene attacked not only mesitylene, but also toluene, anisole, and even benzene. The corresponding diarylamines **6** were obtained in 2–18% yields. These workers subsequently observed appreciable yields (13–38%) of diphenylamines produced in the thermolysis (130–140 °C) of *p*-nitrophenyl; *p*-(trifluoromethyl)phenyl, and *p*-cyanophenyl azide **7** in *N*,*N*-dimethylaniline, 1,3,5-trimethoxybenzene, and mesitylene. The low yields of CH insertion products formed, and the high temperatures required in most of these examples make them incompatible with PAL applications.



5 6



7 8 9

We have observed that the photochemistry of aryl azides is highly sensitive to temperature.[6b,11] At low temperature (−196 °C), photolysis of phenyl azide **1** gave high yields of the triplet nitrene derived products aniline and azobenzene, whereupon products derived from ketenimine **3** were obtained upon photolysis of phenyl azide **1** in solution at warmer temperatures (>−150 °C). We have also observed that (*m*-nitrophenyl)nitrene reacts with frozen polycrystalline (−196 °C) toluene at the benzylic position to give a formal CH insertion adduct **11** in 30% yield. This reaction product was not observed on photolysis of *m*-nitrophenyl azide **10** in toluene solution.[12a] Similar results were obtained upon photolysis of *m*-carbomethoxyphenyl

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(4) Smith, P. A. S. *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic: San Diego, CA, 1984.

(5) Platz, M. S. *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic: San Diego, CA, 1984.

(6) (a) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 5229. (b) Leyva, E.; Platz, M. S.; Persy, G. B.; Wirz, J. *J. Am. Chem. Soc.* **1986**, *108*, 3783. (c) Li, Y.-Z.; Kirby, J. P.; George, M. W.; Poliakoff, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 8092. (d) Meijer, E. W.; Nijhuis, S.; van Vroonhoven, F. C. B. M. *J. Am. Chem. Soc.* **1988**, *110*, 7209.

(7) Doering, W. von E.; Odum, R. A. *Tetrahedron* **1966**, *22*, 81.

(8) Reiser, A.; Leyshon, L. *J. Am. Chem. Soc.* **1970**, *92*, 7487.

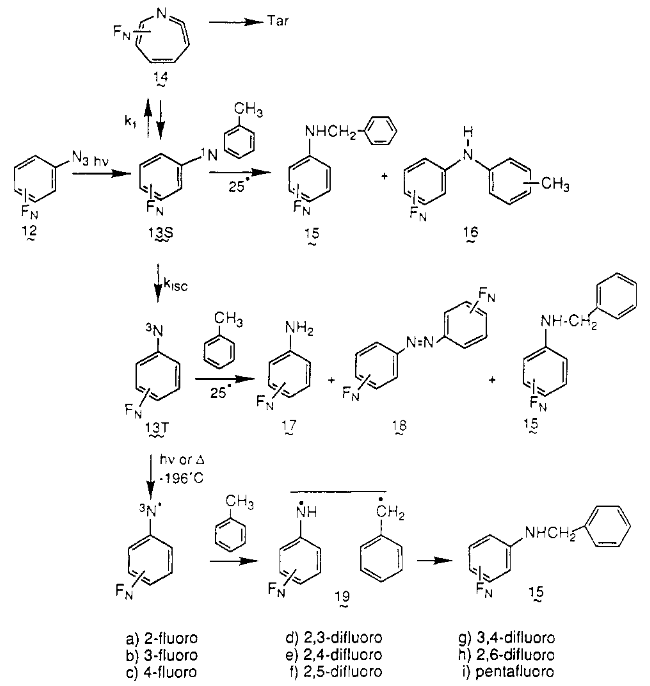
(9) (a) Liang, T.-Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1987**, *109*, 7803. (b) Liang, T.-Y.; Schuster, G. B. *Tetrahedron Lett.* **1986**, *27*, 3325.

(10) (a) Abramovitch, R. A.; Challand, S. R.; Scriven, E. F. V. *J. Am. Chem. Soc.* **1972**, *94*, 1374. (b) Abramovitch, R. A.; Scriven, E. F. V. *Chem. Commun.* **1970**, 787. (c) Abramovitch, R. A.; Challand, S. R.; Scriven, E. F. V. *J. Org. Chem.* **1972**, *37*, 2705.

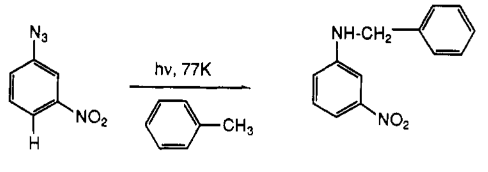
(11) Leyva, E.; Platz, M. S. *Tetrahedron Lett.* **1985**, *26*, 2147.

(12) (a) Torres, M. J.; Zayaz, J.; Platz, M. S. *Tetrahedron Lett.* **1986**, *27*, 791. (b) Kanakarajan, K.; Goodrich, R.; Young, M. J. T.; Soundararajan, S.; Platz, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 6536.

Scheme I

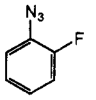


azide in polycrystalline toluene and in toluene solution. Once again a nearly 30% yield of CH insertion adduct could be realized at −196 °C, but no trace of this product could be detected upon photolysis of the azide in toluene at room temperature.[12b]



10 11

Recently we have reported that low-temperature solid-state photolysis of pentafluorophenyl and 2,6-difluorophenyl azide gave nearly quantitative yields of CH insertion products.[13] These results led us to study the photochemistry of fluorinated azides **12a–g** at various temperatures to systematically determine the sensitivity of the yield of insertion product to the position and number of fluorine substituents on the aromatic ring.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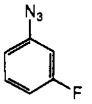
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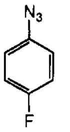
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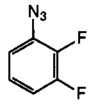
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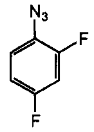
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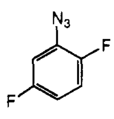
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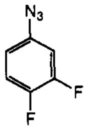
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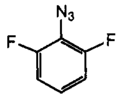
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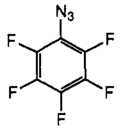
12i

Results

Product Studies in Toluene Solution. Photolysis of azides **12a–i** in toluene at 25 °C gave mostly tar, the corresponding fluorinated anilines **17a–i** and azo compounds **18a–i** (Scheme I). Only low yields of insertion adducts **15a–h** were observed under these conditions (Table I). No other volatile products were detected. It is generally true that the more highly fluorinated the aromatic azide the larger the yield of 1:1 adducts (**15** and **16**) with toluene realized. Moderate yields of diarylamines **16i** were observed upon photolysis of pentafluorophenyl azide **12i**, but photolysis of aryl azides **12a–g** under the same conditions did not give quantifiable amounts of diarylamines **16a–g**.

Table I. Distribution of Products Formed on Photolysis of Fluorinated Phenyl Azides in Toluene at 25 °C[a,b]

azide	17[c] (aniline)	18[c] (azo)	15[c] (adduct)
12a	9	24	4
12b	3	8	traces
12c	traces	7	–
12d	4	16	2
12e	5	24	11
12f	9	16	4
12g	traces	12	traces
12h[12]	17	3	13[d]
12i[12]	12	–	52[d]

[a] Samples were photolyzed in a Rayonet photoreactor with a 350-nm light source for 4 h. [b] Azide concentration: 0.04 M. Diphenylmethane (internal standard) concentration: 0.01 M. [c] Percent yields are absolute relative to internal standard ±1%. [d] Yield includes isomers **16**, see ref 13 and 14.

Table II. Distribution of Products Formed on Photolysis of Fluorinated Phenyl Azides in Toluene at −78 °C[a–c]

azide	17[d] (aniline)	18[d] (azo)	15[d] (adduct)
12a	5	30	–
12b	3	13	traces
12c	3	16	traces
12d	5	35	traces
12e	traces	30	–
12f	3	22	traces
12g	traces	10	traces
12h[12]	16	24	traces
12i[12]	10	17	33[e]

[a] Samples were photolyzed in a Rayonet photoreactor with a 350-nm light source for 4 h. [b] Samples were kept at −78 °C for 45 h. [c] Azide concentration: 0.04 M. Diphenylmethane (internal standard) concentration: 0.01 M. [d] Percent yields are absolute relative to internal standard ±1%. [e] Yield includes isomers **16**, see ref 13.

Upon photolysis at −78 °C some tar was formed in all of the samples (Table II). There was an increase in the yields of azo compounds **18a–g** upon cooling to −78 °C but there was also a corresponding decrease in the yields of the desired insertion adducts **15a–g**. Thus the simple expedient of lowering the temperature does not itself result in increased yields of adducts. These results followed the same product distribution pattern observed with pentafluoro- and 2,6-difluorophenyl azides.[13]

The photolysis of aryl azides **12a–g** at 25 °C under triplet-sensitized conditions led to a decrease in the amount of tar produced and a higher overall material balance of volatile products (Table III). The yields of azo compounds **18a–g** and anilines **17a–g** increased for most of the azides. On the other hand, the yields of insertion products **15a–g** decreased. Thus the formation of the triplet nitrene in solution is not sufficient to raise the yields of insertion products.

The results of solution-phase photolysis experiments are consistent with our previous mechanistic analysis of phenyl azide **1**.[6,10] The relevant aspects of this analysis are summarized in Scheme I. At ambient temperature, photolysis of an aryl azide **12** produces the singlet nitrene **13S**, which

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(13) Leyva, E.; Young, M. J. T.; Platz, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 8307.

Scheme II

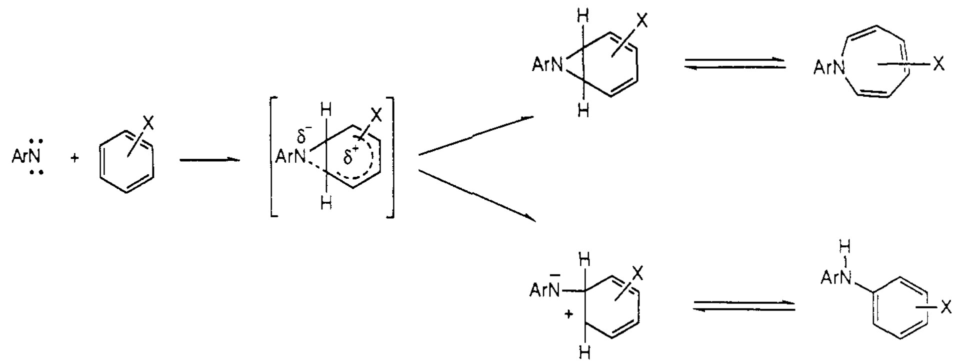

Table III. Distribution of Products Formed on Photolysis of Fluorinated Phenyl Azides in Toluene at 25 °C under Sensitized Conditions^{a-c}

azide	**17**^{d} (aniline)	**18**^{d} (azo)	**15**^{d} (adduct)
12a	10	34	–
12b	4	21	traces
12c	traces	22	traces
12d	6	28	traces
12e	6	48	5
12f	traces	33	traces
12g	8	16	3
12h[12]	54	10	5^e
12i[12]	17	–	8^e

[a] Samples were photolyzed in a Rayonet photoreactor with a 350-nm light source for 4 h. [b] Azide concentration: 0.04 M. Diphenylmethane (internal standard) concentration: 0.01 M. [c] Naphthyl phenyl ketone (0.1 M) used as sensitizer. [d] Percent yields are absolute relative to internal standard ±1%.

Table IV. Distribution of Products Formed on Photolysis of Fluorinated Phenyl Azides in Toluene at −196 °C^{a-c}

azide	**17**^{d} (aniline)	**18**^{d} (azo)	**15**^{d} (adduct)
12a	4	14	35
12b	4	8	8
12c	traces	16	6
12d	traces	16	14
12e	5	18	39
12f	traces	7	25
12g	traces	25	8
12h[12]	traces	6	94
12i[12]	6	8	77

[a] Samples were allowed to stand for 4 days at −196 °C prior to thawing. Samples were photolyzed in a Rayonet photoreactor with a 350-nm light source for 4 h. [b] Samples were kept at 77 K for 4 days after photolysis. [c] Azide concentration: 0.04 M. Diphenylmethane (internal standard) concentration: 0.01 M. [d] Percent yields are absolute relative to internal standard ±1%.

can react with toluene on the aromatic ring or at a benzylic C–H bond. The prevalence of the reaction with toluene mirrors the extent of fluorination of the aryl nitrene. The singlet nitrene may also ring expand to ketenimine **14** or undergo intersystem crossing (ISC) to triplet nitrene **13T** in competition with the reaction with solvent. Once **14** is formed it can polymerize to intractable tars, thus decreasing the overall yield of products. Although triplet sensitization and low temperature (−78 °C) produced the triplet nitrene intermediate, these conditions did not lead to adduct formation. Tar formation is still observed during the sensitized photolysis, thus a second polymerization pathway must be possible.

The formation of diarylamines **16** has been explained as electrophilic attack of the singlet nitrene on the aromatic ring (Scheme II).[8] This mechanism is in agreement with the observation that diarylamines **16** are not formed upon triplet-sensitized photolysis.[13] Net aryl nitrene insertion into an aromatic CH bond has been observed in moderate yields only for the more electrophilic (pentafluorophenyl)nitrene **13iS**.[14]

Product Studies in a Frozen Matrix. Photolysis of azides **12a–g** in frozen toluene at −196 °C gave somewhat different results than photolysis in fluid solution. Some tar was formed with all of the azides studied, and the yields of azo compounds **18a–g** were only moderate (Table IV). However, the yields of insertion products **15a** to **15g** obtained at −196 °C were substantially higher than the yields found in fluid solution with all of the azides studied. Aryl azides **12b**, **12c**, and **12g** lacking fluorine substituents in the ortho position gave the lowest yields (8, 6, and 8%, respectively) of adducts. Azides **12a**, **12d**, **12e**, and **12f** with one fluorine substituent in the ortho position gave much higher yields (35, 14, 39, and 25%, respectively). Nearly quantitative yields (94% and 97%) were observed for azides **12i** and **12j**, which have fluorine substituents in both of the ortho positions.[12] In addition, higher material balances were obtained in low-temperature solids than in solution at room temperature.

The increase in overall yields realized upon drastically lowering the temperature can be explained by a change in the partitioning ratio of the singlet nitrene with temperature (Scheme I). At room temperature k_{isc} is relatively slow and little triplet nitrene **13T** is formed. Under these conditions the putative ketenimine **14** is formed in solution and may polymerize to form tar in the absence of a nucleophile. At very low temperature intersystem crossing is fast relative to all other processes available to the singlet nitrene, thus the yield of **13T** increases. This is demonstrated by the increased yields of the triplet-derived products such as azo compound **18** and insertion adduct **15** observed at −78 °C. The solid-state conditions enhance the yield of adduct **15** by retarding the rate of formation of azo dimer **18**. In the polycrystalline solid, diffusion is quite limited and **13T** can react most efficiently with neighboring molecules of toluene. It is possible that the azo compound is only formed when the matrix is melted. The formation of adduct **15** under matrix conditions can be best visualized as a stepwise process (Scheme I). The triplet nitrene **13T** abstracts a hydrogen atom from toluene (either thermally or photochemically, vide infra) to give an anilino-benzyl radical pair which subsequently combines to give **15**. A triplet aryl nitrene has a very long lifetime in frozen toluene at 77 K. As a consequence it can accumulate in the matrix and eventually compete with unreacted azide for the absorption of light. Thus, under matrix conditions the triplet nitrene can undergo a secondary photochemical reaction. It can undergo either the desired H atom matrix abstraction reaction or ring expansion to the corresponding ketenimine. The missing

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(14) Young, M. J. T. Ph.D. Thesis, The Ohio State University, 1988.

Table V. Distribution of Products Formed on Photolysis of Fluorinated Phenyl Azides in Toluene at −196 °C[a–c] Followed by Immediate Thawing of the Sample

azide	**17**[d] (aniline)	**18**[d] (azo)	**15**[d] (adduct)
12a	7	21	24
12b	4	10	5
12c	traces	18	3
12d	4	19	9
12e	4	21	29
12f	traces	14	16
12g	traces	30	5

[a] Samples were photolyzed in a Rayonet photoreactor with a 350-nm light source for 4 h. [b] Samples were thawed immediately after photolysis. [c] Azide concentration: 0.04 M. Diphenylmethane (internal standard) concentration: 0.01 M. [d] Percent yields are absolute relative to internal standard ±1%.

material balance in the matrix photolysis of azide **12** can be explained by secondary photolysis of **13T** to **14**, which undergoes polymerization upon melting the matrix. In fact, we have observed that triplet phenylnitrene **2T** gives ketenimine **3** upon extended photolysis at 77 K.[6b] This observation agrees with previous IR detection of this species in rare gas matrices.[15]

The higher yields of adducts realized with di-ortho-substituted azides **12h** and **12i** is easily understood on the basis of matrix IR experiments.[15] These studies have demonstrated that ortho substituents suppress the photochemical ring expansion of nitrenes to ketenimines. Thus compounds **12h** and **12i** are the least likely to photochemically ring expand and the most likely to undergo the desired photochemical hydrogen atom abstraction reaction with the toluene matrix.

The distribution of products formed upon photolysis of azides **12a–g** at −196 °C in samples kept frozen for 4 days and in samples thawed immediately after photolysis are shown in Tables IV and V. The overall yields in both conditions were not affected, remaining almost the same. However, the product distribution changed noticeably. The yields of the azo compounds **18a–g** were higher when the samples were thawed immediately after photolysis. On the other hand, standing for long periods of time in the solid state increases the yields of insertion products **15a–g**. When the samples are kept in the solid state, diffusion is limited and a slow thermal reaction to form radical pair **19** is possible. Thawing the samples after photolysis results in the restoration of diffusion, allowing the triplet nitrene to undergo dimerization, thereby increasing the yields of **18**.

Matrix EPR Studies. Various spectroscopic methods have been used to detect the intermediates produced on photolysis of aryl azides. The first spectroscopic identification of triplet phenylnitrene **2T** was obtained by Wasserman and co-workers in 1962.[16] They irradiated phenyl azide **1** in fluorolube at −196 °C in the cavity of an EPR spectrometer and obtained an EPR signal that was stable for at least 18 h after irradiation was discontinued. The signal disappeared on warming the sample as expected for a reactive intermediate. The EPR spectrum had a low-field line (1620 G) corresponding to a $\Delta M = 2$ transition and one high field line (6700 G) corresponding to the $\Delta M = 1$ transition. Photolysis ($\lambda > 295$ nm) of azides **12a–g** in a variety of matrices gave the EPR spectra of the

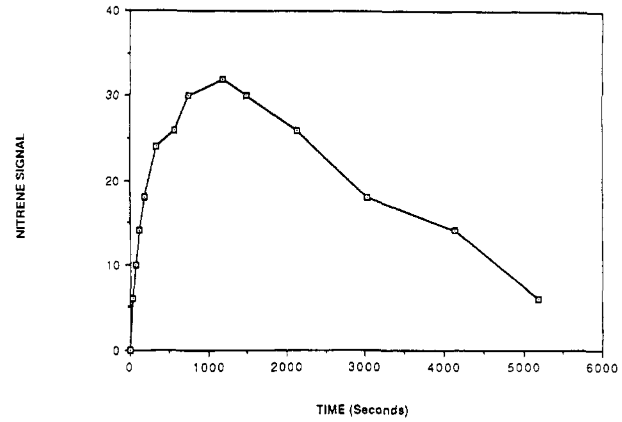

Figure 1. Time dependance of the EPR signal of **13eT** in toluene at −196 °C during continuous irradiation.

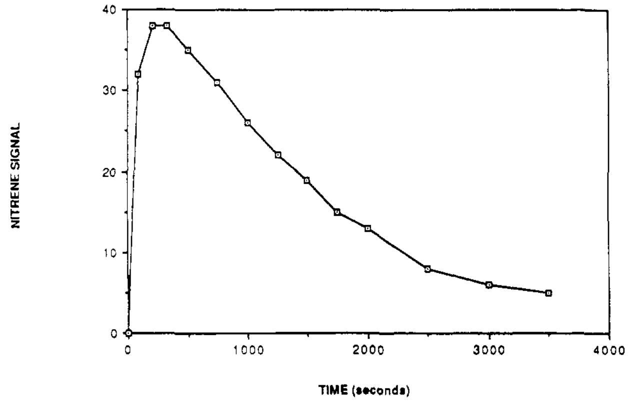

Figure 2. Time dependance of the EPR signal of **13eT** in MTHF at −196 °C during continuous irradiation.

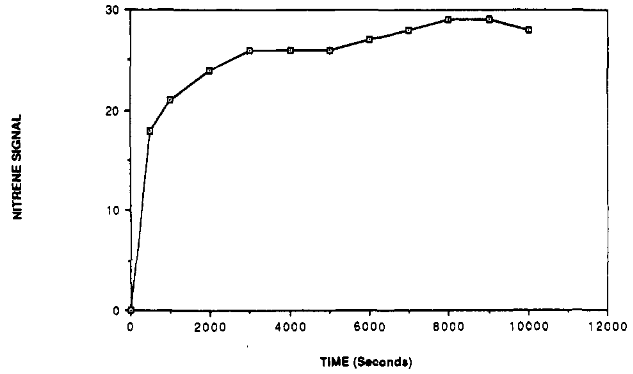

Figure 3. Time dependance of the EPR signal of **13eT** in FBTHF at −196 °C during continuous irradiation.

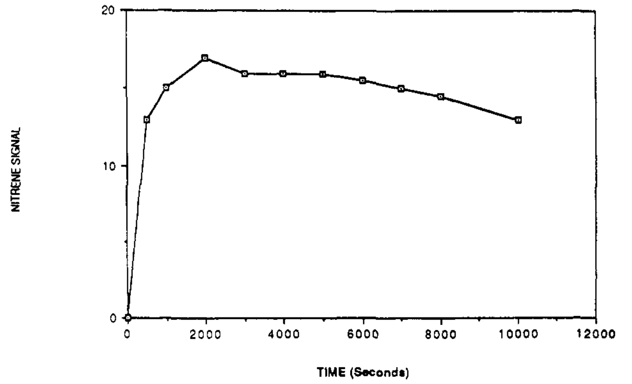

Figure 4. Time dependance of the EPR signal of **13cT** in toluene-d_8 at −196 °C during continuous irradiation.

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(15) (a) Chapman, O. L.; Le Roux, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 282. (b) Donnelly, T.; Dunkin, I. R.; Norwood, D. S. D.; Prentice, A.; Shields, C. J.; Thompson, P. C. P. *J. Chem. Soc., Perkin Trans. 2* **1985**, *26*, 2147.

(16) Smolinsky, G.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 3220.

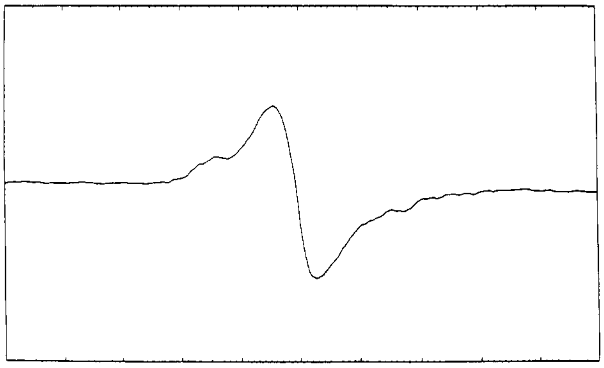

Figure 5. EPR spectrum of the radical pair derived from the photoreaction of **13eT** and toluene. The spectrum is centered at 3270 G and is 400 G wide.

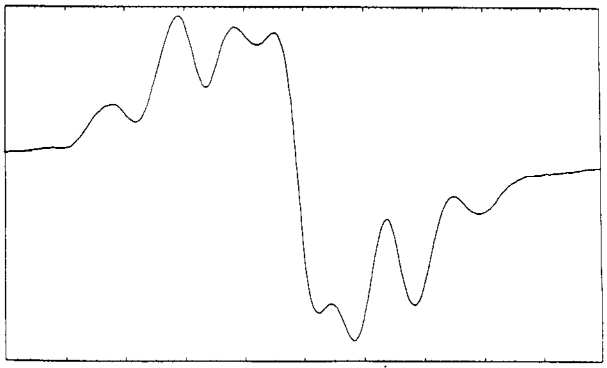

Figure 6. EPR spectrum of the radical pair derived from the photoreaction of **13eT** and MTHF. The spectrum is centered at 3300 G and is 200 G wide.

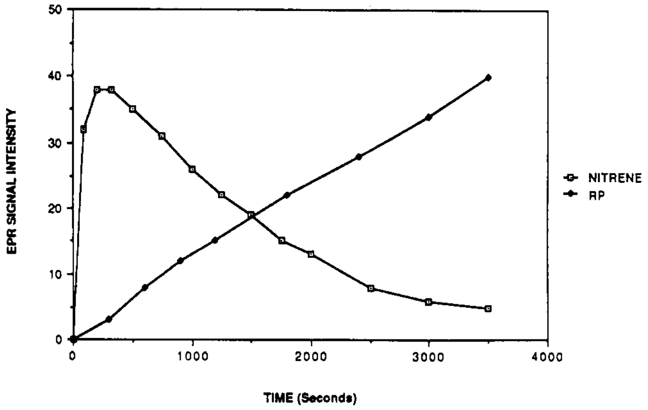

Figure 7. Time dependance of the EPR signals of **13eT** and **19e** in MTHF at -196 °C during continuous irradiation.

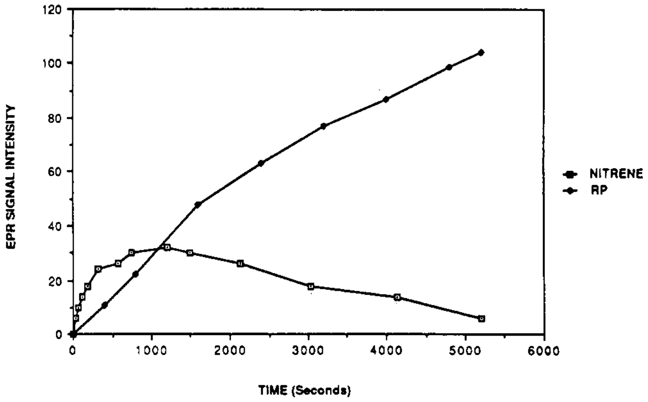

Figure 8. Time dependance of the EPR signals of **13eT** and **19e** in toluene at -196 °C during continuous irradiation.

corresponding triplet nitrenes **13aT–gT**, all of which were stable in the dark for several hours at -196 °C. In frozen toluene, these nitrenes were destroyed by prolonged photolysis as evidenced by the disappearance of their EPR resonance spectra (Figure 1). The same trend was observed in the photolysis of the azides in MTHF at 77 K (Figure 2). In contrast, nitrenes **13aT–gT** were much more stable to prolonged photolysis in perfluoro-2-*n*-butyltetrahydrofuran (FBTHF) and in toluene-d_8 where atom abstraction was less favorable or impossible (Figures 3 and 4). In most cases, the photoinduced disappearance of **13T** in frozen toluene was accompanied by the formation of an EPR spectrum whose zero-field parameter $|D/hc|$ is consistent with an anilino–benzyl radical pair **19**, centered near 3300 G (Figure 5). Radical pair spectra were also observed in MTHF (Figure 6). The relative intensity of the nitrene and the alleged radical pair EPR signals generated upon extended photolysis in MTHF and toluene were measured as a function of irradiation time (Figures 7 and 8). Whereas the EPR signal intensities of the triplet nitrenes and radical pairs both increased following brief irradiation, the triplet EPR signal of the nitrene decayed while the radical pair signal kept growing on continued photolysis. These results are consistent with the mechanism shown in Scheme I in which the radical pair **19** is generated from photolysis of triplet nitrene **13T**. We have observed similar behavior for triplet aryl carbenes at 77 K.[17] Chapman and Dunkin have studied the matrix IR spectra of several ketenimines.[15] It is clear that 2,6-disubstituted phenylnitrenes do not photochemically ring expand at low temperature to form ketenimines. Thus the higher yields of coupling products derived from ortho- and di-ortho-substituted fluorinated azides is easily understood. In these systems the photochemically driven H atom abstraction reactions of the triplet nitrenes compete most effectively with the undesired ring expansion process. It is interesting to note that higher yields of adducts at -196 °C are obtained when the photolyzed samples are allowed to stand in the dark at -196 °C for 4 days following irradiation (Table IV) rather than annealed immediately after photolysis (Table V). This observation implies that there is a slow thermal reaction between the nitrene and the matrix.

Conclusions

Our studies on the photochemistry of fluorinated aryl azides show that these reagents could be useful in photoaffinity labeling work at low temperature. Photolysis of these azides in toluene at ambient temperature gives the singlet nitrene **13S**, which can form adducts with toluene in low yield. At cryogenic temperatures, singlet nitrene **13S** undergoes ISC to **13T** to a larger extent than at ambient temperature. An aryl nitrene **13T** generated in the solid state can accumulate and undergo photochemical H atom abstraction to give radical pairs, which eventually collapse to form CH insertion adducts in moderate yields upon warming the matrix. Our product studies suggest that ortho fluoro substitution, low temperature, and rigid phase are the desired conditions for efficient photoaffinity labeling of hydrocarbons with simple aryl azides.

Experimental Section

General Methods. Melting points were recorded on an electrochemical capillary melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-250

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(17) Barcus, R. L.; Wright, B. B.; Leyva, E.; Platz, M. S. *J. Phys. Chem.* **1987**, *91*, 6677.

(250-MHz) spectrometer. All ^{1}H chemical shifts are reported relative to TMS as an internal standard. ^{19}F NMR spectra were recorded on a Bruker AM-250 (250-MHz) instrument and were proton decoupled. All ^{19}F chemical shifts are reported relative to hexafluorobenzene (162.9 ppm) as an internal standard. Infrared spectra were recorded on a Perkin-Elmer Model 1710 infrared Fourier transform spectrometer. Mass spectra and exact masses were obtained on a V6 70-2505 or a Kratos MS-30 mass spectrometer. Gas chromatographic analyses were performed on a Perkin-Elmer 8500 gas chromatograph equipped with split/splitless injection, a flame ionization detector, and a 30 m × 0.254 mm J&W Scientific fused silica capillary column (5% DB-1701, 0.25 μm). GC/MS spectra were obtained with a Finnegan 4021 gas chromatograph/mass spectrometer.

Materials. Toluene, 2-fluoroaniline, 3-fluoroaniline, 4-fluoroaniline, 2,3-difluoroaniline, 2,4-difluoroaniline, 2,5-difluoroaniline, and 3,4-difluoroaniline were purchased from Aldrich and were used without further purification.

General Procedure for Preparation of Azides 12a–g. All the azides were prepared from the corresponding anilines following a standard literature procedure[18] with only minor modifications. The corresponding aniline (0.023 mol) was dissolved in a warm (40–50 °C) solution of concentrated sulfuric acid (4.0 mL) and concentrated trifluoroacetic acid (20 mL). The amine solution was cooled to room temperature and diazotized with a solution of sodium nitrite (0.03 mol) in 20 mL of water. The solution was stirred for 30 min while kept in an ice–water bath. A solution of sodium azide (0.040 mol) in 15 mL of water was added dropwise to the cold solution. The resulting solution was stirred for 1 h and extracted with ether. The organic extracts were washed with water and a saturated solution of sodium carbonate. The organic solution was dried over magnesium sulfate, and the solvent was removed to yield a yellow oil. The oil was purified by passage through a neutral alumina column using hexane as the eluant.

General Procedure for Preparation of *N*-Benzylanilines 15e–g. The substituted *N*-benzylanilines were all prepared by the method of Houben.[19] The substituted aniline (0.016 mol) and potassium carbonate (0.015 mol) were placed in a round-bottom flask containing 50 mL of water. Benzyl chloride (0.018 mol) was added, and the resulting mixture was refluxed for 12 h. The mixture was extracted with ether. The organic layer was dried over magnesium sulfate, and the solvent was removed to yield a brown oil. The oil was purified by column chromatography with neutral alumina using hexane as the eluant.

General Procedure for Preparation of Azo Compounds 18a–g. Authentic samples of all the azo compounds used in this study were prepared following Birchall's procedure.[20] The corresponding aniline (0.045 mol) and lead tetraacetate (0.068 mol) were placed in a round-bottom flask containing 200 mL of benzene. The dark red solution was refluxed for 2 h and filtered hot. The remaining solid mixture was rinsed several times with benzene. The benzene extracts were combined, and the solvent was removed to yield a red solid. The solid was purified through a neutral alumina column using a (9:1) mixture of hexane/ethyl acetate as the solvent.

2-Fluorophenyl azide (12a): 65%; IR (neat, cm^{-1}) 2120, 2100 ($-N_3$); ^{1}H NMR (acetone-d_6) δ 7.20 (d, 4 H, aromatic); ^{19}F NMR (acetone, ppm) −126.37 (s, 1 F, aromatic); MS *m/e* calculated for $C_6H_4N_3F$ 137.0390, observed 137.0392, difference 0.0002.

3-Fluorophenyl azide (12b): 64%; IR (neat, cm^{-1}) 2120 ($-N_3$); ^{1}H NMR (acetone-d_6) δ 7.43 (q, 1 H, aromatic), 7.8–6.8 (m, 3 H, aromatic); ^{19}F NMR (acetone, ppm) −110.85 (s, 1 F, aromatic); MS *m/e* calculated for $C_6H_4N_3F$ 137.0390, observed 137.0379, difference 0.0011.

4-Fluorophenyl azide (12c): 55%; IR (neat, cm^{-1}) 2120, 2100 ($-N_3$); ^{1}H NMR (acetone-d_6) δ 7.21–7.07 (m, 4 H, aromatic); ^{19}F NMR (acetone, ppm) −117.60 (s, 1 F, aromatic); MS *m/e* calculated for $C_6H_4N_3F$ 137.0390, observed 137.0397, difference 0.0007.

2,3-Difluorophenyl azide (12d): 80%; IR (neat, cm^{-1}) 2120, 2100 ($-N_3$); ^{1}H NMR (acetone-d_6) δ 7.27–7.13 (m, 1 H, aromatic), 7.12–7.03 (m, 2 H, aromatic); ^{19}F NMR (acetone, ppm) −151.59 (d, J = 20 Hz, 1 F, aromatic), −137.05 (d, J = 20 Hz, 1 F, aromatic); MS *m/e* calculated for $C_6H_3N_3F_2$ 155.0296, observed 155.0287, difference 0.0009.

2,4-Difluorophenyl azide (12e): 72%; IR (neat, cm^{-1}) 2120, 2100 ($-N_3$); ^{1}H NMR (acetone-d_6) δ 7.26 (q, 1 H, aromatic), 7.18–7.0 (m, 2 H, aromatic); ^{19}F NMR (acetone, ppm) −121.64 (d, J = 5 Hz, 1 F, aromatic), −113.8 (d, J = 5 Hz, 1 F, aromatic); MS *m/e* calculated for $C_6H_3N_3F_2$ 155.0296, observed 155.0299, difference 0.0003.

2,5-Difluorophenyl azide (12f): 80%; IR (neat, cm^{-1}) 2120 ($-N_3$); ^{1}H NMR (acetone-d_6) δ 7.25–7.15 (m, 1 H, aromatic), 7.03–6.86 (m, 2 H, aromatic); ^{19}F NMR (acetone, ppm) −116.25 (d, J = 2.5 Hz, 1 F, aromatic), −131.68 (d, J = 2.5 Hz, 1 F, aromatic); MS *m/e* calculated for $C_6H_3N_3F_2$ 155.0296, observed 155.0303, difference 0.0007.

3,4-Difluorophenyl azide (12g): 65%; IR (neat, cm^{-1}) 2120, 2100 ($-N_3$); ^{1}H NMR (acetone-d_6) δ 7.36 (q, 1 H, aromatic), 7.09 (q, 1 H, aromatic), 6.97–6.90 (m, 1 H, aromatic); ^{19}F NMR (acetone, ppm) −142.46 (d, J = 22.2 Hz, 1 F, aromatic), −135.32 (d, J = 22.2 Hz, 1 F, aromatic); MS *m/e* calculated for $C_6H_3N_3F_2$ 155.0296, observed 155.0304, difference 0.0008.

***N*-Benzyl-2-fluoroaniline (15a)**: 20%; IR (neat, cm^{-1}) 3400 (–NH–); ^{1}H NMR (acetone-d_6) δ 7.42–7.18 (m, 5 H, aromatic), 7.01–6.86 (m, 2 H, aromatic), 6.70–6.51 (m, 2 H, aromatic), 5.37 (s, 1 H, NH), 4.43 (d, 2 H, CH_2); ^{19}F NMR (acetone, ppm) −135.5 (s, 1 F, aromatic); MS *m/e* calculated for $C_{13}H_{12}NF$ 201.0955, observed 201.0962, difference 0.0007.

***N*-Benzyl-3-fluoroaniline (15b)**: 18%; IR (neat, cm^{-1}) 3400 (–NH–); ^{1}H NMR (acetone-d_6) δ 7.40–7.19 (m, 5 H, aromatic), 7.05 (q, 1 H, aromatic), 6.50–6.25 (m, 3 H, aromatic), 5.78 (s, 1 H, NH), 4.34 (d, 2 H, CH_2); ^{19}F NMR (acetone, ppm) −112.9 (s, 1 F, aromatic); MS *m/e* calculated for $C_{13}H_{12}NF$ 201.0955, observed 201.0956, difference 0.0001.

***N*-Benzyl-4-fluoroaniline (15c)**: 45%; IR (neat, cm^{-1}) 3430 (–NH–); ^{1}H NMR (acetone-d_6) δ 7.39–7.18 (m, 5 H, aromatic), 6.84 (t, 2 H, aromatic), 6.65–6.60 (m, 2 H, aromatic), 5.36 (s, 1 H, NH), 4.31 (d, 2 H, CH_2); ^{19}F NMR (acetone, ppm) −129.0 (s, 1 F, aromatic); MS *m/e* calculated for $C_{13}H_{12}NF$ 201.0955, observed 201.0935, difference 0.0020.

***N*-Benzyl-2,3-difluoroaniline (15d)**: 24%; IR (neat, cm^{-1}) 3410 (–NH–); ^{1}H NMR (acetone-d_6) δ 7.41–7.19 (m, 5 H, aromatic), 6.89–6.79 (m, 1 H, aromatic), 6.49–6.39 (m, 2 H, aromatic), 5.74 (s, 1 H, NH), 4.56 (d, 2 H, CH_2); ^{19}F NMR (acetone, ppm) −161 (d, J = 18 Hz, 1 F, aromatic), −140.60 (d, J = 18 Hz, 1 F, aromatic); MS *m/e* calculated for $C_{13}H_{11}NF_2$ 219.0860, observed 219.0846, difference 0.0014.

***N*-Benzyl-2,4-difluoroaniline (15e)**: 29%; IR (neat, cm^{-1}) 3430 (–NH–); ^{1}H NMR (acetone-d_6) δ 7.43–7.19 (m, 5 H, aromatic), 7.0–6.90 (m, 1 H, aromatic), 6.43–6.35 (m, 1 H, aromatic), 6.29–6.20 (m, 1 H, aromatic), 5.75 (s, 1 H, NH); 4.44 (d, 2 H, CH_2); ^{19}F NMR (acetone, ppm) −140.96 (d, J = 16.7 Hz, 1 F, aromatic), −117.38 (d, J = 16.7 Hz, 1 F, aromatic); MS *m/e* calculated for $C_{13}H_{11}NF_2$ 219.08608, observed 219.0823, difference 0.0037.

***N*-Benzyl-2,5-difluoroaniline (15f)**: 22%; IR (neat, cm^{-1}) 3410 (–NH–); ^{1}H NMR (acetone-d_6) δ 7.42–7.19 (m, 5 H, aromatic), 6.93–6.84 (m, 1 H, aromatic), 6.76–6.57 (m, 2 H, aromatic), 5.28 (s, 1 H, NH), 4.41 (d, 1 H, CH_2); ^{19}F NMR (acetone, ppm) −130.98 (s, 1 F, aromatic), −126.54 (s, 1 F, aromatic); MS *m/e* calculated for $C_{13}H_{11}NF_2$ 219.0860, observed 219.0868, difference 0.0008.

***N*-Benzyl-3,4-difluoroaniline (15g)**: 22%; IR (neat, cm^{-1}) 3430 (–NH–); ^{1}H NMR (acetone-d_6) δ 7.39–7.19 (m, 5 H, aromatic), 7.0 (q, 1 H, aromatic), 6.57–6.48 (m, 1 H, aromatic), 6.45–6.38 (m, 1 H, aromatic); ^{19}F NMR (acetone, ppm) −154.74 (d, J = 23.2 Hz, 1 F, aromatic), −138.12 (d, J = 23.2 Hz, 1 F, aromatic); MS *m/e* calculated for $C_{13}H_{11}NF_2$ 219.0860, observed 219.0865, difference 0.0005.

2,2′-Difluoroazobenzene (18a): 20%; mp 97–98 °C; ^{1}H NMR (acetone-d_6) δ 7.78 (t, 2 H, aromatic), 7.65–7.58 (m, 2 H, aromatic), 7.45–7.23 (m, 4 H, aromatic); ^{19}F NMR (acetone, ppm) −123.8 (s, 2 F, aromatic); MS *m/e* calculated for $C_{12}H_8N_2F_2$ 218.0653, observed 218.0663, difference 0.0010. Anal. Calcd for $C_{12}H_8N_2F_2$: C, 66.03; H, 3.69; N, 12.84; F, 17.42. Found: C, 65.97; H, 3.98; N, 12.38; F, 17.28.

3,3′-Difluoroazobenzene (18b): 34%; mp 60–62 °C; ^{1}H NMR (acetone-d_6) δ 7.81 (d, 2 H, aromatic), 7.70–7.60 (m, 4 H, aromatic), 7.36 (t, 2 H, aromatic); ^{19}F NMR (acetone, ppm) −111.56 (s, 2 F,

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[18] Smith, P. A. S.; Brown, B. B. *J. Am. Chem. Soc.* **1951**, *73*, 2438.

[19] Houben, J.; Basset, W. *Chem. Ber.* **1906**, *39*, 3233.

[20] Birchall, J. M.; Hazeldine, R. N.; Kemm, J. E. G. *J. Chem. Soc. C* **1970**, 449.

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aromatic); MS m/e calculated for $C_{12}H_8N_2F_2$ 218.0653, observed 218.0660, difference 0.0007. Anal. Calcd for $C_{12}H_8N_2F_2$: C, 66.03; H, 3.69; N, 12.84; F, 17.42. Found: C, 66.00; H, 3.85; N, 12.73; F, 17.73.

4,4′-Difluoroazobenzene (18c): 30%; mp 98–99 °C; ^{1}H NMR (acetone-d_6) δ 7.96 (q, 4 H, aromatic), 7.34 (t, 4 H, aromatic); ^{19}F NMR (acetone, ppm) −109.05 (s, 2 F, aromatic); MS m/e calculated for $C_{12}H_8N_2F_2$ 218.0653, observed 218.0662, difference 0.0009. Anal. Calcd for $C_{12}H_8N_2F_2$: C, 66.03; H, 3.69; N, 12.84; F, 17.42. Found: C, 65.98; H, 3.66; N, 12.90; F, 17.27.

2,2′,3,3′-Tetrafluoroazobenzene (18d): 20%; mp 140–142 °C; ^{1}H NMR (acetone-d_6) δ 7.64–7.53 (m, 4 H, aromatic), 7.42–7.32 (m, 2 H, aromatic); ^{19}F NMR (acetone, ppm) −148.68 (d, J = 20.7 Hz, 2 F, aromatic), −137.30 (d, J = 20.7 Hz, 2 F, aromatic); MS m/e calculated for $C_{12}H_6N_2F_4$ 254.0466, observed 254.0476, difference 0.001. Anal. Calcd for $C_{12}H_6N_2F_4$: C, 56.68; H, 2.38; N, 11.02; F, 29.91. Found: C, 56.68; H, 2.42; N, 10.80; F, 29.89.

2,2′,4,4′-Tetrafluoroazobenzene (18e): 20%; mp 115–117 °C; ^{1}H NMR (acetone-d_6) δ 7.54–7.43 (m, 6 H, aromatic); ^{19}F NMR (acetone, ppm) −127.69 (d, J = 17.5 Hz, 2 F, aromatic), −116.51 (d, J = 17.5 Hz, 2 F, aromatic); MS m/e calculated for $C_{12}H_6N_2F_4$ 254.0466, observed 254.0473, difference 0.0007. Anal. Calcd for $C_{12}H_6N_2F_4$: C, 56.68; H, 2.38; N, 11.02; F, 29.91. Found: C, 56.97; H, 2.56; N, 10.71; F, 29.71.

2,2′,5,5′-Tetrafluoroazobenzene (18f): 39%; mp 138–140 °C; ^{1}H NMR (acetone-d_6) δ 8.0–7.82 (m, 2 H, aromatic), 7.36–7.25 (m, 2 H, aromatic), 7.21–7.12 (m, 2 H, aromatic), ^{19}F NMR (acetone, ppm) −118.81 (d, J = 10.1 Hz, 2 F, aromatic), −103.81 (d, J = 10.1 Hz, 2 F, aromatic); MS m/e calculated for $C_{12}H_6N_2F_4$ 254.0466, observed 254.0477, difference 0.0011. Anal. Calcd for $C_{12}H_6N_2F_4$: C, 56.58; H, 2.38; N, 11.02; F, 29.91. Found: C, 57.04; H, 2.56; N, 10.64; F, 29.76.

3,3′,4,4′-Tetrafluoroazobenzene (18g): 39%; mp 65–67 °C; ^{1}H NMR (acetone-d_6) δ 7.89–7.76 (m, 4 H, aromatic), 7.56 (q, 2 H, aromatic); ^{19}F NMR (acetone, ppm) −135.75 (d, J = 22.2 Hz, 2 F, aromatic), −132.84 (d, J = 22.2 Hz, 2 F, aromatic), MS m/e calculated for $C_{12}H_6N_2F_4$ 254.0466, observed 254.0472, difference 0.0006. Anal. Calcd for $C_{12}H_6N_2F_4$: C, 56.68; H, 2.38; N, 11.02; F, 29.91. Found: C, 56.60; H, 2.32; N, 10.97; F, 29.87.

EPR Experiments. All EPR measurements were obtained on a Varian E-112 X-Band Century Series EPR spectrometer equipped with a modified microwave cavity which admitted light through a series of louvres on one side. Samples were sealed in 4-mm suprasil quartz tubes under vacuum after three freeze–pump–thaw cycles to remove oxygen. Samples were irradiated with filtered light ($\lambda > 295$ nm) from a Schoeffel Universal 1000-W Hg–Xe arc lamp. Triplet nitrene spectra were recorded at 10 mW of microwave power while triplet radical pair spectra were recorded at 1 mW of microwave power.

Product Studies. Samples were prepared by putting 0.5 mL of the solution of interest in 6-mm Pyrex tubes which were prewashed with ammonium hydroxide and oven-dried. The solutions were then degassed using three freeze–pump–thaw cycles and then sealed under vacuum. Samples were photolyzed with 350-nm light using Southern New England RPR 3500-Å lamps. The product mixtures were analyzed by gas chromatography. The yields and identities of the products were determined by co-injection of authentic samples and by GC–mass spectroscopy.

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Registry No. **12a**, 3296-04-6; **12b**, 3296-03-5; **12c**, 3296-02-4; **12d**, 123330-49-4; **12e**, 91229-55-9; **12f**, 123330-50-7; **12g**, 123330-51-8; **12h**, 102284-85-5; **12i**, 1423-15-0; **15a**, 123330-52-9; **15b**, 123330-53-0; **15c**, 370-77-4; **15d**, 123330-54-1; **15e**, 123330-55-2; **15f**, 123330-56-3; **15g**, 123330-57-4; **15h**, 115910-96-8; **15i**, 36375-86-7; **16h**, 123330-60-9; **16i**, 123330-61-0; **17a**, 348-54-9; **17b**, 372-19-0; **17c**, 371-40-4; **17d**, 4519-40-8; **17e**, 367-25-9; **17f**, 367-30-6; **17g**, 3863-11-4; **17h**, 5509-65-9; **17i**, 771-60-8; **18a**, 401-44-5; **18b**, 331-21-5; **18c**, 332-07-0; **18d**, 123330-58-5; **18e**, 326-17-0; **18f**, 325-84-8; **18g**, 123330-59-6; **18h**, 42808-62-8; **18i**, 2285-06-5; imidogen, 13774-92-0; hydrogen, 1333-74-0; toluene, 108-88-3; benzyl radical, 2154-56-5; 2,4-difluorophenylamanyl radical, 51460-59-4.

Photoinduced Molecular Transformations. 104.[1] Pathways of the Photorearrangements of Five-Membered Cyclic Steroidal α-Nitro Ketones to *N*-Hydroxy Cyclic Imides, Cyclic Hydroxamic Acid, and Cyclic Imide

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We report on the photolysis of three five-membered and two seven-membered cyclic α-nitro ketones with a steroidal skeleton. The photoreaction in ethanol of two five-membered cyclic steroidal α-nitro ketones that exist largely as the enol forms in ethanol gave the corresponding cyclic *N*-hydroxy imides (57–61%) which arose from photorearrangements. A similar photolysis of a five-membered cyclic steroidal α-nitro ketone that exists exclusively as the keto form in ethanol led to an unprecedented formation of the corresponding cyclic imide (12%) instead of a cyclic *N*-hydroxy imide. The corresponding cyclic α-hydroxyimino ketones (5–18%) are accompanying products in all three photoreactions, while a cyclic hydroxamic acid (11%) is the accompanying product of the cyclic *N*-hydroxy imide in one of the photoreactions. In contrast, photoreactions of the two seven-membered α-nitro steroidal ketones in ethanol gave only the corresponding α-hydroxyimino ketones. The photochemical nitrogen insertions in the photoreactions of cyclic steroidal α-nitro ketones thus depend on their ring size. On the basis of the independent photolysis of 16α- and 16β-hydroxy-5α-androstan-17-one nitrites, as well as quenching experiments with oxygen, we suggest the formation of cyclic hydroxamic acid and cyclic *N*-hydroxy imides is from the enols of the five-membered cyclic steroidal α-nitro ketones. The cyclic imide is formed when 5α-androstane-15,16-dione monooxime is irradiated in ethanol. This first example of a photo-Beckmann rearrangement of a cyclic α-diketone monooxime established the genesis of the cyclic imide.

The photochemistry of α-nitro carbonyl compounds as bichromophoric molecules is of considerable interest since the diverse photochemical behavior of nitroalkanes and nitroolefins has become reasonably well understood.[2]

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