Reactivities of Nitrenes Generated by Photolysis of 2-(ω-Phenylalkyl)phenyl Azides

Shigeru Murata, Ryuichi Yoshidome, Youji Satoh, Noriyasu Kato, and Hideo Tomioka*

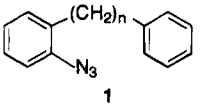
Chemistry Department for Materials, Faculty of Engineering, Mie University, Tsu, Mie 514, Japan

Received June 29, 1994[⊗]

In order to investigate the reactivity of a photolytically generated arylnitrene with an intramolecular CH bond, the photochemistry of 2-(ω-phenylalkyl)phenyl azides (**1a–d**) was examined. Irradiation of **1** in solution revealed that the insertion of the nitrene into an adjacent CH bond to give cyclic compounds **4** and **5** occurs favorably only when a reactive CH bond, such as benzylic, is located close to the nitrenic center. This process can compete with the formation of products derived from triplet nitrene, but not with the capture of didehydroazepine by DEA. On the other hand, irradiation of **1b** in an Ar matrix at 12 K gave a mixture of the CH insertion product **4b** and the didehydroazepine **15**. The origin of the difference in reactivity of the nitrene observed in solutions and in a matrix, and the spin state of the nitrene involved in the CH insertion reaction, are discussed.

The photochemistry of aromatic azides has been of interest due to its application in photoresist systems and in biochemical photoaffinity labeling.[1] Both uses are based on the intermolecular covalent bond formation between nitrenes, which are known to be short-lived intermediates generated by the photolysis of azides, and surrounding macromolecules. In spite of extensive investigation of the photochemistry of phenyl azide and its derivatives,[2,3] the essential features of the mechanism of this bond formation remains controversial.

The insertion of a photolytically generated nitrene into a CH bond is thought to be an important bond-forming reaction in many systems of practical application, (*e.g.*, in the photoresist system involving bis(azide) and partially cyclized polyisoprene[4]). However, several questions arise: (a) why can the nitrene generated photolytically in the photoresist system insert into a CH bond of the polymer, while photolysis of a fluid solution of phenyl azide in a hydrocarbon solvent, such as cyclohexane, gives no CH insertion products and (b) which state of the nitrene is involved in a CH insertion reaction. In order to shed light on the intrinsic reactivity of a photolytically generated nitrene toward a CH bond, we have examined the photochemistry of the aromatic azides having an alkyl side chain adjacent to the reaction center. Although it has been reported that nitrenes induced by thermolysis of 2-alkylphenyl azides[5] or by deoxygenation of 2-alkylnitrobenzenes with triethyl phosphite[6] undergo an insertion into an intramolecular CH bond, few reports of the CH insertion of photochemically generated nitrenes have appeared.[7] In this paper, we wish to report our systematic studies of the photochemical reactions of 2-(ω-phenylalkyl)phenyl azides (**1a–d**) in fluid solutions and



1

a: n = 1, **b**: n = 2, **c**: n = 3, **d**: n = 4

in matrices, wherein it is revealed that the insertion of the photolytically generated nitrene into an adjacent CH bond occurs, although unfavorably. The spin state of the nitrene involved in the CH insertion is also discussed.

Results and Discussion

Photolysis in Cyclohexane. We first examined the photolysis of the azides **1a–d** in cyclohexane, since irradiation in an inert solvent would be favorable for the intramolecular reaction. In general, irradiation of phenyl azide in hydrocarbon solvents gives mainly azobenzene,

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1995.

(1) The photochemistry of aromatic azides has been reviewed; for example: (a) Iddon, B.; Meth-Cohn, O.; Scriven, E. F. V.; Suschitzky, H.; Gallagher, P. T. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 900. (b) Scriven, E. F. V. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1982. (c) *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic Press: New York, 1984. (d) Wentrup, C. *Reactive Molecules*; Wiley: New York, 1984; Chapter 4.

(2) (a) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 5228. (b) Leyva, E.; Platz, M. S.; Persy, G.; Wirz, J. *J. Am. Chem. Soc.* **1986**, *108*, 3783. (c) Shields, C. J.; Chrisope, D. R.; Schuster, G. B.; Dixon, A. J.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 4723. (d) Kanakarajan, K.; Goodrich, R.; Young, M. J. T.; Soundararajan, S.; Platz, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 6536. (e) Li, Y.-Z.; Kirby, J. P.; George, M. W.; Poliakoff, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 8092. (f) Cullin, D. W.; Soundararajan, N.; Platz, M. S.; Miller, T. A. *J. Phys. Chem.* **1990**, *94*, 8890. (g) Marcinek, A.; Leyva, E.; Whitt, D.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 8609.

(3) Polyfluorinated phenyl azides have gained much attention due to their utility as photoaffinity label reagents: (a) Leyva, E.; Young, M. J. T.; Platz, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 8307. (b) Young, M. J. T.; Platz, M. S. *Tetrahedron Lett.* **1989**, *30*, 2199. (c) Cai, S. X.; Keana, J. F. W. *Tetrahedron Lett.* **1989**, *30*, 5409. (d) Soundararajan, N.; Platz, M. S. *J. Org. Chem.* **1990**, *55*, 2034. (e) Keana, J. F. W.; Cai, S. X. *J. Org. Chem.* **1990**, *55*, 3640. (f) Poe, R.; Grayzar, J.; Young, M. J. T.; Leyva, E.; Schnapp, K. A.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 3209. (g) Pinney, K. G.; Katzenellenbogen, J. A. *J. Org. Chem.* **1991**, *56*, 3125. (h) Young, M. J. T.; Platz, M. S. *J. Org. Chem.* **1991**, *56*, 6403. (i) Cai, S. X.; Glenn, D. J.; Keana, J. F. W. *J. Org. Chem.* **1992**, *57*, 1299. (j) Poe, R.; Schnapp, K.; Young, M. J. T.; Grayzar, J.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 5054. (k) Marcinek, A.; Platz, M. S.; Chan, S. Y.; Floresca, R.; Rajagopalan, K.; Golinski, M.; Watt, D. *J. Phys. Chem.* **1994**, *98*, 412.

(4) For studies of chemical mechanism in practical photoresist systems, see, for example: Shimizu, S.; Bird, G. R. *J. Electrochem. Soc.* **1977**, *124*, 1394.

(5) (a) Smolinsky, G. *J. Am. Chem. Soc.* **1961**, *83*, 2489. (b) Smolinsky, G. *J. Org. Chem.* **1961**, *26*, 4108. (c) Smolinsky, G.; Feuer, B. I. *J. Org. Chem.* **1964**, *29*, 3097. (d) Smolinsky, G.; Feuer, B. I. *J. Am. Chem. Soc.* **1964**, *86*, 3085.

(6) (a) Sundberg, R. J. *J. Org. Chem.* **1965**, *30*, 3604. (b) Sundberg, R. J. *Tetrahedron Lett.* **1966**, 477. (c) Smolinsky, G.; Feuer, B. I. *J. Org. Chem.* **1966**, *31*, 3882.

(7) (a) Barton, D. H. R.; Sammes, P. G.; Weingarten, G. G. *J. Chem. Soc. (C)* **1971**, 721. (b) Lindley, J. M.; McRobbie, I. M.; Meth-Cohn, O.; Suschitzky, H. *Tetrahedron Lett.* **1976**, 4513. (c) Lindley, J. M.; McRobbie, I. M., Meth-Cohn, O.; Suschitzky, H. *J. Chem. Soc., Perkin Trans 1* **1977**, 2194. (d) Albini, A.; Bettinetti, G.; Minoli, G. *J. Org. Chem.* **1987**, *52*, 1245. (e) Ciufolini, M. A.; Byrne, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 8016.

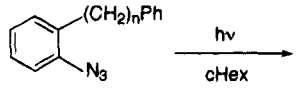
0022-3263/95/1960-1428$09.00/0

Table 1. Photoproducts of 1a–d in Cyclohexane

substrate	yield (%)[a] 2	3	4	others
1a	30	3		
1b		trace	31[b]	
1c	21	trace	10	2[c]
1d	31	trace		2[d]

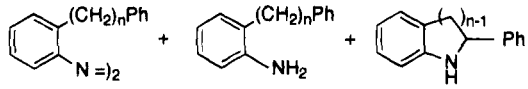
[a] Yield by isolation. [b] 2-Phenylindoline (**4b**; 25%) and 2-phenylindole (**5b**; 6%). [c] Carbazole (2%) and 2-benzylindole (**5c**; trace). [d] 2-(2-Phenylethyl)indole (**5d**; 2%) and carbazole (trace).

the formation of which is rationalized in terms of dimerization of triplet phenylnitrene.[1] A solution of the azides **1a–d** (*ca.* 6×10^{-3} M) in cyclohexane was irradiated with



1

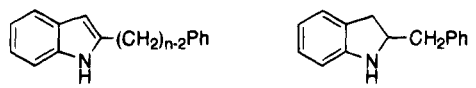
a: n = 1, **b**: n = 2, **c**: n = 3, **d**: n = 4



2 **3** **4**

a high-pressure mercury lamp through a Pyrex filter. After chromatographic separation, photoreaction products were isolated, the distribution of which is shown in Table 1. Interestingly, the product distribution was highly dependent on the chain length of the ω-phenylalkyl group at the 2-position.

Irradiation of 2-azidodiphenylmethane (**1a**) in cyclohexane gave a mixture of the corresponding azobenzene (**2a**) and the aniline (**3a**), both of which were considered to be products of triplet state nitrene. No 10*H*-azepino-[1,2-*a*]indole, which was reported to be a major product of the thermal decomposition of **1a**,[8] could be detected. In contrast, the photolysis of 2-(2-phenylethyl)phenyl azide (**1b**) afforded 2-phenylindoline (**4b**) exclusively, which was formed by intramolecular insertion of the nitrene into a β-CH bond of the 2-phenylethyl group. Some fraction of the indoline was dehydrogenated in the course of photoreaction and separation to give 2-phenylindole (**5b**). However, the yield of intramolecular CH

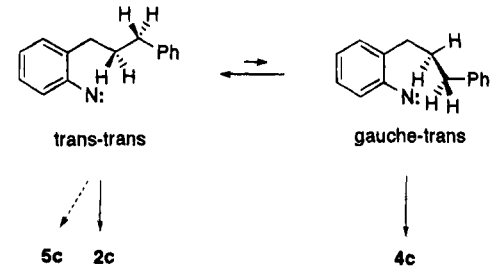


5 **6**

b: n = 2, **c**: n = 3, **d**: n = 4

insertion product was reduced in the photolysis of 2-(3-phenylpropyl)phenyl azide (**1c**), where 2-phenyl-1,2,3,4-tetrahydroquinoline (**4c**), which was formed from intramolecular insertion into a γ-CH bond, was isolated in 10% yield. A major photoreaction product was the corresponding azobenzene **2c**. Further, it should be noted that products derived from intramolecular insertion of the nitrene into a β-CH bond were obtained only scarcely in the photolysis of **1c** in cyclohexane: no 2-benzylindoline (**6**) could be isolated, but only trace amounts of 2-benzylindole (**5c**) were obtained from the photolyzed mixture. The further elongation of the methylene chain in the substituent at the 2-position resulted in a considerable decrease in the formation of intramolecular CH insertion products. Thus, irradiation of 2-(4-phenylbutyl)phenyl azide (**1d**) in cyclohexane gave the corresponding azobenzene (**2d**) almost exclusively, and 2-(2-phenylethyl)indole (**5d**) was obtained in only 2% yield as the sole intramolecular CH insertion product.

Scheme 1



The studies on the photochemistry of a series of 2-(ω-alkylphenyl)phenyl azides (**1a–d**) in cyclohexane revealed the following three points. First, the intramolecular CH insertion of the photochemically generated nitrenes occurs, but is an unfavorable process. Thus, only when reactive hydrogens, such as benzylic hydrogens, are situated close to the nitrenic center, does intramolecular CH insertion occur favorably. In the nitrene generated from **1b**, benzylic β-hydrogens can be located close to the nitrenic center, assuming a free rotation of 2-nitrenophenyl group around the $C_{Ar}-C_{\alpha}$ bond. Therefore, the intramolecular CH insertion can occur smoothly to give 2-phenylindoline (**4b**). However, when considering the conformation of 1,3-disubstituted propanes, it is reasonable to think that the nitrenes generated from **1c** prefer a trans–trans conformation about the $C_{\alpha}-C_{\beta}$ and $C_{\beta}-C_{\gamma}$ bonds, respectively, such that the nitrene cannot interact with reactive benzylic γ-hydrogens (Scheme 1). Despite the favorable location of β-hydrogens for insertion of the nitrene, only trace amounts of 2-benzylindole (**5c**) are obtained, as mentioned above. These observations imply that the rate of reaction with an unreactive β-CH bond is considerably reduced, so that the dimerization of the triplet nitrene to give the azobenzene **2c** predominates. Thus, the 2-phenyltetrahydroquinoline (**4c**) species obtained would originate from the nitrene with a less stable gauche–trans conformation. This would account for a low yield of the intramolecular CH insertion products in the photolysis of **1c** (Scheme 1).

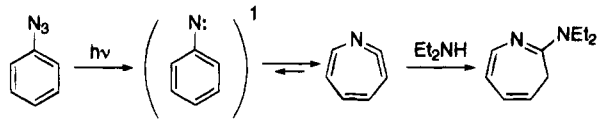
Studies of **1a–d** also showed that no products derived from the reaction of the nitrene with α-hydrogens arose from photolysis. This is due to a high strain energy in the transition state of insertion into an α-CH bond. However, the possibility that an α-hydrogen migrated to the nitrenic center to give the o-quinoid imine derivative, which then polymerized,[5b] cannot be ruled out.

Finally, the nitrenes photolytically generated from **1a–d** cannot add to the π electron of the terminal benzene ring of the substituent at the 2-position. This may be attributed not only to the low electrophilicity of aryl nitrenes, but also to the unfavorable conformation of the nitrenes for addition to the benzene ring, since it has been reported that the nitrenes conformationally in close proximity to an adjacent aromatic ring add to the

(8) Jones, G.; Long, B. D.; Thorne, M. P. *J. Chem. Soc., Perkin Trans. 2* **1992**, 903 and references therein.

double bond of the aromatic ring.[9] We could isolate trace amounts of carbazole in the photolysis of **1c** and **1d**. Although the formation of this compound derives from the intramolecular interaction of the nitrenic center with the terminal benzene ring, the detailed mechanism has yet to be elucidated.

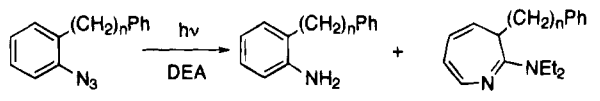
Photolysis in Diethylamine (DEA). When phenyl azide is irradiated in a nucleophilic solvent such as DEA, 2-(diethylamino)-3*H*-azepine is obtained. Recent investigations have revealed that the mechanism of the ring expansion involves a didehydroazepine intermediate **7**,



7

which was directly observed by spectroscopic methods.[2,10] It is generally accepted that upon irradiation of phenyl azide in fluid solutions at room temperature, singlet phenylnitrene is generated and immediately isomerizes to **7**, which is captured by DEA to give the 3*H*-azepine, while in the absence of DEA, **7** regenerates singlet nitrene in competition with polymerization and reaction with the starting azide.[2b,e] If the rate of insertion of the nitrenes generated photolytically from **1a–d** into an adjacent CH bond is comparable to that of isomerization to the didehydroazepines, then the irradiation of **1a–d** in DEA would yield the intramolecular CH insertion products together with the corresponding 3*H*-azepine derivatives. It has been reported that in the photolysis of 2-azidobiphenyl in the presence of DEA, the intramolecular cyclization to give carbazole competes with the 3*H*-azepine formation.[11]

Sundberg and co-workers reported that the irradiation of 2-alkylphenyl azides in DEA afforded a mixture of oxidation products identified as pyridines and 2*H*-azepin-2-ones, rather than 3*H*-azepines, due to the sensitivity of the 1*H*-azepine intermediates to molecular oxygen.[12] They also reported, however, that the formation of oxidation products was avoided by heating the photolyzed mixture with methanol. Thus, we treated the photolysate



1 **3** **8**

of the azides **1a–d** in DEA with boiling methanol according to their procedure. As shown in Table 2, irradiation of the azide **1a–d** in DEA gave the corresponding 3-alkyl-2-(diethylamino)-3*H*-azepines **8**, together with small amounts of 2-alkylanilines **3**. No products that derived from intramolecular insertion of the nitrenes into an adjacent CH bond, such as **4** or **5**,

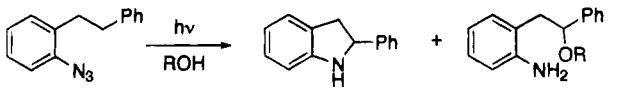
Table 2. Photoproducts of 1a–d in Diethylamine

substrate	yield (%)[a] 3	8
1a	5	21
1b	trace	24
1c	3	12[b]
1d	2	20[b]

[a] Yield by isolation. [b] Trace amounts of carbazole were also isolated.

could be detected.[13] Thus, the photolysis in a nucleophilic solvent which could capture didehydroazepines effectively revealed that the intramolecular CH insertion of the nitrenes photolytically generated from **1b** and **1c** could not compete with the isomerization to the didehydroazepine. This is in contrast to the formation of carbazole from 2-azidobiphenyl. These results suggest to us that the intramolecular CH insertion to give **4b** or **4c** proceeds by a mechanism different from that of formation of carbazole, which has been established to involve a singlet nitrene.[1,11] In order to obtain additional information about the mechanism of the intramolecular CH insertion, further studies were carried out on the photochemistry of **1b** and **1c**.

Photolysis in Alcohols. It is generally known that irradiation of phenyl azide in alcohols gives only aniline and tarry products and that neither singlet phenylnitrene nor didehydroazepine (**7**) can be captured owing to the insufficient electrophilicity of these intermediates to react with alcohols.[14] However, when the azide **1b** was irradiated in methanol, the adduct of the nitrene with methanol was obtained in 37% yield, together with the intramolecular CH insertion product **4b** (9%). The adduct was



1b **4b** **9**

identified as 2-(2-methoxy-2-phenylethyl)aniline (**9**, R = Me) by the ^{1}H NMR and GC-MS data. The formation of the analogous product has been reported in the irradiation of 2-azido-1-methoxyphenazine in ethanol.[7d] The product distribution was dependent on the irradiation time. Thus, longer irradiation resulted in an increased yield of **9** with less of **4b**. This observation implied that **4b** was converted photochemically into **9** in alcohol. However, at least at the early stages of the photoreaction, the adduct **9** obtained originated from the azide **1b**, since the independent irradiation of **4b** in alcohol revealed that the conversion of **4b** into **9** was less efficient than the decomposition of **1b**.[15]

The dependence of the product distribution on the concentration of alcohol in cyclohexane was examined. The result shown in Figure 1 demonstrated that the yield of **9** increased at the expense of **4b** with increasing concentration of alcohol, which implied that both prod-

(9) Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 6317.

(10) (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**, 307. (c) Hayes, J. C.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 5879.

(11) (a) Sundberg, R. J.; Heintzelman, R. W. *J. Org. Chem.* **1974**, *39*, 2546. (b) Sundberg, R. J.; Gillespie, D. W.; DeGraff, B. A. *J. Am. Chem. Soc.* **1975**, *97*, 6193.

(12) Sundberg, R. J.; Suter, S. R.; Brenner, M. *J. Am. Chem. Soc.* **1972**, *94*, 513.

(13) Though 2-phenylindoline (**4b**) was consumed in the photolysis in DEA, it was confirmed that **4b** was less reactive than the azide **1b**.

(14) Though Sundberg and Smith, Jr., reported that irradiation of phenyl azide in methanol gave 2-methoxy-3*H*-azepine in 11% yield, attempts to reproduce this result have been unsuccessful. For the photochemistry of aromatic azides in methanol, see for example: (a) Sundberg, R. J.; Smith, Jr., R. H. *J. Org. Chem.* **1971**, *36*, 295. (b) Purvis, R.; Smalley, R. K.; Strachan, W. A.; Suschitzky, H. *J. Chem. Soc., Perkin Trans. 1* **1978**, 191. See also: refs 3f and 9.

(15) After irradiation of **1b** (4 mg, ca. 4×10^{-3} M) in ethanol for 30 min, 50% of the starting azide was consumed, while ca. 5% of **4b** was converted into **9** under the same conditions.

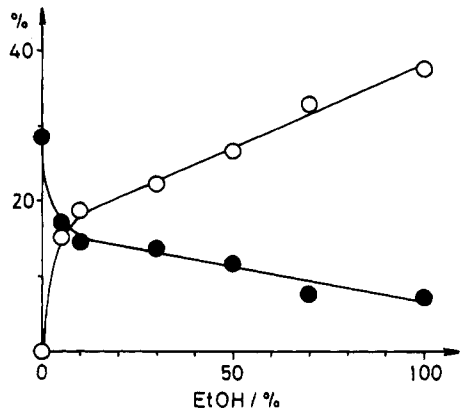
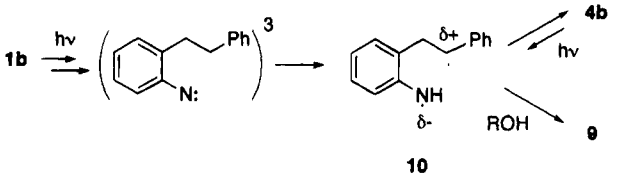


Figure 1. Dependence of the product yields on the concentration of ethanol in the photolysis of **1b** in a cyclohexane–ethanol binary system: **4b** (●); **9** (R = Et) (○).

Scheme 2



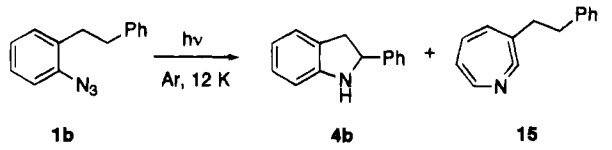
ucts originated from a common reactive intermediate. It is reasonable to think that the product **9** arises from solvent-trapping of the biradical, which should be formed by an intramolecular hydrogen abstraction of the triplet nitrene.[7d] The addition of alcohol can be rationalized by assuming a polarized biradical structure as depicted in **10** in Scheme 2. Since a recombination of the biradical **10** gives **4b**, it appears that intramolecular CH insertion of the nitrene photolytically generated from **1b** occurs by a hydrogen abstraction–recombination mechanism including a triplet state nitrene.

Analogously, irradiation of **1c** in methanol gave the corresponding azobenzene **2c** in 16% yield, 2-phenyltetrahydroquinoline (**4c**) in 15% yield and two kinds of methoxylated anilines, **11** and **12**, in 4 and 13% yields, respectively, together with small amounts of 2-benzylindoline (**6**) (3%) (Scheme 3). Assignment of the two isomeric methoxylated aniline structures was readily made based on ^{1}H NMR and MS fragment patterns. In the ^{1}H NMR spectrum, the methine proton at the γ-position of **11** produced a doublet of doublets at δ 4.13, while **12** revealed a methine proton at the β-position with a multiplet centered at δ 3.62. As discussed for the photolysis of **1b**, the products **4c** and **11** should be derived from a common biradical intermediate **13**, which is formed by the abstraction of an intramolecular benzylic γ-hydrogen by triplet state nitrene (Scheme 3). It is noteworthy that while only small amounts of the cyclization product **6**, which should be derived from a biradical **14** produced by β-hydrogen abstraction, could be obtained, the aniline **12** methoxylated at the β-position was formed in a yield comparable to that of **2c** or **4c**. Thus, it is found that on irradiation of **1c** in methanol, a β-hydrogen abstraction takes place in competition with a γ-hydrogen abstraction and a dimerization to **2c**. This result, contrasting with that obtained in cyclohexane (Scheme 1), can be interpreted in terms of solvent effect on the stabilization of the polarized biradicals. The reason that **14** undergoes the reaction with methanol to give **12** in preference to the recombination to **6** cannot be satisfactorily explained at the present time.[16]

If we assume a hydrogen abstraction–recombination mechanism involving a triplet state nitrene for the formation of the intramolecular CH insertion products, the results obtained in the photolysis of **1b** and **1c** in solutions may be interpreted as follows. It has been known that the isomerization of singlet phenylnitrene, generated photolytically in solution, to didehydroazepine is faster than the intersystem crossing to a triplet state at room temperature.[2b,f] Therefore, products derived from a triplet state nitrene cannot be obtained in DEA, since didehydroazepine is captured with DEA more rapidly than it regenerates a singlet state nitrene.[17] In the absence of strong nucleophiles, didehydroazepine comes to equilibrium with singlet state nitrene, which is deactivated to its triplet state. Thus, the CH insertion products **4b** and **4c** may be obtained in the irradiation of **1b** and **1c**, respectively, in cyclohexane or methanol, but not in DEA.[18,20]

Photochemistry of 1b in an Ar Matrix at 12 K. Since Chapman and Le Roux reported the first observation of the IR spectrum of didehydroazepine (**7**) in an Ar matrix in 1978,[10a] this technique has been a powerful method for studying the photochemistry of azides. In order to gain information about the reactivity of a photolytically generated nitrene toward a CH bond, the photochemistry of **1b** matrix-isolated in Ar at 12 K was examined.

Irradiation (>300 nm) of **1b** in an Ar matrix afforded 2-phenylindoline (**4b**) and a product exhibiting an intense cumulenic band at 1894 cm^{-1}, each of which appeared to be a primary photoproduct (Figure 2). The former was identified by comparison of the IR spectrum with that of the authentic sample matrix-isolated in Ar at 12 K. The product that shows an 1894 cm^{-1} band was tentatively assigned to the didehydroazepine **15**, which was consid-



ered to be a precursor of azepine **8b** obtained by the photolysis in DEA. Further irradiation with longer-

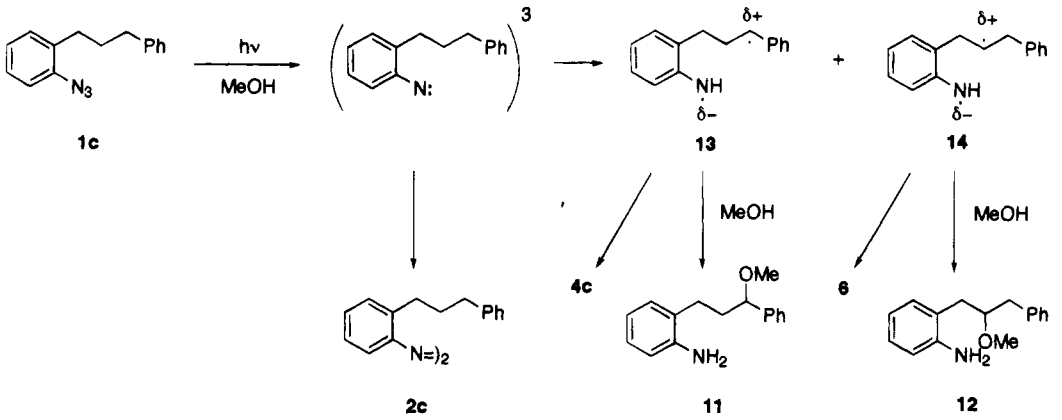
(16) It would be conceivable that the less stable biradical **14** could be formed in methanol by the larger participation of solvent molecules, increasing the contribution of polarized character to the biradical which would accelerate the rate of the reaction with methanol.

(17) Small amounts of the anilines **3** were isolated in the irradiation of **1** in DEA as shown in Table 2. In general, the mechanism of the aniline formation in the irradiation of aromatic azides in DEA is unclear. Two mechanisms have been proposed; hydrogen abstraction of a triplet nitrene and electron transfer from DEA to an excited azide. Our results would be consistent with the latter mechanism. See: Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 5234.

(18) The triplet-sensitized experiment would give a clue to the spin state of the nitrene involved in a CH insertion. However, the photolysis of **1b** in the presence of benzophenone (E_T = 69 kcal/mol) as a triplet sensitizer gave a complex mixture from which no products originated from the azide were identified. This frustrating result is probably due to an inefficient triplet-energy transfer from excited benzophenone to the azide. The triplet energy of phenyl azide has been estimated to be 70–75 kcal/mol: refs 2g and 19. Though irradiation of a benzene solution of **1b** containing a sensitizer with a higher triplet energy, *e.g.*, 4-methoxyacetophenone (E_T = 72 kcal/mol), with >350 nm light ([**1b**] = 5.6 × 10^{-3} M, [sensitizer] = 4.5 × 10^{-2} M) afforded 2-phenylindoline (**4b**), it has not been confirmed that **1b** could be decomposed by a triplet-energy transfer from the sensitizer under these conditions.

(19) (a) Lewis, F. D.; Saunders, Jr., W. H. *J. Am. Chem. Soc.* **1968**, *90*, 7033. (b) Leyshon, L. J.; Reiser, A. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1918.

Scheme 3



wavelength light (>350 nm) caused an increase in intensities of the IR peaks due to **4b** with a decrease in the intensity of the band at 1894 cm^{-1}. This observation may be explained in terms of the regeneration of nitrene from the didehydroazepine **15**. It has been reported that the conversion of phenylnitrene to didehydroazepine is photochemically reversible in matrices at low temperatures.[10c] The indoline **4b** was unreactive even under short-wavelength irradiation (>200 nm).

Thus, it was found that in the photolysis of **1b** in an Ar matrix, the formation of **4b** could compete with the ring-enlargement process to give **15**. This result contrasted with that obtained in the photolysis in solutions, where the formation of **4b** was completely quenched in a solvent that could capture didehydroazepines effectively, *e.g.*, DEA. These observations imply that the intramolecular CH insertion in matrices proceeds by a mechanism different from that in solutions. However, we cannot draw a definitive conclusion concerning the spin state of the nitrene responsible for the CH insertion in matrices because of the fact that didehydroazepine is mainly produced by the photolysis of triplet phenylnitrene in matrices at low temperatures.[10c] Thus, two explanations may be given for the mechanism of the intramolecular CH insertion under these conditions. The first mechanism is a direct insertion of a singlet state nitrene, which competes with intersystem crossing to its triplet state. The second is a hydrogen abstraction–recombination mechanism involving a triplet state nitrene, where the nitrene would abstract the hydrogen in competition with photochemical conversion to the didehydroazepine **15**. Though the facile formation of **4b** as a primary photoproduct appears to support the first mechanism, the second cannot be ruled out since a hydrogen abstraction of a triplet nitrene would proceed smoothly at cryogenic temperatures by a tunneling mechanism.[21]

Furthermore, it should be noted that in matrices at low temperatures, unlike in solutions, molecular motions of **1b**, even the rotation of the 2-azidophenyl group around the $C_{Ar}-C_{\alpha}$ bond, should be frozen. Therefore, upon irradiation, some molecules in which β-benzylic protons are located close to the nitrenic center would give the CH insertion product **4b**, and others would isomerize to **15**.

Conclusions

The photochemistry of 2-(ω-phenylalkyl)phenyl azides (**1a–d**) has been studied to obtain information about the reactivity of a photolytically generated nitrene toward a CH bond. It is known that insertion of a photolytically-generated arylnitrene into a CH bond is an unfavorable process.[1] Thus, photolysis of phenyl azide in a hydrocarbon solvent gives no CH insertion products. Our studies have, however, revealed that arylnitrenes generated by photolysis in solution can insert favorably into the reactive CH bond, such as benzylic, that is situated close to the nitrenic center. Furthermore, it has been found that this process can compete with the formation of products from a triplet nitrene, *i.e.*, the azobenzenes **2** and the alkoxylated anilines **9**, **11**, and **12**, but not with the capture of didehydroazepine by DEA.

It has been reported that nitrenes generated by thermolysis of aryl azides yield CH insertion products.[5] Hall and co-workers established that the insertion of thermally produced phenylnitrene into a hydrocarbon CH bond proceeded by a triplet mechanism,[22] while Smolinsky and Feuer presented evidence for the participation of singlet arylnitrene in intramolecular CH insertion in the thermolysis of 2-(2-methylbutyl)phenyl azide.[5d] Though we have no definitive evidence as to the spin state of the nitrene involved in the photochemical CH insertion at present, the results of the photolysis of **1b** and **1c** in solution are not inconsistent with a hydrogen abstraction–recombination mechanism involving a triplet state nitrene. To validate this possibility, measurement of the kinetic isotope effect and determination of the extent of configurational inversion using an optically active substrate are required, both of which are planned in our laboratory.

In a matrix at low temperature, irradiation of **1b** gave both the didehydroazepine **15** and the intramolecular CH insertion product **4b**. This observation suggests that in matrices where molecular motion is quite restricted, the photolytically-generated nitrene can readily insert into

(20) The CH insertion product **4b**, as well as the methoxylated aniline **9**, was similarly obtained when the azide **1b** was irradiated with a shorter- (>200 nm in a quartz tube) or longer-wavelength light (>350 nm). Moreover, thermolysis of **1b** in 1,2,4-trichlorobenzene at 180 °C exclusively afforded **4b** (75%). These observations seem to imply that a free nitrene is a precursor of intramolecular CH insertion products. However, the possibility that an electronically excited azide participates in the product formation under our irradiation conditions cannot be thoroughly excluded.

(21) It is established that in the case of carbenes triplet CH abstraction at cryogenic temperatures proceeds by the tunneling mechanism: Platz, M. S. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Plenum Press: New York, 1990; Chapter 6.

(22) Hall, J. H.; Hill, J. W.; Fargher, J. M. *J. Am. Chem. Soc.* **1968**, *90*, 5313.

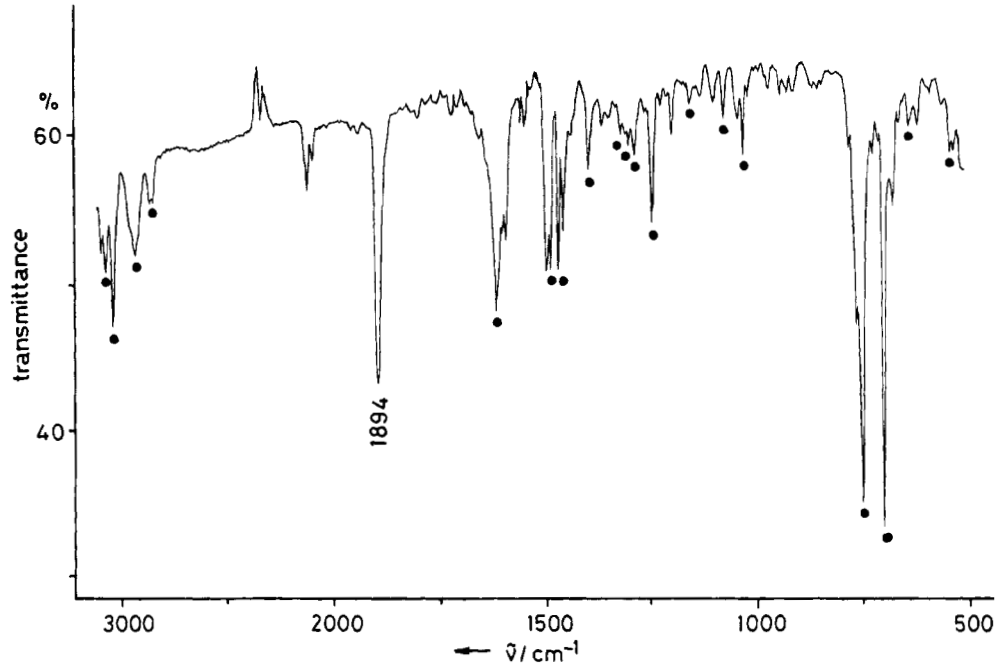


Figure 2. IR spectrum obtained by irradiation (>300 nm; 30 h) of **1b** matrix-isolated in Ar at 12 K. The peaks marked with ● are assigned to the bands due to **4b**.

a CH bond fixed close to the nitrenic center. This may provide the reason for the difference in the reactivities of nitrenes generated in current application systems and in fluid solutions.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded at 100 or 270 MHz. GC-MS spectra were recorded with a GC column prepared from 5% silicone OV-17 on Diasolid L (5.0 mm × 1.0 m). The GC analyses were performed on a column prepared from 5% silicone OV-17 on Diasolid L (5.0 mm × 1.0 m) or 5% PEG-20M on Diasolid L (5.0 mm × 1.0 m). The HPLC analyses were carried out on a JASCO Finepak C_{18}-T5 column. Gel permeation liquid chromatograph (GPC) was performed on a JASCO HLC-01 high-pressure liquid chromatograph equipped with a Shodex GPC H-2001 column. TLC was carried out on a Merk kieselgel 60 PF_{254}, and column chromatography was done on Fuji Davison silica gel BW-127ZH.

Materials. The synthesis of 2-azidodiphenylmethane (**1a**) have previously been reported.[8] The other 2-(ω-phenylalkyl)-phenyl azides (**1b–d**) were prepared in the standard procedure from the corresponding 2-(ω-phenylalkyl)anilines (**3b–d**).[23] In a typical run, ca. 600 mg of the amine (**3b–d**) was dissolved in 2 mL of dioxane, and 10 mL of 6 N sulfuric acid was added to the solution. The mixture was cooled to 0–5 °C, and a solution of 300 mg of $NaNO_2$ in 3 mL of water was added dropwise to the solution. The reaction mixture was stirred for 2 h at this temperature. After removing excess nitrous acid by addition of urea, the cooled solution was added dropwise to a solution of 1 g of NaN_3 in 3 mL of water with stirring at room temperature. After the addition, the reaction mixture was stirred for 2 h. The organic material was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was developed on a silica gel column with hexane to give the azide (**1b–d**) in 80–90% yield. The identity and purity of the new azides **1b–d** were established by ^{1}H NMR and IR spectra. 2-(2-Phenylethyl)phenyl azide (**1b**): colorless granules; mp 22 °C; ^{1}H NMR ($CDCl_3$) δ 2.86 (4H, s), 6.9–7.3 (9H, m); IR (NaCl) 2130, 1490, 1455, 1285, 750, 695 cm^{-1}; UV (cyclohexane) λ_{max} (log ε) 252 (3.98), 280 (3.39), 289 (3.29) nm. 2-(3-Phenylpropyl)phenyl azide (**1c**): colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.8–2.0 (2H, m), 2.6–2.8 (4H, m), 6.9–7.3 (9H, m); IR (NaCl) 2140, 1495, 1460, 1290, 755, 700 cm^{-1}; UV (cyclohexane) λ_{max} (log ε) 252 (3.95), 280 (3.38), 289 (3.28) nm. 2-(4-Phenylbutyl)phenyl azide (**1d**): colorless granules; mp 31 °C; ^{1}H NMR ($CDCl_3$) δ 1.5–1.7 (4H, m), 2.5–2.7 (4H, m), 6.9–7.3 (9H, m); IR (NaCl) 2950, 2130, 1495, 1455, 1290, 750, 700 cm^{-1}.

Irradiations for Preparative Experiments. A solution (20 mL) of the azide (ca. 30 mg) was placed in a Pyrex tube and purged with N_2 for 10 min. It was irradiated with a 300-W high-pressure mercury lamp at room temperature for 1 h, when 70–80% of the starting azide was consumed. The resulting solution was worked up by the following procedure.

(1) Irradiation of 1a–d in Cyclohexane. A solution of 30 mg of the azide in 20 mL of cyclohexane was irradiated. After evaporation of the solvent, the residue was separated by GPC with $CHCl_3$ eluent. The products were identified by ^{1}H NMR and GC-MS. The yield of products shown in Table 1 was determined by isolation on the basis of the reacted material. The identity and purity of the new azobenzenes, **2a**, **2c**, and **2d**, were established by ^{1}H NMR and high-resolution mass spectra. 2,2′-Dibenzylazobenzene (**2a**): orange needles; mp 119 °C; ^{1}H NMR ($CDCl_3$) δ 4.56 (4H, s), 7.1–7.4 (16H, m), 7.60 (2H, d, J = 7.9 Hz); HRMS found M$^+$ 362.1797. $C_{26}H_{22}N_2$ requires M$^+$ 362.1783. 2,2′-Bis(3-Phenylpropyl)azobenzene (**2c**): orange granules; mp 71 °C; ^{1}H NMR ($CDCl_3$) δ 2.03 (4H, quintet, J = 7.7 Hz), 2.72 (4H, t, J = 7.7 Hz), 3.19 (4H, t, J = 7.7 Hz), 7.2–7.4 (16H, m), 7.49 (2H, d, J = 7.9 Hz); HRMS found M$^+$ 418.2420. $C_{30}H_{30}N_2$ requires M$^+$ 418.2409. 2,2′-Bis-(4-phenylbutyl)azobenzene (**2d**): orange needles; mp 82 °C; ^{1}H NMR ($CDCl_3$) δ 1.7–1.8 (8H, m), 2.64 (4H, t, J = 6.9 Hz), 3.19 (4H, t, J = 7.3 Hz), 7.1–7.4 (16H, m), 7.58 (2H, d, J = 7.9 Hz); HRMS found M$^+$ 446.2733. $C_{32}H_{34}N_2$ requires M$^+$ 446.2722. 2-Phenylindoline (**4b**),[24] 2-phenyl-1,2,3,4-tetrahydroquinoline (**4c**),[25] 2-phenylindole (**5b**), 2-benzylindole (**5c**),[26] 2-(2-phenyl-

(23) Ibuki, E.; Ozasa, S.; Fujioka, Y.; Okada, M. *Yakugaku Zasshi* **1980**, *100*, 718.

(24) (a) Fischer, E.; Schmitt, T. *Chem. Ber.* **1888**, *21*, 1075. (b) Adkins, H.; Coonradt, H. L. *J. Am. Chem. Soc.* **1941**, *63*, 1563.

(25) (a) Oldham, W.; Johns, I. B. *J. Am. Chem. Soc.* **1939**, *61*, 3289. (b) Goldstein, S. W.; Dambek, P. J. *Synthesis*, **1989**, 221.

(26) (a) Julian, P. L.; Pikl, J. *J. Am. Chem. Soc.* **1933**, *55*, 2105. (b) Hooper, M.; Pitkethly, W. N. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1607. (c) Augustine, R. L.; Gustavsen, A. J.; Wanat, S. F.; Pattison, I. C.; Houghton, K. S.; Koletar, G. *J. Org. Chem.* **1973**, *38*, 3004.

ethyl)indole (**5d**),[27] and carbazole were identified by comparison of the spectroscopic data with those of authentic material.

(2) Irradiation of 1a–d in DEA. A solution of 30 mg of the azide in 20 mL of DEA was irradiated. The photolyzed solution was transferred under a N_2 atmosphere to a dropping funnel which was attached to a flask containing 20 mL of boiling methanol. The photolyzed solution was added dropwise to the refluxing methanol, and the mixture was refluxed for 1 h. After cooling, the solvent was removed, and the residue was separated by GPC with $CHCl_3$ eluent. The products were identified by ^1H NMR. The yield of products shown in Table 2 was determined by isolation on the basis of the reacted material. The identity and purity of the new azepines **8a–d** were established by ^1H NMR spectra, where the 3-substituted-3*H*-azepine structures were confirmed by comparison with analogous azepines.[12] 2-(Diethylamino)-3-benzyl-3*H*-azepine (**8a**): oil; ^1H NMR ($CDCl_3$) δ 0.98 (6H, t, J = 7.1 Hz), 2.25 (1H, dd, J = 13.2, 6.9 Hz), 2.46 (1H, dd, J = 13.2, 8.6 Hz), 3.18 (4H, brs), 4.21 (1H, m), 5.12 (1H, t, J = 9.2 Hz), 5.73 (1H, dd, J = 7.5, 6.3 Hz), 6.35 (1H, dd, J = 9.2, 6.3 Hz), 7.1–7.3 (6H, m). 2-(Diethylamino)-3-(2-phenylethyl)-3*H*-azepine (**8b**): oil; ^1H NMR ($CDCl_3$) δ 1.05 (6H, t, J = 7.1 Hz), 1.3–1.6 (2H, m), 2.4–2.6 (2H, m), 3.2–3.4 (4H, m), 4.03 (1H, m), 5.12 (1H, t, J = 9.1 Hz), 5.61 (1H, dd, J = 7.8, 6.2 Hz), 6.30 (1H, dd, J = 9.1, 6.2 Hz), 7.05 (1H, d, J = 7.8 Hz), 7.1–7.3 (5H, m). 2-(Diethylamino)-3-(3-phenylpropyl)-3*H*-azepine (**8c**): oil; ^1H NMR ($CDCl_3$) δ 1.11 (6H, t, J = 7.1 Hz), 1.1–1.3 (2H, m), 1.5–1.7 (2H, m), 2.4–2.6 (2H, m), 3.3–3.5 (4H, m), 4.04 (1H, m), 5.09 (1H, t, J = 9.2 Hz), 5.58 (1H, dd, J = 7.6, 6.3 Hz), 6.26 (1H, dd, J = 9.2, 6.3 Hz), 7.02 (1H, d, J = 7.6 Hz), 7.1–7.3 (5H, m). 2-(Diethylamino)-3-(4-phenylbutyl)-3*H*-azepine (**8d**): oil; ^1H NMR ($CDCl_3$) δ 1.11 (6H, t, J = 6.9 Hz), 1.1–1.6 (6H, m), 2.53 (2H, t, J = 7.8 Hz), 3.3–3.5 (4H, m), 4.02 (1H, m), 5.09 (1H, t, J = 9.2 Hz), 5.59 (1H, dd, J = 7.6, 6.3, Hz), 6.26 (1H, dd, J = 9.2, 6.3 Hz), 7.03 (1H, d, J = 7.6 Hz), 7.1–7.3 (5H, m).

(3) Irradiation of 1b and 1c in Methanol. A solution of 28.7 mg (0.129 mmol) of azide **1b** in 20 mL of methanol was irradiated. After evaporation of the solvent, the residue was separated by GPC with $CHCl_3$ eluent to give 1.9 mg (9%) of 2-phenylindoline (**4b**) and 9.2 mg (37%) of 2-(2-methoxy-2-phenylethyl)aniline (**9**, R = Me), together with 4.4 mg of the unchanged starting material (**1b**). The identity and purity of the new methoxylated aniline **9** (R = Me) were established by ^1H NMR and GS-MS spectra. **9** (R = Me): oil; ^1H NMR ($CDCl_3$) δ 2.76 (1H, dd, J = 14.5, 4.0 Hz), 3.07 (1H, dd, J = 14.5, 8.3 Hz), 3.18 (3H, s), 4.38 (1H, dd, J = 8.3, 4.0 Hz), 6.6–6.7 (2H, m), 6.92 (1H, d, J = 6.9 Hz), 7.04 (1H, t, J = 7.6 Hz), 7.2–7.4 (5H, m); GC-MS *m/z* (rel intensity) 227 (M^+, 9), 121 ($M^+ - CH_2C_6H_4NH_2$, 100), 106 ($M^+ -$ CH(OMe)Ph, 15). Irradiation of **1c** (31.7 mg, 0.134 mmol) was carried out in the same manner to give 3.1 mg (16%) of the azobenzene **2c**, 3.8 mg (17%) of the mixture composed of 2-(3-methoxy-3-phenylpropyl)aniline (**11**) and 2-(2-methoxy-3-phenylpropyl)aniline (**12**), 2.9 mg (15%) of 2-phenyl-1,2,3,4-tetrahydroquinoline (**4c**), 0.6 mg (3%) of 2-benzylindoline (**6**), and 0.7 mg (4%) of carbazole, together with 9.4 mg of the unchanged starting material (**1c**). The ratio of the two methoxylated anilines **11** and **12** was determined by the integration of ^1H NMR as 0.29:1. The chromatographical separation of these isomers in a preparative scale was unsuccessful, though the GC-MS spectrum of each isomer was obtained. Thus, the identity and purity of the new methoxylated aniline, **11** and **12**, as well as the new indoline **6**, were established by ^1H NMR and GC-MS spectra. **11**: ^1H NMR ($CDCl_3$) δ 1.9–2.1 (2H, m), 2.5–2.6 (2H, m), 3.24 (3H, s), 4.13 (1H, dd, J = 8.4, 4.8 Hz), 6.6–6.7 (2H, m), 7.0–7.1 (1H, m), 7.2–7.4 (6H, m); GC-MS *m/z* (rel intensity) 241 (M^+, 60), 226 (M^+ – Me, 25), 209 (M^+ – OMe, 33), 135 ($M^+ - CH_2C_6H_4NH_2$, 37), 132 (57), 121 ($M^+ - CH_2$-$CH_2C_6H_4NH_2$, 98), 118 (100), 106 ($M^+ - CH_2CH(OMe)Ph$, 98). **12**: ^1H NMR ($CDCl_3$) δ 2.64 (1H, dd, J = 14.9, 4.0 Hz), 2.72 (1H, dd, J = 14.9, 7.9 Hz), 2.75 (1H, dd, J = 13.7, 6.6 Hz), 2.95 (1H, dd, J = 13.7, 5.9 Hz), 3.24 (3H, s), 3.6–3.7 (1H, m), 6.6–6.7 (2H, m), 6.92 (1H, d, J = 7.6 Hz), 7.0–7.1 (1H, m), 7.2–7.4 (5H, m); GC-MS *m/z* (rel intensity) 241 (M^+, 22), 209 (M^+ – OMe, 11), 135 ($M^+ - CH_2C_6H_4NH_2$, 100), 118 (39). 2-Benzylindoline (**6**): oil; ^1H NMR ($CDCl_3$) δ 2.7–3.0 (3H, m), 3.14 (1H, dd, J = 15.7, 8.4 Hz), 4.0–4.2 (1H, m), 6.58 (1H, d, J = 7.9 Hz), 6.69 (1H, t, J = 7.3 Hz), 7.01 (1H, dd, J = 7.9, 7.3 Hz), 7.09 (1H, d, J = 7.3 Hz), 7.2–7.4 (5H, m); GC-MS *m/z* (rel intensity) 209 (M^+, 5), 118 ($M^+ - CH_2Ph$, 100), 91 (18).

Irradiation for Analytical Experiments. In the experiments for dependence of the product yields on the concentration of alcohol in the photolysis of **1b** in a cyclohexane–alcohol binary system, ethanol was employed on account of the solubility in cyclohexane. A solution (4 mL) of the azide **1b** (4 mg) in a cyclohexane–ethanol binary solvent was placed in a Pyrex tube, purged with N_2 for 10 min, and irradiated for 30 min with a 300-W high-pressure mercury lamp at room temperature. The products were 2-phenylindoline (**4b**) and 2-(2-ethoxy-2-phenylethyl)aniline (**9**, R = Et), which were identified by ^1H NMR and GC-MS. **9** (R = Et): ^1H NMR ($CDCl_3$) δ 1.12 (3H, t, J = 6.9 Hz), 2.75 (1H, dd, J = 14.3, 3.6 Hz), 3.07 (1H, dd, J = 14.3, 8.6 Hz), 3.2–3.4 (2H, m), 4.47 (1H, dd, J = 8.6, 3.6 Hz), 6.6–6.7 (2H, m), 6.91 (1H, d, J = 7.6 Hz), 7.0–7.1 (1H, m), 7.2–7.4 (5H, m); GC-MS *m/z* (rel intensity) 241 (M^+, 8), 135 ($M^+ - CH_2C_6H_4NH_2$, 100), 107 (M^+ – CH-(OEt)Ph, 74). The consumption of the material (ca. 50%) and the yield of products were determined by HPLC on the basis of an internal standard. In these conditions, the photodecomposition of the primary photoproducts was negligible. The results were shown in Figure 1.

Matrix-Isolation Spectroscopy. The apparatus and experimental technique used for matrix-isolation spectroscopy have been described previously.[28] The azide **1b** and 2-phenylindoline **4b** were vaporized under 10^{-6} Torr at room temperature and at 55 °C, respectively. IR data of the starting material and the photoproduct isolated in an Ar matrix at 10 K were as follows. **1b**: 3034w, 2122vs, 2098s, 1492m, 1454w, 1293m, 1287m, 752m, 699m, 653w. **4b**: 3040w, 1616m, 1486s, 1469s, 1398w, 1248m, 1031w, 749s, 702m, 542w.

Acknowledgment. We thank Professor Yoshiro Yamashita and Miss Sachiyo Nomura of the Institute for Molecular Science for the measurement of high-resolution mass spectra. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan, which is gratefully acknowledged.

Supplementary Material Available: ^1H NMR spectra of new products **1b–d**, **2a**, **2c**, **2d**, **6**, **8a–d**, **9** (R = Me and Et), and a mixture of **11** and **12** (15 pages). This material is contained in libraries on microfiche, immediately follows this articles in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9410676

(27) Mohan, B.; Nagarathnam, D.; Vedachalam, M.; Srinivasan, P. C. *Synthesis* **1985**, 188.

(28) Murata, S.; Yamamoto, T.; Tomioka, H. *J. Am. Chem. Soc.* **1993**, *115*, 4013.