5.53 (d, J = 18.2 Hz, 1 H), 6.05 (s, 1 H), 7.64 (dd, J = 18.0, 11.3 Hz, 1 H). ^{13}C NMR ($CDCl_3$) δ 14.2, 60.0, 62.5, 116.1, 119.5, 131.5, 151.6, 166.3; HRMS calcd for $C_8H_{12}O_3$ 156.0786, found 156.0783. **Lactone (*Z*)-18a**: ^{1}H NMR ($CDCl_3$) δ 4.99 (dd, J = 1.8, 0.5 Hz, 2 H), 5.61 (d, J = 11.0 Hz, 1 H), 5.62 (d, J = 17.7 Hz, 1 H), 5.98 (m, 1 H), 6.70 (ddd, J = 17.8, 10.9, 0.7 Hz, 1 H), consistent with literature data.[26] IR and HRMS could not be taken, due to the instability of this compound.

Ethyl 3-(1-Hydroxypropyl)-2,4-pentadienoate ((*E*)-18b) and Corresponding Lactone (*Z*)-18b. The above procedure, using 796.0 mg (2.78 mmol) of 1-(phenylsulfinyl)-2,2,2-trieth-oxyethane,[1] 137.5 mg (1.40 mmol) of hexa-2,3-dien-1-ol, a catalytic amount of 2,4,6-trimethylbenzoic acid, and 2.0 mL of methylene chloride, yielded a crude mixture of (*E*)-18b and (*Z*)-18b (3:1) as a brown oil. Subsequent purification via short-path column chromatography (silica gel, eluting solvent diethyl ether/pentane (1:199, 1:49, 1:9, 1:4)) followed by purification via PTLC (2 × 1500 μm, eluting solvent diethyl ether/hexanes (1.5:1), extraction solvent methylene chloride) yielded compounds (*E*)-18b (74.2 mg, 29%) as a yellow oil and (*Z*)-18b (23.7 mg, 12%) as a yellow oil. **Ester (*E*)-18b**: IR ($CHCl_3$, cm^{-1}) 3601, 3519 (br), 1702; ^{1}H NMR ($CDCl_3$) δ 0.98 (t, J = 7.4 Hz, 3 H), 1.29 (t, J = 7.2 Hz, 3 H), 1.59 (m, 2 H), 1.80 (m, 1 H), 4.18 (qd, J = 7.2, 2.3 Hz, 2 H), 4.61 (m, 1 H), 5.43 (ddd, J = 11.6, 1.5, 1.0 Hz, 1 H), 5.55 (d, J = 18.1 Hz, 1 H), 6.06 (s, 1 H), 7.61 (dd, J = 18.6, 11.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 15.5, 30.4, 60.3, 66.1, 116.1, 119.8, 132.1, 156.2, 166.8; HRMS calcd for $C_{10}H_{16}O_3$ 184.1099, found 184.1103. **Lactone (*Z*)-18b**: IR ($CHCl_3$, cm^{-1}) 1749; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.4 Hz, 3 H), 1.67 (m, 1 H), 2.11 (m, 1 H), 5.15 (m, 1 H), 5.64 (d, J = 11.2 Hz, 1 H), 5.67 (d, J = 17.8 Hz, 1 H), 5.98 (s, 1 H), 6.57 (dd, J = 17.8, 11.1 Hz, 1 H).

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Supplementary Material Available: Characterization of new compounds by NMR (11 pages). Ordering information is given on any current masthead page.

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Photochemical Decomposition of 1-Alkoxy-2-azidophenazines. Addition of Nitrenes to Azides

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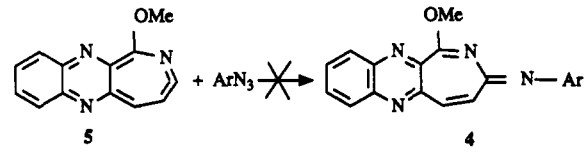
The photolysis of 2-azido-1-methoxyphenazine (**1a**) and its ethoxy homologue (**1b**) takes an unusual course. It involves the addition of a singlet nitrene or one of its cyclic tautomers to the ground-state azide to form the *N*-phenazinyl iminoether **9a** (from **1a**) and a 2-oxazolo[5,4-*a*]phenazinyl derivative of a quinoxalinylpropenenitrile (**10**, from both **1a** and **1b**). Products derived from the triplet nitrene are formed as well. The effects of varying some of the experimental conditions were determined. A mechanism for the photolysis is proposed.

Introduction

For several years we have been interested in the photochemical decomposition of heterocyclic azides, in particular, azidophenazines. Depending on the reaction conditions, such compounds give high yields of either, from the singlet nitrene, products of trapping by nucleophiles or, from the triplet nitrene, dimers and products of trapping by radical scavengers.[1] In contrast, the photolysis of carbocyclic aromatic azides usually gives poor yields of such products.[2]

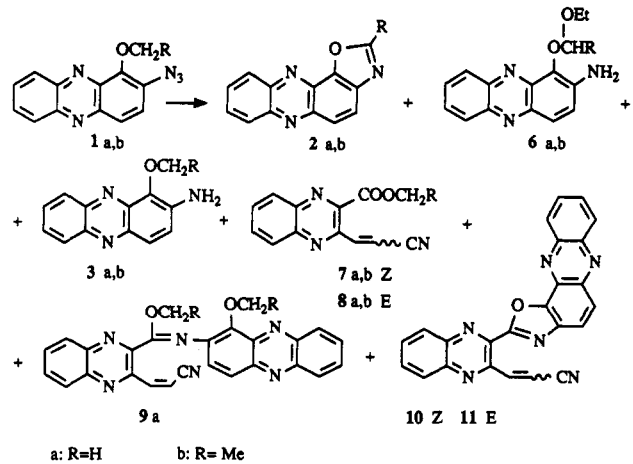
We earlier reported[1a] some results of the photolysis of 2-azido-1-methoxyphenazine (**1a**). Besides the oxazole **2a** and the amine **3a**, which were derived from the triplet nitrene (Scheme I), another major product arose from what appeared to be the coupling of two molecules of the substrate. We assigned an iminoazepine structure (formula **4**) to this compound and postulated that it was formed by the 1,3-dipolar cycloaddition of the ground-state azide to the dehydroazepine **5**, a cyclic isomer of singlet nitrene (Scheme II).

Scheme I



Ar = (1-methoxy-2-phenazinyl)

Scheme II



a: R=H b: R= Me

(1) (a) Albini, A., Bettinetti, G.; Minoli, G. *J. Org. Chem.* **1987**, *52*, 1245. (b) Bettinetti, G. F.; Fasani, E.; Minoli, G.; Pietra, S. *Gazz. Chim. Ital.* **1979**, *109*, 175. (c) Bettinetti, G. F.; Fasani, E.; Minoli, G.; Pietra, S. *Gazz. Chim. Ital.* **1980**, *110*, 135. (d) Albini, A.; Bettinetti, G. F.; Fasani, E.; Pietra, S. *Gazz. Chim. Ital.* **1982**, *112*, 15.

(2) (a) Iddon, B.; Meth-Cohn, O.; Scriven, E. F. V.; Suschitzky, H.; Gallagher, P. T. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 900. (b) Smith, P. A. In *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic Press: Orlando, 1984; p 95. (c) Scriven, E. F. V. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1981; Vol. 2, p 1. (d) Lwowski, W. In *Reactive Intermediates*; Jones, M., Mass, R. A., Eds.; Wiley: New York, 1981. (e) Abramovitch, R. A.; Kyla, E. P. *The Chemistry of the Azido Group*; Patai, S., Ed.; Wiley: New York, 1971; p 256. (f) Wentrup, C. *Adv. Heterocycl. Chem.* **1981**, *28*, 279. (g) Abramovitch, R. A.; Davis, B. A. *Chem. Rev.* **1964**, *64*, 149.

0022-3263/91/1956-6993$02.50/0

Table I. Products of the Photolysis of Azides 1a and 1b

starting material	solvent	T (°C)	products (% yield)
1a	benzene	20	**2a** (20), **3a** (17), **7a** (3), **8a** (1), **9a** (15), **10** + **11** (12)
	EtOH	20	**3a** (34), **6a** (24), **9a** (28)
	MeCN	20	**2a** (tr), **3a** (14), **7a** (8), **8a** (3), **9a** (40), **10** + **11** (21)
	MeCN	−20[a]	**9a** (81)
	MeCN	20, MK[b]	**2a** (20), **3a** (28), **7a** (tr), **8a** (tr), **9a** (12), **10** + **11** (7)
	MeCN	−20, MK[b]	**3a** (5), **9a** (30)
1b	benzene	20	**2b** (16), **3b** (20), **7b** (tr), **10** + **11** (20)
	EtOH	20	**3b** (41), **6b** (21), **7b** (3), **8b** (1)
	MeCN	20	**2b** (12), **3b** (18), **7b** (1), **8b** (tr), **10** + **11** (25)
	MeCN	−20	**2b** (6), **3b** (25), **7b** (5), **8b** (2), **10** + **11** (30)

[a] 66% conversion. [b] In the presence of 10^{-2} M Michler's ketone.

This unusual finding, for, indeed, neither products with a "dimeric nitrene" structure (except for azo compounds derived from triplet nitrenes) nor products of the trapping of a dehydroazepine by means other than the addition of a nucleophile have been previously described,[2] prompted us to undertake a more extensive investigation. This resulted in a revision of the structure originally assigned to **4**. Furthermore, a new type of "dimeric" product, unrelated to the one discovered earlier, was isolated. Conditions under which the yields of the dimeric compounds could be maximized were determined. The formation of such products was rationalized within the framework of the previously proposed mechanism,[1a] which was accordingly expanded.

Results

Photolysis of 2-Azido-1-methoxyphenazine (1a). As shown in Table I, both in benzene and in ethanol the main chemical processes, which together account for about half to two-thirds of the yield, were intra- and intermolecular hydrogen abstraction, which yielded **2a**, **3a**, and, in ethanol, also **6a**. Irradiation of benzene solutions also yielded small amounts of the open-chain nitrile esters **7a** and **8a**. The yields of the "dimeric" product, postulated earlier to have structure **4**, were far from negligible: in benzene and ethanol the yields were 15% and 28%, respectively (Table I, Scheme I).

That the ^{1}H NMR spectrum of *Z* nitrile **7a** was similar to that of compound **4**, and that its IR spectrum showed a very weak absorption due to the cyano group cast doubt on the structure assigned to **4**. Indeed, close examination of the IR spectrum of **4** showed a very weak absorption band at 2219 cm^{-1}. Although some nitriles yield IR spectra which show virtually undetectable CN absorption bands,[3] this is generally not the case for α,β-unsaturated nitriles. Thus, this observation was somewhat surprising. The structure of the "dimer" was therefore revised to the (*Z*)-quinoxalinylpropenenitrile **9a**, which bears an N-substituted iminoether functionality (Scheme I).

Moreover, from photolysis in benzene, two additional "dimeric" products were isolated (12% yield) and characterized. They were geometric isomers, which, like **9a**, incorporated an α,β-unsaturated nitrile functionality but lacked a methoxy group, as their ^{1}H NMR and IR spectra showed. The *Z* isomer constituted ca. 90% of the mixture of the two isomers that was obtained by rapid chromatographic purification of the raw photolysate. However, it slowly isomerized to the *E* isomer, even at room temperature. Complete conversion to the *E* isomer was accomplished by refluxing an ethanol suspension of the mixture of isomers for 3 h. The ^{1}H NMR spectra of both isomers showed that all of the protons, except for two olefinic protons, were attached to aromatic carbons (two sets of four protons on the carbons of the fused benzo rings, and two vicinal protons). The UV spectrum of the *E* isomer (λ_{max} = 279, 318, and 370 nm) showed the presence of a chromophore different from that of the parent phenazine. The analytical data for the *E* isomer were consistent with the formula $C_{24}H_{12}N_6O$. Thus the compound resulted from the coupling of two methoxyphenazinyl nitrenes, $C_{13}H_9N_3O$, formally with the loss of a molecule of dimethyl ether. On the basis of these data, structure **10** was assigned to the *Z* isomer and structure **11** to the *E* isomer.

The effects of changing certain experimental conditions, such as the nature of the solvent, on the photolysis were determined. The product distributions from photolyses in solvents that did not possess an easily abstractable hydrogen atom were qualitatively similar to that from photolyses in benzene. However, the yield of **9a** increased in some cases. The results of irradiating acetonitrile solutions were the most interesting. At 20 °C, only traces of **2a**, a 40% yield of **9a**, an increased proportion of the esters **7a** and **8a**, and a 21% yield of a mixture of **10** and **11** were produced. When the irradiation was performed at low temperature, the yield of **9a** increased. At −20 °C it was produced in 81% yield. Only traces of the other products were detected. Thus, a satisfactory route to **9a** had been found.

When irradiation was performed in the presence of a photosensitizer (Michler's ketone, MK, 10^{-2} M), so that only ca. 2% of the light was directly absorbed by **1a**, the product distribution changed greatly (Table I). Thus, upon irradiation at room temperature, the yield of **9a** decreased to 12%, only traces of **10** and **11** were detected, and the yields of the amine **3a** and the oxazole **2a** increased markedly. Upon irradiation at −20 °C, only **9a** and the amine **3a** were formed.

Studies of the Interconversion of the Products. It was established that no interconversion of the products took place during chromatography on silica gel. Compound **9a** could be hydrolyzed to a mixture of **3a**, **7a**, and **8a** by treatment with mineral acids. Furthermore compound **9a** was found to be reasonably photostable and was not converted to **10** or **11** under the reaction conditions (94% of **9a** was recovered after 10-min irradiation). It should be pointed out that, when photolysis took place in an aprotic solvent, **9a** was found in the raw photolysate whereas **10** was not. New signals (two olefinic doublets and signals due to methoxy groups) were observed in the ^{1}H NMR spectrum of the raw photolysate when it was recorded immediately after irradiation. However, when the raw photolysate was shaken with silica gel for 1 h and then its ^{1}H NMR spectrum was recorded, the new ab-

(3) It is known that the presence of electron-withdrawing groups strongly reduces the intensity of the cyano group absorption. See, for example: Kitson, R. E.; Griffin, N. E. *Anal. Chem.* **1952**, *24*, 335. Thompson, H. W.; Steel, G. *Trans. Faraday Soc.* **1956**, *52*, 1451. In the IR spectrum of a cyclic α-cyano imidate the CN absorption was absent. See: Oberti, R.; Albini, A.; Fasani, E. *J. Heterocycl. Chem.* **1983**, *20*, 1007.

Table II. Products of the Photolysis of Azide 1a in the Presence of Various Aryl Azides (Acetonitrile, −20 °C)

aryl azide (ArN_3) Ar =	products (% yield)
phenyl	**2a** (tr), **3a** (5), **7a** (8), **8a** (tr), **9a** (36)
o-methoxyphenyl	**3a** (8), **7a** (5), **9a** (36)
p-nitrophenyl	**3a** (4), **7a** (8), **9a** (46), **12** (4)
2-naphthyl	**2a** (20), **3a** (7), **7a** (tr), **9a** (13), **13** (13)

sorptions were absent and the characteristic low-field olefinic absorptions due to compound **10** were present.

Photolysis of 2-Azido-1-ethoxyphenazine (1b). The photodecomposition of **1b**, the ethyl homologue of **1a**, differed from that of **1a** in that, of the two expected "dimeric" products, no iminoether (**9b**) was formed, even under conditions that favored the formation of **9a** from **1a**. However, **10** and **11** were obtained in satisfactory yields by irradiation both at room temperature and at −20 °C. (Some colored, rather unstable compounds which together accounted for ca. 15% of the yield were also formed but were not identified.) The "monomeric" products were the amine **3b** and the oxazole **2b**, together with small amounts of the open-chain esters **7b** and **8b**, and, from the irradiation of ethanol solutions, the acetal **6b** (Table I).

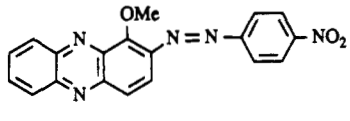
Cross-Coupling Experiments with Different Azides. Because experiments with **1a** confirmed that products formally arising from the coupling of two molecules of nitrene were formed, it was of interest to determine if any "cross-coupled" products similar to **9** or **10** could be formed by the irradiation of a mixture of azides.

In an attempt to discover conditions that favored the formation of the desired products, **1a** was irradiated in acetonitrile solution at −20 °C in the presence of one of several aryl azides that did not absorb light of the wavelength employed in the irradiation (Table II). The course of the photolysis of **1a** was unaffected by the presence of either phenyl or *o*-methoxyphenyl azide. When *p*-nitrophenyl azide was present, the only change was that some of the mixed azo derivative **12** was produced. However, when 2-naphthyl azide was present, the yield of **9a** dropped to 19%, the yield of the oxazole **2a** rose to 20%, and a new product was formed. The spectra of the new compound were similar to those of **9a**, but also showed absorptions attributable to both quinoxaline and naphthalene rings. It was identified as the "cross-coupled" nitrene adduct **13**.

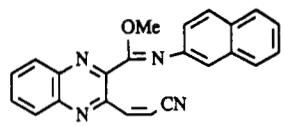
Photolysis of 2-Azidophenazine. To determine how general were the processes that occurred during the photolysis of the alkoxy derivatives, an acetonitrile solution of the parent compound, 2-azidophenazine, was irradiated at −20 °C. Chromatography of the soluble part of the raw photolysate yielded the amine **15** (the main product) and a small amount of the aldehyde **14**. The same products were also isolated after irradiation at rt. However, the ^1H NMR and IR spectra of the raw photolysate showed that the aldehyde **14** was absent, whereas an open-chain derivative that incorporated the *Z*-CH=CHCN group was present. Furthermore TLC of the photolysate showed the presence of a new compound. When the plate was again developed, at right angles to the first development, the spot due to the new compound gave rise to those due to **14** and **15**. Thus a "dimeric" compound, homologous to **9** (bearing H instead of OR), was apparently formed but did not survive chromatography, during which it decomposed to **14** and **15**.

Discussion

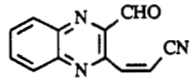
The pathways followed by the triplet nitrenes require little comment. Both inter- and intramolecular hydrogen atom abstraction, to yield the amines **3** and the oxazoles **2**, respectively, are precedented.[2a,4] As expected, the oxazoles **2** are not formed upon irradiation of ethanol solutions, because in ethanol the intermolecular process predominates. In keeping with the low reactivity displayed by aromatic triplet nitrenes ("lazy triplet"),[1,2] the yields of products from the two processes decreased substantially at low temperature. Of course, the mixed azo compound **12**, derived from **1a** and *p*-nitrophenyl azide, is a product of the reaction of the triplet nitrene.



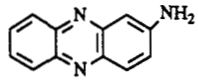
12



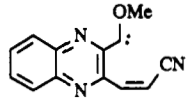
13



14



15



22

As for the pathways followed by the singlet nitrenes, the following points are mechanistically relevant. The products are either "dimers", i.e., **9a** and **10**, or are products derived from "dimeric" precursors, as are **14** and **15** (from **1c**), as well as the nitriles **7** and **8**. The last-named compounds are formed neither by oxidation of the nitrene[5] nor by hydrolysis of **9a**, which is stable under the reaction conditions. Thus, they must arise, together with a portion of the amines **3**, by the mild hydrolysis of some dimeric intermediate. Finally, it must be remembered that **10** is neither related to **9a** nor is it an initial product; rather it arises from a different and, in the absence of a protic solvent, quite stable precursor.

The mechanism depicted in Scheme III, although speculative, does explain the formations of the products in an economical way. The sequence begins with the singlet nitrene **16** (which can also be represented by the dipolar structure **16'**) or its cyclic tautomers, the dehydroazepine **5** and the benzoazirine **17**. The participation of one, or both, of the tautomers explains many reactions of aromatic azides, in particular the addition of nucleophiles.[1,2] In the present case, a bimolecular reaction with a ground-state molecule of the azide **1a** is involved. For example, it should be noted that no "dimeric" products were formed when the initial concentration of the azide was 10^{-5} rather than 10^{-3} M.

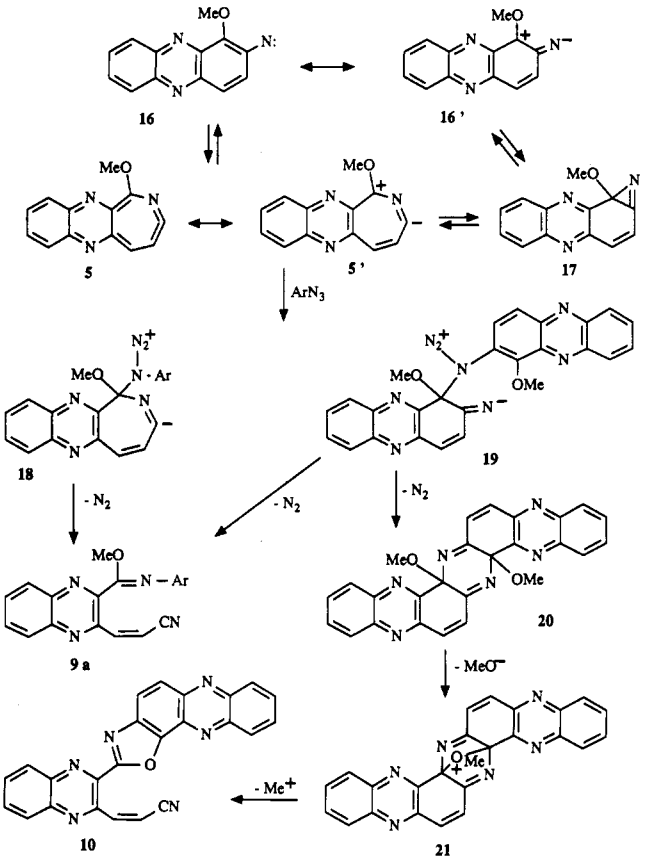
In view of the large effects that changes in the medium, temperature, and structure had on the product distribution, it is likely that **9a** and **10** arise via different paths. The addition of the nitrene to the azide would yield zwitterionic intermediates like **18** and **19**. These would collapse to **9a** via elimination of nitrogen and cleavage of a C–N or C–C σ bond. The same zwitterions might also be the sources of the esters **7** and **8** and a portion of the amines **3** via the action of moisture present in the solvent.

A second path leads from zwitterion **19** to intermediate **20** via loss of nitrogen and intramolecular cyclization. That **19** is formed is apparently not without precedent. The formation of 1,1-dimethoxy-1,2-dihydro-2-iminoanthracene by the photolysis of 1-methoxy-2-azidoanthracene in

(4) Lindley, J. M.; Mc Robbie, I. M.; Meth-Cohn, O.; Suschitzky, H. *J. Chem. Soc., Perkin Trans. 1* **1980**, 982.

(5) The experiments were performed in the absence of oxygen. It was previously observed that, in the presence of oxygen, the reaction takes a different course. See: ref 1b.

Scheme III. Singlet Pathways Followed in the Photolysis of 1-Methoxy-2-phenazinylnitrene



methanol/dioxane may have involved an intermediate similar to **19**.[6] Intermediate **20** may be the unidentified product present in the crude photolysate. Heterolytic cleavage of the C–O bond of the imino acetal function of **20** in the presence of protic solvents or silica gel would lead to a carbocation which could be attacked intramolecularly by the other alkoxy group to afford **21**. Loss of R^+ (Me^+ or Et^+) from the trialkyl oxonium cation **21** and rearrangement would yield **10**. Thus, the unusual formal elimination of R_2O that occurred during the formation of **10** from both **1a** and **1b** would be explained.

An alternative pathway that was considered is that ring opening of **5** to the carbene **22** preceded addition. This is reasonable because structurally similar carbenes are probably intermediates in the formation of 1-cyanocyclopentadienes from phenyl azides, a process which, however, is characteristic of high-temperature pyrolysis rather than of photolysis at room temperature.[7] From carbene **22** another viable path would lead to **9**. However, **22** could not yield **7** and **8** under oxygen-free conditions, as exist in the experiments described here. Besides, the formation of **10** from **22** would require an initial attack on the ether oxygen rather than on the azide nitrogen, which would be followed by other, ill-defined steps. In any event, the carbene pathway does not explain why a precursor of **10**, rather then **10** itself, was present in the photolysate before chromatography.

Thus, the mechanism depicted in Scheme III is favored, even though definitive evidence that demonstrates the existence of the proposed intermediates is lacking, and it does not rationalize that both **9a** and **10** are formed from **1a**, while only **10** is obtained from **1b**, the ethyl homologue of **1a**. Steric factors and, possibly, charge-transfer interactions between the rings may influence both the initial addition of the nitrene to the azide (the key factor is probably a charge-transfer interaction which favors the approach of the cumulene **5** or the benzoazirine **16** to the phenazinyl azide) and in the evolution of the intermediates that follows. The same factors may come into play in the interesting, but, for the moment, not further studied, cross-addition that was observed during the photolysis of **1a** in the presence of 2-naphthyl azide and which yielded compound **13**. It should be noted that under the conditions that gave rise to **13** there was an increase in the yield of **2a**, which possibly was the result of an enhanced rate of intersystem crossing induced by the naphthalene derivative.

In conclusion, a new mode of reaction of singlet nitrenes, i.e. addition to azides, has been identified. The formation of the unusual "dimeric" products **9** and **10** probably is a consequence of the peculiar stability imparted to the nitrenes (both singlet and triplet) by conjugation with the phenazine nucleus, as well as of the propensity for such nitrenes to form charge-transfer complexes. As the results of the experiments with 2-azidophenazine suggest, similar adducts may have been formed in other cases. However, the isolation of such products may prove to be difficult.[8]

The results of this work again demonstrate that good yields of products from the reactions of both triplet and singlet nitrenes can be obtained by the judicious choice of experimental conditions. Furthermore, the results support the notion that not only are singlet nitrenes and their cyclic tautomers in equilibrium, but also so are triplet and singlet nitrenes (see e.g. MK experiment in Table I, line 5). Notice further that hydrogen atom abstraction (a reaction of the triplet) is obviously favored in hydrogen-donating solvents. However, both inter- and intramolecular hydrogen atom abstraction require some energy of activation. Thus, at low temperatures, reactions typical of the singlet nitrene predominate, even when the azide is irradiated in the presence of a photosensitizer (see Table I, line 6).

Experimental Section

General. The solvents were spectroscopic grade and were distilled before use. Column chromatography was performed with silica gel 60 HR (Merck). Compounds **1a** and 2-azidophenazine were prepared as described.[1a,b] Compound **1b** was prepared in a manner similar to that used to prepare the methoxy derivative **1a** via the following intermediates:

1-Ethoxy-2-nitrophenazine from 1-(*N*-pyrazolyl)-2-nitrophenazine[9] by treatment with NaOEt/EtOH: yellow crystals; mp 131–132 °C (EtOH); 65%. Anal. Calcd for $C_{14}H_{11}N_3O_3$: C, 62.45; H, 4.12; N, 15.61. Found: C, 62.62; H, 4.18; N, 15.97.

2-Amino-1-ethoxyphenazine: orange crystals; mp 137–138 °C (benzene); 87%. Anal. Calcd for $C_{14}H_{13}N_3O$: C, 70.27; H, 5.48; N, 17.56. Found: C, 70.00; H, 5.51; N, 17.81.

2-Azido-1-ethoxyphenazine: soft yellow needles; mp 126–127 °C dec (EtOH); 75%. Anal. Calcd for $C_{14}H_{11}N_5O$: C, 63.38; H, 4.18; N, 26.40. Found: C, 63.58; H, 4.32; N, 26.42.

(6) Rigaudy, J.; Igier, C.; Barcelo, J. *Tetrahedron Lett.* **1979**, 1837.
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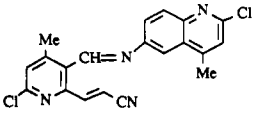
(8) Compound **23**, an analogue of **9**, was obtained from the photolysis of 2-chloro-4-methyl-6-azidoquinoline. See: Hayes, R.; Schofield, J. M.; Smalley, R. C.; Scopes, D. I. C. *Tetrahedron* **1990**, *46*, 2089.



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(9) Pietra, S.; Casiraghi, G. *Gazz. Chim. Ital.* **1970**, *100*, 119.

Table III. Spectroscopic Characteristics at the New Products

compd	IR (cm^{-1})	^1H NMR (δ, ppm)
2b	1587, 1525	2.90 (s, 3 H), 7.75–8.6 (m, 6 H)
3b	3477, 3321, 1637	1.5 (t, 3 H, J = 6 Hz), 1.55 (s, 2 H), 4.55 (q, 2 H, J = 6 Hz), 7.3–8.4 (m, 6 H)
6b	3470, 3350, 1640	1.2 (t, 3 H, J = 6 Hz), 2.67 (d, 3 H, J = 5.5 Hz), 3.95 (q, 2 H, J = 6 Hz) 4.7 (br s, 2 H), 6.07 (q, 1 H, J = 5.5 Hz), 7.2–8.3 (m, 6 H)
7b	2219, 1717	1.5 (t, 3 H, J = 6 Hz), 4.58 (q, 2 H, J = 6 Hz), 5.82 (d, 1 H, J = 12 Hz), 7.75–8.5 (m, 4 H), 8.1 (d, 1 H, J = 12 Hz)
8b	2219, 1717	1.5 (t, 3 H, J = 6 Hz), 4.6 (q, 2 H, J = 6 Hz), 6.92 (d, 1 H, J = 16 Hz), 7.4–8.9 (m, 4 H), 8.35 (d, 1 H, J = 16 Hz)
10	2217	6.06 (d, 1 H, J = 12 Hz), 7.7–8.6 (m, 10 H), 8.99 (d, 1 H, J = 12 Hz)
11	2219	7.1 (d, 1 H, J = 16 Hz), 7.7–8.6 (m, 10 H), 9.12 (d, 1 H, J = 16 Hz)
12	1522, 1343	4.8 (s, 3 H), 7.95 d and 8.42 (AA'XX', 4 H), 8.1 (d, 1 H, J = 9 Hz), 7.9–8.2 (m, 4 H), 8.4 (d, 1 H, J = 9 Hz)
13	2222, 1670	4.2 (s, 3 H), 5.7 (d, 1 H, J = 12 Hz), 6.8–8.2 (m, 11 H), 7.35 (d, 1 H, J = 12 Hz)

General Procedure for the Photochemical Decomposition of Azides 1a and 1b. The solvent (170 mL) was deaerated by boiling and, after a small quantity (20 mL) had been distilled, was cooled to rt under Ar. The azide and, if required, a second azide (in the cross-addition experiments), or Michler's ketone (in the sensitized experiments) were introduced. The solution (4×10^{-3} M in 1) was purged with Ar for 30 min and then was irradiated with a medium-pressure Hg lamp (125 W) through a Pyrex filter until the starting material (**1a** or **1b**) disappeared (TLC). When required, the solution was cooled to −20 °C and then was irradiated. After irradiation, the solvent was evaporated at rt under reduced pressure. The residue was chromatographed on 150 g of silica gel (benzene/AcOEt, from 9:1 to 7:3; or cyclohexane/AcOEt, from 9:1 to 1:1).

Photolysis of 1a (150 mg) in MeCN at rt. Irradiation for 8 min and column chromatography (benzene/AcOEt) afforded, in order of elution: **8a** (4 mg), colorless needles, mp 188–191 °C;[1a] **7a** (12 mg), colorless needles, mp 110–113 °C;[1a] a mixture of 3-[3-(2-oxazolo[5,4-*a*]phenazinyl)-2-quinoxalinyl]-2-propenenitriles (**10** and **11**, 25 mg), a light yellow solid that, upon refluxing in EtOH for 3 h, was converted into the pure *E* isomer **11**, a light yellow microcrystalline solid, mp 283–285 °C ($EtNO_2$), MS m/z 400 [Anal. Calcd for $C_{24}H_{12}N_6O$: C, 71.99; H, 3.02; N, 20.99. Found: C, 71.84; H, 3.07; N, 20.76]; **2a** (3 mg), light yellow needles, mp 214–215 °C (cyclohexane);[1a] 3-[3-[[(1-methoxy-2-phenazinyl)imino]methoxymethyl]-2-quinoxalinyl]-2-propenenitrile (**9a**, 54 mg) yellow fluffy needles, mp 220–222 °C (benzene/cyclohexane, 1:1);[1a] **3a** (19 mg), red needles, mp 146–147 °C (benzene/cyclohexane, 1:1).[1a]

Photodecomposition of 1a (150 mg) in MeCN at −20 °C in the Presence of *p*-Nitrophenyl Azide (10^{-2} M). Irradiation for 20 min and column chromatography (cyclohexane/AcOEt) afforded the mixed azo derivative **12** (10 mg): orange crystals, mp 250 °C (benzene/cyclohexane, 1:1), MS m/z 359. Anal. Calcd for $C_{19}H_{13}N_5O_3$: C, 63.51; H, 3.65; N, 19.49. Found: C, 63.21; H, 3.73; N, 19.38. The other products are listed in Table II.

Photodecomposition of 1a (150 mg) in MeCN at −20 °C in the Presence of 2-Naphthyl Azide (8×10^{-3} M). Irradiation for 20 min and column chromatography (cyclohexane/AcOEt) afforded **13** (28 mg): light yellow needles; mp 147–148 °C (benzene/cyclohexane, 1:1), MS m/z 364. Anal. Calcd for $C_{23}H_{16}N_4O$: C, 75.81; H, 4.43; N, 15.38. Found: C, 76.00; H, 4.20; N, 15.10. The other products are listed in Table II.

Photolysis of 1b at rt. In MeCN: irradiation of **1b** (160 mg) for 8 min and column chromatography (benzene/AcOEt) afforded, in order of elution: **8b** (1 mg), colorless crystals; mp 89–92 °C. Anal. Calcd for $C_{14}H_{11}N_3O_2$: C, 66.39; H, 4.38; N, 16.59. Found: C, 66.72; H, 4.45; N, 16.32. Compound **7b** (2 mg), colorless crystals; mp 161–163 °C. Anal. Calcd for $C_{14}H_{11}N_3O_2$. Found: C, 66.20; H, 4.49; N, 16.41. Compounds **10** and **11**, an inseparable mixture (30 mg). An orange glass; further chromatography of this glassy material on 15 g of silica gel (cyclohexane/acetone, 8:2) afforded **2b** (17 mg), light yellow needles; mp 221–222 °C (cyclohexane). Anal. Calcd for $C_{14}H_9N_3O$: C, 71.48; H, 3.86; N, 17.86. Found: C, 71.61; H, 3.82; N, 18.01. The amine **3b** (27 mg). In EtOH: irradiation of **1b** (160 mg) for 9 min and column chromatography (benzene/AcOEt) gave, besides **3b**, **7b**, and **8b** (see Table I), the amine **6b** (36 mg): red needles; mp 118–119 °C (cyclohexane/benzene, 1:1). Anal. Calcd for $C_{16}H_{17}N_3O_2$: C, 67.82; H, 6.05; N, 14.83. Found: C, 67.82; H, 6.06; N, 14.77.

Photochemical Decomposition of 2-Azidophenazine in MeCN. Irradiation of a CH_3CN solution of 2-azidophenazine (150 mg) for 20 min at −20 °C, as described in the general procedure, gave an orange-brown suspension. Filtration of the mixture and column chromatography of the filtrate (benzene/AcOEt) afforded the aldehyde **14** (10 mg, 7%)[1b] and 2-aminophenazine (**15**, 36 mg, 27%).[1b] After irradiation at rt the same products, **14** (25 mg, 17%) and **15** (35 mg, 26%), were obtained.

Hydrolytic Cleavage of Compound 9a. To a suspension of **9a** (50 mg) and MeOH (10 mL) was added 10% aqueous HCl (0.1 mL). The mixture was stirred for 1 h at rt. The red solution that resulted was allowed to stand overnight. The solution was then neutralized by the introduction of aqueous NH_3 and then was diluted with water. The orange solution that resulted was extracted with benzene. Concentration of the extract and column chromatography of the residue afforded **8a** (4 mg, 25%), **7a** (10 mg, 62%), and the amine **3a** (12 mg, 80%).[1a]

Identification of the Photoproducts. The spectroscopic characteristics of the new compounds are listed in Table III.

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Registry No. 1a, 107383-59-5; **1b**, 136721-36-3; **2a**, 136721-41-0; **2b**, 136721-48-7; **3a**, 136721-43-2; **3b**, 136721-35-2; **6a**, 136721-51-2; **6b**, 136721-49-8; **7a**, 136721-38-5; **7b**, 136721-47-6; **8a**, 136721-37-4; **8b**, 136721-46-5; **9a**, 136721-42-1; **10**, 136721-39-6; **11**, 136721-40-9; **12**, 136721-44-3; **13**, 136721-45-4; **14**, 136721-50-1; **15**, 2876-23-5; 1-ethoxy-2-nitrophenazine, 136721-34-1; 1-(*N*-pyrazolyl)-2-nitrophenazine, 27447-80-9; *p*-nitrophenyl azide, 1516-60-5; 2-naphthyl azide, 20937-86-4; phenyl azide, 622-37-7; *o*-methoxyphenyl azide, 20442-97-1; 2-azidophenazine, 6494-70-8.