Hz, CHOBn), 3.71 (3 H, s, $CH_3CCO$), 4.29 and 4.55 (2 H, AB q, $J_{AB}$ = 12.0 Hz, $CH_2OBn$), 5.10 (1 H, d, $J$ = 11.4 Hz, cis H of C=$CH_2$), 5.21 (1 H, d, $J$ = 16.8 Hz, trans H of C=$CH_2$), 5.58 (1 H, dd, $J$ = 8.3, 15.3 Hz, C=CH), 6.17 (1 H, dd, $J$ = 10.5, 15.2 Hz, C=CH), 6.31–6.43 (1 H, m, C=CH), 6.50–6.58 (1 H, m, C=CH), 7.25–7.34 (5 H, m, aryl H). Anal. Calcd for $C_{22}H_{30}O_3$: C, 77.16; H, 8.83. Found: C, 77.23; H, 8.84.

**(2*E*,8*E*)-(4*S*,6*S*,7*S*)-2,4,6-Trimethyl-7-(benzyloxy)-2,8,10-undecatrien-1-ol (38).** To a solution of 108 mg (0.316 mmol) of ester **37** in 5 mL of ether at −78 °C was added 0.83 mL (0.83 mmol) of 1 M DIBAH in hexanes dropwise over 5 min. Stirring was continued for 35 min at −78 °C, and the mixture was quenched with 1 mL of saturated Rochelle's salt solution, extracted into ether, and dried over $MgSO_4$. Chromatography on a 1 × 15 cm column of silica gel with 50% ether–hexane afforded the allylic alcohol **38** in quantitative yield: $[\alpha]^{22}_D$ −3.1° (*c* 2.67, $CH_2Cl_2$); IR (film) $\nu$ 3340, 2950, 2845, 2840, 1600, 1450, 1375 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ 0.87 and 0.88 (6 H, d and d, $J$ = 6.9 and 6.6 Hz, $CHCH_3$), 1.01 and 1.41 (2 H, m), 1.29 (1 H, br s, OH), 1.59 (3 H, d, $J$ = 1.4 Hz, vinyl $CH_3$), 1.79 (1 H, m), 2.45 (1 H, m), 3.59 (1 H, dd, $J$ = 5.6, 8.2 Hz, CHOBn), 3.94 (2 H, br s, $CH_2OH$), 4.30 and 4.56 (2 H, AB q, $J_{AB}$ = 12.1 Hz, $OCH_2Ph$), 5.08–5.24 (3 H, m, C=$CH_2$ and $HOCH_2C(CH_3)$=C*H*), 5.60 (1 H, dd, $J$ = 8.3, 15.3 Hz, C=CH), 6.17 (1 H, dd, $J$ = 10.5, 15.3 Hz, C=CH), 6.31–6.44 (1 H, m, C=CH), 7.23–7.34 (5 H, m, aryl H). Anal. Calcd for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62. Found: C, 80.34; H, 9.64.

**(2*E*,8*E*)-(4*S*,6*S*,7*S*)-2,4,6-Trimethyl-7-(benzyloxy)-2,8,10-undecatrienal (1g).** Trienol **38** (59 mg, 0.19 mmol) was oxidized by the method of Swern[12] with 40 μL (0.46 mmol) of oxalyl chloride, 50 μL (0.71 mmol) of $Me_2SO$, and 240 μL (1.7 mmol) of triethylamine in 2 mL of $CH_2Cl_2$ as described above. Purification by chromatography on a 1 × 10 cm column of silica gel with 10% ether–hexane as eluant gave 53 mg (89%) of the aldehyde **1g**: $[\alpha]_D$ −3.79° (*c* 2.72, $CH_2Cl_2$); IR (film) $\nu$ 2950, 2910, 2850, 2700, 1690, 1640, 1605, 1460 $cm^{-1}$; $^1H$ NMR (300 MHz) $\delta$ 0.88 (3 H, d, $J$ = 6.8 Hz, $CHCH_3$), 0.99 (3 H, d, $J$ = 6.6 Hz, $CHCH_3$), 1.10–1.24 (1 H, m), 1.55–1.72 (2 H, m), 1.67 (3 H, d, $J$ = 1.3 Hz, vinyl $CH_3$), 2.77 (1 H, m), 3.54 (1 H, dd, $J$ = 6.1, 8.2 Hz, CHOBn), 4.28 and 4.56 (2 H, AB q, $J_{AB}$ = 12.1 Hz, $OCH_2Ph$), 5.11 (1 H, d, $J$ = 11.5 Hz, cis H of C=$CH_2$), 5.22 (1 H, d, $J$ = 16.7 Hz, trans H of C=$CH_2$), 5.58 (1 H, dd, $J$ = 8.4, 15.3 Hz, C=CH), 6.12–6.40 (3 H, m), 7.24–7.31 (5 H, m, aryl H). Anal. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.65; H, 9.09.

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# Inter- and Intramolecular Reactions of Nitrenes and Their Cyclic Isomers in the Photodecomposition of Some Substituted 2-Azidophenazines

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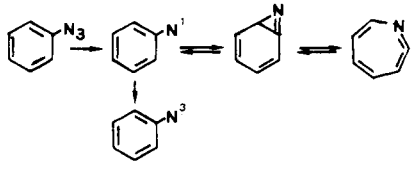
The photodecomposition of 2-azido-1-(3,5-dimethylpyrazolyl)phenazine (**1a**) and 2-azido-1-methoxyphenazine (**1b**) is investigated in benzene and ethanol and in the presence of acids or bases. This is a suitable model for the chemical characterization of nitrenes and their cyclic isomers (benzoazirines and dehydroazepines) formed under these conditions. In an unreactive medium, singlet nitrene from **1a** is trapped intramolecularly to yield the heteropentalene **2**, but in ethanol substitution of the azido group via excited azide and addition to the azirine to give the aziridine **6** (yielding the oxidation product **5** during workup) are observed. In the presence of acids phenazine imines **10** and **11** (undergoing hydrolysis to **8** and **9**) are obtained through the nitrenium cation. In bases, addition to the dehydroazepine takes place to give the ethoxyazepine **13**. In the case of **1b**, the dehydroazepine is trapped via an unprecedented cycloaddition with the azide (yielding **18**) or reacts with bases to yield the dimeric product **28**. Triplet nitrene reactions (inter- or intramolecular hydrogen abstraction, reaction with oxygen to yield the rearranged nitroso derivative **22**) are more important from **1b**. Substituent and solvent effects are discussed in connection with recent hypotheses on the equilibrium between different reactive species from the decomposition of azides.

## Introduction

Photochemical decomposition of aromatic azides is a subject of active research in organic chemistry[1] as well as in applicative areas such as cross-linking of polymers[2] and photochemical labeling in biochemistry.[3]

**Scheme I**




The synthetic outcome of the photodecomposition of azides depends widely on the structure of the starting material and the conditions of the experiments, untractable "tars" accounting in several cases for a large portion of the

(1) (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) Lwoski, W. In *Reactive Intermediates*; Jones, M., Mass, R. A. Eds.; Wiley: New York, 1981. (e) Abramovitch, R. A.; Kyba, E. P. In *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.

(2) Breslow, D. S., in ref 1b, p 491.

(3) (a) Knowles, J. R. *Acc. Chem. Res.* **1972**, *5*, 155. (b) Bayley, H.; Staros, J. V., in ref 1b, p 432.

0022-3263/87/1952-1245$01.50/0 

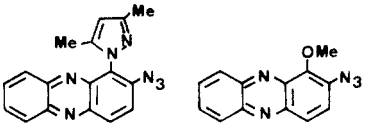
material balance. Nevertheless, several general processes have long been recognized and have been firmly attributed to either the singlet or the triplet state of the nitrene on the basis of sensitization experiments or kinetic studies.[1] As an example, reaction with nucleophiles and intramolecular electrophilic attack have been attributed to the former species and hydrogen abstraction as well as dimerization to the azo derivatives to the latter.

Actually, the situation is more complex in that various spectroscopic and chemical evidences suggest that in some cases singlet nitrene isomerizes to different cyclic intermediates such as benzoazirines and dehydroazepines before final reaction.[4] Two recent papers by Schuster, based mainly on laser flash photolysis evidence on phenyl, naphthyl, and pyrenyl azide, convincingly proposed that singlet nitrene is in fact *in equilibrium* with its cyclic isomers.[5] Trapping of the latter species by nucleophiles leads to adducts; this failing, intersystem crossing to the triplet state intervenes (Scheme I).

We have been concerned for some time with the photodecomposition of phenazinyl azides[6] and have observed that, analogously to what is observed with other heterocyclic azides,[7] the output of isolable products is often higher than with the carbocyclic analogues.

In a previous study,[8] we considered the photodecomposition of 2-azidophenazine bearing in position 1 a dimethylpyrazole ring as this system was expected to offer the chance of distinguishing, via intramolecular reactions, the reactivity of the singlet and the triplet states of the nitrene, as the former would react with the lone pair of the pyrazole nitrogen atom and the latter with the activated pyrazole methyl group.[9] In fact, we found that both direct irradiation and triplet sensitization of 2-azido-1-(1,3-dimethylpyrazolyl)phenazine (**1a**) in "inert" solvents result almost exclusively in intramolecular electrophilic attack.

In the present paper we discuss the concurrence of inter- and intramolecular reaction and singlet and triplet nitrene reactions in photochemistry of **1a** and of 2-azido-1-methoxyphenazine (**1b**). The latter compound lacks a site for




1a 1b

intramolecular electrophilic attack, while intramolecular hydrogen abstraction is possible. Both compounds were studied in benzene and in ethanol. Complex mixtures of products were formed, and new kinds of processes were observed as well as known ones. All of these can be rationalized through the reaction of one of the species of Scheme I, so that these results allow a discussion of the factors affecting the equilibrium between the different reactive intermediates.

**Table I. Preparative Results from the Irradiation of Phenazinyl Azides 1a–c**

| starting material | solvent, conditions[a] | products (% yield) |
|---|---|---|
| 1a | cyclohexane[b] | **2** (73), **3a** (5) |
| | tetralin[b] | **2** (71), **3a** (18) |
| | acetonitrile[b] | **2** (41), **3a** (11) |
| | benzene | **2** (64), **3a** (3) |
| | ethanol | **2** (14), **3a** (17), **4** (12), **5** (40) |
| | ethanol, $2 \times 10^{-2}$ M $CF_3COOH$ | **2** (2), **3a** (25), **8** (16), **9** (14) |
| | ethanol, $2 \times 10^{-2}$ M EtONa | **2** (22), **3a** (30), **13** (18) |
| 1b | benzene | **3b** (17), **14** (20), **18** (15), **20** (3), **21** (3) |
| | benzene[c] | **3b** (16), **14** (12), **18** (10), **20** (1), **21** (3), **22** (42), **26** (1) |
| | ethanol | **3b** (34), **18** (29), **27** (24) |
| | ethanol, $2 \times 10^{-2}$ M $CF_3COOH$ | **3b** (23), **18** (31), **27** (20) |
| | ethanol, $2 \times 10^{-2}$ M EtONa | **3b** (47), **27** (2), **28** (11) |
| 1c | benzene[d] | tars |
| | benzene[c,d] | **3c** (3), **31** (57), **32** (5), **33** (6) |
| | ethanol[e] | **3c** (2), **34** (7) |
| | ethanol, 0.15 M HCl[e] | **3c** (4), **34** (16), **35** (35) |
| | methanol, 0.1 M MeONa[e] | **3c** (2), **36** (15) |

[a] Solution previously degassed by boiling and flushing with Ar, unless otherwise specified. [b] From ref 8. [c] Air-equilibrated solution. [d] From ref 6a. [e] From ref 6c.

## Results

The products obtained by photodecomposition of azides **1a** and **1b** are shown in Schemes II–V (in the schemes only the ring initially carrying the azido group is indicated; Py = 1-(1,3-dimethylpyrazolyl)). Isolated yields after chromatographic separation are reported in Table I.

**Photodecomposition of 2-Azido-1-(1,3-dimethylpyrazolyl)phenazine (1a).** Intramolecular electrophilic attack onto the neighboring pyrazolyl nitrogen atom largely predominates in the photodecomposition of this azide, and of the other potential intramolecular or intermolecular pathways, only reduction to amine appears as a minor process. Thus, 1,3-dimethyl-5*H*-pyrazolo[1′,2′:1,2]-1,2,3-triazolo[5,4-*a*]phenazin-4-ium inner salt (**2**)[8] was obtained in 64% yield along with 3% of the amine **3a** on photolysis of **1a** in degassed benzene.[10a] Similar results had previously been obtained in other "inert" media.[8]

Photodecomposition of **1a** in degassed ethanol takes a different course. The yield of the amine **3a** was observed to increase to 17%, as expected in a hydrogen-donating solvent, while product **2** dropped to 14%[10b] and two other

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(5) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 5228, 5234.

(6) (a) Bettinetti, G. F.; Fasani, E.; Minoli, G.; Pietra, S. *Gazz. Chim. Ital.* **1979**, *109*, 175. (b) Bettinetti, G. F.; Fasani, E.; Minoli, G.; Pietra, S. *Gazz. Chim. Ital.* **1980**, *110*, 135. (c) Albini, A.; Bettinetti, G. F.; Fasani, E.; Pietra, S. *Gazz. Chim. Ital.* **1982**, *112*, 15.

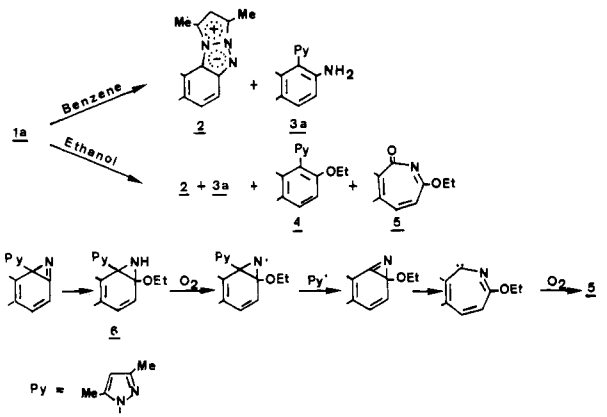
(7) (a) Khan, Z. U.; Patel, D. I.; Smalley, R. K.; Scriven, E. F. V.; Suschitzky, H. *J. Chem. Soc., Perkin Trans. 1* **1983**, 4. (b) Sawanishi, H.; Hirai, T.; Tsuchiya, T. *Heterocycles* **1982**, *19*, 2071 and therein cited references.

(8) Albini, A.; Bettinetti, G. F.; Minoli, G. *J. Chem. Soc., Perkin Trans. 1* **1981**, 4.

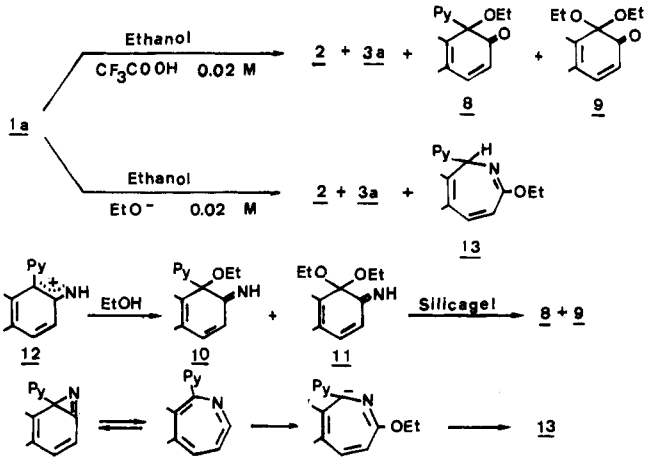
(9) (a) This model has been proposed by Suschitzky et al. in the case of 1-(2-nitrenophenyl)-3,5-dimethilpyrazole, ref 9b. (b) Lindley, J. M.; Mc Robbie, I. M.; Meth-Cohn, O.; Suschitzky, H. *J. Chem. Soc., Perkin Trans. 1* **1980**, 982.

(10) (a) In the presence of oxygen, product **2** undergoes efficient self-sensitized photooxidation. Albini, A.; Bettinetti, G. F.; Minoli, G.; Pietra, S. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2904. (b) In these conditions compound **2** is photostable. c) We exclude that product **5** arises from oxidation of a 2*H*-azepine, as such compounds, when isolated, (see for instance product **13**) are stable to oxygen and workup (under these conditions).

Scheme II



Scheme III



products were formed in 12% and 40% yield. The first one was recognized as 1-(1,3-dimethylpyrazolyl)-2-ethoxyphenazine (4) by comparison with an authentic sample obtained by thermal reaction (see Experimental Section). This product apparently arises through photonucleophilic substitution onto the intact azide, as **1a** does not significantly react in ethanolic solution at room temperature.

The second and major product was identified as 3-ethoxy-1-oxoazepino[3,4-*b*]quinoxaline (**5**) on the basis of analytical and spectroscopic evidence (see Experimental Section for more detail). The source of this product is less straightforward. The pyrazolyl group has been eliminated (an equivalent amount of pyrazole was separated from the reaction mixture) and an oxidation has taken place. This requires that compound **5** arises from a primary photoproduct which undergoes a further reaction during workup in the presence of oxygen. The more likely candidate for this intermediate is the ethoxypyrazolylaziridine **6**, arising from solvent addition to the azirine, in accordance with previous reports.[1b] A possible mechanism for the conversion of this product into azepinone **5** is outlined in Scheme II.[10c]

As shown above, in a nucleophilic medium, intermolecular reactions largely predominate over intramolecular electrophilic attack.

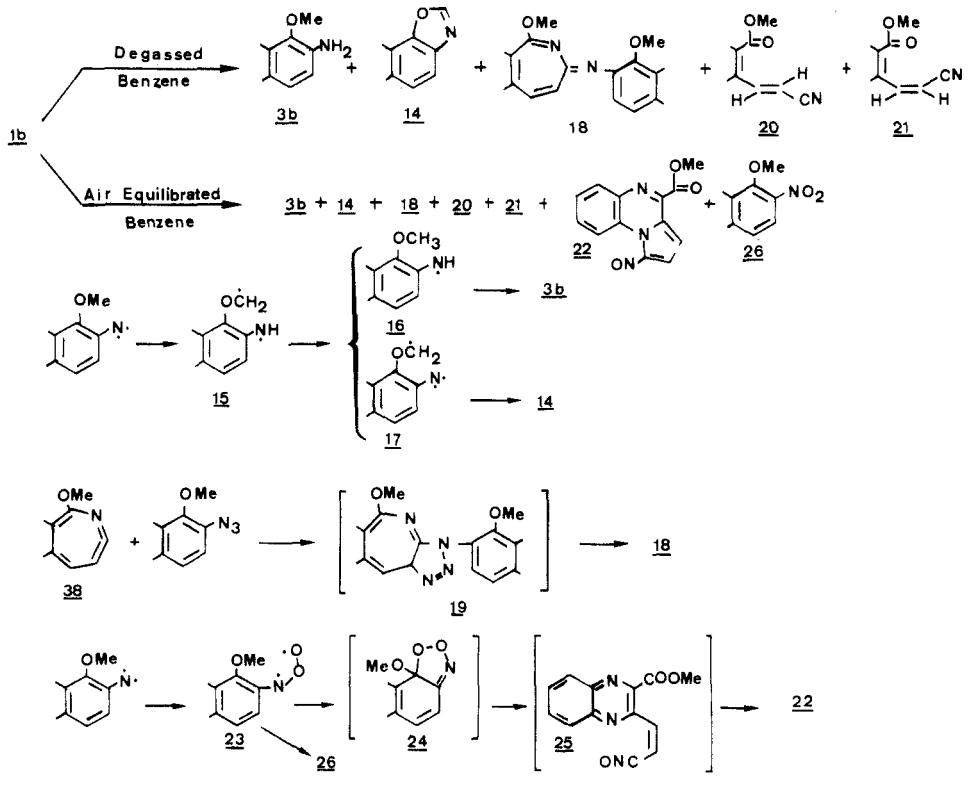
A further change in the chemical output was effected by changing the pH of the solution. Thus, in ethanol containing $2 \times 10^{-2}$ M trifluoroacetic acid, the yield of product **2** dropped to 2%, reduction to the amine **3a** grew to 25%, and no compounds **4** and **5** were formed. Two new products, obtained in 16% and 14% yield, were recognized as substituted 1,2-dihydrophenazin-2-one, viz., the 1-(1,3-dimethylpyrazolyl)-1-ethoxy (**8**) and the 1,1-diethoxy (**9**) derivative, on the basis of spectroscopic evidence. It is reasonable to assume that products **8** and **9** arise from silica gel catalyzed hydrolysis of the corresponding imines **10** and **11** during chromatographic separation of the photolyzate. The imines in turn arise from solvent attack onto the nitrenium ion **12**.

The results from the decomposition of **1a** in ethanol containing $2 \times 10^{-2}$ M sodium ethoxide are again different. Product **2** accounted for 22% and the amine **3a** for 30%, and a new product, 1*H*-1-(1,3-dimethylpyrazolyl)-3-ethoxyazepino[3,4-*b*]quinoxaline (**13**), was obtained in 18% yield. This may arise either from nucleophilic attack onto the azirine and subsequent isomerization to the stable seven-membered ring anion or, more likely, by direct attack onto the dehydroazepine (Scheme III).

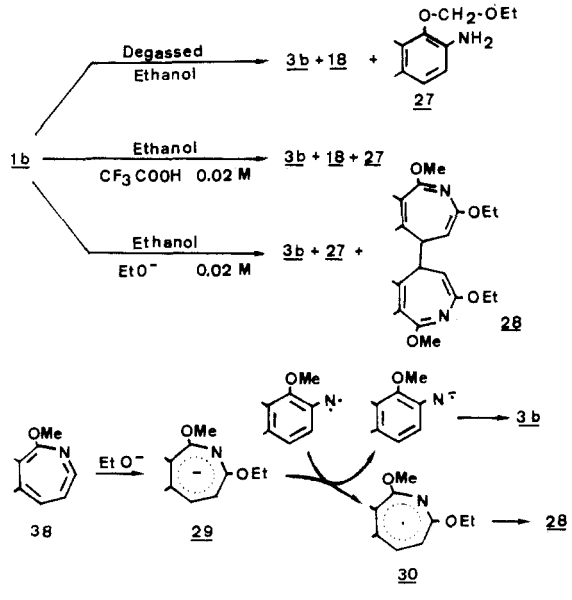
**Photodecomposition of 2-Azido-1-methoxyphenazine (1b).** While a single process dominates the photochemistry of **1a** in inert media, several processes were observed for **1b**. Photodecomposition in degassed benzene led to a complex mixture (Scheme IV). Besides the amine **3b** (17%), there were two major products. The first one (20% yield) analyzed to be $C_{13}H_7N_3O$ and spectroscopic properties suggested the structure of oxazolo[4,5-*a*]-phenazine (**14**). The first step for the formation of **14** is an intramolecular hydrogen abstraction to yield biradical **15**. Since the corresponding dihydro derivative of oxazole **14** was not detected among the reaction products, we assume that **15** does not cyclize to the dihydro derivative but rather disproportionates to radicals **16** and **17**, which further react to the amine **3b** and oxazole **14**, respectively (Scheme IV). This explains the observed formation of the amine **3b** in relatively high yield even in non-hydrogen-donating solvent, whereas no amine is formed from the parent 2-azidophenazine (**1c**) in benzene.[6a] The second product (15% yield, $M_r$, 446, $C_{26}H_{18}N_6O_2$) formally corresponds to two units of methoxyphenazinylnitrene. Inspection of the NMR spectrum showed that in one unit the phenazine ring is preserved, while in the other an azepine ring is present. On this and other evidence, structure **18** was assigned to this product. This apparently arises from the cycloaddition reaction of the dehydroazepine **38** onto a molecule of intact azide, and nitrogen elimination from the intermediate triazoline **19** (Scheme IV). The yield of product **18** dropped, as expected, with decreasing azide concentration and was very low for [**1b**] $< 10^{-3}$ M. Minor products under these conditions were two isomeric 3-(3-carbomethoxy-2-quinoxalinyl)propenenitriles **20** and **21**, resulting from oxidative cleavage of the ring carrying the azido group. This kind of process was already observed as a minor pathway also in the photodecomposition of 2-azidophenazine (**1c**).[6a] The low yield of these products discouraged any attempt to retrace the precursor and the mechanism by which they are formed.

When the photodecomposition was carried out in air-equilibrated benzene, the yields of main products **3b**, **14**, and **1**, were slightly diminished. Under these conditions the main product (42% yield) was 4-carbomethoxy-1-nitrosopyrrolo[1,2-*a*]quinoxaline (**22**), together with a minor amount of the nitro derivative **26**. These compounds are formed from the reaction of triplet nitrene with oxygen via a single intermediate, namely, the biradical **23**, which can give rise to the nitro derivative **26** by a nitrogen–oxygen bond reorganization and to the pyrroloquinoxaline **22** through the cycloadduct **24**, C1–C2 bond fission with formation of the nitrile oxide **25**, and cyclization onto the nitrogen atom of the resulting quinoxaline, as already observed in the photodecomposition of **1c**.[6a] The reaction mixture contained also small amounts of products **20** and **21** (Scheme IV).

Scheme IV



Scheme V



Photodecomposition of **1b** in degassed ethanol (Scheme V) led to the amine **3b** and to product **18** in higher yield than in degassed benzene, and to another amine, viz. 1-(ethoxymethoxy)-2-aminophenazine (**27**), apparently arising from solvent-trapping of biradical **15**.

In contrast to the case of **1a**, addition of $2 \times 10^{-2}$ M trifluoroacetic acid to the ethanolic solution did not significantly affect the course of the photodecomposition of azide **1b**, nor there was any important change in product yield. A change was observed in the presence of $2 \times 10^{-2}$ M sodium ethoxide. Reduction to the amine **3b** greatly predominated, while product **27** was reduced to 1.5%, product **18** was absent, and a new product was obtained in 11% yield. The base peak in the mass spectrum of this compound is 268 (formally nitrene + EtO), but the molecular peak is twice as much. The NMR spectrum likewise suggests a dimeric structure, and more particularly structure **28**, H4 and H5 absorbing at $\delta$ 4.5 and 4.65. The formation of product **28** can be rationalized as involving addition of an ethoxy anion to the dehydroazepine and oxidation of the resulting anion **29** by some species, likely by triplet nitrene. This would account both for the increased yield of the amine **3b** and formation of product **28** through coupling of the stable radical **30** (Scheme V).

## Discussion

For the sake of comparison, some of the results obtained in previous work[6a] on the photodecomposition of 2-azidophenazine (**1c**) are reported again in Scheme VI and in Table I. In the previous section, it has been attempted to rationalize every one of the isolated products with some primary processes, either inter- or intramolecular, starting from one of the species in Scheme I. The results of the classification are collected in Table II and Scheme VII. These data can be commented on as follows. In only one case, is nucleophilic substitution onto the azide excited state fast enough to compete, although inefficiently (ratio 1:6), with azido group cleavage. In every other instance, the reaction can be attributed to the nitrene, either singlet or triplet, or its cyclic isomers.

Aromatic azides in the absence of nucleophiles yield in general products arising from triplet nitrene. This is true also with the presently considered phenazinylnitrenes, although the reactions observed are qualitatively different. Thus, formation of the azo derivative is at most a minor process (≤1% from **1a**). Intermolecular hydrogen abstraction to yield the amines obviously depends on the hydrogen-donating properties of the solvent (see Table I). However, this is a minor reaction from **1c** and is more important from **1a**, and particularly from **1b**, since it is initiated by an intramolecular mechanism (see below).

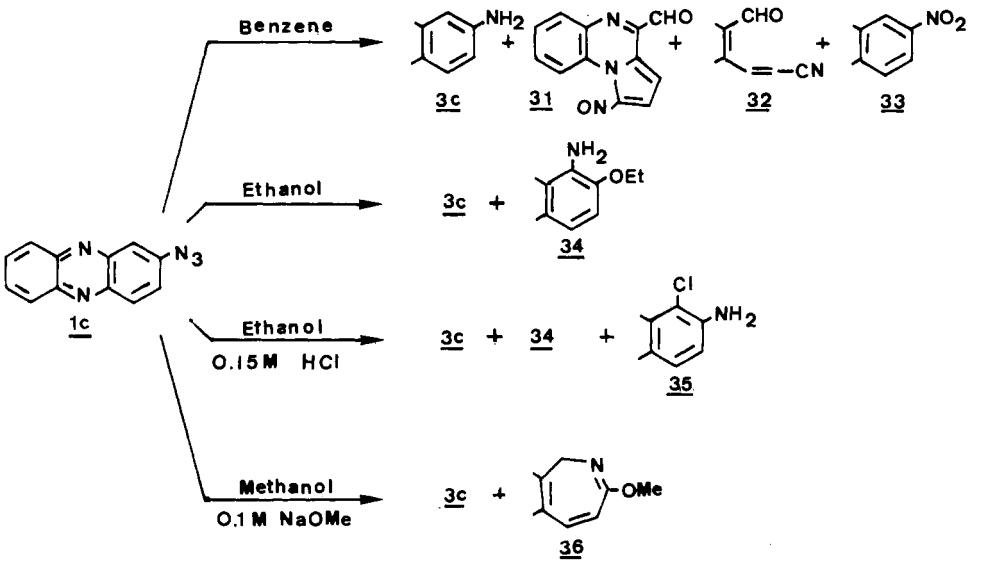
The inefficiency of azo formation might be due to experimental conditions, as this process has been demonstrated to depend on light intensity,[5] but this is not a

**Table II. Different Pathways in the Photodecomposition of Phenazinyl Azides 1a-c**

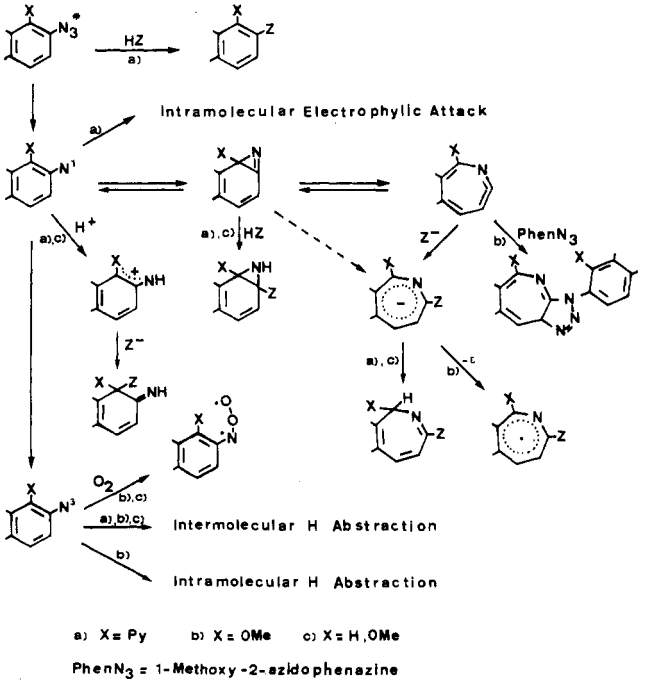
| azide | solvent | excited azide | singlet nitrene | azirine | dehydro-azepine | nitrenium cation | triplet nitrene: intra-molecular H-abstraction | triplet nitrene: inter-molecular H-abstraction | reaction with oxygen |
|---|---|---|---|---|---|---|---|---|---|
| 1a | benzene | | 2 (64) | | | | | 3a (3) | |
| 1b | benzene | | | | 18 (15) | | 14 (20) | 3b (17) | |
| 1b | benzene[a] | | | | 18 (10) | | 14 (12) | 3b (16) | 22 + 26 (43) |
| 1c | benzene[a] | | | | | | | 3c (1) | 31 + 33 (63) |
| 1a | ethanol | 4 (12) | 2 (14) | 5 (40) | | | | 3a (13) | |
| 1b | ethanol | | | | 18 (29) | | 27 (24) | 3b (34) | |
| 1c | ethanol | | | 34 (7) | | | | 3c (2) | |
| 1a | ethanol, $H^+$ | | 2 (2) | | | 8 + 9 (30) | | 3a (25) | |
| 1b | ethanol, $H^+$ | | | | 18 (31) | | 27 (20) | 3b (23) | |
| 1c | ethanol, $H^+$ | | | 34 (16) | | 35 (35) | | 3c (4) | |
| 1a | ethanol, $EtO^-$ | | 2 (22) | | 13 (18) | | | 3a (30) | |
| 1b | ethanol, $EtO^-$ | | | | 28 (11) | | 27 (2) | 3b (47) | |
| 1c | methanol, $MeO^-$ | | | | 36 (15) | | | 3c (2) | |

[a] Air-equilibrated solvent. In the other cases, degassed solutions were irradiated.

**Scheme VI**

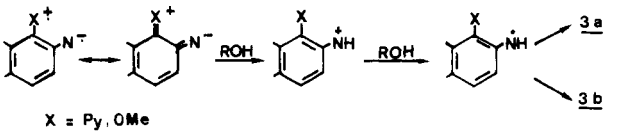



**Scheme VII**

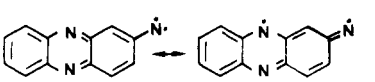



sufficient explanation and a different chemical reactivity must be invoked.

**Scheme VIII**




The peculiar reactivity of triplet phenazinylnitrene can be rationalized on the basis of its low energy (at higher temperature hydrogen abstraction becomes significant or predominant for **1c**) and its pronounced biradical character, likely due to extended conjugation, as in mesomeric formula **37**.



**37**

The radical character is apparent in the reaction with oxygen, mainly leading to the nitrile oxide **25** as reported above. Formation of a nitro derivative had been previously reported as a minor pathway for some carbocyclic aromatic azides.[12] The present results suggest that reaction with

(11) The results from the photolysis of **1a** in air-equilibrated ethanol are qualitatively the same as in deaerated solution, except than product **2** is consumed under this condition, ref 10.

(12) Abramovitch, R. A.; Challand, S. R. *J. Chem. Soc., Chem. Commun.* **1972**, 964.

oxygen might be rather general and, failing intramolecular trapping, polymerization of the nitrile oxide leads to part of the usually observed tars.

As for reduction to the amine, the greater efficiency of this reaction with **1a** and **1b** with respect to **1c** might be in part due to intramolecular electron transfer followed by protonation by the solvent, rather than to direct intermolecular hydrogen abstraction, according to Scheme VIII.

Electron transfer from the pyrazole ring to the phenazinylnitrene moiety is so fast that even intramolecular hydrogen abstraction from the activated methyl group does not take place, contrary to the case of 1(*o*-nitrenophenyl)dimethylpyrazole.[9b]

Amine formation by hydrogen abstraction by triplet nitrene is significant only in good hydrogen-donating solvent, e.g., in tetralin.

As for the nitrene singlet state, this is trapped efficiently by intramolecular electrophilic attack in the case of **1a** just as it happens wherever an aromatic or heterocyclic ring is present in the ortho position according to the well-known model of *o*-nitrenobiphenyl cyclization.[1a]

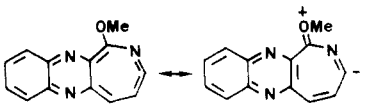
A second reaction pathway involves protonated singlet nitrene. Part of the change in the product distribution observed in acidic medium can be explained by protonation of the azirine (see below) enhancing the rate of addition (e.g., higher yield of product **34** from **1c** in acidic ethanol). However, products **10** and **11** from **1a**, and in particular product **35**, arising from the addition of the weakly nucleophilic chloride anion onto **1c**, require that phenazinylnitrene is largely protonated under this condition.[13]

In the other cases, observed products involve reaction of cyclic isomers of nitrene and can be readily divided into two groups: (i) formation of aziridines, through addition of a nucleophile onto azirines, (ii) products arising from dehydroazepines.

The aziridines than undergo heterolytic cleavage to yield 1-amino-2-substituted phenazines such as **34** from **1c** or homolytic cleavage as in the case of aziridine **6** from **1a**.

As for reactions attributable to dehydroazepine, the more characteristic is the cycloaddition onto the azido group observed in the case of methoxy derivative **1b**.

To our knowledge this is the first unambigous chemical evidence for this kind of intermediate, previously detected in the case of phenyl azide by low temperature spectroscopy,[4c] and suggests that the chemistry of this species is richer than hitherto suspected. [**Note added in proof**: Further support for this mechanism has been obtained through trapping of the dehydroazepine from **1b** by *another* azide (2-naphthyl azide).] Probably the presently




**38**

observed cycloaddition is due to a stabilization of the dehydroazepine from **1b** as can be rationalized by the importance of mesomeric formulae such as **38**.

This stabilization must be important as no reactions attributed to the azirine or, in acidic conditions, to the nitrenium ion are observed from **1b**. With the azides **1a** and **1c**, a reaction attributed to the dehydroazepine is observed only in the presence of bases and leads to the 1*H*-3-substituted azepines **13** and **36**. Other nucleophilic additions have been similarly rationalized,[14] although in principle these products could arise also from addition to the azirine followed by ring enlargement. However, at least in the present case, this seems unlikely as in these conditions the analogous product **28** is formed from **1b**, whereas this compound does not yield under neutral or acidic conditions products arising from the azirine.

## Conclusion

We have shown in this paper that, although the diversity of processes occurring in the decomposition of phenazinyl azides **1a–c** may appear at first sight confusing, all of the reactions discussed can be understood as arising from the different species in Scheme I. Moreover, the new reactions recognized throw new light on the chemistry of nitrenes and their cyclic isomers. This is particularly the case for the unambiguous evidence for the dehydroazepine obtained through a new cycloaddition reaction. The nature of the aromatic ring (carbocyclic or heterocyclic), the pattern of substitution, and the presence of intra- or intermolecular nucleophiles are important in determining the contribution of the different intermediates to the reactions actually observed in each case.

## Experimental Section

**General.** UV–vis spectra were recorded on a Hitachi Perkin-Elmer 200 spectrophotometer, $^1$H NMR spectra ($CDCl_3$) on a Brucker WP80 instrument using $(CH_3)_4Si$ as an internal standard, IR spectra (nujol) on a Perkin-Elmer 257 spectrophotometer, and mass spectra on a Du Pont 492 spectrometer. Melting points are uncorrected. Commercial (Carlo Erba) spectroscopic grade benzene and absolute ethanol were used as received. Column chromatography was performed with silica gel 60 HR (Merck) and preparative TLC using a Chromatotron (Morrison Research) appartus, eluting with benzene–ethyl acetate (9:1 to 6:4 mixtures) in the case of the photolysate from **1a** and cyclohexane–ethyl acetate (8:2 to 1:1 mixtures) for **1b**. The products are reported following the order of elution.

**Photochemical Decomposition of 2-Azido-1-(3,5-dimethylpyrazolyl)phenazine (1a).** Benzene (160 mL) was degassed by boiling and cooling under argon, 160 mg of product **1a**[8] was added, and the resulting solution was further purged with argon for 20 min and irradiated by means of a medium pressure mercury arc (Helios Italquartz, 125 W) through a Pyrex filter until the starting material had disappeared (TLC, 5 min). After concentration to 10 mL under reduced pressure, dark blue crystals of 1,3-dimethyl-1-5*H*-pyrazolo [1′,2′:1,2]1,2,3-triazolo[3,2-*a*]-phenazin-4-ium inner salt[8] (**2**, 79 mg) were obtained overnight. Chromatography of the filtrate yielded an additional portion of this compound (16 mg) and 2-amino-1-(3,5-dimethylpyrazolyl)-phenazine (**3a**, 4 mg).[8]

Photolysis of **1a** in degassed ethanol under similar conditions, evaporation of the solvent, and chromatography of the residue yielded the following products: 3-ethoxy-1-oxoazepino[3,4-*b*]-quinoxaline (**5**, 50 mg), white crystals from benzene [mp 133–134 °C; NMR $\delta$ 1.40 (t, 3 H), 4.45 (q, 2 H), 6.85 (d, H4), 7.45 (d, H5, $J_{4,5}$ = 11, 5 Hz), 7.80–8.50 (m, 4 H); IR 1690, 1640, 1620 cm$^{-1}$. Anal. Calcd for $C_{14}H_{11}N_3O_2$: C, 66.39; H, 4.38; N, 16.59. Found: C, 66.20; H, 4.49; N, 16.45. Final proof of the structure of **5** was obtained by analogy with a single-crystal structure determination];[15] compound **2** (21 mg); 1,3-dimethylpyrazole (19 mg); 1-(1,3-dimethylpyrazolyl)-2-ethoxyphenazine (**4**, 19 mg), identical with the product obtained through thermal reaction (see below); and compound **3a** (25 mg).

Photolysis of **1a** in degassed ethanol containing $2 \times 10^{-2}$ M trifuoroacetic acid followed by neutralization with potassium

(13) For a discussion of the chemistry of arylnitrenium cations, see: Abramovitch, R. A.; Jeyaraman, R., in ref 1b, p 297.

(14) Rigaudy, J.; Igier, C.; Barcelo, J. *Tetrahedron Lett.* **1979**, 1837 and therein cited references.

(15) Personal communication by Dr. B. Bovio, Pavia. The structure determination was carried out on the corresponding propoxy derivative, from which single crystals of convenient size are easily grown.

carbonate, evaporation of the solvent, and chromatography yielded the following products: 1,1-diethoxy-1,2-dihydrophenazin-2-one (**9**, 21 mg), colorless crystals [mp 122–124 °C from ethanol; NMR $\delta$ 1.25 (t, 6 H), 3.80 (q, 4 H), 6.70 (d, H3), 7.05 (d, H4, $J_{3,4}$ = 10 Hz); IR 1725 cm$^{-1}$. Anal. Calcd for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.34; H, 5.68; N, 10.01]; 1-(1,3-dimethylpyrazolyl)-1-ethoxy-1,2-dihydrophenazin-2-one (**8**, 27 mg) [mp 200 °C from ethanol; NMR $\delta$ 1.25 (t, 3 H), 2.10 (s, 3 H), 2.50 (s, 3 H), 3.75 (q, 2 H), 5.90 (s, 1 H), 7.15 (AB system, H3 and H4); IR 1725 cm$^{-1}$. Anal. Calcd for $C_{19}H_{18}N_4O_2$: C, 68.24; H, 5.42; N, 16.76. Found: C, 68.05; H, 5.55; N, 16.58]; product **2** (3 mg); and the amine **3a** (39 mg).

Photolysis of **1a** in degassed ethanol containing $2 \times 10^{-2}$ M sodium ethoxide, followed by neutralization with acetic acid and evaporation of the solvent under reduced pressure and chromatography, yielded the following products: compound **2** (33 mg); 1*H*-1-(1,3-dimethylpyrazolyl)-3-ethoxyazepino[3,4-*b*]quinoxaline (**13**, 30 mg), colorless needles from cyclohexane [mp 158–159 °C; NMR $\delta$ 1.27 (t, 3 H), 2.25 (s, 3 H), 2.62 (s, 3 H), 4.20 (q, 2 H), 6.06 (s, 1 H), 6.72 (s, 1 H), 6.75 (d, H4), 7.57 (d, H5, $J_{4,5}$ = 10 Hz); IR 1640, 1630 cm$^{-1}$. Anal. Calcd for $C_{19}H_{19}N_5O$: C, 68.45; H, 5.74; N, 21.01. Found: C, 68.67; H, 5.77; N, 21.01].

**Thermal Reaction of 1a with Sodium Ethoxide.** Compound **1a** (160 mg) was added to a 0.5 M solution of sodium ethoxide in ethanol (20 mL). No reaction was detected (TLC) after 2 h at room temperature. Reaction was almost complete after 14 days. Evaporation of the solvent and chromatography of the residue yielded the starting material (12 mg) [1-(1,3-dimethylpyrazolyl)-2-ethoxyphenazine (**4**, 92 mg, 60% yield), orange needles from cyclohexane: mp 165–166 °C; NMR $\delta$ 1.3 (t, 3 H), 2.05 (s, 3 H), 2.40 (s, 3 H), 4.20 (q, 2 H), 6.15 (s, 1 H), 7.50–8.50 (m, 6 H); IR 1630 cm$^{-1}$. Anal. Calcd for $C_{19}H_{18}N_4O$: C, 71.67; H, 5.70; N, 17.60. Found: C, 71.62; H, 5.66; N, 17.56] and amine **3a** (43 mg, 30%).

**2-Azido-1-methoxyphenazine (1b).** 1-Methoxy-2-nitrophenazine (**26**)[16] (1 g) was dissolved in 200 mL of ethanol and hydrogenated at room temperature and pressure in the presence of 100 mg of 10% palladium on charcoal. Evaporation of the solvent and recrystallization from benzene–cyclohexane yielded 0.85 g (95%) of 2-amino-1-methoxyphenazine (**3b**), mp 146–147 °C: NMR $\delta$ 4.15 (s, 3 H), 4.55 (br s, 2 H), 7.25–8.40 (m, 6 H); IR 3380, 3300, 3200, 1635, 1605 cm$^{-1}$. Anal. Calcd for $C_{13}H_{11}N_3O$: C, 69.32; H, 4.92; N, 18.66. Found: C, 69.21; H, 4.89; N, 18.70.

The amine (0.325 g) was dissolved in acetic acid (5 mL) and water (5 mL) was added. The clear solution was cooled to 5 °C and 5 mL of 40% fluoboric acid was added. The suspension thus obtained was cooled to −5 °C and was dropwise added with 0.12 g of sodium nitrite in 1 mL of water. After 10 min the solid was filtered, suspended in 10 mL acetic acid, cooled to 5 °C, and treated with 0.39 g of sodium azide. After 15 min of stirring, the suspension was added with 10 g of ice and neutralized with concentrated ammonia while cooling. The solid was filtered, dissolved in benzene, and chromatographed on a short alumina column eluting with benzene. Recrystallization of the yellow band from benzene yielded the title compound, 0.245 g (64%), mp 127 °C; NMR $\delta$ 4.35 (s, 3 H), 7.45–8.45 (m, 6 H); IR 2140, 1625, 1600 cm$^{-1}$. Anal. Calcd for $C_{13}H_9N_5O$: C, 62.14; H, 3.61; N, 27.88. Found: C, 61.68; H, 3.62; N, 27.80.

**Photolysis of the Azide 1b.** Experimental conditions are the same as for the corresponding experiments with **1a**. The products obtained are the following, starting from 125 mg of the azide in 160 mL of solvent.

Photolysis in degassed benzene: *trans*-3-[2-(3-carbomethoxyquinoxalinyl)] propenenitrile (**20**, 4 mg), colorless crystals [mp 188–189 °C; NMR $\delta$ 4.15 (s, 3 H), olefinic signals at $\delta$ 6.95 (d) and 8:45 (d, $J$ = 16 Hz), 7.85–8.30 (m, 4 H); IR 2210, 1720 cm$^{-1}$. Anal. Calcd for $C_{13}H_9N_3O_2$: C, 65.26; H, 3.79; N, 17.51. Found: C, 65.41; H, 3.82; N, 17.46]; *cis*-3-[2-(3-carbomethoxyquinoxalinyl)]-propenenitrile (**21**, 4 mg) colorless crystals [mp 112–113 °C; NMR $\delta$ 4.15 (s, 3 H), olefinic signals at $\delta$ 5.9 (d) and 8.0 (d, $J$ = 11.5 Hz), 7.85–8.45 (m, 4 H); IR 2210 and 1740 cm$^{-1}$. Anal. Calcd for $C_{13}H_9N_3O_2$: C, 65.26; H, 3.79; N, 17.51. Found: C, 65.05; H, 3.73; N, 17.41]; oxazolo[4,5-*a*]phenazine (**14**, 22 mg), light yellow crystals from cyclohexane [mp 214–215 °C; NMR $\delta$ 8.25 (s, H2), 7.75–8.65 (m, 6 H); IR 3080, 1530 cm$^{-1}$; mass spectrum, $m/z$ 221 (M$^+$). Anal. Calcd for $C_{13}H_7N_3O$: C, 70.58; H, 3.19; N, 19.00. Found: C, 70.38; H, 3.15; N, 18.86. N 2-(1-methoxyphenazinyl)-3*H*-1-methoxy-3-iminoazepino[3,4-*b*]quinoxaline (**18**, 17 mg), yellow needles from cyclohexane [mp 220–222 °C; NMR $\delta$ 4.05 (s, 3 H), 4.25 (s, 3 H), 5.85 (d, H4), 7.6 (d, H5, $J_{4,5}$ = 11 Hz), 7.50–8.30 (m, 10 H); the presence of one azepine ring is indicated by two doublets at 5.85 and 7.6; H3 and H4 of the intact phenazine ring absorb at 7.70; IR, 1675 cm$^{-1}$; mass spectrum, $m/z$ 446 (M$^+$). Anal. Calcd for $C_{26}H_{18}N_6O_2$: C, 69.94; H, 4.06; N, 18.83. Found: C, 70.03; H, 4.05; N, 18.76]; product **3b** (19 mg).

Photolysis in air-equilibrated benzene: products **20** (1 mg); **21** (4 mg); **14** (14 mg); **18** (11 mg); 1-nitroso-4-carbomethoxypyrrolo[1,2-*a*]quinoxaline (**22**, 53 mg) yellow needles from cyclohexane [mp 189–190 °C; NMR $\delta$ 4.15 (s, 3 H), 6.65 (d, H2), 7.6 (d, H3, $J_{2,3}$ = 5.5 Hz), 7.75–8.50 (m, 4 H); IR, 1730 cm$^{-1}$. Anal. Calcd for $C_{13}H_9N_3O_3$: C, 61.17; H, 3.55; N, 16.47. Found: C, 60.98; H, 3.57; N, 16.38]; 1-methoxy-2-nitrophenazine (**26**, 1 mg); and amine **3b** (19.5 mg).

Photolysis in degassed ethanol: compound **18** (32 mg); 1-(ethoxymethoxy)-2-aminophenazine (**27**, 32 mg) [red needles from benzene–cyclohexane, mp 126–127 °C; NMR $\delta$ 1.27 (t, 3 H), 4.97 (q, 2 H), 4.65 (br s, 2 H) 5.75 (s, 2 H), 7.25–8.30 (m, 6 H); IR 3430, 3320, 3200, 1635, 1605 cm$^{-1}$. Anal. Calcd for $C_{15}H_{15}N_3O_2$: C, 66.90; H, 5.61; N, 15.61. Found: C, 66.95; H, 5.71; N, 15.66]; compound **3b** (38 mg).

Photolysis in degassed ethanol containing trifluoracetic acid: compounds **18** (33 mg); **27** (34 mg); **3b** (25 mg).

Photolysis in degassed ethanol containing sodium ethoxide: compound **27** (3 mg); 1-methoxy-3-ethoxy-5-[5-(1-methoxy-3-ethoxyazepino[3,4-*b*]quinoxalinyl)]azepino[3,4-*b*]quinoxaline (**28**, 22 mg), yellow needles from ethanol [mp 175–176 °C; NMR $\delta$ 1.35 (t, 6 H), protons in positions 4, 5, 4′, and 5′ observed as a second-order system centered at $\delta$ 4.5 and 4.65, 7.50–8.25 (m, 8 H); IR, 1620, 1605 cm$^{-1}$. Anal. Calcd for $C_{30}H_{28}N_6O_4$: C, 67.15; H, 5.26; N, 15.66. Found: C, 66.94; H, 5.19; N, 15.72].

**Acknowledgment.** This work was supported in part by a grant from the Italian Department of Education.

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