***exo*-7-Phenyl-1-methyl-2,6-dioxabicyclo[3.2.0]heptane (*exo*-8a)**: ^{1}H NMR ($CDCl_3$) δ 0.88 (s, 3 H), 1.80 (m, J = 4.0, 9.1 Hz, 1 H), 2.14 (m, J = 5.6, 13.7 Hz, 1 H), 4.29-4.36 (m, 2 H), 4.99 (d, J = 4.0 Hz, 1 H), 5.44 (s, 1 H), 7.19-7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 17.8 (q), 34.1 (t), 67.7 (t), 89.3 (d), 89.5 (s), 90.9 (d), 125.3 (d), 127.6 (d), 128.4 (d), 138.8 (s); IR (CCl_4, endo/exo) 3020, 2920, 1605, 1505, 1470, 1400, 1220, 1050, 825 cm^{-1}; MS (m/z, endo/exo) 190 (M^+), 134, 105, 91, 84, 77, 69, 43. Anal. ($C_{12}H_{14}O_2$) Calcd: C, 75.76; H, 7.42. Found: C, 75.20; H, 6.92.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft (Projekt Gr 881/2-1 and 2-2), the Fonds der Chemischen Industrie, and the Universitätsbund Würzburg. We thank Prof. C. Doubleday, Jr. and Prof. S. S. Shaik for helpful and stimulating comments and encouragement.

Chemistry of Nitrenes Generated by the Photocleavage of Both Azides and a Five-Membered Heterocycle

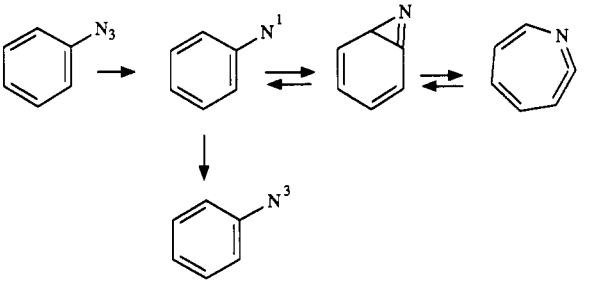
A. Albini, G. Bettinetti,* and G. Minoli

Contribution from the Department of Organic Chemistry, The University of Pavia, I-27100 Pavia, Italy. *Received October 16, 1990. Revised Manuscript Received May 2, 1991*

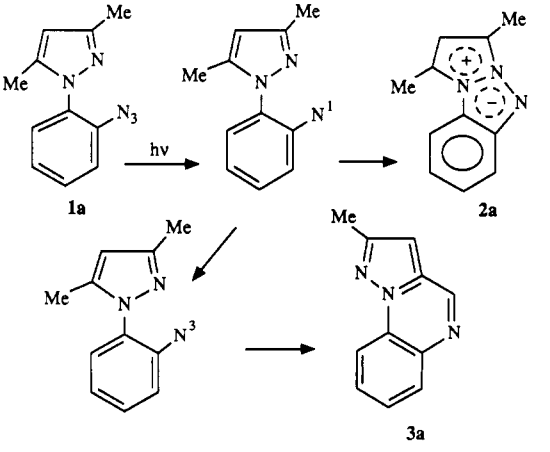
Abstract: Pyrazolo[1,2-*a*]benzotriazole and some of its derivatives (**2a-c**) are photochemically cleaved to form 2-(1-pyrazolyl)phenylnitrenes, which are also obtained through a more conventional path by photodecomposition of the pyrazolylphenyl azides (**1a-c**). Product studies and laser flash photolysis analysis of nitrenes from both sources show that there is competition between fast intramolecular reclosure to heterocycles **2** and rearrangement to dehydroazepines. The latter species are trapped by nucleophiles, or otherwise slowly rearrange back to the nitrenes (conformational factors affect these processes). The (quite unreactive) triplet nitrenes are identified spectroscopically and possibly are in equilibrium with the previous transients.

The study of the photodecomposition of aromatic azides has gradually revealed various chemical paths that require the involvement of different intermediates.[1-5] Thus the reactivities of singlet (e.g. electrophilic attack on aromatics) and triplet nitrene (e.g. coupling to yield azo derivatives) have been distinguished one from the other. In order to rationalize the addition of nucleophiles, it has been proposed that bond reorganization of the nitrene to a bicyclic azirine should precede the reaction.[6] Following this, matrix isolation[7] and flash photolytic investigation,[8] as well as preparative studies,[9,10] have supported the intervention of both azirines and dehydroazepines. Recent work on phenyl, 2-naphthyl, and pyrenyl azide suggests that these rearranged intermediates are actually in equilibrium with singlet nitrene[11] (Scheme I). We rationalized the photochemistry of some phenazinyl azides through a related scheme.[12]

Scheme I



Scheme II



The available evidence for the occurrence of these rearranged intermediates in solution has been mainly indirect (e.g. relatively

(1) Iddon, B.; Meth-Cohn, O.; Scriven, E. F. V.; Suschitzky, H.; Gallagher, P. T. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 900.
(2) Smith, P. A. In *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic Press: Orlando, 1984; Chapter 3.
(3) Scriven, E. F. V. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1981; Vol. 2, Chapter 1.
(4) Lwowski, W. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1981; Chapter 8.
(5) Wentrup, C. *Adv. Heterocycl. Chem.* **1981**, *28*, 279.
(6) Huisgen, R.; Vossius, D.; Appl, M. *Chem. Ber.* **1958**, *91*, 1. Huisgen, R.; Appl, M. *Ibid.* **1958**, *91*, 12.
(7) (a) Chapman, O. L.; Le Roux, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 282 and 6245. (b) Chapman, O. L., Sheridan, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 3690. (c) Dunkin, I. R.; Thompson, P. C. P. *J. Chem. Soc., Chem. Commun.* **1980**, 499. (d) Wentrup, C. Reference 2, Chapter 8. (e) Wentrup, C.; Winter, H. W. *J. Am. Chem. Soc.* **1980**, *102*, 6159. (f) Wentrup, C.; Thĕtaz, C.; Tagliaferri, E.; Lindner, H. J.; Kitscke, B.; Winter, H. W.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 566.
(8) (a) Sundberg, R. J.; Heintzelman, R. W. *J. Org. Chem.* **1974**, *39*, 2546. (b) De Graff, B. A.; Gillespie, D. W.; Sundberg, R. J. *J. Am. Chem. Soc.* **1974**, *95*, 7491. (c) Sumitani, M.; Nagakura, S.; Yoshihara, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2995. (d) Nielsen, P. E.; Buchard, O. *Photochem. Photobiol.* **1982**, *35*, 317.
(9) (a) Sundberg, R. J.; Suter, S. R.; Brenner, M. *J. Am. Chem. Soc.* **1972**, *94*, 513. (b) Carrol, S. E.; Nay, B.; Scriven, E. F. V.; Suschitzky, H. *Tetrahedron Lett.* **1977**, 943. (c) Rigaudy, J.; Igier, C.; Barcelo, J. *Tetrahedron Lett.* **1975**, 3845. (d) Rigaudy, J.; Igier, C.; Barcelo, J. *Tetrahedron Lett.* **1979**, 1837. (e) Crow, W. D.; Wentrup, C. *Tetrahedron Lett.* **1968**, 6149. (f) von Doering, W. E.; Odum, R. A. *Tetrahedron* **1966**, *22*, 81.
(10) (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. (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.
(11) (a) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 5228 and 5234. (b) Leyva, E.; Platz, M.; Persy, G.; Wirz, J. *J. Am. Chem. Soc.* **1986**, *108*, 5783.
(12) Albini, A.; Bettinetti, G.; Minoli, G. *J. Org. Chem.* **1987**, *52*, 1245.

0002-7863/91/1513-6928$02.50/0

Table I. Preparative Experiments

(A) From the Azides **1**

substrate	solvent (additive)	irradiation time (min)	converted **1** (%)	products (%) on converted **1**
1a	EtOH	30	100	**2a** (66), **4a** (9)
	MeCN	30	70	**2a** (58)
	C_6H_{12}	30	63	**2a** (53), **4a** (1)
	C_6H_{12} (DPA 6×10^{-2} M)	30	81	**2a** (7), **3a** (tr), **4a** (tr), **5a** (26)
	MeCN (Ph_2CO 5×10^{-3} M)	60	56	**2a** (5), **3a** (10), **4a** (6), **6a** (74)
	MeCN (PhCOMe 5×10^{-3} M)	60	54	**2a** (7), **3a** (11), **4a** (7), **6a** (70)
1b	MeCN	40	84	**2b** (53), **3b** (tr), **6b** (5)
	C_6H_6	60	84	**2b** (39), **3b** (1)
	MeCN (DPA 6×10^{-2} M)	50	82	**2b** (53), **3b** (tr), **5b** (1), **6b** (tr)
1c	MeCN	40	95	**2c** (31), **6c** (14)
	MeCN (DPA 6×10^{-2} M)	60	90	**2c** (28), **4c** (5), **6c** (9), **7c** (4)

(B) From the Heteropentalenes **2**

substrate	solvent (additive)	irradiation time (h)	converted **2** (%)	products (%) on converted **2**
2a	MeCN	15	72	**3a** (7), **4a** (9)
	i-PrOH	8	100	**3a** (10), **4a** (30)
	C_6H_6	14	86	**3a** (17), **4a** (18)
	C_6H_6 (DPA 6×10^{-2} M)	3.5	25	**3a** (8), **4a** (10), **5a** (25)
2b	*i*-PrOH	14	95	**3b** (5), **4b** (26)
	C_6H_6	5	100	**3b** (35), **4b** (33)
	C_6H_6 (DPA 6×10^{-2} M)	5	49	**3b** (26), **4b** (34), **5b** (tr)
2c	C_6H_6	3.5	77	**6c** (52)
	C_6H_6 (DPA 6×10^{-2} M)	4	65	**6c** (43), **4c** (5), **7c** (3)

slow formation of the end products arising from them as shown by flash photolysis),[11] while direct spectroscopic evidence is generally limited to frozen media.

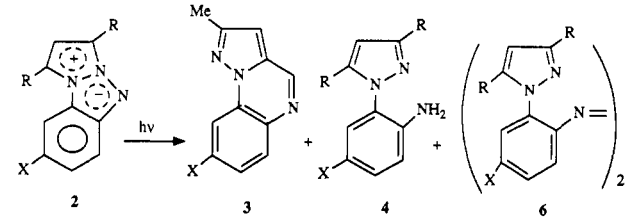
Support for this scheme could be the generation of nitrenes and their cyclic isomers by photolysis under similar conditions from an independent chemical source different from the azides. It occurred to us that a heterocycle reported several years ago by Suschitzky and colleagues[13] might offer an opportunity for this aim. These authors used 1-(2-azidophenyl)-3,5-dimethylpyrazole (**1a**) as a tool for distinguishing singlet and triplet nitrene through their competing intramolecular reactions. Thus, singlet nitrene (an electrophile) cyclizes onto the heterocyclic nitrogen atom to yield 1,3-dimethylpyrazolo[1,2-*a*]benzotriazole (**2a**), while triplet nitrene abstracts a hydrogen from the methyl group in position 3 and finally yields 1-methylpyrazolo[1,2-*a*]quinoxaline (**3a**) (Scheme II). Though the reported experimental conditions were not optimized (see below) and the conclusion oversimplified, the reasoning is correct and it is consistent with the observed effect of substituents on the benzene ring and with the results obtained from sensitized irradiation.[13]

Thus, heterocycle **2a** can be regarded as an electronic isomer of singlet nitrene (from which it arises), and we considered the hypothesis that photochemical excitation might revert the reaction and produce the latter species again through a method alternative to azide fragmentation. This turned out to be the case and here we present a report of the results from steady-state irradiation and laser flash photolysis experiments on **2a**, some related heterocycles, and the corresponding azides **1**.

Results

Preparative Irradiation. The irradiated substrates and the products formed are shown in Scheme III. 1,3-Dimethylpyrazolo[1,2-*a*]benzotriazole (**2a**) is rather photostable, but it is consumed by prolonged irradiation and yields 1-methylpyrazolo[1,2-*a*]quinoxaline (**3a**) and 1-(2-aminophenyl)-3,5-dimethylpyrazole (**4a**) in roughly equal amounts in inert solvents (see Table I). Direct irradiation of the corresponding azide **1a** forms **2a** in good yields with a minute amount of products **3a** and **4a**. The photochemistry of both **1a** and **2a** is substantially unaffected by the nature of the solvent (see also ref 14), except that **4a** predominates over **3a** in hydrogen-donating solvents. When looking for intermolecular trapping of intermediates, we

Scheme III



a: R = Me, X = H
b: R = Me, X = Cl
c: R = H, X = H

Table II. Photophysical and Photochemical Data

substrate	singlet energy (kcal/mol)	fluorescence quantum yield	reaction quantum yield
2a	72.9	10^{-4}	1×10^{-3}
2b	69	10^{-3}	1.3×10^{-3}
2c	73.8	10^{-4}	2×10^{-2}

observed that in the presence of 0.1 M di-*n*-propylamine (DPA), the yield of **3a** and **4a** from **2a** is lowered, and a new product, identified as the azepine **5a**, is obtained in a 25% yield (see the Experimental Section for structure assignment). Correspondingly, irradiation of **1a** under this condition yields 7% of **2a** and 26% of **5a**.

As it is shown in Table I, the chloroheteropentalene **2b** exhibits a photochemistry similar to that of **2a**, with the difference that DPA has a much smaller effect and the azepine **5b** is obtained in trace amounts. Correspondingly, the azide **1b** yields only **2b** and small amounts of the quinoxaline **3b** and the azo derivative **6b**, with traces of **5b** in the presence of DPA.

Pyrazolo[1,2-*a*]benzotriazole (**2c**) yields an azo derivative **6c**. In the presence of DPA, **6c** remains the main product, but an addition takes place as a side process leading to tiny amounts of an adduct together with the amine. The spectroscopic properties of this product differ largely from those of **5a,b**, and the alternative azepine structure **7c** is proposed for it. As for the azide **1c**, this yields **2c** as the main product, along with some azo **6c** and, in the presence of DPA, a small amount of compound **7c**.

Steady-State Measurements. The heteropentalenes **2a–c** show a strong vibrationally resolved absorption band in the region 320–400 nm (Figure 1). The chloro derivative **2b** shows a weak fluorescence in solution ($\Phi_F = 10^{-3}$), while with the other two

(13) Lindley, J. M.; McRobbie, I. M.; Meth-Cohn, O.; Suschitzky, H. *J. Chem. Soc., Perkin Trans. 1* **1980**, 982.
(14) Albini, A.; Bettinetti, G.; Minoli, G. *Chem. Lett.* **1981**, 301.

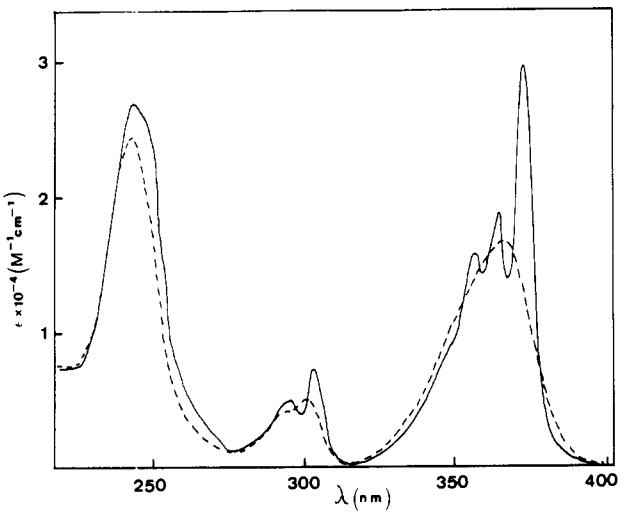


Figure 1. Absorption spectra of compound **2c** in cyclohexane (–) and in acetonitrile (---).

Table III. Observed Transients

(A) From the Heteropentalenes **2**

substrate	solvent	% bleached	rate of recovery: k, s^{-1}
2a	EtOH	42	2.2×10^4
	MeCN	36	9.5×10^3
	CH_2Cl_2	30	9.3×10^3
	C_6H_{12}	87	7×10^2
2b	MeCN	24	1.8×10^4
	C_6H_{12}	55	1.3×10^3
2c	MeCN	40	85
	C_6H_{12}	20	79

(B) From the Azides **1**

substrate	solvent	% of the "slow" process	rate of grow-in: k (s^{-1})
1a	EtOH	44	2.9×10^4
	MeCN	36	5.5×10^4
	CH_2Cl_2	37	5.3×10^4
	C_6H_{12}	39	1.5×10^4
		38	3.9×10^3
		6	8×10^2
1b	EtOH	52	2.4×10^4
	MeCN	44	3×10^4
	C_6H_{12}	54	1.3×10^4
		7	5×10^3
1c	MeCN	3	5×10^4
		93	8.2×10^3
	C_6H_{12}	67	4×10^3
		6	30

heteropentalenes, emission is barely detectable. At 77 K in glass, the fluoresence of compounds **2a–c** is more intense, but there is no phosphorescence. The quantum yield for the photodecomposition of compounds **2a,b** is ca. 10^{-3}, and it is 1 order of magnitude larger for **2c**, (Table II).

Flash Photolysis Experiments. Excitation at 355 nm of the heteropentalene **2a** by the output of a Nd–YAG laser (third harmonic, 8-ns pulse duration) shows a conspicuous reversible bleaching. Under our conditions, where a 5×10^{-5} M acetonitrile solution is used, the absorption of **2a** decreases by 36% after one flash. Virtually complete recovery takes place with a first-order process, $k = 9.5 \times 10^3$ s^{-1} (Table III, Figure 2). A similar phenomenon is observed in other solvents, and the measured rate of recovery drops by a factor of 30 with decreasing polarity from ethanol to cyclohexane.

Formation of product **2a** has been monitored at 370 nm after photolysing the azide **1a** with the fourth harmonic of the laser (266 nm) under otherwise identical conditions. It has been observed that a part of the heteropentalene is formed within the flash duration, and another part by a slower process (rate ca. 10^4 s^{-1}). In fact, the "slow" part of the formation of **2a** in cyclohexane is better accounted for by two first-order processes that give the main contribution, with a third slower component having a minor role (Table III, Figure 3).

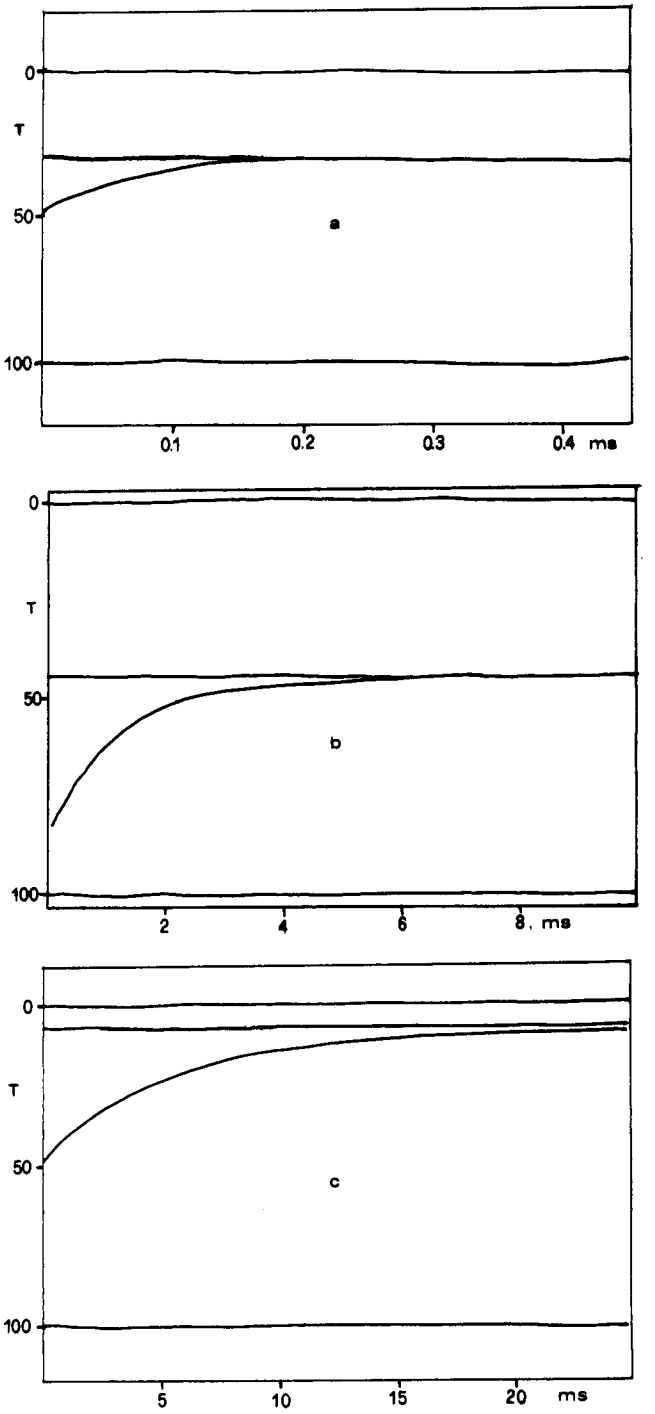
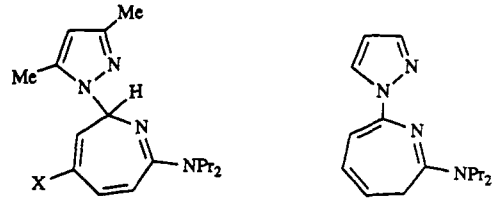
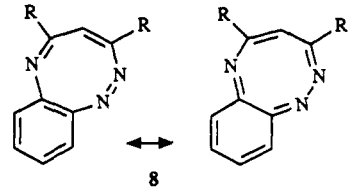


Figure 2. Oscilloscope traces showing the reversible bleaching (measured at 370 nm): a, heteropentalene **2a** in acetonitrile; b, the same in cyclohexane; c, heteropentalene **2c** in acetonitrile. The first trace is obtained by laser flash photolysis, the other ones by conventional lamp discharge flash photolysis (see the Experimental Section).

The reaction in the presence of DPA is not so easy to monitor due to partial superimposition of the absorption spectra of the products **2a** (formed in smaller amounts but with higher ϵ) and **5a**. Observation of the time evolution of the 370-nm absorption in the presence of various concentrations of DPA gives an approximate value of 1.5×10^7 M^{-1} s^{-1} for the second-order rate constant for the reaction of a precursor of both compounds with the amine.





The transients observed with the chloro derivatives **2b** and **1b** are similar to those of **2a** and **1a**, respectively. With the non-methylated heteropentalene **2c** there are some differences, since recovery of the absorption takes place during a slow process both in acetonitrile and in cyclohexane, and also the rate is markedly lower than with the other heteropentalenes. The corresponding azide **1c** behaves similarly to the other azides, and the part of the absorption of **2c** that is not formed within the flash duration grows at a relatively fast (and polarity dependent) rate, with the further addition of a slower component in cyclohexane. Another peculiarity of **1c** and **2c** is that a weak, but relatively long-lived transient absorption (ca. 470–550 nm, $\tau_{1/2}$ ca. 30 ms) is observed after the flash (see Figure 4).

Sensitized Photolysis of Azide 1a. Flash photolysis experiments show that azide **1a** quenches the triplet state of benzophenone at a rate of 10^9 M^{-1} s^{-1} (see Figure 5). Thus, energy transfer is efficient and produces azide triplets. Preparative experiments (see Table I) show that the product distribution changes greatly under triplet sensitization, with the azo derivative **6a** now being by far the main one. Flash photolysis experiments under conditions involving absorption of most of the light by the sensitizer (acetophenone in this case) reveal a weak transient absorption around 530 nm ($\tau_{1/2}$ 3.5 ms; see Figure 4).

Discussion

The thermal chemistry (typically electrophilic substitution and cycloaddition) of the various classes of heteropentalenes, aromatic analogues of the pentalene dianion, has been largely investigated and reviewed.[15,16] In particular, several results have been reported for pyrazolotriazoles **2**.[17] However, little is known about the photochemistry of these compounds. From their aromatic character and the high extinction coefficient of the first electronic transition (Figure 1), one might expect that compounds **2** fluoresce efficiently and undergo no monomolecular photoreaction. However, the observed emission is weak (though, as expected, short-lived, <5 ns) and the apparent photostability under steady-state irradiation is only the result of fast thermal reversion of the photoproduct(s), as is shown by flash investigations.

Obviously, some labile product arises from a rearrangement of **2**; one might, for example, consider electrocyclic ring opening to yield benzotriazacyclooctatetraenes **8**. However, both steady-state and flash experiments support the idea that the same species are formed both from heteropentalenes **2** and from azides **1**. We suggest that heteropentalenes **2** cleave with virtually unitary quantum yield (which seems realistic as shown by the fact that, in some cases, e.g. **2a** in cyclohexane, a flash actually bleaches about 90% of the substrate absorption) to give the corresponding nitrene. One can, in fact, compare the recovery of bleached **2** with the "slow" part of the formation of **2** from the azides. Table III shows that the ratio between the extent of the fast ($k > 10^8$ s^{-1}) and the slow ($k \simeq 10^4$ s^{-1}) component is the same in both cases, and the observed rates are sufficiently close one to another. Furthermore, the side products from the irradiation of the azides and the products obtained from prolonged irradiation of the heteropentalenes are the same under all the conditions studied, and trapping experiments also lead to parallel results.

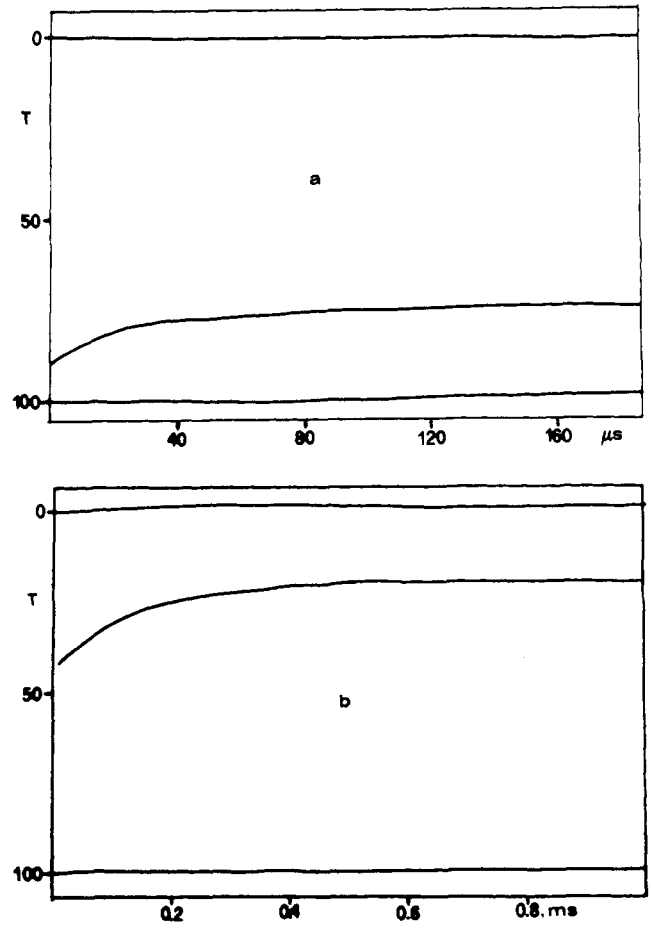


Figure 3. Oscilloscope traces showing the "instantaneous" and the "slow" parts of the grow-in of the absorption at 370 nm after laser excitation of azide **1a** (not absorbing at this wavelength): a, in acetonitrile; b, in cyclohexane.

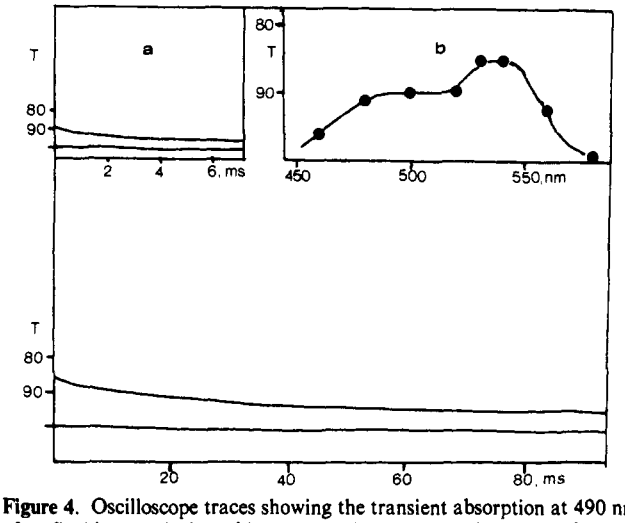


Figure 4. Oscilloscope traces showing the transient absorption at 490 nm after flashing a solution of heteropentalene **2c** in cyclohexane. Inset a, transient absorption observed at 530 nm after flashing a solution of acetophenone (1.35×10^{-2} M) and azide **1a** (2×10^{-3} M) in acetonitrile. Inset b, absorbance spectrum observed 5 ms after flash under the same conditions as in the previous experiment.

(15) Ramsden, C. *Tetrahedron* **1977**, *33*, 3203.
(16) Elguero, J.; Claramunt, R. M.; Summers, A. J. H. *Adv. Heterocycl. Chem.* **1978**, *22*, 183.
(17) (a) Albini, A.; Bettinetti, G.; Minoli, G. *J. Org. Chem.* **1984**, *49*, 2670. (b) Albini, A.; Bettinetti, G.; Minoli, G. *J. Org. Chem.* **1983**, *48*, 1080.

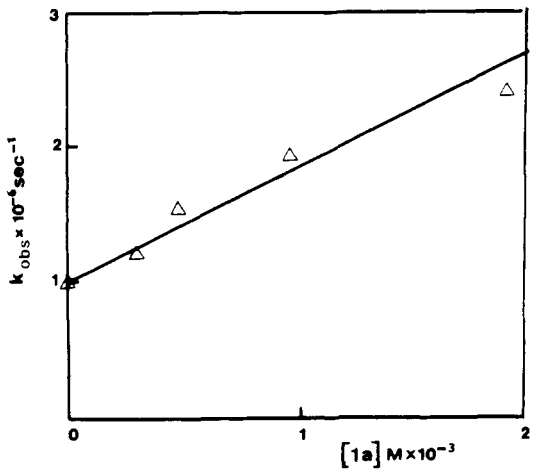
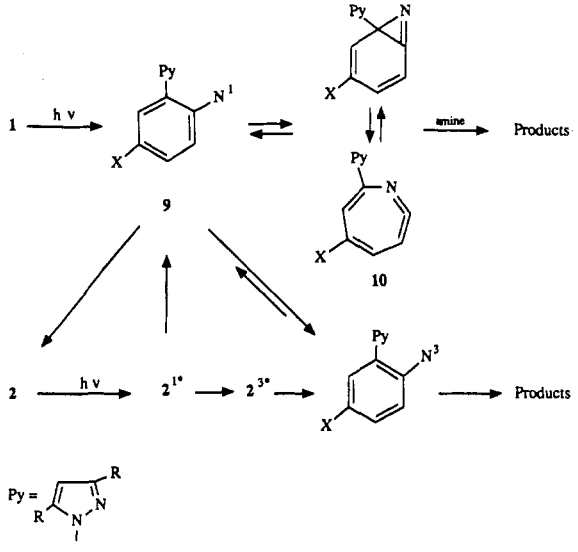


Figure 5. Rate constants for quenching of benzophenone triplet (monitored at 532 nm) at increasing **1a** concentrations.

Scheme IV

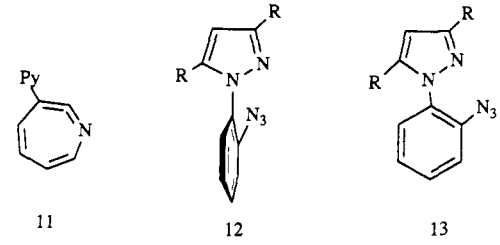


This requires that the photoreaction of **2** is in fact the cleavage of the N(4)–N(5) bond to yield a nitrene.[18] Thus, as hypothesized, these compounds are an entry to nitrenes, which is an alternative to the photolysis of azides **1**, thus offering a complementary way to study, or to check, the chemical behavior of nitrenes and of the rich pool of related species.

Singlet nitrenes **9** that are formed from either source (see Scheme IV) undergo fast electrophilic cyclization to yield compounds **2** (the reaction is instantaneous under our conditions, at a rate $>10^8$ s^{-1}). However, a competitive rearrangement takes place and leads to a longer lived species, which finally reverts to **9** (and thus to **2**) unless it is trapped by DPA to yield an azepine. This evidence and the analogy with the reaction of aryl azides[11] identify this species as being a dehydroazepine **10** (or the corresponding benzoazirine). Decreasing the solvent polarity moderately decreases the rates both of cyclization of **9** to **2** and of rearrangement of **10** to **9** in the case of the **1a–2a** system, while there is little effect on the other two pairs of derivatives.

Another long-lived intermediate is formed in low yields from the singlet nitrene, and its presence is not only indirectly revealed by a further (minor) contribution to the formation of **2** observed in some cases, but also directly evidenced by its absorption around 500 nm, which is apparent with **1c** and **2c**. The increase of a similar absorption when "authentic" triplet nitrene is produced from the triplet state of azide **1a** (see the sensitized experiments, Figure 4) supports the identification of this species as being a triplet nitrene. Likewise, the chemical behavior is typical of the "lazy" triplet state of aryl nitrenes[1] viz. the coupling to azo derivative is the main reaction, and the inefficient intermolecular hydrogen abstraction gives a minor contribution.

Several comments should be made about the chemistry that has been observed. As for the dehydroazepine, it should be remarked that its formation is regioselective, and the trapping products constantly arise from intermediate **10** and not from isomeric **11**. This points to the importance of electronic factors



in the attack on the phenyl ring. It might appear surprising that, in the presence of an attractive alternative, such as electrophilic attack at the pyrazole nitrogen, closure onto the phenyl ring takes place at all.

A reasonable explanation for this lies in conformational factors. Repulsion between the pyrazole methyl group and phenyl ortho hydrogen makes **12** the preferred conformation for azides **1a** and **1b** and for the nitrenes that arise from them. Ring closure onto the nitrogen, therefore, is a relatively slow process, since first the rotation of the pyrazole ring, in order to attain planarity, is required. This fact provides an opportunity for a competing attack onto the phenyl ring. Likewise, once created from the heteropentalene, the nitrene in part recloses directly, but also in part reaches the more stable conformation **12**, and this again results in the formation of some dehydroazepine.

However, when the nonmethylated derivative **2c** is photolyzed, there is no steric hindering to prevent the reclosure of singlet nitrene, and the formation of dehydroazepine is much less important (see e.g. the low yield of trapping products). As for the azide **1c**, both conformers **12** and **13** are equally important if there is no interaction between the heterocycle and the azido group, as it is indicated by the spectroscopic properties of this compound and the other azides **1**. Photolysis of the former conformer leads to the "wrong" nitrene, thereby giving a chance to the attack onto the ring, as revealed by the presence of the appropriate "slow" grow-in of **2c** in flash photolysis (though trapping by DPA still remains inefficient).

Electronic factors are also important, and indeed when the electrophilic character of singlet nitrene is enhanced, as is the case for the **1b**/**2b** system, ring closure to produce the heteropentalene is faster, virtually independent of polarity and leaves no room for intermolecular trapping.

As for triplet nitrenes, their identification is hampered in the present systems by the strong absorption of heteropentalenes **2**, which limits the window available to detect such species. The transient absorption at ca. 500 nm monitored in the present case fits in reasonably well with the long-wavelength (and weakest) absorption of triplet phenylnitrene.[1] Interestingly, formation of triplet nitrene from **2c** is more important than from the methylated derivatives **2a**,**b**, and this is the cause of the increase by one order of magnitude in the quantum yield for the decomposition of the former compound, since in the absence of nucleophiles, the triplet pathway is the only one that leads to an irreversible reaction. Comparison with the results from azide **1c** suggests that this is due to an enhanced contribution of the heteropentalene triplet state, rather than to an increased intersystem crossing from singlet to triplet nitrene after the cleavage.

(18) Preparation of nitrenes by photochemical cleavage of N–N or N–O bonds has been previously reported, though on models only distantly related to the present one (these include indazoles, ref 19a; anthranils, ref 19b; oxaziridines, ref 19c).

(19) (a) Heinzelmann, W.; Märky, M.; Gilgen, P. *Helv. Chim. Acta* **1976**, *59*, 2362. (b) Berwick, M. A. *J. Am. Chem. Soc.* **1971**, *93*, 5780. (c) Splitter, J. S.; Calvin, M. *Tetrahedron Lett.* **1960**, 1445.

(20) Lynch, B. M.; Hung, Y. Y. *J. Heterocycl. Chem.* **1965**, *2*, 218.

Conclusions

The mechanism discussed above is oversimplified. Indeed, the rates observed for the formation of heteropentalenes **2** from azides **1** and for the regeneration of bleached **2** are very close one to the other in some cases, but in other ones differ by as much as a factor of 10. Furthermore, the "slow" grown-in of **2** is multicomponent when formed from azides in apolar solvents. However, we are inclined to attribute these differences to the contribution of different conformations with different relevant barriers to interconversion and to the presence of both dehydroazepines and benzazirines, and we conclude that this work supports the notion that singlet nitrenes and cyclic isomer(s) are in equilibrium in solution. This pool of transients can be reached both by photolysis of the azides **1** and by photoisomerization of the heteropentalenes **2**.

Furthermore, the triplet nitrenes also appear to cross back to the singlet nitrenes in this case. Though this is generally not assumed to be a viable path, its occurrence with these substrates may be a consequence of the high intramolecular reactivity of the singlets, as opposed to the chemical inertness of the triplets.

Two main results have been obtained in this work. First, the efficient (ϕ = ca. 1) cleavage of heteropentalenes **2** has hardly any precedent (unless photofragmentations of open-chain ylides are considered), and, by showing a radical difference in the chemical properties of ground and singlet excited states of these substrates, fosters further investigation of the virtually unknown photochemistry of heteropentalenes.

Second, the fact that for the first time the same nitrenes have been photochemically generated and characterized both from azides and from a different precursor under identical conditions, as well as the fact that the same pool of transients can be reached by both paths, lends further support to the current rationalization of nitrene chemistry.

Experimental Section

UV–visible spectra were recorded on a Hitachi Perkin-Elmer 200 spectrophotometer. Fluorescence spectra were taken on an Aminco-Bowman MPF spectrofluorimeter. IR spectra were recorded on Perkin-Elmer Model 197 or Model 881 spectrophotometers. ^{1}H NMR spectra were obtained on a Bruker WP80 instrument with Me_4Si as the internal standard, and mass spectra were determined on a Finnigan Mat 8222 spectrometer. Melting points are uncorrected. Commercial (C. Erba) spectroscopic grade solvents were used after distillation. Di-*n*-propylamine (C. Erba pure grade reagent) was further purified by repeated fractional distillation from KOH. Column chromatography was performed with silica gel 60 HR (Merck) and preparative TLC using a Chromatotron (Morrison Research) apparatus, eluting with benzene–ethyl acetate (9:1 to 8:2) mixtures. Azides **1** and heteropentalenes **2** were prepared and purified as described elsewhere.[13,17b]

Photochemical Decomposition of 1-(2-Azidophenyl)-3,5-dimethylpyrazole (1a). To anhydrous cyclohexane (160 mL) deaerated by boiling and cooled under a stream of argon was added **1a** (213 mg), and after 15 min of additional flushing, the resulting solution (6.25×10^{-3} M) was irradiated through a quartz jacket by means of a low-pressure mercury arc (Helios Italquartz 15 W) under an argon stream. The reaction mixture was evaporated under reduced pressure at room temperature, and the residue was chromatographed on a silica gel column, eluting with a cyclohexane–ethyl acetate (8:2) mixture. In order of elution, the starting material **1a** (79 mg), 1,3-dimethyl-5*H*-pyrazolo[1,2-*a*]benzotriazol-4-ium inner salt (**2a**) (62 mg), and the amine **4a** (1 mg) were isolated. In the other solvents, the yields reported in Table I were obtained.

Photolysis of 1a in the Presence of Di-*n*-propylamine. In the same way as above, a solution of **1a** (213 mg, 6.25×10^{-3} M) in cyclohexane (160 mL) was photolyzed in the presence of di-*n*-propylamine (1.3 mL, 6×10^{-2} M). The chromatographic separation of the photolysate afforded 2-(3,5-dimethylpyrazolyl)-7-(di-*n*-propylamino)-2*H*-azepine (**5a**) (136 mg) as cream needles: mp 69–70 °C (petroleum ether); IR (Nujol) 1595, 1545 cm^{-1}; UV (MeCN) λ 302 nm ($\epsilon = 7.5 \times 10^3$); ^{1}H NMR ($CDCl_3$) δ 4.0 (d, H-2, $J_{2,3}$ = 6 Hz), 5.8 (dd, H-5), 5.90 (pyrazole H), 6.3 (dd, H-3), 6.35 (dd, H-4), 7.3 (d, H-6, $J_{5,6}$ = 8 Hz), besides the aliphatic protons. Anal. Calcd for $C_{17}H_{26}N_4$: C, 71.29; H, 9.15; N, 19.56. Found: C, 71.11; H, 9.36; N, 19.67. The other products were eluted as follows: unreacted **1a** (40 mg), traces of compound **3a**, heteropentalene **2a** (24 mg), and traces of the amine **4a** in the yields reported in Table I.

Sensitized Photodecomposition of 1a. A solution of **1a** (300 mg, 4.7×10^{-3} M) in MeCN (300 mL) in the presence of acetophenone (180 mg, 5×10^{-3} M) was irradiated by means of a Pyrex-filtered medium-pressure mercury arc (Philips HPK 125 W). Chromatographic separation of the reaction mixture was performed on a silica gel column, eluting the sensitizer with carbon tetrachloride and then going on with benzene–ethyl acetate (8:2) mixture to isolate the products in this order: unreacted **1a** (138 mg), the pyrazoloquinoxaline **3a** (15 mg), compound **2a** (10 mg), the amine **4a** (10 mg), and finally the azoderivative **6a** (49 mg) in the yields reported in Table I. Following the same procedure the irradiation of **1a** in the presence of benzophenone (273 mg, 5×10^{-3} M) and chromatographic separation gave unreacted **1a** (132 mg), **3a** (14 mg), **2a** (10 mg), **4a** (9 mg), and **6a** (54 mg) in the yields reported in Table I.

Photochemical Decomposition of 1-(2-Azido-5-chlorophenyl)-3,5-dimethylpyrazole (1b). Photolysis of **1b** (300 mg, 4×10^{-3} M) in MeCN (300 mL) as described for **1a**, followed by chromatographic separation on a silica gel column eluting with benzene–ethyl acetate (8:2) mixture, afforded (in order of elution) unreacted **1b** (48 mg) and 2,2′-bis(3,5-dimethylpyrazolyl)-4,4′-dichloroazobenzene (**6b**) (12 mg), which was further purified by means of preparative TLC, eluting with a cyclohexane–ethyl acetate (8:2) mixture and obtained as orange needles: mp 205 °C dec (cyclohexane); IR (Nujol) 1590, 935 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.0 and 2.35 (s, pyrazole methyl groups), 6.05 (s, pyrazole H), 7.27–7.65 (m, 3 H, aromatics); M$^+$ m/z = 438. Anal. Calcd for $C_{22}H_{20}N_6Cl_2$: C, 60.14; H, 4.58; N, 19.13. Found: C, 59.89; H, 4.45; N, 19.00. Then traces of 8-chloro-2-methylpyrazoloquinoxaline (**3b**) and compound **2b** (117 mg) were eluted in this order in the yields reported in Table I.

Photolysis of 1b in the Presence of Di-*n*-propylamine. In the same way as for **1a**, a solution of **1b** (300 mg, 4×10^{-3} M) in MeCN (300 mL) was photolyzed in the presence of di-*n*-propylamine (2.5 mL, 6×10^{-2} M). Chromatographic separation as above gave a reddish oily compound (4 mg), which after purification by preparative TLC eluting with benzene–ethyl acetate (8:2) mixture was recognized as 2-(3,5-dimethylpyrazolyl)-4-chloro-7-(di-*n*-propylamino-2*H*-azepine (**5b**): IR (film) 1660, 1590, 1560 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.35 (d, H-3), 7.1 (d, H-6), besides aliphatic protons; M$^+$ m/z = 320. Anal. Calcd for $C_{17}H_{25}N_4Cl$: C, 63.63, H, 7.85; N, 17.48. Found: C, 63.78; H, 7.90; N, 17.41. Further elution gave starting material **1b** (53 mg), compound **3b** (1 mg), and 8-chloro-1,3-dimethyl-5*H*-pyrazolo[1,2-*a*]benzotriazol-4-ium inner salt (**2b**) (117 mg) in the yields reported in Table I.

Photochemical Decomposition of 1-(2-Azidophenyl)pyrazole (1c). Photolysis of **1c** (300 mg, 5.4×10^{-3} M) in MeCN (300 mL) was performed as described for **1a**; chromatographic separation eluting with cyclohexane–ethyl acetate (8:2) mixture gave unreacted **1c** (8 mg), pyrazolo[1,2-*a*]benzotriazole (**2c**) (77 mg), and 2,2′-bis(pyrazol-1-yl)azobenzene (**6c**) (36 mg) as red-orange needles: mp 164–166 °C (EtOH) (lit.[20] mp 167 °C) IR (Nujol) 1590 cm^{-1}; UV (MeCN) λ_{max} 235 ($\epsilon = 4.9 \times 10^3$), 256 ($\epsilon = 4.8 \times 10^3$), 330 nm ($\epsilon = 2.8 \times 10^3$). The yields are reported in Table I.

Photolysis of 1c in the Presence of Di-*n*-propylamine. Irradiation of **1c** (300 mg, 5.4×10^{-3} M) in MeCN (300 mL) in the presence of di-*n*-propylamine (2.5 mL, 6×10^{-2} M) was carried out as described above. Column chromatography of the photolizate, eluting with a benzene–ethyl acetate (9:1) mixture, gave as the first fraction an orange yellow oil, which was further purified by preparative TLC eluting with a benzene–ethyl acetate (8:2) mixture, and was recognized as 6*H*-2-pyrazolyl-7-(di-*n*-propylamino)azepine (**7c**) (15 mg): IR (film) 1610, 1565, 1560 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.85 (d, CH_2), 5.1 (dt, H-5), 6.5 (dd, H-4), 6.7 (d, H-3), 6.4, 7.6, and 8.1 (pyrazole H's), besides the aliphatic protons; M$^+$ m/z = 258. Anal. Calcd for $C_{15}H_{22}N_4$: C, 69.73; H, 8.58; N, 21.69. Found: C, 69.87; H, 8.64; N, 21.53. Unreacted **1c** (50 mg), pyrazolo[1,2-*a*]benzotriazole (**2c**) (65 mg), compound **6c** (20 mg), and the amine **4c** (12 mg) were then eluted in the yields reported in Table I.

Photolysis of the Heteropentalenes 2. In anhydrous MeCN (300 mL), anhydrous **2a** (300 mg, 5.4×10^{-3} M) was deaerated by boiling and cooled under a stream of argon. The resulting solution was irradiated by means of a Pyrex-filtered medium-pressure mercury arc (Phylips HPK 125W) under argon stream. The reaction mixture was evaporated under reduced pressure at room temperature and the residue was chromatographed on a silica gel column, eluting with cyclohexane–ethyl acetate (8:2) mixture to yield in order of elution compounds **3a** (15 mg), **2a** (84 mg), and **4a** (20 mg). The same procedure has been adopted for the other solvents and for compounds **2b** (300 mg, 4.5×10^{-3} M) and **2c** (300 mg, 6.3×10^{-3} M). The isolated compounds and yields are reported in Table I.

Photolysis of Heteropentalenes 2 in the Presence of Di-*n*-propylamine. In the same way as described for heteropentalenes **2**, a solution of **2a** (300 mg, 5.4×10^{-3} M) (300 mL) in benzene was photolyzed in the presence of di-*n*-propylamine (2.5 mL, 6×10^{-2} M). Elution as above gave products **5a** (26 mg), **3a** (5 mg), **2a** (261 mg), and **4a** (7 mg). The same

procedure has been adopted for compounds **2b** (300 mg, 4.5×10^{-3} M) and **2c** (300 mg, 6.3×10^{-3} M). The products and the yields from chromatographic separation are gathered in Table I.

Flash Photolysis Experiments. The laser flash photolysis studies were carried out by using the third (355 nm) and the fourth (266 nm) harmonics of a Q-switched Nd-YAG laser (Model HY 200 JK Lasers Ltd. Lumonics). The detection system consisted of a laser kinetic spectrometer (Model K 347 Applied Photophysics) and an oscilloscope (Tektronix Model 2467 connected to a C 1001 video camera). The trace was registered through an IBM PC/AT.

In the nanosecond experiments, solutions of the heteropentalenes **2** of ca. 5×10^{-5} M in the appropriate solvent (corresponding to an absorbance of ca. 0.4 at the excitation wavelength) were excited by a single shot using the third harmonic (355 nm) of the Nd-YAG laser (the duration and energy of the pulse were approximately 8 ns and 30 mJ, respectively) and analyzed at 370 nm through a Schott glass filter WC295 for compounds **2**, or at the convenient wavelength for the nitrenes and ketone triplets (see text). The optical beam had a path length of 1 cm in the cell and was at a right angle to the excitation pulse.

Solutions of the azides **1** in the appropriate solvent ca. 5×10^{-5} M were excited as described above by using the fourth harmonic (266 nm, 20 mJ pulse^{-1}) and analyzed at 370 nm through a Schott glass filter WG 345. The sample solution was replaced after each shot.

Conventional flash photolysis was carried out by means of an Applied Photophysic K-20 apparatus, using solutions ca. 10^{-5} M of the substrates **1** or **2** in the appropriate solvent in cylindrical tubes, analyzing at 370 nm through the above-mentioned filters. The optical path was 10 cm; the sample solution was replaced after each shot. The kinetic constants for the decay of the transients were obtained manually from oscilloscope traces.

Acknowledgment. This work was supported by the Ministero Pubblica Istruzione, Rome. We thank Prof. J. Wirz (Basel) for preliminary measurements.

Registry No. 1a, 78564-50-8; **1b**, 60418-40-8; **1c**, 60418-63-5; **2a**, 60418-46-4; **2b**, 60418-48-6; **2c**, 1738-57-4; **3a**, 78564-51-9; **3b**, 60418-49-7; **4a**, 60418-47-5; **4b**, 60450-52-4; **4c**, 54705-91-8; **5a**, 134817-12-2; **5b**, 134817-13-3; **6a**, 78564-52-0; **6b**, 134817-11-1; **6c**, 1738-59-6; **7c**, 134817-14-4; **10**, 134817-15-5; imidogen, 13774-92-0; benzophenone, 119-61-9; dipropylamine, 142-84-7; acetophenone, 98-86-2; 2-(3,5-dimethylpyrazolyl)phenylnitrene, 78564-49-5.

$O_2^{\bullet-}$ Addition to Ketomalonate Leads to Decarboxylation: A Chain Reaction in Oxygenated Aqueous Solution

Man Nien Schuchmann, Heinz-Peter Schuchmann, Martina Hess, and Clemens von Sonntag*

Contribution from the Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim a. d. Ruhr, Germany. *Received January 14, 1991. Revised Manuscript Received May 21, 1991*

Abstract: Superoxide radical anion, $O_2^{\bullet-}$, was generated radiolytically in oxygenated aqueous formate solutions. In its reaction with ketomalonate ion, oxalic monoperacid and carbon dioxide are formed via a chain reaction. The chain length increases linearly with (dose rate)$^{-1/2}$, i.e. (rate of $O_2^{\bullet-}$ generation)$^{-1/2}$, as well as ketomalonate concentration. Typically, at a dose rate of 0.055 Gy s^{-1} and a ketomalonate concentration of 8×10^{-3} mol dm^{-3} at pH 10 (formate concentration 0.1 mol dm^{-3}), $G(CO_2) = 150 \times 10^{-7}$ mol J^{-1} is found. It is suggested that the propagation steps of this unexpected chain reaction are addition of $O_2^{\bullet-}$ to the keto group of the ketomalonate ion, followed by fragmentation of this adduct into oxalic monoperacid and $CO_2^{\bullet-}$, the latter reducing O_2 and so regenerating $O_2^{\bullet-}$. A propagation rate constant of about 150 dm^3 mol^{-1} s^{-1} has been estimated.

Introduction

The reactions of the superoxide radical anion, $O_2^{\bullet-}$, are attracting increasing attention since they are believed to be implicated in biological cell damage inflicted under normal metabolic conditions or by ionizing radiation.[1,2] In aqueous solutions, $O_2^{\bullet-}$ readily undergoes electron-transfer reactions; otherwise, however, it is quite inert compared to other free radicals (for a review see ref 3), especially with respect to hydrogen abstraction, as the H–O_2^- bond dissociation energy is below 70 kcal mol^{-1} (gas phase[4-6]). Where such a reaction *is* observed (e.g., with *n*-propylgallate), it is believed to be due to an addition reaction, followed by HO_2^- (H_2O_2) elimination.[7] $O_2^{\bullet-}$ is also known (so far only in *nonaqueous solvents*) to act as a nucleophile (for a review see ref 3), leading, e.g., to ester cleavage under alkoxide expulsion and formation of a peroxyacyl radical.[8] In α-keto- and α-hydroxyketones and -esters, $O_2^{\bullet-}$ can bring about oxidative C–C bond cleavage,[9,10] again in nonaqueous solvents.

A well-known reaction *in aqueous solution* leading to $HO_2^{\bullet}/O_2^{\bullet-}$ is its elimination from α-hydroxyalkylperoxyl radicals (reactions 1–3).[11,12] This process plays a major role in the peroxyl radical chemistry of aqueous solutions since many peroxyl radicals which carry an H atom but not an OH group in the α-position eventually are still converted into α-hydroxyalkylperoxyl radicals.[2]

$$R_2C(OH)O_2^{\bullet} \rightarrow R_2C{=}O + HO_2^{\bullet} \quad (1)$$

$$R_2C(OH)O_2^{\bullet} + OH^- \rightarrow R_2C(O^-)O_2^{\bullet} + H_2O \quad (2)$$

$$R_2C(O^-)O_2^{\bullet} \rightarrow R_2C{=}O + O_2^{\bullet-} \quad (3)$$

In the course of a radiation chemical study of hydroxymalonic acid where the $O_2^{\bullet-}$ elimination sequence (1–3) is also operative,[13]

(1) *Oxygen Radicals in Biology and Medicine, Basic Life Sciences, Vol 49*; Simic, M. G., Taylor, K. A., Ward, J. F., von Sonntag, C., Eds.; Plenum Press: New York, 1988.
(2) von Sonntag, C. *The Chemical Basis of Radiation Biology*; Taylor and Francis: London, 1987.
(3) Frimer, A. A. *The Chemistry of Functional Groups, Peroxides*; Patai, S., Ed.; Wiley and Sons: London, 1983, p 429.
(4) Merenyi, G.; Lind, J. *J. Phys. Chem.* **1990**, *94*, 5412.
(5) Nash, C. P.; Volman, D. H. *J. Phys. Chem.* **1990**, *94*, 5412.
(6) Golden, D. M.; Bierbaum, V. M.; Howard, C. J. *J. Phys. Chem.* **1990**, *94*, 5413.
(7) Deeble, D. J.; Parsons, B. J.; Phillips, G. O.; Schuchmann, H.-P.; von Sonntag, C. *Int. J. Radiat. Biol.* **1988**, *54*, 179.
(8) Gibian, M. J.; Sawyer, D. T.; Ungermann, T.; Tangpoonpholvivat, R.; Morrison, M. M. *J. Am. Chem. Soc.* **1979**, *101*, 640.
(9) San Filippo, J.; Chern, C.-I.; Valentine, J. S. *J. Org. Chem.* **1976**, *41*, 1077.
(10) Sawyer, D. T.; Stamp, J. J.; Menton, K. A. *J. Org. Chem.* **1983**, *48*, 3733.
(11) Bothe, E.; Schuchmann, M. N.; Schulte-Frohlinde, D.; von Sonntag, C. *Photochem. Photobiol.* **1978**, *28*, 639.
(12) Bielski, B. H. J. *Methods Enzymol.* **1985**, *105*, 81.

0002-7863/91/1513-6934$02.50/0