of water until the volume of the organic layer was ca. 12 mL. The organic layer was dried overnight with $MgSO_4$. GLC separation (75 °C) of 2.0 mL of the ethereal solution (total volume after drying 11 mL) gave 0.15 g of **12** as a colorless volatile liquid (calculated total yield 0.83 g, 64%): ^1H NMR ($CDCl_3$) δ 5.13 (d quintet, J_{HF} = 56.5 Hz, J_{HH} = 6.2 Hz, 1 H, CHF); 4.95 (m, 2 H, $CH_2{=}$), 3.10–2.96 (m, 4 H, CH_2); ^{19}F NMR ($CDCl_3$) δ −170.6 (d m, J_{HF} = 56.9 Hz, CHF); HRMS (EI) m/e calcd for C_5H_7F 86.0532, found 86.0539.

Supplementary Material Available: ^1H NMR spectra of compounds **2**–**12** as well as an Ortep plot for compound **9** (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

The Photochemical Reaction between Aromatic Nitriles and Allylsilane

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The results obtained from the irradiation of aromatic nitriles and allyltrimethylsilane (ATMS) depend on the redox parameters of these molecules and their singlet energies. The reaction between 1-naphthalenecarbonitrile (NN) and ATMS in apolar solvents leads to [2 + 2] cycloaddition at positions 1 and 2 (via the exciplex); in polar solvents, electron transfer becomes a possibility, and loss of the trimethylsilyl cation followed by allylation of NN at positions 2 and 4 is also observed. When naphthalene-1,4-dicarbonitrile (NDN) is used, electron-transfer-initiated allylation (both addition and cyano group substitution) is the main pathway, but in apolar solvents cycloaddition at positions 4a and 5 occurs as a minor pathway. The reaction with benzene-1,2,4,5-tetracarbonitrile (BTN) gives substitution of an allyl for a cyano group as the only process. Finally, with both NDN and BTN and a high ATMS concentration in apolar solvents, the reaction pathway changes to photosensitized [2 + 2] dimerization of ATMS, proposed to occur via a terplex. Rationalizations for the observed reactions (including regiochemistry of addition and cycloaddition and nature of the intermediates) are offered.

In contrast to the variety of processes observed with benzene derivatives, the photoreactions between naphthalenes and alkenes are limited to [2 + 2] cycloadditions at positions 1 and 2;[2,3] with dienes, both [2 + 2] and [4 + 4] cycloadditions are observed.[4] Under conditions favoring electron transfer new paths become available. Thus, with naphthalenenitriles and arylalkenes the stabilized radical cations of the latter compounds are formed and undergo ionic addition and dimerization.[5] (However, we recently observed that cycloaddition takes place competitively in these systems as well).[3m] In other cases, the alkene radical cation is fragmented. Thus, with naphthalene-1,4-dicarbonitrile (NDN) and 2,3-dimethylbutene, the radical cation deprotonates and the alkenyl radical adds to NDN;[6] similarly, when allyltrimethylsilane (ATMS) is used as the donor, desilylation and addition of the allyl radical to NDN take place (Scheme I).[7]

Scheme I

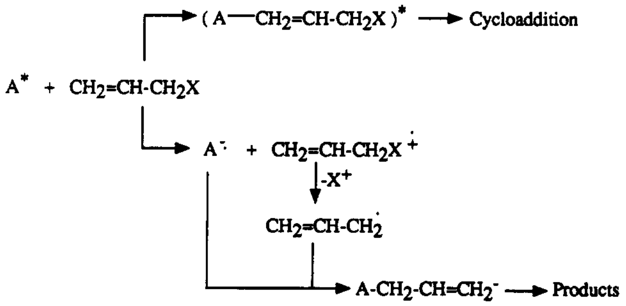

Table I. Products (Isolated Yield) from the Irradiation of Arenecarbonitriles in the Presence of 0.1 M Allyltrimethylsilane

arene	solvent	products (% yield)[a]
NN	MeCN	**1** (8), **2** (12), **3** (29), **4** (2), **5** (20)
NN	C_6H_6	**1** (23), **2** (35)
NDN	MeCN[b]	**6** (40), **7** (15), **8** (8), **9** (8)
NDN	C_6H_6	**6** (8), **7** (13), **8** (2), **9** (2), **10** (5), **12** (27),[c] **13** (23)[c]
BTN	MeCN	**11** (61)
BTN	CH_2Cl_2	**11** (85), **12** (79),[c] **13** (63)[c]

[a] Calculated on the converted nitriles. [b] In acetonitrile containing 0.1% D_2O the yields are unchanged, but compounds **7**–**9** are replaced by the deuterated analogues **7′**–**9′**. [c] Molar percentage of ATMS dimerized per mol of ATMS chemically reacting with the nitriles.

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(1) (a) University of Pavia. (b) University of Torino.

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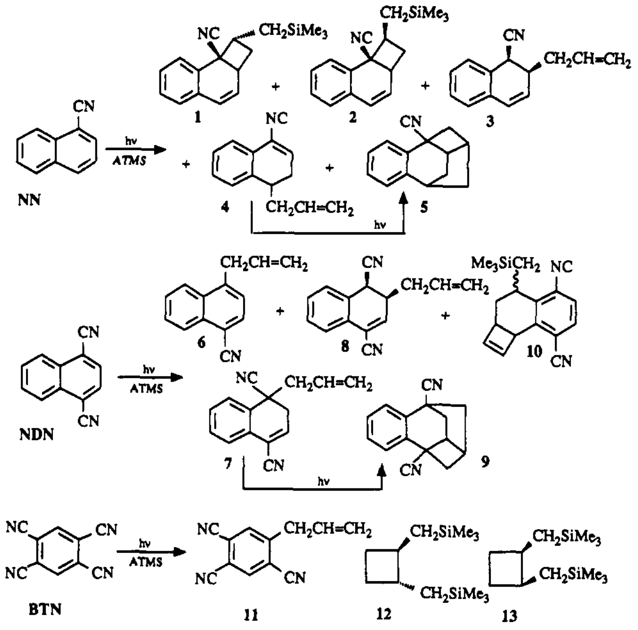
Scheme II



Some time ago we enbarked on a study of the competition between exciplex and radical ion chemistry in the photochemistry of aromatics.[3m,4d,8] We now report our results using ATMS in the presence of two naphthalene light-absorbers, NDN and naphthalene-1-carbonitrile (NN), and in the presence of a "model" electron acceptor, benzene-1,2,4,5-tetracarbonitrile (BTN) for the sake of comparison, under various experimental conditions.

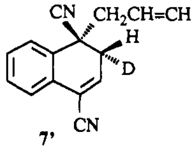
Results

The irradiation of NN in acetonitrile in the presence of 0.1 M ATMS gave a complex mixture which was chromatographically separated to yield five products (see Scheme II and isolated yields in Table I). Two of these products involved addition of the reagents, as shown by elemental analysis and mass spectra. The NMR spectra clearly showed that both compounds resulted from [2 + 2] addition at positions 1 and 2 of the naphthalene ring and that the regiochemistry was the same. (Thus, the angular methine is vicinal to a methylene group in both cases; see Experimental Section). Assigning the stereochemistry of the two products, which were formed in similar amounts, was not possible on the basis of the spectra, nor did the appropriate NOE experiments help in this regard. However, comparison of the spectra in deuteriochloroform and hexadeuteriobenzene evidenced a large effect on the chemical shifts of the two methine groups in only one of the stereoisomers, which was therefore assumed to be the endo adduct 1, and a much smaller effect for the exo adduct 2 in which these protons are more hindered (see Table V in Experimental Section). The complete assignments for the ^{13}C NMR spectra through (C–H) correlated experiments are also reported in the Experimental Section and may be of some help since such data are not available in the literature for related compounds.

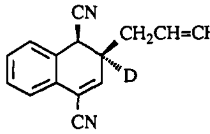
The other compounds isolated were silicon-free. These included the main product, an oil recognized as *cis*-2-allyl-1,2-dihydronaphthalene-1-carbonitrile (3, note the relatively large coupling constants between the protons in positions 1 and 2). The second product in order of abundance contained no olefinic and nine aliphatic protons (three methine and three diastereotopic methylene groups). This is clearly compatible with a tricyclo[3.2.2.$0^{3,7}$]nonene structure (product 5 in this case), as previously reported, from the secondary intramolecular cycloaddition of 1-alkenyl-1,2-dihydronaphthalene-1,4-dinitriles.[6,7b] Indeed, the fifth product, obtained in low yields, contained an allyl group and one further olefinic proton. All other spectroscopic properties supported the structure of 4-(2-propenyl)-3,4-dihydronaphthalene-1-carbonitrile (4) for this compound. The yield of product 4 was higher at lower NDN conversion, in which case product 5 was present only in traces. Separate irradiation of compound 4 yielded the above-mentioned cage compound, which was accordingly recognized as structure 5.

A simpler mixture was obtained when the irradiation was carried out in benzene. The two cyclobutane adducts 1 and 2 were obtained in fair yield, and the desilylated compounds 3 to 5 obtained in negligible amounts.

The analogous irradiation of NDN in acetonitrile gave only silicon-free products. These were 4-(2-propenyl)-naphthalene-1-carbonitrile (6), both 1- and 2-(2-propenyl)-1,2-dihydronaphthalene-1,4-dicarbonitriles (7 and 8, in the latter case the cis isomer), as well as the cage compound 9, formed, as in the previous case, from adduct 7 through a secondary photocycloaddition. Products 6, 7, and 9, but not product 8, have been previously reported by Mizuno from the irradiation of the same system.[7b] When the irradiation was carried out in acetonitrile containing 0.1% D_2O products 7–9 were obtained as the selectively monodeuterated derivatives 7′–9′. The stereochemistry of the cage derivative 9′ is easily deduced from the NMR spectrum, which also allows the assignment for compound 7′. Products 6–9 were also obtained upon irradiation in benzene, although in different and, in general, lower yields. In this case, however, a small amount of an adduct preserving the trimethylsilyl group was obtained. This compound contained only two (vicinal) aromatic protons; two olefinic protons with a small (2.8-Hz) coupling constant supported the presence of a cyclobutene moiety; the methylene group α to the silicon atom was coupled to a benzylic proton; a further diastereotopic methylene and two methine groups were present. Analysis of the ^1H and ^{13}C NMR spectra (see Experimental Section) left no doubt concerning structure 10 for this compound (see, for example, the coupling between the angular methine groups and between these and the olefinic protons).



7'



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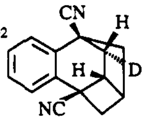

9'

Irradiation of BTN with ATMS in acetonitrile yielded only the allyl tricarbonitrile 11. The low solubility of BTN in benzene discouraged running experiments in that solvent, and irradiations were carried out in moderately polar solvents such as dichloromethane and ethyl acetate. Under these conditions compound 11 was again the only aromatic product obtained, but two other volatile compounds were also present. These could be separated by VPC, though we were not successful with other separation techniques. Mass spectrometry, as well as ^1H and ^{13}C NMR spectra (confirmed by H–H and C–H correlated experiments), allowed the identification of the two products (formed in ca. 1:1 ratio) as the two stereoisomeric bis[(trimethylsilyl)methyl]cyclobutanes arising from the head-to-head [2 + 2] dimerization of ATMS (structures 12, 13); comparison with literature data allowed assignment of the

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Table II. Quantum Yield for Product Formation

arene	[ATMS]	solvent	quantum yield[a] cycloaddition	addition	substitution	ATMS dimerization
NN	0.1	MeCN	0.008 (1 + 2)	0.024 (3 + 4 + 5)		
NN	0.1	C_6H_6	0.012 (1 + 2)			
NDN	0.1	MeCN		0.045 (7 + 8 + 9)	0.075 (6)	
NDN	0.1	C_6H_6	0.018 (10)	0.011 (7 + 8 + 9)	0.005 (6)	0.024 (12 + 13)
BTN	0.1	MeCN			0.065 (11)	
BTN	0.1	CH_2Cl_2			0.03 (11)	0.08 (12 + 13)
BTN	0.3	CH_2Cl_2			0.002 (11)	0.18 (12 + 13)

[a] The quantum yield is reported according to the type of process observed (sum of the quantum yields of the products indicated).

Table III. Fluorescence Quenching of the Arenes by ATMS

arene	(E_{red} (S_1) vs SCE)[a]	solvent	ΔG_{et}, eV	K_{sv}, M^{-1}	k_q, M^{-1} s^{-1}
NN	(1.55, V)	C_6H_6	+0.53	3.8	4×10^8
		MeCN	−0.27	20	2.2×10^9
NDN	(2.14, V)	C_6H_6	−0.16	15.6	1.6×10^9
		MeCN	−0.86	86	8.6×10^9
BTN	(3.1, V)	CH_2Cl_2	−1.62	44	4×10^9
		MeCN	−1.82	153	1.4×10^{10}

[a] Defined as $E_{red}(S_1) = E_{red}(S_0) + E_{exc}$.

Table IV. Quantum Yield for Dimer Formation

arene	[ATMS]	solvent	Φ_a	Φ_d
NDN	0.05	C_6H_6	0.025	0.015
	0.1		0.034	0.024
	0.2		0.035	0.07
	0.3		0.038	0.11
	0.5		0.04	0.135
BTN	0.05	CH_2Cl_2	0.038	0.06
	0.1		0.03	0.08
	0.2			0.14
	0.3		0.002	0.18

stereochemistry (see Experimental Section). The yield of the dimers increased at the expense of product 11 when a higher starting ATMS concentration was used. In view of this result, experiments with NDN in benzene were repeated in the presence of higher donor concentrations. Cyclobutanes 12 and 13 were indeed obtained, their yield depending on the starting ATMS concentration in a manner similar to that observed in the BTN experiments.

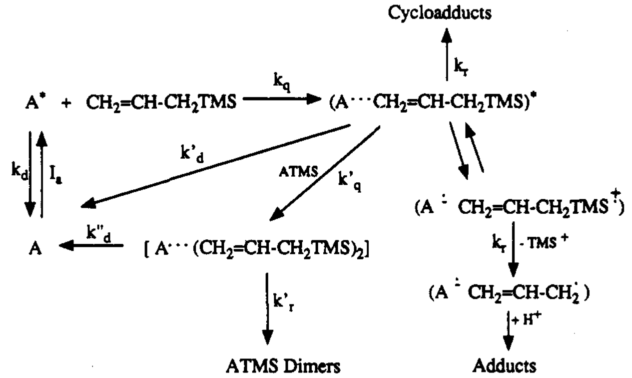
In order to facilitate solving the mechanistic question, steady-state measurements were carried out. These included quantum yield measurements for the formation of the photoproducts under various conditions (determined from VPC or HPLC measurements of the product yields in low-conversion experiments) and fluorescence quenching of the nitriles by ATMS in both acetonitrile and benzene (Tables II and III).

Discussion

ATMS is a much better donor than monosubstituted alkenes and quenches the fluorescence of the nitriles under all the conditions studied, whereas, for example, 1-hexene has virtually no effect on NN luminescence. All the reactions observed arise from the singlet state of the arene, and, as is often the case in the photochemistry of naphthalenes, a low quantum yield is obtained. However, as is apparent from Table II, the course of the reaction depends greatly on the conditions.

General Course of the Reaction. Table III compares the observed fluorescence quenching constants with the free energy change for electron transfer to the lowest excited singlet state of the arene, as calculated from the Weller equation. As expected, the rate for S_1 quenching approaches the diffusion-controlled limit for $\Delta G < -10$ kcal M^{-1}, while the process is much slower for near to thermoneutral electron transfer. No change in the emission spectrum is observed upon adding the quencher, and thus there is no direct evidence for an exciplex.[9] However, the occurrence of [2 + 2] cycloaddition exclusively under conditions which would imply a limited charge transfer (see Table II and III) and analogy with literature suggest that [2 + 2] cycloaddition occurs via a weakly stabilized exciplex.[2,3d] On the other hand, when full electron transfer is favored the main reaction leads to allyl(dihydro)arenes. It is reasonable to assume that this reaction involves loss of the trimethylsilyl cation from the initial radical cation and addition of the allyl radical to the arene radical anion. The polarity of the solvent exerts a stronger effect in this case than in the previous, and in the opposite direction. Scheme III shows a mechanism which can account for these observations.

Scheme III



[2 + 2] Cycloaddition. The observance of different types of cycloadditions in the case of benzene derivatives has found theoretical rationalization,[10] whereas no similar theory is available for naphthalene derivatives. Indeed, the fact that in this case the reaction is generally limited to [2 + 2] addition at positions 1 and 2 could simply be a consequence of the greater rigidity of the naphthalene skeleton in comparison with benzene, making overlap of the alkene with nonvicinal positions negligible (the lack of photoisomerizations in naphthalene can be similarly explained). The foregoing holds true for singlet-state reactions, with which we are concerned here; in fact 1,4-cycloaddition is observed with the triplet state of 1-acetylnaphthalene.[11] What remains to be rationalized is the regiochemistry of the reaction, yielding either "head-to-head" or "head-to-tail" adducts (formulas 14 and 15 for 1-substituted naphthalenes). Previous workers have obtained products of type 14 from 1-methoxynaphthalene

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(9) Exciplex emission has been detected from NN and some alkenes: Taylor, G. N. *Chem. Phys. Lett.* 1971, *10*, 355. Ware, W. R.; Watt, D.; Holmes, J. D. *J. Am. Chem. Soc.* 1974, *96*, 7853.

(10) (a) Houck, K. N. *Pure Appl. Chem.* 1982, 54, 1633. (b) Mattay, J. *Tetrahedron* 1985, *41*, 2393 and 2405.

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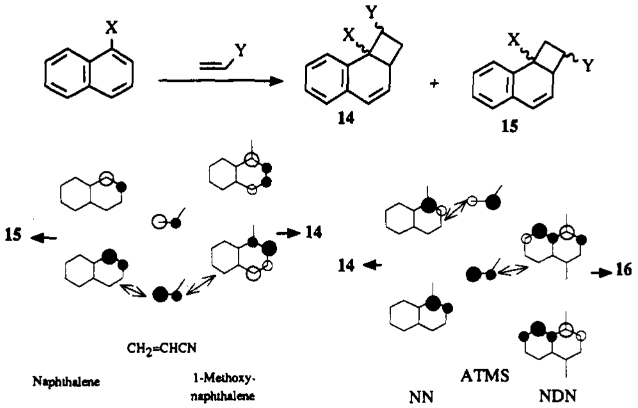
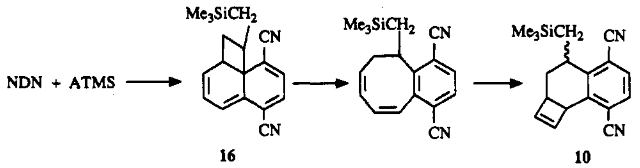


Figure 1. Regiochemistry of the [2 + 2] photocycloadditions between naphthalenes and monosubstituted alkenes. Frontier molecular orbital for typical cases (the most important interactions are indicated by double arrows).

Scheme IV

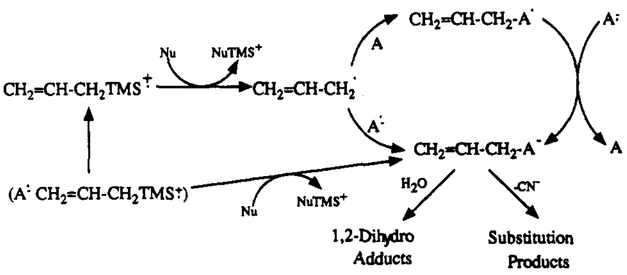


and acrylonitrile[3] and of type **15** (as the major product, with a small amount of **14**) from naphthalene and acrylonitrile (see Figure 1).[3a,b] These results would follow from a predominantly $HOMO_{arene}$ - $HOMO_{alkene}$ interaction and reflect an inversion in the order of C_1 and C_2 coefficients in the naphthalenes involved (Figure 1). Such an MO interaction becomes insignificant in the case of the naphthalenenitriles, and both homologous HOMO–HOMO and LUMO–LUMO interactions come into play, with the latter dictating the regiochemistry in the NN–ATMS reaction, in which only head-to-head adducts are formed. In this regard it appears reasonable that with styrenes both interactions are important since the FMOs are more closely spaced and, as a result, both adducts are formed.[3m]

In the reaction with NDN an adduct is formed only in benzene, and even then in low yield, as expected in view of the favorable electron transfer (see Table III). The compound isolated (**10**) is obviously not a primary product; its formation can be rationalized as involving two sequential electrocyclic rearrangements from a primary adduct **16** (the first step restores aromaticity, see Scheme IV). Indeed, the stabilizing effect of a further cyano group is expected to make the crossed interaction ($LUMO_{arene}$ - $HOMO_{alkene}$) more important, besides lowering the yield of the exciplex mediated cycloaddition in comparison to full electron-transfer-initiated allylation, as is indeed observed. In this case, the interaction localized at atoms C_{4a}–C_5, which have the same sign in the LUMO, is apparently dominant (Figure 1).

Allyl Group Addition. As previously mentioned, this process involves cleavage of the ATMS radical cation and attack by the allyl radical; however, a detailed outlining of the mechanism requires a thorough discussion. It has been amply demonstrated that photoinduced electron transfer facilitates fragmentation and, in particular, that loss of a trialkylsilyl cation takes place under such conditions from various silanes.[4d,12] It has been pointed out for the case of benzyltrimethylsilane that a considerable energetic barrier remains for the fragmentation of the radical cation.[12c] A fortiori this holds for $ATMS^{\bullet+}$, where the enthalpy change for fragmentation is around 30–35 kcal M^{-1}.[13]

Scheme V



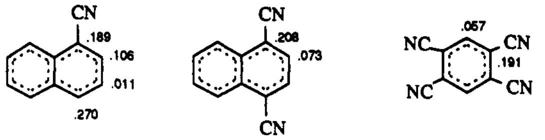


Figure 2. Spin density in the radical anions of some arenecarbonitriles, calculated according to: McLachan, A. D. *Mol. Phys.* **1958**, *1*, 233.

$$CH_2{=}CH{-}CH_2TMS^{\bullet+} \rightarrow CH_2{=}CH{-}CH_2^{\bullet} + TMS^+ \qquad (1)$$

However, in both cases the calculation is based on gas-phase data,[13] and since the solvation enthalpies for the charged reagent (the π radical cation) and the product (the trimethylsilyl cation) are probably quite different, it is doubtful that such an evaluation is accurate for solution experiments. Certainly, the possibility must be taken into account that the process observed is different from the simple unimolecular decomposition shown in eq 1, particularly since, in the case of some (*p*-methoxybenzyl)trialkylsilanes, it has been found that nucleophiles decrease the lifetime of the radical cation, while not changing the quantum yield of benzylation.[12c] In the present case there is no positive evidence for a nucleophile-assisted radical cation, though traces of water may play such a role. However, with NDN and BTN allylation occurs also in benzene, though with a lower quantum yield than in acetonitrile. At present we prefer the hypothesis wherein fragmentation occurs in the radical ion pair (see below).

As for the second step, attack on the arene, this can be envisaged in two ways, i.e., either direct reaction with the acceptor radical anion ($A^{\bullet-}$) followed by protonation (by traces of moisture, see D_2O experiments) or cyanide anion loss or alternatively attack on the neutral acceptor followed by reduction of the radical by the persisting radical anion $A^{\bullet-}$ and then as above (Scheme V). The two paths lead to the same result, with the latter being clearly favored by kinetic factors if the reaction involves the free-radical ions, while the former may be favored if addition takes place within the initially formed radical ion pair.

As for the regiochemistry of the attack, this involves positions 2 and 4 in NN; these are the unsubstituted

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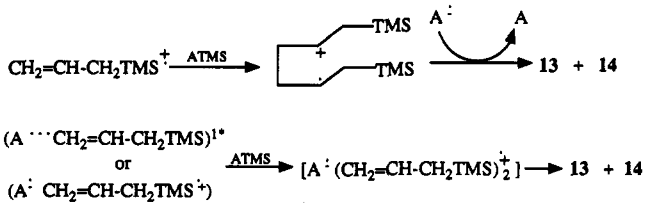
[12] (a) Mariano, P. S. *Org. Photochem.* **1987**, *9*, 1. (b) Hasegawa, E.; Yoon, U. C.; Mariano, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 406. (c) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P.; Mattes, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 8973.

[13] Calculated from the expression BDE ($ATMS^{\bullet+}$) = BDE(ATMS) - IP (ATMS) + IP($Me_3Si^{\bullet}$) = AP(Me_3Si^+) - IP(ATMS) where AP is the appearance potential of the cation in the mass spectrum. For AP(Me_3Si^+), values of 10.63,[13a] 10.03,[13b] and 10.09 eV[13c] have been reported, and for IP (ATMS), the values are 8.85[13d] and 9.0 eV.[13c] This leads to an estimate for BDE ($ATMS^{\bullet+}$) between 41 and 24 kcal M^{-1}, obviously reported for the gas phase. (a) Hess, G. G.; Lampe, F. W.; Sommer, L. H. *J. Am. Chem. Soc.* **1965**, *85*, 5237. (b) Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 2085. (c) Distefano, G. *Inorg. Chem.* **1970**, *9*, 1919. (d) Bock, H. *J. Organomet. Chem.* **1968**, *13*, 87. (d) Weidner, U.; Schweig, A. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 146.

Scheme VI



positions with the higher spin densities in NN$^{\bullet-}$ (Figure 2), but would also be the favored positions for radical attack onto neutral NN. In the NDN radical anion, spin density at position 1 is higher and at position 2 lower with respect to NN$^{\bullet-}$, thus explaining the important role of ipso attack (not observed with NN) in this case. The results of the reactions with NN, in which attack at unsubstituted positions takes place exclusively, clearly show that the fact that ipso attack had been reported in the literature to be the main, or only, path is due to the limitation in the examples considered up to now.

Since spectroscopic identification of the intermediates failed, an unambigous assignment of the detailed mechanism is impossible. However, several facts militate for the in-cage mechanism. These include the high chemical yield even with low arene concentration, the fact that unimolecular cleavage of the radical cation encounters a high barrier, while concerted $SiMe_3^+$ elimination (or rather transfer to MeCN or to the traces of water present)–radical addition to A$^{\bullet-}$ would afford a viable alternative, as well as the close similarity in the case of NDN between the reaction with ATMS and the reaction with toluene or benzylsilane, where the benzyl analogues of products **7** and **8** (and in the presence of D_2O, of products **7′** and **8′**) were obtained[14] and where there are indications for an in-cage mechanism.

ATMS Dimerization and Kinetic Discussion. The [2 + 2] dimerization of ATMS occurs efficiently (see Table IV) under suitable conditions (in nonpolar or moderately polar solvents, in the presence of either NDN or BTN and high ATMS concentration). This is a sensitized reaction (the arene is not consumed) and takes place at the expense of the previously discussed reactions, which involve consumption of both reagents. Under these conditions the quantum yield for adduct formation (Φ_a) increases with [ATMS] in the NDN case because a larger portion of NDN is quenched when [ATMS] increases, while with BTN, where the K_{SV} is larger Φ_a actually drops in the range of concentrations considered.

Several hypotheses could be considered. A triplet mechanism is precluded on energetic grounds. The reaction may involve the alkene radical cation, and indeed several examples of head-to-head [2 + 2] dimerizations by such a pathway are known.[5a,e,15] If desilylation is slow in apolar solvents, the radical cation might interact with a neutral molecule of ATMS according to Scheme VI. However, since the dimerization competes with the addition reaction, which has been envisaged as an in-cage process, and it occurs even under conditions where separation of the radical ions is unlikely to be fast (apolar medium), it appears reasonable that ATMS quenches the same intermediate as in the previous reactions, i.e., the exciplex–radical ion pair, and that the reaction occurs via a ternary excited complex, a mechanism for which there is also precedent.[16] While we are currently investigating the scope of the dimerization, this reaction is useful for the present discussion since it allows the evaluation of the kinetic parameters of the general mechanism (Scheme III).

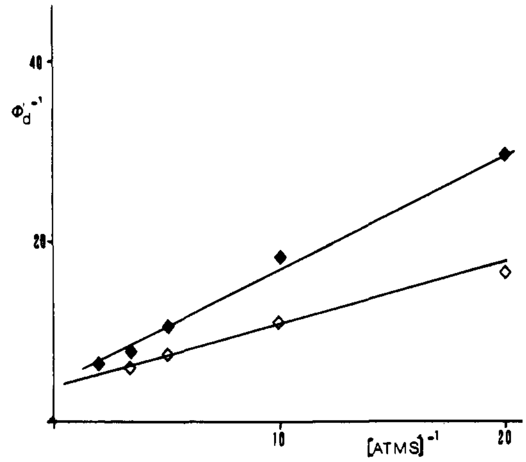


Figure 3. Doubly reciprocal plot for the corrected quantum yield of ATMS dimerization vs ATMS: (◇) BTN as sensitizer, solvent dichloromethane; (◆) NDN as sensitizer, benzene solvent.

According to this scheme, the quantum yield for dimer formation is

$$\Phi_d = \frac{k_q[\mathrm{ATMS}]}{k_q[\mathrm{ATMS}] + k_d}\,\frac{k'_q[\mathrm{ATMS}]}{k'_q[\mathrm{ATMS}] + k'_d + k_r}\,\frac{k'_r}{k'_r + k''_d}$$

and correcting for partial quenching of the acceptor singlet state through the parameter Φ'_d the following relationship

$$\Phi'_d = \Phi_d\left(1 + \frac{1}{K_{sv}[\mathrm{ATMS}]}\right)$$

results

$$\Phi'^{-1}_d = \frac{k'_r + k''_d}{k'_r}\left(1 + \frac{k'_d + k_r}{k'_q[\mathrm{ATMS}]}\right)$$

The corresponding doubly reciprocal plots are reported in Figure 3. The intercept vs slope value gives the ratio $k'_q/(k'_d + k_r)$, and this is 3.8 M^{-1} for NDN and 8.5 M^{-1} for BTN. Since ATMS is expected to quench the highly polar exciplex at a diffusion-controlled rate this suggests a short lifetime for such species, ca. 1 ns for (NDN ATMS)* and 2 ns for (BTN TMS)*. These lifetimes are considerably shorter than those of the corresponding monomeric excited states. This observation is consistent with the representation of these complexes as being only weakly stabilized. Orbital overlap and molecular deformation are less important with naphthalenes than with benzenes, the charge-transfer component is more significant, and these states are better represented as radical ion pairs than as complexes. Accordingly, they do not emit and their chemical reactivity is low (from the extrapolated quantum

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Table V. Solvent Effect in the ^{1}H-NMR Spectrum of Adducts 1 and 2

adduct	proton	δ (C_6D_6)	($CDCl_3$)
1	H-2a	2.75	3.4
	H-1	2.6	3
2	H-2a	3.2	3.5
	H-1	3.35	3.4

yield of adduct formation one obtains k_r/k'_d ca. 0.07 for NN and ca. 0.05 for NDN in benzene). The interaction with a second molecule of ATMS is more effective in inducing chemical reaction: thus, k'_r/k''_d is ca. 0.17 for NDN and 0.22 for BTN (from the intercepts in Figure 3).

In conclusion, allyltrimethylsilane, being a reasonably good donor and with a facile cleavage pathway available via the radical cation, enhances our understanding of the nature of polar exciplexes, at least insofar as mechanistic indications can be drawn from product studies. For the reasons discussed above the photoaddition reactions of naphthalenes have poor synthetic value, in contrast with the large potential that photoadditions of benzenes have. On the other hand, reactions photosensitized by naphthalenes, including the presently reported ATMS dimerization and many other known examples, may surely be developed into preparatively interesting processes.

Experimental Section

NN and ATMS were commercial products. NDN and BTN were prepared and purified as previously described. Spectrograde acetonitrile (Carlo Erba) was used as obtained or dried by refluxing over CaH_2. For NMR data, J values are given in Hz.

Preparative Irradiations. Aliquots (80 mL) of solutions containing the arene and 1.27 mL of ATMS (0.1 M) were deoxygenated by flushing with argon, capped with a rubber septum, and irradiated by means of a multilamp apparatus fitted with six 15-W phosphor-coated lamps (center of emission 320 nm). After a convenient time the solvent was evaporated and the raw photolysate chromatographed on a flash silica gel column (50 g) eluting with cyclohexane–ethyl acetate mixtures of increasing polarity. The following products were obtained.

From 245 mg of NN (0.02 M) in acetonitrile after 16 h irradiation. Unreacted starting material (135 mg). *endo*-1-[(Trimethylsilyl)methyl]-1,2,2a,8b-tetrahydrocyclobuta[*a*]naphthalene-8b-carbonitrile (1): oil (15.5 mg, 8%); ^{1}H-NMR (C_6D_6) δ –0.5 (s, $SiMe_3$), 0.6 (dd, J_{gem} = 14, J_{vic} = 3) and 0.9 (t, J_{gem} = J_{vic} = 14) (CH_2Si), 1.5 (ddd, $J_{2,2a}$ = 3, J_{gem} = 11, $J_{1,2}$ = 8, H-2 endo), 1.9 (ddd, $J_{2,2a}$ = 9, $J_{1,2}$ = J_{gem} = 11, H-2 exo) 2.6, (dddt, $J_{1,2a}$ = 1, J_{1,CH_2} = 3 and 14, $J_{1,2\text{-cis}}$ = 10, $J_{1,2\text{-trans}}$ = 10, H-1), 2.75 (m, $J_{2a,4}$ = 2, $J_{2a,3}$ = 4 $J_{2a,2\text{-cis}}$ = 9, $J_{2a,2\text{-trans}}$ = 9, $J_{1,3}$ = 1, H-2a), 5.0 (dd, $J_{3,4}$ = 10, $J_{2a,3}$ = 4, H-3), 5.58 (dd $J_{3,4}$ = 10, $J_{2a,3}$ = 2), no NOE effect by irradiation at δ 0.9; ^{13}C-NMR ($CDCl_3$) δ –1.03 (Me_3Si), 19.8 (CH_2Si), 37.2 (C-1), 38.2 (C-2), 44.9 (C-2a), 125.9 (C-4), 127.5 (C-3), 127.3, 127.9, 128.3, 128.4 (aromatic CH). Anal. Calcd for $C_{17}H_{21}NSi$:C, 76.55; H, 7.92, N, 5.24. Found: C, 76.85; H, 8.10; N, 5.10.

Exo isomer 2: oil (23 mg, 12%); ^{1}H-NMR (C_6D_6) δ –0.5 (s, $SiMe_3$), 0.5 (t, J_{vic} = J_{gem} = 14), and 0.75 (dd, J_{gem} = 14, J_{vic} = 3) (CH_2Si), 1.55 (dt, $J_{2,2a\text{-cis}}$ = 9, $J_{1,2\text{-trans}}$ = 9, J_{gem} = 11, H-2 endo), 2.25 (dt, $J_{2,2a\text{-trans}}$ = 9, $J_{1,2\text{-cis}}$ = 9, J_{gem} = 11 H-2 *exo*), 3.2 (dt, $J_{2,2a\text{-cis}}$ = 9, $J_{2,2a\text{-trans}}$ = 9, J_{gem} = 11, H-2a), 3.35 (ddt, J_{1,CH_2} = 3 and 14, $J_{1,2\text{-trans}}$ = 9, $J_{1,2\text{-cis}}$ = 9, H-1), 5.5 (dd, $J_{3,4}$ = 10, $J_{2a,3}$ = 5, H-3), 6.1 (d, $J_{3,4}$ = 10, H-4), small NOE effect on H-1 and H-2 by irradiation at δ 0.75, no effect by irradiation at δ 0.5; ^{13}C-NMR ($CDCl_3$) δ –1.0 ($SiMe_3$), 20.0 (CH_2Si), 36.7 (C-1), 37.7 (C-2) 47.5 (C-2a) 126 (C-3) 127 (C-4), 127.9, 128, 128.5, 130.1 (aromatic CH). Anal. Found: C, 76.45; H, 7.90; N, 5.10. The assignment of the stereochemistry to compounds 1 and 2 is mainly based on the solvent effects reported in Table V, in which the large shielding in C_6D_6 of the less hindered protons of compound 1 is apparent.

cis-1,2-Dihydro-2-(2-propenyl)naphthalene-1-carbonitrile (3): oil (40.5 mg, 29%); ^{1}H-NMR ($CDCl_3$) δ 2.35 and 2.5 (ABXY system, J_{vic} = 7, J_{vic} = 7, CH_2), 2.72 (m, H-2), 4.02 (d, $J_{1,2}$ = 6, H-1), 5.1 (dd, J_{gem} = 2, J_{cis} = 10) and 5.2 (dd, J_{gem} = 2, J_{trans} = 17) (=CH_2), 5.8 (ddd, J_{cis} = 10, J_{trans} = 17, J_{vic} = 7, -CH=), 5.9 (dd, $J_{2,3}$ = 4, $J_{3,4}$ = 10, H-3), 6.6 (dd, $J_{2,4}$ = 2, $J_{3,4}$ = 10, H-4). Anal. Calcd for $C_{14}H_{13}N$: C, 86.11; H, 6.71; N, 7.17. Found: C, 86,10; H, 6.85; N, 7.05.

3,4-Dihydro-4-(2-propenyl)naphthalene-1-carbonitrile (4): oil (3 mg, 2%), see below for identification.

Tetracyclo[6.3.2.0^{2,7}.0^{10,13}]trideca-2,4,6-triene-8-carbonitrile (5) (28 mg, 20%): ^{1}H-NMR ($CDCl_3$) δ 1.55 (d, J_{gem} = 12.5) and 1.85 (dt, J_{gem} = 12.5, $J_{1,12}$ = $J_{12,13}$ = 4.5) (H_2-12), 1.75 (d, J_{gem} = 14) and 2.03 (dddd, J_{gem} = 14, $J_{10,11}$ = 9, $J_{1,11}$ = 5, $J_{9,11}$ = 1.5) (H_2-11), 1.68 (dt, J_{gem} = 11, $J_{9,10}$ = 1.5, $J_{9,13}$ = 1.5) and 3.13 (ddd, J_{gem} 11, $J_{9,11}$ = 1.5) (H_2-9), 2.78 (m, $J_{9,10}$ = 9 and 1.5, $J_{10,11}$ = 1 and 9, $J_{10,13}$ = 5, H-10), 3.7 (ddd, $J_{10,13}$ = 5, $J_{12,13}$ = 4.5 and 1.5, H-13). Assignments confirmed by COSY and double irradiation experiments. Anal. Found: C, 85.95; H, 6.70; N, 7.00.

When the irradiation of a similar solution was limited to 7 h the unreacted starting material was 190 mg, and among the products there was almost no product 5 but a larger amount of compound 4, an oil, was present (10 mg, 14%); ^{1}H-NMR ($CDCl_3$) δ 2.5 (ddd, J_{gem} = 18, $J_{2,3}$ = 6, $J_{3,4}$ = 4), and 2.6 (ddd, J_{gem} = 18, $J_{2,3}$ = 4, $J_{3,4}$ = 7) (H_2-3), 2.25 (m, CH_2), 2.9 (m, H-4), 4.9 (dddd, J_{trans} = 17, J_{all} = 1.5 and 3, J_{gem} = 2) and 5.1 (J_{cis} = 10, J_{all} = 1 and 2, J_{gem} = 2) (=CH_2), 5.75 (m, –CH=), 6.8 (dd, $J_{2,3}$ = 4 and 6, H-2); ^{13}C-NMR ($CDCl_3$) δ 28.1 (–CH_2), 36.0 (C-4), 38.8 (C-3), 117.4 (=CH_2), 125.0, 127.3, 127.8, 129.2, 135.6, 142.4 (vinylic and aromatic CH). Anal. Found: C, 86.00, H, 6.80; N, 7.00.

From NN (147 mg, 0.012 M) in benzene after 30 h of irradiation. Unreacted starting material (103 mg). Compounds 1 (17.5 mg, 23%) and 2 (29 mg, 35%).

From NDN (230 mg, 0.013 M) in acetonitrile, after 3 h of irradiation. Unreacted starting material (20 mg). Compounds 6 (91 mg, 40%), 7 (39 mg, 15%), and 9 (21 mg, 8%), all corresponding in their physical properties to those reported by Mizuno et al.,[7b] as well as *cis*-1,2-dihydro-2-(2-propenyl)naphthalene-1,4-dicarbonitrile (8): oil (21 mg, 8%); ^{1}H-NMR ($CDCl_3$) δ 2.45 (m, CH_2), 2.9 (m, $J_{1,2}$ = 6, $J_{2,3}$ = 4, H-2), 4.1 (d, $J_{1,2}$ = 6, H-1), 5.2 dd (J_{cis} = 8, J_{gem} = 2) and 5.25 (dd, J_{trans} = 16, J_{gem} = 2) (=CH_2), 6.75 (d, $J_{2,3}$ = 4, H-3). Anal. Calcd for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49, N, 12.72. Found: C, 81.90; H, 5.55; N, 12.60. For the deuterated derivatives, the key factors were the following: 1,2-Dihydro-1-(2-propenyl)naphthalene-1,4-dicarbonitrile (2-d_1, *cis*-7′), 2.95 (d, J = 8, replacing part of an ABX system in compound 7), 6.72 (d, replacing a dd). *cis*-1,2-Dihydro-2-(2-propenyl)naphthalene-1,4-dicarbonitrile (2-d_1) (8′), ^{1}H-NMR, no signal at δ 4.1 (H-1, see above). Tetracyclo[6.4.0.1^{2,5}.0^{4,7}]trideca-1(8),9,11-triene-2,7-dicarbonitrile (9′): ^{1}H-NMR 2.33 (d, $J_{3,4}$ = 4.5, 3-H, replacing an AB system at 2.03 and 2.33 in 9; only the 2.03 signal has a significant coupling constant with the proton in position 4, and therefore is cis to it).

From NDN (150 mg, 0.0105 M) in benzene after 24 h of irradiation. Unreacted starting material (25 mg). Products 6 (11 mg, 8%), 7 (20 mg, 13%), 8 (3 mg, 2%), 9 (3 mg, 2%). 2a,3,4,8b-Tetrahydro-4-trimethylsilylmethylcyclobuta[*a*]naphthalene-5,8-dicarbonitrile (10): oil (10 mg, 5%); ^{1}H-NMR (C_6D_6) δ –0.3 (s, $SiMe_3$) 0.78 (ddd, J_{gem} = 14, $J_{2a,3}$ = 11, $J_{3,4}$ = 4), and 1.55 (ddd, J_{gem} = 14, $J_{2a,3}$ = 8, $J_{3,4}$ = 3) (H_2-3), 2.65 (m, $J_{2a,3}$ = 8 and 11, $J_{2a,8b}$ = 5, $J_{2,2a}$ = 1, $J_{1,2a}$ = 0.5, H-2a), 3.05 (ddt, $J_{3,4}$ = 3 and 4, J_{4,CH_2} = 4 and 12, H-4), 3.45 (ddd, $J_{2a,8b}$ = 5, $J_{1,8b}$ = 1, $J_{2,8b}$ = 1.8, H-8b), 5.6 (ddd, $J_{1,2}$ = 2.8, $J_{2.8b}$ = 1.8, $J_{2,2a}$ = 1, H-2), 6.35 (ddd, $J_{1,2}$ = 2.8, $J_{1,8b}$ = 1, $J_{1.2a}$ = 0.5) 7.01 (AB system, aromatic CH) and ($CDCl_3$) 0.9 (dd, J_{gem} = 15, J_{4,CH_2} = 12), and 0.7 (dd, J_{gem} = 15, J_{4,CH_2} = 4) (CH_2Si). ^{13}C-NMR ($CDCl_3$) δ –0.9 (Me_3Si), 23.2 (CH_2Si), 31.3 (C-3), 36.2, 38.5, 42.2 (C-2a, C-4, C-8b), 135.7 (C-1), 142.5 (C-2), 130.4 (C-6), 130.1 (C-7), 116.7, 117 (C-5 and C-8), 143.3, 150.9 (C-8 and C-9), 115, 116.2 (CN). Anal. Calcd for $C_{18}H_{20}N_2Si$: C, 73.93; H, 6.89; N, 9.58. Found: C, 73.80; H, 6.95; N, 9.35. The coupling constants of the two methylene protons in position 3 with the protons in positions 2a and 4 are quite similar to one another, and therefore we are unable to determine the stereochemistry of this compound. In an identical experiment the solvent was evaporated and the residue submitted to bulb-to-bulb distillation at reduced (30 mmHg) pressure to yield a mixture of products 12 and 13 (see below, 40 mg, ratio 1.2).

From BTN (142 mg, 0.1 M) in acetonitrile after 3 h of irradiation. Unreacted starting material (71 mg). 5-(2-Propenyl)benzene-1,2,4-tricarbonitrile (11, 47 mg, 61%), colorless crystals, mp 178–80 °C (from ethanol). ^{1}H-NMR δ 3.7 (AB system, J_{CH_2CH} = 6, CH_2), 5.25 (dd, J_{gem} = 2, J_{trans} = 15), and 5.35 (dd, J_{gem} = 2, J_{cis} = 8) (=CH_2), 5.9 (ddd, J_{CH_2CH} = 6, J_{trans} = 15, J_{cis} = 8, =CH–), 7.8 (s, H-6), 8.05 (s, H-3). Anal. Calcd for $C_{12}H_7N_3$: C, 74.60; H, 3.65; N, 21.75. Found: C, 74.50; H, 3.60; N 21.85.

From BTN (142 mg, 0.1 M) in dichloromethane after 8 h of irradiation. Unreacted starting material (92 mg); product **11** (46 mg, 85%). In an identical experiment, the solvent was evaporated, and the residue was submitted to bulb-to-bulb distillation at reduced (30 mmHg) pressure. From the distillate were obtained two volatile compounds separated by VPC. *trans*-1,2-Bis[(trimethylsilyl)methyl]cyclobutane (**12**, 25 mg): M$^+$ m/z 228: ^{1}H-NMR ($CDCl_3$) δ 1.35, 1.8 and 1.95 (three m, AA′BB′CC′ system), 0.5 (dd, J_{gem} = 14, J_{CH_2CH} = 10), and 0.83 (dd, J_{gem} = 14, J_{CH_2CH} = 4) (CH_2Si); ^{13}C-NMR ($CDCl_3$) δ −0.8 (Me_3Si), 24 (CH_2Si), 28.3 (C-3), 43.1 (C-1). Cis isomer of compound **12** (**13**, 20 mg), M$^+$ m/z 228: ^{1}H NMR ($CDCl_3$) δ 1.5, 2.0, and 2.4 (three m, AA′BB′CC′ system), 0.5 (dd, J_{gem} = 14, J_{vic} = 5), 0,62 (J_{gem} = 14, J_{vic} = 10) (CH_2Si); ^{13}C-NMR ($CDCl_3$) δ −0.9 (Me_3Si), 17.3 (CH_2Si), 27.3 (C-3), 35.3 (C-1). Compare with tabulated values for *cis*- and *trans*-1,2-dimethylcyclobutane δ 26.6 (C-3) and 32.2 (C-1) and, respectively, 26.8 (C-3) and 39.2 (C-1).

Irradiation of Compound 4. Compound **4** (8 mg) in 25 mL of acetonitrile was irradiated as above for 90 min. Evaporation of the solvent gave compound **5** (quantitative yield) identical in its spectroscopic properties to the sample obtained in the NN-ATMS irradiation.

Quantum Yield of Reaction. Aliquots (5 mL) of solution in quartz tubes were prepared as above and irradiated in a merry-go-round apparatus inserted in the multilamp apparatus described above. Chemical reaction was evaluated by VPC and light intensity by ferrioxalate actinometry.

Fluorescence Measurements. Fluorescence intensities were measured by means of an Aminco-Bowman MPF spectrofluorimeter using 1-cm optical path spectrophotometric cells degassed by five freeze–degas–thaw cycles.

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Photochemistry of Matrix-Isolated (α-Diazobenzyl)phosphonate. Observation and Reactions of Phosphonylphenylcarbene, Phosphonyl Phenyl Ketone Oxide, and Phenylphosphonyldioxirane

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Photolysis of dimethyl α-diazobenzylphosphonate (**1**) in an Ar matrix at 10 K resulted in the appearance of new absorption bands at 1268, 788, and 536 cm^{-1}, attributable to the carbene **2**. The assignment was based on the observation that the new absorptions disappeared upon thawing of the CO-containing matrix to produce the ketene **3**, which can be generated by photolysis of (α-diazophenacyl)phosphonate **4**. Photolysis of **1** in an Ar matrix doped with 20% O_2 at 10 K produced benzoylphosphonate **5** along with benzoyl phosphate **8**. Generation of **2** in a 0.3% O_2-containing matrix, followed by warming of the matrix to 35 K in the dark, resulted in the total disappearance of the band arising from **2** and the concurrent appearance of a new intermediate, identified as the carbonyl oxide **6**. Photolysis of **6** with visible light (λ > 480 nm) gave the corresponding dioxirane **7**, which was converted to the ester **8** by further irradiation (λ > 350 nm); none of the phosphate **9**, expected to arise via phenyl migration in the photoisomerization of **7**, was detected.

Phosphorylcarbenes, readily available from the photolysis or thermolysis of phosphoryl diazo compounds, have been the focus of considerable interest because they can be used not only to introduce the phosphoryl function into organic compounds,[1] as in the phosphorylcyclopropanation of alkenes or arenes, but also as potential photolabile mimics of phosphate derivatives.[2] In this regard, the chemistry of phosphorylcarbenes seems to have been thoroughly investigated. However, the direct observation and characterization of phosphorylcarbenes has not yet been accomplished, to the best of our knowledge, in spite of the fact that there has been an increasing number of reports concerning the direct observation, characterization, and kinetic analysis of many fundamental types of carbenes using either laser flash photolysis techniques[3] or matrix isolation spectroscopy.[4] In the course of our studies on the chemistry of phosphorylcarbenes,[5] we explored the photochemical generation of phenylphosphonylcarbene under matrix isolation conditions. We wish to report herein the characterization of this carbene, its thermal reactions with CO and O_2, and spectroscopic evidence for the sequential formation from it of a carbonyl oxide and a dioxirane.

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