

FLASH PHOTOLYSIS STUDIES OF NITRILE IMINES AND RELATED INTERMEDIATES PHOTOGENERATED FROM SYDNONES AND TETRAZOLES IN FLUID SOLUTIONS[†]

K. BHATTACHARYYA^a, D. RAMAIAH^b, P. K. DAS^{a†} and M. V. GEORGE^{a,b,c†}

^aRadiation Laboratory and ^cChemistry Department, University of Notre Dame, Notre Dame, IN 46556 (U.S.A.)

^bChemistry Department, Indian Institute of Technology, Kanpur 208016 (India)

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Summary

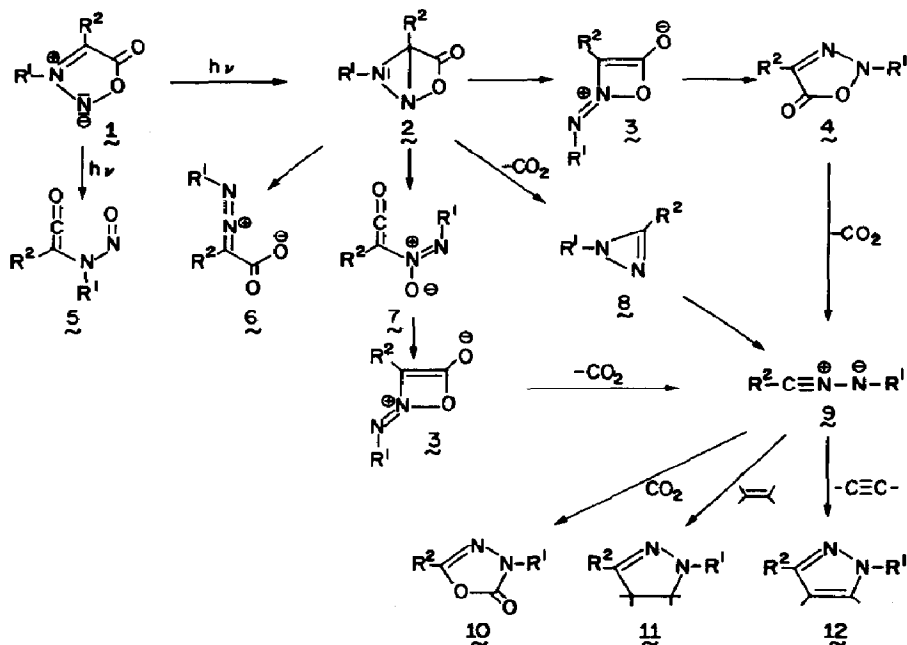
The spectral and kinetic behavior of nitrile imines photogenerated from sydnones and tetrazoles in fluid solutions has been studied by laser and lamp flash photolysis. The nitrile imines are characterized by lifetimes of milliseconds and are quenchable by the dipolarophile dimethyl acetylenedicarboxylate ($k_q = (5 - 9) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for *N,C*-diarylnitrile imines in benzene) and by carboxylic acids ($k_q = 10^8 - (2 \times 10^9) \text{ M}^{-1} \text{ s}^{-1}$ with trifluoroacetic acid in benzene and acetonitrile). The phototransformation of 3,4-diarylsydnones to the corresponding *N,C*-diarylnitrile imines occurs rapidly (within nanoseconds of laser excitation); this suggests that bicyclic diaziridine, diazirine or 1,2,3-oxadiazolin-5-one intermediates, postulated in the literature as precursors for nitrile imines, are either very short lived or not involved at all. The laser flash photolysis of the sydnones unsubstituted at the 4-position or bearing a methyl group at this position gives rise to additional, fast-decaying, transient species ($\tau = 0.3 - 4 \mu\text{s}$ in benzene) which become progressively longer lived upon interaction with hydroxylic reagents (water, alcohols and carboxylic acids). Possible assignments of these transient species in terms of ylide structures are discussed in the light of the results of steady state photolysis at low temperatures.

1. Introduction

Since the first report by Krauch *et al.* [1] regarding the photoisomerization of 3-phenylsydnone to Δ^2 -1,3,4-oxadiazolin-5-one, the photochemistry of sydnones (1,2,3-oxadiazol-5-ones, **1** in Scheme I) has been a topic of extensive research by several groups of workers [2 - 11]. The intermediate of central interest in sydnone photochemistry appears to be the nitrile imine **9**

[†] Dedicated to Professor Rolf Huisgen on the occasion of his 65th birthday.

[‡] Authors to whom correspondence should be addressed.



Scheme I.

produced via several postulated precursors, namely bicyclic diaziridines (2) [1 - 6, 9, 10], diazirines (8) [1 - 11] or 1,2,3-oxadiazolin-5-ones (4) [7, 8]. The photogeneration of nitrile imines from sydnone has been established by their 3 + 2-cycloaddition reactions with alkene and alkyne derivatives leading to pyrazolines and pyrazoles respectively [2 - 6, 9, 11]. A few other intermediates have been postulated in connection with the photochemistry [1 - 11] and the photochromism [11, 12] of sydnone. These include (i) the ketenes (5 and 7) put forward by Gotthardt and Reiter [10] to explain the novel phototransformation of 3-amino-4-(phenylthio)sydnone to their isomers possessing 2-aza-1,3-diazoniacyclopentadiene-1,4-diolate structures and (ii) the extended ylide system 6 proposed by Trozzolo *et al.* [11] to interpret the blue coloration produced upon photolysis of 3-(3-pyridyl)sydnone in a KBr disc at 77 K (followed by warming).

Tetrazoles (13) have been commonly used as thermal and photochemical precursors of nitrile imines [6, 13 - 24]. Under thermolytic conditions, nitrile imines produced from tetrazoles have been trapped by dipolarophiles (alkene or alkyne derivatives) and a variety of HX-type reagents, including primary and secondary amines, phenols, thiophenols and carboxylic acids [13 - 16]. Although the photolytic nitrogen extrusion to *N,C*-diphenylnitrile imine is well established in the case of 2,5-diphenyltetrazole [6, 13, 21], the published reports on steady state photochemical studies of 5-phenyltetrazole and 2-methyl-5-phenyltetrazole and failures to trap the corresponding nitrile imines cast doubt on the involvement of these intermediates in the photochemistry of these two tetrazole systems [22, 23]. Low temperature IR and UV spectroscopic studies have led to the character-

ization of nitrile imines photolytically formed from 2,5-diphenyltetrazoles and 2-phenyltetrazoles as well as from related systems in polymeric or glassy matrices at 10 - 85 K [18 - 20].

In spite of the widespread interest in the photochemistry of sydrones and tetrazoles, as far as we know, no attempt has been made to characterize the related photointermediates in fluid solutions. We have undertaken a time-resolved study, based on laser and lamp flash photolysis, to generate information primarily on the spectral and kinetic behavior of nitrile imines photogenerated from sydrones and tetrazoles. The results are presented in this paper. Interestingly, besides the transient absorptions that are best assigned to long-lived nitrile imines, we have observed in some cases fast-decaying transients in the nanosecond time domain; the latter suggest that the photochemistry of some of the sydrones is more complex than revealed in steady state irradiation studies in fluid solutions.

The sydrones and tetrazoles under study are shown in Fig. 1.

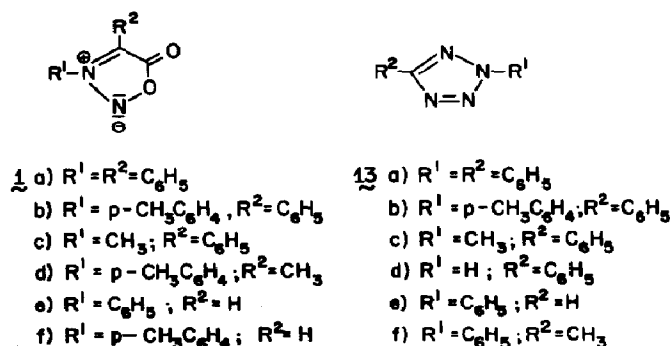


Fig. 1. Sydrones and tetrazoles under study.

2. Experimental details

The sydrones [25 - 29] and tetrazoles [30 - 36] were prepared by methods similar to those described in the literature [25 - 36]. To prepare 2-phenyltetrazole (13e) the procedure from the literature [36] was modified as follows. To a mixture of glyoxalic acid phenylhydrazone (3 g; 18.3 mmol) and 2,4,6-tribromophenyl azide (6.6 g; 18.5 mmol) in absolute alcohol (50 ml) was added a cold solution of sodium ethoxide (0.85 g Na in 20 ml absolute EtOH) at about 25 °C with stirring. The reaction mixture was kept at 60 - 65 °C for 4 h. Addition of water (200 ml) after cooling gave 2,4,6-tribromoaniline quantitatively. To the dark-red filtrate (after removal of tribromoaniline) was added concentrated HCl (50 ml; pH 3 - 4) to give 2-phenyltetrazole-5-carboxylic acid (2.78 g; 80%; melting point, 138 - 139 °C). Thermolysis of 2-phenyltetrazole-5-carboxylic acid (2.75 g; 14.5 mmol) at 150 - 155 °C in a sealed tube for 0.5 h gave a black residue. Addition of water (150 ml), extraction of the resultant dark-red oil with dichloro-

methane and evaporation of the solvent gave a residue which upon distillation under vacuum gave 1.57 g (75%) 2-phenyltetrazole (boiling point, 110 - 111 °C at 10 mm).

Benzene (Aldrich), methanol (Aldrich) and cyclohexane (MCB), all spectral grade, were used as received. Acetonitrile (spectral grade) and 2-methyltetrahydrofuran, both purchased from Aldrich, were distilled over P₂O₅ and LiAlH₄ respectively. For some experiments, the distilled acetonitrile was passed through a column of basic alumina (Woelm B, Akt I) before use. The other solvents and reagents used in this study were the best grades commercially available and were subjected to standard purification procedures before use.

The absorption spectra were recorded using a Cary 219 spectrophotometer. For spectral measurements and steady state photolysis at 77 K, the rectangular quartz cells of path length 3 mm which contained the solutions were immersed in liquid nitrogen in dewars equipped with flat-faced quartz windows. For steady state irradiation, the excitation source was a medium pressure mercury lamp (Bausch and Lomb SP-200) coupled with a Bausch and Lomb monochromator (33-86-07) and Corning filters. For room temperature (295 K) photolysis and absorption spectral measurements, square cells (1 cm × 1 cm) were commonly used.

For laser flash photolysis we mostly used pulsed outputs from a UV-400 Moletron nitrogen (337.1 nm; 2 - 3 mJ; about 8 ns) or a Lambda Physik EMG 101 MCS excimer (308 nm; 50 mJ or less; about 20 ns; Xe-Cl) laser system. For some experiments, the laser excitation was also carried out at 355 nm (about 6 ns; third harmonic), 266 nm (about 6 ns; fourth harmonic) using a Quanta-Ray Nd-YAG system or at 248 nm (about 20 ns; Kr-F) using the Lambda Physik system. The outputs from the latter laser sources were suitably attenuated to 20 mJ per pulse or less and defocused to minimize multiphoton processes. The details of the kinetic spectrophotometer and the data collection system are available in previous publications [37, 38] from the Radiation Laboratory. For transient absorption spectra requiring wavelength-by-wavelength measurements with a large number of laser shots, use was made of a flow system consisting of a reservoir which filled the rectangular quartz cell (path length, about 3 mm) continuously. For kinetics, static cells (path length, 1 - 3 mm) containing 1 - 2 ml of the solutions for photolysis were used. Unless we intended to study the effect of oxygen, the solutions were deaerated by saturating with high purity argon. The conventional lamp flash photolysis set-up has been described elsewhere [39].

3. Results

Of the sydnones under study (1a - 1f in Fig. 1), those substituted by phenyl/*p*-tolyl groups at both the 3- and the 4-positions (*i.e.* 1a and 1b) show ground state absorption maxima at 341 - 342 nm ($\epsilon_{\max} \approx 11 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) in benzene. The others (1c - 1f) have their absorption maxima

relatively blue shifted ($\lambda_{\max} = 326$ nm and $\epsilon_{\max} = 15 \times 10^3$ M⁻¹ cm⁻¹ for 1c and $\lambda_{\max} = 316 - 320$ nm and $\epsilon_{\max} = (5 - 6) \times 10^3$ M⁻¹ cm⁻¹ for 1d - 1f in benzene). All of the sydnone substrates could be conveniently excited at the laser wavelength 308 and 337.1 nm using benzene solutions of concentrations of 1 mM or below. In contrast, the tetrazoles 13a - 13d do not absorb significantly at wavelengths longer than 330 nm (except for the weak n, π^* transitions in 13a and 13b). For these systems, the direct laser excitation was carried out at 308, 266 or 248 nm. For 2,5-diaryltetrazoles, (13a and 13b), sensitization was possible with 337.1 nm or 355 nm laser excitation using benzophenone or *p*-methoxyacetophenone as a sensitizer (see below).

3.1. Laser flash photolysis of sydrones 1a - 1c

Upon 337.1 nm or 308 nm laser flash photolysis, solutions of sydrones 1a and 1b produce long-lived transient species characterized by absorption maxima at 375 - 380 nm (see Figs. 2(A) and 2(B)). In various solvents (*e.g.* benzene, methanol and acetonitrile), these transient photoproducts are formed rapidly (almost within the duration of the laser pulse) and undergo very little or no decay (5% or less) over 100 μ s or so. Oxygen (2 mM or less) has practically no effect on their yields or decay kinetics. Based on the similarity of the spectra and the kinetics with those of transients photogenerated from

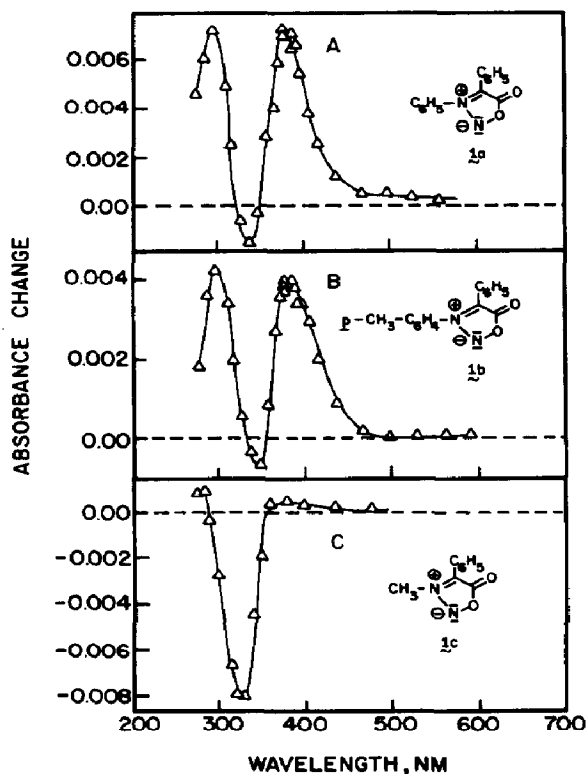


Fig. 2. Transient absorption spectra observed at 0.5 - 100 μ s following 308 nm laser flash photolysis of (A) 1a, (B) 1b and (C) 1c in benzene.

tetrazoles, as well as their quenching behavior (to be discussed in detail below), we assign the 375 - 380 nm species as *N,C*-diarylnitrile imines.

From a low temperature steady state photolysis study of 2,5-diphenyl-tetrazole in EPA glass at 77 K, the extinction coefficient ϵ_{NI} at the absorption maximum (378 nm) of *N,C*-diphenylnitrile imine has been reported [18] to be $17.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. Assuming that ϵ_{NI} at room temperature is not very different from the value at 77 K, we have estimated the photochemical yields ϕ_{P} of the nitrile imines from sydnone 1a and 1b. Laser flash photolysis (337.1 nm) of solutions of benzophenone and sydnone 1a and 1b in benzene (optically matched with each other at 337.1 nm) gave transient absorbance changes (end of pulse) due to benzophenone triplets at 532 nm and changes due to *N,C*-diarylnitrile imines at 375 - 380 nm. Use was made of the equation

$$\phi_{\text{P}} = \phi_{\text{T}} \frac{\epsilon_{\text{T}}}{\epsilon_{\text{NI}}} \frac{\Delta A_{\text{NI}}}{\Delta A_{\text{T}}} \quad (1)$$

where ϕ_{T} is the triplet yield of benzophenone in benzene (taken to be unity), ϵ_{T} is the extinction coefficient of benzophenone triplet ($7.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 532 nm in benzene [40]) and ΔA_{NI} and ΔA_{T} are the absorbance changes due to nitrile imines and benzophenone triplets respectively. For both 1a and 1b, the ϕ_{P} were found to be surprisingly low (0.05 in benzene). As is evident from Figs. 2(A) and 2(B), in the short-wavelength region around 300 nm (where the sydnone ground state absorption spectra show minima), positive absorbance changes can be observed as a result of the laser flash photolysis. When we consider the fact that *N,C*-diphenylnitrile imine has only a minor band system in this spectral region (the ϵ_{max} in EPA glass at 77 K are $6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ and $5.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 308 nm and 298 nm respectively [18]), we are led to the conclusion that photoproducts other than nitrile imines are also formed in a parallel manner as a result of laser flash photolysis. We should, however, note that the monitoring of absorption changes in the region of ground state absorption is fraught with complications from the secondary photochemistry of products accumulating in the photolysis region as a result of the action of the analyzing light (pulsed) prior to the arrival of the laser pulse. Hence, this was avoided in most of our experiments and suitable cut-off filters were used to minimize the absorption of analyzing light by the substrates.

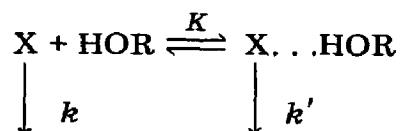
In a companion study [41], we have shown that, under energy transfer sensitization, sydnone 1a - 1f form short-lived triplets ($\lambda_{\text{max}}^{\text{T}} = 380 - 400 \text{ nm}$ and $\tau_{\text{T}} = 0.2 - 2 \mu\text{s}$ in benzene) quenchable by oxygen ($k_{\text{q}, \text{O}_2}^{\text{T}} = (1.7 - 2.0) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in benzene). Transient phenomena attributable to these triplets are not observed under direct excitation. The facts that the transient absorbance changes lack initial growth components on the short time scale of triplet decay and that oxygen has no effect on their magnitudes establish that the triplets are not involved in the photochemistry of the sydnone 1a under direct excitation.

The laser flash photolysis (337.1 or 308 nm) of sydnone 1c in benzene or methanol does not lead to any transient phenomena in terms of positive absorbance change at 350 nm or above. Only the bleaching of the ground state is observed at 290 - 350 nm (Fig. 2(C)). The steady state photolysis of this sydnone in benzene is known to produce its isomer, 4-methyl-2-phenyl- Δ^2 -1,3,4-oxadiazolin-5-one [24]. In terms of the mechanism of Krauch *et al.* [1], one may invoke the intermediacy of *N*-methyl-*C*-phenylnitrile imine (9, $R_1 \equiv \text{CH}_3$ and $R_2 \equiv \text{C}_6\text{H}_5$, see Scheme I) that is trapped by carbon dioxide photo-extruded from the sydnone. It appears that the absorption spectrum of the nitrile imine in this case is located at short wavelengths (shorter than 350 nm, see below) and remains buried under the ground state absorption spectrum of the parent sydnone.

3.2. Laser flash photolysis of sydnones 1d - 1f

For each of the sydnones 1d - 1f in benzene, dual transient behavior is observed upon 337.1 or 308 nm laser flash photolysis. An initial relatively fast decay of transient absorption over microseconds is followed by a long-lived component which remains nearly "permanent" on our longest time scale (about 100 μs). The transient spectra and kinetics are illustrated in Fig. 3. The short-lived component can be fitted very well to first-order kinetics; the decay lifetimes are given in Table 1. Note that the absorption spectra of the short-lived components (Fig. 3) are more extended into the visible region than their long-lived counterparts (*i.e.* residual absorptions).

The decay kinetics of the short-lived components remain unaffected in the presence of oxygen, di-*tert*-butylnitroxy radicals or ferrocene. Since these reagents have been shown to be efficient quenchers of sydnone triplets [41], the lack of a quenching effect rules out the assignment of a triplet for the fast-decaying transients. Interestingly, upon gradual addition of alcohols at millimolar concentrations, the decay of these transients becomes progressively slower. The transient spectra and kinetics in the presence of low concentrations of methanol are presented in Fig. 4. A plausible explanation for the observed effect of alcohols may be sought in terms of the reversible formation of a complex that is much longer lived than the uncomplexed transient. This is shown in Scheme II.



Scheme II.

X stands for the transient species and k and k' represent the rate constants for its decay in free and complexed forms respectively. Based on the assumption that the equilibration process is much faster than the decay of X and

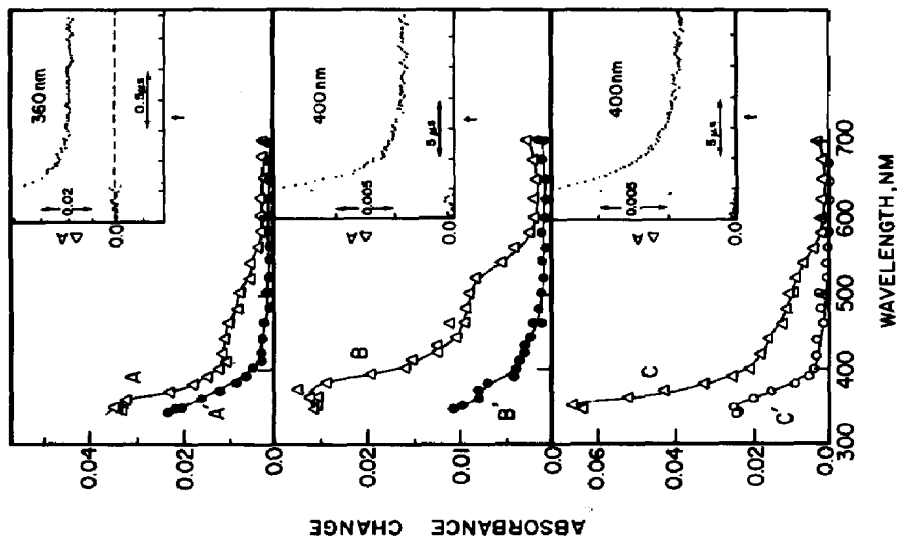
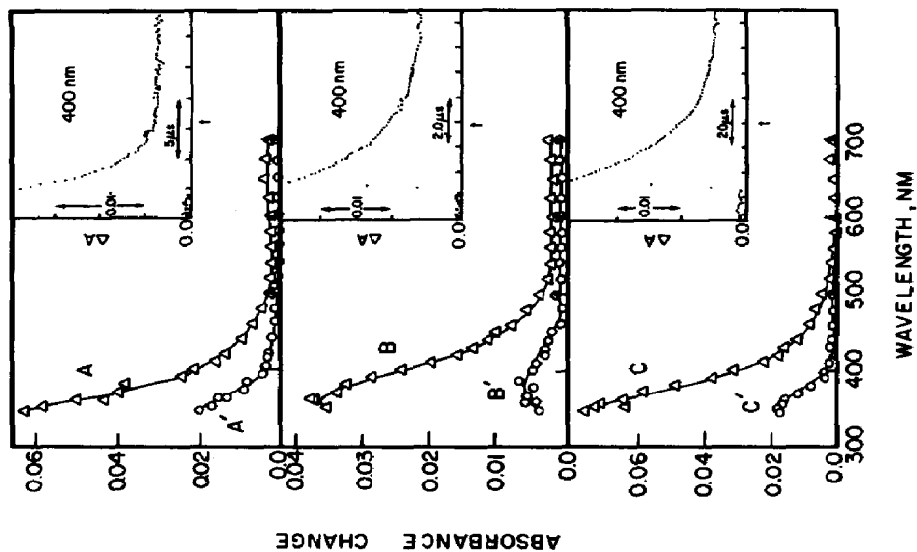


Fig. 3. Transient absorption spectra observed upon 337.1 nm laser flash photolysis of (A,A') 1d, (B,B') 1e and (C,C') 1f in benzene (A - C, end-of-pulse; A' - C', following the completion of the initial fast component). The insets show representative kinetic traces monitored at the wavelengths indicated.

Fig. 4. Transient absorption spectra observed upon 337.1 nm laser flash photolysis of (A,A') 1d in benzene + 0.10 M methanol, (B,B') 1e in benzene + 0.10 M methanol and (C,C') 1f in benzene + 0.05 M methanol. The insets show representative kinetic traces monitored at the wavelengths mentioned.

TABLE 1

Data concerning lifetimes of short-lived transients photogenerated from sydnones 1d - 1f and their complexation with alcohols (temperature, 295 K)

Sydnone substrate	Solvent	τ (μs)	K (M^{-1})	
			MeOH	<i>t</i> -BuOH
1d	Benzene	0.33	33 ± 1	8.0 ± 1
	Benzene + 0.05 M MeOH	0.92		
	Acetonitrile	5.3		
1e	Benzene	1.9	33 ± 2	13 ± 2
	Benzene + 0.05 M MeOH	4.3		
	Acetonitrile	60		
1f	Benzene	4.1	31 ± 2	21 ± 2
	Benzene + 0.05 M MeOH	9.7		
	Acetonitrile	100		

X. .HOR, one can show that the observed rate constant k_{obsd} for the decay of transient absorption due to X, X. .HOR or the composite X + X. .HOR is given by the equation

$$k_{\text{obsd}} = \frac{k + k'K[\text{ROH}]}{1 + K[\text{ROH}]} \quad (2a)$$

The decay behavior at relatively high [ROH] suggests that k' is negligible. Under this condition, eqn. (2a) takes the simplified form

$$\frac{k}{k_{\text{obsd}}} = 1 + K[\text{ROH}] \quad (2b)$$

Figure 5 shows the plots of k/k_{obsd} vs. [ROH], with methanol as the reagent in benzene. Within our experimental errors, the plots are linear (correlation coefficient, better than 0.99) and suggest almost identical K values (slopes) for the three sydnone substrates. Similar plots are also obtained with *tert*-butanol as the reagent. In this case, however, the K differ considerably among the three substrates. The transients under consideration become longer lived on going from benzene to acetonitrile; the lengthening of their lifetimes upon gradual addition of water, alcohols or carboxylic acids is also noted in acetonitrile. Interestingly, in the presence of 1 - 3 mM trifluoroacetic acid, hints of growth kinetics ($\tau = 0.5 - 1 \mu\text{s}$) appear at 370 - 390 nm in the course of laser flash photolysis of 1d or 1e in acetonitrile. This suggests that the initially produced transient interacts with the carboxylic acid.

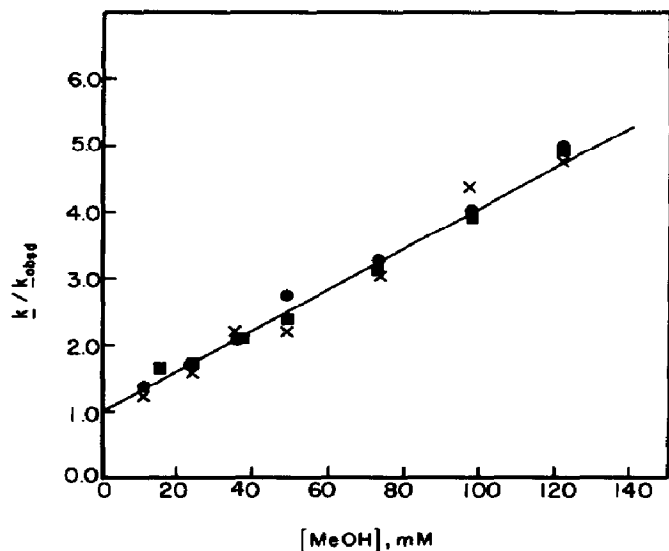


Fig. 5. Plots based on eqn. (2b) (●, 1d; ×, 1e; ■, 1f). The straight line drawn is the least-squares best linear fit of data points corresponding to 1f (solvent, benzene).

3.3. Sensitized and direct laser excitation of tetrazoles 13a - 13f

Of the tetrazoles under study, only the 2,5-diaryl-substituted compounds (*i.e.* 13a and 13b) act as efficient quenchers for benzophenone and *p*-methoxyacetophenone triplets. The quenching rate constants k_q^T obtained from the linear dependence of the pseudo-first-order rate constants of ketone triplet decay on the tetrazole concentrations are given in Table 2.

TABLE 2

Bimolecular rate constants for the quenching of benzophenone and *p*-methoxyacetophenone triplets by tetrazoles in benzene at 295 K

Tetrazole	$k_q^T (\times 10^9 \text{ M}^{-1} \text{ s}^{-1})$	
	Benzophenone	<i>p</i> -Methoxyacetophenone
13a	0.41	5.4
13b	0.88	5.4
13c	< 0.002	< 0.005
13d	< 0.002	< 0.03
13e	0.05	0.53
13f	0.18	0.89

The *p*-methoxyacetophenone and benzophenone triplets were monitored by their absorptions at 390 nm and 532 nm respectively. The probable mechanisms for the quenching of aromatic carbonyl triplets by tetrazoles are energy transfer and charge transfer. In the latter case, the tetrazoles are

expected to behave as electron donors. From the onset of the lowest-lying weakly allowed band system of 13a and 13b, their lowest energies E_S are estimated at 70 - 71 kcal mol⁻¹. Thus, although the transition responsible for this band system ($\epsilon_{\max} = 28 \text{ M}^{-1} \text{ cm}^{-1}$ at 354 nm for 13a in benzene) appears to be of n, π^* origin, and hence is characterized by a small singlet-triplet separation (typically 5 - 10 kcal mol⁻¹ for aza-aromatics [42]), it is expected that the triplet energy E_T of tetrazoles 13a and 13b is lower than that of benzophenone (69 kcal mol⁻¹). The k_q data (Table 2) suggest the proximity of the E_T of benzophenone to that of 13a and 13b. The 0,0 bands discernible in the absorption spectra of 13c and 13d in EPA glass at 77 K are located at 282 nm (*i.e.* 101 kcal mol⁻¹). For these tetrazoles, the E_T appear to be too high for efficient energy transfer from triplets of either *p*-methoxyacetophenone or benzophenone. Tetrazoles 13e and 13f are intermediate in their behavior as quenchers for the ketone triplets. The rate constants for quenching, $(0.5 - 9) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Table 2), are below the limit of diffusion control and this suggests that the E_T of these tetrazoles are above, but close to, the E_T of *p*-methoxyacetophenone. In this context, it is worth noting that the triplet energies of aliphatic azo compounds are in the vicinity of 53 kcal mol⁻¹ [43].

Upon 337.1 nm or 355 nm laser flash photolysis of benzophenone in the presence of 1 - 10 mM of tetrazoles 13a or 13b in benzene, growths of long-lived transient absorption are observed at 350 - 420 nm. These growths are concomitant with the enhanced decay of benzophenone triplet monitored at 532 nm. Long-lived transient absorption at 350 - 420 nm is also produced under sensitization by *p*-methoxyacetophenone (Fig. 6(A)); this is attributable to *N,C*-diarylnitrile imines formed as a result of fast extrusion of N₂ from the triplets of 13a or 13b. This is based on the similarity of the spectra to those of products obtained by direct photolysis of tetrazoles at room temperature as well as at low temperatures (see below). A comparison of absorbance changes due to benzophenone triplets at 532 nm with those at 370 - 380 nm due to *N,C*-diarylnitrile imines derived via energy transfer from the former to 13a or 13b gave a value of $7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ for the extinction coefficient of the two nitrile imines at 380 nm in benzene. Note that this value is less than half that ($17.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 378 nm) estimated for *N,C*-diphenylnitrile imine in EPA glass at 77 K [18].

Direct laser excitation (248, 266 or 308 nm) of 13a or 13b in benzene or acetonitrile gives transient absorption spectra (Figs. 6(B) and 6(C)) with major maxima at about 370 - 375 nm. The transients are very long lived ($\tau > 500 \mu\text{s}$) and are reminiscent of those observed under benzophenone triplet sensitization of 13a or 13b and under direct excitation of 1a or 1b. Interestingly, under both sensitization and direct excitation, the transient spectra attributable to *N,C*-diarylnitrile imines in fluid solutions at 295 K show a second absorption maximum at about 320 nm. This maximum is missing in the low temperature spectra of the nitrile imines photogenerated from the tetrazoles in glass at 77 K (see below). As a matter of fact, the short-wavelength maximum (320 nm) is more prominent than its longer-

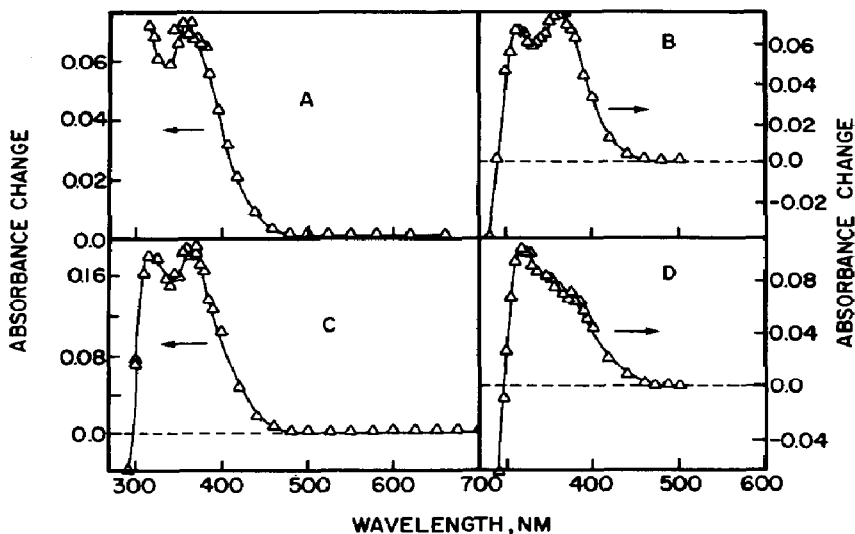


Fig. 6. Transient absorption spectra at 2 - 5 μ s following (A) 337.1 nm laser flash photolysis of *p*-methoxyacetophenone in the presence of 1 mM 13a, and 248 nm laser flash photolysis of (B) 13a in acetonitrile, (C) 13b in acetonitrile and (D) 13a in cyclohexane.

wavelength counterpart (370 nm) in such solvents as cyclohexane (Fig. 6(D)), 2-methyltetrahydrofuran and methanol. The *N,C*-diarylnitrile imines upon reaction with acids give rise to transients (probably protonated forms) with intense maxima at 320 nm, and in the course of flash photolysis of the tetrazoles we occasionally observed growths of transient absorption at or near this wavelength (ascribable to reactions with adventitious acid impurities). In order to sort out the spurious origin of the 320 nm peak, experiments were performed with 13a in acetonitrile that had been freshly passed through a column of basic alumina and in aqueous acetonitrile (about 1% water) containing about 0.1 mM NaOH. The transient spectra under these conditions were no different from those presented in Fig. 6(C). Also, the relative intensity of the 320 nm peak with respect to that at 370 nm for the transient photogenerated from 13a in acetonitrile by 248 nm laser pulses remained unchanged upon varying the laser intensity both with and without a 300 nm cut-off filter (Corning 0-54) in the path of the analyzing light (before it reached the photolysis cell). These findings suggest that the 320 nm peak is not due to a secondary transient produced from a photoproduct (e.g. nitrile imine).

Upon laser flash photolysis in acetonitrile, tetrazoles 13c - 13e produce transients with absorption maxima considerably blue shifted relative to those from 13a and 13b. These are shown in Fig. 7. In the case of 13d, the major transient has its principal absorption maximum (315 nm) red shifted relative to that in the case of 13c ($\lambda_{\text{max}} = 295$ nm). It displays an additional minor band system in the visible region (450 - 600 nm). Furthermore, the decay of this transient occurs relatively rapidly ($\tau = 5$ μ s) and is enhanced in the

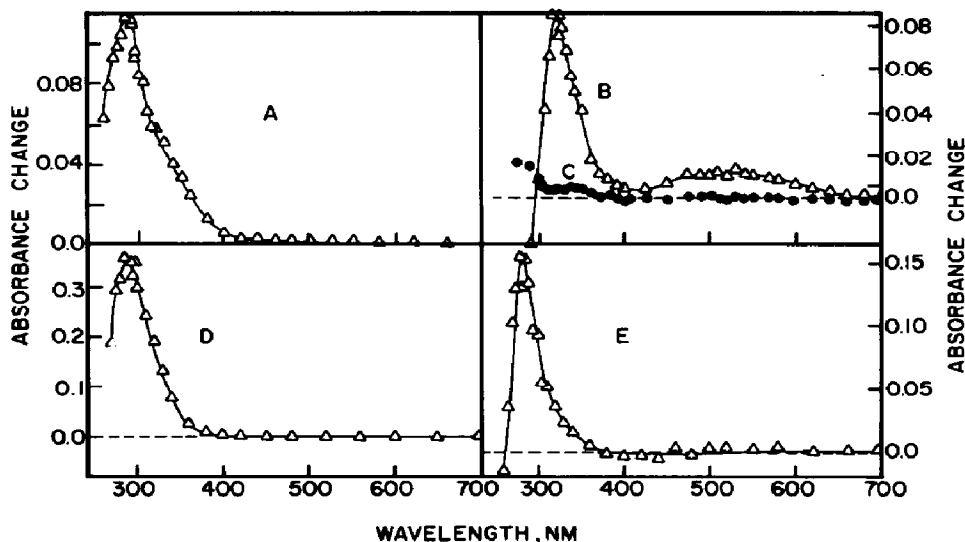


Fig. 7. Transient absorption spectra upon 248 nm laser flash photolysis of (A) 13c, (B,C) 13d, (D) 13e and (E) 13f in acetonitrile. The spectra correspond to (A) 5, (B) 0.2, (C) 7, (D) 5 and (E) 5 μ s following the laser flash.

presence of oxygen ($k_{q,O_2} = 1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile). It seems probable that this oxygen-quenchable, relatively long lived, species originates from the tautomeric form of 13d, namely 14a (Fig. 8) while the residual absorption following its decay corresponds to C-phenylnitrile imine.

The evidence for the involvement of the tautomer 14a comes from the laser flash photolysis of its methyl analogue 14b (obtained as a byproduct in the course of the synthesis of 13c). The tetrazole 14b produces an oxygen-quenchable transient having spectral and kinetic behavior very similar to that in the case of 13d, namely λ_{max} of 320 nm (major) and 520 nm (minor), a lifetime of 7.5 μ s and $k_{q,O_2} = 1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The transient spectrum in acetonitrile is shown in Fig. 9(A). We note that for tetrazoles unsubstituted at the 2-position the tautomeric form 14 is known to predominate over the form 13d [44]. The most plausible assignment for the major transient observed in the case of 13d and 14b lies in terms of the nitrene 15a or 15b produced via photoextrusion of nitrogen. A similar nitrene (15c) has been implicated in the photochemical transformation of the tetrazole 14c to 2-phenylbenzimidazole and diphenylcarbodiimide [45].

The 308 nm laser flash photolysis of benzene solutions of 13a or 13b optically matched with a benzene solution of benzophenone led to estimates of quantum yields of photoextrusion of nitrogen from 13a and 13b (against $\phi_T = 1$ for benzophenone). Based on a value of $1.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for ϵ_{NI} at 370 nm, values of 0.36 and 0.29 were obtained for quantum yields of 13a and 13b respectively. Note that the low values may be a reflection of the fact that the assumed ϵ_{NI} is incorrect (*i.e.* much higher than the actual value in fluid solutions, see Section 4).

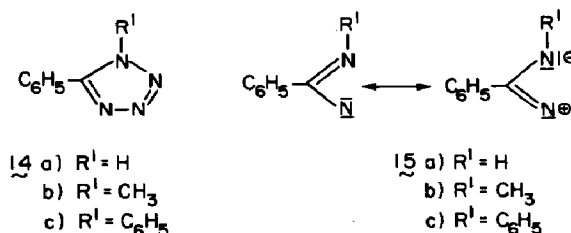


Fig. 8. Compounds 14 and 15.

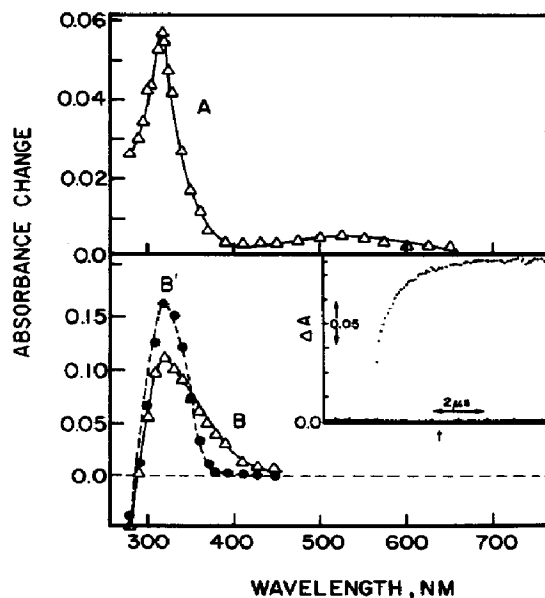


Fig. 9. Transient absorption spectra upon (A) 266 nm laser flash photolysis of 14b in acetonitrile and (B,B') 248 nm laser flash photolysis of 13a in the presence of 4.2 mM trifluoroacetic acid in acetonitrile. The spectra correspond to (A) 1, (B) 0.5 and (B') 6 μs following the laser flash. Inset, kinetic trace for growth of transient absorption at 320 nm in the last case.

3.4. Quenching behavior of nitrile imines

The chemical trapping of nitrile imines by alkene or alkyne derivatives (dipolarophiles), nitriles and HX-type molecules is well known [13 - 19, 45 - 48]. The laser flash photolysis (337.1 nm) of 1a and 1b in neat benzonitrile shows that the photogenerated 380 nm species do not undergo any appreciable decay over 100 μs or so in this solvent ($\tau > 500 \mu s$). This behavior suggests that the kinetics of the reaction of *N,C*-diarylnitrile imines with benzonitrile leading to 3-phenyl-1,2,4-triazoles [15] are very slow ($k_q < 10^2 M^{-1} s^{-1}$). Also, over about 100 μs , the decay of laser-flash-photolytic *N,C*-diphenylnitrile imine from 1a in benzene is found to be slightly enhanced in the presence of excess dimethyl acetylenedicarboxylate (DMAD; about 1 M), suggesting its slow quenching by the dipolarophile. However, the changes in the decay kinetics on this time scale are too small for reliable measurements of the quenching rate constants to be made.

For precise measurements of the rate constants for the quenching of *N,C*-diarylnitrile imines by DMAD, conventional lamp flash photolysis ($\lambda_{ex} = 300 - 350 \text{ nm}$) was used with sydnone 1a, 1b and 1e and tetrazole 13a as substrates in benzene. In these experiments, the concentrations of the sydnone were 0.06 - 0.12 mM while the tetrazole (0.18 mM) was used in the presence of benzophenone (2.8 mM) sensitizer. The decay of nitrile imines was followed at 380 - 390 nm over milliseconds as a function of

DMAD concentration (0 - 60 mM). The quenching rate constants k_q were obtained from the slopes of the linear plots of the observed pseudo-first-order decay rate constants against [DMAD]. For 1a, 1b and 13a, the k_q data are given in Table 3. Note that k_q in the case of 1a ($4.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) is practically the same as that in the case of 13a ($5.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$); this establishes that the same *N,C*-diphenylnitrile imine is photogenerated from the two substrates (as expected). Interestingly, the long-lived transient in the case of 1e, presumably *C*-phenylnitrile imine (see below), was found to be practically non-quenchable by DMAD at the concentrations employed (60 mM or lower).

Not surprisingly, carboxylic acids are found to be efficient quenchers for nitrile imines. In particular, we have obtained k_q data with trifluoroacetic acid as the quencher. The kinetics of decay of transient absorptions due to nitrile imines was followed as a function of the acid. The k_q data are compiled in Table 3. Corresponding to the decay of *N,C*-diarylnitrile imine transient absorption at wavelengths longer than 350 nm in the presence of trifluoroacetic acid, growths of absorption were observed at shorter wavelengths. This is illustrated by the transient spectra in the case of 13a in Figs. 9(B) and 9(B'). Apparently, the product of protonation has a maximum at 320 nm. Benzoic and acetic acids are found to be weaker quenchers for *N,C*-diarylnitrile imines. The k_q values for the two acids are $8.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $2.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ respectively, with 1a as the substrate in acetonitrile. The reactivity of *N,C*-diarylnitrile imines with diethylamine is found to be similar, the k_q values being $1.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $0.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ with 1a and 1b as the substrates respectively (in benzene).

As noted earlier, upon gradual addition of acids, the fast transient absorptions in the case of sydnone 1d - 1f become progressively longer lived. The quenching effect of acids on the slow components (presumably,

TABLE 3

Bimolecular rate constants for the quenching of nitrile imines at 295 K

Nitrile imine precursor	Solvent	k_q ($\text{M}^{-1} \text{ s}^{-1}$)	
		DMAD	TFA
1a	Benzene	4.9×10^3	2.4×10^9
1a	Acetonitrile		2.4×10^8
1b	Benzene	8.7×10^3	2.0×10^9
1b	Acetonitrile		3.1×10^8
13a	Benzene	5.3×10^3	2.2×10^9
13a	Acetonitrile		2.3×10^8
13b	Acetonitrile		3.8×10^8
13c	Acetonitrile		4.4×10^9
13d	Acetonitrile		9.4×10^7
13f	Acetonitrile		1.5×10^9

nitrile imines) could not be studied in these cases because of this complication. Interestingly, the 320 nm transients in the cases of 13d and 14b (assigned as nitrenes 15a and 15b) are quenched by trifluoroacetic acid with rate constants of $1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ respectively (in acetonitrile).

3.5. Steady state photolysis of tetrazoles and sydnone at 77 K

Upon steady state photolysis (253 or 280 nm) of tetrazoles 13a - 13c in EPA or 2-methyltetrahydrofuran (2-MTHF) glasses at 77 K, photoproducts are produced with the absorption spectra shown in Fig. 10. The photoproduct absorption spectrum ($\lambda_{\text{max}} = 375 \text{ nm}$ in EPA at 77 K) in the case of

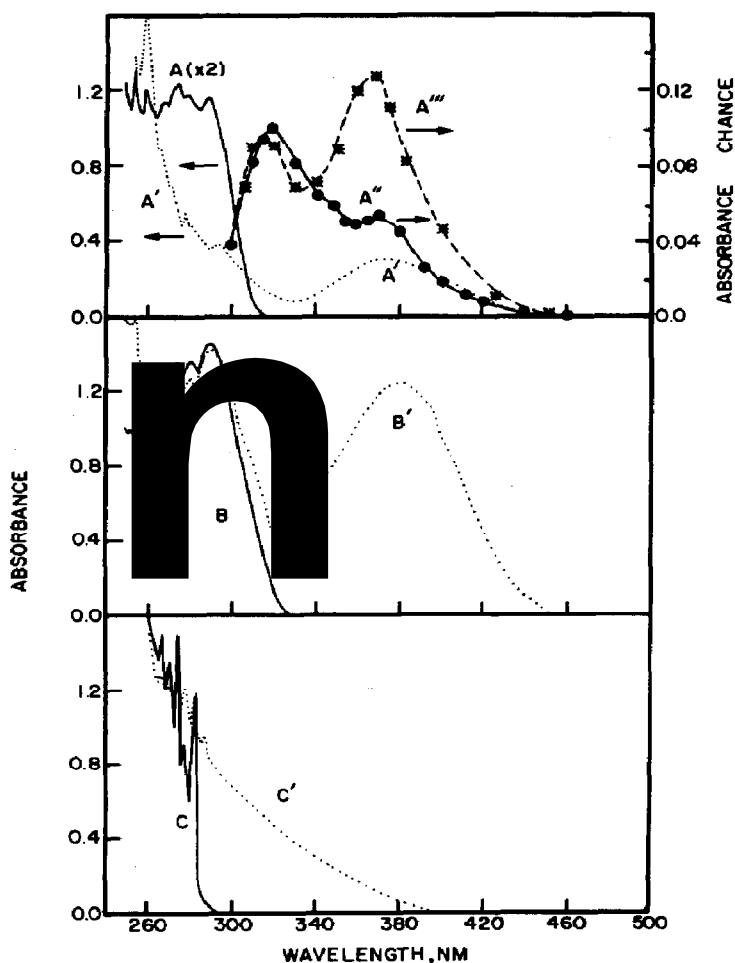


Fig. 10. Absorption spectral changes at 77 K upon steady state photolysis (253 nm) of (A,A') 13a in 2-MTHF, (B,B') 13b in EPA and (C,C') 13c in 2-MTHF (A - C, before photolysis; A' - C', after about 1 h photolysis). The transient spectra A'' and A''' were obtained at 5 μs following 248 nm laser flash photolysis of 13a in 2-MTHF at 295 K and 160 K respectively.

13a is found to resemble the spectra of the same nitrile imine or related imines under similar conditions reported in the literature [18, 20]. Upon warming the photolyzed glasses in the case of 13a or 13b in 2-MTHF to 110 - 112 K and recooling them to 77 K, the absorption spectra of *N,C*-diarylnitrile imines are recovered unchanged in shape and location. For comparison, in Figs. 10(A'') and 10(A''') we have shown the spectra of *N,C*-diphenylnitrile imine photogenerated from 13a in 2-MTHF by 248 nm laser flash photolysis at room temperature (295 K) and at 160 K. Note that upon lowering the temperature the relative intensity of the 320 nm peak is reduced. Tetrazole 13d proved to be photoresistant to prolonged 253 nm photolysis in EPA or 2-MTHF glass at 77 K. In the case of 13e or 13f, although bleaching was observed in the region of ground state absorption, no significant absorption developed at longer wavelengths.

Sydnone 1a - 1e were also subjected to 320 and 366 nm photolysis in 2-MTHF and EPA at 77 K in order to see if the diaziridine formation and/or carbon dioxide elimination occurs at this low temperature. For sydnones 1a and 1b, no change occurs in the long-wavelength band system (300 - 380 nm) upon prolonged irradiation (366 nm) at 77 K. Also, the intensity of their blue fluorescence does not undergo any significant reduction during irradiation at 77 K. Upon warming the photolyzed glass to room temperature, the spectrum of the unphotolyzed sydnone is fully recovered. Under similar conditions of irradiation in fluid solutions at room temperature, photodegradation of the sydnone occurs readily, as is evident from the loss of absorption at 300 - 380 nm and the appearance of new absorption bands at below 320 nm. All these results suggest that sydnones 1a and 1b are resistant to phototransformation to the bicyclic form (diaziridine) and/or loss of carbon dioxide in the low temperature glass.

The results of the photolysis (320 nm) of 1d - 1f in EPA or 2-MTHF glass are interesting. As shown in Fig. 11, photobleaching of these sydnones occurs readily at low temperatures. The photoproduct (or one of the photoproducts) in the case of 1d as well as that of 1f is characterized by a sharp absorption peak at 314 - 315 nm. This peak is absent in the case of 1e and appears to be linked with the *p*-tolyl group. Upon warming the photolyzed glass (in all three cases) to 110 - 120 K, a yellow-to-red coloration develops. Upon recooling to 77 K, broad absorption spectra ($\lambda_{\max} = 315 - 330$ nm) extending well into the visible are obtained. Upon warming to a higher temperature (210 - 215 K), the yellow-to-red coloration fades away and the absorptions in the visible region mostly disappear (as seen by recooling to 77 K and recording the spectra at this temperature). We note that the absorption changes found for sydnones 1d - 1f are reminiscent of those documented by Trozzolo *et al.* for 3-(3-pyridyl)sydnone in a KBr disc, except that the final coloration in the latter case is blue ($\lambda_{\max} = 630$ nm) and is persistent in the disc at room temperature. Sydnone 1d also undergoes photobleaching at 77 K, but the process is slow and no visible color develops upon warming the photolyzed glass.

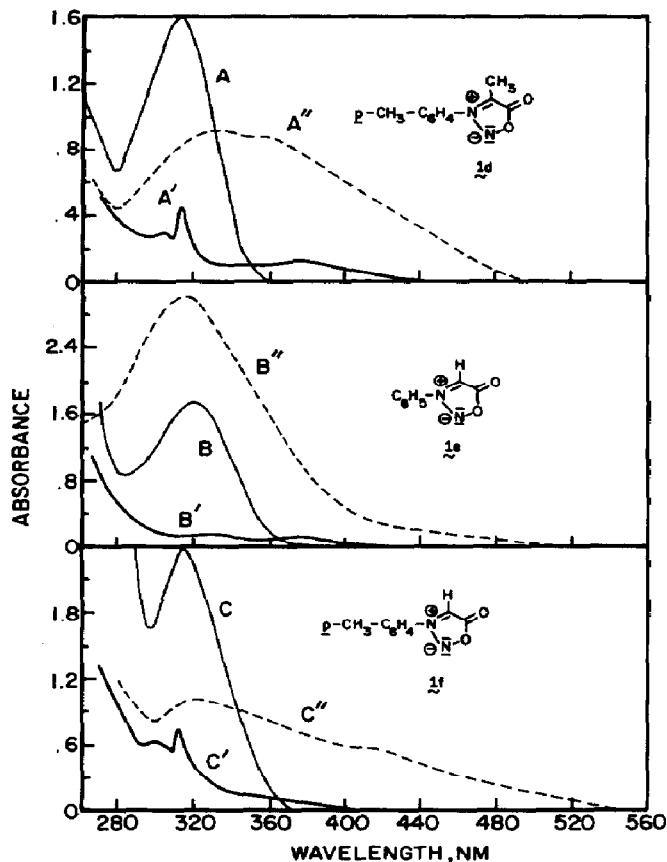


Fig. 11. Absorption spectral changes upon steady state photolysis (320 nm) of (A - A'') 1d, (B - B'') 1e and (C - C'') 1f in EPA glass at 77 K (A - C, before photolysis; A' - C', after about 1 h photolysis; A'' - C'', after slow warming to 110 - 115 K and then recooling to 77 K).

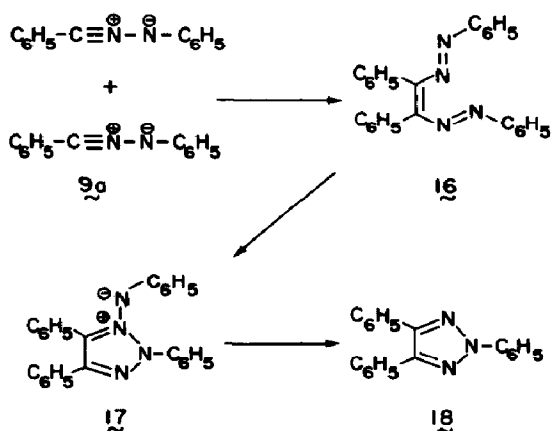
4. Discussion

The assignment of the slowly decaying species ($\lambda_{\max} = 375 - 380$ nm), photogenerated from sydnone 1a and 1b, to nitrile imines rests on the similarity of its spectral and kinetic behavior to those of the products of photolysis of the corresponding tetrazoles 13a and 13b (at both room temperature and 77 K). Previous studies [18 - 20] based on IR and UV spectroscopy have confirmed that photoextrusion of nitrogen from tetrazole 13a and analogous systems takes place at low temperatures leading to *N,C*-diarylnitrile imines. Our results show that in fluid solutions at room temperature *N,C*-diarylnitrile imine intermediates are quite long lived with lifetimes in the millisecond time domain (in the absence of a dipolarophilic or electrophilic quencher). From chemical and spectral evidence, the principal mode of decay of *N,C*-diphenylnitrile imine is recognized to be its head-to-head dimerization leading to 1,2-bis(phenylazo)-1,2-diphenylethylene (16) [6, 18,

22] (see Scheme III). The latter, upon photolysis, loses phenyl nitrene via a cyclized intermediate (17) to give 2,4,5-triphenyl-1,2,3-triazole (18).

Our results show that the photoextrusion of carbon dioxide from sydnones 1a and 1b leading to nitrile imines occurs very quickly (*i.e.* within the duration of the nanosecond laser pulses). This implies that the postulated intermediates 2 - 4 or 8 (Scheme I) are either very short lived or are not involved in the phototransformation of the sydnones to nitrile imines. In particular, species 2 - 4 and 8 are expected to absorb only in the UV region (below 350 nm). If any of them were to act as a relatively slow precursor for the nitrile imine the intermediacy would manifest itself as a growth process for the transient absorption due to the nitrile imines at longer wavelengths (350 - 450 nm).

Based on the evidence available to us, it is not possible to arrive at an unequivocal interpretation for the fast transient absorption processes observed in the case of sydnones 1d - 1f. The fact that the transient absorption extends to long wavelengths in the visible (up to 600 nm in benzene) rules out assignment in terms of any of the intermediates 2, 4, 6, 8 or 9 ($R_2 \equiv H$ or CH_3). Note that *N*-phenylnitrile imine and *C*-methyl-*N*-phenylnitrile imine absorb at short wavelengths ($\lambda_{max} = 290$ nm) and possess long lifetimes ($\tau > 500$ μs) when photogenerated from tetrazoles 13e and 13f in fluid solutions. An explanation in terms of ketene structure 7 with zwitterionic character seems untenable because alcohols and acids render the transients in question longer lived rather than quenching them. It is possible that the fast-decaying transient is an ylide of structure 3 or 6. The lengthening of lifetimes upon addition of alcohols is not surprising because such behavior has been observed for azomethine ylide systems derived from benzoylaziridines [49]. We note that sydnones 1d - 1f which develop coloration upon steady state photolysis at low temperatures are also the substrates that produce the non-triplet-like fast-decaying transients upon laser flash photolysis at room temperature. The absorption spectra of the photoproducts under the two conditions are also reasonably similar, suggesting that the same species may be responsible for the low temperature photochromism and the room-tempera-



Scheme III.

ture fast transient behavior. We tend to favor an assignment to structure 6 because, with such a structure, one can explain the red shift in the absorption on going from 1e to 1d and 1f in terms of greater delocalization of the positive charge induced by the *p*-tolyl group.

The present study shows that the transient spectra of *N,C*-diarylnitrile imines photogenerated from the corresponding tetrazoles at room temperature are significantly dissimilar to those in glass at 77 K. The difference lies in the prominence of the 320 nm band system in fluid solutions at room temperature. One reason for the lack of spectral similarity may be that the nitrile imine when photogenerated from a tetrazole in rigid glass possesses a structure (namely, bent) different from that (namely, linear) in fluid solutions. This is ruled out by the fact that upon softening the glass by warming to 110 - 112 K and recooling the absorption spectra remain unchanged. An explanation in terms of formation of the dimer, *i.e.* 16 (Scheme III), in fluid solutions seems unlikely on the basis of the following. In the spectral region 300 - 450 nm, 16 shows dual maxima, at 340 nm (major) and 400 nm (minor), in EPA at 170 K [18]. These do not agree well with the maxima, namely 320 nm and 375 nm, seen for the laser-flash-photolytic transient from 13a in solution at 295 K. More importantly, we do not observe any kinetics associated with dimer formation or monomer decay and the transient spectra remain practically unchanged in the 100 μ s or so following the laser flash. Prompt formation of 16 through loss of two N₂ molecules from a ground state dimer of 13a is not supported because of the lack of dependence of the transient spectra on the concentration of 13a. It is possible that at room temperature (295 K) the nitrile imine is in fast equilibrium with the small amount of the diazine 8 present, the latter contributing in the short-wavelength region. Alternatively, the intrinsic spectra of *N,C*-diarylnitrile imines are strongly temperature dependent. In both cases, ϵ_{NI} at room temperature would be very different from that determined from photolysis at 77 K. Thus, the quantum yields of nitrile imine formation from sydnones 1a and 1b or tetrazoles 13a and 13b estimated on the basis of ϵ_{NI} at 77 K should be considered as very approximate.

Acknowledgments

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