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Kinetics and Mechanism of the Addition of Amines to Carbon Disulfide in Ethanol

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The reactions of morpholine, benzylamine, and pyrrolidine with carbon disulfide are studied in ethanol, at 25 °C, ionic strength 0.0024 M (maintained with lithium chloride). The reactions are found to proceed through the dithiocarbamic acid intermediate **1**, which yields the dithiocarbamate anion **2** by proton loss to the amine. The reactions of the substrate with morpholine and benzylamine exhibit reversibility, due to protonation of **2** (to yield **1**) by the corresponding conjugate acid of the amine. Also, a parallel reversible path between reactants and **2** is found for the latter reactions. This is interpreted as ethoxide anion catalysis of amine attack in the forward step and general-acid catalysis by ethanol in the reverse one. In the reaction with pyrrolidine, the formation of **1** is the rate-determining step, and **1** gives **2** irreversibly. No catalysis by ethoxide anion is found for this reaction. Pyrrolidine is ca. 200-fold more nucleophilic than piperidine toward carbon disulfide. Comparison of this value with the ones toward other substrates is made. Tetramethylenedithiocarbamate is found to be much more stable than the piperidino analogue toward decomposition. The stabilities of both are analyzed and compared with those shown by other compounds possessing the two amino moieties.

Introduction

Although the kinetics of decomposition of dithiocarbamates in aqueous solution has been subject to much study[1-5] (eq 1, where R^1 or R^2 can be a hydrogen atom),

$$R^1R^2NCS_2^- \overset{H^+}{\rightleftharpoons} R^1R^2NH + CS_2 \qquad (1)$$

little is known about the reverse reaction, i.e., addition reactions of amines to carbon disulfide. We are aware of only a few works on the latter reactions,[2,6] with two of them involving amino acids as nucleophiles.[6] The influence of the solvent on the mechanism of both steps has received much less attention, the decomposition of dithiocarbamates being studied only in methanol–water[3,4] and dioxane–water[3] mixtures.

Following previous work in our laboratory on the reaction of carbon disulfide with piperidine in ethanol,[7] we report in this paper the reactions of the same substrate with pyrrolidine, morpholine, and benzylamine in ethanol in an attempt to shed more light on the mechanism of amine addition to carbon disulfide in this solvent.

Experimental Section

Materials. Pyrrolidine, morpholine, and benzylamine were distilled over potassium hydroxide. All other reagents were purified as previously described.[7]

The ammonium salts of tetramethylene-, oxydiethylene-, and benzyldithiocarbamates were prepared by a standard procedure.[8,9] The IR and ^{1}H NMR spectra of these compounds were in good agreement with their structures.

Kinetic Measurements. The kinetics were followed by recording the dithiocarbamate increase at 290–294 nm by means of a Pye Unicam SP 1800 spectrophotometer, as previously described.[7]

All reactions were found to follow pseudo-first-order kinetics. The total concentration of the amine (free base plus cationic forms) was at least 20-fold in excess over that of the substrate. The pseudo-first-order rate constants observed (k_{obsd}) were determined by means of "infinity" plots, except in the slowest reactions where Guggenheim plots were employed. The plots remained linear for at least three half-lives, and those resulting with correlation coefficients worse than 0.999 were discarded. In order to be sure that equilibrium was reached and carbon disulfide neither escaped nor was oxidized, tightly stoppered cells (Hellma 110-QS) were used, and some of the slow reactions were followed for 10 half-lives. No noticeable absorbance changes were found after 6 half-lives.

The experimental conditions of the reactions and the k_{obsd} obtained are shown in Table I.

Product Studies. The ammonium salts of oxydiethylene-, benzyl-, and tetramethylenedithiocarbamates were found to be the stable products of the kinetic reactions. This was achieved by comparison of the UV spectra of the kinetic solutions at infinity time with those of authentic samples (prepared as in Materials) in the same experimental conditions of the kinetic reactions.

Results

The reactions of amines with carbon disulfide under the conditions of the present work are subject to the rate law given by eq 2, where k_{obsd} and k_N are the pseudo-first-order

$$k_{obsd} = k_0 + k_N[N] \qquad (2)$$

and the second-order rate constants observed, respectively, k_0 is the rate constant in the absence of amine, and N represents the amine free-base form.

The values of k_0 and k_N were obtained as the intercept and the slope, respectively, of linear plots of k_{obsd} vs. molar concentration of amine free base, at constant molar fraction of the free base. Table II shows the values of k_0 and k_N obtained for the reactions of the three amines under study.

In the reactions of the substrate with benzylamine and morpholine, k_0 and k_N exhibited a dependence on the free-amine fraction. Plots of k_0 vs. $[NH^+]/[N]$ and k_N vs. $[N]/[NH^+]$ (where NH^+ represents the conjugate acid of the amine) gave straight lines with correlation coefficients 0.996–0.9996.

The reactions of the substrate with pyrrolidine did not show any dependence of k_N on the free-amine fraction and the value of k_0 was too small to be measured (Table II). The final value of k_N was obtained, in this case, as the slope of a plot of k_{obsd} vs. [N], including all the runs at the three

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Table I. Experimental Conditions and k_{obsd} for the Reactions of Carbon Disulfide[a] with Amines in Ethanol at 25 °C, Ionic Strength 0.0024 M (Maintained with Lithium Chloride)

amine	$10^3[N]_{tot}$,[b] M	free-base[c] fraction	$10^3 k_{obsd}$, s^{-1}	number of runs
morpholine	5.8-9.6	0.813	3.45-3.88	16
	1.9-9.6	0.873	2.44-3.06	17
	1.9-9.6	0.935	1.55-2.67	11
benzylamine	2.4-4.8	0.620	0.08-0.13	5
	2.4-4.8	0.750	0.09-0.15	5
	2.9-4.8	0.875	0.11-0.18	4
pyrrolidine	1.2-4.8	0.490	1.88-9.73	5
	1.2-4.3	0.620	2.60-10.28	4
	1.2-4.8	0.745	2.70-13.70	5

[a] The initial substrate concentration was (0.5-1.5) × 10^{-4} M. [b] Range of concentration of total amine (free-base plus acidic forms). [c] Molar fraction of amine free base from the total amine.

Table II. Values of k_N and k_0 at Various Free-Amine Fractions for the Aminolysis of Carbon Disulfide in Ethanol at 25 °C, Ionic Strength 0.0024 M (Maintained with Lithium Chloride)[a]

amine	free-base fraction	k_N, s^{-1} M^{-1}	k_0, s^{-1}
morpholine	0.813	4.7 × 10^{-2}	3.4 × 10^{-3}
	0.873	7.4 × 10^{-2}	2.4 × 10^{-3}
	0.935	14.5 × 10^{-2}	1.2 × 10^{-3}
benzylamine	0.620	3.3 × 10^{-2}	3.5 × 10^{-5}
	0.750	3.6 × 10^{-2}	1.9 × 10^{-5}
	0.875	4.3 × 10^{-2}	2.8 × 10^{-6}
pyrrolidine	0.490	4.4	c
	0.620	4.0	c
	0.745	4.1	c
		4.0 ± 0.4[b]	

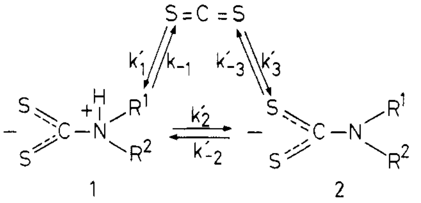
[a] The rate constants were obtained as slopes and intercepts of plots of eq 2 at a given free-amine fraction by least-squares analysis. [b] Value obtained as slope of a plot of eq 2, which included all the points (for the three free-amine fractions) by least-squares treatment. The error is the standard deviation. [c] Negligible values under the experimental conditions.

different free-amine fractions (14 points). The final value of k_N is also shown in Table II.

The reactions of the substrate with morpholine and benzylamine exhibited reversibility as evidenced by the shapes of the absorbance at infinity time (A_∞) vs. [N] curves for these reactions at constant initial substrate concentration. The shapes of these curves are in accord with an equation obtained in the reactions of the substrate with piperidine in the same experimental conditions as in the present reactions.[7]

Considering the dependence of the rate constants observed on the free-amine concentration and on the amine fractions and the dependence of A_∞ on these variables, a scheme of reactions can be envisaged for morpholine and benzylamine (Scheme I). This is the same scheme as the one found in the reactions of the substrate with piperidine.[7]

Scheme I



$$k'_1 = k_1[HNR^1R^2]$$
$$k'_2 = k_2[HNR^1R^2]$$
$$k'_{-2} = k_{-2}[H_2^+NR^1R^2]$$
$$k'_3 = k_3[EtO^-][HNR^1R^2]$$
$$k'_{-3} = k_{-3}[EtOH]$$

From the application of the steady-state approximation to the dithiocarbamic acid intermediate 1, together with the assumption that $k_{-1} \ll k_2[N]$ and the comparison of the resulting k_{obsd} with eq 2, eq 3 and 4 results,[7] where K_{-2}

$$k_0 = k'_{-3} + k_{-1}K_{-2}[NH^+][N]^{-1} \quad (3)$$

$$k_N = k_1 + k_3K_b[N][NH^+]^{-1} \quad (4)$$

$= k_{-2}/k_2$ and $K_b = [NH^+][EtO^-]/[N]$. Table III shows the values of the rate constants obtained as intercepts and slopes of plots of eq 3 and 4.

Equivalent expressions to eq 3 and 4 can be derived from Scheme I by assuming $k'_2 = k_2[EtO^-]$ and $k'_{-2} = k_{-2}[EtOH]$. The same dependence of k_0 and k_N on the amine ratios (eq 3 and 4) was found in the reactions of the substrate with piperidine under the same experimental conditions.[7]

Since in the reactions of the substrate with pyrrolidine, k_0 was negligible and k_N was approximately constant (Table II) under the experimental conditions employed, eq 3 and 4 lead to $k'_{-3} \approx k_{-1}K_{-2} \approx k_3K_b \approx 0$, and $k_N = k_1$ for these reactions. Since K_b (basicity constant) for pyr-

Table III. Values of the Rate Constants of Scheme I for the Reactions of Carbon Disulfide with Amines[a]

amine	k_1, s^{-1} M^{-1}	k_1K_2, s^{-1}	k'_{-3}, s^{-1}	$10^3 k_3K_b$, s^{-1} M^{-1}	$10^6 k_3$,[b] s^{-1} M^{-1}	pK_a[c]
morpholine	(5.9 ± 3) × 10^{-3}	(1.3 ± 0.2) × 10^{-2}	(3.5 ± 2) × 10^{-4}	9.7 ± 0.5	63 ± 3	8.3
benzylamine	(3.0 ± 0.2) × 10^{-2}	(6.8 ± 1.4) × 10^{-5}	$<10^{-6}$[d]	1.8 ± 0.2	1.1 ± 0.1	9.3
piperidine	(1.7 ± 2) × 10^{-2}	(1.0 ± 0.1) × 10^{-3}	(3.0 ± 6) × 10^{-5}	150 ± 20	1.5 ± 0.1	11.1
pyrrolidine	4.0 ± 0.4					11.3

[a] Experimental conditions as in Table II. Values obtained as slopes and intercepts of plots of eq 3 and 4, by least squares treatment, and from ref 7 (piperidine). Errors shown are standard deviations. [b] Values obtained by dividing k_3K_b by K_b. The K_b values of the amines in ethanol were obtained from $K_b = K_{EtOH}/K_a$, where K_a is the acidity constant of the conjugate acid of the amine and $K_{EtOH} = 10^{-19.1}$ is the ionic product of ethanol in the same solvent.[11] The pK_a values in ethanol at 25 °C were assumed to be 9.3, 10.3, and 12.1 for morpholinium, benzylammonium, and piperidinium ions, respectively, i.e., one unit higher[11] than their pK_a values in water (shown in the last column of this table). [c] pK_a values in water, at 25 °C.[12] [d] The value and standard deviation obtained for this rate constant was (5.0 ± 5.5) × 10^{-6} s^{-1}.

rolidine is not zero, it follows that $k_3 \approx 0$, which together with $k_{-3} \approx 0$ leaves Scheme I for the pyrrolidine reaction with only the left-hand side (steps 1 and 2 only). The rate law observed implies $k_2[\mathrm{N}] \gg k_{-1}$, therefore the rate-determining step is the pyrrolidine attack on the substrate (k_1 step).

Since, for the pyrrolidine reactions, $k_{-1}K_{-2} = k_{-1}k_{-2}/k_2 \approx 0$ and $k_{-1}/k_2 \approx 0$,[10] it follows that $k_{-2} \gtrsim 0$. Therefore, in the reactions with pyrrolidine, two situations regarding the second step of Scheme I can arise: either it is practically irreversible toward dithiocarbamate or it is an equilibrium step during the reactions. Taking into account that A_∞ does not show any dependence on $[\mathrm{N}]/[\mathrm{NH}^+]$, the equilibrium between **1** and **2** for the pyrrolidine reactions can be ruled out under the conditions of the experiments.

In the hydrolysis of dithiocarbamates,[4] monothiocarbamates,[5] and carbamates[5] of basic amines, it was found that an equilibrium step occurs between the carbamate derivatives and their conjugate acids followed by the slow decomposition of the latter toward amine and $\mathrm{CX_2}$ (X = oxygen and/or sulfur atoms). This reaction scheme is in accord with the one found for the reactions of carbon disulfide with morpholine and benzylamine (this work) and with piperidine,[7] where $k_2[\mathrm{N}] \gg k_{-1}$, which effectively means a rapid equilibrium between **1** and **2** (Scheme I).

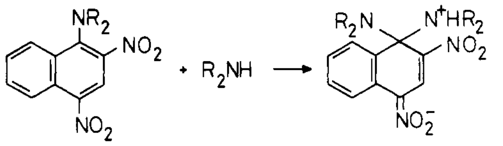
Discussion

The k_3 step of Scheme I has been found likely to be amine attack on the substrate base catalyzed by ethoxide anion.[7] If this is a concerted process, microscopic reversibility demands that ethanol acts as an acid catalyst in the reverse (k_{-3}) reaction. The value of k_{-3} should decrease with increasing basicity of the leaving group (amine) of the dithiocarbamate when similar structures are compared. In accordance to this, Table III shows that the value of k'_{-3} for the morpholino derivative is larger than those for the more basic benzyl- and pentamethylenedithiocarbamates. The situation is not so clear when the values for the piperidino and benzylamino derivatives are compared in view of the uncertainty in the determination of the former.

Pyrrolidine is ca. 200-fold more nucleophilic toward carbon disulfide than piperidine in spite of being only slightly more basic (Table III). The lack of a k_3 step for the reactions with pyrrolidine is in accord with the behavior exhibited by the most basic amines in their reactions with carboxylic acid derivatives. They do not show any term other than the uncatalyzed nucleophilic reaction.[13]

The higher value of k_3 for morpholine relative to the other more basic amines (Table III) is in accord with its larger acidity and also with the principle that "catalysis occurs where it is most needed",[14] since morpholine is the least nucleophilic of the amines as indicated by the k_1 values of Table III.

The remarkable nucleophilic reactivity of pyrrolidine compared to piperidine toward a carbonyl or thiocarbonyl carbon is unprecedented to our knowledge. Pyrrolidine is only twice as reactive as piperidine toward carbonyl sulfide.[15] In the reactions of these amines with aromatic carbon centers such as 2,4-dinitrophenyl phenyl ether[16] and 2,4-dinitro-1-naphthyl ethyl ether,[17] pyrrolidine shows an enhanced nucleophilic reactivity of only 2–3-fold relative to piperidine, although for the overall reactions pyrrolidine shows a spectacular higher reactivity. This higher overall rate was attributed to the superior ability of the pyrrolidino moiety, in the tetrahedral intermediate formed, to expel the ethoxide or phenolate leaving group. A remarkably higher nucleophilicity of pyrrolidine compared to piperidine (ca. 400-fold) was found in the reactions of these amines with their *N*-(2,4-dinitro-1-naphthyl) derivatives[18] (eq 5), although the electrophilic center of the substrate is different from the one described in this paper.



(5)

The lack of reversibility found for the reactions with pyrrolidine under the experimental conditions used can be explained through the higher stability toward solvolysis of tetramethylenedithiocarbamate relative to the other dithiocarbamates. This superior stability is reflected in the much slower rate of decomposition of the pyrrolidino adduct than the piperidino one in acidic aqueous methanolic solutions at 25 °C.[19,20] In 98% methanol–water solution the second-order rate constant for acid decomposition of tetramethylenedithiocarbamate[19] is $k_\mathrm{H} = 0.14$ $\mathrm{s^{-1}\,M^{-1}}$. This value can be compared to the corresponding one in the acid methanolysis of piperidinedithiocarbamate:[20] $k_\mathrm{H} = 1.93 \times 10^3\ \mathrm{s^{-1}\,M^{-1}}$. Also, in acidic aqueous solution at 25 °C, the pyrrolidino adduct decomposes much more slowly[3] ($k_\mathrm{H} = 3.5 \times 10^{-3}\ \mathrm{s^{-1}\,M^{-1}}$) than the piperidino one[4] ($k_\mathrm{H} \approx 50\ \mathrm{s^{-1}\,M^{-1}}$).

The acid-catalyzed decomposition of dithiocarbamates of cyclic secondary amines in aqueous solution at 30 °C exhibits a linear Brönsted-type plot (log k_H vs. basicity of the amine leaving group) with a small negative slope.[4,5] The line does not include tetramethylenedithiocarbamate, which should give a large negative deviation (see above). *N*-alkyldithiocarbamates show much less reactivity than the cyclic secondary amino derivatives on the same plot.[5] These results are in agreement with our findings. If log $k_{-1}K_{-2}$ vs. pK_a of the conjugate acid of the amine is plotted for the present reactions (Table III) and a straight line is drawn through the piperidino and morpholino derivatives, the line shows a small negative slope, and a large negative deviation is exhibited by benzyldithiocarbamate.

A Brönsted-type plot for the k_{-3} step (log k'_{-3} vs. basicity of the amine leaving group, Table III) looks very similar to the one found for $k_{-1}K_{-2}$, but this must be taken with caution in view of the uncertainty in the k'_{-3} value for pentamethylenedithiocarbamate.

When log k_3 is plotted against basicity of the amine (Table III), again a similar picture obtains. The straight line drawn through morpholine and piperidine has a negative slope, and benzylamine shows a substantial negative deviation to the line, although not as large as in the case of the Brönsted-type plot for $k_{-1}K_{-2}$.

As far as the k_1 step of Scheme I is concerned, a Brönsted-type plot including the four amines of Table III can be drawn. Unfortunately, the large error obtained in

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[10] The fact that $k_{-1}/k_2[\mathrm{N}] \approx 0$ with $[\mathrm{N}] \approx 10^{-3}$ M makes k_{-1}/k_2 even nearer to zero.

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[19] This value was obtained from Figure 3 of ref 3, where $k_\mathrm{obsd} = 0.014$ $\mathrm{s^{-1}}$. Since $[\mathrm{MeOH_2^+}] \approx 0.1$ M, $k_\mathrm{H} \approx 0.14\ \mathrm{s^{-1}\,M^{-1}}$.

[20] From ref 4, in pure methaol $k_\mathrm{obsd} = 1.93 \times 10^{-2}\ \mathrm{s^{-1}}$ when $[\mathrm{MeOH_2^+}] \approx 10^{-5}$ M. From these figures, $k_\mathrm{H} \approx 1.93 \times 10^3\ \mathrm{s^{-1}\,M^{-1}}$.

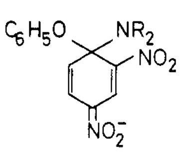
the determination of k_1 for piperidine makes the interpretation of this plot rather uncertain. Nevertheless, it seems that the most likely straight line through morpholine and piperidine would have a small positive slope. Both benzylamine and pyrrolidine would show rate enhancements relative to this straight line. In fact, these two amines will show positive deviations to any straight line drawn through morpholine and piperidine.

The small negative Brönsted slope for $k_{-1}K_{-2}$ and the small positive one for k_1 can be interpreted through an early transition state for the nucleophilic reactions, which means a late transition state for the decomposition of the dithiocarbamates. There should be, therefore, little charge development on the sulfur and nitrogen atoms of the transition-state structure. The same conclusion was reached by Jencks and co-workers for the acid decomposition of carbamates and mono- and dithiocarbamates of basic aliphatic amines.[5]

The large nucleophilic rate enhancement (k_1) of the reaction with pyrrolidine relative to the other reactions means that the transition state for this reaction must be even closer to reactants than the corresponding state for the reactions with the other amines, according to the Hammond postulate.[21] Both the transition state and the cationic adduct 1 of Scheme I for the reactions of pyrrolidine must be stabilized relative to the corresponding structures in the reactions of the other amines, whereas this relative stabilization does not take place in the reactants.

In order to account for the slow decomposition of tetramethylenedithiocarbamate compared to the other adducts, it is also necessary to assume that the former compound is much more stable than the dithiocarbamates of morpholine, benzylamine, and piperidine. Furthermore, the relative stabilization of product 2 of Scheme I for the reactions of pyrrolidine must be larger than for intermediate 1, since K_2 ($= k_2/k_{-2}$) is much larger for the pyrrolidino than for the other amino derivatives (see Results). The value of k_2 should not vary significantly with the nature of the amine, since this step involves the donation of a proton from the ammonium moity of intermediate 1 to the corresponding conjugate amine. Therefore, the value of k_{-2} must be much smaller for tetramethylenedithiocarbamate than for the other amino derivatives. This means that the unshared electron pair on the nitrogen atom of product 2 must be strongly delocalized into the dithiocarbonyl moiety of the pyrrolidino compound compared to the other dithiocarbamates, hence the relatively higher difficulty of its protonation by the pyrrolidinium ion.

The great stability of tetramethylenedithiocarbamate toward protonation and, therefore, toward decomposition is evidenced by its slower rate of solvolysis compared to the piperidine analogue. This must be due to the greater ability of the pyrrolidino moiety compared to the piperidino one to conjugate toward the dithiocarbonyl group of the molecule. The above also occurs when replacing the dithiocarbonyl moiety by an aromatic ring. Bunnett and co-workers found that in the reactions of piperidine and pyrrolidine with 2,4-dinitro-1-naphthyl ethyl and 2,4-dinitrophenyl phenyl ethers, pyrrolidine shows an outstanding higher reactivity.[16,17] This was attributed to the greater ability of the pyrrolidino moieties of 3 and 4 compared to the piperidino one to expel the phenoxy and ethoxy groups, respectively. In other words, it seems that for the products of these reactions, the contribution of canonical forms of coplanar geometry for the amino moiety such as 5 are much more important for the pyrrolidino than for the piperidino derivatives.



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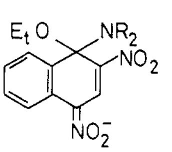

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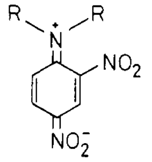

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Although dithiocarbamates are different from aromatic amines, nevertheless, we think that structures similar to 5 have much greater contribution in tetramethylenedithiocarbamate than in the piperidino analogue. This results in a greater difficulty of protonation on the amino moiety of the former.

Acknowledgment. This research was financially supported by Dirección de Investigación de la Universidad Católica de Chile (DIUC), to which we are indebted.

Registry No. Carbon disulfide, 75-15-0; morpholine, 110-91-8; benzylamine, 100-46-9; pyrrolidine, 123-75-1.

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A Procedure for Gas-Phase Dehalogenation of Organic Dihalides with Alkali Metal Vapors Using Microwave and/or Ultrasound Excitation and Matrix Isolation of Products

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Gas-phase dehalogenation of organic dihalides with alkali metal vapors in excess argon is promoted by microwave and/or ultrasound excitation. The products were deposited on a cold window along with excess solid argon. The use of the method is demonstrated on three α,ω-diiodoalkanes. The procedure is useful for the preparation of small amounts of highly strained olefins and ring compounds from their dihalo precursors.

Biradicals and biradical-like species are believed to play a pivotal role in various thermal processes and in very many photochemical processes encountered in organic chemistry.[2-4] In spite of their generally acknowledged

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