Photochemical Reactions of Arenecarbonitriles with Aliphatic Amines. 2. Effect of Amine Structure on Aminyl vs. α-Aminoalkyl Radical Formation

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Abstract: The photochemical reactions of 9-phenanthrenecarbonitrile with several secondary and primary amines and triethylamine have been investigated. Rate constants for fluorescence quenching by secondary and primary amines decrease with amine α-alkylation in spite of increased electron-donor ability of the more substituted amines. This trend is attributed to a steric effect on the equilibrium constant for reversible exciplex formation. The reactions of secondary and primary amines in nonpolar solvent result in selective N–H vs. α-C–H transfer from amine to arene, via a singlet exciplex. The ratio of α-C–H/N–H transfer increases with α-alkylation and increased solvent polarity and is larger for secondary vs. primary amines. The behavior of the intermediate free radical pairs is also dependent upon amine structure and solvent polarity.

Abstraction of a hydrogen atom from a primary or secondary amine can give rise to either an aminyl or α-aminoalkyl radical (eq 1).[1-4] On the basis of current estimates for N–H vs. α-C–H

$$R_2CHNHR' \xrightarrow{-H\cdot} R_2CH\dot{N}R' \text{ or } R_2\dot{C}NHR' \qquad (1)$$

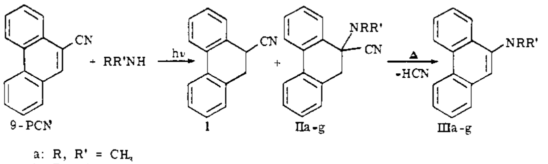
homolytic bond dissociation energies (e.g., $DH° = 96$ kal/mol for Me_2N–H[5] and 87 kcal/mol for $MeNHCH_2$–H[6]) α-aminoalkyl radical formation should be the thermodynamically favored process for both primary and secondary amines. In accord with this prediction, the reactions of primary or secondary amines with *tert*-butoxyl radical[1] or triplet benzophenone[2] yield predominantly the more stable α-aminoalkyl radicals. In contrast, the reactions of numerous singlet arenes with secondary amines yield predominantly the less stable aminyl radicals.[7] In the preceding article selective aminyl radical formation was concluded to be characteristic of relatively nonpolar singlet arene–diethylamine exciplexes (heteroexcimers).[4] A possible rationale for selective N–H transfer in these exciplexes is provided by the recent proposal of Okada, Karaki, and Mataga[8] that the amine N–H is hydrogen bonded to the arene π orbitals. Such a special exciplex geometry might account for selective (kinetically controlled) N–H vs. α-C–H transfer. Increased solvent polarity favors α-aminoalkyl vs. aminyl radical formation, possibly due to increased exciplex polarity and the disruption of N–H hydrogen bonding between the amine and arene.

We report here the results of our investigations of the reactions of singlet 9-phenanthrenecarbonitrile (9-PCN) with several secondary and primary amines and triethylamine. Stabilization of the α-aminoalkyl radical by α-branching or allyl (but not benzyl) resonance favors α-C–H vs. N–H transfer from secondary amines. Greater selectivity for N–H vs. α-C–H transfer is observed for primary vs. secondary amines. Radical pair termination reactions are dependent upon N and α-C alkylation and upon solvent polarity. These results serve to elucidate the effects of amine structure on the formation and behavior of aminyl and α-aminoalkyl radicals.

Results

Fluorescence Quenching. The fluorescence of 9-PCN is quenched by primary, secondary, and tertiary aliphatic amines. Values of $k_{qs}\tau_s$ obtained from the least-squares slopes of fluorescence-quenching Stern–Volmer plots in deoxygenated benzene or acetonitrile solution are given in Table I. The fluorescence quenching rate constants (k_{qs}) are calculated using the measured lifetimes for 9-PCN in benzene (15 ns)[9] and acetonitrile (24 ns)[10] solution. Values of k_{qs} for tertiary and secondary amines approach the rate of diffusion in benzene (1.6×10^{10} M^{-1} s^{-1}) and acetonitrile (2.9×10^{10} M^{-1} s^{-1}) solution.[11] Distinctly lower values of k_{qs} are observed for primary amines, requiring the use of higher amine concentrations (≤ 0.2 M) to observe appreciable fluorescence quenching. Weak exciplex emission ($\lambda_{max} = 560$ nm) was observed upon quenching of 9-PCN by triethylamine in benzene solution,[12] but could not be detected for any of the secondary or primary amines in benzene or acetonitrile solution.

Reactions of 9-Phenanthrenecarbonitrile with Secondary Amines. The reaction of singlet 9-PCN with diethylamine in benzene solution to yield 9,10-dihydrophenanthrene-9-carbonitrile (I) and 9-(diethylamino)-9,10-dihydrophenanthrene-9-carbonitrile (IIb) has previously been reported.[3,4] Analogous reduction and addition products are formed upon reaction of singlet 9-PCN with dimethylamine, diisopropylamine, dibenzylamine, and diallylamine (eq 2). In all cases heating or chromatography of the adducts (II) led to quantitative loss of HCN to yield the substitution



(2)

a: R, R' = CH_3
b: R, R' = CH_2CH_3
c: R. R' = $CH(CH_3)_2$
d: R, R' = CH_2Ph
e: R, R' = $CH_2CH{=}CH_2$
f: R = H, R' = $CH_2CH_2CH_3$
g: R = H. R' = $CH(CH_3)_2$

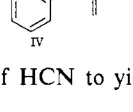


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Table I. Fluorescence Quenching of 9-Phenanthrenecarbonitrile by Amines

amine	IP,[a] eV	$k_{qs}\tau_s$,[b] M^{-1}, C_6H_6	$10^{-9}k_{qs}$,[c] $M^{-1}\ s^{-1}$	$k_{qs}\tau_s$,[b] M^{-1}, CH_3CN	$10^{9}k_{qs}$,[c] $M^{-1}\ s^{-1}$
triethylamine	7.82	188	12	305	13
dimethylamine	8.24	167	11	207	8.6
piperidine	8.04	140	9.3		
diethylamine	8.01	119	7.9	205	8.5
diisopropylamine	7.73	73	4.9	165	6.9
diisopropylamine-*N-d*		67	4.5	160	6.7
diallylamine		52	3.5		
2,2,6,6-tetramethylpiperidine	7.59	75	5.0		
n-propylamine	8.78	1.4	0.09	14	0.59
isopropylamine	8.72	0.88	0.06	8.5	0.35
tert-butylamine	8.64	0.43	0.03	5.8	0.24

[a] Data from ref 18 except for piperidine and tetramethylpiperidine for which values are from ref 19 and are normalized for the scale of ref 18. [b] Least-squares slope of Stern–Volmer plot. [c] Calculated from Stern–Volmer slope and measured singlet lifetime.[8,9]

Table II. Quantum Yields for Product Formation from 9-Phenanthrenecarbonitrile and Aliphatic Amines[a]

amine	Φ_I, C_6H_6	Φ_{III}, C_6H_6	Φ_I, CH_3CN	Φ_{III}, CH_3CN
dimethylamine	0.0029	0.056	0.00037	0.0003
diethylamine	0.0032	0.026	0.0031	
diisopropylamine	0.0039	0.0012	0.0090	
diisopropylamine-*N-d*	0.0030	0.00087	0.0084	
dibenzylamine	0.0076	0.0047	0.012	0.0006
diallylamine	0.0067	0.047	0.0046	
isopropylamine	0.00026	0.00035	0.010	
triethylamine	0.00079		0.0079	

[a] Values for deoxygenated solutions of 9-PCN (0.01 M) and amines (0.12 M tertiary or secondary amine and 0.45 M primary amine). Limits of error for relative values are small (<20%). Limits of error for absolute values increase with decreasing quantum yield (e.g., 0.01 ± 0.003, 0.001 ± 0.001).

Table III. Deuterium-Labeling Results[a]

amine	solvent	9-PCN, % D_{10}	I, % D_{10}	% D_9
diethylamine-*N-d*	C_6H_6	33	108	42
diisopropylamine-*N-d*	C_6H_6	30	64	44
dibenzylamine-*N-d*	C_6H_6	33	118	78
diallylamine-*N-d*	C_6H_6	31	67	68
diethylamine-*N-d*	CH_3CN	<10	52	25
diisopropylamine-*N-d*	CH_3CN	13	20	70
dibenzylamine-*N-d*	CH_3CN	30	103	80
diallylamine-*N-d*	CH_3CN	13	<10	92

[a] Deuterium content in recovered 9-PCN and I by ^{1}H NMR peak integration compared to undeuterated samples (±10%).

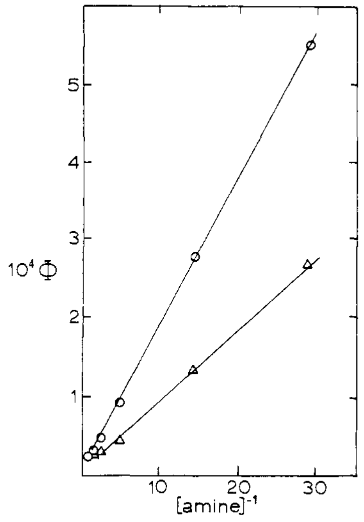


Figure 1. Amine concentration dependence of the quantum yields for formation of reduction product I (○) and substitution product IIIg (△) from the reaction of 9-phenanthrenecarbonitrile with isopropylamine in benzene solution.

products (III). Also formed were the *N*-alkylidene amines derived from amine oxidation. In the case of diallylamine, two substitution products could be resolved by analytical GC. The minor product displayed a mass spectral fragmentation pattern similar to those of IIIa–d and is tentatively assigned structure IIIe. The major product was assigned structure IV on the basis of its ^{1}H NMR and mass spectra. Irradiation of 9-PCN and 2,2,6,6-tetramethylpiperidine does not result in formation of reduction or addition products.

Quantum yields for the formation of products I and III from the reaction of 9-PCN with secondary amines in benzene and acetonitrile solution are summarized in Table II. In all cases values or Φ_{III} decrease with increasing solvent polarity. Only for dimethylamine and dibenzylamine can III be detected in acetonitrile solution. As is the case in the reaction of 9-PCN with diethylamine,[4] the quantum yield for formation of I from 9-PCN and diisopropylamine displays a minimum at a solvent polarity $\epsilon \sim 8$ and increases in both more and less polar solvents.

Irradiation of 9-PCN (0.016 M) with N-deuterated secondary amines (0.10 M) results in the formation of I with deuterium incorporation at C-10 and C-9 and recovered 9-PCN with deuterium incorporation at C-10. The results obtained with several amines at ≥90% conversion of 9-PCN to products are summarized in Table III. Deuterium exchange in 9-PCN can account for C-10 deuteration levels in I which exceed 100%, however, this contribution should be no more than half the level of D_{10} deuterium incorporation in recovered 9-PCN (≤16%).

Reactions of 9-Phenanthrenecarbonitrile with Primary Amines. Irradiation of 9-PCN (0.015 M) with *n*-propyl- or isopropylamine (0.45 M) results in the formation of the reduction product I and the substitution products IIIf,g (eq 2). Addition products analogous to IIa–e are presumed to be intermediates in the formation of IIIIf,g but were not isolated or characterized. Quantum yields for product formation with isopropylamine are reported in Table II. The quantum yields formation of both I and IIIg display the normal linear relationship between Φ^{-1} and $[\text{amine}]^{-1}$ (Figure 1), indicative of a singlet state reaction mechanism for the formation of both products. As a consequence of the very low quantum yields and curvature at high amine concentrations, reliable kinetic data cannot be obtained from the intercept/slope ratio of Figure 1. The quantum yield for the formation of IIIg decreases with increasing solvent polarity, while the quantum yield for the formation of I increases with increasing solvent polarity (Figure 2).

Irradiation of 9-PCN with either *n*-$PrND_2$ or *i*-$PrND_2$ in benzene solution results in extensive C-10 deuteration of both recovered 9-PCN (>60%) and product I (>150%). Irradiation of 9-PCN with *i*-$PrND_2$ in acetonitrile results in a somewhat lower, but substantial extent of C-10 deuteration at C-10 in recovered 9-PCN (~40%) and product I (100%). These levels of deuterium incorporation are substantially higher than those observed with secondary amines (Table III).

Reaction of 9-Phenanthrenecarbonitrile with Triethylamine. Irradiation of 9-PCN with triethylamine in benzene or acetonitrile solution results in the formation of I but no 9-PCN–amine adduct

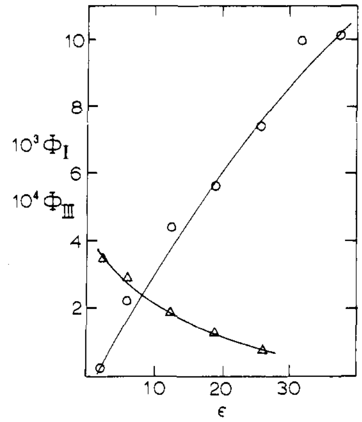


Figure 2. Effect of solvent polarity on the quantum yield for formation of reduction product I (○) and substitution product IIIg (△) from the reaction of 9-phenanthrenecarbonitrile and isopropylamine.

or substitution product. The quantum yield for formation of I in benzene solution (Table II) is substantially lower than for diethylamine, whereas, in acetonitrile solution the quantum yield for formation of I with triethylamine is greater than that for diethylamine.

Discussion

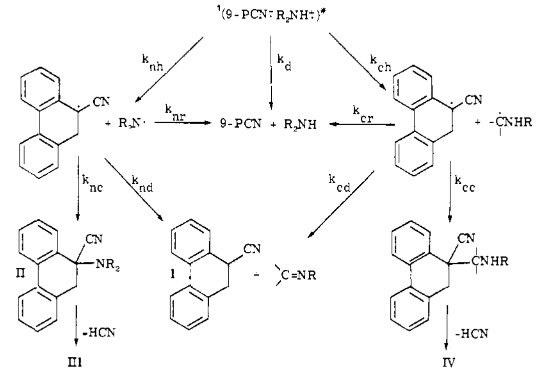
The observation of diffusion-controlled quenching and exciplex emission for the reaction of singlet 9-PCN with triethylamine is indicative of the formation of a charge-transfer stabilized exciplex.[13-15] The free energy for exciplex formation in nonpolar solvent can be calculated from Weller's equation (eq 3),[13c] where

$$-\Delta G_{ex} = {}^1E_A{}^* - (E_A{}^{red} - E_D{}^{ox}) - 0.32 \pm 0.1 \text{ eV} \qquad (3)$$

${}^1E_A{}^*$ and $E_A{}^{red}$ are the singlet energy (3.43 eV) and reduction potential (−1.91 V vs. Ag/AgCl in acetonitrile solution[16]) of 9-PCN and $E_D{}^{ox}$ is the amine oxidation potential. Using values of $E_D{}^{ox}$ = 0.66 V for triethylamine and 1.01 V for diethylamine (vs. Ag/AgCl in acetonitrile solution[17]), values of $-\Delta G_{ex}$ = 0.5 eV for triethylamine and 0.2 eV for diethylamine are obtained. While the oxidation potentials of primary amines have not been measured, they are expected to be at least 0.5 V higher than those for secondary amines on the basis of ionization potential differences (Table I).[18] Thus electron-transfer quenching of singlet 9-PCN by primary amines should be endothermic by ≥0.3 eV, in accord with the low values of k_{qs} (Table I). Only in the case of the primary amines is rate enhancement in polar vs. nonpolar solvent observed.

Within the series of secondary and primary amines investigated, rate constants for quenching of 9-PCN decrease slightly with decreasing amine ionization potential (Table I), contrary to expectations for electron-transfer quenching.[13-15] Similar observations for more limited sets of secondary amines have been reported for quenching of singlet *trans*-stilbene[7e] and benzothiophenes[19] by secondary amines. These observations were attributed to a steric effect on the fluorescence-quenching process[19] or exciplex-decay processes.[7e] A steric effect of unspecified origin is supported by the decrease in fluorescence-quenching rate constant with α-substitution and the larger rate constant for piperidine vs. diethylamine. The recent investigation of steric effects on the photophysics of pyrene-*N*,*N*-dimethylaniline exciplexes by Cheung and Ware[20] established that the most significant effect of di-*tert*-butyl substitution of the amine was to retard the exciplex dissociation process and thus increase the equilibrium constant for reversible exciplex formation. This effect is attributed to changes in the entropies of solvation, which may also be responsible for the steric effect observed in the present investigation.

Scheme I



A plausible mechanism for the formation of reduction (I) and addition (II) products via a common singlet exciplex intermediate is shown in Scheme I. Transfer of N–H from amine to 9-PCN (k_{nh}) yields an aminyl radical, while transfer of α-C–H (k_{ch}) yields an α-aminoalkyl radical. In the preceeding article we described the use of deuterium-labeled diethylamine to establish that N–H transfer is the exclusive reaction observed in nonpolar solvent, while N–H and α-C–H transfer occur to comparable extents in polar solvent.[4] The solvent-induced change in exciplex behavior was attributed to the formation and reaction of a relatively nonpolar exciplex in nonpolar solvent and a pure charge-transfer exciplex (radical ion pair) in polar solvent. The geometry of the exciplex may also change due to amine–solvent hydrogen bonding.

The results of quantum yield (Table II) and deuterium-labeling studies (Table III) for the reaction of singlet 9-PCN with several secondary and primary amines indicate that the competition between N–H and α-C–H hydrogen abstraction is dependent upon the amine structure as well as solvent polarity. The deuterium-labeling results in Table III can be used to provide rough estimates of the k_{nh}/k_{ch} ratios. Values obtained (assuming a negligibly small kinetic isotope effect[4]) are k_{nh}/k_{ch} > 10 for diethylamine and dibenzylamine and ca. 2 for diisopropylamine and diallylamine in benzene solution. In acetonitrile solution the k_{nh}/k_{ch} ratios are ca. 2 for diethylamine, >5 for dibenzylamine, 0.2 for diisopropylamine, and <0.1 for diallylamine. The decrease in k_{nh}/k_{ch} for diisopropylamine or diallylamine vs. diethylamine is in accord with expected decrease in the α-C–H bond strength with α-alkylation or allylic stabilization. A similar decrease in k_{nh}/k_{ch} might have been expected for dibenzylamine but is not observed. The observation of enhanced α-C–H abstraction for diallylamine but not dibenzylamine finds an analogy in the reactions of singlet *trans*-stilbene with *N*,*N*-dimethylallylamine and *N*,*N*-dimethylbenzylamine in benzene solution.[21] The former reaction results in highly selective formation of the dimethylaminoallyl radical while the latter fails to yield the dimethylaminobenzyl radical. The absence of benzyl radical formation was attributed to steric inhibition of resonance as a result of nonbonded interactions between the ortho hydrogens of the phenyl ring and the *N*-methyl groups.[21] A similar explanation can account for the small extent of α-C–H transfer observed for dibenzylamine.

The 9-cyano-9,10-dihydrophenanthren-9-yl–aminyl radical pair formed upon N–H transfer can combine to yield adduct II (k_{nc}), disproportionate to yield I and an imine (k_{nd}), or revert to starting

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materials (k_{nr}, Scheme I). Quantum yields for the formation of substitution products IIIa–c decrease with α-substitution ($Me_2NH > Et_2NH > i\text{-}Pr_2NH$) while quantum yields for the formation of I increase with α-substitution in benzene solution (Table II). The decrease in Φ_{III} with α-alkylation cannot be attributed entirely to a change in N–H vs. α-C–H transfer as N–H transfer is the dominant reaction even for diisopropylamine in benzene solution. A simple steric effect on the ratio of aminyl radical combination/disproportionation[22] (Scheme I, $k_{nc}/(k_{nd} + k_{nr})$ can account for the observed effect of amine structure on Φ_{III}. Further evidence for a steric effect on radical pair combination is provided by the observation that 2,2,6,6-tetramethylpiperidine quenches the fluorescence of 9-PCN with a rate constant similar to that for diisopropylamine (Table I) but fails to yield any reaction products. Irradiation of 9-PCN with partially N-deuterated tetramethylpiperidine in benzene solution results in C-10 deuteration of recovered 9-PCN. Evidently N–H transfer occurs, but the resultant aminyl radical can neither disproportionate, due to the absence of α-hydrogens, nor combine, due to steric hindrance.

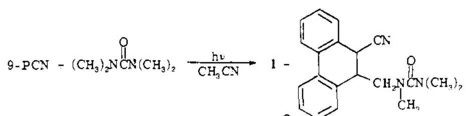
The phenanthren-9-yl-α-aminoalkyl radical pair formed upon α-C–H transfer can also combine to yield an adduct (k_{cc}), disproportionate to yield I and an imine (k_{cd}), or revert to starting materials (k_{cr}). Deuterium-labeling studies indicate that α-C–H transfer occurs to an appreciable extent in benzene solution only with diisopropylamine and diallylamine. The fact that adduct formation (IV) is observed wth the latter but not the former amine is indicative of a steric effect on radical pair combination vs. disproportionation ($k_{cc}/k_{cd} + k_{cr}$) for α-aminoalkyl radicals, as is the case for aminyl radicals. Increased solvent polarity affects radical pair termination reactions as well as the competition between N–H and α-C–H transfer. Radical pair combination products can be detected in acetonitrile solution only in the reactions of dimethylamine and dibenzylamine with 9-PCN (Table II). In the preceeding article we suggested that electron transfer from the aminyl or α-aminoalkyl radical to the phenanthren-9-yl radical to yield an ion pair followed by proton transfer could account for the selective formation of reduction product I and an imine in polar solvents.[4] Oxidation of an aminyl radical to a dialkylnitrogen cation should be less favorable for dimethylamine or dibenzylamine than for diethylamine or diisopropylamine, providing a possible explanation for the observation of radical pair combination products from the former but not the latter amines.

The reactions of 9-PCN with primary amines have not been investigated as thoroughly as those with secondary amines; however, the mechanisms of these reactions appear to be similar. The observation of fluorescence quenching of 9-PCN by primary amines and the linear plots of Φ_I^{-1} and Φ_{IIIg}^{-1} vs. $[\text{amine}]^{-1}$ (Figure 1) are indicative of a common singlet exciplex intermediate in the formation of I and IIIg. The low quantum yields for product formation with isopropylamine (Table II) are due in part to incomplete singlet quenching (0.45 M amine quenches ca. 30% of singlet 9-PCN). The quantum yield for the formation of IIIg decreases less rapidly with increasing solvent polarity than the quantum yields for formation of IIIb or IIIc from the reaction of 9-PCN with secondary amines.[4] The less polar primary amine–9-PCN exciplex is apparently less sensitive to changes in solvent polarity than are the more polar secondary amine–9-PCN exciplexes. Similar differential solvent effects have been observed for cycloaddition reactions from exciplexes of different polarity.[23,24]

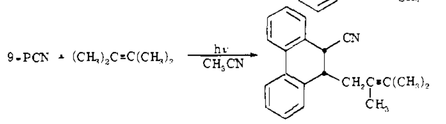
Both the N–H and α-C–H homolytic bond dissociation energies of primary amines are larger than those for secondary amines (DH° = 103 kcal/mol for MeNH–H vs. 96 kcal/mol for Me_2N–H[5] and 94 kcal/mol for H_2NCH_2–H vs. 87 kcal/mol for $MeNHCH_2$–H[6]). Thus both aminyl and α-aminoalkyl radical formation should be thermodynamically less favorable for primary vs. secondary amines. The large extent of C-10 deuteration both in recovered 9-PCN and I obtained with $n\text{-}PrND_2$ and $i\text{-}PrND_2$ indicates that N–H transfer is the dominant reaction pathway for both amines in benzene and acetonitrile solution. Thus primary amines are more selective than secondary amines toward N–H vs. α-C–H transfer. The large extent of C-10 deuteration of recovered 9-PCN also indicates that reabstraction of hydrogen to yield starting materials (Scheme I, k_{nr}) is a more important radical pair termination pathway for primary than for secondary amines. The larger ratio of $k_{nr}/(k_{nc} + k_{nd})$ for primary vs. secondary amines is consistent with the difference in N–H homolytic bond dissociation energies. Thus the low quantum yield for reaction of singlet arenes with primary amines[7] may reflect highly reversible N–H abstraction as well as inefficient singlet quenching.

The reaction of singlet -PCN with triethylamine results in the formation of I but no addition products in both polar and nonpolar solvents. The low quantum yield for formation of I in benzene solution (Table II) is consistent with highly inefficient α-C–H transfer observed in the reactions of 9-PCN with primary and secondary amines and of other singlet arenes with tertiary amines in nonpolar solvents.[7] The increase in quantum yield with increasing solvent polarity is consistent with the proposal that α-C–H transfer is more efficient for the pure charge-transfer exciplex (radical ion pair) formed in polar solvent than for the heteroexcimer formed in nonpolar solvent.[4] The absence of radical pair combination products might be due to either steric hindrance of bond formation[22] or rapid radical pair electron transfer followed by proton transfer to yield I and *N*,*N*-diethylethenamine.[4]

An α-C–H addition product has been reported to be formed in high yield upon reaction of triplet 9-PCN with tetramethylurea (eq 4).[10] The regiochemistry of addition is opposite to that



(4)



(5)

observed in the reactions of singlet 9-PCN with secondary amines but is the same as that observed in the reaction of singlet 9-PCN with 2,3-dimethyl-2-butene (eq 5).[25] The regio- and stereoselectivity of the latter reaction was attributed to deprotonation of the alkene cation radical by solvent to yield an allyl radical. Covalent bonding of the allyl radical and 9-PCN anion radical yields (regioselectively) an α-cyanocarbanion which is protonated (stereoselectively) to yield the adduct.[25] An analogous mechanism might account for the regiochemistry of addition of 9-PCN and tetramethylurea.

In summary, the reactions of singlet 9-PCN with secondary and primary amines are highly dependent upon amine structure and solvent polarity. The predominant reaction observed in nonpolar solvent for all of the amines investigated is N–H transfer to yield an aminyl radical. The formation of aminyl radicals rather than the thermodynamically more stable α-aminoalkyl radicals is attributed to N–H hydrogen bonding of the amine to 9-PCN in the singlet exciplex intermediate.[4,8] The ratio of α-C–H/N–H transfer is larger for α-branched or allyl vs. unsubstituted secondary amines and for secondary vs. primary amines. A similar conclusion was reached by Cohen and Stone[2b] in their detailed investigation of the reaction of triplet benzophenone with amines. The ratio of α-C–H/N–H transfer also increases with increasing solvent polarity, plausibly due to a change in the electronic structure and solvation of the exciplex. The termination reactions of the intermediate free radical pairs are dependent upon amine structure and solvent polarity. The combination/disproportionation ratios for both aminyl and α-aminoalkyl radicals decrease with increasing α-substitution and increasing solvent polarity. The ratio of disproportionation to starting materials vs. product formation is substantially larger for primary vs. secondary aminyl

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radicals. The results of the preceeding article[4] establish that both the competition between N–H vs. α-C–H transfer and the behavior of the resultant aminyl and α-aminoalkyl radicals are also dependent upon the structure of the excited arene reactant.

In reflecting upon the numerous investigations of aminyl vs. α-aminoalkyl radical formation from aliphatic amines (eq 1), we are reminded of the ancient Indian parable of the elephant and the blind men who attempted to describe the elephant after touching one of its parts. The use of singlet arenes[7] to probe the behavior of aliphatic amines led to the conclusion that aminyl radical formation was their characteristic reaction, whereas the use of triplet benzophenone[2] or alkoxyl radicals led to the conclusion that α-aminoalkyl radical formation was their characteristic reaction. While both observations are correct, the behavior of aliphatic amines, like the appearance of the elephant, cannot be fully characterized on the basis of a single observation.

Experimental Section

General procedures are the same as described in the preceeding article.[4] Primary amine fluorescence-quenching and quantum yields were determined on samples that were degassed by three freeze–pump–thaw cycles. Primary amine fluorescence-quenching constants ($k_{qs}\tau_s$) are determined from the initial portion of the Stern–Volmer plots since upwards curvature occurs at high amine concentrations.

Amines. Diethylamine (Aldrich), diisopropylamine (Aldrich), 2,2,6,6-tetramethylpiperidine (Aldrich), *n*-propylamine (Aldrich), isopropylamine (Aldrich), *tert*-butylamine (Aldrich), and triethylamine (Aldrich) were distilled from NaOH prior to use. Dimethylamine (Eastman) was used without further purification.

Deuterated Amines. Diethylamine, diisopropylamine, isopropylamine, and *n*-propylamine were all N deuterated by exchanging twice with a 5-fold excess of D_2O (Aldrich, 99.8 atom % D), the amine being distilled from the D_2O each time. The amines were dried over barium oxide and distilled. This resulted in >97% deuteration in all cases (by NMR). 2,2,6,6-Tetramethylpiperidine was N deuterated by treatment with *n*-butyllithium in hexane followed by quenching with D_2O.

***N*,*N*-Dimethyl-9-phenanthrenamine (IIIa).** Irradiation of 9-PCN with dimethylamine by the standard procedure affords IIIa [^{1}H NMR ($CDCl_3$) δ 7.24–8.73 (m, 9 H), 2.94 (s, 6 H); mass spectrum (EI, 70 eV), *m/e* 221 (100), 178 (27)] and I.

***N*,*N*-Diisopropyl-9-phenanthrenamine (IIIc).** Irradiation of 9-PCN with diisopropylamine by the standard procedure affords IIIc [^{1}H NMR ($CDCl_3$) δ 7.25–8.71 (m, 9 H), 3.73 septet, $J = 6.4$ Hz, 2 H), 1.05 (d, $J = 6.4$ Hz, 12 H); mass spectrum (EI, 70 eV), *m/e* 277 (28), 262 (100), 220 (50), 207 (30)] and I.

***N*,*N*-Dibenzyl-9-phenanthrenamine (IIId).** Irradiation of 9-PCN with dibenzylamine by the standard procedure affords IIId [^{1}H NMR ($CDCl_3$) δ 7.12–8.70 (m, 19 H), 4.34 (s, 4 H); mass spectrum (EI, 70 eV), *m/e* 91 (100)] and I.

***N*-Allyl-1-(9-phenanthryl)allylamine) (IV).** Irradiation of 9-PCN with diallylamine by the standard procedure affords IV [^{1}H NMR ($CDCl_3$) δ 7.20–8.82 (m, 9 H), 5.69–6.12 (m, 2 H), 5.07–5.32 (m, 4 H), 3.81 (d, $J = 5.9$ Hz, 4 H); mass spectrum (EI, 70 eV), *m/e* 273 (48), 230 (100), 215 (100)] and I. Also detected by GC–MS was IIIe [mass spectrum (EI, 70 eV, *m/e* 273 (100), 258 (49), 204 (85)].

***N*-*n*-Propyl-9-phenanthrenamine (IIIf).** Irradiation of 9-PCN with *n*-propylamine by the standard procedure affords IIIf [^{1}H NMR ($CDCl_3$) δ 7.24–8.76 (m, 8 H), 6.77 (s, 1 H), 3.34 (t, $J = 7.0$ Hz, 2 H), 1.85 (sextet, $J = 7.2$ Hz, 2 H), 1.12 (t, $J = 7.0$ Hz, 3 H); mass spectrum (EI, 70 eV), *m/e* 236 (38), 235 (50), 207 (56), 206 (100), 178 (40)] and I.

***N*-Isopropyl-9-phenanthrenamine (IIIg).** Irradiation of 9-PCN with isopropylamine by the standard procedure affords IIIg [^{1}H NMR ($CDCl_3$) δ 6.94–8.73 (m, 9 H), 3.92 (septet $J = 6.2$ Hz, 1 H), 1.41 (d, $J = 6.2$ Hz, 6 H); mass spectrum (EI, 70 eV), *m/e* 236 (28), 235 (66), 221 (40), 220 (100) 178 (19)] and I.

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Registry No. I, 56666-55-8; IIIa, 87884-68-2; IIIc, 25943-37-7; IIId, 87884-69-3; IIIf, 87884-71-7; IIIg, 87884-72-8; IV, 87884-70-6; 9-PCN, 2510-55-6; dimethylamine, 124-40-3; diethylamine, 109-89-7; diisopropylamine, 108-18-9; diisopropylamine-*N-d*, 25837-82-5; dibenzylamine, 103-49-1; diallylamine, 124-02-7; isopropylamine, 75-31-0; triethylamine, 121-44-8; piperidine, 110-89-4; 2,2,6,6-tetramethylpiperidine, 768-66-1; propylamine, 107-10-8; *tert*-butylamine, 75-64-9; diethylamine-*N-d*, 997-11-5; dibenzylamine-*N-d*, 87884-66-0; diallylamine-*N-d*, 87884-67-1.

Reaction of Diphenylcarbene with Methanol[1]

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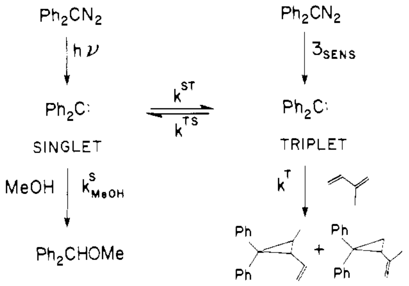
Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. *Received March 22, 1983*

Abstract: The reaction of triplet diphenylcarbene with methanol is believed to proceed via thermal excitation to the singlet state followed by reaction of that state with the alcohol. Analysis of the related reaction kinetics led to a reported enthalpy difference of 3–5 kcal mol^{-1} between the singlet and its triplet ground state. We report measurements of the activation energy, E_{obsd}, for reaction of triplet diphenylcarbene with methanol in various solvents and find, for example, $E_{obsd} = 1.66 \pm 0.20$ kcal mol^{-1} in acetonitrile. These and other results are inconsistent with published interpretations of the data and dictate a reevaluation of earlier experiments and the mechanistic conclusions drawn from them.

The nature of the energy gap between singlet and triplet diphenylcarbene has been a subject of interest for some years.[2-8] Electron paramagnetic resonance studies have shown that the carbene has a triplet ground state,[9-12] and the consensus of current opinion supports the idea that the triplet and singlet states are

Scheme I



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