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Primary and Tertiary Amines as Catalysts of Hydrogen Transfer in the Photocyclization of 1,1-Diarylethylenes

Sir:

In a previous communication we have shown that 1-(α-naphthyl)-1-phenylethylene (I) yields 1-phenylacenaphthylene (II) by irradiation in the presence of iodine and oxygen.[1] In the absence of the oxidant, direct irradiation of a degassed cyclohexane solution of I slowly leads to a mixture of II and 1-phenylacenaphthene (III).[2] This cyclization is not triplet sensitized (nor quenched by oxygen) and it might therefore be ascribed to a short-lived species such as the S$_1$ state.[3]

We were interested to know whether the formation of exciplexes or radical ions from the interaction of photoexcited I with amines would favor or inhibit the photocyclization to III. We have found that addition of amines[4] to a degassed cyclohexane solution of I accelerates the photocyclization of I to give III as the almost exclusive product. We wish to report here[6] the preliminary results of a study of the scope of the reaction and of the mechanism of this unprecedented catalysis of a photocyclization by amines.

1. Scope of the Reaction. A number of experiments, summarized in Table I, were performed to test the potential synthetic value of this reaction which generates five-membered carbocyclic rings. The cyclization proceeds with high yield with R = Ph or CN, if it involves an α-naphthyl or 1-pyrenyl aromatic nucleus. The failure of reactions 7–9 originates, probably, from unfavorable electronic interactions for the cyclization. Diaminoalkanes are the most effective catalysts.

2. Mechanism. The simplest and best documented system was 1-(α-naphthyl)-1-phenylethylene (I) which was used as a model.

Quantum yields were measured at 313 nm in standard conditions described in Table II, with valerophenone as actinometer.[7]

When their alkyl groups are not too bulky, tertiary amines are efficient catalysts of the photocyclization; for example, Et$_3$N and Dabco increase the quantum yield ϕ_{III}, respectively, $\simeq$20 times and $\simeq$40 times relative to the uncatalyzed reaction, but n-Pr$_3$N is far less efficient. These amines are known to be good quenchers of the fluorescent state of arenes. As expected, I gives a fluorescent exciplex with Et$_3$N in cyclohexane[8], λ_{max} 440 nm. The Stern–Volmer plot for the amine quenching of monomer fluorescence gives $k_q\tau$ = 4.63 M^{-1}. The S$_1$ lifetime τ of I in cyclohexane was measured[9] to be τ = 1.2 × 10^{-9} s from which we derive k_q = 3.86 × 10^9 M^{-1} s^{-1}.

The formation of an exciplex is not sufficient to induce a catalytic effect, since dimethyl sulfide and 1,3-cyclohexadiene, which are efficient quenchers of S$_1$ states of arenes and have a lower ionization potential than primary alkylamines,[11] do not catalyze the reaction. Moreover, the quenching of the S$_1$ state of I is not a prerequisite to the reaction: with 1,3-diaminopropane in acetonitrile (at concentrations up to 0.22 M) the

Table I[a]
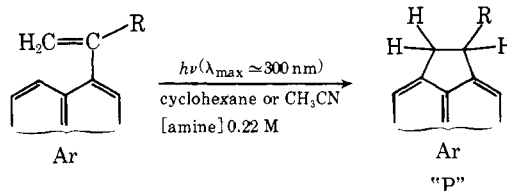
Expt	Ar	R	Solvent	Amine	"P" yield, %
1	α-Naphthyl	Ph	CH	Et$_3$N	80
2	α-Naphthyl	Ph	CH	n-PrNH$_2$	90
3	α-Naphthyl	Ph	AN	n-PrNH$_2$	95
4	4-Methoxy (α-naphthyl)	Ph	CH	Et$_3$N	70
5	5-Acenaphthenyl	Ph	CH	Et$_3$N	85
6	1-Pyrenyl	Ph	CH	NH$_2$(CH$_2$)$_3$NH$_2$[b]	60
7	9-Phenanthryl	Ph	CH	NH$_2$(CH$_2$)$_3$NH$_2$[b]	0[c]
8	5-Chrysenyl	Ph	CH	NH$_2$(CH$_2$)$_3$NH$_2$[b]	0[c]
9	3-Fluoranthenyl	Ph	CH	NH$_2$(CH$_2$)$_3$NH$_2$[b]	0[c]
10	α-Naphthyl	α-Naphthyl	CH	NH$_2$(CH$_2$)$_3$NH$_2$[b]	85
11	α-Naphthyl	CH$_3$	CH	NH$_2$(CH$_2$)$_3$NH$_2$[b]	0
12	α-Naphthyl	CN	CH	NH$_2$(CH$_2$)$_3$NH$_2$[b]	95

[a] Irradiation were carried out with a Rayonet with RUL lamps: $\lambda_{max} \simeq 300$ nm; exposure time $\simeq$3 h (expt 1–5), 18 h (expt 6–12); CH = cyclohexane, AN = acetonitrile. [b] The diamine is not completely miscible with CH. [c] Extended irradiation gives rise to the reduction of the double bond.

Table II. Quantum Yields of Formation of II and III by Irradiation (313 nm) of I (5 × 10^{-3} M) in Cyclohexane (CH) or Acetonitrile (AN) in the Presence of Electron Donors (0.22 M)

| Electron donors	Solvent	ϕ_{II}[a]	ϕ_{III}[a]
None	CH	0.014 ± 0.005	0.005 ± 0.002
	AN	0.008 ± 0.002	0.002 ± 0.001
	CH[b]	0.03 ± 0.003	≤0.001
Et$_3$N	CH	0.02 ± 0.003	0.12 ± 0.02
	AN	0.004 ± 0.001	0.26 ± 0.02
	CH[b]	0.13 ± 0.02	≤0.001
n-PrNH$_2$	CH	0.01 ± 0.002	0.11 ± 0.02
Dabco (0.0125 M)	CH	0.02 ± 0.004	0.22 ± 0.02
NH$_2$(CH$_2$)$_3$NH$_2$	CH[c]	0.007 ± 0.002	0.31 ± 0.02
	AN	≤0.001	0.39 ± 0.04
NH$_2$(CH$_2$)$_4$NH$_2$	CH[c]	0.006 ± 0.002	0.34 ± 0.02
Pyridine	CH	0.003 ± 0.002	0.005 ± 0.002
Me$_2$S	CH	0.009 ± 0.002	0.002 ± 0.001
⬡	CH	0.006 ± 0.002	≤0.001

[a] Degassed solutions by four freeze and thaw cycles. The amount of II and III formed after 1–4% (CH) or 5–11% (AN) conversion is determined by VPC. Valerophenone is used as actinometer.[7] [b] Air saturated. [c] The diaminoalkanes are not completely miscible with CH.

monomer fluorescence is not measurably quenched, whereas the quantum yield ϕ_{III} is 0.39 at [1,3-diaminopropane] of 0.22 M. These results indicate that there is no relation between the ionization potential and the effectiveness of the catalyst. On the contrary, the catalytic capacity appears to correlate with the basicity. The diaminoalkanes, which are the most effective amines have much higher gas-phase basicities than primary amines.[12] Even if the difference is less in solution, the monoprotonated forms of these amines exist largely as cyclic internally hydrogen-bonded species even in water.[13] Pyridine, which is slightly basic, does not catalyze the cyclization.

Other bases, KOH or K$_2$CO$_3$ (0.22 M) in MeOH–H$_2$O (4:1 v/v), increase ϕ_{III} about three times. Since the media are different, one cannot compare the efficiencies of catalysis of bases in aqueous methanol with those of amines in cyclohexane.

Scheme I
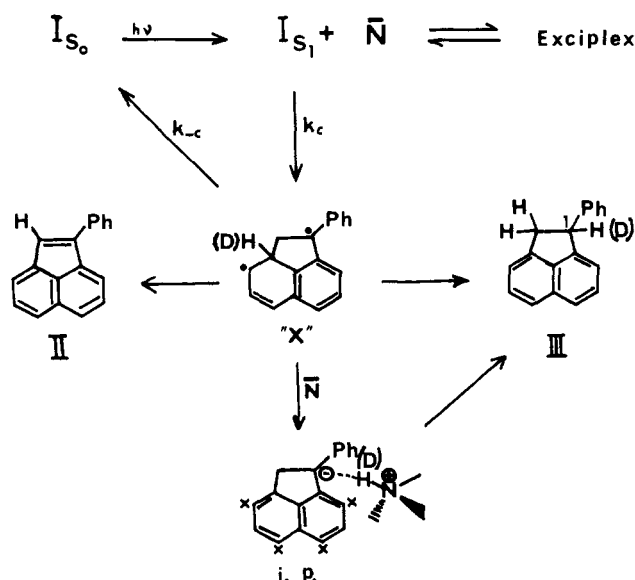
All the compounds (Table I) which do not cyclize in the absence of the amine, do not cyclize when it is present; so the effect of the catalyst is not to induce the cyclization, but to enhance and direct the photocyclization to III.

We propose (Scheme I) that I, in the S_1 state, is transformed into the diradical[14] ("X") which, in the absence of amine, very inefficiently gives II and III and reverts primarily to I. With amine present, it generates an ion pair (i. p.) which collapses rapidly into III. This scheme is also consistent with the following labeling experiments.

A. Starting from compound I having a perdeuterated naphthalene ring (named I(D)) and using Et_3N in the standard conditions, we obtained III containing $\simeq 100\%$ D in position 1.[16] This shows that the hydrogen atom on vertex 1 does not come from the solvent (cyclohexane) or from the alkyl chain of the amine,[17] but from the ring.

B. From I(D) and n-$PrNH_2$ (in cyclohexane) one gets III containing 45% D on vertex 1. The same percentage of deuterium is observed if $NH_2(CH_2)_3NH_2$ is used instead of n-$PrNH_2$.

C. Finally I(H) (with no deuterium) irradiated in the presence of n-$PrND_2$ leads to III, with $\sim$55% D in position 1.

The results B and C clearly show that amines play a chemical role in transferring H from the ring to vertex 1. With primary amines the % D (H) is not the statistical one; moreover in expt B one would have expected a deuterium content lower than 33% from isotopic effect. A rationale would be that the newly formed D-N^+ bond has a greater probability to generate a hydrogen bond between the carbanion and the ammonium cation. It is also likely that amines undergo very fast acid–base equilibria, the starred vertices (see i. p.) being protonated with the result of an enrichment in deuterium content of the alkyl ammonium ions before irreversible protonation of the carbanion in position 1.[18]

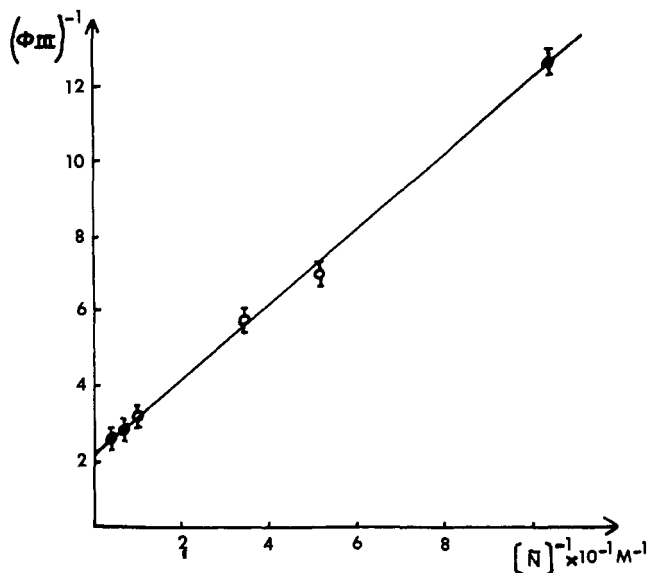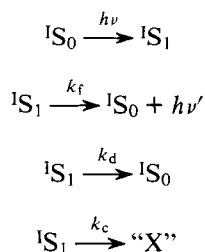This mechanism is expressed by the following kinetic scheme:

$$^1S_0 \xrightarrow{h\nu} {}^1S_1$$

$$^1S_1 \xrightarrow{k_f} {}^1S_0 + h\nu'$$

$$^1S_1 \xrightarrow{k_d} {}^1S_0$$

$$^1S_1 \xrightarrow{k_c} \text{"X"}$$

Figure 1. ϕ_{III} is given as a function of 1,3-diaminopropane concentration (from 10^{-2} to 0.22 M) in CH_3CN. Irradiations were carried out in a merry-go-round at 313 nm with valerophenone as actinometer.[7] The amount of III formed, after 5 to 11% conversion, is measured by VPC with p-terphenyl as internal standard.

$$\text{"X"} \xrightarrow{k_{-c}} {}^1S_0$$

$$\text{"X"} + \bar{N} \xrightarrow{k_H} III$$
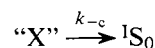
ϕ_{III} is much smaller in the absence of amine catalysts than in their presence. The direct conversion of "X" to III is omitted in this scheme, since at the concentration of amine used in these experiments (10^{-2}–3×10^{-1} M) the extent of direct conversion is known to be negligible.

Under stationary-state approximation, a linear correlation is expected between $1/\phi_{III}$ and $1/[\bar{N}]$.

$$\frac{1}{\phi_{III}} = \frac{1}{k_c\tau} + \frac{k_{-c}}{k_c\tau k_H}\frac{1}{[\bar{N}]} \text{ where } \tau = \frac{1}{k_f + k_d + k_c}$$

With 1,3-diaminopropane ($\bar{N}$) in CH_3CN as solvent, our data gave a linear plot of $1/\phi_{III}$ vs. $1/[\bar{N}]$ with an intercept of 2.2 and a slope of 0.095 M from which we deduced $k_c = 3.79 \times 10^8$ s^{-1} and $k_{-c}/k_H = 0.043$ M (assuming $\tau = 1.2 \times 10^{-9}$ s) (Figure 1).

Additional experiments are necessary to go deeper into the mechanism: for example, flash photolysis to try to detect the postulated intermediate "X" and to see whether the exciplex formation, when it occurs, is a pure competitive process of the "X" formation as assumed here or an additional way to III.

In conclusion, we believe that primary and tertiary amines play a catalyzing role in abstracting a proton of a diradical intermediate preventing this species from reverting efficiently to initial arylethylene. This is, to our knowledge, the first report of this base catalysis in a photocyclization reaction.[20] This reaction has been shown to be liable to extension to compounds other than I. Further investigations of the mechanism and possible synthetic applications are under way.

References and Notes

(1) (a) R. Lapouyade, R. Koussini, and J. C. Rayez, *J. Chem. Soc., Chem. Commun.*, 676 (1975). (b) Since the preceding communication, the very inefficient photocyclization of 1-(9-phenanthryl)-1-phenylethylene has been

reported: W. H. Laarhoven and Th. J. H. M. Cuppen, *Recl. Trav. Chim. Pays-Bas*, **95**, 165 (1976).

(2) Similar oxidative and nonoxidative photocyclizations have been observed with 1-(α-naphthyl) acrylates but they involve an α,β-unsaturated ester chromophore: (a) E. Groveinstein, Jr, Th. C. Campbell, and T. Shibata, *J. Org. Chem.*, **34**, 2418 (1969); W. C. Fleming, W. W. Lee, and D. W. Henry, *ibid.*, **38**, 4404 (1973).

(3) We postulate that the formation of the new bond is the first step of the reaction; the intermediate obtained cannot easily transfer its hydrogen to form III so that elimination of H_2 can compete. In accord with this mechanism ϕ_{II}/ϕ_{III} is quasi-constant whatever the solvent is and, if I has a perdeuterated naphthalene ring, the photoproduct III has ∼80% D on the carbon which bears the phenyl ring.

(4) With secondary amines (Et_2NH) one observes a number of products, even at the beginning of the reaction, probably because protonation occurs rapidly in exciplex before and after cyclization. It has been shown that an important step in the decay of arene–secondary amine exciplexes involves the proton transfer from the amine to the arene.[5]

(5) N. C. Yang and J. Libman, *J. Am. Chem. Soc.*, **95**, 5783 (1973).

(6) An account of this work was given at the VIth IUPAC Conference on Photochemistry, Aix en Provence, France, July 1976.

(7) P. J. Wagner and A. E. Kemppainen, *J. Am. Chem. Soc.*, **90**, 5896 (1968).

(8) The quenching of the fluorescence of I by Et_3N in cyclohexane was observed with a Perkin-Elmer MPF3 without correction of the spectrum system. The samples were degassed by a slow nitrogen current.

(9) Fluorescence lifetime of I has been measured with the single photon technique described elsewhere.[10]

(10) C. Lewis, W. R. Ware, L. J. Doemeny, and T. L. Nemzek, *Rev. Sci. Instrum.*, **44**, 107 (1973).

(11) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Hesson, K. Drail and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions", U.S. Department of Commerce, National Bureau of Standards, Washington, D.C., 1969.

(12) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **95**, 3504 (1973).

(13) J. Hine and W. S. Li, *J. Org. Chem.*, **40**, 1795 (1975).

(14) This species is described as a diradical for simplicity, but it may have a zwitterionic character.[15]

(15) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

(16) Estimation of deuterium content was made by mass spectra and NMR.

(17) A. Couture, A. Lablache-Combier, and H. Ofenberg, *Tetrahedron*, **31**, 2023 (1975).

(18) Kinetic protonation of the acenaphthylene dianion involves the naphthalene ring,[19] but we do not know of similar studies with acenaphthenyl monoanion.

(19) (a) L. D. Kershner, J. M. Gaidis, and H. H. Freedman, *J. Am. Chem. Soc.*, **94**, 985 (1972); (b) T. S. Cantrell, *Tetrahedron Lett.*, 1803 (1973); (c) C. V. Ristagno and R. G. Lawler, *ibid.*, 159 (1973).

(20) With amines, arenes usually form exciplexes and the photoproducts generally result from reduction or reductive amination of the aromatic part.[5,21]

(21) (a) S. G. Cohen, A. Parola, and G. H. Parsons, Jr., *Chem. Rev.*, **73**, 141 (1973); (b) J. A. Barltrop, *Pure Appl. Chem.*, **33**, 179 (1973); (c) N. C. Yang, D. M. Shold, and B. Kim, *J. Am. Chem. Soc.*, **98**, 6587 (1976).

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1

2

Table I. ^{13}C NMR Chemical Shifts[a] and $^{195}Pt-^{13}C$ Coupling Constants[b]

	1	2
	A. bipy	
C(2)	154.95 (NO)	157.57 (34)
C(6)	147.73 (9)	148.36 (27)
C(4)	144.91 (<5)	143.05 (6)
C(5)	129.63 (21)	128.68 (32)
C(3)	126.78 (17)	125.35 (28)
	B. Aliphatic Amine Ligand[c]	
CH(a)	45.19 (20)	44.24 (24)
CH_2(b)	37.33 (8)	35.11 (52)
CH_2(c)	33.60 (16	29.40 (<6)
CH(d)	42.17 (19)	14.60 (<6)

[a] In parts per million vs. TMS external standard. [b] In hertz, given in parentheses after chemical shifts; NO, not observed owing to signal saturation. [c] Relative intensity of a:b:c:d, 2:1:2:1.

Structural Characterization of a Novel Platinum(IV) Complex Produced by Deprotonation of Coordinated Amino Groups of the Rigid Ligand *cis,cis*-1,3,5-Triaminocyclohexane

Sir:

We describe herein details of the preparation and structural characterization of a novel octahedral platinum(IV) complex, **1**, which resulted from the aqueous solution reaction of *cis,cis*-1,3,5-triaminocyclohexane (tach) with dichloro-(bipy)platinum(II), where bipy = 2,2'-bipyridyl. This complex is unique in two respects. First, the platinum(II) to platinum(IV) oxidation occurred under mild conditions (probably air oxidation) in contrast to the normal requirements of strong oxidants to effect this conversion.[1] Secondly, deprotonation of two amine donors occurred readily in aqueous solution. Such an acidity of coordinated amino groups is unusual in that, where similar deprotonation reactions are known to occur, a strong base is generally found to be necessary to effect proton removal.[2,3] A discussion of the evidence leading to structure **1**, derived from mutually complementary information from
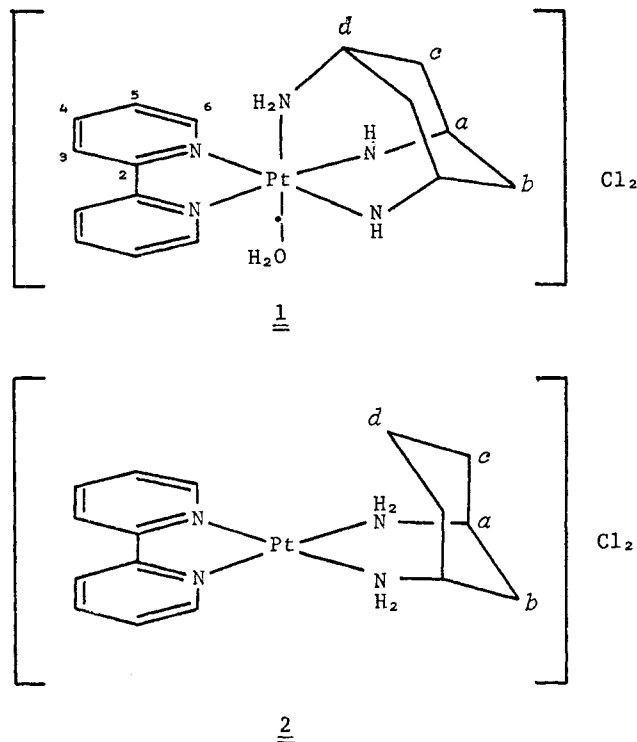
NMR and ESCA spectroscopy and an x-ray crystal structure analysis, is presented.

Complex **1** was prepared by reacting a stoichiometric quantity of the tach ligand with dichloro(bipy)platinum(II) in aqueous solution by a synthetic procedure analogous to that employed to produce a wide variety of square-planar platinum(II) complexes of bipy and aliphatic ligands.[4] Elemental analysis[5] for the yellow crystalline product was consistent with the formulation of one bipy, one tach, two chlorine atoms, and four water molecules per platinum atom. This formulation is in accord with the 100-MHz ^1H NMR spectrum in aqueous (D_2O) solution. Moreover, the excellent resolution and lack of contact shifts in this spectrum attest to the diamagnetic nature of the complex.

Data from the 25.2-MHz ^{13}C NMR spectrum of **1** and an analogous square-planar platinum(II) complex, **2**, of bipy and *cis*-1,3-diaminocyclohexane (dach) are presented in Table I. The multiplicity and relative intensities of the resonances are indicative of symmetrical binding arrangements for the bipy and tach moieties in **1**. The tridentate nature of the coordinated tach in **1** can be discerned from the similarity of the 19-Hz