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XII   XIII
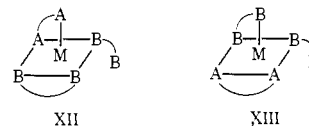
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Solvent Specific Photochemistry Involving an Intramolecular Amino Ketone Triplet Exciplex[1]

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Abstract: β-Naphthyl γ-dimethylaminopropyl ketone (**1**) undergoes inefficient ($\Phi \leq 0.01$), unquenchable type II photoelimination to 2-acetonaphthone in protic and aprotic solvents. The efficiency of **1** as a photosensitizer indicates that it forms long-lived ($\tau \geq 10^{-6}$ s) triplets in good yield ($\Phi_{isc} = 0.76$–0.88). Only in protic solvents does this easily quenchable triplet yield acetonaphthone ($\Phi = 0.17$ in methanol). It is concluded that the π,π^* triplet undergoes efficient CT interaction with the amine group in all solvents; only specific protonation of the exciplex catalyzes its rearrangement into a diradical. The lack of such rearrangement in aprotic solvents indicates a rather restricted cyclic geometry to the exciplex.

It is now well established that the triplet states of ketones are quenched by charge transfer (CT) interactions with amines, with efficient photoreduction often following.[2] Whereas the reactivity differences between n,π^* and π,π^* ketone triplets are now pretty well defined for hydrogen abstraction reactions,[3] they are not so well defined for CT reactions. Thermodynamic factors (redox potentials and electronic excitation energy) clearly affect quenching rate constants,[4] but from the limited data in the literature it is not possible to tell whether any fundamental reactivity differences exist between the two triplet types.

Another aspect of CT quenching of triplet ketones which is not well understood involves the structure of the nonluminescent exciplex presumably formed in the quenching process. In this regard, the photochemistry of amino ketones is particularly interesting because of the conformational limitations of intramolecular bifunctional reactions.

In this paper we report the strongly solvent dependent photochemistry of β-naphthyl γ-dimethylaminopropyl ketone, **1**. This compound was chosen because the π,π^* lowest triplets of naphthyl ketones do not abstract hydrogen atoms directly[5,6] and because γ-amino phenyl ketones undergo facile intramolecular CT triplet quenching.[7]

Results

Irradiation at 313 or 365 nm of degassed benzene or acetonitrile solutions 0.02–0.05 M in **1** results in inefficient ($\Phi =$
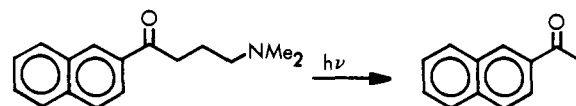
0.010), completely unquenchable (by 3.4 M 1,3-pentadiene) type II elimination[8] to 2-acetonaphthone. The quantum yield is unaffected by 0.56 M pyridine. We presume that some cyclobutanol is also formed[9] but did not analyze for it. In methanol as solvent, the type II quantum yield is 0.17, 0.163 of which is readily quenchable by low concentrations of dienes and stilbene, both of which quench triplet naphthyl ketones.[10] After subtraction of the residual unquenchable reaction, linear Stern–Volmer plots were obtained for the quenchable portion of the reaction, with slope ($k_q\tau$) values of 780 M^{-1} for 1,3-pentadiene and 6100 M^{-1} for *trans*-stilbene. In methanol-*O-d*, the total quantum yield is only 0.12; in 2,2,2-trifluoroethanol, 0.05. Table I lists quantum yields in benzene as a function of added methanol concentration.

In benzene, 0.05 M **1** is 76 $\pm$ 2% as efficient as 0.05 M benzophenone or 2-acetonaphthone at photosensitizing the cis–trans isomerization of 0.04–0.20 M 1,3 pentadiene.[11] Consequently, the intersystem crossing yield of **1** is 0.76 relative to 1.0 for 2-acetonaphthone.[12] In methanol, 0.03 M **1** is 88% as efficient as 0.03 M benzophenone at sensitizing the isomerization of 0.2 M diene. In benzene, 10^{-3} M **1** is 30% as effective as benzophenone and 2-acetonaphthone at sensitizing

Table I. 2-Acetonaphthone Quantum Yields from **1** in Mixed Benzene–Methanol Solvents

[CH$_3$OH], M	Φ_{II}	[CH$_3$OH], M	Φ_{II}
0	0.010 ± 0.003	7.5	0.084
0.25	0.010	12.5	0.11
1.25	0.021	17.5	0.14
2.5	0.033	22.5	0.16
5.0	0.059	25	0.17 ± 0.01

the phosphorescence of biacetyl (measured at 516 nm) in concentrations ranging from 0.01 to 0.0002 M.

The polarographic reduction potential of **1**, like that of 2-acetonaphthone, is -1.80 eV (vs. SCE) in DMF with tetrabutylammonium iodide as supporting electrolyte. The phosphorescence spectrum of **1** at 77 K is identical with that of 2-acetonaphthone, with 0–0 band at 482 nm.[5] The absorption spectrum of **1** is also identical with that of 2-acetonaphthone. As noted before,[5] there is no distinct n,π^* band; it is partially buried under the fairly strong, structured π,π^* transition with peaks at 324 and 340 nm. Figure 1 compares the near-uv absorption of equal concentrations of 2-acetonaphthone and methyl 2-naphthoate. The long wavelength tail of the ketone spectrum presumably represents the long wavelength part of the n,π^* band, since there is no such tail in the ester spectrum.

Discussion

The photochemistry of **1** bears a superficial resemblance to that of γ-dimethylaminobutyrophenone (**2**), which also undergoes solvent dependent type II photoelimination.[7] In **2**, most or all of the reaction can be ascribed to direct γ-hydrogen atom abstraction by a quenchable n,π^* triplet. In **1**, however, there is some unquenchable reaction in all solvents and no triplet reaction except in protic solvents. The latter difference is particularly informative.

Excited States of 1. The lowest triplet at 59.3 kcal in 2-acetonaphthone has long been recognized as a perturbed naphthalene π,π^* state[5] and is surely the same in **1**. The exact position of the carbonyl n,π^* triplet can only be estimated. An absorption band at 382 nm (74.5 kcal) has been observed in the phosphorescence excitation spectrum of 2-naphthaldehyde and assigned as the ^{3}n,π^* 0–0 band.[13] We have already summarized the evidence that, because of geometric differences between n,π^* triplets and ground states, emission 0–0 bands for ketones are 3–4 kcal lower than the corresponding absorption 0–0 bands.[3] Consequently, we estimate a n,π^* triplet energy of some 71 kcal/mol for **1**.

Although naphthyl ketones are generally regarded to have n,π^* lowest singlets,[6] there is no published evidence for this conclusion. Simple inspection of the uv spectrum of **1** or of 2-acetonaphthone does not reveal any distinct n,π^* transition. No ^{1}n,π^* band is apparent in the reported phosphorescence excitation spectrum of naphthaldehyde, although the first band in the $^1\pi,\pi^*$ transition was misassigned as such.[13] As Figure 1 shows, there is weak absorption ($\epsilon_{360} \sim 40$ M^{-1} cm^{-1}) from 350 to 380 nm in 2-acetonaphthone whereas there is no such corresponding absorption in methyl 2-naphthoate. The ester was chosen as the naphthalene derivative which would most closely mimic the π,π^* transitions of **1** without having any n,π^* transitions. There are five distinct peaks visible in the perturbed ^{1}L$_b$ band of both ester and ketone, with those in the ketone occurring 7 nm higher than those in the ester. The π,π^* transition in the ketone is much broader than that in the ester. This behavior is common when the upper vibrational levels of the lower electronic state can mix in with a higher electronic state.[14] We are now confident that the lowest singlet of 2-naphthyl ketones is basically n,π^* in nature. It lies only a few kilocalories lower than the ^{1}L$_b$ π,π^* singlet.
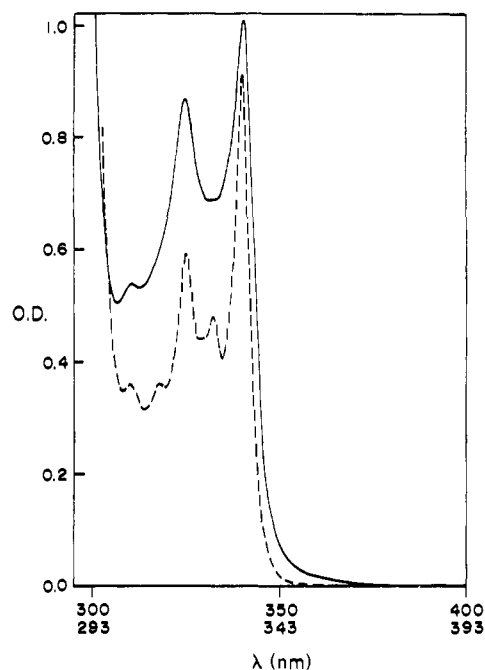

Figure 1. Absorption spectra of 2-acetonaphthone (—) and methyl 2-naphthoate (- - -), each 0.0006 M in heptane. Ester spectrum is offset 7 nm to higher wavelength.

Unquenchable Reaction. The small amount of unquenchable type II elimination observed from **1** in all solvents seems to be characteristic of naphthyl alkyl ketones and has been ascribed to n,π^* singlet hydrogen abstraction barely competing with intersystem crossing.[6] It is also possible that some γ-hydrogen abstraction by the n,π^* triplet manages to compete with internal conversion to the lowest triplet. In fact, with the rate of hydrogen abstraction in triplet **2** known to be 10^9 s^{-1},[7] some 1% of the n,π^* triplets in **1** could react if the rate of internal conversion equaled 10^{11} s^{-1}. This interpretation would require significant population of T$_2$ by intersystem crossing. This possibility is quite real, given El-Sayed's latest results on intersystem crossing in benzophenone.[15] Sensitization studies could shed further light on this problem. Unfortunately, quenching of sensitizers by the tertiary amine group in **1** precluded any readily interpretable results.

Triplet Reaction. Intersystem crossing is less than 100% efficient in **1**, but is more efficient than in **2**. Some intramolecular CT quenching of the excited singlets presumably occurs.[7] The ratio of rates for intersystem crossing vs. singlet quenching is twice as large in **1** (3:1) as in **2** (1.4:1) and is doubled by methanol in both, but it is not possible to evaluate changes in any one rate constant, especially when the quenching processes may well be rotationally controlled.[16]

Unlike **2**, **1** forms very long-lived triplets. Their long lifetime is evident from the concentration independence of the sensitized biacetyl emission; even 0.0002 M biacetyl quenches triplet **1** completely. (The 30% emission yield relative to the other sensitizers results because the amino group of **1** quenches triplet biacetyl at a rate competitive with its normal decay.[17]) With the rate constant for the 4 kcal exothermic energy transfer from triplet **1** to biacetyl assumed to be 5×10^9 M^{-1} s^{-1} in benzene,[18] τ_T for **1** may be as long as 10^{-5} s. The bimolecular rate constant for CT quenching of triplet 2-acetonaphthone by triethylamine is approximately 1×10^5 M^{-1} s^{-1} in benzene and 6×10^5 M^{-1} s^{-1} in acetonitrile,[19] so triplet **1** should undergo intramolecular quenching by its own amino group with a rate on the order of 10^5 to 10^6 s^{-1}.[7] With a self-quenching rate constant of 2.5×10^5 M^{-1} s^{-1} for 2-acetonaphthone,[20] the total contribution to the triplet decay rate of **1**

from interactions with both the carbonyl and the amino groups of 0.02–0.05 M *ground state* **1** would be only $1-2 \times 10^4$ s^{-1}. Thus triplet **1** should undergo very efficient intramolecular CT quenching and exciplex formation.
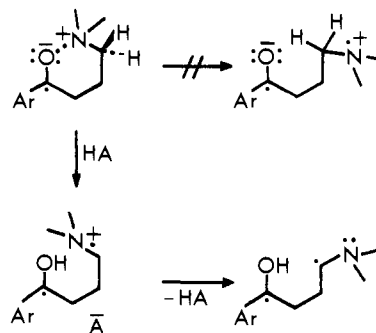
The lack of any type II products from triplet **1** indicates not only the expected lack of direct γ-hydrogen abstraction but also the lack of any rearrangement of the exciplex to diradical. Since bimolecular reduction of triplet naphthyl ketones by amines leads to efficient radical formation,[19] the cyclic exciplex formed from **1** must be restricted to conformations in which the hydrogens α to the nitrogen are kept farther than bonding distance from the carbonyl oxygen, such that 1,5-proton transfer is impossible. There is some evidence that stereoelectronic requirements affect rates of CT quenching,[21] but these results are the first which demonstrate structural requirements so severe as to prevent a normally efficient chemical decay channel of an excited CT complex. We have previously suggested that little diradical formation can occur from the 2-derived triplet exciplex,[7] but the competing direct hydrogen abstraction prevented any quantitative conclusions.

It is possible that the initial geometries of the exciplexes from **1** and **2** differ, with the nitrogen approaching the electron deficient carbonyl n-orbital in **1**,[21] the α-naphthyl carbon in **1**.[22] However, the exciplexes may have similar equilibrium geometries, since the partial negative charge in each must reside largely on oxygen.
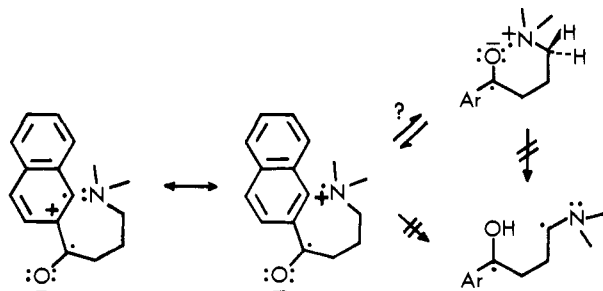
Exciplex Protonation. The most significant aspect of the photochemistry of **1** is that methanol allows the lowest triplet to react with moderate efficiency. The quenching results show that energy transfer to 1,3-pentadiene is, as expected,[10] slower than diffusion controlled. Since energy transfer from triplet 2-acetonaphthone to *trans*-stilbene is diffusion controlled,[23] k_q in methanol can be assumed to equal 7.5×10^9 M^{-1} s^{-1}.[24] The quenching results thus indicate a triplet decay rate of 1.2 $\times 10^6$ s^{-1} for **1**. This rate is what would be expected[7] for intramolecular CT quenching given the published rate constants for bimolecular quenching of triplet acylnaphthalenes by amines.[19] Methanol would not enhance direct γ-hydrogen atom abstraction.[3] Therefore we must conclude that intramolecular exciplex formation takes place in all solvents but that only in protic solvents such as methanol does the exciplex rearrange to a 1,4-diradical. Since acetonitrile does not affect quantum yields and since the quantum yield in methanol-*O-d* is only 70% that in normal methanol, specific hydrogen bonding to or actual protonation of the oxygen in the exciplex must be responsible rather than a simple dissociation of the exciplex into a solvated radical-ion pair. Protonation of the partially negative oxygen is perhaps most likely in view of the acid-catalyzed addition of benzene to α-trifluoroacetophenone,[25] in which methanol is also an effective catalyst.

The gradual rise in Φ_{II} for **1** as a function of added methanol is further evidence that the solvent effect involves specific catalysis. Methanol (0.5 M) is sufficient to force all type II 1,4-diradicals on to product.[31] The value of $(0.86 - \Phi)$ represents the quantum yield for radiationless decay from the triplet, which decay is quenched by methanol. The slope of the Stern–Volmer plot of $0.86/(0.86 - \Phi)$ vs. methanol concen-

tration equals 0.015 M^{-1} and, if our interpretation of the solvent effect is correct, represents the rate constant for protonation of the exciplex times the exciplex lifetime. Unfortunately, neither value can be estimated even roughly. It is interesting that the more acidic trifluoroethanol has a smaller solvent effect than methanol. It may hydrogen bond so strongly to the nitrogen lone pair that CT quenching is suppressed. This phenomenon is well documented for n,π* triplets[7,26] but has not been established for π,π* triplets.

Hydrogen Abstraction vs. CT Quenching in Triplet 2. We previously suggested that the 0.25 quantum yield for **2** in methanol might involve some similar solvation of the n,π* derived exciplex as well as direct hydrogen abstraction.[7] With **1** the conclusion is unequivocal because of the lack of any competing direct triplet state γ-hydrogen abstraction. In fact, the behavior of **1** now allows us to better sort out the competing reactions of triplet **2**. We can assume that the same fraction of triplet exciplexes formed undergoes type II elimination in methanol in **2** as observed for **1**. This fraction is the triplet quantum yield divided by the intersystem crossing yield, 0.163/0.88 (19%). Equation 1 describes how the triplet quantum yield in **2** depends on the competition between hydrogen abstraction and CT interaction, with $\Phi_{ISC} = 0.72$ in methanol.[7] This analysis indicates that k_{CT} is four times larger than k_H.

$$\frac{0.25}{0.72} = \frac{k_H}{k_H + k_{CT}} + \frac{0.19 k_{CT}}{k_H + k_{CT}} \tag{1}$$

Summary

We have described a simple photoreaction which is made allowed only by specific solvation of an excited CT complex. External protonation of exciplexes may be quite common[25,27] and we have evidence that it is necessary for the production of CIDNP signals in several systems.[28] Its necessity in **1** limits the structural possibilities of exciplexes formed from triplet ketones and amines.

Experimental Section

Chemicals. Amino ketone **1** was prepared by addition of β-naphthyl Grignard reagent to γ-dimethylaminobutyronitrile. In a 500-ml three-necked flask fitted with stirrer, reflux condenser, and dropping funnel was placed 5.86 g (0.24 g-atom) of magnesium turnings, 30 ml of anhydrous ether, and a crystal of iodine. The system was then flushed with nitrogen and kept under nitrogen throughout. A mixture of 50 ml of ether, 4 g of 2-bromonaphthalene, and 0.5 ml of ethylene bromide was added and the whole solution was refluxed until Grignard formation began. Then the remainder of the 2-bromonaphthalene (total 54 g, 0.25 mol) in 100 ml of ether was added dropwise so as to maintain refluxing. The solution was refluxed for 30 min after addition was complete. Then 21.6 g (0.19 mol) of γ-dimethylaminobutyronitrile (Aldrich) in 100 ml of ether was added over 30 min. The resulting solution was then refluxed for 14 h. After being cooled, it was poured into 75 ml of cold water containing 21.5 g of ammonium chloride. After all solids were dissolved, the ether was evaporated. The aqueous solution was heated on a steam bath for 1 h to hydrolyze the imine. Free ketone was then extracted into ether. Hydrochloric acid was

added to the water solution, which was heated two more hours and then brought back to pH 8 with sodium carbonate. This solution was extracted with ether. The combined ether extracts were extracted with cold 2 N HCl. The aqueous extracts were then neutralized and the amino ketone was extracted with ether. The ether solution was dried over potassium carbonate and then flash evaporated. The residue was distilled through a 10-cm Vigreux column at 0.04 Torr. Slightly yellow liquid (40 g, 80%) was collected from 128 to 135 °C. The distillate was decolored by being passed through alumina. It was redistilled; bp 135° (0.10 Torr). Crude amino ketone was also purified by recrystallization of its hydrochloride salt from methanol-2-butanone. Free 1 was regenerated as needed by treating the salt under nitrogen with cold aqueous sodium hydroxide. VPC analysis showed <0.3% impurities: ir (KBr pellet) 2810, 2760, 1677, 860, 820, 747 cm^{-1}; uv (heptane) λ_{max} 238 nm (ϵ 29 100) 246 (3500) 281 (5100) 324 (1200) 340 (1400); ^{1}H NMR (CCl$_4$) δ 1.87 (quintet, 2 H, $J = 7$ Hz, C–CH$_2$-C) 2.21 (s, 6 H, NMe$_2$) 2.33 (t, 2 H, $J = 7$ Hz, CH$_2$CO) 3.07 (t, 2 H, $J = 7$ Hz, CH$_2$-N) 7.43-8.47 (complex, 7 H, naphthyl); MS (70 eV) m/e 241, 155, 127, 71, 58 (base). The mass spectral fragmentation pattern is very similar to that of 2.[29]

Solvents were purified as in earlier work.[3] Baker *trans*-stilbene was used as received. Aldrich 1,3-pentadiene was passed through alumina and then distilled for quenching purposes; Chemical Samples 99.7% cis was used as received for intersystem crossing measurements. Eastman white label benzophenone was recrystallized from petroleum ether. Eastman 2-acetonaphthone was dissolved in ethanol, treated with decolorizing charcoal, and then recrystallized three times each first from aqueous ethanol and then from ligroin. Aldrich biacetyl was simply distilled prior to being used.

Irradiation Procedures. Solutions containing measured concentrations of ketone, internal standard, and any other additives were prepared in volumetric flasks. Aliquots (2.8 ml) were syringed into previously constricted 13 × 100 mm Pyrex culture tubes. The samples were attached to a vacuum line, degassed by four freeze-pump-thaw cycles, and sealed. The sealed samples were placed in a merry-go-round apparatus[30] immersed in a room temperature water bath and irradiated with a Hanovia 450-W medium pressure mercury arc contained in a water-cooled quartz immersion well. The 313-mm line was isolated with a filter solution containing 0.002 M potassium chromate in 5% aqueous potassium carbonate; the 365-mm line was isolated with Corning 7-83 filter combinations.

Actinometry. Samples containing 0.1 M valerophenone and 0.005 M tetradecane in benzene were irradiated in parallel with the samples containing 1. The quantum yield for formation of acetophenone is 0.33.[31]

Analytical Procedures. Formation of 2-acetonaphthone was monitored by vapor phase chromatography (VPC). A 5 ft × ½ in. steel column packed with 5% SE-30 on 60/80 mesh, acid-washed, DMCS-treated Chromosorb W held at 190-200 °C was used. Octa-

decane was the internal standard. Acetophenone formation was monitored as usual.[31] Cis-trans isomerization of pentadiene was also monitored as usual.[32] In all runs conversions were 10% or less.

Biacetyl phosphorescence was monitored on an Aminco-Bowman spectrophotofluorometer. Sensitizer concentrations were adjusted so that total optical density at 320 nm (excitation wavelength) equaled 0.7. Emission at 516 nm in samples with no biacetyl was negligible.

The uv spectra were recorded in 1-cm cells on a Cary 17 spectrometer.

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(1) This work was supported by NSF Grant No. GP-19580.
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