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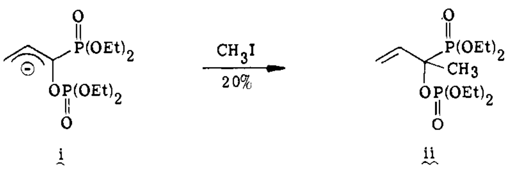

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Competing Triplet Reactions in Azidoketones

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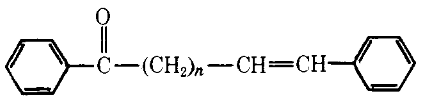
Abstract: The photochemistry of three α-benzoyl-ω-azidoalkanes $PhCO(CH_2)_nN_3$ has been studied. With 365-nm irradiation two competitive processes occur from the triplet ketone: γ-hydrogen abstraction to yield Norrish type II products and energy transfer to azide to yield nitrene products. The rate constant for the latter decreases an order of magnitude for each additional methylene between $n = 3$ and $n = 5$. This rate decrease is interpreted to reflect the strain in medium-sized rings. The effects of δ- and γ-azido on the rate constant for γ-hydrogen abstraction indicate a σ_I value of 0.46 for N_3 and little resonance stabilization of an adjacent carbon radical.

For years, there has been widespread interest among photochemists in bifunctional and bichromophoric compounds.[1] Nonetheless, there have been few investigations in which the positions of the two chromophores on a molecular skeleton have been varied systematically so that rate constants for interactions between the two groups can be compared to their distance apart.[2,3] One such study showed that the rate of intramolecular triplet energy transfer in ω-styrenylalkyl phenyl ketones decreases as the number of methylenes connecting the two chromophores increases from 2 to 4.[2] These energy transfer rate constants are probably controlled by rates of rotation, since the corresponding bimolecular process, being exothermic, is diffusion controlled.[4]



In this paper we report the photochemistry of three ω-azidoalkyl phenyl ketones. These compounds display the expected competition between carbonyl and azide (nitrene) photochemistry. Moreover, since energy transfer from triplet ketones to azides is two orders of magnitude slower than diffusion controlled,[5] the variation in rates of intramolecular energy transfer reflects conformational equilibrium rather than rotational kinetics.

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Table I. Variations in Acetophenone Quantum Yields[a]

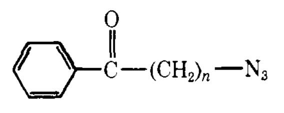
δ-Azidovalerophenone[b]	
conversion, %	Φ_{11}[c]
9	0.16
13	0.13
17	0.10
γ-Azidobutyrophenone	
[γ-AB], M	Φ_{11}
0.03	0.0049 ± 0.0006
0.05	0.0046
0.07	0.0042 ± 0.0003
0.10	0.0030 ± 0.0001

[a] In benzene, 365 nm. [b] 0.05 M. [c] ±0.01.

Table II. Quantum Yields for $PhCO(CH_2)_nN_3$[a]

n	$k_q\tau$, M^{-1}	Φ_{isc}	Φ_{-K}	Φ_{imine}	Φ_{11}	Φ_{11}^{max}[b]
3	11 ± 1 (15 ± 2)[e]	0.80	0.29[c]	0.20[d]	0.0060[c]	0.012[c]
4	111[f] (101)[e]	0.98		0.02	0.20[f]	0.32[f]
5	93	1[g]	0.36		0.34	0.93

[a] 0.07 M in benzene, 365 nm. [b] 0.5 M pyridine added. [c] Extrapolated to zero [γ-AB]. [d] 2:1 2-phenylpyrrole–2-phenylpyrroline. [e] From sensitization studies. [f] Extrapolated to zero conversion. [g] Assumed.



γ-AB, n = 3
δ-AV, n = 4
ε-AH, n = 5

Results

γ-Azidobutyrophenone (γ-AB) was prepared by treating the ethylene ketal of γ-chlorobutyrophenone with sodium azide. δ-Azidovalerophenone (δ-AV) and ε-azidohexanophenone (ε-AH) were prepared directly from the ω-chloro ketones. The UV spectra of all three azidoketones showed no significant differences from that of an equimolar mixture of valerophenone and n-butyl azide. At 313 nm, the ketone n,π* transition contributes an extinction coefficient of 42 M^{-1} cm^{-1}, while the tail of the azide absorption (λ_{max} 285 nm) contributes only 7 M^{-1} cm^{-1}. At 365 nm only the carbonyl absorbs.

Photoproducts. Irradiation of degassed benzene solutions 0.05-0.10 M in ε-AH at 365 nm produced primarily acetophenone and small quantities of what, by their GC retention times, were assumed to be the expected[6] cyclobutanol coproducts. The acetophenone accounted for 90% of reacted ε-AH.

Comparable solutions of δ-AV gave, with 365-nm excitation, primarily acetophenone. A small amount of the cyclic imine 2-phenyl-3,4,5,6-tetrahydropyridine was identified by GC/mass spectrometry. The only other volatile substance detected by GC analysis was unreacted δ-AV.

Comparable solutions of γ-AB gave primarily an oligomeric, brown oil. Volatile products account for only 70% of reacted γ-AB, with 2-phenyl-Δ^1-pyrroline and 2-phenylpyrrole being the major products, acetophenone being a minor product, and a fourth unidentified product being formed in ⅓ the yield of the pyrrole. The azidoketone itself was stable to GC analysis with a flame ionization detector but partially pyrolyzed to the pyrroline on a thermal conductivity detector.

Irradiation of γ-AB at 313 nm produced the same products in a material balance of only 60% and with 1.5 times as much 2-phenylpyrrole relative to the other products. At both wavelengths, actual yields of acetophenone were constant with increasing conversion whereas yields of the two cyclic amines decreased.

Quantum Yields. Since 313-nm excitation directly excites the azido group and gives a much larger proportion of products derived from excited azide, most quantitative measurements were made at 365 nm. Quantum yields were measured relative to valerophenone actinometers.[7]

For δ-AV, acetophenone quantum yields decreased with increasing conversion, as indicated in Table I. Consequently, the quantum yields listed in Table II were extrapolated to zero conversion. Quenching by the imine product accounts for some of the conversion dependence. p-Fluorophenylpyrroline was found to quench the photoelimination of butyrophenone with a Stern-Volmer slope of 265 M^{-1}, i.e., 44% as efficiently as "diffusion-controlled" quenchers.[8] We assume a comparable quenching efficiency for the cyclic imine formed from δ-AV. Since imine accounts for only 10% of the products, however, not enough is produced to be responsible for all the effect.

Product quantum yields from γ-AB did not vary appreciably with conversion. However, they did show a small decrease with increasing azidoketone concentration (Table I). The acetophenone yield in Table II was extrapolated to zero ketone concentration. The cause of the concentration effect is obscure. Butyl azide quenches butyrophenone with a Stern-Volmer slope ($k_q\tau$ value) of only 12 M^{-1}; since τ = 130 ns,[8] k_q is on the order of 1 × 10^7 M^{-1} s^{-1}, half the literature value for quenching of triplet acetophenone.[5] Therefore, bimolecular quenching of triplet γ-AB by ground-state γ-AB is unlikely, given the short triplet lifetime of γ-AB (see below).

Quantum yields of acetophenone are doubled by 0.5 M pyridine, the usual effect of added Lewis base.[9] The maximum values listed in Table II for the γ- and δ-azidoketones are extrapolated to zero concentration and conversion.

Quenching Studies. Benzene solutions 0.07 M in azidoketone and containing various concentrations of 1-methylnaphthalene were irradiated in parallel at 365 nm. Linear Stern-Volmer plots of relative acetophenone quantum yields provided values of $k_q\tau$. In the case of γ-AB, 2-phenylpyrrole formation was quenched with the same efficiency as was acetophenone at 10% total conversion (Figure 1). The $k_q\tau$ value listed for δ-AV in Table II was extrapolated to zero conversion by increasing the measured value at 6% conversion by the same 14% found when extrapolating quantum yields. The $k_q\tau$ value for γ-AB was not extrapolated to zero ketone concentration since there is no evidence that triplet ketone is affected by ground-state ketone. Such a correction would raise the measured value no more than 40%, i.e., to 16 M^{-1}.

Sensitization Studies. Figure 2 displays the standard double reciprocal plots[10] for cis-trans isomerization of *cis*-1,3-pentadiene sensitized by 0.07 M γ-AB and δ-AV. Parallel irradiation at 365 nm of 0.07 M acetophenone-pentadiene (ϕ_{isc} = 1)[11] provided actinometry. Reciprocal intercepts are listed as ϕ_{isc} values in Table II. The intercept/slope values yield the $k_t\tau$ values listed in Table II and are in good agreement with the $k_q\tau$ values obtained in the quenching studies. Under the conditions employed there is no detectable disappearance of δ-AV and only a few percent of γ-AB. Actual percent isomerizations of diene ranged from 3 to 15%. The yellow color characteristic of irradiated γ-AB solutions was absent in all solutions containing diene, even though not all triplet ketone was quenched. Presumably the diene traps the small amount of nitrene formed and thus prevents any oligomerization. Correction for the resulting loss of diene would raise ϕ_{isc} at most 20% and lower $k_q\tau$ values a corresponding amount.

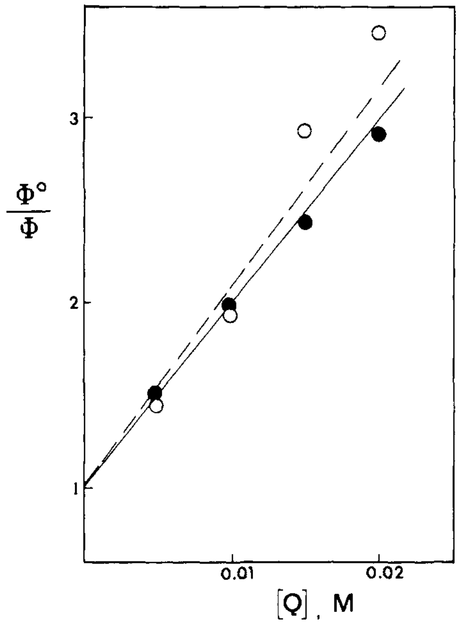
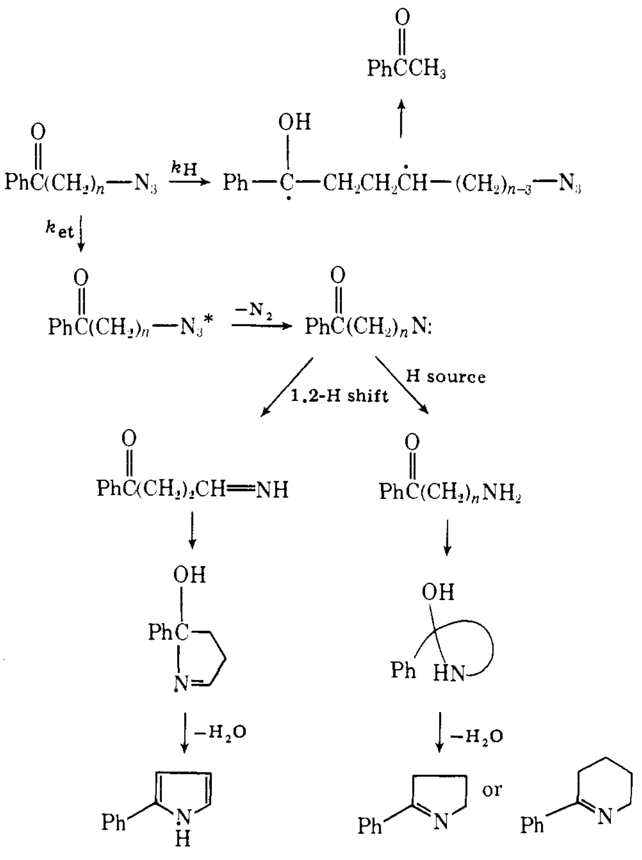


Figure 1. Stern-Volmer quenching of products from γ-azidobutyrophenone: ○, acetophenone; ●, 2-phenylpyrrole.

Discussion

Since phenyl ketones sensitize the loss of nitrogen from alkyl azides,[5] the photochemistry of these three ω-azidoketones is best interpreted as displaying a varying competition between two triplet ketone reactions: γ-hydrogen abstraction and energy transfer to the azido group. The triplet azides yield nitrenes which can rearrange to imines,[12] pick up hydrogen to yield amines,[13] and attack ground-state azide like other triplet nitrenes.[13] Cyclization of the ω-amino ketones would yield the observed cyclic imines; cyclization of the γ-imino ketone would yield the pyrrole.[14]

Scheme I



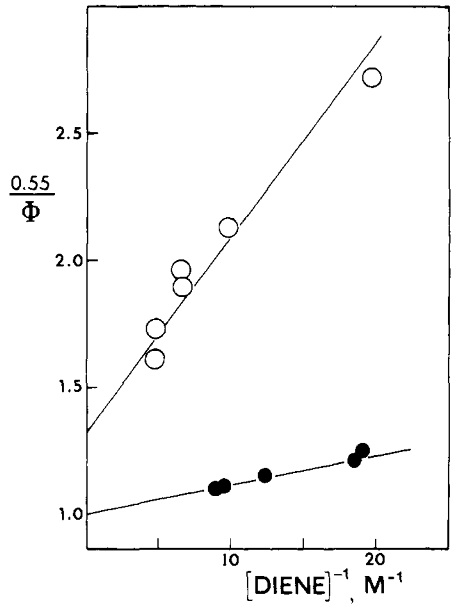


Figure 2. Sensitization plots for 0.07 M azidoketones: ○, γ-AB; ●, δ-AV.

Table III. Kinetic Parameters for $PhCO(CH_2)_nN_3$

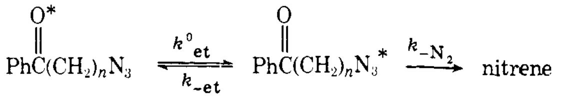
n	$1/\tau$, 10^8 s^{-1}	k_H, 10^8 s^{-1}	k_{et}, 10^8 s^{-1} [a]
3	3.8 ± 0.5	0.05	3.7
4	0.47 ± 0.03	0.18	0.29
5	0.54 ± 0.02	0.54	<0.03
∞ [b]	1.5	1.5	

[a] See text for possible contributions to measured rate constants. [b] Hexanophenone as model compound, ref 7.

Undoubtedly further work could maximize heterocycle yields, perhaps discover other products such as azo compounds[13] or their decomposition products, and better characterize the mechanisms of the nitrene reactions. However, the main purpose of this study was to explore the efficiency of intramolecular energy transfer to the azido group. Characterization of heterocyclic products expected from a nitrene confirms that this energy transfer is the predominant mode of triplet decay in γ-AB, a minor mode in δ-AV, and negligible in ε-AH.

Triplet Lifetimes. The quenching and sensitization studies gave comparable values for $k_q\tau$ and $k_t\tau$. Since $k_q = k_t = 5 \times 10^9$ M^{-1} s^{-1} for energy transfer from phenyl ketones to conjugated dienes and to naphthalene in benzene at room temperature,[8,15,16] we can calculate the overall triplet decay rates listed in Table III. Alkyl azides have higher triplet energies than do phenyl ketones;[5] so any quenching of excitation localized on the ω-azido group would be similarly diffusion controlled, although we suspect the triplet azides of being too short lived for appreciable bimolecular quenching. This possibility introduces the problem of the potential reversibility of energy transfer between the two chromophores.

Lewis and Saunders concluded that energy transfer from phenyl ketones to alkyl azides is several kilocalories per mole *endothermic*.[5] Although it was not widely recognized at that time, it is now well known that any endothermic energy transfer is usually reversible.[10,17] In this case, exothermic back transfer from triplet azide to carbonyl should be very fast, but the extent of reversibility depends on how fast nitrogen is lost from triplet azide. There are three possibilities: (1) $k_{-et} \gg k_{-N_2}$; (2) $k_{-et} \ll k_{-N_2}$; (3) $k_{-et} \approx k_{-N_2}$.



$$\overset{O^*}{\overset{\|}{\mathrm{PhC}}}\mathrm{(CH_2)}_n\mathrm{N_3} \underset{k_{-\mathrm{et}}}{\overset{k^0{}_{\mathrm{et}}}{\rightleftharpoons}} \overset{O}{\overset{\|}{\mathrm{PhC}}}\mathrm{(CH_2)}_n\mathrm{N_3}^* \xrightarrow{k_{-\mathrm{N_2}}} \text{nitrene}$$

The first possibility is complete equilibration of excitation[18] and is ruled out by the results. Triplet decay rates and quantum yields would be defined by the equations

$$1/\tau_{\mathrm{eq}} = \chi_{\mathrm{CO}}k_{\mathrm{H}} + \chi_{\mathrm{N_3}}k_{-\mathrm{N_2}} \quad (1)$$

$$\Phi_{\mathrm{II}}{}^{\mathrm{eq}} = \chi_{\mathrm{CO}}k_{\mathrm{H}}\tau_{\mathrm{eq}} \quad (2)$$

where χ_{CO} and $\chi_{\mathrm{N_3}}$ are the fractions of excitation on each functional group, and it is assumed that each triplet undergoes only one chemical reaction. There is no reason to suspect that $k_{-\mathrm{N_2}}$, χ_{CO}, or $\chi_{\mathrm{N_3}}$ would vary among the three ketones. Given the electron-withdrawing nature of the azido group,[19] the values of k_{H} would increase in the order γ-AB < δ-AV < ϵ-AH.[7] However, the observed $1/\tau$ values decrease in that order. Moreover, the 100-fold variation in type II quantum yields is much bigger than any previously observed[7] variation in k_{H} values. In fact, any analysis must conclude that $k_{\mathrm{H}} \sim k_{\mathrm{et}}$, so that a model involving complete equilibration cannot obtain.

The fact that pyrrole and acetophenone formation from γ-AB are quenched with comparable efficiencies suggests either complete equilibration (just ruled out) or completely irreversible energy transfer. We cannot rule out partially reversible energy transfer and can merely set a maximum triplet lifetime for the azide group of ≤ 1 ns. Any larger value would have allowed observation of a distinctly quadratic[10] Stern-Volmer plot for quenching of the 2-phenylpyrrole from γ-AB.

In any event, we can divide triplet lifetimes into a straightforward competition between hydrogen abstraction and energy transfer to azide, which may or may not be partially reversible, and discuss observed rates of energy transfer.

$$1/\tau = k_{\mathrm{H}} + k_{\mathrm{et}} \quad (3)$$

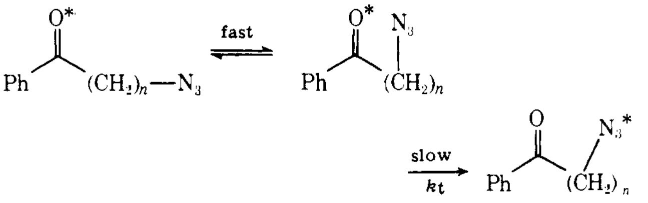
$$k_{\mathrm{et}} = k^0{}_{\mathrm{et}}\left(\frac{k_{-\mathrm{N_2}}}{k_{-\mathrm{et}} + k_{-\mathrm{N_2}}}\right) \quad (4)$$

$$\Phi_{\mathrm{II}}{}^{\mathrm{max}} = \phi_{\mathrm{isc}}k_{\mathrm{H}}\tau \quad (5)$$

Values of k_{H} can be extracted from τ by application of eq 5[7] and are listed in Table III. The remainder of $1/\tau$ is ascribed to k_{et},[20] since in the absence of intramolecular interaction the triplet carbonyl only abstracts γ hydrogens. Of course, the value of $(1/\tau - k_{\mathrm{H}})$ really equals $(k_{\mathrm{et}} + k_{\mathrm{x}})$, where k_{x} is the rate constant for any other reaction between triplet ketone and azide. Lewis and Saunders found that only 56% of the quenching of triplet acetophenone by alkyl azides led to loss of nitrogen.[4] They hypothesized that some bent triplet azide was formed with too little energy to lose nitrogen. If that were the case, 44% of the energy transfer could be almost completely reversible. Unfortunately, no variations in sensitizer concentration, which would detect reversibility,[8,10] were reported. It is also possible that 44% of the quenching interaction involves some process other than energy transfer. The value for k_{et} listed in Table III therefore may include some quenching besides energy transfer, although the ubiquitous charge transfer quenching[15] is unlikely here because of the high oxidation potential of the azido group. Whatever the exact composition of k_{et}, our main interest is in comparing the various intramolecular $k_{\mathrm{et}}{}^{\mathrm{obsd}}$ values with each other and with the bimolecular value.

Relative Rates of Intramolecular Energy Transfer. As the numbers in Table III show, the value of k_{et} decreases by at least an order of magnitude for each additional methylene interposed between benzoyl and azide groups for $n = 3$-5. The value of 2.9×10^7 s^{-1} for $n = 4$ is comparable to the reported[5] bimolecular rate constant of 2-3×10^7 M^{-1} s^{-1} and indicates that a δ-azido group is effectively 1 M. A similar observation was made for δ-amino ketones.[20]

Scheme II



$$k_{\mathrm{et}} = \sum_i \chi_{\mathrm{f}i}k_{\mathrm{t}i} \quad (1)$$

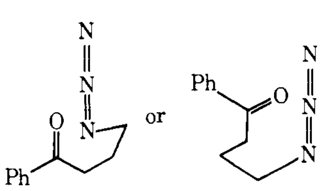
$$\chi_{\mathrm{f}}\ (\text{total}) = 1 - \chi_{\mathrm{u}}\ (\text{total}) \quad (2)$$

The bimolecular rate constant is determined by the efficiency of energy transfer (or other quenching) during a solution encounter ($\leq 0.2\%$ for triplet phenyl alkyl ketones and alkyl azides). This intrinsic inefficiency indicates that the intramolecular process occurs only a small fraction of the times in which conformations allowing sufficient orbital overlap are attained. Therefore, like rate constants for normal "slow" ground-state reactions, the measured k_{et} values are dominated by conformational equilibria, as indicated in Scheme II.

Scheme II recognizes that there are stretched-out conformations unfavorable for energy transfer and favorable cyclic conformations. The actual rate constant for energy transfer is a sum over all favorable conformations. Since the rate constant for triplet energy transfer decreases an order of magnitude for every additional 1 Å between donor and acceptor,[21] favorable conformations require close approach of the two chromophores. We assume that the number of such conformations is always small and becomes an increasingly small fraction of the total conformations available as n increases.

The contribution of each individual conformation to the total process depends both on the fractional population of that conformer ($\chi_{\mathrm{f}i}$) and on the k_{t} value for that particular geometry. The maximum k_{t} value ($\sim 10^{11}$ s^{-1})[21,22] presumably applies only to those conformations in which the two chromophores can approach as close as the 4-Å sum of their π systems' van der Waals radii and with the optimum (as yet unknown) relative orientation.[20] The χ_{f} value for each such conformation is determined by its free energy relative to those of all available conformations. Since bringing two chromophores close together necessarily involves cyclic conformations, the χ_{f} values must partially reflect the various steric strain factors which affect different-sized rings.

With the above considerations in mind, we propose that the tenfold decreases in $k_{\mathrm{et}}{}^{\mathrm{obsd}}$ for each additional methylene reflect primarily the increasing strain in medium-sized rings. Unfortunately, the optimum orientation for energy transfer between carbonyl and azide is not known. Therefore, we really do not know how many atoms comprise the "ring" in the best conformation for any particular value of n. The uncertainty is magnified by the linear structure of the azide group.[23]



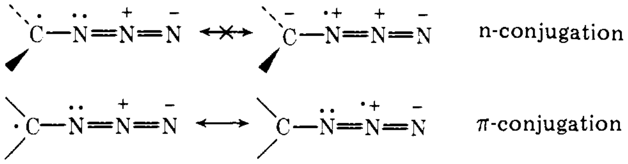
An alternative explanation of decreasing $k_{\mathrm{et}}{}^{\mathrm{obsd}}$ with increasing n invokes the additional entropy loss for each additional frozen rotation in the cyclic conformation for reaction.[24,25] Entropy loss in energy transfer probably is not as important as it is in chemical reactions involving covalent bond formation; several conformations are possible in which energy transfer can occur, whereas bond formation generally requires one or a few conformations.

The importance of ring strain in determining the value of k_{ct}^{obsd} would show up best in the azidoketones where $n = 1$ and 2. Unfortunately we were unable to purify either compound without its decomposing. Saunders has determined that some α-azido aryl ketones form long-lived triplets.[26] The resulting conclusion that k_{et} is low agrees with similar observations on α-amino[20] and α-styrenyl[2] ketones and suggests that, in general, the strain inherent in small rings slows intramolecular interaction of α-substituted triplet excited ketones.

We are currently studying keto amines and keto sulfides with the expectation that the localized lone pairs on S and N will allow a better dissection of the factors which govern intramolecular quenching.

Azide Substituent Effect on k_H Values. We demonstrated earlier[7] a very good linear free energy relationship between the rate constant for triplet state γ-hydrogen abstraction in δ-substituted valerophenones and the σ_I value for the substituents: $\log (k/k_0) = -1.85\ \sigma_I$. The k_H value for δ-AV indicates a σ_I value for N_3 of 0.46. A similar relationship was found for ϵ-substituted hexanophenones: $\log (k/k_0) = -0.76\ \sigma_I$. The k_H value for ϵ-AH also indicates a σ_I value for N_3 of 0.46. The good fit of both azidoketones with the same σ_I value, together with the excellent earlier correlation, suggests that we have measured a reliable σ_I value, one very close to that (0.44) determined indirectly from σ_m and σ_p values.[19]

Resonance Effect of N_3. As described earlier,[7] one can extrapolate a ρ value of -4.3 for γ-hydrogen abstraction in γ-substituted butyrophenone triplets. Therefore, we would expect $\log k/k_0 = \sigma\rho = -2.0$ in γ-AB. Triplet γ-AB actually reacts 4% as fast as triplet valerophenone, four times faster than predicted solely by the inductive effect of the azido group. Therefore, we deduce a fourfold kinetic resonance factor for N_3 presumably due to conjugation of its π electrons with the incipient p orbital on the γ carbon. Similar small resonance factors were found for other π-conjugating substituents, whereas n-conjugating substituents (including Cl, with a similar σ_I value) show considerably larger resonance factors.[7] This comparison strongly suggests that the lone pair on azido does not stabilize a radical on the adjacent carbon. That such is the case is not surprising, since two adjacent positive nitrogens would result.



Experimental Section

Chemicals. Benzene (Mallinckrodt nanograde) was washed with sulfuric acid and distilled from P_2O_5. Pyridine (Mallinckrodt) was distilled from barium oxide.

Aldrich 1-methylnaphthalene and Chemical Samples Co. *cis*-1,3-pentadiene were used as received. Valerophenone and acetophenone were available from earlier studies.[7]

Butyl azide was prepared by treating *n*-butyl bromide with sodium azide in 6:1 methylcarbitol-water.[27]

2-(*p*-Fluorophenyl)Δ^1-pyrroline was prepared by adding γ-chlorobutyronitrile to *p*-fluorophenylmagnesium bromide and then heating the resultant imine salt in xylene at 100 °C.[28] Product was obtained by distillation: bp 77 °C (0.2 Torr); IR 1650 cm^{-1}; ^{1}H NMR (CCl_4) δ 2.00 (m, 2 H), 3.00 (t, 2 H), 4.00 (t, 2 H), 7.60 (m, 4 H).

γ-Azidobutyrophenone was synthesized as follows. The ketal of γ-chlorobutyrophenone (Aldrich) and ethylene glycol was prepared and added to DMF containing a 10% excess of sodium azide. The mixture was heated at 80 °C for 24 h; it was then cooled, poured into chloroform, and extracted with water and saturated aqueous sodium chloride. After the chloroform was removed, the azidoketal was added to a 50:50 mixture of THF and 0.2 N HCl, stirred for 2 days, and then neutralized with NH_4OH. The THF was distilled off; the remaining aqueous solution was extracted with ether. γ-AB was collected by vacuum distillation (50% yield) and then purified by being passed through alumina and redistilled: bp 122 °C (0.03 Torr); IR 1680, 2100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.94 (m, 2 H), 3.00 (t, 2 H), 3.40 (t, 2 H), 7.70 (m, 5 H); UV (heptane) λ_{max} 325 nm (ϵ 50), 278 (1000), 240 (10 000); MS *m/e* 161.

δ-Azidovalerophenone was prepared similarly by treating δ-chlorovalerophenone[7] in DMF with sodium azide. The crude δ-AV was passed through alumina, then recrystallized twice from cold hexane, mp 22–23 °C. The oily ketone was dried under vacuum for 2 days, then vacuum distilled: bp 140 °C (0.08 Torr); IR 1690, 2100 cm^{-1}; ^{1}H ($CDCl_3$) δ 1.80 (m, 4 H), 2.92 (t, 2 H), 3.30 (t, 2 H), 7.70 (m, 5 H); UV (heptane) λ_{max} 325 nm (ϵ 55), 276 (1100), 238 (16 000); MS *m/e* 175.

ϵ-Azidohexanophenone was prepared from ϵ-chlorohexanophenone[7] in the same way in 55% yield: mp 27 °C; bp 146 °C (0.08 Torr); IR 1700, 2100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.50 (m, 6 H), 2.90 (t, 2 H), 3.20 (t, 2 H), 7.70 (m, 5 H); UV (heptane) λ_{max} 325 nm (ϵ 50), 276 (900), 238 (16 000); MS *m/e* 189.

Identification of Photoproducts from γ-AB. Acetophenone and 2-phenyl-Δ^1-pyrroline[29] were collected by preparative GC of irradiated γ-AB solutions and were identified by their spectroscopic properties. To isolate other GC-volatile products, degassed tubes containing 0.07 M ketone were irradiated at 365 nm for 2 weeks. After removal of benzene, 1.0 g of brown oil remained. It was chromatographed through 100 g of alumina. Pure benzene eluted acetophenone, the pyrroline, and γ-AB. Ethyl acetate-benzene (20:80 by volume) eluted a brown oil which contained 2-phenylpyrrole. Nothing else was eluted even with methanol.

The pyrrole was vacuum sublimed from the brown oil and then resublimed. It was identified by comparison of its properties to those in the literature:[30] mp 115–118 °C (lit. 129 °C); IR 3425 cm^{-1}; ^{1}H NMR δ 6.15–6.65 (m, 3 H), 7.30 (broad s, 5 H); MS *m/e* 143.

The brown oil (common to reactions involving azides[31]) was not volatile enough to produce any GC signals. Its IR showed C=O, N_3, and either NH or OH absorbances; its NMR was nearly identical with that of γ-AB.

Procedures. Quantum yield determinations, quenching studies, and sensitization studies all were performed as previously described.[20] All quantitative irradiations were performed on a "merry-go-round", with Corning no. 7-83 filters to isolate the 365-nm region of an Hanovia 450-W mercury arc. An Infotronics Model CRS-208 digital integrator was used during GC analysis. UV spectra were measured in a Unicam Model SP-800 spectrometer.

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Proton Transfers of Substituted Ammonium Salts. 14. The 1,*cis*-2,6-Trimethylpiperidinium Ion in Anhydrous Acidic Dimethyl Sulfoxide

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Abstract: The kinetics of nitrogen inversion of the title compound has been studied at 25 °C in acidic Me_2SO using variable pH (from −0.3 to 7.7) and piperidine concentrations C_0 (0.2–0.5 M). The two isomeric piperidinium cations AH^+ and BH^+, where the *N*-methyl is in equatorial or axial position, respectively, are observed either by DNMR using a solution of both isomers in equilibrium or by equilibration NMR using a solution initially containing one isomer (AH^+) only. In both cases, the interconversion (i) is brought to within the appropriate time scale through protonation of the nitrogen atom according to

$$AH^+ \underset{k_{NB}}{\overset{k_{NA}}{\rightleftarrows}} BH^+ \text{ (i) } AH^+ \underset{k_p}{\overset{k_d}{\rightleftarrows}} A \underset{k_B}{\overset{k_A}{\rightleftarrows}} B \underset{k_d}{\overset{k_p}{\rightleftarrows}} BH^+ \text{ (ii)}$$

the scheme in (ii). Three different laws are obtained: $k_{NA} + k_{NB} = 120.4 \times 10^{-7} C_0/[H^+]$ or 3×10^{-4} or $3.5 \times 10^{-4}/[H^+]$ (s^{-1}) according to the pH range investigated (pH >2 or 0 < pH < 2 or pH < 0, respectively). They can be accounted for when the deprotonation and reprotonation rates are taken into consideration: $k_d = k_3$ [piperidine] + k_1, and $k_p = k_3$[piperidinium ion] + k_{-1}, where $k_3 = 2.70 \times 10^4$ M^{-1} s^{-1}, $k_1 = 3 \times 10^4$ s^{-1} and $k_{-1} = 6.7 \times 10^5$ M^{-1} s^{-1} refer to the reactions

$$AH^+ \text{ (or } BH^+) + (A + B \xrightarrow{k_3} A \text{ (or B)} + (AH^+ + BH^+) \text{ and } AH^+ \text{ (or } BH^+) + Me_2SO \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A \text{ (or B)} + Me_2SO\cdots H^+$$

Compared to previous data in aqueous solutions, the proton transfer and nitrogen inversion rates are respectively decreased and increased by four and three orders of magnitude. These results illustrate the importance of water as a small bridging molecule both allowing fast proton transfers within sterically hindered acid–base pairs and promoting the formation of associated species, $A\cdots H_2O\cdots AH^+$, which are not likely to undergo inversion.

Introduction

Studies of proton transfer in aprotic solvents have been performed mainly for the purpose of comparison with aqueous solutions. One of the objectives of such studies is to try to elucidate by comparison the role of the water molecule in these transfers.[1] On account of its amphoteric properties and of its small size, this molecule may be tentatively assumed to play the role of an intermediary proton vector between an acid AH and a base B, thus facilitating the exchange and increasing its rate according to the equation

$$AH + H{-}O{-}H + B \rightleftarrows A + H{-}O{-}H + HB$$

This assumed role could be of fundamental importance in biological media[2] where enzyme catalysis often involves the protonation and deprotonation of the active site in an aqueous environment at a fixed pH.

The enhancement of proton transfer by an interstitial water molecule has been clearly demonstrated for the first time by Grunwald and co-workers, using methylammonium ions (AH^+) in aqueous acidic solutions of variable pH.[3] The deprotonation of AH^+ was accounted for by the set of reactions

$$AH^+ + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A + H_3O^+ \qquad \text{(R1)}$$

$$AH^+ + OH^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} A + H_2O \qquad \text{(R2)}$$

$$AH^+ + A \underset{k_3}{\overset{k_3}{\rightleftarrows}} A + AH^+ \qquad \text{(R3)}$$

$$AH^+ + H{-}O{-}H + A \underset{k_3'}{\overset{k_3'}{\rightleftarrows}} A + H{-}O{-}H + AH^+ \qquad \text{(R'3)}$$

among which mechanism R'3 is of the type defined above (where B is replaced by the conjugate base A of AH^+). Mechanisms R3 and R'3 only were predominant in moderately acidic solutions (pH ≃ 3-5). The weight of reaction R'3 compared to that of R3 strongly depends on the structure of the ammonium salt, from about 10% (NH_4^+) to 50%

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