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Photolysis of Reluctant Azoalkanes. Effect of Structure on Photochemical Loss of Nitrogen from 2,3-Diazabicyclo[2.2.2]oct-2-ene Derivatives

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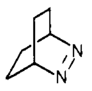
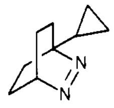
Abstract: Azoalkanes containing the bicyclo[2.2.2] skeleton often prove to be remarkably stable toward loss of nitrogen. These derivatives of 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) also exhibit fluorescence whose lifetime extends to 600 ns. This paper is an attempt to understand the effect of fused rings and bridgehead substituents on the photochemical and photophysical properties of DBO. The main factor controlling quantum yields of nitrogen is a 6–11 kcal mol^{-1} activation barrier that differs for the singlet and triplet states and that seems to mimic the barrier to ground-state deazatization. The product distribution for DBO derivatives is rationalized on the basis of interconverting singlet 1,4-biradicaloids.

Whereas most azoalkanes lose nitrogen photochemically with relative ease,[1] a number of cases have been discovered where deazatization proceeds with low efficiency. Most of these so-called "reluctant azoalkanes" contain the 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) skeleton. We have shown previously[2,3] that the singlet state of such compounds possesses a thermal barrier to deazatization. The present work deals mainly with compounds **1**–**8**, which were chosen to assess the effect of bridgehead substituents and fused rings on the photochemistry of DBO. All of these DBO derivatives exhibit fluorescence, which serves as a convenient probe of singlet-derived processes. Although the relationship between structure and the various excited-state rate constants is complex, a rough correlation emerges between photochemical and thermal stability. The photochemistry of these compounds is rationalized in terms of a thermally activated crossing from the $^1(n,\pi^*)$ and $^3(n,\pi^*)$ state to dissociative surfaces.


DBO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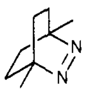
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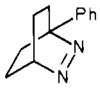
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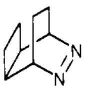
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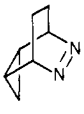
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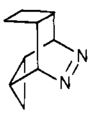
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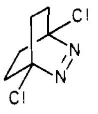
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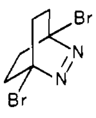
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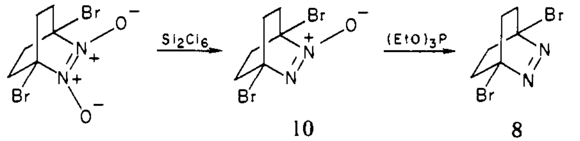
Synthesis of Compounds

DBO,[4] **1**,[5] **2**,[6] **3**,[7] **4**,[8] **5**,[7] **6**,[9] and **7**[10] have all been reported previously. Br$_2$DBO (**8**) was made by bromination[11] of cyclohexane-1,4-dione dioxime to afford **9** in low yield. Successive reduction with Si$_2$Cl$_6$[12] and (EtO)$_3$P gave **8**. Attempts to prepare the corresponding diiodo compound from 1,4-diiodo-1,3-cyclohexadiene[13] and *N*-methyltriazolinedione were not successful.



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Results

Table I shows triplet-sensitized quantum yields (Φ_r^S) for DBO, **2**, and **4** as a function of temperature. Fitting the data (cf. Figure 1) to eq 1[3] yielded the activation energies shown in Table II.

$$\ln (1/\Phi_r - 1) = \ln (k_d/A) + E_a/RT \qquad (1)$$

Because we had not previously encountered an azoalkane where the quantum yield of sensitized photolysis exceeded that of direct irradiation, the high Φ_r's for **2** in Table I came as a surprise. (Φ_r for direct irradiation of **2** at 25 °C is about 0.02.) The trend was confirmed by laser irradiation (337 nm) of **2** at 64.8 °C, giving $\Phi_r(\text{direct}) \equiv \Phi_r^D = 0.137$ and $\Phi_r(\text{sensitized}) \equiv \Phi_r^S = 0.272$. In contrast, the same experiment at 66.5 °C with DBO led to $\Phi_r^D = 0.063$ and $\Phi_r^S = 0.048$. It was later discovered that **5** also shows $\Phi_r^S > \Phi_r^D$ so that this behavior can no longer be considered exceptional.

A complication in the above experiments is that the observed quantum yield can depend on the extent of conversion, as reported earlier for DBO.[4] This effect is attributed to formation of singlet quenchers[4] and, as seen in Table III, is significant only for direct irradiation of DBO. In this case Φ_r^D is a bit higher than Φ_r^S at zero conversion, but for **2**, triplet sensitization is definitely more efficient than direct irradiation. These results confirm that the different slopes in Figure 1 are real and that only by coincidence are the direct and sensitized lines so close in DBO. In general then, the two photolysis modes exhibit different activation energies.

The most remarkable property of DBO is its intense, extremely long-lived fluorescence.[4,14] Because most of the lifetimes (τ_f) could

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Table I. Benzophenone-Sensitized Deazatization of DBO Derivatives

compd	$\Phi_r{}^{S\,a}$ (temp, °C)
DBO	0.0054 (7.0), 0.013 (23.0), 0.040 (46.0), 0.073 (63.0)
2	0.028 (6.0), 0.061 (23.6), 0.246 (57.0), 0.436 (77.0)
4	0.134 (6.0), 0.223 (22.7), 0.521 (57.0), 0.609 (77.0)

[a] Nitrogen quantum yield in benzene by using 313-nm light.

Table II. Activation Energy for Deazatization of DBO Derivatives[a]

compd	$E_a{}^{D\,b,c}$	$E_a{}^{S\,b}$	$\mathrm{int}^{D\,c,d}$	$\mathrm{int}^{S\,d}$
DBO	8.6	9.0	−10.3	−11.0
2	10.2	9.2	−13.6	−12.8
4	7.4	6.6	−11.5	−10.0

[a] D = direct irradiation; S = sensitized by benzophenone. [b] kcal mol^{-1}. [c] Cf. ref 3. [d] Intercept from eq 1.

Table III. Nitrogen Quantum Yields as a Function of Conversion in Benzene

compd[a]	T, °C	mode	% conversion	Φ_r
DBO	39	dir[b]	6.2	0.034
			11.6	0.031
			19.0	0.026
			27.9	0.022
DBO	39	sens[c]	4.0	0.032
			7.1	0.029
			14.9	0.030
			29.4	0.030
2	25	dir[b]	4.8	0.024
			9.4	0.024
			17.3	0.022
			29.5	0.019
2	39	dir[b]	4.0	0.055
			8.0	0.055
			14.6	0.055

[a] Concentration = 0.03 M. [b] 366 nm. [c] 313 nm with benzophenone sensitizer.

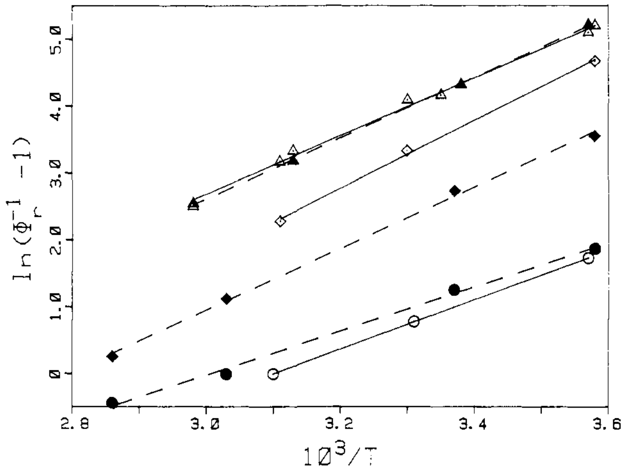
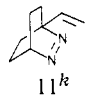
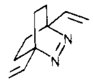


Figure 1. Temperature-dependent quantum yields plotted according to eq 1. Open symbols, direct irradiation; solid symbols, benzophenone sensitized; △, DBO; ◇, **2**; ○, **4**.

Table IV. Temperature-Dependent Fluorescence Lifetimes (ns) in Benzene

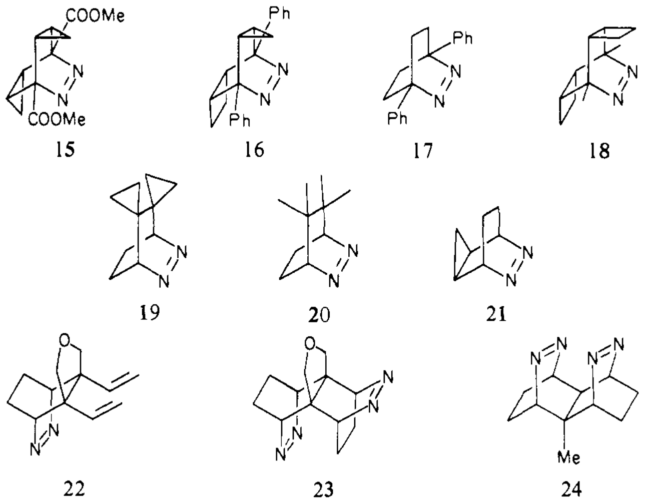
compd	τ_f (T, °C)
1	478 (12.6), 423 (20.6), 398 (25.4), 357 (29.2), 297 (37.6)
2	723 (5.7), 667 (19.8), 555 (51.2), 433 (65.4)

Table V. Photochemical Parameters for DBO Derivatives at 25 °C[a]

compd	$\Phi_r{}^{D\,b}$	$\Phi_r{}^{S\,b}$	$\tau_f{}^c$	$\Phi_f{}^d$	10^{-5}-$k_f{}^e$
DBO	0.018,[f] 0.022[g]	0.014[g,h]	434	0.39	9.0
1-Me DBO			500	0.44	8.8
1	0.16	0.12	398	0.20	5.0
1[i]			526	0.23	4.4
2	0.024,[f] 0.014[j]	0.069[h]	599	0.53	8.8
3	1.0	0.82	2.5	0.0014	5.6
4	0.28	0.24[h]	302	0.18	6.0
5	0.022	0.083	155	0.097	6.2
6	0.28		118	0.066	5.6
7	0.020	0.068	58	0.033	5.7
7[i]	0.10		464	0.19	4.1
8	0.022		60	0.032	5.3
 11[k]	1.0	0.75	0.56	0.0009	16
 12[k]	1.0		0.53	0.0014	26

[a] In benzene unless otherwise specified. [b] Nitrogen quantum yield under direct (D) and benzophenone sensitized (S) irradiation. [c] Fluorescence lifetime, ns. [d] Fluorescence quantum yield. [e] Rate constant for fluorescence, s^{-1}. [f] This work. [g] Reference 4. [h] Interpolated from Table I. [i] In acetonitrile. [j] Reference 2. [k] Reference 3.

Chart I



be measured in our laboratory by pulsed laser excitation and monitoring the decay with an oscilloscope, this technique was applied to all of the DBO derivatives available.[15] As seen in Table IV, τ_f of **1** and **2** decreases considerably at elevated temperature, indicating an activation energy for some singlet-derived process. Fluorescence lifetime measurements were used to show that DBO singlets are rapidly quenched by 2,2,6,6-tetramethylpiperidine-1-oxyl ($k_q = 4.2 \times 10^9$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) and CBr_4 ($k_q = 1.0 \times 10^{10}$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$). Very recently, it was found that even CCl_4 is a moderately efficient quencher of excited singlet **1** ($k_q = 1.9 \times 10^7$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$).[16]

Lifetimes of all DBO derivatives studied are shown in Table V, along with quantum yields for fluorescence (Φ_f) and deazatization (Φ_r). It was found for compounds **2**, **4**, **5**, and **6** that $\Phi_r{}^D$

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(15) The fluorescence lifetime of **3**, **11**, and **12** was determined by 353-nm picosecond laser excitation at the CFKR in Austin, TX.

(16) This observation raises the possibility that the excited singlet state of DBO derivatives reacts with CCl_4. If the same is true of the triplet state, such a reaction might account for the dichlorinated hydrocarbon found in the benzophenone sensitized irradiation of **1** in CCl_4.[5] These hypotheses are being subjected to experimental test.

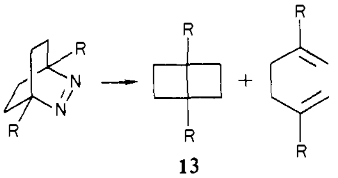
Table VI. Product Distributions (%) from DBO Derivatives

compd	mode	13	14
DBO	dir	42	58
	dir	42[a]	58
	sens	33	67
	sens	27[a]	73[a]
1	dir	30	65
	sens[b]	18	21
2	dir	39	61
	sens	54	46
3	dir	0	100[c]
4	dir[d]	22	53[e]
	dir[f]	38	38[e]
	sens[g]	9	70[e]
5	dir		+[h]
	sens		+[h]
7	dir[i]	~33	~33
11	dir[j]	0	100
15	dir[k,l]	95	4
	sens[k,m]	27	42
16	dir[n]	0	100[o]
17	dir[c,p]	0	100
18	dir[q]	100	0
19	dir[r]	66	32
20	dir[r]	29	71[s]
21	dir[t]	20[u]	60
22	dir[v]	33	22
23	dir[v]	0	100[w]
24	dir, sens	+[x]	+[x]

[a] Reference 4. [b] Reference 5. The only other product is 4-propylidene-1-cyclohexene. [c] Irradiated at 6 °C in C_6D_6 and monitored by NMR. [d] In pentane, ref 19. 1,2-Divinylcyclobutane and *cis*-1,5-cyclooctadiene are also formed. [e] *cis,trans*-1,5-cyclooctadiene. [f] In hexane, ref 20. [g] In pentane with biacetyl sensitizer, ref 20. [h] Only 1,4-cycloheptadiene could be identified; see text. [i] Estimated data for perfluoromethylcyclohexane, ref 10. [j] At −78 °C in acetone-d_6, ref 3. [k] Reference 21. [l] In methanol. [m] Acetone sensitized. [n] In $CDCl_3$ at −60 °C, ref 22. [o] The cyclobutane ring remains intact. [p] Reference 23. [q] At −15 °C in ether, ref 24. [r] Reference 25. [s] 38% 3,3,4,4-tetramethylhexa-1,5-diene and 33% 2,7-dimethylocta-2,6-diene. [t] Reference 26. [u] Anti isomer. [v] Reference 27. [w] Product is **22**. [x] Both products formed but no quantitative data given; ref 28.

equalled Φ for azoalkane disappearance. Benzene appears to be a weak fluorescence quencher since τ_f in this solvent is about 30% shorter than in acetonitrile for compounds **1**, **2**, and **4**.[14] A surprisingly large solvent effect was found recently for **7**, its τ_f in acetonitrile being 8 times that in benzene. Since dienes have long been known to quench azoalkane fluorescence via a singlet exciplex,[17,18] the electron-withdrawing chlorines in **7** may allow such a mechanism even with benzene.

The organic compounds resulting from deazatization of DBO's are of two main types: bicyclo[2.2.0]hexanes (**13**) and 1,5-hexadienes (**14**).



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We have determined the product ratio under direct and sensitized irradiation for several DBO derivatives. These results and others from the literature are included in Table VI. Considerable effort was expended to identify the products from **5**, which generally gave three GC peaks. Although all of them appeared by GC/MS to be C_7H_{10} compounds, heating the mixture did not destroy the early peaks, mitigating against tricycloheptanes.[26] In dilute solution, the products could not be distilled away from the solvent, but in concentrated solution, the photolysis quantum yield tended toward zero, due presumably to quenching by azo photoreduction products. Irradiation of **5** in the gas phase revealed that 83% of the volatile material was 1,4-cycloheptadiene while the remaining 17% consisted of five compounds, which were not identified.

Scheme I

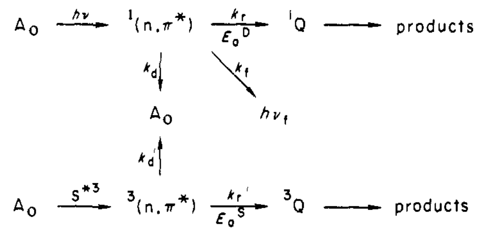

Table VII. Photochemical Parameters at 25 °C Based on Scheme I

compound	$10^{-5}k_r$, s^{-1}	Φ_d	$10^{-5}k_d$, s^{-1}
DBO	0.41	0.59	14
1-MeDBO[a]	0.40	0.54	11
1	4.0	0.64	16
2	0.40	0.45	7.5
3	4000	0	0
4	9.3	0.54	18
5	1.4	0.88	57
6	24	0.65	55
7	3.4	0.95	160
7[b]	2.2	0.71	15
8	3.7	0.95	158
11	18000	0	0
12	19000	0	0

[a] Values calculated on the assumption that Φ_r^D for 1-MeDBO is 0.02. [b] In CH_3CN.

Discussion

According to Table V, the fluorescence rate constants for DBO derivatives lie within a factor of 2 except for those bearing bridgehead vinyl substituents. Compounds **11** and **12** emit very weakly, leading to possible errors in measurement of τ_f and Φ_f. Since it is already known that k_f for DBO agrees reasonably well with the value calculated by integrating the absorption spectrum,[29] no further comments will be made about k_f.

Any mechanism for photolysis of DBO's in solution must take into account the following experimental observations: (1) direct and sensitized photolyses are not coupled; that is, either one may show a larger Φ_r (Table V), (2) direct photolysis exhibits an activation barrier that differs from the barrier found on triplet sensitization (Table II), (3) the products of direct and triplet-sensitized irradiation are the same, but their relative amounts may differ considerably (Table VI), (4) fluorescence lifetimes are very long but are decreased at elevated temperature (Table IV) and by structural changes in the DBO (Table V). Scheme I is the

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Table VIII. Quenching of Sensitizer Triplets by DBO and 7

compd	sensitizer	E_T, kcal mol^{-1}	$10^{-8}k_q$, M^{-1} s^{-1}	ref
DBO	biacetyl^a	54.9	20	4
	biacetyl		6.7	2
	biacetyl		5.5	this work
7	biacetyl		0.27	this work
DBO	chrysene^b	56.6	17	this work
7	chrysene		2.2	this work
DBO	9-fluorenone^b	53.3	0.18	this work

^{a} By quenching of phosphorescence lifetime. ^{b} By kinetic spectroscopy.

simplest one that we have been able to devise to accommodate these observations. Direct irradiation populates the $^1(n,\pi^*)$ state, which decays, fluoresces, or decomposes via some dissociative state ^{1}Q. Triplet sensitization behaves analogously except that the $^3(n,\pi^*)$ state does not emit. Since the (n,π^*) states must surmount different barriers of several kcal mol^{-1}, the differing temperature dependence of direct and sensitized irradiation is rationalized. The observed barriers are smaller than those found for photolysis of most aliphatic ketones.[30]

Scheme I allows us to calculate k_d and k_r in addition to the k_f values already presented in Table V. Thus k_r is given as Φ_r^D/τ_f, Φ_d (quantum yield of radiationless decay from the singlet) as $1 - \Phi_r^D - \Phi_f$, and k_d as Φ_d/τ_f. The results, which are displayed in Table VII, show a complex dependence on structure.

Looking first at k_d, we note that increasing methyl substitution at the bridgehead position of DBO diminishes radiationless decay. This trend is analogous to the effect of deuteration on the phosphorescence lifetime of aromatic hydrocarbons[31] and suggests that α-hydrogens facilitate decay of the $^1(n,\pi^*)$ state. The k_d values for **3**, **11**, and **12** are subject to considerable uncertainty because Φ_r^D for these compounds is close to unity. Since Φ_d is $1 - \Phi_r^D - \Phi_f$, small errors in Φ_r^D will translate into large errors in Φ_d and hence k_d. Nevertheless, it is clear that singlet decay is a minor process for compounds **3**, **11**, and **12**.

Bridgehead halogens increase k_d relative to that for **2** in both benzene and acetonitrile. Φ_d of **2** in acetonitrile can be calculated as 0.28 from its known Φ_r^D of 0.016[3] and Φ_f of 0.70.[14] This Φ_d and the literature τ_f[14] lead to $k_d = 3.7 \times 10^5$ s^{-1}. Thus bridgehead chlorine enhances k_d by at least 4-fold, but judging from the results in benzene, bromine is no more effective than chlorine. The enhanced k_d in the halogen compounds might be explained if decay were a two-step process: slow intersystem crossing (isc) followed by rapid triplet decay. Even though heavy atoms are not expected to accelerate $^1(n,\pi^*) \rightarrow {}^3(n,\pi^*)$ isc,[32] we searched for phosphorescence from **7** and **8**. As in all such previous attempts, these experiments failed.

If not a heavy atom effect, bridgehead halogens might accelerate isc by narrowing the singlet–triplet energy gap (ΔE_{S-T}). The long singlet lifetime of DBO shows that isc is highly unfavorable; hence, even a minor perturbation of the energy levels could lead to a 4 fold enhancement of k_{isc}. That this idea is incorrect is readily shown by the following results. According to their UV wavelength maxima, both **7** and **8** possess a 2.7 kcal mol^{-1} higher singlet energy than DBO. We estimated the triplet energy (E_T) difference between **7** and DBO by quenching sensitizers of known E_T, with the results shown in Table VIII. The log of these k_q's was plotted vs. sensitizer triplet energy in the usual manner,[33-35] the slopes of the falloff region was taken as 0.73 kcal mol^{-1},[33,34] and the

Table IX. Activation Free Energy for Thermolysis of DBO Derivatives

compd	$\Delta G^\ddagger$(100 °C), kcal mol^{-1}	ref
DBO	40.4	38
	41.0	6
1	40.3	7
2	39.5	6
3	32.8	7
4	34.3	9
5	42.0	7
6	37.2	9
11	31.3	39
12	28.2	39
21	20.0	40

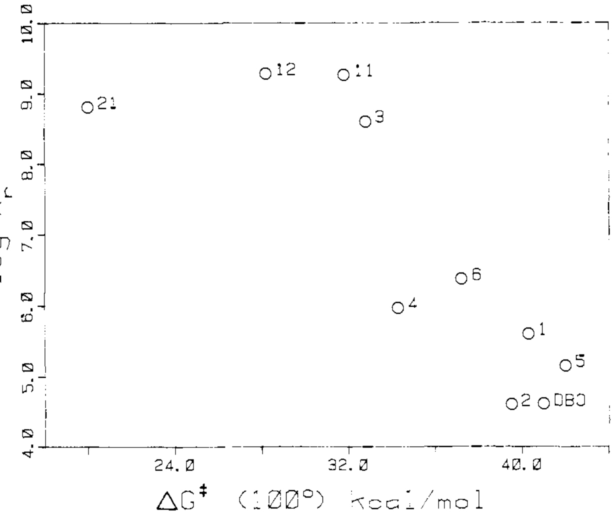
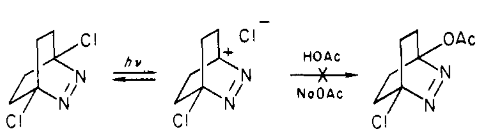


Figure 2. Correlations of photochemical with thermal stability of DBO derivatives. $\Delta G^\ddagger$ is from Table IX while k_r is taken from Table VII.

diffusion-controlled limit was assumed to be log $k_q = 9.5$.[35] For a case like this where energy transfer is irreversible, E_T of the quencher should be taken as the break in the curve as in stilbene,[34] not below the break as in biacetyl.[33] This analysis leads to E_T = 56.5 kcal mol^{-1} for DBO (lit.[4] 54.5 kcal mol^{-1}) and 58.0 kcal mol^{-1} for **7**. Because the E_T difference between **7** and DBO is only 1.5 kcal mol^{-1}, the ΔE_{S-T} of **7** is larger than that in DBO. Thus the idea that bridgehead halogen enhances k_{isc} by decreasing ΔE_{ST} is rendered highly unlikely. Still another explanation for the enhanced k_d of **7** and **8** is reversible photochemical ionization of halide, by analogy to the known process[36] in acyclic azoalkanes. Unfortunately, attempts to trap the expected cation **25** met with failure. Therefore we can only suggest that chlorine and bromine atoms accelerate internal conversion of the $^1(n,\pi^*)$ state. A similar conclusion was reached by Givens and co-workers[37] for halogenated β,γ-unsaturated ketones.



7 25

Turning now to the k_r values in Table VII, the reader will notice that deazatization is especially rapid for compounds **3**, **11**, and **12**. Our previously suggested[2] correlation of photochemical with

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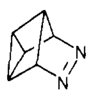
thermal reactivity of DBO's can now be examined more closely. Activation free energies for thermolysis are given in Table IX while a plot of log k_r from Table VII vs. ΔG^* is shown in Figure 2. To calculate k_r for **21**, we used $\Phi_r^D = 0.85$ and $\tau_f = 1.3$ ns. This lifetime is a maximum because the thermal instability of **21** dictated that τ_f be determined at −78 °C. Although the correlation of log k_r with ΔG^* is frustratingly crude, we can say that the most thermally labile DBO's are the most photochemically labile. In terms of Scheme I, this suggests that the barrier between the $^1(n,\pi^*)$ state and ^1Q mimics the behavior of the ground state.^{2} Apparently there is some other factor at work here, but its nature is not understood; for example, **5** is more stable thermally than DBO yet it is less stable photochemically.

The high k_r of **6** is due more to the exo cyclobutyl ring than to the endo cyclopropyl. Thus an exo cyclobutyl (**4**) enhances k_r by a factor of 23 (Table VII) whereas an endo cyclopropyl (**5**) gives only a 3.4-fold enhancement. Multiplying these two factors by k_r for DBO predicts that $k_r = 3.2 \times 10^6$ s^{-1} for **6**, which is not far from the observed value of 2.4×10^6 s^{-1}. The reactivity-enhancing effects of the two fused rings are therefore multiplicative. The high quantum yield for deazatization of **21** as well as its short singlet lifetime demonstrate that in contrast to Tanida's conclusion,^{26} the cyclopropyl ring plays an important role in the photochemistry of this compound. Finally, the increased k_r for **7** and **8** relative to DBO could be due to the stabilizing effect of halogen on an attached carbon radical.^{41}

It is unclear why the lifetime of the $^3(n,\pi^*)$ state seems to be so short in DBO,^{4} despite the fact that triplet-sensitized deazatization is an activated process. Thus from Scheme I and multiplicity considerations, one would expect k_d' to be less than k_d, which we know to be 1.4×10^6 s^{-1} (Table VII). Since triplet sensitized photolysis is inefficient, k_d' is the major pathway of the $^3(n,\pi^*)$ state. It follows that τ_p should be about 0.7 μs, yet neither emission^{42} nor transient absorption^{43} has been observed for DBO.^{44} The lack of phosphorescence could be due to its low rate constant ($\sim 10^2$ by analogy to other $^3(n,\pi^*)$ states)^{45} relative to k_d while the absence of transient absorption is explicable if direct irradiation of DBO does not populate the $^3(n,\pi^*)$ state. None of the experiments described here require isc from $^1(n,\pi^*)$ to $^3(n,\pi^*)$; in fact, the 20 kcal mol^{-1} energy gap and the forbidden nature of the process^{45} speak gainst it. Rau has further suggested that a planar azo group is the least likely to undergo $^1(n,\pi^*)$ to $^3(n,\pi^*)$ isc.^{46} It is amusing that evidence exists for isc in azoalkanes **26**^{47} and **27**;^{28} however, these rigid components are not DBO derivatives, and their triplet reaction is mostly rearrangement rather than deazatization. It would be gratifying to rationalize the chemistry of **26** and **27** on the basis of a modification of Scheme I, but such an explanation evades us at present.



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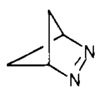
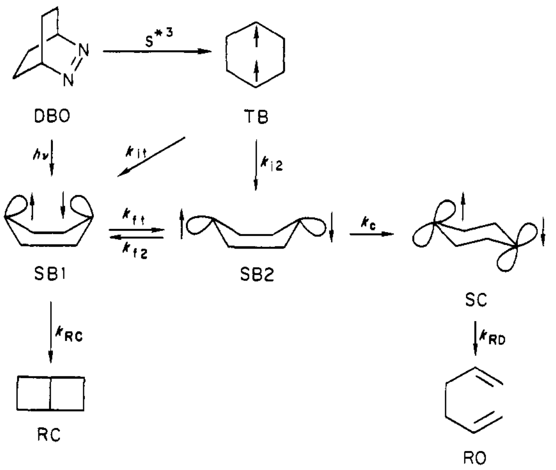


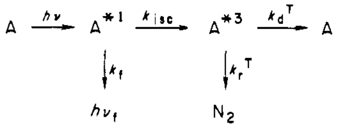
27

As seen in Table VI, the ratio of bicyclohexanes (**13**) to 1,5-hexadienes (**14**) varies widely, depending on azoalkane structure and photolysis mode. Two of the observed structural effects can be explained on the basis of Scheme II, which is the best we have been able to devise. The key intermediates are the two Jahn–Teller isomers of the singlet biradical (SB1 and SB2), which were postulated by Dewar in theoretical studies of the Cope rearrangement.^{49} These biradicaloids interconvert over a barrier with rate constants k_{f1} and k_{f2}. The triplet biradical (TB) must not go exclusively to the same species (SB1) produced by direct irradiation of DBO because there would be no way to explain different product ratios in direct vs. sensitized photolysis. In Scheme II, the ratio of ring closure (RC) to ring opening (RO) depends upon k_{f1}/k_{RC} and k_c/k_{f2} for direct irradiation and additionally in some ill-understood manner on k_{i2}/k_{i1} for the sensitized reaction.

Scheme II



Scheme III



The most striking effect in Table VI is that good radical-stabilizing substituents at the bridgehead (**3**, **11**, **16**, **17**) swing the product distribution totally to the side of RO. In considering this problem earlier,^{3} we suggested that such substituents might facilitate concerted photocycloreversion. This would predict a shorter τ_f for **12** than for **11**, in conflict with experiment. Scheme II provides a more appealing rationale. SB1 owes its stability to a through-space, direct interaction between the singly occupied atomic orbitals while SB2 is dominated by through-bond, indirect interactions. A radical-stabilizing substituent should decrease the through-space coupling in SB1, thus lowering k_{RC}. At the same time, such a substituent will make the singly occupied orbitals of SB2 more p-like, thus stabilizing SB2 and enhancing k_{f1}. As seen in Table VI, even one cyclopropyl group (**1**) causes a measurable increase in ring opening while a phenyl group (**3**) leaves no detectable amount of ring closure.

Fused rings as in **15** and **18** favor ring closure because they inhibit conformational inversion (k_c) to the chair biradical (SC). Thus any SB2 which happens to form is shuttled back to SB1 and ring closure. The phenyl groups of **16** apparently exert a stronger effect than the fused rings, since **16** gives exclusive ring opening. On the other hand, the weaker radical stabilizing group carbomethoxy in **19** succombs to the influence of two fused cyclopropyl rings. One fused ring is insufficient to inhibit k_c as seen from the results for **4** and **21**.

Relationship to Earlier Mechanisms and to Theory

Several years ago, Clark and Steel^4 reported that Φ_r for DBO in the gas phase decreased at elevated pressures while the fluorescence intensity was independent of pressure. These results were rationalized nicely by Scheme III, wherein triplet decay (k_d^T) increases with pressure, thus lowering Φ_r but not Φ_f. Scheme III cannot apply in solution, for it predicts that both direct and sensitized photolysis proceed via a common $^3(n,\pi^*)$ excited state,

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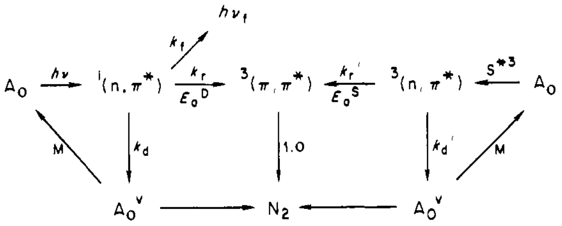
Scheme IV



in conflict with several experimental results noted above. For example, Φ_r^D cannot exceed Φ_r^S according to Scheme III, but four such cases appear in Table V.

We have previously employed theoretical results obtained by Bigot et al.[50] to rationalize the photochemical behavior of DBO. Although their prediction of a barrier for sensitized and direct irradiation agrees with experiment, both photolysis modes were said to proceed via the $^3(\pi,\pi^*)$ state. This mechanism would lead to different product distributions only if the $^3(\pi,\pi^*)$ state were produced with a different geometry under direct versus sensitized irradiation. Though possible, this hypothesis requires abandoning the appealing spin correlation effect explanation[51,52] for azoalkane **1**.[5] Moreover, the change in product distribution can be rather large as in **4** or **15** (Table VI). One must wonder how much geometric flexibility is allowable in the $^3(\pi,\pi^*)$ state of such compounds.

The gas-phase results[4] and the calculations of Bigot et al.[50] can be accommodated by Scheme IV. In contrast to the suggestion of Clark and Steel,[4] Scheme IV shows the pressure-quenchable species as a vibrationally excited ground state (A_0^v) rather than a triplet state. Previously A_0^v was dismissed because its RRKM calculated lifetime was much longer than that of the quenchable species. The reliability of such calculations for azoalkanes has since been questioned;[53] moreover, A_0^v is an accepted intermediate in acyclic azoalkane photochemistry.[1] The quantum yield of DBO fluorescence is about 0.5 in both the gas phase and solution; hence, the other half of the $^1(n,\pi^*)$ states decay to A_0^v, which is deactivated to A_0 at high pressures (M) or in solution. Whereas gas-phase photolysis occurs mostly via A_0^v, the much less efficient solution-phase reaction is an activated process. Aside from making deactivation a two-step process via A_0^v, Scheme IV differs from Scheme I only in the nature of the decomposing state. Scheme IV invokes decomposition from different geometries of the $^3(\pi,\pi^*)$ state whereas Scheme I employs different spin states. Although ^{1}Q and ^{3}Q might be the biradicals SB1 and TB in Scheme II, analysis of azoalkane photolysis at this level of detail is not presently possible.

In conclusion, we offer the following generalizations about decomposition of DBO derivatives in solution: (1) direct and sensitized photolyses exhibit sizable but different activation energies, (2) these activation barriers are the main factors governing deazatization efficiency, (3) a scheme in which the $^1(n,\pi^*)$ and $^3(n,\pi^*)$ bound states cross onto singlet and triplet dissociative surfaces will rationalize the solution-phase results, (4) a rough correlation exists between photochemical and thermal deazatization rates, (5) bridgehead halogens shorten the fluorescence lifetime of DBO, probably by accelerating internal conversion, and (6) radical-stabilizing bridgehead substituents favor the formation of 1,5-hexadienes while multiple fused rings favor bicyclo[2.2.0]hexanes.

Experimental Section

General. Melting points were taken on a Mel-Temp in capillary tubes and are uncorrected. NMR spectra were recorded in $CDCl_3$ on a Varian EM390 or a Jeol FX90Q FT spectrometer. UV spectra were taken on a Cary 17 spectrometer while fluorescence spectra were recorded on a Hitachi MPF-2A fluorimeter.

Because no detailed procedure for making **6** has been published,[9] we report the four step synthesis below.

***exo*-7,8-Dicarbomethoxy-7,8-diazatricyclo[4.2.2.0^{2,5}]dec-9-ene.** 1,3,5-Cyclooctatriene[54] (1.98 g, 18.7 mmol) and ethyl propionate (10 mL) were added to a 25-mL flask fitted with a reflux condenser, nitrogen inlet, and dropping funnel. This solution was heated to reflux and dimethyl azodicarboxylate (2.73 g, 18.7 mmol) in 5 mL of ethyl propionate was added over a 20-min period. The resulting orange solution was reluxed overnight. Rotoevaporation of solvent followed by strong evacuation yielded an orange oil. This compound, which was pure by NMR, was used in the next step without further purification: NMR δ 1.30–1.63 (m, 2 H), 1.83–2.35 (m, 2 H), 2.63–3.10 (m, 2 H), 3.72 (s, 6 H), 4.68–5.00 (m, 2 H), 6.40–6.95 (m, 2 H).

An ethereal solution of diazomethane was generated from 0.6 g (6 mmol) of nitrosomethylurea.[55] The diazomethane was added to the olefin (1.18 g, 4.68 mmol), which was dissolved in 30 mL of ether in a 100-mL pressure bottle. After the bottle was capped, the yellow solution was stirred overnight at 80–85 °C. A white, insoluble solid formed on the sides of the bottle, and the yellow diazomethane color was discharged. Filtration followed by rotoevaporation yielded an oil containing about 50% starting material (NMR analysis). The oil was dissolved in ether and reacted with additional diazomethane. After rotoevaporation and pumping under full vacuum, the crude adduct (1.06 g, 78%) was isolated as a yellow, foamy oil. Combined crude adduct (4.08 g) from several reactions was purified by chromatography on Florisil (EtOAc eluent). The fractions of R_f = 0.20 by TLC (EtOAc development) were combined and rotoevaporated to yield 4-methyl-2,4,6,10,11-pentaazopentacyclo-[5.5.4.0^{2,6}.0^{8,12}.0^{13,16}]hexadec-10-ene-3,5-dione (1.30 g) as a colorless, foamy oil: UV (CH_3CN), λ^{max} 324 nm (ϵ 376).

The above pyrazoline (1.27 g, 4.70 mmol) was dissolved in 100 mL of acetonitrile. Photolysis for 11 h in a Pyrex photochemical apparatus resulted in complete destruction of the pyrazoline absorption. Rotoevaporation of the solvent and pumping under full vacuum yielded crude deazatized material (1.01 g, 87%) as an off-white semisolid of suitable purity for the next reaction. A sample was purified by preparative TLC (EtOAc), removing several minor, low-R_f components. The cyclopropane showed R_f 0.40; NMR δ 0.34–0.77 (m, 2 H), 1.36–1.72 (m, 2 H), 1.83–2.30 (m, 4 H), 2.56–2.97 (m, 2 H), 3.62 (s, 6 H), 4.20–4.49 (m, 2 H); MS, *m/e* 266 (m^+), 207 ($m^+ - CO_2Me$), 153 ($m^+ - CO_2Me, C_2H_4$), 59 (CO_2Me^+).

2,3-Diazatetracyclo[2.3.4.0^{5,8}.0^{9,11}]undec-2-ene (6). The copper complex precursor to **6** was prepared from 101mg of the above cyclopropane by the NaOMe–Me_2SO method[6] (70 °C, overnight). The complex was decomposed with concentrated NH_4OH to afford **6** (11.7 mg, 21%) as white crystals after purification by sublimation (30–60 °C (0.2 mm)). A second sublimation yielded material, mp 59–60 °C (lit.[9] mp 59.5–60.5 °C).

1,4-Dibromo-2,3-diazabicyclo[2.2.2]hex-2-ene *N,N'*-Dioxide (9). Bromination of 1,4-cyclohexanedione dioxime (10 g, 0.070 mmol) by the procedure of Piloty and Steinbock[11] yielded **13** (0.71 g, 2.6%) as a white powder along with *trans*-1,4-dibromo-1,4-nitrosocyclohexane (9.6 g, 36%) as deep-blue crystals. The diazoxy compound was pure enough for use in the next step. A sample recrystallized from methanol was white needles: mp 129–130 °C dec; IR (KBr) 1442, 1398, 1345 (cis diazoxy) cm^{-1}; UV (MeOH) λ_{max} 272 nm (ϵ 7.02 × 10^3).

1,4-Dibromo-2,3-diazabicyclo[2.2.2]oct-2-ene *N*-Oxide (10). A 50-mL flask fitted with a nitrogen inlet and rubber septum was heated with a heat gun under a strong nitrogen flow. When the flask had cooled, it was charged with **9** (0.554 g, 1.85 mmol) and 40 mL of chloroform (freshly distilled from P_2O_5). Hexachlorodisilane (0.80 ml, 4.8 mmol) was then added via a disposable syringe. The heterogeneous mixture was stirred overnight. After 1 h, the reaction mixture had turned homogeneous. The reaction was quenched with 15 ml of 1 M NaOH (**caution:** exothermic reaction), the inorganics were filtered off, and the layers were separated. The organic layer was washed with water and dried (K_2CO_3), and the solvent was rotoevaporated to yield **10** (0.530 g, 100%) as a white solid. A sample recrystallized from methanol had mp 213–215 °C dec: NMR δ 2.53 (m); IR (KBr) 1478, 1445 (N=N), 1330 (d), 1275 (d) (N—O) cm^{-1}; UV (benzene) λ_{max} 232 nm (ϵ 6.74 × 10^3); calcd for $C_6H_8Br_2NO$ (m^+ - NO), *m/e* 251.9023; found, 251.9020.

1,4-Dibromo-2,3-diazabicyclo[2.2.2]oct-2-ene (8). The procedure of Lüttke and Schabacker[10] was used. To a 25-mL flask was added **10** (390 mg, 1.37 mmol) and 8 mL of triethyl phosphite. A reflux condensor and nitrogen inlet were attached, and the mixture was heated to reflux for

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1 h. After cooling to room temperature, the phosphorus compounds were removed under vacuum, yielding a semisolid residue. This was taken up in hot methanol. The azo compound (264 mg, 72%) was isolated as long needles. A second recrystallization furnished material, mp 210–211 °C. During a study of the fluorescence properties of this compound, the presence of an impurity was revealed in the excitation spectrum. Sublimation (105–130 °C (0.05 mm)) removed this impurity; NMR δ 2.21 (AB q); UV (benzene) λ_{max} 366 nm (ϵ 129); MS, m/e 238, 240, 242 ($m^+ - N_2$); calcd for $C_6H_8Br_2$ ($m^+ - N_2$), 237.8992; found, 237.8990.

Nitrogen quantum yields were determined on a photochemical merry-go-round using a Hanovia 450-W medium-pressure mercury arc lamp and filters to isolate the desired wavelength (366 nm direct or 313 nm sensitized). Solutions were degassed and sealed in Pyrex tubes, N_2 evolution being measured with a Toepler pump and gas buret. The initial absorbance was arranged to be about 3 and conversions were kept below 20%. A solution of 2,3-diazabicyclo[2.2.1]hept-2-ene plus benzophenone was employed as the actinometer ($\Phi_r = 1.0$). The temperature of the merry-go-round water bath was regulated to ±0.1 °C with a RFL Industries proportional controller.

Fluorescence lifetimes were determined utilizing a Lambda Physik EMG 101 nitrogen (337 nm) or xenon fluoride (351 nm) excimer laser and a Hewlett-Packard HP1741A storage oscilloscope. The desired emission was isolated wtih a Bausch and Lomb grating monochromator. The sample was degassed in a 1 cm^2 cell equipped with a glass well that protruded into the solution. Temperature was monitored by measuring the resistance of a calibrated thermistor placed in the well. The temperature of the cell was regulated by a cooling–heating block connected to a Neslab circulating bath. The scope traces were photographed and digitized to produce data files that were analyzed on a PDP 11/70 computer and a Hewlett-Packard 2648A graphics terminal. All fluorescence decays were first order.

Product Studies. Solutions of DBO in C_6H_6 or **2** in C_6H_5F were degassed and sealed in Pyrex tubes. Irradiation was done using a Hanovia 450-W mercury lamp and appropriate filters to isolate the 366-nm (direct) or 313-nm (Ph_2CO sensitized) line. Products were analyzed on an Antek 300 FID gas chromatograph with $^1/_8$ in. × 20 ft. stainless steel column of 20% XE-60 on Chromosorb P at 80 °C. DBO gave two peaks,[4] 1,5-hexadiene being identified by comparison of retention time with that of the known compound. Products of **2** were isolated by preparative GC (15% XE-60, 20 ft × 0.25 in., 80 °C) and their NMR spectra compared with those of the known compounds.[56] The first peak (retention time 13.3 min) was 1,4-dimethylbicyclo[2.2.0]hexane and the second (retention time 20.0 min) was 2,5-dimethyl-1,5-hexadiene.

A solution of **17** in C_6D_6 was irradiated at 366 nm for 20 min at 6 °C. An NMR of the solution showed δ 2.74 (s, 4 H), 5.36 (br s, 2 H), 5.67 (d, J = 2 Hz, 2 H), 7.60 (m, 10 H). On the basis of this spectrum, the product is assigned as 2,5-diphenylhexa-1,5-diene, a known substance.[57] The same product was formed on heating **17** to 200 °C. A similar experiment using azoalkane **3** gave an NMR spectrum corresponding to the known hydrocarbon 2-phenyl-1,5-hexadiene.[58]

Attempted Trapping of Cation 25. 7 (20 mg) was added to 3 mL of a saturated solution of NaOAc in AcOH. A few drops of CH_2Cl_2 were required to keep all reactants in solution. The mixture was irradiated for 2 h through Pyrex, with a Hanovia 450-W lamp. AcOH was then evaporated, and ~1 mL of $CDCl_3$ was added to the remaining solid. After filtration through K_2CO_3, NMR showed that no detectable amount of bridgehead acetate had formed (absence of δ 2.0 peak).

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Registry No. 1, 87373-47-5; **2**, 49570-30-1; **3**, 87373-48-6; **4**, 25863-08-5; **5**, 87420-89-1; **6**, 39898-44-7; **7**, 3993-62-2; **8**, 87373-49-7; **9**, 87373-52-2; **10**, 87373-55-5; **13** (R = Br), 87373-53-3; **DBO**, 3310-62-1; biacetyl, 431-03-8; chrysene, 218-01-9; 9-fluorenone, 486-25-9; 1,3,5-cyclooctatriene, 1871-52-9; dimethyl azodicarboxylate, 2446-84-6; *exo*-7,8-dicarboxymethoxy-7,8-diazatricyclo[4.2.2.0^{2,5}]dec-9-ene, 87373-50-0; 4-methyl-2,4,6,10-11-pentaazapentacyclo[5.5.4.0^{2,6}.0^{8,12}.0^{13,16}]hexadec-10-ene-3,5-dione, 87373-51-1; *trans*-1,4-dibromo-1,4-dinitrosocyclohexane, 87373-54-4.

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Reaction of Nucleophiles with Electron Acceptors by S_N2 or Electron Transfer (ET) Mechanisms: *tert*-Butyl Peroxybenzoate/Dimethyl Sulfide and Benzoyl Peroxide/*N*,*N*-Dimethylaniline Systems[1,2]

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Abstract: This paper is one of a series that probes the reactions of nucleophiles with peroxides, reactions that can occur either by an initial S_N2 reaction or by an electron-transfer (ET) reaction. The products and kinetics are reported for the reaction of dimethyl sulfide and a series of ring-substituted aryl methyl sulfides with *tert*-butyl peroxybenzoate (TBP) and four ring-substituted TPB's. Kinetic analysis allows the separation of the rate constants for unimolecular homolysis (k_1) and those for the decomposition of the TBP by the sulfide (k_2). The bimolecular reaction is accelerated by electron-withdrawing substituents in the TBP; for example, when 3,5-$(NO_2)_2$-TBP is used, k_2/k_1 is 12000. The products that are formed are consistent with a radical process; however, this evidence is not regarded as conclusive. Experiments with both limiting galvinoxyl and excess galvinoxyl, as well as with styrene, indicate that radicals are produced in sulfide–TBP reactions, but the yield of radicals is small (see Table VII). Solvent effects (Table I) and substituent effects (Table II) are not useful for distinguishing S_N2 and ET pathways. The kinetic isotope effect produced by substituting deuterium in the nucleophile is reported for the $(CD_3)_2S$ reaction with TBP and $(NO_2)_2$-TBP and also for the reaction of dimethylaniline-d_6 with benzoyl peroxide. This isotope effect is suggested to be a more reliable probe of the nature of the initial reaction (i.e., S_N2 or ET). Surprisingly, the isotope effects indicate that the dimethylaniline–BPO system involves an S_N2 reaction and the dimethyl sulfide–TBP system involves ET, although the former pair gives about a 10-fold higher yield of free radicals.

In recent years, a lengthening list of reactions that had been thought to occur by ionic reactions has been found to involve free-radical chain reactions, at least under some conditions.[3] Some of the most interesting reactions that are of this type are sub-