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(12) ^{1}H NMR (δ, $CDCl_3$): 7.09–7.71 (m, 20 H), 4.06 (d, 1 H, $J_{^{31}P-^1H}$ = 12.7 Hz). ^{13}C NMR (C_6D_6): 11.0 ppm (d, $J_{^{31}P-^{13}C}$ = 24.1 Hz), plus CO and phenyl resonances. IR (cm^{-1}, THF): 2023 (m), 1930 (m), 1905 (vs). A portion of **12** was recrystallized from benzene, mp 115–120 °C dec. Anal. Calcd for $C_{29}H_{21}FeO_4P$: C, 66.95; H, 4.07; Fe, 10.73; P, 5.95. Found: C, 67.07; H, 4.68; Fe, 11.33; P, 6.18.
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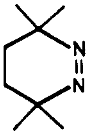
Received May 18, 1979

Enhancement of Decomposition Quantum Yields of "Reluctant" Azoalkanes

Sir:

Whereas irradiation of azoalkanes generally leads to efficient loss of nitrogen, six-membered azoalkanes decompose with low quantum yield (Φ_r).[1,2] This ring-size effect seems not to depend on whether the azo linkage is incorporated into a monocyclic or bicyclic system, as illustrated for compounds **1**, **2**, DBO, and DBH. Since analogues of DBO (e.g. compounds **3–6**) are also known to be photostable,[7-9] or to react slowly,[10] considerable interest has arisen[7,11] in finding methods for decomposing these "reluctant" azoalkanes. We report here that Φ_r for six-membered azoalkanes can be enhanced substantially either by modifying their structure so as to render them more labile thermally or by raising the temperature during photolysis. These measures are effective because the lowest excited singlet state encounters a barrier to loss of nitrogen.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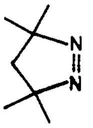
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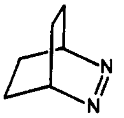
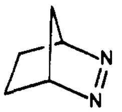
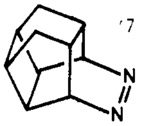

DBO[6]


DBH[6]

Φ_r 0.008 0.98 0.022 1.0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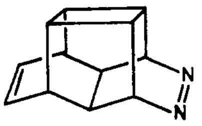
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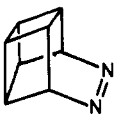
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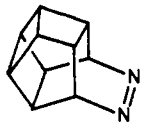
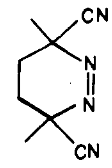

6[10]

Table I. Data for Photochemical and Thermal Decomposition of Azoalkanes

compd	Φ_r[a]	solvent	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
1	0.008[b]	benzene	36.3[c]	11.3
	0.0085[d]	*n*-butyl acetate		
7	0.2[d]	ethyl acetate	21.2[e]	5.9[e]
8	0.2[d]	ethyl acetate	(23)[f]	(7)[f]
DBO	0.022[g]	isooctane	44.3[c]	9.5[c]
9	0.014[h]	benzene	43.7[b]	11.4[b]
	0.0065[d]	*n*-butyl acetate		
10	0.3[d]	benzene	40.8[i]	10.3[i]
11	0.3[d]	benzene	38.6[i]	11[i]
	0.20[j]	hexane		
12	0.9[d]	benzene	34.2[k]	7.7[k]
13	0.8[d]	benzene	32.6[l]	(10)
14	0.9[d]	ethyl acetate	21.5[m]	4.1[m]

[a] Quantum yield for nitrogen formation. [b] Reference 3. [c] Average of values tabulated in ref 3. [d] This work. [e] Reference 12. [f] Calculated from data for the 3,6-dimethyl analogue[13] ($t_{1/2}$ = 30 min at −10 °C; calculated $\Delta G^{\ddagger}$ = 19.45 kcal mol^{-1}). $\Delta G^{\ddagger}$ for **8** is estimated[3] to be 21.15 kcal mol^{-1} and $\Delta S^{\ddagger}$ is assumed to be 7 eu. [g] Reference 4. [h] Reference 1. [i] Reference 14. [j] Reference 15. [k] Reference 16 [l] Based on our measured $k = 9.7 \times 10^{-5}$ s^{-1} at 100.2 °C and an assumed $\Delta S^{\ddagger}$ of 10 eu; cf. ref 17. [m] Reference 18.

As seen in Table 1, the thermal lability of **1** and DBO was increased by two kinds of structural changes: placing radical-stabilizing groups at the α-carbon atoms or incorporating a strained ring into their structure. In the monocyclic series, Φ_r for **7** and **8** (determined at −78 °C) is 25-fold greater than for model compound **1**. Even larger effects are observed in the bicyclo[2.2.2] series, as demonstrated by comparison of DBO and **9** with **12–14**.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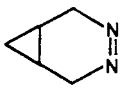
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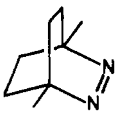
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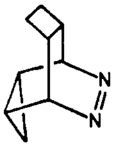
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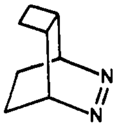
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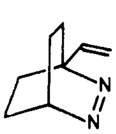
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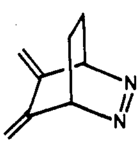
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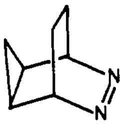
14

Taking advantage of the fact that rigid cyclic azoalkanes fluoresce,[15] we studied the emission properties of DBO and **9–14** in hopes of clarifying the mechanism by which thermal lability influences Φ_r. All of these compounds exhibited fluorescence spectra of the same general shape and λ_{max}, but emission from **12–14** was much weaker than from DBO and **9–11**. Since the radiative rate constant k_f is safely assumed to be invariant for the series,[15] we conclude from the formula $\Phi_f = k_f\tau_f$ that **12–14** have a much shorter τ_f than DBO and **9–11**. This was verified experimentally for DBO, **11**, and **12**, whose measured lifetime in degassed benzene was 460, 330, and 0.5, respectively.[19] It follows that the *rate* of some excited singlet

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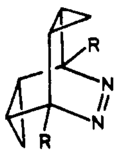
Table II. Temperature Dependence of Azoalkane Nitrogen Quantum Yields

compd	temp, °C	Φ_r	solvent	E_a*, kcal mol^{-1}
1	30	0.0085	*n*-butyl acetate	2.0
	110	0.017	*n*-butyl acetate	
2	6.4	0.96	benzene	~0
	30.0	0.90	benzene	
	59.9	0.99	benzene	
9	7	0.0055	acetonitrile	7.9
	44.6	0.0245	acetonitrile	
	67.0	0.066	acetonitrile	
18	5.0	0.31	acetonitrile	10.0
	31.0	0.67	acetonitrile	
	51.5	0.86	acetonitrile	
19	6.4	0.49	benzene	2.2
	30.0	0.55	benzene	
	59.9	0.645	benzene	

(A^{*1}) process is accelerated in compounds **12–14**. Although this process might be intersystem crossing to a decomposing triplet state, one would not expect the structural modifications employed to affect significantly the energy and interconversion rates of azoalkane electronic states. Not only are the absorption spectra of DBO and **9–14** similar, but DBO and **12** quench biacetyl phosphorescence at similar rates, implying that their triplet energy is the same.[20] (For DBO in benzene, $k_q = 6.7 \times 10^8$ M^{-1} s^{-1}; lit.[4] in isooctane, $k_q = 2.0 \times 10^9$; for **12**, $k_q = 4.4 \times 10^8$.) Decomposition through a vibrationally excited ground state (A_0^v) is also unlikely because the vinyl group in **12** is not expected to accelerate internal conversion $A^{*1} \rightarrow A_0^v$. A recent suggestion[21] that the decomposing state of **9** precedes the fluorescing state is inconsistent with the decrease in τ_f on introducing a bridgehead vinyl group, which should enhance deazatization from the precursor of A^{*1}. In our view, it is most reasonable that weaker C–N bonds (i.e., lower $\Delta H^{\ddagger}$) accelerate direct loss of N_2 from A^{*1}. From the formula $\Phi_r = k_r\tau_f$, the quantum yields in Table I, and the measured values of τ_f, we calculate that the rate constant (k_r) for deazatization of excited DBO, **11**, and **12** is 4.8×10^4, 9.1×10^5, and 1.8×10^9 s^{-1}, respectively.

The fact that exocyclic fused cyclopropane rings accelerate thermolysis of azoalkanes whereas endocyclic rings do not suggested that a photochemical comparison of **14**[22-24] with its endocyclic isomer would be of interest. Because *endo*-**14** is unfortunately not a known compound, we irradiated **10**[14] and found its Φ_r to be considerably below that of **14**. It is likely that **10** would have decomposed less efficiently were the exo cyclobutane ring absent, judging from the identical Φ_r of **10** and **11**[14,25-27] (cf. Table I). Whereas an endo cyclopropyl ring aids neither thermolysis nor photolysis, an exo cyclobutyl ring increases Φ_r 15-fold, though it lowers $\Delta H^{\ddagger}$ by only 3-5 kcal mol^{-1}. Irradiation of **15**[28] and **16**[29] produces hydrocarbons, but the fact that no Φ_r has been reported makes comparison with the present results difficult. Moreover, the data for **12** suggest that the bridgehead substituents would increase Φ_r, thereby obscuring any effect of the endo cyclopropyl ring.



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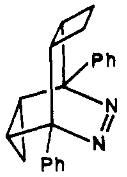
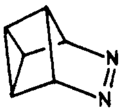


16

Photolysis at elevated temperatures is a method for enhancing Φ_r for reluctant azoalkanes without modifying their structure. Turro and co-workers demonstrated this effect for compounds **3**[7] and **17**[11] and then used the temperature dependence of fluorescence intensity to calculate the activation energy (E_a*) for decomposition of the excited singlet state in favorable cases.[30] We have employed temperature dependence of Φ_r to determine E_a* for **9**, which cannot be done by fluorescence.[30] Furthermore, new results on **18** allow us to compare E_a* deduced by these two methods.



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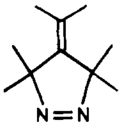

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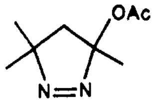
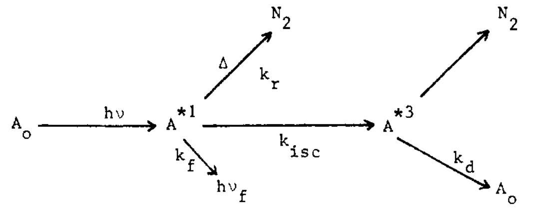


19

As shown in Table II, Φ_r for all azoalkanes examined increases monotonically as the temperature is raised. If one assumes that the singlet state fluoresces, decays, or undergoes thermally activated decomposition,[31] a plot of ln $[\Phi_r^{-1} - 1]$ vs. T^{-1} should be linear with slope equal to E_a^*/R. We find that E_a* for **18** in CH_3CN is 10.0 kcal mol^{-1}, in reasonable agreement with the value of 7.9 kcal mol^{-1} deduced from fluorescence measurements.[33] Since the sum of Φ_f and Φ_r is much below unity at low temperatures ($\Phi_f = 0.3$ at −6.1 °C[30]), some other singlet decay process is important for **18** under these conditions. The sharp decline in Φ_r with temperature explains why 4-methylene-1-pyrazoline gave only a feeble ESR spectrum of trimethylenemethane on irradiation at −196 °C[34] and why lengthy irradiation of DBO[35] or another analogue of **18**[32] under similar conditions produced no ESR signals.

To rationalize the dependence of Φ_r on thermal lability of the azoalkane and on temperature, we postulate that Steel's mechanism[4] for photolysis of DBO must be modified by inclusion of thermally activated decomposition from A^{*1}. On account of the high barrier for this process in **9** and presumably DBO, the singlet state either fluoresces or goes to A^{*3}, which



is deactivated in solution. Raising the temperature enhances decomposition from A^{*1} at the expense of fluorescence. Greater thermal lability of the azoalkane also increases k_r, as shown dramatically by comparison of DBO, **11**, and **12** (see above). Apparently the barrier to decomposition of A^{*1} mimics the behavior of the ground state, as postulated for the triplet state of acyclic azoalkanes.[36] Indeed, compound **12** shows no barrier to decomposition of A^{*1}, its Φ_r being the same at 25 and −78 °C. A recently calculated potential energy diagram for the one bond homolysis of diimide[37] is in accord with our results on DBO and **12** since the crossing point of the $^1n,\pi^*$ surface with the dissociating $^3\pi,\pi^*$ curve should be lowered when the incipient radicals are stabilized. However, application of the published diagrams[37] to such compounds as **14** is fraught with difficulties.[38]

Whereas the above mechanism explains the results for bicyclic azoalkanes, further consideration of Tables I and II reveals that **1** has both a low Φ_r and a low E_a*. We attribute the low Φ_r of **1** mostly to its molecular flexibility which allows N=N twisting and rapid radiationless decay.[3,39] In fact this process is so facile that it wastes 80% of the absorbed photons in thermally labile compounds **7** and **8**. Because **1** and its derivatives do not fluoresce, we cannot calculate k_r and therefore cannot rule out decomposition via a hot ground state.[1] By analogy to the case of DBH vs. DBO,[1] the highly efficient, temperature-independent photolysis of **2** is attributed to its rigidity and to its >12 kcal mol^{-1} higher singlet energy than **1**. Finally, we note that **18** shows a high Φ_r despite its high E_a^*. Although this anomalous behavior suggests an unusually large Arrhenius *A* factor for decomposition of A^{*1}, few *A* factors for excited-state reactions are presently available, let alone interpretable.[40]

Acknowledgment. Financial support by The Robert A. Welch Foundation, The National Science Foundation, and the Alfred P. Sloan Foundation is gratefully acknowledged. We thank Dr. David J. Bishop for carrying out preliminary experiments on **7** and **8**, Professors J. P. Snyder and W. R. Roth for providing a sample of **13**, and Professor A. M. Halpern for fluorescence lifetime measurements.

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(39) Attempts to detect *trans*-**1** by matrix isolation IR have been unsuccessful. We thank Professor Orville Chapman and Mr. Richard Hayes for carrying out these experiments.
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Received January 2, 1979

One-Electron Oxidation of Vinylidene–Carbene Complexes of Iron Porphyrins. Isolation of Complexes Spectrally Analogous to Catalase and Horseradish Peroxidase Compounds I

Sir:

The reactions of catalases and peroxidases with various two-electron oxidants lead to intermediate iron complexes, called compounds I and II, which retain, respectively, 2 and 1 oxidizing equiv above the native Fe(III) hemoprotein.[1] The knowledge of the structure and reactivity of these intermediates appears especially important since they play a key role in the catalytic function of the corresponding hemoproteins. From their spectroscopic properties,[2] compounds II of catalase and peroxidases are generally believed to be porphyrin–iron(IV) complexes with an oxygenated exogenous ligand which could be an oxo or an OH ligand. The structures of compounds I, which could be considered formally as iron(V) porphyrin complexes, are even less clear. Cytochrome *c* peroxidase compound I has been depicted as an iron(IV) porphyrin complex with a free radical of an amino acid residue in the vicinity of the heme iron.[3] Horseradish peroxidase (HRP) and catalase (CAT) compounds I have been described as iron(IV) [porphyrin π cation radical] complexes, because of their abnormal electronic absorption spectra which resemble those of magnesium, nickel, or cobalt porphyrin π cation radicals.[4] Iron porphyrin π cation radicals[5] have also been proposed as intermediates in electron transfers by cytochromes.[4d-f]

The carbon analogues of porphyrin–iron oxo species, porphyrin–iron(IV)=O, possibly present in CAT and HRP compounds II, are the carbene complexes [porphyrin–iron(II)$\leftarrow$CRR′], which can be considered, at least formally,[6] as [porphyrin–iron(IV)=CRR′] complexes. Evidence has been presented in favor of the involvement of such cytochrome P450–carbene complexes,[7] and we have isolated a number of stable iron porphyrin–carbene complexes.[8] The latter exhibit visible spectra quite similar to those of compounds II but are considerably more stable. We thus could expect that their one-electron oxidation would lead to iron porphyrin complexes analogous to HRP and catalase compounds I, but also more stable. The present paper describes the preparation of stable iron porphyrin complexes from the one-electron oxidation of the vinylidene–carbene complexes Fe[porphyrin] [C=C(p-$\mathrm{ClC_6H_4}$)$_2$][8c] by ferric or cupric chloride, which exhibit visible spectra similar to those of catalase or HRP compounds I.

As shown in Figure 1a, the progressive addition of 1 equiv of $\mathrm{CuCl_2}$ in acetonitrile to a benzenic solution of complex **1**, Fe[TPP[9]][C=C(p-$\mathrm{ClC_6H_4}$)$_2$],[8c] leads to a gradual transformation, with isobestic points at 377, 430, 521 and 557 nm, of the characteristic visible spectrum of complex **1** into that of a new complex, **2**. In a typical preparative experiment, complex **2** was obtained from reaction of complex **1** (10^{-4} M in benzene) with 1 equiv of $\mathrm{FeCl_3}$ (10^{-1} M in acetonitrile, added progressively within 5 h), followed by solvent evaporation, column chromatography on silica gel (elution with benzene and benzene–acetone (70:30) affording respectively un-

0002-7863/79/1501-6437$01.00/0