PHOTOCHEMICAL DECOMPOSITION AND ISOMERIZATION OF ALIPHATIC AZO COMPOUNDS

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Abstract – Incorporation of the azo group into the bicyclo[2.2.2]octane skeleton leads to "reluctant" azoalkanes which undergo photochemical loss of nitrogen with low quantum efficiency. The barrier to singlet decomposition which these compounds possess can be surmounted by raising the temperature or can be lowered by making the azoalkane more labile thermally. The only products detected thus far from bridgehead vinyl substituted 2,3-diazabicyclo[2.2.2]oct-2-enes are those of ring opening. Some of the properties of cis 1-azobicyclo[2.2.1]heptane, an extraordinarily stable acyclic cis azoalkane, are described.

INTRODUCTION

Photolysis of azoalkanes is a clean and general method for producing biradicals and unstable hydrocarbons, as shown by the examples below (Ref. 1).
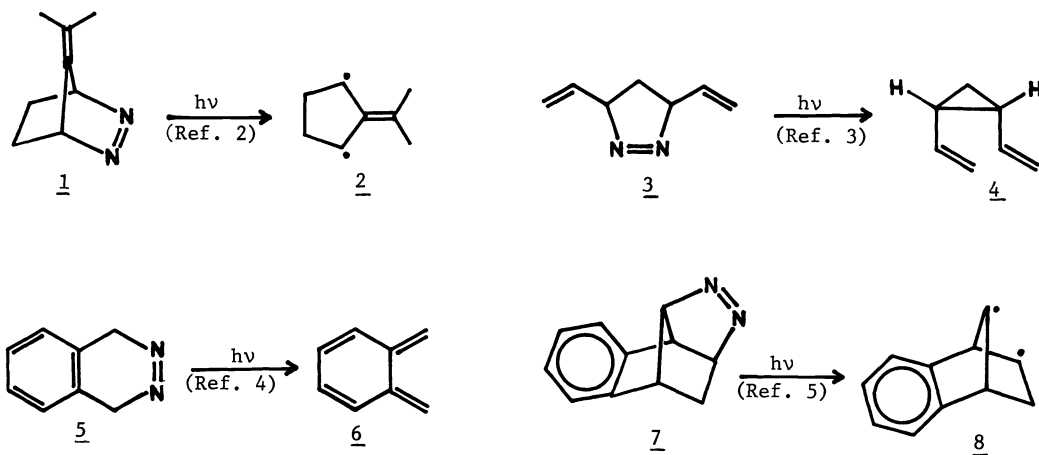
There are a few azo compounds which lose nitrogen with particular difficulty however, and the common feature of these exceptional cases (eg 9-12) seems to be incorporation of the azo linkage into a bicyclo[2.2.2]octane structure. Since these "reluctant" azoalkanes mar what
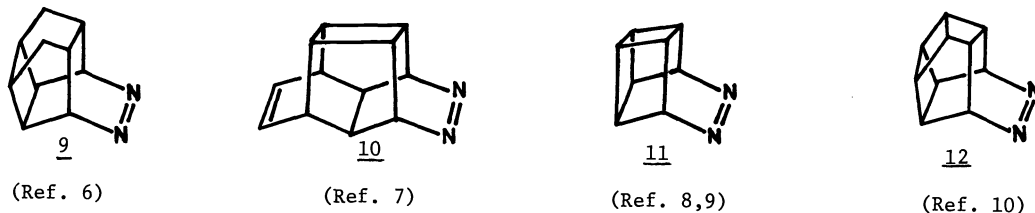

is otherwise a useful technique, we have sought to understand the reason for their inertness and hopefully to overcome the problem.

The nitrogen quantum yields (Φ_r) for the well-studied parent compounds 2,3-diazabicyclo [2.2.1]hept-2-ene (DBH) and 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) typify this reactivity

Φ_r 1.0   0.022

difference. Whereas irradiation of DBH in solution produces bicyclo[2.1.0]pentane rapidly in high yield (Ref. 11), DBO fluoresces strongly and goes slowly to a mixture of 1,5-hexadiene and bicyclo[2.2.0]hexane (Ref. 12). At 5.5°K, DBH gives the cyclopentan-1,3-diyl biradical but DBO produces no species observable by esr (Ref. 13). Photoreduction probably competes with deazatization of excited singlet DBO in hydrogen-donating solvents, as was found in the dichloro analog 13 (Ref. 14).
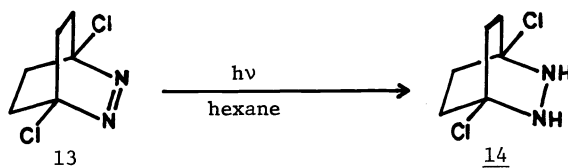
THE EFFECT OF BRIDGEHEAD VINYL GROUPS

Our approach to enhancing deazatization of DBO was to stabilize the incipient radical sites by making them allylic. The expectation that such a structural change might be effective was based on our earlier study (Ref. 15) of the acyclic allylic azo compound 15, whose triplet state was found to lose nitrogen much more readily than that of azo-tert-butane (ATB). Note that even a single allyl group (compound 16) produced the same increase in Φ_r

$\Phi_r(\emptyset_2CO$ sensitized)   0.11   0.02   0.10
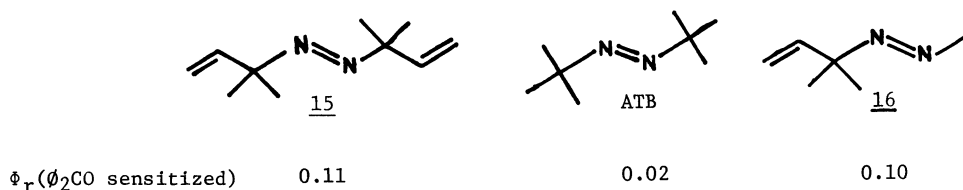
as found for 15, suggesting that the excited triplet state undergoes initial scission of one C-N bond.

The required analogs of DBO, though readily conceived, are not easily synthesized; in fact, our earliest efforts date from 1972. Ultimately, compounds 17 and 18 were made by the routes outlined below (Ref. 16). As shown by the data in Table 1, 17 and 18 were far more labile
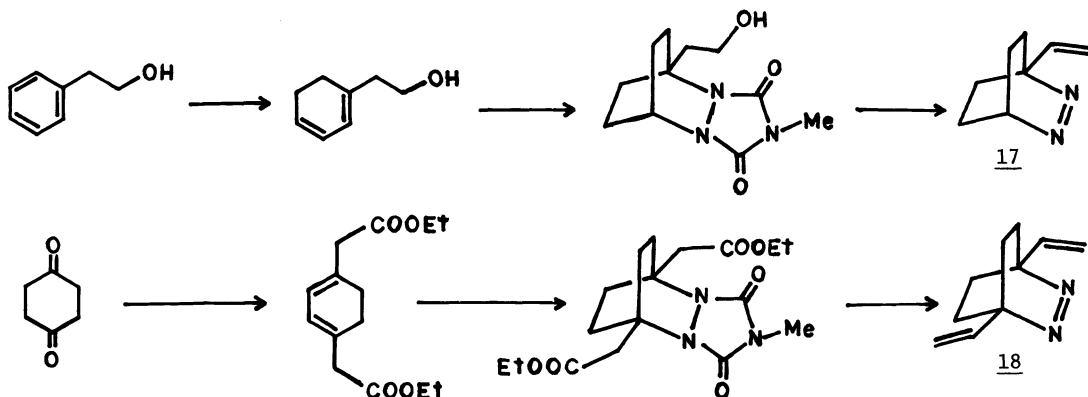
thermally than DBO but were still easily handled at ambient temperature.

TABLE 1.   Thermolysis of 2,3-diazabicyclo[2.2.2]oct-2-enes[a]

Compound	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$ (150°) kcal mol^{-1}
DBO	45.0±0.2	10.6±0.4	40.4
17	34.2±0.8	7.7±2.0	30.9
18	28.8±0.3	1.5±0.8	28.2

a. based on kinetic runs in xylene at 5-7 temperatures
    spanning a 20-30° range (Ref. 16).

With the thermolysis kinetics of 17 and 18 well in hand, we began the photochemical study of these compounds (Ref. 17). Their absorption and emission spectra fall in the same region as those of DBO itself (Fig. 1); however, fluorescence from 17 and 18 is at least a hundred
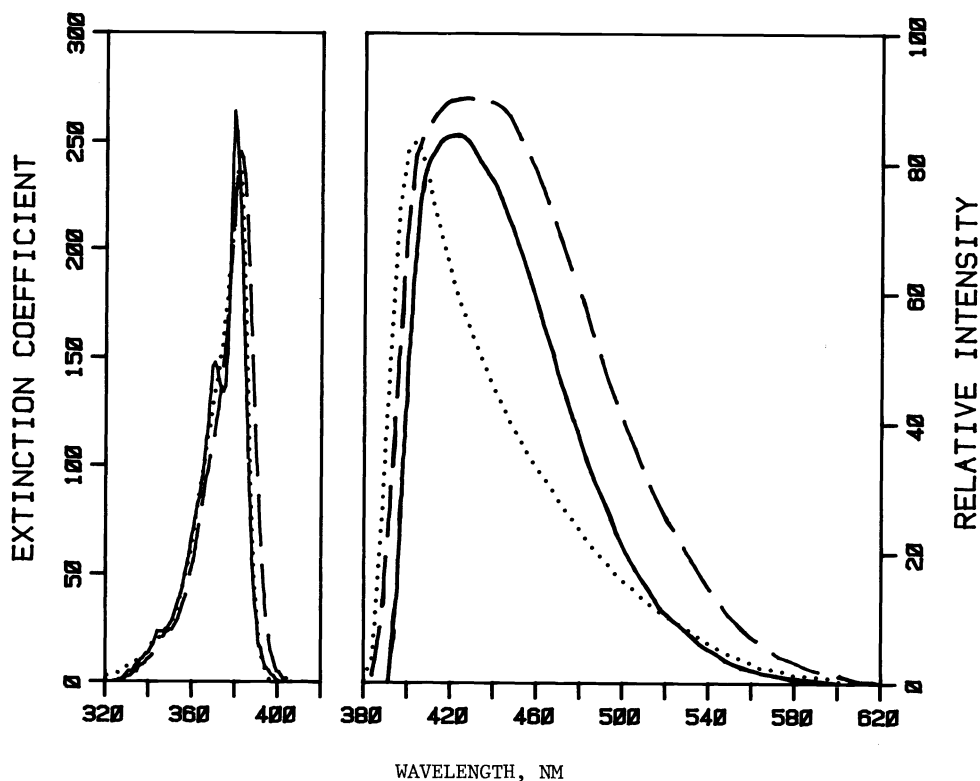

Fig. 1. Absorption and emission spectra of DBO(—), 17 (.....), and 18 (----) in benzene at 25°. λ_{max}, ϵ : DBO 379,264; 17 381,238; 18 382,245. Emission was excited at 337 nm. 17 and 18 were run on the same sensitivity but DBO was ca. 10^2 more intense.

times less intense than from DBO. The weak emission of the substituted compounds was shown to be real by the similarity of their absorption and excitation spectra, though a small contribution from impurities cannot be ruled out. Since the radiative rate constant k_f is generally about 10^6 for azoalkanes (Ref. 18) these observations suggest that some nonradiative process is accelerated in 17 and 18. Determination of Φ_r quickly revealed that this accelerated process was loss of nitrogen ; in fact, further measurements (Table 2) allowed us to quantify most of the photochemical pathways.

It is noteworthy that incorporation of a single bridgehead vinyl group into DBO enhances Φ_r by about 70 fold and lowers both Φ_f and τ_f by 2-3 orders of magnitude. Whereas k_f remains in the expected range of 10^6, k_r goes up by nearly 10^5. A key feature of Table 2 is that the second vinyl group causes no further enhancement of k_r. Since this situation is remarkably similar to that found in decomposition of triplet acyclic azoalkanes (see above),

TABLE 2. Photochemical parameters for 2,3-diazabicyclo[2.2.2]oct-2-enes[a]

Compound	Φ_r	Φ_f	τ_f, nsec	k_r, sec^{-1}[b]	k_f, sec^{-1}[c]
DBO	0.013	0.39	434	3.0×10^4	9×10^{5}[d]
17	0.9	0.0009	0.56	1.6×10^9	1.6×10^6
18	0.9	0.0014	0.53	1.7×10^9	2.6×10^6

a. In benzene at 25°. b. $k_r = \Phi_r/\tau_f$. c. $k_f = \Phi_f/\tau_f$. d. The literature
values are 6.1×10^5 sec^{-1} in isooctane (Ref. 12) and 1.2×10^6 sec^{-1} in
water (Ref. 18).

it is expedient to invoke the same explanation, namely, that one C-N bond breaks in the
rate-determining step.

The question of one bond versus two bond thermolysis of azoalkanes has received much study
(Ref. 1); however, little is known about the photochemical mechanism (Ref. 2). Most of the
present results are accomodated by a published calculation of the potential energy curves
for the one-bond homolysis of cis diimide (Ref. 19). As shown in Fig. 2, the $^1n,\pi^*$ state
produced by irradiation fragments only after surmounting an activation barrier and crossing
at A onto the $^3\pi,\pi^*$ curve. A similar calculation, though not without its flaws (Ref. 15),
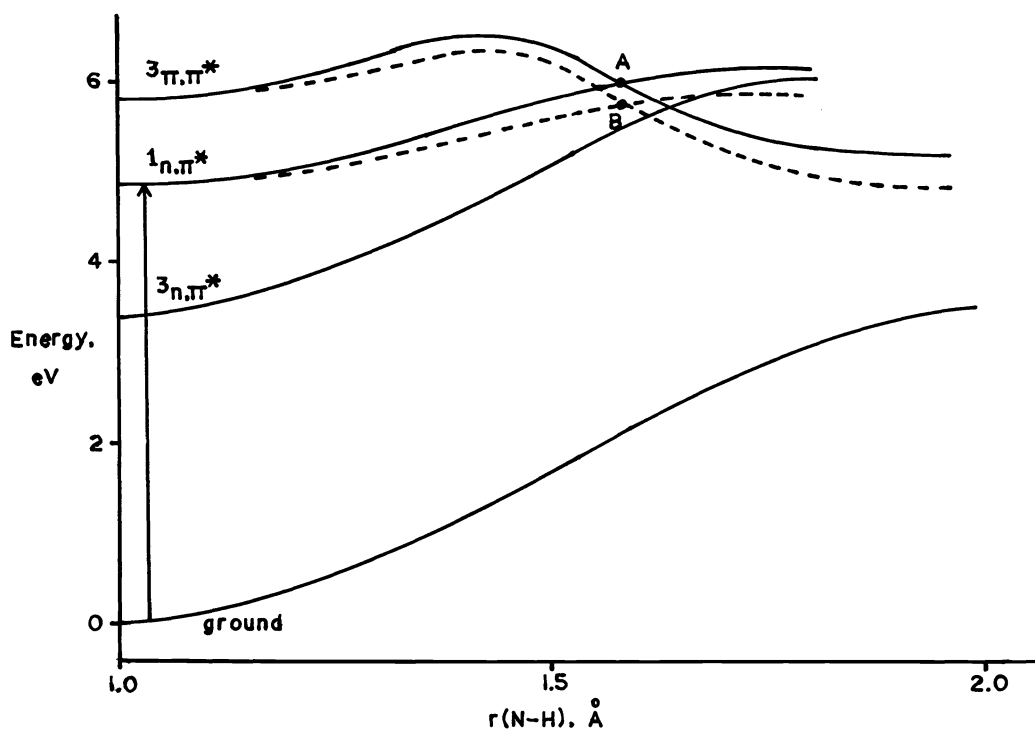
Fig. 2. Potential energy curves for one bond homolysis of diimide.
Dashed lines indicate the predicted effect of enhanced thermal lability.

predicts a greater activation energy for concerted elongation of both C-N bonds. Although
no effort has been made to detect the proposed intermediate 19 of the one-bond mechanism,
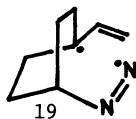
previous studies of diazenyl radicals suggest that their lifetime is exceedingly short
(Ref. 20).

The presence of an activation barrier in Fig. 2 leads to two interesting suggestions:
a) photolysis should become more efficient at elevated temperatures (Ref. 21) and b) ther-
mally labile azoalkanes should exhibit greater k_r values at a given temperature. Thus

allylic stabilization of one incipient radical should lower both the $^1n,\pi^*$ and $^3\pi,\pi^*$ curves so that they resemble the dashed lines in Fig. 2. Since crossing now occurs at point B instead of A, k_r is expected to increase, exactly as seen in Table 2. Note that the vertical $^1n,\pi^*$ state energy is unaffected by bridgehead vinyl substitution, as evidenced by the similar uv spectra of DBO, 17 and 18, (cf. Fig. 1).

In order to test suggestion a), we measured quantum yields for photolysis of DBO and its analogs 20 and 21 at several temperatures; the results are shown in Table 3.
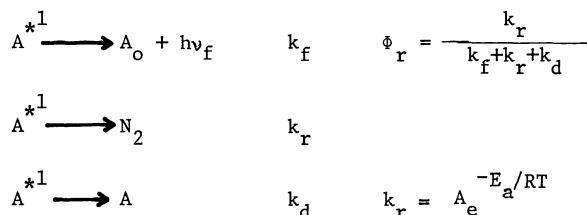

20   21

TABLE 3. Photolysis of DBO and related compounds in benzene at 366 nm.

Compound	Temp., °C	Φ_r	E_a, kcal mol^{-1}	$\ln\left(\dfrac{k_f+k_d}{A}\right)$
DBO	6.2	0.0055	8.6±0.3	-10.2±1.0
	29.7	0.016		
	47.9	0.040		
20	6.2	0.0093	10.2±0.4	-13.6±0.6
	29.7	0.035		
	47.9	0.093		
21	7.0	0.15	7.7±0.2	-12.1±0.3
	29.3	0.32		
	49.3	0.52		

For each compound, the data were treated by the following scheme:

Scheme 1.

$$^1A^* \longrightarrow A_o + h\nu_f \qquad k_f \qquad \Phi_r = \frac{k_r}{k_f+k_r+k_d}$$

$$^1A^* \longrightarrow N_2 \qquad k_r$$

$$^1A^* \longrightarrow A \qquad k_d \qquad k_r = A e^{-E_a/RT}$$

These equations, coupled with the assumption that k_f and k_d are independent of temperature, lead to

$$\ln(\Phi_r^{-1}-1) = \ln\left(\frac{k_f + k_d}{A}\right) + \frac{E_a}{RT}$$

Thus a plot of $\ln(\Phi_r^{-1}-1)$ versus T^{-1} should have a slope equal to E_a/R and an intercept related to k_f,k_d, and A. As seen in Table 3, all three compounds gave linear plots corresponding to a substantial activation energy for photolysis. Not only is this result in accord with Fig. 2, but it suggests that irradiation at elevated temperatures is a useful device for decomposing reluctant azoalkanes (Ref. 6). Furthermore it explains why DBO undergoes no photolysis at low temperatures (Ref. 13). By way of historical perspective, it should be noted that activation energies for photolysis of acyclic azoalkanes in the gas phase have been known for decades (Ref. 22, 23).

Measuring the temperature dependence of fluorescence intensity is another means of obtaining E_a (Ref. 21); however, it is inapplicable in the present case because k_f is such an important contributor to τ_f that the numerator and denominator in the expression

$$\Phi_f = \frac{k_f}{k_f + k_d + k_r} \qquad (2)$$

vary in a nearly parallel fashion. Thus changes in k_r due to temperature have little effect on Φ_f.

As mentioned above, Fig. 2 suggests that the more thermally labile compounds 17 and 18 will exhibit a lower activation energy than DBO. Irradiation of 17 at -78° gave the same Φ_r as at 25°; moreover, the singlet lifetime of both compounds was virtually independent of temperature. Thus for 17, τ_f = 2.4 nsec at 25° and 3.6 nsec at -78° while for 18, τ_f = 2.6 nsec at 25° and 2.7 nsec at -78°. These values, which were obtained in toluene on a different day from the ones in Table 2, are about five times longer; however, the discrepancy does not affect any of the present conclusions. Since deazatization is the major reaction of 17 and 18, the insensitivity of τ_f to temperature implies that this reaction encounters no activation barrier. In terms of Fig. 2, this means that point B is lowered to the vicinity of the ^{1}n,π^* state energy at the equilibrium C-N distance.

Steel et al. (Ref. 12) have reported that the inefficient decomposition of DBO in solution originates from both the singlet and triplet state. It is conceivable therefore, that the role of bridgehead vinyl groups is to enhance intersystem crossing (ISC) to a decomposing triplet. Although the triplet state of 17 and probably 18 is unstable to deazatization (Φ_r = 0.75 for benzophenone or p-methoxyacetophenone sensitization of 17), there is no good reason to expect that bridgehead vinyl groups accelerate ISC, especially since the singlet and triplet state energy are the same as for DBO (Ref. 17). It is not surprising that deazatization of triplet 17 is much more efficient than this process in DBO (Φ_r = 0.033 in CH$_3$CN) because according to Fig. 2, the barrier to decomposition of the ^{3}n,π^* state should be lowered by incipient radical stabilization just as effectively as the ^{1}n,π^* state.

Since triplet DBO undergoes very little decomposition and does not phosphoresce, its major fate must be radiationless decay. One suggested mechanism for this decay (Ref. 12) is reversible cleavage to a diazenyl radical. As shown below, the Φ_r data demand that such reversal be highly effective for DBO but not for 17. However, it is not apparent why 19
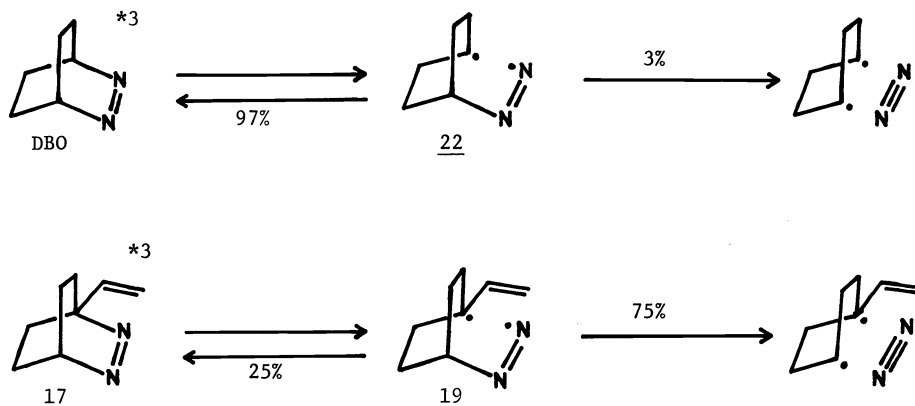
should lose N$_2$ much more often than 22 does. Both this argument and the high barrier seen in Fig. 2 indicate that reversible cleavage is not a likely mechanism for decay of triplet DBO. When formed in solution, the ^{3}n,π^* state is left with no choice but to revert to ground state, a process which occurs exclusively by a radiationless pathway. By analogy with the photoinert hydrocarbon bicyclo[2.2.2]oct-2-ene (Ref. 24), we presume that deactivation by twisting is more facile than expected in this seemingly rigid skeleton. It follows from this discussion that the process to which we have referred simply as decay (k$_d$) in scheme 1 could consist of ISC followed by triplet decay (Ref. 12).

Having discussed the activation energies for photolysis, we shall look briefly at the A factors. The last column in Table 3 allows calculation of A if k$_f$ and k$_d$ are known. From scheme 1 and the equation $k_r = \Phi_r / \tau_f$, it follows that

$$k_f + k_d = (1-\Phi_r)/\tau_f. \qquad (3)$$

This equation is conveniently applied to the reluctant azo compounds because errors in the small Φ_r values are unimportant. For 17 and 18, we know that k$_r$ dominates the singlet reaction pathways and that E$_a$ is negligible; thus, A = k$_r$. Even if the intercept in eq. (1) is not very accurate, the A factors in Table 4 for DBO and 20 seem higher than those for 17 and 18. No ready explanation for this difference comes to mind, particularly in view of the value for 21. Nevertheless, all of the A factors, which correspond to $\Delta^{\ddagger}$ = -5 to -18 eu, are lower than expected for a single bond homolysis, perhaps a consequence of the spin-forbidden crossing in Fig. 2 (Ref. 25).

TABLE 4. Parameters used to calculate excited state A values

Compound	τ_f, nsec	Φ_r	$k_f + k_d$[b]	A[c]
DBO	434	0.013	2.3×10^6	6.0×10^{10}
20	599	0.026	1.6×10^6	1.3×10^{12}
21	302	0.29	2.4×10^6	4.1×10^{11}
17	0.56	0.9	1.8×10^8	1.6×10^9
18	0.53	0.9	1.8×10^8	1.7×10^9

a. Calculated at 25° from data in Table 3. b. From eq. 3.
c. Arrhenius A factor (sec^{-1}) for excited state deazatization.

The values shown in Table 4 for $(k_f + k_d)$ of 17 and 18 are 100 times larger than those for other azoalkanes. Since we know that k_f is about 10^6, it appears that bridgehead vinyl groups enhance k_d. However, these values depend strongly on Φ_r. For example, if Φ_r were 0.999 instead of 0.9, k_d would be reduced to $\sim 10^6$. Although repeated measurements of Φ_r never gave values above 0.9, we cannot rule out a systematic error.

It will be noted that 21 exhibits a value of Φ_r intermediate between those for the reluctant azoalkanes and the bridgehead vinyl compounds. This result supports the correlation of Φ_r with thermal lability because $\Delta G^{\ddagger}$ for thermolysis of 21 is 33.9 kcal mol^{-1} (Ref. 26; cf. also Table 1). As seen in Tables 3 and 4, the reason why Φ_r is higher for 21 than DBO is that E_a is smaller and A is greater, leading to a 32 fold increase in k_r. Enhanced decomposition from 21 occurs at the expense of fluorescence ($\Phi_f = 0.18$) and decay ($\Phi_d = 0.53$) but k_d is not diminished by the possibly greater skeletal rigidity of 21 relative to DBO.

In light of the results described above, it is useful to consider the photochemistry of 20 in greater detail. The lifetimes and quantum yields for this and many other azoalkanes (Ref. 18) depend strongly on the nature of the solvent employed. As seen from the Φ_f and τ_f

TABLE 5. Solvent-dependent photochemistry of 20

Solvent	τ_f	Φ_f	Φ_{-azo}	Φ_r
CH_3CN	780[a], 740[b]	0.7[a,b]	0.15[a]	0.016[c]
C_6H_6	599[c], 660[a]	0.53[c]	0.025[c]	0.026[c]
CH_3OH	14[a], 30[b]	0.01[a]	0.25[a]	0.0015[c]
CH_3OD	165[a]	0.10[a]	0.20[a]	

a. Ref. 25. b. Ref. 18. c. This work

data in Table 5, methanol seems to be a good singlet quencher; however, it was said not to change the quantum yield for azoalkane disappearance (Φ_{-azo}) from the value in CH_3CN (Ref. 27). This result was rationalized in terms of Scheme 2 in which the decomposing state (A_N^*) precedes the fluorescing state. Interestingly, Scheme 2 is exactly the opposite of the one required to explain the gas phase photolysis of DBO (Ref. 12). In the latter instance, addi-

Scheme 2.

$$A \xrightarrow{h\nu} A_N^* \longrightarrow A^{*1} \longrightarrow h\nu_f$$

with $A_N^* \downarrow \to N_2$ and $A^{*1} \downarrow^{MeOH} \to A$
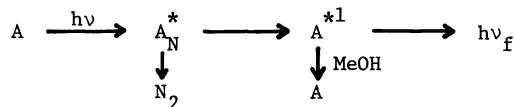
tion of inert gas diminished decomposition but left fluorescence unaffected, suggesting that decomposition follows intersystem crossing. If A_N^*, presumably an excited state whose energy is not yet randomized among the various vibrational modes of the molecule (Ref. 28), is important in solution, it certainly must be so in the gas phase; however, the sum of Φ_f and decomposition from the quenchable state (A^{*3}) is unity. This leaves no role for A_N^* in the gas phase.

Since a nonrandom state helps to explain the photochemistry of acylic azoalkanes in solution (Ref. 1, 28) it should not be readily dismissed in DBO derivatives. Nevertheless, the existing data can be rationalized nicely without invoking these species. For example, if Scheme 2 were correct, one would expect incorporation of bridgehead vinyl groups to facili-

tate loss of nitrogen from A_N^*. The lifetime of A^{*1} would then be unaffected as Φ_r increased, in sharp contrast to the observed trend (Table 2). Earlier work on the photolysis of DBO in solution showed that fluorescence is quenched by cyclohexa-1,3-diene (Ref. 11) or the photo-chemically formed quencher (Ref. 12) to the same extent as decomposition. These processes would not exhibit the same sensitivity to quenchers if deazatization originated from A_N^* and fluorescence from A^{*1}.

Several other observations speak against Scheme 2: the quantum yield for azoalkane disappearance in CH_3CN or CH_3OH is higher than that of N_2 or hydrocarbon formation (Table 5 and Ref. 12), methanol as solvent actually enhances azoalkane disappearance and diminishes nitrogen formation and irradiated solutions of 20 in methanol turn yellow. Furthermore, it is likely that most of the Φ_{-azo} results in Table 5 are too high because DBO exhibits a value of only 0.068 in acetonitrile (Ref. 12). It is therefore apparent that DBO analogs can react with certain solvents to produce nitrogen-containing photoproducts, (cf. 13 → 14). We propose that Scheme 3 is more consistent with the data in Table 5 than Scheme 2 is. Here the use of CH_3OH as solvent should decrease Φ_f, τ_f and Φ_r to the same extent, more or less the observed

Scheme 3.

$$A \xrightarrow{h\nu} A^{*1} \xrightarrow{MeOH} A^* \cdot MeOH \xrightarrow{25\%} product$$

trend. Although MeOD is only one tenth as effective as MeOH at forming a $A^* \cdot MeOH$ hydrogen bonded complex, both complexes go to products with about 25% efficiency.

PRODUCT STUDIES

If 17 and 18 behaved like DBO, their photochemical products would be derived by ring closure and opening of the expected diradicals 23 and 26. These species are of interest as possible

Calc'd ΔH_f, kcal mol^{-1}

	17	23	24	25
	55.9	57.3	47.4	33.5

	18	26	27	28	29
	72.0	59.5	64.0	46.8	54.5

intermediates in the Cope rearrangement (Ref. 21). The ultimate products from 18 might be bicyclohexane 27, which we calculate to be thermodynamically less stable than 26 (Ref. 30), tetraene 28, whose thermal reactions are under investigation (Ref. 31), and finally the recently synthesized anti-Bredt compound 29 (Ref. 32). We have found that irradiation of 18 at 25° produces only tetraene 28, as judged by nmr comparison with an authentic sample. Although a considerable number of compounds similar to 27 are known (Ref. 33-35), it seemed possible that 27 might be a thermally labile intermediate between 18 and 28. We therefore irradiated 18 at -78° and ran the nmr spectrum of the product at low temperatures but only 28 was seen. H. D. Martin (Ref. 36) reported recently that irradiation of 30 in frozen benzene caused ring closure but that the product in fluid solution arose by ring cleavage. Unfortunately, irradiation of 18 in frozen benzene led only to tetraene 28. Professor Orville Chapman and Richard A. Hayes at UCLA kindly agreed to monitor the photolysis of 18 at 26°K by matrix isolation infrared spectroscopy; however, the observed product spectrum still corresponded to that of 28. Irradiation of 17 at -78° in CD_3COCD_3 with 366 nm light also gave only ring opening, judging by comparison with an authentic sample of 25 (note a). These low temperature results, coupled with our eventual synthesis of 24 (see below) are convincing evidence that neither 24 nor 27 are intermediates on the pathway to 25 and 28. Why do we

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Note a.: The authors thank Professor Jack W. Timberlake, University of New Orleans, for the sample of 25.

observe no ring closure products from 17 and 18 when DBO and 20 give both a 1,5-hexadiene and a bicyclo[2.2.0]hexane (Ref. 12)?

Stabilization of the diradical by allylic resonance does not seem to be the answer because the ratio of cleavage to closure in the Norrish Type II reaction (Ref. 37) or in six-membered monocyclic azoalkanes (Ref. 1) shows no particular dependence on resonance delocalization of the biradical. Conformational effects (Ref. 38) are not likely either, in view of the similar product distribution from DBO and 20. Triplet diradicals undergo more cleavage than singlet diradicals from DBO (Ref. 12) and a six-membered azoalkane (Ref. 39); however, even the pure triplet reaction gives 25% ring closure. Spin multiplicity differences are therefore not the answer. A more appealing explanation is that diradicals 23 and 25 do not lie on the decomposition pathway but that the unstabilized cyclohexan-1,4-diyl does. Thus concerted cycloreversion might be facilitated in 17 and 18, in the same way that radical stabilizing groups accelerate the Cope rearrangement (Ref. 40). Of course we have earlier postulated diazenyl radical 19 as the key intermediate and this species might fragment to
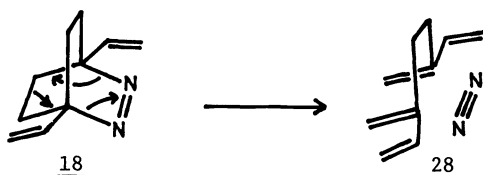
give the most stable products. It follows that either DBO does not give a similar diazenyl radical (22) or that if it does, 22 behaves differently from 19. An esr study of the photolysis of 17 and 18 at low temperatures might be of help in sorting out these possibilities.

Although photolysis of 17 and 18 did not produce any bicyclo[2.2.0]hexanes, these compounds are sufficiently interesting to warrant independent synthesis. Our attempts to prepare 27 from the known 1,4-bishydroxymethylenebicyclo[2.2.0]hexane (Ref. 41) using selenium chemistry (Ref. 42) or the Wittig reaction (Ref. 43), were not fruitful. We did succeed, however, in synthesizing 24 by the Wittig route. This compound underwent thermal rearrangement at 33.5°C with a half life of 8 hours, demonstrating that it would have been detected in the photolysis of 17. Using literature data, one calculates that 27 should have a half life at -78°C of 3.7 min. and would be exceedingly stable at 26°K. The relevant data are summarized in Table 6.

TABLE 6. Activation parameters for cyclobutane thermolysis

Compound	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ eu	$\Delta G^{\ddagger}$ (100°C)	Ref
cyclobutane	61.1	9.1	57.7	44
vinylcyclobutane	48.6	5.4	46.6	45
trans divinylcyclobutane	33.7	-2	34.4	46,47
cis divinyl cyclobutane	23.1	-11.7	27.5	47
bicyclo[2.2.0]hexane	36.0	1.5	35.4	48
1-vinyl bicyclo[2.2.0] hexane (23)			24.5[a]	this work
1,4-divinylbicyclo [2.2.0]hexane (26)			(13.5)	estimated

a. Based on one determination only.

Each added vinyl group in the monocyclic series lowers $\Delta G^{\ddagger}$ by about 11 kcal mol^{-1}, corresponding to one allyl resonance energy. Since a similar decrease in $\Delta G^{\ddagger}$ occurs on adding a vinyl group to bicyclo[2.2.0]hexane, it seems reasonable to expect another decrease of this magnitude in 27. Even if the geometry of 27 were as favorable for Cope rearrangement as that of cis divinylcyclobutane, the half life of 27 would still be many years at 26°K.

To summarize the above discussion, we have found that bridgehead vinyl substitution greatly enhances the photolability of DBO. The results are consistent with initial cleavage of only one C-N bond, leading to a diazenyl radical. In accord with a theoretical calculation, DBO exhibits a barrier to decomposition of S^{*1} which can be surmounted by raising the temperature during irradiation. The only photoproducts found to date are triene 25 and tetraene 28, and these do not seem to arise via vinylbicyclohexanes 24 and 27.

ISOMERIZATION

Unlike their bicyclic counterparts, acyclic azoalkanes can undergo cis-trans isomerization. Although the cis isomer of azobenzene has been known since 1937, (Ref. 49) it was only in 1964 that Hutton and Steel (Ref. 50) reported the first aliphatic analog, cis azomethane. Both this compound and cis azoisopropane have since been studied carefully (Ref. 51). In 1969, Mill and Stringham (Ref. 52) made the important discovery that azo-tert-butane (ATB) underwent photoisomerization to a labile cis isomer, which lost nitrogen even at 0°C.

In collaboration with Professor Jack W. Timberlake at the University of New Orleans, we have studied some acyclic cis azoalkanes which were expected to isomerize thermally back to trans, without forming nitrogen (Ref. 53). The compounds chosen were 1-azobicycloalkanes, in which the resulting radicals would be at the bridgehead. This structural feature is known from studies of perester thermolysis (Ref. 54), aldehyde decarbonylation (Ref. 55) and others (Ref. 56) to destabilize radicals. In trans azoalkanes, thermolysis rates reflect both radical stability (Ref. 57) and the requirement of planarity in the transition state (Ref. 58).

The case of azo-1-norbornane 31 is a particularly interesting one.

31t   31c
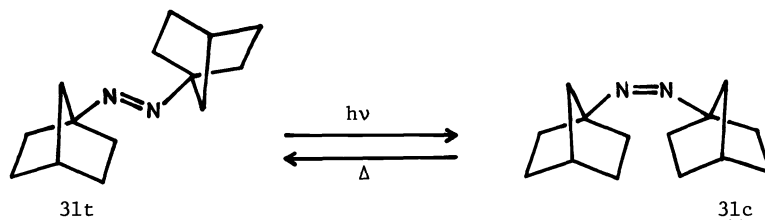
Irradiation of 31t in hexane at 366 nm and 25°C caused the solution to become intensely yellow. Column chromatography allowed isolation of 31c, which proved to be stable for months at room temperature. As is generally true for cis azoalkanes, the extinction coefficient of 31c was several times that of 31t and the absorption maximum was at substantially longer wavelength 31t λ_{max} = 364 nm, ϵ = 15; 31c λ_{max} = 423 nm, ϵ = 88). Differential scanning calorimetry (DSC) allowed determination for the first time of the enthalpy difference between two azoalkane isomers, in this case 12.6 kcal mol^{-1}. We suspect that approximately 8 kcal mol^{-1} is due to the inherent cis-trans difference and the rest represents repulsion between norbornyl groups. After solid 31c had reverted to solid 31t in the DSC instrument, the melting behavior of 31t at 166° indicated less than 0.3% impurities. This result confirms our observation that heating 31c in solution leads to no evolution of nitrogen. Thus the behavior of 31c is precisely the opposite of that of cis ATB, whose exclusive fate is deazatization.

The fact that 31c is so stable makes it an appealing compound for further study. Uv-visible spectroscopy was used to monitor the thermal reversion of 31c to 31t in xylene at 80-102°C, yielding the activation parameters $\Delta H^{\ddagger}$ = 30.3±0.5 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 0.8±1.3 eu. Analogy with azo-1-adamantane and azoisopropane suggest that 31c will also revert cleanly to 31t under visible irradiation; in fact, the yellow color of all of our cis azoalkanes fades when they are stored under ambient light.

Fogel and Steel (Ref. 51) have reported for azoisopropane that $\Phi_{t \to c} \approx \Phi_{c \to t} \approx 0.5$ under direct irradiation but that $\Phi_{t \to c}$ = 0.04 and $\Phi_{c \to t}$ = 0.70 for benzophenone sensitization. Since the reaction proceeds much more efficiently in the exothermic direction, a Schenck mechanism (Ref. 51) could possibly be involved. We found, however, that 31c isomerizes to 31t under benzophenone or thioxanthone sensitization with quantum yields of 0.87 and 0.77 respectively. Since thioxanthone has a π,π^{*} lowest triplet state, the Schenck mechanism is unlikely. Furthermore, triplet sensitized cis→trans isomerization proceeds readily in cyclic systems 32 (Ref. 60) and 33 (Ref. 61), in which the trans isomer is of equal or higher energy than the cis. Thus one can now say that the photostationary state for direct irradiation of acyclic azoalkanes is very different from that for triplet sensitization. The simplest
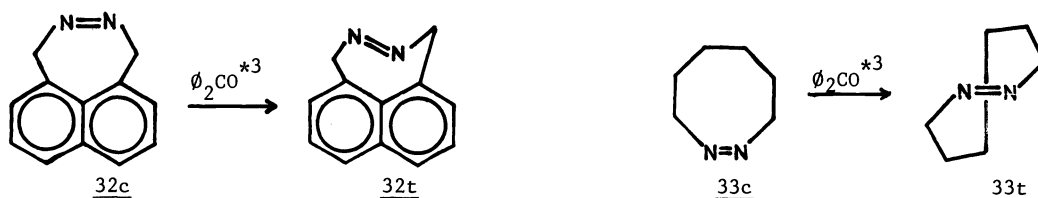
explanation for this observation is that direct isomerization occurs from the azoalkane n,π^* singlet state, before intersystem crossing.

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