hydrogen atoms were taken from the International Tables for X-Ray Crystallography.[42] Hydrogen atoms scattering factors were those of Stewart, Davison, and Simpson.[43] Computer-generated perspective drawings were obtained by using a PLUTO 78 program.[44]

Bond angles, additional bond lengths, and the final values of positional and thermal parameters are given in the supplementary material.

Acknowledgment. We extend our special thanks to Dr. Jordi Frigola, Department of Medicinal Chemistry, Laboratorios Dr. Esteve, S. A., Barcelona, for the helpful discussions and for recording the ^{13}C NMR spectra. Thermogravimetry experiments were kindly determined by Dr. Josê Luis Serrano, Facultad de Quimica, Universidad de Zaragoza. We are indebted to the Ministerio de Educaciôn y Ciencia for a postgraduate scholarship to I.D.

Registry No. 3, 105958-17-6; 4, 67766-29-4; 5, 109929-49-9; 6, 105958-19-8; 7, 105958-20-1; 8, 105958-21-2; 9, 105958-22-3; 10, 105958-23-4; 11 (ion 1+), 109929-50-2; 12 (ion 1+), 109959-83-3; 13 (ion 1+), 109929-51-3; 14, 105958-24-5; 15, 105958-25-6; 16, 67766-30-7; 17, 105958-26-7; 18, 105958-28-9; 19, 109959-82-2; 20, 109929-47-7; 21, 109929-48-8; 22, 31230-17-8; 23, 61-82-5; 24, 4418-61-5; 25, 1455-77-2; 26, 448-61-3; 27, 105958-31-4; 28, 105958-32-5; 29, 89419-81-8; 30, 109929-40-0; 31, 934-32-7; 32, 29096-75-1; 33, 105958-33-6; 34, 105958-35-8; 35, 107553-43-5; 36, 109929-41-1; 37, 4857-06-1; 38, 39791-96-3; 39, 21539-80-0; 40, 105958-29-0; 41, 2963-77-1; 42, 109929-42-2; 43, 109929-44-4; 44, 109929-46-6.

Supplementary Material Available: ^{1}H NMR data of *N*-azolylpyridinium salts (Table V); ^{13}C NMR data of *N*-azolylpyridinium salts (Table VI); ^{1}H NMR data of pyridinium azolate inner salts (Table VII); ^{13}C NMR data of pyridinium azolate inner salts (Table VIII); unit cell perspective view showing selected intermolecular contacts for compound 3 (Figure 3); elemental analysis for all the *N*-azolylpyridinium salts and the pyridinium azolate inner salts synthesized (Table X); total charges at $\theta_{\min}$ for 3, 5–10 (Table XI); plot of the total energy vs. torsional angle θ in compound 7 (Figure 4); crystallographic data for the pyridinium benzimidazolate inner salts 3 and 17, the final values of positional parameters (Table XII and XIII), thermal parameters (Table XIV and XV), and bond distances and angles (Table XVI and XVII) (15 pages). Ordering information is given on any current masthead page. Structure factors tables are available from the authors.

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Fluorescence Quenching and Photoreactions of 2,3-Diazabicyclo[2.2.2]oct-2-enes. A Case of Charge Transfer and Hydrogen Atom Transfer

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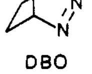
A variety of organic compounds have been found to quench the long-lived fluorescence of 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO), but photochemical reactions take place only with good hydrogen atom donors and tetrahalomethanes. A hydrogen isotope effect on k_q of 1.7–3.0 was observed with 1,3- and 1,4-cyclohexadiene. While both quenchers photoreduced DBO, the 1,3-isomer also dimerized to a mixture characteristic of triplet diene. The results are rationalized in terms of the usual encounter complex and ion pair except that the former can undergo hydrogen transfer or react with 1,3-cyclohexadiene. A second case of photochemically induced electron transfer fragmentation was found in the reaction of 1-phenyl-DBO with bromotrichloromethane.

2,3-Diazabicyclo[2.2.2]oct-2-ene (DBO) was first prepared by Cohen and Zand in 1962.[1] Unlike typical azoalkanes,[2,3] this compound exhibits a low quantum yield for loss of nitrogen in solution; hence, DBO and many of its derivatives have been termed "reluctant azoalkanes". The photoreactions of some substituted DBO's are nevertheless interesting because unusual biradical and electron-transfer reactions take place.[4] Loss of an electron from azoalkanes produces the radical cations, whose chemistry is now beginning to unfold.[4-8]



DBO

The extraordinary long-lived, fluorescent singlet state of DBO can be quenched with such substances as olefins,[9,10] halocarbons,[4,11] and hydrazines.[12] The quenching effiency of olefins has been explained quantitatively on the

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Table I. Quenching of DBO Fluorescence

quencher	solvent[a]	$10^7 k_q$, M^{-1} s^{-1} [b]	quencher	solvent[a]	$10^7 k_q$, M^{-1} s^{-1} [b]
1,3-cyclohexadiene	I	17 (24)[4] (26)[9]	1,1-diphenylethylene	A	1.8
1,3-cyclohexadiene-d_8	I	8.2	1,1-diphenylethylene	I	7.6
1,3-cyclohexadiene	A	3.2 (4.4)[4]	quadricyclene	I	1.6[10]
1,3-cyclohexadiene-d_8	A	1.9	benzene	I	<0.004[9]
1,4-cyclohexadiene	I	4.1	*p*-dimethoxybenzene	A	0.27[4]
1,4-cyclohexadiene-d_8	I	1.5	chlorobenzene	A	0.010[4]
1,4-cyclohexadiene	A	1.7 (1.8)[4]	benzotrichloride	A	5.5[4]
1,4-cyclohexadiene-d_8	A	0.56	benzonitrile	A	0.28[4]
cyclopentadiene	I	5.6[9]	*p*-dicyanobenzene	A	247[4]
piperylene	I	3.0[9]	dimethyl phthalate	A	3.1
cyclopentene	I	0.87[9]	1,1-dimethylhydrazine	A	100[12]
cyclohexene	I	0.84[9]	1,2-dimethylhydrazine	A	340[12]
cyclohexene	A	0.19	carbon tetrabromide	A	1000[4]
cis-2-butene	I	0.19[9]	bromotrichloromethane	A	700
1-hexene	I	0.12 (0.098)[9]	tetranitromethane	A	2300
1-hexene	A	0.059	benzoyl peroxide	A	84
1-octene	I	0.055[9]	di-*tert*-butyl peroxide	A	0.91
styrene	A	0.3	tetramethylpiperidine-1-oxyl	A	420
trans-stilbene	A	1.4			

[a] A = acetonitrile, I = isooctane. [b] Values are from this work except where a reference is cited.

Table II. Fluorescence Quenching of DBO Derivatives in Acetonitrile

fluorescer	quencher	$E_{1/2}$, V[a]	$10^7 k_q$, M^{-1} s^{-1}
DBO	benzonitrile	−2.35	0.28
DBO	dimethyl phthalate	−1.93	3.1
DBO	*p*-dicyanobenzene	−1.60	247
1	benzene	2.04	0.13[b]
1	anisole	1.76	1.6
1	*m*-dimethoxybenzene	1.49	23
1	*p*-dimethoxybenzene	1.34	147

[a] Reduction or oxidation potential of quencher versus SCE. [b] In neat benzene.

Table III. Nitrogen Quantum Yields for DBO with Quenchers in Acetonitrile[a]

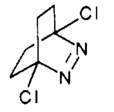
azoalkane	quencher	quencher concn, M	Φ_{N_2}
DBO	none		0.018[b]
DBO	benzotrichloride	0.141	0.0085
DBO	*p*-dicyanobenzene	0.074[c]	4.6×10^{-7}
DBO	*p*-dicyanobenzene[d]	0.042	0.0038[e]
DBO	*p*-dicyanobenzene	0.073[c]	3.2×10^{-4} [f]
1	*p*-dimethoxybenzene	0.138[c]	1.3×10^{-7}
1	*p*-dimethoxybenzene	0.138[c]	9.8×10^{-4} [f]
DBO	TCNE[g]	0.0097	2.6×10^{-4}
1	TCNE	0.013	0.034
1	TCNE	0.0089	0.0024[f]
DBO	TMPDA[h]	0.010	2.2×10^{-4}
DBO	TMPDA	0.0073	5.8×10^{-4} [f]
1	TMPDA	0.0078	0.0012
1	TMPDA	0.0087	0.0015[f]

[a] DBO irradiated at 366 nm. [b] Value in benzene from ref 4. 1,4-Dimethyl-DBO exhibits $\Phi_{N_2} = 0.016$ in acetonitrile. [c] UV monitoring showed negligible disappearance of azo absorption. [d] *p*-Dicyanobenzene irradiated at 254 nm where DBO absorption is minimal. [e] Absorbance of solution increased gradually during irradiation, making an accurate determination of DBO disappearance impossible. However, it is certain that DBO reacts very slowly. [f] In methanol. [g] Tetracyanoethylene. [h] Tetramethyl-*p*-phenylenediamine.

basis of charge transfer from olefin to DBO.[13] We now report additional data on the interaction of DBO singlets with a variety of compounds. Although photochemistry is not a usual consequence of this interaction, both electron transfer and hydrogen atom transfer take place in some cases.

Results

Table I shows quenching rate constants (k_q) of DBO fluorescence by many substances. Half of the values are collected from the literature while the remainder are newly determined by either the intensity or lifetime method. Clearly, both electron-rich and electron-deficient compounds can quench DBO singlets, with k_q spanning 5 orders of magnitude. Fluorescence quenching was also examined for some methoxybenzenes with 1,4-dichloro-DBO (1), yielding results included in Table II.



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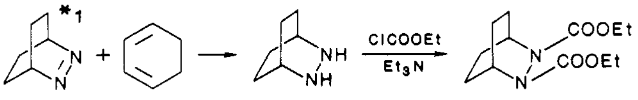
Because fluorescence quenching was so common, it was important to check whether any chemistry resulted from irradiation of DBO's with quenchers. The data in Table III reveal that the nitrogen quantum yield of these reactions is very low; moreover, UV monitoring of selected mixtures showed little disappearance of the azo chromophore. In contrast to these results, irradiation of DBO in neat 1,3-cyclohexadiene produced a cloudy, yellow solution and a 2% yield of nitrogen. Because of the color, we could only calculate from a UV spectrum of the final solution that the minimum quantum yield for DBO disappearance was 0.021. Addition of ethyl chloroformate and triethylamine allowed trapping of the photoreduction product **2** as a 22% yield of carbamate **3**.[14] Although several GC



2 3

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Table IV. Cyclohexadiene Dimer Product Distributions[a]

sensitizer	4	5	6	7	reference
benzophenone[b]	tr	16	62	22	this work
benzophenone[b]		20	60	20	15
DCN[c]	79	21	tr	0	this work
DCN[c]	69	11	20[d]		16
DCNA[e]	77	23	0	0	17
direct $h\nu$ (>330 nm)		40	44	23	18
DBO[f]	tr	11	68	20	this work
DBO[g]	tr	7	74	19	this work
DBO[b]	27	12	44	16	this work

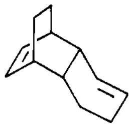
[a] Data for this work given in percent of total dimer GC peak area. [b] In neat 1,3-CHD. [c] 1,4-Dicyanonaphthalene in acetonitrile. [d] Total of 6 and 7. [e] 9,10-Dicyanoanthracene in CH_2Cl_2. [f] With 1.1 M 1,3-CHD in isooctane. [g] With 1.1 M 1,3-CHD in acetonitrile.

Table V. Isotope Effects on k_q of DBO Fluorescence

quencher	solvent[a]	k_q^H/k_q^D [b]
1,3-CHD	I	2.1
1,3-CHD	A	1.7
1,4-CHD	I	2.7
1,4-CHD	A	3.0

[a] A = acetonitrile, I = isooctane. [b] Calculated from data in Table I.

peaks in this mixture remain unidentified, the formation of cyclohexadiene dimers **4–7** was confirmed by comparison with authentic samples (cf. Tables IV and VI).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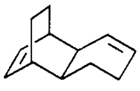
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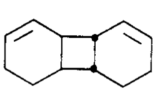
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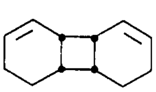
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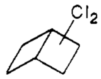
Since we have previously reported the photoreaction of 1-cyclopropyl-DBO with CCl_4,[4] an attempt was made to analyze the products of DBO itself with CCl_4. Extended irradiation of this mixture gave an unstable oil, which was subjected to column chromatography followed by preparative GC. Ultimately, a stable, clear oil was isolated in very low yield and was shown by GC not to be 1,4-dichlorocyclohexane. Its mass spectrum and ^1H and ^{13}C NMR spectra suggested a saturated, dichloro bicyclic hydrocarbon such as **8** or **9**. Unfortunately, the complexity



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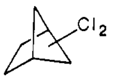

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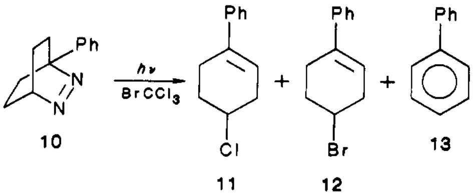
of the NMR spectra and the presence of impurities precluded a detailed structural assignment, though the two known isomers of dichlorobicyclo[2.2.1]hexane[19] could be ruled out.

Greater success was achieved in the photoreaction of 1-phenyl-DBO (**10**) with bromotrichloromethane. Reverse-phase HPLC revealed at least a dozen peaks, of which products **11–13** could be isolated. Identification



was achieved by comparison with authentic samples. Although **11** had been synthesized previously,[20] we had to make **12** from 4-bromocyclohexanone. The absolute product yields were determined with fluorene as an internal standard: **11**, 1.4%; **12**, 2.7%; and **13**, 2.1%.

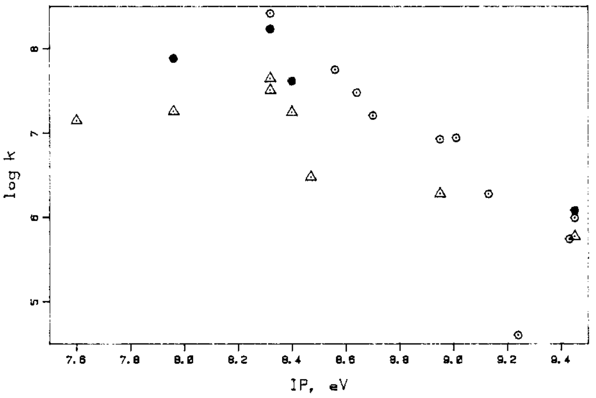


Figure 1. Log of the quenching rate constant of DBO fluorescence vs. ionization potential of quencher. (⊙) Data from ref 13 in isooctane. (●) This work in isooctane. (△) This work in acetonitrile. Only values for hydrocarbons in Table I are plotted.

Discussion

On the basis of the linearity of plot of ln $[k_q/(k_{\text{dif}} - k_q)]$ vs. ionization potential (IP), Evans[13] concluded that quenching of DBO fluorescence by olefins is charge transfer in nature. When k_q is considerably smaller than the diffusion-controlled rate constant, k_{dif}, Evans' plot is equivalent to the more usual log k_q vs. IP plot. Figure 1 (open circles) shows that the latter two quantities are indeed correlated for olefins ($k_q < 3 \times 10^8$ M^{-1} s^{-1}, Table I) in isooctane solvent and that our new values for 1,3-cyclohexadiene (1,3-CHD) and 1-hexene agree with earlier ones.[9] Although these data support Evans' interpretation, we were concerned about the known ability of excited singlet DBO to abstract hydrogen,[4,12] leading to possible attack on the solvent or quencher.

To check for a solvent effect, the k_q values in acetonitrile were also plotted vs. IP in Figure 1. The limited olefin data still appear somewhat linear, though all k_q's are 2–5-fold slower than in isooctane. However, consideration of a wider range of quenchers reveals a great deal of scatter. Especially alarming was the low k_q of poor hydrogen-donating olefins such as styrene, stilbene, and 1,1-diphenylethylene. These results raised the question of whether hydrogen abstraction might contribute to k_q in other cases.

Four additional experiments show that hydrogen abstraction is indeed significant with cyclohexadienes. (1) Despite the published comment that quenching of DBO fluorescence by 1,3-CHD leads to no chemical reaction,[9] we isolate a 22% yield of **3** from an irradiated mixture of

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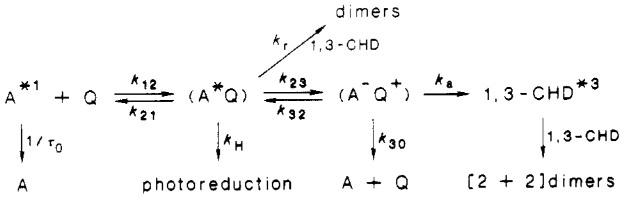
Table VI. Characterization of 1,3-CHD Dimers

compd	retn time, min[a]	chemical shift[b]		
		CH_2	CH	olefinic
4	50.5	23.53, 25.49, 26.41, 27.36	36.60, 36.92, 39.19, 40.29	128.17, 132.26, 132.83, 134.01
5	55.4	18.55, 21.17, 24.91, 25.89	33.06, 35.17, 35.51, 36.71	130.11, 131.95, 134.43, 135.68
6	52.3	21.35, 22.10	31.94, 39.31	126.73, 130.29
7	67.1	21.74, 23.13	35.25, 35.71	128.40, 128.66

[a] On 0.125 in. × 6 m 15% Apiezon L. Oven 158 °C, detector and injector 160 °C, He flow 90 mL/min. [b] In $CDCl_3$. Assignments confirmed by INEPT.

Scheme I



these compounds, after trapping of the hydrazine. (2) Use of 1,4-CHD as solvent raises the quantum yield of DBO disappearance over four fold to 0.079 from its value of 0.018 in benzene and leads after trapping to a 76% yield of **3**.[4] (3) We find a deuterium isotope effect of 2–3 for both 1,3- and 1,4-CHD quenching DBO fluorescence (cf. Table V). (4) Flash photolysis of DBO in acetonitrile containing 0.51 M 1,4-CHD produces a signal with a 49 ns rise time at 326 nm, corresponding to the cyclohexadienyl radical.[21]

Before postulating a mechanism to rationalize these data, we must note that the other products of DBO and 1,3-CHD are the diene dimers **4**–**7**. As seen in Table IV, these dimers are produced in a ratio characteristic of 1,3-CHD triplets,[15] not of radical cations.[22,23] Even a solvent change from isooctane to acetonitrile does not enhance formation of **4** or **5** as one would expect if free diene radical cations were involved.[16,24] Both photoreduction of DBO and dimerization of 1,3-CHD originate from the S_1 state of DBO because intersystem crossing in these azoalkanes is neither efficient nor rapid; for example, $\Phi_{isc} < 0.082$ for 1-cyclopropyl-DBO.[4] Moreover, neat (10.5 M) 1,3-CHD can be calculated from the first entries in Table I to quench >99.8% of the DBO singlets. Any reaction from triplet DBO could not have a quantum yield above 0.002, yet the observed quantum yield of DBO disappearance was at least 10 times this value.

As shown in Scheme I, we propose that DBO^{*1} and ground-state 1,3-CHD form an encounter complex (A^*Q) that has charge-transfer character and that can undergo hydrogen atom transfer (k_H) or electron transfer.[25,26] The resulting ion pair (A^-Q^+) either decays to starting materials or self-annihilates (k_a), liberating excited triplet 1,3-CHD. At high concentrations of 1,3-CHD, reaction (k_r) of the diene with (A^*Q) is the most probable route to the dimers in view of the enhanced yield of **4** in neat 1,3-CHD (Table IV) and Schuster's closely related work on 1,4-dicyanonaphthalene.[16]

For most quenchers other than 1,3-CHD k_r is unimportant, k_a can be included in k_{30}, and k_H is omitted if the quencher has no abstractable hydrogens. Since none of the chemical reactions is essential to fluorescence quenching, we can understand why substances like stilbene and styrene are still quenchers. Although the ion pair (A^-Q^+) for typical charge-transfer exciplexes actually lies at high energy than (A^*Q) in solvents with dielectric constant below 7,[27] it is included for three reasons: (1) to rationalize the rough correlation between k_q and the donor–acceptor properties of Q (cf. Table 2 and the discussion below), (2) to explain the inverse solvent effect on k_q (slower quenching in acetonitrile than isooctane), and (3) to provide a means for generating triplet 1,3-CHD. A scheme with (A^*Q) as the sole intermediate leads to equations of precisely the same form as (2) and (3) below but either decay or hydrogen transfer within the complex would have to depend on the donor–acceptor properties of Q.[27] In fact, the latter phenomemon has been invoked in the quenching of triplet ketones by olefins.[28] The formation of free ions cannot be an important process because even in acetonitrile, dimer **4**, which is characteristic of $1,3\text{-}CHD^{\cdot+}$, is found only in trace amounts.

Using the steady-state assumption and neglecting k_r, one can derive eq 1, which is analogous to Weller's equation[29] for the apparent Stern–Volmer fluorescence quenching rate constant k_q. F represents the fraction of (A^-Q^+) that

$$k_q = \frac{k_{12}(k_H + k_{23}F)}{k_H + k_{23}F + k_{21}} \qquad (1)$$

decays or reacts; that is $F = (k_a + k_{30})/(k_a + k_{30} + k_{32})$. If k_{21} is small, eq 1 shows that k_q will not depend on k_H or k_{23}, but our observation of an isotope effect (Table V) shows that k_q does depend on k_H. The measured isotope effect (k_q^H/k_q^D) is not equal to the one for the photoreduction step (k_H/k_D), but instead these quantities are related in a complex way. However, dividing eq 1 for H by that for D and making the assumption that k_{21} is much larger than k_H gives the simpler equation:

$$\frac{k_q^H}{k_q^D} = \frac{k_H + k_{23}F}{k_D + k_{23}F} \qquad (2)$$

The absence of any noticeable disagreement between Stern–Volmer slopes obtained by steady-state and transient techniques[30] implies that k_{21} is surely larger than 10^9 s^{-1}, a value that exceeds even the rate of hydrogen abstraction by *tert*-butoxyl radicals.[31] Thus, eq 2 is likely to be valid. Moreover, Wagner and co-workers[28] have nicely shown that sizeable isotope effects are consistent with reversible complexation, i.e., large k_{21}. The observed isotope effect is therefore less than k_H/k_D except when $k_{23}F$ happens to be small, in which case fluorescence quenching provides the correct value of k_H/k_D. We cannot conclude

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that our results fall into the latter regime since other factors can reduce the observed isotope effect below its theoretical maximum of ~7. However, it is certain that k_H/k_D is at least 1.7.

Scheme I can account for the fact that irradiation of DBO in 1,4-CHD increases the quantum yield of azoalkane disappearance over the value in benzene. The relationship between Φ_{-A} and k_H is expressed in eq 3. Here F' is the

$$\frac{1}{\Phi_{-A}} = \left(\frac{1}{1-F'}\right)\left(1 + \frac{k_{23}F}{k_H} + \frac{k_{23}F'}{k_H}\right) \qquad (3)$$

fraction of initially formed A* that fluoresces or decays, namely, $(1/\tau_0)/(1/\tau_0 + k_{12}[Q])$ while F has the same meaning as in eq 1 except that k_a is zero because no dimers form with 1,4-CHD. More rapid hydrogen abstraction obviously increases Φ_{-A}, in accord with experiment.

It is clear from Table I that k_q depends strongly on the nature of the quencher. Assuming no chemical reaction ($k_r = k_a = k_H = 0$) and $k_{21} \gg k_{23}F$, we can rewrite eq 1 as

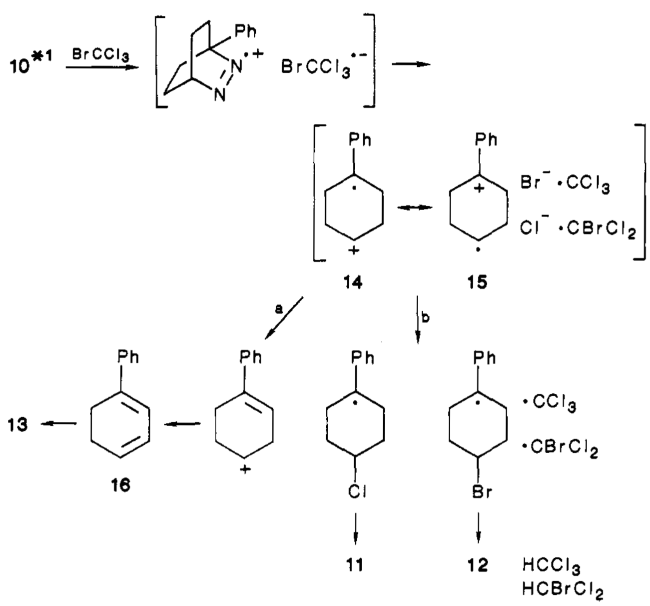
$$k_q = \frac{k_{12}}{k_{21}} k_{23} \frac{k_{30}}{k_{30} + k_{32}} \qquad (4)$$

Equation 4 predicts a complex dependence of k_q on quencher structure. Thus, k_q is affected by the equilibrium constant for forming encounter complexes, the rate of electron transfer, and the fraction of ion pairs that decays. Within a series of closely related molecules, it is possible that the first and last terms are more or less constant, allowing a correlation of the type seen by Evans[13] (Figure 1). Changing the solvent from isooctane to acetonitrile probably decreases the first term more than it increases k_{23} since k_q is distinctly lower in acetonitrile. This trend contrasts with previously reported effects.[26,32-35] It is also likely that the intrinsic reorganization energy differs for cross-electron transfer within each electron donor–acceptor pair,[34] causing quenchers of different structural types to fall on different lines in Figure 1.

Despite the absence of a simple structure–reactivity relationship in Table I, the electron-donating and -accepting properties of the quencher are clearly important. As seen in Table II, compounds that are more easily reduced are better quenchers of DBO fluorescence while those that are more easily oxidized are better quenchers of singlet **1**. In other words, charge transfer in DBO's can be either to or from the quencher. The electron-withdrawing chlorine atoms of **1** allow *p*-dimethoxybenzene to quench S_1 of **1** over 500 times faster than in the case of DBO. Because the oxidation of azoalkanes is electrochemically irreversible and their reduction has hardly been studied, insufficient information is available to calculate the free energy of electron transfer by the Weller equation. The trend in Table II is nevertheless interesting in light of recent work on the chemistry of azoalkane radical cations.[4-8]

We have proposed that the reaction of 1-cyclopropyl-DBO with CCl_4 proceeds via the radical cation.[4] Unfortunately, DBO itself did not react cleanly with CCl_4, probably because its radical cation does not lose nitrogen very rapidly.[8] Reasoning that a radical stabilizing group at the bridgehead should facilitate deazatation, we selected compound **10** as a potential second case of photochemical electron transfer fragmentation of an azoalkane. However the singlet lifetime of **10** is so short (2.5 ns)[11] that CCl_4 would not be a fast enough quencher to intercept S_1 efficiently, assuming that k_q has the same value (1.9×10^7 M^{-1} s^{-1}) found for 1-cyclopropyl-DBO.[4] We therefore irradiated **10** in $BrCCl_3$, a very much faster quencher than CCl_4 (cf. Table I). Although the product mixture was complex and the isolated yield was low, the brominated product **12** was obtained in greater amount than the chlorinated one **11**. A possible mechanism is shown in Scheme II. The azoalkane radical cation and the bromotrichloromethane radical anion are both unstable, but it is not clear how these species fragment. Although either pathway a or pathway b will lead to the halogenated products, it may be preferable to invoke step a for the formation of biphenyl, though the mechanism of the last oxidation (**16** → **13**) is unknown.

Scheme II



Since DBO's are appealing precursors to hydrocarbon radical cations (e.g., **14** ↔ **15**), we attempted to detect such species by laser flash photolysis. However, 337-nm irradiation of DBO in CCl_4 revealed no transients between 80 and 610 nm with a lifetime beyond 1 μs. Flash photolysis of **10** in cyclohexane at 266 nm showed a sharp transient absorption at 285 nm with a lifetime of 230 ns. By analogy with other benzylic biradicals,[36,37] this transient is very likely due to 1-phenyl-1,4-cyclohexanediyl. A flash photolysis study of **10** in $BrCCl_3$ is under way.

In summary, we find that a wide variety of compounds quench the fluoresence of DBO ($k_q = 10^5$–10^{10}) but that only in a few cases does any photochemical reaction take place. Excited singlet DBO is photoreduced by such good hydrogen donors as the cyclohexadienes, and the observed quenching rate constant k_q is affected by this reaction. A mechanism involving an encounter complex and an ion pair explains these results, the deuterium isotope effect on k_q, and to some degree, the dependence of k_q on the electron donor–acceptor properties of the quencher. A second case of photochemical electron transfer fragmentation has been found with 1-phenyl-DBO and $BrCCl_3$.

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Experimental Section

General Methods. NMR spectra were obtained in $CDCl_3$ on a JEOL FX-90Q and on an IBM AF300 FT NMR instrument. UV spectra were recorded on a Cary 17 spectrophotometer, emission spectra on a Perkin-Elmer MPF-2A fluorimeter, and low-resolution mass spectra on a Finnigan 3300 GC/MS system.

The acetonitrile and benzene used in photochemical studies were gold label, spectrophotometric grade (Aldrich Chemical Co.), and the isooctane was purified by two distillations. The sensitizers were purified by recrystallization or zone refining, and the quenchers were recrystallized or distilled before use.

Fluorescence Quenching. The quenching rate constants were determined from intensity measurements of solutions of DBO and its derivatives in the presence of quenchers under nitrogen. Fluorescence lifetimes were also used to calculate k_q. The values of τ_f were determined with a Lambda Physik EMG-101 laser at 337 nm to excite sealed, degassed solutions of DBO and its derivatives in the presence of quenchers. After the emitted light passed through a Bausch & Lomb grating monochromator, it was detected with a 1P28 photomultiplier. The electrical signal was displayed on a Hewlett-Packard 1741A oscilloscope and photographs of the traces were digitized into a PDP-11/70 computer. The lifetimes were calculated by a least-squares routine using about 60 data points.

Nitrogen Quantum Yields. Nitrogen quantum yields were determined on a photochemical merry-go-round by using a Hanovia 450-W medium-pressure mercury arc lamp with a 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate solution filter to isolate 366-nm light. A homemade reactor consisting of three GE low-pressure mercury lamps without a filter was used for 254-nm light. Solutions were degassed at least three times and sealed in Pyrex or quartz tubes, N_2 evolution being measured with a Toepler pump and gas buret. The initial absorbance was arranged to be about 2.0 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 ($\Phi_r = 1.0$).

Analysis of 3. A 2.6-mL solution of 0.0066 M DBO and 0.0013 M bibenzyl (internal standard) in 1,3-cyclohexadiene in a Pyrex tube was degassed and irradiated until the azo absorption had disappeared. After determination of the nitrogen yield with a Toepler pump and gas buret, the solution was thawed under a nitrogen atmosphere, and 50 μL of triethylamine and 50 μL of ethyl chloroformate were added. The solution was poured into 5 mL of H_2O, and the organic layer was analyzed by GC (OV-17, over temperature 190 °C). Authentic **3** was prepared according to the literature.[14]

1,3-Cyclohexadiene Dimers. Solutions of 10 mg of DBO and 265 mg (1.1 M) of 1,3-cyclohexadiene in 3 mL of isooctane or acetonitrile in Pyrex tubes were degassed and irradiated for 290 min with a Hanovia 450-W mercury arc lamp. After irradiations, it was found by UV that over 95% of the DBO had decomposed. In reference experiments, a solution of 0.5 mg of 1,4-dicyanonaphthalene and 265 mg of 1,3-cyclohexadiene in 3 mL of acetonitrile (1.1×10^{-3} and 1.1 M, respectively) and a separate solution of a trace amount of benzophenone in 3 mL of 1,3-cyclohexadiene were irradiated for 5 min with a Hanovia mercury arc lamp. Production of dimers was monitored by GC/MS (OV-17 column), and cyclohexadiene dimer product distributions were determined by GC (SF-96 capillary column) analysis.

To verify the structure of the dimers, **4** and **5** were isolated by preparative GC (15% Apiezon L, 158 °C) of an irradiated solution of 1,3-CHD and 9,10-dicyanoanthracene. The ^{1}H NMR spectra were compared with those reported by Valentine et al.[15] Dimers **6** and **7** were isolated similarly from the benzophenone sensitized irradiation of 1,3-CHD. Because retention times and ^{13}C NMR spectra have not been given previously, these data are shown in Table VI.

Irradiation of DBO in CCl_4. A solution of 2.2 g of DBO in 200 mL of CCl_4 was irradiated at 366 nm for 18 h with an Oriel 500-W mercury arc lamp with filters to isolate 366-nm light. After concentrating the reaction solution, the residue was washed with water and extracted with ether. Removal of the ether afforded a black oil, which was filtered through an alumina column, eluting with ether. The eluted solution was dried over $MgSO_4$, filtered, and concentrated to yield 500 mg of pale yellow oil. GC analysis (OV-17, oven 205 °C) of this oil revealed only two dominant products (retention time 30.0 and 39.0 min, area ratio 5.4:1), and the larger peak was isolated by preparative GC: ^{1}H NMR δ 1.6–2.8 (m, 6 H), 4.0–4.5 (m, 2 H); MS, *m/e* (relative abundance) 75 (13), 77 (15), 78 (8), 79 (100), 80 (8), 88 (7.5), 114 (13), 115 (13), 149 (5), 150 (14), 151 (6), 152 (8). The compound appeared to have structure **8** or **9**.

Irradiation of 1-Phenyl-DBO in Bromotrichloromethane. A solution of 100 mg of **10** in 10 mL of freshly distilled $CBrCl_3$ was irradiated at 366 nm for 5 h under a nitrogen purge. HPLC analysis of the photolysate (ODS column) revealed at least 12 products. The three largest peaks were separated by preparative HPLC and were identified as biphenyl, 4-chloro-1-phenylcyclohexene, and 4-bromo-1-phenylcyclohexene by comparison of HPLC retention times, ^{1}H NMR spectra, and mass spectra with those of authentic materials.

4-Bromocyclohexanol. A mixture of 28.8 g of 1,4-cyclohexanediol and 100 g of 48% hydrobromic acid was vigorously mixed in a stoppered flask until the solution became homogeneous, and then the solution was heated at 70 °C for 48 h. The reaction solution was extracted with three 100-mL portions of $CHCl_3$, and the combined organic layers were dried over K_2CO_3 and rotary evaporated. The crude, brown oil was distilled, giving 13.8 g (31%) of clear oil: bp 68–79 °C (0.1 mm); NMR δ 1.2–2.7 (m, 9 H), 3.4–4.7 (m, 2 H).

4-Bromocyclohexanone. To a suspension of 21.8 g of PCC[38] in 120 mL of dry CH_2Cl_2 was added 13.8 g of 4-bromocyclohexanol in 30 mL of dry CH_2Cl_2. The reaction mixture turned black, and a deposit formed on the vessel walls during the course of 2 h. The solution was filtered through a Celite pad, and the residue was washed with a few portions of ether. The combined solution was dried and evaporated. Distillation of the dark brown oil led to 8.69 g (63%) of pale yellow oil: bp 100–110 °C (18 mm); ^{1}H NMR δ 1.20–3.0 (m, 8 H), 4.1–4.8 (m, 1 H).

4-Bromo-1-phenyl-1-cyclohexanol. To a 200-mL three-necked flask equipped with a dropping funnel, thermometer, magnetic stirrer, and N_2 inlet was added 40 mL of dry THF and 18 mL of 1.37 M PhLi in ether/benzene. The solution was cooled to −78 °C, and a solution of 4.35 g of 4-bromocyclohexanone in 30 mL of dry THF was added dropwise over 1 h, maintaining the temperature between −70 and −75 °C. The temperature was raised to 20 °C, the mixture was stirred for 1 h, and then the solution was poured into 200 mL of H_2O and extracted twice with 100-mL portions of ether. The combined organic solution was dried over K_2CO_3 and rotary evaporated. Distillation of the crude product afforded 1.37 g (22%) of pale yellow oil: bp 136–150 °C (0.1 mm); ^{1}H NMR δ 1.35–2.80 (m, 9 H), 3.90–4.30 (m, 1 H), 7.10–7.70 (m, 5 H).

4-Bromo-1-phenyl-1-cyclohexene. A 1.37-g portion of 4-bromo-1-phenyl-1-cyclohexanol and 180 mg of *p*-toluenesulfonic acid were dissolved in 80 mL of benzene, and the solution was refluxed with a Dean Stark trap for 2 h. The reaction solution was washed with aqueous sodium bicarbonate and water, and then it was dried over $MgSO_4$ and concentrated. Distillation of the residue afforded 751 mg (56%) of clear oil: bp 99–104 °C (0.1 mm); ^{1}H NMR δ 2.00–3.10 (m, 6 H), 4.28–4.64 (m, 1 H) 5.84–6.10 (m, 1 H), 7.10–7.60 (m, 5 H).

Perdeuteriocyclohexadienes. To a solution of 0.32 g of anhydrous potassium *tert*-butoxide in 10 g of DMSO-d_6 was added 2 g of 1,4-cyclohexadiene in 20 mL of dry pentane, and the mixture was stirred for 140 min under a N_2 atmosphere. The DMSO layer was separated from the reaction solution. To the pentane layer was added a solution of 0.32 g of anhydrous potassium *tert*-butoxide in 10 g of DMSO-d_6, and the fresh mixture was stirred for 130 min under N_2. The pentane layer was separated, washed with H_2O, and dried over $MgSO_4$. Removal of the pentane by distillation yielded 1.47 g of clear oil. Deuteriated 1,3- (388 mg) and 1,4- (147 mg) cyclohexadiene were isolated by preparative GC (column; Apiezon L, oven 140 °C). The deuterium content of these products was found to be 94% and 95%, respectively, by NMR (external standard $CHCl_3$).

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Registry No. 1, 3993-62-2; 2, 280-49-9; 3, 3310-59-6; 4, 703-35-5; 5, 703-36-6; 6, 670-79-1; 7, 704-53-0; DBO, 3310-62-1; 1-phenyl-DBO, 87373-48-6; tetramethylpiperidine-1-oxyl, 2564-83-2; 4-bromo-1-phenylcyclohexene, 110174-56-6; 4-bromocyclohexanol, 89599-47-3; 4-bromo-1-phenyl-1-cyclohexanol, 110174-57-7; perdeuterated 1,3-cyclohexadiene, 17647-18-6; perdeuterated 1,4-cyclohexadiene, 2102-12-7; deuterium, 7782-39-0; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1; cyclopentadiene, 542-92-7; piperylene, 504-60-9; cyclopentene, 142-29-0; cyclohexene, 110-83-8; *cis*-2-butene, 590-18-1; 1-hexene, 592-41-6; 1-octene, 111-66-0; styrene, 100-42-5; *trans*-stilbene, 103-30-0; 1,1-diphenylethylene, 530-48-3; quadricyclene, 278-06-8; benzene, 71-43-2; *p*-dimethoxybenzene, 150-78-7; chlorobenzene, 108-90-7; benzotrichloride, 98-07-7; benzonitrile, 100-47-0; *p*-dicyanobenzene, 623-26-7; dimethyl phthalate, 131-11-3; 1,1-dimethylhydrazine, 57-14-7; 1,2-dimethylhydrazine, 540-73-8; carbon tetrabromide, 558-13-4; bromotrichloromethane, 75-62-7; tetranitromethane, 509-14-8; benzoyl peroxide, 94-36-0; di-*tert*-butyl peroxide, 110-05-4; *m*-dimethoxybenzene, 151-10-0; tetracyanoethylene, 670-54-2; tetramethyl-*p*-phenylenediamine, 100-22-1; benzophenone, 119-61-9; 1,4-dicyanonaphthalene, 3029-30-9; carbon tetrachloride, 56-23-5; biphenyl, 92-52-4; 4-chloro-1-phenylcyclohexene, 15619-36-0; 4-bromocyclohexanone, 22460-52-2; 1,4-cyclohexanediol, 556-48-9.

Notes

A Short, Efficient Synthesis of (1*S*,3*S*,5*R*)- and (1*S*,3*R*,5*R*)-1,3-Dimethyl-2,9-dioxabicyclo[3.3.1]nonane

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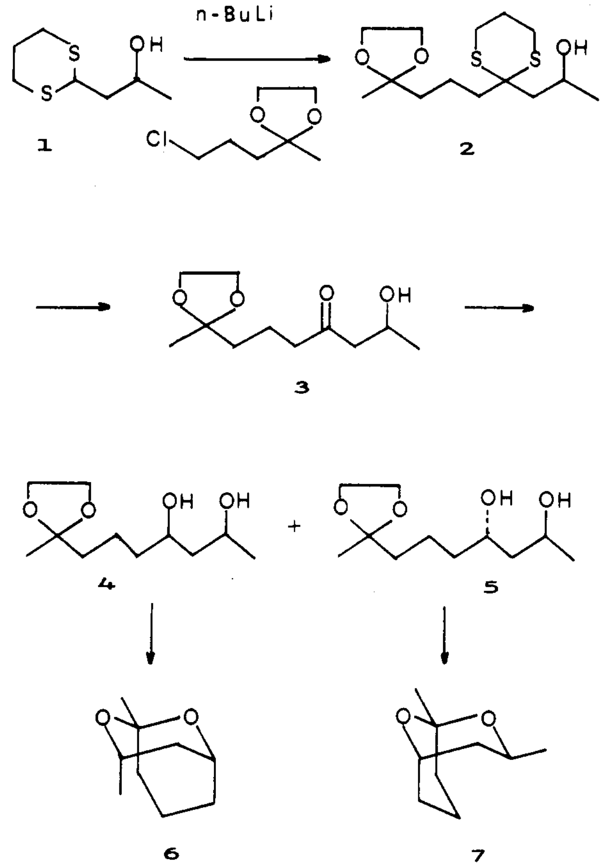
endo-1,3-Dimethyl-2,9-dioxabicyclo[3.3.1]nonane (**6**) is an interesting biologically active substance isolated from Norway spruce infested by *Trypodendron lineatum* Oliv.[1] The relative stereochemistry of the natural product was established by comparison of the NMR data of racemic synthetic *endo*-**6** and *exo*-**7** with that of the natural product.[2] The absolute stereochemistry is unknown, although all of the enantiomers were synthesized from glucose.[3]

In this paper we provide details of our syntheses of (1*S*,3*S*,5*R*)-**6** and (1*S*,3*R*,5*R*)-**7**, demonstrating the usefulness of (*R*)-1-(1,3-dithian-2-yl)-2-hydroxypropane [(*R*)-**1**, (*R*)-DHP] and (*S*)-1-(1,3-dithian-2-yl)-2-hydroxypropane [(*S*)-**1** (*S*)-DHP] as chiral building blocks in the synthesis of enantiomerically pure compounds (Scheme I). (*S*)-DHP[4] and (*R*)-DHP[5] are both available in high enantiomeric purity by microbial reduction of dithianylacetone. For this reason, we chose to synthesize the *endo*-(1*S*,3*S*,5*R*)-**6** from (*S*)-DHP and the *exo*-(1*S*,3*R*,5*R*)-**7** from (*R*)-DHP. The reaction of the dilithium salt of **1** with the commercially available 2-(3-chloropropyl)-2-methyl-1,3-dioxolane gave **2** in high yield. The conversion of **2** into the hydroxy ketone **3** requires very mild conditions to avoid the hydrolysis of the 1,3-dioxolanyl group. The right conditions were achieved by using a 4 M water solution of mercury perchlorate and controlling the pH with solid calcium carbonate. This hydrolytic procedure has the advantage of the methods using mercury oxide or lead dioxide with boron trifluoride etherate (they are very fast) and of the method using mercury dichloride and calcium carbonate (it is very mild), and furthermore it needs only a slight excess of the mercury salt. The hydroxy ketone **3** obtained by this method is sufficiently pure to be used in the subsequent step. The reduction of the β-hydroxy ketone **3** with zinc borohydride provides the *syn*-diol **4** with good selectivity. The anti isomer **5** can be obtained only with a poor selectivity (2:1 = anti:syn) by reducing the hydroxy ketone **3** with sodium triacetoxyborohydride in acetic acid[6]

Scheme I



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