

with 70/30 acetone/water at 1.2 mL/min. Two major and at least four minor compounds were present in this fraction. The first major compound ($R_f = 13.9$ min) had a visible spectrum reminiscent of a tetrahydroporphyrin [594 nm (71), 554 (26), 486 (14) 472 (16), 454 (15), 410 (78), 384 (100), 80/20 acetone/water], but the HPLC retention time was much less than would be expected for **2b**. Thus, it might be a minor isomeric nickel(II) isobacteriochlorin. The second major product ($R_f = 17.9$ min) appeared to be a nickel(II) hexahydrophorphyrin by its visible spectrum [586 nm (37), 556 (29), 538 (32), 462 (18), 430 (13), 402 (84), 385 (72), 353 (100), 80/20 acetone/water] and was reinjected to provide pure material for NMR study. However, the NMR spectrum was not clean, and further attempts to characterize the δ -*meso*-methylhexahydrophorphyrins were abandoned. A previous Raney Ni reduction of **1c** in methanol at 70 °C had also yielded as small amount of a similar compound: UV λ_{\max} (CH₂Cl₂) 582 nm (32), 546 (27), 460 (13), 402 (92), 387 (73), 371 (61), 356 (100); MS, m/e (%) 625 (73, M⁺, ⁵⁸Ni).

Analytical Data. **3c**: UV λ_{\max} (CH₂Cl₂, rel absorbance) 600 nm (38.2), (10), 520 (7.3), 402 (100); MS, m/e (%) 611 (20%), 609 (34), 608 (39), 607 (47, M⁺, ⁵⁸Ni), 606 (47), 507 (11), 506 (16), 504 (36), 492 (16), 491 (19), 489 (37); NMR (360 MHz, CDCl₃ see Table IV.

3a: UV λ_{\max} (CH₂Cl₂, rel absorbance) 644 nm (20.3), 588 (3.3), 502 (9.5), 400 (100); MS, m/e (%) 551 (100%, bp, M⁺), 536 (19, M⁺ - CH₃), 463 (12, M⁺ - CH₂CH₂CO₂Me); NMR (360 MHz, CDCl₃) see Table IV.

2b: obtained as a solid from acetone/water, mp, 142-144 °C; UV λ_{\max} (CH₂Cl₂) 598 nm (ϵ 3.58 × 10⁴), 554 (1.45 × 10⁴), 478 (1.09 × 10⁴), 414 (4.10 × 10⁴), 393 (5.90 × 10⁴); MS m/e (%) 625 (32%), 624 (28, M⁺, ⁶⁰Ni), 623 (85), 622 (37, M⁺, ⁵⁸Ni), 621 (22), 520 (14), 508 (11), 507 (11), 477 (12), 465 (12), 464 (18), 463 (23), 462 (13); NMR (360 MHz, CDCl₃) see Table II. Anal. Calcd for C₃₅H₄₀N₄NiO₃: C, 67.43; H, 6.46; N, 8.99. Found: C, 67.09; H, 6.43; N, 8.83.

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Registry No. **1c**, 96806-62-1; **2b** (tcc), 96866-31-8; **3a**, 96896-95-6; **3c**, 96866-32-9; **4**, 96866-33-0; **5**, 96806-63-2; **9b**, 96893-69-5; **10a**, 13566-43-3; **10b**, 47823-49-4; **10c**, 96866-35-2; **11a**, 96866-34-1; **12**, 96896-96-7.

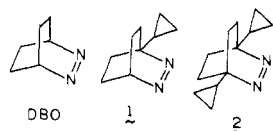
“Spring-Loaded” Biradicals. The Radical and Electron-Transfer Photochemistry of Bridgehead Cyclopropyl-Substituted 2,3-Diazabicyclo[2.2.2]oct-2-enes (DBO's)

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Abstract: Bridgehead cyclopropyl-substituted 2,3-diazabicyclo[2.2.2]oct-2-enes **1** and **2** have been synthesized from 1-cyclopropyl-1,3-cyclohexadiene and 1,4-dicyclopropyl-1,3-cyclohexadiene. Irradiation of these azoalkanes leads to 1,4-biradicals which undergo single- and double-cyclopropylcarbinyl rearrangement. The lifetime of the resulting 1,7- and 1,10-biradicals has been determined by using a combination of “free radical clock” and trapping techniques. Irradiation of **1** in CCl₄ provides the first case of photochemically induced electron-transfer fragmentation of an azoalkane and the first bimolecular reaction of an azoalkane triplet state. Even the triplet state of the unsubstituted 2,3-diazabicyclo[2.2.2]oct-2-ene can be intercepted by a good hydrogen donor such as 1,4-cyclohexadiene.

When the azo group is part of a bicyclo[2.2.2] skeleton as in 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO), loss of nitrogen is difficult both thermally and photochemically.¹⁻⁵ Photolysis of such



“reluctant” azoalkanes can be accelerated by employing elevated temperatures⁶⁻⁸ and short-wavelength irradiation⁹ or by modifying the structure to make the compounds more labile thermally.^{8,10}

(1) Turro, N. J.; Liu, K. C.; Cherry, W.; Liu, J. M.; Jacobson, B. *Tetrahedron Lett.* **1978**, 555.

(2) Berson, J. A.; Davis, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 3658.

(3) Snyder, J. P. *Diss. Abstr.* **1966**, *26*, 5728.

(4) Allred, E. L.; Beck, B. R. *Tetrahedron Lett.* **1974**, 437.

(5) Turro, N. J.; Renner, C. A.; Waddell, W. H.; Katz, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 4320.

(6) Engel, P. S.; Nalepa, C. J.; Leckonby, R. A.; Chae, W. K. *J. Am. Chem. Soc.* **1979**, *101*, 6435.

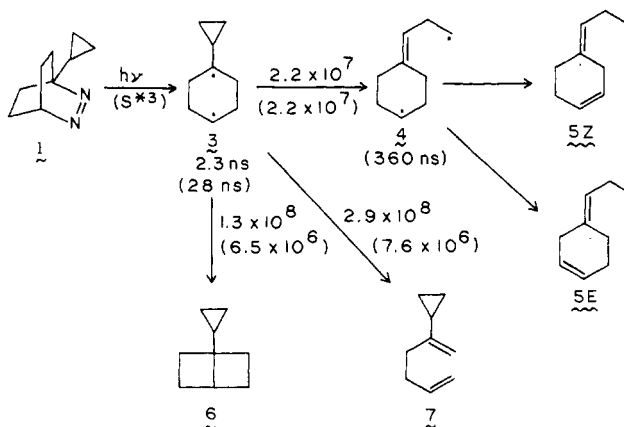
(7) Engel, P. S.; Nalepa, C. J. *Pure Appl. Chem.* **1980**, *52*, 2621.

(8) Engel, P. S.; Horsey, D. W.; Keys, D. E.; Nalepa, C. J.; Soltero, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 7108.

(9) Adam, W.; Mazenod, F. P. *J. Am. Chem. Soc.* **1980**, *102*, 7131.

(10) McElwee-White, L.; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 3466.

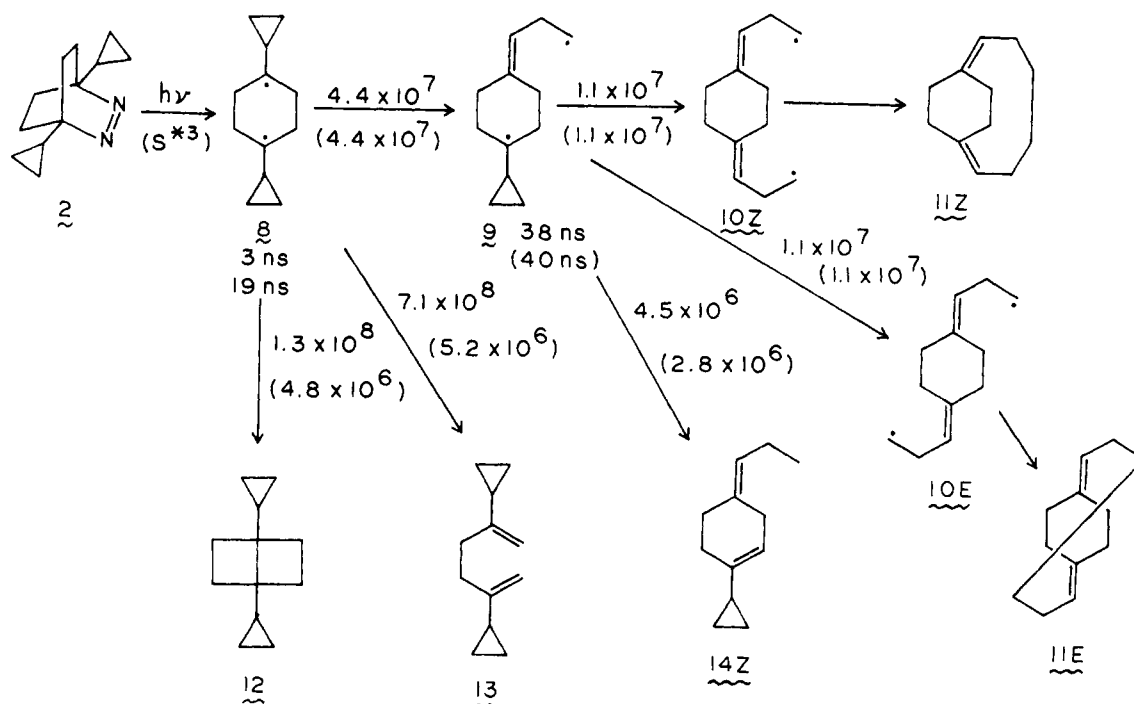
Scheme I. Biradical Rate Constants (s⁻¹) and Lifetimes for Direct and (Triplet-Sensitized) Photolysis of **1**



In the course of studying the photochemistry of bridgehead-substituted DBO's, we prepared compounds **1** and **2**, whose cyclopropyl groups not only enhance photoreactivity but also have a drastic effect on the product distribution. We already reported¹¹

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Scheme II. Biradical Rate Constants (s^{-1}) and Lifetimes for Direct and (Triplet-Sensitized) Photolysis of **2**

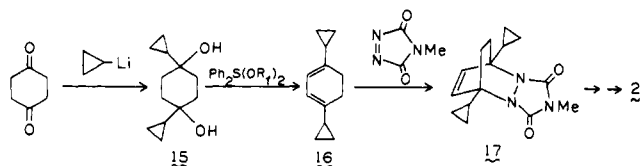


that **1** yields diene **5Z** via cyclopropylcarbinyl rearrangement of the initially formed 1,4-biradical **3** (cf. Scheme I). In effect, the driving force for the rearrangement of **3** to **4** "spring-loads" **3** and diverts it away from the usual bicyclo[2.2.2]hexane (**6**) and 1,5-hexadiene (**7**) products.^{12,13} Compound **2** then should produce the doubly spring-loaded 1,4-biradical **8** which could open to 1,10-biradicals **10E** and **10Z** (cf. Scheme II). Since the radical centers suddenly find themselves separated by a considerable distance, we anticipated that recombination would be disfavored.

The present report concerns the photochemical reactions of **1** and **2**, including successful trapping of their derived 1,7- and 1,10-biradicals. It has proven possible to calculate the lifetime and rate constants of several singlet and triplet biradicals by employing the "free radical clock" technique.¹⁴ The results with carbon tetrachloride, initially thought to represent biradical trapping,¹¹ are reinterpreted as the first electron-transfer photochemistry of azoalkanes and the first bimolecular reaction of an azoalkane triplet state. A reinvestigation of the parent DBO reveals that even its triplet state can be intercepted by the good hydrogen donor 1,4-cyclohexadiene (1,4-CHD).

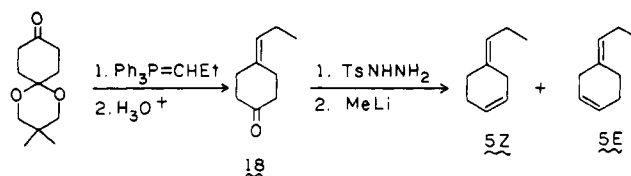
Synthesis of Compounds

DBO derivatives **1** and **2** were prepared from the appropriate 1,3-cyclohexadienes by the usual triazolinedione route. Since the detailed synthesis of **1** has already been published,¹⁵ we report here only the preparation of **2**. Cyclohexane-1,4-dione was converted with cyclopropyllithium to a presumed stereoisomeric mixture of diols **15**. Although one of them could be isolated

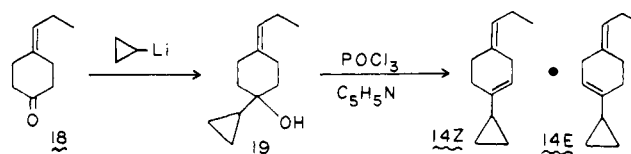


crystalline, we did not concern ourselves with its detailed structure but instead dehydrated it to diene **16**. Martin's reagent, bis-[2,2,2-trifluoro-1-phenyl-1-(trifluoromethyl)ethoxy]diphenyl sulfuran, proved superior to the other dehydrating reagents tried.¹⁶ Diels-Alder reaction of **16** with *N*-methyltriazolinedione^{15,17} afforded the adduct **17** which was converted by hydrogenation and hydrolysis to **2**. Our ability to produce **2** in quantity was limited by the low overall yield of this sequence (9%) and by the scarcity of the sulfuran.

Besides the azoalkanes, it was necessary to synthesize a number of authentic compounds for comparison with those isolated from the photolyses of **1** and **2**. The route to **5** is shown below. After



separation by preparative GC, the isomers were clearly distinguished by nuclear Overhauser effects (cf. Table X). The preparation of **14** employed 4-propylidenecyclohexanone (**18**), an intermediate already made in the above sequence. Although these



diene isomers were readily separable only by analytical GC, the two product peaks could be assigned structures by correlating the GC trace with the NMR spectrum of unequal mixtures of **14E** and **14Z**. Thus, the side-chain olefinic proton of **14E** and **14Z** fell at δ 5.20 and 5.13, respectively, while the analogous protons of **5E** and **5Z** occurred at δ 5.24 and 5.16. Similarly, the doubly

(12) Cyclopropylcarbinyl rearrangements of ketone-derived 1,4-biradicals are known; cf.: Wagner, P. J. In "Rearrangements in Ground and Excited States"; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 395.

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(16) Martin, J. C.; Arhart, R. J.; Franz, J. A.; Perozzi, E. F.; Kaplan, L. *J. Org. Synth.* **1977**, *57*, 22. Arhard, R. J.; Martin, J. C. *J. Am. Chem. Soc.* **1972**, *94*, 5003. We are most grateful to Prof. Martin and to Dr. Richard A. Hayes for generous samples of this reagent and its precursor.

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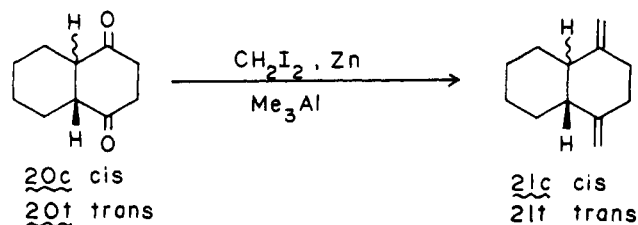
Table I. Product Yields^a from **1**

solvent	photolysis mode	temp, °C	6	7	5Z	5E
benzene	direct ^b	10	31	64	5	<1
		25 ^c	30	65	5	<1
		53	27	69	4	<1
benzene	sensitized ^d	9.5	45	39	9	7
		25	18	21	53	8
		54	10	11	68	12
hexadecane	thermolysis	230		98	2	
benzene ^e	direct ^b	-1	19	53	25	4
benzene	sensitized ^f	25	11	14	76	trace
1,4-cyclohexadiene	sensitized ^f	25	11	14	56 ^g	0
CCl ₄ ^h	sensitized ^f	25	6	51	42	0

^aGC peak area ratios normalized to total 100%. ^b366 nm. ^cUse of biphenyl as an internal GC standard showed that the observed products accounted for 99% of the consumed azoalkane. ^dBenzophenone or *p*-methoxyacetophenone at 313 nm. ^eRatio of GC peak areas on irradiation in frozen benzene. ^f2-Acetonaphthone at 313 nm. ^gThe remaining 20% of product was propylidenecyclohexane. ^hAll products listed were minor; see text.

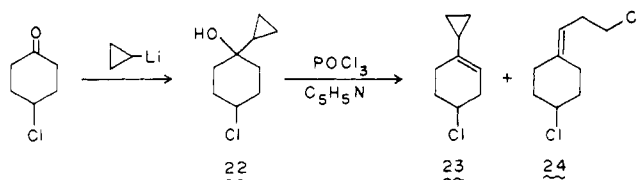
allylic carbon of **14E** and **14Z** exhibited a chemical shift of 35.20 and 33.05 ppm while those of **5E** and **5Z** were located at 35.39 and 32.91 ppm. Finally, the *Z* isomer of both sets of compounds showed the shorter GC retention time on a XE-60 column. An authentic sample of 1,4-dipropylidenecyclohexane was prepared via a Wittig reaction with **18**; however, we were unable to separate the *Z* and *E* isomers on a variety of GC columns.

cis- and *trans*-1,4-Dimethylenedecalin (**21c**, **21t**) were thermal rearrangement products whose structure was important to this study. To avoid epimerization during synthesis of the authentic



samples, the methylenation procedure of Nozaki and co-workers¹⁸ was applied to the known *cis*- and *trans*-decalin-1,4-dione.^{19,20}

An attempt to prepare the chloroolefin **23** produced mainly **24**. Thus, 4-chlorocyclohexanone²¹ was reacted with cyclopropyllithium to afford a diastereomeric mixture of chloro alcohols **22**. De-



hydration of either diastereomer with POCl₃ in pyridine gave **23** as the minor product. Presumably **24** arose via a cyclopropylcarbinyl cation rearrangement. As it turned out, both **23** and **24** were valuable authentic compounds.

Results

Products from 1. Direct- and triplet-sensitized irradiation of approximately 0.1 M solutions of **1** gave the products shown in Scheme I in the yields recorded in Table I. With the exception of the reaction in CCl₄ (see below), all these photolysis were clean and produced hydrocarbons in high yield. The structure proof

Table II. Starting Material and Products (mmol × 100) for Irradiation of **1** in CCl₄^a

time, min	1	23	24
0	4.88	<i>b</i>	<i>b</i>
15	4.56	<i>b</i>	<i>b</i>
45	3.55	0.16	0.25
70	3.20	0.13	0.34
100	2.56	0.21	0.43
130	2.12	0.17	0.59
190	1.69	0.27	0.98
250	1.20	0.36	1.11

^aInitial solution contained 0.0488 mmol of **1**, 0.0812 mmol of benzophenone, and 0.107 mmol of octadecane (internal standard) in 0.8 mL of CCl₄. ^bUndetectable.

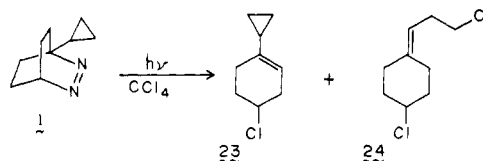
Table III. Starting Material and Products (mmol × 100) for Irradiation of **1** + **23** + **24** in CCl₄

time, min	1	23	24
0	4.88	9.52	0.59
15	4.80	9.34	0.43
45	3.83	8.37	0.79
100	3.14	8.33	0.94
130	2.77	8.49	1.16
190	2.16	8.25	1.31
250	1.81	8.57	1.53

^aInitial solution was identical with that of Table II except that 0.0952 mmol of a 16:1 mixture of **23** and **24** was added.

of **5Z** and its configurational isomer **5E** rests on authentic synthesis and the NOE measurements described in the Experimental Section. The structures of **6** and **7** are based on ¹H NMR and mass spectra. Thermolysis at 206 °C for 2.5 h of neat **6** isolated from irradiated **1** gave only **7**, in accord with the usual behavior of bicyclo[2.2.2]hexanes.²² Thermolysis of **1**, on the other hand, yielded 2% **5Z**, along with the expected **7**. Unlike the results reported²³ for some DBO derivatives, we found no increase in the bicyclohexane yield on irradiation in frozen benzene (cf. Table I, fourth entry). Triplet-sensitized irradiation in 1,4-cyclohexadiene solvent diverted 20% of the product from **5Z** to propylidenecyclohexane, suggesting that biradical **4** had been trapped.

In CCl₄, both direct and sensitized photolysis produced an unknown, water-soluble, reddish solid. Its yield under direct irradiation was 33% by weight, based on starting **1**. The incomplete formation of gaseous nitrogen in the CCl₄ irradiations (see below) indicated that this reddish solid contained nitrogen while its ¹³C NMR in D₂O showed 14 peaks ranging in chemical shift from 0 to 54 ppm. The hydrocarbons listed in Table I were reduced to very minor GC peaks in CCl₄, the main products now being 1-cyclopropyl-4-chlorocyclohexene (**23**) and 4-chloro-(3-chloropropylidene)cyclohexane (**24**). A number of other small



GC peaks were observed, but only hexachloroethane was identified by retention time and mass spectroscopy. It was found that the ratio of **23** to **24** changed from 5.7:1 on direct photolysis to 0.31:1 on 2-acetonaphthone-sensitized irradiation. In view of the facile formation of **24** during the authentic synthesis of **23**, we entertained the possibility that **24** was a secondary photolysis product. The evolution of these products with time showed no induction period for **24** (cf. Table II); moreover, spiking the initial solution of **1** plus benzophenone in CCl₄ with **23** led to only a small decrease in the amount of **23** after 4 h of irradiation. The rate at which **24** formed was the same as in the sample lacking **23**

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Table IV. Product Yields^a (%) from **2**

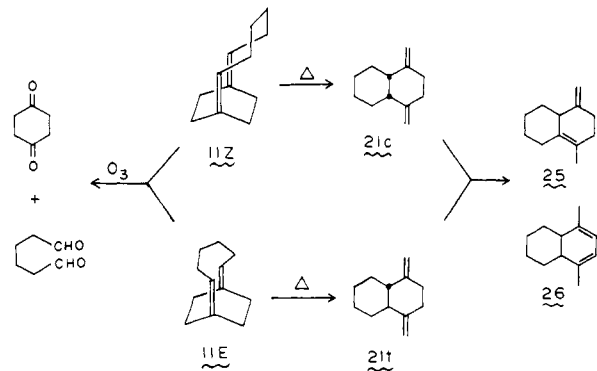
solvent	photolysis mode	temp, °C	11 ^b	12	13	14
benzene	direct ^c	25	4	15	81	1
benzene	sensitized ^d	25	72	9	10	9 ^e
hexadecane	thermolysis	233			99.7	0.3

^aGC peak area ratios normalized to total 100%. ^bTotal of **11Z** and **11E**, which are present in equal amounts. ^c366 nm. ^dBenzophenone or *p*-methoxyacetophenone at 313 nm. The actual total product yield was shown to be 98% in a 2-acetonaphthone-sensitized irradiation by using the sensitizer as an internal GC standard. ^e2.7:1 mixture of **14Z** and **14E**.

initially (cf. Table III). It is concluded that both **23** and **24** are primary photolysis products.

Products from 2. Irradiation of **2** led to the hydrocarbons shown in Scheme II in the yields recorded in Table IV. The structure of bicyclohexane **12** is supported by its rearrangement²² to **13** on heating at 178 °C for 2 h. Surprisingly, the ¹H NMR spectrum of **12** revealed the four cyclobutyl methylene groups as a singlet at 1.8 ppm. The ¹³C NMR of this compound exhibited three peaks, consistent with its symmetrical structure and a long relaxation time for the quaternary carbons. Both **14Z** and **14E** were present in the sensitized photolysate in a 2.7:1 ratio. The NMR spectra of **13** and **14** were consistent with the structures assigned; moreover, an authentic sample of **14** was available from the synthesis described above.

On account of their thermal lability, isolation of the isomers **11Z** and **11E** from the triplet-sensitized irradiation of **2** was no simple matter. A mixture of **11Z** and **11E** was collected by preparative GC despite a badly tailing peak contaminating these compounds. The ¹H and ¹³C NMR spectra suggested a highly symmetrical structure with impurities. Re-injection of the preparative sample revealed two additional peaks which were shown by coincidence of retention time to be the two dimethylenedecalins **21c** and **21t**. Thermolysis at 95 ± 10 °C of a preparative GC sample of **11** dissolved in C₆D₆ was monitored by ¹H NMR and GC. It was apparent that **11** was rearranging to **21** but that **21c** and **21t** were themselves thermally labile, rearranging to various isomers, two of which were tentatively identified as **25** and **26**.



Finally, the sensitized irradiation of **2** was monitored by NMR, revealing roughly equal amounts of **11Z** and **11E** but no **21**. The badly tailing GC peak mentioned above is therefore attributed to a Cope rearrangement occurring on the GC column.

To verify the structure of these important Bredt olefins,²⁴ a preparative GC sample of **11** was ozonolyzed. GC analysis of the products after triphenylphosphine workup showed the presence of 1,4-cyclohexanedione and adipaldehyde, the latter prepared by similar ozonolysis of cyclohexene. The NMR spectrum of the ozonolysis product from **11** confirmed the formation of these carbonyl compounds by the characteristic singlet of 1,4-cyclohexanedione and an aldehyde peak at 9.78 ppm. Although the lability of **11** prevented us from assigning the NMR or GC peaks to a particular isomer, the NMR spectrum of crude photolysate

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Table V. Absorption and Fluorescence Parameters for DBO Derivatives^a

compd	λ _{max} , nm	ε	τ _f , ns	Φ _f
DBO	380	304	436	0.39
1	383	186	402	0.20
2	384	144	632	0.21

^aIn benzene.

Table VI. Quantum Yields for Direct Photolysis of DBO Derivatives at 25 °C

compd	solvent	Φ _r (D) ^a	N ₂ yield, %	Φ _{azo} ^{init b}
DBO	C ₆ H ₆	0.018	90 ^c	0.018
DBO	1,4-CHD ^d	0	1 ^c	0.079
DBO	CH ₃ CN ^e	4.6 × 10 ⁻⁷		
DBO	CH ₃ CN ^f	8.5 × 10 ⁻³		
1	C ₆ H ₆	0.16	100 ^g	0.16 ^h
1	CH ₃ CN	0.17	94 ^c	0.20
1	CH ₃ CN ⁱ	0.021	87 ^c	0.026
1	CCl ₄	0.032	44 ^j	0.15
2	C ₆ H ₆	0.16	100 ^g	0.16 ^h
27	C ₆ H ₆	0.023	96 ^k	0.024
27	CCl ₄	0.028	41 ^l	0.14

^aNitrogen quantum yield for direct irradiation. ^bInitial quantum yield of azoalkane disappearance determined by UV spectroscopy. ^cFor complete disappearance of azoalkane. ^d1,4-Cyclohexadiene. At least 76% of the reacted DBO goes to the corresponding hydrazine. ^eWith 0.0738 M *p*-dicyanobenzene. ^fWith 0.141 M PhCCl₃. ^gFrom hydrocarbon yield. ^hCalculated from Φ_r and N₂ yield. ⁱWith 0.100 M *p*-dicyanobenzene. ^j32% conversion. ^kCalculated from Φ_r and Φ_{azo}^{init}. ^l24% conversion.

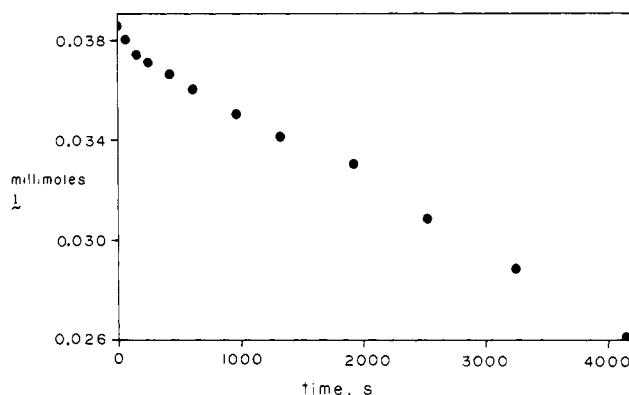


Figure 1. Irradiation of **1** in CCl₄ at 25 °C and 366 nm monitored by UV at 383 nm.

shows that **2** gives **11Z** and **11E** in approximately equal amounts. Attempts to synthesize **11** met with failure, though a more vigorous effort might succeed.^{24,25} Triplet-sensitized irradiation of **2** in 1,4-CHD solvent led to a new GC peak identified as 1,4-dipropylidene-cyclohexane, suggesting that the 1,10-biradical **10** had been trapped.

Mechanistic Studies

DBO derivatives exhibit intense, long-lived fluorescence,^{8,26,27} and as seen in Table V, compounds **1** and **2** are no exception. The cyclopropyl groups cause only a minor shift of the absorption maximum but diminish the extinction coefficient considerably. The quantum yield for loss of nitrogen (Φ_r, Table VI) is enhanced by nearly an order of magnitude on incorporation of either one or two bridgehead cyclopropyls. Although deazitation is essentially quantitative in benzene and acetonitrile, the nitrogen yield in CCl₄ is only about 40%. These N₂ yields were determined by first monitoring azoalkane disappearance by UV spectroscopy.

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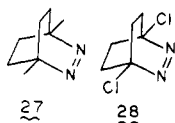
Table VII. Quantum Yields for Triplet-Sensitized Photolysis of DBO Derivatives at 25 °C

compd	solvent	$\Phi_r(S)^a$	N ₂ yield, %	conversion, % ^b	$\Phi_{-azo}^{init\ c}$
DBO ^d	C ₆ H ₆	0.014	100	100	0.016
DBO ^d	1,4-CHD ^e	0.0066	58	100	0.016
1 ^f	C ₆ H ₆	0.12			
1 ^d	CCl ₄	0.087	78	23	0.10
2 ^f	C ₆ H ₆	0.14			
2 ^f	C ₆ H ₆	0.069			
2 ^d	CCl ₄	0.051	86	24	0.065

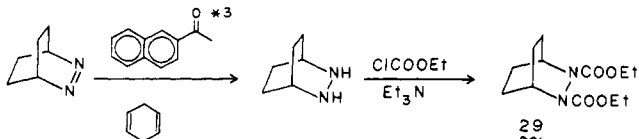
^aNitrogen quantum yield for sensitized irradiation. ^bPercent of azoalkane decomposed for Φ_r and N₂ yield determination. ^cInitial quantum yield of azoalkane disappearance by UV. ^d2-Acetonaphthone sensitizer. ^e1,4-Cyclohexadiene. At least 20% of the reacted DBO goes to the hydrazine. ^fBenzophenone sensitizer.

As seen in Figure 1, the initial rate of azoalkane disappearance in CCl₄ is greater than that at later times. This initial slope was converted to the Φ_{-azo}^{init} values in Table VI, using the measured light intensity. The irradiations were stopped when the red precipitate began to form, and the nitrogen was measured with a Töpler pump and gas buret. Dividing the amount of nitrogen produced by the amount of azoalkane reacted gave the N₂ yields. Because of the red precipitate, the overall quantum yields ($\Phi_r(D)$) in CCl₄ fell at higher conversions. It will be important for the later discussion to note that CCl₄ does not diminish Φ_{-azo}^{init} for **1**; in fact, this solvent enhances disappearance of **27**. Addition of *p*-dicyanobenzene, on the other hand, does quench the photoreaction of **1**.

Because DBO itself is far more easily obtained than **1** or **2**, several mechanistic studies were carried out on the parent compound. The good hydrogen donor 1,4-cyclohexadiene (1,4-CHD) completely suppresses nitrogen formation from DBO but enhances the quantum yield of azoalkane disappearance relative to its value in benzene. Although photoreduction of DBO was suspected long



ago,²⁷ this reaction has actually been proven only in the case of 1,4-dichloro-DBO (**28**).²⁸ We added ethyl chloroformate and triethylamine to a freshly irradiated solution of DBO in 1,4-CHD and obtained a 76% GC yield of 2,3-dicarboethoxy-2,3-diazabicyclo[2.2.2]octane (**29**). An authentic sample of this material



was available from the Diels-Alder reaction of ethylazodicarboxylate with 1,3-cyclohexadiene followed by catalytic hydrogenation. Surprisingly, the photoreduction of DBO could also be triplet-sensitized (cf. Table VII) though more than half of the azoalkane still lost nitrogen. Like the triplet-sensitized reaction of **1** with CCl₄, this observation shows that some azoalkane triplets survive long enough to be intercepted. Comparison of Tables VI and VII supports our earlier observation⁸ that those azoalkanes whose singlet state is photolabile are also subject to efficient triplet sensitization. The sensitized reactions of **1** and **27** in CCl₄ give a higher nitrogen yield and are cleaner than direct irradiation, but the red precipitate still forms at high conversions.

A number of compounds were found to quench DBO fluorescence. The data in Table VIII mostly for acetonitrile solvent add to those published years ago²⁹⁻³¹ for olefins in isoctane. Although

Table VIII. Quenching of DBO Fluorescence Lifetime in CH₃CN

quencher	concn, M	τ_f , ns	$10^7 k_q$, M ⁻¹ s ⁻¹
none	0	682	
1,3-cyclohexadiene	0.0315	356	4.3
1,3-cyclohexadiene	0.0840	192	4.4
1,3-cyclohexadiene ^a	0.0315	96	24
1,3-cyclohexadiene ^b			26
<i>p</i> -dimethoxybenzene	0.122	556	0.27
1,4-cyclohexadiene	0.0317	493	1.8
chlorobenzene	9.84	406	0.010
PhCCl ₃	0.0762	168	5.9
<i>p</i> -dicyanobenzene	0.00172	175	247
benzonitrile	0.0166	661	0.28
CBr ₄	6.92×10^{-4}	117	1000

^aIn isoctane, $\tau_f^0 = 335$ ns. ^bValue in isoctane from ref 30.

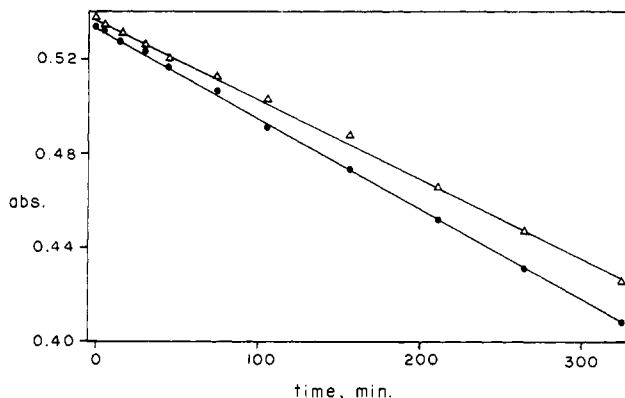


Figure 2. Irradiation of DBO (4.76×10^{-3} M) + 2-acetonaphthone (1.22×10^{-3} M) in acetonitrile at 25 °C and 313 nm. Loss of DBO was monitored by UV at 380 nm: (Δ) with added *p*-dicyanobenzene (0.101 M).

both electron donors and acceptors decrease the fluorescence lifetimes of DBO, CBr₄ is the most effective compound found to date. It is significant that CCl₄ quenches the fluorescence of **1**, giving a reasonable Stern-Volmer plot with $k_q = 1.9 \times 10^7$ M⁻¹ s⁻¹. To ascertain whether a good fluorescence quencher might affect the triplet-sensitized photolysis, a sample of DBO was irradiated in acetonitrile with and without added *p*-dicyanobenzene. It is apparent from Figure 2 that the disappearance rate of DBO sensitized by 2-acetonaphthone is not enhanced by *p*-dicyanobenzene.

Discussion

The product distributions in Tables I and IV can be rationalized on the basis of a spin correlation effect^{32,33} in the initially formed 1,4-biradicals **3** and **8**. Although the first intermediate from DBO's may be a diazenyl radical, we have no evidence that its lifetime is sufficient to influence the product distribution. The rates of all the reactions of **3** and **8** can be calculated from the product yields at 25 °C and the estimated rate¹¹ (2.2×10^7 s⁻¹) of the **3** → **4** rearrangement, giving the values summarized in Schemes I and II. The calculation is straightforward for **3** since the competing first-order reactions require that the rate constant be proportional to the product yield.³⁴ In the case of **8**, a statistical factor of 2 is applied to the cyclopropylcarbonyl rearrangement rate because either of the cyclopropyl rings can open. The equal yield of **11Z** and **11E** seen by NMR dictates that the total rearrangement rate of **9** be partitioned half to each isomer of **11**.

The reciprocal of the sum of the rate constants for disappearance of any biradical in Schemes I and II equals its lifetime. In accord with the notion that intersystem crossing is the rate-determining step for reactions of triplet biradicals,^{35,36} the triplet lifetime of

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(29) Evans, T. R. *J. Am. Chem. Soc.* **1971**, 93, 2081.

(30) Solomon, B. S.; Thomas, T. F.; Steel, C. *J. Am. Chem. Soc.* **1968**, 90, 2249.

(31) Solomon, B. S.; Steel, C.; Weller, A. *Chem. Commun.* **1969**, 927.

(32) Engel, P. S. *Chem. Rev.* **1980**, 80, 99.

(33) Schultz, P. G.; Dervan, P. B. *J. Am. Chem. Soc.* **1982**, 104, 6660.

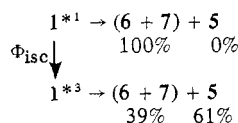
(34) The total of **5Z** and **5E** and the total of **14Z** and **14E** were used in the calculations.

the 1,4-biradicals is roughly an order of magnitude longer than that of the singlets. Acyclic 1,3-biradicals must be shorter-lived³⁷ than the values found here because even triplet 3-cyclopropyl-1-pyrazolines give no cyclopropylcarbinyl rearrangement products.³⁸

The product distribution for the triplet-sensitized reaction (Table I) depends upon temperature whereas that for direct irradiation is virtually independent of temperature. A possible reason for this difference is that cyclopropylcarbinyl rearrangement is favorable only when the π -like bonds of the cyclopropane ring can overlap with the cyclohexyl radical center, that is, in the bisected conformation.³⁹ If **1** exists mainly in some other conformation, as seems likely, a rotation about the cyclopropane to DBO bond will be needed between the time that **1** loses N_2 and the time that rearrangement occurs. Rotation of such a heavily substituted system would probably be slower than the normal closure and cleavage rates of singlet **3**⁴⁰ and yet would exhibit only a minimal temperature dependence. Thus, higher temperatures would have little influence on the product distribution, which is determined prior to cyclopropylcarbinyl rearrangement. This rationalization is in accord with the analytical solution of the Curtin-Hammett system.⁴¹

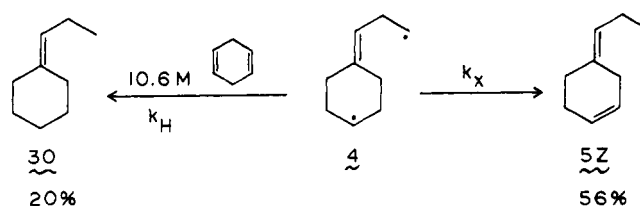
For the triplet-sensitized reaction, the cyclopropyl ring approaches rotational equilibrium and rearrangement competes with spin inversion. One can apply the Arrhenius equation to the relative rearrangement rate **3** \rightarrow **4** as reflected in the sensitized yield of **5**. The resulting activation energy of 7 ± 3 kcal mol⁻¹ is reasonable in light of the 5.9 kcal mol⁻¹ barrier for the cyclopropylcarbinyl radical itself.⁴² Since this calculation assumes a temperature-independent triplet biradical lifetime in the absence of cyclopropylcarbinyl rearrangement, we hasten to add that ketone-derived triplet 1,4-biradicals exhibit a lifetime of ~ 30 ns over a 140 °C range.³⁵

Intersystem crossing (ISC) in DBO's must not be very efficient;⁴³ otherwise, both direct and sensitized irradiation would give the same product distribution. One can calculate a maximum Φ_{isc} by the following method. Suppose the photochemistry of **1** could be described by the scheme below. The triplet-state (3)



product distribution of 39% (**6** + **7**) and 61% **5** is taken from the fifth line of Table I. Since **5** is most important in the triplet-sensitized reaction, let us attribute any **5** seen upon direct irradiation (actual yield 5%) to ISC of **1**. The ratio of (**6** + **7**) to **5** is then $[100(1 - \Phi_{isc}) + 39(\Phi_{isc})] : [0(1 - \Phi_{isc}) + 61(\Phi_{isc})] = 95:5$. Thus, Φ_{isc} of **1** would be 0.082 if the above scheme were applicable. The only other product study that requires a Φ_{isc} this low was on a highly functionalized DBO ($\Phi_{isc} < 0.094$).⁴⁴ If Φ_{isc} of **1** was actually zero, as we suspect, the formation of **5** under direct irradiation means that even singlet 1,4-biradicals can be diverted by cyclopropylcarbinyl rearrangement. The question remains of how triplet **3** proceeds to products. Most likely, this biradical undergoes rate-determining spin inversion followed by ring closure to **6** or opening to **7**. The singlet biradical formed by ISC cannot be the same one produced on direct irradiation of **1**, for direct and sensitized photolysis give **6** and **7** in different ratios (Table I). Perhaps singlet **3** "remembers" its origin;³⁵ that is, its geometry

Scheme III



may not be the same when formed from **1** as from triplet **3**. Alternately, triplet **3** might go directly to products, as suggested for cycloalkanones.^{45,47}

Dienes **5** and **14** appear to arise from intramolecular disproportionation of the 1,7-biradicals **4** and **9**. According to molecular models, formation of the *Z* isomer is geometrically more feasible than the long-distance hydrogen transfer needed to form the *E* isomer. Since the *E* diene is definitely present under triplet-sensitized irradiation, we considered alternate mechanisms by which it might arise: (a) secondary photosensitized isomerization of *Z* to *E*;⁴⁸ (b) bimolecular disproportionation of two 1,7-biradicals; and (c) a chain mechanism wherein a molecule of **4** abstracts hydrogen from carbon 4 of **1**. To test mechanism a, **1** was irradiated with benzophenone, and the products were monitored by GC over a period much greater than the usual irradiation time. The fact that **5E**/**5Z** barely increased in this control experiment argues against secondary photoisomerization. Since mechanism b can be ruled out on the basis of short biradical lifetimes while c has no precedent in azoalkane chemistry, we are presently inclined toward long-distance intramolecular disproportionation of **4** and **9**. The ring strain encountered in forming **5Z** should be roughly that of *trans*-cyclononene (14 kcal mol⁻¹), while the analogous figure for **5E** should be the strain of *trans*-cycloheptene (27 kcal mol⁻¹).²⁴ Despite the great exothermicity of intramolecular disproportionation (60 kcal mol⁻¹), the double bond of **4** and **9** would have to twist with unusual ease if **5E** is to form competitively with **5Z**. The proposed mechanism is consistent with the formation of **5E** when **1** is irradiated directly in frozen benzene. The matrix apparently increases the lifetime of singlet **4** so that it occasionally finds itself in a geometry distorted enough to give **5E**. The enhanced yield of **5Z** relative to **6** and **7** suggests that the lifetime of **3** is also increased in a matrix. Related cases of product alteration in a frozen matrix have been reported.²³

We were intrigued that even the most favorable hydrogen transfer in 1,7-biradicals **4** and **9** had to occur over the seemingly prohibitive distance of 3 Å. With the idea in mind that **4** might be long-lived and hence trapable by atom transfer, we irradiated **1** in neat 1,4-CHD and in CCl_4 . The 1,4-CHD result in Table I argues strongly that **4** was trapped since 20% of **5** was replaced by propylidencyclohexane (**30**). If we knew the trapping rate constant (k_H) (Scheme III), the rate of intramolecular disproportionation (k_x) would be calculable from the product ratio.^{48a} Unfortunately, nothing relevant was known about 1,4-CHD at the outset of this study, save that it is a good hydrogen atom donor⁴⁹ capable of intercepting biradicals.⁵⁰ It was therefore gratifying to note that the results from **2** allow us to solve the problem in reverse, thus providing a value for k_H . According to

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(46) Doubleday, C.; McIver, J. W.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 3768.

(47) deKanter, F. J. J.; Kaptein, R. *J. Am. Chem. Soc.* **1982**, *104*, 4759.

(48) Caldwell, R. A. *J. Am. Chem. Soc.* **1970**, *92*, 1439. (a) The calculation assumes that **30** is the only trapping product. Although no internal standard was added, the irradiated solution remained clear and no unexplained GC peaks appeared. Moreover, products **6** and **7** are unlikely to be affected by the solvent change. Since the decrease in **5Z** equals the increase in **30**, there is no room for another trapping product.

(49) 1,4-Cyclohexadiene donates hydrogen 60 times faster to *tert*-butoxyl radicals than does cumene or cyclopentane. Paul, H.; Small, R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520.

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(37) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688.

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(39) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: New York, 1981; p 407.

(40) Dervan, P. B.; Santilli, D. S. *J. Am. Chem. Soc.* **1980**, *102*, 3863.

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(43) Intersystem crossing is also negligible in 2,3-diazabicyclo[2.2.1]-hept-2-ene, according to CIDNP results in ref 37.

(44) Gousetis, C.; Sauer, J. *Tetrahedron Lett.* **1979**, 1295.

Scheme II, the products of **9** lead to an estimate of its k_x in a second use of the "biradical clock" technique.¹⁴ Thus, the product ratio **11**:**14** coupled with an estimated cyclopropylcarbinyl rearrangement rate constant of $2.2 \times 10^7 \text{ s}^{-1}$ yields the figure $k_x = 2.8 \times 10^6 \text{ s}^{-1}$ for triplet **9**. The k_x value should be approximately the same for **4** so that the relative yields of **5Z** and **30** provide the desired k_H as $9.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. This is a high value for hydrogen transfer between carbon radicals but is in good accord with a recent direct measurement of $k_H = 1.3 \times 10^5$ and $5.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for the reaction of 1,4-CHD with methyl and ethyl radicals, respectively.⁵¹ The reciprocal of k_x gives the lifetime of **4** in unreactive solvents as 0.36 μs . Despite this long lifetime, reclosure of **4** to **3** cannot compete with intramolecular disproportionation, for the former has a rate constant of only $1.7 \times 10^3 \text{ s}^{-1}$.⁵²

Biradical **9** is of similar structure to **4**, but its lifetime is shortened so much by the availability of a second cyclopropylcarbinyl rearrangement that **9** could not be trapped by neat 1,4-CHD in the triplet-sensitized photolysis of **2**. However, this hydrogen-donating solvent diverts the resulting 1,10-biradical **10** to a 0.77:1 ratio of 1,4-dipropylidene-cyclohexane to dienes **11**. Although our inability to separate the *Z* and *E* isomers of 1,4-dipropylidene-cyclohexane prevents lifetime determination of **10Z** and **10E** individually, application of Scheme III with $k_H = 10^5 \text{ M}^{-1} \text{ s}^{-1}$ gives $\tau = 730 \text{ ns}$ for one or both of the 1,10-biradicals.

At first glance, the results of irradiating **1** in CCl_4 also seem to indicate trapping of biradical **4**. Although a reduction in hydrocarbon yield and formation of **24** are just what one would expect from chlorine atom donation to **4**, experiments to be described below disprove this mechanism. We tried CCl_4 first as a biradical trap to avoid possible photoreduction of the azo linkage by hydrocarbons.²⁷ Indeed, photoreduction is so efficient for singlet **1** in 1,4-CHD solvent that none of the usual hydrocarbon products can be detected. Unlike direct irradiation, the sensitized photolysis did not actually require CCl_4 as a biradical trap because earlier work²⁷ showed that triplet DBO was unreactive toward isooctane. However, we now find that 1,4-CHD reacts with triplet DBO, though 58% deazotization still occurs (cf. Table VII). Photoreduction of triplet DBO is a significant observation, for no bimolecular reaction of a triplet azoalkane has been reported heretofore. In view of the higher quantum yield (Φ_r^S) for **1** than DBO, we propose that the majority of triplet **1** undergoes normal deazotization in neat 1,4-CHD and that trapping of **4** by hydrogen atom transfer is straightforward.

There soon arose two indications that CCl_4 was not simply trapping biradical **4**: CCl_4 is too poor an atom donor to intercept a biradical (**4**) of 0.36- μs lifetime and chloroalkene **23** is certainly not a trapping product of biradical **3**, whose lifetime is only 28 ns. Based on literature values,⁵³ we estimated the chlorine atom transfer rate constant at $1.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, leading to an astoundingly long triplet biradical (**4**) lifetime of 0.45 ms.¹¹ It has recently been found that CCl_4 is 1–2 orders of magnitude better a chlorine atom donor in solution than previously thought.⁵⁴ One can readily calculate the expected ratio of **24** to **5** if **4** is the precursor of both products. Competing first- and second-order reactions as in Scheme III with 10.5 M CCl_4 replacing 1,4-CHD leads to the equation $[(5.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1})(10.5 \text{ M})]/2.8 \times 10^6 \text{ s}^{-1} = 0.22$. Since the observed ratio of **24** to **5** was 6.32, there is too much chlorinated product to rationalize simply as biradical trapping. Instead, we postulate that triplet **1** reacts with CCl_4 , just as triplet DBO reacted with 1,4-CHD. These important reactions imply that the elusive azoalkane triplet state^{32,55} can have

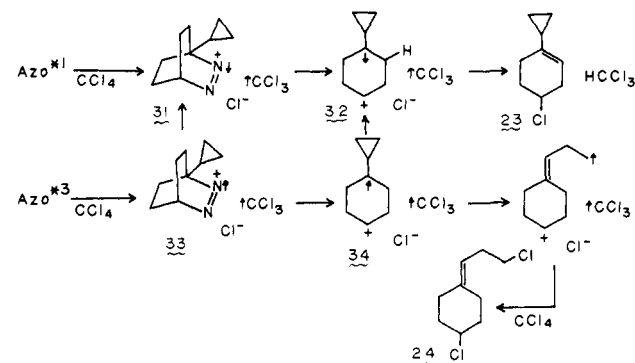
(51) Hawari, J. A.; Engel, P. S.; Griller, D. *Int. J. Chem. Kinet.*, in press.

(52) This conclusion assumes that the equilibrium constant for opening of **3** is the same as for the parent cyclopropylcarbinyl radical (1.3×10^4 at 25 $^\circ\text{C}$).⁴²

(53) Ingold, K. U. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p 84. Macken, K. V.; Sidebottom, H. W. *Int. J. Chem. Kinet.* **1979**, *11*, 511. Matheson, I.; Tedder, J.; Sidebottom, H. *Int. J. Chem. Kinet.* **1982**, *14*, 1033; **1983**, *15*, 905. Frith, P. G.; McLaughlin, K. A. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 87.

(54) Hawari, J. A.; Davis, S.; Engel, P. S.; Gilbert, B. C.; Griller, D. *J. Am. Chem. Soc.*, in press.

Scheme IV. Reaction of Singlet and Triplet **1** with CCl_4



a lifetime of at least a few nanoseconds.

In the case of direct irradiation, the combination of photophysics and photochemistry provided direct proof that singlet **1** reacts with CCl_4 to produce **23** and **24**. The rate constant for CCl_4 quenching the fluorescence of **1** was $1.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. This figure is considerably below the diffusion-controlled limit, but it is still fast enough to divert 99% of the long-lived azoalkane singlet states by interaction with CCl_4 . The calculation is shown below.

$$\frac{k_q[\text{CCl}_4]}{k_q[\text{CCl}_4] + \tau_f^{-1}} = \frac{(1.9 \times 10^7)(10.5)}{(1.9 \times 10^7)(10.5) + (402 \times 10^{-9})^{-1}} = 99\% \quad (1)$$

Although the majority of singlet excited **1** interacts with CCl_4 , it is still possible that the products seen in CCl_4 arise from the 1% which is not quenched. In that case, the maximum quantum yield for reaction would be 0.01; however, Table VI shows an initial Φ for azoalkane disappearance of 0.15. Although Φ_r is only 0.032, that value was obtained at 32% conversion, by which time the solution was a hazy yellow, obscuring the light. Singlet excited **1** clearly reacts with CCl_4 , and we suggest that the mechanism is the first electron-transfer photochemistry of an azoalkane.

As illustrated in Scheme IV, the excited singlet state of **1** is presumed to transfer an electron to CCl_4 , which immediately dissociates.^{56–58} The azoalkane radical cation **31** loses N_2 , producing singlet radical ion pair **32**. With no spin barrier to product formation, disproportionation and ion recombination of **32** leads to **23**, the observed major product of direct irradiation. A similar sequence starting from triplet azoalkane produces **34**, which is much more likely to undergo cyclopropylcarbinyl rearrangement on account of the spin inversion barrier to forming **23**. Following rearrangement, the opened radical cation undergoes ion recombination with Cl^- and chlorine abstraction from the solvent to give **24**.

Azoalkane radical cations have not been reported previously, though the anions are known^{59,60} and azobenzene radical cation has been seen by ESR.⁶¹ The mass spectra of many azoalkanes exhibit a molecular ion⁶² but electrochemical oxidation of all azo compounds tried, save azobenzene,⁶³ was irreversible.⁶⁴ While

(55) Durr, H.; Ruge, B. *Top. Curr. Chem.* **1976**, *66*, 53.

(56) Gaines, A. F.; Kay, J.; Page, F. M. *Trans. Faraday Soc.* **1966**, *62*, 874.

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(58) Hamill, W. H.; Guarino, J. P.; Ronayne, M. R.; Ward, J. A. *Disc. Faraday Soc.* **1963**, *36*, 169.

(59) Gerlock, J. G.; Janzen, E. G.; Ruff, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 2558.

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(63) Kuder, J. E.; Gibson, H. W.; Wychick, D. *J. Org. Chem.* **1975**, *40*, 875. Cressman, P. J.; Hartmann, G. C.; Kuder, J. E.; Saeva, F. D.; Wychick, D. *J. Chem. Phys.* **1974**, *61*, 2740. Wawzonek, S.; McIntyre, T. W. *J. Electrochem. Soc.* **1967**, *114*, 1025. Stradins, J. P.; Glezer, V. T. In "Encyclopedia of Electrochemistry of the Elements"; Bard, A. J., Ed.; Marcel Dekker: New York, 1979; Vol. 13, p 163.

this work was in progress, Prof. Henry Shine informed us that thianthrene radical cation oxidizes some azoalkanes to their unstable radical cation.⁶⁵ We postulate in Scheme IV that **31** loses nitrogen, but the rate of this reaction is uncertain and is likely to depend on azoalkane structure.

In view of the facile reaction of **1** with CCl₄, it seemed worthwhile to examine other electron acceptors. Such compounds as α,α,α-trichlorotoluene and *p*-dicyanobenzene (*p*-DCB) also proved to be quenchers of DBO fluorescence (Table VIII), but also they drastically decreased the nitrogen quantum yield, Φ_N (Table VI, entries 1, 3, and 4). In the case of *p*-DCB, for example, its singlet quenching rate constant for **1** should be similar to the 2.47 × 10⁹ M⁻¹ s⁻¹ found for DBO. Combining this value in an equation analogous to (1) with the known lifetime of **1** in acetonitrile (526 ns)⁸ and a *p*-DCB concentration of 0.10 M reveals that over 99% of singlet **1** interacts with *p*-DCB in the seventh entry of Table VI. Since this much *p*-DCB decreases Φ_N from 0.17 to 0.021, it is clear that the quenching complex gives little nitrogen. Moreover, the complex leads to little chemistry in which nitrogen is retained, since the initial quantum yield for disappearance of **1** is reduced from 0.20 to 0.026. We conclude that CCl₄ is much more efficient than other electron acceptors in its reaction with **1**.

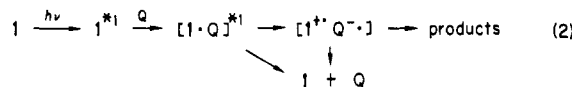
CCl₄ is a widely studied quencher of excited states of aromatic hydrocarbons,⁶⁶⁻⁷⁰ amines,^{71,72} and ketones.⁷³⁻⁷⁵ Irradiation of the mixtures generally leads to reactions⁷⁶⁻⁸⁰ that can be classified as photochemically induced electron-transfer fragmentations.^{81,82} Although amines, hydrocarbons, and di-*tert*-butyl nitroxide⁸³ are known to form ground-state charge-transfer (CT) complexes with CCl₄, we could detect no new bands in a careful study of DBO in CCl₄.⁸⁴ The same was true for α,α,α-trichlorotoluene and *p*-dicyanobenzene; moreover, the fluorescence spectrum of DBO was unchanged in shape by addition of any of these quenchers. The higher ionization potential⁸⁵ of azoalkanes than amines

Table IX. Identification of GC Columns

designation	column and size
A	20% XE-60, 0.125 in. × 20 ft
B	20 M Carbowax capillary
C	20% TCEP on Chromosorb-P, 0.25 in. × 20 ft
D	15% OV-17, 0.25 in. × 8 ft
E	30% Carbowax, 0.25 in. × 12 ft
F	SE-54 Capillary, 25-m fused silica (Hewlett-Packard)
G	15% XE-60, 0.25 in. × 15 ft
H	15% XF-1150, 0.25 in. × 10 ft
I	10% SE-30, 0.125 in. × 5 ft (Antek)

suggests that ground-state CT complexes are less likely for azoalkanes.

Electron acceptors (Q) are presumed to quench the fluorescence of **1** by forming an excited CT complex which usually decays to ground state (cf. eq 2). If electron transfer occurs within the



complex, the radical ion pair thus formed must undergo rapid reverse electron transfer; otherwise, photochemical reactions would be expected. The unique aspect of CCl₄ is the instability of its radical anion,⁵⁶⁻⁵⁸ causing dissociation to dominate over reverse electron transfer.⁸⁶ One might expect that the spin multiplicity of the radical ion pair would influence its fate.⁸² Thus, reverse electron transfer should be more important in the singlet (**31**) than in the triplet (**33**) radical ion pair (cf. Scheme IV). *p*-Dicyanobenzene failed to react even with triplet DBO (cf. Figure 2), suggesting that radical ion pairs were never formed or that spin inversion followed by back electron transfer was faster than dissociation of DBO⁺.

The quenching of DBO fluorescence is not confined to electron acceptors; for example, the quenching rate constants for dienes³¹ could be correlated nicely with diene ionization potential (IP).²⁹ We suspect that quenching is not simply a matter of IP because *p*-dimethoxybenzene (IP = 7.90 eV) is a better electron donor than 1,3-cyclohexadiene (IP = 8.32 eV) yet the latter is a better quencher (cf. Table VIII). It is also surprising to note that 1,3-cyclohexadiene quenches DBO*¹ 5 times faster in isooctane than in acetonitrile, suggesting that hydrogen abstraction from solvent or quencher may be important. A more careful study of fluorescence quenching, analogous to the work of Monroe and Turro on biacetyl,⁸⁷ is now in progress.

In summary, we have found that the usual ring closure and scission of cyclohexane-1,4-diyl biradicals can be diverted by cyclopropylcarbonyl rearrangement. Lifetimes of these fascinating intermediates and rate constants for many of their reactions have been obtained by using the free radical clock technique. Because the 1,7-biradical **4** must undergo intramolecular disproportionation over a distance of 3 Å, it survives for 360 ns, long enough to be trapped by 1,4-cyclohexadiene. The doubly "spring-loaded" cyclohexane-1,4-diyl **8** rearranges via a long-lived 1,10-biradical **10** to Bredt olefins **11** which undergo thermal Cope rearrangement to 1,4-dimethylenedecalins. To our surprise, irradiation of **1** in carbon tetrachloride gave chlorinated olefins **23** and **24** in the first electron-transfer photoreaction of an azoalkane. The triplet-sensitized reaction of **1** with CCl₄ and of DBO with 1,4-CHD represent the first bimolecular processes observed for an azoalkane triplet state. Although these species are short-lived, direct observation is now recognized as a possibility. It is amusing that this class of azoalkanes, which acquired the uncomplimentary name of "reluctant",¹⁻⁵ have turned out to exhibit a rich chemistry of their own. Admittedly, as many questions have been raised by the present results as have been answered; hence, further work on DBO derivatives is in progress.

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Experimental Section

General. Melting points were determined with a Me-Temp apparatus and are uncorrected. NMR spectra were obtained in CDCl₃ on a JEOL FX-90Q Fourier transform spectrometer. UV spectra were recorded on a Cary 17 spectrophotometer, emission spectra on a Perkin-Elmer MPF-2A fluorimeter, low-resolution mass spectra on a Finnigan 3300 mass spectrometer, and high-resolution mass spectra on a CEC Du Pont 21-110B spectrometer. Photochemical experiments were carried out by using a 450-W Hanovia lamp or a 500-W short arc mercury lamp employing either NiSO₄/K₂CrO₄ (313 nm) or 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate/Corning 7-54 (366 nm) filter combinations. Nitrogen quantum yields were determined as described earlier.⁸ GC work was conducted on an Antec 300 gas chromatograph equipped with TC and FID detectors. The GC columns used in this work are listed in Table IX and will be referred to by letter.

The acetonitrile and benzene used in photochemical studies were gold label, spectrophotometric grade (Aldrich Chemical Co.). The triplet sensitizers were purified by recrystallization or zone refining.

Syntheses. The preparations of DBO,¹⁷ 1,4-dimethyl-DBO (27),^{88,89} and 1-cyclopropyl-DBO (1)¹⁵ have been described previously.

1,4-Dicyclopropyl-1,4-cyclohexanediol (15). To a stirred solution of 15.0 g of cyclopropyl bromide in 200 mL of anhydrous THF under N₂ at -78 °C was added 60 mL of 2.6 M *t*-BuLi in pentane. After 1.5 h, a solution of 5.6 g of 1,4-cyclohexanedione in 25 mL of THF was added, and the reaction solution was stirred for an additional 7 h at -78 °C, warmed to room temperature, and stirred overnight. The reaction was quenched by pouring carefully into 400 mL of H₂O. The layers were separated, and the aqueous fraction was extracted with two 200-mL portions of ether. The combined organic layers were dried over MgSO₄, filtered, and rotary-evaporated to yield 9.3 g of oily, yellow crystals. Recrystallization from 25 mL of hexane containing a few drops of EtOAc afforded 5.2 g (56%) of white crystals: NMR δ 0.12–0.44 (m, 8 H), 0.76–1.18 (m, 4 H), 1.60 (s, 8 H).

1,7-Dicyclopropyl-4-methyl-2,4,6-triazatricyclo[5.2.2.0^{2,6}]undec-8-ene-3,5-dione (17). To a solution of 0.946 g of 15 in 60 mL of chloroform in a drybox was added 7.0 g of bis[2,2,2-trifluoro-1-phenyl-1-(trifluoromethyl)ethoxy]diphenylsulfurane.¹⁶ The reaction solution immediately turned black. The flask was stoppered, removed from the drybox, and stirred at room temperature for 4 h. After the mixture was washed with 2 × 50-mL portions of 20% aqueous NaOH and the CHCl₃ layer dried with MgSO₄, the solvent was removed by rotary evaporation to yield a black oil. The oil was bulb-to-bulb distilled at 5 torr below 50 °C to yield a clear oil. To this oil was added 5% *N*-methyltriazaolinedione^{15,17} in EtOAc until a faint red color persisted. The solvent was removed in vacuo, and the residue was recrystallized from acetone, yielding 0.689 g (52%) of white crystals, mp 143–144.5 °C: ¹H NMR δ 0.30–1.00 (m, 8 H), 1.28–2.20 (m, 6 H), 2.96 (s, 3 H), 5.97 (s, 2 H); ¹³C NMR δ 2.34, 3.60, 14.27, 24.99, 29.59, 131.23; exact mass calcd for C₁₅H₁₉N₃O₂ (M⁺) *m/e* 273.1477, found 273.1477, calcd (M⁺ + 1, ¹³C) *m/e* 274.1511, found 247.1510.

1,4-Dicyclopropyl-1,3-cyclohexadiene (16). A pure sample of this diene was isolated by preparative GC (column D, oven temperature 181 °C) of the bulb-to-bulb distilled oil mentioned above: NMR δ 0.32–0.74 (m, 8 H), 1.22–1.58 (m, 2 H), 1.94 (s, 4 H), 5.63 (s, 2 H); ¹³C NMR δ 5.20, 16.66, 24.66, 117.78, 137.92; exact mass calcd for C₁₂H₁₆ (M⁺) *m/e* 160.1252, found 160.1253.

1,7-Dicyclopropyl-4-methyl-2,4,6-triazatricyclo[5.2.2.0^{2,6}]undecane-3,5-dione. To a solution of 2.0 g 17 in 50 mL of absolute EtOH was added a small amount of activated charcoal. After swirling briefly, the charcoal was removed by filtration through a Celite pad. The olefin was then hydrogenated at atmospheric pressure by using 5% Pd/C as catalyst. After hydrogen uptake was complete, the catalyst was removed by filtration through the same Celite pad used above. The EtOH was removed by rotary evaporation to yield white crystals. These were recrystallized from cyclohexane to give pure product in 87.5% yield, mp 90–92 °C: NMR δ 0.32–0.76 (m, 8 H), 1.00–2.00 (m, 10 H), 3.04 (s, 3 H); exact mass calcd for C₁₅H₂₁N₃O₂ (M⁺) *m/e* 275.1634, found 275.1637.

1,4-Dicyclopropyl-2,3-diazabicyclo[2.2.2]oct-2-ene (2). The crude crystals of hydrogenated 17 were dissolved in 60 mL of *i*-PrOH, and 4.6 g of KOH pellets was added.⁹⁰ The reaction was heated at reflux overnight. After cooling to room temperature, the solids were removed by filtration and were washed with several portions of methanol. The solvent was then removed by rotary evaporation. The oil obtained was diluted with 100 mL of H₂O and then extracted with 3 × 100-mL por-

Table X. % NOE Enhancements^a

compd	H _a	H _b	H _c
5Z		X	0.1
5Z	8.9	-1.2	X
5Z	X	7.6	5.6
5E		X	29.8
5E	-0.2	21.6	X
5E	X	4.6	-2.1

^a "X" indicates irradiated protons.

tions of CH₂Cl₂. The combined CH₂Cl₂ fractions were dried over MgSO₄, and the solvent was rotary-evaporated to give a yellow solid. Low-temperature (-78 °C) recrystallization from pentane afforded 0.487 g (35%) of 2 as white crystals, mp 109–111 °C: ¹H NMR δ 0.68–1.76 (m, 18 H); ¹³C NMR δ 1.50, 18.22, 27.83; exact mass calcd for C₁₂H₁₈N₂ (M⁺) *m/e* 190.1470, found 190.1468, calcd (M⁺ - N₂) *m/e* 162.1409, found 162.1410.

3,3-Dimethyl-9-propylidene-1,5-dioxaspiro[5.5]undecane. Following the procedure of Crawford and Tokunaga,⁹¹ a 0.3-g portion of 47% NaH in mineral oil under N₂ was washed twice with dry pentane to remove the oil. To the NaH was added 25 mL of dry Me₂SO (distilled from CaH₂), and the mixture was heated at 50 °C until H₂ evolution ceased. Then 2.0 g of *n*-propyltriphenylphosphonium bromide⁹² was slowly added. The resulting bright-orange solution was heated at 50 °C under N₂ for 45 min. To the solution was added 0.98 g of 3,3-dimethyl-1,5-dioxaspiro[5.5]undecan-9-one^{93,94} in 15 mL of dry Me₂SO. After stirring for 2 h, the reaction solution was poured into 300 mL of H₂O and filtered through Celite. The filtrate was extracted with 3 × 75-mL portions of pentane. The combined pentane fractions were dried over MgSO₄, filtered, and concentrated to yield 1.09 g of slightly yellow crystals. The product could be purified by distillation through a short-path apparatus, bp 100–108 °C (0.1 mmHg): NMR δ 0.80–1.00 (m, 9 H), 1.72–2.28 (m, 10 H), 3.52 (s, 4 H), 5.11 (t, 1 H, *J* = 7.2 Hz).

4-Propylidene-1-cyclohexanone (18). The crude olefinic ketal obtained above (1.09 g) was dissolved in 25 mL of acetone and 10 drops of concentrated HCl were added. The solution was refluxed under N₂ for 30 min. The cooled reaction solution was diluted with 100 mL of water and extracted with 2 × 75-mL portions of ether. The combined ether fractions were dried over MgSO₄, filtered, and concentrated to yield a yellow oil. Purification could be accomplished by short-path distillation, bp 55–58 °C (0.18 mmHg): NMR δ 0.99 (t, 3 H, *J* = 7.2 Hz), 1.80–2.15 (m, 6 H), 2.43 (br s, 4 H), 5.33 (t, 1 H, *J* = 7.2 Hz).

4-Propylidene-1-cyclohexene (5, Z and E Isomeric Mixture). Following the procedure of Dauben et al.,⁹⁵ the crude sample of 18 obtained above was dissolved in 200 mL of THF. To this solution was added 1.89 g of *p*-toluene-sulfonylhydrazide and four drops of concentrated HCl. The solution was then refluxed for 15 h under N₂ through a Soxhlet extractor containing 4-Å molecular sieves. The solution was cooled to 0 °C, and 30 mL of 1.6 M MeLi in pentane was slowly added. The reaction solution was stirred vigorously at 0 °C for 30 min, warmed to room temperature, and stirred for an additional 1.5 h. Excess water was added, and the resulting mixture was stirred for 30 min at room temperature. The layers were separated, and the aqueous layer was extracted with 2 × 75-mL portions of ether. The combined organic fractions were dried over MgSO₄, filtered, and concentrated to yield a dark brown oil. Purification of the oil by preparative GC (column C, oven programmed from 75 to 100 °C, 1 °C/min) yielded the Z and E isomers as clear oils: 5Z retention time 50 min; NMR δ 0.96 (t, 3 H, *J* = 7.2 Hz), 1.85–2.38 (m, 6 H), 2.75 (br s, 2 H), 5.16 (t, 1 H, *J* = 7.2 Hz), 5.68 (br s, 2 H); 5E retention time 56 min; NMR δ 0.96 (t, 3 H, *J* = 7.2 Hz), 1.86–2.48 (m, 6 H), 2.70 (br s, 2 H), 5.24 (t, 1 H, *J* = 7.2 Hz), 5.67 (br s, 2 H).

Nuclear Overhauser Effect Study on 5E and 5Z. The separate samples of 5E and 5Z in CDCl₃ were degassed by five freeze-thaw cycles and were sealed into NMR tubes. Each proton resonance was irradiated, and the area of the other peaks was determined by using five integrations. A pulse delay of 80 ms ensured that totally relaxed spectra were obtained. The data are shown in Table X with the proton assignments below.

1-Cyclopropyl-4-propylidencyclohexanol (19). To a stirred solution of 7.0 g of cyclopropyl bromide in 120 mL of THF at -78 °C under N₂ was added 55 mL of 1.6 M *t*-BuLi in pentane, and the mixture was

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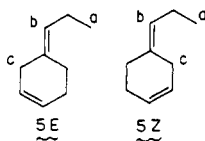
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stirred for 2 h. A solution of 2.3 g of **18** in 10 mL of THF was added, and stirring was continued at -78°C for 4 h. The mixture was allowed to warm slowly to room temperature, and it was then stirred for 10 h. The solution was poured into saturated aqueous NH_4Cl and was extracted with ether. The combined ethereal layers were dried over MgSO_4 and filtered, and the solvent was removed by rotary evaporation. The resulting yellow oil was purified by short-path distillation at 0.18 torr, bp $76\text{--}79^{\circ}\text{C}$, to produce 1.44 g (47.8%) **19**: ^1H NMR δ 0.22–0.44 (m, 4 H), 0.72–1.10 (m, 4 H), 1.14–2.58 (m, 11 H), 5.13 (t, 1 H, $J = 7.2$ Hz); ^{13}C NMR δ 0.08, 14.86, 20.57, 21.69, 23.59, 31.98, 38.08, 38.76, 70.08, 123.93, 137.68.

1-Cyclopropyl-4-propylidene-1-cyclohexene (14E and 14Z). To a stirred solution of 0.166 g of **19** in 10 mL of dry pyridine at 25°C under N_2 was slowly added 0.20 mL of POCl_3 . The solution was stirred at room temperature for 8 h and then quenched by carefully adding H_2O . Workup consisted of extracting with $2 \times 75\text{-mL}$ portions of pentane, washing the combined pentane layers with $2 \times 20\text{ mL}$ of 3 N HCl, drying over MgSO_4 , and removing of the pentane. Pure **12** was obtained from the yellow oil by preparative GC (column D, oven 155°C) to produce 39.7 mg (26.6%) of **14E** and **14Z** in roughly equal amounts: ^1H NMR δ 0.33–0.60 (m, 4 H), 0.79–1.06 (t, 3 H, $J = 7.2$ Hz), 1.11–1.46 (m, 1 H), 1.75–2.44 (m, 6 H), 2.70 (br s, 2 H), 5.00–5.48 (m, 2 H), olefinic protons; (**14Z**) 5.13 (t, 1 H, $J = 7.2$ Hz), and (**14E**) 5.20 (t, 1 H, $J = 7.2$ Hz); ^{13}C NMR δ (**14Z**) 4.18, 4.28, 14.42, 17.15, 20.71, 27.69, 28.42, 33.05, 118.51, 124.66, 134.95, 138.71, (**14E**) 4.18, 4.28, 14.86, 17.05, 20.37, 25.25, 28.57, 35.20, 119.59, 123.93, 135.15, 138.32.

1,4-Dipropylidene-cyclohexane (Z and E Isomeric Mixture). Following the procedures given above for 3,3-dimethyl-9-propylidene-1,5-dioxaspiro[5.5]undecane, 0.55 g of 60% NaH was reacted with 25 mL of Me_2SO for 2.5 h at 40°C . A 4.1-g portion of *n*-propyltriphenylphosphonium bromide was added and the mixture was heated at 40°C for 1 h. After cooling the stirred mixture to the lowest possible temperature without freezing it, 1.1 g of 4-propylidene-cyclohexanone (**18**) in 10 mL of Me_2SO was added, and the mixture was allowed to warm to 25°C . The solution was stirred for 3 h and worked up according to the aforementioned procedure. The crude product, consisting of white crystals and a pale yellow oil, was triturated with 10 mL of hexane. After filtration, rotary evaporation, and short-path distillation, 0.39 g of product was obtained, bp $93\text{--}95^{\circ}\text{C}/14\text{ mmHg}$: NMR δ 0.96 (t, 6 H, $J = 7.6$ Hz), 1.86–2.24 (m, 12 H), 5.15 (t, 2 H, $J = 7.1$ Hz); ^{13}C NMR 14.88, 20.62, 28.97, 29.78, 37.32, 38.29, 124.25, 124.36, 138.29; MS, m/e (rel abundance) 164 (100), 135 (57.3), 121 (49.3), 107 (48.6), 93 (92.8), 79 (86.1), 67 (32.5), 41 (30.7). Attempted separation of the *E* and *Z* isomers failed on a packed TCEP GC column and on SF-96 and SE-54 capillary columns.

cis-1,4-Dimethylenedecalin (21c). To a stirred solution of 2.0 g of CH_2I_2 in 25 mL of dry THF under N_2 was carefully added 1.9 g of activated Zn dust, following the procedure of Takai et al.¹⁸ After the mixture had cooled to room temperature, 1.3 mL of 2 M Me_3Al in toluene was carefully added dropwise to prevent an exotherm. After cooling the mixture to room temperature, a solution of 0.203 g of *cis*-decalin-1,4-dione (**20c**)⁹⁶ in 5 mL of THF was added, and the reaction was stirred for 9 h. The resulting slurry was filtered through a Celite pad, 50 mL of ether added, and the organic layer washed twice with 3% HCl, twice with H_2O , dried over K_2CO_3 , and filtered. The solvent was removed by rotary evaporation to leave a brown oil. Filtration through a short alumina column eluting with petroleum ether and subsequent solvent removal yielded 75.5 mg (38%) of clear oil: ^1H NMR δ 1.12–2.59 (m, 14 H), 4.76 (br s, 4 H); ^{13}C NMR δ 24.13, 28.22, 34.86, 45.05, 108.03, 150.37.

trans-1,4-Dimethylenedecalin (21t). The method of Takai et al.¹⁸ was applied to 1.3 g of *trans*-decalin-1,4-dione²⁰ as described immediately above. Filtration of the crude, brown, oily product through a short alumina column eluting with petroleum ether yielded 0.4 g (32.3%) of clear oil: ^1H NMR δ 1.00–2.56 (m, 14 H), 14.68 (d, 4 H, $J = 5.4$ Hz); ^{13}C NMR δ 26.22, 29.69, 38.18, 47.59, 105.10, 152.27.

***n*-Propylidene-cyclohexane (30).**⁹⁷ A 4.0-g portion of 47% NaH dispersion in mineral oil was washed 3 times with dry pentane under N_2 ,

and 40 mL of dry Me_2SO was added.⁹¹ The slurry was stirred under N_2 at 40°C for 2.5 h, and a 30-g portion of *n*-propyltriphenylphosphonium bromide⁹² was then added. The mixture was stirred at 40°C for 1 h and cooled to room temperature; then 7.2 g cyclohexanone was added, and the solution was stirred for 1 h at 25°C . The solution was poured into 300 mL of H_2O , filtered through a Celite pad, and extracted with three 200-mL portions of pentane. The combined pentane fractions were dried over MgSO_4 , filtered, and concentrated to yield 3.6 g (40%) of slightly yellow oil. A small portion was short-path-distilled at 31 torr, and the product was collected at $66.5\text{--}68^{\circ}\text{C}$ as a clear oil: NMR δ 0.95 (t, 3 H, $J = 7.2$ Hz), 1.54 (br s, 6 H), 1.84–2.28 (m, 6 H), 5.08 (t, 1 H, $J = 7.2$ Hz).

4-Chlorocyclohexanone. To a suspension of 14.5 g of PCC⁹⁸ in 80 mL of dry CH_2Cl_2 was added 6.2 g of 4-chlorocyclohexanol⁹⁹ in 20 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 mixture was filtered through Celite, washing the deposits in the reaction flask with several portions of ether. Rotary evaporation of the solvent left 7.4 g of brown oil. Distillation through a short Vigreux column yielded 1.9 g (31.1%) of 4-chlorocyclohexanone, bp $83\text{--}88^{\circ}\text{C}$ (12 mmHg) [lit.²¹ $96\text{--}98^{\circ}\text{C}$ (20 mmHg)]: NMR δ 1.20–3.0 (m, 8 H), 3.90–4.40 (m, 1 H).

4-Chloro-1-cyclopropyl-1-cyclohexanol (22). To a stirred solution of 13.0 g of cyclopropyl bromide in 60 mL of dry THF at -78°C under N_2 was added 60 mL of 1.6 M *t*-BuLi in pentane. The resulting solution was stirred at -78°C for 2 h, a 3.2-g portion of 4-chlorocyclohexanone in 20 mL of dry THF was added, and the solution was warmed to 25°C . After stirring overnight, the solution was poured into 200 mL of H_2O and extracted with two 100-mL portions of ether. The combined ether layers were dried over MgSO_4 and filtered, and the ether was removed by rotary evaporation to yield a yellow oil. After short-path distillation at 0.2 torr, 2.3 g (50%) of clear oil was obtained, bp $78\text{--}82^{\circ}\text{C}$. GC analysis (column H, oven 184°C) of the oil showed a minor component (28%) with a retention time of 28.5 min (peak A) and a major component (64%) with a retention time of 42.0 min (peak B). Compounds A and B were isolated by preparative GC, and the isolated samples were reinjected to verify that they were single compounds. Both preparative samples were identified as isomers of **22** by ^1H and ^{13}C NMR and mass spectral analysis. Peak A: NMR δ (^1H) 0.28–0.48 (m, 4 H), 0.76–1.08 (m, 1 H), 1.28–2.20 (m, 9 H), 4.42 (br s, 1 H); ^{13}C NMR δ 0.08, 22.08, 30.27, 31.93, 59.69, 69.25; MS, m/e (rel abundance) 120 (44.2), 138 (6.3), 156 (1.3); exact mass calcd for $\text{C}_9\text{H}_{15}\text{CO}$ m/e 174.0811, found 174.0813, calcd ($\text{M}^+ - \text{H}_2\text{O}$) m/e 156.0706, found 156.0707, calcd ($\text{M}^+ - \text{HCl}$) m/e 138.1045, found 138.1042. Peak B: ^1H NMR δ 0.26–0.46 (m, 4 H), 0.70–1.02 (m, 1 H), 1.30–2.18 (m, 9 H), 3.68–4.05 (m, 1 H); ^{13}C NMR δ 0.18, 21.78, 32.47, 36.57, 59.25, 68.27; MS, m/e (rel abundance) 120 (31.8), 138 (8.2), 156 (5.0); exact mass calcd for $\text{C}_9\text{H}_{15}\text{ClO}$ (M^+) m/e 174.0811, found 174.0813, calcd ($\text{M}^+ - \text{H}_2\text{O}$) m/e 156.0706, found 156.0707, calcd ($\text{M}^+ - \text{HCl}$) m/e 138.1045, found 138.1042.

4-Chloro-1-cyclopropyl-1-cyclohexene (23). A 103.6-mg portion of **22** (peak B from above) was dissolved in 2 mL of dry pyridine. To this solution was added dropwise 1.5 mL of freshly distilled POCl_3 . The resulting solution was heated at 40°C under N_2 for 12 h. The solution was cooled to room temperature, diluted carefully with 10 mL of 1.5 N HCl, and extracted with $2 \times 15\text{-mL}$ portions of ether. The combined ether fractions were washed with 10 mL of H_2O , dried over K_2CO_3 , filtered, and concentrated to yield a yellow oil. The oil was bulb-to-bulb distilled at 0.2 torr to a liquid N_2 trap to give 51.5 mg of clear liquid. GC analysis (column H, oven 184°C) revealed two products with retention times of 6.3 (32%) and 21.6 min (68%). Each peak was isolated pure by preparative GC, as shown by reinjection on the same column. The 6.3-min peak was identified as 4-chloro-1-cyclopropyl-1-cyclohexene (**23**) by mass spectral and NMR (^1H and ^{13}C) analysis. The 21.6-min peak was identified as **24** by spectral comparison with the product obtained from the sensitized photolysis of **1** in CCl_4 . From the GC analysis, the yield of the desired compound (**23**) could be calculated as 17.9%.

Similarly, when peak A was used in this dehydration procedure, **23** was obtained in an overall yield of 15.8%, the remainder again being **24**. **23**: ^1H NMR 0.32–0.66 (m, 4 H), 1.11–1.48 (m, 1 H), 1.70–2.78 (m, 6 H), 4.00–4.39 (m, 1 H), 5.32 (br s, 1 H); ^{13}C NMR δ 4.47, 4.62, 16.91, 25.88, 32.56, 35.69, 56.76, 116.37, 138.32; exact mass calcd. for $\text{C}_9\text{H}_{13}\text{Cl}$ (M^+) m/e 156.0706, found 156.0707, calcd ($\text{M}^+ + 2$; ^{37}Cl) m/e 158.0676, found 158.0678.

Product Studies of 1. A solution of 165.2 mg of **1** in 10 mL of benzene was irradiated in a Pyrex cell at 25°C using an Oriel 500-W short-arc mercury lamp without filter solutions. Irradiation was discontinued when the azo compound was no longer observed by UV (~ 12 h). GC analysis of the photolysate (column A, oven 45°C) revealed three products (re-

(96) Prepared from *cis*-decalin-2,6-diene-1,4-dione¹⁹ by zinc/acetic acid reduction followed by catalytic hydrogenation.²⁰

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tention times 70.2, 77.7, and 113.2 min; area ratio 30:65:5). The solvent was removed by rotary evaporation and the residual oil separated by preparative GC. The first peak (70.2 min) was identified as 1-cyclopropylbicyclo[2.2.0]hexane (**6**), the second (77.7 min) as 2-cyclopropyl-1,5-hexadiene (**7**), and the third (113.2 min) as (Z)-4-propylidene-1-cyclohexene (**5Z**). The NMR spectrum of **5Z** was identical with that of authentic material (see above). Diene **7** was identified by ^1H NMR: δ 0.32–0.72 (m, 4 H), 1.12–1.52 (m, 1 H), 1.90–2.40 (m, 4 H), 4.64 (s, 2 H), 4.84–5.16 (m, 2 H), 5.58–6.10 (m, 1 H). Upon rf irradiation of the multiplet at 1.90–2.40 ppm, the multiplet at 5.58–6.10 ppm collapsed into a doublet of doublets, and the multiplet at 4.84–5.16 ppm also became first order. $J_{\text{cis}} = 10$, $J_{\text{trans}} = 17$, and $F_{\text{gem}} = 1.8$ Hz could be found in the simplified pattern. 1-Cyclopropylbicyclo[2.2.0]hexane (**6**) was identified by ^1H NMR and the fact that it was isomeric with the other decomposition products as found by mass spectroscopy. As supportive evidence for the structure, thermolysis of **6** at 206 °C for 2.5 h gave only **7**.

A triplet-sensitized product study was accomplished by preparing a solution of 125.6 mg of **1** and 235.7 mg of benzophenone in 10 mL of benzene. The degassed and sealed sample was then irradiated with the Hanovia lamp at 313 nm at 25 °C. GC analysis of the crude photolysate (same column and conditions as used above) revealed four products (retention times 70.2, 77.7, 113.2, and 118.2 min; area ratio 18:21:53:8). The first three peaks were already identified in the direct irradiation product study, and the last peak was assigned as the *E* isomer of 4-propylidene-1-cyclohexene (**5E**) by comparing its retention time with that of an authentic sample. It was found that the $^3(\pi,\pi^*)$ sensitizer *p*-methoxyacetophenone gave the same product distribution as benzophenone.

Product Studies of 2. A solution of **2** in benzene was degassed and sealed into a Pyrex tube. After 366-nm irradiation, the products were identified by GC. Four peaks were observed (column D, oven 150 °C) with retention times 9.6, 12.3, 18.7, and 29.0 min and area ratio 14.5:80.8:0.8:3.9. All peaks were determined by GC/MS to be isomers with $M^+ = 162$. The first two were isolated by preparative GC (column E, oven 150 °C) and were identified as 1,4-dicyclopropylbicyclo[2.2.0]hexane (**12**) and 2,5-dicyclopropylhexa-1,5-diene (**13**). **12**: ^1H NMR δ 0.10–0.45 (m, 8 H), 0.70–0.95 (m, 2 H), 1.80 (s, 8 H); ^{13}C NMR δ 0.2, 13.8, 27.9. Thermolysis of isolated **12** at 178 °C in benzene- d_6 for 2 h gave exclusively **13**. **13**: ^1H NMR 0.35–0.75 (m, 8 H), 1.18–1.60 (m, 2 H), 2.21 (s, 4 H), 4.63 (br s, 4 H). The two later peaks were identified in the triplet-sensitized product studies where their yields were larger.

The triplet products from **2** were obtained from irradiations in benzene sensitized with either benzophenone or *p*-methoxyacetophenone. The GC trace of the crude photolysate revealed the same products as in the direct irradiation; however, the area ratios were significantly altered (15.1:21.3:14.7:48.9). In addition, the trace exhibited a badly tailing peak which also occurred on several other columns regardless of GC conditions. Analysis of the crude photolysate under mild conditions on a capillary column revealed a product ratio of 8.8:9.7:9.2:72.3 (retention times 14.2, 20.7, 33.7, and 41.1 min; column F, oven 68 °C, injector 123 °C). The 33.7-min peak was identified by comparing its retention time in crude photolysates with that of authentic 1-cyclopropyl-4-propylidene-1-cyclohexene (**14**) (column D, oven 155 °C, and column A, oven 120 °C). Column A showed that both isomers of **14** were present (2.7:1 ratio of **14Z** to **14E**).

The last peak, with a retention time of 42 min, was collected by preparative GC (column D, oven 151 °C) of the crude photolysate. NMR analysis indicated a very symmetrical compound with impurities. **11E** and **11Z**: ^1H NMR δ 1.50–2.70 (m, 16 H), 4.86–5.19 (m, 1 H), and 8.26 (t, 1 H, $J = 7.2$ Hz); ^{13}C NMR δ 27.88, 31.39, 32.47, 35.64, 129.44. Re-injection of the preparative GC sample under analytical conditions revealed two additional peaks (retention times of 13.7 and 15.3 min) which did not correspond to any of the other known decomposition products. Their retention times would place these peaks under the broad peak that was interfering with GC analysis mentioned above. Since it appeared that **11** was rearranging on the GC, a preparative sample of **11** was diluted in benzene- d_6 , degassed, sealed in an NMR tube, and thermolyzed at 197 °C in a sand bath for 2.75 h. GC comparison of the thermolysate with authentic samples of **21c** and **21t** showed that **21t** was the thermolysis product of **11Z**. However, we later found that high temperatures isomerize **21c** to **21t**.

In order to check the product composition without the danger of thermal rearrangements, the sensitized photolysis of **2** was conducted in benzene- d_6 with monitoring by NMR. Decalins **21c** and **21t** were absent, but **11E** and **11Z** were present in approximately equal amounts. Attempted isolation of **11** by preparative GC caused the rearrangement products to appear as above, firmly establishing that rearrangements occur on the GC.

Another sample of crude photolysate was thermolyzed at roughly 100 °C, and the reaction was monitored by NMR and GC (column F, oven 71 °C). Not only was **11** rearranging to **21**, but several other minor products were observed that were also seen from independent thermolysis of **21c** and **21t**. Those minor products have been tentatively identified by NMR and mass spectrometry as isomers of **21** which contain one or two endocyclic double bonds, such as **25** and **26**.

The structure of **11** is further supported by degradation. A small GC isolated sample of **21** was ozonized and worked up with triphenylphosphine. The products were compared by GC with that obtained from ozonolysis of cyclohexene. Identity of retention times and NMR analysis confirmed the presence of adipaldehyde in both samples. An extra peak in the ozonized sample of **21** was identified as 1,4-cyclohexanedione by injection of the authentic material and by NMR.

Biradical Trapping with 1,4-Cyclohexadiene. A solution of 14 mg of **1** and 16 mg of 2-acetonaphthone in 2 mL of 1,4-CHD was irradiated at 313 nm under an argon purge. NMR monitoring revealed that decomposition of **1** was complete after 11 h. A reference solution of 12.1 mg of **1** and 25.1 mg of 2-acetonaphthone in 2 mL of benzene was thoroughly degassed, sealed, and irradiated at 313 nm for 24 h. GC analysis (column G, oven 109 °C) showed that the product ratio 6:7:5 in benzene was 11:14:76. The same peaks plus a new one of 24.3-min retention time were found in 1,4-CHD (retention times 22.5, 20.4, 32.4, and 24.3 min, ratio 11:14:56:20). Identification of the new product (**30**) was afforded by comparison of retention time with that of an authentic sample of propylidene-cyclohexane.

A solution of 11.7 mg of **2** and 22.7 mg of 2-acetonaphthone in 2 mL of 1,4-CHD was irradiated at 313 nm as in the case of **1**. GC on column D revealed all the peaks previously seen in benzene, plus a new peak falling between products **12** and **13**. Its retention time on columns D and I and its mass spectrum were the same as those of authentic 1,4-dipropylidene-cyclohexane. The area ratio of products **12**, **13**, **14**, and **11** and the new peak was 6.6:6.8:11.9:42.1:32.5.

Products from Irradiation of 1 in CCl₄. A solution of 208.3 mg of **1** in 2 mL of CCl₄ was irradiated at 366 nm by using the Oriel short-arc mercury lamp and filters. The solution formed a reddish solid on the walls of the tube as the photolysis progressed. GC analysis of the photolysate (column G, oven programmed from 130 to 195 °C/min) revealed about eight products but only two were dominant (retention time 25.2 and 38.0 min; area ratio 5.7:1). The largest peak was separated by preparative GC and was identified as 4-chloro-1-cyclopropyl-1-cyclohexene (**23**) by comparison of GC retention time, ^1H and ^{13}C NMR spectra, and mass spectrum with that of authentic material.

The triplet-sensitized product study was carried out by irradiating a solution of 98.9 mg of **1** and 203.8 mg of benzophenone in 10 mL of CCl₄ at 313 nm. The reddish solid mentioned above also formed here. GC analysis as above of the crude photolysate revealed that the two dominant peaks in the complex mixture were the same as those seen in the direct photolysis; however, the area ratio had changed to 1:3.2. The second peak was isolated by preparative GC and identified as 4-chloro-1-(3-chloropropylidene)cyclohexane (**24**) by NMR and mass spectral analysis: NMR δ 1.64–2.72 (m, 10 H), 3.49 (t, 2 H, $J = 7.2$ Hz), 4.04–4.36 (m, 1 H), 5.16 (t, 1 H). The 500-MHz proton NMR¹⁰⁰ and decoupling experiments support the structure: MS, *m/e* (rel abundance) 41 (52.9), 79 (100.0), 107 (55.0), 143 (4.24), 145 (1.36), 192 (1.45), 194 (0.79), 196 (0.22). A minor peak in the direct photolysate was identified as hexachloroethane by comparing GC retention times and mass spectra with those of an authentic sample.

To monitor the time evolution of products formed during the sensitized photolysis of **1** in CCl₄, two tubes were prepared, each containing 0.04883 mmol of **1**, 0.08117 mmol of benzophenone, and 0.1069 mmol of octadecane (as internal standard) in CCl₄. To one tube was added 0.09515 mmol of **23** which contained 0.05847 mmol of **24**. After purging with N₂, both tubes were irradiated at 313 nm in the merry-go-round. The photolyses were monitored by GC (column I, oven 150 °C). The areas of the peaks (Table II) were obtained relative to octadecane by computer integration.

To determine the amount of reddish solid formed during the direct photolysis, a solution of 40.7 mg of **1** in 4.2 mL of CCl₄ was prepared. The solution was degassed, sealed, and irradiated for 20 h at 366 nm with the Oriel lamp. The tube was rotated slowly during photolysis. After opening the tube, the solid was collected by filtration and found to weigh 16.0 mg.

Fluorescence lifetime determinations were carried out by using a Lambda Physik EMG 101 nitrogen laser to excite sealed, degassed solutions of DBO and its derivatives. After passing through a Bausch & Lomb monochromator, the emitted light 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 fluorescence lifetimes were calculated

by a least-squares routine by using about 60 data points. The following results were obtained for fluorescence quenching of **1** by CCl₄ in benzene at 25 °C: concentration of CCl₄ (M), τ_f (ns) 0, 416; 0.087, 213; 0.247, 121; 0.870, 51.

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Registry No. **1**, 87373-47-5; **2**, 87433-32-7; **5E**, 83632-67-1; **5Z**, 83615-88-7; **6**, 83615-86-5; **7**, 83615-87-6; **11E**, 97012-28-7; **11Z**,

97012-29-8; **12**, 97012-26-5; **13**, 97012-27-6; **14E**, 97012-17-4; **14Z**, 97012-18-5; *cis*-**15**, 97012-11-8; *trans*-**15**, 97012-30-1; **16**, 97012-13-0; **17**, 97012-12-9; **17** (dihydro derivative), 97042-30-3; **18**, 97012-15-2; **19**, 97012-16-3; **20c**, 2717-36-4; **20t**, 6751-42-4; **21c**, 97012-21-0; **21t**, 97012-22-1; *cis*-**22**, 97012-23-2; *trans*-**22**, 97012-24-3; **23**, 97012-25-4; **24**, 83615-90-1; **27**, 49570-30-1; **30**, 2129-93-3; 1,4-CHD, 628-41-1; 1,3-CHD, 592-57-4; DBO, 3310-62-1; Ph₂S(OC(CF₃)₂Ph)₂, 32133-82-7; Ph₃PC₃H₇-n⁺Br⁻, 6228-47-3; *p*-C₆H₄(OCH₃)₂, 150-78-7; PhCl, 108-90-7; PhCCl₃, 98-07-7; *p*-C₆H₄(CN)₂, 623-26-7; PhCN, 100-47-0; CBr₄, 558-13-4; cyclopropyl bromide, 4333-56-6; 1,4-cyclohexanedione, 637-88-7; *N*-methyltriazolinedione, 13274-43-6; 3,3-dimethyl-1,5-dioxaspiro[5.5]undecan-9-one, 69225-59-8; 3,3-dimethyl-9-propylidene-7,5-dioxaspiro[5.5]undecane, 97012-14-1; (*Z,Z*)-1,4-dipropylidene-cyclohexane, 97012-19-6; (*E,E*)-1,4-dipropylidene-cyclohexane, 97012-20-9; cyclohexanone, 108-94-1; 4-chlorocyclohexanol, 30485-71-3; 4-chlorocyclohexanone, 21299-26-3.

(100) We thank Prof. Peter B. Dervan for obtaining these spectra.

Onium Ylide Chemistry. 4.¹ Alkylhalonium Methylides

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Abstract: Alkylhalonium methylides were generated by two independent routes, proving their formation through derived product analysis. The reaction of singlet methylene, produced by photolysis of diazomethane, with methyl and ethyl halides gives in competition with C-H insertion evidence of methylenation of the halogen atom, i.e., alkylhalonium methylide formation. The unstable halonium methylides are immediately protonated or alkylated in the reaction medium to give dialkylhalonium ions which then undergo cleavage to the corresponding alkyl halides. Methylidonium methylide was also generated via the deprotonation of dimethylidonium hexafluoroantimonate with sodium hydride in competition with the expected methylation of fluoride and hydride, giving the major products. Subsequent methylation of the methylidonium methylide by excess dimethylidonium ion gives methylethylidonium ion followed by cleavage leading to the formation of ethyl halides and via hydride reduction to ethane, respectively. Attempted formation of alkylhalonium methylides via fluoride cleavage of methyl[(trimethylsilyl)methyl]halonium hexafluoroantimonates was unsuccessful due to ready disproportionation of the halonium ions.

Karele and Neilands have reported the preparation of arylidonium ylides from active methylene compounds and iodosobenzene.^{2a} Hayashi later improved the method for generating arylidonium ylides and studied the thermal and Cu-catalyzed decomposition of these iodonium ylides.^{2b} Halonium ylides have been proposed as intermediates in the formation of benzoquinones from the photolysis of 3,5-diisobutylbenzene 1,4-diazooxide with bromophenols,^{3a} isopropyl bromide,^{3b} or iodobenzene.^{3b} Several other stable arylhalonium ylides have been prepared.⁴

Chloronium ylides have been suggested as intermediates in the photochemical addition of ethyl diazoacetate in chloro-substituted methanes.⁵ The alkoxy-carbonyl-carbene was proposed to attack a chlorine atom of the substituted methane solvent leading to the chloronium ylide which then undergoes intramolecular rearrangement, probably involving a radical pair. This mechanism

was later supported by ¹³C CIDNP studies.^{6a} Roth has described the abstraction of chlorine by singlet methylene from chloroform to proceed through a singlet radical pair, as evidenced by CIDNP.^{6b}

Olah et al. reported the first generation of methylhalonium methylides as reaction intermediates in the hydrogen-deuterium exchange of the corresponding dimethylhalonium ions in deuterated sulfuric acid.⁷

In our continued study of reactive onium ylide intermediates, we report here a mechanistic study of the generation of alkylhalonium ylides via two independent routes, proving their formation through derived products (albeit being by necessity in instances only minor ones).

Results and Discussion

Reaction of Methylene with Alkyl Halides. The gas-phase reaction of methylene with methyl chloride^{8a} takes place pre-

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