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STATE-DEPENDENT PHOTOCHEMISTRY OF HIGHLY FLUORINATED BICYCLO[4.2.0]OCTA-2,4-DIENES

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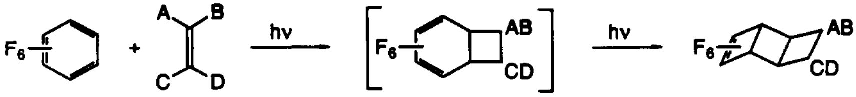
SUMMARY

A series of 1,2,3,4,5,6-hexafluorobicyclo[4.2.0]octa-2,4-dienes was subjected to direct irradiation with ultraviolet light and to triplet sensitization. While all of the dienes cyclized smoothly upon direct irradiation to tricyclo[4.2.0.0^{2,5}]oct-3-enes, their behavior when triplet sensitized was strongly dependent upon the substituents in the 7- and 8-positions. Responses included no reaction, cyclization to tricyclooctene, and fragmentation to hexafluorobenzene plus olefin. Fragmentation occurred only when geminal chlorines were present at the 7-position. This observation is consistent with the view that the four-membered ring opens homolytically at the C_6-C_7 bond, and only if sufficient stabilization is available for a radical center at the 7-position.

INTRODUCTION

Photocycloaddition of olefins to benzene can take place in 1,2-, 1,3- or 1,4-fashion [1], but hexafluorobenzene shows a strong preference for 1,2-addition [2-5]. Broad in scope, the hexafluorobenzene-olefin reaction has yielded a variety of valuable synthetic intermediates. The initially formed cycloadducts, 1,2,3,4,5,6-hexafluorobicyclo[4.2.0]octa-2,4-dienes, photocyclize under the reaction conditions to give *anti*-tricyclo[4.2.0.0^{2,5}]oct-3-enes, the products normally isolated (Equation 1). In some reactions of this type, rates and yields have been found to vary capriciously.



(1)

The present photochemical study of diene intermediates formed in the hexafluorobenzene-olefin reaction was undertaken in the hope of gaining a fuller mechanistic understanding of the overall transformation, and perhaps improving it as a result.

While carrying out the photocycloaddition of trichloroethylene to hexafluorobenzene, we accidentally discovered that introduction of air into the nitrogen-filled apparatus caused a reaction

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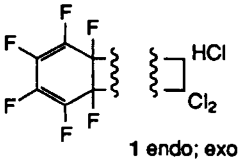
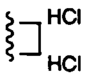
which had become extremely sluggish to run smoothly again. The implication that oxygen was responsible suggested an explanation. As an excellent quencher of triplet states, oxygen might inhibit a triplet reaction which opposes the desired cycloaddition [6]. Specifically, the bicyclic diene formed initially might photocyclize to product via a singlet excited state, but fragment to starting materials if excited to a triplet state. The investigation described here was designed to test this idea.

RESULTS AND DISCUSSION

The dienes we examined were all prepared by thermal ring opening of tricyclooctenes which were products of the hexafluorobenzene-olefin photoreaction. The orbital-topology-forbidden disrotatory ring opening occurred essentially quantitatively at about 160°. All of the dienes (**1** - **5**) bore chloro and/or fluoro substituents at the 7- and 8-positions. Choices were limited by a decision

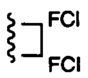


1 endo; exo



2a endo, cis

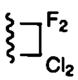
2b trans



3 trans;

exo, cis;

endo, cis



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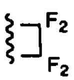

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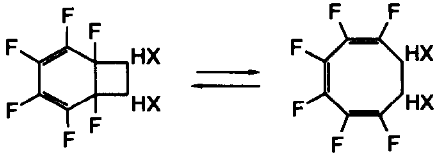
to omit compounds which exist in thermal equilibrium with a detectable amount of their cycloocta-1,3,5-triene valence isomers because of the complications the trienes might introduce into the photochemistry. In particular, the unsubstituted **6** and the endo, cis-difluoro analog **7** were excluded because the equilibrium constant for triene formation is much greater than unity and approximately unity, respectively, for these compounds[5].



6 X = H

7 X = F (endo, cis)

With the exception of **4**, all of the dienes employed in this study had previously been synthesized in our laboratory [7]. To prepare diene **4**, a neat mixture of hexafluorobenzene and 1,1-dichlorodifluoroethylene was irradiated with a Vycor-filtered medium-pressure mercury arc to give 7,7-dichlorooctafluorotricyclo[4.2.0.0^{2,5}]oct-3-ene (**8**) in 76% yield after distillation. Heating **8** under reflux gave **4** in 98% yield. ^{19}F NMR assignments for **4** and **8** are presented in Tables I and II, respectively. They are accompanied by assignments for the three stereoisomers of

3 (Table I) and its tricyclic precursor 9 (Table II). The task of assigning these spectra was guided by generalizations discussed elsewhere [5], and aided in the cases of 3 and 9 by partial resolution of the stereoisomeric mixture by preparative gas chromatography.

TABLE I

^{19}F NMR chemical shift assignments for dichlorooctafluorobicyclo[4.2.0]octa-2,4-dienes

Isomer	F_3, F_4	F_2, F_5	F_1, F_6	F_7, F_8
3 (exo-7, endo-8)[a]	147.6, 149.4	~154.5	168.5, 182.4	113.5, 119.0
3 (exo-7,8)	148.3	154.9	168.0	124.5
3 (endo-7,8)	148.5	154-155	182.4[b]	128.6
4 (7,7)	146.7, 150.6	153.2, 154.7	173.9, 174.7	107.4, 108.5[c]

[a] Ratio of the 3 isomers obtained, in order listed: 20 : 5 : 1. [b] Value uncertain. [c] J_{gem} = 194 Hz.

TABLE II

^{19}F NMR chemical shift assignments for dichlorooctafluoro-*anti*-tricyclo[4.2.0.$0^{2,5}$]oct-3-enes

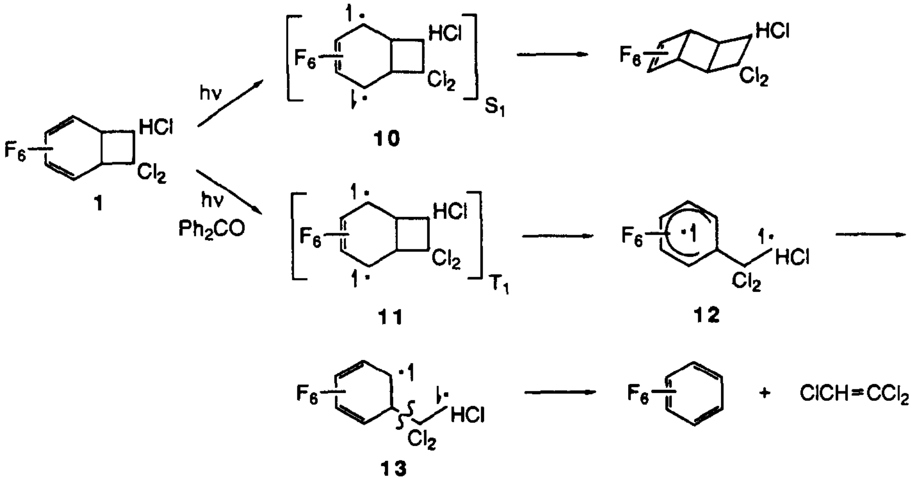
Isomer	F_3, F_4	F_2, F_5	F_1, F_6	F_7, F_8
9 (exo-7, endo-8)[a]	118-119	188.7 (F_2)	178.3 (F_1)	113.5, 113.6
		185.7 (F_5)	166.1 (F_6)	
9 (endo-7,8)	118-119	188.5	176.2	127.0
9 (exo-7,8)	~119.3-119.5	185.7	167.2	~119.3-119.5
8 (7,7)	119.5, 120.2	185.8 (F_2)	179.0 (F_1)	106.0 (F_8 endo)[b]
		189.5 (F_5)	167.0 (F_6)	110.5 (F_8 exo)[b]

[a] Ratio of the 9 isomers obtained, in the order listed: 16 : 4 : 1. [b] J_{gem} = 206 Hz.

The light source for all photoreactions was a medium-pressure mercury arc, and all were carried out in Pyrex NMR tubes in acetonitrile. This solvent was chosen both for its optical and ^{19}F NMR transparency and for its resistance to hydrogen atom abstraction. For photosensitized reactions, benzophenone was the sensitizer and a 340 nm cutoff filter was used to assure that only the sensitizer absorbed light. Representative of the dienes studied, 3 displayed an absorption maximum in isooctane at 278 nm ($\varepsilon = 2000$) which tailed out to 320 nm. Thus, the long-wavelength side of the absorption band is accessible to Pyrex-filtered radiation, but absorption beyond 340 nm (particularly in the presence of benzophenone at high concentration) is negligible.

Direct irradiation of dienes **1** - **5** gave good to essentially quantitative yields of the corresponding tricyclooctenes. In the least clean of these transformations, **2a** gave 79% of the tricyclooctene by ^{19}F NMR. No hexafluorobenzene formation was detected in any of these reactions, so fragmentation to benzene and olefin does not occur in the lowest singlet excited state of these compounds.

In sharp contrast, trichlorodiene **1**, a 4 : 1 mixture of endo and exo isomers at C_8, gave no tricyclooctene whatever when triplet sensitized to 20% conversion. The emergence of a single strong NMR signal corresponding to hexafluorobenzene revealed that the fragmentation reaction postulated at the outset does indeed occur in the triplet state, cleanly in this case. The dichotomy in reaction pathway for **1** can be rationalized as shown in Scheme I. Because all electrons are paired in the S_1 state of the diene (**10**), cyclization can occur rapidly and without impediment. For a molecule in the T_1 state (**11**), however, cyclization is not possible until intersystem crossing takes place; thus the excited species has an opportunity to explore other options. Whereas bond formation requires that the bonding electrons be paired, bond cleavage suffers from no such constraint. Hence opening of the four-membered ring, with concomitant strain relief, to give a triplet diradical (**12**) is an attractive option. After intersystem crossing, the resulting singlet diradical (**13**) can either reclose to give starting diene or fragment with the assistance of aromatization as a driving force to yield hexafluorobenzene and olefin.



SCHEME I.

Diene family **1** - **5** responded in divergent ways to triplet sensitization, in contrast to the rather uniform response to direct excitation. Stereoisomers **2a** and **2b** resisted both cyclization and fragmentation, showing no reaction after 12-13 hours. Likewise diene **3** was unchanged after the same period of time. On the other hand, after just 3 hours the isomeric diene **4** was 33% converted: 25% to fragmentation products and 8% to tricyclooctene. In this case both fragmentation products were detected by ^{19}F NMR since the olefin as well as the benzene contained fluorine. Finally, fully fluorinated diene **5** responded to triplet sensitization in yet another way, cyclizing cleanly and quite rapidly to tricyclooctene as it had done in its S_1 state. Thus, the consequences of triplet sensitization span the range from exclusive fragmentation through no reaction to exclusive cyclization.

Since the S_1 state of a diene lies far above its T_1 state [8], and is therefore not accessible thermally from T_1, cyclization originating from the latter state implies bond formation taking place in the (vibrationally excited) ground state. In the triplet state the cyclohexadiene ring may distort to a boat conformation to relieve interelectronic repulsion [9]. Intersystem crossing occurring in this geometry could lead directly to the tricyclic product*.

It is striking that isomeric systems **3** and **4** behave so differently upon triplet sensitization**, but an explanation for the fragmentation of **4** is suggested by the fact that the two dienes which undergo this reaction are the only two which have *geminal* chlorines on the four-membered ring. The stability of the diradical formed upon scission of the four-membered ring, e.g. **12**, may be the critical factor which determines whether fragmentation can compete with other possible fates of the triplet state. Chlorine in the alpha position is more effective than either hydrogen or fluorine at stabilizing a carbon free radical [10], as indicated by the bond dissociation energies in Table III Dissociation energies of bonds to both hydrogen and chlorine are shown to make it clear that a dramatic change in the atom bonded to carbon does not greatly change the apparent relative stabilities of the $\cdot CY_3$ radicals. Table III reveals that the trichloromethyl radical is roughly 10 kcal/mole stabler than either the methyl or the trifluoromethyl radical. Certainly the stability differences among diradical **12** and its analogs derived from dienes **1**- **5** are much smaller than this,

TABLE III

Bond dissociation energies of methanes[a]

	CH_3	CF_3	CCl_3
H	105.1 ± 0.2	106.7 ± 1	95.8 ± 1
Cl	84.6 ± 0.2	86.2 ± 3	73.1 ± 1.8

[a] Kcal/mole. D. F. McMillen and D. M. Golden, Ann. Rev. Phys. Chem., 33 (1982) 493.

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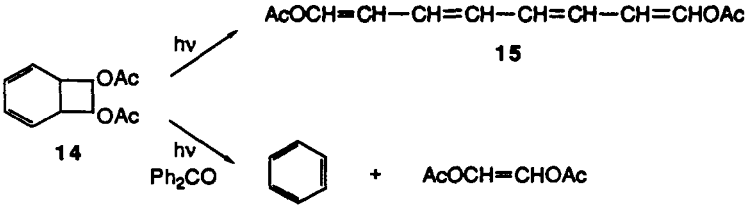
*A similar argument has been advanced to explain the triplet-sensitized cyclization of another cyclic diene [13]

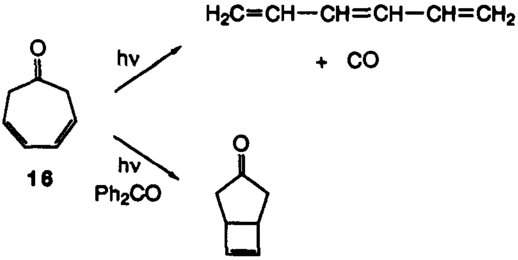
When triplet sensitized, diene **3, which was contaminated with **4** because the starting olefin contained a small amount of the unsymmetrical isomer [3], gave a ^{19}F NMR signal for this 1,1-dichloro isomer at 87.3 ppm but none for cis- or trans-1,2-dichlorodifluoroethylene (104 and 119 ppm, respectively). The contrasting behavior of **3** and **4** was thus confirmed.

but differences of two or three kilocalories/mole could alter completely the fate of an excited state. We therefore propose that the unique triplet state behavior of 1 and 4 is traceable to the modestly greater stability of the derived triplet diradicals relative to those which could form from the other dienes in the series.

To our knowledge there is no close precedent for the kind of dichotomy in excited state behavior exhibited by dienes 1 and 4, but related state-dependent photochemistry is well recognized. For example, direct irradiation of 7,8-diacetoxybicyclo[4.2.0]octa-2,4-diene (14) results in ring cleavage to open-chain tetraene 15 [11], but triplet sensitization elicits behavior parallel to that of 1 and 4: fragmentation to benzene and the 1,2-diacetoxyethylenes [12]



Cyclohepta-3,5-dienone (16) presents an interesting contrast to the photochemical behavior of 1 and 4. Here fragmentation is a singlet state reaction and cyclization a consequence of triplet sensitization [13, 14]



Whether our findings help explain the idiosyncrasies of the hexafluorobenzene photocycloadditions described at the outset is not yet clear. They may, indeed, in cases where fragmentation of the intermediate bicyclo[4.2.0]octa-2,4-diene occurs in the triplet state, as those dienes may be triplet sensitized by hexafluorobenzene.

EXPERIMENTAL

The monitoring of photoreactions by ^{19}F NMR spectra was carried out at 56.2 MHz using a JEOL FX60Q Fourier transform instrument. Chemical shifts reported in Tables I and II were obtained at 282.2 MHz using a Varian XL300 spectrometer with deuteriochloroform as solvent and trichlorofluoromethane (Freon 11) as internal standard; they are reported in parts-per-million upfield from the reference. Mass spectra were measured with a Finnigan Model 4023 quadrupole mass spectrometer. Preparative gas chromatography was performed on a Hewlett-Packard Model 5750 instrument equipped with a 1/4" x 25' 20% QF-1-on-Chromasorb W-HP 80/100 column and thermal conductivity detector. Microanalytical data were obtained from Spang Microanalytical Laboratory, Eagle Harbor, Michigan.

Solvents and reagents used in this work were reagent grade. Perfluorobenzene was purchased from Fairfield Chemical and 1,1-dichlorodifluoroethylene from PCR. Dienes **1**, **2a**, **2b**, **3** and **5** were synthesized according to procedures in the literature cited; the last was a gift from Dr. M. M. Rahman.

7,7-Dichlorooctafluoro-*anti*-tricyclo[4.2.0.0^{2,5}]oct-3-ene

The apparatus was a photochemical reactor which comprised a cylindrical 3-neck Pyrex vessel containing in its central neck a water-cooled quartz well which surrounded the source, a Hanovia 679A36 450-W medium-pressure mercury lamp fitted with a Vycor filter. About 50 ml mercury was placed in the reaction vessel in order to raise the level of the reaction mixture to that of the lamp. The assembly was cooled externally as well as internally by cold water.

A mixture of hexafluorobenzene (28.65 g, 0.154 mol) and 1,1-dichlorodifluoroethylene (21.3 g, 0.160 mol) was placed in the photoreactor and irradiated for 14 days under nitrogen. The solution was diluted with isopentane (100 ml), washed with 10% aqueous Na_2CO_3 (30 ml), and dried over $MgSO_4$. Solvent was removed by distillation and the remaining liquid was distilled through a Vigreux column (6 x 1/2") to give 37.09 g (0.116 mole, 76% yield) of colorless olefin, b.p. 50_{25}-$55^{o}{}_{20}$. ^{19}F NMR indicated no contamination by hexafluorobenzene. IR (neat): 1770, 1380, 1320, 1175, 1060, 1010, 860, 805, 725 cm^{-1}. MS m/e 318 (M^+), 283 (M^+-Cl), 248 ($C_8F_8^+$), 233 ($C_7F_6Cl^+$), 186 ($C_6F_6^+$, base), 132 ($C_2F_2Cl_2^+$). Analysis: Found: C, 30.09; Cl, 22.33%. $C_8F_8Cl_2$ requires C, 30.12; Cl, 22.23%.

7,7-Dichlorooctafluorobicyclo[4.2.0]octa-2,4-diene (4)

The olefin prepared above (2.0 g, 6.3 mmol) was heated under reflux in a nitrogen atmosphere for 17.5 h. As indicated by ^{19}F NMR, the reaction was complete and the light tan liquid product comprised **4** (98%) and hexafluorobenzene (2%). Distillation through a Vigreux column (6 x 1/2") gave a colorless diene, b.p. 24_{15}-$26^{o}{}_{10}$, still contaminated with a little of the benzene. A pure sample was prepared by preparative gas chromatography (oven temp. 60-150°, 30°/min; inj., 200°; det. 250°). IR (neat): 1755, 1705, 1405, 1360, 1305, 1200, 1000, 915, 880, 845, 755 cm^{-1}. MS m/e: 318 (M^+), 233 ($C_7F_6Cl^+$), 186 ($C_6F_6^+$, base), 179 ($C_7F_5^+$), 132 ($C_2F_2Cl_2^+$), 117 ($C_5F_3^+$), 93 ($C_3F_3^+$), 69 (CF_3^+). Analysis: Found: C, 29.90; Cl, 22.12; F, 47.31%. $C_8F_8Cl_2$ requires C, 30.12; Cl, 22.23; F, 47.65%.

General procedure for irradiations

Solutions of dienes **1** - **5** in acetonitrile, typically ~0.1 M, in 5 mm Pyrex NMR tubes were flushed thoroughly with nitrogen and capped snugly. All irradiations were carried out using the light source and water-cooled quartz well described above, with sample tubes mounted close to the well. For triplet sensitization, the solutions also contained ≥ 1.0 mmol benzophenone (typically ~5 equivalents to assure that no light was absorbed by the diene), and a 2 x 2" Corning #7380 340 nm cutoff filter was interposed between the quartz well and the sample.

ACKNOWLEDGEMENTS

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REFERENCES

1 D. Bryce-Smith and A. Gilbert, Tetrahedron, 33 (1977) 2459.

2 M. Zupan and B. Sket, Isr. J. Chem., 17 (1978) 92.

3 D. M. Lemal, J. M. Buzby, A. C. Barefoot, III, M. W. Grayston and E. D. Laganis, J. Org. Chem., 45 (1980) 3118.

4 A. C. Barefoot, III, W. D. Saunders, John M. Buzby, M. W. Grayston and D. M. Lemal, J. Org. Chem., 45 (1980) 4292.

5 M. M. Rahman, B. A. Secor, K. M. Morgan, P. R. Shafer and D. M. Lemal, submitted to J. Am. Chem. Soc.

6 N. J. Turro, Modern Molecular Photochemistry, Benjamin/Cummings, Menlo Park, California, 1978, pp. 589-91.

7 For **1**, G. D. Goldman, T. D. Cohen and D. M. Lemal, manuscript in preparation; for **2**, N. E. Takenaka, R. Hamlin and D. M. Lemal, to be published; for **3**, see [3]; for **5**, see [5].

8 J. A. Barltrop and J. D. Coyle, Principles of Photochemistry, John Wiley, New York, 1975, p 228

9 Diene triplet states tend to distort from planar geometry. A. Devaquet, Topics in Current Chemistry, 54 (1975) 1.

10 This point was clearly made in an early paper on cycloadditions of haloolefins to dienes by P. D. Bartlett, L. K. Montgomery and B. Seidel, J. Am. Chem. Soc., 86 (1964) 616.

11 D. H. R. Barton, Helv. Chim. Acta, 42 (1959) 2604.

12 R. A. Caldwell, J. Org. Chem., 34 (1969) 1886.

13 D. I. Schuster and D. J. Blythin, J. Org. Chem., 35 (1970) 3190.

14 For a recent review of intramolecular diene photochemistry, see W. H. Laarhoven in A. Padwa (ed.), Organic Photochemistry, Vol. 9, Marcel Dekker, New York, 1987, Ch. 2, p. 129.