prepared from the corresponding ketones with CH_3MgI. The preparation of 12-*exo*-CH_3-*endo*-OH is typical. To the Grignard reagent, prepared from 0.5 g of Mg and 3.0 g of CH_3I in 15 mL of absolute ether is added 3.0 g of ketone 6-oxo, and the mixture is refluxed for 2 h. After the usual workup, the crude product is purified by distillation in vacuo, bp 84 °C (1 Torr) to give 2.5 g (76%) of an oil.

The methylene compounds 12-CH_2 and 13-CH_2 were prepared from the corresponding ketones by the Wittig reaction. The preparation of 13-CH_2 is typical. The Wittig reagent was prepared from 11.5 g of triphenylphosphonium bromide and 30 mL of *n*-butyllithium (15%) in 100 mL of absolute THF under an N_2 atmosphere. 6-oxo, 4.0 g, dissolved in 80 mL of absolute THF is added and the mixture stirred for 25 h at room temperature. H_2O is added and the product extracted with ether. After the usual workup, distillation in vacuo, bp 71–75 °C (15 Torr), gave 2.0 g (51%) of a liquid product.

Tertiary alcohols 12-*endo*-CH_3-*exo*-OH and 13-*endo*-CH_3-*exo*-OH are obtained from the corresponding methylene compounds by oxymercuration/demercuration using the standard procedure described above.

The four 3,5-dinitrobenzoates 12-*exo*-CH_3-*endo*-ODNB, 12-*endo*-CH_3-*exo*-ODNB, 13-*exo*-CH_3-*endo*-ODNB, and 13-*endo*-CH_3-*exo*-ODNB were prepared from the corresponding alcohols by the standard procedure. They were crystallized several times from ligroin. Some of the physical properties of the compounds are summarized in Table VII.

Acknowledgment. A travel scholarship from the DAAD to one of us (Y.A.) was helpful for this work. The work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Registry No. 3-OBs, 840-88-0; 3-OTs, 959-42-2; 4-OBs, 840-89-1; 4-OTs, 840-90-4; 6-*exo*-OBs, 60494-06-6; 6-*endo*-OBs, 60537-04-4; 6-*exo*-OAc, 67594-59-6; 6-*exo*-OH, 67594-60-9; 7-*exo*-OTr, 60494-07-7; 7-*endo*-OTr, 60494-08-8; 7-*exo*-OAc, 111718-77-5; 7-*exo*-OH, 111718-78-6; 9-*exo*-CN-*exo*-OBs, 78376-59-7; 9-*exo*-CN-*endo*-OBs, 78419-47-3; 9-*endo*-CN-*exo*-OBs, 78419-48-4; 9-*endo*-CN-*endo*-OBs, 78376-60-0; 9-*exo*-CN-*exo*-OH, 60178-80-5; 9-*endo*-CN-*exo*-OH, 60209-06-5; 11-OBs, 111718-76-4; 11-OH, 111819-64-8; 12-*endo*-ODNB, 60537-05-5; 13-ODNB, 111819-63-7; 14-*exo*-ODNB, 60494-09-9; 14-*endo*-ODNB, 60494-10-2; 2-norbornyl cation, 24321-81-1.

Notes

Addition of Fluorenylidene to Hexafluorobenzene and an Answer to the Question: How Does Hexafluorobenzene Influence the Reactions of Diazofluorene with Olefins?

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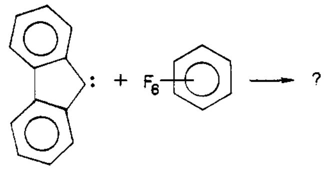
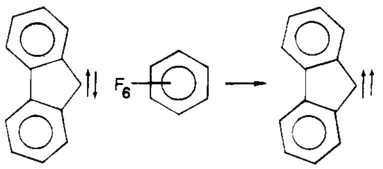
Received May 26, 1987

The structure of the product of addition of fluorenylidene to hexafluorobenzene is of interest in relation to the question: How does hexafluorobenzene influence the reactivity of fluorenylidene toward olefins?



Jones and Rettig suggested that hexafluorobenzene was an inert moderator, increasing the number of nonreactive collisions of the carbene and thus enhancing the relaxation of excited singlet to ground-state triplet fluorenylidene.[1]



That hexafluorobenzene is *not* inert to fluorenylidene, however, is clear from the report by Griller et al. that an adduct is formed in ca. 20% yield, but no structural information was provided.[2] Direct kinetic measurements on triplet fluorenylidene by Griller and Schuster established that hexafluorobenzene is ca. 1–2 orders of magnitude *less* reactive toward the carbene than more traditional trapping agents such as monoolefins, dienes, and alcohols.[2,3] The reaction of fluorenylidene with hexafluorobenzene is, however, quite rapid, the lifetime of the triplet carbene in C_6F_6 being only 95 ns.[3]

We have found that the presence of hexafluorobenzene dramatically alters the stereochemistry of fluorenylidene addition to *cis*-1,2-dichloroethylene.[4] We also observed that chemical combination of fluorenylidene and hexafluorobenzene at low temperature leads to a species whose ESR spectrum could be recorded, but whose structure could not be assigned from the spectrum.[4] These observations led to the suggestion that the role of hexafluorobenzene might be to reversibly form a complex that could act as a carbenoid, mimicking a triplet carbene.[4] Such a complex could also give rise to the previously uncharacterized stable adduct of fluorenylidene to hexafluorobenzene noted by Griller and ourselves,[2,4] and we thus set out to establish its structure.

Results and Discussion

Irradiation of 0.05 M solutions of diazofluorene in hexafluorobenzene with the uranium glass-filtered radiation from a 450-W medium-pressure mercury lamp yielded two major products, bifluorenylidene (40%), and 2,3,4,5,6,7-

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[1] Jones, M., Jr.; Rettig, K. R. *J. Am. Chem. Soc.* **1965**, *87*, 4013 and 4015.

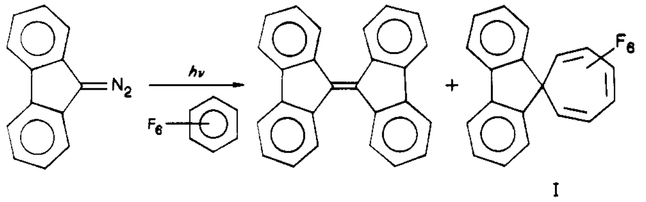
[2] Griller, D.; Montgomery, C. R.; Scaiano, J. C.; Platz, M. S.; Hadel, L. *J. Am. Chem. Soc.* **1982**, *104*, 6813.

[3] Zupancic, J. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1980**, *102*, 5958.

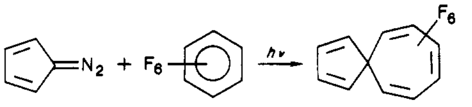
[4] Gaspar, P. P.; Lin, C.-T.; Whitsel Dunbar, B. L.; Mack, D. P.; Balasubramanian, P. *J. Am. Chem. Soc.* **1984**, *106*, 2128.

0022-3263/88/1953-0675$01.50/0

hexafluorospiro[cyclohepta-2,4,6-triene-1,9′-fluorene] (I) (27% and 36%). A ca. 0.5% yield of another fluorine-containing product was detected by ^{19}F NMR spectroscopy, but was not isolated or identified.

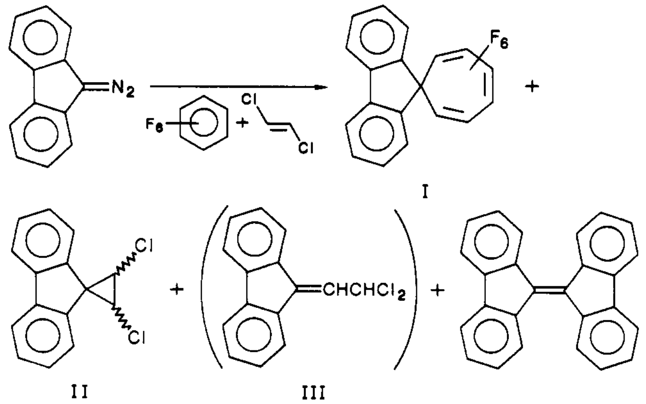


Product I, while in an impure state, is rather unstable, and this may have led to earlier reports that several products resulted from reaction of fluorenylidene and hexafluorobenzene.[4] The spiro adduct I was isolated by flash chromatography and purified by recrystalization. That it has the structure of a cycloheptatriene rather than a norcaradiene was suggested by comparison of its ^{19}F NMR spectrum with that of the cyclopentadienylidene adduct to hexafluorobenzene earlier reported.[5]



The structure of I was fully elucidated by single-crystal X-ray diffraction analysis. The puckered seven-member ring of I is seen clearly in Figure 1. The C_2–C_1–C_7 bond angle is 109.4° and the C_2–C_7 bond distance is 2.48 Å, both incompatible with a norcaradiene structure. The bond distances within the cycloheptatriene ring alternate as expected: $r(C_1–C_2) = 1.526$ (5) Å, $r(C_2–C_3) = 1.313$ (5) Å, $r(C_3–C_4) = 1.444$ (6) Å, $r(C_4–C_5) = 1.323$ (5) Å, $r(C_5–C_6) = 1.432$ (6) Å, $r(C_6–C_7) = 1.322$ (5) Å, $r(C_7–C_1) = 1.518$ (5) Å.

To determine relative reactivity, competition experiments were carried out with mixtures of *trans*-1,2-dichloroethylene and hexafluorobenzene as substrates for reaction with diazofluorene. From an 80:20 mol % mixture of C_6F_6 and *trans*-1,2-dichloroethylene, a 13% yield of I was obtained together with a combined yield of 16% of the cyclopropane adducts (90% trans, 10% cis) II of 1,2-dichloroethylene and a 23% yield of bifluorenylidene.



Special means are required to detect the other known product from this system, 9-(2,2-dichloroethylidene)fluorene (III), due to interferences in the ^1H NMR spectrum,[4] and its yield was not determined in these experiments. From a 60:40 mol % mixture of C_6F_6 and *trans*-$C_2H_2Cl_2$, the yields of I, II, and bifluorenylidene were 9%, 27%, and 20% respectively.

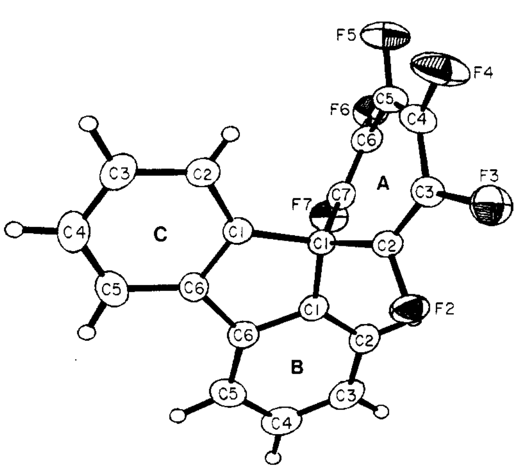
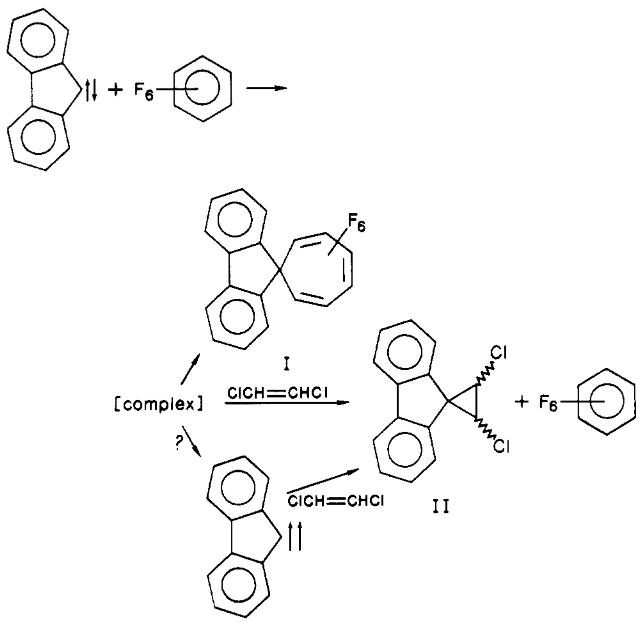


Figure 1. ORTEP drawing of 2,3,4,5,6,7-hexafluorospiro[cyclohepta-2,4,6-triene-1,9′-fluorene].

Scheme I



From both these experiments *trans*-1,2-dichloroethylene is seen to be ca. 5 times as reactive as hexafluorobenzene with respect to product formation, and this is the same relative reactivity that was previously gauged from the effect of hexafluorobenzene on the stereospecificity of cyclopropanation of *cis*-1,2-dichloroethylene.[4] This suggests that both the formation of the hexafluorobenzene adduct I and the decrease in the stereospecificity of cyclopropanation of *cis*-1,2-dichloroethylene are related to reaction of fluorenylidene with hexafluorobenzene, forming an intermediate complex.

Two effects are possible and are illustrated in Scheme I.

While the intermediate complex might be thought to act as a catalyst for the conversion of singlet to triplet fluorenylidene, this role seems unlikely, given the weight of the evidence previously presented for rapid intersystem crossing from singlet to triplet fluorenylidene.[3,4] It is more probable that the complex reacts directly with the 1,2-dichloroethylenes, acting as a carbenoid. Such a scheme gives rise to the observed linear decrease in the stereospecificity of cyclopropanation of *cis*-$C_2H_2Cl_2$ already reported[4] and the apparent nonlinear increase in the yield of I with increasing C_6F_6 concentration observed in the present experiments.

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(5) Jones, M., Jr. *J. Org. Chem.* **1968**, *33*, 2338.

Conclusion

In summary, we have determined that a single adduct with a tropilidene structure, 2,3,4,5,6,7-hexafluorospiro[cyclohepta-2,4,6-triene-1,9′-fluorene] (I), is formed from photolysis of diazofluorene in hexafluorobenzene. The relative reactivity of hexafluorobenzene and *trans*-1,2-dichloroethylene toward fluorenylidene determined from product ratios in a competition experiment is ca. 1:5, which is similar to the effect of hexafluorobenzene in reducing the fraction of cis cyclopropane adduct from the photolysis of diazofluorene in mixtures of *cis*-1,2-dichloroethylene and hexafluorobenzene. These results suggest that the role of hexafluorobenzene in reducing the stereospecificity of addition by singlet fluorenylidene is to form an intermediate complex that can react as a carbenoid with 1,2-dichloroethylene.

Experimental Section

General Procedures. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-FX100 miltinuclear 100-MHz FT spectrometer. The mass spectrum was recorded on a Finnegan 3200 quadrupole instrument.

Preparation of 9-Diazofluorene. The procedure of Moss and Joyce was utilized.[6] Recrystalization from petroleum ether gave red needles, mp 97–98 °C (lit. mp 98–99 °C).[6]

Irradiation of 9-Diazofluorene in Hexafluorobenzene. 9-Diazofluorene (1.37 g) was dissolved in 140 mL of hexafluorobenzene, producing a solution 0.051 M in diazo compound. This was deoxygenated by bubbling pure nitrogen through it for $^3/_4$ h in an immersion reactor prior to irradiation for 24 h with a 450-W Hanovia medium-pressure mercury lamp from which wavelengths < 330 nm were filtered by a uranium glass sleeve. The lamp and filter sleeve were housed in a water-cooled quartz immersion well. Throughout the irradiation, pure nitrogen was bubbled through the reaction mixture. Following the irradiation, the reaction mixture was concentrated to 20 mL by vacuum distillation, and the remaining hexafluorobenzene was removed by bulb-to-bulb distillation on a vacuum line. The product was isolated by flash chromatography on a 1 × 6 in. silica gel column with *n*-hexane as eluent and recrystalized from *n*-hexane, affording white needles of 2,3,4,5,6,7-hexafluorospiro[cyclohepta-2,4,6-triene-1,9′-fluorene] (I) that turned yellow at 95 °C and melted at 119–120 °C: ^{1}H NMR (C_6D_6) δ 7.37 (m); ^{19}F NMR (C_6D_6) (chemical shifts relative to $CFCl_3$) −120.7 (t, 2 F), 2 F), −155.7 (m, 2 F), −156.9 (m, 2 F); MS (70 eV), *m/e* 352 (1.9), 351 (15.4), 350 (P, 93.4), 349 (23.4), 332 (15.3), 331 (49.2), 330 (16.5), 329 (25.7), 301 (19.4), 300 (100), 299 (10.2), 298 (11.8), 281 (12.2), 280 (28.3), 260 (10.0), 184 (13.9), 183 (95.0), 175 (11.0), 164 (44.4), 163 (46.9), 156 (32.7), 150 (51.7), 149 (22.8), 140 (77.0), 137 (22.1), 131 (17.8), 127 (11.7), 125 (18.9), 117 (12.2), 115 (12.8), 105 (11.0), 99 (11.5), 98 (11.2), 87 (13.6), 86 (11.9), 75 (17.6), 74 (17.9), 69 (13.6), 63 (22.4), 62 (11.0), 51 (18.1), 50 (12.0). Anal. Calcd for $C_{19}H_8F_6$: C, 65.15; H, 2.30; F, 32.56. Found: C, 64.84; H, 2.46; F, 32.74.

X-ray Analysis. The compound I crystallizes in the orthorhombic space group $P2_12_12_1$, with a = 6.736 (4) Å; b = 18.816 (7) Å; c = 11.982 (5) Å; V = 1503 (2) Å^3; Z = 4. A total of 2764 independent reflections were collected at 22 °C on a Nicolet P3 diffractometer with Mo Kα radiation and the omega scan data collection technique with a maximum 2θ angle of 50°. The structure was solved by using the MULTAN direct methods programs and refined by using 1805 reflections with $F_o^2 > 3\sigma(F_o^2)$ to give final discrepancy indices of R = 0.026 and R_w = 0.031 for 258 variables representing 25 anisotropic non-hydrogen atoms and eight hydrogen atoms with fixed isotropic thermal parameters. Tables of data collection and structure solving details and atomic positional and thermal parameters are provided as supplementary material.

Yields. Yields of product I were determined by ^{19}F NMR integration of the signal due to F-2 and F-7 in concentrated reaction mixtures relative to a *p*-nitrofluorobenzene internal standard. In a typical experiment 0.2 g of diazofluorene was dissolved in 20.83 mL of hexafluorobenzene and sealed in a Pyrex ampule after three freeze–pump–thaw cycles on a vacuum line. After 4 h of irradiation as described above, the hexafluorobenzene was removed in vacuo, and the remainder of the reaction mixture was dissolved in C_6D_6 and 5 μL of *p*-nitrofluorobenzene added. Integration of the ^{19}F NMR spectrum gave the product yields upon normalization. The same procedure was employed to obtain the yield of I from competition experiments in which diazofluorene was irradiated in mixtures of hexafluorobenzene and *trans*-1,2-dichloroethylene. The yields of *cis*- and *trans*-2,3-dichlorospiro[cyclopropane-1,9′-fluorene] and bifluorenylidene were determined as previously described[4] by integration of the peaks in the ^{1}H NMR spectrum at δ 4.09 and 4.17 (2 H) for the cyclopropanes and δ 8.15–8.45 (2 H) for the bifluorenylidene relative to 5 μL of toluene as the internal standard. The stereospecificity of cyclopropanation was determined from the ratio of the peaks at δ 4.09 (cis) and 4.17 (trans). Probable errors in the determination of these yields are ±7%.

Acknowledgment. We are grateful to the National Science Foundation for financial support under Grants CHE-8414358 (Washington University) and CHE-8318345 (Princeton).

Registry No. I, 88413-56-3; *cis*-II, 87319-63-9; *trans*-II, 87319-64-0; III, 87319-65-1; C_6F_6, 392-56-3; (*E*)-ClCH=CHCl, 156-60-5; 9-diazofluorene, 832-80-4; bifluorenylidene, 746-47-4; fluorenylidene, 2762-16-5.

Supplementary Material Available: X-ray crystallographic procedures, tables of data collection and structure solving details, and atomic postional and thermal parameters (9 pages); table of structure factors (4 pages). Ordering information is given on any current masthead page.

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[6] Moss, R. A.; Joyce, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 4475.

A Comparative Evaluation of Some Ortho Directing Groups for Cubane

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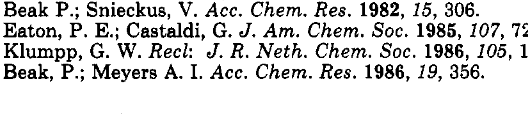
The "ortho lithiation" technique has been widely used for the regiospecific substitution of electrophilic groups in both aromatic and nonaromatic systems.[1-6] This procedure is based upon the observation that certain functional groups X promote the lithiation of an adjacent ("ortho") carbon, which is then susceptible to electrophilic attack.



$$-\overset{X}{\underset{|}{\overset{|}{C}}}-\overset{H}{\underset{|}{\overset{|}{C}}}- \xrightarrow{R-Li} -\overset{X}{\underset{|}{\overset{|}{C}}}-\overset{Li}{\underset{|}{\overset{|}{C}}}- \xrightarrow{E^+} -\overset{X}{\underset{|}{\overset{|}{C}}}-\overset{E}{\underset{|}{\overset{|}{C}}}-$$

The role of the directing group X is believed to include (a) enhancement of the acidity of the α-hydrogens, thus promoting its replacement by Li$^+$, and (b) stabilization of the lithiated intermediate, in which the ortho carbon is

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[1] Gilman, H.; Morton, J. W. *Org. React.* (*N.Y.*) **1954**, *8*, 258.
[2] Gschwend, H. W.; Rodriguez, H. R. *Org. React.* (*N.Y.*) **1979**, *26*,1.
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[4] Eaton, P. E.; Castaldi, G. *J. Am. Chem. Soc.* **1985**, *107*, 724.
[5] Klumpp, G. W. *Recl: J. R. Neth. Chem. Soc.* **1986**, *105*, 1.
[6] Beak, P.; Meyers A. I. *Acc. Chem. Res.* **1986**, *19*, 356.