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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A Comparative Evaluation of Some Ortho Directing Groups for Cubane

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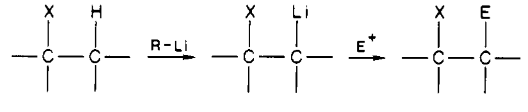
Received April 17, 1987

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.



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.
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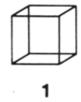
activated toward electrophilic attack by means of an interaction between X and the lithium.[3,5,7] Accordingly, it is anticipated that effective directing groups should be characterized by strong inductive electron-withdrawing tendencies and also by a capacity for coordinating with metals, for example, through lone pairs. Tertiary amide groups, for instance, have been found to be particularly good directing groups.[5-9]

Our objective in this work has been to carry out, by a computational procedure, comparative evaluation of several different functional groups in terms of their abilities to promote ortho substitution on cubane (**1**, a strained polyhedrane system). We have focused particularly upon the ortho-lithiated intermediate that is formed in each case, represented by structure **2a–d**.



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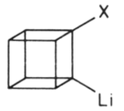

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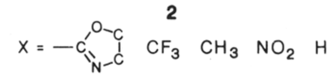

a **b** **c** **d** **e**

The oxazoline and the trifluoromethyl groups (**a** and **b**, respectively) are known to be good directing agents.[3] CH_3 is not expected to show such activity and is included primarily to serve as a point of reference. It would be particularly interesting if NO_2 should show signs of being an effective directing group, since this would have important implications for the synthesis of polynitro polyhedranes.

Methods

We have computed optimized structures for the four molecules **2a–d**, by using an ab initio self consistent field molecular orbital procedure (GAUSSIAN 82).[10] Because of the size of the system being studied, the optimizations were carried out at the STO-3G level. (The structures will be provided for interested readers upon request.) These geometries were used to calculate the STO-5G molecular electrostatic potential of each system in the diagonal plane passing through the two substituted carbons.

The electrostatic potential that is created at any point $\vec{r}$ in the space around a molecule by its nuclei and electrons is expressed rigorously by eq 1. Where Z_A is the charge

$$V(\vec{r}) = \sum_{A} \frac{Z_A}{|\vec{R}_A - \vec{r}|} - \int \frac{\rho(\vec{r}\,')d\vec{r}\,'}{|\vec{r}\,' - \vec{r}|} \qquad (1)$$

on nucleus A, located at $\vec{R}_A$, and $\rho(\vec{r})$ is the electronic density function of the molecule, which we obtain computationally. The first term on the right side of eq 1 represents the contribution of the nuclei, while the second gives that of the electrons. Thus an approaching electrophile will tend initially to go to those regions in which $V(\vec{r})$ is negative, in which the effect of the electrons is dominant, and especially to those points at which $V(\vec{r})$ reaches its most negative (minimum) values. The electrostatic potential is now widely used in interpreting and predicting molecular reactive properties.[11-13] It is important to note that $V(\vec{r})$ is a real physical property and can be determined experimentally as well as computationally.[13]

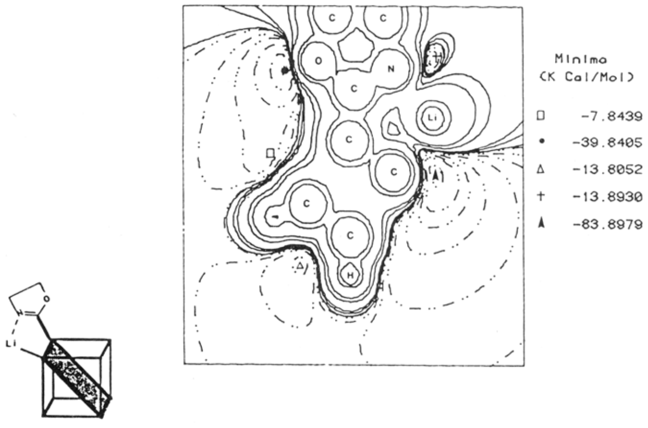

Figure 1. Calculated electrostatic potential of 1-lithio-1-(2-oxazolinyl)cubane (**2a**) in a diagonal plane, as shown. Dashed contours correspond to negative potentials; the zero contour is shown. The magnitude of the other contours are in kcal/mol: −50.2, −37.6, −25.1, −12.5, −6.3, −3.1, −0.6, 3.1, 6.3, 31.4, 62.7, 314.0, 627.0. The locations and values of the minima are indicated.

Results and Discussion

In an earlier study,[7] we presented the electrostatic potential of lithiocubane (**2e**) and pointed out the very unusual feature of a relatively strong negative region (minimum = −38 kcal/mol) associated with a carbon (the one that is lithiated). We showed further that when an amide is present on an adjacent carbon, it interacts with the lithium to stabilize the system. This interaction causes the lithium to shift somewhat toward the amide oxygen; the calculated Li–O separation is 1.80 Å, considerably less than the sum of the lithium and oxygen van der Waals radii, 3.3 Å.[14] As a result, there is created a channel of strongly negative electrostatic potential, with a minimum of −83 kcal/mol, leading to the lithiated carbon. Thus the amide group clearly has the effect of activating the molecule toward electrophilic attack on an ortho carbon. (For a tertiary amide, the channel minimum was −85 kcal/mol.[7])

Figure 1 shows that the situation in the case of 2-lithio-1-(2-oxazolinyl)cubane (**2a**) is very similar to that described above for the amide directing groups. The lithium is shifted toward the oxazoline nitrogen (the Li-N separation is 1.86 Å, with the sum of the van der Waals radii being 3.4 Å),[14] and there is again a strong negative channel leading to the lithiated carbon, with a minimum of −83 kcal/mol. In terms of these factors, then, 2-oxazoline **a** should be a good directing group, as indeed it is known to be.[3]

It is seen in Figure 1 that there are also other negative regions in **2a**, in addition to that associated with the lithiated carbon. These can be attributed to the lone pairs of the oxazoline oxygen and nitrogen and also to the unsubstituted C–C bond. With regard to the latter, we have found that the C–C bonds in strained hydrocarbons in general, and also in some of their derivatives (e.g. **2a**), have negative electrostatic potentials near their midpoints.[15-19]

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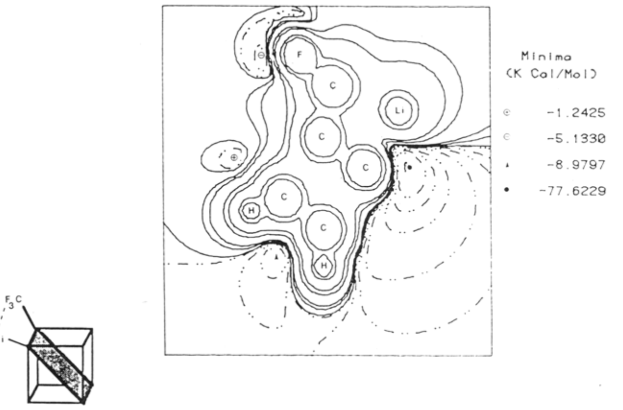

Figure 2. Calculated electrostatic potential of 2-lithio-1-(trifluoromethyl)cubane (**2b**) in a diagonal plane, as shown. Dashed contours correspond to negative potentials; the zero contour is shown. The magnitude of the other contours are in kcal/mol: −50.2, −37.6, −25.1, −12.5, −6.3, −3.1, −0.6, 3.1, 6.3, 31.4, 62.7, 314.0, 627.0. The locations and values of the minima are indicated.

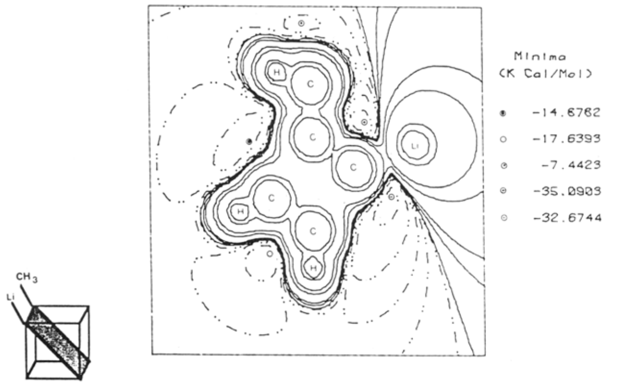

Figure 3. Calculated electrostatic potential of 2-lithio-1-methylcubane (**2c**) in a diagonal plane, as shown. Dashed contours correspond to negative potentials; the zero contour is shown. The magnitude of the other contours are in kcal/mol: −12.5, −6.3, −3.1, −0.6, 3.1, 6.3, 31.4, 62.7, 314.0, 627.0. The locations and values of the minima are indicated.

These are fully consistent with the observed reactive behavior of these molecules toward electrophiles.

In the present context, the key feature of Figure 1 is the negative channel to the lithiated carbon. This represents an important aspect of the activation of the ortho carbon by the 2-oxazoline directing group. When the latter is replaced by CF_3 as the directing agent (structure **2b**), this feature is modified to only a minor extent (Figure 2). The minimum near the ortho carbon is now −78 kcal/mol, which still corresponds to a very significant activation of this position toward electrophilic attack.

In marked constrast is the situation when CH_3 tries to take on the role of the directing group (**2c**). There is now no shifting of the lithium atom and no strongly negative channel to the ortho carbon (Figure 3); the minimum in that spatial region is now −33 kcal/mol. The picture is very much the same as that obtained earlier for lithiocubane.[7] There is clearly no activation of the ortho position.

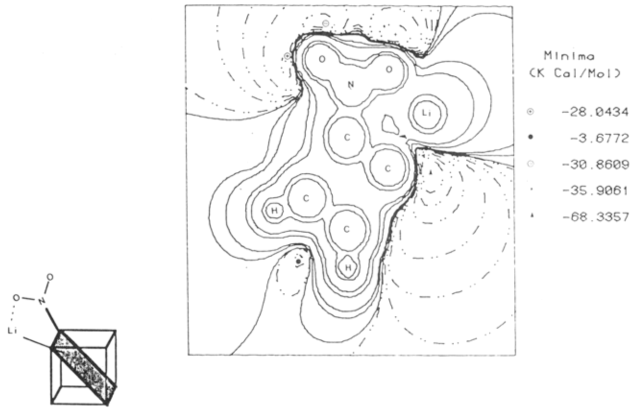

Figure 4. Calculated electrostatic potential of 2-lithio-1-nitrocubane (**2d**) in a diagonal plane, as shown. Dashed contours correspond to negative potentials; the zero contour is shown. The magnitude of the other contours are in kcal/mol: −37.6, −25.1, −12.5, −6.3, −3.1, −0.6, 3.1, 6.3, 31.4, 63.0, 314.0, 627.0. The locations and values of the minima are indicated.

Finally, Figure 4 shows the electrostatic potential for 2-lithio-1-nitrocubane (**2d**). There is again an interaction between the two substituents; the lithium is only 1.76 Å from the oxygen, while the sum of the van der Waals radii is 3.3 Å.[14] This produces a channel of negative potential to the lithiated (ortho) carbon, with a minimum of −68 kcal/mol (compared to −38 kcal/mol in that region for lithiocubane, without any second substituent). Thus NO_2 does definitely activate the ortho position toward electrophilic attack, although not as well as 2-oxazoline and CF_3.

Summary

We have carried out a computational assessment of the relative ortho directing powers of four different functional groups in terms of their tendencies to interact with an adjacent lithium substituent, thereby producing a channel of strongly negative electrostatic potential leading to the lithiated (ortho) carbon. In terms of the factors examined in this analysis, it appears that the nitro group should have at least a moderate ortho-directing capability.

Acknowledgment. We greatly appreciate very helpful discussions with Dr. Jane S. Murray. We also thank the U.S. Army Research Office for partial support of this work.

Registry No. **2a**, 111976-24-0; **2b**, 111976-25-1; **2c**, 111976-26-2; **2d**, 111976-27-3; CF_3, 2264-21-3; NO_2, 10102-44-0; CH_3, 2229-07-4; 2-oxazoline, 504-77-8.

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Isolation of a Ketene Imine from the Decomposition of a Vinyl Azide

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Received June 22, 1987

Hassner and co-workers[1] have discussed recently the thermolysis of vinyl azides and suggested empirical rules for the formation of azirines and rearranged nitriles in this reaction. Whereas the thermal or photochemical loss of nitrogen is most likely a concerted process leading to an azirine,[2] formation of nitriles or of heterocyclic compounds

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