H, 8.20; N, 4.56; S, 10.43. Found: C, 46.83; H, 8.15; N, 4.33; S, 10.36.

3(*S*)-[1(*R*)-(*tert*-Butyldimethylsiloxy)ethyl]-4-(*R*)-[[(ethylthio)thiocarbonyl]thio]-2-oxoazetidinone (11). Sodium hydroxide (11.8 g, 0.296 mol) was dissolved in water (170 mL) and cooled to 2 °C. Ethanethiol (24.5 mL, 0.318 mol) was added over 5 min, and the solution stirred for 30 min. Carbon disulfide (26.7 mL, 0.444 mol) was then rapidly charged, and the yellow solution stirred for 60 min. Sulfone 1 (22.7 g, 0.074 mol) in methylene chloride (340 mL was added in one portion to the rapidly stirring 0 °C solution which was allowed to warm to 20 °C. After 18 h the reaction was complete, and the phases were separated. The aqueous layer was extracted with methylene chloride (2 × 125 mL). The combined organic extracts were washed with water (2 × 125 mL) and dried over Na_2SO_4. A yellow solid (24.1 g) was obtained upon solvent removal under vacuum. Recrystallization from hexane (410 mL) afforded yellow "cottonlike" crystals (18.15 g, 67%), mp 122-123 °C; IR ($CHCl_3$) 3411, 2950, 2928, 2857, 1776, 1462, 1083 cm^{-1}; ^1H NMR (250 MHz) 6.59 (b s, 1 H), 5.67 (d, J = 2.5 Hz, 1 H) 4.29 (m, 1 H), 3.37 (q, J = 7.4 Hz, 2 H), 3.21 (t, J = 3 Hz, 1 H), 1.37 (t, J = 7.4 Hz, 3 H), 1.21 (d, J = 6.2 Hz, 3 H), 0.88 (s, 9 H), 0.08 (s, 6 H). Anal. Calcd for $C_{14}H_{27}NO_2S_3Si$: C, 45.99; H, 7.44; N, 3.83; S, 26.31. Found: C, 46.05; H, 7.21; N, 3.82; S, 26.83.

Supplementary Material Available: Coordinates and bond distances and angles for 1 (1 page). Ordering information is given on any current masthead page.

Rearrangements of Azidoquinones. Generation of a Benzyne Intermediate

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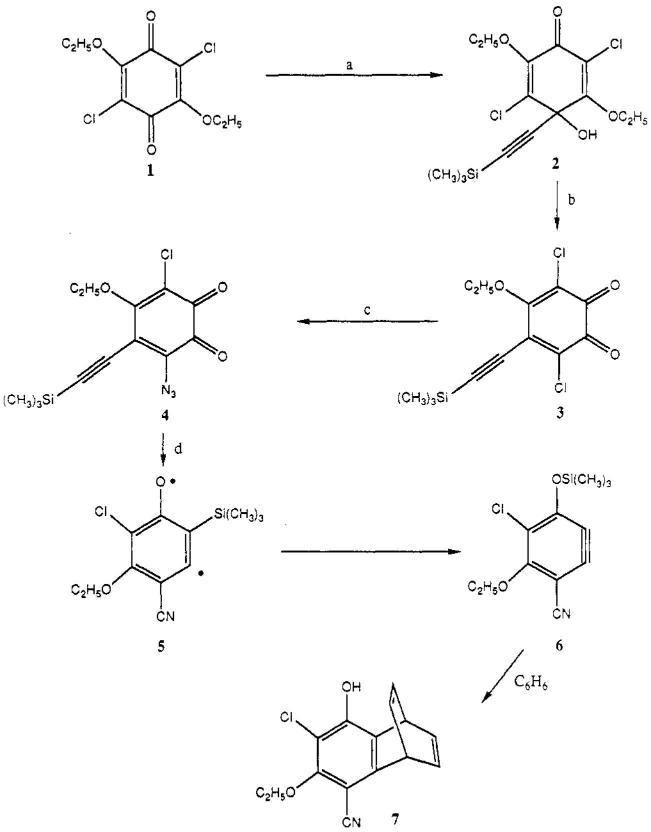
Reported here is a rearrangement envisaged to involve the unique generation of a benzyne intermediate from an azidoquinone precursor.[1] Specifically, 3-azido-6-chloro-5-ethoxy-4-[(trimethylsilyl)ethynyl]-1,2-benzoquinone (4) was prepared as outlined in Scheme I (1 → 2 → 3 → 4) and subjected to thermolysis in refluxing benzene; the bicyclic compound 7 was thus obtained in 38% isolated yield.[2] This unusual transformation is considered to proceed via the diradical intermediate 5, which suffers a trimethylsilyl shift from carbon to oxygen to give the benzyne 6. This then undergoes a Diels-Alder cycloaddition to the solvent resulting in adduct 7.

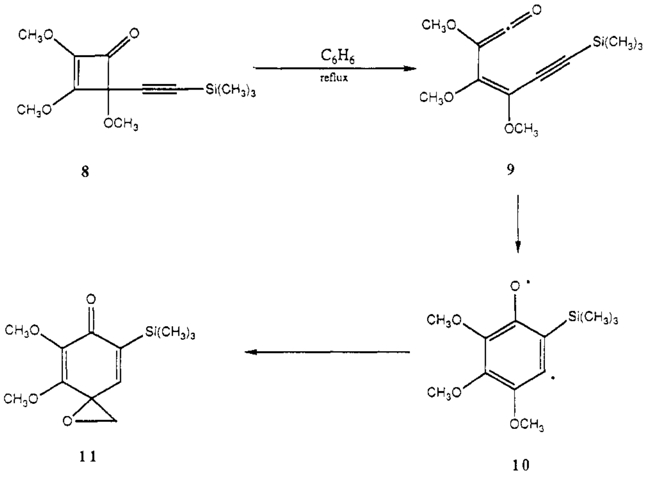
The structure of 7 is based upon its characteristic spectral properties. Of particular importance is the ^1H NMR and ^{13}C NMR data. The former shows absorptions due to the two bridgehead and four vinyl protons as two symmetrical multiplets at 5.25-5.29 and 5.36-5.39 and as a multiplet at 6.89-6.91 ppm, and the latter showed two vinyl carbon absorptions as required by the symmetry of structure 7. Thus, the [4 + 2] cycloaddition of 6 to benzene rather than a [2 + 2] mode is established.

Scheme I



[a] Lithium (trimethylsilyl)acetylide, THF, −78 °C. [b] TFAA, H_2SO_4, ambient temperature. [c] Na N_3, acetone, −78 °C. [d] Refluxing benzene.

Scheme II



The mechanism suggested above for the conversion of 4 to 7 finds precedence with respect to the formation of the diradical 5 and the cycloaddition of benzynes to benzene.[3,4] However, to our knowledge, formation of benzyne 6 from the diradical 5 is unique.

For comparison, it is of interest to note that the related diradical 10 (Scheme II) does not rearrange to a benzyne intermediate.[3] This diradical was generated from the cyclobutenone 8, which upon electrocyclic ring opening gives ketene 9, and this subsequently leads to the diradical 10. Rather than silyl migration to a benzyne, this diradical undergoes an intramolecular hydrogen atom transfer and

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(1) Azidoquinones have received extensive study and have been observed to function as precursors to a variety of other products. However, no example of their conversion to benzynes has been reported. For reviews of azidoquinone chemistry see: (a) Moore, H. W. *Chem. Soc. Rev.* **1973**, *2*, 415. (b) Moore, H. W.; Decker, O. H. W. *Chem. Rev.* **1986**, *86*, 821.

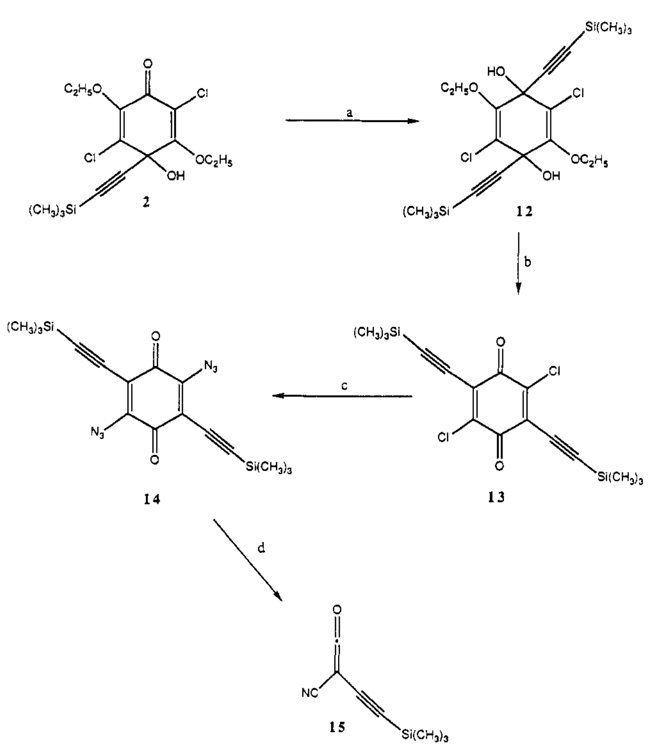
(2) Synthesis of substituted quinones by this method has been reported previously. See: Moore, H. W.; Sing, Y. L.; Sidhu, R. S. *J. Org. Chem.* **1980**, *45*, 5057.

(3) Foland, L. D.; Karlsson, J. O.; Perri, S. T.; Schwabe, R.; Xu, S. L.; Patil, S.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 975.

(4) For an example of the [4 + 2] cycloaddition of benzyne to benzene see: Friedman, L.; Lindow, D. F. *Ibid.* **1968**, *90*, 2329.

0022-3263/90/1955-0370$02.50/0

Scheme III



^{a}NaH, THF, 0 °C; lithium (trimethylsilyl)acetylide, THF, −78 °C. ^{b}NH$_4$Cl. ^{c}NaN$_3$, acetone, 0 °C. ^{d}Refluxing benzene.

ultimately gives the spiroepoxide **11**.

In an attempt to extend the benzyne synthesis outlined here, 2,5-diazido-3,6-bis[(trimethylsilyl)ethynyl]-1,4-benzoquinone (**14**) was prepared (**2** → **12** → **13**) and subjected to thermolysis (refluxing benzene) in the presence of diphenylacetylene (Scheme III). On the basis of analogies from our laboratory, **14** was anticipated to give the alkynyl ketene **15**, which in turn was expected to lead to a diradical directly related to **5** via an electrocyclic ring opening of 4-[(trimethylsilyl)ethynyl]-4-cyano-2,3-diphenylcyclobutenone to the corresponding conjugated ketene intermediate.[5] Unfortunately, a complex mixture of products resulted from this experiment. As a result, at this time the generation of benzynes via the migration of trialkylsilyl groups in diradicals of structural type **5** may be limited in synthetic scope. Nevertheless, the conversion of **4** to **7** remains an interesting mechanistic puzzle.

Experimental Section

2,5-Dichloro-3,6-diethoxy-4-hydroxy-4-[(trimethylsilyl)ethynyl]-2,5-cyclohexadien-1-one (2). A solution of 2.69 mL (0.019 mol) of (trimethylsilyl)acetylene in 75 mL of dry THF, under an argon atmosphere, was stirred at −78 °C while 16 mL of *n*-butyllithium (1.19 M in hexanes) was added dropwise. The solution was stirred for 15 min and then transferred slowly, via cannula, to a rapidly stirred solution of 5.0 g (0.019 mol) of 2,5-dichloro-3,6-diethoxy-2,5-cyclohexadiene-1,4-dione (**1**) in 300 mL of dry THF at −78 °C. The stirring was continued for 2 h at −78 °C before the reaction was quenched with 100 mL of 10% ammonium chloride. The THF layer was washed twice with water, dried over anhydrous magnesium sulfate, and concentrated. The residue was absorbed onto silica gel and subjected to flash chromatography (4:1 dichloromethane/hexanes) to give 3.75 g (53%) of light yellow crystals; mp 103–104 °C; ^{1}H NMR δ 4.77 (dq, J = 2.8, 7 Hz, 1 H), 4.59 (dq, J = 2.8, 7 Hz, 1 H), 4.19 (dq, J = 2.5, 7 Hz, 1 H), 4.10 (dq, J = 2.5, 7 Hz, 1 H), 3.44 (s, 1 H), 1.46 (t, J = 7 Hz, 3 H), 1.36 (t, J = 7 Hz, 3 H), 0.10 (s, 9 H); IR 3380 (br), 2980 (m), 2900 (w), 1650 (s), 1580 (s), 1280 (s), 1020 (s) cm^{-1}; MS, m/z 326 (EI), 327 (CI); MS exact mass calcd for $C_{15}H_{20}Cl_2O_4Si$ 362.05077, found 362.0501.

3,6-Dichloro-4-ethoxy-5-[(trimethylsilyl)ethynyl]-3,5-cyclohexadiene-1,2-dione (3). A solution of 1.0 g (2.76 mmol) of **2** in 75 mL of ethyl ether was stirred at room temperature while 0.47 mL (3.31 mmol) of trifluoroacetic anhydride was added. The solution was stirred for 15 min before 1 drop of concentrated sulfuric acid was added. After an additional 15 min of stirring, the solution was washed twice with water, dried over anhydrous magnesium sulfate, and concentrated. Recrystallization from ether/hexanes affords 0.80 g (92%) of red crystals; mp 90–91 °C; ^{1}H NMR 4.61 (q, J = 7 Hz, 2 H), 1.49 (t, J = 7 Hz, 3 H), 0.31 (s, 9 H); IR 1670 (s), 1590 (m), 1530 (m), 1290 (s), 840 (s) cm^{-1}; MS, m/z 318 (EI) (hydroquinone), m/z 319 (CI) (hydroquinone); MS exact mass calcd for $C_{13}H_{14}Cl_2O_3Si$ 316.00891, found 316.0078.

3-Azido-6-chloro-4-ethoxy-5-[(trimethylsilyl)ethynyl]-3,5-cyclohexadiene-1,2-dione (4). A solution of 0.10 g (0.32 mmol) of **3** in 20 mL of acetone was stirred at −78 °C. Sodium azide (22.8 mg, 0.35 mmol) was dissolved in 1 mL of water. The azide solution was added to **3**. After stirring for an hour, the reaction mixture was diluted with ether. The solution was washed twice with water, dried over anhydrous magnesium sulfate, and concentrated to give 0.10 g (97%) of a purple liquid: ^{1}H NMR δ 4.58 (q, J = 7 Hz, 2 H), 1.47 (t, J = 7 Hz, 3 H), 0.29 (s, 9 H); IR 2980 (w), 2100 (s), 1670 (s), 1580 (s), 1530 (m), 1010 (s), 840 (s) cm^{-1}; MS, m/z 267 (EI ketene), 296 (CI, nitrene), 268 (CI, ketene).

2-Chloro-4-cyano-3-ethoxy-1-hydroxy-5,8-dihydro-5,8-ethenonaphthalene (7). A solution of 0.24 g (0.74 mmol) of **4** in 75 mL of dry benzene was added dropwise to 400 mL of refluxing benzene while under an argon atmosphere. The solution was heated at reflux for 2.5 h. The reaction mixture was concentrated, and the residue absorbed onto silica gel and subjected to flash chromatography (7:3 hexanes/ethyl acetate) to afford 75 mg (38%) of tan crystals: mp 121–121.5 °C; ^{1}H NMR δ 6.89–6.91 (m, 4 H), 6.18 (s, 1 H), 5.36–5.39 (m, 1 H), 5.25–5.29 (m, 1 H), 4.16 (q, J = 7 Hz, 2 H), 1.44 (t, J = 7 Hz, 3 H); ^{13}C 183.33, 153.36, 153.32, 148.87, 140.09, 139.17, 130.48, 111.02, 96.16, 71.26, 47,50, 42.68, 15.57; IR 3360 (br), 3060 (w) 2980 (m), 2210 (s), 1580 (s), 1430 (s), 1170 (s), 1100 (s), 1020 (s), 740 (s), 700 (s) cm^{-1}; MS, m/z 273 (EI), 274 (CI); MS exact mass calcd for $C_{15}H_{12}ClNO_2$ 273.055 64, found 273.0558.

2,5-Dichloro-3,6-bis[(trimethylsilyl)ethynyl]-2,5-cyclohexadiene-1,4-dione (13). A solution of 3.0 g (8.29 mmol) of **2** in 300 mL of dry THF, under an argon atmosphere, was stirred at 0 °C while 0.36 g (9.12 mmol) of sodium hydride was added. To the solution was added dropwise, via cannula, lithium (trimethylsilyl)acetylene that had been prepared from the addition of 7.3 mL (1.19 M in hexanes) of *n*-butyllithium to a solution of 1.29 mL (9.12 mmol) of (trimethylsilyl)acetylene in 75 mL of dry THF at −78 °C. After the addition was completed, the solution was stirred for 45 min at 0 °C before being quenched with 100 mL of 10% ammonium chloride. The organic layer was washed twice with water, dried over anhydrous magnesium sulfate, and concentrated. The residue was dissolved in 150 mL of THF and stirred at room temperature while 1 mL of concentrated sulfuric acid was added. The solution was heated at 64 °C for 1.5 h. The solution was washed once with saturated sodium bicarbonate and three times with water. The organic layer was dried over anhydrous magnesium sulfate and concentrated. The residue was absorbed onto silica gel and subjected to flash chromatography (1:1 dichloromethane/hexanes) to give 1.57 g (52%) of red crystals: mp 167.5–169 °C; ^{1}H NMR δ 0.29 (s, 18 H); IR 3340 (w), 2970 (m), 2900 (w), 1680 (s), 1550 (s), 1280 (s), 1250 (s), 1180 (s), 955 (s), 850 (br) cm^{-1}; MS, m/z 369 (CI), 368 (EI); MS exact mass calcd for $C_{16}H_{18}Cl_2O_2Si_2$ 368.022 23, found 368.0228.

2,5-Diazido-3,6-bis[(trimethylsilyl)ethynyl]-2,5-cyclohexadiene-1,4-dione (14). A solution of 0.25 g (0.68 mmol) of **13** in 30 mL of acetone was stirred at 0 °C while 93 mg (1.43 mmol) of sodium azide in 1 mL of water was added dropwise. After a few minutes, the solution was diluted with water to precipitate out of solution a red solid. Vacuum filtration affords 0.25 g (96%) of a red solid: ^{1}H NMR δ 0.28 (s, 18 H); IR 3300 (w), 2960 (m), 2450 (w), 2260 (m), 2210 (m), 2160 (s), 2100 (s), 1650 (s), 1550

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[5] See the following and references cited therein: Moore, H. W.; Chow, K.; Nguyen, N. V. *J. Org. Chem.* **1987**, *52*, 2537.

(s), 1360 (br), 1280 (br), 1250 (s), 1160 (s), 1010 (s), 920 (s), 850 (br) cm^{-1}; MS, m/z 163 (ketene, EI), 329 (nitrene of hydroquinone, CI), 164 (ketene, CI).

Acknowledgment. We thank the National Institutes of Health (GM-36312 and CA-11890) for financial support of this work.

Registry No. 1, 20764-96-9; 2, 123834-45-7; 3, 123834-46-8; 4, 123834-47-9; 6, 123834-48-0; 7, 123834-49-1; 13, 123834-50-4; 14, 123834-51-5; lithium (trimethylsilyl)acetylide, 54655-07-1; (trimethylsilyl)acetylene, 1066-54-2.

Comparison of Reactions of Difluorocarbene with *cis*- and *trans*-Cyclooctene

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Difluorocarbene is an unusually stable and chemically selective carbene occurring as a ground-state singlet.[1] When generated in situ from triphenylphosphine, difluorodibromomethane, and inorganic fluoride salts in triglyme, it forms cyclopropanes in high yield from tri- and tetraalkyl olefins (e.g., 74–79% from 2,3-dimethyl-2-butene) and in low yield from symmetrically dialkylated olefins (*cis*-2-butene, 6%; *trans*-2-butene, 12%; cyclohexene, 21%).[2,3]

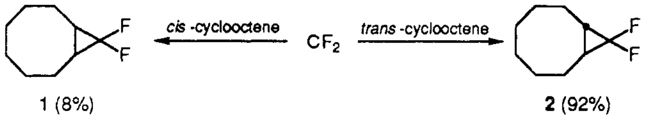
This paper summarizes the findings of an investigation of the reactions of CF_2 generated as above with *cis*- and *trans*-cyclooctene. The main purposes of the investigation are 2-fold: first, investigation of the effect of distortion of an olefinic linkage on the yield of the cyclopropanation reaction; second, generation of an "extra-strained" trans-fused bicyclo[6.1.0]nonane. This idea follows from the effects of geminal fluorines, which lengthen the vicinal bond of a cyclopropane and increase its strain by ca. 10 kcal/mol.[4-8] Thus, while the extra strain in *trans*-bicyclo[6.1.0]octane relative to the cis isomer is at most 1 kcal/mol,[9] it may be possible that inclusion of the fusion-bond-weakening fluoro substituents might enhance this difference.

The use of the Burton method[2] for generating CF_2 was suggested by two factors. First, once the 9,9-difluoro-*trans*-bicyclo[6.1.0]nonane is synthesized, exposure to temperatures above 60 °C might induce geometrical isomerization as observed for *trans*-2,3-dimethyl-1,1-difluorocyclopropane.[4] Secondly, if one were to employ the Seyferth reaction,[10] which involves phase transfer and attack of the alkene by CF_3^-, it is likely that geometrical isomerization would occur prior to ring closure as observed for CCl_2 and CBr_2 attack on *cis,trans*-1,5-cyclooctadiene.[11]

Experimental Section

trans-Cyclooctene was synthesized and purified according to a published procedure.[12] *cis*-Cyclooctene, triphenylphosphine, dibromodifluoromethane, potassium fluoride, and triglyme were obtained from Fluka Chemical Co., and 1-methylcyclohexene was purchased from Aldrich Chemical Co. *cis*-Cyclooctene and 1-methylcyclohexene were distilled prior to use. Triphenylphosphine was recrystallized from absolute ethanol, potassium fluoride was heated in a crucible over a flame and allowed to cool in a vacuum desiccator, and triglyme was dried over 5A molecular sieves. The reaction was carried out according to literature procedures,[3] the crude mixtures were distilled at room temperature at ca. 6 mm, and the distillate was trapped at −78 °C. Subsequent purification was done by gas chromatography (6 ft × $^1/_8$ in. OD ab5 100/110 mesh, apiezon b 5% w/w); column initial temperature 75 °C, increased 20 °C/min to 230 °C; injector 250 °C, detector 280 °C.

Scheme I



7,7-Difluoro-1-methylbicyclo[4.1.0]heptane: mass spectrum, m/e 104 (base peak) ($C_5H_6F_2$), 146 (M) (27), 131 (82), 118 (33), 117 (50), 103 (44), 91 (41), 90 (61), 81 (41), 77 (50), 68 (46), 67 (72), 55 (58); ^{19}F NMR ($CDCl_3$, relative to $CFCl_3$; $CF_3C_6H_5$ was used as an external standard and 63.7 ppm added to place the chemical shifts on the $CFCl_3$ scale) 145.3 (d, 1 F, $^2J_{FF}$ = 151 Hz), 135.9 ppm (dd, 1 F, $^2J_{FF}$ = 152 Hz, $^2J_{HF}$ = 15 Hz); ^1H NMR ($CDCl_3$, TMS): 1.1 ppm (s, 3 H), other peaks 1.05–1.8 ppm (9 H). The Yield based upon the GC chromatogram was 22%.

***cis*-9,9-Difluorobicyclo[6.1.0]nonane (1)**: mass spectrum, m/e 41 (base peak), 160 (M) (5), 90 ($C_4H_4F_2$) (94), 81 (54), 77 (79), 67 (51), 55 (77), 54 (42), 51 (38), 39 (88); ^{19}F NMR [$CDCl_3$, relative to $CFCl_3$ (see above); $CF_3C_6H_5$ was used as external standard] 154.2 (d, 1 F, $^2J_{FF}$ = 151 Hz), 126.1 ppm (dt, 1 F, $^2J_{FF}$ = 151 Hz, $^2J_{HF}$ = 15 Hz). The yield based upon the GC chromatogram was 8%. The ^{19}F NMR spectrum is in agreement with published data on this compound[13] with the larger $^2J_{HF}$ tentatively assigned to the exo fluorine by analogy to the monofluoro analogues.[14] Other spectral data are also published.[10]

***trans*-9,9-Difluorobicyclo[6.1.0]nonane (2)**: mass spectrum, m/e 90 (base peak) ($C_4H_4F_2$), 160 (M) (2.6), 81 (44), 77 (61), 67 (40), 55 (48), 41 (56), 39 (48); ^{19}F NMR [$CDCl_3$, relative to $CFCl_3$ (see above)] 139.0 ppm (broadened singlet with some splitting); ^1H NMR ($CDCl_3$, TMS) 1.0–1.25 (complex group of peaks, 8 H), 1.47 (m, 2 H), 1.9–2.0 ppm (m, 4 H). The yield based upon the GC chromatogram was 92%.

Discussion

The yield of the CF_2 reaction with *trans*-cyclooctene is much higher than for *cis*-cyclooctene (Scheme I). It is probably easiest to understand this in terms of the ionization energies of the olefins[15] and frontier orbital analysis known to be applicable to carbene–olefin reactions.[16] Thus, the adiabatic ionization energies for 2,3-dimethyl-2-butene (8.30 eV), 2-methyl-2-butene (8.67 eV), and 1-methylcyclohexene (8.67 eV) are relatively low. In contrast,

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