3330 (NH), 1750, 1716, and 1683 (C=O); NMR ($CDCl_3$) δ 1.25 (t, 3 H), 3.78 (s, 3 H), 4.25 (q, 2 H), 4.51 (s, 2 H).

Anal. Calcd for $C_{13}H_{16}N_2O_5$: C, 55.70; H, 5.75; N, 9.99. Found: C, 55.74; H, 5.71; N, 9.98.

Elution of the column with benzene–chloroform (1:1) gave an additional 0.2051 g (14.3%) of the above hydrazine.

A second portion of the crude reaction mixture (0.8882 g) was dissolved in 10 mL of ether and stirred for 2 h at room temperature with 10 drops of 5% hydrochloric acid. The solution was dried over magnesium sulfate. The ether was evaporated and the residue was chromatographed on alumina. Elution with benzene–chloroform (7:3) gave 0.4010 g (45.1%) of *N*-carboethoxy-*N*-(carbomethoxymethyl)-*N'*-benzoylhydrazine, mp 78–80 °C. This product was identical with the above pure material (IR, NMR, mmp).

Registry No.—3, 67859-20-5; **6,** 67859-21-6; **8,** 67859-22-7; **9,** 67859-23-8; **10,** 67859-24-9; **11a,** 67859-25-0; **11b,** 67859-26-1; **12a,** 67859-27-2; **12b,** 67859-28-3; **13,** 67859-29-4; **14,** 67859-30-7; **15,** 67859-31-8; *N*-(carbomethoxybenzyl)-*N'*-benzoylhydrazine, 67859-32-9; ethyl benzoylazocarboxylate, 10465-85-7; phenylketene dimethyl acetal, 13049-41-7; phenylketene diethyl thioacetal, 66750-44-5; bromoketene diethyl acetal, 42520-11-6; chloroketene diethyl acetal, 42520-09-2; ketene dimethyl acetal, 922-69-0; benzoylhydrazine, 613-94-5; methyl α-chlorophenylacetate, 7476-66-6; ethyl chloroformate, 541-41-3; 1,1-di(*N*-morpholinyl)ethylene, 14212-87-4; *N*-acetylmorpholine, 1696-20-4; ethyl benzoylhydrazinylcarboxylate, 10465-97-1; 2-(phenylmethylene)-1,3-dioxolane, 4362-17-8.

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Notes

2-Fluoro-3-phenyl-2-cyclobutenylidene. Generation via the Bamford–Stevens Reaction and Addition to Olefins

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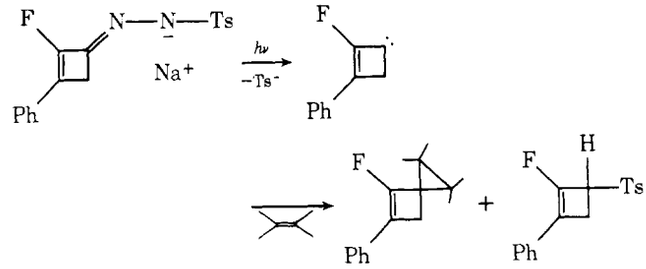
It has been noted that reference to cyclobutenylidene is "conspicuous by its absence from the literature".[1] Only two previous reports pertinent to its chemistry have been noted. Addition to alkenes and alkynes of the species generated by halogen–metal exchange of hexachlorocyclobutene and 3-*H*-pentachlorocylobutene has been found.[2] Unsubstituted cyclobutenylidene, when prepared by deoxygenation of cyclobutenone with atomic carbon, rearranges to vinylacetylene.[3]

While vinylmethylene has been shown by ESR spectroscopy to possess a triplet ground state,[4] the small bond angle at the divalent carbon of cyclobutenylidene and the interaction of the p orbital of the divalent carbon with the π system of the double bond should serve to stabilize the lowest singlet state of cyclobutenylidene.[5] The generation of 2-fluoro-3-phenyl-2-cyclobutenylidene is reported here as well as its stereochemistry of addition and relative reactivity toward several olefins.

2-Fluoro-3-phenyl-2-cyclobutenone was converted to the sodium salt of its tosylhydrazone by standard procedures. When suspensions of the tosylhydrazone salt in olefins were irradiated with ultraviolet light, spirohexenes were formed in high yields, reported in Table I. Irradiation of tosylhydrazone salts in aprotic media has been shown to produce carbenes, via diazoalkanes. Thus we may formulate the transformations as:



Most of the olefin addition products are unstable, darkening within a few hours under air. An adduct of satisfactory analytical purity was obtained only from 1,1-dichloro-2,2-difluoroethylene. The other adducts were characterized spectroscopically immediately after differential precipitation of the only other product detected, the sulfone, which is also pro-

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Table I. Product Yields from Irradiation of the Sodium Salt of 2-Fluoro-3-phenyl-2-cyclobutenone Tosylhydrazone in Various Olefins and Relative Reactivities of the Olefins

substrate	registry no.	yield of spiro-hexene, %[a]	relative reactivity[b]
styrene	100-42-5	71.3	
1,1-dichloro-2,2-difluoro-ethylene	79-35-6	59.1	
cyclohexene	110-83-8	54.9	
cis-2-butene	590-18-1	87.7	
trans-2-butene	624-64-6	80.3	1.0
1,3-butadiene	106-99-0	82.5	4.2
chlorotrifluorethylene	79-38-9	64.5	0.72
trimethylsilylethylene	754-05-2	66.8	0.49

[a] Yields from reaction mixtures containing a single olefin. [b] Based on relative yields from reaction mixtures containing *trans*-2-butene and a second olefin in molar ratios 0.6 to 1.7.

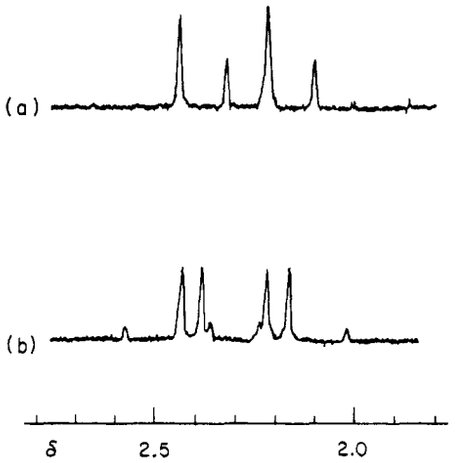
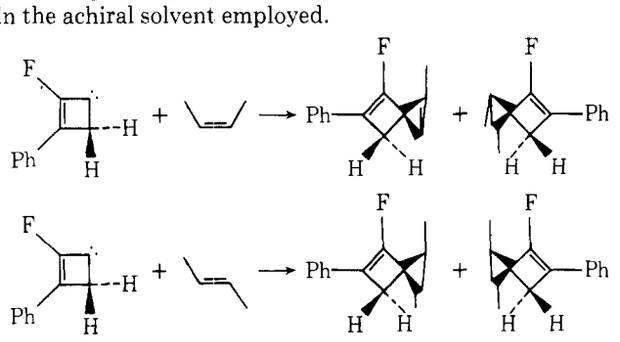


Figure 1. Cyclobutene ring methylene portion of 60 MHz NMR spectra of products of addition of 2-fluoro-3-phenyl-2-cyclobutenylidene to (a) *cis*- and (b) *trans*-2-butene.

duced in yields up to 72% when a suspension of the tosylhydrazone salt in dry tetrahydrofuran is irradiated. Sulfones have been obtained from other tosylhydrazone salts decomposed under aprotic conditions.[6]

Spirohexenes were isolated as stereoisomeric mixtures with less than 10% impurities. Structures were assigned on the basis of ^1H and ^{19}F NMR spectra as well as infrared and ultraviolet spectroscopic data. The transannular coupling between the methylene protons at the 4 position and the fluorine atom at the 2 position of the cyclobutene ring, together with the corresponding chemical shifts, provided a reliable means for ascertaining that a product retained the cyclobutene ring. The NMR splitting patterns for the cyclopropane rings of the product molecules are complex, but isomeric ring-opened unsaturated structures are precluded by the chemical shifts.

The stereochemistry of addition to olefins of the presumed carbene intermediate was examined by studying reactions with *cis*- and *trans*-2-butene. The NMR spectra of the products indicated the formation of a pair of spirohexene products from *cis*-butene and a different product from *trans*-butene. The cyclobutene ring methylene proton signals are illustrated in Figure 1. The spectra are consistent with the formation of a pair of epimeric products from addition to the *cis*-olefin, while addition to the *trans*-olefin gives an enantiomeric pair of products whose NMR spectra are identical in the achiral solvent employed.

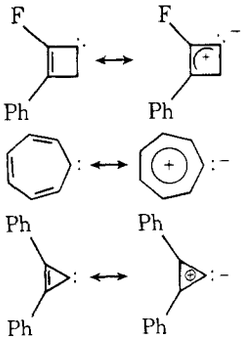


While none of the product from the *trans*-olefin was detected from the *cis*-olefin, and vice versa, the limit of detectability by NMR of the cross product was determined to be 3 to 4%. Thus the stereospecificity of addition is greater than 96%. It may be inferred from the Skell postulate[7] that the cyclobutenylidene underwent addition from a singlet electronic state.

Whether the reacting state is the ground state of the carbene has not been established. Attempts to observe an ESR signal from the triplet state of the carbene following irradiation at 77 K of frozen matrices containing sodium or lithium salts of the tosylhydrazone failed in a variety of hosts including ethers, perfluoro ethers, hydrocarbons and fluorocarbons. Only a free spin signal was observed under conditions which allowed the ESR spectrum of diphenylmethylene to be readily observed from benzophenone tosylhydrazone lithium salt.

When the cyclobutenone tosylhydrazine lithium salt was irradiated in a 2-methyltetrahydrofuran matrix at 77 K a bright yellow color was observed, and an absorption maximum at 390 nm was recorded. The absorption peak and the yellow color disappeared irreversibly when the matrix was thawed for a few seconds and refrozen. The identity of the colored intermediate could not be inferred from the UV spectrum, but the free carbene seems more likely than the related diazo compound, which would be expected to survive the thaw–freeze cycle.

No marked preference for "electron-rich" vs. "electron-poor" olefins was noted when the carbene precursor was irradiated in olefin mixtures (see Table I). Perhaps the effects of the fluorine substituent cause 2-fluoro-3-phenyl-3-cyclobutenylidene to be less nucleophilic than cycloheptatrienylidene[8] and 2,3-diphenylcyclopropenylidene,[9] carbenes for which canonical structures emphasizing the delocalization of the adjacent π system onto the divalent carbon can also be drawn.



The results reported here indicate that the photolysis of the sodium salt of 2-fluoro-3-phenyl-2-cyclobutenone tosylhydrazone generates a species believed to be 2-fluoro-3-phenyl-2-cyclobutenylidene that behaves like a "normal" singlet carbene.

Experimental Section

Spectra. Magnetic resonance spectra were determined on Varian-A60 (protons) and Perkin-Elmer R-10 (^{19}F at 56.4 MHz) spec-

trometers. Fluorine chemical shifts are reported in ppm upfield from trichlorofluoromethane. Infrared spectra were measured on a Perkin-Elmer 457 grating spectrophotometer and ultraviolet spectra on a Carey 14 instrument. Mass spectra were recorded on a Varian M66 cycloidal mass spectrometer.

2-Fluoro-3-phenyl-2-cyclobutenone Tosylhydrazone. 2-Fluoro-3-phenyl-2-cyclobutenone[10] (30.0 g, 0.186 mol) and 34.5 g (0.186 mol) of 4-toluenesulfonylhydrazine in 300 mL of absolute EtOH was refluxed for 2 h. The pale yellow precipitate obtained upon cooling the reaction mixture (crude yield 55.2 g, 90.4%) was recrystallized from EtOH: mp 220.0–220.3 °C; UV (EtOH, nm) λ_{max} 219 (ϵ 2.59 × 10^4), 311 (ϵ 3.43 × 10^4); IR (KBr) 3217 (s), 1720 (s), 1630 (m), 1600 (m), 1495 (s), 1455 (s), 1440 (m), 1420 (s), 1370 (s), 1340 (s), 1175 (s), 1137 (m), 1070 (s), 915 (s), 817 (s), 765 (s), 745 (s), 693 (s) cm^{-1}; NMR (Me_2SO-d_6) δ 7.92–7.40 (multiplet, 9 H, aromatic), 3.78–3.37 (broad singlet, 1 H, N–H), 3.07 (doublet, J_{FH} = 13.20 ± 0.05 Hz, 2 H, cyclobutene CH_2), 2.42 (singlet, 3 H, tosyl CH_3).

Photolysis of the Sodium Salt of 2-Fluoro-3-phenyl-2-cyclobutenone Tosylhydrazone in the Presence of Olefins. Reactions were generally carried out in the Pyrex tube (25 cm long × 3 cm i.d.) in which the sodium salt was prepared. To the base-washed, rinsed, and dried tube was added, under nitrogen, a solution of the tosylhydrazone in 10 mL of dry tetrahydrofuran (THF) and a suspension in 3 mL of dry THF of an equivalent of sodium hydride obtained by washing a 57% oil dispersion of the hydride with dry THF. The mixture was stirred with a magnetic stirring bar for 30 min and then the solvent was removed at room temperature under vacuum (20 μ). Olefin was transferred by trap-to-trap distillation into the reaction tube, and the resulting suspension of the tosylhydrazone sodium salt in olefin was degassed by several freeze–pump–thaw cycles before the tube was sealed. The sealed reaction tube was mounted in a water bath maintained at room temperature next to a quartz immersion well containing a 450-W Hanovia medium-pressure mercury lamp. After irradiation the reaction tube was cooled in a dry ice–acetone bath, opened, and allowed to warm to room temperature with evaporation of excess olefin. The residue was taken up in ether and washed with a saturated sodium chloride solution. Any unreacted starting material appears as a suspension of solid tosylhydrazone and was recovered by filtration. Evaporation of the solvent gave the spirohexenes and a small amount of the sulfone, 1-toluenesulfonyl-2-fluoro-3-phenyl-2-cyclobutene. The sulfone was removed by precipitation with CCl_4, in which the spirohexenes dissolved, and filtration. Evaporation of the CCl_4 gave quite pure products.

1,1-Dichloro-2,2,4-trifluoro-5-phenylspirohex-4-ene. 1,1-Dichloro-2,2-difluoroethylene (25 mL), the sodium salt from 450 mg (1.36 mmol) of 2-fluoro-3-phenyl-2-cyclobutenone tosylhydrazone, and 1 molar equiv of NaH were employed and irradiation lasted 5 h. Tosylhydrazone (34.4 mg, 7.6%) was recovered and 225.1 mg (59.1%) of 1,1-dichloro-2,2,4-trifluoro-5-phenylspirohex-4-ene was obtained as cubic crystals, mp 61–62 °C after recrystallization from boiling EtOH: UV (EtOH, nm) λ_{max} 212 (ϵ 1.78 × 10^4), 218 (ϵ 1.28 × 10^4), 263 (ϵ 2.52 × 10^3); IR (KBr) 1700 (s, cyclobutenyl C=C stretch), 1592 (w), 1492 (s), 1450 (s, phenyl C=C stretch), 1438 (s, cyclobutenyl methylene C–H out-of-plane bend), 1340 (s), 1330 (s), 1310 (s), 1270 (s), 1210 (s), 1185 (m), 1120 (s), 1100 (s), 1085 (m), 1060 (s), 1033 (s, cyclopropyl ring deformation), 1000 (w), 980 (s), 820 (s), 761 (s), 740 (s), 710 (s), 689 (s), 650 (s), 620 (s) cm^{-1}; ^1H NMR (CCl_4) δ 7.32 (singlet, 5 H, aromatic), 2.71 (doublet of doublets, J_{F_1H} = 12.85 ± 0.05, J_{F_2H} 1.65 ± 0.05 Hz, 2 H, cyclobutene CH_2); ^{19}F NMR ($CDCl_3$) δ 95.43 (triplet of doublets, $J_{F_1F_2}$ = 2.93 ± 0.02, J_{F_1H} = 12.52 ± 0.02 Hz, 1 F, cyclobutenyl F_1), 129.29 (doublet, $J_{F_2F_3}$ = 228.4 ± 0.1 Hz, 1 F, cyclopropyl geminate F_3 anti to cyclobutene CH_2), 133.70 (doublet of quintets, $J_{F_2F_3}$ = 228.4 ± 0.1, J_{F_2H} 1.50 ± 0.02, $J_{F_1F_2}$ 2.93 ± 0.02 Hz, cyclopropyl geminate F_2 syn to cyclobutene CH_2); mass spectrum (15 eV) parent ion at *m/e* 278, calculated for $C_{12}H_7F_3{}^{35}Cl_2$ 278, intensity ratio calculated for two chlorines I_{278}–I_{280}–I_{282} = 9.53:6.17:1.00, found 9.51:6.13:1.00. Anal. Calcd for $C_{12}H_7F_3Cl_2$: C, 51.64; H, 2.52. Found: C, 51.86; H, 2.48.

***syn-* and *anti-cis*-1,2-Dimethyl-4-fluoro-5-phenylspirohex-4-ene.** *cis*-2-Butene (12 mL), the sodium salt from 150 mg (0.454 mmol) of tosylhydrazone, and 1 molar equiv of NaH were employed and irradiation lasted 4 h. Tosylhydrazone (20 mg, 13%) was recovered and 9.5 mg (7%) of sulfone isolated. A crude yield of 79.7 mg (87.7%) of a mixture of *syn-* and *anti-cis*-1,2-dimethyl-4-fluoro-5-phenylspirohex-4-ene was purified by column chromatography on neutral alumina with elution by hexane. The colorless liquid product darkened within 1 h in air: UV (EtOH, nm) λ_{max} 233 (ϵ 6.90 × 10^3), 267 (ϵ 1.27 × 10^4); IR (neat, NaCl plates) 1690 (s, cyclobutenyl C=C stretch), 1597 (w), 1493 (s), 1450 (s, phenyl C=C stretch), 1380 (m), 1365 (s), 1345 (s), 1290 (s), 1210 (m), 1170 (s), 1155 (s), 1135 (s), 1085 (s), 1050 (m, cyclopropyl ring deformation), 763 (s), 699 (s, monosubstituted phenyl) cm^{-1}; NMR (CCl_4) δ 7.22 (multiplet, 5 H, aromatic), 2.35 and 2.22 (pair of doublets with identical splitting J_{FH} 13.8 ± 0.1 Hz, 2 H, area ratio of the two doublets 2.4, cyclobutene CH_2, one doublet due to syn the other to anti), 1.24 (multiplet, 8 H, cyclopropyl CH_3 and CH).

***trans*-1,2-Dimethyl-4-fluoro-5-phenylspirohex-4-ene.** *trans*-2-Butene (12 mL), the sodium salt from 150 mg (0.454 mmol) of tosylhydrazone, and 1 molar equiv of NaH were employed and irradiation lasted 3.5 h. Tosylhydrazone (5.2 mg, 3.5%) was recovered and 7.2 mg (5.5%) of sulfone and 70.7 mg (80.3%) of *trans*-1,2-dimethyl-4-fluoro-5-phenylspirohex-4-ene were isolated. Chromatography on alumina gave a colorless product that darkened within an hour. An analytical sample was prepared by a second round of column chromatography followed by preparative thin-layer chromatography on silica gel with elution by *n*-heptane: UV (EtOH, nm) λ_{max} 267 (ϵ 1.26 × 10^4); IR (neat, NaCl plates) 1688 (s, cyclobutenyl C=C stretch), 1595 (m), 1491 (m), 1450 (s, aromatic C=C stretch), 1388 (m), 1350 (s), 1330 (s), 1290 (m), 1185 (m), 1150 (s), 1090 (m), 1050 (m, cyclopropyl ring deformation), 920 (w), 900 (w), 880 (w), 800 (w), 780 (w), 762 (s), 698 (s, monosubstituted phenyl) cm^{-1}; NMR (CCl_4) δ 7.18 (multiplet, 5 H, aromatic), 2.33 (two AB quartets, $J_{FH_a} \simeq J_{FH_b}$ 13.75 ± 0.05, J_{ab} 9.10 ± 0.05 Hz $\Delta\nu_{ab}$ = 0.145 ppm, 2 H, cyclobutene CH_2), 1.50–0.76 (multiplet, 8 H, cyclopropyl CH_3 and CH). Anal. Calcd for $C_{14}H_{15}F$: C, 83.13; H, 7.43. Found: C, 82.20; H, 7.44.

***syn-* and *anti*-Spiro[2-fluoro-3-phenyl-2-cyclobutene-1,7′-norcarane].** Cyclohexene (50 mL), the sodium salt from 1.00 g (3.04 mmol) of tosylhydrazone, and 1 equivalent of NaH was employed and the reaction mixture placed in a Pyrex jacket surrounding the immersion well and deoxygenated with a nitrogen stream. A Pyrex filter sleeve surrounded the mercury lamp during the 4 h irradiation. Spiro[2-fluoro-3-phenyl-3-cyclobutene-1,7′-norcarane] (379 mg, 54.9%) was obtained as a colorless oil upon column chromatography on alumina with hexane eluent: IR (neat, NaCl plates) 1808 (m), 1690 (s, cyclobutenyl C=C stretch), 1594 (m), 1490 (s), 1448 (s, aromatic C=C stretch), 1350–1280 (s, multiplet), 1220 (m), 1177 (s), 1150 (s), 1119 (m), 1110 (m), 1091 (m), 1082 (s), 1065 (m), 1055 (s), 1031 (s), 900 (m), 845 (w), 762 (s), 695 (s, monosubstituted phenyl) cm^{-1}; NMR (CCl_4) δ 7.28 (multiplet, 5 H, aromatic), 2.32 and 2.28 (two doublets, J_{FH} 13.9 ± 0.1 and 14.1 ± 0.1 Hz, 2 H, area ratio of the two doublets 1.5, cyclobutene CH_2 for syn and anti isomers), 2.0–1.1 (multiplet, 10 H, norcarane).

***syn-* and *anti*-4-Fluoro-5-phenyl-1-vinylspirohex-4-ene.** 1,3-Butadiene (50 mL), 300 mg (0.908 mmol) of tosylhydrazone, and 1 equiv of NaH were employed, and irradiation lasted 3.5 h. Sulfone (31.1 mg, 11.3%) and 150.2 mg (82.5%) of 4-fluoro-5-phenyl-1-vinylspirohex-4-ene was obtained as an oil: UV (EtOH) λ_{max} 255 nm (ϵ 2.44 × 10^4); IR ($CHCl_3$, NaCl plates) 1822 (w), 1775 (w), 1690 (s, cyclobutenyl C=C stretch), 1636 (w, vinyl C=C stretch), 1601 (w), 1594 (w), 1451 (m, aromatic C=C stretch), 1390 (w), 1355 (m), 1341 (m), 1330 (m), 1305 (m), 1285 (m), 1220 (s), 1185 (m), 1170 (m), 1145 (m), 1080 (m), 913 (m), 762 (s) cm^{-1}; NMR (CCl_4) δ 8.20–6.90 (multiplet, 5 H, aromatic), 6.20–4.80 (multiplet, 3 H, CH=CH_2), 2.67–2.22 (two AB quartets centered at 2.41, $J_{Fa} \simeq J_{Fb}$ 13.90 ± 0.05 Hz, *syn*-vinyl, and another multiplet centered at 2.47, *anti*-vinyl, 2 H, cyclobutene CH_2), 2.1–0.6 (multiplet, 3 H, cyclopropyl).

***syn-* and *anti*-1-Chloro-1,2,2,4-tetrafluoro-5-phenylspirohex-4-ene.** Chlorotrifluoroethylene (25 mL), 450 mg (1.36 mmol) of tosylhydrazone, and 1 equiv amount of NaH was used and irradiation lasted 4 h. Sulfone (9.8 mg, 2.4%) and 251.4 mg (64.5%) of 1-chloro 1,2,2,4-tetrafluoro-5-phenylspirohex-4-ene (as an oil) were isolated: UV (EtOH) λ_{max} 257 nm (ϵ 2.67 × 10^4); IR (neat, NaCl plates) 1703 (s, cyclobutenyl C=C stretch), 1601 (w), 1497 (m), 1450 (s, aromatic C=C stretch), 1350 (s), 1332 (s), 1315 (m), 1285 (m), 1235 (s), 1190 (m), 1175 (s), 1160 (s), 1135 (s), 1110 (w), 1068 (m), 1035 (s, doublet, C–F stretch), 1005 (m), 990 (m), 980 (m), 920 (w), 855 (s), 840 (s), 768 (s, C–Cl stretch), 745 (s), 698 (s, monosubstituted phenyl) cm^{-1}; NMR ($CDCl_3$) δ 7.60–7.15 (multiplet, 5 H, aromatic), 2.85–2.47 (a pair of doublets centered at 2.68 for the *syn*-chloro isomer, cyclobutene CH_2 coupled to the cyclobutene F, J_{FH} 13.05 ± 0.05 Hz, and to one (syn-) cyclopropyl F, J_{FH} = 1.40 ± 0.05 Hz; also a pair of double doublets centered at 2.60, equal in area to the peaks centered at 2.68, for the *anti*-chloro isomer, cyclobutene CH_2 coupled to two cyclopropyl F's and the cyclobutene F).

***syn-* and *anti*-4-Fluoro-1-trimethylsilyl-5-phenylspirohex-4-ene.** Trimethylvinylsilane (10 mL), 450 mg (1.36 mmol) of tosylhydrazone, and 1 equiv of NaH were employed and irradiation lasted 4.5 h. Sulfone (47 mg, 12%), 7.2 mg of tosylhydrazone (1.8%), and 220.7 mg (66.8%) of 4-fluoro-1-trimethylsilyl-5-phenylspirohex-4-ene were isolated: UV (EtOH, nm) λ_{max} 264 (ϵ 2.02 × 10^4); IR

(neat, NaCl plates) 1823 (m), 1691 (s, cyclobutenyl C=C stretch), 1600 (w), 1495 (m), 1451 (m, aromatic C=C stretch), 1397 (m), 1341 (w), 1325 (m), 1307 (m), 1288 (m), 1268 and 1252 (s, Si–CH_3 deformation), 1222 (s), 1142 (m), 1038 (m), 841 (s, CH_3 rocking), 761 (s, Si–C stretch), 698 (s, monosubstituted phenyl) cm^{-1}; NMR ($CDCl_3$) δ 8.00–6.90 (multiplet, 5 H, aromatic), 2.67–2.26 (two doublets, one centered at 2.50, J_{FH} = 13.40 ± 0.05 Hz, the other at 2.45, J_{FH} = 13.80 ± 0.05 Hz, area ratio 1:3, 2 H, cyclobutene CH_2 for *anti*- and *syn*-$Si(CH_3)_3$ isomers, respectively), 1.34–0.22 (multiplet, 3 H, cyclopropyl), 0.08 (singlet, 9 H, $Si(CH_3)_3$).

***syn*- and *anti*-4-Fluoro-1,5-diphenylspirohex-4-ene.** Freshly distilled styrene (180 mL), the sodium salt from 1.00 g (3.04 mmol) of tosylhydrazone, and 1 equiv of NaH were employed and the irradiation (3.5 h) carried out as described for cyclohexene substrate. Column chromatography on neutral alumina with hexane eluent yielded 540 mg (71.3%) of a mixture of *syn*- and *anti*-4-fluoro-1,5-diphenylspirohex-4-ene as an oil: UV (EtOH) λ_{max} 268 nm (ϵ 3.02 × 10^4); IR (neat, NaCl plates) 1688 (s, cyclobutenyl C=C stretch), 1600 (m), 1494 (s), 1447 (m, aromatic C=C stretch), 1027 (m, cyclopropyl ring deformation), 1940 (w), 1867 (w), 1795 (w), 1735 (w), 760 (s, monosubstituted phenyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.18 (multiplet 10 H, aromatic), 2.40 (a pair of AB quartets, $J_{FHa} \simeq J_{FHb}$ 13.50 ± 0.05, J_{ab} = 8.90 ± 0.05 Hz, $\Delta\nu_{ab}$ = 0.10 ppm, 2 H, cyclobutene CH_2), 2.44–2.05 and 1.77–1.16 (multiplet, 3 H, cyclopropyl); ^{19}F NMR ($CDCl_3$) δ 91.02 (triplet of doublets, $J_{FH_1} \simeq J_{FH_2}$ 14.02 ± 0.02, J_{FH_3} = 2.10 ± 0.02 Hz, 1F, anti), 98.84 (triplet, J_{FH} = 13.80 ± 0.02 Hz, 1F, syn), ratio of peak areas, *anti*-F–*syn*F = 1:2; mass spectrum (15 eV) parent ion at *m/e* 250, calcd for $C_{16}H_{15}F$, 250.

Competition Experiments. Olefin pairs were employed under the reaction conditions used for single olefins, and the reactivity ratios were determined from the ratios of integrated peak areas in the NMR spectra of product mixtures, normalized for the relative substrate concentrations. Peaks used for the determination of yield ratios were well defined in the spectra of both the pure products and in the product mixtures. The olefin pairs each contained *trans*-2-butene together with 1,3-butadiene, chlorotrifluoroethylene, and trimethylvinylsilane, respectively.

Photolysis of the Tosylhydrazone Salt in Tetrahydrofuran. Dry tetrahydrofuran (180 mL), 1.00 g (3.04 mmol) of tosylhydrazone, and 1 equiv of NaH were employed in a Pyrex jacket surrounding the immersion well. Irradiation (3 h) was carried out as described for cyclohexene substrate. *p*-Tolyl 3-(2-fluoro-1-phenyl)cyclobutenyl sulfone (662 mg, 72.4%) was obtained: mp 135.0–135.5 °C after recrystallization from benzene; UV (EtOH) λ_{max} 217 (ϵ 5.73 × 10^4), 230 (ϵ 4.99 × 10^4), 257 nm (ϵ 6.94 × 10^4); IR (KBr) 3025 (m, C–H stretch), 1592 (m), 1490 (m), 1446 (m, phenyl C=C stretch), 1305 (s), 1152 (m, antisymmetric and symmetric stretch, respectively, of S=O in $-SO_2-$), 816 (m), 732 (s), 618 (w), 474 (m, para-substituted phenyl), 766 (s), 694 (s), 605 (m), 436 (m, monosubstituted phenyl), 559 (s, $-SO_2-$ scissor), 507 ($-SO_2-$ wag), 1325 (s, C–F stretch) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.30–7.08 (tolyl AB quartet centered at 7.60, J = 8.8 ± 0.1 Hz $\Delta\nu$-0.49 ppm, and a singlet at 7.30, 9 H, aromatic), 4.55 (quintet of two overlapping triplets, J_{FH} = 6.1 ± 0.1, J_{HH} = 3.1 ± 0.1 Hz, 1 H, CH), 2.64 (doublet of doublets, J_{FH} = 13.8 ± 0.1, J_{HH} = 3.1 ± 0.1 Hz 2 H, CH_2); ^{19}F NMR ($CDCl_3$) δ 92.64 (triplet of doublets, J_{FH_1} = 13.98 ± 0.02, J_{FH_2} 6.23 ± 0.02 Hz); mass spectrum (70 eV) parent ion at *m/e* 302. Anal. Calcd for $C_{17}H_{15}SO_2F$: C, 67.52; H, 5.00. Found: C, 67.35; H, 5.12.

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Registry No.—2-Fluoro-3-phenyl-2-cyclobutenone tosylhydrazone, 56291-31-7; 1,1-dichloro-2,2,4-trifluoro-5-phenylspirohex-4-ene, 67773-55-1; *syn-cis*-1,2-dimethyl-4-fluoro-5-phenylspirohex-4-ene, 67773-56-2; *anti-cis*-1,2-dimethyl-4-fluoro-5-phenylspirohex-4-ene, 67814-61-3; *trans*-1,2-dimethyl-4-fluoro-5-phenylspirohex-4-ene, 67814-62-4; *syn*-spiro[2-fluoro-3-phenyl-2-cyclobutene-1,7′-norcarnane], 67773-57-3; *anti*-spiro[2-fluoro-3-phenyl-2-cyclobutene-1,7′-norcarnane], 67814-63-5; *syn*-4-fluoro-5-phenyl-1-vinylspirohex-4-ene, 67773-58-4; *anti*-4-fluoro-5-phenyl-1-vinylspirohex-4-ene, 67773-59-5; *syn*-1-chloro-1,2,2,4-tetrafluoro-5-phenylspirohex-4-ene, 67773-60-8; *anti*-1-chloro-1,2,2,4-tetrafluoro-5-phenylspirohex-4-ene, 67773-61-9; *syn*-4-fluoro-1-trimethylsilyl-5-phenylspirohex-4-ene, 67773-62-0; *anti*-4-fluoro-1-trimethylsilyl-5-phenylspirohex-4-ene, 67773-63-1; *syn*-4-fluoro-1,5-diphenylspirohex-4-ene, 67773-64-2; *anti*-4-fluoro-1,5-diphenylspirohex-4-ene, 67773-65-3; *p*-tolyl-3-(2-fluoro-1-phenyl)cyclobutenyl sulfone, 67773-66-4; 2-fluoro-3-phenyl-2-cyclobutenone, 771-65-3; 4-toluenesulfonylhydrazine, 1576-35-8; 2-fluoro-3-phenyl-2-cyclobutenone tosylhydrazone sodium salt, 67773-67-5.

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Synthesis of (*R*)- and (*S*)-Epichlorohydrin

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Recently there has been increasing interest in the synthesis of small chiral fragments which can be incorporated with retention of chirality into natural products and compounds of synthetic and medicinal interest.[1] Examples include the synthesis of (*R*)-recifeiolide[2] from (*R*)-methyloxirane[3] and the synthesis of (*S,S*)-vermiculin[4] from (*S*)-(2-bromoethyl)-oxirane.[5] The use of chiral oxiranes is particularly attractive since subsequent reactions do not involve the chiral center. Recognizing the potential importance of such chiral intermediates, we report herein the synthesis of both (*R*)- and (*S*)-epichlorohydrin (chloromethyloxirane).

Epichlorohydrin has been widely used in organic synthesis. Its reaction with nucleophiles yields substituted 2-propanols,[6] 2,3-epoxypropanes,[6] or, in specific cases, heterocyclic compounds.[7] Epichlorohydrin has also found wide application in the field of medicinal chemistry.[8] From these examples, it is apparent that the ready availability of chiral epichlorohydrin would hold great potential in synthetic organic chemistry. Although (*R*)-(−)-epichlorohydrin has been reported,[9] the synthesis, which involves a resolution, is cumbersome and impractical. The reported specific rotation ($[\alpha]^{18}_D$ −25.6°) is also much lower than that which we have observed ($[\alpha]^{23}_D$ −34.3°).

The synthetic scheme (Scheme I) is relatively straightforward and amenable to large scale preparation; however, several points require some comment. The cleavage of the bisacetonide of D-mannitol (1) followed by reduction of the intermediate aldehyde to give 2 has been carried out previously

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