Remarkable Enhancement of Dienophilicity by the Trifluoromethanesulfonyl Group. Phenyl(trifluoromethanesulfonyl)acetylene

Richard S. Glass* and Douglas L. Smith

Department of Chemistry, The University of Arizona, Tucson, Arizona 85721

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Phenyl(trifluoromethanesulfonyl)acetylene, prepared from the lithium salt of phenylacetylene and trifluoromethanesulfonic acid anhydride, undergoes exceptionally facile Diels–Alder reactions with tetraphenylcyclopentadienone, 1,3-diphenylisobenzofuran, cyclopentadiene, and 1,3-cyclohexadiene. The rates of these reactions and those of the corresponding reactions with other $C_6H_5C{\equiv}CX$ derivatives were measured and compared. The rate of reaction of phenyl(trifluoromethanesulfonyl)acetylene with cyclopentadiene in ethyl acetate at room temperature was found to be 1.7 times as fast as the rate of reaction of dimethyl acetylenedicarboxylate with this diene. The reasons for the remarkable dienophilicity of phenyl(trifluoromethanesulfonyl)acetylene are discussed.

In the usual Diels–Alder reaction (as opposed to the Diels–Alder reaction with inverse electron demand)[1] electron-withdrawing groups on the dienophile increase the rate of reaction.[1c,2] Thus, Becker and coworkers[3] found that the rate of reaction of methyl esters of substituted phenyl propiolates with tetraphenylcyclopentadienone correlated with Hammett σ constants, and even better with σ^- constants, to give a positive ρ value for the reaction. Dudkowski and Becker reported[4] that increasing the electron-withdrawing power of Y in $C_6H_5C{\equiv}CY$ increased the rate of reaction with tetraphenylcyclopentadienone.

Since the trifluoromethanesulfonyl group is an unusually potent electron-withdrawing group, as evidenced by its extraordinarily large σ constant,[5] dienophiles with such a substituent might undergo especially facile Diels–Alder reactions. This has been found to be the case for phenyl(trifluoromethanesulfonyl)acetylene.[6]

Results

Phenyl(trifluoromethanesulfonyl)acetylene was prepared by treating the lithium salt of phenylacetylene with trifluoromethanesulfonic acid anhydride. The ir, nmr, and mass spectra support this structural assignment. In addition, controlled catalytic hydrogenation of this acetylene produced *cis*-2-phenyl(1-trifluoromethanesulfonyl)ethylene, and reaction of this acetylene with benzenethiol in the presence of sodium thiophenoxide yielded a crystalline monoadduct.

As illustrated in Tables I and II phenyl(trifluoromethanesulfonyl)acetylene reacts faster with tetraphenylcyclopentadienone[7] and 1,3-diphenylisobenzofuran than any other phenylacetylene investigated. Phenyl(trifluoromethanesulfonyl)acetylene reacts 235 and 5.4 times faster than phenylpropioloyl chloride, the next most reactive acetylene studied,[8] with 1,3-diphenylisobenzofuran at 108° and tetraphenylcyclopentadienone at 174°, respectively. Furthermore, phenyl(trifluoromethanesulfonyl)acetylene reacts readily with cyclopentadiene in toluene at 24.0–24.1° with a second-order rate constant of 2.41×10^{-3} l. mol^{-1} sec^{-1}, whereas phenylpropioloyl chloride undergoes no appreciable reaction with cyclopentadiene at room temperature even after 24 hr. Phenyl(trifluoromethanesulfonyl)acetylene reacts 65 times faster than phenylpropioloyl chloride with 1,3-cyclohexadiene at 81.0–81.5° in benzene (the second-order rate constants were 1.68×10^{-3} and 2.58×10^{-5} l. mol^{-1} sec^{-1}, respectively). Surprisingly, phenyl(trifluoromethanesulfonyl)acetylene even reacts faster with cyclopentadiene than does dimethyl acetylenedicarboxylate. In a competition experiment at room temperature phenyl(trifluoromethanesulfonyl)acetylene proved 1.7 times more reactive than dimethyl acetylenedicarboxylate.[9]

Each of the reactions studied kinetically was run on a preparative scale and the product was isolated and characterized. For the reactions with tetraphenylcyclopentadienone, compounds **2a–e** were isolated in good yields. The reactions with 1,3-diphenylisobenzofuran afforded good

Table I
Second-Order Rate Constants for the Reactions[a] of $C_6H_5C{\equiv}CX$ with Tetraphenylcyclopentadienone

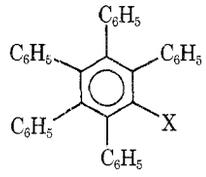
Compd	X	$k_2 \times 10^3$, l. mol^{-1} sec^{-1}
1a	SO_2CF_3	38.7
1b	COCl	15.0
1c	CN	11.0
1d	CHO	2.70[b]
1e	CO_2CH_3	1.56[c]
1f	$Si(CH_3)_3$	*d*

[a] All reactions were run in *p*-cymene as solvent at a temperature of 174.0–174.5° and with an initial concentration of acetylene of 8.10×10^{-2} mol l.$^{-1}$ except for the reaction of **1a** in which the initial concentration of acetylene was 3.85×10^{-2} mol l.$^{-1}$ [b] Dudkowski and Becker report[4] a rate constant of 1.69×10^{-3} l. mol^{-1} sec^{-1} for this reaction. [c] Dudkowski and Becker report[4] a rate constant of 1.27×10^{-3} l. mol^{-1} sec^{-1} for this reaction. [d] There was no appreciable reaction after 48 hr.

Table II
Second-Order Rate Constants for the Reactions[a] of $C_6H_5C{\equiv}CX$ with 1,3-Diphenylisobenzofuran

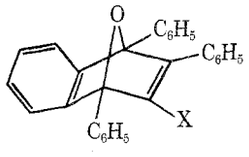
Compd	X	$k_2 \times 10^3$, l. mol^{-1} sec^{-1}
1a	SO_2CF_3	6.01[b]
		13.6[c]
		27.1[d]
		2940[e]
1b	COCl	12.5
1c	CN	7.04
1d	CHO	1.67
1e	CO_2CH_3	0.690
1f	$Si(CH_3)_3$	*f*

[a] All reactions were run in toluene as solvent at a temperature of 107.5–108.0° except where indicated otherwise. The initial concentration of acetylene was 8.10×10^{-2} mol l.$^{-1}$ for **1a** and **1b** and 2.31×10^{-1} mol l.$^{-1}$ for **1c–f**. [b] Temperature of 23.5°. [c] Temperature of 31.0°. [d] Temperature of 41.0°. [e] Value at 108.0° extrapolated from the data obtained at lower temperatures: E_a = 16.2 kcal mol^{-1} and $A = 4.42 \times 10^9$. [f] There was no appreciable reaction after 48 hr.



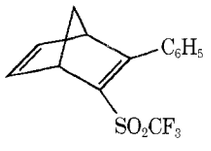
2a, X = SO_2CF_3
b, X = COCl
c, X = CN
d, X = CHO
e, X = CO_2CH_3

yields of adducts **3a–e.** Reaction of phenyl(trifluoromethanesulfonyl)acetylene with cyclopentadiene and 1,3-



3a, X = SO_2CF_3
b, X = COCl
c, X = CN
d, X = CHO
e, X = CO_2CH_3

cyclohexadiene produced adducts **4** and **5a,** respectively. Phenylpropioloyl chloride and 1,3-cyclohexadiene afforded adduct **5b,** isolated as **5c.**



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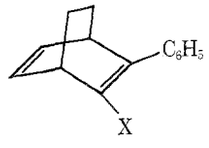

5a, X = SO_2CF_3
b, X = COCl
c, X = CO_2CH_3

Discussion

The remarkable facility with which phenyl(trifluoromethanesulfonyl)acetylene undergoes Diels–Alder reactions is ascribable to the electron-withdrawing electronic effect[10] of the trifluoromethanesulfonyl group. The electronic effect of the sulfonyl group is responsible as well for the enhanced dienophilicity of double bonds appended with chlorosulfonyl[11] or alkyl or aryl sulfonyl groups,[11,12] the marked dienophilicity of aryl sulfonyl cyanides,[13] at least in part for the potent dienophilicity of thiophene 1,1-dioxide,[14] and the high reactivity of chlorosulfonyl isocyanate[15] in cycloaddition reactions. As already pointed out electron-withdrawing groups on the dienophile enhance its dienophilicity. An attractive explanation of this effect is in terms of perturbation molecular orbital theory.[16] The rate of reaction will depend on the magnitude of the energy gap between the highest occupied molecular orbital of the diene and the lowest unoccupied molecular orbital of the dienophile. Thus electron-attracting substituents on the dienophile lower the energy of the lowest unoccupied molecular orbital and, thereby, lessen the energy gap between this orbital and the highest occupied molecular orbital of the diene in the usual Diels–Alder reactions.

Note should be made that the sulfonyl group enhances dienophilicity despite its unfavorable steric and field effects. Nucleophilic substitution at the carbon of α-substituted sulfones is usually extraordinarily difficult[17] (except if the displacement is intramolecular, as in the Ramberg–Bäcklund reaction,[18] or if an exceptionally good leaving group is attached to the α carbon, such as in an α-diazonium ion[19] or α-trifluoromethanesulfonate[20]). This difficulty has been attributed to the steric and field effect of the sulfone group. Nevertheless, in the Diels–Alder reaction these unfavorable effects are overwhelmed by the favorable electronic effect.[21] The reason for this may be that, as suggested by Meyers,[22] the steric effect of the sulfonyl group is small and the field effect of the negatively charged oxygen atoms accounts for the difficulty in effecting nucleophilic displacement at the carbon of α-substituted sulfones. Such a field effect would be expected to strongly disfavor the approach of nucleophiles but the effect on the approach of 1,3-dienes would be relatively modest.

Alternatively, for the Diels–Alder reactions of phenyl(trifluoromethanesulfonyl)acetylene an unsymmetrical transition state[23] could maximize the rate enhancing electronic effect and minimize the steric and field effects of the trifluormethanesulfonyl group. In such a transition state the distance between C-1 of the diene and the carbon bearing the phenyl group in the acetylene would be less than the distance between C-4 of the diene and the carbon bearing the trifluoromethanesulfonyl group. Furthermore, the carbon bearing the trifluoromethanesulfonyl group would have a partial negative charge which the trifluoromethanesulfonyl group could stabilize by inductive and resonance effects.[24] Note, however, that Becker and coworkers[3b,c] proposed that the transition state for the reaction of tetraphenylcyclopentadienone with methyl esters of substituted phenyl propiolates is unsymmetrical but in the opposite sense to that proposed here.

Experimental Section

All reactions were run under anhydrous conditions and under an argon atmosphere. Elemental microanalyses were performed by analysts at Spang Microanalytical Laboratory, Ann Arbor, Mich. Molecular weights were determined using a Hewlett-Packard Model 302B vapor pressure osmometer. Infrared spectra were taken on a Perkin-Elmer Model 337 ir spectrophotometer. Proton nmr spectra were recorded using a Varian Model T-60 nmr spectrometer and employing tetramethylsilane as an internal standard. Mass spectra were determined employing a Hitachi Perkin-Elmer Model RMU-6E double focusing mass spectrometer. All melting points are corrected and were determined using a Thomas-Hoover melting point apparatus.

Phenyl(trifluoromethanesulfonyl)acetylene (1a). In a 250-ml three-necked flask, fitted with a pressure-equilibrating addition funnel, a rubber septum, and a gas inlet, were placed *n*-butyllithium (2.74 g, 42.8 mmol) and dry diethyl ether (100 ml). In the addition funnel were placed trifluoromethanesulfonic acid anhydride[25] (12.00 g, 42.8 mmol) and diethyl ether (100 ml). To the solution in the flask, chilled in a Dry Ice–acetone bath, was added freshly distilled phenylacetylene (4.70 ml, 4.36 g, 42.8 mmol) dropwise from a syringe. After stirring for 1 hr at −78°, the solution of anhydride was added dropwise and cautiously over a period of 1 hr to the solution of salt at −78°. The mixture was then stirred 0.5 hr longer at −78°, brought to room temperature, and then stirred for an additional 0.5 hr.

The reaction mixture was extracted successively with several 50-ml portions of water and brine. The combined extracts were washed with ether and the ether layers were combined and dried over anhydrous magnesium sulfate. Evaporation of the solvent left a dark oil. Two distillations through a short Vigreux column under reduced pressure (bp 57–62° (0.1 mm)) gave a very lightly colored oil (7.25 g, 72.5%): ir (neat) 2165 (C≡C), 1370 (SO_2), 1195–1230 (CF_3), 1110 (SO_2) cm^{-1}; nmr ($CDCl_3$) δ 7.18–7.72 (m); mass spectrum *m/e* 234 (P), 165 (P − 69), 101 (P − 133).

The product crystallized with difficulty to give a solid of mp 31°. This material darkened on standing at room temperature under nitrogen but could be stored indefinitely when packed in powdered Dry Ice.

Catalytic Hydrogenation of 1a. In a 50-ml three-necked flask were placed glacial acetic acid (10 ml) and 5% palladium-on-charcoal (200 mg). The flask was attached to a catalytic hydrogenator

and the catalyst was saturated with hydrogen. Then **1a** (234 mg, 1.0 mmol) in acetic acid (2 ml) was added by syringe. The system was allowed to take up hydrogen until such uptake ceased. The volume of hydrogen consumed was 37.6 ml (1.68 mmol), corrected to STP.

The catalyst was filtered and the filtrate was taken up in 50 ml of diethyl ether. This solution was extracted successively with several 30-ml portions of saturated aqueous sodium bicarbonate solution, water, and brine. The ether layer was then dried over anhydrous magnesium sulfate. Evaporation of the solvent left a dark oil which was purified by preparative glpc on a 5 ft × 0.25 in. 3% SE-30 on Chromosorb W (80–100 mesh) column: ir (neat) 1370 (SO_2), 1185–1210 (CF_3), 1110 (SO_2), 680 (cis-disubstituted ethylene) cm^{-1}; nmr (CCl_4) δ 7.24–7.78 (m, 6, five aromatic H and one vinyl H), 6.40, 6.20 (d, 1, J = 12 Hz, vinyl H, collapsed to singlet at δ 6.30 when irradiated at δ 7.50); mass spectrum m/e 236 (P), 167 (P − 69), 103 (P − 133).

Anal. Calcd for $C_9H_7F_3O_2S$: C, 45.76; H, 2.97. Found: C, 46.06; H, 2.91.

Addition of Benzenethiol to 1a. In a 25-ml round-bottom flask were placed **1a** (468 mg, 2.0 mmol) and dry tetrahydrofuran (7 ml). The flask was fitted with a pressure-equilibrating addition funnel containing benzenethiol (220 mg, 2.0 mmol), sodium thiophenoxide (10 mg), and tetrahydrofuran (7 ml). The solution of benzenethiol was added dropwise over a period of 0.5 hr to the solution of **1a.**

The solvent was evaporated and diethyl ether (25 ml) was added to the resulting oil. This solution was extracted successively with several 20-ml portions of water and brine. The ether layer was dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness. The residue was dissolved in benzene (5 ml) and chromatographed on silica gel (35 g). Hexane (100 ml), followed by 2:8 benzene–hexane (300 ml), eluted two bands: one containing benzenethiol and the other phenyl disulfide (both identified by tlc). Additional amounts of 2:8 benzene–hexane eluted the adduct of **1a** with benzenethiol. Evaporation of the solvents followed by two recrystallizations from CCl_4–hexane gave colorless crystals (453 mg, 66%): mp 114–115°; ir (KBr) 1540 (C=C), 1355 (SO_2), 1180–1200 (CF_3), 1105 (SO_2) cm^{-1}; nmr (CCl_4) δ 7.56 (s, 5), 7.40 (s, 5), 5.40 (s, 1); mass spectrum m/e 344 (P), 275 (P − 69), 211 (P − 133), 178 (P − 166), 102 (P − 242).

Anal. Calcd for $C_{15}H_{11}F_3O_2S_2$: C, 52.33; H, 3.20; S, 18.60. Found: C, 52.44; H, 3.18; S, 18.56.

Kinetic Studies. The acetylenes other than **1a** used in the kinetic studies were prepared by known procedures. Phenylpropioloyl chloride was made from phenylpropiolic acid and PCl_5[26] and was converted into both the corresponding amide[27] and methyl ester (bp 55° (0.22 mm)), the latter by addition of 1 equiv each of methanol and triethylamine. Phenylpropiolamide was dehydrated to the corresponding nitrile.[28] Finally, **1f** was prepared from phenylacetylene.[29] Phenylpropiolaldehyde, supplied by Aldrich Chemical Co., was distilled before use.

Tetraphenylcyclopentadienone and 1,3-diphenylisobenzofuran were recrystallized to constant melting point, while cyclopentadiene and 1,3-cyclohexadiene were purified by distillation prior to use.

The solvents (*p*-cymene, toluene, and benzene) were each purified by washing with aqueous potassium permanganate solution, 2 *N* sulfuric acid solution, and water. This was followed by drying over anhydrous magnesium sulfate, heating at reflux over calcium hydride, and then distilling from calcium hydride.

The reagents were dissolved in the appropriate amount of solvent and were placed in a three-necked flask which was fitted with a reflux condenser and a thermometer. Each solution contained an equal concentration of acetylene and diene. The flask was flushed with argon and immediately placed in an insulated bath which had been preheated to a constant temperature. Zero time was taken to be that time at which constant internal temperature was reached.

The reactions were followed by measuring the change in ir absorption in the region 2500 to 2000 cm^{-1} of an accurately diluted (with 100 μl of solvent) measured (30–60 μl) aliquot as a function of time. The size of the aliquot removed depended on the initial concentration of reactant, which varied from 3.85×10^{-2} to 0.231 mol $l.^{-1}$.

The competition between **1a** and dimethyl acetylenedicarboxylate for cyclopentadiene was conducted by placing **1a** (117 mg, 0.5 mmol) and dimethyl acetylenedicarboxylate (71 mg, 0.5 mmol) together with cyclopentadiene (26.4 mg, 0.4 mmol) in ethyl acetate (6.2 ml) in a stoppered 10-ml round-bottom flask under argon. The mixture was stirred for 24 hr at room temperature. The ethyl acetate was evaporated and the residue (224.8 mg) taken up in chloroform (25.0 ml). The ir spectrum of this solution was measured and the concentrations of reactants remaining and products formed were calculated by comparing the absorptions at selected wavelengths with spectra of known concentration for the pure compounds. The wavenumbers chosen were: 2170 cm^{-1} for **1a,** 894 cm^{-1} for dimethyl acetylenedicarboxylate, and 1620 cm^{-1} for dimethyl norborna-2,5-diene-2,3-dicarboxylate. In addition, the amounts of the products formed were determined by isolation. The final amounts of materials were: 0.25 mmol of **1a,** 0.34 mmol of dimethyl acetylenedicarboxylate, 0.24 mmol of **4,** and 0.16 mmol of dimethyl norborna-2,5-diene-2,3-dicarboxylate.

Product Studies. All adducts **2a–5c** were prepared in a similar manner. The diene (3 mmol) and the acetylene (3 mmol) were dissolved in the appropriate solvent (13 ml) and were placed in a round-bottom flask fitted with a reflux condenser. The solvents used were *p*-cymene for **2a–e,** toluene for **3a–e,** and benzene for **4** and **5a,b.** The solution was then placed under an argon atmosphere and heated at reflux for 48 hr with the exception of **4** which was maintained at room temperature for 24 hr and **5b** which was heated at reflux for 100 hr.

After removal of the solvent the crude product was recrystallized to constant melting point. Toluene was used as recrystallization solvent for **2a–e,** and **3a–e,** while petroleum ether was used for **4.** Adducts **5a** and **5c** were purified by chromatography as described below. **5a** was then recrystallized from petroleum ether, while **5c** was distilled.

The adduct from dimethyl acetylenedicarboxylate and cyclopentadiene was prepared according to the literature.[30]

Pentaphenyl Trifluoromethanesulfone (2a): 1.55 g (87.8%); mp 360–362°; ir (KBr) 1360 (SO_2), 1205 (CF_3), 1110 (SO_2) cm^{-1}; nmr ($CDCl_3$) δ 7.08 (s, 10), 6.78 (s, 15); mass spectrum m/e 590 (P), 521 (P − 69), 457 (P − 133).

Anal. Calcd for $C_{37}H_{25}F_3O_2S$: C, 75.26; H, 4.24; S, 5.42. Found: C, 75.39; H, 3.99; S, 5.18.

Pentaphenylbenzoyl Chloride (2b): 1.29 g (83.0%); mp 285–286°; ir (KBr) 1730 (C=O) cm^{-1}; nmr ($CDCl_3$) δ 7.16 (m, 10), 6.82 (m, 15); mass spectrum m/e, no parent at 520, 485 (P − 35), 457 (P − 63). This material was converted to **2e.** The spectra (ir and nmr) of this material are the same as those of authentic **2e.** Furthermore, the mixture melting point with authentic **2e** is undepressed.

Pentaphenylbenzonitrile (2c): 1.21 g (83.5%); mp 280–281° (lit.[31] mp 271–272°).

Pentaphenylbenzaldehyde (2d): 1.30 g (89.4%); mp 263° (lit.[4] mp 265°).

Methyl Pentaphenylbenzoate (2e): 1.37 g (88.6%); mp 344–345° (lit.[4] mp 342°).

Trifluoromethyl (1,2,4-Triphenyl-1,4-epoxynaphthalene)-3-sulfone (3a): 1.39 g (86.2%); mp 192–193°; ir (KBr) 1570 (C=C), 1355 (SO_2), 1185–1200 (CF_3), 1105 (SO_2) cm^{-1}; nmr ($CDCl_3$) δ 7.02–7.80 (m); mass spectrum m/e, no parent at 504, 371 (P − 133).

Anal. Calcd for $C_{29}H_{19}F_3O_3S$: C, 69.05; H, 3.77; S, 6.35; mol wt, 504. Found: C, 69.05; H, 3.91; S, 6.25; mol wt, 510.

1,2,4-Triphenyl-1,4-epoxynaphthalene-3-carboxylic Acid Chloride (3b): 0.97 g (74.5%); mp 177–178° dec; ir (KBr) 1710–1765 broad doublet (C=O), 1570 (C=C) cm^{-1}; nmr (CCl_4) δ 7.02–7.96 (m); mass spectrum m/e, no parent at 434, 399 (P − 35), 371 (P − 63), 270 (P − 164).

Anal. Calcd for $C_{29}H_{19}ClO_2$: C, 80.18; H, 4.38; Cl, 8.07; mol wt, 434. Found: C, 80.10; H, 4.41; Cl, 8.04; mol wt, 431.

1,2,4-Triphenyl-1,4-epoxynaphthalene-3-carbonitrile (3c): 1.02 g (85.5%); mp 189–190° dec; ir (KBr) 2190 (C≡N), 1570 (C=C) cm^{-1}; nmr ($CDCl_3$) δ 7.02–7.84 (m); mass spectrum m/e 397 (P), 319 (P − 78), 270 (P − 127).

Anal. Calcd for $C_{29}H_{19}NO$: C, 87.66; H, 4.79; N, 3.53; mol wt, 397. Found: C, 87.64; H, 4.93; N, 3.29; mol wt, 383.

1,2,4-Triphenyl-1,4-epoxynaphthalene-3-carboxaldehyde (3d): 1.04 g (87.0%); mp 161–162°; ir (KBr) 2810 (C(=O)H), 1655 (C=O), 1570 (C=C) cm^{-1}; nmr ($CDCl_3$) δ 9.70 (s, 1), 7.00–7.98 (m, 19); mass spectrum m/e 400 (P), 372 (P − 28), 270 (P − 130).

Anal. Calcd for $C_{29}H_{20}O_2$: C, 87.00; H, 5.00; mol wt, 400. Found: C, 86.91; H, 5.29; mol wt, 413.

Methyl 1,2,4-Triphenyl-1,4-epoxynaphthalene-3-carboxylate (3e): 1.12 g (86.5%); mp 81–82°; ir (KBr) 1700 (C=O), 1570 (C=C) cm^{-1}; nmr (CCl_4) δ 6.92–7.88 (m, 19), 3.40 (s, 3); mass spectrum m/e, no parent at 430, 399 (P − 31), 371 (P − 59), 270 (P − 160).

Anal. Calcd for $C_{30}H_{22}O_3$: C, 83.72; H, 5.12; mol wt, 430. Found: C, 83.58; H, 5.32; mol wt, 445.

Trifluoromethyl 3-Phenylbicyclo[2.2.1]hepta-2,5-dienyl 2-Sulfone (4): 0.846 g (94.0%); mp 75–76°; ir (KBr) 1590, 1560 (C=C), 1365 (SO_2), 1172–1205 (CF_3), 1110 (SO_2) cm^{-1}; nmr (CCl_4) δ 7.40 (s, 5), 7.00 (m, 2), 3.99, 4.18 (d, 2, J = 11 Hz), 2.10, 2.20, 2.41, 2.56 (m, 2); mass spectrum m/e 300 (P), 231 (P − 69), 167 (P − 133), 66 (P − 234).

Anal. Calcd for $C_{14}H_{11}F_3O_2S$: C, 56.00; H, 3.67; S, 10.67; mol wt, 300. Found: C, 56.02; H, 3.82; S, 10.76; mol wt, 300.

Trifluoromethyl 3-phenylbicyclo[2.2.2]octa-2,5-dienyl 2-sulfone (5a) was eluted with 200 ml 8:2 hexane–benzene from a column of 35 g of silica gel: 0.674 g (71.5%); mp 71–72°; ir (KBr) 1620, 1580 (C=C), 1355 (SO_2), 1175–1200 (CF_3), 1118 (SO_2) cm^{-1}; nmr ($CDCl_3$) δ 7.32 (m, 5), 6.50 (m, 2), 4.00, 4.35 (broad d, 2), 1.65 (m, 4); mass spectrum m/e 314 (P), 286 (P − 28), 260 metastable (corresponds to 314 → 286), 245 (P − 69), 217 (P − 97), 181 (P − 133), 153 (P − 161).

Anal. Calcd for $C_{15}H_{13}F_3O_2S$: C, 57.32; H, 4.14; S, 10.19. Found: C, 57.37; H, 4.16; S, 10.11.

Methyl 3-Phenylbicyclo[2.2.2]octa-2,5-diene-2-carboxylate (5c): from 1,3-cyclohexadiene and phenylpropioloyl chloride, followed by methanol and triethylamine; purified by two successive column chromatographs each on 35 g of silica gel. The first involved elution with 200 ml of benzene, while the second involved elution with 500 ml of 1:1 hexane–benzene. The product was the second band eluted in the second chromatography: 0.257 g (35.7%); ir (neat) 1695 (C=O), 1620, 1605 (C=C) cm^{-1}; nmr (CCl_4) δ 7.20 (m, 5), 6.35 (m, 2), 3.90, 4.20 (broad d, 2), 3.55 (s, 3), 1.60 (m, 4); mass spectrum m/e 240 (P), 212 (P − 28), 181 (P − 59), 152 (P − 88).

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Registry No.—1a, 52843-77-3; **1a** monoadduct with benzenethiol, 52855-91-1; **1b,** 7299-58-3; **1c,** 935-02-4; **1d,** 2579-22-8; **1e,** 4891-38-7; **2a,** 52843-78-4; **2b,** 52843-79-5; **2c,** 52843-80-8; **2d,** 52843-81-9; **2e,** 2857-85-4; **3a,** 52843-82-0; **3b,** 52920-69-1; **3c,** 52843-83-1; **3d,** 52843-84-2; **3e,** 52843-85-3; **4,** 52843-86-4; **5a,** 52843-87-5; **5c,** 52843-88-6; tetraphenylcyclopentadienone, 479-33-4; 1,3-diphenylisobenzofuran, 5471-63-6; cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; trifluoromethanesulfonic acid anhydride, 358-23-6; phenylacetylene, 536-74-3; *cis*-2-phenyl-1-trifluoromethanesulfonylethylene, 52843-89-7; benzenethiol, 108-98-5.

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