Elution with CH_2Cl_2 gave 0.17 g (14%) of **10** as a faint yellow oil, which solidified on standing in a refrigerator: mp 94–96 °C (from hexane); ^1H NMR (CCl_4) δ 0.85 (d, 12), 1.1–1.9 (m, 6 H), 3.1–3.7 (m, 4 H), 3.88 (s, 2 H), 6.89 (s, 2 H), 6.9–7.5 (m, 6 H). Anal. Calcd for $C_{25}H_{32}O_2S_4$: C, 60.94; H, 6.55. Found: C, 60.72; H, 6.39.

4,4'-Methylenebis(1,2-diiodobenzene) (11). To a stirred and gently refluxed solution of 1.27 g (5 mmol) of iodine, 0.70 g (6 mmol) of isoamyl nitrite in 100 mL of 1,2-dichloroethane was added a solution of 0.72 g (2.5 mmol) of **4** in 12 mL of dioxane over a period of 20 min. The mixture was refluxed for 1 h, cooled, and filtered to remove insoluble materials formed. The filtrate was washed with aqueous 5% $Na_2S_2O_4$ (2 × 25 mL) and water (2 × 25 mL) and dried over $MgSO_4$. The solvent was evaporated and the resulting solid residue was purified by column chromatography (CCl_4, silica gel) to provide 0.47 g (29%) of **11** as white crystals, mp 180–182 °C (from benzene). A solution of **11** in benzene turned pink on standing at room temperature because the compound liberates molecular iodine. A satisfactory elemental analysis could not be obtained for this compound. The following is the most satisfactory among several attempts. Anal. Calcd for $C_{13}H_8I_4$: C, 23.24; H, 1.20; I, 75.56. Found: C, 24.26; H, 1.39; I, 74.51. IR (KBr) 1448, 1375, 1256, 1085, 1000, 896, 802 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80 (s, 2 H, methylene), 6.8 (d, 2 H, aromatic, 7.2–8.1 (m, 4 H, aromatic).

Methylenebis[(phenylthio)benzene] (12). A solution of 0.72 g (2.5 mmol) of **4** in 12 mL of dioxane was added to a stirred and refluxed solution of 1.38 g (10 mmol) of ethyl phenyl sulfide and 0.70 g (6 mmol) of isoamyl nitrite in 100 mL of 1,2-dichloroethane over a period of 20 min. The mixture was refluxed for 1 h and then evaporated to leave a red oil. The oil was dissolved in benzene (50 mL), washed with 5% KOH (2 × 30 mL) and water (2 × 30 mL), and dried. The benzene was evaporated and the residual oil was chromatographed on a column of silica gel. Elution with CCl_4 gave a mixture of **12** and ethyl phenyl sulfide, which was subjected to fractional distillation (Kugelrohr). Ethyl phenyl sulfide was distilled at 75 °C (3 mmHg) and **12** at 200 °C (0.05 mmHg) as a viscous oil which solidified in a refrigerator: 0.20 g (21%); mp 95–102 °C (from hexane); ^1H NMR (CCl_4) δ 3.85 (br, s, 2 H, methylene), 6.9–7.6 (m, 16 H). Anal. Calcd for $C_{25}H_{20}S_2$: C, 78.08; H, 5.24. Found: C, 77.82; H, 5.43.

4,4'-Methylenebis(1,2-dichloro-1,2-dihydrobenzocyclobutene) (13). To a stirred and gently refluxed mixture of *trans*-1,2-dichloroethylene (20 mL), isoamyl nitrite (0.70 g, 6 mmol), and 1,2-dichloroethane (100 mL) was added a solution of 0.72 g (2.5 mmol) of **4** in 12 mL of dioxane over a period of 20 min. The mixture was refluxed for 1 h, cooled, and filtered to remove insoluble materials formed. The filtrate was evaporated to leave an oily residue, which was chromatographed on a column of silica gel. Elution with CCl_4 gave 20 mg (2.2%) of the *trans,trans*-**13** and 7 mg (0.8%) of the *cis,trans*-**13**. The reaction was repeated five times on this scale. The results are truly reproducible and the above two products were repeatedly obtained in the ratio described.

trans,trans-**13**: mp 121–127 °C (from hexane); white granules; ^1H NMR (CCl_4) δ 4.00 (s, 2 H, methylene), 5.14 (s, 4 H, cyclobutyl H), 7.0–7.2 (m, 6 H, aromatic); MS, *m/e* (relative intensity) 360 (52), 358 (100), 356 (77) (M^+), 323 (15), 298 (25), 296 (25), 262 (38), 251 (20), 215 (30), 191 (35), 189 (35); high-resolution mass spectrum, calcd for $C_{17}H_{12}Cl_4$ 359.9636, 357.9666, and 355.9696, found 359.9626, 357.9628, and 355.9695.

cis,trans-**13**: mp 149–158 °C (from hexane); white granules; ^1H NMR (CCl_4) δ 4.00 (s, 2 H, methylene), 5.14 (s, 2 H, cyclobutyl H), 5.57 (s, 2 H, cyclobutyl H), 7.0–7.2 (m, 6 H, aromatic); MS, *m/e* (relative intensity) 360 (52), 358 (100), 356 (76) (M^+), 323 (16), 285 (15), 262 (21), 249 (20), 215 (36), 189 (23); high-resolution mass spectrum, calcd for $C_{17}H_{12}Cl_4$ 359.9636, 357.9666, and 355.9696, found 359.9604, 357.9641, and 355.9680.

Registry No. **4**, 7330-46-3; **5**, 92958-37-7; **6**, 92958-38-8; **7**, 92958-39-9; **8**, 92958-40-2; **9**, 92958-41-3; **10**, 92958-42-4; **11**, 92958-43-5; **12**, 92958-44-6; **13**, 92958-45-7; $Cl(CH_2)_2Cl$, 107-06-2; *trans*-ClCH=CHCl, 156-60-5; $TiCl_4$, 7550-45-0; $LiAlH_4$, 16853-85-3; CS_2, 75-15-0; I_2, 7553-56-2; EtSPh, 622-38-8; isoamyl nitrite, 110-46-3; tetraphenylcyclopentadienone, 479-33-4; anthracene, 120-12-7; 2,5-dimethylfuran, 625-86-5; isoamyl alcohol, 123-51-3; dioxane, 123-91-1.

Application of the Peterson Olefination to the Preparation of Substituted Triafulvenes from Methoxycyclopropenylium Triflates

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Received June 12, 1984

Three new unusually substituted triafulvenes were prepared by reacting methoxycyclopropenylium triflates with α-silyl substituted anions. The mode of a nucleophilic attack varied, depending on the anion. Attack occurred at the methoxy substituted carbon, yielding the desired triafulvene, the methoxy methyl group, yielding the cyclopropenone and the methyl substituted anion, or the alkyl/aryl substituted carbon. The latter rearranged upon heating in CH_3CN to give the desired triafulvene. These reactions are discussed in detail.

Triafulvenes represent the simplest cross-conjugated cyclic hydrocarbons and have therefore been of considerable theoretical and synthetic interest.[2] The recent reports by Billups[3] and Staley[4] and co-workers on the elegant synthesis of the long sought after parent triafulvene, C_4H_4, prompted us to report a new method for the preparation of novel exocyclic substituted triafulvenes.

Although a variety of methods, prominent among them the Wittig olefination of diphenylcyclopropenone[5] and the condensation of activated methylene compounds such as $(CN)_2CH_2$ with ethoxycyclopropenylium ions,[6] have been used for the synthesis of substituted triafulvenes, the well-known Peterson olefination[7,8] has, to our knowledge, not been employed. Since this method is an excellent

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0022-3263/84/1949-5087$01.50/0

Table I. Formation of Triafulvenes 9 and Adducts 10

reagents	R	X	Y	9,10	%9[a]	%10[a]
1a/2b	C_6H_5	$C_6H_5SO_2$	Me_3Si	a	70	0
1a/2c	C_6H_5	p-$CH_3C_6H_4SO_2$	SCH_3	b	26	50
1b/2a	t-Bu	$S(CH_2)_3S$		c	26	28

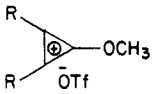
[a] Isolated yields.

means of olefin synthesis we set out to examine its application to triafulvene synthesis.

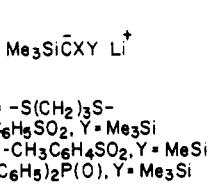
It is known[9] that ring substituted cyclopropenones react with certain nucleophiles, in particular lithium reagents, in a conjugate manner resulting in ring opened products. Hence, we considered alkoxycyclopropenylium salts better substrates than the precursor cyclopropenones themselves.

Results and Discussion

The reactions of methoxycyclopropenylium triflates 1 with a variety of α-silyl substituted anions 2 were examined.

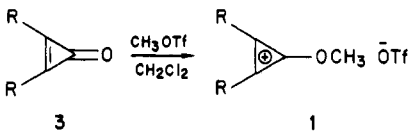


1a, R = C_6H_5
b, R = t-Bu



2a, X,Y = $-S(CH_2)_3S-$
b, X = $C_6H_5SO_2$, Y = Me_3Si
c, X = p-$CH_3C_6H_4SO_2$, Y = MeSi
d, X = $(C_6H_5)_2P(O)$, Y = Me_3Si

Triflates **1a** and **1b** were obtained as stable crystalline salts by addition of methyl triflate to the corresponding cyclopropenones[10,11] **3**.



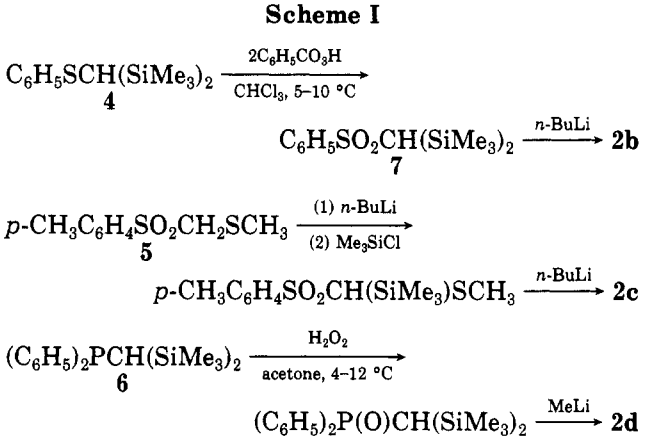
3 1

The necessary precursors to anions **2** were obtained as follows. The precursor to **2a**, 2-(trimethylsilyl)-1,3-dithiane, is commercially available. The required sulfone, **7**, for **2b** was made by perbenzoic acid oxidation of the known sulfide, **4**. Silylation of **5**, a known compound,[14] gave the precursor for **2c**. Oxidation of phosphine[15] **6** with hydrogen peroxide gave the desired phosphine oxide as shown in Scheme I.

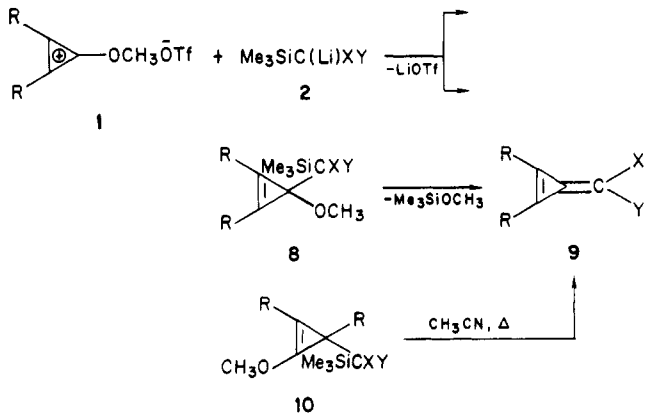
Anions **2a–c** were formed by deprotonation with n-BuLi at low temperature while **2d** was formed by deprotonation with MeLi at 0 °C under argon. The solid salt 1 was added to the solution of anions **2** at low temperature under argon.

Nucleophilic attack of anions **2** on the substituted cyclopropenylium salts 1 can occur either at the O-substituted carbon or the R-substituted carbon as shown in Scheme II.

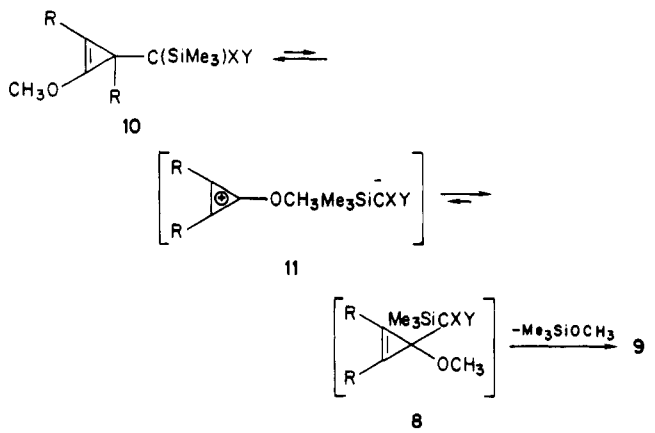
Scheme I



Scheme II



Scheme III



Attack at the O-substituted position followed by elimination of Me_3SiOMe results in the desired substituted triafulvenes **9**, whereas attack at the R-substituted position gives adduct **10**. As seen in Table I, in two of the three cases, both products were observed.

Interestingly, upon prolonged standing in chloroform solution at room temperature or in refluxing acetonitrile in a few hours cyclopropenes **10** rearrange nearly quantitatively to the corresponding triafulvenes **9**. A reasonable mechanism for this rearrangement is shown in Scheme III.

Reionization of adduct **10** to ion pair **11** followed by collapse to **8** gives the same intermediate as in the direct Peterson olefination in Scheme II, and upon loss of Me_3SiOCH_3 affords triafulvenes **9**. The possible driving force for this unusual rearrangement derives from the fact that both cyclopropenylium cations and the α-silyl substituted anions **2** are very stable species. Therefore, the

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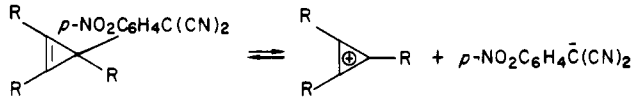
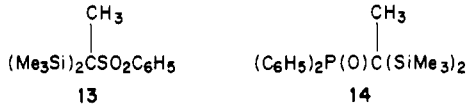
energy difference between ion pair **11** and covalent structures **10** or **8** must be relatively small and the rearrangement can occur under mild conditions. Recently Arnett and co-workers[16] in an elegant study provided convincing evidence for such a direct bond heterolysis of a very weak carbon–carbon bond in the ionization of triafulvene **12**. This rearrangement of **10** to **9** increases the



12, R = Me or C_6H_5

overall yield and therefore improves the utility of the Peterson olefination in triafulvene synthesis.

Finally, in two instances, namely the interaction of **1b** with **2b** and **1a** with **2d** no triafulvene was observed at all. Instead only starting cyclopropenones **3b** and **3a** and the corresponding methylated anions **13** and **14** were observed.



The presence of these products clearly implies that nucleophilic attack has occurred on the methyl group rather than the cyclopropenylium cation.

Unfortunately, these last results limit the scope and usefulness of the Peterson olefination for the formation of triafulvenes. This is particularly true since it is not possible to a priori predict if nucleophilic attack by a particular substituted anion will occur on the methyl group resulting in demethylation or on the cyclopropenylium cation giving the desired triafulvene. This problem may be circumvented by use of oxycyclopropenylium salts other than methoxy substituted ones, which should be less susceptible to such dealkylation.

In summary, we have shown the Peterson olefination as a useful method, albeit limited in scope, for the formation of certain exo substituted triafulvenes. Three unique triafulvenes were prepared in good yield by this method. A novel rearrangement involving cyclopropenylium ions and stabilized carbanion ion pairs was postulated. The chemistry of these triafulvenes as well as further application of the Peterson olefination to related systems is under active investigation.

Experimental Section

General Methods. All melting points are uncorrected. IR spectra were obtained on a Perkin-Elmer 298 spectrometer. Proton NMR were obtained on a Varian EM-390, ^{13}C on a Varian SC-300 spectrometer, and both are reported relative to internal Me_4Si. Mass spectra were obtained on a VG Micromass 7070 system. All solvents were purified prior to use by standard procedures.

Diphenylmethoxycyclopropenylium Triflate (1a). To a solution of 10.32 g (50 mmol) of diphenylcyclopropenone[10] in 100 mL of dry ethylene chloride was added 9.03 g (6.23 mL, 55 mmol) of methyl triflate under stirring at room temperature. After completion of the addition the mixture was heated to its boiling point and then allowed to cool slowly. Crystallization was completed at −20 °C. The colorless crystals were filtered under argon, washed with a small amount of cold ethylene chloride, and dried over an inert atmosphere yielding 17.0 g (92%). On heating in a sealed capillary tube the compound started to decompose at 120–130 °C and melted with formation of a brown oil at 163–169 °C: IR (KBr) 3060, 2960, 1889, 1592, 1577, 1508, 1438, 1390, 1255, 1160, 1020, 850, 760 718, 680, 660, 636 cm^{-1}.

Di-*tert*-butylmethoxycyclopropenylium Triflate (1b). A mixture of 8.31 g (50 mmol) di-*tert*-butylcyclopropenone[11] and 9.03 g (6.23 mL, 55 mmol) of methyl triflate in 50 mL of dry methylene chloride was stirred for 2 h at room temperature. The solvent and the excess alkylating reagent were distilled off under vacuum and the residue was crystallized from dry THF under an argon atmosphere yielding 12.39 g (75%) of colorless, very hygroscopic crystals: mp 111–114 °C (sealed capillary tube); IR (KBr) 2967, 1873, 1520, 1488, 1460, 1408, 1390, 1369, 1312, 1260, 1225, 1151, 1030, 1011, 878, 813, 757, 739, 640 cm^{-1}.

Bis(trimethylsilyl)(phenylsulfonyl)methane (2b). A solution of 13.43 g (50 mmol) of bis(trimethylsilyl)methyl phenyl sulfide[13] (**4**) in 50 mL of chloroform was added dropwise to an ice cold 0.5 M solution of perbenzoic acid in chloroform[12] (220 mL = 110 mmol) at such a rate that the temperature of the reaction mixture was maintained between +5 and +10 °C. After the addition was complete the clear solution was stirred for 5 more min in the ice bath and then for 45 min at room temperature. The solvent was removed under vacuum and the residue dissolved in 100 mL of hot ethanol. On cooling to −15 °C, 7.20 g of colorless needles crystallized. The mother liquor, on concentration to about 75 mL volume and addition of 12 mL of water, gave a second crop of 4.50 g of **2b** as colorless plates. The combined yield was 11.7 g (78%): mp 107–108 °C; IR (KBr) 3060, 2980, 2955, 2900, 2880, 1480, 1444, 1407, 1315, 1280, 1265, 1250, 1132, 1103, 1086, 1071, 1000, 978, 850, 800, 760, 742, 695, 655, 623 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.93–7.80 (m, 2 H), 7.63–7.43 (m, 3 H), 2.70 (s, 1 H), 0.20 (s, 18 H).

[(4-Methylphenyl)sulfonyl](trimethylsilyl)methyl Methyl Sulfide (2c). A solution of 3.25 g (15 mmol) of [(4-methylphenyl)sulfonyl]methyl methyl sulfide in 40 mL of dry THF was cooled to −78 °C. A solution of 6.2 mL (16 mmol) of 2.6 M *n*-butyllithium in hexane was added dropwise to the stirred solution followed by stirring for an additional 90 min. At the end of this period 2.4 mL (2.06 g, 19 mmol) of chlorotrimethylsilane was injected via a syringe. After 3 min the cold bath was removed and the reaction mixture was stirred for 2 h at room temperature and then poured on 200 mL of ice water. The product was collected by extracting first with 70 mL of CH_2Cl_2 and then twice more with 50 mL of methylene chloride. The combined organic layers were washed with 50 mL of water, dried over magnesium sulfate, and evaporated under vaccum. The residue, on crystallization from 50 mL of ether gave 2.68 g of colorless product. The mother liquor was concentrated to a volume of 20 mL and 50 mL of pentane was added, on cooling a second crop of 1.11 g of **2c** crystallized. The combined yield was 3.79 g (88%): mp 109–111 °C; IR (KBr) 2960, 2918, 1591, 1490, 1425, 1400, 1310, 1300, 1286, 1247, 1140, 1082, 1067, 1055, 1020, 970, 964, 850, 820, 803, 771, 749, 710, 647, 610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.00 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H), 7.43 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H), 3.23 (s, 1 H), 2.47 (s, 3 H), 1.72 (s, 3 H), 0.33 (s, 9 H).

[Bis(trimethylsilyl)methyl]diphenylphosphine Oxide (2d). A solution of 17.23 g (50 mmol) of [bis(trimethylsilyl)methyl]-diphenylphosphine in 200 mL of acetone was cooled to +4 °C in an ice bath. While the solution was stirred, 11.64 g (60 mmol) of a 17% hydrogen peroxide solution in water was added dropwise over a period of 15 min, which caused the temperature to rise to 10–12 °C at times. The ice bath was then removed and the reaction mixture stirred for an additional 30 min at room temperature and then poured on 750 mL of water. The crude product was collected by filtration, air dried, and dissolved in 75 mL of boiling ethanol; 18 mL of water was added under stirring and the solution was allowed to cool to room temperature. After completing the crystallization at −20 °C, 16.41 g (89%) of **2d** was obtained by filtration as colorless crystals: mp 122–124 °C; IR (KBr) 3055, 2980, 2960, 2900, 1482, 1437, 1250, 1176, 1114, 1097, 1070, 1010, 848, 789, 759, 746, 724, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.90–7.57 (m, 4 H), 7.47–7.27 (m, 6 H), 1.31 (d, $^2J_{P,H}$ = 12.5 Hz, 1 H), 0.00 (s, 18 H).

Triafulvene 9a. A solution of 9.02 g (30 mmol) of sulfone **2b** in 150 mL of DME/THF (4:1) was cooled to −78 °C. Then 12 mL of 2.6 M *n*-butyllithium in hexane (31.2 mmol) was added dropwise to the well stirred solution and the temperature was kept below −70 °C. After stirring an additional 1 h at −78 °C, 12.24 g (33 mmol) of cyclopropenylium salt **1a** was added in one portion

(16) Arnett, E. M.; Troughton, E. B.; McPhail, A. T.; Molter, K. E. *J. Am. Chem. Soc.* **1983**, *105*, 6172.

under argon. The reaction mixture was kept at −78 °C for 1.5 h, 0 °C for 0.5 h, and finally at room temperature for 1.0 h. The solvent was then removed in vacuo under argon to leave a semisolid residue which was extracted three times with 400-mL portions of dry boiling *n*-hexane. The clear, orange-yellow hexane extracts were combined and allowed to cool slowly. Crystallization was completed at −15 °C. Filtration under argon gave 8.70 g (70%) **9a** as yellow crystals: mp 95.5–97.5 °C; IR (KBr) 3060, 2950, 2895, 1810, 1500, 1472, 1440, 1340, 1272, 1248, 1123, 1083, 950, 927, 840, 764, 725, 710, 690, 676, 638, 615, 610 cm^{-1}; ^1H NMR (CD_3CN) δ 8.33–8.15 (m, 2 H), 7.97–7.77 (m, 4 H), 7.68–7.37 (m, 9 H), 0.13 (s, 9 H); MS (70 eV), *m/e* 417 (15), 416 (55), 401 (10), 291 (12), 263 (12), 259 (11), 217 (34), 215 (10), 202 (15), 178 (12), 759 (10), 135 (33), 105 (12), 97 (100), 78 (11), 77 (29), 75 (17), 73 (27), 59 (16), 51 (14), 44 (10), 43 (11).

Generation of Lithio[(4-methylphenyl)sulfonyl](trimethylsilyl)methyl Methyl Sulfide (2c) and Its Reaction with Diphenylmethoxycyclopropenylium Triflate (1a). A solution of 1.44 g (5 mmol) of sulfide **2c** in 25 mL of DME/THF (4:1) was cooled to −78 °C. Then 2 mL of 2.6 M *n*-butyllithium in hexane was added dropwise while the temperature was kept below −70 °C. After the reaction had stirred an additional hour at −78 °C, 2.04 g (5.5 mmol) of cyclopropenylium salt **1a** was added in one portion under argon. Stirring was continued for 90 min at −78 °C, 30 min at 0 °C, and 1 h at room temperature. The solvent was then removed under vacuum. The residue was dissolved in 80 mL of ether and washed twice with 30 mL of water. The water layers were then extracted with 40 mL of ether and the combined organic layers were dried over magnesium sulfate. The ether was evaporated in vacuo and the crude product was dissolved in 25 mL of ether. When the mixture had cooled to −25 °C, 1.28 g (50%) of pale yellow crystals formed slowly and were isolated by filtration. The compound turned intense yellow on heating and decomposed rapidly above 100 °C. The mother liquor was concentrated to a volume of about 10 mL and pentane (10 mL) was added under stirring. Crystallization of 1,2-diphenyl-3-[[(4-methylphenyl)sulfonyl](methylthio)methylene]-cyclopropene (**9b**) began at room temperature and was completed at −25 °C. The yield of **9b** was 0.52 g (26%) as yellow crystals: mp 175–176.5 °C (the compound became soft at 148–150 °C, but did not melt).

10b: IR (KBr) 3060, 3030, 2983, 2960, 2924, 2900, 2820, 1782, 1593, 1572, 1490, 1485, 1443, 1397, 1302, 1292, 1283, 1260, 1249, 1228, 1180, 1133, 1090, 1080, 1045 1020, 960, 859, 810, 762, 741, 710, 692, 642, 630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.13–7.13 (m, 14 H), 2.88 (s, 3 H), 2.40 (s, 3 H), 1.87 (s, 3 H), 0.20 (s, 9 H); ^{13}C NMR ($CDCl_3$, −10 °C) δ 143.74, 138.59, 131.65, 130.04, 129.88, 129.61, 129.44, 129.29, 129.08, 128.96, 128.56, 124.90, 76.04, 69.44, 49.83, 21.72, 16.12, 1.21. **9b**: IR (KBr) 3060, 2980, 2920, 1838, (sh 2853 and 1770), 1598, 1574, 1510, 1477, 1446, 1351, 1308, 1282, 1179, 1150, 1135 1090, 1048, 1021, 962, 934, 811, 774, 763 750, 721, 710 699, 688, 664 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.60–8.25 (m, 4 H), 7.88 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.67–7.50 (m, 6 H), 7.22 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 2.36 (s, 3 H), 2.28 (s, 3 H); MS (70 eV), *m/e* 406 (4), 405 (9), 404 (33), 250 (12), 249 (62), 235 (18), 234 (100), 202 (13), 189 (24), 91 (19), 65 (10).

Reaction of 2-Lithio-2-(trimethylsilyl)-1,3-dithiane (2a) with Di-*tert*-butylmethoxycyclopropenylium Triflate (1b). A solution of 10 mmol of **2a**[17] in 24 mL of THF/hexane was cooled to −75 °C and 3.41 g (10.3 mmol) of cyclopropenylium salt **1b** was added under argon at such a rate that the temperature of the reaction mixture stayed between −75 and −62 °C. After the addition was complete stirring was continued for 30 min at −78 °C, 30 min at 0 °C, and 100 min at room temperature. Then 2 mL of water was added and the THF and the hexane were removed in vacuo. The residue was dissolved in 100 mL of ether and extracted twice with 25 mL of water. After drying of the ether phase over magnesium sulfate and evaporation of the solvent a pale yellow oil was obtained. Column chromatography on 155 g of silica gel (Davisil™62, column 2.3 × 101 cm) with 800 mL of methylene chloride/hexanes (1:1) as eluant gave two fractions. Fraction one consisted of 1.06 g (28%) of 2-(2,3-di-*tert*-butyl-1-methoxycyclopropen-3-yl)-2-(trimethylsilyl)-1,3-dithiane (**10c**), as colorless crystals: mp 83–83.5 °C (methanol); IR (KBr) 2997, 2968, 2922, 2860, 2813, 1843, 1477, 1443 1430, 1416, 1385, 1357, 1296, 1270, 1241, 1210, 1185, 1070, 1030, 982, 958, 919, 880, 847, 809, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.90 (s, 3 H), 3.12–2.43 (m, 4 H), 2.10–1.70 (m, 2 H), 1.35 (s, 9 H), 1.11 (s, 9 H), 0.37 (s, 9 H); calcd $C_{15}H_{24}{}^{32}S_2$ 268.1319, found 268.1346 ± 0.0025. Fraction two contained 0.71 g (26%) of 2-(1,2-di-*tert*-butylcyclopropenylidene)-1,3-dithiane (**9c**) as colorless crystals: mp 115–116 °C (from pentane or acetonitrile); IR (KBr) 2964, 2910, 2867, 2815, 1860, 1830, 1810, 1574, 1481, 1463 (sh 1450), 1429, 1420, 1393, 1367, 1268, 1241, 1204, 1140, 1075, 1038, 1020, 942, 911 (sh 916), 872, 840, 648 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.83–2.63 (m, 4 H), 2.30–1.98 (m, 2 H), 1.30 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 142.29, 131.70 65.73, 32.60, 31.99, 28.83, 27.58; MS (70 eV), *m/e* 270 (10), 269 (18), 268 (100), 211 (13), 194 (31) 137 (27), 91 (12), 77 (11), 57 (26) 55 (10), 45 (12), 43 (14), 41 (50), 39 (23), 32 (14), 29 (22); calcd $C_{11}H_{14}{}^{32}S_2$ 211.06515, found 211.0594 ± 0.0050.

Thermolysis of the 1-Methoxycyclopropenes 10b,c. A solution of 1 mmol of **10b** or **10c** was refluxed in 5 mL of acetonitrile for 1.5 h (**10b**) and 75 h (**10c**), respectively. The clear solutions were then cooled to −25 °C, which resulted in crystalization of 75% of **9b** or 63% of **9c**. The mother liquor of **9b** on concentration and crystallization from 10 mL of ether gave a second crop of 15% **9b**.

Reaction of [Bis(trimethylsilyl)(phenylsulfonyl)-methyl]lithium (2b) with Di-*tert*-butylmethoxycyclopropenylium Triflate (1b). To a solution of 5 mmol of **2b** in 25 mL of DME/THF (4:1) was added 1.82 g (5.5 mmol) of cyclopropenylium salt **1b** at a rate such that the temperature did not rise above −65 °C. The reaction mixture was stirred for an additional 3 h at −78 °C and for 1.5 h at room temperature. After evaporation of the solvent the residue was extracted three times with 30-mL portions of warm (35–40 °C) *n*-hexane. The hexane extracts contained 1-(phenylsulfonyl)-1,1-bis(trimethylsilyl)ethane (**13**), which was slightly contaminated with di-*tert*-butylcyclopropenone (**3b**) and starting material **2b**. Concentration of the combined extracts to about 12 mL and cooling to −20 °C rsulted in the crystallization of 0.88 g (56%) of compound **13** as colorless needles: mp 82–83 °C; IR (KBr) 3060, 2945, 2900, 2877, 1582, 1474, 1460, 1441, 1402, 1376, 1290, 1282, 1263, 1248, 1131, 1090, 1067, 1000, 835, 780, 755, 730, 691, 678 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.93–7.77 (m, 2 H), 7.62–7.41 (m, 3 H), 1.50 (s, 3 H), 0.13 (s, 18 H). The hexane insoluble part of the crude reaction product was suspended in 100 mL of methylene chloride and extracted once with 30 mL of saturated sodium carbonate solution and then four times with 30-mL portions of water. The organic layer was dried over magnesium sulfate and then evaporated and the residue sublimed in vacuo to give 0.5 g of di-*tert*-butylcyclopropenone (**3b**), identified by comparison with the authentic material.

Acknowledgment. Partial support by the NSF (CHE81-03596) and a NATO grant are greatly appreciated.

Registry No. **1a**, 93039-27-1; **1b**, 93039-28-2; **2a**, 34410-04-3; **2b**, 93039-29-3; **2c**, 93039-30-6; **2d**, 93039-31-7; **4**, 62761-90-4; **5**, 59662-65-6; **6**, 70530-40-4; **9a**, 93039-32-8; **9b**, 93039-33-9; **9c**, 93039-36-2; **10b**, 93039-34-0; **10c**, 93039-35-1; **13**, 93039-37-3; **14**, 93039-38-4; CF_3SO_2OMe, 333-27-7; diphenylcyclopropenone, 886-38-4; di-*tert*-butylcyclopropenone, 19985-79-6.

(17) Corey, E. J.; Seeback, D.; Freedman, R. *J. Am. Chem. Soc.* **1967**, *89*, 434 and references therein.