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Reactions of Some Sulfur(II)- and Iodine(III)-containing Electrophiles with *endo*-Tricyclo[6.2.1.0^{2,7}]undeca-4,9-diene-3,6-dione

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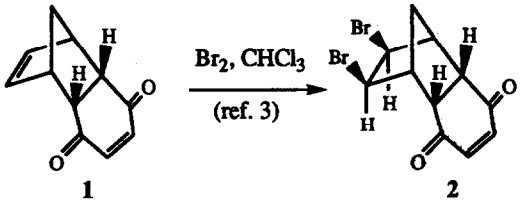
Abstract. Reaction of ArSCl (Ar = phenyl or *ortho*-nitrophenyl) with*endo*-tricyclo[6.2.1.0^{2,7}]-undeca-4,9-diene-3,6-dione (**1**) results in *anti* addition across the norbornene carbon-carbon double bond with concomitant aromatization of the cyclohexenedione ring, thereby affording **4** (87%) and **5** (63%), respectively. The corresponding reaction of PhSCl with **1** in the presence of added Ag(I) proceeds via polar addition across the norbornene carbon-carbon double bond with concomitant intramolecular nucleophilic trapping of an intermediate episulfonium ion by a distant C=O group, thereby affording **6** (57% yield). The reaction of $PhICl_2$ with **1**, when carried out in the presence of $SbCl_5$ or $AgBF_4$, proceeds with concomitant Wagner-Meerwein rearrangement and aromatization to afford adducts **7a** and **8**, respectively.

Introduction. *endo*-Tricyclo[6.2.1.0^{2,7}]undeca-4,9-diene-3,6-dione (**1**), the exclusive product that results via Diels-Alder [4 + 2] cycloaddition of cyclopentadiene to *p*-benzoquinone,[1] has been employed frequently as an intermediate in the synthesis of substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes.[2] In addition, the mode of addition of electrophiles to the isolated [norbornene C(2)-C(3)] carbon-carbon double bond in **1** has been studied. Interestingly, the addition of Br_2 (1 equivalent) to **1** has been reported by Singh and Verma[3] to afford exclusively the corresponding dibromide, **2**, which results via stereoselective *exo,cis* addition (Scheme 1).

Scheme 1



1 **2**

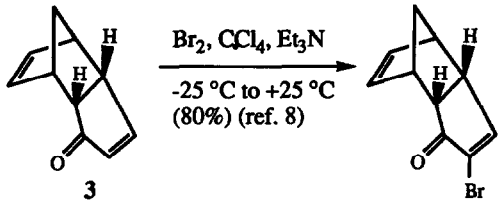
This mode of addition is unusual, since electrophilic addition of bromine to nonconjugated alkenes generally proceeds stereoselectively *anti* (via the corresponding bromonium ion intermediate)[4] and only

rarely stereoselectively *syn*.[5,6a] Polar additions of Cl_2 and Br_2 to norbornenes and to benzonorbornenes frequently are accompanied by Wagner-Meerwein rearrangements, a result which implicates a carbocation intermediate.[6]

The reported[3] course of the reaction of **1** with Br_2 contrasts markedly with that of the corresponding reaction of *endo*-tricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-one (**3**). Thus, reaction of **3** with Br_2[7,8] results in exclusive addition across the (electron-poor) eneone carbon-carbon double bond, leaving the isolated (and relatively electron-rich) norbornene carbon-carbon double bond unscathed (Scheme 2). The unusual behavior of **3** in this regard has been accounted for in terms of "steric and electronic constraints present in *endo*-tricyclodecadienones".[8]

Although Singh and Verma[3] provided convincing proof of the structure of adduct **2**, they failed to suggest any mechanistic rationalization to account for the observed stereochemistry of the electrophilic addition of Br_2 to **1**. In an effort to gain additional insight into the mechanism of this process, we have investigated a variety of electrophilic additions to **1** (*vide infra*).

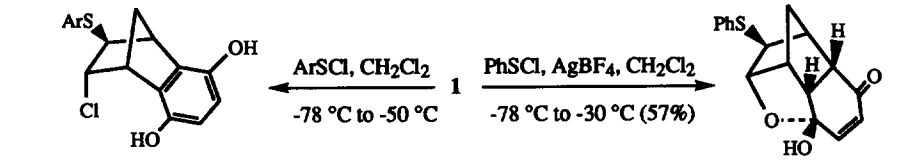
Scheme 2



Results and Discussion. Electrophilic additions of arylsulfenyl chlorides (ArSCl, Ar = phenyl and 2-nitrophenyl) and of $PhICl_2$ to **1** under a variety of experimental conditions have been investigated. The results obtained via these studies are summarized in Scheme 3. Thus, reaction of **1** with PhSCl in the presence of Ag(I)[9] results in polar addition across the norbornene carbon-carbon double bond with concomitant intramolecular nucleophilic trapping of a cationic intermediate by a distant C=O group, thereby affording **6** (57% yield). In the absence of added Ag(I), *anti* addition of ArSCl (Ar = phenyl or *ortho*-nitrophenyl) occurs, accompanied by aromatization of the cyclohexenedione ring. The corresponding reaction of **1** with $PhICl_2$,[10] when performed in the presence of either Sb(V) or Ag(I), proceeds with concomitant Wagner-Meerwein rearrangement and also results in the formation of an aromatized product (**7a** and **8**, respectively).

The results of earlier studies of additions of arenesulfenyl halides to norbornenes and benzonorbornadienes have been reported by Kwart and Miller[11a] and, more recently, by Zefirov and coworkers.[12,13] In general, *anti* addition of ArSX (X = halogen) to the norbornene carbon-carbon double bond occurs in these systems. Simple 1,2-additions to norbornenes often are accompanied by nortricyclene formation and, occasionally, by the formation of Wagner-Meerwein rearranged products.

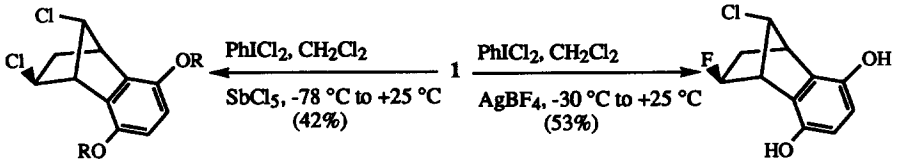
Scheme 3



4 [Ar = C_6H_5 (87%)]

5 [Ar = 2-$NO_2(C_6H_4)$ (63%)]

6

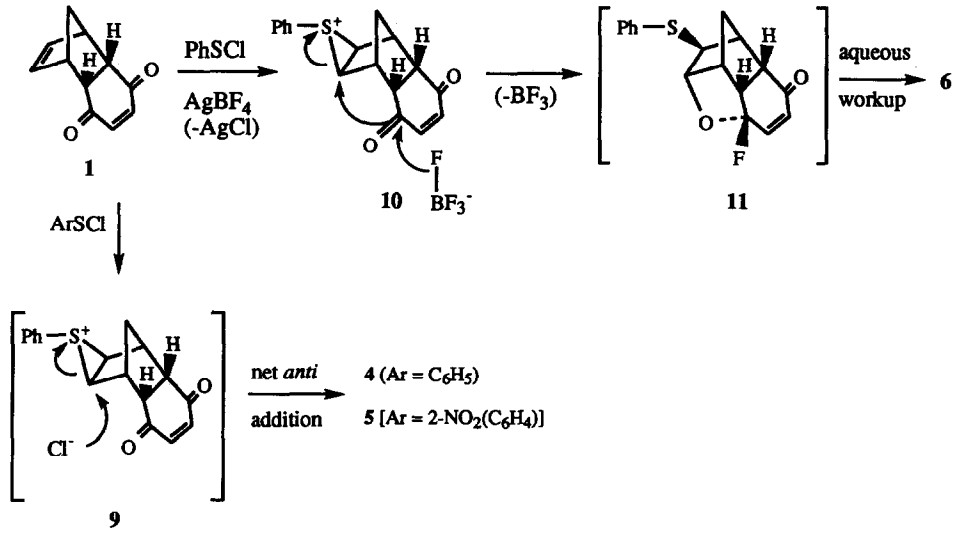


7a: R = H
7b: R = C(O)CH_3

8

Mechanistic rationalization for the course of the reactions of **1** with ArSCl is shown in Scheme 4. The absence of Wagner-Meerwein rearranged adducts lends credence to the suggestion that intermediate episulfonium (i. e., thiiranium) ions are formed in these reactions (see **9** and **10** in Scheme 4). As expected,[11] subsequent intermolecular nucleophilic trapping of **9** by Cl^- occurs exclusively at the *endo* face of the episulfonium ion. This results in stereoselective *anti* addition across the norbornene carbon-carbon double bond, as required to account for the formation of **4** and **5**. In contrast, episulfonium ion **10** is paired with a counter ion (BF_4^-) which is a relatively poor nucleophile. Nucleophilic transfer of F^- from BF_4^- might occur in a manner that results in the formation of **11**, which survives intact until aqueous workup provides the necessary nucleophilic agent that ultimately produces the observed product, **6**. The suggestion that BF_4^- might serve as a source of nucleophilic F^- is supported by our observation that a fluoroalkane, **8**, is obtained via the reaction of **1** with $PhICl_2$-$AgBF_4$ (Scheme 3).

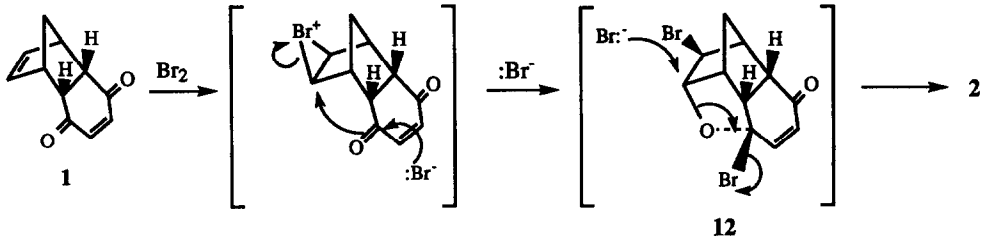
Scheme 4



The reaction of **1** with $PhICl_2$, when performed in the presence of powerful Lewis acids (e.g., $SbCl_5$ and$AgBF_4$), appears to proceed in stepwise fashion by way of a cationic intermediate. The intermediacy of a carbocation is suggested by the fact that the products (i.e., **7a** and **8**, respectively) are formed with concomitant Wagner-Meerwein skeletal rearrangement.[6]

Some Thoughts on the Mechanism of Bromination of 1. Although different electrophiles were used in the present study, we nevertheless believe that our results may bear directly upon the question of the stereochemistry of electrophilic bromination of **1**.[3] Of particular significance in this regard is the possible incursion of an intermediate which results via intramolecular nucleophilic trapping of an epsulfonium ion intermediate by a distant enedione C=O group.[12] This situation finds close analogy in the course of the reaction of **1** with PhSCl when this reaction is performed in the presence of Ag(I) (Scheme 4). Thus, in the case of bromination, an intermediate, **12**, that is closely analogous to **6** might be formed, which subsequently undergoes nucleophilic attack by Br^- to afford **2** (see Scheme 5). In this way, the observed[3] net *syn* addition of Br_2 to **1** might be rationalized.

Scheme 5



Experimental Section

Melting points are uncorrected. NMR spectra were recorded on a Varian Gemini 200 spectrometer which was operated at 200 MHz for ^{1}H (Me_4Si internal standard), 50 MHz for ^{13}C (Me_4Si internal standard), and 282 MHz for ^{19}F NMR spectra ($CFCl_3$ external standard). IR spectra were obtained on a Nicolet model 20-SXB Fourier transform infrared spectrophotometer. Dichloromethane was distilled under nitrogen from CaH_2. Phenyliodine(III)dichloride ($PhICl_2$) was obtained via the reaction of iodobenzene with chlorine by following a literature procedure.[14] Compound **1** was synthesized via Diels-Alder cycloaddition of cyclopentadiene to *p*-benzoquinone.[15] Phenyl- and *o*-nitrophenylsulfenyl chlorides were obtained from corresponding disulfides.[16] Elemental microanalyses were performed by M-H-W Laboratories, Phoenix, AZ.

3,6-Dihydroxy-*exo*-9-(phenylthio)-*endo*-10-chlorotricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5-triene (4). A solution of **1** (0.944 g, 5.43 mmol) in CH_2Cl_2 (8 mL) was cooled to -78 °C by application of an external dry ice-acetone cold bath. To this cooled solution was added dropwise with stirring a solution of PhSCl (776 mg, 5.37 mmol) in CH_2Cl_2 (2 ml). The reaction mixture was allowed to warm gradually to -50 °C and then was stirred at this termperature for 4 h. The cold bath was removed, and the reaction mixture was allowed to warm gradually to room temperature and then stirred at this temperature for 1 h. The reaction mixture was concentrated *in vacuo*, thereby affording crude **4** as a yellow oil. Upon trituration with $CHCl_3$-hexane, the crude product solidified. This solid was collected by suction filtration, air-dried, and then recrystallized from $CHCl_3$-hexane. Pure **4** was thereby obtained as colorless flakes (1.5 g, 87%): mp 99-100 °C; IR (KBr) 3296 (br, m), 1633 (m), 1457 (s), 1288 (s), 1224 (s), 846 (s), 738 cm^{-1} (s); ^{1}H NMR (acetone-d_6) δ 1.95 (m, 1H), 2.15 (dt, J = 9.9, 1.4 Hz, 1 H), 3.11 (t, J = 3.1 Hz, 1 H), 3.61 (s, 1 H), 3.92 (m, 1 H), 4.45 (t, J = 3.7 Hz, 1 H), 6.52 (*AB*, J_{AB} = 8.5 Hz, 1 H), 6.56 (*AB*, J_{AB} = 8.5 Hz, 1 H), 7.20-7.50 (m, 5 H), 7.65 (s, 1 H), 7.82 (s, 1 H); ^{13}C NMR (acetone-d_6) δ 46.34 (t), 47.41 (d), 48.96 (d),

57.68 (d), 65.52 (d), 115.7 (d), 116.1 (d), 127.1 (d), 129.8 (d), 130.0 (s), 130.1 (d), 132.9 (s), 136.6 (s), 144.4 (s), 147.5 (s). Anal. Calcd for $C_{17}H_{15}ClO_2S$: C, 64.04; H, 4.74. Found: C, 64.10; H, 4.83.

3,6-Dihydroxy-*exo*-9-(2-nitrophenylthio)-*endo*-10-chloro-tricyclo[6.2.1.0.^{2,7}]undeca-2(7),3,5-triene (5). A mixture of **1** (562 mg, 3.23 mmol) and *o*-nitrobenzenesulfenyl chloride[16] (628 mg, 3.31 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 40 h. The reaction mixture was washed sequentially with saturated aqueous $NaHCO_3$ (10 mL) and water (20 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue, a yellow oil, was purified via column chromatography on silica gel by using 10-50% EtOAc-hexane (gradient elution scheme). Pure **5** (0.74 g, 63%) was thereby obtained as a yellow microcrystalline solid: mp 204-205 °C (dec); IR (KBr) 3443 (br, m), 1499 (s), 1302 (s), 1147 (s), 731 cm^{-1} (s); ^1H NMR (acetone-d_6) δ 1.98 (m, 1 H), 2.15 (dt, J = 10.2, 1.5 Hz, 1 H), 3.19 (t, J = 3.3 Hz, 1 H), 3.65 (s, 1 H), 3.98 (m, 1 H), 4.58 (t, J = 3.7 Hz, 1 H), 6.54 (AB, J_{AB} = 8.6 Hz, 1 H), 6.65 (AB, J_{AB} = 8.6 Hz, 1 H), 7.40-7.90 (m, 3 H), 7.70 (s, 1 H), 7.95 (s, 1 H), 8.25 (dd, J = 8.5, 1.4 Hz, 1 H); ^{13}C NMR (acetone-d_6) δ 46.21 (t), 47.21 (d), 49.00 (d), 56.58 (d), 64.46 (d), 116.0 (d), 116.4 (d), 126.4 (d), 126.7 (d), 129.3 (d), 130.0 (s), 132.9 (s), 134.8 (d), 136.7 (s), 144.5 (s), 147.4 (s), 147.8 (s). Anal Calcd for $C_{17}H_{14}ClNO_4S$: C, 56.12; H, 3.88. Found: C, 56.30; H, 3.81. The structure of **5** has been established unequivocally by application of single crystal X-ray crystallographic methods (*vide infra*).

2-Oxa-3-hydroxy-12-phenylthio-tetracyclo[7.3.0.0^{3,8}.0^{7,11}]dodec-4-en-6-one (6). To A suspension of $AgBF_4$ (175 mg, 0.9 mmol) in CH_2Cl_2 (3 mL) under argon was cooled to -78 °C by application of an external dry ice-acetone cold bath. To this cold suspension was added dropwise with stirring a solution of phenylsulfenyl chloride (PhSCl, 132 mg, 0.91 mmol) in CH_2Cl_2 (1 mL). The resulting mixture was stirred at -78 °C for 0.5 h after the addition of PhSCl had been completed. A solution of **1** (158 mg, 0.91 mmol) in CH_2Cl_2 (1 mL) then was added, and the reaction mixture was stirred at -78 °C for 1 h. The reaction mixture then was allowed for warm gradually to -30 °C, and a solution of water (0.5 mL) in CH_3CN (2.5 mL) was added dropwise. The resulting mixture was stirred at -30 °C for 0.5 h after the addition of aqueous CH_3CN had been completed. The cold bath was removed, and the reaction mixture was allowed to warm gradually to room temperature and stirred at this temperature for an additional 2 h. Water (5 mL) was added, and the resulting suspension was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue, a pale yellow oil, gradually solidified upon trituration with 1:1 $CHCl_3$-hexane. The resulting

solid was collected by suction filtration, air-dried, and then the residue was purified via column chromatography on silica gel by using 17% EtOAc-hexane as eluent. Pure **6** (155 mg, 57%) was thereby obtained as a colorless microcrystalline solid: mp 179-180 °C; IR (KBr): 3366 (br, m), 1633 (m), 1429 (s), 1259 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 1.70 (m, 1 H), 2.22 (dt, J = 11.3, 1.4 Hz, 1 H), 2.80 (s, 1 H), 2.88 (m, 2 H), 3.12 (m, 2 H), 3.30 (m, 1 H), 4.46 (d, J = 4.9 Hz, 1 H), 6.09 (*AB*, J_{AB} = 10.2 Hz, 1 H), 6.92 (*AB*, J_{AB} = 10.2 Hz, 1 H), 7.10-7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 34.90 (t), 45.49 (d), 47.32 (d), 48.07 (d), 49.00 (d), 51.32 (d), 87.65 (d), 100.9 (s), 126.1 (d), 128.7 (d), 129.1 (d), 129.7 (d), 134.8 (s), 149.7 (d), 197.9 (s). Anal. Calcd for $C_{17}H_{16}O_3S$: C, 67.98; H, 5.37. Found: C, 67.75; H, 5.50. The structures of two polymorphic forms of **6** have been established unequivocally by application of single crystal X-ray crystallographic methods (*vide infra*).

3,6-Dihydroxy-*exo*-9-*syn*-11-dichlorotricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5-triene (7a). A solution of freshly prepared[14] $PhICl_2$ (0.41 g, 1.49 mmol) in CH_2Cl_2 (10 mL) under argon was cooled to -78 °C by application of an external dry ice-acetone cold bath. To this cold solution was added with stirring $SbCl_5$ (1.5 mL of a 1.0 M solution in CH_2Cl_2, 1.5 mmol). The reaction mixture immediately darkened upon addition of this $SbCl_5$ solution. To the resulting mixture was added dropwise a solution of **1** (260 mg, 1.49 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was stirred at -78 °C for 0.5 h after the addition of **1** had been completed. The cold bath then was removed, and the reaction mixture was allowed to warm gradually to room temperature. Saturated aqueous $NaHCO_3$ (10 mL) was added, and the resulting mixture was extracted with $CHCl_3$ (3 x 15 mL). The combined organic extracts were dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue, a dark brown oil, was purified via column chromatography on silica gel by eluting with 9% EtOAc-hexane. Recrystallization of the material thereby obtained from $CHCl_3$-hexane afforded pure **7a** (153 mg, 42%) as a colorless microcrystalline solid: mp 83-84 °C; IR (KBr) 3312 (br, m), 3035 (m), 1604 (m), 1495 (s), 1381 (m), 1246 (m), 1036 (s), 807 cm^{-1} (s); ^{1}H NMR (acetone-d_6) δ 2.22 (dd, J = 13.0, 8.1 Hz, 1 H), 2.55 (dt, J = 13.1, 3.8 Hz, 1H), 3.68 (m, 1 H), 3.79 (t, J = 1.6 Hz, 1H), 3.90 (ddd, J = 8.0, 4.4, 1.2 Hz, 1 H), 4.15 (t, J = 1.2 Hz, 1 H), 6.56 (s, 2 H), 7.95 (br s, 2 H); ^{13}C NMR (acetone-d_6) δ 36.65 (t), 47.68 (d), 53.93 (d), 57.56 (d), 66.91 (d), 116.3 (d), 117.0 (d), 129.1 (s), 130.8 (s), 144.8 (s), 145.0 (s). The structure of **7a** has been established unequivocally by application of single crystal X-ray crystallographic methods (*vide infra*).

Compound **7a** was further characterized as the corresponding di-*O*-acetyl derivative, **7b**. Thus, a mixture of **7a** (100 mg, 0.4 mmol), Et_3N (242 mg, 2.4 mmol) and *N,N*-dimethylaminopyridine (15 mg,

catalytic amount) in dry CH_2Cl_2 (10 mL) was cooled to 0°C by application of an external ice-water bath. To this cooled mixture was added dropwise with stirring acetic anhydride (Ac_2O, 102 mg, 1.2 mmol). After the addition of Ac_2O had been completed, the cold bath was removed. The reaction mixture was allowed to warm gradually to room temperature, and stirring was continued for 12 h. The reaction mixture was diluted with water (25 mL), and the resulting aqueous suspension was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were washed sequentially with 10% aqueous HCl (10 mL) , water (20 mL) and brine (25 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue thereby obtained was purified via column chromatography on silica gel by eluting with 15% EtOAc-hexane. Pure **7b** (124 mg, 95 %) was thereby obtained as a colorless microcrystalline solid: mp 155-156 °C; IR (KBr) 2997 (w), 2944 (w), 1761 (s), 1481 (s), 1439 (w), 1365 (m), 1296 (m), 1174 (vs), 1032 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 2.28 (s, 3 H), 2.32 (s, 3 H), 2.21-2.42 (m, 1 H), 2.62 (dt, J = 13.0, 4.0 Hz, 1 H), 3.45 (bs, 1 H), 3.57 (bs, 1 H), 4.01 (dd, J = 9.2, 5.6 Hz, 1 H), 4.06 (br s, 1 H), 6.87 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.76 (q, 2 C), 35.01 (t), 40.07 (d), 54.12 (d), 55.49 (d), 65.71 (d), 121.41 (d), 121.95 (d), 135.25 (s), 137.11 (s), 141.81 (s), 142.04 (s), 168.71 (s, 2 C); Anal. Calcd for $C_{15}H_{14}Cl_2O_2$: C, 54.73; H, 4.29; Found: C, 54.95; H, 4.20.

3,6-Dihydroxy-*exo*-9-fluoro-*syn*-11-chlorotricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5-triene (8). A suspension of $AgBF_4$ (125 mg, 0.64 mmol) in dry CH_2Cl_2 (3 mL) under argon was cooled to -30 °C by appli-cation of an external dry ice-acetone cold bath. To this cold solution was added portionwise with stirring freshly prepared[14] solid $PhICl_2$ (175 mg, 0.64 mmol), and the resulting mixture was stirred under argon at -30 °C for 0.5 h. Compound **1** (112 mg, 0.64 mmol) then was added, and the resulting mixture was stirred under argon for an additional 2 h. The external cold bath was removed, and the reaction mixture was allowed to warm gradually to room temperature and then stirred for 0.5 h at this temperature. Water (20 mL) was added, and the resulting aqueous suspension was extracted with $CHCl_3$ (3 x 20 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue, a yellow oil, was purified via column chromatography on silica gel by eluting with 9% EtOAc-hexane. Pure **8** was thereby obtained as a colorless microcrystalline solid (78 mg, 53%): mp 143-145 °C; IR (KBr) 3268 (br, m), 1668 (m), 1499 (s), 1239 (m), 1055 (s), 844 cm^{-1} (s); ^1H NMR (acetone-d_6) δ 2.05 (m, 1 H), 2.40 (ddt, J = 30.3, 13.2, 2.8 Hz, 1 H), 3.65 (br s, 1 H), 3.88 (d, J = 7.0 Hz, 1 H), 4.19 (s, 1 H), 4.73 (dd, J_{HF} = 56.2 Hz, J_{HH} = 6.7 Hz, 1 H), 6.55 (s, 2 H), 7.78 (s, 1 H), 7.94 (s, 1 H); ^{13}C NMR (acetone-d_6) δ 34.28 (d, J = 21.2 Hz), 46.85 (s), 52.64 (d, J = 21.5 Hz), 67.03 (s), 95.01 (d, J =

194.8 Hz), 116.5 (s), 117.3 (s), 126.4 (s), 126.6 (s), 132.7 (s), 145.5 (d, J = 37.2 Hz); ^{19}F NMR (acetone-d_6) δ 3.32 (dddd, J = 56.4, 30.2, 12.1, 7.2 Hz, 1 F). Anal. Calcd for $C_{11}H_{10}ClFO_2$: C, 57.89; H, 4.42. Found: C, 57.78; H, 4.55. The structure of **8** has been established unequivocally by application of single crystal X-ray crystallographic methods (*vide infra*).

X-ray Structure Determination of 5, 6, 7a, and 8. All data were collected on an Enraf-Nonius CAD-4 diffractometer by using Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Standard procedures developed in our laboratory for this purpose have been described previously.[17] X-ray data thereby obtained for **5, 6, 7a,** and **8** are presented in Table 1.

Table 1. X-ray structure data for **5, 6 (polymorphs A and B), 7a,** and **8.**

Compound	**5**	**6 (polymorph A)**	**6 (polymorph B)**	**7a**	**8**
Formula	$C_{21}H_{22}ClNO_6S$	$C_{17}H_{16}O_3S$	$C_{17}H_{16}O_3S$	$C_{11}H_{10}Cl_2O_2 \cdot H_2O$	$C_{11}H_{10}ClFO_2$
Size (mm)	.08 x .10 x .22	.08 x .12 x .62	.07 x .22 x .48	.05 x .07 x .21	.08 x .12 x .33
Space Group	P1	Pbca	$P2_1P2_1P2_1$	P1	Pc
a (Å)	7.435 (2)	9.0202 (7)	6.7333 (9)	6.496 (1)	7.1579 (8)
b (Å)	7.454 (2)	13.0568 (9)	8.0319 (6)	7.391 (3)	18.3040 (8)
c (Å)	19.120 (4)	24.551 (2)	26.078 (2)	12.178 (2)	11.325 (1)
a (°)	83.16 (1)			81.02 (3)	
b (°)	87.74 (2)			83.33 (1)	90.250 (9)
g (°)	80.82 (20			81.94 (30	
V (Å^3)	1038 (1)	2851.5 (3)	1410.3 (3)	569.2 (3)	1483.7 (7)
Z	2	8	4	2	6
D_C (g-cm^{-3})	1.445	1.380	1.415	1.535	1.536
m (cm^{-1})	3.15	2.20	2.26	5.58	3.72
$2q_{max}$	40	44	44	44	44
Total refl.	1926	2064	1055	1383	2063
Unique refl.	1926	2064	1055	1085	1898
R_{int}	- -	- -	- -	- -	0.032
I ≥ 3s(I)	632	1141	828	1085	1002
Parameters	121	160	105	115	194
R, wR	.0767, .0875	.0504, .0495	.0497, .0491	.1275, .1596	.0795, .0875
$(D/s)_{max}$	<0.01	<0.01	<0.01	<0.01	<0.01
r_{min}; r_{max}	0.38, -0.30	0.44, -0.32	0.34, -0.40	0.83, -0.76	0.83, -0.72

Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods [SIR[18] (**6, polymorph B**), MULTAN[19] (**6, polymorph A**), and SHELXS-86[20] (**5** and **8**)]. In each case, the model was refined by using full-matrix least-squares techniques. The treatment of thermal parameters was based upon a number of observed data. Thus, anisotropic parameters were incorporated for the S and O atoms in **6, polymorph B**, the Cl atom in **8**, all non-hydrogen and non-phenyl carbons in **6, polymorph A**, and in **5**. Sufficient data were available to enable anisotropic treatment of all non-hydrogen atoms. Hydrogen atoms were located on difference maps and then included

in the model in idealized positions [U(H) = 1.3 B_{eq}(C)]. All computations other than those specified were performed by using MolEN.[21] Scattering facters were taken from the usual sources.[22,23]

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References and Footnotes

1. (a) Cookson, R. C.; Crundwell, E.; Hill, R. R.; Hudec, J. *J. Chem. Soc.* **1964,** 3062. (b) Marchand, A. P.; Allen, R. W. *J. Org. Chem.* **1974,** *39,* 1596.
2. For a review, see: Marchand, A. P. In *Advances in Theoretically Interesting Molecules;* Thummel, R. P., Ed.; JAI: Greenwich, CT; 1989, Vol. 1, pp. 357-399.
3. Singh, N.; Verma, S. M. *Indian J. Chem.* **1980,** *19B,* 290.
4. Reviews: (a) Ruasse, M.-F. *Adv. Phys. Org. Chem.* **1993,** *28,* 207. (b) Ruasse, M.-F. *Acc. Chem. Res.* **1990,** *23,* 87 and references cited therein. (c) de la Mare, P. B. D.; Bolton, R. *Electrophilic Addition to Unsaturated Systems,* 2nd ed.; Elsevier: New York, 1982, pp 136-197. (d) Schmid, G. H. *The Chemistry of Functional Groups. Supplement A: The Chemistry of Double-Bonded Functional Groups,* Patai, S., Ed.; Wiley-Interscience: New York, 1989, pp. 695-706. (e) Schmid, G. H.; Garratt, D. G. "The Chemistry of Functional Groups. Supplement A: *The Chemistry of Functional Groups. Supplement A: The Chemistry of Double-Bonded Functional Groups,* Patai, S., Ed.; Wiley-Interscience: New York, 1977, pp. 754-785.
5. Smart, B. E. *J. Org. Chem.* **1973,** *38,* 2027.
6. e. g., See: (a) Cristol, S. J.; Nachtigall, G. W. *J. Org. Chem.* **1967,** *32,* 3727. (b) Caple, R.; Hsu, F. M.; Ilenda, C. S. *J. Org. Chem.* **1968,** *33,* 4111. (c) Tanner, D. D.; Gidley, G. C. *J. Org. Chem.* **1968,** *33,* 38.
7. Paquette, L. A.; Ward, J. S. J. Org. Chem. 1972, 37, 3569.
8. Dols, P. P. M. A.; Klunder, A. J. H.; Zwanenburg, B. *Tetrahedron* **1993,** *49,* 11373.
9. Effenberger, F.; Russ, W. *Chem. Ber.* **1982,** *115,* 3719.
10. Zefirov, N. S.; Koz'min, A. S.; Kasumov, T.; Potekhin, K. A.; Sorokin, V. D.; Brel, V. K.; Abramkin, E. V.; Struchkov, Yu. T.; Zhdankin, V. V.; Stang, P. J. *J. Org. Chem.* **1992,** *57,* 2433.
11. (a) Kwart, H. C.; Miller, R. K. *J. Am. Chem. Soc.* **1956,** *78,* 5678. (b) Cristol, S. J.; Arganbright, R. P.; Brindell, G. D.; Heitz, R. M. *J. Am. Chem. Soc.* **1957,** *79,* 6035. (c) Mueller, W. H.; Butler, P. E. *J. Am. Chem. Soc.* **1966,** *88,* 2866.
12. (a) Zefirov, N. S.; Sadovaya, N. K.; Magerramov, A. M.; Bodrikov, I. V.; Karataschov, V. R. *Tetrahedron* **1975,** *31,* 2948. (b) Zefirov, N. S.; Sadovaya, N. K.; Navgorodtseva, A..; Bodrikov, I. V.*Tetrahedron* **1978,** *34,* 1373.
13. For a critical reappraisal of the episulfonium ion mechanism of addition of RSCl to carbon-carbon double bonds, see: Smit, W. A.; Zefirov, N. S.; Bodrikov, I. V.; Krimer, M. Z. *Acc. Chem. Res.* **1979,** *12,* 282.
14. Lucas, H. J.; Kennedy, E. R. *Org. Syn., Coll. Vol. 3,* Wiley: New York, 1955, pp 482-483.
15. Marchand, A. P.; Allen, R. W. *J. Org. Chem.* **1974,** *39,* 1596.
16. Hubacher, M. H. *Org. Syn., Coll. Vol. 2,* Wiley: New York, 1943, pp 455-457.
17. Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993,** *115,* 4971.
18. Burla, M. C.; Carnalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Cryst.* **1989,** *22,* 389.
19. Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; DeClerq, J. P.; Woolfson, M. M. *MULTAN80, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data;* University of York, England; 1980.
20 Sheldrick, G. M. In: *Crystallographic Computing,* Sheldrick, G. M.; Krüger, C.; Goddard, R., Eds. OUP, 1985, pp. 184-189.
21. *MolEN, An Interactive Structure Soltuion Program,* Enraf-Nonius: Delft, The Nether-lands; 1990.
22. Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography; Vol. IV;* Kynoch Press: Birmingham; 1974, Table 2.
23. Tables of atomic coordinates and isotropic thermal parameters, bond lengths, bond angles,anisotropic thermal parameters, H-atom coordinates, and isotropic thermal parameters for **5, 6 (polymorphs A and B), 7a,** and **8** are available upon request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CV2 1EW, U. K. Requests should be accompanied by the full literature citation for this article.

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