Stereochemistry of the Electrophilic Homoallylic Chlorination Reaction of Sterically Congested Alkenes with Benzenesulfenyl Chloride: The Structure of the Phenylthiiranium Ion Intermediate

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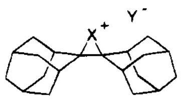
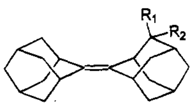
A methyl-substituted derivative (**4**) of the sterically congested alkene adamanylideneadamantane (Ad=Ad; **2**) has been synthesized. Upon reaction with PhSCl, **4** shows a remarkable selectivity; only two of the remaining 15 homoallylic positions undergo reaction to give chlorinated products. The phenylthiiranium ion of the parent alkene Ad=Ad has been prepared and characterized by single-crystal X-ray diffraction and ^{1}H and ^{13}C NMR spectroscopy as its triflate salt (**1d**). Crystal data for $[(C_{10}H_{14})_2S(C_6H_5)][SO_3CF_3]$: triclinic, space group $P\bar{1}$; $Z = 4$; $a = 10.983(3)$ Å; $b = 14.988(3)$ Å; $c = 16.059(6)$ Å; $\alpha = 95.60(2)°$; $\beta = 93.39(2)°$; $\gamma = 108.98(2)°$; $V = 2476$ Å^3; $T = 216$ K; $R_F = 0.052$ for 4840 data ($I_o \geq 2.5\sigma(I_o)$) and 633 variables. The dimensions of the thiiranium (SC_2) rings are S–C range 1.909(3)-1.937(3) Å; $\langle C-C \rangle = 1.500$ Å; $\langle C-S-C \rangle = 46.1°$; C–C–S range 66.3(2)–67.9(2)°. The crystallographically independent cations display similarly asymmetric dispositions of the phenyl group: $C-S-C_{ipso}$ are 108.5(2)°, 116.7(2)°, and 112.9(2)°, 117.6(2)° respectively; $S-C_{ipso} = 1.789(3)$ Å in both cases. In both cations the plane of the phenyl ring is approximately orthogonal to the plane of the thiiranium ring but nearly coplanar with one of the ring S–C bonds.

Introduction

We are interested in the mechanism of electrophilic addition to alkenes, and especially in the structure and reactivity of any intermediates formed during the reaction. The use of sterically congested alkenes has allowed the isolation and characterization of several intrinsically reactive intermediates formed during the electrophilic addition reaction, i.e. **1a**,[1] **1b**,[2,3] and **1c**.[3] Here the normal product forming steps have been slowed down or stopped altogether by severe steric crowding at the stage of the reactive intermediate.



1a: X=Br; Y=Br_3
1b: X=Br; Y=OTrf
1c: X=I; Y=OTrf
1d: X=SPh; Y=OTrf



2: R_1=R_2=H
3: R_1=H; R_2=Cl
4: R_1=CH_3; R_2=H
5: R_1=H; R_2=CH_3

Adamantylideneadamantane (Ad=Ad; **2**) was reported in 1969 to give a stable bromonium ion tribromide salt when treated with bromine, as opposed to the normal dibromide/bromosolvate products.[1] This ion has been characterized by single-crystal X-ray diffraction.[4] Recently, it has been shown that the tribromide anion in **1a** can be trapped with methyl trifluoromethanesulfonate (triflate), which replaces the Br_3^- anion with nearly nonnucleophilic $CF_3SO_3^-$ anion to give **1b**.[2,3] The counteranion of the iodonium ion has also been trapped using silver triflate to give **1c**.[3] Ad=Ad has also been reported to react with several electrophilic reagents to yield a homoallylic substitution product (**3**), instead of the normal products of addition. The reagents used include benzenesulfenyl chloride,[5] benzeneselenenyl chloride,[6] and NCS.[7] A possible reaction pathway leading to the substitution product **3** (for the reaction of PhSCl) is shown in Scheme 1.

We accordingly decided to isolate and structurally characterize the proposed thiiranium ion intermediate using methyl triflate to trap the chloride anion. Thus, we should prevent the formation of any product that requires the presence of chloride ion acting as a nucleophile or as a base.

We were also interested in the stereochemical course of the homoallylic substitution reaction. Clearly with Ad=Ad itself, there is no means of probing whether syn (arrow a, Scheme 1) or anti elimination (arrow b) is occurring to form the proposed cyclopropylcarbinyl thioether followed by opening of the cyclopropyl ring with chloride ion (either in a concerted fashion or by a stepwise mechanism). We envisioned that a pseudoaxial methyl derivative of Ad=Ad (with respect to the double bond) **4** would allow the stereochemistry of the homoallylic chlorination reaction to be determined.

Interestingly, Ad=Ad has been reported to react with both SCl_2 and S_2Cl_2 in chloroform and dichloromethane to provide good to excellent yields of **6**. Here the thiirane

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(6) We find that in contrast to the report in the literature (Garrett, D. G. *Tetrahedron Lett.* **1979**, *23*, 285), the reaction of benzeneselenenyl chloride with Ad=Ad gives an almost quantitative yield of **3**. In a footnote, Lopez, L.; Troisi, L.; Mele, G. *Tetrahedron Lett.* **1991**, *32*, 117–120; communicated a similar result.

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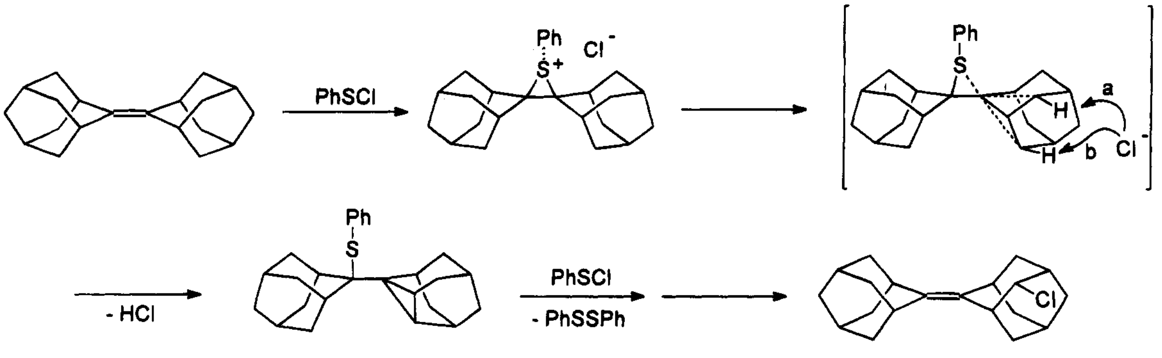
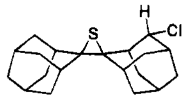
0022-3263/94/1959-7108$04.50/0

Scheme 1



ring and the chlorine substituent are on the same face of the molecule as shown by single-crystal X-ray diffraction, thus implying that the stereochemistry was determined by an initial syn reaction.[8,9]



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Experimental Section

(a) Materials and Methods. All NMR spectra reported in this manuscript were run on a Bruker AMX-400 spectrometer. Spectra were acquired using either $CDCl_3$ or CD_2Cl_2 as solvent and as the internal reference. Multiplicity assignments for ^{13}C NMR spectra were made using a DEPT pulse sequence.[10] 2-D ^1H NMR COSY[11] and NOESY[12] (800 ms mixing time) phase sensitive spectra were acquired using standard pulse sequences. All melting points are uncorrected.

1′-Phenyldispiro[tricyclo[3.3.1.1^{3,7}]decane-2,2′-thiiranium-3′,2″-tricyclo[3.3.1.1^{3,7}]decane] Trifluoromethanesulfonate (1d). To a solution of 2-(tricyclo[3.3.1.1^{3,7}]decylidene)tricyclo[3.3.1.1^{3,7}]decane (**2**)[13] (1.6 g, 6 mmol) in dry dichloromethane (40 mL) were added methyl trifluoromethanesulfonate (10 mL; 1 N solution in dichloromethane) and benzenesulfenyl chloride[14] (0.742 g, 5.13 mmol). The reaction mixture was stirred for 10 min until the color of benzenesulfenyl chloride had disappeared. Volatiles were removed under reduced pressure, and the residue was washed with hexane and then ether (to remove the excess alkene). The solid residue was purified by recrystallization from CH_2Cl_2/Et_2O to give a colorless hygroscopic solid (2.6 g; 96%), mp = 137 °C dec. ^1H NMR (400 MHz; CD_2Cl_2) δ 1.68–1.74 (m, 2H), 1.90–2.00 (m, 5H), 2.11–2.19 (m, 5H), 2.20–2.38 (m, 10H), 2.48 (m, 2H), 2.56 (m, 2H), 2.95 (m, 2H), 7.58–7.68 (m, 2H), 7.68–7.76 (m, 3H). ^{13}C NMR (100 MHz; CD_2Cl_2) δ 133.7 (Ar), 132.4 (Ar), 131.7 (Ar), 120.6 (Ar), 105.1 (C), 39.8 (CH_2), 39.2 (CH_2), 38.7 (CH_2), 37.1 (CH_2), 36.6 (CH_2), 35.5 (CH), 31.7 (CH), 27.1 (2CH). Anal. Calcd for $C_{27}H_{33}F_3S_2O_3$: C, 61.57; H, 6.32. Found: C, 61.57; H, 6.37.

(1*R,2*R**)-2-Hydroxy-4-(tricyclo[3.3.1.1^{3,7}]decylidene)tricyclo[3.3.1.1^{3,7}]decane (7).** (1*R**,2*R**)-2-Chloro-4-tricyclo[3.3.1.1^{3,7}]decylidene)tricyclo[3.3.1.1^{3,7}]decane (**3**)[7] (6.2 g) and Ag_2O (8.4 g) in THF (150 mL) and H_2O (50 mL) were heated at reflux for 6 h. The precipitate was filtered and the solvent evaporated. The product was extracted with EtOAc (2 x 200 mL) and dried (Na_2SO_4). Removal of the solvent gave 6.0 g of crude product (theoretical 5.83 g), which was used directly for the next step. The alcohol (1.0 g) was purified by recrystallization from MeOH to give a white solid (0.75 g): mp = 210–213 °C (lit.[15] mp 214–215 °C). ^1H NMR (400 MHz; $CDCl_3$) δ 1.42–1.48 (m, 1H), 1.52–1.72 (m, 8H), 1.75–1.96 (m, 11H), 2.08–2.20 (m, 2H), 2.84 (bs, 1H), 2.88 (bs, 3H), 3.74 (t, 1H). ^{13}C NMR (100 MHz; $CDCl_3$) δ 136.01, 130.98, 74.95, 39.78 (CH_2), 39.69 (CH_2), 39.66 (CH_2), 39.62 (CH_2), 39.28 (CH_2), 38.66 (CH_2), 37.27 (CH_2), 37.01 (CH_2), 34.56 (CH), 32.58 (CH_2), 32.49 (CH), 32.21 (CH), 30.67 (CH_2), 30.67 (CH), 28.52 (2CH), 27.83 (CH).

2-Oxo-4-(tricyclo[3.3.1.1^{3,7}]decylidene)tricyclo[3.3.1.1^{3,7}]decane (8). The alcohol **7** (5.0 g) was treated with $Na_2Cr_2O_7$ (5.0 g) and a mixture containing concd H_2SO_4 (5 mL) in Et_2O (200 mL) and H_2O (30 mL). After 1 h of stirring, the Et_2O layer was washed with H_2O and saturated NaCl and dried ($MgSO_4$). The product was purified by flash column chromatography (silica; eluant hexane, followed by 5% EtOAc in hexane) to give a white solid (4.1 g, 82%): mp = 154–155 °C (lit.[15] mp 158–160 °C). ^1H NMR (400 MHz; $CDCl_3$) δ 1.60–1.72 (m, 4H), 1.78–2.15 (m, 17H), 2.59 (bs, 1H), 2.85–2.92 (m, 2H), 3.05 (bs, 1H), 3.60 (bs, 1H).

4-Methylene-2-(tricyclo[3.3.1.1^{3,7}]decylidene)tricyclo[3.3.1.1^{3,7}]decane (9). The ketone **8** (4.4g, 15.6 mmol) in dry CH_2Cl_2 (30 mL) was added to a methylenation reagent prepared according to the procedure of Lombardo.[16] This mixture was stirred at rt for 2 h. The product was purified by flash column chromatography (silica; eluant hexane) to give a white solid (3.5 g, 80%): mp = 98–99 °C. ^1H NMR (400 MHz; $CDCl_3$) δ 1.61–1.79 (m, 6H), 1.79–2.00 (m, 15H), 2.53 (bs, 1H), 2.86 (bs, 1H), 2.95 (bs, 1H), 2.98 (bs, 1H), 3.50 (bs, 1H), 4.43 (d, J = 2Hz, 1H), 4.48 (d, J = 2Hz, 1H), MS m/z 280. Anal. calcd for $C_{21}H_{28}$: C, 89.94; H, 10.06. Found: C, 89.92; H, 9.93.

(1*R,4*R**)-4-(Hydroxymethyl)-2-(tricyclo[3.3.1.1^{3,7}]decylidenetricyclo[3.3.1.1^{3,7}]decane (10a).** A solution of the methylene compound **9** (3.8 g, 13.6 mmol) in hexane (100 mL) was treated with BH_3 (20 mL; 1 N in THF). After the solution was stirred at rt for 10 min, a solution of H_2O_2 (10 mL; 30%) and NaOH (1N; 10 mL) was added dropwise and the mixture stirred for a further 1 h. The product was extracted with EtOAc (3 × 200 mL), dried (Na_2SO_4), and filtered. Evaporation of the solvent under reduced pressure afforded a mixture of the 4*R* and 4*S* isomers in a 1.1:1 ratio. TLC (silica gel; 10% EtOAc in hexane) showed a $\Delta R_f \approx 0.06$, with $R_f = 0.24$ (4*R*) and $R_f = 0.18$ (4*S*). Separation by flash column chromatography (silica: eluant 5% EtOAc in hexane) gave the 4*R* isomer (**10a**; 1.10 g), a mixture of the 4*R* and 4*S* isomers (0.69 g), and the 4*S* isomer (**10b**; 1.16 g), for a total of 2.95 g (combined yield = 74%).

4*R* isomer: mp = 133–134 °C. ^1H NMR (400 MHz; $CDCl_3$) δ 1.60–2.00 (m, 23H), 2.84 (bs, 1H), 2.87 (bs, 2H), 2.91 (bs, 1H), 3.53 (dd, J = 6.8 Hz, J = 10.5 Hz, 1H), 3.59 (dd, J = 6.8 Hz, J = 11.3 Hz, 1H). Anal. Calcd for $C_{21}H_{30}O$: C, 84.51; H, 10.13. Found: C, 84.41; H, 10.25.

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4*S* isomer: mp = 118−119 °C. ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.60−1.98 (m, 23H), 2.81−2.96 (b, 4H), 3.76 (dd, *J* = 6.8 Hz, *J* = 11.3 Hz, 1H), 3.80 (dd, *J* = 6.8 Hz, *J* = 11.3 Hz, 1H). Anal. Calcd for $C_{21}H_{30}O$: C, 84.51; H, 10.13. Found: C, 84.30; H, 10.25.

(1*R,4*R**)-4-[[(4-Toluenesulfonyl)oxy]methyl]-2-(tricyclo[3.3.1.1^{3,7}]decylidene)tricyclo[3.3.1.1^{3,7}]decane (11a).** **10a** (1.0 g, 3.4 mmol) and TsCl (1.3 g, 6.8 mmol) in dry pyridine (10 mL) were stirred overnight. Then MeOH (40 mL) was added, and the solution was cooled to −5 °C. After leaving overnight, crystallization was complete, and the product was collected as white crystals (1.39 g, 91%) mp =138−139 °C. ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.40−1.50 (m, 3H), 1.52−1.64 (m, 4H), 1.67−1.94 (m, 15H), 2.09−2.16 (m, 1H), 2.43 (s, 3H), 2.76 (bs, 3H), 2.82 (bs, 1H), 3.88 (dd, *J* = 6.8 Hz, *J* = 10.0 Hz, 1H), 3.93 (dd, *J* = 6.8 Hz, *J* = 10.0 Hz, 1H), 7.32 (m, 2H), 7.76 (m, 2H). Anal. Calcd for $C_{28}H_{36}O_3S$: C, 74.30; H, 8.02. Found: C, 74.33; H, 8.14.

(1*R,4*R**)-4-Methyl-2-(tricyclo[3.3.1.1^{3,7}]decylidene)tricyclo[3.3.1.1^{3,7}]decane (4).** The tosylate **11a** (1.39 g, 3.1 mmol) and $NaBH_4$ (0.60 g) in dry DMSO (30 mL) were heated to 100 °C for 12 h. The product was extracted with hexane, washed with water, and dried ($MgSO_4$). The product was purified by flash column chromatography (silica; eluant hexane) to give a white solid (0.82 g, 94%). mp = 106−107 °C. ^{1}H NMR (400 MHz; $CDCl_3$) δ 0.89 (d, *J* = 8Hz, 3H), 1.55−1.75 (m, 8H), 1.76−1.95 (m, 15H), 2.62 (bs, 1H), 2.80 (bs, 1H), 2.86 (bs, 1H), 2.93 (bs, 1H). MS *m/z* 282. ^{13}C NMR (100 MHz; $CDCl_3$) δ 136.4, 130.3, 41.1 (CH), 41.0 (CH_2), 40.5 (CH_2), 40.2_4 (CH_2), 40.2 ($2CH_2$), 39.7 (CH_2), 39.4 (CH_2), 38.3 (CH), 37.8 (CH_2), 34.7 (CH), 33.7 (CH_2), 32.7 (CH), 32.5 (CH), 32.4 (CH), 29.2_3 (CH), 29.1_7 (CH), 28.8 (CH), 19.5 (CH_3). Anal. Calcd for $C_{21}H_{30}$: C, 89.30; H, 10.70. Found: C, 89.26; H, 10.72.

(1*R,4*S**)-4-[[(4-Toluenesulfonyl)oxy]methyl]-2-(tricyclo[3.3.1.1^{3,7}]decylidene)tricyclo[3.3.1.1^{3,7}]decane (11b).** The same procedure as above was applied for the tosylation reaction using **10b** (0.85 g), TsCl (1.30 g), and pyridine (10 mL) to give **11b** as white crystals (1.18 g, 91%): mp = 148−149 °C. ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.39 (bd, *J* = 13Hz, 1H), 1.50−1.98 (m, 22H), 2.45 (s, 3H), 2.74 (bs, 1H), 2.80 (bs, 1H), 2.86 (bs, 1H), 2.89 (bs, 1H), 4.15 (dd, *J* = 0.5 Hz, *J* = 8Hz, 2H), 7.34 (d, *J* = 8Hz, 2H), 7.80 (d, *J* = 8 Hz, 2H). Anal. Calcd for $C_{28}H_{36}O_3S$: C, 74.30; H, 8.02. Found: C, 74.45; H, 8.14.

(1*R,4*S**)-4-Methyl-2-(tricyclo[3.3.1.1^{3,7}]decylidene)tricyclo[3.3.1.1^{3,7}]decane (5).** The same procedure as above was applied for the reductive detosylation using **11b** (1.18 g), $NaBH_4$ (0.50 g) and DMSO (30 mL) to give **5** as a white solid (0.68 g, 92%). mp = 117−118 °C. ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.08 (d, *J* = 8Hz, 3H), 1.36−1.42 (m, 1H), 1.50−1.56 (m, 1H), 1.60−1.71 (m, 7H), 1.72−1.89 (m, 10H), 1.89−1.94 (m, 2H), 1.95−2.07 (m, 2H), 2.58 (bs, 1H), 2.90 (bs, 3H). MS *m/z* 282. ^{13}C NMR (100 MHz; $CDCl_3$) δ 134.9, 133.4, 41.1 (CH_2), 40.8 (CH), 40.6 (CH_2), 40.1_4 (CH_2), 40.1 (CH_2), 40.0_5 ($2CH_2$), 37.9 (CH_2), 37.8 (CH), 34.3 (CH), 33.0 (CH_2), 32.6 (CH), 32.5 (CH), 31.9 (CH), 31.2 (CH_2), 29.2 (3CH), 18.7 (CH_3). Anal. Calcd for $C_{21}H_{30}$: C, 89.30; H, 10.70. Found: C, 89.29; H, 10.68.

Reaction of 4 with Benzenesulfenyl Chloride. The pseudoaxial methyl derivative **4** (relative configuration 1*R*,4*R*; 226 mg; 0.8 mmol) and PhSCl (200 μL; 1.76 mmol) in dry dichloromethane (8 mL) were stirred under an inert atmosphere for 3 days. Evaporation of the volatiles gave a residue which was purified by flash column chromatography (silica; eluant hexane) to give a mixture of monochlorinated products **12** and **13** (233 mg; 92%) and starting material (18 mg; 8%). The mixture of monochlorinated products showed a mp = 81−84 °C. ^{1}H NMR (400 MHz; $CDCl_3$) for the only two observable resonances with a chemical shift ≥3.00, δ 4.19 (bs, relative integration 22 ± 5%) and δ 4.31 (bs, relative integration 78±5%). MS *m/z* 316 (100), 317 (25.4), 318 (36.6), 319 (7.9). Anal. Calcd for $C_{21}H_{29}Cl$: C, 79.59; H, 9.22. Found: C, 79.40; H, 9.36.

This mixture of monochlorinated products (73 mg, 0.23 mmol) and PhSCl (100 μL; 0.88 mmol) in dry dichloromethane (3 mL) was stirred under an inert atmosphere for 3 days. Evaporation of the volatiles gave a residue which was purified by flash column chromatography (silica; eluant hexane) to give a dichlorinated product ***rel*-(1*R*,2*R*,4*S*,6*R*)-2,4-dichloro-6-methyl-9-(tricyclo[3.3.1.1^{3,7}]decylidene)tricyclo[3.3.1.1^{3,7}]decane (14)** as a white crystalline solid (57 mg; 70%): mp = 134−135 °C dec. ^{1}H NMR (400 MHz; $CDCl_3$) δ 0.92 (d, *J* = 7 Hz, 3H), 1.55−1.73 (m, 6H), 1.80−1.98 (m, 8H), 2.07−2.18 (m, 2H), 2.20−2.27 (m 1H), 2.32 (bs, 1H), 2.46−2.55 (m 1H), 2.80 (bs, 1H), 2.84 (bs, 1H), 2.90 (bs, 1H), 2.92 (bs, 1H), 4.02 (bs, 1H), 4.13 (bs, 1H). MS *m/z* 350 (100), 351 (23.3), 352 (65.0), 353 (15.8), 354 (12.5). Anal. Calcd for $C_{21}H_{28}Cl_2$: C, 71.79; H, 8.03. Found: C, 71.86; H, 8.03.

Regiochemistry of the first chlorination product was shown by reacting the mixture of monochlorinated products (75 mg, 0.24 mmol) and Ag_2O (0.2 g) in THF (10 mL) and H_2O (5 mL) at reflux for 3 days. The precipitate was removed by filtration, and the product was purified by flash column chromatography (silica; 5% EtOAc in hexane) to give a white solid (67 mg; 96%). This solid and *p*-nitrobenzoyl chloride (100 mg) in dry pyridine (1 mL) were stirred at rt for 2 days. The product was extracted with EtOAc (3 × 10 mL), washed with 5% HCl, H_2O, and 1 N NaOH, and dried ($MgSO_4$). Purification by flash column chromatography (silica; 5% EtOAc in hexane) gave a light yellow solid (93 mg; 93%). Two recrystallizations from MeOH/hexane increased the ratio of the major:minor products from 4:1 to ≈10:1: mp = 118−120 °C. ^{1}H NMR (400 MHz; toluene-d_8, major product peaks only) δ 0.96 (d, *J* = 7 Hz, 3H), 1.45−1.92 (m, 19H), 2.15−2.23 (m, 1H), 2.32−2.40 (m, 1H), 2.66 (bs, 1H), 2.80 (bs, 1H), 2.87 (bs, 1H), 3.02 (bs, 1H), 5.16 (bs, 1H), 7.68 (m, 2H), 7.80 (m, 2H).

Crystallography. Crystals suitable for structural analysis were obtained by addition at ambient temperature of ethyl acetate (200 μL/mg) to a solution of **1d** in dichloromethane (60 μL/mg). To this mixture was added hexane (~20 μL/mg) until the solution became turbid, then addition of a small quantity of ethyl acetate clarified the solution, and this mixture was left undisturbed at rt overnight, after which crystallization was complete. The selected crystal was rapidly transferred from the mother liquor and carefully wedged, using a trace of apiezon grease as an adhesive, in a glass capillary tube which was then sealed and mounted on the diffractometer. Data were recorded at 216 K with an Enraf Nonius CAD4F diffractometer equipped with an in-house modified low-temperature attachment and using graphite-monochromatized Mo Kα radiation. Two intensity standards were measured every hour of exposure time and fluctuated by ±2.5% during the course of the measurements. The data were corrected for absorption by the Gaussian integration method.[17] Data reduction included corrections for intensity scale variation and for Lorentz and polarization effects.

The structure was solved using direct methods. Coordinates and anisotropic thermal parameters for all non-hydrogen atoms were refined. The net along-bond component of thermal motion for all pairs of mutually bonded non-hydrogen atoms was restrained toward zero. Hydrogen atoms were placed in calculated positions 0.95 Å from their respective carbon atoms and with isotropic temperature factors initially proportionate to the carbon-atom equivalent isotropic temperature factors. Coordinate shifts for the hydrogen atoms were subsequently linked with those for their respectively bound carbon atoms. A mean isotropic temperature factor for all hydrogen atoms was refined and its shifts were applied to the individual values.

Analysis of the observed and calculated structure factors revealed a scattering of bad data which we attribute to the random occurrence of low temperature "spikes" arising from water-condensation and ice buildups in the apparatus during this week-long experiment under conditions of widely varying humidity. A Robust-Resistant[18] weighting scheme was therefore applied in the latter cycles of refinement. This method gave zero weight to 58 reflections and yields slightly lower values (zero-weight reflections included) of both R_F and R_{wF} than do either unit weights or weighting schemes based on counting statistics. $\langle w(|F_o| - |F_c|)^2 \rangle$ was near constant as a

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(17) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 180−182.

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Table 1. Crystallographic Details for the Structure Determination of [*Ph*S{($C_{10}H_{14})_2$}][SO_3CF_3] at 216 K

formula	$S_2F_3O_3C_{27}H_{33}$	crystal system	triclinic
fw	526.67	space group	$P\bar{1}$
a (Å)[a]	10.983(3)	ϱ_c (g cm^{-3})	1.413
b (Å)	14.988(3)	λ(Mo Kα_1) (Å)	0.70930
c (Å)	16.059(6)	μ(Mo Kα) (cm^{-1})	2.5
α (°a0	95.60(2)	min−max 2θ (°)	4−46
β (°)	93.39(2)	transmission[b]	0.912−0.943
γ (°)	108.98(2)	crystal dim. (mm)	0.30 × 0.33 × 0.36
V (Å^3)	2476	R_F[c]	0.052
Z	4	R_{wF}[d]	0.056
temp (K)	216		

[a] Cell dimensions were determined from 24 reflections (36° ≤ 2θ ≤ 40°). [b] The data were corrected for the effects of absorption by the Gaussian integration method. [c] $R_F = \sum|(|F_o| - |F_c|)|/\sum|F_o|$, for 4840 data ($I_o \geq 2.5\sigma(I_o)$). [d] $R_{wF} = [\sum(w(|F_o| - |F_c|)^2)/\sum(wF_o{}^2)]^{1/2}$ for 4840 data ($I_o \geq 2.5\sigma(I_o)$), where $w = w'(1 - (\Delta F/6\sigma(F))^2)^2$, $w' = [1.01t_0(x) + 1.03t_1(x)]^{-1}$, $t_i(x)$ are the terms of the Chebyshev series, $x = F_c/F_c(\max)$, and $\sigma(F)$ is an estimated standard deviation of F determined from the fitting to obtain the coefficients of the Chebyshev series. When w is calculated to be negative, it is reassigned as 0. Fifty-eight reflections had zero weight on this basis.

function of both $|F_o|$ and sin θ/λ. Final full matrix least squares refinement of 633 parameters for 4840 data ($I_o \geq 2.5\sigma(I_o)$) and 82 restraints converged at $R = 0.052$ with a maximum |shift/error| of 0.01.

The programs used for absorption corrections, data reduction, structure solution, and plot generation were from the NRCVAX Crystal Structure System.[19] Refinement was performed using CRYSTALS.[20] Complex scattering factors for neutral atoms[21] were used in the calculation of structure factors. Computations were carried out on MicroVAX-II and 80486 computers.

Results

Crystallographic details for the thiiranium salt **1d** are summarized in Table 1. Final fractional atomic coordinates for the non-hydrogen atoms are listed in Table 2. The asymmetric unit consists of two cations and anions. There are no interionic contacts significantly less than the corresponding sums of accepted van der Waals radii. The two independent [*Ph*S{($C_{10}H_{14})_2$}]$^+$ ions are very similar in both dimensions and conformation. One of these cations is depicted in Figure 1 as representative of both. A one-to-one comparison of selected bond distances and angles for the two cations is given in Table 3.

We decided to differentiate between the two faces of the alkene using a methyl substituent. Shown in Scheme 2 is the synthetic route taken to give the desired alkene **4**. The stereochemistry of the two methyl derivatives **4** and **5** was determined using ^{13}C NMR chemical shifts. For the pseudoaxial methyl isomer **4**, there is one CH_2 resonance (δ 33.7) that is shielded by more than 4 ppm relative to the remaining eight CH_2 carbons ($\delta \geq 37.8$), while the pseudoequatorial isomer **5** has two upfield CH_2 resonances (δ 31.2 and 33.0). That either one or two CH_2 carbons are shielded relative to the seven/eight remaining CH_2 groups is explained by the γ-gauche effect.[22] These assignments have also been confirmed by 2-D NOESY

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors (Å^2) for the Non-Hydrogen Atoms of [*Ph*S{($C_{10}H_{14})_2$}][SO_3CF_3] at 216 K

atom	x	y	z	U_{eq}[a]
S(10)	0.29271(9)	0.69073(6)	0.50878(6)	0.0388
S(20	0.19673(10)	0.21946(7)	1.01379(7)	0.0460
S(100)	0.10065(8)	0.73358(6)	0.30531(5)	0.0310
S(200)	0.02785(8)	0.89892(6)	0.73023(6)	0.0334
F(11)	0.5315(3)	0.7305(2)	0.5733(2)	0.0710
F(12)	0.4228(3)	0.5814(2)	0.5537(2)	0.0675
F(13)	0.4915(3)	0.6559(2)	0.4492(2)	0.0687
F(21)	0.3737(4)	0.3350(3)	1.1238(2)	0.1084
F(22)	0.3908(3)	0.3736(2)	1.0013(2)	0.0791
F(23)	0.4448(3)	0.2566(3)	1.0341(3)	0.1013
O(11)	0.2059(3)	0.6078(2)	0.4584(2)	0.0586
O(12)	0.3288(3)	0.7754(2)	0.4682(2)	0.0511
O(13)	0.2635(3)	0.7041(2)	0.5939(2)	0.0550
O(21)	0.1987(4)	0.1871(3)	0.9278(2)	0.0795
O(22)	0.1832(4)	0.1485(2)	1.0680(2)	0.0743
O(23)	0.1209(3)	0.2800(2)	1.0232(3)	0.0747
C(10)	0.4416(4)	0.6636(3)	0.5218(3)	0.0478
C(20)	0.3600(4)	0.2980(3)	1.0428(3)	0.0610
C(110)	0.1044(3)	0.6352(2)	0.2188(2)	0.0284
C(111)	0.1521(3)	0.6753(2)	0.1381(2)	0.0314
C(112)	0.1227(4)	0.5910(3)	0.0687(2)	0.0350
C(113)	0.1925(4)	0.5231(3)	0.0936(2)	0.0364
C(114)	0.3380(4)	0.5754(3)	0.1060(3)	0.0422
C(115)	0.3683(4)	0.6588(3)	0.1753(3)	0.0414
C(116)	0.3230(4)	0.6238(3)	0.2578(2)	0.0417
C(117)	0.1770(3)	0.5708(3)	0.2467(2)	0.0350
C(118)	0.1455(4)	0.4872(3)	0.1756(2)	0.0391
C(119)	0.2986(3)	0.7269(3)	0.1511(2)	0.0365
C(120)	−0.0287(3)	0.6257(2)	0.2426(2)	0.0291
C(121)	−0.1354(3)	0.6330(2)	0.1818(2)	0.0318
C(122)	−0.2130(3)	0.5305(3)	0.1416(2)	0.0383
C(123)	−0.2742(3)	0.4689(3)	0.2084(3)	0.0404
C(124)	−0.3631(4)	0.5127(3)	0.2545(3)	0.0485
C(125)	−0.2840(4)	0.6134(3)	0.2962(3)	0.0453
C(126)	−0.1766(4)	0.6082(3)	0.3580(2)	0.0408
C(127)	−0.0859(3)	0.5644(2)	0.3122(2)	0.0338
C(128)	−0.1662(4)	0.4642(3)	0.2706(2)	0.0404
C(129)	−0.2244(3)	0.6758(3)	0.2289(2)	0.0398
C(131)	0.1377(3)	0.8434(2)	0.2614(2)	0.0313
C(132)	0.0700(4)	0.8638(3)	0.1946(2)	0.0363
C(133)	0.1181(4)	0.9517(3)	0.1670(3)	0.0407
C(134)	0.2289(4)	1.0193(3)	0.2064(3)	0.0434
C(135)	0.2922(4)	1.0009(3)	0.2763(3)	0.0447
C(136)	0.2483(3)	0.9120(3)	0.3040(2)	0.0392
C(210)	0.1994(3)	0.9167(2)	0.7775(2)	0.0297
C(211)	0.2279(3)	0.8246(2)	0.7832(2)	0.0335
C(212)	0.3728(3)	0.8502(3)	0.8078(3)	0.0419
C(213)	0.4110(4)	0.9129(3)	0.8927(3)	0.0448
C(214)	0.3362(4)	0.8584(3)	0.9596(3)	0.0492
C(215)	0.1914(4)	0.8335(3)	0.9364(2)	0.0427
C(216)	0.1589(4)	0.9246(3)	0.9296(2)	0.0420
C(217)	0.2326(3)	0.9794(3)	0.8622(2)	0.0369
C(218)	0.3792(4)	1.0031(3)	0.8858(3)	0.0444
C(219)	0.1519(4)	0.7713(3)	0.8513(2)	0.0395
C(220)	0.1960(3)	0.9590(2)	0.6966(2)	0.0298
C(221)	0.2382(3)	0.9209(2)	0.6159(2)	0.0343
C(222)	0.3807(4)	0.9812(3)	0.6123(3)	0.0438
C(223)	0.3954(4)	1.0851(3)	0.6096(3)	0.0473
C(224)	0.3127(4)	1.0950(3)	0.5337(3)	0.0510
C(225)	0.1720(4)	1.0378(3)	0.5387(3)	0.0434
C(226)	0.1266(4)	1.0742(3)	0.6192(2)	0.0401
C(227)	0.2086(3)	1.0640(2)	0.6969(2)	0.0353
C(228)	0.3512(4)	1.1219(3)	0.6903(3)	0.0412
C(229)	0.1560(4)	0.9325(3)	0.5399(2)	0.0387
C(231)	−0.0572(3)	0.7791(2)	0.6852(2)	0.0343
C(232)	−0.0193(4)	0.7228(3)	0.6254(2)	0.0444
C(233)	−0.1033(4)	0.6331(3)	0.5950(3)	0.0454
C(234)	−0.2248(4)	0.6010(3)	0.6220(3)	0.0456
C(235)	−0.2619(4)	0.6569(3)	0.6814(3)	0.0485
C(236)	−0.1777(3)	0.7457(3)	0.7139(3)	0.0415

[a] U_{eq} is the cube root of the product of the principal axes of the thermal ellipsoid.

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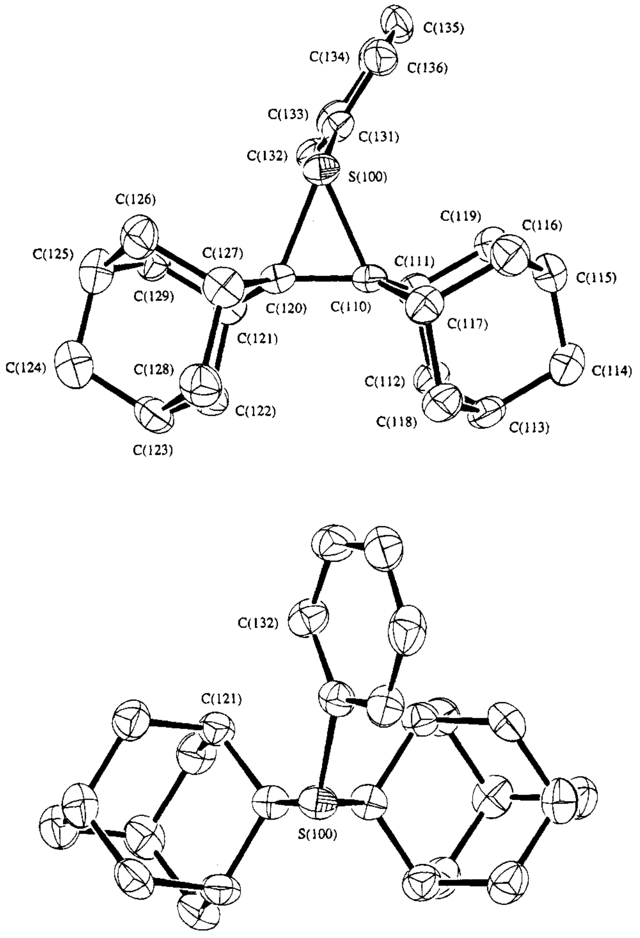
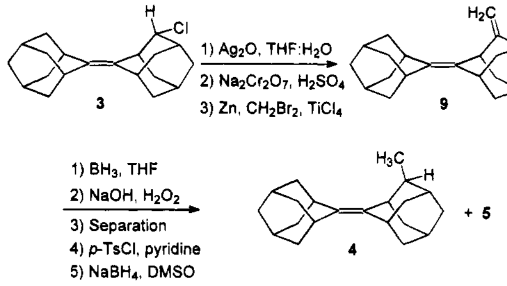


Figure 1. (a, Top) Molecular structure of one of the [*Ph*S{$(C_{10}H_{14})_2$}]$^+$ cations, 50% enclosure ellipsoids are shown. Hydrogen atoms are excluded for clarity. (b, Bottom) View of the same cation from directly above the thiiranium ring.

Scheme 2



experiments, where the methyl group in **4** showed NOE cross-peaks to two allylic protons, whereas the CH_3 group in **5** showed a cross-peak to only one allylic proton.

The products of chlorination of **4** (including isolated yields) when treated under different conditions (see experimental section) with PhSCl are summarized in Scheme 3. The regio- and stereochemistries of the products were determined by 2-D ^{1}H NMR spectroscopy. Shown in Figures 2, 3, and 4 are the phase sensitive 2-D 400 MHz ^{1}H NMR COSY and NOESY spectra of **14**. The regiochemistry of **14** is established by the labeled cross-peaks in the ^{1}H COSY (Figure 2), where the path shown traces the connectivity of the protons (H_a-H_g) which are labeled in Figure 5. The stereochemistry is established by the cross-peak (H_d-H_f) in Figure 3 which shows that both C*H*Cl protons are spatially close. Consequently, the only structure which fits both of the 2-D spectra is **14** (Figure 5). The cross-peak (H_c-H_i) identifies the allylic proton H_i on the adjacent adamantyl ring. Further conformation of the pseudoaxial orientation of the methyl substituent is shown by the cross peaks labeled H_a-H_c, and H_a-H_i in Figure 4, which show that an NOE exists between the methyl group and two of the allylic protons H_c and H_i (Figure 5). The regioselectivity of the two chlorination sites in **4** was determined by converting the mixture of monochlorinated products via their respective alcohols to the *p*-nitrobenzoyl esters. Two recrystallizations of the mixture of esters from methanol/ether enriched the major:minor ratio from approximately 4:1 to 10:1. The 2-D COSY spectrum (see Experimental Section for the chemical shifts observed in the ^{1}H NMR spectrum) showed that for the major isomer the proton centered at δ 2.36 was correlated with both the methyl group (δ 0.96) and the allylic proton at δ 3.02. The allylic proton (δ 3.02) was also correlated with the proton (C*H*O*p*NB) at δ 5.16. Thus, the major product of the

Table 3. Selected Bond Distances (Å) and Angles (deg) for [*Ph*S{$(C_{10}H_{14})_2$}][SO_3CF_3] at 216 K

cation 1		cation 2	
S(100)–C(110)	1.937(3)	S(200)–C(210)	1.913(3)
S(100)–C(120)	1.914(3)	S(200)–C(220)	1.909(3)
S(100)–C(131)	1.789(3)	S(200)–C(231)	1.789(3)
C(110)–C(120)	1.498(5)[a,b]	C(210)–C(220)	1.503(5)
C(120)–S(100)–C(110)	45.8(2)	C(220)–S(200)–C(210)	46.3(2)
C(131)–S(100)–C(110)	108.5(2)	C(231)–S(200)–C(210)	112.9(2)
C(131)–S(100)–C(120)	116.7(2)	C(231)–S(200)–C(220)	117.6(2)
C(111)–C(110)–S(100)	112.2(2)	C(211)–C(210)–S(200)	114.1(2)
C(117)–C(110)–S(100)	114.7(2)	C(217)–C(210)–S(200)	111.9(2)
C(117)–C(110)–C(111)[c]	111.0(3)	C(217)–C(210)–C(211)	111.2(3)
C(120)–C(110)–S(100)	66.3(2)	C(220)–C(210)–S(200)	66.7(2)
C(120)–C(110)–C(111)	121.5(3)	C(220)–C(210)–C(211)	122.9(3)
C(120)–C(110)–C(117)	122.3(3)	C(220)–C(210)–C(217)	121.0(3)
C(110)–C(120)–S(100)	67.9(2)	C(210)–C(220)–S(200)	67.0(2)
C(121)–C(120)–S(100)	123.7(2)	C(221)–C(220)–S(200)	120.8(2)
C(121)–C(120)–C(110)	123.3(3)	C(221)–C(220)–C(210)	122.9(3)
C(127)–C(120)–S(100)	102.5(2)	C(227)–C(220)–S(200)	105.3(2)
C(127)–C(120)–C(110)	120.3(3)	C(227)–C(220)–C(210)	121.0(3)
C(127)–C(120)–C(121)	110.9(3)	C(227)–C(220)–C(221)	111.1(3)
C(132)–C(131)–S(100)	127.4(3)	C(232)–C(231)–S(200)	128.5(3)
C(136)–C(131)–S(100)	111.4(3)	C(236)–C(231)–S(200)	111.2(3)
C(136)–C(131)–C(132)[d]	121.2(3)	C(236)–C(231)–C(232)	120.2(3)

[a] Unlisted C(sp^3) – C(sp^3) range from 1.514(6) to 1.549(5) Å. [b] C(sp^2) – C(sp^2) range from 1.374(6) to 1.398(5) Å. [c] Unlisted C(sp^3) – C(sp^3) – C(sp^3) range from 106.0(3) to 111.0(3)°. [d] Unlisted C(sp^2) – C(sp^2) – C(sp^2) range from 118.7(4) to 121.0(4)°.

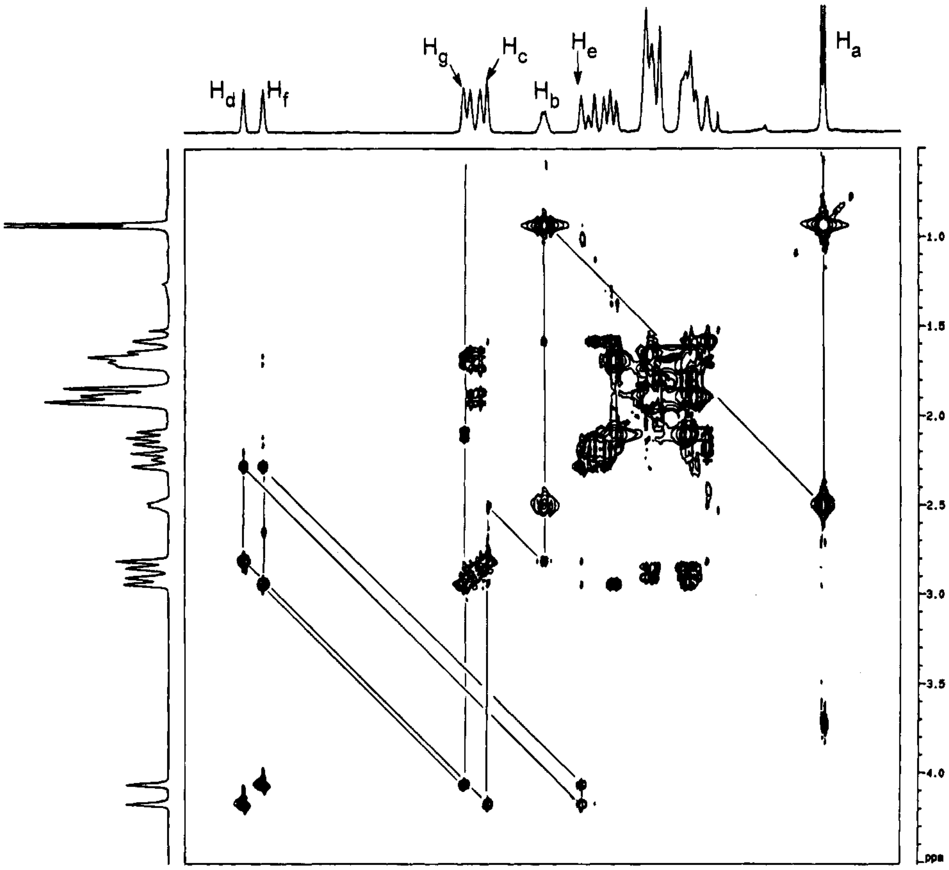
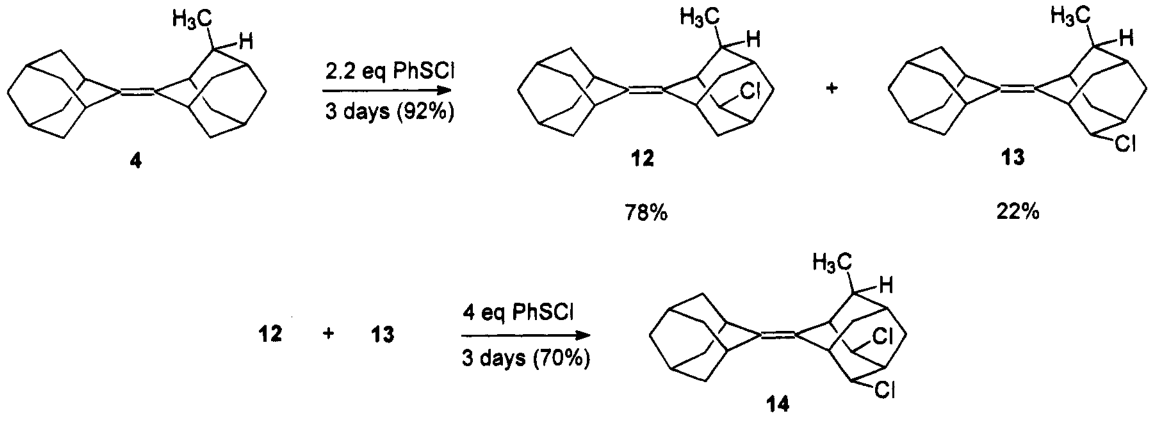


Figure 2. 400 MHz two-dimensional ^1H NMR COSY spectrum of **14**.

Scheme 3



initial chlorination reaction is **12**. To check for any unexpected rearrangement during the hydrolysis reactions of **12** and **13**, the mixture (10:1) of the nitrobenzoyl esters was subjected to basic hydrolysis, followed by chlorination with $SOCl_2$. The resulting major chlorinated product had an identical ^1H NMR spectrum to the major product from the initial chlorination experiments (i.e. **12**).

Discussion

Within the three-membered thiiranium rings of **1d**, the S–C bond lengths appear to be shorter and the C–C bond lengths longer than those in the analogous phenylthiiranium cation of 1,2-dimethylacenaphthylene[23] (S–C 1.970, 1.987 Å; C–C 1.472 Å; no esds given). This suggests that the present case represents a more advanced stage in the electrophilic addition to the olefin. Predictably the C–S bond lengths in **6** are shorter still (1.847(9), 1.850(9) Å) although the corresponding C–C bond (1.50(1) Å) is not significantly different from those in **1d**.[8] Of the two independent cations in the present case, only one displays significant asymmetry of the S–C bond lengths (as did also the 1,2-dimethylacenaphthylene derivative). There does not appear to be a simple explanation for this difference, but it is perhaps a manifestation of the different crystal environments for the two cations and the packing of the phenyl rings. In this regard it should be noted that the only other significant difference in the arrangement about the sulfur atoms is between the C(131)–S(100)–C(110) angle (108.5(2)°) and the analogous C(231)–S(200)–C(210) angle (112.9(2)°).

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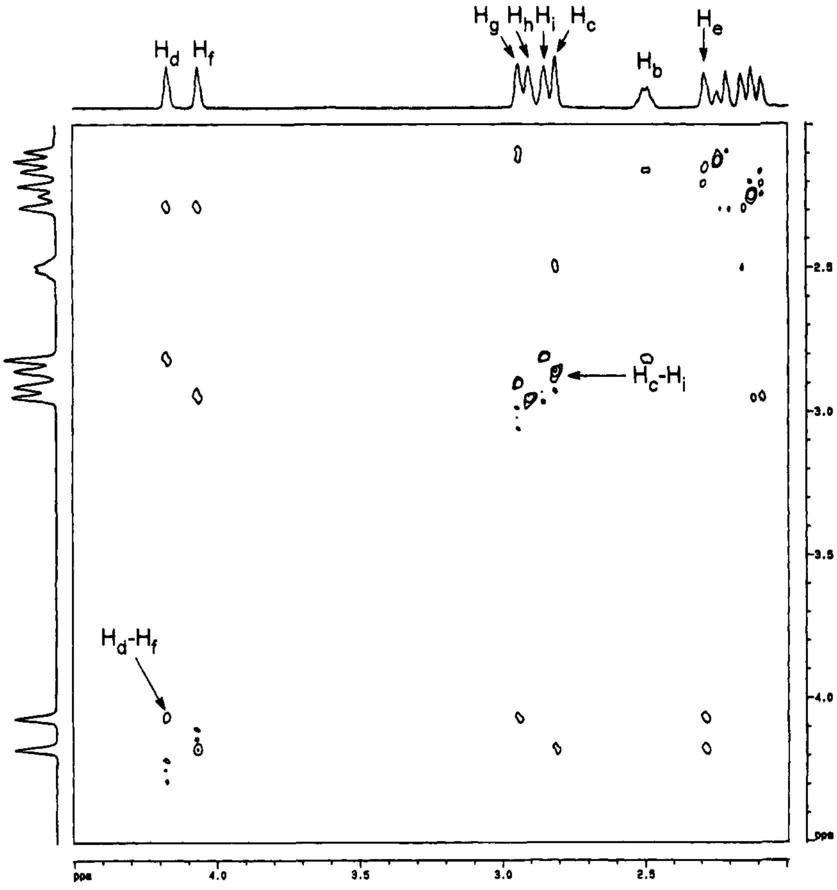

Figure 3. Expanded region of the 400 MHz two-dimensional phase sensitive ^1H NMR NOESY spectrum of 14 (only the negative peaks are shown for clarity).

The interaction of PhS^+ with the double bond of Ad=Ad in the present structure appears to be of a similar magnitude to the analogous interaction of Br^+, in the triflate salts of the bromonium ion of Ad=Ad. However, the present interaction appears to be stronger than the interaction of I^+ in the triflate salt of the iodonium cation of Ad=Ad on the basis of a comparison of the observed C−S, C−Br, and C−I bond distances with the corresponding S, Br, and I covalent radii, as well as the central C−C bond length in the different cations. Such differences may be partly attributed to the iodine−water interaction observed in the iodonium case.[3]

The most striking feature of the cationic structure of **1d** is the asymmetric orientation of the phenyl group. The two independent cations are remarkably similar in this respect, suggesting that this particular conformation represents an energy minimum for the molecule. Besides the one-to-one comparison of the bond angles at sulfur and at the carbon atoms bonded to it (given in Table 2), respective bond torsion angles also show a close similarity:[24] for example, the approximate eclipsing of one of the thiiranium S−C bonds by the phenyl ring (C(120)−S(100)−C(131)−C(132) 11.4(2)° and C(220)−S(200)−C(231)−C(232) 2.4(2)°; *cf.* C(110)−S(100)−C(131)−C(132) 60.5(2)° and C(210)−S(200)−C(231)−C(232) 53.7(2)°). Note, also, that the plane of the phenyl ring and that of the thiiranium ring are approximately mutually orthogonal in both cases (the respective dihedral angles are 87° and 81°).

An interesting, and apparently related, feature is the small twist in the orientation of one of the adamantyl groups away from a symmetrical disposition with respect to the plane of the thiiranium ring. This is shown by the dihedral angle of 101(2)° between the S(100)−C(110)−C(120) and the C(121)−C(120)−C(127) planes as compared with 89(2)° between the S(100)−C(110)−C(120) and C(111)−C(110)−C(117) planes. This twist can be seen in Figure 1. The analogous angles in the second independent cation are 98(2)° and 90(2)°, respectively. Such a twist is not clearly evident in any of the reported structures based on the Ad=Ad skelton which contain a three-membered ring,[25] $[Br\{(C_{10}H_{14})_2\}][Br_3]$ (**1a**),[4] $[Br\{(C_{10}H_{14})_2\}][O_3SCF_3]$ (**1b**),[3] $[I\{(C_{10}H_{14})_2\}][O_3SCF_3]$ (**1c**),[3] $[S\{(C_{10}H_{14})(C_{10}H_{13}Cl)\}]$ (**6**),[8] or $[O\{(C_{10}H_{14})_2\}]$,[26] and could arise in the phenylthiiranium cation as a consequence of the preferred orientation of the phenyl group, *vide supra*.[27] For example there appears to be a ~2.0 Å H−H intramolecular contact between the hydrogen atom on C(132) and that on C(121) and a similar distance for the second cation. There is an asymmetry in the bond

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[24] The actual set of unique coordinates for the second cation given in Table 2 (atom labels 200−236) happens to correspond to a molecule of opposite hand to that of the first cation, shown in Figure 1 (both hands of course being equally present in the crystal for either molecule). The signs of the torsion angles for the second cation, given here, refer to its inversion-symmetry equivalent.

[25] Not surprisingly in the corresponding dioxetane the adamantyl rings are twisted with respect to each other: Hess, J.; Vos, A. *Acta. Crystallogr., Sect. B* **1977**, *33*, 3527−3530.

[26] Watson, W. H.; Nagl, A. *Acta. Crystallogr., Sect. C* **1988**, *44*, 1627−1629.

[27] The author has deposited atomic coordinates for structure **1d** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

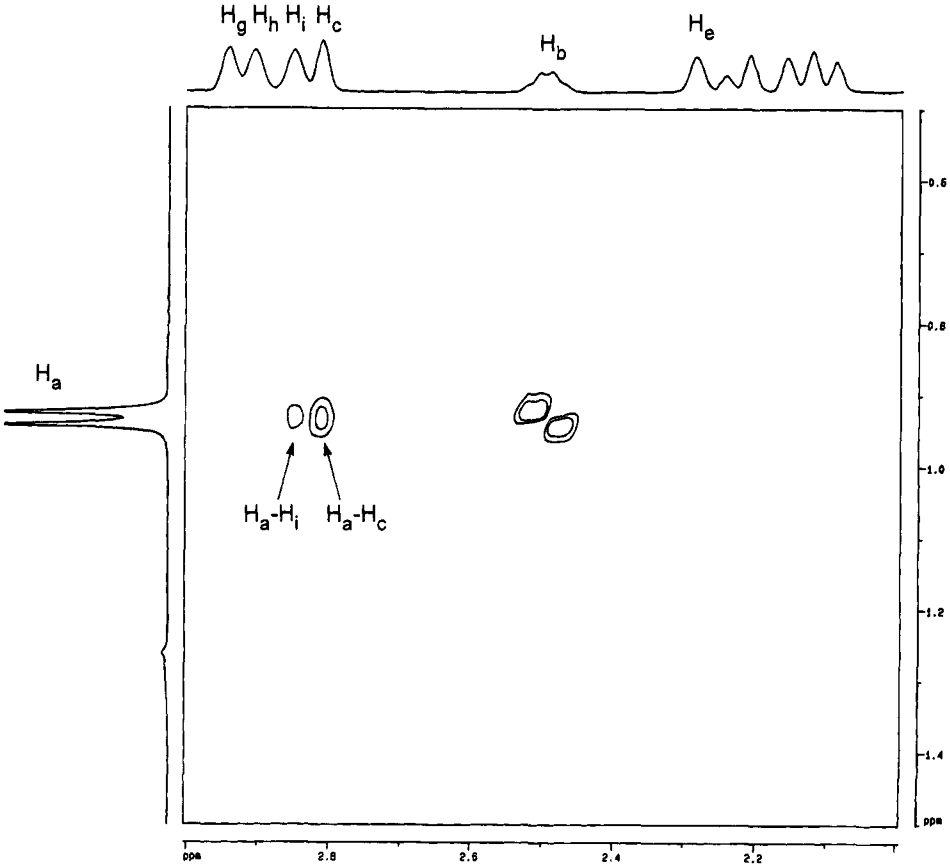

Figure 4. Expanded region of the 400 MHz two-dimensional phase sensitive ^{1}H NMR NOESY spectrum of 14 (only the negative peaks are shown for clarity).

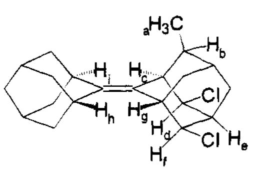

Figure 5. Structure of 14 showing the protons assigned using the two-dimensional NMR spectra shown in Figures 2–4.

angles at the *ipso* carbon atom of the phenyl ring (C(132)–C(131)–S(100) 127.4(3)° and C(136)–C(131)–S(100) 111.4(3)°; C(232)–C(231)–S(200) 128.5(3)° and C(236)–C(231)–S(200) 111.2(3)°) corresponding to an in-plane bending of the phenyl ring away from C(121). The fact that this latter interaction is not alleviated by rotation of the phenyl group about the S–C$_{\text{ipso}}$ bond in either independent cation suggests that the observed conformation represents particularly favorable orbital interactions between the phenyl and thiiranium fragments. However, the ^{1}H NMR spectrum in CD_2Cl_2 shows an apparent plane of symmetry which bisects the thiiranium ring at all temperatures investigated down to −90 °C. This leads to the conclusion that if the lowest energy conformation of the thiiranium ring in solution has a nonsymmetrically disposed phenyl ring (as shown in Figure 1), then there is no large activational barrier for phenyl group motion to symmetrize the ion.

The pseudoaxial methyl group in **4** differentiates the two faces of the alkene, and the only possible face which the electrophile PhSCl could attack to give a thiiranium ion intermediate is the same one that the methyl substituent is attached to. Electrophilic attack on the opposite face to the methyl substituent would require that the methyl group (at the stage of the thiiranium ion intermediate) be forced to reside in a prohibitively crowded environment. This is best explained by reference to the crystal structure of **1d** where the two pairs of hydrogen atoms on the backside of the thiiranium ring (one attached to C(112) and C(122); as well as C(118) and C(128), see Figure 1) are calculated to be separated by approximately 2.2 Å (i.e., within van der Waals contact). Consequently, it is energetically unfavorable for a methyl group to occupy one of these positions.

The observations that chlorination of **4** produces only two monochlorinated products (out of a possible 8 pseudoequatorial positions) in quantitative yield and that when reacted with an excess of PhSCl a single dichlorinated product is produced show the regioselectivity and stereospecificity of this homoallylic reaction. The best rational for the observed results is that the reaction is stereospecific for the substitution of a pseudoequatorial proton on the opposing face to that which addition of the PhSCl electrophile occurs (vide supra), i.e., proton removal occurs via pathway b (Scheme 1). The reaction is regiospecific for the substitution on the same adamantyl ring as the methyl substituent and is regioselective for the substitution of the position on the same side as the methyl in the substituted adamantyl ring. That chlorination is only observed in the same ring as the methyl substituent indicates that proton removal is probably concerted with the thiiranium ring opening, which for steric reasons is energetically constrained to open away from the methyl substituent (or a severe 1,3 diaxial interaction would result).

A possible explanation for the regioselectivity of chlorination of **4** to give **12** and **13** in a ratio of ≈3.5:1 can be seen with reference to Figure 6. The view displayed in

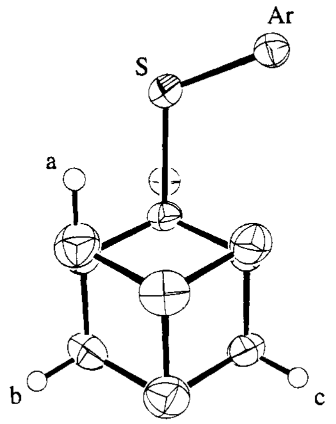

Figure 6. Molecular structure of one of the adamantane rings of the $[Ph\text{S}\{(\text{C}_{10}\text{H}_{14})_2\}]^+$ cations. View is orthogonal to that in Figure 1 and 50% enclosure ellipsoids are shown. Three hydrogen atoms are included for the discussion on reactivity of **14** (see text).

Figure 6 (only one of the adamantyl rings of **1d** is shown for clarity) is nearly orthogonal to those shown in Figure 1; also shown are the calculated positions of three protons (labeled a, b, and c), where a is in a pseudoaxial position and represents the position of the methyl substituent while b and c are pseudoequatorial and show the reactive positions for chlorination. The lowest-energy phenylthiiranium ion from the reaction of **4** and PhSCl should for steric reasons place the phenyl ring as shown in Figure 6. Proton abstraction from either position (b or c) probably occurs simultaneously with the opening of the thiiranium ring. In order to maximize the orbital interactions at the transition state for this reaction, the adamantyl ring shown should rotate to align the breaking C−S, and C−H bonds. This relative rotation of the two adamantyl rings should be energetically more facile to place the hydrogen labeled b (Figure 6) antiperiplanar to the breaking C−S bond, rather than the hydrogen labeled c. Therefore more substitution is observed to give **12** rather than **13**, although the difference in free energy of activation ($\delta\Delta G^{\ddagger}$) for these two possible substitutions at 25 °C is only approximately 750 cal mol^{-1}.

Conclusions

The homoallylic chlorination reaction of sterically congested alkenes with benzenesulfenyl chloride proceeds stereospecifically, with the chlorine substitution occurring on the opposite face of the alkene to which the initial electrophilic attack took place. The regioselectivity for this reaction is controlled by the sterically driven ring opening of the thiiranium ion intermediate.

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