

of **9a** (2.30 g, 10.0 mmol) in 20 mL of CH_2Cl_2 . During dropwise addition of a solution of Br_2 (0.62 mL, 12 mmol) in CH_2Cl_2 (50 mL) a precipitate is formed, and the mixture is stirred for 20 h at ambient temperature. After filtration, the solution is washed with 20% aqueous NaHSO_3 solution (2 mL) and concd aqueous ammonia (2 mL) and then dried over CaCl_2 . Evaporation of the solvent and distillation yields 2.10 g (88%) of **11a** with a bp (bath) 80–100 °C (20 mmHg), which crystallizes in the refrigerator (mp 29.5–30 °C): $^1\text{H NMR}$ (CCl_4) δ 1.13 (s, 6 H), 1.17 (s, 6 H), 1.87 (s, 2 H); $^{13}\text{C NMR}$ (CDCl_3) δ 28.36 (q), 29.12 (q), 45.26 (s), 45.62 (s), 51.54 (t), 128.07 (s), 138.66 (s); MS (70 eV) m/e (rel intensity) 240, 238, 236 (2, 10, 8, M^+), 225 (11), 223 (49), 221 (38), 144 (31), 142 (100).

1-Chloro-2-iodo-3,3,5,5-tetramethylcyclopentene (11b). Silver trifluoroacetate (7.74 g, 35.0 mmol) was added to a solution of **9a** (4.90 g, 21.2 mmol) in 100 mL of CH_2Cl_2 . A solution of I_2 (8.83 g, 34.8 mmol) in CH_2Cl_2 (150 mL) was added dropwise and stirred for 4 h at ambient temperature. The suspension was washed with 20% aqueous NaHSO_3 solution (100 mL), filtered, and once more washed with 20% aqueous NaHSO_3 solution (100 mL). The organic layer was then washed with water (200 mL) and concd aqueous NH_3 (150 mL) and was dried over CaCl_2 . After evaporation of the solvent, the residue was distilled to give 5.25 g (87%) of **11b** with bp (bath) 90–105 °C (3.5 mmHg), which crystallizes in the refrigerator: mp 26–28 °C (from ether); $^1\text{H NMR}$ (CCl_4) δ 1.12 (s, 6 H), 1.20 (s, 6 H), 1.95 (s, 2 H); $^{13}\text{C NMR}$ δ 28.52 (q), 30.40 (q), 46.56 (s), 47.51 (s), 50.42 (t), 109.09 (s), 145.73 (s); MS (90 eV) m/e (rel intensity) 286, 284 (12, 43, M^+), 271 (31), 269 (100), 144 (43), 143 (25), 142 (48), 127 (27).

5-Chloro-3,3,5-trimethyl-1-(trimethylsilyl)-1-hexyne (12). Isobutene (1.25 g, 22.3 mmol) was introduced into a 0.5 M solution of BCl_3 in dry CH_2Cl_2 (10 mL) at -78 °C. A solution of **7** (2.58 g, 14.8 mmol) in CH_2Cl_2 (20 mL) was added dropwise to give a brown solution. After being stirred at -78 °C for 2 d, the mixture was poured into water, and the organic layer was separated, washed with water, and dried over $\text{CaCl}_2/\text{NaHCO}_3$. Distillation gave 0.40 g of unreacted **7** and 2.12 g (74% with respect to converted **7**) of **12** with bp (bath) 45–52 °C (0.01 mmHg): IR (neat) 2960, 2920, 2880, 2150, 1250, 885, 845, 790, 760 cm^{-1} ; $^1\text{H NMR}$ (CCl_4) δ 0.10 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 1.31 (s, 6 H, 3- CH_3), 1.73 (s, 6 H, $\text{C}(\text{CH}_3)_2\text{Cl}$), 2.00 (s, 2 H, CH_2); MS (96 eV) m/e (rel intensity) 230, 232 (13, 4, M^+), 215, 217 (57, 19), 179 (7), 159, 161 (29, 9), 139 (22), 123 (22), 122 (47), 121 (38), 119 (19), 117 (52), 107 (67), 97 (73), 95 (23), 93 (68), 91 (28), 73 (100).

7-Chloro-3,3-dimethyl-1-(trimethylsilyl)hept-5(E)-1-ene (13). 1,3-Butadiene (1.08 g, 20.0 mmol) and SnCl_4 (1.0 g, 3.8 mmol) were dissolved in CH_2Cl_2 (30 mL) at -78 °C. A solution of **7** (3.50 g, 20.0 mmol) in CH_2Cl_2 (20 mL) was added dropwise within 30 min, and the mixture was stirred for 4 h at -78 °C. The solution was poured into water (150 mL), and after separation of the two layers, the aqueous layer was extracted with CH_2Cl_2 . The organic layers were dried over MgSO_4 and evaporated. Bulb-to-bulb distillation yielded **13** (1.89 g, 41%), a colorless liquid with bp (bath) 50 °C (0.1 mmHg): IR (neat) 3030, 2960, 2920, 2160, 1440, 1250, 970, 920, 840, 760 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 200 MHz) δ 0.13 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 1.17 (s, 6 H, 3- CH_3), 2.15 (d, $J = 7.0$ Hz, 2 H, 4-H), 4.07 (d, $J = 6.9$ Hz, 2 H, 7-H), 5.60–5.95 (m, 2 H, 5-H, 6-H); $^{13}\text{C NMR}$ (CDCl_3) δ 0.26 (q, $\text{Si}(\text{CH}_3)_3$), 28.83 (q, 3- CH_3), 31.82 (s, C-3), 45.10, 45.62 (2 t, C-4, C-7), 84.01 (s, C-1), 113.64 (s, C-2), 128.70, 132.17 (2 d, C-5, C-6); MS (70 eV) m/e (rel intensity) 228, 230 (2, 1, M^+), 159, 161 (6, 3), 139 (100), 97 (83), 75 (27). Anal. Calcd for $\text{C}_{12}\text{H}_{21}\text{ClSi}$: C, 62.99; H, 9.25. Found: C, 62.26; H, 9.21.

3-Chloro-4,4-dimethyl-2-(trimethylsilyl)bicyclo[3.2.1]-octa-2,6-diene (16). A solution of **7** (2.62 g, 15.0 mmol) in dry CH_2Cl_2 (20 mL) was added dropwise to a solution of BCl_3 (1.2 g, 10 mmol) in CH_2Cl_2 (20 mL) at -10 °C. Cyclopentadiene (0.99 g, 15.0 mmol) dissolved in CH_2Cl_2 (100 mL) was then added within 1 h, and the solution was stirred for another hour at -10 °C. The mixture was poured into water (100 mL), and the organic layer was extracted with two 50-mL portions of CH_2Cl_2 . After the CH_2Cl_2 solutions were dried over MgSO_4 , the solvent was evaporated, and the residue was dissolved in hexane (100 mL) and passed through silica (KG 60, 70–230 mesh, column $l = 10$ cm and $d = 2.5$ cm). Evaporation of the solvent and distillation yielded **16** (950 mg, 26%), a colorless oil with bp (bath) 50 °C (0.02 mmHg): IR (neat) 2960, 2860, 1570, 1250, 1055, 930, 920,

870, 840, 730 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 0.19 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.99, 1.27 (2s, 6 H, CH_3), 1.75–1.9 (m, 2 H, 8-H), 2.52 (mc, 1 H, 5-H), 2.87 (mc, 1 H, 1-H), 5.83 (1 H, dd, $J_{6,7} = 5.6$ Hz, $J_{5,6} = 2.7$ Hz, 1 H, 6-H), 6.22 (dd, $J_{6,7} = 5.6$ Hz, $J_{1,7} = 2.7$ Hz, 1 H, 7-H); $^{13}\text{C NMR}$ (CDCl_3) δ -0.21 (q, $\text{Si}(\text{CH}_3)_3$), 23.34, 28.52 (2 q, 4- CH_3), 39.45 (t, C-8), 42.21 (s, C-4), 43.78 (d, C-1), 51.72 (d, C-5), 131.18, 140.40 (2 d, C-6, C-7), 139.03 (s, C-2), 149.09 (s, C-3); MS (70 eV) m/e (rel intensity) 240, 242 (11, 4, M^+), 225, 227 (3, 1), 159, 161 (13, 5), 132 (40), 119, 121 (48, 15), 117 (71), 93 (37), 73 (100). Anal. Calcd for $\text{C}_{13}\text{H}_{21}\text{ClSi}$: C, 64.83; H, 8.79. Found: C, 64.76; H, 8.93.

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Registry No. **7**, 18387-63-8; **8a**, 115-11-7; **8b**, 513-35-9; **8c**, 873-66-5; **8d**, 624-64-6; **8e**, 693-89-0; **9a**, 137649-22-0; **9b**, 137649-23-1; **9c**, 137649-24-2; **9d**, 137649-25-3; **9e**, 137649-26-4; **10a**, 137649-27-5; **10c**, 137649-28-6; **11a**, 137649-29-7; **11b**, 137649-30-0; **12**, 137649-31-1; **13**, 137649-32-2; **16**, 137649-33-3; 2-methyl-4-(trimethylsilyl)-3-butyn-2-ol, 5272-33-3; 2-methyl-3-butyn-2-ol, 115-19-5; 1,3-butadiene, 106-99-0; cyclopentadiene, 542-92-7.

Temperature-Controlled Synthesis of 4,7-Dioxatricyclo[3.2.1.0^{3,6}]octane Derivatives

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Interest in the chemistry of 7-oxanorbornenic systems has increased in recent years especially due to the large array of molecules of biological relevance that may be synthesized from these bicycles.¹ This has been possible because they contain valuable stereochemical information in their rigid skeleton and they are readily available as optically pure starting materials.² Additions of soft electrophiles to 7-oxanorbornenic derivatives have been thoroughly studied. In most cases the reaction occurs with complete regio- and stereocontrol to afford synthetically useful adducts (A or B) (Scheme I). This behavior has been attributed to the steric and electronic characteristics of the substituents at C-2.³ These studies have been also extended to the norbornenic analogues.⁴

In connection with our interest in the development of new synthetic methodologies from oxanorbornenic derivatives,⁵ particularly those with sulfur and selenium,⁶ and with our broader interest in vinyl sulfoxides⁷ we required efficient regiocontrolled routes to oxabicyclic functionalized vinyl sulfides,⁸ immediate precursors of the corresponding sulfoxides and sulfones.⁹ For this purpose, the facile but not highly selective intramolecular cyclization of 2-*exo*-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-ol (**1**, Table I, entry 1) upon reaction with PhSCl was considered an interesting possibility, provided we could render the cyclization synthetically useful. Furthermore, it was envisioned that subsequent deprotonation of the sulfur-containing oxetanes should produce oxanorbornenic vinyl sulfides by preferential β -elimination of the oxetane oxygen due to the highly strained character of the four-membered ring. On the other hand, control of the addition reaction would

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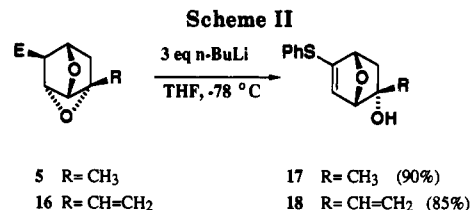
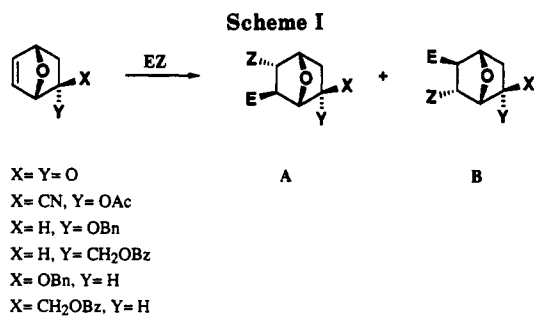
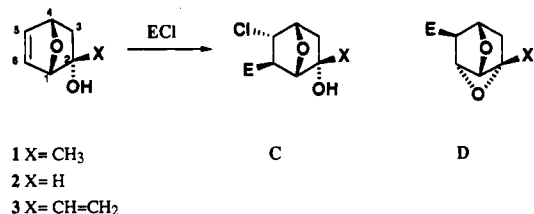


Table I. Reaction between 2-endo-7-Oxanorbornenols and Electrophiles^a



entry	substr	ECl	solvent	temp °C	C	D	C:D ratio ^b
1 ^b	1	PhSeCl	CHCl ₃	rt	4	5	20:80
2	1	2-NBSeCl	CHCl ₃	rt	6	7	19:81
3	1	2,4-DNBSeCl	CHCl ₃	rt	8	9	13:87
4	1	PhSeCl	CHCl ₃	-50 °C		5	-:100
5 ^b	1	PhSeCl	CHCl ₃	rt	10	11	80:20
6	1	PhSeCl	CH ₂ Cl ₂	-78 °C	10	11	10:90
7	1	PhSeCl	CH ₃ CN	rt	10	11	92:8
8	1	PhSeCl	CH ₃ CN	reflux	10	11	95:5
9	2	PhSeCl	CHCl ₃	rt	12	13	84:16
10	2	PhSeCl	CH ₂ Cl ₂	-78 °C	12	13	58:42
11	2	PhSeCl	CHCl ₃	rt	14	15	50:50
12	2	PhSeCl	CH ₂ Cl ₂	-78 °C	14	15	33:67
13 ^c	2	PhSeCl	CH ₂ Cl ₂	-78 °C	14	15	17:83
14	3	PhSeCl	CH ₂ Cl ₂	-78 °C	16		-:100

^aAll reactions afforded excellent combined yields (75–95%) of pure final products. ^bMeasured by integration of the 300-MHz ¹H NMR spectra of the crude reaction mixtures. ^cThe reaction was carried out on the preformed lithium alkoxide (2/*n*-BuLi/CH₂Cl₂/-78 °C).

permit, from a single starting material, access to bicyclic adducts by chloride attack on the episulfonium or epi-

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selenonium intermediates¹⁰ or to 4,7-dioxatricyclo-[3.2.1.0^{3,6}]octane derivatives, which are potential herbicides.¹¹ With this objective in mind we undertook a systematic study of these electrophilic additions, and the results obtained are shown in Table I.

We have previously reported that methylcarbinol 1 and PhSeCl (CHCl₃/rt) afforded a 20:80 mixture of adduct 4 and oxetane 5^{4b} (Table I, entry 1). In an attempt to favor oxetane formation, we tested harder sulfur electrophiles¹² such as 2-nitrobenzenesulfonyl chloride, which did not increase the ratio of oxetane appreciably, and the even harder 2,4-dinitrobenzenesulfonyl chloride, which augmented the ratio to 13:87 in favor of oxetane 9 (entries 2 and 3). These reactions required longer reaction times (overnight) and an excess (2 equiv) of electrophile.

The effect of lowering the reaction temperature was then examined. Conducting the experiment at -50 °C provided an excellent yield (93%) of oxetane 5 with no trace of bicyclic adduct 4 in the crude product (entry 4). Even PhSeCl rendered a satisfactory 84% yield of a 10:90 mixture where tricyclic oxetane 11 was the major product, when the experiment was performed at -78 °C¹³ (entries 5 and 6). This is in contrast to the reaction of PhSeCl at room temperature where the reaction yielded a 80:20 mixture favoring adduct 10 over the intramolecular cyclization product. This dramatic change in selectivity with temperature is noteworthy and, to the best of our knowledge, unprecedented for sulfo- and seleno-etherifications. Furthermore, changing the solvent to CH₃CN inverted the 10:11 ratio to 92:8, further enhanced to 95:5 when the reaction was carried out under reflux

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(8) Oxanorbornenic vinyl sulfides are available from 3-(phenylsulfenyl)furans, see: McDougal, P. G.; Oh, Y.-L.; Van Derveer, D. *J. Org. Chem.* 1989, 54, 91–97. However, the preparation of 3-(phenylsulfenyl)furans is rather lengthy. Additionally, to the best of our knowledge, the cycloadditions between these furans and unreactive ketene equivalents have not been studied.

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(11) Le Drian, C.; Vogel, P. *Helv. Chim. Acta* 1988, 71, 1399–1405. (12) Alcohol 1 gives good yields of the corresponding bromo oxetanes upon reaction with a hard electrophile such as bromine. See: Arjona, O.; Fernández de la Pradilla, R.; García, L.; Mallo, A.; Plumet, J. *J. Chem. Soc., Perkin Trans. 2* 1989, 1315–1318.

(13) When oxetane 11 was treated with 1 equiv of PhSeCl in CH₂Cl₂, a 50:50 mixture of 10 and 11 after 1 day at reflux was obtained; this result indicates that oxetanes D are formed under kinetic control.

(entries 7 and 8). Thus, simple control of solvent and temperature provides selenenyl oxetanes D and adducts C with synthetically useful selectivities.

To extend the scope of the methodology, we examined secondary carbinol 2^{2c} and found less tendency toward intramolecular cyclization. When the reaction was carried out with PhSeCl under standard conditions a 84:16 mixture of 12:13 was obtained; even at low temperature a 58:42 mixture of adduct and oxetane was produced. PhSCL (CHCl₃/room temperature) gave a 50:50 mixture 14 and 15. At low temperature the amount of oxetane 15 was increased slightly (33:67, 14:15). Oxetane formation was improved when the addition of PhSCL was conducted on the preformed lithium alkoxide of 2 (*n*-BuLi/CH₂Cl₂/-78 °C) and produced a 17:83 mixture of carbinol 14 and tricyclic oxetane 15 (entries 9-13). These results may be rationalized in terms of small skeletal distortions that place the alcohol functionality farther from the reactive episulfonium ion. Vinyl-substituted tertiary alcohol 3^{6a} behaved similarly to methylcarbinol 1, and a good yield of the 4,7-dioxatricyclo[3.2.1.0^{3,6}]octane derivative 16 was obtained at -78 °C (entry 14); however, in this case the amount of electrophile (PhSCL) had to be strictly controlled to avoid addition to the exocyclic double bond.

Finally, we conducted preliminary experiments to test whether oxetanes D could serve as precursors of oxanorbornenic vinyl sulfides. Treatment of 5 (Scheme II) with 3 equiv of *n*-BuLi in THF at -78 °C resulted in a clean conversion to vinyl sulfide 17 (90% yield of pure compound after a simple chromatography). Similarly, oxetane 16 afforded 85% of pure vinyl sulfide 18. We are currently addressing the synthetic utility of these products and of the related oxanorbornenic vinyl sulfoxides. These results will be published in due course.

In conclusion, an efficient method for the synthesis of tricyclic oxetanes derived from 7-oxanorbornenic systems has been described. This intramolecular cyclization is favored by low temperature and chlorinated solvents, even for soft selenium electrophiles. This process is less effective for secondary alcohols like 2, although the use of base to preform the alkoxide afforded oxetanes in fair yields. In some cases, the reaction can be directed to the bicyclic adduct C by a change in the solvent and reaction temperature (CH₃CN/reflux). Additionally, treatment of these sulfide oxetanes with base efficiently yields 7-oxanorbornenic vinyl sulfides.

Experimental Section

General. For procedures and conditions, see refs 3b and c. PhSeCl, 2-NO₂C₆H₄SCL, and 2,4-(NO₂)₂C₆H₃SCL were purchased from Aldrich. The resulting products were separated chromatographically and fully characterized. Analytical TLC was carried out on 0.20-mm E. Merck precoated silica gel plates (60 F-254). All the NMR spectra were recorded in CDCl₃. All the new compounds are racemic and are numbered arbitrarily to facilitate comparison of the data.

5-endo-Chloro-6-exo-[(2,4-dinitrophenyl)sulfonyl]-2-exo-methyl-7-oxabicyclo[2.2.1]heptan-2-endo-ol (8) and 2-exo-[(2,4-Dinitrophenyl)sulfonyl]-5-exo-methyl-4,7-dioxatricyclo[3.2.1.0^{3,6}]octane (9). From 1 and 2,4-DNBSCl, a 13:87 separable mixture of 8 and 9 was obtained in 88% combined yield. Data of 8, *R*_f = 0.26 (CH₂Cl₂). ¹H NMR: δ 1.53 (3 H, s, CH₃), 1.91 (1 H, ddd, *J* = 13.4, 5.8, 1.5 Hz, H-3x), 2.40 (1 H, d, *J* = 4.9, 1.5 Hz, H-5), 4.01 (1 H, s, H-1), 4.18 (1 H, td, *J* = 4.9, 1.5 Hz, H-5), 4.39 (1 H, d, *J* = 4.6 Hz, H-6), 4.68 (1 H, td, *J* = 5.4, 1.5 Hz, H-4), 7.86 (1 H, d, *J* = 9.0 Hz, ArH), 8.41 (1 H, dd, *J* = 9.0, 2.4 Hz, ArH), 9.11 (1 H, d, *J* = 2.4 Hz, ArH). ¹³C NMR: δ 29.4, 39.1, 50.1, 61.0, 78.0, 81.9, 89.4, 121.7, 127.5, 127.9, 144.2, 145.8. IR (CHCl₃): 3620, 3020, 2930, 1590, 1520, 1340, 1010 cm⁻¹. Anal. Calcd for C₁₃H₁₃ClN₂O₆S: C, 43.28; H, 3.63; N, 7.76. Found: C, 43.04; H, 3.78; N, 7.70. Data of 9, mp 159-161 °C. *R*_f = 0.35 (CH₂Cl₂). ¹H

NMR: δ 1.49 (1 H, s, CH₃), 1.79 (1 H, dd, *J* = 12.7, 4.6 Hz, H-3x), 2.23 (1 H, d, *J* = 12.7 Hz, H-3n), 3.82 (1 H, s, H-5), 4.65 (1 H, dd, *J* = 3.4, 1.7 Hz, H-6), 5.08 (1 H, dd, *J* = 4.6, 1.2 Hz, H-4), 5.17 (1 H, d, *J* = 3.7 Hz, H-1), 7.65 (1 H, *J* = 9.0 Hz, ArH), 8.36 (1 H, dd, *J* = 9.0, 2.7 Hz, ArH), 9.05 (1 H, d, *J* = 2.4 Hz, ArH). ¹³C NMR: δ 20.9, 44.0, 51.6, 80.6, 81.5, 83.4, 92.9, 121.9, 127.0, 142.1, 144.2, 144.7. IR (CHCl₃): 3090, 3010, 2980, 1590, 1520, 1340, 1050, 980 cm⁻¹. Anal. Calcd for C₁₃H₁₂N₂O₆S: C, 48.15; H, 3.73; N, 8.64. Found: C, 48.18; H, 3.61; N, 8.15.

2-exo-(Phenylsulfonyl)-5-exo-vinyl-4,7-dioxatricyclo[3.2.1.0^{3,6}]octane (16). From 3 and PhSCL, 16 was obtained in 80% yield, mp 83-84 °C. *R*_f = 0.28 (hexane/ethyl acetate (5:1)). ¹H NMR: δ 1.84 (1 H, dd, *J* = 12.8, 4.6 Hz, H-3x), 2.09 (1 H, d, *J* = 12.8 Hz, H-3n), 3.70 (1 H, s, H-5), 4.63 (1 H, dd, *J* = 3.5, 1.6 Hz, H-6), 5.00 (1 H, dt, *J* = 4.6, 1.3 Hz, H-4), 5.19 (1 H, dd, *J* = 3.2, 1.0 Hz, H-1), 5.21 (1 H, dd, *J* = 10.8, 1.5 Hz, H-2'cis), 5.31 (1 H, dd, *J* = 17.3, 1.5 Hz, H-2'trans), 5.89 (1 H, dd, *J* = 17.3, 10.8 Hz, H-1'), 7.20-7.50 (5 H, m, ArH). ¹³C NMR: δ 42.8, 53.5, 81.3, 82.3, 83.8, 93.4, 116.0, 126.8, 129.0, 130.5, 130.6, 135.3. IR (KBr): 3000, 1590, 1490, 1060, 750 cm⁻¹. Anal. Calcd. for C₁₄H₁₄O₂S: C, 68.27; H, 5.73. Found: C, 67.95; H, 5.69.

5-(Phenylsulfonyl)-2-exo-vinyl-7-oxabicyclo[2.2.1]hept-5-en-2-endo-ol (18). From 16 and *n*-BuLi, 18 was obtained in 85% yield, mp 70-71 °C. *R*_f = 0.36 (hexane/ethyl acetate (5:1)). ¹H NMR: δ 1.44 (1 H, d, *J* = 12.1 Hz, H-3n), 1.68 (1 H, brs, OH), 2.13 (1 H, dd, *J* = 12.1, 4.9 Hz, H-3x), 4.57 (1 H, dd, *J* = 1.9, 1.0 Hz, H-1), 4.77 (1 H, brd, *J* = 4.9 Hz, H-4), 5.14 (1 H, dd, *J* = 10.8, 1.2 Hz, H-2'trans), 5.33 (1 H, dd, *J* = 17.4, 1.2 Hz, H-2'cis), 6.14 (1 H, dd, *J* = 17.4, 10.2 Hz, H-1'), 6.24 (1 H, d, *J* = 1.9 Hz, H-6), 7.25-7.49 (5 H, m, ArH). ¹³C NMR: δ 42.7, 80.4, 82.1, 86.3, 111.6, 127.8, 129.0, 129.3, 131.2, 132.6, 143.3, 145.9. IR (CHCl₃): 3420, 3050, 2950, 1720, 1640, 1580, 1560, 1480, 1440, 1010, 930, 900 cm⁻¹. Anal. Calcd for C₁₄H₁₄O₂S: C, 68.27; H, 5.73. Found: C, 68.11; H, 5.73.

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Supplementary Material Available: Experimental and spectroscopic data for compounds 6, 7, 12-15, and 17 (2 pages). Ordering information is given on any current masthead page.

On Pentaorganylstiborane. 2. Reactions of Pentaorganylstiboranes with Acyl Chlorides and Ketones[†]

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Introduction

It has been shown that quaternary stibonium salts have a much greater tendency to form pentaorganylstiboranes than the corresponding phosphonium and arsonium salts.¹ Generally, for phosphorus and arsenic, the ylides are produced on treating their quaternary salts with either LDA (lithium diisopropylamide), *t*-BuOK, or RLi (*R* = alkyl, aryl). However, for antimony, treatment of the quaternary stibonium salts with the less nucleophilic strong base LDA or *t*-BuOK affords stibonium ylides, while with the strong nucleophilic base RLi pentaorganylstiboranes are produced. Although many pentaorganylstiboranes are known, scarce attention has been paid to their application

[†]This paper is the 97th report on the studies of the synthetic application of elementoorganic compounds of 15th and 16th groups.