°C; R_f 0.36; $[\alpha]^{25}_D$ −13.2° (c 1.00, pyridine); IR (KBr) 1782, 1773; MS, 272 (M^+); ^1H NMR (DMSO-d_6) 7.79 (2 H, d, J = 9), 7.50 (2 H, d, J = 9), 5.96 (1 H, br, D_2O exchanges), 5.51 (1 H, d, J = 4.5), 4.39 (1 H, dd, J = 2.5, 8), 4.31 (1 H, dd, J = 2.5, 4.5), 4.13 (1 H, d, J = 8), 2.43 (3 H, s); ^{13}C (DMSO-d_6) 170.3, 145.3, 132,5, 130.0, 127.8, 75.1, 72.9, 67.1, 21.0. Anal. Calcd for $C_{11}H_{12}O_6S$: C, 48.52; H, 4.44; S, 11.78. Found: C, 48.74; H, 4.51; S, 12.00.

Chromatography of the mother liquors from **11** on silica gel (ethyl acetate–hexane) and recrystallization from ethyl acetate afforded **12**: mp 119–122 °C; R_f 0.46; IR 1781; MS 255 (M^+ + 1); ^1H NMR 7.82 (2 H, d, J = 7), 7.39 (2 H, d, J = 7), 7.24 (1 H, dd), 4,86 (2 H, dd), 2.43 (3 H, s); ^{13}C NMR 165.9, 146.6, 137.3, 132.0, 130.18, 128.6, 67.5, 21.8. Anal. Calcd for $C_{11}H_{10}O_6S$; C, 51.96; H, 3.96; S, 12.61. Found: C, 52.04; H, 3.93, S, 12.38.

Ethyl 4-Hydroxy-2(*S*),3(*R*)-epoxybutyrate (1). As a slurry, tosylate **11** (25.0g) in absolute ethanol[12c] and tetrahydrofuran (430 mL/75 mL, respectively) was treated with sodium ethoxide (12.2 mL of 0.82 N in ethanol, 0 °C, over 2 h) after which the solution became homogeneous and TLC indicated the presence of **13** (R_f 0.21). Additional ethoxide solution (101 mL over 30 min, −30 °C) was added. After 2 h the reaction was quenched with acetic acid (0.7 mL, pH = 7). All volatiles were evaporated (<25 °C, 5 mm) and the solids treated with ethyl acetate–hexane (2:1, 200 mL). Gravity filtration of one-half of this mixture thru silica (100 g, 230–400 mesh) using hexane and then ethyl acetate–hexane as eluent afforded chromatographically pure **1** (6.43 g, 95%). Alternatively, the remaining half was filtered, volatiles were removed under vacuum, and the material was recrystallized from ether–hexane, affording pure **1** (6.16 g, 91%): R_f 0.35; mp 47–49 °C (lit.[3a] mp *ent*-**1**, 45–46 °C); $[\alpha]^{25}_D$ +33.1° (c 1.00, ethanol) (lit.[3a] *ent*-**1**, $[\alpha]^{20}_D$ −33.8° (c 1.00, ethanol)); IR 1743, 1210; MS, 147 (M^+ +1); HPLC analysis[13] >99% ee; ^1H NMR ($CDCl_3$–D_2O) 4.24 (2 H, m), 3.96 (1 H, dd, J = 2, 12), 3.73 (1 H, dd, J = 4, 12), 3.54 (1 H, d, J = 1), 3.38 (1 H, ddd, J = 1, 2, 4); ^{13}C NMR 14.1, 50.3, 58.0, 60.2, 61.8, 169.08. Anal. Calcd for $C_6H_{10}O_4$: C, 49.31; H, 6.90. Found: C, 49.23; H, 6.85.

If an excess of ethoxide was employed compound **14** was isolated (>5%) by silica gel chromatography (R_f 0.30) and was characterized by benzoylation (1 equiv of benzoyl chloride in dry methylene chloride with 1.2 equiv of pyridine), affording **15**: mp 99–102 °C; R_f 0.87; $[\alpha]^{25}_D$ +63° (c 1.00, MeOH); IR 1748, 1726; MS 350 (M^+); ^1H NMR 3.58 (1 H, d, J = 1.5), 3.43 (2 H, d, J = 1.5), 1.31 (3 H, t, J = 7); ^{13}C NMR 167.84, 165.95, 133.47, 119.80, 129.26, 128.53, 63.89, 62.82, 64.00, 55.40, 54.44, 50.83, 50.59, 14.07. Anal. Calcd for $C_{17}H_{18}O_8$: C, 58.28; H, 5.18. Found: C, 58.49; H, 5.31.

Methyl 4-hydroxy-2(*S*),2(*R*)-epoxybutyrate (16) was prepared from **11** (10 g in 1:4 tetrahydrofuran–methanol, 150 mL, −10 to −25 °C), using sodium methoxide in methanol (8.0 mL, 25% wt, Aldrich), affording **16** (4.88g, 91%) after silica gel filtration as above: mp 19–20 °C; R_f 0.29; $[\alpha]^{25}_D$ +36.9° (c 1, MeOH); IR 1748; MS 132 (M^+); ^1H NMR (MeOH-d_4) 3.82 (1 H, dd, J = 4, 12), 3.76 (3 H, s), 3.62 (1 H, dd, J = 4,12), 3.51 (1 H, d, J = 1), 3.27 (1 H, m); ^{13}C NMR 169.41, 60.08, 58.00, 52.59, 50.07. Anal. Calcd for $C_5H_8O_4$; C, 45.46; H, 6.10. Found: C, 45.57; H, 6.14.

Benzyl 4-hydroxy-2(*S*),3(*R*)-epoxybutyrate (17) was prepared from 31.5 g of **11** in benzyl alcohol (312 g) and THF (500 mL) as above, affording **17** (90%) after chromatography (Waters Prep 500): mp: 39–42 °C; R_f 0.42; $[\alpha]^{25}_D$ +22.4° (c 1.00, $CHCl_3$); IR 3599 (nonbonded), 1748; UV 258 (230), 208 (7900); MS 208 (M^+); ^1H NMR 7.36 (5 H, s), 3.56 (1 H, d, J = 1); ^{13}C NMR 168.84, 135.00, 128.63; 128.48, 67.38, 60.04, 58.07, 50.16. Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45: H, 5.81. Found: C, 62.23; H, 5.73.

Allyl 4-hydroxy-2(*S*),3(*R*)-epoxybutyrate (18) was prepared from **11** (2.30 g) in allyl alcohol (58 g) and THF (50 mL, −25 °C) with sodium allyloxide (68.2 mL, 0.124 M), affording **18** (1.24 g, 93%) after silica gel filtration: R_f 0.38; $[\alpha]^{25}_D$ +27.4° (c 1, $CHCl_3$); IR 1748, 1197; ^1H NMR 5.91 and 5.32 (3 H, m), 4.68 (2 H, m), 3.98 (1 H, dd, J = 2, 11). 3.68 (1 H, J = 4, 11), 3.77 (2 H, J = 2), 3.42 (1 H, m); ^{13}C NMR 168.5, 131.3, 119.3, 66.2, 60.1, 57.9, 50.1. Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 52.78; H, 6.18.

3-Methylbutyl 4-hydroxy-2(*S*),2(*R*)-epoxybutyrate (19) was prepared from **11** (20.0 g) isoamyl alcohol–THF (38:62, w/w) at −9 to −17 °C with sodium isoamylate (0.34 M, 205 mL), affording **19** (12.64 g, 92%): R_f 0.48; $[\alpha]^{25}_D$ = +22.4° (c 1.00, MeOH); IR, 1743; MS, 189 (M^+ + 1); ^1H NMR ($CDCl_3$ + D_2O) δ 3.96 (1 H, dd, J = 2,12), 3.80 (1 H, dd, J = 4, 12); ^{13}C NMR δ 169.18, 64.56, 60.22, 58.08, 50.29, 37.21, 25.08, 22.51, 22.48. Anal. Calcd for $C_9H_{16}O_4$: C, 57.43, H, 8.57. Found: C, 57.64, H, 8.46.

2-Methoxyethyl 4-hydroxy-2(*S*),3(*R*)-epoxybutyrate (20) was prepared from **11** (13 g) in 2-methoxyethanol (400 mL), using sodium 2-methoxyethanolate (0.65 M, 74 mL, −20 °C), affording **20** (5.89 g, 70%) after flash chromatography: R_f 0.30; $[\alpha]^{25}_D$ +27.1° (c 1.00 $CHCl_3$); IR 1750, 1227; MS 177 (M^+ + 1); ^1H NMR ($CDCl_3$ + D_2O) 3.96 (1 H, dd, J = 4, 12), 3.74 (1 H, dd, J = 4, 12), 3.40 (3 H, s); ^{13}C NMR 168.9, 70.1, 64.6, 60.1, 59.0, 58.1, 50.1. Anal. Calcd for $C_7H_{12}O_5$: C, 47.73; H, 6.87. Found: C, 47.51; H, 6.71.

Acknowledgment. We thank Prof K. B. Sharpless for helpful suggestions and comments in advance of publication of his work. We also thank co-workers mentioned in refs 1c and 2b for gainful insights and the Molecular Structure Division of Eli Lilly and Company.

Fine-Tuned Remote Control of Electrophilic Additions to Substituted Norbornenes

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Received April 2, 1991

The chemistry of bicyclo[2.2.1]heptane derivatives continues to attract considerable attention both from mechanistic[1] and synthetic standpoints.[2] Recent developments in the preparation of optically pure norbornenes by asymmetric Diels–Alder processes[3] as well as by enzymatic protocols[4] should render these intermediates even more ubiquitous in organic synthesis, especially if new regio- and stereocontrolled functionalizations are developed. While the outcome of the electrophilic additions of sulfur and selenium halides to ketone **1** and its cyanoacetoxy precursor **2** have been thoroughly studied.[5,6] other simple norbornenic substrates such as compounds **3–10** (Scheme I) have not be examined. In connection with our involvement in the chemistry of bicyclic compounds, particularly oxanorbornenic derivatives[7] we undertook the research described here in parallel to a previous report.[7c]

Readily available norbornenic substrates **3–10**[8] (Scheme I) were selected for this study. Based upon previous knowledge on these processes,[5–7,9] we anticipated that endo-substituted systems **3–5** and **10** would allow for complete steric control producing exclusively adducts arising from endo attack of the nucleophile on C-5 (A, Table I). Alternatively, exo-substituted substrates **6** and **7** were expected to display some regioselectivity in favor of the opposite isomers **B** possibly due to electronic reasons.[10] Hydroxymethyl derivatives **8** and **9**, on the other hand, were expected to show a small selectivity in favor of isomers A.[7c] However, we guessed that the substitution of an oxygen bridge for a methylene could alter the selectivity of these processes, especially for exo-substituted substrates free of strong endo steric requirements, and therefore governed by a delicate interplay of steric and electronic effects. Table I gathers the results obtained in the course of this study.

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0022-3263/91/1956-6227$02.50/0

Scheme I

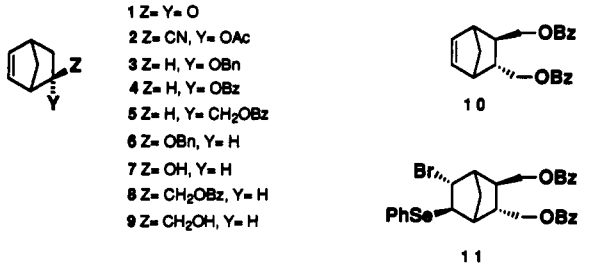
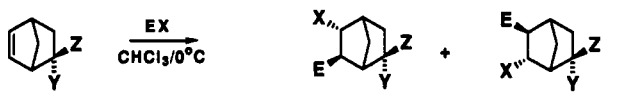


Table I. Electrophilic Additions to Substituted Norbornenes 3-10



entry	substrate	EX	A	B	A:B ratio[a]	yield[b] (%)
1[c]	3	PhSeBr	12		1:0	85
2	4	PhSeBr	13		1:0	80
3	5	PhSeBr	14		1:0	75
4[c,d]	6	PhSeBr	15	16	1:6	82
5[c,d]	6	PhSeBr	15	16	1:7.2	80
6[c,d]	7	PhSeBr	17	18	1:10	80
7[c,d]	7	PhSCl	19	20	1:15	87
8	8	PhSeBr	21	22	7:1	75
9[d]	8	PhSeBr	21	22	25:1	85
10[d]	9	PhSeBr	23	24	10:1	82
11[d]	9	PhSCl	25	26	8.2:1	70
12	10	PhSeBr	11		1:0	80

[a] Measured by integration of the 300-MHz ^1H NMR spectra of the crude reaction mixtures. [b] Yields refer to pure isolated adducts. [c] Small amounts (5–25% included in the yield, see Experimental Section) of uncharacterized isomeric byproducts were obtained. [d] The reaction was carried out in CH_2Cl_2 at −78 °C.

Treatment of endo benzyl ether **3** with PhSeBr (entry 1) gave rise to adduct **12** along with ca. 25% of isomeric byproducts whose structure did not appear to be of type B, presumably arising from Wagner–Meerwein rearrangement of the intermediate episelenonium ion. Changing the protecting group to a benzoate (entry 2) afforded an excellent yield of **13**, thus circumventing this problem. Similarly, endo (benzoyloxy)methyl substrate **5** displayed complete steric control to yield exclusively adduct **14**.

The reaction of exo benzyl ether **6** produced a 1:6 mixture favoring adduct B with significantly higher selectivity than its oxanorbornenic analogue (1:3.6[7c]). Lowering the temperature to −78 °C produced a slight increase in the ratio obtained (entry 5). Furthermore, commercially available alcohol **7** displayed a striking selectivity (1:10, entry 6) when the reaction was conducted at −78 °C in CH_2Cl_2. The harder electrophile PhSCl showed a significant increase in the ratio of isomer B (entry 7).

At this stage the behavior of hydroxymethyl derivatives **8** and **9** was examined. Benzoate **8** exhibited an unexpectedly high selectivity favoring isomer A (entry 8). Moreover, lowering the temperature to −78 °C (entry 9) afforded almost exclusively adduct **21**. Even alcohol **9** gave rise to **23** (PhSeBr) and **25** (PhSCl) with synthetically useful ratios (entry 10 and 11).[11]

Finally, dibenzoate **10**, which was considered to be a good test of the relative importance of endo steric control in light of the above results, was treated with PhSeBr (entry 12) to produce exclusively adduct **11**. This result clearly demonstrates the decisive influence of endo substituents on the regioselectivity of the process.

The assignment of the regio- and stereochemistry of the addition products derived from their spectral data (see Experimental Section) with the aid of selective decoupling experiments and DNOE measurements. For example, *exo*-benzyl ether **15** showed a 7.8% enhancement on H-2 upon irradiation of H-6; isomeric ether **16** displayed a 5.7% enhancement on H-3n upon irradiation of H-5.

While at present a definitive mechanistic proposal remains elusive, it is possible to tentatively advance a qualitative rationale for the above results. First, *exo*-benzyloxy and hydroxy groups behave as remote eletrondonating substituents[10] with enhanced selectivity in norbornenic derivatives vsmthe corresponding oxanorbornenes. This enhancement may derive from the elimination of electrostatic repulsions caused by the 7-oxygen bridge lone pairs, thus diminishing small unfavorable distortions in the geometry of the molecule. Second, *exo*-(hydroxymethyl)norbornene derivatives favor incorporation of the nucleophile at C-5 with remarkable regioselectivity; in this case, exo substitution may cause a small but nonetheless significant distortion of the bicyclic system resulting in an important steric bias at the endo face of the molecule particularly for norbornenic sub-

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(8) Benzyl ethers **3** and **6** were prepared from the corresponding alcohols (NaH, BnBr, DMF). Benzoates **4**, **5**, and **8** were prepared from the corresponding alcohols (BzCl, pyridine). Dibenzoate **10** was prepared from the corresponding diacid chloride (LAH, THF; BzCl, pyridine).

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(10) Carrupt, P. A.; Vogel, P.; *Tetrahedron Lett.* **1982**, *23*, 2563–2566.

(11) It was found that adducts derived from exo-substituted substrates slowly isomerized upon standing at room temperature, both in solution and neat. For instance, the initial ratio for **17**:**18** (1:10) changed to 1:4 after 2 days at room temperature.

strates.[12] At any rate, we have shown that the selectivity of these synthetically useful reactions[5-7,13] applied to readily available substrates may be fine tuned to a larger extent than could have been anticipated.[14]

Experimental Section

General. For procedures and conditions, see ref 7c. 5-Norbornen-2-ol (exo/endo), 5-norbornen-2-methanol (endo/exo), *trans*-3,6-endomethylene-1,2,3,6-tetrahydrophthalic chloride, and PhSeBr were purchased from Aldrich. PhSCl was prepared by the literature procedure.[15] All experiments involving hydroxymethyl derivatives **5**, **8**, **9** were effected on the mixtures of isomers; the resulting adducts were subsequently separated chromatographically and fully characterized.[16] It should be mentioned that a number of methods to produce endo[17] or exo[18] ester precursors to **5**, **8**, and **9** are known in the literature. All new compounds described in this report are racemic and are numbered arbitrarily to facilitate comparison of the data.

2-*endo*-3-*exo*-Bis[(benzoyloxy)methyl]-5-*endo*-bromo-6-*exo*-(phenylselenyl)bicyclo[2.2.1]heptane (11). The reaction was carried out in $CHCl_3$ at 0 °C. The reaction mixture was purified by chromatography on silica gel (80%, white solid). R_f: 0.3 (hexane/Et_2O (3:1). Mp: 124–125 °C. IR ($CHCl_3$): 3080, 2980, 1740, 1620, 1560, 1500, 1290, 1130 cm^{-1}. ^1H NMR (C_6D_6): δ 1.14 (dm, 1 H, J = 11.1 Hz, H-7syn), 1.55 (apdd, J = 11.1 Hz, H-7anti), 1.73 (m, 1 H, H-2), 1.99 (apdd, 1 H, J = 4.3, 1.3 Hz, H-4), 2.24 (m, 1 H, H-1), 2.32 (apqd, 1 H, J = 7.4, 1.5 Hz, H-3), 3.70 (dd, 1 H, J = 4.4, 3.0 Hz, H-6), 3.92–3.96 (m, 2 H, H-3'), 3.98 (t, 1 H, J = 4.3 Hz, H-5), 4.17 (dd, 1 H, J = 11.5, 10.3 Hz, H-2'), 4.48 (dd, 1 H, J = 11.5, 6.0 Hz, H-2'), 6.83–6.87 (m, 3 H, ArH), 7.04–7.18 (m, 6 H, ArH), 7.45–7.48 (m, 3 H, ArH), 7.96–8.00 (m, 2 H, ArH), 8.20–8.23 (m, 2 H, ArH). DNOE between H-7anti/H-7syn, 25%; H-7anti/H-5, 9.9%; H-7anti/H-1, 6.2%; H-7anti/H-4, 4.3%; H-7anti/H-2, -9.3; H-6/ArH, 1.9%; H-6/H-3n, 2.8%; H-6/H-2', 7.8%; H-6/H-1, 3.6%; H-6/H-5, 2.2%. ^{13}C NMR ($CDCl_3$): δ 35.1, 38.3, 44.1, 46.8, 47.5, 47.6, 58.4, 63.5, 66.6, 127.6, 127.7, 128.2, 128.3, 129.0, 129.5, 129.7, 129.8, 131.4, 132.9, 133.0, 133.9, 166.0, 166.3. Anal. Calcd for $C_{29}H_{27}BrO_4Se$: C, 58.21; H, 4.55; Br, 13.35. Found: C, 58.40; H, 4.27; Br, 13.03.

2-*endo*-(Benzoyloxy)-5-*endo*-bromo-6-*exo*-(phenylselenyl)bicyclo[2.2.1]heptane (13). The reaction was carried out in $CHCl_3$ at 0 °C. The reaction mixture was purified by chromatography on silica gel (80% yield, white solid). R_f: 0.36 (hexane/AcOEt (5:1). Mp: 95–96 °C. IR ($CHCl_3$): 2960, 1710, 1280, 1120, 670 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.68 (dm, 1 H, J = 11.2 Hz, H-7syn), 1.92 (dm, 1 H, J = 11.2 Hz, H-7anti), 2.07 (dt, 1 H, J = 14.2, 3.7 Hz, H-3n), 2.19 (dddd, 1 H, J = 14.2, 9.9, 4.4, 1.9 Hz, H-3x), 2.57 (m, 1 H, H-4), 2.73 (m, 1 H, H-1), 3.94 (dd, 1 H, J = 4.8, 1.8 Hz, H-6), 4.32 (td, 1 H, J = 4.4, 1.8 Hz, H-5), 5.29 (dt, 1 H, J = 10.0, 4.1 Hz, H-2), 7.26–7.28 (m, 2 H, ArH), 7.44–7.63 (m, 6 H, ArH), 8.00–8.03 (m, 2 H, ArH). DNOE between H-5/H-7anti, 2.8%; H-5/H-6, 4.4%; H-5/H-4, 5.0%; H-6//H-1, 2.8%; H-6/H-3n, 1.1%; H-6/ArH, 2.3%; H-2/H-7syn, 3.3%; H-2/H-3x, 5.5%. ^{13}C NMR ($CDCl_3$): δ 30.8, 34.7, 45.0, 46.4, 48.4, 58.4, 74.8, 127.5, 128.4, 129.1, 129.5, 129.7, 130.0, 133.1, 133.3, 166.1. Anal. Calcd for $C_{20}H_{19}BrO_2Se$: C, 53.35; H, 4.25. Found: C, 53.58; H, 4.17.

5-*endo*-Bromo-6-*exo*-(phenylselenyl)bicyclo[2.2.1]heptan-2-*exo*-ol (17) and 6-*endo*-Bromo-5-*exo*-(phenylselenyl)bicyclo[2.2.1]heptan-2-*exo*-ol (18). The reaction was carried out in CH_2Cl_2 at -78 °C. The crude product was purified by chromatography on silica gel to yield a 1:10 inseparable mixture of **17**:**18** along with 6% of uncharacterized isomeric products (80%, combined yield). R_f: 0.33 (hexane/Et_2O (1:1)). IR ($CHCl_3$): 3600, 3400, 2960, 1470, 1440, 1080, 1050 cm^{-1}. **Data of 17.** ^1H NMR ($CDCl_3$): δ 2.23 (br s, 1 H, H-1), 2.98 (dd, 1 H, J = 4.5, 2.6 Hz, H-6), 3.84 (dm, 1 H, J = 6.9 Hz, H-2), 4.09 (td, J = 4.1, 1.8 Hz, H-5). ^{13}C NMR ($CDCl_3$): δ 32.2, 36.5, 44.0, 49.6, 52.2, 57.9, 73.1. **Data of 18.** ^1H NMR ($CDCl_3$): δ 1.53 (dm, 1 H, J = 13.6 Hz, H-3x), 1.76–1.79 (m, 2 H, H-7syn, H-7anti), 1.88 (ddd, 1 H, J = 13.6, 7.0, 2.2 Hz, H-3n), 2.01 (br s, 1 H, O*H*), 2.34 (br d, 1 H, J = 3.9 Hz, H-4), 2.45 (br d, 1 H, J = 4.4 Hz, H-1), 3.17 (dd, 1 H, J = 4.0, 2.4 Hz, H-5), 4.15 (t, 1 H, J = 4.3 Hz, H-6), 4.5 (dm, 1 H, J = 6.8 Hz, H-2), 7.25–7.32 (m, 3 H, ArH), 7.52–7.60 (m, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 32.8, 41.9, 43.5, 51.8, 53.5, 54.9, 70.3, 127.7, 134.3, 134.7.

2-*exo*-[(Benzoyloxy)methyl]-5-*endo*-bromo-6-*exo*-(phenylselenenyl)bicyclo[2.2.1]heptane (21) and 2-*exo*-[(Benzoyloxy)methyl]-6-*endo*-bromo-5-*exo*-(phenylselenenyl)bicyclo[2.2.1]heptane (22). The reaction was carried out in CH_2Cl_2 at -78 °C. The crude product was purified by chromatography on silica gel to produce a 25:1 mixture of **21**:**22** (85% combined yield). R_f: 0.18 (hexane/Et_2O (10:1)). IR($CDCl_3$): 2960, 1710, 1450, 1310, 1260, 1110 cm^{-1}. **Data of 21.** ^1H NMR ($CDCl_3$): δ 1.20–1.29 (dm, 1 H, J = 13.0 Hz, H-3x), 1.62 (dm, 1 H, J = 11.1 Hz, H-7syn), 1.85 (dm, 1 H, J = 11.1 Hz, H-7anti), 2.13 (m, 1 H, H-2), 2.29 (ddd, 1 H, J = 13.0, 8.7, 2.5 Hz, H-3x), 2.37 (br s, 1 H, H-1), 2.55 (br t, 1 H, J = 3.6 Hz, H-4), 3.35 (t, 1 H, J = 3.4 Hz, H-6), 4.03 (dd, 1 H, J = 11.1, 9.4 Hz, H-2'), 4.18 (dd, 1 H, J = 11.0, 6.1 Hz, H-2'), 4.21–4.27 (m, 3 H, H-5, 2H-2') 7.26–7.33 (m, 3 H, ArH), 7.43–7.49 (m, 2 H, ArH), 7.54–7.89 (m, 3 H, ArH), 7.95–8.07 (m, 2 H, ArH). ^{13}C NMR ($CDCl_3$): δ 28.6, 33.0, 41.0, 44.7, 46.3, 54.4, 58.2, 66.9, 127.6, 128.4, 129.1, 129.5, 130.1, 133.0, 134.0, 166.4. **Data of 22.** ^1H NMR ($CDCl_3$): δ 1.39 (dt, 1 H, J = 13.1, 4.6 Hz, H-3x), 1.54–1.58 (m, 1 H, H-7syn), 1.66–1.70 (m, 1 H, H-3n), 1.75 (dm, 1 H, J = 11.0 Hz, H-7anti), 2.39 (m, 1 H, H-1 or H-4), 2.49 (dm, 1 H, J = 4.1 Hz, H-1 or H-4), 2.81 (m, 1 H, H-2), 3.25 (dd, 1 H, J = 4.6, 2.8 Hz, H-5), 4.21–4.27 (m, 3 H, H-6, 2H-2'). ^{13}C NMR ($CDCl_3$): δ 33.3, 34.0, 35.0, 44.7, 47.2, 53.7, 58.8, 67.1.

Acknowledgment. Support of this research by D.G.I.C.Y.T. (Grant PB89-0099) and by the C.S.I.C. is gratefully acknowledged. We thank the Universidad Complutense for a doctoral fellowship to A.V.

Registry No. **3**, 135560-43-9; **4**, 135560-44-0; **5**, 135560-45-1; **6**, 135560-46-2; **7**, 87392-59-4; **8**, 135560-47-3; **9**, 69831-10-3; **10**, 135560-48-4; **11**, 135560-49-5; **12**, 135560-50-8; **13**, 135560-51-9; **14**, 135560-52-0; **15**, 135560-53-1; **16**, 135560-54-2; **17**, 135560-55-3; **18**, 135560-56-4; **19**, 135583-74-3; **20**, 135583-75-4; **21**, 135560-57-5; **22**, 135560-58-6; **23**, 135560-59-7; **24**, 135560-60-0; **25**, 135583-61-8; **26**, 135560-61-1; PhSeBr, 34837-55-3; PhSCl, 4972-29-6; *endo*-5-norbornen-2-ol, 69769-90-0; *endo*-5-norbornene-2-methanol, 42070-72-4; *trans*-3,6-endomethylene-1,2,3,6-tetrahydrophthaloyl chloride, 4582-21-2.

Supplementary Material Available: Experimental and spectroscopic data for compounds **12**, **14**, **15**, **19**, **20**, and **23–26** (4 pages). Ordering information is given on any current masthead page.

(12) It should be pointed out that the substitution of an oxygen for a methylene bridge brings about a lengthening of the C(1)–X(7) bond (X = O, CH_2), thus altering the geometry of the molecule. See: Arjona, O.; Mallo, A.; Manzano, C.; Plumet, J.; Galbis, J.; Jaime, C. *J. Chem. Soc., Perkin Trans. 2*, **1988**, 865–868.

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(14) For an example of long-range substituent effects on oxanorbornenic derivatives, see: Ferrari, T.; Vogel, P. *Tetrahedron Lett.* **1986**, *27*, 5507–5508.

(15) Fieser and Fieser, *Reagents for Organic Synthesis*; John Wiley & Sons: New York, 1975; Vol. 5, p 523.

(16) Upon treatment with PhSeBr and PhSCl, 5-norbornen-2-*endo*-methanol afforded products of intramolecular cyclization, as described previously. See for 5-*exo*-(phenylthio)-3-oxatricyclo[4.2.0.$0^{4,8}$]nonane: Tuladhar, S. M.; Fallis, A. G. *Can. J. Chem.* **1987**, *65*, 1833–1837. For 5-*exo*-(phenylselenyl)-3-oxatricyclo[4.2.0.$0^{4,8}$]nonane: Nicolau, K. C.; Magolda, R. L.; Sipio, W. J.; Barnette, W. E.; Lysenko, Z.; Joullie, M. M. *J. Am. Chem. Soc.* **1980**, *102*, 3784–3793.

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