148 (8) ($M^+ - CO_2$), 126 (15 ($M^+ - C_5H_6$), 105 (17) (M^+ - iPr - CO_2), 83 (74) ($C_4H_3O_2$), 66 (100) (C_5H_6).

7,7-Diphenyl-3-(1-methylethyl)-2-oxa-5,6-diazaspiro[3.4]-oct-5-en-1-one (11b). A solution of 220 mg (1.74 mmol) of **5b** in 5 mL of acetonitrile was treated with 339 mg (1.74 mmol) of diphenyldiazomethane in 5 mL of acetonitrile. The mixture was stirred at 20 °C until the color disappeared and the $CuCN/CH_3CN$ spray[8] revealed a positive azo test. The solvent was removed by evaporation (ca. 20 °C (15 Torr)) and the crude product was recrystallized from methanol to yield 350 mg (63%) of colorless needles: mp 100–102 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 0.56 (d, J = 6.6 Hz, 3 H), 1.08 (d, J = 6.6 Hz, 3 H), 1.86 (d septet, J = 8.6, 6.7 Hz, 1 H), 2.49 and 2.87 (AB-system, J = 14.3 Hz, 2 H), 4.81 (dd, J = 8.9 Hz, 1 H), 7.25–7.35 (m, 10 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.5 (q), 17.7 (q), 28.7 (d), 33.7 (t), 83.0 (d), 104.1 (s), 106.2 (s), 126.4 (d), 127.0 (d), 127.5 (2 × d), 127.9 (2 × d), 128.7 (2 × d), 128.9 (2 × d), 141.3 (s), 143.0 (s), 165.5 (s); IR (CCl_4) ν 3070, 3035, 2970, 1835 cm^{-1}; MS (70 eV) m/z 292 (6) ($M^+ - N_2$), 248 (61) ($M^+ - N_2 - CO_2$), 233 (47) ($M^+ - N_2 - CO_2 - CH_3$), 205 (100) ($M^+ - N_2 - CO_2$ - iPr), 43 (22) (iPr). Anal. Calcd for $C_{20}H_{20}N_2O_2$ (320.4): C, 74.98; H, 6.29; N, 8.74. Found: C, 74.68; H, 6.22; N, 8.44.

Ethenylidenecyclohexane (12c) and Ethenylidenetricyclo[3.3.1.1^{3,7}]decane (12d). Samples of 60.0 mg (0.394 mmol) of **5c** or 90.0 mg (0.441 mmol) of **5d** were placed in a flask and heated at 100 °C (0.1 Torr) to volatilize the α-methylene β-lactone into a 20-cm quartz tube kept at 400 °C. The pyrolysates were collected in a liquid-air-cooled receiving flask to afford 33 mg (87%) or 64 mg (91%) of the corresponding allenes **12c,d**, which were identified by comparison with the reported spectral data.[9]

(*E*)-5-Ethylidenebicyclo[2.2.1]hept-2-ene (13a) and (*E*)-5-(2-Methylpropylidene)bicyclo[2.2.1]hept-2-ene (13b). Samples of 36.0 mg (0.219 mmol) of an exo/endo mixture **9a** or 128 mg (0.666 mmol) of an exo/endo mixture **9b** were placed in a flask and heated to 180 °C (0.1 Torr) to volatilize the β-lactones into a 20-cm quartz tube kept at 400 °C. The pyrolysates were collected in a liquid-air-cooled receiving flask to afford 23 mg (87%) or 66.5 mg (67%) of the corresponding (*E*)-alkylidenenorbornenes **13a,b** as colorless liquids, identified by comparison with the reported spectral data[10] in the case of **13a** or by NOE irradiation experiments (degassed, sealed tubes) for **13b**. **Norbornene 13b**: ^1H NMR (400 MHz, $CDCl_3$) δ 0.82 (dd, J = 6.7, 0.4 Hz, 3 H), 0.88 (dd, J = 6.7, 0.4 Hz, 3 H), 1.28 (dm, J = 8.0 Hz, 1 H), 1.46 (dddd, J = 8.0, 3.0, 1.6, 1.4 Hz, 1 H), 1.60 (dddd, J = 14.4, 2.9, 2.3, 0.4 Hz, 1 H), 2.08 (ddd, J = 14.5, 3.5, 2.3 Hz, 1 H), 2.18 (d septet, J = 9.0, 6.7 Hz, 1 H), 2.89 (m, 1 H), 2.97 (m, 1 H), 5.11 (dddd, J = 9.0, 2.3, 2.3, 0.7 H, 1 H), 5.96 (ddd, J = 5.6, 3.0, 0.4 Hz, 1 H), 6.00 (dd, J = 5.5, 2.5 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 22.9 (q), 23.1 (q), 29.3 (d), 30.8 (t), 41.8 (d), 50.1 (t), 50.5 (d), 126.6 (d), 134.6 (d), 135.6 (d), 138.7 (s); IR (CCl_4) ν 3070, 2980, 1625 cm^{-1}; MS (70 eV) m/z 148 (100) (M^+), 133 (51) ($M^+ - CH_3$), 105 (88) (M^+ - iPr), 92 (62) ($M^+ - C_4H_8$), 66 (97) (C_5H_6).

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft (SFB 347 "Selektive Reaktionen Metall-aktivierter Moleküle") and the Fonds der Chemischen Industrie is gratefully appreciated.

Registry No. **5a**, 117203-16-4; **5b**, 117203-18-6; **5c**, 135638-62-9; **5d**, 135638-63-0; **6b** (OMe), 71385-30-3; **6b** (OEt), 135638-64-1; **6b** (PhNH), 135638-65-2; *cis*-**7b**, 135638-66-3; *trans*-**7b**, 135638-67-4; *cis*-**8b**, 135638-68-5; *trans*-**8b**, 135638-69-6; *exo*-**9a**, 135638-70-9; *endo*-**9a**, 135684-12-7; *exo*-**9b**, 135638-71-0; *endo*-**9b**, 135684-13-8; **10d**, 126255-71-8; **11b**, 135638-72-1; **12c**, 5664-20-0; **12d**, 59556-21-7; (*E*)-**13a**, 28304-67-8; (*E*)-**13b**, 135638-73-2; $PhNH_2$, 62-53-3; PhSH, 108-98-5; $(Ph)_2CN{=}NH$, 883-40-9; cyclopentadiene, 542-92-7.

Supplementary Material Available: X-ray crystallographic data for thietanone **10d** consisting of the structural parameters, six tables that include atomic coordinates and equivalent isotropic displacement parameters, bond lengths, bond angles, anisotropic displacement parameters and H-atom coordinates, and isotropic displacement parameters, and ^1H NMR spectral data for compounds **9a** and **9b** (10 pages). Ordering information is given on any current masthead page.

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Novel Formation of Isomeric Bicyclo[3.2.0]heptan-1-ols from Phenyl Vinyl Sulfoxide and the Cyclopentanone Lithium Enolate Generated by Conjugate Addition of Lithiated (*E*)-But-2-enyldiphenylphosphine Oxide to 2-Methylcyclopent-2-enone

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Whereas the title enolate **2** in THF reacts at −10 °C with 2 equiv of phenyl vinyl sulfone to provide the hydrindanol **9** (9%), it reacts with 1 equiv of phenyl vinyl sulfoxide to give 7-(phenylsulfinyl)bicyclo[3.2.0]heptan-1-ol sulfoxides **11** and **12** (50% overall) and adduct **10** (10%). The yield of the bicycloheptanols decreases to 35% in the dark and increases to 68% under irradiation. Their formation is entirely suppressed by HMPA. Stereochemistry of **12** was provided by X-ray crystallography of the derived sulfone **14**. Base-induced ring opening of the sulfone in the presence of phenyl vinyl sulfone gives the alkylated cyclopentanones **17**, **18**, and **21** and the bicyclo[2.2.1]heptanone **20**. The bicyclo[3.2.0]heptanols **11** and **12** are considered to arise by intramolecular nucleophilic or single electron transfer processes.

Introduction

The enolate **2**, generated by conjugate addition of lithiated (*E*)-but-2-enyldiphenylphosphine oxide (**1**) to 2-methylcyclopent-2-enone in THF, reacts efficiently with β-sulfonyl or β-chlorovinyl ketones to provide adducts that have been converted into hydrindanone precursors of vitamin D.[1,2] However, the preparations have the drawback

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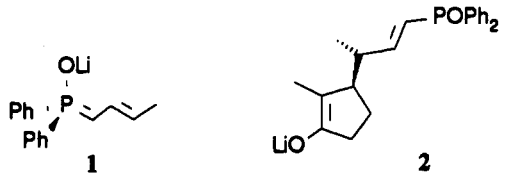
that a carbonyl transposition from C9 to C8 (steroid numbering) must be carried out on the hydrindanone to provide the CD precursor.[3-5]



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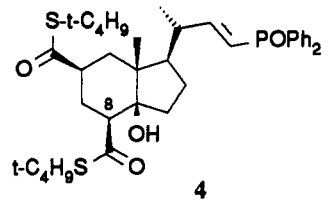

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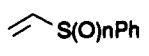
The problem can in principle be overcome as follows. We have observed that 2 mol of *tert*-butyl thioacrylate **3** reacts with **2** to give the hydrindanol **4**.[2,6] Thus, vinyl sulfone and sulfoxide electrophiles **5** and **6** should react in the same way as **3** to provide hydrindanols now bearing substituents strategically located for transformation into known CD intermediates with carbonyl[4] or sulfonyl[5] groups at C-8.



5; n = 1

6; n = 2

However, the sulfone **5** does not undergo sequential conjugate addition–ring closure with the lithium enolate of cyclohexanone,[7] although it does react in a different manner with the kinetic lithium dienolate of cyclohexenone.[8] Sulfoxide **6** undergoes conjugate addition with carbanion nucleophiles[9] in the same way as sulfone **5**.[10] Although reaction of **6** with ketone enolates has not been recorded, the closely related aryl vinyl selenoxides react with primary and secondary lithium enolates to generate α-selenoxide carbanions. An ensuing proton transfer generates a new enolate, which displaces selenoxide to provide α-ketocyclopropanes.[11]

Results

The enolate **2**[1,2,6] at −10 °C reacted with sulfone **5** (2 equiv) to give a complex mixture of products containing adduct **7** (55%)[2] and the hydrindanol **9** (9%, after isolation by HPLC). Stereochemical identity of **9** follows from the similarity of its NMR spectrum to that of hydrindanol **4**.[2,6] Signals due to H4 (δ 3.18 ppm) and H6 (δ 3.02) (hydrindanol numbering) display trans-diaxial couplings of 13.5 and 12.5 Hz, respectively, to H5β. H6 has an additional coupling of 12.5 Hz to H7β. Thus the phenylsulfonyl groups are cis and equatorial. Stereochemistry of ring fusion follows from the mode of reaction. The enolate **2** reacts through the face away from the phosphinoyl side chain with 2 equiv of the vinyl sulfone to generate lithiated sulfone **8**. The pseudoaxial methyl group on the cyclopentanone ring causes cis closure of the six-membered ring to take place. The relative configuration of *RS* at C1′ follows from the strict stereochemical control operating during the conjugate addition of the lithiated phosphine oxide.[1,2,6]

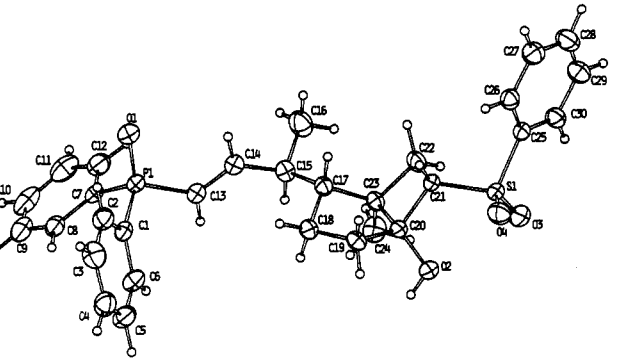
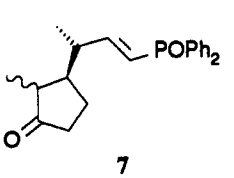


Figure 1. ORTEP plot of (1*RS*,1′*RS*,4*RS*,7*SR*)-5-methyl-4-[1′-methyl-3′-(diphenylphosphinoyl)prop-2′-enyl]-7-(phenylsulfonyl)bicyclo[3.2.0]heptan-1-ol (**14**) with crystallographic numbering.



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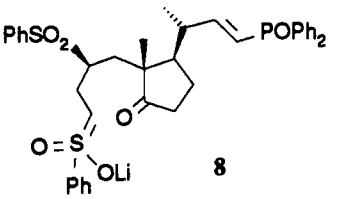

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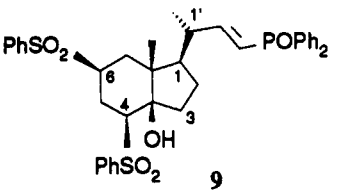

9

The reaction of the sulfoxide **6** was strikingly different from that of sulfone **5**. Treatment of **2** at −10 °C in THF under laboratory lighting with **6** gave **7** (26%), the "monoalkylated" product **10** (10%), and the bicyclo[3.2.0]heptanol sulfoxides **11** (23%) and **12** (27%) as single stereoisomers. The sulfoxide analogue of hydrindanol **9** was not formed. Sulfoxide **11** and **12** were characterized as sulfones **13** and **14**. Relative configuration of **14** was given by an X-ray structural determination. The ORTEP plot (Figure 1) shows the cis-fused bicyclo[3.2.0]heptane system with the entire ensemble of substituents on the same face. The relative configuration of *RS* at C1′ [C(15) in Figure 1] is also evident. Intramolecular hydrogen bonding in the crystal between the hydroxyl and sulfone groups is not evident. There is, however, a strong inter-

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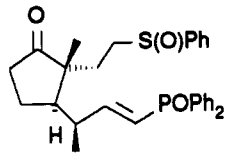

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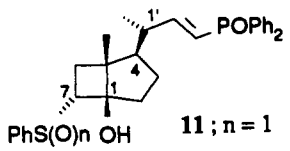
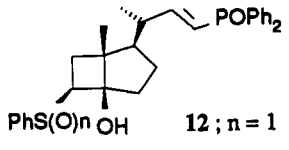


11 ; n = 1



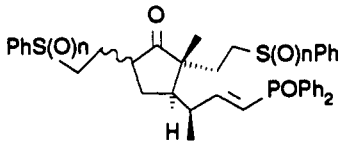
12 ; n = 1

13 ; n = 2

14 ; n = 2

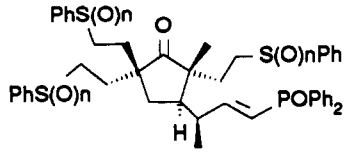
molecular hydrogen bond between the hydroxyl group and the oxygen atom of the phosphine oxide [O(1)···O(2) 2.665 Å, O(1)···HO(2) 1.82 Å]. In solution, a hydrogen bond could form between the hydroxyl and the sulfone; the O(2)···O(3) distance is only 2.839 Å, and this will be further reduced by rotation about the S–C bond. The four-membered ring is significantly distorted from planarity; the average deviation from the least-squares plane is 0.08 Å. The five-membered ring is also puckered with atoms deviating by up to 0.26 Å from planarity. Considerable steric strain is evident in the fused ring system, and this is most notably manifest in the common bond [C(20)–C(23)], which is 1.573 (3) Å long. This constitution of sulfone **13** follows from the close similarity of its NMR data with that of **14**. In particular, the three-proton connectivity of the cyclobutyl system is clearly apparent in the signals due to H6β (δ 1.71), H6α (1.97), and H7β (3.80). Geminal and vicinal couplings of 12.0 and 10.0 Hz, respectively, are apparent in the first two signals. The last contains both vicinal (10 Hz) and long range "*W*" couplings (1 Hz to H2β). The long range coupling is absent in compound **14**. In addition, preirradiation at δ 1.71 (H6β) gave enhancements at 1.97 (H6α, 8%) and at 3.80 ppm (H7β, 3.4%). The complementary NOE experiment—preirradiation at δ 3.81 (H7β)—gave enhancements at 1.71 (H6β, 6.1%) and at 1.17 (5-CH_3, 1.7%). Both the long-range coupling and the NOE results unambiguously indicate the stereochemistry is as in **13**.

Several experiments were carried out to probe formation of the bicyclic products. Reaction of **6** with **2** in the dark gave the bicyclics **11** (7%) and **12** (28%), and diastereomeric mixtures of the alkylated products **15** (25%) and **16** (32%), characterized as the sulfones **17** and **18**. Under



15; n = 1

17; n = 2

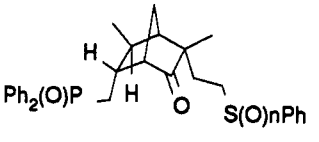


16; n = 1

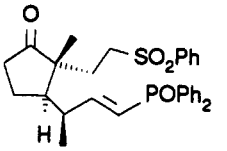
18; n = 2

irradiation from a tungsten lamp, products **11** (25%) and **12** (43%) were obtained in increased yield, together with **7** (13%) and **10** (12%). Next, the lithiated phosphine oxide **1** was generated in the presence of HMPA and treated with enone and then the vinyl sulfoxide **6** to give **16** (85%) and a product tentatively identified as the bicyclo[2.2.1]heptanone **19** (5%). Treatment of the enolate **2** with ClTi(O-*i*-Pr)$_3$ followed by **6** enhanced formation of **7** (62%) at the expense of the bicyclic products (10%); this probably reflects destruction of the enolate rather than suppression of reaction with the sulfoxide.

The unexpected formation of the bicyclics **11** and **12** thwarted our aim to generate the sulfoxide analogue of hydrindanol **9**. Another attempt to prepare **9** was therefore made through base-induced ring opening of sulfone **14** in the presence of vinyl sulfone **6**. Ring opening of the alkoxide from **14** will generate the lithiated sulfone, which we hoped to intercept through reaction with the sulfone electrophile to provide **8**, the precursor of **9**. However, treatment of a mixture of **6** and **14** in DMF with NaH at −10 °C gave the ring-opened, trialkylated product **18** (49%), and a single diastereomer of the bicyclo[2.2.1]-heptanone **20** (36%). In contrast, addition of the reactants in THF to LDA in THF gave only the product of ring opening, the sulfone **21** (81%). The formation of **18** and



19; n = 1



21

20; n = 2

20 clearly involves intra- or intermolecular equilibrating proton transfer to the incipient lithiated sulfone from C5 (cyclopentanone numbering) of the ketone arising by ring opening of the alkoxide of **14**. Intermolecular addition of the enolate to the vinyl sulfone **6** or intramolecular addition to the vinyl phosphine oxide side chain gives the products. Reactions corresponding to the last have been thoroughly examined in this laboratory.[12] The complexity of the NMR spectrum of **21** prevented stereochemical assignments from being made, but relative configuration is believed to be as depicted. We have shown that in closely related systems stereochemistry of the intramolecular cyclization is controlled by conformation of the vinyl phosphine oxide side chain in the enolate precursor.[12] Compound **9** was not formed.

Discussion

The formation of the bicyclics **11** and **12** under such mild conditions is noteworthy. Construction of such systems bearing a bridgehead hydroxyl normally involves thermal or photochemical [2 + 2] cycloaddition of activated ketenes to cyclopentenyl silyl ethers,[13] or a ketene acetal to cyclopentenyl acetate.[14] Other methods require intramolecular reductive coupling of cycloheptane-1,4-diones,[15] ciné-substitution and hydrolysis of 6,6-dichlorobicyclo-[3.2.0]heptan-7-one,[16] and solvolysis of (cyclopentenyl)ethyl tosylate.[17] Aside from the single example of an aldol

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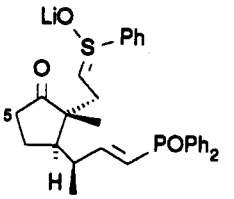
reaction driven by an ensuing reduction of the carbonyl in the aldol product,[18] we are unaware of examples of intramolecular addition of a carbanion to a carbonyl group leading to the bicyclo[3.2.0]heptane skeleton. That the vinyl sulfoxide only undergoes this reaction indicates involvement of a tight reactant complex in which the highly polar vinyl sulfoxide occupies a coordination site on the Li^+ associated with the enolate 2 plays an important role. Nucleophilic addition of the enolate to the vinyl sulfoxide generates the lithiated sulfoxide 22, which now has Li^+



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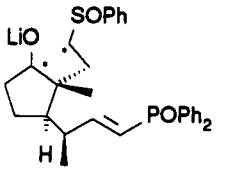
associated with the sulfoxide oxygen. Carbonyl complexation then drives the reaction along the carbonyl addition pathway leading to the bicycloheptanol. The importance of tight ion pairing is demonstrated by the dramatic effect of HMPA, which diverts the reaction entirely away from cycloaddition. The lower dipole of the sulfone renders ion pairing and carbonyl complexation less important, so that intermolecular reactions only are observed with the adduct from vinyl sulfone 5 and enolate 2.[19] Alternatively, reaction of 5 with 2 to generate the lithiated bicyclic alkoxides of 13 and 14 may take place, but both because of the inferior ability of the sulfone group to stabilize the bicyclic alkoxide through intramolecular chelation of Li^+, and because of the greater stability of the lithiated sulfone corresponding to 22, their formation is reversible, and other products are eventually obtained. The lithiated sulfoxide alkoxides of 11 and 12 on the other hand will be stabilized by intramolecular chelation between the alkoxide and the sulfoxide group.[20]

The intriguing enhancement of yields of the bicyclo[3.2.0]heptanols upon irradiation indicates that electron transfer via a charge transfer or donor–acceptor complex *either* between the enolate and the vinyl sulfoxide *or*, in an intramolecular sense, between the lithiated α-sulfinyl anion and the carbonyl group in 22 may play a role in this reaction. In both cases, complex formation and stability is reliant upon the presence of Li^+. In the first case, electron transfer leads via an enol radical–radical ion pair to 22. In the second case, intramolecular electron transfer in 22 leads to diradical 23, which couples to provide the alkoxide precursors of 11 and 12. In the absence of photostimulation, intramolecular proton transfer in 22 from C5 to the lithiated sulfoxide competes, which leads to the alkylated products 15 and 16. The lack of formation of



23

these products in the irradiated reaction mixtures suggests that the *intramolecular* complex formation and electron transfer involving 22 is, remarkably, the more likely of the two pathways.

From both preparative and mechanistic viewpoints, the reactions are important, and further investigations are clearly required.

Experimental Section

The general experimental conditions,[1,2] the preparation of (*E*)-but-2-enyldiphenylphosphine oxide[21] and characterization of the epimers of product 7[2] have been described elsewhere.

Enolate Trapping with Phenyl Vinyl Sulfone (5). Generation of lithiated phosphine oxide 1 from the parent phosphine oxide (666 mg, 2.60 mmol, 1.0 equiv) in THF (30 mL) and C_4H_9Li and its reaction with 2-methylcyclopentenone (250 mg, 2.60 mmol) were carried out as previously described.[1,2] At −10 °C, the solution of the resulting enolate 2 was treated dropwise with 5 (958 mg, 2.2 equiv) in THF (3 mL) over 5 min. The orange solution was stirred at −10 °C for 45 min and after an aqueous NH_4Cl quench, was extracted with ethyl acetate (3 × 50 mL). The organic phase was washed with water (2 × 100 mL) and brine (100 mL) and dried (Na_2SO_4). Removal of the solvent under reduced pressure left the crude products whose purification by flash chromatography with 99:1 ethyl acetate–methanol afforded the product mixture as a cream foam (1.674 g, 94%). Analytical HPLC with 397:3 ethyl acetate–methanol (Whatman Partisil 5 column, 1.5 mL/min, 1000 psi) indicated the presence of a complex mixture of product fractions and one fraction consisting of a mixture of isomers of the simple addition product 7[2] (55%). Preparative HPLC of the complex mixture of 224:1 ethyl acetate–methanol (Whatman Partisil 10 M20 column, 13.5 mL/min, 900 psi) partially resolved the fractions. The fraction containing hydrindanol 9 was purified further by preparative HPLC with 92:8 ethyl acetate–petroleum ether (Whatman Partisil 10 M20 column, 13.5 mL/min, 1400 psi) to give a white solid (160 mg, 9%; t_R 49.5 min). Recrystallization from ethyl acetate–ether gave (**1*RS*,1′*RS*,2′*E*,3a*SR*,4*SR*,6-*SR*,7a*RS*)-7a-methyl-1-[1′-methyl-3′-(diphenylphosphinoyl)prop-2′-enyl]-4,6-bis(phenylsulfonyl)octahydro-1*H*-inden-3a-ol (9)** as fine white needles, mp 142.5–145 °C. ^1H NMR: δ 0.82 (3 H, d, $J_{1'\text{-Me},1'}$ = 6.80 Hz, 1′-CH_3), 0.96 (3 H, s, 7a-CH_3), 1.40 (1 H, dddd, $J_{2\beta,2\alpha}$ = 12.0, $J_{2\beta,3\beta}$ = 12.0, $J_{2\beta,1}$ = 9.0, $J_{2\beta,3\alpha}$ = 2.5 Hz, H2β), 1.52 (1 H, ddd, $J_{1,1'}$ = 9.0, $J_{1,2\beta}$ = 9.0, $J_{1,2\alpha}$ = 1.0 Hz, H1), 1.59–2.06 (6 H, m, H2α, H3β, H5α, H5β, H7α, H7β), 2.30–2.40 (1 H, m, H1′), 2.71 (1 H, ddd, $J_{3\alpha,3\alpha}$ = 13.0, $J_{3\alpha,2\alpha}$ = 9.5, $J_{3\alpha,2\beta}$ = 2.5 Hz, H3α), 3.02 (1 H, dddd, $J_{6\alpha,5\alpha}$ = 12.5, $J_{6\alpha,7\alpha}$ = 12.5, $J_{6\alpha,5\beta}$ = 3.0 Hz, $J_{6\alpha,7\beta}$ = 3.0 Hz, H6α), 3.18 (1 H, dd, $J_{4\alpha,5\alpha}$ = 13.5, $J_{4\alpha,5\beta}$ = 4.0 Hz, H4α), 3.73 (1 H, br s, $W_{h/2}$ = 10.5 Hz, OH), 6.141 (1 H, ddd, $J_{3',P}$ = 24.5, $J_{3',2'}$ = 17.0, $J_{3',1'}$ = 1.0 Hz, H3′), 6.47 (1 H, ddd, $J_{2',P}$ = 19.5, $J_{2',3'}$ = 17.0, $J_{2',1'}$ = 8.5 Hz, H2′), 7.45–7.92 (20 H, m, ArH). HRMS: calcd for $C_{38}H_{41}O_6PS_2$ 688.2082, found, 688.2068. Anal. Calcd for $C_{38}H_{41}O_6PS_2$: C, 66.26; H, 6.00. Found: C, 66.14; H, 5.90.

Enolate Trapping with Phenyl Vinyl Sulfoxide (6). (i) Under Laboratory Lighting. The reaction was carried out in a three-necked round-bottom flask immersed in an ethanol cooling bath contained within a flat Pyrex basin and exposed to neon laboratory lighting. The enolate 2 from the phosphine oxide (666 mg, 1.0 equiv) and the enone (250 mg, 2.60 mmol) was treated at −10 °C with 6 (1.19 g, 3.0 equiv) in THF (3 mL) at a rate such that the temperature remained at −10 °C. The reaction mixture was stirred for 45 min at −10 °C and then worked up as described above to give the crude product mixture, radial chromatography of which with 25:1 ethyl acetate–methanol gave sulfoxide 6 (95

(18) Bianco, A.; Guiso, M.; Iavarone, C.; Marini-Bettelo, R.; Trogolo, C. *Tetrahedron* **1979**, *35*, 1121.

(19) The superior Li^+ chelating ability of lithiated sulfoxide vis-a-vis lithiated sulfone is dramatically apparent in the differing regiochemical outcomes of the reactions of the respective reagents with cyclic enones: Binns, M. R.; Haynes, R. K.; Katsifis, A. G.; Schober, P. A.; Vonwiller, S. C. *J. Org. Chem.* **1989**, *54*, 1960 and references therein.

(20) We acknowledge pertinent comments from a referee. As noted above, independent generation of the lithiated sulfone corresponding to 22 by ring opening of the bicycloheptanol lithium alkoxide of 14 in the presence of 5 leads only to 21. This outcome stands in contrast to that of the reaction of 5 with 2, which yields a complex mixture of products containing a small amount of hydrindanol 9. Although this at first sight implies that bicycloheptanol sulfones are not formed as intermediates in the latter reaction, we note that sulfone 5 cannot be recovered from the ring-opening reaction involving the lithium alkoxide of 14. It evidently undergoes competing decomposition, perhaps engendered by LDA, under the reaction conditions; thus an issue of dichotomous reaction pathways for the respective reactions is beclouded.

(21) Binns, M. R.; Haynes, R. K.; Katsifis, A. G.; Schober, P. A.; Vonwiller, S. C. *J. Am. Chem. Soc.* **1988**, *110*, 5411.

mg), a 1:1 mixture of epimers of the simple addition product 7 as a colorless viscous gum (241 mg, 26%) and a mixture of products 10–12 (878 mg, 67%), which included side products (about 5%). Preparative HPLC of the last with 25:1 ethyl acetate–methanol (Whatman Partisil 10 M20 column, 13.5 mL/min, 1200 psi) gave firstly a 1:1 mixture of diastereomers of **(1′*RS*,2*RS*,2′*E*,3*SR*)-2-methyl-3-[1′-methyl-3′-(diphenylphosphinoyl)prop-2′-enyl]-2-[2″-(phenylsulfinyl)ethyl]cyclopentan-1-one (10)** as a white foam (131 mg, 10%, t_R 119 min). ^{1}H NMR: δ 0.96 (3 H, s, 2-CH_3), 1.10 (3 H, d, $J_{1'\text{-Me},1'}$ = 7.0 Hz, 1′-CH_3), 1.43–1.55 (1 H, m, H4β), 1.76–1.83 (3 H, m, H3, H4α, H1″), 1.94 (1 H, ddd, $J_{5\beta,5\alpha}$ = 18.0, $J_{5\beta,4\beta}$ = 8.5, $J_{5\beta,4\alpha}$ = 2.5 Hz, H5β), 2.17 (1 H, ddd, $J_{1'',1''}$ = 14.0, $J_{1'',2''}$ = 12.5, $J_{1'',2''}$ = 4.5 Hz, H1″), 2.29 (1 H, ddd, $J_{5\alpha,5\beta}$ = 18.0, $J_{5\alpha,4\alpha}$ = 8.5, $J_{5\alpha,4\beta}$ = 2.5 Hz, H5α), 2.52 (1 H, dddq, $J_{1',2'}$ = 8.5, $J_{1',1'\text{-Me}}$ = 7.0, $J_{1',3}$ = 4.5, $J_{1',3'}$ = 1.0 Hz, H1′), 2.63 (1 H, ddd, $J_{2'',2''}$ = 13.0, $J_{2'',1''}$ = 12.5, $J_{2'',1''}$ = 4.5 Hz, H2″), 2.74 (1 H, ddd, $J_{2'',2''}$ = 13.0, $J_{2'',1''}$ = 12.5, $J_{2'',1''}$ = 4.5 Hz, H2″), 6.24 (1 H, ddd, $J_{3',P}$ = 24.5, $J_{3',2'}$ = 17.5, $J_{3',1'}$ = 1.0 Hz, H3′), 6.61 (1 H, ddd, $J_{2',P}$ = 19.5, $J_{2',3'}$ = 17.5, $J_{2',1'}$ = 8.5 Hz, H2′), 7.43–7.56 (9 H, m, ArH meta, para), 7.57–7.60 (2 H, m, S(O)Ph ortho), 7.63–7.70 (4 H, m, P(O)Ph ortho). The compound was characterized as the sulfone 21 described below.

The next fraction was **(1*RS*,1′*RS*,2′*E*,4*RS*,5*RS*,7*RS*)-5-methyl-4-[1′-methyl-3′-(diphenylphosphinoyl)prop-2′-enyl]-7-(phenylsulfinyl)bicyclo[3.2.0]heptan-1-ol (11)**, a white foam (302 mg, 23%; t_R 127.5 min). ^{1}H NMR: δ 1.11 (3 H, d, $J_{1'\text{-Me},1'}$ = 6.5 Hz, 1′-CH_3), 1.14 (3 H, s, 5-CH_3), 1.37–1.50 (2 H, m, H6α, H6β), 1.59–1.70 (2 H, m, H2β, H3β), 1.74–1.80 (1 H, m, H4), 1.90–2.01 (1 H, m, H3α), 2.035 (1 H, br s, $W_{h/2}$ = 39 Hz, OH), 2.56–2.60 (1 H, m, H1′), 2.64–2.75 (1 H, m, H2α), 3.48 (1 H, dd, $J_{7\beta,6\alpha}$ = 10.0, $J_{7\beta,6\beta}$ = 10.0 Hz, H7β), 6.21 (1 H, ddd, $J_{3',P}$ = 24.5, $J_{3',2'}$ = 17.5, $J_{3',1'}$ = 1.0 Hz, H3′), 6.70 (1 H, ddd, $J_{2',P}$ = 19.5, $J_{2',3'}$ = 17.5, $J_{2',1'}$ = 7.0 Hz, H2′), 7.42–7.55 (9 H, m, ArH meta, para), 7.61–7.72 (6 H, m, ArH ortho). The compound was characterized as the sulfone 13, prepared as follows. Product 11 (25 mg, 0.049 mmol) in CH_2Cl_2 (0.5 mL) was added to a stirred solution of *m*-CPBA (80%, 21 mg, 0.098 mmol) in CH_2Cl_2 (5 mL) at 0 °C under N_2. The white suspension was stirred at 0 °C for 1.5 h and then warmed to room temperature. The mixture was diluted with ether to a total volume of 30 mL, washed with aqueous $NaHCO_3$ (saturated, 2 × 20 mL), water (2 × 20 mL), and brine (20 mL), and then dried (Na_2SO_4). Removal of the solvent under reduced pressure left a viscous gum, flash chromatography of which with 99:1 ethyl acetate–methanol afforded the sulfone, a white brittle foam, as a single diastereoisomer (22 mg, 86%). An analytical sample of **(1*RS*,1′*RS*,2′*E*,4*RS*,5*RS*,7*RS*)-5-methyl-4-[1′-methyl-3′-(diphenylphosphinoyl)prop-2′-enyl]-7-(phenylsulfonyl)bicyclo[3.2.0]heptan-1-ol (13)** was obtained by preparative HPLC with 99:1 ethyl acetate–methanol (Whatman Partisil 10 M20 column, 13.5 mL/min, 1100 psi) followed by recrystallization from ethyl acetate–ether as a white crystalline solid, mp 157–159 °C, t_R 55 min. ^{1}H NMR: δ 1.13 (3 H, d, $J_{1'\text{-Me},1'}$ = 6.8 Hz, 1′-CH_3), 1.17 (3 H, s, 5-CH_3), 1.42–1.52 (1 H, m, H2β), 1.57–1.65 (1 H, m, H3β), 1.71 (1 H, dd, $J_{6\beta,6\alpha}$ = 12.0, $J_{6\beta,7\beta}$ = 10.0 Hz, H6β), 1.83–1.88 (1 H, m, H4), 1.97 (1 H, dd, $J_{6\alpha,6\beta}$ = 12.0, $J_{6\alpha,7\beta}$ = 10.0 Hz, H6α), 2.07–2.16 (1 H, m, H3α), 2.63–2.72 (1 H, m, H1′), 2.92 (1 H, ddd, $J_{2\alpha,2\beta}$ = 15.0, $J_{2\alpha,3\alpha}$ = 8.0, $J_{2\alpha,3\beta}$ = 2.5 Hz, H2α), 3.80 (1 H, ddd, $J_{7\beta,6\alpha}$ = 10.0, $J_{7\beta,6\beta}$ = 10.0, $J_{7\beta,2\beta}$ = 1.0 Hz, H7), 6.22 (1 H, ddd, $J_{3',P}$ = 26.5, $J_{3',2'}$ = 17.5, $J_{3',1'}$ = 1.5 Hz, H3′), 6.79 (1 H, ddd, $J_{2',P}$ = 20.5, $J_{2',3'}$ = 17.5, $J_{2',1'}$ = 6.5 Hz, H2′), 7.42–7.56 (8 H, m, P(O)Ph meta, para, SO_2Ph meta), 7.59–7.69 (5 H, m, P(O)Ph ortho, SO_2Ph para), 7.86–7.90 (2 H, m, SO_2Ph, ortho), OH not observed. Preirradiation at δ 1.71 (H6β) gave enhancements at δ 1.97 (H6α) of 7.6% and at δ 3.80 (H7β) of 3.4%. Preirradiation at δ 3.81 (H7β) gave enhancements at δ 1.71 (H6β) of 6.1%, and δ 1.17 (5-CH_3) of 1.7%. HRMS: calcd for $C_{30}H_{33}O_4PS$ 520.1837, found 520.1846. Anal. Calcd for $C_{30}H_{33}O_4PS$: C, 69.21; H, 6.39. Found: C, 68.98; H, 6.50.

The next fraction was compound 12, **(1*RS*,1′*RS*,2′*E*,4*RS*,5*RS*,7*SR*)-5-methyl-4-[1′-methyl-3′-(diphenylphosphinoyl)prop-2′-enyl]-7-(phenylsulfinyl)bicyclo[3.2.0]heptan-1-ol**, a white foam (354 mg, 27%; t_R 171 min). ^{1}H NMR: δ 1.08 (3 H, d, $J_{1'\text{-Me},1'}$ = 7.0 Hz, 1′-CH_3), 1.16 (3 H, s, 5-CH_3), 1.38–1.48 (1 H, m, H3β), 1.56–1.62 (2 H, m, H2β, H3α), 1.63–1.70 (1 H, m, H4), 1.71–1.81 (1 H, m, H2α), 1.87 (1 H, dd, $J_{6\beta,6\alpha}$ = 13.0, $J_{6\beta,7\alpha}$ = 9.5 Hz, H6β), 2.19 (1 H, dd, $J_{6\alpha,6\beta}$ = 13.0, $J_{6\alpha,7\alpha}$ = 8.0 Hz, H6α), 2.46 (1 H, dddq, $J_{1',2'}$ = 8.0, $J_{1',1'\text{-Me}}$ = 7.0, $J_{1',4}$ = 4.5, $J_{1',3'}$ = 1.0 Hz, H1′), 3.23 (1 H, dd, $J_{7\alpha,6\beta}$ = 9.5, $J_{7\alpha,6\alpha}$ = 8.0 Hz, H7α), 5.02 (1 H, br s, $W_{h/2}$ = 12.0 Hz, OH), 6.62 (1 H, ddd, $J_{3',P}$ = 24.5, $J_{3',2'}$ = 17.5, $J_{3',1'}$ = 1.0 Hz, H3′), 6.57 (1 H, ddd, $J_{2',P}$ = 19.5, $J_{2',3'}$ = 17.5, $J_{2',1'}$ = 8.0 Hz, H2′), 7.40–7.55 (9 H, m, ArH, meta, para), 7.62–7.72 (6 H, m, ArH ortho). Preirradiation at δ 1.16 (5-CH_3) gave enhancements at δ 1.56–1.62 (H2β) of 1.7%, at δ 1.67 (H4) of 2.3%, at δ 1.87 (H6β) of 2.2%, at δ 2.19 (H6α) of 1.7%, and at δ 7.4–7.7 (Ph) of 8.9%. The compound was characterized as the sulfone 14. Thus, oxidation of the sulfoxide (95 mg, 0.188 mmol) with *m*-CPBA (80%, 81 mg, 2.0 equiv) in CH_2Cl_2 as described above gave a viscous gum, flash chromatography of which with 99:1 ethyl acetate–methanol gave the sulfone as a single diastereomer (88 mg, 90%). An analytical sample was prepared by preparative HPLC with 99:1 ethyl acetate–methanol (Whatman Partisil 10 M20 column, 13.5 mL/min, 1100 psi) followed by recrystallization from ethyl acetate–ether. The product, **(1*RS*,1′*RS*,2′*E*,4*RS*,5*RS*,7*SR*)-5-methyl-4-[1′-methyl-3′-(diphenylphosphinoyl)prop-2′-enyl]-7-(phenylsulfonyl)bicyclo[3.2.0]heptan-1-ol (14)**, was thereby obtained as white needles, mp 163.5–165 °C, t_R 60 min. ^{1}H NMR: δ 1.09 (3 H, d, $J_{1'\text{-Me},1'}$ = 6.8 Hz, 1′-CH_3), 1.185 (3 H, s, 5-CH_3), 1.45–1.55 (1 H, m, H3β), 1.56–1.65 (2 H, m, H2β, H3α), 1.65–1.75 (2 H, m, H2α, H4), 1.88 (1 H, dd, $J_{6\beta,6\alpha}$ = 13.0, $J_{6\beta,7\alpha}$ = 9.5 Hz, H6β), 2.34 (1 H, dd, $J_{6\alpha,6\beta}$ = 13.0, $J_{6\alpha,7\alpha}$ = 8.0 Hz, H6α), 2.49 (1 H, dddq, $J_{1',2'}$ = 8.0, $J_{1',4}$ = 6.8, $J_{1',1'\text{-Me}}$ = 6.8, $J_{1',3'}$ = 1.0 Hz, H1′), 3.68 (1 H, dd, $J_{7\alpha,6\beta}$ = 9.5, $J_{7\alpha,6\alpha}$ = 8.0 Hz, H7α), 4.11 (1 H, br s, $W_{h/2}$ = 9.0 Hz, OH), 6.19 (1 H, ddd, $J_{3',P}$ = 24.5, $J_{3',2'}$ = 17.5, $J_{3',1'}$ = 1.0 Hz, H3′), 6.57 (1 H, ddd, $J_{2',P}$ = 19.5, $J_{2',3'}$ = 17.5, $J_{2',1'}$ = 8.0 Hz, H2′), 7.41–7.59 (8 H, m, P(O)Ph meta, para, SO_2Ph meta), 7.62–7.71 (5 H, m, P(O)Ph ortho, SO_2Ph para), 7.93–7.97 (2 H, m, SO_2Ph, ortho). HRMS: calcd for $C_{30}H_{33}O_4PS$ 520.1837, found 520.1834. Anal. Calcd for $C_{30}H_{33}O_4PS$: C, 69.21; H, 6.39. Found: C, 69.58; H, 6.60.

(ii) In the Dark. Enolate 2 was generated from the phosphine oxide (333 mg, 1.0 equiv) and enone (125 mg, 1.30 mmol) in THF (20 mL) as previously described. The whole reaction vessel was covered with a double layer of aluminum foil. Sulfoxide 6 (600 mg, 3.0 equiv) in THF was injected via syringe at a rate such that the temperature of the reaction mixture remained at −10 °C. The reaction mixture was stirred for 50 min at −10 °C and then worked up in the usual way. The crude product mixture was submitted to flash chromatography with 25:1 ethyl acetate–methanol and subsequently to preparative HPLC with 24:1 and then 47:3 ethyl acetate–methanol (Whatman Partisil 10 M20 column, 13.5 mL/min, 900 psi) to give firstly the bicyclics 11 (46 mg, 7%), and 12 (184 mg, 28%). The next fraction was a mixture of diastereomers of the dialkylated product 15 contaminated with minor amounts of the trialkylated product 16 (231 mg, 25%). Because it could not be obtained in a pure state, the sulfoxide 15 (100 mg, 0.15 mmol) was converted into the sulfone 17 for characterization according to the usual method. **(1′*RS*,2*RS*,2′*E*,3*SR*,5*RS* or 5*SR*)-2-Methyl-3-[1′-methyl-3′-(diphenylphosphinoyl)prop-2′-enyl]-2,5-bis[2″-(phenylsulfonyl)ethyl]cyclopentan-1-one (17)** was obtained as a single diastereoisomer and as a brittle foam (95 mg, 92%). An analytical sample (t_R 112 min) was obtained by preparative HPLC with ethyl acetate (Whatman Partisil 10 M20 column, 13.5 mL/min, 1100 psi). ^{1}H NMR: δ 0.87 (3 H, s, 2-CH_3), 1.11 (3 H, d, $J_{1'\text{-Me},1'}$ = 6.25 Hz, 1′-CH_3), 1.10–1.19 (1 H, m, H4β), 1.66 (1 H, dddd, $J_{1''',1'''}$ = 14.0, $J_{1''',2'''}$ = 10.5, $J_{1''',5}$ = 7.3, $J_{1''',2'''}$ = 5.0 Hz, H1‴), 1.73 (1 H, ddd, $J_{3,4\beta}$ = 11.8, $J_{3,1'}$ = 8.5, $J_{3,4\alpha}$ = 5.2 Hz, H3), 1.84 (1 H, ddd, $J_{1'',1''}$ = 14.0, $J_{1'',2''}$ = 12.5, $J_{1'',2''}$ = 4.5 Hz, H1″), 1.96–2.14 (4 H, m, H4α, H5, H1″, H1‴), 2.42–2.52 (1 H, m, H1′), 2.90 (1 H, ddd, $J_{2'',2''}$ = 14.0, $J_{2'',1''}$ = 12.5, $J_{2'',1''}$ = 4.5 Hz, H2″), 3.05 (1 H, ddd, $J_{2''',2'''}$ = 14.0, $J_{2''',1'''}$ = 10.5, $J_{2''',1'''}$ = 5.0 Hz, H2‴), 3.19 (1 H, ddd, $J_{2''',2'''}$ = 14.0, $J_{2''',1'''}$ = 10.5, $J_{2''',1'''}$ = 5.0 Hz, H2‴), 3.20 (1 H, ddd, $J_{2'',2''}$ = 14.0, $J_{2'',1''}$ = 12.5, $J_{2'',1''}$ = 4.5 Hz, H2″), 6.27 (1 H, ddd, $J_{3',P}$ = 25.0, $J_{3',2'}$ = 17.0, $J_{3',1'}$ = 1.0 Hz, H3′), 6.66 (1 H, ddd, $J_{2',P}$ = 19.0, $J_{2',3'}$ = 17.0, $J_{2',1'}$ = 9.0 Hz, H2′), 7.45–7.52 (4 H, m, P(O)Ph meta), 7.53–7.61 (6 H, m, P(O)Ph para, SO_2Ph meta), 7.64–7.72 (6 H, m, P(O)Ph ortho, SO_2Ph para), 7.86–7.90 (4 H, m, SO_2Ph, ortho). Anal. Calcd for $C_{38}H_{41}O_6PS_2$: C, 66.26; H, 6.00. Found: C, 66.35; H, 6.05.

The next fraction was a complex mixture of diastereoisomers of the trialkylated product 16 (337 mg, 32%; t_R 99 min), obtained as a foam contaminated with minor amounts of the dialkylated

product **15** and other products (ca. 7%). Because it could not be obtained in a pure state, it was characterized as the sulfone **18**. Thus the sulfoxide diastereomers (469 mg, 0.715 mmol) were oxidized with *m*-CPBA, and the crude product was subjected to flash chromatography as described above to give the product sulfone, a brittle foam, as a single diastereomer (490 mg, 87%). An analytical sample of **(1′*RS*,2*RS*,2′*E*,3*SR*)-2-methyl-3-[1′-methyl-3′-(diphenylphosphinoyl)prop-2′-enyl]-2,5,5-tris-[2″-(phenylsulfonyl)ethyl]cyclopentan-1-one (18)** (t_R 54 min) was obtained by preparative HPLC with ethyl acetate (Whatman Partisil 10 M20 column, 13.5 mL/min, 1100 psi). ^{1}H NMR: δ 0.88 (3 H, s, 2-CH_3), 1.09 (3 H, d, $J_{1'\text{-Me},1'}$ = 6.8 Hz, 1′-CH_3), 1.36 (1 H, dd, $J_{4\beta,3}$ = 13.0, $J_{4\beta,4\alpha}$ = 13.0 Hz, H4β), 1.51 (1 H, ddd, $J_{1''',1'''}$ = 14.0, $J_{1''',2'''}$ = 11.0, $J_{1''',2'''}$ = 5.0 Hz, H1′′′), 1.57–1.83 (5 H, m, H3, H4α, H1′′′, H1′′′′), 1.81 (1 H, ddd, $J_{1'',1''}$ = 13.5, $J_{1'',2''}$ = 12.5, $J_{1'',2''}$ = 4.5 Hz, H1″), 2.12 (1 H, ddd, $J_{1'',1''}$ = 13.5, $J_{1'',2''}$ = 12.5, $J_{1'',2''}$ = 4.5 Hz, H1″), 2.36–2.48 (1 H, m, H1′), 2.725 (1 H, ddd, $J_{2''',2'''}$ = 13.5, $J_{2''',1'''}$ = 12.0, $J_{2''',1'''}$ = 4.5 Hz, H2′′′), 2.74–2.93 (3 H, m, H2″, H2′′′′, H2′′′′), 2.935 (1 H, ddd, $J_{2'',2''}$ = 13.5, $J_{2''',1'''}$ = 12.0, $J_{2''',1'''}$ = 4.5 Hz, H2′′′), 3.17 (1 H, ddd, $J_{2'',2''}$ = 13.5, $J_{2'',1''}$ = 12.5, $J_{2'',1''}$ = 4.5 Hz, H2″), 6.26 (1 H, ddd, $J_{3',P}$ = 24.0, $J_{3',2'}$ = 17.0, $J_{3',1'}$ = 1.0 Hz, H3′), 6.60 (1 H, ddd, $J_{2',P}$ = 19.0, $J_{2',3'}$ = 17.0, $J_{2',1'}$ = 9.0 Hz, H2′), 7.33–7.73 (19 H, m, P(O)Ph ortho, ArH, meta, para), 7.80–7.93 (6 H, m, SO_2Ph, ortho). Anal. Calcd for $C_{46}H_{49}O_8PS_3$: C, 64.47; H, 5.76. Found: C, 64.29; H, 6.29.

(iii) Under Irradiation. The enolate **2** was generated from the phosphine oxide (333 mg, 1.0 equiv) and enone (125 mg, 1.30 mmol) in THF (20 mL) in a reaction vessel immersed in an ethanol cooling bath in a flat Pyrex basin. This was then irradiated with a high-intensity photoflood lamp (Phillips 6-in. Agraphoto BM, 500 W) mounted at a distance of ca. 6 cm from the flask. The temperature of the reaction mixture was maintained at −10 °C with the aid of an external thermostated cooling unit immersed in the cooling bath. Sulfoxide **6** (600 mg, 3.0 equiv) in THF (1 mL) was added at a rate such that the temperature remained at −10 °C. The reaction mixture was stirred for 45 min at −10 °C and worked up as described above to give a viscous gum, flash chromatography of which with 24:1 ethyl acetate–methanol afforded unchanged sulfoxide **6** (300 mg) and the mixture of products as a foam (648 mg, 99%). Analytical HPLC with 96.5:3.5 ethyl acetate–methanol (Whatman Partisil 5 column, 1.5 mL/min, 1500 psi) indicated the presence of the following products, in order of elution: a 1:1 mixture of epimers of adduct **7** (13%), other unidentified products (ca. 6%), monoalkylated product **10** (12%), and bicyclics **11** (25%) and **12** (43%).

(iv) In the Presence of HMPA. Lithiated phosphine oxide **1** was generated from the phosphine oxide (333 mg, 1.0 equiv) in THF (20 mL) containing HMPA (0.43 mL, 2.0 equiv) and treated with 2-methylcyclopentenone (125 mg, 1.30 mmol) in THF (1 mL) at −78 °C under N_2.[1,2] At −10 °C sulfoxide **6** (600 mg, 3.0 equiv) was added at a rate such that the temperature remained at −10 °C. The reaction mixture was stirred for 1 h at −10 °C and then worked up in the usual way to leave a foam, flash chromatography of which with 25:1 and then 9:1 ethyl acetate–methanol afforded the product mixture as a brittle foam (946 mg, 90%). Preparative HPLC of this mixture with 47:3 ethyl acetate–methanol (Whatman Partisil 10 M20 column, 13.5 mL/min, 1100 psi) gave firstly a mixture of two diastereomers of a product identified by comparison of its NMR spectra with those of related compounds[12] as **3,5-dimethyl-6-[1′-(diphenylphosphinoyl)-methyl]-3-[2″-(phenylsulfinyl)ethyl]bicyclo[2.2.1]heptan-2-one (19)**, a foam (33 mg, 5%, t_R 44 min). ^{1}H NMR: δ 0.97, 0.99 (3 H, s, 3-CH_3), 1.06 (3 H, d, $J_{5\text{-Me},5}$ = 6.7 Hz, 5-CH_3), 1.636, 1.637 (1 H, ddd, $J_{1',1'}$ = 13.5, $J_{1',2'}$ = 12.0, $J_{1',2'}$ = 4.5 Hz, H1′), 1.69–1.78 (1 H, m, H7), 1.78–1.98 (4 H, m, H1, H5, H7, H1′), 1.99–2.15 (2 H, m, H6, H1″), 2.28–2.32, 2.34–2.37 (1 H, m, H4), 2.35, 2.36 (1 H, ddd, $J_{1'',P}$ = 15.0, $J_{1'',1''}$ = 14.5, $J_{1'',6}$ = 4.0 Hz, H1″), 2.74, 2.79 (1 H, ddd, $J_{2',2'}$ = 13.0, $J_{2',1'}$ = 12.0, $J_{2',1'}$ = 4.5 Hz, H2′), 7.46–7.66 (11 H, m, P(O)Ph meta, para, S(O)Ph ortho, meta, para), 7.76–7.82 (4 H, m, P(O)Ph ortho).

The next fraction consisted solely of the trialkylated product **16** (894 mg, 85%). This was oxidized to the sulfone **18** as described above.

Ring-Opening Reactions. (i) With NaH. A suspension of NaH (9 mg, 0.34 mmol, obtained from a 55% dispersion in oil and washed with hexanes prior to use) in DMF (1 mL) was added to a stirred solution of the bicyclic sulfone **14** (100 mg, 0.19 mmol) and sulfone **5** (35 mg, 1.1 equiv) in DMF (5 mL) under N_2 at −10 °C. The mixture was stirred at −10 °C for 3.0 h, during which time it changed color from pale yellow to purple. The mixture was quenched with aqueous NH_4Cl (saturated, 20 mL) and worked up with ethyl acetate in the usual way to give a brown gummy foam. Flash chromatography with 99:1 ethyl acetate–methanol gave the product mixture as a foam (128 mg), analysis of which by HPLC with ethyl acetate (Whatman Partisil 5 column, 1.5 mL/min) indicated the presence of single diastereoisomers of the trialkylated sulfone **18** (49%) and the bicyclo[2.2.1]heptanone sulfone **20** (36%). Preparative HPLC with ethyl acetate (Whatman Partisil 10 M20, 13.5 mL/min, 900 psi) gave **3,5-dimethyl-6-[1′-(diphenylphosphinoyl)methyl]-3-[2″-(phenylsulfonyl)ethyl]bicyclo[2.2.1]heptan-2-one (20)** (t_R 75 min) as a white foam. ^{1}H NMR: δ 0.92 (3 H, s, 3-CH_3), 1.02 (3 H, d, $J_{5\text{-Me},5}$ = 7.0 Hz, 5-CH_3), 1.69–1.89 (5 H, m, H4, H5, H7, H1′, H1′), 1.94–2.11 (3 H, m, H6, H7, H1″), 2.29–2.33 (1 H, m, H1), 2.35 (1 H, ddd, $J_{1'',1''}$ = 15.0, $J_{1'',P}$ = 10.0, $J_{1'',6}$ = 4.0 Hz, H1″), 3.04–3.19 (2 H, m, H2′, H2′), 7.42–7.60 (8 H, m, P(O)Ph meta, para, SO_2Ph, meta), 7.64–7.77 (5 H, m, P(O)Ph ortho, SO_2Ph para), 7.85–7.90 (2 H, m, SO_2Ph ortho). Anal. Calcd for $C_{30}H_{33}O_4PS$: C, 69.21; H, 6.39. Found: C, 68.92; H, 6.44.

(ii) With LDA. A solution of the bicyclic sulfone **14** (31 mg, 0.058 mmol) and sulfone **6** (19 mg, 2.0 equiv) in THF (1 mL) was added dropwise over 5 min to a stirred solution of LDA (from diisopropylamine, 10 μL, 1.0 equiv and C_4H_9Li, 1.8 M, 32 μL) in THF (10 mL) at −20 °C under N_2. The yellow mixture was stirred at −20 °C for 2.5 h and then worked up to give a yellow viscous oil. Purification by flash chromatography with ethyl acetate gave **(1′*RS*,2*RS*,2′*E*,3*SR*)-2-methyl-3-[1′-methyl-3′-(diphenylphosphinoyl)prop-2′-enyl]-2-[2″-(phenylsulfonyl)ethyl]-cyclopentan-1-one (21)** as a colorless gum (25 mg, 81%). ^{1}H NMR: δ 0.92 (3 H, s, 2-CH_3), 1.13 (3 H, d, $J_{1'\text{-Me},1'}$ = 6.5 Hz, 1′-CH_3), 1.43–1.56 (1 H, m, H4β), 1.79 (1 H, ddd, $J_{3,4\alpha}$ = 11.5, $J_{3,1'}$ = 8.0, $J_{3,4\beta}$ = 5.5 Hz, H3), 1.865 (1 H, ddd, $J_{1'',1''}$ = 14.0, $J_{1'',2''}$ = 12.5, $J_{1'',2''}$ = 4.0 Hz, H1″), 1.92–2.06 (2 H, m, H4α, H5β), 2.09 (1 H, ddd, $J_{1'',1''}$ = 14.0, $J_{1'',2''}$ = 12.5, $J_{1'',2''}$ = 4.0 Hz, H1″), 2.21–2.34 (1 H, m, H5α), 2.48–2.58 (1 H, m, H1′), 2.94 (1 H, ddd, $J_{2'',2''}$ = 13.0, $J_{2'',1''}$ = 12.5, $J_{2'',1''}$ = 4.0 Hz, H2″), 3.22 (1 H, ddd, $J_{2'',2''}$ = 13.0, $J_{2'',1''}$ = 12.5, $J_{2'',1''}$ = 4.0 Hz, H2″), 6.27 (1 H, ddd, $J_{3',P}$ = 24.5, $J_{3',2'}$ = 17.0, $J_{2',1'}$ <1.0 Hz, H3′), 6.645 (1 H, ddd, $J_{2',P}$ = 19.5, $J_{2',3'}$ = 17.0, $J_{2',1'}$ = 8.5 Hz, H2′), 7.43–7.61 (8 H, m, P(O)Ph meta, para, SO_2Ph meta), 7.64–7.72 (5 H, m, P(O)Ph ortho, SO_2Ph para), 7.87–7.92 (2 H, m, SO_2Ph ortho). HRMS: calcd for $C_{30}H_{33}O_4PS$ 520.1837, found 520.1848.

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Registry No. **2**, 135480-97-6; **5**, 5535-48-8; **6**, 20451-53-0; **7** (isomer 1), 131228-06-3; **7** (isomer 2), 131321-10-3; **9**, 135455-37-7; **10** (isomer 1), 135455-38-8; **10** (isomer 2), 135557-38-9; **11**, 135455-39-9; **12**, 135557-36-7; **13**, 135455-40-2; **14**, 135557-37-8; **15**, 135455-41-3; **16**, 135455-42-4; **17**, 135455-43-5; **18**, 135455-44-6; **19**, 135455-45-7; **20**, 135455-46-8; **21**, 135455-47-9; (*E*)-2-butenyldiphenylphosphine oxide, 17668-60-9; 2-methyl-2-cyclopenten-1-one, 1120-73-6.

Supplementary Material Available: Infrared, ^{13}C NMR, and mass spectral data for compounds **10–15** and **17–21**, 400-MHz ^{1}H NMR spectrum of compound **21**, and crystallographic data for compound **14**, including an ORTEP plot, tables of positional parameters, bond lengths and angles, thermal parameters, hydrogen atom positional and thermal parameters, and details of least-squares planes calculations (15 pages). Ordering information is given on any current masthead page.