α-Methylene β-Lactones as Masked Allenes and Allene Equivalents: Some Selected Chemical Transformations

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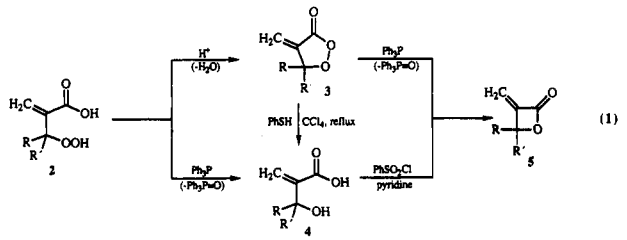
Selective chemical transformations have been performed on a number of α-methylene β-lactones to illustrate that these highly functionalized heterocycles serve as useful building blocks in organic synthesis. Thus, thermal decarboxylation of these "masked allenes" provides a useful regioselective preparation of allenes with a predetermined substitution pattern. Nucleophilic addition takes place at the carbonyl group with ring opening, but free-radical addition, e.g., thiophenol, and electrophilic addition, e.g., bromine, proceed at the exomethylene group with preservation of the β-lactone ring. [4 + 2] Cycloaddition with cyclopentadiene affords the expected β-lactones, which on thermal decarboxylation lead to 2-alkylidenenorbornenes. This regio- and stereoselective transformation establishes the α-methylene β-lactones as valuable *allene equivalents*. The α-methylene β-lactones serve also as dipolarophiles by undergoing readily 1,3-dipolar cycloaddition with diazoalkanes. Reaction with Lawesson's reagent affords a hitherto unknown α-methylene β-(*S*)-lactone.

In the preceeding paper[1] we described convenient preparations of the hitherto unknown α-methylene β-lactones **5** (eq 1) from the corresponding β-hydroperoxy acids



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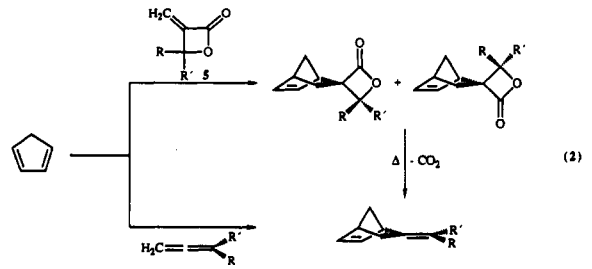
2. The purpose of the present work is to take advantage of the high degree of functionality contained in the novel heterocyclic system **5** for synthetic exploitation. On one hand, the α-methylene β-lactones **5** represent *masked allenes* through facile decarboxylation,[2] and on the other, they constitute *allene equivalents*. For example, nucleophilic, free radical, or electrophilic addition at the exomethylenic terminal (Michael-type addition) would lead to intact β-lactones. Since the regiochemistry is fixed through the β-lactone vice and a stereogenic β-carbon site (different R and R′ groups) should provide stereochemical differentiation in the addition step, the regio- and stereoselective synthesis of allene-derived products becomes feasible. Furthermore, these synthetic building blocks should serve as dienophiles in [4 + 2] and 1,3-dipolar cycloadditions, in which again a stereogenic β-carbon center should promote diastereoselectivity. In eq 2 the utilization of the α-methylene β-lactones as *allene equivalents* in [4 + 2] cycloadditions with 1,3-cyclodienes is exhibited.



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Finally, these β-lactones also possess a heterodiene functionality, the α,β-enone moiety, which provides an opportunity to explore [4 + 2] cycloadditions with electron-rich dienophiles. Also, such cycloadditions should generate interesting chemistry for synthetic applications.

Results and Discussion

The reactions of the α-methylene β-lactones **5** toward nucleophiles, radicals, electrophiles, and cyclophiles are summarized in the rosette of Figure 1, together with the thermal decarboxylation into allenes. The broad scope in reactivity of these functionalized β-lactones is clearly evident from these diverse transformations. The detailed results shall now be given for the transformations A–G.

Transformation A: Reaction with Nucleophiles. Nucleophiles like RO^- and $ArNH_2$ attack the α-methylene β-lactone **5b** at the electrophilic carbonyl site, analogous to the β-propiolactones.[3] For example, the reaction of **5b** with sodium methoxide or ethoxide afforded the β-hydroxy esters **6b** (MeO, EtO), while aniline led to the β-hydroxy amide **6b** (PhNH). Toward potassium cyanide and azide, the α-methylene β-lactone **5b** was unreactive under the conditions at which it does not deteriorate by competing side reactions. Even under phase-transfer catalysis only the intact β-lactone **5b** was reisolated.

Transformation B: Photochemical Addition of Thiophenol. The addition of thiophenol to the exomethylenic double bond with preservation of the four-membered ring occurred by a photochemically initiated free-radical reaction. On irradiation of β-lactone **5b** and thiophenol at 300 nm (Rayonett photoreactor), the diastereomeric β-lactones **7b** were obtained in 66% yield. The carbonyl frequency at 1840 cm^{-1} and the AB patterns at δ 3.16/3.46 and 3.22/3.35 of the two diastereomers are characteristic for the proposed structure.

Transformation C: Electrophilic Addition of Bromine. Among electrophiles, only the reaction of bromine with β-lactone **5b** was carried out. As expected, the addition of bromine was slow; nevertheless, the diastereomeric dibromides **8b** were obtained in 62% yield. Again, the characteristic carbonyl frequency at 1850 cm^{-1} and the

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(2) Adam, W.; Baeza, J.; Liu, J.-C. *J. Am. Chem. Soc.* **1972**, *94*, 2000.
(3) Kröper, H. In *Methoden der Organischen Chemie, (Houben-Weyl)*; Müller, E., Ed.; G. Thieme Verlag: Stuttgart, 1963; Vol. VI/2, p 527.

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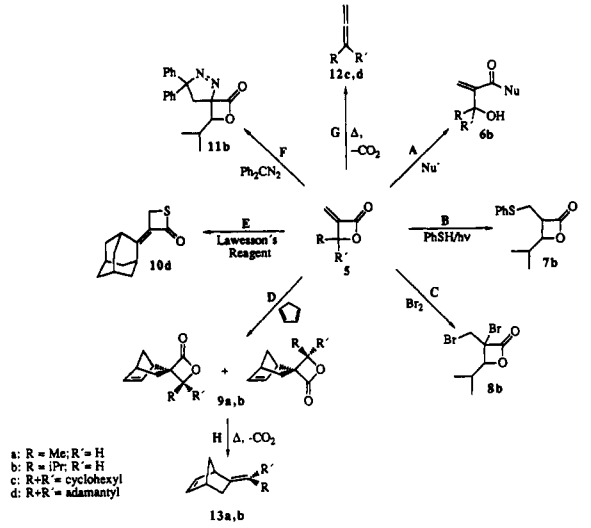

Figure 1. Chemical transformations of α-methylene β-lactones **5**.

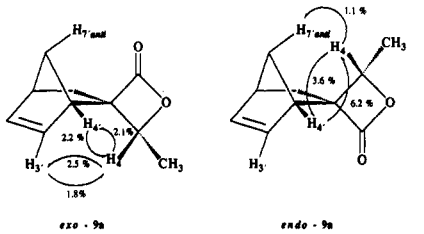

Figure 2. Structure assignment of cycloadduct **9a** by NOE.

AB patterns at δ 3.79/4.00 and 3.91/3.98 of the two diastereomers confirm this structure assignment.

Transformation D: [4 + 2] Cycloaddition with Cyclopentadiene. The exomethylenic double bond of β-lactones **5a,b** was expected to serve as dienophile, and indeed [4 + 2] cycloaddition with cyclopentadiene took place to give the diastereomeric norbornene adducts **9a,b**. Even with a large excess of cyclopentadiene, this Diels–Alder reaction proceeded slowly (at ca. 20 °C after 20 d ca. 48% conversion); however, when $Ti(OiPr)_4$ was utilized as Lewis acid catalyst, the cycloaddition was facilitated significantly (at ca. 20 °C after 9 h ca. 71%). The carbonyl frequency at 1812 cm^{-1} clearly speaks for the β-lactone structure.

The α-methylene β-lactone **5** dienophile preferred *exo* cycloaddition. The *exo/endo* ratio was 75:25 for **9a** and only 67:33 for **9b**, but the latter in the presence of the Lewis acid $Ti(OiPr)_4$. The stereochemistry of *exo/endo*-**9a** was established by NOE experiments (Figure 2). No NOE effects were observed for the 3-H′ proton in the *endo*-**9a** diastereomer.

It is important for the mechanistic rationalization of the stereochemical course of the cycloaddition to note that the β-alkyl substituent R in the cycloadduct **9** possesses the anti configuration with respect to the norbornene methylene bridge. Thus, while the *exo/endo* diastereoselectivity is moderate, but normal for acrylate-type dienophiles,[4] the α-methylene β-lactones **5** exhibit a very high diastereofacial bias by approaching the diene partner opposite the β-alkyl substituent. As the *exo* and *endo* transition states (TS; Figure 3) reveal, as a consequence of this sterically controlled approach, the β-alkyl substituents must be located anti to the methylene bridge in the *exo*- and *endo*-**9** cycloadducts.

(4) Meek, J. S.; Trapp, W. B. *J. Am. Chem. Soc.* **1957**, *79*, 3909.

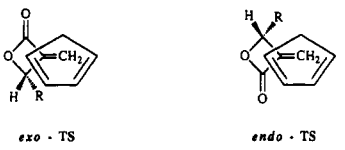

Figure 3. Exo/endo transition states of the cycloaddition of α-methylene β-lactones **5** with cyclopentadiene.

In view of the fact that β-lactones readily decarboxylate at moderate temperatures to afford alkenes stereospecifically,[2] the cycloadducts *exo/endo*-**9a,b** were submitted to vacuum flash pyrolysis at 400 °C (0.1 Torr). The expected (*E*)-alkylidene-substituted norbornenes **13a,b** were obtained exclusively and essentially quantitatively from a mixture of corresponding *exo/endo*-**9a,b**. Therefore, by starting from cyclopentadiene, this constitutes an efficient diastereoselective synthesis of (*E*)-alkylidenenorbornenes **13a,b**, which establishes the readily available α-methylene-β-lactones (cf. preceeding paper[1]) as useful *allene equivalents*.[5]

Transformation E: Reaction with Lawesson's Reagent. On treatment with Lawesson's reagent (LR), the β-lactone **5d** was converted in 37% yield into the novel β-thio lactone **10d**, the first example of this sulfur heterocycle. In addition to our preliminary report,[6] we include here as well the full X-ray structural data (cf. supplementary material). The four-membered ring is clearly evident, although in view of the significantly longer carbon-sulfur bond, the ring is highly unsymmetrical compared to the oxygen analogue.[1,6]

Transformation F: Cycloaddition with 1,3-Dipolarophiles. While phenyl azide was unreactive toward the α-methylene β-lactones **5b**, with diphenyldiazomethane in acetonitrile the Δ^1-pyrazoline **11b** was obtained in 63% yield. The carbonyl frequency at 1835 cm^{-1} indicates the β-lactone moiety, the UV absorption (λ_{max} = 323 nm; n,π* transition) reveals the cyclic azo functionality, and the AB patterns at δ 2.49/2.87 confirm this structure assignment.

Transformation G: Thermal Decarboxylation to Allenes. As *masked allenes*, the α-methylene β-lactones **5** were expected to release the allenes on decarboxylation. Indeed, on pyrolysis at 400 °C (0.1 Torr) by volatilizing the β-lactones **5c,d** through a hot tube, they cleanly decarboxylated and afforded the corresponding allenes **12c,d** in high yield. Comparison of the spectral data reported for the authentic substances served for identification.

In summary, the selected chemical transformations that are portrayed in the rosette of Figure 1 suffice to illustrate the synthetic potential of the α-methylene β-lactones **5**. The availability of these functionalized building blocks (cf. preceeding paper[1]) should facilitate the development of preparatively useful synthetic methodology. A novel feature is their use as *allene equivalents* in diastereoselective synthesis.

Experimental Section

All melting points and boiling points are uncorrected. Solvents were purified according to standard procedures.

Methyl 3-Hydroxy-4-methyl-2-methylenepentanoate (6b-(MeO)). To a solution of 100 mg (0.800 mmol) of oxetan-2-one **5b** in 5 mL of absolute ether was added a suspension of 54.0 mg (1.00 mmol) of sodium methoxide in 5 mL of absolute ether at 20 °C. The mixture was allowed to stir for 10 min. After hydrolysis with 5 mL of 5% aqueous NH_4Cl solution, the organic

(5) (a) Bonjouklian, R.; Ruden, R. A. *J. Org. Chem.* **1977**, *42*, 4095. (b) Snider, B. B. *J. Org. Chem.* **1973**, *38*, 3961. (c) Philips, J. C.; Oku, M. *J. Am. Chem. Soc.* **1972**, *94*, 1012. (d) Cunico, R. F.; Dexheimer, E. M. *Organometal. Chem. Synth.* **1971**, *1*, 253.

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layer was separated, dried ($MgSO_4$), and evaporated (ca. 20 °C (15 Torr)). Purification of the residue by Kugelrohr distillation at 75–80 °C (0.1 Torr) (lit.[7a] 78–80 °C (4 Torr)) yielded 107 mg (85%) of a colorless liquid, characterized by comparing the spectral data with the literature.[7b]

Ethyl 3-Hydroxy-4-methyl-2-methylenepentanoate (6b-(EtO)). Following the above procedure, 500 mg (3.96 mmol) of oxetan-2-one **5b** and 270 mg (4.00 mmol) of sodium ethoxide in 5 mL of EtOH gave (1 h stirring at 20 °C) 400 mg (64%) of a colorless liquid (Kugelrohr distillation at 180 °C (0.1 Torr): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.79 (d, J = 6.7 Hz, 3 H), 0.83 (d, J = 6.7 Hz, 3 H), 1.22 (t, J = 7.1 Hz, 3 H), 1.80 (d septet, J = 6.7 Hz, 1 H), 3.00 (br s, 1 H), 4.12 (d, J = 6.4 Hz, 1 H), 4.30 (q, J = 7.1 Hz, 2 H), 5.67 (d, J = 1.0 Hz, 1 H), 6.15 (d, J = 1.0 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0 (q), 17.2 (q), 19.4 (q), 32.6 (d), 60.6 (t), 76.7 (d), 125.3 (t), 142.0 (s), 166.6 (s). IR (CCl_4) ν 3700–3100, 2970, 1710, 1625 cm^{-1}; MS (70 eV) m/z = 172 (0.4) (M^+), 129 (78) (M^+ – iPr), 83 (100) (C_6H_{11}), 55, (26) (C_3H_3O), 43 (17) (iPr). Anal. Calcd for $C_9H_{16}O_3$ (172.2): C, 62.77; H, 9.36. Found: C, 63.25; H, 9.45.

***N*-Phenyl-3-hydroxy-4-methyl-2-methylenepentanamide (6b(PhNH)).** A sample of 50.0 mg (0.400 mmol) of oxetan-2-one **5b** in 1 mL Of $CDCl_3$ was mixed with 38.0 mg (0.400 mmol) of freshly distilled aniline. After the mixture was heated for 3 h under reflux, the solvent was evaporated. Purification of the residue by column chromatography on silica gel ((32–63 μm), 50:1 adsorbant/substrate ratio, 1:1 CH_2Cl_2/ether solvent mixture as eluant, at 20 °C, R_f 0.71) yielded 57.0 mg (65%) of colorless needles: mp 100–101 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.84 (d, J = 6.8 Hz, 3 H), 1.05 (d, J = 6.8 Hz, 3 H), 1.97 (d septet, J = 8.4, 6.7 Hz, 1 H), 3.42 (d, J = 5.0 Hz, 1 H), 4.04 (dd, J = 8.5, 4.9 Hz, 1 H), 5.46 (s, 1 H), 6.05 (s, 1 H), 7.10–7.55 (m, 5 H), 8.99 (br s, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 18.9 (q), 19.6 (q), 32.5 (d), 80.6 (d), 120.3 (d), 123.3 (t), 124.5 (d), 129.0 (d), 144.4 (s), 165.7 (s), 172.3 (s); IR (CCl_4) ν 3430, 2965, 1675, 1625, 1603 cm^{-1}; MS (70 eV) m/z 219 (20) (M^+), 201 (6) ($M^+ - H_2O$), 176 (51) (M^+ – iPr), 93 (100) ($PhNH_2$), 77 (13) (Ph), 55 (18). Anal. Calcd for $C_{13}H_{17}NO_2$ (219.4): C, 71.21; H, 7.81; N, 6.39. Found: C, 71.71; H, 7.72; N, 6.26.

***cis*- and *trans*-4-(1-Methylethyl)-3-[(phenylthio)-methyl]-1-oxetan-2-ones (7b).** A mixture of 50.0 mg (0.400 mmol) of oxetan-2-one **5b** and 44.0 mg (0.400 mmol) of thiophenol was irradiated at 35 °C in a Rayonet photoreactor at 300 nm for 3 d. After this time, 78% conversion of **5b** (monitored by NMR) was achieved, which did not increase on further photolysis. The product was purified first by column chromatography on silica gel ((32–63 μm), 50:1 adsorbant/substrate ratio 50:1, 1:1 CH_2Cl_2/petroleum ether (30–70) solvent mixture as eluant, at 15 °C, R_f 0.32), and subsequently by Kugelrohr distillation (170 °C (0.1 Torr)) to yield 49 mg (66%) of a pale yellow oil as a 80:20 mixture of diastereomers. **Major isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (d, J = 6.8 Hz, 3 H), 1.01 (d, J = 6.8 Hz, 3 H), 1.89 (d septet, J = 7.8, 6.7 Hz, 1 H), 3.16 and 3.46 (AB part of ABX, J = 14.9, 11.4, 4.5 Hz, 2 H), 3.45 (m, 1 H), 4.00 (dd, J = 7.9, 3.7 Hz, 1 H), 7.20–7.40 (m, 5 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 17.2 (q), 17.8 (q), 31.8 (t), 32.1 (d), 53.2 (d), 82.8 (d), 127.0 (d), 129.3 (d), 129.8 (d), 134.3 (s), 169.5 (s). **Minor isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (d, J = 6.5 Hz, 3 H), 1.08 (d, J = 6.5 Hz, 3 H), 2.06 (d septet, J = 10.2, 6.6 Hz, 1 H), 3.22 and 3.35 (AB part of ABX, J = 13.7, 8.4, 6.5 Hz, 2 H), 3.84 (X part of ABX, J = 8.6, 6.4 Hz, 1 H), 4.20 (dd, J = 10.1, 6.3 Hz, 1 H), 7.20–7.40 (m, 5 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 18.4 (q), 18.9 (q), 28.3 (t), 28.8 (d), 51.7 (d), 80.6 (d), 127.2 (d), 129.3 (d), 130.5 (d), 134.3 (s), 169.5 (s); IR (CCl_4) ν 3080, 2975, 1840, 1585 cm^{-1}; MS (70 eV) m/z 236 (2) (M^+), 192 (21) ($M^+ - CO_2$), 149 (4), ($M^+ - CO_2$ – iPr), 110 (46) (PhSH), 109 (12) (PhS), 84 (14) ($C_4H_4O_2$), 83 (57) ($M^+ - CO_2$ – PhS), 55 (100) (C_3H_3O), 43 (28) (iPr). Anal. Calcd for $C_{13}H_{16}O_2S$ (236.3): C, 66.07; H, 6.82. Found: C, 65.96; H, 6.68.

***cis*- and *trans*-3-Bromo-3-(bromomethyl)-4-(1-methylethyl)-1-oxetan-2-one (8b).** To 500 mg (3.96 mmol) of **5b** and 5 mg of hydroquinone in 5 mL of CCl_4 was added under exclusion of light 634 mg (3.96 mmol) of Br_2 in 5 mL of CCl_4. The reaction mixture was stirred at 20 °C until the color had disappeared (20 d). The solvent was evaporated (ca. 20 °C (15 Torr)). Purification of the residue by column chromatography on silica gel ((32–63 μm), 50:1 adsorbant substrate ratio, 10:10:1 CH_2Cl_2/petroleum ether (30–50)/acetic ester solvent mixture as eluant, at 10 °C, R_f 0.70) yielded 620 mg (62%) of a pale yellow liquid as 70:30 mixture of diastereomers. **Major isomer:** ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.02 (d, J = 6.6 Hz, 3 H), 1.13 (d, J = 6.6 Hz, 3 H), 2.16 (m, 1 H), 3.79 and 4.00 (AB-system, J = 11.4 Hz, 2 H), 4.25 (d, J = 10.4 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 17.4 (q), 18.4 (q), 31.6 (d), 32.1 (t), 63.7 (s), 84.1 (d), 164.4 (s). **Minor isomer:** ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.08 (d, J = 6.1 Hz, 3 H), 1.11 (d, J = 6.1 Hz, 3 H), 2.44 (m, 1 H), 3.91 and 3.98 (AB-system, J = 12.0 Hz, 2 H), 4.54 (d, J = 10.9 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 18.1 (q), 18.9 (q), 28.5 (t), 28.7 (d), 59.9 (s), 91.5 (d), 164.1 (s); IR (CCl_4) ν 2970, 2940, 1850, 1470 cm^{-1}; MS (70 eV) m/z 245, 243, 241 (0.8, 1.0, 0.8) (M^+ – iPr), 216, 214, 212 (2,4,2) ($M^+ - C_4H_8O$), 163, 161 (58, 59) (M^+ – Br – iPr), 135, 133 (32, 32) (M^+ – Br – iPr –CO), 43 (47) (iPr). Anal. Calcd for $C_7H_{10}Br_2O_2$ (286.0): C, 29.40; H, 3.52. Found: C, 29.95; H, 3.45.

4′-Methylspiro[bicyclo[2.2.1]hept-5-ene-2,3′-oxetan-2′-one] (9a). A solution of 26.0 mg (0.265 mmol) of **5a** and 1.00 g (15.1 mmol) of freshly distilled cyclopentadiene in 20 mL of absolute CH_2Cl_2 was stirred at 20 °C for 14 d. The solvent was evaporated (ca. 20 °C (15 Torr)), and the residue was purified by Kugelrohr distillation (100 °C (0.1 Torr)) to yield 21.0 mg (48%) of a colorless liquid as a 75:25 mixture of *exo*/*endo* diastereomers. **Exo isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (d, J = 6.3 Hz, 3 H), 1.42 (dd, J = 12.4, 3.1 Hz, 1 H), 1.48 (m, 1 H), 1.78 (dddd, J = 8.8, 1.5, 1.4, 0.6 Hz, 1 H), 2.05 (ddd, J = 12.4, 3.7, 0.3 Hz, 1 H), 2.99 (m, 1 H), 3.45 (m, 1 H), 4.43 (q, J = 6.3 Hz, 1 H), 6.10 (dd, J = 5.6, 2.9 Hz, 1 H), 6.36 (dd, J = 5.7, 3.0 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.3 (q), 32.5 (t), 42.1 (d), 47.6 (t), 49.4 (d), 62.3 (s), 77.0 (d), 132.0 (d), 139.6 (d), 176.4 (s). **Endo isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (dm, J = 8.5 Hz, 1 H), 1.50 (d, J = 6.3 Hz, 3 H), 1.50 (m, 1 H), 1.54 (m, 1 H), 1.93 (dd, J = 12.6, 3.6 Hz, 1 H), 2.99 (m, 1 H), 3.18 (m, 1 H), 4.55 (q, J = 6.3 Hz, 1 H), 6.20 (dd, J = 5.5, 2.7 Hz, 1 H), 6.36 (dd, J = 5.7, 3.0 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.8 (q), 33.0 (t), 42.6 (d), 48.4 (t), 52.1 (d), 63.0 (s), 78.7 (d), 132.2 (d), 141.2 (d), 176.4 (s); IR (CCl_4) ν 3070, 2975, 1820 cm^{-1}; MS (70 eV) m/z 164 (3) (M^+), 149 (1) ($M^+ - CH_3$) 120 (9) ($M^+ - CO_2$), 105 (9) ($M^+ - CH_3 - CO_2$), 66 (100) (C_5H_6).

4′-(1-Methylethyl)spiro[bicyclo[2.2.1]hept-5-ene-2,3′-oxetan-2′-one] (9b). A solution of 300 mg (2.38 mmol) of **5b** and 157 mg (2.38 mmol) of freshly distilled cyclopentadiene in 15 mL of absolute CH_2Cl_2 was treated with 1 mL of $Ti(iPrO)_4$ and stirred for 9 h at 20 °C. After evaporation (ca. 20 °C (15 Torr)) of the solvent, the residue was taken up in 10 mL of ether, 15 mL of water was added, and the solution was stirred for 15 min. The white precipitate (TiO_2) was removed by filtration over Celite, and the solvent together with the generated iPrOH was removed by evaporation (ca. 20 °C (15 Torr)). The crude product was purified by Kugelrohr distillation (180 °C (0.1 Torr)) to yield 327 mg (71%) of a colorless liquid as a 67:33 mixture of *exo*/*endo* diastereomers. These diastereomers were separated by flash column chromatography on silica gel ((32–63 μm), 100:1 adsorbant substrate ratio, 95:5 heptane/acetic ester solvent mixture as eluent, R_f(*exo*) 0.57, R_f(*endo*) 0.51). **Exo isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75 (d, J = 6.6 Hz, 3 H), 0.99 (d, J = 6.6 Hz, 3 H), 1.46 (m, 1 H), 1.50 (m, 1 H), 1.70 (d septet, J = 9.6, 6.6 Hz, 1 H), 1.80 (dddd, J = 8.6, 1.4, 1.4, 0.7 Hz, 1 H), 2.02 (dd, J = 12.4, 3.4 Hz, 1 H), 2.98 (br m, 1 H), 3.21 (br m, 1 H), 3.89 (d, J = 9.5 Hz, 1 H), 6.06 (dd, J = 5.7, 3.0 Hz, 1 H), 6.38 (dd, J = 5.6, 3.1 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 18.1 (q), 18.4 (q), 30.1 (d), 31.8 (t), 42.2 (d), 47.1 (t), 50.1 (d), 61.6 (s), 85.4 (d), 133.0 (d), 140.8 (d), 176.5 (s); IR (CCl_4) ν 3060, 2980, 2870, 1814 cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_2$ (192.3): C, 74.97; H 8.47. Found: C, 74.62; H, 8.52. **Endo isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (d, J = 6.6 Hz, 3 H), 1.06 (d, J = 6.6 Hz, 3 H), 1.31 (m, 1 H), 1.50 (m, 2 H), 1.93 (d septet, J = 8.6, 6.6 Hz, 1 H), 2.01 (dd, J = 12.4, 3.7 Hz, 1 H), 3.01 (br m, 1 H), 3.13 (br m, 1 H), 4.00 (d, J = 8.7 Hz, 1 H), 6.19 (dd, J = 5.6, 2.6 Hz, 1 H), 6.34 (dd, J = 5.6, 2.5 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 18.1 (q), 18.6 (q), 30.3 (d), 32.3 (t), 42.7 (d), 48.3 (t), 52.0 (d), 62.2 (s), 87.1 (d), 132.3 (d), 139.4 (d), 175.5 (s); IR (CCl_4) ν 3070, 2970, 2870, 1817 cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_2$ (192.3): C, 74.97; H, 8.47. Found: C, 74.71, H, 8.39. MS (70 eV) for the *exo*/*endo* mixture: m/z 192 (3) (M^+), 149 (16) (M^+ – iPr),

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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).

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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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