the reported procedure.[26] Further, this conjugate adduct (cis/trans = 21:79) was treated with a solution of sodium methoxide in methanol under reflux for 4 h. The mixture was poured into pentane and water, and the pentane layer was analyzed by GLC. This showed that 20% of the cis isomer had been converted to the more stable trans isomer.[26] Authentic samples for 5-alkyl-2-methylcyclohexanone (R = Et, *n*-Bu, *t*-Bu, and Ph) are prepared by the conjugate addition of R_2CuLi to 6-methyl-2-cyclohexenone. Their stereochemical assignments were made by the base-catalyzed conversion of the cis/trans mixtures to the stable trans isomer.[26] The isomeric ratio of 5-alkyl-2-methylcyclohexanone (R = Et and *t*-Bu) were determined by capillary GLC analysis: 5-ethyl-2-methylcyclohexanone: t_R (trans) = 10.1 min, t_R (cis) = 10.7 min at 80 °C; 5-*tert*-butyl-2-methylcyclohexanone: t_R (trans) = 17.5 min, t_R (cis) = 18.2 min at 80 °C. In contrast, the cis/trans ratio of 5-alkyl-2-methylcyclohexanone (R = *n*-Bu, Ph, and CH_2COO-*t*-Bu) were established by comparison with the doublet peaks of the 2-methyl group in 500 MHz ^1H NMR: 5-*n*-butyl-2-methylcyclohexanone: δ 1.02 (trans), 1.06 (cis); 2-methyl-5-phenylcyclohexanone: δ 1.09 (trans), 1.17 (cis); *tert*-butyl (4-methyl-3-oxocyclohexyl)acetate: δ 1.02 (trans), 0.91 (cis). In the conjugate addition to (*S*)-(−)-carvone with MAD/MeLi, the high trans selectivity (>95%), which referred to the stereochemistries of the 3,5-dialkyl substituents, was confirmed by GLC comparison with the authentic material of (3*S*,5*S*)-5-isopropenyl-2,3-dimethylcyclohexanone. This material was synthesized by the conjugate addition of Me_2CuLi to carvone.[44] The stereochemical assignments at the 3,5-dialkyl substituents in 3-*sec*-butyl-5-isopropenyl-2-methylcyclohexanone and 3,5-diisopropenyl-2-methylcyclohexanone were made in a similar manner as described above. Authentic *trans*-3-methyl-4-triphenylsiloxycyclopentanone was prepared by the conjugate addition of Me_2CuLi (4 equiv) in ether to 4-triphenylsiloxy-2-cyclopentenone at −78 °C for 30 min: ^1H NMR (CCl_4) δ 7.25–7.63 (15 H, m, Ph), 4.12 (1 H, q, J = 5.2 Hz, CH–O), 2.21 (2 H, d, J = 6.2 Hz, $CH_2C{=}O$), 0.92 (3 H, d, J = 6.2 Hz, CH_3CH). On the other hand, the conjugate adduct derived by the reaction of 4-triphenylsiloxy-2-cyclopentenone with MAD/MeLi exhibited the CH–O peaks at δ 4.12 (q, J = 5.2 Hz) and 4.45 (m) corresponding to the trans and cis isomers in a ratio of 63:37. In a similar manner, the trans/cis ratio of 3-*tert*-butyl-4-triphenylsiloxycyclopentanone was established by ^1H NMR analysis to be 76:24: ^1H NMR (CCl_4) δ 4.72 (m, cis CH–O), 4.43 (m, trans CH–O).

Conjugate Addition of *t*-BuLi to Benzyl Methacrylate. The reaction was carried out in a similar manner as described in the conjugate addition of organolithium to enone. The crude product was purified by column chromatography on silica gel (ether/hexane = 1:30 as eluant) to give benzyl 2,5,5-trimethylhexanoate in 71% yield: ^1H NMR (CCl_4) δ 7.25 (5 H, s, Ar–H), 5.00 (2 H, s, $ArCH_2$), 1.12 (3 H, d, J = 6.5 Hz, CH_3), 0.83 (9 H, s, *t*-Bu); IR (liquid film) 1737, 1454, 1369, 1188, 1151, 696 cm^{-1}. Anal. ($C_{13}H_{22}O_2$) C, H.

Reaction of (*E*,*E*)-1-Phenyl-2,4-hexadien-1-one with MAD/*t*-BuLi. The MAD-mediated conjugate addition of *t*-BuLi to the dienone was carried out in a like manner as described in the general method for conjugate addition of organolithium to enone. The ratio of 1,6-, 1,4-, and 1,2-adducts was determined by ^1H NMR analysis of their mixture based on the peaks of isolated C=C–H (δ 5.09–6.27), $C{=}C{-}CH_2{-}C{=}O$ (δ 3.51–3.69), and $C{=}C{-}CH_3$ (δ 1.54, J = 5 Hz).

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A Model for the Diastereofacial Differentiation in the Alkylation of Endocyclic Enolate

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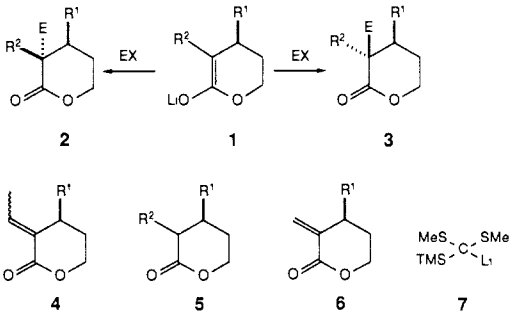
Abstract: There is a consensus of opinion that an alkylation of endocyclic enolates **1** with an asymmetric center at the β-position affords the products **2** with an entry of electrophile E trans to the substituent (R^1). A series of endocyclic enolates **1** with nonchiral exo-allylic substituents (R^2) varying from methyl to $CH_2C(SMe)_2SiMe_3$ have been examined with respect to their diastereofacial differentiation in alkylation (trans to R^1 (**2**) and/or cis to R^1 (**3**)). The complete reverse of diastereofacial differentiation was realized in the alkylation of **1** with bulky nonchiral exo-allylic substituent ($R^2 = CH_2C(SMe)_2SiMe_3$), providing **3** in an extremely high selectivity. On the other hand, the usual, but higher diastereofacial differentiation was realized in the alkylation of **1** with a vinyl substituent ($R^2 = CH{=}CH_2$). It was found that the reverse and normal diastereofacial differentiations can be simply rationalized by considering the conformation of **1** as shown in A.

An intriguing facet of alkylation of **1** is the manner through which the asymmetric center renders the face of the adjacent enolate π-system stereochemically nonequivalent.[1] The preferred production of **2** arising from alkylation trans to R^1 is the established understanding and, in fact, constitutes an important protocol in complex synthesis.[2] We now report the unprecedented and extremely efficient diastereofacial differentiation in the alkylation of **1**, providing **3** with an entry of electrophile cis to R^1, based on the notion of controlling stereochemistry by the *nonchiral* exo-allylic substituent with the specific conformation.[3] Furthermore

Scheme I



molecular mechanics calculations were performed on **1** and appear to be generally consistent with the experimental results. The *reverse* of diastereofacial differentiation demonstrated here requires a revision of the common understanding above (see Scheme I).

Results

A series of endocyclic enolates **1** with nonchiral exo-allylic substituents (R^2) varying from methyl to $CH_2C(SMe)_2SiMe_3$ have

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Table I. Diastereoselective Alkylation of the Enolates **1** to **2** (trans to R^1) and/or **3** (cis to R^1)

entry	1	method[a]	R^1	R^2	EX	% 2[b]	% 3[b]	total yield % (2 + 3)
1	**1a**[c]	A	Ph	$CH{=}CH_2$	MeI	>99.5	0.5	86
2	**1b**[d]	A	Ph	Me	EtI	>99.5	0.5	80
3	**1c**[d]	A	Ph	Et	MeI	98.0	2.0	91
4	**1d**[e]	B	Ph	$CH_2C(SMe)_2SiMe_3$	MeI	3.0	97.0	40[f]
5	**1e**[c]	A	Me	$CH{=}CH_2$	MeI	91.0	9.0	71
6	**1f**[d]	A	Me	Me	EtI	83.0	17.0	56
7	**1g**[d]	A	Me	Et	MeI	33.0	67.0	55
8	**1h**[d,g]	A	Me	$CH_2CH(SMe)_2$	MeI	1.0	99.0	82
9	**1i**[e]	B	Me	$CH_2C(SMe)_2SiMe_3$	MeI	0.5	>99.5	80
10	**1e**[c]	A	Me	$CH{=}CH_2$	allylBr	99.0	1.0	44[h]
11	**1e**[c]	A	Me	$CH{=}CH_2$	$PhCH_2Br$	98.0	2.0	69
12	**1i**[e]	B	Me	$CH_2C(SMe)_2SiMe_3$	allylBr	0.5	>99.5	75
13	**1i**[e]	B	Me	$CH_2C(SMe)_2SiMe_3$	$PhCH_2Br$	3.0	97.0	50

[a] A: lithiated the corresponding lactone (**4** or **5**) with LDA in THF in the presence of HMPA (2–5 equiv) at −78 °C; B: prepared by the reaction of **6** with **7** in THF at −78 °C. [b] Ratios were determined by GLC (OV1, 20 m) and NMR. Detection limits were ±0.25%. [c] Generated from **4**. [d] Generated from **5**. [e] Generated from **6**. [f] Overall yield from **6** (R^1 = Ph) to **3c** (R^1 = Ph, R^2 = Et, E = Me) (conjugate addition of **7**, methylation of enolate, protodesilylation (Bu_4NF), and then Raney nickel reduction). [g] Prepared by the LDA lithiation of the corresponding lactone (**5**: R^1 = Me, R^2 = $CH_2CH(SMe)_2$) obtained from **6** (R^1 = Me) via conjugate addition of **7**, protonation, and then protodesilylation (Bu_4NF). [h] γ-Alkylation product was obtained in 37%.

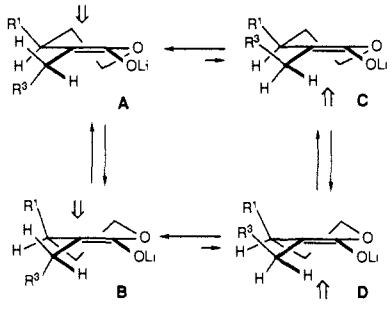
been examined with respect to their diastereofacial differentiation in alkylation (trans to R^1 (**2**) and/or cis to R^1 (**3**)). The enolates **1** were generated from the lactones **4–6** by the two methods, A and B (vide infra). Methylation of the enolate (**1a**: R^1 = Ph, R^2 = $CH{=}CH_2$) bearing a vinyl substituent, generated from **4** by the lithiation with lithium diisopropylamide (LDA) in the presence of hexamethylphosphoric triamide (HMPA) (method A), with methyl iodide in THF afforded **2a** as a single diastereomer (entry 1 in the Table I). Ethylation of **1b** (R^1 = Ph, R^2 = Me) also provided **2b**. Methylation of **1c** (R^1 = Ph, R^2 = Et) bearing the ethyl substituent with methyl iodide gave **2c** and **3c** in the ratio of 98:2. The reverse of diastereofacial differentiation was observed in the methylation of **1d** (R^1 = Ph, R^2 = $CH_2C(SMe)_2SiMe_3$), generated from **6** by the conjugate addition of **7**[4] (method B), affording **3d** and **2d** in a ratio of 97:3. The structure was confirmed by reduction (Raney-nickel or H_2–Pd/C) to 3-substituted 2-ethyl-2-methyl-5-pentanolides (**2** or **3**: R^1 = Me, Ph; R^2, E = Me, Et). The diastereomeric ratio was determined by capillary gas chromatography and NMR.

Additional examples are given in Table I.[5] Thus, the reaction of **1a,e** bearing a vinyl substituent (R^2 = $CH{=}CH_2$) proceeded, as expected, with high diastereofacial differentiation to provide **2** (trans-alkylation to R^1) (entries 1, 5, 10, 11). The reverse (cis-alkylation) and extremely high diastereofacial differentiation was realized in the alkylation of **1d,h,i** bearing the bulky dithioacetal substituent at R^2, producing **3** (entries 4, 8, 9, 12, 13).[6] It was surprising that an electrophile was introduced cis in spite of the bulky phenyl group (R^1 = Ph, entry 4), demonstrating the generality of the present diastereofacial differentiation. Furthermore, a variety of electrophiles were found to alkylate in a similar fashion. Since the lactones (**4–6**) are available in optically active form,[7] the present reaction provides either enantiomer in a high efficiency.

Discussion

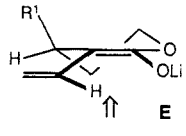
The diastereofacial differentiation in **1** is primarily controlled by the relative size of the two groups, H and R^1, on the adjacent asymmetric center. However, the facial preference is apparently influenced by the size of the exo-allylic substituent (R^2) as demonstrated above. When the R^2 is a group other than H or methyl, the enolate **1** would assume the more stable conformations A and

Scheme II



B rather than C and D. The C–H bond at the exo-allylic position is coplanar with the enolate π-system due to the allylic strain,[8,9] and R^3 would be antiperiplanar to R^1, to minimize steric interactions (see Scheme II).

In a specific conformation A or B, *facial entry is controlled by the steric balance between R^1 on the asymmetric carbon and R^3 on the nonasymmetric carbon.* Hence, an entry of an electrophile cis to R^1 and trans to R^3 would be essentially dictated by the bulkier R^3 (=$C(SMe)_2SiMe_3$) on the *nonasymmetric* carbon. Hyperconjugative effects of the σ-bond (C–CS (=C-R_3)) on a transition state[1,10] cannot be ruled out at this time, but the transition state would be readily attainable from A based on the least motion principle. The usual, but higher selectivities of **1a,e** (R^2 = $CH{=}CH_2$) compared to **1b,c,f** (R^2 = Me, Et) could be attributed to the planarity of the exo-allylic position as shown in E. The rationalization is consistent with the reactantlike transition state in the alkylation.[11]



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(9) For the application of the allylic strain concept in stereoselective alkylation, see: Fleming, I.; Lewis, J. J. *J. Chem. Soc., Chem. Commun.* **1985**, 149. Yamamoto, Y.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1984**, 904. Kim, D.; Chun, M. W.; Chung, W.-K. *Tetrahedron Lett.* **1986**, *27*, 943. Eyer, M.; Seebach, D. *J. Am. Chem. Soc.* **1985**, *107*, 3601. Meyers, A. I.; Barner, B. A. *J. Org. Chem.* **1986**, *51*, 120.
(10) McGarvey, G.; Williams, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 1435. Vedejs, E.; McClure, C. K. *J. Am. Chem. Soc.* **1986**, *108*, 1095. Morizawa, Y.; Yasuda, A.; Uchida, K. *Tetrahedron Lett.* **1986**, *27*, 1833. Houk, K. N. *Pure Appl. Chem.* **1983**, *55*, 277.

It is also noteworthy that the reverse of diastereofacial differentiation is observed in the methylation of **1g** (R^1 = Me, R^2 = Et, entry 7), in contrast to the normal and high differentiation exhibited by **1c** (R^1 = Ph, R^2 = Et, entry 3). This strongly indicates that the so-called product development control (thermodynamic control) is probably not operative in the present alkylation.

In support of this rationalization for the stereochemical alkylation, molecular mechanics calculations on **1** (R^1 = Me, R^3 = *t*-Bu) were performed by using Allinger MM2 force field.[12] The conformations A and B with comparable energy were shown to be of lowest steric energy by a factor of 3.5 kcal/mol over C and D.[13] The conformation E was also shown to be most stable.[13]

Conclusion

In summary, it is important to note that the diastereofacial differentiation is controlled by the exo-allylic position for the specific conformation of the nonasymmetric carbon center of an enolate. We believe that the reversal of diastereofacial differentiation and stereochemical rationalization demonstrated in this work will stimulate further advances in this important area of chemistry.[14,15]

Experimental Section[16]

2-Ethylidene-3-methyl-5-pentanolide (4, R^1 = Me). To a solution of LDA (13.1 mmol) in THF (10 mL) was added 3-methyl-5-pentanolide[7,17] (1.0 g, 8.76 mmol) in THF (10 mL). After having been stirred for 30 min at −78 °C, acetaldehyde (0.98 mL, 17.5 mmol) was added. The mixture was stirred at −78 °C for 20 min and was quenched with saturated aqueous ammonium chloride. Extraction with ethyl acetate and concentration afforded a yellow oil (3.0 g).

To a solution of the yellow oil above, triethylamine (4.9 mL, 35.0 mmol), and (4-dimethylamino)pyridine (20 mg) in methylene chloride (25 mL) was added methanesulfonyl chloride (1.4 mL, 17.5 mmol). After having been stirred for 1 h at room temperature, water (10 mL) was added. The separated organic layer was successively washed with 10% aqueous hydrochloric acid, saturated aqueous sodium bicarbonate, and saturated aqueous sodium chloride. Concentration afforded a brown oil (2.0 g).

A mixture of the brown oil above and DBU (1.3 mL, 8.8 mmol) in benzene (20 mL) was stirred for 1 h at room temperature. The entire mixture was successively washed with 10% aqueous hydrochloric acid, saturated aqueous sodium bicarbonate, and saturated aqueous sodium chloride. Concentration and purification through silica gel column chromatography (benzene–ethyl acetate = 10:1) afforded a pale yellow oil of **4** (R^1 = Me) (690 mg, 56%) as a 1:1 mixture of *Z* and *E* isomers: NMR ($CDCl_3$) δ 0.84–2.36 (m, CH_2CH_2O, 2 H), 1.13 (d, J = 7.1 Hz, CH_3, $^3/_2$ H), 1.17 (d, J = 6.9 Hz, CH_3, $^3/_2$ H), 1.84 (dd, J = 0.7, 7.4 Hz, $CH_3CH{=}C$, $^3/_2$ H), 2.08 (dd, J = 1.5, 7.4 Hz, $CH_3CH{=}C$, $^3/_2$ H), 2.65–3.32 (m, $CHCH_3$, 1 H), 3.94–4.56 (m, CH_2O, 2 H), 6.20 (dq, J = 1.5, 7.1 Hz, $CH{=}C$, $^1/_2$ H), 7.05 (dq, J = 1.5, 7.4 Hz, $CH{=}C$, $^1/_2$ H); IR (neat, film) 1720, 1640 cm^{-1}; MS, calcd for $C_8H_{12}O_2$ 140.0838, found 140.0878.

2-Ethylidene-3-phenyl-5-pentanolide (4, R^1 = Ph) was prepared in 69% yield as a yellow oil in the similar way as that of preparation of **4** (R^1 = Me): NMR ($CDCl_3$) δ 1.59 (dd, J = 0.9, 7.4 Hz, CH_3, 3 H), 1.70–2.56 (m, CH_2CH_2O, 2 H), 4.04–4.36 (m, CH_2O, CHPh, 3 H), 7.06–7.48 (m, Ph, $CH{=}C$, 6 H); IR (neat, film) 1720, 1630 cm^{-1}; MS, calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0999.

3-Methyl-2-methylene-5-pentanolide (6, R^1 = Me). To a cooled (−78 °C) solution of LDA (26.3 mmol) in THF (40 mL) was added a solution of 3-methyl-5-pentanolide[7,17] (2.0 g, 17.5 mmol) in THF (20 mL). After stirring at −78 °C for 30 min, carbon dioxide gas was introduced via cannula over a period of 30 min. The mixture was acidified with 10% aqueous hydrochloric acid and extracted with ethyl acetate. The combined extracts were concentrated to leave a yellow oil (3.63 g).

A mixture of an oil above, 35% aqueous formalin (17 mL, 19.2 mmol), and triethylamine (9 mL, 87.5 mmol) was stirred at 80 °C for 1 h. After the addition of sodium acetate (1.58 g, 19.3 mmol) and acetic acid (15 mL), the entire mixture was stirred at 80 °C for 30 min and was poured into saturated aqueous sodium chloride. After extraction with ethyl acetate, the extracts were washed successively with 10% aqueous hydrochloric acid, saturated aqueous sodium bicarbonate, and saturated aqueous sodium chloride and dried over magnesium sulfate. Concentration and purification through silica gel column chromatography (benzene–ethyl acetate = 20:1) afforded **6** (R^1 = Me) (1.10 g, 50%) as a colorless oil: NMR ($CDCl_3$) δ 1.25 (d, J = 6.6 Hz, CH_3, 3 H), 1.47–2.17 (m, CH_2CHO, 2 H), 2.55–2.96 (m, $CHCH_3$, 1 H), 4.16–4.58 (m, CH_2O, 2 H), 5.63 (dd, J = 1.2, 2.2 Hz, $CH_2{=}C$, 1 H), 6.48 (dd, J = 1.2, 2.2 Hz, $CH_2{=}C$, 1 H); IR (neat, film) 1720, 1620 cm^{-1}; MS, calcd for $C_7H_{10}O_2$ 126.0639, found 126.0659.

2-Methylene-3-phenyl-5-pentanolide (6, R^1 = Ph) was prepared in 35% yield as pale yellow needles (mp 55–57 °C) from 3-phenyl-5-pentanolide[7,17] in the similar way as that of preparation of **4** (R^1 = Me) (formaldehyde gas was used instead of acetaldehyde): NMR ($CDCl_3$) δ 2.09–2.35 (m, CH_2CH_2O, 2 H), 3.81–4.11 (m, CHPh, 1 H), 4.34–4.51 (m, CH_2O, 2 H), 5.33–5.41 and 6.58–6.67 (m, $CH_2{=}C$, each 1 H), 7.12–7.49 (m, Ph, 5 H); IR (Nujol, film) 1720 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.58; H, 6.43. Found: C, 76.37; H, 6.50.

2,3-Dimethyl-5-pentanolide (5, R^1, R^2 = Me). To a cooled (−78 °C) solution of LDA (26.3 mmol) in THF (30 mL) was added a solution of 3-methyl-5-pentanolide[7,17] (2.85 g, 25.0 mmol) in THF (30 mL). After stirring for 1 h at −78 °C, HMPA (5.22 mL, 30.0 mmol) and methyl iodide (1.71 mL, 27.5 mmol) were added. The mixture was stirred at −50 °C for 2 h, and the reaction was quenched with saturated aqueous ammonium chloride. Extractive workup (methylene chloride) and purification through silica gel column chromatography (hexane–ether = 2:1) afforded **5** (R^1, R^2 = Me) (2.44 g, 76%) as a colorless oil (bp 140 °C/2 mmHg). NMR and IR were identical with those of *trans*-**5** (R^1, R^2 = Me) reported.[18]

2-Ethyl-3-methyl-5-pentanolide (5, R^1 = Me, R^2 = Et) was prepared in 51% yield as a colorless oil as a separable (silica gel column chromatography (hexane–ethyl acetate = 4:1)) 26:1 mixture of major trans and cis isomers in the similar way as that for **5** (R^1, R^2 = Me) (ethyl iodide was used instead of methyl iodide): NMR (trans isomer) ($CDCl_3$) δ 0.97 (t, J = 7.2 Hz, CH_3, 3 H), 1.09 (d, J = 5.9 Hz, CH_3, 3 H), 1.2–2.6 (m, 6 H), 4.0–4.6 (m, 2 H); IR (neat, film) 1730 cm^{-1}; MS, 142 (M^+). Cis isomer 0.89 (d, J = 6.0 Hz, CH_3, 3 H), 1.00 (t, J = 7.3 Hz, CH_3, 3 H), 1.15–2.8 (m, 6 H), 3.2–4.5 (m, 2 H); IR (neat, film) 1725 cm^{-1}; MS, 142 (M^+).

2-Methyl-3-phenyl-5-pentanolide (5, R^1 = Ph, R^2 = Me) was prepared in 83% yield as a pale yellow oil in the similar way as that for **5** (R^1, R^2 = Me): NMR ($CDCl_3$) δ 1.14 (d, J = 6.6 Hz, CH_3, 3 H), 1.97–2.30 (m, CH_2CH_2O, 2 H), 2.53–2.96 (m, CHPh, $CHCH_3$, 2 H), 4.36 and 4.55 (dd, J = 5.4, 11.3 Hz, CH_2O, each 1 H), 7.11–7.48 (m, Ph, 5 H); IR (neat, film) 1720 cm^{-1}; MS, calcd for $C_{12}H_{14}O_2$ 190.0991, found 190.0991.

2-Ethyl-3-phenyl-5-pentanolide (5, R^1 = Ph, R^2 = Et) was prepared in 66% yield as a pale yellow oil in the similar way as that for **5** (R^1, R^2 = Me): NMR ($CDCl_3$) δ 0.92 (t, J = 7.4 Hz, CH_3, 3 H), 1.16–3.16 (m, 6 H), 4.12–4.61 (m, CH_2O, 2 H), 7.00–7.46 (m, Ph, 5 H); IR (neat, film) 1720 cm^{-1}; MS, calcd for $C_{13}H_{16}O_2$ 204.1151, found 204.1158.

2-(2,2-Bis(methylthio)ethyl)-3-methyl-5-pentanolide (5, R^1 = Me, R^2 = $CH_2CH(SCH_3)_2$) was prepared in 63% yield as a pale yellow oil in the similar way as that for **3** (R^1, E = CH_3, R^2 = $CH_2CH(SCH_3)_2$) (acetic acid was used instead of methyl iodide): NMR ($CDCl_3$) δ 1.13 (d, J = 6.1 Hz, CH_3, 3 H), 1.53–2.64 (m, 6 H), 2.07 and 2.16 (s, SCH_3, each 3 H), 4.03 (dd, J = 4.3, 11.0 Hz, $CH(SCH_3)_2$, 1 H), 4.24–4.42 (m, CH_2O, 2 H); IR (neat, film) 1720 cm^{-1}; MS, calcd for $C_{10}H_{18}O_2S_2$ 234.0749, found 234.0761.

General Alkylation Procedure by Method A (Entries 1–3, 5–8, 10, and 11). To a cooled (−78 °C) solution of LDA (1.80 mmol) and HMPA (1.0 mL, 6.0 mmol) in THF (6 mL) was added a solution of **4** (or **5**)

(11) Caine, D.; Huff, B. J. L. *Tetrahedron Lett.* **1966**, 4695; **1967**, 3399. Bare, T. M.; Herskey, N. D.; House, H. O.; Swain, C. G. *J. Org. Chem.* **1972**, *37*, 997.

(12) For computation, OLi was treated as O^-, and parameters developed by Still (Still, W. C.; Galynker, I. *Tetrahedron* **1981**, *23*, 3981) were used. We are grateful to Prof. Eiji Osawa, Department of Chemistry, Hokkaido University, for providing us with the MM2 program.

(13) The dihedral angles of H—C—C═C were around 20° and 30° for conformations A and B, placing the C–R^3 bond nearly perpendicular to the plane of the enolate. The dihedral angle of H—C(═)—C═C was around 0° for E, placing the vinyl group on the plane of the enolate.

(14) Application of this concept to other cyclic systems is the subject of the future studies.

(15) A somewhat related phenomena has been reported. Meyers, A. I.; Oppenlaender, T. *J. Am. Chem. Soc.* **1986**, *108*, 1989.

(16) The compounds described are racemic. A Hitachi 263-50 gas chromatograph (capillary glass column OV1, 20 m, nitrogen carrier gas) was used for the determination of the isomer ratio of **2** and **3**.

(17) Bailey, D. M.; Johnson, R. E. *J. Org. Chem.* **1970**, *35*, 3574. Frimer, A. A.; Bartlett, P. D.; Boschung, A. F.; Jewett, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 7983.

(18) Tamaru, Y.; Furukawa, Y.; Mizutani, M.; Kitao, O.; Yoshida, Z. *J. Org. Chem.* **1983**, *48*, 3631.

(1.50 mmol) in THF (2 mL). After having been stirred at −78 °C for 50 min, alkyl halide (6.0 mmol) was added. The mixture was stirred at −78 °C for 30 min and was allowed to warm up to −20 °C over a period of 2 h. The reaction was quenched with saturated aqueous ammonium chloride and extracted with ethyl acetate. The combined extracts were washed successively with 10% aqueous hydrochloric acid, saturated aqueous sodium bicarbonate, and saturated aqueous sodium chloride. Concentration and purification through silica gel column chromatography (benzene–ethyl acetate = 10:1) afforded **2** as a major product (**3** in runs 7 and 8).

***cis*-2-Methyl-3-phenyl-2-vinyl-5-pentanolide (2a, R¹ = Ph, R² = CH=CH₂, E = Me) (entry 1)** was obtained in 86% yield as colorless needles (mp 101–102 °C). No isomer was detected by NMR and GLC and was confirmed by analyzing the corresponding reduction product: ^{1}H NMR ($CDCl_3$) δ 1.34 (s, CH_3, 3 H), 2.76–3.07 and 3.32–3.80 (m, CH_2CH_2O, each 1 H), 3.09 (dd, J = 2.9, 12.5 Hz, CHPh, 1 H), 4.12–4.68 (m, CH_2O, 2 H), 4.92–5.32 (m, CH_2=CH, 2 H), 5.64 (dd, J = 10.0, 17.2 Hz, CH_2=CH, 1 H), 7.00–7.52 (m, Ph, 5 H); ^{13}C NMR ($CDCl_3$) δ 23.4 (q), 26.0 (t), 48.0 (d), 51.1 (s), 68.6 (t), 116.5 (t), 127.0 (d), 127.7 (d), 128.9 (d), 137.4 (d), 138.4 (s), 173.3 (s); IR (KBr) 1720 cm^{-1}; MS, calcd for $C_{14}H_{16}O_2$ 216.1151, found 216.1152.

***trans*-2-Ethyl-2-methyl-3-phenyl-5-pentanolide (2b, R¹ = Ph, R² = Me, E = Et) (entry 2)** was obtained in 80% yield as colorless prisms (mp 89–90 °C). No isomer was detected by GLC (180 °C, 63 mL/min, retention time 10.3 and 10.5 min for **2** and **3**): ^{1}H NMR ($CDCl_3$) δ 1.06 (s, CH_3, 3 H), 1.07 (t, J = 7.3 Hz, CH_3, 3 H), 1.20–2.70 (m, 4 H), 3.32 (dd, J = 3.3, 11.9 Hz, CHPh, 1 H), 4.20–4.62 (m, CH_2O, 2 H), 7.02–7.54 (m, Ph, 5 H); ^{13}C NMR ($CDCl_3$) δ 9.3 (q), 22.8 (q), 26.0 (t), 30.5 (t), 42.8 (d), 48.2 (s), 68.5 (t), 126.8 (d), 127.9 (d), 128.5 (d), 139.4 (s), 176.0 (s); IR ($CHCl_3$) 1720 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.95; H, 8.38.

***cis*-2-Ethyl-2-methyl-3-phenyl-5-pentanolide (2c, R¹ = Ph, R² = Et, E = Me) (entry 3)** was obtained in 91% yield as colorless plates (mp 73.5–74.5 °C). The ratio of 98:2 was determined by NMR and GLC (see above): ^{1}H NMR ($CDCl_3$) δ 0.80 (t, J = 7.4 Hz, CH_3, 3 H), 1.27 (s, CH_3, 3 H), 1.08–2.66 (m, 4 H), 3.14 (dd, J = 4.2, 10.5 Hz, CHPh, 1 H), 4.20–4.66 (m, CH_2O, 2 H), 6.92–7.48 (m, Ph, 5 H); ^{13}C NMR ($CDCl_3$) δ 8.5 (q), 23.0 (q), 25.8 (t), 26.6 (t), 46.0 (s), 48.2 (d), 67.9 (t), 126.9 (d), 127.9 (d), 128.8 (d), 139.2 (s), 175.2 (s); IR (KBr) 1720 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.09; H, 8.35.

***cis*-2,3-Dimethyl-2-vinyl-5-pentanolide (2e, R¹, E = Me, R² = CH=CH₂) (entry 5)** was obtained in 71% yield as a colorless oil. The ratio of 91:9 was determined by NMR (^{1}H NMR δ 1.42 and 1.30, ^{13}C NMR δ 27.7 and 27.1 for quaternary methyl signals of **2** and **3**, respectively): ^{1}H NMR of **2** ($CDCl_3$) δ 0.76–2.28 (m, CH_2CH_2O, $CHCH_3$, 3 H), 1.02 (d, J = 6.1 Hz, CH_3, 3 H), 1.42 (s, CH_3, 3 H), 4.10–4.56 (m, CH_2O, 2 H), 4.96–5.30 (m, CH_2=C, 2 H), 5.89 (dd, J = 10.8, 17.4 Hz, CH=C, 1 H); ^{13}C NMR ($CDCl_3$) δ 15.5 (q), 22.4 (q), 27.7 (t), 36.6 (d), 50.2 (s), 68.3 (t), 116.6 (t), 136.5 (d), 174.0 (s); IR (neat, film) 1725, 1635 cm^{-1}; MS, calcd for $C_9H_{14}O_2$ 154.0994, found 154.0999.

***trans*-2-Ethyl-2,3-dimethyl-5-pentanolide (2f, R¹ = Me, R² = Me, E = Et) (entry 6)** was obtained in 56% yield as a colorless oil. The ratio of 83:17 was determined by NMR and GLC (see reduction of **2** (R² = CH=CH₂)).

2-Ethyl-2,3-dimethyl-5-pentanolide (2g, R¹, E = Me, R² = Et) (entry 7) was obtained in 55% yield as a colorless oil. The ratio of 33:67 was determined by NMR and GLC (see reduction of **2** (R² = CH=CH₂)).

***trans*-2-(2,2-Bis(methylthio)ethyl)-2,3-dimethyl-5-pentanolide (3h, R¹ = Me, R² = CH₂CH(SMe)₂, E = Me) (entry 8)** was obtained in 82% yield as a colorless oil. All spectral data were identical with those obtained by method B (entry 9). The ratio of 99:1 was determined by NMR and GLC (see reduction of **2** (R² = CH=CH₂)).

***cis*-2-Allyl-3-methyl-2-vinyl-5-pentanolide (2, R¹ = Me, R² = CH=CH₂, E = CH₂CH=CH₂) (entry 10)** was obtained in 44% yield (γ-alkylation product was obtained in 37% yield) as a colorless oil. The ratio of 99:1 was determined by analyzing the corresponding reduction product: ^{1}H NMR ($CDCl_3$) δ 0.98 (t, J = 6.6 Hz, CH_3, 3 H), 1.44–3.04 (m, 5 H), 4.06–4.52 (m, CH_2O, 2 H), 4.96–5.40 (m, CH_2=CH, 4 H), 5.48–6.00 (m, CH_2=CH, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.7 (q), 27.4 (t), 31.6 (d), 39.0 (t), 54.1 (s), 68.7 (t), 117.1 (t), 118.5 (t), 133.5 (d), 136.2 (d), 172.5 (s); IR (neat, film) 1720 cm^{-1}; MS, calcd for $C_{11}H_{16}O_2$ 180.1148, found 180.1138.

***cis*-2-Benzyl-3-methyl-2-vinyl-5-pentanolide (2, R¹ = Me, R² = CH=CH₂, E = CH₂Ph) (entry 11)** was obtained in 69% yield as a colorless oil. The ratio of 98:2 was determined by analyzing the corresponding reduction product: ^{1}H NMR ($CDCl_3$) δ 1.05 (d, J = 6.4 Hz, CH_3, 3 H), 1.36–2.31 (m, 3 H), 2.79 and 3.67 (d, J = 13.8 Hz, CH_2Ph, each 1 H), 3.78–4.40 (m, CH_2O, 2 H), 5.26 (d, J = 17.2 Hz, CH_2=CH, 1 H), 5.35 (d, J = 10.8 Hz, CH_2=CH, 1 H), 5.93 (q, J = 10.8, 17.2 Hz, CH_2=CH, 1 H), 7.25 (s, Ph, 5 H); ^{13}C NMR ($CDCl_3$) δ 15.3 (q), 27.4 (t), 31.1 (d), 40.0 (t), 56.2 (s), 68.9 (t), 117.3 (t), 126.5 (d), 128.2 (d), 130.1 (d), 136.9 (s and d), 172.6 (s); IR (neat, film) 1725 cm^{-1}; MS, calcd for $C_{15}H_{18}O_2$ 230.1305, found 230.1298.

General Reduction Procedure of 2 (R² = CH=CH₂). A solution of **2** (R² = CH=CH₂) (1 mmol) (obtained in the entries 1, 5, 10, and 11) was stirred in ethanol (10 mL) over 10% Pd/C (20 mg) under hydrogen atmosphere for 12 h. Filtration through Celite pad and purification through silica gel column chromatography (ethyl acetate–hexane = 1:4) afforded **2** (R² = Et).

***cis*-2-Ethyl-2-methyl-3-phenyl-5-pentanolide (2, R¹ = Ph, R² = Et, E = Me)** was obtained in 98% yield as colorless plates (mp 73.5–74.5 °C) from **2a** (entry 1). No isomer was detected by NMR and GLC (see above). Spectral data were identical with those of **2c** (entry 3).

***cis*-2-Ethyl-2,3-dimethyl-5-pentanolide (2, R¹, E = Me, R² = Et)** was obtained in 78% yield as a colorless oil from **2e** (entry 5). The ratio of 10:1 was determined by NMR (^{1}H NMR δ 1.32 and 1.16, ^{13}C NMR δ 22.8 and 20.9 for quaternary methyl signals of **2** and **3**, respectively) and further by capillary column GLC (OV1, 20 m, 146 °C, 50 mL/min, retention time 10.8 and 10.5 min for **2** and **3**, respectively): ^{1}H NMR (for major **2**) ($CDCl_3$) δ 0.90 (t, J = 7.6 Hz, CH_3, 3 H), 1.04 (d, J = 6.6 Hz, CH_3, 3 H), 1.32 (s, CH_3, 3 H), 1.32–2.18 (m, 5 H), 4.12–4.54 (m, CH_2O, 2 H); ^{13}C NMR ($CDCl_3$) δ 8.8 (q), 15.4 (q), 22.8 (q), 26.3 (t), 27.5 (t), 35.9 (d), 45.8 (s), 67.7 (t), 175.9 (s); IR (neat, film) 1730 cm^{-1}; MS, calcd for $C_9H_{16}O_2$ 156.1148, found 156.1145.

***trans*-2-Ethyl-3-methyl-2-propyl-5-pentanolide (2, R¹ = Me, R² = Et, E = Pr)** was obtained in 96% yield as a colorless oil from **2** (entry 10). The ratio of 99:1 was determined by GLC (OV1, 20 m, 200 °C, 40 mL/min retention time 7.3 and 7.6 min for **2** and **3**, respectively): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 7.5 Hz, CH_3, 3 H), 0.92 (t, J = 7.1 Hz, CH_3, 3 H), 1.01 (d, J = 7.0 Hz, CH_3, 3 H), 1.17–1.41 (m, $CH_3CH_2CH_2$, 3 H), 1.54 (dq, J = 7.7, 14.1 Hz, CH_3CH_2, 1 H), 1.75 (dq, J = 7.3, 14.3 Hz, $CH_3CH_2CH_2$, 1 H), 1.77–1.94 (m, CH_2CH_2O, CH_2CH_2, 3 H), 2.12–2.20 (m, $CHCH_3$, 1 H), 4.27 (ddd, J = 4.8, 9.9, 11.4 Hz, CH_2O, 1 H), 4.38 (ddd, J = 4.0, 5.5, 11.4 Hz, CH_2O, 1 H); ^{13}C NMR ($CDCl_3$) δ 9.3 (q), 14.5 (q), 15.1 (q), 18.0 (t), 26.5 (t), 27.7 (t), 32.1 (d), 37.3 (t), 49.8 (s), 68.2 (t), 174.9 (s); IR (neat, film) 1725 cm^{-1}; MS, calcd for $C_{11}H_{20}O_2$ 184.1464, found 184.1416.

***trans*-2-Benzyl-2-ethyl-3-methyl-5-pentanolide (2, R¹ = Me, R² = Et, E = CH₂Ph)** was obtained in 97% yield as a colorless oil from **2** (entry 11). The ratio of 98:2 was determined by HPLC (Waters Radial Pak 8SI 5 μ, 2 mL/min, ethyl acetate–hexane = 1:4, 256 nm, retention time 7.8 and 9.9 min for **2** and **3**, respectively): ^{1}H NMR ($CDCl_3$) δ 1.03 (t, J = 7.8 Hz, CH_3, 3 H), 1.06 (d, J = 7.0 Hz, CH_3, 3 H), 1.34–2.58 (m, 5 H), 2.53 and 3.49 (d, J = 13.8 Hz, CH_2Ph, each 1 H), 3.64–3.98 (m, CH_2O, 1 H), 4.10–4.36 (m, CH_2O, 1 H), 7.03–7.42 (m, Ph, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.3 (q), 15.1 (q), 28.4 (t), 28.7 (t), 31.5 (d), 41.8 (t), 52.0 (s), 68.6 (t), 126.3 (d), 128.1 (d), 129.9 (d), 137.9 (s), 174.6 (s); IR (neat, film) 1725 cm^{-1}; MS, calcd for $C_{15}H_{20}O_2$ 232.1463, found 232.1466.

General Alkylation Procedure by Method B (Entries 4, 9, 12, and 13). To a solution of trimethylsilylbis(methylthio)methane[4,6] (1.78 mmol) in THF (6 mL) was added a hexane solution of butyllithium (1.78 mmol) at −10 °C. After stirring at −10 °C for 1 h, a solution of **6** (1.48 mmol) in THF (2 mL) was added at −78 °C. After having been stirred for 0.75 h, hexamethylphosphoric triamide (HMPA) (2.96 mmol) and alkyl halide (5.92 mmol) were added. The mixture was allowed to warmup to −20 °C over a period of 4 h. A 1 M THF solution of tetrabutylammonium fluoride (2.22 mmol) was added, and the mixture was stirred for 0.5 h at room temperature. Extractive workup and following column chromatography afforded **3** (R² = $CH_2CH(SMe)_2$).

***trans*-2-(2,2-Bis(methylthio)ethyl)-2-methyl-3-phenyl-5-pentanolide (3d, R¹ = Ph, R² = CH₂CH(SMe)₂, E = Me) (entry 4)** obtained as above was directly reduced to **3** (R¹ = Ph, R² = Et, E = Me) in 40% overall yield. The ratio of 97:3 was determined by GLC (see entry 2). The major product was identical with the compound obtained in entry 2.

***trans*-2-(2,2-Bis(methylthio)ethyl)-2,3-dimethyl-5-pentanolide (3i, R¹ = Me, R² = CH₂CH(SMe)₂, E = Me) (entry 9)** was obtained in 80% yield as the sole product: ^{1}H NMR ($CDCl_3$) δ 0.97 (d, J = 6.6 Hz, CH_3, 3 H), 1.17 (s, CH_3, 3 H), 1.99 and 2.13 (s, CH_3S, each 3 H), 1.48–2.44 (m, 4 H), 2.61 (dd, J = 11.5, 14.7 Hz, $CH_2CH(SCH_3)_2$, 1 H), 3.72 (dd, J = 4.7, 11.5 Hz, $CH(SCH_3)_2$, 1 H), 4.26–4.45 (m, CH_2O, 2 H); ^{13}C NMR ($CDCl_3$) δ 10.5 (q), 13.5 (q), 15.1 (q), 21.9 (q), 27.8 (t), 31.1 (d), 40.3 (t), 45.8 (s), 50.6 (d), 68.5 (t), 175.4 (s); IR (neat, film) 1720 cm^{-1}; MS, calcd for $C_{11}H_{20}O_2S_2$ 248.0903, found 248.0877.

***trans*-2-Allyl-2-(2,2-bis(methylthio)ethyl)-3-methyl-5-pentanolide (3, R¹ = Me, R² = CH₂CH(SMe)₂, E = CH₂CH=CH₂) (entry 12)** was obtained in 75% yield as a pale yellow oil. The ratio was determined by GLC of the corresponding reduction product: ^{1}H NMR ($CDCl_3$) δ 1.56 (d, J = 6.6 Hz, CH_3, 3 H), 1.48–2.44 (m, 5 H), 1.87 (dd, J = 4.9, 14.8 Hz, $CH_2CH(SMe_2)$, 1 H), 1.99 and 2.13 (s, CH_3S, each 3 H), 2.54 (dd,

J = 11.3, 14.8 Hz, $CH_2CH(SCH_3)_2$, 1 H), 3.70 (dd, J = 4.9, 11.3 Hz, $CH(SCH_3)_2$, 1 H), 4.28-4.49 (m, CH_2O, 2 H), 4.92-5.23 (m, CH_2=CH, 2 H), 5.58-6.07 (m, CH_2=CH, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.4 (q), 13.7 (q), 15.1 (q), 28.2 (t), 31.6 (d), 39.4 (t), 40.3 (t), 48.9 (s), 50.7 (d), 68.7 (t), 117.8 (t), 133.8 (d), 173.5 (s); IR (neat, film) 1720 cm^{-1}; MS, calcd for $C_{13}H_{22}O_2S_2$ 274.1062, found 274.1064.

***trans*-2-Benzyl-2-(2,2-bis(methylthio)ethyl)-3-methyl-5-pentanolide (3, R^1 = Me, R^2 = $CH_2CH(SMe)_2$, E = CH_2Ph) (entry 13)** was obtained in 50% yield as a pale yellow oil. The ratio was determined by GLC of the corresponding reduction product: ^1H NMR ($CDCl_3$) δ 1.18 (d, J = 7.1 Hz, CH_3, 3 H), 1.26-2.74 (m, 7 H), 1.96 and 2.12 (s, CH_3S, each 3 H), 2.88 (s, CH_2Ph, 2 H), 3.70 (dd, J = 4.9, 11.3 Hz, $CH(SCH_3)_2$, 1 H), 4.08-4.53 (m, CH_2O, 2 H), 7.20 (br s, Ph, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.5 (q), 13.6 (q), 15.1 (q), 27.5 (t), 31.6 (d), 39.8 (t), 41.7 (t), 50.5 (s), 50.7 (d), 68.9 (t), 126.5 (d), 127.8 (d), 130.1 (d), 136.8 (s), 173.4 (s); IR (neat, film) 1720 cm^{-1}; MS, calcd for $C_{17}H_{24}O_2S_2$ 324.1218, found 324.1231.

General Reduction Procedure of 3 (R^2 = $CH_2CH(SMe)_2$). A crude product **3** (0.10 g) (obtained in entries 4, 8, 9, 12, and 13) was heated under reflux over Raney nickel W4 in ethanol (4 mL) for 5 h. Filtration through Celite pad and concentration afforded a yellow oil. Purification through silica gel column chromatography (ethyl acetate-hexane = 1:4) afforded **3** (R^2 = Et) as a colorless oil.

***trans*-2-Ethyl-2,3-dimethyl-5-pentanolide (3, R^1, E = Me, R^2 = Et)** was obtained in 74% yield in two steps from **6** via **3** (entry 9) as a colorless oil. No isomer was detected by NMR (^1H, ^{13}C) and GLC (see reduction of **2** (R^2 = CH=CH_2)): ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 7.4 Hz, CH_3, 3 H), 0.97 (d, J = 6.6 Hz, CH_3, 3 H), 1.16 (s, CH_3, 3 H), 1.20-2.31 (m, 5 H), 4.08-4.50 (m, CH_2O, 2 H); ^{13}C NMR ($CDCl_3$) δ 9.1 (q), 15.3 (q), 20.9 (q), 27.6 (t), 30.2 (t), 31.3 (d), 47.3 (s), 68.4 (t), 176.4 (s); IR (neat, film) 1720 cm^{-1}; MS, calcd for $C_9H_{16}O_2$ 156.1148, found 156.1130.

***cis*-2-Ethyl-3-methyl-2-propyl-5-pentanolide (3, R^1 = Me, R^2 = Et, E = Pr)** was obtained in 79% yield as a colorless oil from **3** (entry 12). No isomer was detected by GLC (see reduction of **2** (R^2 = CH=CH_2)): ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.3 Hz, CH_3, 3 H), 0.90 (t, J = 7.3 Hz, CH_3, 3 H), 1.01 (d, J = 7.0 Hz, CH_3, 3 H), 1.24-1.37 (m, $CH_3CH_2CH_2$, 2 H), 1.37-1.47 (m, $CH_3CH_2CH_2$, 1 H), 1.45 (dq, J = 7.3, 14.6 Hz, CH_3CH_2, 1 H), 1.65 (ddd, J = 5.8, 11.0, 13.6 Hz, $CH_3CH_2CH_2$, 1 H), 1.75-1.95 (m, CH_2, 2 H), 1.96 (dq, J = 7.3, 14.6 Hz, CH_3CH_2, 1 H), 2.14-2.21 (m, CH_3CH_2, 1 H), 4.27 (ddd, J = 4.8, 10.3, 11.4 Hz, CH_2O, 1 H), 4.38 (ddd, J = 4.0, 5.5, 11.4 Hz, CH_2O, 1 H); ^{13}C NMR ($CDCl_3$) δ 9.2 (q), 14.8 (q), 15.1 (q), 18.1 (t), 27.2 (t), 28.3 (t), 31.5 (d), 36.2 (t), 50.0 (s), 68.2 (t), 174.9 (s); IR (neat, film) 1725 cm^{-1}; MS, calcd for $C_{11}H_{20}O_2$ 184.1464, found 184.1520.

***cis*-2-Benzyl-2-ethyl-3-methyl-5-pentanolide (3, R^1 = Me, R^2 = Et, E = CH_2Ph)** was obtained in 78% yield as a colorless oil from **3** (entry 13). The ratio of 97:3 was determined by HPLC (see reduction of **2** (R^2 = CH=CH_2)): ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 7.4 Hz, CH_3, 3 H), 1.14 (d, J = 6.9 Hz, CH_3, 3 H), 1.30-2.46 (m, 5 H), 2.91 (s, CH_2Ph, 2 H), 4.07-4.49 (m, CH_2O, 2 H), 7.04-7.44 (m, Ph, 5 H); ^{13}C NMR ($CDCl_3$) δ 9.0 (q), 14.9 (q), 27.1 (t), 28.1 (t), 31.2 (d), 40.4 (t), 51.8 (s), 68.7 (t), 126.3 (d), 127.7 (d), 130.0 (d), 137.2 (s), 174.0 (s); IR (neat, film) 1725 cm^{-1}; MS, calcd for $C_{15}H_{20}O_2$ 232.1464, found 232.1467.

Arylcyclopropane Photochemistry. Unusual Aromatic Substituent Effects on the Photochemical Rearrangement of (2-Arylcyclopropyl)methyl Acetates to 1-Arylhomoallyl Acetates

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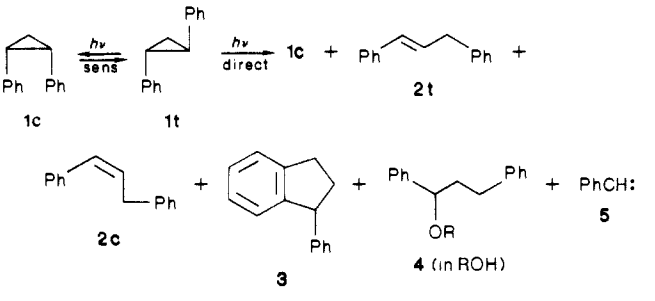
Abstract: Irradiation of *trans*-(2-arylcyclopropyl)methyl acetates **6a** (Ar = Ph), **6b** (Ar = *p*-OMePh), **6c** (*m*-OMePh), **6d** (*p*-MePh), **6e** (*m*-MePh), **6f** (*p*-CNPh), **6g** (*m*-CNPh), and **6h** (*m*-CF_3Ph) affords in every case but **6c** a 4-butenyl-1-aryl acetate (**7a,b,d-h**) via an ionic mechanism from the singlet state. Similar rearrangements occurred with *exo*-(1,1a,6,6a-tetrahydrocycloprop[*a*]inden-1-yl)methyl acetate (**14a**) and the 4-cyano derivative (**14b**). Excited state reaction rate constants were determined from reactant fluorescence lifetimes and product quantum yields. A large rate increase relative to **6a** or **14a** was found for the cyano and trifluoromethyl derivatives **6f-h** and **14b**. It is concluded that the rate-determining step involves conversion of the initially formed aromatic excited state to a reactive cyclopropane excited state and that cyclopropane to aromatic ring charge transfer enhances this process.

Early studies of the photochemistry of arylcyclopropanes revealed a fascinating array of reactions.[1] Many of them are exemplified in the photochemistry of *trans*-1,2-diphenylcyclopropane (**1t**), easily the most studied of all arylcyclopropanes[1,2] (Scheme I). One of the most interesting aspects of the photochemistry of **1** is that reactions of apparently quite distinct electronic character occur from the same (singlet) manifold; that

Scheme I



is, while all reactions involve fission of a cyclopropane bond, the pathways to **1c**, **2**, **3**, and **5** are most easily visualized as radical-like or concerted and not involving any highly polar intermediates, whereas the process leading to **4** is ionic.[2]

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