Lithium 3-Lithio-3-tosylalkanoates: β-Acylvinyl Anion Equivalents of β-Lithiated α,β-Unsaturated Carboxylic Acids†

Pedro Bonete and Carmen Nájera*

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain

Received January 3, 1994®

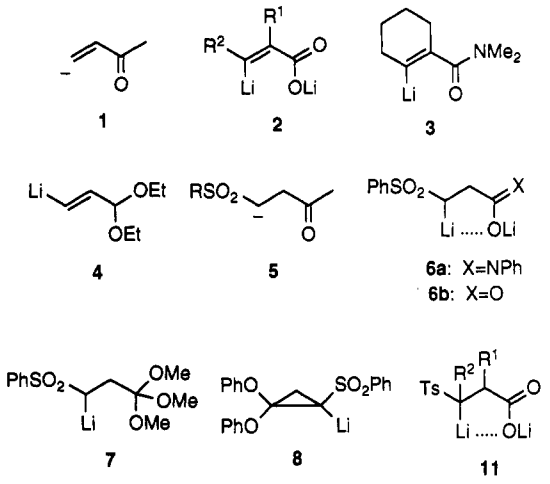
The dilithiation of β-tosylated propanoic, 2-methylpropanoic, and butanoic acid **10** with *n*-butyllithium at −78 °C leads to the corresponding lithium 3-lithio-3-tosylalkanoates **11**. They react with different electrophilic reagents (deuterium oxide, iodine, trimethylchlorosilane, alkyl halides, and acyl chlorides) to give the corresponding 3-substituted tosylated alkanoic acids **12**. When carbonyl compounds are allowed to react with intermediates **11** followed by *in situ* lactonization with trifluoroacetic anhydride and base-promoted elimination α,β-butenolides are obtained. This methodology is applied to the direct synthesis of the rosefuran lactone precursor **14cg**, the *O*-benzyl derivative of (±)-umbelactone (**14ch**), and (±)-andirolactone (**14ci**). The alkylation and acylation reactions of organolithium compounds **11** followed by esterification with hydrogen chloride in methanol and treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) afford α,β- and/or β,γ-unsaturated esters **17** and/or **18** and unsaturated 4-keto esters **19**, respectively. The last methodology has been applied to the synthesis of the unsaturated 4-keto ester **19ae** precursor of the seco acid of (±)-pyrenophorin (**22**).

Introduction

β-Acylvinyl anions of the type **1** are umpoled d^3 reagents[1] which are appropriate intermediates to provide α,β-unsaturated functionality.[2] Unsubstituted derivatives cannot be prepared by kinetic deprotonation of acrylic systems due to the formation of α-acylvinyl anions thermodynamically more stable than the β-ones.[3] Thus, the presence of an electron-donating[3,4] or -withdrawing[5] group in the β-position of the starting α,β-unsaturated carbonyl compound is necessary. However, organolithium compounds such as **2**,[6] **3**,[7] and **4**[5a] have been prepared by bromine–lithium exchange and the last one also by tin–lithium transmetalation[8] (Chart 1). β-Lithiated acrylic (**2a**, $R^1 = R^2 = H$) and crotonic (**2c**, $R^1 = H$, $R^2 = Me$) acids are obtained in low yield because of competition with the elimination reaction to give acetylenic carboxylates.[6a]

A good alternative strategy for β-acylvinyl anions is to use homoenolates[2] stabilized by the sulfone[9] group of the type **5**[10] as β-acylvinyl anion equivalents. The starting sulfones are stable and crystalline compounds and can be easily prepared by simple addition of a sulfinic acid to the α,β-unsaturated carbonyl compound, and the sulfone group can be finally removed by base-mediated elimination. Amide **6a**,[11] orthoester **7**,[12] and cyclopropanone ketal **8**[13] have been used as useful synthetic equivalents for β-lithi-

Chart 1



† Dedicated to Professor E. J. Corey on his 65th birthday.

® Abstract published in *Advance ACS Abstracts*, April 15, 1994.

(1) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239–258.

(2) (a) Werstiuk, N. H. *Tetrahedron* **1983**, *39*, 205–268. (b) Stowell, J. C. *Chem. Rev.* **1984**, *84*, 409–435. (c) Hoppe, D. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 932–948. (d) Werstiuk, N. H. In *Umpoled Synthons*; Hase, T. A., Ed.; John Wiley & Sons: New York, 1987; pp 173–216. (e) Nájera, C.; Yus, M. *Trends Org. Chem.* **1991**, *2*, 155–181.

(3) See, for instance: Feit, B. A.; Haag, B.; Kast, J.; Schmidt, R. R. *J. Chem. Soc., Perkin Trans. 1* **1986**, 2027–2036.

(4) See, for instance: Barua, N. C.; Schmidt, R. R. *Synthesis* **1986**, 1067–1070 and references cited therein.

(5) (a) Meyers, A. I.; Spohn, R. F. *J. Org. Chem.* **1985**, *50*, 4872–4877. (b) Richardson, S. K.; Jeganathan, A.; Watt, D. S. *Tetrahedron Lett.* **1987**, *28*, 2335–2338. (c) Nájera, C.; Yus, M. *J. Org. Chem.* **1988**, *53*, 4708–4715. (d) Nájera, C.; Yus, M. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1387–1391. (e) Parrain, J. L.; Beaudet, I.; Duchêne, A.; Watrelot, S.; Quintard, J. P. *Tetrahedron Lett.* **1993**, *34*, 5445–5448.

(6) Caine, D.; Frobese, A. S. *Tetrahedron Lett.* **1978**, 5167–5170. (b) Caine, D.; Frobese, A. S.; Ukachukwu, V. C. *J. Org. Chem.* **1983**, *48*, 740–741. (c) Caine, D.; Ukachukwu, V. C. *Tetrahedron Lett.* **1984**, *25*, 4357–4360.

(7) Baker, W. R.; Coates, R. M. *J. Org. Chem.* **1979**, *44*, 1022–1024.

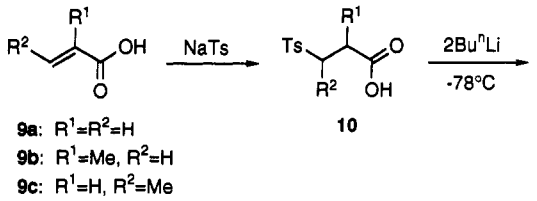
(8) Parrain, J. L.; Duchêne, A.; Quintard, J. P. *J. Chem. Soc., Perkin Trans. 1* **1990**, 187–189.

(9) For reviews about sulfones see: (a) Schank, K. In *Methoden der Organischen Chemie (Houben-Weyl)*; George Thieme Verlag: Stuttgart, 1985, Vol. E/11. (b) *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappoport, Z., Stirling, C., Eds.; J. Wiley & Sons: Chichester, 1988. (c) Simpkins, N. S. In *Sulphones in Organic Synthesis*; Pergamon Press: Oxford, 1993.

(10) (a) Kondo, K.; Tunemoto, D. *Tetrahedron Lett.* **1975**, 1007–1010. (b) Kondo, K.; Tunemoto, D. *Tetrahedron Lett.* **1975**, 1397–1400. (c) Julia, M.; Badet, B. *Bull. Soc. Chim. Fr.* **1975**, 1363–1366. (d) Kondo, K.; Saito, E.; Tunemoto, D. *Tetrahedron Lett.* **1975**, 2275–2278. (e) Fayos, J.; Clardy, J.; Dolby, L. J.; Farnham, T. *J. Org. Chem.* **1977**, *42*, 1349–1352. (f) Kotake, H.; Inomata, K.; Oayama, S.; Kinushita, H. *Chem. Lett.* **1977**, 73–76. (g) Inomata, K.; Aoyama, S.; Kotake, H. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 930–932. (h) Menicagli, R.; Wis, M. L.; Lardicci, L.; Botteghi, C.; Caccia, G. *J. Chem. Soc., Perkin Trans. 1* **1979**, 847–850. (i) Cooper, G. K.; Dolby, L. J. *J. Org. Chem.* **1979**, *44*, 3414–3416. (j) Yoshida, T.; Saito, S. *Chem. Lett.* **1982**, 165–168. (l) Nokami, J.; Ono, T.; Kurihara, H.; Wakabayashi, S. *Chem. Lett.* **1982**, 607–608. (m) Yoshida, T.; Saito, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3931–3932. (n) Fürst, A.; Labler, L.; Meier, W. *Helv. Chim. Acta* **1982**, *65*, 1499–1521. (o) Otera, J.; Mandai, T.; Shiba, M.; Saito, T.; Shimohata, K.; Takemor, K.; Kawasaki, Y. *Organometallics* **1983**, *2*, 332–336. (p) Craig, D.; Etheridge, C. J.; Smith, A. M. *Tetrahedron Lett.* **1992**, *33*, 7445–7446. (q) Semmelhack, M. F.; Knochel, P.; Singleton, T. *Tetrahedron Lett.* **1993**, *34*, 5051–5054.

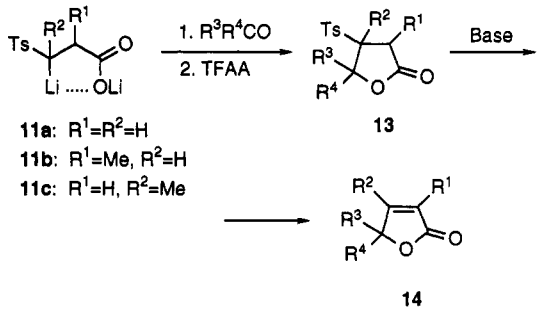
0022-3263/94/1959-3202$04.50/0

Scheme 1



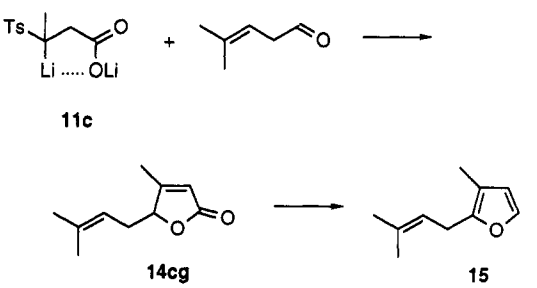
9a: R^1=R^2=H
9b: R^1=Me, R^2=H
9c: R^1=H, R^2=Me

Scheme 2



11a: R^1=R^2=H
11b: R^1=Me, R^2=H
11c: R^1=H, R^2=Me

Scheme 3



ated acrylic acid (Chart 1). However, the simplest and first described anion **6b**,[14] prepared by lithiation of 3-(phenylsulfonyl)propanoic acid with LDA at −50 °C and characterized by deuterolysis,[15] afforded an adduct in low yield (37%) with cyclopentanone as the only electrophile tried. We have studied the general preparation of organolithium derivatives of type **11** from the corresponding sulfones **10** derived from representative α,β-unsaturated carboxylic acids **9** and their synthetic applications as β-acylvinyl anion equivalents.[16]

Results and Discussion

The reaction of sulfones **10a–c**, prepared by addition of sodium *p*-toluenesulfinate in EtOH or HOAc to α,β-unsaturated carboxylic acids **9a–c**,[17] with BuLi[18] (1:2 molar ratio) in THF at −78 °C yielded the corresponding lithium 3-lithio-3-tosylalkanoates **11**. These were chemically characterized by reaction with D_2O to lead to deuterated compounds **12aa**, **12ba**, and **12ca** (Scheme 1 and Table 1, entries 1, 13, and 16). The *in situ* reaction of intermediates **11** with other electrophiles such as I_2, TMSCl, alkyl halides, and carboxylic acid chlorides followed by acidic hydrolysis afforded compounds **12** (Scheme 1 and Table 1). The alkylation reaction with BuI was carried out in the presence of HMPA, and in the case of compounds **12ba–bj** (Table 1, entries 13–15), derived from methacrylic acid (**9b**), they were obtained as mixture of diastereoisomers (*ca.* 3:1).

The addition of organolithium compounds **11** to carbonyl compounds was applied to the synthesis of α,β-butenolides. By reaction of intermediates **11** with aldehydes or ketones at −78 °C to −40 °C[19] followed by *in situ* lactonization with TFAA (1:2 molar ratio) at −40 °C, diastereomeric lactones **13**[20] were obtained (Scheme 2). Lactones **13** derived from aldehydes were isolated and treated with DBU or Et_3N in CH_2Cl_2 affording the corresponding butenolides **14**[22] (Scheme 2 and Table 2). In the case of lactones derived from ketones the elimination of *p*-toluenesulfinic acid was carried out *in situ* by addition of a 10-fold excess of Et_3N at −20 °C to the reaction mixture. This methodology has been applied to the synthesis of naturally occurring α,β-butenolides such as the lactone precursor **14cg** of rosefuran (**15**),[30] the *O*-benzyl derivative **14ch** of (±)-umbelactone (**16**),[31] and (±)-andirolactone (**14ci**).[32]

The α,β-butenolide **14cg**[27] was prepared starting from intermediate **11c** (derived from crotonic acid **9c** *via* its tosylated derivative **10c**) by reaction with 4-methyl-3-pentenal[34] in 40% yield (Table 2, entry 9). This butenolide

(11) Tanaka, K.; Wakita, H.; Yoda, H.; Kaji, A. *Chem. Lett.* **1984**, 1359–1362.
(12) (a) De Lombaert, S.; Nemery, I.; Rockens, B.; Carretero, J. C.; Kimmel, T.; Ghosez, L. *Tetrahedron Lett.* **1986**, *27*, 5099–5102. (b) Carretero, J. C.; De Lombaert, S.; Ghosez, L. *Tetrahedron Lett.* **1987**, *28*, 2135–2138. (c) Carretero, J. C.; Ghosez, L. *Tetrahedron Lett.* **1988**, *29*, 2059–2062.
(13) Pohmakotr, M.; Ratchataphusit, J. *Tetrahedron* **1993**, *49*, 6473–6482.
(14) Iwai, K.; Kosugi, H.; Miyazaki, A.; Uda, H. *Synth. Commun.* **1976**, *6*, 357–363.
(15) The reaction takes place in 72% yield, but the amount of deuterium incorporation is not indicated.[14]
(16) For preliminary communication, see: Bonete, P.; Nájera, C. *Tetrahedron Lett.* **1992**, *33*, 4065–4068.
(17) Kamogawa, H.; Kusaka, H.; Nanasawa, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3379–3380.
(18) When the lithiation of compound **10a** was carried out with LDA[14] at −78 °C and the resulting intermediate **11a** was treated with D_2O compound **12aa** was obtained in 87% yield with 72% of deuterium incorporation.
(19) The addition of intermediates **11** to ketones is a reversible process at temperatures above −40 °C.[12c]
(20) The reductive desulfonylation of the corresponding phenylsulfonyl derivatives of lactones **13** to γ-lactones has been carried out with sodium amalgam[12b] following the general procedure reported by Trost *et al.*[21]
(21) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1970**, 3477–3480.
(22) Intermediates **6a**[11] and **7**[12b] have also been used in the synthesis of butenolides.
(23) Solladié, G.; Fréchou, C.; Demailly, G.; Greck, C. *J. Org. Chem.* **1986**, *51*, 1912–1914.
(24) Canonne, P.; Bélanger, D.; Lemay, G. *J. Org. Chem.* **1982**, *47*, 3953–3959.
(25) Musierowicz, S.; Wróblewski, A. E. *Tetrahedron* **1978**, *34*, 461–465.
(26) Kresze, G.; Kloimstein, L.; Runge, W. *Ann. Chem.* **1976**, 979–986.
(27) (a) Gedge, D. R.; Pattenden, G. *Tetrahedron Lett.* **1977**, 4443–4446. (b) Takano, S.; Morimoto, M.; Satoh, S.; Ogasawara, K. *Chem. Lett.* **1984**, 1261–1262.
(28) Ortuño, R. M.; Bigorra, J.; Font, J. *Tetrahedron* **1987**, *43*, 2199–2202.
(29) For syntheses, see: Orduña, A.; Zepeda, G.; Tamariz, J. *Synthesis* **1993**, 375–377 and references cited therein.
(30) Component of the oil of rose. For syntheses, see: Marshall, J. A.; DuBay, W. J. *J. Org. Chem.* **1993**, *58*, 3602–3603 and references cited therein.
(31) (+)-Umbelactone[28] has been isolated from *Memycelon Umbelatum* Burm, the crude extract of this plant has activity against Ranikhe disease virus and spasmolytic and antiamphetamine activity.[6b]
(32) Andirolactone has been isolated from *Cedrus libanotica* wood and has potential biological and medicinal properties.[33]
(33) Avcibasi, H.; Anil, H.; Toprak, M. *Phytochemistry* **1987**, *26*, 2852–2854.
(34) Obtained by oxidation of 4-methyl-3-penten-1-ol (Aldrich) with PCC.[35]
(35) Adams, L. L.; Luzzio, F. A. *J. Org. Chem.* **1989**, *54*, 5387–5390.

Table 1. Reaction of Tosylated Lithium Homoenolates 11 with Electrophiles

entry	intermediate	electrophile	product no.	product X	yield,[a] %	R_f[b] or mp,[c] °C
1	**11a**	D_2O	**12aa**	D	91[d]	113–115
2	**11a**	I_2	**12ab**	I	62[e]	147–148
3	**11a**	Me_3SiCl	**12ac**	Me_3Si	35	107–108
4	**11a**	MeI	**10c**	Me	85	133–134
5	**11a**	CH_2=$CHCH_2Br$	**12ad**	CH_2=$CHCH_2$	36	87–88
6	**11a**	BuI[f]	**12ae**	Bu	76[g]	0.35
7	**11a**	$PhCH_2Br$	**12af**	$PhCH_2$	60[e]	160–161
8	**11a**	(*E*)-PhCH=$CHCH_2Br$	**12ag**	(*E*)-PhCH=$CHCH_2$	69[e]	139–140
9	**11a**	PrCOCl	**12ah**	PrCO	63[e]	130–131
10	**11a**	i-PrCOCl	**12ai**	i-PrCO	66[e]	131–132
11	**11a**	PhCOCl	**12aj**	PhCO	56[e]	155–156[h]
12	**11a**	n-$C_8H_{17}COCl$	**12ak**	n-$C_8H_{17}CO$	57[i]	113–114
13	**11b**	D_2O	**12ba**[j]	D	82[k]	115–116
14	**11b**	$PhCH_2Br$	**12bf**[j]	$PhCH_2$	65[e]	177–178[l]
15	**11b**	PhCOCl	**12bj**[j]	PhCO	75[e]	140–142[l]
16	**11c**	D_2O	**12ca**	D	89[m]	129–131
17	**11c**	PhCOCl	**12cj**	PhCO	61[e]	159–161

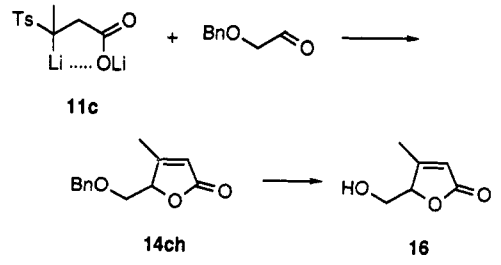
[a] Isolated yield based on starting sulfone **10**, after column chromatography; silica gel. [b] Hexane–AcOEt/2:1. [c] Hexane–CH_2Cl_2. [d] 98% of deuterium incorporation (^1H NMR). [e] After recrystallization. [f] In the presence of HMPA. [g] Crude compound; it was transformed into the corresponding unsaturated ester **17**. [h] Lit.[5d] mp 153–155 °C. [i] Reversed-phase silica gel. [j] Mixture of diastereomers (*ca.* 3:1 ^{13}C NMR). [k] 98% of deuterium incorporation (MS). [l] For the main diastereomer. [m] 97% of deuterium incorporation (MS).

Table 2. Synthesis of α,β-Butenolides 14

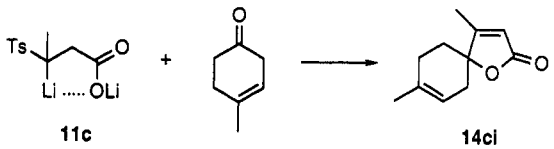
entry	base (time, h)	intermediate	carbonyl compd	product no.	R^3	R^4	yield,[a] %	R_f[b]
1	DBU (0.5)	**11a**	i-PrCHO	**14aa**	i-Pr	H	68	0.51[c]
2	Et_3N (20)	**11a**	t-BuCHO	**14ab**	t-Bu	H	50[d]	0.61[e]
3	DBU (1.5)	**11a**	n-$C_5H_{11}CHO$	**14ac**	n-C_5H_{11}	H	35	0.63[f]
4	Et_3N (3)[g]	**11a**	cyclopentanone	**14ad**	$-(CH_2)_4-$		90	0.59[h]
5	Et_3N (30)	**11a**	cyclohexanone	**14ae**	$-(CH_2)_5-$		72	0.54[i]
6	Et_3N (20)	**11a**	PhCOEt	**14af**	Ph	Et	76	0.55[j]
7	Et_3N (12)	**11b**	PhCOEt	**14bf**	Ph	Et	53	0.57[k,l]
8	Et_3N (12)	**11c**	PhCOEt	**14cf**	Ph	Et	76	0.56[m]
9	Et_3N (12)	**11c**	Me_2C=$CHCH_2CHO$	**14cg**	Me_2C=$CHCH_2$	H	40	0.39[n]
10	Et_3N (12)	**11c**	$PhCH_2OCH_2CHO$	**14ch**	$PhCH_2OCH_2$	H	31	0.41[o]
11	Et_3N (12)	**11c**	4-methyl-3-cyclohexanone	**14ci**			25	0.62[p]

[a] Isolated yield based on starting sulfone **10**, after column chromatography; silica gel. [b] Hexane/AcOEt = 2/1. [c] Lit.[10p]. [d] The synthesis was carried out without isolation of lactone **13ab**. [e] Lit.[23] mp 59–61 °C. [f] Lit.[23] [g] Under reflux. [h] Lit.[24] bp 116 °C/7 mmHg. [i] Lit.[24] 124 °C/7 mmHg. [j] Lit.[25] bp (bath) 120–125 °C/0.1 mmHg. [k] Bp 130 °C/0.1 Torr (Kugelrohr). [l] Lit.[26] [m] bp 145 °C/0.1 Torr. [n] Lit.[27] bp 130 °C/0.08 Torr. [o] Lit.[28] [p] Lit.[29] mp 48–49 °C.

Scheme 4



Scheme 5



14cg had already been converted to the corresponding rosefuran (**15**) by reduction with DIBALH in 80% yield[27] (Scheme 3).

The (±)-umbelactone *O*-benzyl derivative (**14ch**)[6b] was prepared by reaction of dianion **11c** with 2-(benzyloxy)-acetaldehyde in 31% yield (Table 2, entry 10); subsequent hydrogenolysis of the benzyl group gave umbelactone **16**[6b] (Scheme 4).

Finally, the terpenoid spirobutenolide (±)-andirolactone (**14ci**)[32] was also prepared from organolithium compound **11c** and 4-methylcyclohex-3-en-1-one[36] in 25% yield (Scheme 5 and Table 2, entry 11). This synthesis is more direct than others previously described.[29]

We have studied other applications of organolithium compounds **11** as β-acylvinyl anion equivalents in alkylation and acylation reactions. In the first case the reaction of alkyl halides with intermediates **11** was followed by esterification with a 5 M solution of HCl in CH_3OH followed by DBU-mediated elimination in CH_2Cl_2 affording α,β- and/or β,γ-unsaturated methyl esters **17** and/or **18**,[37,38] depending on the structure of the alkyl halide (Scheme 6 and Table 3). With *n*-alkyl halides such as BuI

(36) Corey, E. J.; Watt, D. S. *J. Am. Chem. Soc.* **1973**, *95*, 2303–2311.

(37) Similar results have been obtained with 2-(diethylamino)-4-(phenylsulfonyl)-2-butenenitrile: De Lombaert, S.; Ghosez, L. *Tetrahedron Lett.* **1984**, *25*, 3475–3478.

(38) A recent work reports that treatment of homologous phenyl esters with DBU in THF gives mixtures (*ca.* 6:1) of α,β- and β,γ-unsaturated esters.[13]

(39) De Kimpe, N.; Schamp, N. *J. Org. Chem.* **1975**, *40*, 3749–3755.

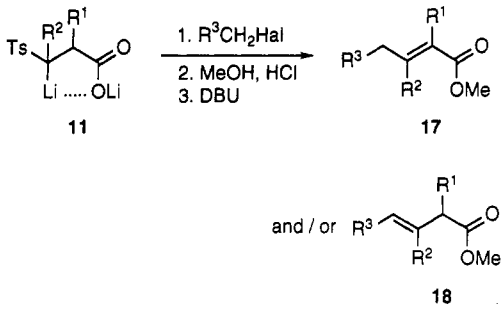
(40) Murali, D.; Khrishna Rao, R. S. *Synthesis* **1987**, 254–256.

(41) Hoye, T. R.; Richardson, W. S. *J. Org. Chem.* **1989**, *54*, 688–693.

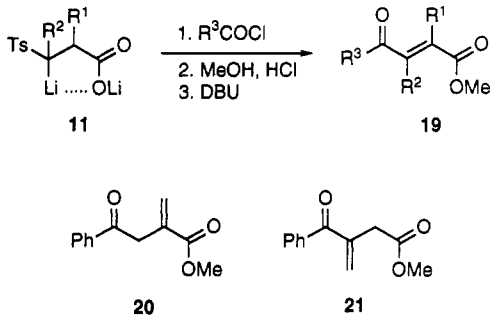
(42) Chiusoli, G. P.; Salerno, G.; Giroldini, W.; Pallini, L. *J. Organomet. Chem.* **1981**, *219*, C16–C20.

(43) Najafi, M. R.; Wang, M.-L.; Zweifel, G. *J. Org. Chem.* **1991**, *56*, 2468–2476.

Scheme 6



Scheme 7



and with methallyl bromide, α,β-unsaturated esters **17** were mainly or exclusively obtained, the configuration for compounds **17aa**, **17ab**, and **17ba** being *E* (Table 3, entries 1, 2, and 6). When benzyl or allyl bromides such as benzyl, 3,3-dimethylallyl, and cinnamyl bromide were used as alkylating reagents, β,γ-unsaturated esters **18** were mainly or exclusively obtained (Table 3, entries 3–5, 7, and 9). For derivatives of acrylic acid (**9a**) only esters **18ac**, **18ad**, and **18ae** were mainly or exclusively obtained with the *E*-configuration. However, in the case of alkylation of methacrylic and crotonic acid derivatives with benzyl bromide, mixtures of esters **17** and **18** were obtained. The configuration of compounds **17bd** and **18bd** derived from methacrylic acid was *E* and for compounds **17cd** and **18cd** derived from crotonic acid was a 1:1 mixture of *Z*:*E* diastereoisomers.

The acylation reaction of dianions **11** followed by esterification with a 5 M HCl in CH_3OH and DBU elimination of *p*-toluenesulfinic acid led to unsaturated 4-keto esters **19** (Scheme 7 and Table 4). In the case of acrylic acid derivatives **19aa–ae** (Table 4, entries 1–5) the β-elimination reaction was stereoselective and unsaturated ketoesters with *E*-configuration were produced. Only in the case of compound **19af** (Table 4, entry 6) was a mixture (*Z*:*E* = 3:7) of diastereoisomers obtained. In the case of the reaction of methacrylic and crotonic acid intermediates **11b** and **11c** with benzoyl chloride mixtures of *Z*:*E* diastereoisomers **19bd** and **19cd** together with regioisomers **20** and **21** were formed (Scheme 7 and Table 4, entries 7 and 8).

This methodology has been applied to the synthesis of the precursor **19ae** of the seco acid of (±)-pyrenophorin (**22**).[56] Thus, when intermediate **11a** was allowed to react with acid chloride **23** (prepared from γ-valerolactone[57]) the corresponding 4-keto ester **19ae** was stereoselectively obtained (Scheme 8 and Table 4, entry 5). A similar strategy was reported by Stille using Pd-catalyzed coupling of a β-(tributylstannyl)acrylate with acyl chloride **23**.[57]

From the results described in this paper we conclude that 3-tosyl adducts of α,β-unsaturated acids are readily available and stable starting materials for the preparation of 3-lithiated 3-tosyl lithium alkanoates, which are versatile β-acylvinyl anion equivalents, especially useful in the synthesis of α,β-butenolides, unsaturated esters, and 4-keto esters.

Experimental Section

General. Melting points were obtained with a Reichert Thermovar apparatus and are uncorrected. IR spectra were obtained on a Pye Unicam SP3-200 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer with TMS as internal standard and using $CDCl_3$ as solvent. ^{13}C-NMR assignments were made on the basis of DEPT experiments. MS spectra were measured in a Hewlett-Packard 5988A by GLC or direct injection (EI, 70 eV). Elemental analyses were performed by the Microanalyses Service of the University of Alicante. GC analyses were determined with a Hewlett-Packard HP-5890 instrument equipped with a 25-m WCOT capillary column (0.22-mm diameter, 0.2-μm film thickness OV-101 stationary phase) using N_2 (2 mL/min) as the carrier gas, $T_{injector}$ = 270 °C, T_{column} = 60 °C, and a range of 60–270 °C (15 °C/min). TLC was carried out on Schleicher & Schuell F1500/LS 254 plates coated with a 0.2-mm layer of silica gel, using a mixture of hexane/EtOAc (2:1) as eluent, and UV visualization. Column chromatography was performed using 70–270-mesh silica gel 60 and hexane/EtOAc as eluent. All starting materials were of the best grade available (Aldrich, Fluka) and were used without further purification. THF was dried with $LiAlH_4$ under Ar atmosphere, and CH_2Cl_2 was dried over P_2O_5.

Preparation of 3-Tosylalkanoic Acids (10). General Procedure. A mixture of α,β-unsaturated acid **9** (20 mmol) and sodium *p*-toluenesulfinate hydrate (Aldrich, 4.2 g, *ca.* 20 mmol) in EtOH (for **10a**, 25 mL) or HOAc (for **10b,c**, 50 mL) was stirred for 1 d at rt (for **10a**) or under reflux (for **10b,c**). In the case of compound **10a** the precipitate was filtered (G-3), washed with EtOH (5 mL), dissolved in H_2O (50 mL), acidifed with 2 N HCl (50 mL), and extracted with ether (3 × 40 mL). In the case of compound **10b,c** the reaction mixture was extracted with ether (100 mL) and the organic layer washed with 2 N aqueous HCl (50 mL) and water (4 × 40 mL). The organic layer was finally dried (Na_2SO_4) and evaporated to afford crude compounds **10** which were purified by recrystallization from hexane/dichloromethane.

3-Tosylpropanoic acid (10a): 72% yield; mp 113–114 °C; IR ($CHCl_3$) 3700–2300, 1700, 1310, 1140 cm^{-1}; ^1H NMR δ 2.45 (s,

(44) Negishi, E.; Matsushita, H.; Okukado, N. *Tetrahedron Lett.* **1981**, *22*, 2715–2718.
(45) Van der Veen, R. H.; Cerfontain, H. *J. Org. Chem.* **1985**, *50*, 342–346.
(46) Anderson, R. J.; Corbin, V. L.; Cotterrell, G.; Cox, G. R.; Henrick, C. A.; Schaub, F.; Siddall, J. B. *J. Am. Chem. Soc.* **1975**, *97*, 1197–1204.
(47) Franke, A.; Mattern, G.; Traber, W. *Helv. Chim. Acta* **1975**, *58*, 278–283.
(48) Salomon, M. F.; Pardo, S. N.; Salomon, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 3797–3802.
(49) Kulinkovich, O. G.; Tischenko, I. G.; Romashin, I. N.; Savitskaya, L. N. *Synthesis* **1986**, 378–379.
(50) Montecatini Edison S. p. A. It. Patent, 796247, 1967; *Chem. Abstr.* **1967**, *76*, 72045k.
(51) Bennet, G. B.; Mason, R. B. *J. Org. Chem.* **1977**, *42*, 1919–1922.
(52) Landini, D.; Quici, S.; Rolla, F. *Synthesis* **1975**, 397–399.
(53) Machinaga, N.; Kibayashi, C. *Tetrahedron Lett.* **1993**, *34*, 841–844.
(54) Sestrick, M. R.; Miller, M.; Hegedus, L. S. *J. Am. Chem. Soc.* **1992**, *114*, 4079–4088.
(55) El-Ghandour, N.; Henri-Rousseau, O.; Soulier, J. *Bull. Soc. Chem. Fr.* **1972**, *7*, 2817–2829.

(56) The macrolide dilactone (−)-pyrenophorin is an antifungal antibiotic produced by the plant pathogenic fungi *Pyrenophora avenae* and *Stemphylium radicinum*. For syntheses see ref 53 and references cited therein.
(57) Labadié, J. W.; Tueting, D.; Stille, J. K. *J. Org. Chem.* **1983**, *48*, 4634–4642.

Table 3. Synthesis of Unsaturated Esters 17 and 18

entry	intermediate	R^3CH_2Hal	product no.	product formula	yield,[a] %	R_f[b]
1	**11a**	BuI	**17aa**	(*E*)-BuCH=CHCO$_2$Me	66	0.80[c]
2	**11a**	H_2C=C(Me)CH_2Br	**17ab**	(*E*)-Me_2C=CHCH=$CHCO_2Me$		
			18ab	(*E*)-CH_2=CMeCH=$CHCH_2CO_2Me$	51[d]	0.80[e,f]
3	**11a**	Me_2C=$CHCH_2Br$	**18ac**	Me_2C=CHCH=$CHCH_2CO_2Me$	25	0.76[g,h]
4	**11a**	$PhCH_2Br$	**18ad**	(*E*)-PhCH=$CHCH_2CO_2Me$	50	0.73[i]
5	**11a**	(*E*)-PhCH=$CHCH_2Br$	**18ae**	PhCH=CHCH=$CHCH_2CO_2Me$	38	0.78[j,k]
6	**11b**	BuI	**17ba**	(*E*)-BuCH=$CMeCO_2Me$	54	0.83[l]
7	**11b**	$PhCH_2Br$	**17bd**	(*E*)-$PhCH_2CH$=$CMeCO_2Me$		
			18bd	(*E*)-PhCH=$CHCHMeCO_2Me$	44[m]	0.80[e,n]
8	**11c**	BuI	**17ca**	Bu(Me)C=$CHCO_2Me$	52	0.82[o,p]
9	**11c**	$PhCH_2Br$	**17cd**	$PhCH_2C$(Me)=$CHCO_2Me$		
			18cd	PhCH=C(Me)CH_2CO_2Me	35[q]	0.76[e,r]

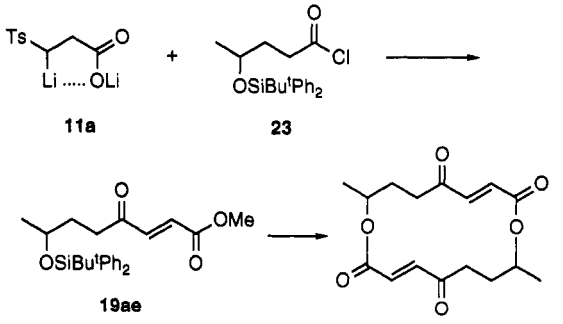
[a] Isoalted yield after flash chromatography (silica gel), based on starting sulfone **10**. [b] Hexane:AcOEt/2:1. [c] Lit.[39] [d] Overall yield for compounds **17ab** and **18ab** obtained in 12:1 molar ratio (^{13}C NMR). [e] Could not be separated. [f] Compound **17ab**: lit.[40] bp 108 °C/25 mmHg. [g] Mixture of *Z*:*E* diastereomers (1:2.5, ^{1}H NMR). [h] Lit.[37] [i] Lit.[41] bp 104–106 °C/1.7 mmHg. [j] Mixture of *E*,*E*:*Z*,*E* diastereomers (5:1, ^{1}H NMR). [k] Lit.[42] [l] Lit.[43] bp 65–70 °C/2 mmHg. [m] Overall yield for compounds **17bd** and **18bd** obtained in 1:1 molar ratio (GC). [n] Compound **17bd**, lit.[44]; compound **18bd**, lit.[45] [o] Obtained as mixture of *Z*:*E* diastereomers (1:1.9, GC). [p] Lit.,[46] bp (bath) 55 °C/10 mmHg. [q] Compounds **17cd** and **18cd** were obtained in 1:13 molar ratio (GC) as mixture of *Z*:*E* diastereomers (1:1, GC). [r] Compound **17cd**, lit.[47]; compound **18cd**, lit.[48]

Table 4. Synthesis of Unsaturated 4-Keto Esters 19

entry	intermediate	product no.	R^3	yield,[a] %	R_f,[b] or mp,[c] °C
1	**11a**	**19aa**	n-Pr	60	38–39[d]
2	**11a**	**19ab**	i-Pr	42	0.68[e]
3	**11a**	**19ac**	t-Bu	80	0.76[f]
4	**11a**	**19ad**	Ph	48	30–31[g,h]
5	**11a**	**19ae**	CH_3C(OSiBu-*t*-Ph_2)HCH_2CH_2	61	0.79[i]
6	**11a**	**19af**[j]	n-C_8H_{17}	35	55–56[k]
7	**11b**	**19bd**[l]	Ph	45[m]	*n*, *o*
8	**11c**	**19cd**[p]	Ph	35[q]	*r*, *o*

[a] Isolated yield after flash chromatography on silica gel, based on starting sulfone **10**. [b] Hexane/AcOEt = 2/1. [c] Hexane. [d] Lit.[49] mp 38–39.5 °C. [e] Lit.[50] [f] Lit.[51] bp 65–70 °C/0.1 Torr. [g] From hexane/ether. [h] Lit.[52] mp 31 °C. [i] Lit.[53] [j] Mixture of *Z*:*E* diastereomers (3:7, GLC) separated by flash chromatography and recrystallization. [k] For *Z*-diastereoisomer, lit.[54] [l] Mixture of *Z*:*E* diastereoisomers (1:2, GC). [m] 12% of compound **20** was also obtained. [n] R_f = 0.70 and 0.77 for *Z* and *E* diastereoisomers, respectively. [o] Lit.[55] [p] Mixture of *Z*:*E* diastereoisomers (1:1, GC). [q] 7% of compound **21** was also obtained. [r] R_f = 0.70 and 0.76 for *Z* and *E* diastereoisomers, respectively.

Scheme 8



3H), 2.78 (t, *J* = 7.6 Hz, 2H), 3.39 (t, *J* = 7.6 Hz, 2H), 7.37, 7.79 (2d, *J* = 8.3 Hz, 4H), 8.36 (br s, 1H); ^{13}C NMR δ 21.62, 27.60, 51.20, 128.15, 130.08, 135.27, 145.27, 175.36; *m*/*z* 228 (M$^+$, 3), 156 (29), 155 (13), 139 (20), 108 (10), 107 (13), 92 (48), 91 (100), 77 (13), 72 (35), 65 (49), 63 (18), 56 (10), 55 (33), 45 (25), 44 (10). Anal. Calcd for $C_{10}H_{12}O_4S$: C, 52.62; H, 5.30. Found: C, 52.36; H, 5.41.

2-Methyl-3-tosylpropanoic acid (10b): 45% yield; mp 116–117 °C; IR ($CHCl_3$) 3400–2400, 1710, 1300, 1140 cm^{-1}; ^{1}H NMR δ 1.36 (d, *J* = 7.1 Hz, 3H), 2.45 (s, 3H), 2.96–3.10 (m with dd at 3.07 *J* = 16.2, 5.6 Hz, 2H), 3.66 (dd, *J* = 16.2, 6.2 Hz, 1H), 7.37, 7.80 (2d, *J* = 8.2 Hz, 4H), 9.60 (br s, 1H); ^{13}C NMR δ 17.59, 21.62, 34.67, 58.44, 128.09, 129.99, 136.03, 145.09, 179.25; *m*/*z* 242 (M$^+$, 5), 173 (17), 156 (24), 155 (17), 139 (18), 92 (42), 91 (100), 89 (11), 87 (11), 86 (11), 63 (11), 45 (18), 41 (24). Anal. Calcd for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.84. Found: C, 54.00; H, 5.94.

3-Tosylbutanoic acid (10c): 75% yield; IR ($CHCl_3$) 3400–2500, 1710, 1300, 1140 cm^{-1}; ^{1}H NMR δ 1.32 (d, *J* = 6.8 Hz, 3H), 2.45 (m with s at 2.45, 4H), 3.04 (dd, *J* = 16.7, 4.2 Hz, 1H), 3.54 (m, 1H), 7.37, 7.76 (2d, *J* = 8.0 Hz, 4H), 10.05 (br s, 1H); ^{13}C NMR δ 13.81, 21.53, 34.31, 56.26, 128.95, 129.86, 133.15, 145.15, 175.36; *m*/*z* 242 (M$^+$, 9), 156 (24), 139 (13), 107 (10), 92 (98), 91 (100), 89 (14), 87 (59), 69 (53), 65 (47), 63 (13), 45 (29), 43 (22), 41 (20). Anal. Calcd for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.84. Found: C, 54.86; H, 6.10.

Preparation of 3-Tosylated Lithium 3-Lithioalkanoates 11 and Reaction with Electrophiles. Isolation of Compounds 10c and 12. General Procedure. To a solution of compound **10** (1 mmol) in dry THF (15 mL) was slowly added a 1.6 M solution of *n*-BuLi in hexane (1.4 mL, 2.2 mmol) at −78 °C under Ar. The resulting yellow solution was stirred for 1 h, and then the electrophile was added (see Table 1). The reaction mixture was allowed to rise to rt overnight, quenched with 2 N aqueous HCl (5 mL), and extracted with ether (3 × 15 mL). The organic layer[58] was dried (Na_2SO_4) and evaporated to give crude compounds **10c** and **12** which were purified by recrystallization, except for compound **12aj** which was purified by column chromatography on reversed-phase silica gel. Compounds **12ae**, **12be**, and **12ce** were transformed into compounds **17** without purification. Physical data are included in Table 1; spectral and analytical data follow.

3-Deuterio-3-tosylpropanoic acid (12aa): IR ($CHCl_3$) 3600–2600, 1700, 1310, 1145 cm^{-1}; ^{1}H NMR δ 2.44 (s, 3H), 2.76 (d, *J* = 7.6 Hz, 2H), 3.39 (t, *J* = 7.6 Hz, 1H), 7.36, 7.77 (2d, *J* = 8.1 Hz, 4H), 10.46 (br s, 1H); ^{13}C NMR δ 21.46, 27.42, 50.76 (t, *J* = 21.7 Hz), 127.98, 129.96, 135.02, 145.17, 175.20; *m*/*z* 229 (M$^+$, 6), 156 (22), 155 (17), 92 (16), 91 (100), 65 (29), 57 (19), 45 (12). Anal. Calcd for $C_{10}H_{11}DO_4S$: C, 52.39; H/D, 5.72. Found: C, 52.17; H/D, 5.38.

3-Iodo-3-tosylpropanoic acid (12ab): IR (Nujol) 3400–2500, 1700, 1310, 1140 cm^{-1}; ^{1}H NMR δ 2.48 (s, 3H), 3.09 (dd, *J* = 17.4, 10.2 Hz, 1H), 3.61 (dd, *J* = 17.4, 3.9 Hz, 1H), 5.27 (dd, *J* = 10.2, 3.9 Hz, 1H), 7.40, 7.86 (2d, *J* = 8.2 Hz, 4H), 8.57 (br s, 1H); ^{13}C NMR δ 24.76, 34.06, 39.69, 130.00, 130.86, 146.22, 173.82; *m*/*z* 354 (M$^+$, 26), 326 (10), 172 (14), 155 (17), 139 (92), 128 (16), 127 (16), 92 (38), 91 (100), 89 (16), 77 (13), 65 (54), 63 (17), 45 (17). Anal. Calcd for $C_{10}H_{11}IO_4S$: C, 33.91; H, 3.13. Found: C, 33.00; H, 3.14.

3-Tosyl-3-(trimethylsilyl)propanoic acid (12ac): IR (film) 3500–2500, 1705, 1300, 1140 cm^{-1}; ^{1}H NMR δ 0.28 (s, 9H), 2.37

(58) When alkyl halides were used as electrophiles the organic layer was extracted with 0.5 M NaOH (3 × 30 mL). The aqueous extracts were combined, acidulated with concd HCl and extracted with ether (3 × 15 mL). The organic layer was washed with 2 N HCl (3 × 10 mL), dried (Na_2SO_4), and evaporated to give crude compounds **12**.

(s, 3H), 2.60 (dd, J = 18.2, 5.3 Hz, 1H), 2.73 (dd, J = 18.2, 6.6 Hz, 1H), 3.28 (dd, J = 6.6, 5.3 Hz, 1H), 7.26, 7.73 (2d, J = 8.0 Hz, 4H), 9.69 (br s, 1H); ^{13}C NMR δ −1.47, 21.40, 31.00, 51.72, 128.02, 129.53, 137.02, 144.17, 175.92; m/z 300 (M^+, <1), 285 (21), 255 (50), 228 (11), 195 (13), 180 (18), 149 (32), 140 (11), 139 (98), 129 (100), 118 (10), 92 (14), 91 (63), 89 (10), 77 (12), 75 (73), 74 (10), 73 (98), 65 (27), 13 (13), 55 (17), 45 (27), 43 (16). Anal. Calcd for $C_{13}H_{20}O_4SSi$: C, 51.97; H, 6.71. Found: C, 52.10; H, 6.84.

3-Tosyl-5-hexenoic acid (12ad): IR ($CHCl_3$) 3600–2700, 3060, 3020, 1710, 1635, 1295, 1145 cm^{-1}; ^{1}H NMR δ 2.27, 2.70 (2m, 2H), 2.46 (s, 3H), 2.60, 2.90 (2dd, J = 17.3, 6.3 Hz, 2H), 3.62 (m, 1H), 5.10 (d, J = 16.7 Hz, 1H), 5.11 (d, J = 10.5 Hz, 1H), 5.69 (m, 1H), 7.38, 7.95 (2d, J = 8.0 Hz, 4H), 10.51 (br s, 1H); ^{13}C NMR δ 21.64, 32.17, 32.78, 59.92, 119.56, 129.07, 129.96, 132.42, 133.91, 145.26, 175.75; m/z 269 (M^+ + 1, <1), 210 (M^+ − CH_2COOH), 157 (46), 140 (29), 139 (22), 113 (39), 111 (29), 95 (10), 92 (38), 91 (61), 71 (100), 70 (10), 67 (50), 65 (38), 43 (13), 41 (26). Anal. Calcd for $C_{13}H_{16}O_4S$: C, 58.19; H, 6.01. Found: C, 57.82; H, 6.11.

3-Tosylheptanoic acid (12ae): IR ($CHCl_3$) 3500–2500, 1700, 1300, 1140 cm^{-1}; ^{1}H NMR δ 0.84 (t, J = 7.0 Hz, 3H), 1.25–1.70 (m, 6H) 2.44 (s, 3H), 2.53 (dd, J = 17.2, 6.7 Hz, 1H), 2.91 (dd, J = 17.2, 6.0 Hz, 1H), 3.55 (m, 1H), 7.36, 7.77 (2d, J = 8.3 Hz, 4H), 10.49 (br s, 1H); ^{13}C NMR δ 13.47, 21.43, 22.16, 28.02, 28.29, 32.99, 60.62, 128.81, 129.75, 133.84, 144.96, 175.62; m/z 284 (M^+, <1), 157 (38), 155 (13), 140 (12), 139 (43), 133 (10), 129 (64), 123 (11), 111 (65), 93 (11), 92 (60), 91 (100), 89 (15), 87 (13), 83 (75), 77 (12), 73 (14), 69 (47), 63 (11), 55 (44), 45 (13), 43 (15), 41 (33).

4-Phenyl-3-tosylbutanoic acid (12af): IR ($CHCl_3$) 3500–2500, 1705, 1300, 1140 cm^{-1}; ^{1}H NMR δ 2.40–2.50 (m with s at 2.40, 4H), 2.68 (dd, J = 13.9, 10.9 Hz, 1H), 2.82 (dd, J = 17.3, 7.4 Hz, 1H), 3.33 (dd, J = 13.9, 4.2 Hz, 1H), 3.84 (m, 1H), 7.06–7.80 (m with d at 7.07, J = 6.9 Hz and 2d at 7.33, 7.78, J = 8.0 Hz, 9H), 9.66 (br s, 1H); ^{13}C NMR δ 21.54, 32.16, 34.15, 62.05, 127.19, 128.71, 128.97, 129.11, 129.89, 133.81, 135.66, 145.26, 175.74; m/z 318 (M^+, <1), 163 (21), 162 (94), 161 (50), 157 (36), 145 (12), 121 (10), 120 (11), 118 (19), 117 (100), 116 (11), 115 (42), 92 (14), 91 (79), 77 (14), 65 (35). Anal. Calcd for $C_{17}H_{18}O_4S$: C, 64.13; H, 5.70. Found: C, 64.71; H, 5.36.

(*E*)-6-Phenyl-3-tosyl-5-hexenoic acid (12ag): IR (Nujol) 3300–2200, 1700, 1600, 1300, 1140 cm^{-1}; ^{1}H NMR δ 2.36–2.46 (m with s at 2.42, 4H), 2.55 (dd, J = 17.1, 7.3 Hz, 1H), 2.81 (m, 1H), 2.90 (dd, J = 17.1, 5.6 Hz, 1H), 3.65 (m, 1H), 5.95 (ddd, J = 15.8, 8.4, 6.3 Hz, 1H), 6.36 (d, J = 15.8 Hz, 1H), 7.21 (m, 5H), 7.35, 7.78 (2d, J = 8.1 Hz, 4H), 8.80 (br s, 1H); ^{13}C NMR δ 21.59, 32.22, 32.36, 60.41, 123.74, 126.18, 127.65, 128.47, 129.02, 129.97, 133.96, 134.21, 136.41, 145.30, 175.84; m/z 344 (M^+, <1), 188 (38), 143 (11), 129 (19), 128 (100), 115 (12), 91 (22), 65 (10). Anal. Calcd for $C_{19}H_{20}O_4S$: C, 66.26; H, 5.85. Found: C, 65.92; H, 5.71.

4-Oxo-3-tosylheptanoic acid (12ah): IR (Nujol) 3500–2500, 1725, 1705, 1305, 1175 cm^{-1}; ^{1}H NMR δ 0.90 (t, J = 7.4 Hz, 3H), 1.60 (m, 2H), 2.45 (s, 3H), 2.62–3.07 (m, 4H), 4.53 (dd, J = 11.1, 3.2 Hz, 1H), 7.36, 7.63 (2d, J = 8.0 Hz, 4H), 8.59 (br s, 1H); ^{13}C NMR δ 13.24, 16.54, 21.62, 31.96, 46.65, 69.86, 129.20, 129.91, 132.68, 145.95, 174.60, 200.98; m/z 298 (M^+, <1), 210 (58), 155 (11), 139 (21), 119 (15), 99 (12), 97 (10), 92 (19), 91 (87), 89 (10), 71 (100), 65 (39), 55 (25), 43 (51), 41 (21). Anal. Calcd for $C_{14}H_{18}O_5S$: C, 56.36; H, 6.08. Found: C, 56.67; H, 6.15.

5-Methyl-4-oxo-3-tosylhexanoic acid (12ai): IR ($CHCl_3$) 3500–2400, 1695, 1300, 1135 cm^{-1}; ^{1}H NMR δ 1.12, 1.15 (2d, J = 6.9 Hz, 6H), 2.44 (s, 3H), 2.84 (dd, J = 17.5, 3.4 Hz, 1H), 2.99 (dd, J = 17.5, 10.8 Hz, 1H), 3.23 (sept, J = 6.9 Hz, 1H), 4.77 (dd, J = 10.8, 3.4 Hz, 1H), 7.35, 7.61 (2d, J = 8.2 Hz, 4H), 7.75 (br s, 1H); ^{13}C NMR δ 17.24, 18.78, 21.53, 31.80, 42.02, 68.35, 129.04, 129.88, 132.59, 145.94, 174.67, 204.95; m/z 255 (M^+ − C_3H_7, 1), 210 (57), 183 (10), 157 (17), 155 (21), 139 (37), 92 (19), 91 (100), 89 (11), 71 (81), 65 (33), 55 (32), 43 (67), 41 (22). Anal. Calcd for $C_{14}H_{18}O_5S$: C, 56.36; H, 6.08. Found: C, 55.62; H, 6.40.

4-Oxo-4-phenyl-3-tosylbutanoic acid (12aj):[6d] IR (Nujol) 3600–2500, 1770, 1665, 1300, 1140 cm^{-1}; ^{1}H NMR δ 2.39 (s, 3H), 3.13 (dd, J = 17.6, 3.8 Hz, 1H), 3.26 (dd, J = 17.6, 10.4 Hz, 1H), 5.45 (dd, J = 10.4, 3.8 Hz, 1H), 7.22–7.91 (m with d at 7.24, J = 8.1 Hz, t at 7.41, J = 7.6 Hz and d at 7.90, J = 7.6 Hz, 9H), 9.84 (br s, 1H); ^{13}C NMR δ 21.61, 32.34, 65.64, 128.55, 129.24, 129.41, 129.74, 132.76, 133.95, 136.25, 145.89, 175.26, 191.08; m/z 268 (M^+ − SO_2, <1), 105 (100), 91 (24), 73 (24), 65 (13), 51 (11). Anal. Calcd for $C_{17}H_{16}O_5S$: C, 61.43; H, 4.85. Found: C, 61.07; H, 4.88.

3-Tosyl-4-oxododecanoic acid (12ak): IR ($CHCl_3$) 3440–2700, 1710, 1300, 1135 cm^{-1}; ^{1}H NMR δ 0.88 (t, J = 6.5 Hz, 3H), 1.26 (m, 10H), 1.55 (m, 2H), 2.45 (s, 3H), 2.66 (dt, J = 18.4, 7.1 Hz, 1H), 2.87 (dd, J = 17.6, 3.2 Hz, 1H), 2.93 (dt, J = 18.4, 8.1 Hz, 1H), 3.02 (dd, J = 17.6, 11.1 Hz, 1H), 4.51 (dd, J = 11.1, 3.2 Hz, 1H), 7.36, 7.62 (2d, J = 8.1 Hz, 4H), 10.13 (br s, 1H); ^{13}C NMR δ 14.03, 21.64, 22.58, 23.11, 28.72, 29.04, 29.23, 31.74, 31.92, 44.82, 69.87, 129.22, 129.94, 132.69, 145.99, 175.41, 201.05; m/z 270 (M^+ − C_7H_{14}, 1), 210 (29), 188 (12), 157 (10), 155 (13), 141 (53), 139 (42), 114 (13), 111 (10), 99 (15), 98 (13), 97 (17), 96 (11), 92 (28), 91 (100), 83 (20), 81 (16), 71 (59), 70 (16), 69 (13), 67 (12), 65 (36), 57 (66), 55 (80), 53 (11), 43 (58), 42 (10), 41 (54). Anal. Calcd for $C_{19}H_{28}O_5S$: C, 61.93; H, 7.66. Found: C, 61.63; H, 7.96.

3-Deuterio-2-methyl-3-tosylpropanoic acid (12ba): IR ($CHCl_3$) 3400–2400, 1705, 1300, 1140 cm^{-1}; ^{1}H NMR δ 1.35 (d, J = 7.0 Hz, 3H), 2.45 (s, 3H), 3.05 (m, 2H), 7.36, 7.79 (2d, J = 8.2 Hz, 4H), 9.83, (br s, 1H); ^{13}C NMR δ 17.50, 21.55, 34.56, 58.10 (t, J = 21.1 Hz), 128.02, 129.94, 135.94, 145.06, 179.11; m/z 243 (M^+, 4.6), 242 (0.1), 173 (19), 156 (29), 155 (17), 139 (11), 92 (61), 91 (100), 89 (13), 70 (10), 65 (37), 63 (12), 45 (16), 42 (17). Anal. Calcd for $C_{11}H_{13}DO_4S$: C, 54.30; H/D, 6.21. Found: C, 54.16; H/D, 6.43.

2-Methyl-4-phenyl-3-tosylbutanoic acid (12bf): (main diastereomer) IR ($CHCl_3$) 3300–2450, 1695, 1305, 1295, 1285, 1140 cm^{-1}; ^{1}H NMR δ 1.49 (d, J = 7.3 Hz, 3H), 2.42 (s, 3H), 2.67 (q d, J = 7.3, 2.6 Hz, 1H), 3.01 (dd, J = 14.4, 11.2 Hz, 1H), 3.15 (dd, J = 14.4, 4.4 Hz, 1H), 4.13 (ddd, J = 11.2, 4.4, 2.6 Hz, 1H), 7.01 (d, J = 7.8 Hz, 2H), 7.22 (m, 3H), 7.33, 7.79 (2d, J = 8.2 Hz, 4H), 10.52 (br s, 1H); ^{13}C NMR δ 10.31, 21.64, 32.57, 37.45, 66.83, 127.21, 128.56, 128.67, 128.93, 129.87, 136.01, 136.31, 144.91, 177.76; m/z 259 (M^+ − $C_3H_5O_2$, 1), 176 (45), 175 (10), 157 (33), 133 (12), 131 (78), 92 (13), 91 (100), 77 (11), 65 (20).

2-Methyl-4-oxo-4-phenyl-3-tosylbutanoic acid (12bj): (main diastereomer) IR (Nujol) 3300–2450, 1690, 1660, 1295, 1140 cm^{-1}; ^{1}H NMR δ 1.65 (d, J = 7.2 Hz, 3H), 2.33 (s, 3H), 3.39 (m, 1H), 5.20 (d, J = 10.1 Hz, 1H), 7.13–7.75 (m, 9H), 8.23 (br s, 1H); ^{13}C NMR δ 16.22, 21.54, 40.11, 71.50, 128.28, 128.84, 129.52, 133.36, 133.73, 136.70, 145.66, 179.10, 193.19; m/z 328 (M^+ − H_2O, <1), 282, (M^+−SO_2, 2), 224 (10), 105 (100), 91 (22), 77 (31). Anal. Calcd for $C_{18}H_{18}O_5S$: C, 62.41; H, 5.24. Found: C, 61.64; H, 5.41.

3-Deuterio-3-tosylbutanoic acid (12ca): IR ($CHCl_3$) 3400–2500, 1710, 1300, 1140 cm^{-1}; ^{1}H NMR δ 1.31 (s, 3H), 2.43 (m, with s 2.45, 4H), 3.03 (d, J = 16.7 Hz, 1H), 7.37, 7.76 (2d, J = 8.2 Hz, 4H), 9.45 (br s, 1H); ^{13}C NMR δ 13.71, 21.55, 34.28, 56.25 (t, J = 21.6 Hz), 128.98, 129.88, 133.22, 145.17, 175.23; m/z 243 (M^+, 10), 242 (0.3), 156 (18), 139 (16), 93 (17), 92 (100), 91 (64), 89 (14), 88 (48), 70 (38), 65 (44), 63 (14), 44 (25), 43 (32), 42 (27), 41 (41). Anal. Calcd for $C_{11}H_{13}DO_4S$: C, 54.30; H/D, 6.21. Found: C, 54.12; H/D, 6.04.

4-Phenyl-3-methyl-4-oxo-3-tosylbutanoic acid (12cj): IR ($CHCl_3$) 3400–2500, 1700, 1665, 1300, 1135 cm^{-1}(SO_2); ^{1}H NMR δ 1.92 (s, 3H), 2.44 (s, 3H), 2.84, 3.54 (2d, J = 17.2 Hz, 2H), 7.30–7.85 (m, 9H), 8.96 (br s, 1H); ^{13}C NMR δ 18.48, 21.69, 40.85, 73.77, 128.04, 128.55, 129.60, 130.65, 130.90, 131.65, 138.15, 145.94, 174.85, 198.81; m/z 282 (M^+ − SO_2, <1), 224 (20), 105 (100), 91 (15), 77 (28). Anal. Calcd for $C_{18}H_{18}O_5S$: C, 62.41; H, 5.24. Found: C, 61.81; H, 5.41.

Synthesis of α,β-Butenolides 14. General Procedure. To the *in situ* generated organolithium compound 11 was added at −78 °C the carbonyl compound (1.1 mmol) and the reaction mixture allowed to warm to −40 °C (2–3 h). TFAA (0.28 mL, 2 mmol) was then added and the resulting solution stirred for 1 h at −40 to −20 °C. Et_3N (1.4 mL, 10 mmol) or DBU (0.16 mL, 1 mmol) was then added and the bath removed (see Table 2). The solution was poured into an aqueous saturated solution of $NaHCO_3$ and extracted with ether (2 × 15 mL). The organic layers were combined and washed successively with saturated aqueous $NaHCO_3$, 2 N aqueous HCl, and brine, dried (Na_2SO_4) and evaported. The resulting residue was purified by column chromatography on silica gel to afford pure butenolides 14. Physical data are included in Table 2; spectral data follow.

5-Isopropyl-2(5*H*)-furanone (14aa):[10p] IR ($CHCl_3$) 3070, 1740, 1590, 825 cm^{-1}; ^{1}H NMR δ 1.00 (d, J = 6.8 Hz, 6H), 2.04 (septet, J = 6.8 Hz, 1H), 4.87 (ddd, J = 5.8, 1.9, 1.4 Hz, 1H), 6.14 (dd, J = 5.8, 1.9 Hz, 1H), 7.49 (dd, J = 5.8, 1.4 Hz, 1H); ^{13}C NMR

δ 17.36, 17.72, 31.43, 87.85, 121.98, 154.93, 173.06; *m/z* 126 (M^+, 1), 97 (17), 85 (14), 84 (100), 85 (15), 56 (15), 55 (36), 43 (32), 41 (32).

5-*tert*-Butyl-2(5*H*)-furanone (14ab):[23] IR (film) 3080, 1745, 1600, 825 cm^{-1}; ^1H NMR δ 0.99 (s, 9H), 4.73 (dd, *J* = 2.1, 1.5 Hz, 1H), 6.15 (dd, *J* = 5.8, 2.1 Hz, 1H), 7.50 (dd, *J* = 5.8, 1.5 Hz, 1H); ^{13}C NMR δ 25.26; 34.71, 90.78, 122.33, 154.30, 173.09; *m/z* 125 ($M^+ - CH_3$, 4), 97 (10), 84 (43), 57 (100), 55 (13), 43 (10), 41 (44).

5-Pentyl-2(5*H*)-furanone (14ac):[23] IR ($CHCl_3$) 3080, 1750, 1595, 820 cm^{-1}; ^1H NMR δ 0.90 (t, *J* = 6.9 Hz, 3H), 1.26–2.80 (m, 8H), 5.04 (m, 1H), 6.10 (dd, *J* = 5.7, 1.9 Hz, 1H), 7.46 (dd, *J* = 5.7, 1.3 Hz, 1H); ^{13}C NMR δ 13.87, 22.36, 24.60, 31.41, 33.11, 83.41, 121.47, 156.27, 173.13; *m/z* 154 (M^+, 1), 126, (14), 125 (44), 99 (18), 98 (10), 97 (16), 94 (10), 84 (100), 83 (24), 71 (10), 55 (58), 43 (21), 41 (23).

5,5-Tetramethylene-2(5*H*)-furanone (14ad):[24] IR (film) 3080, 1740, 1600, 820 cm^{-1}; ^1H NMR δ 1.80–2.05 (m, 8H), 6.00 (d, *J* = 5.6 Hz, 1H), 7.37 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR δ 24.66, 36.78, 96.78, 120.24, 158.94, 172.54; *m/z* 138 (M^+, 85), 110 (20), 109 (20), 97 (10), 96 (12), 95 (11), 94 (48), 82 (90), 81 (100), 68 (49), 67 (48), 66 (32), 55 (26), 54 (62), 53 (23), 51 (10), 42 (11), 41 (18).

5,5-Pentamethylene-2(5*H*)-furanone (14ae):[24] IR ($CHCl_3$) 3040, 1745, 1595, 830 cm^{-1}; ^1H NMR δ 1.60–1.85 (m, 10H), 6.00 (d, *J* = 5.6 Hz, 1H), 7.50 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR δ 22.26, 24.40, 34.39, 88.43, 112.98, 160.64, 172.38; *m/z* 152 (M^+, 100), 124 (40), 123 (15), 110 (13), 109 (23), 97 (39), 96 (40), 95 (23), 82 (77), 81 (94), 80 (40), 79 (13), 69 (14), 68 (47), 67 (24), 55 (33), 54 (51), 53 (24), 51 (11), 41 (29).

5-Ethyl-5-phenyl-2(5*H*)-furanone (14af):[25] IR (film) 3060, 1750, 1590, 820 cm^{-1}; ^1H NMR δ 0.88 (t, *J* = 7.4 Hz, 3H), 2.04, 2.18 (2quintet, *J* = 7.4 Hz, 2H), 6.07 (d, *J* = 5.6 Hz, 1H), 7.26–7.46 (m, 5H), 7.62 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR δ 7.97, 32.71, 91.91, 120.01, 124.98, 128.09, 128.75, 138.81, 159.20, 172.42; *m/z* 188 (M^+, 44), 160 (32), 159 (100), 131 (73), 115 (15), 105 (62), 103 (49), 77 (80), 76 (10), 63 (11), 54 (11), 51 (37), 50 (13).

5-Ethyl-3-methyl-5-phenyl-2(5*H*)-furanone (14bf):[26] IR ($CHCl_3$) 3050, 3020, 1750, 1650, 1590, 835 cm^{-1}; ^1H NMR δ 0.86 (t, *J* = 7.3 Hz, 3H), 1.90–2.05 (m with d at 1.92, *J* = 1.6 Hz, 4H), 2.12 (quintet, *J* = 7.3 Hz, 1H), 7.3 (m, 6H); ^{13}C NMR δ 8.06, 10.52; 33.08, 89.46, 125.01, 127.86, 128.52, 128.65, 139.60, 151.83, 173.71; *m/z* 202 (M^+, 4), 174 (13), 173 (100), 145 (17), 117 (10), 115 (11), 105 (84), 77 (57), 51 (19).

5-Ethyl-4-methyl-5-phenyl-2(5*H*)-furanone (14cf): IR ($CHCl_3$) 3050, 1750, 1635, 1590, 835 cm^{-1}; ^1H NMR δ 0.91 (t, *J* = 7.3 Hz, 3H), 1.91 (d, *J* = 1.4 Hz, 3H), 2.12, 2.35 (2 quintets, *J* = 7.3 Hz, 2H), 5.79 (q, *J* = 1.3 Hz, 1H), 7.35 (m, 5H); ^{13}C NMR δ 7.43, 13.40, 28.28, 92.29, 116.01, 125.16, 128.29, 128.75, 137.89, 171.67, 172.96; *m/z* 202 (M^+, 15), 173 (100), 145 (12), 115 (10), 105 (52), 77 (32), 51 (11).

5-(3-Methyl-2-butenyl)-4-methyl-2(5*H*)-furanone (14cg):[27] IR ($CHCl_3$) 3090, 1750, 1640 cm^{-1}; ^1H NMR δ 1.64 (s, 3H), 1.70 (d, *J* = 1.4 Hz, 3H), 2.05 (dd, *J* = 1.4, 0.8 Hz, 3H), 2.32 (m, 1H), 2.64 (m, 1H), 4.86 (t, *J* = 5.3 Hz, 1H), 5.03 (m, 1H), 5.81 (quintet, *J* = 1.4 Hz, 1H); ^{13}C NMR δ 13.92, 18.00, 25.77, 30.34, 84.28, 116.07, 117.32, 136.26, 168.17, 173.14; *m/z* 166 (M^+, 16), 98 (65), 97 (15), 69 (100), 53 (16), 41 (91).

(±)-*O*-Benzyl umbelactone (14ch):[28] IR (film) 3070, 3050, 1750, 1640, 840 cm^{-1}; ^1H NMR δ 2.00 (dd, *J* = 1.5, 0.7 Hz, 3H), 3.64 (dd, *J* = 11.0, 4.3 Hz, 1H), 3.72 (dd, *J* = 11.0, 3.5 Hz, 1H), 4.55, 4.52 (2d, *J* = 12.0 Hz, 2H), 4.85 (m, 1H), 5.78 (m, 1H), 7.24 (m, 5H); ^{13}C NMR δ 14.01, 68.24, 73.64, 83.66, 117.78, 127.64, 127.85, 128.41, 137.29, 166.35, 172.89; *m/z* 218 (M^+, 1), 112 (7), 92 (10), 91 (100), 65 (9), 41 (7).

(±)-Andirolactone (14ci):[29] IR ($CHCl_3$) 3010, 1640, 1745 cm^{-1}; ^1H NMR δ 1.50–1.78 (m with br s at 1.70, 4H), 1.82–2.10 (m with d *J* = 1.4 Hz, 6H), 2.38 (m, 2H), 5.35 (m, 1H), 5.73 (q, *J* = 1.4 Hz, 1H); ^{13}C NMR δ 13.26, 23.33, 26.88, 29.81, 33.09, 87.16, 116.37, 116.48, 133.93, 172.30, 172.57; *m/z* 178 (M^+, 23), 111 (36), 69 (10), 68 (100), 67 (39), 53 (10), 41 (10).

Synthesis of Unsaturated Esters 17 and 18 and Ketoesters 19. General Procedure. A solution of crude **12** in 5 M methanolic HCl (2 mL)[59] was stirred at room temperature until esterification was complete (monitored by TLC). The reaction mixture was dissolved in ether (30 mL), dried (Na_2SO_4), and evaporated to yield crude esters which were dissolved in CH_2Cl_2 (10 mL). To this solution was added at 0 °C DBU (0.17 mL, 1.1 mmol), and the solution was stirred at rt until elimination was complete. The reaction mixture was poured into an aqueous saturated solution of $NaHCO_3$ (25 mL) and extracted with ether (3 × 10 mL). The ethereal layer was washed with 2 N aqueous HCl and brine, dried (Na_2SO_4), and evaporated to yield crude compounds **17–19** which were purified by column chromatography on silica gel. Physical data are included in Tables 3 and 4; spectral data follow.

Methyl (*E*)-2-heptenoate (17aa):[39] IR ($CHCl_3$) 3020, 1725, 1655, 985 cm^{-1}; ^1H NMR δ 0.84 (t, *J* = 7.2 Hz, 3H), 1.20–1.42 (m, 4H), 3.13 (qd, *J* = 7.0, 1.6 Hz, 2H), 3.65 (s, 3H), 5.75 (dt, *J* = 15.7, 1.6 Hz, 1H), 6.90 (dt, *J* = 15.7, 7.0 Hz, 1H); ^{13}C NMR δ 13.73, 22.13, 30.07, 31.84, 51.29, 120.78, 149.71, 167.13; *m/z* 142 (M^+, 12), 113 (62), 111 (47), 110 (27), 101 (17), 100 (14), 87 (100), 82 (20), 81 (15), 74 (33), 69 (32), 68 (27), 69 (25), 56 (17), 55 (79), 53 (17), 43 (15), 41 (38).

Methyl (*E*)-5-methyl-2,4-hexadienoate (17ab):[40] IR (film) 3060, 3020, 1730, 1640, 1615, 975 cm^{-1}; ^1H NMR δ 1.80, 1.82 (2s, 6H), 3.66 (s, 3H), 5.69 (d, *J* = 15.1 Hz, 1H), 5.91 (d, *J* = 11.6 Hz, 1H), 7.49 (dd, *J* = 15.1, 11.6 Hz, 1H); ^{13}C NMR δ 18.85, 26.45, 51.27, 118.02, 123.64, 141.14, 146.36, 168.02; *m/z* 140 (M^+, 27), 125 (42), 109 (29), 81 (100), 80 (48), 79 (76), 77 (20), 66 (10), 65 (19), 59 (12), 55 (13), 53 (41), 51 (9), 50 (11), 41 (41).

Methyl (*Z,E*)-6-methyl-3,5-heptadienonate (18ac):[37] ^1H NMR δ 1.74, 1.77, 1.82 (3s, 6H), 3.12 (d, *J* = 7.4 Hz, 2H), 3.23 (d, *J* = 7.5 Hz, 2H), 3.68, 3.69 (2s, 3H), 5.47 (dt, *J* = 10.6, 7.5 Hz, 1H), 5.61 (dt, *J* = 15.0, 7.4 Hz, 1H), 5.82 (d, *J* = 10.9 Hz, 1H), 5.99 (dd, *J* = 11.4, 1.1 Hz, 1H), 6.34 (m, 1H); ^{13}C NMR δ 18.20; 18.24, 25.90, 26.35, 32.10, 38.15, 51.81, 51.85, 119.18, 119.57, 121.82, 124.30, 127.59, 130.38, 135.32, 137.74, 172.31.

Methyl (*E*)-4-phenyl-3-butenoate (18ad):[41] IR (film) 3030, 1730, 1600, 970 cm^{-1}; ^1H NMR δ 3.23 (d, *J* = 7.0 Hz, 2H), 3.69 (s, 3H), 6.28 (dt, *J* = 15.9, 7.0 Hz, 1H), 6.47 (d, *J* = 15.9 Hz, 1H), 7.20–7.37 (m, 5H); ^{13}C NMR δ 38.07, 51.75, 121.54, 126.16, 127.44, 128.41, 133.35, 136.69, 171.82; *m/z* 176 (M^+, 29), 134 (10), 117 (100), 116 (13), 115 (53), 91 (19).

Methyl (*E,E*)-4-phenyl-3,5-pentadienoate (18ae):[42] IR (film) 3060, 3030, 1730, 1640, 1600, 985 cm^{-1}; ^1H NMR δ 3.19 (d, *J* = 7.3 Hz, 2H), 3.71 (s, 3H), 5.91 (dt, *J* = 15.0, 7.3 Hz, 1H), 6.30 (dd, *J* = 15.0, 10.4 Hz, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.77 (dd, *J* = 15.6, 10.4 Hz, 1H), 7.3 (m, 5H); ^{13}C NMR δ 38.00, 51.90, 126.32, 127.51, 128.26, 128.57, 132.16, 134.00, 171.90; *m/z* 202 (M^+, 10), 143 (23), 142 (32), 141 (26), 129 (17), 128 (100), 115 (37), 111 (26), 98 (12), 91 (20), 65 (13), 59 (13), 51 (19).

Methyl (*E*)-2-methyl-2-heptenoate (17ba):[43] IR ($CHCl_3$) 3020, 1705, 1640 cm^{-1}; ^1H NMR δ 0.91 (t, *J* = 7.1 Hz, 3H), 1.25–1.45 (m, 4H), 1.83 (br s, 3H), 2.17 (q, *J* = 7.3 Hz, 2H), 3.73 (s, 3H), 6.77 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR δ 12.27, 13.81, 22.37, 28.31, 30.66, 51.58, 127.36, 142.72, 168.71; *m/z* 156 (M^+, 38), 127 (61), 125 (36), 101 (100), 99 (15), 97 (13), 96 (14), 95 (32), 88 (69), 83 (11), 82 (16), 81 (15), 73 (12), 69 (20), 67 (24), 59 (22), 56 (12), 55 (82), 54 (11), 53 (22), 43 (13), 41 (31).

Methyl (*E*)-4-oxo-2-heptenoate (19aa):[49] IR ($CHCl_3$) 3050, 3010, 1720, 1670, 1640, 990 cm^{-1}; ^1H NMR δ 0.95 (t, *J* = 7.3 Hz, 3H), 1.68 (sextet, *J* = 7.3 Hz, 2H), 2.62 (t, *J* = 7.3 Hz, 2H), 3.82 (s, 3H), 6.68, 7.07 (2d, *J* = 16.0 Hz, 2H); ^{13}C NMR δ 13.58, 17.11, 43.43, 52.28, 130.10, 139.52, 166.01, 199.62; *m/z* 156 (M^+, <1), 128 (18), 125 (10), 113 (100), 97 (50), 85 (25), 59 (21), 55 (19), 54 (12), 53 (11), 43 (47), 41 (16).

Methyl (*E*)-5-methyl-4-oxo-2-hexenoate (19ab):[50] IR (film) 3060, 1715, 1680, 1620, 975 cm^{-1}; ^1H NMR δ 1.16 (d, *J* = 6.9 Hz, 6H), 2.86 (m, 1H), 3.82 (s, 3H), 6.75, 7.20 (2d, *J* = 15.9 Hz, 2H); ^{13}C NMR δ 17.72, 39.95, 52.21, 130.30, 138.12, 165.98, 202.71; *m/z* 156 (M^+, 2), 125 (10), 114 (41), 113 (100), 97 (10), 85 (28), 82 (12), 59 (18), 55 (19), 54 (14), 53 (10), 43 (27), 41 (23).

Methyl (*E*)-5,5-dimethyl-4-oxo-2-hexenoate (19ac):[51] IR (film) 3085, 1720, 1690, 1630, 1615, 985 cm^{-1}; ^1H NMR δ 1.20 (s, 9H), 3.81 (s, 3H), 6.78, 7.52 (2d, *J* = 15.4 Hz, 2H); ^{13}C NMR δ 25.65, 43.55, 52.19, 130.90, 135.57, 166.10, 203.53; *m/z* 170 (M^+, <1), 114 (100), 86 (10), 85 (10), 57 (40), 41 (19).

Methyl (*E*)-4-oxo-4-phenyl-2-butenoate (19ad):[52] IR (film) 3060, 1715, 1665, 1620, 1590, 1570, 975 cm^{-1}; ^1H NMR δ 3.85 (s, 3H), 6.90, 7.93 (2d, *J* = 15.6 Hz, 2H), 7.52 (deformed t, *J* = 7.5

(59) When the solution was not homogeneous CH_2Cl_2 (1 mL) was added.

Hz, 2H), 7.63 (deformed t, J = 7.5 Hz, 1H), 8.00 (d, J = 7.5 Hz, 2H); ^{13}C NMR δ 52.32, 128.87, 132.02, 133.84, 136.57, 141.23, 165.98, 189.38; m/z 190 (M^+, 21), 131 (15), 130 (10), 105 (100), 77 (51), 51 (19).

Methyl (*E*)-4-oxo-7-[(diphenyl-*tert*-butylsilyl)oxy]-2-octenoate (19ae):[53] IR ($CHCl_3$) 3050, 1720, 1690, 1590, 985 cm^{-1}; ^{1}H NMR δ 1.05 (s, 9H), 1.06 (d, J = 6.0 Hz, 3H), 1.76 (m, 2H), 2.63 (m, 2H), 3.82 (s, 3H), 3.93 (sextet, J = 6.0 Hz, 1H), 6.58, 6.98 (2d, J = 16.1 Hz, 2H), 7.52 (m, 10H); ^{13}C NMR δ 19.26, 23.26, 27.01, 32.71, 37.27, 52.31, 68.47, 127.49, 127.63, 129.57, 127.66, 130.05, 134.78, 135.78, 135.85, 139.53, 166.02, 199.52; m/z 367 ($M^+ - C_4H_9$, 7), 200 (63), 197 (11), 183 (12), 181 (24), 153 (13), 137 (19), 135 (23), 123 (14), 121 (10), 113 (71), 105 (38), 91 (10), 85 (28), 82 (13), 81 (16), 79 (11), 78 (19), 77 (46), 59 (42), 57 (100), 55 (31), 54 (13), 53 (16), 45 (15), 43 (15), 41 (80).

Methyl (*E*)-4-oxo-2-dodecenoate (19af): IR ($CHCl_3$) 3020, 1725, 1700, 1640, 1625, 985 cm^{-1}; ^{1}H NMR δ 0.88 (t, J = 6.4 Hz, 3H), 1.28 (m, 10H), 1.63 (m, 2H), 2.62 (t, J = 7.3 Hz, 2H), 3.82 (s, 3H), 6.67, 7.07 (2d, J = 16.0 Hz, 2H); ^{13}C NMR δ 14.05, 22.61, 23.68, 29.07, 29.10, 29.29, 31.77, 41.66, 52.31, 130.10, 139.54, 166.05, 199.80; m/z 195 ($M^+ - CH_3O$, 5), 167 (55), 155 (17), 137 (19), 129 (18), 128 (100), 123 (17), 113 (84), 97 (28), 96 (33), 85 (24), 81 (12), 69 (10), 59 (16), 43 (19), 41 (24).

Methyl (*Z*)-4-oxo-2-dodecenoate (19af):[54] IR ($CHCl_3$) 3030, 1720, 1700, 1625, 815 cm^{-1}; ^{1}H NMR δ 0.88 (t, J = 6.7 Hz, 3H), 1.27 (m, 10H), 1.64 (m, 2H), 2.60 (t, J = 7.4 Hz, 2H), 3.75 (s, 3H), 6.02, 6.49 (2d, J = 8.0 Hz, 2H); ^{13}C NMR δ 14.06, 22.62, 23.30, 29.10 (×2), 29.35, 31.80, 42.69, 52.03, 124.34, 141.81, 165.77, 203.74; m/z 195 ($M^+ - CH_3O$, <1), 155 (14), 128 (22), 123 (17), 113 (100), 97 (12), 96 (27), 55 (12), 41 (12).

Methyl (*E*)-2-methyl-4-phenyl-4-oxobutenoate (19bd):[55] IR ($CHCl_3$), 3060, 3020, 1725, 1665, 1615 cm^{-1}; ^{1}H NMR δ 2.17 (br s, 3H), 3.83 (s, 3H), 7.47 (deformed t, J = 7.8 Hz, 2H), 7.57 (deformed t, J = 7.8 Hz, 1H), 7.70 (br s, 1H), 7.94 (d, J = 7.8 Hz, 2H); ^{13}C NMR δ 14.74, 52.57, 128.51, 128.76, 132.00, 133.56, 137.44, 140.40, 167.88, 192.44; m/z 204 (M^+, 5), 172 (18), 145 (18), 144 (15), 117 (11), 116 (12), 115 (16), 105 (100), 77 (79), 59 (13), 51 (47), 50 (15).

Methyl (*Z*)-2-methyl-4-phenyl-4-oxobutenoate (19bd):[55] IR ($CHCl_3$) 3040, 3020, 1720, 1660, 1610, 845 cm^{-1} (C=O); ^{1}H NMR δ 2.13 (br s, 3H), 3.62 (s, 3H), 6.74 (br s, 1H), 7.45 (deformed t, J = 7.7 Hz, 2H), 7.55 (deformed t, J = 7.7 Hz, 1H), 7.93 (d, J = 7.7 Hz, 2H); ^{13}C NMR δ 20.15, 52.10, 128.53, 128.64, 130.53, 133.25, 136.70, 140.43, 168.55, 191.70; m/z 204 (M^+, 23), 173 (12), 145 (13), 127 (22), 117 (13), 116 (14), 115 (19), 105 (100), 77 (93), 59 (17), 51 (53), 50 (21).

Methyl 2-methylidene-4-phenyl-4-oxobutanoate (20): IR ($CHCl_3$) 3060, 3010, 1720, 1680, 1630, 1590, 1570, 945 cm^{-1}; ^{1}H NMR δ 3.76 (s, 3H), 4.01 (s, 2H), 5.70, 6.41 (2m, 2H), 7.47 (deformed t, J = 7.3 Hz, 2H), 7.58 (deformed t, J = 7.3 Hz, 1H), 7.99 (d, J = 7.3 Hz, 2H); ^{13}C NMR δ 41.70, 52.12, 128.26, 128.59, 128.64, 133.27, 134.52, 136.48, 166.90, 196.79; m/z 204 (M^+, <1), 105 (100), 77 (80), 51 (29), 50 (12).

Methyl (*E*)-3-methyl-4-oxo-4-phenylbutenoate (19cd):[55] IR ($CHCl_3$) 3020, 1700, 1650, 1580 cm^{-1}; ^{1}H NMR δ 2.14 (d, J = 1.6 Hz, 3H), 3.54 (s, 3H), 6.02 (q, J = 1.6 Hz, 1H), 7.48 (deformed t, J = 7.4 Hz, 2H), 7.58 (deformed t, J = 7.4 Hz, 1H), 7.90 (d, J = 7.4 Hz, 2H); ^{13}C NMR δ 21.72, 51.60, 119.08, 128.59, 128.81, 133.56, 134.47, 155.50, 165.23, 198.22; m/z 204 (M^+, 15), 106 (10), 105 (100), 77 (61), 51 (18).

Methyl (*Z*)-3-methyl-4-oxo-4-phenylbutenoate (19cd):[55] IR (film) 3600, 1720, 1660, 1595, 1580 cm^{-1}; ^{1}H NMR δ 2.41 (d, J = 1.5 Hz, 3H), 3.76 (s, 3H), 6.16 (q, J = 1.5 Hz, 1H), 7.40–7.80 (m, 5H); ^{13}C NMR δ 15.49, 51.62, 124.92, 128.52, 129.59, 133.16, 135.80, 152.15, 166.22, 197.83; m/z 204 (M^+, 4), 172 (18), 144 (12), 105 (100), 77 (59), 51 (21).

Acknowledgment. We thank DGICYT (Projects PB88-0287 and PB91-0751) from the Spanish Ministerio de Educación y Ciencia (MEC) for financial support. P.B. thanks the Generalitat Valenciana for a predoctoral fellowship.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of **14cf**, **17ab**, **18ab**, **18ac**, **19af**, **19cd**, **20**, and **21** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.