by subjection of the residue to the above reaction conditions provided an additional 116 mg (16%) of crystalline **53**: TLC (ether) R_f 0.41; ^{1}H NMR (470 MHz) 7.88 (d, 2 H, 7.6 Hz), 7.68 (t, 1 H, 7.4 Hz), 7.57 (t, 2 H, 7.7 Hz), 6.78–6.69 (m, 1 H), 6.61 (d, 1 H, 8.1 Hz), 5.29 (br s, 1 H), 4.31 (br d, 1 H, 5.9 Hz), 4.15–4.02 (m, 2 H), 3.83–3.82 (br s, 3 H total, CRI), 3.54 (s, 3 H), 3.31–2.95 (cm, 3 H), 285–2.83 (s, 3 H total, CRI), 2.72–2.56 (m, 3 H), 2.35–2.16 (cm, 1 H), 2.06 (d, 1 H, 18.2 Hz), 1.90–1.83 (um, 1 H), 1.57 (dd, 1 H, 18.2, 6.7 Hz), 1.02–0.87 (cm, 2 H), 0.01 (s, 9 H); ^{13}C NMR (50 MHz) 156.28 (e), 154.12 (e), 145.07 (e), 143.04 (e), 137.86 (e), 133.76 (o), 129.24 (o), 128.96 (o), 128.75, 128.66 (e, CRI), 123.86 (e), 120.22 (o), 114.56 (o), 91.33 (o), 88.36 (o), 70.65 (e), 63.15 (e), 56.50 (o), 54.63 (o), 48.59 (e), 45.33 (br e), 34.35 (br o), 33.83 (e), 28.40 (e), 25.72 (e), 22.78 (e), 17.69 (e), −1.55 (o); IR ($CHCl_3$) 3.31 (m), 3.38 (m), 5.84 (s), 5.95 (s), 6.10 (w), 6.22 (w), 6.63 (m), 6.92 (m), 7.35 (m), 7.72 (m), 7.80 (m), 8.58 (m), 8.72 (s), 9.20 (m), 11.00 (s), 11.60 (m), 11.90 (m) μm; mass spectrum, m/z (relative intensity) [CI] 600 (M^+ + 1, 7), 572 (48), 430 (33), 358 (83), 314 (100); [EI] 599 (M^+, 1) 255 (18), 174 (12), 73 (100); high-resolution mass spectrum (m/z), calcd for $C_{31}H_{41}NO_7SSi$ 599.2373, found 599.2381.

***(dl)*-3,5-Dimethoxy-9b(*S*)-[2-[methyl(((2-(trimethylsilyl)ethyl)oxy)carbonyl)amino]ethyl]-3a(*R*),8,9,9b-tetrahydrophenanthro[4,4a,4b,5-*bcd*]furan (54).** A solution of **53** (275 mg, 0.46 mmol) in THF (15 mL) under argon was treated with potassium *tert*-butoxide solution (2.2 M in THF, 0.85 mL, 1.87 mmol, 4.1 equiv). After 3 h the reaction mixture was poured into saturation $NaHCO_3$ solution and extracted with dichloromethane, and the combined extract was dried (Na_2SO_4). Filtration followed by evaporation and flash chromatography [ether/hexane/triethylamine (2%)] afforded 190 mg (91%) of **54**: TLC (ether) R_f 0.62; ^{1}H NMR (470 MHz) 6.61 (br d, 1 H, 7.9 Hz), 6.57 (br d, 1 H, 7.9 Hz), 5.53 (br s, 2 H), 5.02 (d, 1 H, 6.4 Hz), 4.15 (dt, 2 H, 9.0, 2.9 Hz), 3.83 (s, 3 H), 3.60 (br s, 3 H), 3.47–3.38 (um, 1 H), 3.32–3.22 (um, 1 H), 3.18–2.75 (overlapping br m, 3 H), 2.88, 2.86 (br s, 3 H total, CRI), 2.49–2.40 (cm, 1 H), 2.24–2.15 (um, 1 H), 1.87 (dt, 1 H, 12.3, 4.9 Hz), 1.00 (um, 2 H), 0.04 (s, 9 H); ^{13}C NMR (50 MHz) 156.32 (e), 151.40 (e), 145.02 (e), 142.74 (e), 133.94 (e), 131.84 (e), 127.22 (e), 119.54 (o), 115.87 (o), 112.11 (o), 96.35 (o), 88.22 (o), 63.38 (e), 56.19 (o), 54.83 (o), 50.15 (e), 45.22 (br e), 35.59 (br e), 34.45 (br o), 26.19 (e), 17.74 (e), −1.58 (o); IR (neat) 3.40 (br s), 5.85 (s), 5.94 (s), 6.02 (m), 6.15 (m), 6.20 (s), 6.67 (s), 6.90 (s), 7.15 (s), 8.78 (s), 9.10 (s), 9.62 (br s) μm; mass spectrum, m/z (relative intensity) [CI] 458 (M^+ + 1, 65), 430 (100), 314 (4), 174 (12); [EI] 457 (M^+, 1), 429 (1), 174 (11), 116 (11), 73 (100); high-resolution mass spectrum (m/z), calcd for $C_{25}H_{35}NO_5Si$ 457.2284, found 457.2280.

Acknowledgment. Support for this investigation was provided by the National Institutes of Health (Grant GM-32693). We thank Dr. Tamim Braish and Mark Anderson for spectral assistance.

Supplementary Material Available: Experimental procedures for the compounds listed in the General section of the Experimental Section (48 pages). Ordering information is given on any current masthead page.

(*E*)-4-Lithio-4-tosylbutenone Dimethyl Ketal: A New and Versatile β-Acylvinyl Anion Equivalent in Organic Synthesis

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Received March 15, 1988

The lithiation of (*E*)-4-tosylbutenone dimethyl ketal (**12**) with methyllithium at −20 °C led to the new β-acylvinyl anion equivalent (*E*)-4-lithio-4-tosylbutenone dimethyl ketal (**13**). The treatment of intermediate **13** with different electrophilic reagents (water, deuterium oxide, trimethylchlorosilane, methyl iodide or allyl bromide, aldehydes, acetic anhydride, carboxylic acid chlorides, ethyl chloroformate, phenyl isocyanate, or dimethyl disulfide) afforded, after careful hydrolysis, the corresponding functionalized ketal derivatives **12–21** or **22**. When the alkylation reaction of **13** with different alkyl halides was followed by acid hydrolysis, the expected alkylated tosyl ketones **23** were obtained directly. In the case of the reaction of the anion **13** with aldehydes, the in situ acid hydrolysis yielded 3-tosylfurans **25**. Monoprotected enediones **18** and keto ester **19** were deprotected by treatment with aqueous trifluoroacetic acid leading to cis-configurated enediones **27** or keto ester **28**. Finally, under basic conditions, compound **27** underwent cyclization to the corresponding cyclopentenones **29**. All the above-described transformations take place in a stereoselective manner yielding either the *E* products or the corresponding cyclized products. This result is consistent with a stereoselective formation of the (*Z*)-vinyllithium **13**, which reacts in an S_E process with retention of configuration.

Introduction

The chemistry of β-acylvinyl anion equivalents of the type **1** has received great attention recently because of their ability to provide the α,β-unsaturated acyl functionality.[1] Intermediates of this type can also be considered as sp^2-hybridized homoenolate equivalents.[1] In general, the corresponding organolithium derivatives have been prepared by starting directly from β-functionalzed α,β-unsaturated carbonyl compounds or their derivatives through two ways: (a) a kinetic β-deprotonation to afford intermediates of the type **2b,c**,[3] **3**,[3-5] **4**,[4,5] **5**,[4,5] **6**,[5] **7**,[6,7] or **8**;[8] (b) a bromine–lithium exchange reaction to give the unsub-

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(1) (a) Stowell, J. C. *Chem. Rev.* **1984**, *84*, 409. (b) Hoppe, D. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 932.

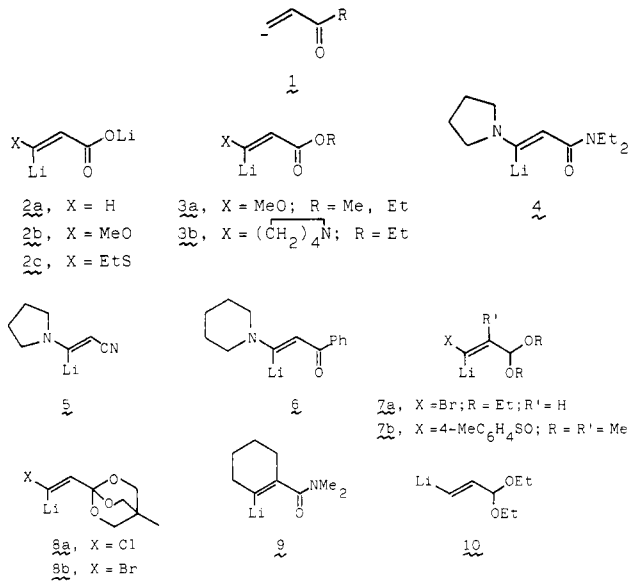
(2) For the corresponding sp^3 equivalents, see, for instance: (a) Barluenga, J.; Rubiera, C.; Fernández, J. R.; Yus, M. *J. Chem. Soc., Chem. Commun.* **1987**, 425. (b) Carretero, J. C.; De Lombaert, S.; Ghosez, L. *Tetrahedron Lett.* **1987**, *28*, 2135.

(3) (a) Barua, N. C.; Evertz, K.; Huttner, G.; Schmidt, R. R. *Chem. Ber.* **1987**, *120*, 213. (b) Schmidt, R. R.; Hirsenkorn, R. *Tetrahedron Lett.* **1984**, *25*, 4357.

(4) Schmidt, R. R.; Talbiersky, J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 171; **1977**, *16*, 853; **1978**, *17*, 204.

(5) Schmidt, R. R.; Talbiersky, J.; Russegger, P. *Tetrahedron Lett.* **1979**, 4273.

0022-3263/88/1953-4708$01.50/0

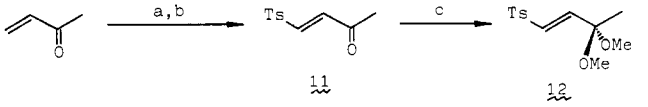


stituted derivatives **2a**,[9] **9**,[10] or **10**.[6] All these intermediates must be prepared at low temperature in order to avoid side reactions, most notably rearrangement to the thermodynamically more stable α-anion.[3-5] In the present paper, we describe the preparation and synthetic applications of a very stable new lithiated β-tosyl acylvinyl anion equivalent **13** derived from methyl vinyl ketone. Our strategy follows a defensive strategy as recently defined by Hoppe;[1b] that is, we temporarily mask the carbonyl group as a ketal.[11]

Results and Discussion

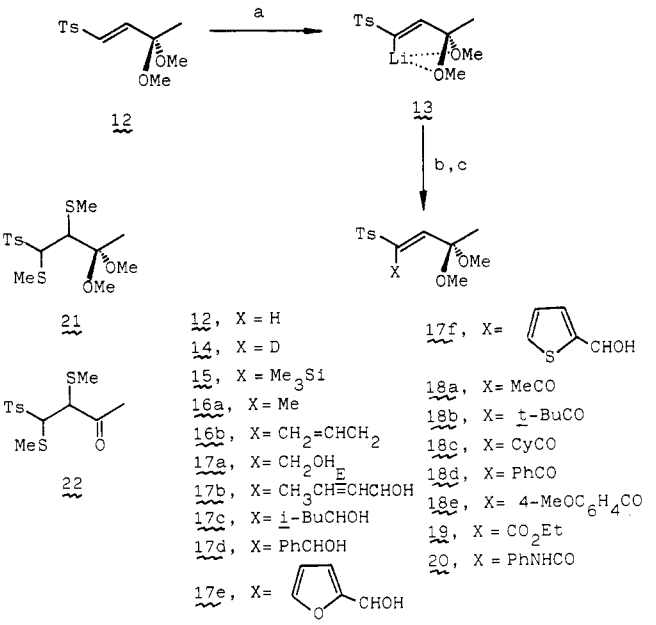
The tandem iodosulfonylation–dehydroiodination of methyl vinyl ketone[12a] led stereoselectively to the corresponding (*E*)-4-tosyl-3-buten-2-one (**11**), which by ketalization with trimethyl orthoformate[13] yielded the corresponding dimethyl ketal **12** (Scheme I). The lithiation of this starting material **12** with methyllithium in the presence of lithium bromide at −20 °C followed by quenching with a variety of electrophiles afforded regio- and stereoselectively the products **12–20** (see Scheme II and Table I). When water was used as electrophile (Table I, entry 1), the same starting material **12** was recovered, the stereochemistry being *E*; this result, together with the ability for cyclization of products **17** and **18** (see below), is a definitive proof of the obtained stereochemistry in products **12–20**. The final hydrolysis in the workup has to be carried out carefully (see Experimental Section) in order to avoid deprotection of the ketal moiety; we think that the monoprotected systems **14–20** may be useful in organic synthesis [see, for instance, products **18** (Table I, entries 12–16) bearing two carbonyl groups, one of them regioselectively protected]. In the case of the reaction with crotonaldehyde (Table I, entry 7), only the corresponding 1,2-addition was observed, yielding product **17b**. Finally,

Scheme I[a]



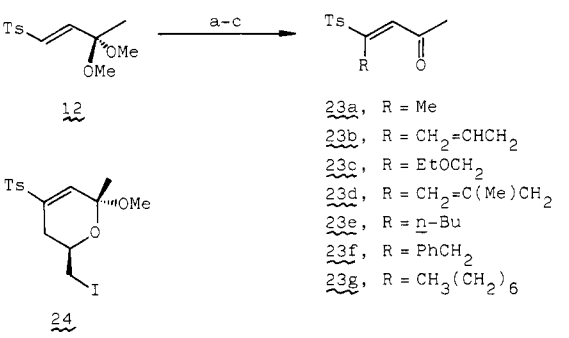
[a] Reagents: (a) NaTs, I_2; (b) Et_3N; (c) $HC(OMe)_3$.

Scheme II[a]



[a] Reagents: (a) MeLi–LiBr, THF, −20 °C; (b) E^+ = H_2O, D_2O, Me_3SiCl, MeI, CH_2=$CHCH_2Br$, CH_2O, (*E*)-CH_3CH=$CHCHO$, *i*-BuCHO, PhCHO, furfural, 2-thiophenecarbaldehyde, Ac_2O, *t*-BuCOCl, CyCOCl, PhCOCl, 4-$MeOC_6H_4COCl$, $ClCO_2Et$, PhNCO, Me_2S_2, −20 or −40 to 20 °C; (c) H_2O.

Scheme III[a]



[a] Reagents: (a) MeLi–LiBr, THF, −20 °C; (b) RHal = MeI, CH_2=$CHCH_2Br$, $EtOCH_2Cl$, CH_2=$C(Me)CH_2Cl$, *n*-BuBr, $PhCH_2Cl$, $CH_3(CH_2)_6I$, $\overline{OCH_2CHCH_2Cl}$ −20 to 20 °C, 1–24 h; (c) HCl–H_2O, 2–24 h.

when dimethyl disulfide was used as electrophilic reagent, compound **21** was obtained, arising from the addition of the in situ generated methyl sulfide anion to the compound of the type **14** (X = MeS) initially formed. On the other hand, when product **21** was chromatographed on silica gel for purification, the corresponding deprotected ketone **22** was isolated, this case being the only one in which chromatographic deprotection was observed (Table I, entry 19).

The observed stereoselectivity is in agreement with the literature data for stabilization of such lithiated systems by intramolecular complexation.[7,14] The treatment of

(6) Meyers, A. I.; Spohn, R. F. *J. Org. Chem.* **1985**, *50*, 4872.
(7) (a) Solladié, G.; Moine, G. *J. Am. Chem. Soc.* **1984**, *106*, 6097. (b) McDougal, P. G.; Oh, Y.-I. *Tetrahedron Lett.* **1986**, *27*, 139.
(8) Richardson, S. K.; Jeganathan, A.; Watt, D. S. *Tetrahedron Lett.* **1987**, *28*, 2335.
(9) Caine, D.; Frobese, A. S. *Tetrahedron Lett.* **1978**, 5167.
(10) Baker, W. R.; Coates, R. M. *J. Org. Chem.* **1979**, *44*, 1022.
(11) A preliminary communication on this work has been published: Nájera, C.; Yus, M. *Tetrahedron Lett.* **1987**, *28*, 6709.
(12) (a) Nájera, C.; Baldó, B.; Yus, M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1029. (b) Haynes, R. K.; Vonwiller, S. C. *J. Chem. Soc., Chem. Commun.* **1987**, 92.
(13) Giordano, C.; Castaldi, G.; Casagrande, F.; Belli, A. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2575.
(14) For an excellent review, see: Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356.

Table I. Reaction of Intermediate 13 with Electrophiles. Isolation of Products 12-21

entry	electrophile	product no.	yield,[a] %	mp,[b] °C (solvent)
1	H_2O	**12**[c]	95	99–100 (hexane–CCl_4)
2	D_2O	**14**	93	98–99 (hexane–CCl_4)
3	Me_3SiCl	**15**	85	135 (hexane–CCl_4)
4	MeI	**16a**	96	36–38 (hexane–CCl_4)
5	CH_2=$CHCH_2Br$	**16b**	81	oil[d]
6	CH_2O	**17a**	86	54–55 (hexane–CCl_4)
7	(*E*)-CH_3CH=CHCHO	**17b**	79	oil[e]
8	*i*-BuCHO	**17c**	84	oil[e]
9	PhCHO	**17d**	80	90–91 (hexane–CH_2Cl_2)
10		**17e**	80	88–89 (hexane–CCl_4)
11		**17f**	71	117–118 (hexane–CCl_4)
12	$(MeCO)_2O$	**18a**	78 (82[f])	oil[g]
13[h]	*t*-BuCOCl	**18b**	84	108–109 (hexane–CCl_4)
14[h]	CyCOCl[i]	**18c**	81	109–110 (hexane–CCl_4)
15	PhCOCl	**18d**	90	112–113 (hexane–CCl_4)
16[h]	4-$MeOC_6H_4COCl$	**18e**	76	145–147 (hexane–ether)
17[h]	$ClCO_2Et$	**19**	75[f]	oil[j]
18[h]	PhNCO	**20**	90[f]	160–161 dec (hexane–CH_2Cl_2)
19	Me_2S_2	**21**	88[f,k]	oil[k]

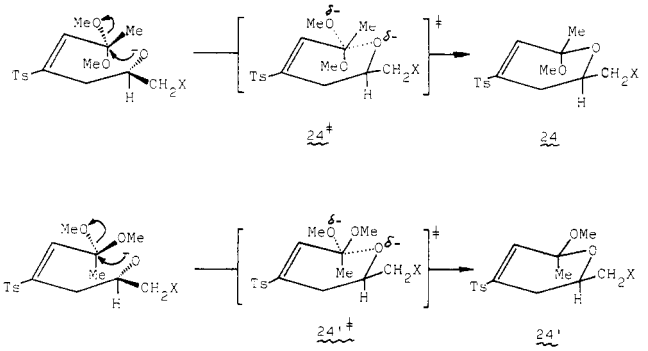
[a] Isolated yield (after flash chromatography; silica gel, hexane–ether) based on starting material **12**. [b] Uncorrected. [c] Prepared via intermediate **13** after hydrolysis (X = H_2O). [d] TLC R_f 0.33 (hexane–ether, 1/1). [e] TLC R_f 0.30 (hexane–ether, 1/2). [f] Isolated crude yield; the product was homogeneous by TLC and pure by NMR. [g] TLC R_f 0.35 (hexane–ether, 1/1). [h] The reaction of intermediate **13** with this electrophile was carried out at −40 to 20 °C (see general procedure in Experimental Section). [i] Cy = cyclohexyl. [j] TLC R_f 0.40 (hexane–ether, 1/2). [k] After silica gel flash chromatography, the corresponding deprotected ketone **22** was isolated as an oil, TLC R_f 0.53 (hexane–ether, 1/2), in 64% overall yield.

intermediate **13** with a variety of electrophiles yielded products **12–20** with retention of stereochemistry (Scheme II); the results show that the internal interaction between the lithium atom and both methoxy groups[5,14] in **13** inhibits inversion in the carbanionic center[15] yielding the expected products arising from an S_E reaction on an sp^2 carbanionic atom with retention of configuration.[16]

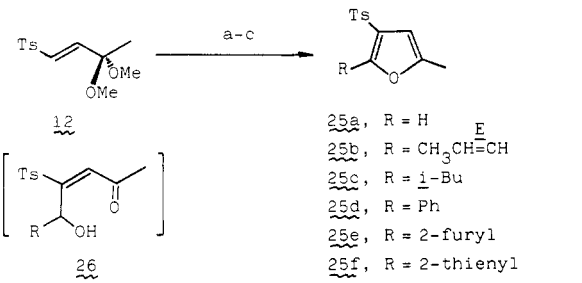
The possibility of obtaining the corresponding deprotected systems directly was studied initially in the case of the reaction with alkyl halides. This was of particular interest to us due to our interest in the use of 3-tosylvinyl ketones of the type **11** as β-acylvinyl cationic equivalents.[12] Thus, the in situ acid hydrolysis of the initially formed alkylated system of the type **16** (Scheme II) led to the expected deprotected products **23** (Scheme III and Table II). The indicated stereochemistry for products **23** (Scheme III) has been confirmed by the obtaining of cyclized compound **24** when epichlorohydrin was used as the alkylating agent, by comparison with literature data (for **23a**),[12a] and by means of experiments using difference nuclear Overhauser effects wherein a negative effect between the olefinic proton on the C-3 carbon and the protons of the group R directly attached to the C-4 carbon was observed.

(15) Caramella, P.; Houk, K.N. *Tetrahedron Lett.* **1981**, *22*, 819.
(16) (a) Schlosser, M.; Hammer, E. *Helv. Chim. Acta* **1974**, *57*, 2547. (b) Corey, E. J.; Widiger, G. N. *J. Org. Chem.* **1975**, *40*, 2975. (c) Barluenga, J.; Fernández, J. R.; Yus, M. *J. Chem. Soc., Perkin Trans. 1*, **1985**, 447.

Scheme IV

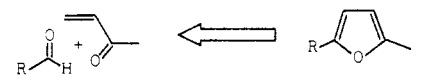


Scheme V[a]



[a] Reagents: (a) MeLi–LiBr, THF, −20 °C; (b) RCHO, −20 °C; (c) HCl–H_2O, overnight.

Scheme VI



Interestingly, the cyclic dihydropyran derivative **24** obtained from epichlorohydrin alkylation was isolated as the sole stereoisomer. The assigned stereochemistry is based on a strong positive nuclear Overhauser effect between the methyl and the iodomethyl groups. A rationalization for the obtention of stereoisomer **24** is presented in Scheme IV. Initially, the expected opening of the epoxide by the carbanion at the less hindered position probably takes place, followed by cyclization through the more favored transition state **24‡**, yielding the product **24**. The other possibility through **24′‡**, with the more bulky methyl group[17] in the pseudoaxial position, does not take place due to steric requirements. In addition to this, product **24** is thermodynamically more stable than **24′** because the pseudoaxial anomeric position of the methoxy group is favored by stereoelectronic effects (Scheme IV).[18] Finally, the chlorine–iodine exchange to give **24** can be explained because the initially used methyllithium was prepared by starting from methyl iodide; so, during the whole process **12** → **24**, an S_N reaction by the iodide anion with formation of the corresponding iodinated product takes place. This type of substitution has been observed in other similar processes.[19,20]

Interest in the furan unit is great due to both its occurrence in a variety of biologically active natural prod-

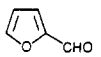
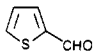
(17) (a) Booth, H.; Everett, J. R. *J. Chem. Soc., Chem. Commun.* **1976**, 278. (b) Schneider, H. J.; Hoppen, V. *Tetrahedron Lett.* **1974**, 579.
(18) See, for instance: Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon: Oxford, 1983; Chapter 2.
(19) Barluenga, J.; Concellón, J. M.; Fernández-Simón, J. L.; Yus, M. *J. Chem. Soc., Chem. Commun.* **1988**, *536*.
(20) Another possibility suggested by one of the referees is that the initially formed chlorohydrin collapses to an epoxide which then opens to an iodohydrin. The iodohydrin then cyclizes to **24** without incorporation of the iodide through an S_N2 displacement of a chloride. We thank this referee for this suggestion.

Table II. Preparation of Products 23 and 24

entry	RHal	reaction time: *t* (RHal)	reaction time: *t* (H_3O^+)	product: no.	product: yield,[a] %	product: mp,[b] °C (solvent)
1	MeI	1 h	3 h	**23a**	88	oil[c]
2	CH_2=$CHCH_2Br$	5 h	2 h	**23b**	87	oil[d]
3	$EtOCH_2Cl$	1 day	4 h	**23c**	80	oil[e]
4	CH_2=$C(CH_3)CH_2Cl$	1 day	4 h	**23d**	76	oil[f]
5	*n*-BuBr	1 day	2 h	**23e**	75	48–49 (hexane–CCl_4)
6	$PhCH_2Cl$	6 h	1 day	**23f**	72	oil[d]
7	$CH_3(CH_2)_6I$	1 h	2 h	**23g**	70	oil[g]
8	$\overline{OCH_2CHCH_2Cl}$	1 day		**24**	74	116–117 dec (hexane–CCl_4)

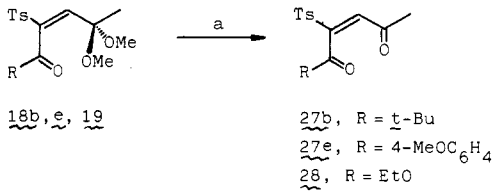
[a] Isolated yield (after flash chromatography; silica gel, hexane–ether) based on starting material **12**. [b] Uncorrected. [c] TLC R_f 0.34 (hexane–ether, 1/2); lit.,[12a] oil. [d] TLC R_f 0.54 (hexane–ether, 1/4). [e] TLC R_f 0.30 (hexane–ether, 1/2). [f] TLC R_f 0.40 (hexane–ether, 1/2). [g] TLC R_f 0.62 (hexane–ether, 1/4).

Table III. Preparation of 3-Tosylfurans 25

entry	RCHO	product: no.	product: yield,[a] %	product: mp,[b] °C (solvent)
1	CH_2O[c]	**25a**	89[d]	103–104 (ether)
2	$CH_3CH\overset{E}{=}$ CHCHO	**25b**	82[d]	87–88 (hexane–CCl_4)
3	*i*-BuCHO	**25c**	78	56–57 (hexane–CCl_4)
4	PhCHO	**25d**	80	142–143 (hexane–CH_2Cl_2)
5		**25e**	75	106–107 (hexane–CCl_4)
6		**25f**	50	105–107 (hexane–CCl_4)

[a] Isolated yield (after flash chromatography; silica gel, hexane–ether) based on starting material **12**. [b] Uncorrected. [c] Paraformaldehyde was used. [d] Isolated crude yield; product was homogeneous by TLC and pure by NMR.

Scheme VII[a]



18b,e, 19

27b, R = t-Bu
27e, R = 4-$MeOC_6H_4$
28, R = EtO

[a] Reagent: (a) CF_3CO_2H–H_2O.

ucts[21] and its utility as a synthetic intermediate.[22,23] Consequently, we explored the in situ acid hydrolysis of compounds **17** to prepare the corresponding substituted 3-tosylfurans.[7b] Thus, after quenching of the lithiated intermediate **13** with different aldehydes, the reaction mixture was treated with 1 N hydrochloric acid overnight to yield the furan products **25** (Scheme V and Table III). The furans most likely arise from cyclization and dehydration of keto alcohol **26**. 3-(Arylsulfonyl)furans of the type **25** have been described only very recently[24] and are interesting because the directing effect of the sulfone functionality in the furan ring allows for regioselective functionalization, either in metalation or in acylation reactions. On the other hand, since the tosyl moiety can be easily removed by reductive cleavage,[24b] this methodology represents an efficient route to furans from butenone and aldehydes (Scheme VI).[25]

Table IV. Preparation of 1,4-Enedicarbonyl Compounds 27 and 28

entry	starting material	product: no.	product: yield,[a] %	product: TLC R_f[b]
1	**18b**	**27b**	81	0.62
2	**18e**	**27e**	93[c]	0.44
3	**19**	**28**	80	0.57

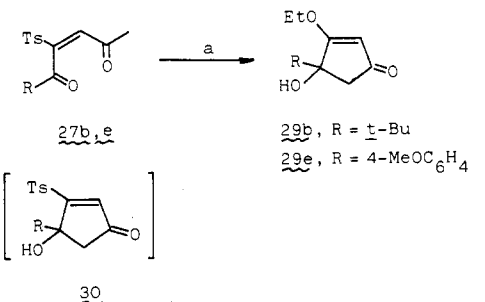
[a] Isolated crude yield based on starting material **12**, precursor of protected systems **18** and **19**; the product was an oil homogeneous by TLC and pure by NMR. [b] Hexane–ether, 1/10. [c] Based on compound **18e**.

Table V. Preparation of Substituted Cyclopentenones 29

entry	starting material	product: no.	product: yield,[a] %	product: mp,[b] °C (hexane–$CHCl_3$)
1	**27b**	**29b**	55	76–78
2	**27e**	**29e**	70	83–85

[a] Isolated yield (after flash chromatography; silica gel, hexane–ether) based on starting enedione **27**. [b] Uncorrected.

Scheme VIII[a]



27b,e

29b, R = t-Bu
29e, R = 4-$MeOC_6H_4$

30

[a] Reagents: (a) NaOH–EtOH.

Finally, we have studied the possibility of obtaining 1,4-enedicarbonyl derivatives by hydrolysis of compounds **18** or **19** and studied their potential use as precursors to substituted cyclopentenones. Thus, treatment of compounds **18b,e** or **19** with aqueous trifluoroacetic acid gave the expected products **27b,e** or **28**, respectively. When the same procedure was applied to the analogous compounds containing hydrogen atoms α to the carbonyl group (for instance, **18a,c**), an intractable mixture of reaction products was obtained (Scheme VII and Table IV).

In the case of compounds **27**, the stereochemistry was corroborated chemically by a cyclization reaction. Treatment of enediones **27** with sodium hydroxide in ethanol yielded the functionalized cyclopentenones **29**. Nucleophilic substitution of the sulfone moiety by the

(21) (a) Dean, F. M.; Sargent, M. V. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, 1984; Vol. 4, p 531. (b) Crews, P.; Naylor, S. *Prog. Chem. Org. Nat. Prod.* **1985**, *48*, 203.
(22) Reference 21a, p 619.
(23) Tanis, S. P.; Head, D. B. *Tetrahedron Lett.* **1984**, *25*, 4451 and references cited therein.
(24) (a) Hartman, G. D.; Halczenko, W. *Tetrahedron Lett.* **1987**, *28*, 3241. (b) McCombie, S. W.; Shankar, B. B.; Ganguly, A. K. *Tetrahedron Lett.* **1987**, *28*, 4123.
(25) Inomata, K.; Aoyama, S.; Kotake, H. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 930.

ethoxy group can take place either on the starting enedione **27** or following cyclization to compound **30** (Scheme VIII and Table V).

Unsubstituted enedicarbonyl compounds have occasionally been employed as intermediates in the synthesis of cyclopentenone derivatives[26] due to their difficult preparation in the necessary cis configuration and their easy cis–trans isomerization.[27]

Conclusions

(*E*)-4-Lithio-4-tosylbutenone dimethyl ketal is a useful β-acylvinyl anion equivalent for organic synthesis and therefore represents a new d^3 reagent[28] with reactivity umpolung when compared to the corresponding α,β-unsaturated carbonyl precursor. Through the reaction of this intermediate with electrophiles, a wide series of sulfonyl-containing derivatives including furans and cyclopentenones have been prepared in a regio- and stereoselective manner. These results show that a variety of functionalized organic compounds are accessible from the readily available methyl vinyl ketone via this new methodology.

Experimental Section

General Methods. Melting points were obtained with a Büchi-Tottoli capillary melting point apparatus and are uncorrected. Flash column chromatography was done on Merck grade 60 silica gel (230–400 mesh), and TLC analyses were obtained with Merck 60F-254 precoated silica gel on aluminum sheets (visualization by UV). Infrared spectra were recorded on a Perkin-Elmer 577 spectrometer. ^1H and ^{13}C NMR spectra were obtained on Varian FT-80 and Bruker AC-300 spectrometers. When CCl_4 was used as solvent, a D_2O capillary was employed as lock reference. Chemical shifts are reported as δ values in parts per million relative to tetramethylsilane (δ = 0.0) as an internal standard. For ^1H NMR, data are reported as follows: chemical shift (multiplicity, coupling constants, integrated intensity, assignment); assignments were confirmed by double resonance experiments. ^{13}C NMR assignments were done on the basis of off resonance (FT-80) or DEPT (AC-300) experiments. Mass spectra were obtained with a Hewlett-Packard 5987A spectrometer at 70 eV. Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer.

Methyllithium was prepared in ether from methyl iodide (Aldrich) and lithium wire (Merck). Electrophilic reagents were commercially available (Aldrich, Fluka) of the best grade and were used without further purification. Ether was dried successively with anhydrous calcium chloride, sodium sulfate, sodium, and finally a K–Na (K_3Na) liquid alloy[29] under reflux. Following distillation, it was stored under argon. Tetrahydrofuran (THF) was dried successively with anhydrous calcium chloride and sodium sulfate. It was then distilled from lithium aluminum hydride and distilled and stored under argon. Reactions that involve organolithium reagents were carried out in an argon atmosphere by using oven- or flame-dried glassware.

(*E*)-4-Tosylbutenone Dimethyl Ketal (12). A solution of 4-tosyl-3-buten-2-one[12a] (7.15 g, 30 mmol), trimethyl orthoformate (6.8 mL, 60 mmol), and *p*-toluenesulfonic acid monohydrate (0.34 g, 1.8 mmol) in absolute methanol (100 mL) was heated at 50 °C for 1 day. The reaction mixture was evaporated in vacuo, and the residue was dissolved in dichloromethane (100 mL). The resulting solution was washed with a saturated aqueous solution of $NaHCO_3$, dried over anhydrous Na_2SO_4, and evaporated till dryness to give 7.54 g (93%) of the title compound as a brown solid. Recrystallization from chloroform–hexane gave beige crystals: mp 99–100 °C; IR (Nujol) 3060, 1590, 980 (CH=C), 1300, 1150 cm^{-1} (SO_2); ^1H NMR (80 MHz, $CDCl_3$) δ 1.35 (s, 3 H, CH_3CO), 2.4 (s, 3 H, CH_3Ar), 3.1 (s, 6 H, 2 CH_3O), 6.6, 6.65 (2 d, J = 15 Hz, 2 H, CH=CH), 7.3, 7.7 (2 d, J = 8 H, 4 H, aromatic H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 21.7, 23.0 (CH_3Ar, CH_3CO), 48.7 (2 CH_3O), 97.8 (CO), 126.6, 129.1, 136.5, 143.4 (aromatic C), 132.8, 144.0 (CH=CH); MS, m/z 255 ($M^+ - CH_3$, 19), 239 (33), 139 (36), 115 (96), 99 (32), 89 (90), 83 (100), 43 (39). Anal. Calcd for $C_{13}H_{18}O_4S$: C, 57.76; H, 6.71. Found: C, 58.0; H, 6.9.

Preparation of (*E*)-4-Lithio-4-tosylbutenone Dimethyl Ketal and Reaction with Electrophiles. Isolation of Products 12–22. General Procedure. Methyllithium (2.2 mmol) in ether was added dropwise to a stirred solution of crude (*E*)-4-tosylbutenone dimethyl ketal (**12**) (0.54 g, 2 mmol) and lithium bromide (0.19 g, 2.2 mmol) in THF (10 mL) at −20 °C. After 10 min, the corresponding electrophilic reagent (2 mmol)[30] was added at −20 °C[31] and the mixture stirred for 30 min at the same temperature and 30 min at room temperature. The resulting solution was quenched with water and extracted with dichloromethane (2 × 25 mL). The organic layer was washed with water, dried over anhydrous Na_2SO_4, and evaporated in vacuo to afford compounds **12–22**, which were purified by recrystallization or by flash chromatography on silica gel. Yields and melting points are reported in Table I. Spectral and analytical data follow.

(*E*)-4-Deuterio-4-tosylbutenone dimethyl ketal (14): IR (Nujol) 3060, 1590, 825 (CH=C), 1310, 1150 cm^{-1} (SO_2); ^1H NMR (80 MHz, CCl_4) δ 1.3 (s, 3 H, CH_3CO), 2.4 (s, 3 H, CH_3Ar), 3.05 (s, 6 H, 2 CH_3O), 6.6 (s, 1 H, CHCO), 7.3–7.7 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 21.55, 22.8 (CH_3CO, CH_3Ar), 49.3 (2 CH_3O), 98.6 (CO), 127.6, 129.8, 137.6, 144.8 (aromatic C), 133.3 (t, J_{CD} = 28.1 Hz, CD), 145.0 (CHCO); MS, m/z 256 ($M^+ - CH_3$, 8), 240 (15), 139 (37), 116 (75), 100 (26), 89 (77), 84 (100), 43 (41).

(*E*)-4-Tosyl-4-(trimethylsilyl)butenone dimethyl ketal (15): IR (Nujol) 3040, 1580, 820 (CH=C), 1280, 1130 cm^{-1} (SO_2); ^1H NMR (80 MHz, CCl_4) δ 0.05 (s, 9 H, 3 CH_3Si), 1.35 (s, 3 H, CH_3CO), 2.4 (s, 3 H, CH_3Ar), 3.15 (s, 6 H, 2 CH_3O), 6.95 (s, 1 H, CHCO), 7.25, 7.65 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR (20 MHz, CCl_4) δ 1.9 (3 CH_3Si), 21.6, 22.2 (CH_3CO, CH_3Ar), 49.0 (2 CH_3O), 100.5 (CO), 127.0, 129.5, 137.9, 143.7 (aromatic C), 147.0, 156.0 (CH=C); MS, m/z 342 (M^+, 1), 295 (41), 171 (43), 155 (33), 89 (100), 43 (20). Anal. Calcd for $C_{16}H_{26}O_4SSi$: C, 56.10; H, 7.65. Found: C, 55.6; H, 7.5.

(*E*)-4-Tosylpent-3-en-2-one dimethyl ketal (16a): IR (Nujol) 3050, 1590, 810 (CH=C), 1300, 1150 cm^{-1} (SO_2); ^1H NMR (80 MHz, $CDCl_3$) δ 1.35 (s, 3 H, CH_3CO), 1.95 (s, 3 H, CH_3C=C), 2.4 (s, 3 H, CH_3Ar), 3.1 (s, 6 H, 2 CH_3O), 6.7 (m, 1 H, CHCO), 7.3, 7.7 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 11.8 (CH_3C=C), 21.2, 22.2 (CH_3CO, CH_3Ar), 48.4 (2 CH_3O), 100.2 (CO), 127.6, 129.5, 135.7, 143.9 (aromatic C), 139.5, 141.0 (CH=C); MS, m/z 269 ($M^+ - CH_3$, 9), 129 (74), 97 (100), 89 (72), 83 (20), 43 (33). Anal. Calcd for $C_{14}H_{20}O_4S$: C, 59.13; H, 7.09. Found: C, 59.0; H, 7.2.

(*E*)-4-Tosylhepta-3,6-dien-2-one dimethyl ketal (16b): IR (film) 3050, 1635, 1590, 810 (CH=C), 1310, 1150 cm^{-1} (SO_2); ^1H NMR (80 MHz, CCl_4) δ 1.3 (s, 3 H, CH_3CO), 2.35 (s, 3 H, CH_3Ar), 3.1 (s, 8 H, 2 CH_3O, CH_2CS), 4.7, 5.4 (2 m, 3 H, $CH=CH_2$), 6.65 (s, 1 H, CHCO), 7.2, 7.65 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 21.2, 22.5 (CH_3CO, CH_3Ar), 30.6 (CH_2CS), 48.7 (2 CH_3O), 100.8 (CO), 115.9 (CH_2=C), 127.9, 129.5, 134.5, 136.7, 141.4, 143.5, 144.2 (aromatic C, CH=C, $CH=CH_2$); MS, m/z 295 ($M^+ - CH_3$, 2), 155 (11), 139 (15), 123 (100), 91 (19), 89 (36), 43 (35).

(*E*)-5-Hydroxy-4-tosylpent-3-en-2-one dimethyl ketal (17a): IR (CCl_4) 3500 (OH), 3040, 1590, 820 (CH=C), 1310, 1150 cm^{-1} (SO_2); ^1H NMR (80 MHz, CCl_4) δ 1.35 (s, 3 H, CH_3CO), 2.3 (s, 3 H, CH_3Ar), 3.1 (s, 6 H, 2 CH_3O), 3.5 (br s, 1 H, OH), 4.2 (s, 2 H, CH_2), 6.7 (s, 1 H, CHCO), 7.25, 7.7 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR (20 MHz, CCl_4) δ 22.6, 24.1 (CH_3CO, CH_3Ar), 50.0 (2 CH_3O), 55.6 (CH_2), 101.0 (CO), 128.9, 130.5, 137.7, 143.9, 145.8 (aromatic C, CH=C); MS, m/z 285 ($M^+ - CH_3$, 5), 145 (28), 129 (23), 113 (90), 91 (25), 89 (100), 83 (22), 55 (21), 43 (46). Anal. Calcd for $C_{14}H_{20}O_5S$: C, 55.98; H, 6.71. Found: C, 56.2; H, 6.8.

(*E,E*)-5-Hydroxy-4-tosylocta-3,6-dien-2-one dimethyl ketal (17b): IR (CCl_4) 3460 (OH), 3030, 1665, 1590, 970, 810 (CH=C),

(26) D'Ascoli, R.; D'Auria, M.; De Mico, A.; Piancatelli, G.; Scettri, A. *J. Org. Chem.* **1980**, *45*, 4500.
(27) Floyd, M. B. *J. Org. Chem.* **1978**, *43*, 1641.
(28) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239.
(29) Gilman, H.; Young, R. W. *J. Org. Chem.* **1936**, *1*, 315.
(30) When water or deuterium oxide was used as electrophile, a large excess (ca. 10 mmol) was added.
(31) In the case of acyl chlorides, the reagent was added at −40 °C.

1310, 1300, 1150 cm^{-1} (SO_2); ^1H NMR (80 MHz, CCl_4) δ 1.35 (s, 3 H, CH_3CO), 1.5 (d, J = 6 Hz, 3 H, CH_3CH), 2.35 (s, 3 H, CH_3Ar), 3.1 (s, 6 H, 2 CH_3O), 3.7 (br s, 1 H, OH), 5.0 (m, 1 H, CHO), 5.4 (m, 2 H, CH=CH), 6.5 (s, 1 H, CHCO), 7.25, 7.65 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR (20 MHz, CCl_4) δ 18.8 (CH_3CH), 22.7, 24.0 (CH_3CO, CH_3Ar), 50.0, 50.5 (2 CH_3O), 68.7 (CHO), 101.5 (CO), 126.45, 131.8 (CH=CH), 128.3, 129.6, 138.3, 142.4, 144.2, 144.7 (aromatic C, CH=C); MS, m/z 308 ($M^+ - CH_3OH$, 6), 276 (37), 197 (21), 153 (24), 139 (42), 122 (40), 121 (20), 111 (28), 105 (23), 91 (74), 90 (22), 77 (42), 65 (32), 43 (100).

(*E*)-5-Hydroxy-7-methyl-4-tosyloct-3-en-2-one dimethyl ketal (17c): IR (Nujol) 3420 (OH), 1590, 870, 820 (CH=C), 1300, 1140 cm^{-1} (SO_2); ^1H NMR (300 MHz, $CDCl_3$) δ 0.83, 0.88 (2 d, J = 7.5 Hz, 6 H, 2 CH_3CH), 1.20–1.85 (m with s at δ 1.44, 6 H, CH_3CO, $CHCH_3$, CH_2), 2.40 (s, 3 H, CH_3Ar), 3.19 (s, 6 H, 2 CH_3O), 3.42 (d, J = 12 Hz, 1 H, OH), 4.44 (t, J = 12 Hz, 1 H, CHO), 6.49 (s, 1 H, CHCO), 7.25, 7.63 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 21.2, 22.5, 22.8, 23.7, 24.9 (2 CH_3CH, CH_3CO, CH_3Ar, CH_2, $CHCH_3$), 49.3 (2 CH_3O), 66.7 (CHO), 100.8 (CO), 127.6, 129.5, 137.9, 140.7, 144.2, 149.2 (aromatic C, CH=C); MS, m/z 341 ($M^+ - CH_3$, 2), 267 (100), 169 (25), 139 (70), 112 (45), 111 (95), 91 (30), 89 (65), 85 (24), 83 (32), 43 (56).

(*E*)-5-Hydroxy-5-phenyl-4-tosylpent-3-en-2-one dimethyl ketal (17d): IR (Nujol) 3400 (OH), 3040, 1640, 1590, 1490, 810 (CH=C), 1300, 1140 cm^{-1} (SO_2); ^1H NMR (80 MHz, $CDCl_3$) δ 1.1 (s, 3 H, CH_3CO), 2.4 (s, 3 H, CH_3Ar), 3.1, 3.25 (2 s, 6 H, 2 CH_3O), 4.6 (d, J = 12 Hz, 1 H, OH), 5.9 (d, J = 12 Hz, 1 H, CHO), 7.05 (s, 1 H, CHCO), 7.1–8.1 (m, 9 H, aromatic H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 21.2, 21.9 (CH_3CO, CH_3Ar), 48.5, 49.0 (2 CH_3O), 68.4 (CHO), 100.8 (CO), 125.1, 126.4, 127.3, 127.6, 129.4, 136.7, 141.7, 143.5, 144.2, 148.5 (aromatic C, CH=C); MS, m/z 344 ($M^+ - CH_3OH$, 37), 189 (40), 158 (45), 157 (83), 129 (35), 105 (43), 91 (36), 89 (100), 83 (25), 77 (23), 43 (48). Anal. Calcd for $C_{20}H_{24}O_5S$: C, 63.81; H, 6.43. Found: C, 63.5; H, 6.5.

(*E*)-5-(2-Furyl)-5-hydroxy-4-tosylpent-3-en-2-one dimethyl ketal (17e): IR (Nujol) 3500 (OH), 3100, 1600, 820 (CH=C), 1300, 1130 cm^{-1} (SO_2); ^1H NMR (80 MHz, $CDCl_3$) δ 1.4 (s, 3 H, CH_3CO), 2.4 (s, 3 H, CH_3Ar), 3.2, 3.25 (2 s, 6 H, 2 CH_3O), 4.8 (d, J = 12 Hz, 1 H, OH), 5.9 (d, J = 12 Hz, 1 H, CHOH), 6.3, 7.7 (2 m, 3 H, furanic H), 7.2 (s, 1 H, $CHCOCH_3$), 7.3, 7.65 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR (20 MHz, CCl_4) δ 22.2, 23.5 (CH_3CO, CH_3Ar), 49.7, 50.2 (2 CH_3O), 64.7 (CHOH), 101.5 ($COCH_3$), 107.4, 110.5, 128.3, 130.2, 137.7, 142.05, 144.5, 145.2, 146.4, 154.5 (aromatic and furanic C, CH=C); MS, m/z 334 ($M^+ - CH_3OH$, 46), 179 (38), 151 (22), 148 (73), 147 (54), 139 (33), 119 (28), 105 (40), 101 (24), 98 (50), 95 (44), 91 (80), 89 (70), 83 (46), 65 (30), 43 (100). Anal. Calcd for $C_{18}H_{22}O_6S$: C, 59.00; H, 6.05. Found: C, 58.7; H, 6.0.

(*E*)-5-Hydroxy-5-(2-thienyl)-4-tosylpent-3-en-2-one dimethyl ketal (17f): IR ($CHCl_3$) 3300 (OH), 3040, 1585, 1490, 810 (CH=C), 1300, 1150 cm^{-1} (SO_2); ^1H NMR (80 MHz, $CDCl_3$) δ 1.3 (s, 3 H, CH_3CO), 2.4 (s, 3 H, CH_3Ar), 3.2, 3.25 (2 s, 6 H, 2 CH_3O), 5.2 (d, J = 12 Hz, 1 H, OH), 6.0 (d, J = 12 Hz, 1 H, CHO), 6.8–7.9 (m with 2 d at δ 7.3, 7.7, J = 8 Hz, 8 H, aromatic and thienylic H, CHCO); ^{13}C NMR (20 MHz, $CDCl_3$) δ 21.8, 22.4 (CH_3CO, CH_3Ar), 49.2, 50.0 (2 CH_3O), 66.4 (CHO), 101.0 (CO), 124.1, 124.4, 126.3, 127.9, 129.7, 136.3, 143.1, 144.1, 146.6, 147.5 (aromatic and thienylic C, CH=C); MS, m/z 350 ($M^+ - CH_3OH$, 63), 266 (21), 195 (28), 163 (100), 162 (43), 135 (60), 111 (66), 91 (49), 89 (70), 83 (30), 65 (20), 43 (55). Anal. Calcd for $C_{18}H_{22}O_5S_2$: C, 56.52; H, 5.80. Found: C, 56.5; H, 5.6.

(*E*)-5,5-Dimethoxy-3-tosylhex-3-en-2-one (18a): IR (CCl_4) 3060, 1630, 1590, 820 (CH=C), 1710 (C=O), 1315, 1140 cm^{-1} (SO_2); ^1H NMR (80 MHz, CCl_4) δ 1.3 (s, 3 H, CH_3CO), 2.3, 2.35 (2 s, 6 H, CH_3CO, CH_3Ar), 3.05 (s, 6 H, 2 CH_3O), 6.4 (s, 1 H, CHCO), 7.25, 7.6 (2 d, J =8 Hz, 4 H, aromatic H); ^{13}C NMR (20 MHz, CCl_4) δ 21.9, 22.6 (CH_3CO, CH_3Ar), 32.1 (CH_3C=O), 49.4 (2 CH_3O), 100.0 (CO), 128.3, 129.7, 136.8, 145.0 (aromatic C), 141.1, 148.1 (CH=C), 197.0 (C=O); MS, m/z 312 (M^+, 1), 141 (19), 125 (33), 89 (100), 83 (75), 43 (35).

(*E*)-2,2-Dimethyl-6,6-dimethoxy-4-tosylhept-4-en-3-one (18b): IR ($CDCl_3$) 3030, 1640, 1595 (CH=C), 1690 (C=O), 1320, 1150 cm^{-1} (SO_2); ^1H NMR (300 MHz, $CDCl_3$) δ 1.19 (s, 9 H, 3 CH_3CC=O), 1.33 (s, 3 H, CH_3CO), 2.34 (s, 3 H, CH_3Ar), 2.90, 3.09 (2 s, 6 H, 2 CH_3O), 6.53 (s, 1 H, CHCO), 7.23, 7.60 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.54, 22.14 (CH_3CO, CH_3Ar), 27.61 (3 CH_3CC=O), 44.65 (CC=O), 49.23, 49.49 (2 CH_3O), 99.43 (CO), 128.27, 129.58, 136.14, 141.78, 144.72, 146.21 (aromatic C, CH=C), 207.59 (C=O); MS, m/z 339 ($M^+ - CH_3$, 2), 266 (100), 265 (24), 141 (50), 139 (56), 111 (31), 83 (45). Anal. Calcd for $C_{18}H_{26}O_5S$: C, 60.99; H, 7.39. Found: C, 60.7; H, 7.3.

(*E*)-1-Cyclohexyl-4,4-dimethoxy-2-tosylpent-2-en-1-one (18c): IR ($CDCl_3$) 3020, 1640, 1600 (CH=C), 1700 (C=O), 1320, 1150 cm^{-1} (SO_2); ^1H NMR (300 MHz, $CDCl_3$) δ 1.00–2.10 (m with s at δ 2.35, 4 H, CHC=O, CH_3Ar), 3.00 (s, 6 H, 2 CH_3O), 6.62 (s, 1 H, CHO), 7.25, 7.61 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.48, 22.19 (CH_3CO, CH_3Ar), 25.82, 25.89, 28.01 (5 CH_2), 49.30 (2 CH_3O), 51.86 (CHC=O), 99.55 (CO), 128.15, 129.60, 136.77, 143.01, 144.63, 146.48 (aromatic C, CH=C), 202.54 (C=O); MS, m/z 365 ($M^+ - CH_3$, 4), 297 (52), 266 (48), 265 (61), 193 (20), 141 (94), 139 (100), 111 (30), 91 (20), 89 (50), 83 (55), 43 (21). Anal. Calcd for $C_{20}H_{28}O_5S$: C, 63.13; H, 7.42. Found: C, 63.4; H, 7.5.

(*E*)-4,4-Dimethoxy-1-phenyl-2-tosylpent-2-en-1-one (18d): IR (Nujol) 3060, 1600, 1580, 825, 760, 680 (CH=C), 1665 (C=O), 1320, 1310, 1150 cm^{-1} (SO_2); ^1H NMR (80 MHz, $CDCl_3$) δ 1.3 (s, 3 H, CH_3CO), 2.45 (s, 3 H, CH_3Ar), 2.95 (s, 6 H, 2 CH_3O), 7.05 (s, 1 H, CHCO), 7.2–8.0 (m, 9 H, aromatic H); ^{13}C NMR (20 MHz, CCl_4) δ 22.2, 22.9 (CH_3CO, CH_3Ar), 49.7 (2 CH_3O), 99.9 (CO), 128.3, 128.6, 128.95, 129.9, 130.8, 133.0, 134.9, 137.4, 138.1, 144.2, 144.9, 145.8 (aromatic C, CH=C), 188.5 (C=O); MS, m/z 359 ($M^+ - CH_3$, 6), 187 (25), 145 (50), 105 (20), 89 (100), 43 (20). Anal. Calcd for $C_{20}H_{22}O_5S$: C, 64.15; H, 5.92. Found: C, 64.0; H, 5.8.

(*E*)-4,4-Dimethoxy-1-(4-methoxyphenyl)-2-tosylpent-2-en-1-one (18e): IR ($CDCl_3$) 3030, 1600, 1595, 1530 (CH=C), 1680 (C=O), 1330, 1160 cm^{-1} (SO_2); ^1H NMR (300 MHz, $CDCl_3$) δ 1.32 (s, 3 H, CH_3CO), 2.42 (s, 3 H, CH_3Ar), 2.93 (s, 6 H, 2 CH_3OCCH_3), 3.84 (s, 3 H, CH_3OAr), 6.87, 7.63 (m and d, J = 8 Hz, 5 H, CHCO, $CH_3OC_6H_4$), 7.28, 7.84 (2 d, J = 8 Hz, 4 H, $CH_3C_6H_4$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.65, 22.05 (CH_3CO, CH_3Ar), 49.12, 55.27 (3 CH_3O), 99.71 (CO), 113.37, 128.60, 129.60, 130.63, 131.48, 136.41, 143.27, 144.49, 145.40, 163.52 (aromatic C, CH=C), 187.90 (C=O); MS, m/z 404 (M^+, 8), 374 (37), 233 (25), 217 (51), 175 (51), 135 (57), 89 (100). Anal. Calcd for $C_{21}H_{24}O_6S$: C, 62.36; H, 5.98. Found: C, 62.5; H, 5.8.

Ethyl (*E*)-4,4-dimethoxy-2-tosylpent-2-enoate (19): IR ($CDCl_3$) 3020, 1650, 1600 (CH=C), 1740 (C=O), 1340, 1160 cm^{-1} (SO_2); ^1H NMR (300 MHz, $CDCl_3$) δ 1.15 (t, J = 7 Hz, 3 H, CH_3CH_2), 1.38 (s, 3 H, CH_3CO), 2.34 (s, 3 H, CH_3Ar), 3.04 (s, 6 H, 2 CH_3O), 4.11 (q, J = 7 Hz, 2 H, CH_2), 6.77 (s, 1 H, CHCO), 7.25, 7.66 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.71 (CH_3CH_2), 21.42, 21.85 (CH_3CO, CH_3Ar), 49.27 (2 CH_3O), 61.76 (CH_2), 99.69 (CO), 128.27, 129.56, 136.22, 140.30, 144.43, 144.79 (aromatic C, CH=C), 162.25 (C=O); MS, m/z 327 ($M^+ - CH_3$, 19), 187 (30), 172 (24), 155 (22), 137 (22), 139 (60), 91 (27), 89 (100), 83 (32), 43 (24).

(*E*)-*N*-Phenyl-4,4-dimethoxy-2-tosylpent-2-enamide (20): IR ($CDCl_3$) 3340 (NH), 3060, 3030, 1640, 1600, 1530 (CH=C), 1680 (C=O), 1320, 1150 cm^{-1} (SO_2); ^1H NMR (300 MHz, $CDCl_3$) δ 1.51 (s, 3 H, CH_3CO), 2.41 (s, 3 H, CH_3Ar), 3.18 (s, 6 H, 2 CH_3O), 6.99 (s, 1 H, CHCO), 7.12, 7.30 (2 m, 5 H, C_6H_5N), 7.46, 7.76 (2 d, J = 8 Hz, 4 H, $CH_3C_6H_4$), 8.02 (br s, 1 H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.64, 22.29 (CH_3CO, CH_3Ar), 49.63 (2 CH_3O), 100.21 (CO), 120.10, 124.76, 128.39, 128.96, 129.91, 135.39, 137.25, 142.46, 144.32, 145.18 (aromatic C, CH=C), 159.23 (C=O); MS, m/z 389 (M^+, 4), 357 (22), 278 (77), 141 (62), 139 (100), 93 (21), 91 (30), 89 (23), 43 (23). Anal. Calcd for $C_{20}H_{23}NO_5S$: C, 61.72; H, 5.95; N, 3.60. Found: C, 61.4; H, 5.9; N, 3.7.

3,4-Bis(methylthio)-4-tosylbutan-2-one dimethyl ketal (21): ^1H NMR (80 MHz, CCl_4) δ 1.3 (s, 3 H, CH_3CO), 2.0, 2.05 (2 s, 6 H, 2 CH_3S), 2.4 (s, 3 H, CH_3Ar), 3.15, 3.2 (2 s, 6 H, 2 CH_3O), 3.5 (m, 2 H, 2 CHS), 7.3, 7.85 (2 d, J = 9 Hz, 4 H, aromatic H); ^{13}C NMR (20 MHz, CCl_4) δ 19.4 (2 CH_3S, CH_3CO), 22.25 (CH_3Ar), 48.45, 49.0 (2 CH_3O), 52.2 ($CHSO_2$), 74.7 (CHCO), 104.9 (CO), 129.6, 130.5, 135.2, 145.2 (aromatic C); MS, m/z 318 ($M^+ - CH_3OCH_3$, 2), 163 (56), 121 (100), 120 (24), 91 (20), 43 (50).

3,4-Bis(methylthio)-4-tosylbutan-2-one (22): IR (CCl_4) 3030, 1590, 1500, 815 (CH=C), 1710 (C=O), 1300, 1140 cm^{-1} (SO_2); ^1H NMR (80 MHz, CCl_4) δ 1.85 (s, 3 H, CH_3C=O), 2.3, 2.35, 2.4 (3 s, 9 H, CH_3Ar, 2 CH_3S), 3.8, 4.3 (2 d, J = 11 Hz, 2 H, 2 CHS), 7.3, 7.75 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR (20 MHz, CCl_4) δ 13.5, 14.9 (2 CH_3S), 22.6 (CH_3Ar), 28.5 (CH_3C=O), 49.1

(CHC=O), 67.8 ($CHSO_2$), 129.9, 135.2, 145.2 (aromatic C), 196.3 (C=O); MS, *m/z* the same as for **21**.

Preparation of Compounds 23 and 24. General Procedure. Intermediate **13** was prepared as described above for **12–22**. The resulting solution of **13** (2 mmol) was treated with the corresponding alkyl halide (2.2 mmol) for 1–24 h (see Table II), the temperature being allowed to rise from −20 to 20 °C. The resulting mixture was then hydrolyzed with water (5 mL) and stirred with 1 N hydrochloric acid (10 mL) for 2–24 h (see Table II).[32] Then it was extracted with dichloromethane (2 × 25 mL), and the organic layer was washed with saturated aqueous $NaHCO_3$ and water, dried over anhydrous Na_2SO_4, and evaporated in vacuo to yield compounds **23** and **24**, which were purified by flash chromatography on silica gel and recrystallized. Yields, melting points, and R_f values are described in Table II. Spectral and analytical data follow.

(*E*)-4-Tosylhepta-3,6-dien-2-one (23b): IR ($CDCl_3$) 3080, 3060, 1640, 1615, 1600 (CH=C), 1710 (C=O), 1320, 1305, 1150 cm^{-1} (SO_2); ^1H NMR (300 MHz, $CDCl_3$) δ 2.23, 2.29 (2 s, 6 H, 2 CH_3), 3.24, 3.25 (2 d, *J* = 6.5 Hz, 2 H, CH_2C=C), 4.74 (m, 2 H, CH_2=C), 5.42 (m, 1 H, C*H*=CH_2), 7.20 (s, 1 H, CHC=O), 7.22, 7.64 (2 d, *J* = 8 Hz, 4 H, aromatic H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.13 (CH_3Ar), 30.75 (CH_2C=C), 31.63 (CH_3C=O), 116.91 (CH_2=C), 128.39, 129.63, 134.49, 144.85 (aromatic C), 130.70, 132.14 (CHC=O, CH=CH_2), 151.65 (CCH_2), 196.96 (C=O); MS, *m/z* 264 (M^+, 8), 222 (36), 157 (98), 139 (85), 91 (55), 66 (42), 65 (46), 43 (100).

(*E*)-5-Ethoxy-4-tosylpent-3-en-2-one (23c): IR ($CDCl_3$) 3040, 1630, 1600, 820 (CH=C), 1710 (C=O), 1320, 1305, 1160 cm^{-1} (SO_2); ^1H NMR (300 MHz, $CDCl_3$) δ 0.78 (t, *J* = 7 Hz, 3 H, CH_3CH_2), 2.24, 2.29 (2 s, 6 H, CH_3C=O, CH_3Ar), 3.08 (q, *J* = 7 Hz, 2 H, CH_2O), 4.28 (s, 2 H, CH_2CS), 7.22, 7.67 (2 d, *J* = 8 Hz, 4 H, aromatic H), 7.23 (s, 1 H, CHC=O); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.91 (CH_3CH_2), 20.92 (CH_3Ar), 30.66 (CH_3C=O), 62.89, 65.55 (2 CH_2), 127.92, 129.23, 135.58, 144.39 (aromatic C), 135.25, 147.17 (CH=C), 197.87 (C=O); MS, *m/z* 282 (M^+, 2), 236 (39), 139 (28), 99 (27), 91 (61), 83 (42), 71 (34), 65 (37), 55 (25), 43 (100).

(*E*)-6-Methyl-4-tosylhepta-3,6-dien-2-one (23d): IR ($CDCl_3$) 3080, 3060, 3040, 1650, 1610, 1600, 820 (CH=C), 1705 (C=O), 1310, 1150 cm^{-1} (SO_2); ^1H NMR (300 MHz, $CDCl_3$) δ 1.55 (s, 3 H, CH_3C=C), 2.33, 2.39 (2 s, 6 H, CH_3C=O, CH_3Ar), 3.37 (s, 2 H, CH_2CS), 4.46, 4.60 (2 s, 2 H, CH_2=C), 7.31, 7.75 (2 d, *J* = 8 Hz, 4 H, aromatic H), 7.41 (s, 1 H, CHC=O); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.92, 21.70 (2 CH_3C=C), 31.21 (CH_3C=O), 33.67 (CH_2CS), 111.75 (CH_2=C), 128.23, 129.34, 134.63, 144.53 (aromatic C), 132.19 (CHC=O), 139.43 (C=CH_2), 150.78 (C=CH), 196.87 (C=O); MS, *m/z* 278 (M^+, 2), 157 (15), 139 (36), 123 (78), 91 (39), 79 (15), 65 (24), 43 (100).

(*E*)-4-Tosyloct-3-en-2-one (23e): IR (CCl_4) 3040, 1605, 1595, 810 (CH=C), 1695 (C=O), 1320, 1300, 1150 cm^{-1} (SO_2); ^1H NMR (300 MHz, CCl_4) δ 0.69 (t, *J* = 7 Hz, 3 H, CH_3CH_2), 1.14 (m, 4 H, $CH_2CH_2CH_3$), 2.17 (s, 3 H, CH_3C=O), 2.20–2.35 (m with s at δ 2.29, 5 H, CH_3Ar, CH_2C=C), 7.02 (s, 1 H, CHCO), 7.17, 7.57 (2 d, *J* = 8 Hz, 4 H, aromatic H); ^{13}C NMR (75 MHz, CCl_4) δ 13.45 (CH_3CH_2), 21.41 (CH_3Ar), 22.65, 27.16, 31.85 (3 CH_2), 31.09 (CH_3C=O), 128.57, 129.70, 135.74, 144.26 (aromatic C), 129.51, 151.58 (CH=C), 195.89 (C=O); MS, *m/z* 280 (M^+, 4), 139 (18), 125 (100), 91 (25), 43 (65). Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.25; H, 7.19. Found: C, 64.1; H, 6.9.

(*E*)-5-Phenyl-4-tosylpent-3-en-2-one (23f): IR ($CDCl_3$) 3060, 3030, 1615, 1600, 815 (CH=C), 1700 (C=O), 1315, 1300, 1150 cm^{-1} SO_2); ^1H NMR (300 MHz, $CDCl_3$) δ 2.27, 2.29 (2 s, 6 H, 2 CH_3), 4.02 (s, 2 H, CH_2), 6.90–7.60 (m with s at δ 7.42 and d at δ 7.52, *J* = 8 Hz, 10 H, aromatic H, CHCO); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.19 (CH_3Ar), 31.62 (CH_3C=O), 32.29 (CH_2), 126.02, 127.85, 128.22, 128.43, 129.45, 132.32, 135.68, 144.55, 152.61 (aromatic C, CH=C), 197.44 (C=O); MS, *m/z* 314 (M^+, 20), 159 (23), 158 (39), 139 (19), 116 (35), 115 (54), 91 (41), 65 (19), 43 (100).

(*E*)-4-Tosylundec-3-en-2-one (23g): IR (film) 3050, 3030, 1610, 1595, 820 (CH=C), 1700 (C=O), 1320, 1310, 1150 cm^{-1} (SO_2); ^1H NMR (300 MHz, CCl_4) δ 0.79 (t, *J* = 6 Hz, 3 H, CH_3CH_2), 1.15 [m, 10 H, $(CH_2)_5CH_3$], 2.10–2.50 (m with 2 s at δ 2.23, 2.35, 8 H, CH_3C=O, CH_3Ar, CH_2CS), 7.06 (s, 1 H, CHC=O), 7.22, 7.62 (2 d, *J* = 8 Hz, 4 H, aromatic H); ^{13}C NMR (75 MHz, CCl_4) δ 14.00 (CH_3CH_2), 21.40 (CH_3Ar), 22.43, 27.45, 28.47, 28.93, 29.49, 31.81 (6 CH_2), 31.44 (CH_3C=O), 128.61, 129.62, 135.88, 144.07 (aromatic C), 129.30, 155.77 (CH=C), 195.65 (C=O); MS, *m/z* 322 (M^+, 6), 280 (20), 157 (100), 139 (48), 95 (25), 91 (32), 43 (76).

***trans*-6-(Iodomethyl)-2-methoxy-2-methyl-4-tosyl-Δ³-dihydropyran (24)**: IR ($CDCl_3$) 3040, 1600 (CH=C), 1320, 1155 cm^{-1} (SO_2); ^1H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 3 H, CH_3CO), 1.98 [ddd, *J* = 17, 11, 2.5 Hz, 1 H, C(5)H_{ax}], 2.27 [dd, *J* = 17, 3.5 Hz, 1 H, C(5)H_{eq}], 2.37 (s, 3 H, CH_3Ar), 3.12 (m, 2 H, CH_2I), 3.27 (s, 3 H, CH_3O), 3.77 (m, 1 H, CHO), 6.71 (d, *J* = 2.5 Hz, 1 H, CHCO), 7.28, 7.67 (2 d, *J* = 8 Hz, 4 H, aromatic H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 6.36 (CH_2I), 21.59, 22.07 (2 CH_3C), 28.46 (CH_2CO), 48.93 (CH_3O), 67.75 (CHO), 96.93 (CO), 128.27, 130.01, 135.06, 136.27, 139.37, 144.87 (aromatic C, CH=C); MS, *m/z* 407 ($M^+ - CH_3$, 8), 391 (21), 267 (100), 139 (72), 97 (32), 91 (27), 66 (15), 65 (23), 43 (38). Anal. Calcd for $C_{15}H_{19}IO_4S$: C, 42.66; H, 4.53. Found: C, 42.6; H, 4.6.

Substituted 3-Tosylfurans 25. General Procedure. Once the intermediate **13** (2 mmol) was prepared as described above, the corresponding aldehyde (2.2 mmol) was added and the mixture was stirred for 2 h at −20 to 20 °C. Then it was treated with water (5 mL) and 1 N hydrochloric acid (10 mL), stirred overnight, and extracted with dichloromethane (2 × 25 mL). The organic layer was washed with water, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The resulting solution was purified by flash chromatography on silica gel and recrystallized to give products **25**. In Table III are summarized yields and melting points for **25**. Spectral and analytical data follow.

2-Methyl-4-tosylfuran (25a): IR (Nujol) 3120, 3080, 1590, 1520, 900, 810 (CH=C), 1315, 1300, 1155 cm^{-1} (SO_2); ^1H NMR (80 MHz, $CDCl_3$) δ 2.4, 2.55 (2 s, 6 H, 2 CH_3), 6.25 (s, 1 H, CH=CO), 7.4, 7.95 (2 d, *J* = 8 Hz, 4 H, aromatic H), 8.0 (s, 1 H, CHO); ^{13}C NMR (20 MHz, CCl_4) δ 13.8 (CH_3CO), 21.9 (CH_3Ar), 104.2, 127.6, 128.4, 130.2, 139.4, 144.4, 155.7 (aromatic and furanic C); MS, *m/z* 238 (M^+ + 2, 6), 236 (M+, 100), 134 (55), 125 (85), 107 (30), 91 (40), 65 (30), 43 (25). Anal. Calcd for $C_{12}H_{12}O_3S$: C, 61.00; H, 5.12. Found: C, 60.8; H, 5.1.

(*E*)-5-Methyl-2-(1-propenyl)-3-tosylfuran (25b): IR (Nujol) 3120, 3050, 1640, 1590, 1530, 960, 820 (CH=C), 1320, 1150 cm^{-1} (SO_2); ^1H NMR (80 MHz, $CDCl_3$) δ 1.95 (d, *J* = 7.5 Hz, 3 H, CH_3CH), 2.25 (s, 3 H, CH_3CO), 2.45 (s, 3 H, CH_3Ar), 6.2 (s, 1 H, CH=CO), 6.6 (m, 1 H, $CHCH_3$), 7.0 (d, *J* = 18 Hz, 1 H, CH=$CHCH_3$), 7.35, 7.9 (2 d, *J* = 8 Hz, 4 H, aromatic H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 13.1 (CH_3CO), 18.7 (CH_3CH=C), 21.2 (CH_3Ar), 105.9, 116.7, 121.7, 126.4, 129.5, 130.7, 139.5, 143.9, 151.7, 152.3 (aromatic and furanic C); MS, *m/z* 278 (M^+ + 2, 5), 276 (M^+, 77), 232 (20), 197 (51), 169 (36), 120 (31), 105 (41), 91 (76), 90 (35), 87 (40), 65 (30), 43 (100). Anal. Calcd for $C_{15}H_{16}O_3S$: C, 65.19; H, 5.84. Found: C, 65.3; H, 6.0.

2-Isobutyl-5-methyl-3-tosylfuran (25c): IR (CCl_4) 3040, 1590, 1560, 1490, 950, 820 (CH=C), 1315, 1150 cm^{-1} (SO_2); ^1H NMR (80 MHz, CCl_4) δ 0.85 (d, *J* = 7.5 Hz, 6 H, 2 CH_3CH), 1.5 (m, 1 H, $CHCH_3$), 2.15, 2.35 (2 s, 6 H, 2 CH_3C), 2.7 (d, *J* = 9 Hz, 2 H, CH_2), 6.0 (s, 1 H, CH=CO), 7.2, 7.7 (2 d, *J* = 8 Hz, 4 H, aromatic H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 13.5 (CH_3CO), 21.6 (CH_3Ar), 22.5 (2 CH_3CH), 28.7 (CH_2), 35.6 ($CHCH_2$), 105.5, 124.2, 127.0, 129.5, 140.7, 143.5, 151.3, 157.6 (aromatic and furanic C); MS, *m/z* 294 (M^+ + 2, 4), 292 (M^+, 57), 250 (100), 249 (57), 139 (50), 102 (20), 95 (25), 94 (20), 91 (45), 65 (24), 43 (80). Anal. Calcd for $C_{16}H_{20}O_3S$: C, 65.50; H, 7.21. Found: C, 65.5; H, 7.4.

2-Phenyl-5-methyl-3-tosylfuran (25d): IR (CCl_4) 3060, 1590, 1540, 1480, 920, 810 (CH=C), 1320, 1150 cm^{-1} (SO_2); ^1H NMR (80 MHz, CCl_4) δ 2.15 (s, 6 H, 2 CH_3), 6.3 (s, 1 H, CH=CO), 6.9–8.0 (m, 9 H, aromatic H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 13.4 (CH_3CO), 21.2 (CH_3Ar), 108.0, 124.2, 126.4, 127.9, 129.5, 135.7, 138.9, 140.7, 143.8, 151.6, 152.5 (aromatic and furanic C); MS, *m/z* 314 (M^+ + 2, 7), 312 (M^+, 100), 129 (56), 128 (47), 127 (21), 105 (25), 91 (21), 77 (26), 43 (30). Anal. Calcd for $C_{18}H_{16}O_3S$: C, 69.21; H, 5.16. Found: C, 69.0; H, 5.2.

2-(2-Furyl)-5-methyl-3-tosylfuran (25e): IR (Nujol) 3150, 1590, 1520, 995, 985, 890, 815 (CH=C), 1310, 1150 cm^{-1} (SO_2); ^1H NMR (80 MHz, $CDCl_3$) δ 2.35, 2.4 (2 s, 6 H, 2 CH_3), 6.45 (s, 1 H, C*H*=CCH_3), 6.55, 7.25, 7.6 (3 m, 3 H, furanic H), 7.3, 7.9 (2 d, *J* = 8 Hz, 4 H, aromatic H); ^{13}C NMR (20 MHz, $CDCl_3$) δ

(32) In the case of compound **24**, the reaction mixture was extracted after quenching with water.

13.4 (CH_3CO), 23.6 (CH_3Ar), 107.6, 111.4, 112.0, 122.6, 126.4, 129.5, 135.7, 138.9, 142.6, 143.5, 144.5, 151.6 (aromatic and furanic C); MS, m/z 304 ($M^+ + 2$, 6), 302 (M^+, 90), 147 (35), 105 (44), 95 (37), 91 (20), 43 (100). Anal. Calcd for $C_{16}H_{14}O_4S$: C, 63.56; H, 4.67. Found: C, 63.2; H, 4.8.

5-Methyl-2-(2-thienyl)-3-tosylfuran (25f): IR ($CDCl_3$) 3100, 3050, 1595, 1560, 1500, 850, 810 (CH=C), 1315, 1150 cm^{-1} (SO_2); ^1H NMR (80 MHz, $CDCl_3$) δ 2.3, 2.35 (2 s, 6 H, 2 CH_3), 6.4 (s, 1 H, CH=CO), 6.9–8.0 (m, 7 H, aromatic and thienylic H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 13.4 (CH_3CO), 21.5 (CH_3Ar), 107.9, 124.7, 126.6, 127.5, 127.9, 128.8, 129.4, 135.0, 138.8, 141.0, 143.8, 150.9 (aromatic, furanic, and thienylic C); MS, m/z 320 ($M^+ + 2$, 12), 318 (M^+, 100), 211 (25), 163 (61), 135 (85), 134 (22), 120 (29), 111 (35), 91 (75), 65 (30), 43 (65). Anal. Calcd for $C_{16}H_{14}O_3S_2$: C, 60.35; H, 4.43. Found: C, 60.4; H, 4.4.

Preparation of Compounds 27 and 28. General Procedure. A solution of the corresponding compound **18** or **19** (1 mmol), trifluoroacetic acid (0.5 mL), and water (0.5 mL) in dichloromethane (20 mL) was stirred for 1 h at room temperature. The reaction mixture was then washed with saturated aqueous $NaHCO_3$ and water. The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuo to yield the crude product **27** or **28** as an oil, which was homogeneous by TLC analysis and spectroscopically pure. Yields and R_f values are included in Table IV. Spectral data follow.

(E)-6,6-Dimethyl-4-tosylhept-3-ene-2,5-dione (27b): IR (film) 3060, 1610, 1590 (CH=C), 1730, 1710 (C=O), 1320, 1145 cm^{-1} (SO_2); ^1H NMR (300 MHz, $CDCl_3$) δ 1.19 (s, 9 H, 3 CH_3CC=O), 2.22, 2.31 (2 s, 6 H, CH_3C=O, CH_3Ar), 7.01 (s, 1 H, CHC=O), 7.22, 7.56 (2 d, J = 8 Hz, 4 H, aromatic H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.39 (CH_3Ar), 27.16 (3 CH_3CC=O), 30.68 (CH_3C=O), 44.66 (CH_3CC=O), 128.70, 129.68, 134.27, 145.57 (aromatic C), 131.39, 154.26 (CH=C), 195.48, 207.97 (2 C=O); MS, m/z 252 ($M^+ - C_4H_8$, 100), 160 (26), 145 (29), 139 (24), 97 (34), 96 (21), 92 (38), 91 (41), 57 (22), 43 (22).

(E)-1-(4-Methoxyphenyl)-2-tosylpent-2-ene-1,4-dione (27e): IR ($CDCl_3$) 3060, 1590, 1500, 830, 810, 800 (CH=C), 1700, 1650 (C=O), 1320, 1145 cm^{-1} (SO_2); ^1H NMR (300 MHz, $CDCl_3$) δ 2.15 (s, 3 H, CH_3C=O), 2.30 (s, 3 H, CH_3Ar), 3.71 (s, 3 H, CH_3O), 6.77, 7.68 (2 d, J = 8.5 Hz, 4 H, $CH_3OC_6H_4$), 7.19, 7.57 (2 d, J = 8 Hz, 4-$CH_3C_6H_4$), 7.26 (s, 1 H, CHC=O); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.47 (CH_3Ar), 30.69 (CH_3C=O), 55.32 (CH_3O), 113.81, 128.50, 128.91, 129.74, 131.50, 132.98, 134.40, 145.60, 152.42, 164.27 (aromatic C, CH=C), 187.86, 194.86 (2 C=O); MS, m/z 358 (M^+, 7), 135 (100).

Ethyl (E)-4-oxo-2-tosylpent-2-enoate (28): IR (film) 3020, 1590, 810 (CH=C), 1700, 1680 (C=O), 1320, 1145 cm^{-1} (SO_2); ^1H NMR (300 MHz, $CDCl_3$) δ 1.08 (t, J = 7 Hz, 3 H, CH_3CH_2), 2.28, 2.32 (2 s, 6 H, CH_3C=O, CH_3Ar), 4.08 (q, J = 7 Hz, 2 H, CH_2), 7.25, 7.71 (2 d, J = 8 Hz, 4 H, aromatic H), 7.45 (s, 1 H, CHC=O); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.03 (CH_3CH_2), 21.1 (CH_3Ar), 29.62 (CH_3C=O), 62.36 (CH_2), 128.58, 129.39, 134.81, 140.94, 141.38, 145.22 (aromatic C, CH=C), 160.36 (CO_2), 196.56 (C=O); MS, m/z 296 (M^+, 2), 203 (32), 155 (73), 139 (29), 131 (23) 117 (23), 99 (22), 91 (100), 85 (24), 64 (24), 43 (55).

Preparation of Cyclopentenones 29. General Procedure. A 0.5 N ethanolic solution of sodium hydroxide (8 mL) was added to a solution of the corresponding compound **27** (1 mmol) in ethanol (5 mL), and the mixture was stirred for 10 min at room temperature. The resulting mixture was dissolved in dichloromethane (25 mL), and the solution was washed with water. The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuo. The resulting residue was purified by flash chromatography on silica gel and recrystallized to afford compound **29**. Yields and melting points are included in Table V. Spectral and analytical data follow.

4-*tert*-Butyl-3-ethoxy-4-hydroxycyclopent-2-enone (29b): IR ($CDCl_3$) 3420 (OH), 1675 (C=O), 1600 cm^{-1} (C=C); ^1H NMR (300 MHz, $CDCl_3$) δ 0.95 (s, 9 H, 3 CH_3C), 1.38 (t, J = 7 Hz, 3 H, CH_3CH_2), 2.34, 2.67 (2 d, J = 18 Hz, 2 H, CH_2C=O), 2.75 (br s, 1 H, OH), 4.00 (q, J = 7 Hz, 2 H, CH_2O), 5.22 (s, 1 H, CHC=O); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.02 (CH_3CH_2), 25.34 (3 CH_3C), 37.08 (CCOH), 47.13 (CH_2C=O), 67.97 (CH_2O), 82.19 (COH), 104.90 (CHC=O), 188.65 ($COCH_2$), 201.95 (C=O); MS, m/z 198 (M^+, 2), 142 (100), 113 (67). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.8; H, 9.1.

3-Ethoxy-4-hydroxy-4-(4-methoxyphenyl)cyclopent-2-enone (29e): IR ($CDCl_3$) 3340 (OH), 3080, 1580, 1500, 830 (CH=C), 1670 cm^{-1} (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 1.28 (t, J = 7 Hz, 3 H, CH_3CH_2), 2.64, 2.84 (2 d, J = 18 Hz, 2 H, CH_2C=O), 3.73 (s, 3 H, CH_3O), 3.79 (br s, 1 H, OH), 4.02, 4.03 (2 q, J = 7 Hz, 2 H, CH_2O), 5.37 (s, 1 H, CHC=O), 6.81, 7.28 (2 d, J = 8.5 Hz, 4 H, aromatic H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.65 (CH_3CH_2), 52.96 (CH_2C=O), 55.08 (CH_3O), 68.19 (CH_2O), 78.44 (COH), 104.55 (CHC=O), 113.73, 125.74, 134.64, 158.89 (aromatic C), 188.02 ($COCH_2$), 202.14 (C=O); MS, m/z 248 (M^+, 45), 219 (21), 135 (100). Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.49. Found: C, 67.5; H, 6.4.

Acknowledgment. We thank Professor J. Barluenga, Departamento de Química Organometálica, Universidad de Oviedo, for financial support and Dr. P. Bernad, Servicio de Espectrometría de Masas, Universidad de Oviedo, for mass spectrometric work.

Registry No. **12**, 115562-91-9; **13**, 115591-06-5; **14**, 115562-92-0; **15**, 115562-93-1; **16a**, 115562-94-2; **16b**, 115562-95-3; **17a**, 115562-96-4; **17b**, 115562-97-5; **17c**, 115562-98-6; **17d**, 115562-99-7; **17e**, 115563-00-3; **17f**, 115563-01-4; **18a**, 115563-02-5; **18b**, 115563-03-6; **18c**, 115563-04-7; **18d**, 115563-05-8; **18e**, 115563-06-9; **19**, 115563-07-0; **20**, 115563-08-1; **21**, 115563-09-2; **22**, 115563-10-5; **23a**, 115563-11-6; **23b**, 115563-12-7; **23c**, 115563-13-8; **2od**, 115563-14-9; **23e**, 115563-15-0; **23f**, 115563-16-1; **23g**, 115563-17-2; **24**, 115591-05-4; **25a**, 115563-18-3; **25b**, 115563-19-4; **25c**, 115563-20-7; **25d**, 115563-21-8; **25e**, 115563-22-9; **25f**, 115563-23-0; **27b**, 115563-24-1; **27e**, 115563-25-2; **28**, 115563-26-3; **29b**, 115563-27-4; **29e**, 115563-28-5; CH_2=$CHCH_2Br$, 106-95-6; CH_2O, 50-00-0; (E)-CH_3CH=CHCHO, 123-73-9; *i*-BuCHO, 590-86-3; PhCHO, 100-52-7; *t*-BuCOCl, 3282-30-2; CyCOCl, 2719-27-9; 4-$MeOC_6H_4COCl$, 100-07-2; PhNCO, 103-71-9; $EtOCH_2Cl$, 3188-13-4; CH_2=$C(CH_3)CH_2Cl$, 563-47-3; $CH_3(CH_2)_6I$, 4282-40-0; 4-tosyl-3-buten-2-one, 88726-07-2; 2-furancarboxaldehyde, 98-01-1; 2-thiophenecarboxaldehyde, 98-03-3; (chloromethyl)oxirane, 106-89-8.