Pergamon

Tetrahedron Vol. 51, No. 9, pp. 2763-2776, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00026-7

Lithiated 3-Tosylpropanal and 4-Tosyl-2-butanone Dimethyl Acetals as β-Acylvinyl Anion Equivalents for the Synthesis of Unsaturated 1,4-Dicarbonyl Compounds and α,β-Butenolides

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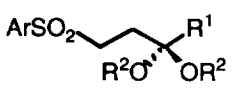
Abstract: The lithiation of 1,1-dimethoxy-3-tosylpropane (**7a**) and 2,2-dimethoxy-4-tosylbutane (**7b**) followed by reaction with acyl chlorides affords, after *p*-toluenesulfinic acid elimination, ene-1,4-dicarbonyl compounds in a stereoselective manner. In the case of compound **7a**, derived from acrolein, sequential monolithiation and reaction with carbonyl compounds give cyclic acetals, which after oxidation and elimination of *p*-toluenesulfinic acid are transformed into α,β-butenolides.

INTRODUCTION

Ketals derived from γ-oxosulfones[1] **1** and **2** are the most simple and stable starting compounds[2] for the preparation of sulfonyl-stabilized homoenolates. Organolithium compounds derived from protected γ-oxosulfones **1** and **2** are excellent β-acylvinyl anion equivalents **3** and **4** of β-lithiated α,β-unsaturated carbonyl compounds[5]. These types of sulfones are easily prepared by Michael addition of a sulfinic acid to α,β-unsaturated carbonyl compounds followed by protection of the carbonyl group[6-15]. Organolithium derivatives of compounds **1** and **2** have been used in many carbon-carbon bonds forming reactions, e.g.: (a) in alkylation reactions by means of alkyl halides[6], tosylates[7], epoxides[8], and chlorotrimethylsilane[9] for the synthesis of saturated[6b] and α,β-unsaturated carbonyl compounds[6a-e,9] such as (+)-nuciferal[6a], *cis*-jasmone[6e], 25-hydroxycholesterol[7a], (+)-*exo*-brevicomin[7b] and δ-lactols[8], (b) in Michael addition reactions to substituted cyclopentenones for the synthesis of 15-oxoprostaglandin F_1[10], (c) in addition to carbonyl compounds to give furans[11], such as dendrolasin[11a], and 4-hydroxycyclopentenones[12], (d) in the arylation reaction, with a tricarbonylchromium complex, of N-silylated indole for the synthesis of clavicipitic acid precursors[13], and (e) in acylation reaction with esters[14] and ethyl chloroformate[15] for the synthesis of saturated 1,4-dicarbonyl compounds[14] and the γ-hydroxybutenolide moiety of strigol[15], respectively.



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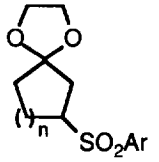

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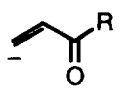

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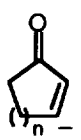

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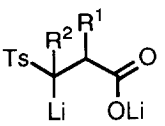
We have recently reported the synthetic applications of lithium 3-lithio-3-tosylalkanoates **5** as β-acylvinyl anion equivalents **6** of β-lithiated α,β-unsaturated carboxylic acids, in the addition to carbonyl compounds and in alkylation and acylation reactions, for the synthesis of α,β-butenolides, α,β and β,γ-unsaturated esters and 4-oxo-2-alkenoates, such as *O*-benzyl derivative of umbelactone, andirolactone, rosefuran lactone and the seco acid of (±)-pyrenoforin[16]. In connection with these studies, we describe here the synthesis of ene-1,4-dicarbonyl compounds[17] and α,β-butenolides[23] by means of organolithium compounds derived from protected γ-oxosulfones.



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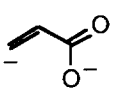

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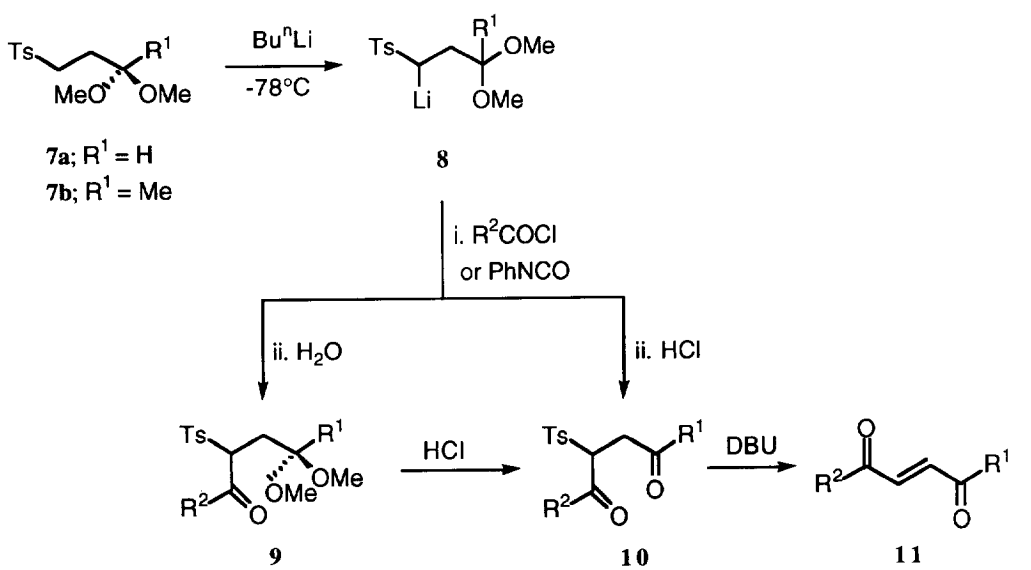
RESULTS AND DISCUSSION

When 3-tosylpropanal and 4-tosyl-2-butanone dimethyl acetals (**7a** and **7b**) were allowed to react with n-butyllithium at -78°C in THF the corresponding organolithium intermediates **8** were obtained, which reacted with acyl chlorides to give after quenching with water or with 1 N hydrochloric acid monoprotected or unprotected 1,4-dicarbonyl compounds **9** or **10**, respectively (Scheme 1 and Table 1). Starting acetals were prepared[9] by addition of sodium *p*-toluenesulfinate to acrolein and methyl vinyl ketone followed by acetalization with methyl orthoformate in 85 and 80% yield, respectively. In the case of compound **7a** better yields were obtained when



Scheme 1

Table 1. Preparation of Compounds **9**, **10**, and **12**.

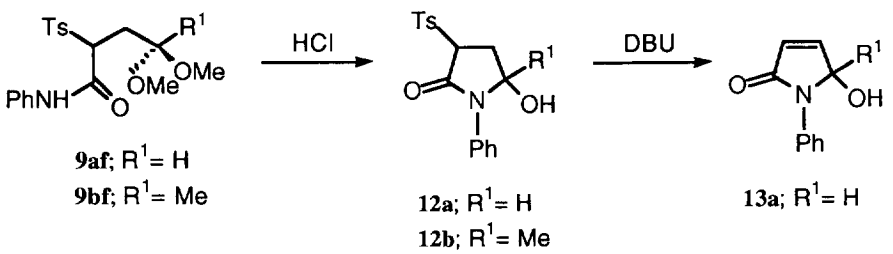
Entry	Starting sulfone	Electrophile	Product No.	R^1	R^2	Yield (%)[a]	Mp (°C)[b] or R_f[c]
1	**7a**	n-PrCOCl	**9aa**	H	n-Pr	79	0.47
2			**10aa**			99[d]	0.45
3	**7a**	*i*-PrCOCl	**9ab**	H	*i*-Pr	63	0.48
4			**10ab**			80[d,e]	0.44
5	**7a**	*t*-BuCOCl	**9ac**	H	*t*-Bu	91	0.46
6			**10ac**			95	0.34
7	**7a**	PhCOCl	**9ad**	H	Ph	75	0.40
8			**10ad**			73[d]	0.30
9	**7a**	$PhCH_2COCl$	**9ae**	H	$PhCH_2$	83[e]	0.41
10	**7a**	PhNCO	**9af**	H	PhNH	81	138-140
11			**12a**			83[d]	0.30[f]
12	**7b**	n-PrCOCl	**10ba**	Me	n-Pr	73	77-78
13	**7b**	*i*-PrCOCl	**10bb**	Me	*i*-Pr	75	118-119
14	**7b**	*t*-BuCOCl	**10bc**	Me	*t*-Bu	72	117-118
15	**7b**	PhCOCl	**10bd**	Me	Ph	88	94-95
16	**7b**	PhNCO	**9bf**	Me	PhNH	83	121-123
17			**10bf**			96[d]	157-158[g]
18			**12b**			36	0.29
19	**7b**	$EtCO_2Cl$	**10bg**	Me	EtO	81	0.39

[a] Based on starting sulfone **7**, after column chromatography (silica gel, hexane/ether). [b] Hexane/CH_2Cl_2. [c] Hexane/EtOAc: 2/1. [d] Based on pure compound **9**. [e] Hydrolysis was carried out with 50% $HClO_4$ in dioxane (1/1). [f] Hexane/EtOAc: 1/1. [g] Hexane/EtOAc.

the deprotonotation was carried out with two equiv of butyllithium, probably due to the acidity of the hydrogen in α-position to the sulfonyl group in compounds **9**[14], which provokes the protonation of **8a**. However, there is no evidence that a dilitiathed intermediate has been formed at -78°C, because after deuterolysis with deuterium oxide or with d4-methanol only the monodeuterated acetal derived of **7a** was obtained.

In the case of the 4-oxoaldehydes **10aa-ad**, derived from acrolein, mainly decomposition was observed when they were purified by column chromatography, for this reason were isolated and purified as acetals **9aa-ad** which were transformed into compounds **10** after hydrolysis with 4 N hydrochloric acid in THF (1/1). The methyl vinyl ketone derivatives were isolated and purified as 1,4-diketones **10ba-bg** (Table 1, entries 12-15, 17, and 19).

When phenylisocyanate was used as electrophile with intermediate **8a** followed by hydrolysis with 5% HCl lactam **12a** was isolated as mixture of diastereomers (Scheme 2 and Table 1, entry 11). The same reaction with intermediate **8b** led to the formation of compound **10bf** after acidic hydrolysis, whereas if the reaction was quenched with water compound **9bf** was isolated which after hydrolysis with 5% HCl afforded also lactam **12b** as mixture of diastereomers (Scheme 2 and Table 1, entries 17, 16, and 18, respectively).



9af; R^1= H
9bf; R^1= Me

12a; R^1= H
12b; R^1= Me

13a; R^1= H

Scheme 2

Basic elimination reaction of *p*-toluenesulfinic acid was carried out by treatment of compounds **10** with triethylamine for aldehyde derivatives or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) for ketone derivatives to give unsaturated 1,4-dicarbonyl compounds **11** (Scheme 1 and Table 2). Lactam **12a** was transformed under the same reaction conditions into the α,β-unsaturated lactam **13a**, whereas the basic elimination of **12b** failed (Scheme 2 and Table 2).

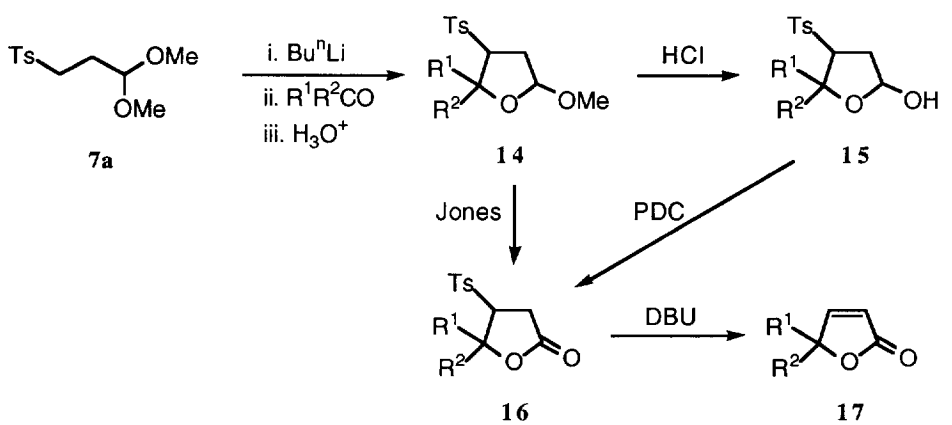
We also have studied the synthesis of α,β-butenolides starting from acrolein derivative **7a**. The reaction of compound **7a** with one equiv of n-butyllithium at -78°C followed by addition of carbonyl compounds as electrophiles gave after acidic hydrolysis cyclic acetals **14**, which were treated with Jones reagent to provide lactones **16** in the case of ketones (Scheme 3 and Table 3). When aldehydes were used as electrophiles acetals **14** suffered oxidation to the corresponding 4-oxoacids under Jones oxidation conditions. In these cases compounds **14a** and **14b** have to be first hydrolyzed with 6N HCl to lactols **15**, which were transformed into lactones **16** by oxidation with pyridinium dichromate (PDC)[4]. Butyrolactones **16** were finally treated with DBU to afford α,β-unsaturated butenolides **17**[16] (Scheme 3 and Table 3).

In conclusion, this simple methodology allows the stereoselective synthesis of unsaturated (*E*)-1,4-dicarbonyl compounds and butenolides by means of organolithium compounds derived from γ-oxosulfones and starting from α,β-unsaturated carbonyl compounds.

Table 2. Synthesis of Unsaturated 1,4-Dicarbonyl Compounds **11** and Lactam **13a**.

Entry	No.	R^1	R^2	Yield (%)[a]	Mp (°C)[b] or R_f[c]	Lit.
1	**11aa**	H	n-Pr	98[d]	0.68	24
2	**11ac**	H	*t*-Bu	97[d]	0.61	25
3	**11ad**	H	Ph	88[d]	0.49	5b
4	**13a**	H	PhNH	60	132-135	26
5	**11ba**	Me	n-Pr	75	0.61	27
6	**11bb**	Me	*i*-Pr	96	0.59	22, 28
7	**11bc**	Me	*t*-Bu	83	0.63	29
8	**11bd**	Me	Ph	99	0.56	30
9	**11bf**	Me	PhNH	68	163-164	31
10	**11bg**	Me	EtO	62	0.64	32

[a] Based on compound **10** or **12** after column chromatography. [b] Hexane/CH_2Cl_2. [c] Hexane/EtOAc: 2/1. [d] The elimination was carried out with Et_3N.



Scheme 3

Table 3. Synthesis of α,β-Butenolides[16b].

R^1	R^2	No.	Yield (%)[a]	No.	Yield (%)[b]	No.	Yield (%)[c]	No.	Yield (%)[d]
i-Pr	H	**14a**	89	**15a**	89	**16a**[e]	90[f]	**17a**	85
n-C_5H_{11}	H	**14b**	95	**15b**	81	**16b**[g]	90[f]	**17b**	95
$(CH_2)_5$		**14c**	95	-	-	**16c**	88[h]	**17c**	98
Ph	Me	**14d**	99	-	-	**16d**[e]	82[h]	**17d**	99

[a] Isolated crude yield, based on starting compound **7a**. [b] Based on compound **14**, after column chromatography. [c] Based on compound **15**. [d] Based on compound **16**, after column chromatography. [e] Diastereomers ratio: 1/1. [f] Isolated crude yield. [g] Diastereomers ratio: 3/2. [h] After column chromatography.

EXPERIMENTAL

General. Melting points were obtained with a Reichert Thermovar apparatus and are uncorrected. IR spectra were obtained as films in a Pye Unicam SP3-200 spectrophotometer. ^1H and ^{13}C spectra were recorded on a Bruker AC-300 spectrometer with $SiMe_4$ 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 (EI, 70eV). Elemental analyses were performed by the Microanalyses Service at the University of Alicante. Chromatographic analysis (GLC) were determined with a Hewlett-Packard HP-5890 instrument equipped with a 25 m WCOT capillary column (0.22 mm diam., 0.2μm film thickness OV-101 stationary phase) using nitrogen (2 ml/min) as the carrier gas, $T_{injector}$=270°C, T_{column}=60°C, and 60-270 (15°C/min). Thin layer chromatography (TLC) was carried out on Schleicher &Schuell F1500/LS 254 plates coated with a 0.2 mm layer of silica gel and UV visualization. Column chromatography was performed using silica gel 60 of 70-270 mesh and hexane/ether as eluant. All starting materials were commercially available (Aldrich, Fluka) of the best grade and were used without further purification. THF was dried with $LiAlH_4$ under argon atmosphere. Methanol was dried with magnesium turnings under argon.

Preparation of γ-Oxosulfones Acetals 7a and 7b. General Procedure. A mixture of sodium *p*-toluenesulfinate (6.0 g, 33 mmol) and the α,β-unsaturated carbonyl compound (30 mmol) in acetic acid (45 ml) was stirred for 12 h. When methyl vinyl ketone was used as carbonyl compound, the reaction mixture was stirred under reflux for 1 d in acetic acid (2.0 ml, 33 mmol) and water (20 ml). Then, ether (150 ml) was added and the reaction mixture was washed with saturated aqueous $NaHCO_3$ and water. The organic layer was dried over Na_2SO_4, evaporated and the resulting residue was used in the ketalization reaction without further purification. A solution of the γ-oxosulfone (10 mmol), trimethyl orthoformate (2.26 ml, 20 mmol) and *p*-toluenesulfonic acid (80 mg, 0.6 mmol) in dry methanol (35 ml) was stirred 20 h at 50°C. Then, solvents were evaporated *in vacuo*

(15 torr), the resulting residue was dissolved in ether (50 ml) and the organic layer was washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4) and evaporated to yield compounds **7a** and **7b**, which were obtained in 85% and 80% yield respectively.

1,1-Dimethoxy-3-tosylpropane (7a): R_f 0.37 (Hex/AcOEt 2:1) ν 2820 (CHO), 1300 and 1140 cm^{-1} (SO_2); δ_H 1.98 (m, 2H, CH_2CH), 2.44 (s, 3H, CH_3Ar), 3.15 (m, 2H, CH_2S), 3.28 (s, 6H, 2xCH_3O), 4.40 (t, *J*=5.0Hz, 1H, CH_2CH), 7.36 and 7.77 (2d, *J*=8.0Hz, 4H, ArH); δ_C 21.3 (CH_3Ar), 26.0 (CH_2CH), 51.4 (CH_2S), 53.4 (2xCH_3O), 102.3 ($CHCH_2$), 127.8, 129.7, 135.8 and 144.5 (ArC); *m/z* 258 (M^+, <1%), 91 (19), 75 (100), 71 (51), 65 (13) and 41 (13) (Found: M^+ 258.0923. Calcd. for $C_{12}H_{18}O_4S$, 258.0926).

2,2-Dimethoxy-4-tosylbutane (7b): R_f 0.40 (Hex/AcOEt 2:1) ν 2820 (CHO), 1290 and 1145 cm^{-1} (SO_2); δ_H 1.20 (s, 3H, CH_3CCH_2), 1.98 (m, 2H, CH_2CCH_3), 2.45 (s, 3H, CH_3Ar); 3.07-3.48 (m with s at 3.11, 8H, CH_2S and 2xCH_3O), 7.36 and 7.79 (2d, *J*=8,0Hz, 4H, ArH); δ_C 21.0, 21.6 (CH_3Ar and CH_3CCH_2), 29.5 (CH_2CCH_3), 48.2 (2xCH_3O), 52.3 (CH_2S), 100.2 (CCH_2), 128.1, 129.9, 136.0 and 144.9 (ArC); *m/z* 241 (M^+-OCH_3, 10%), 101 (20), 91 (51), 89 (100), 86 (13), 85 (80), 71 (14), 65 (29), 55 (26) and 43 (62) (Found: M^+-OCH_3 241.0903. Calcd. for $C_{12}H_{17}O_3S$, 241.0898).

Preparation of Compounds 9, 10 and 12. General Procedure. To a solution of ketal **7a** or **7b** (1 mmol) in dry THF (5 ml) was slowly added a 1.6 M solution of *n*-BuLi (1.25 ml, 2 mmol or 0.63 ml, 1 mmol, respectively) at -78°C under Ar. The resulting yellow solution was stirred for 1h, and then the electrophile was added. The reaction mixture was allowed to rise rt overnight, quenched with water (20 ml) and extracted with ether (3x20 ml). The organic layer was dried (Na_2SO_4) and evaporated to give crude compounds **9**, which were purified by column chromatography on silica gel. In the case of ketal **7b** the reaction was quenched with 2N HCl (5 ml) and stirred 1h at rt., extracted with ether (3x15 ml), dried (Na_2SO_4) and evaporated to give crude compounds **10**, which were purified by column chromatography. Pure compounds **9** (0.5 mmol) were dissolved in THF (5 ml) and aqueous 4N HCl (5 ml) was added and stirred at rt untill complete hydrolysis. Then water (20 ml) was added and the resulting solution was extracted with ether (3x20 ml), the ethereal layers were dried over Na_2SO_4 and evaporated to yield pure compounds **10**. Pure compound **9af** or **9bf** (0.5 mmol) was dissolved in THF (5 ml) and aqueous 6N HCl (5 ml) was added and stirred under reflux, extracted with ether (3x20 ml), dried over Na_2SO_4 and evaporated to yield pure compounds **12**, which were purified by column chromatography. Yields and physical data are included in Table 1, analytical and spectral data follow.

1,1-Dimethoxy-3-tosyl-4-heptanone (9aa): ν 2820 (CHO), 1710 (C=O), 1300 and 1140 cm^{-1} (SO_2); δ_H 0.91 (t, *J*=7.4Hz, 3H, CH_3CH_2), 1.58 (sext, *J*=7.2Hz, 2H, CH_2CH_3), 2.20 (m, 2H, CH_2C=O), 2.45 (s, 3H, CH_3Ar), 2.58, 2.80 (2m, 2H, CH_2CH), 3.19, 3.25 (2s, 6H, 2xCH_3O), 4.28 (m, 2H, CHS and $CHCH_2$), 7.35 and 7.65 (2d, *J*=8.1Hz, 4H, ArH); δ_C 13.4 (CH_3CH_2), 16.5 (CH_2CH_3), 21.6 (CH_3Ar), 30.6 (CH_2CH), 46.9 (CH_2C=O), 53.2, 54.1 (2xCH_3O), 70.1 (CHS), 102.0 ($CHOCH_3$), 129.4, 129.6, 133.3, 145.4 (ArC) and 201.7 (C=O); *m/z* 297 (M^+-OCH_3, 1%), 173 (29), 75 (100) and 71 (66) (Found: M^+-OCH_3 297.1161. Calcd. for $C_{15}H_{21}O_4S$ 297.1161).

2-Methyl-6,6-dimethoxy-4-tosyl-3-hexanone (9ab): ν 2820 (CHO), 1710 (C=O), 1310 and 1140 cm^{-1} (SO_2); δ_H 1.11, 1.12 [2d, *J*=6.8Hz, 6H, $(CH_3)_2CH$], 2.16 (m, 2H, CH_2), 2.44 (s, 3H, CH_3Ar), 3.05 (m, 1H, CHC=O), 3.18, 3.23 (2s, 6H, 2xCH_3O), 4.19 (t, *J*=5.0Hz, 1H, CHO), 4.52 (dd, *J*=10.1, 3.4Hz, 1H, CHS), 7.34 and 7.64 (2d, *J*=8.1Hz, 4H, ArH); δ_C 17.1, 18.0 [$(CH_3)_2CH$], 21.4 (CH_3Ar), 30.5 (CH_2), 42.5

(*C*HC=O), 52.6, 53.7 (2xCH_3O), 68.4 (CHS), 101.4 (*C*HOCH_3), 129.3, 129.5, 133.2, 145.2 (ArC) and 205.4 (C=O); *m/z* 297 (M^+-OCH_3, 1%), 173 (32), 141 (14), 129 (40), 109 (12), 99 (10), 91 (30), 81 (14), 75 (100), 71 (60), 65 (15), 55 (10), 43 (26) and 41 (16).

6,6-Dimethoxy-2,2-dimethyl-4-tosyl-3-hexanone (9ac): ν ($CHCl_3$) 2850 (CHO), 1695 (C=O), 1310 and 1140 cm^{-1} (SO_2); δ_H 1.25 [s, 9H, $(CH_3)_3C$], 2.08 (ddd, *J*=13.7, 9.1, 5.3Hz, 1H, 1xCH_2), 2.15 (ddd, *J*=13.7, 5.3, 4.2Hz, 1H, 1xCH_2), 2.45 (s, 3H, C*H*$_3$Ar), 3.19, 3.25 (2s, 6H, 2xCH_3O), 4.24 (t, *J*=5.3Hz, 1H, C*H*CH_2), 4.84 (dd, *J*=9.1, 4.2Hz, CHS), 7.35 and 7.65 (2d, *J*=8.3Hz, 4H, ArH); δ_C 21.6 (*C*H_3Ar), 27.1 [(*C*H_3)$_3$C], 32.9 (CH_2), 45.5 (*C*CH_3), 52.8, 54.0 (2xCH_3O), 65.0 (CHS), 101.6 (*C*HOCH_3), 129.5, 129.8, 133.6, 145.2 (ArC) and 208.7 (C=O); *m/z* 299 (M^+-OCH_3, 1%), 175 (30), 143 (18), 85 (60), 75 (100), 57 (81), 42 (26) and 40 (41).

4,4-Dimethoxy-1-phenyl-2-tosyl-1-butanone (9ad): ν ($CHCl_3$) 2830 (CHO), 1675 (C=O), 1305 and 1145 cm^{-1} (SO_2); δ_H 2.35-2.50 (m with s at 2.40, 5H, C*H*$_3$Ar and CH_2), 3.13, 3.22 (2s, 6H, 2xCH_3O), 4.30 (t, *J*=7.0Hz, 1H, C*H*CH_2), 5.25 (dd, *J*=9.0, 4.5Hz, 1H, CHS) and 7.25-7.95 (m, 9H, ArH); δ_C 21.8 (*C*H_3Ar), 31.7 (CH_2), 53.6, 54.1 (2xCH_3O), 65.4 (CHS), 102.1 (*C*HOCH_3), 128.2, 128.4, 128.7, 129.4, 129.5, 133.2, 134.0, 145.4 (ArC) and 192.5 (C=O). *m/z* 331 (M^+-OCH_3, <1%), 207 (23), 175 (10), 147 (11) ,105 (32), 91 (15), 77 (18), 75 (100) and 71 (13).

5,5-Dimethoxy-1-phenyl-3-tosyl-2-pentanone (9ae): ν ($CHCl_3$) 1710 (C=O), 1300 and 1135 cm^{-1} (SO_2); δ_H 2.13 (m, 2H, C*H*$_2$CH), 2.36 (s, 3H, C*H*$_3$Ar), 3.00, 3.13 (2s, 6H, 2xCH_3O), 3.92, 3.99 (2d, *J*=15.2Hz, 2H, CH_2C=O), 4.05 (t, *J*=4.8Hz, 1H, C*H*CH_2), 4.38 (dd, *J*=10.7, 2.7Hz, 1H, CHS) and 7.00-7.70 (m with 2d at 7.10 and 7.55, *J*=8.2Hz, 9H, ArH); δ_C 21.6 (*C*H_3Ar), 30.7 (*C*H_2CH), 51.4 (*C*H_2C=O), 53.6, 53.9 (2xCH_3O), 69.3 (CHS), 101.9 (*C*HOCH_3), 127.2, 128.5, 129.5, 129.7, 132.9, 133.2, 145.5 (ArC) and 199.2 (C=O); *m/z* 360 (M^+-CH_3OH, <1%), 183 (21), 173 (13), 156 (15), 155 (15), 145 (14), 139 (27), 117 (15), 115 (16), 107 (20), 105 (64), 99 (16), 92 (27), 91 (100), 89 (14), 85 (14), 79 (16), 77 (41), 71 (57), 65 (32), 66 (10), 55 (17), 51 (13) and 41 (12).

N-*Phenyl-4,4-dimethoxy-2-tosylbutanamide (9af)*: ν ($CHCl_3$) 3310 (NH), 2800 (CHO), 1655 (C=O), 1310 and 1130 cm^{-1} (SO_2); δ_H 2.30 (m,2H, CH_2), 2.42 (s, 3H, C*H*$_3$Ar), 3.29, 3.32 (2s, 6H, 2xCH_3O), 4.10 (dd, *J*=8.8, 4.9Hz, 1H, C*H*CH_2), 4.50 (dd, *J*=6.3, 5.1Hz, 1H, CHS), 7.15 (tt, *J*=7.4, 1.2Hz, 1H, *p*-PhN), 7.33 (m, 4H, *m*-PhN, 2x *p*-CH_3*Ph*), 7.72 (d, *J*=8.2Hz, 2H, 2x *p*-CH_3*Ph*) and 8.25 (broad s, 1H, NH); δ_C 21.7 (*C*H_3Ar), 29.8 (CH_2), 52.6, 54.1 (2xCH_3O), 68.1 (CHS), 101.7 (*C*HOCH_3), 120.1, 125.0, 129.1, 129.2, 130.0, 132.9, 137.2, 145.8 (ArC) and 161.7 (C=O); *m/z* 377 (M^+, 3%), 281 (18), 236 (12), 190 (33), 158 (20), 139 (11), 132 (20), 129 (36), 101 (18), 93 (59), 92 (19), 91 (53), 89 (21), 83 (12), 77 (19), 75 (100), 71 (19), 69 (13), 65 (31), 57 (15), 55 (33), 47 (25), 45 (11), 43 (11) and 41 (20). Anal. Calcd. for $C_{19}H_{23}O_5SN$: C, 60.46; H, 6.14. Found: C, 60.46; H, 6.39.

N-*Phenyl-4,4-dimethoxy-2-tosylpentanamide (9bf)*: ν ($CHCl_3$) 3330 (NH), 1670 (C=O), 1310 and 1140 cm^{-1} (SO_2); δ_H 1.24 (s, 3H, C*H*$_3$CH$_2$), 2.40 (m with s at 2.42, 5H, C*H*$_3$Ar, CH_2), 3.14, 3.19 (2s, 6H, 2xCH_3O), 4.09 (dd, *J*=7.2, 4.7Hz, 1H, CHS), 7.13 (tt, *J*=7.0, 1.3Hz, 1H, *p*-PhN), 7.31 (m, 4H, *m*-PhN, 2x *p*-CH_3*Ph*), 7.48 (m, 2H, 2xPhN), 7.72 (d, *J*=8.5Hz, 2H, 2x *p*-CH_3*Ph*) and 8.21 (broad s, 1H, NH); δ_C 21.2, 21.7 (*C*H_3CH_2 and *C*H_3Ar), 33.1 (CH_2), 48.5, 48.7 (2xCH_3O), 69.1 (CHS), 100.4 (*C*OCH_3), 120.1, 124.9, 129.0, 129.4, 129.8, 133.0, 137.4, 145.6 (ArC) and 162.4 (C=O); *m/z* 391 (M^+, 1%), 295 (31), 204 (48), 188 (15), 172 (24), 144 (76), 143 (23), 132 (46), 111 (17), 97 (14), 94 (10), 93 (38), 92 (20), 91 (52), 89 (100),

83 (23), 77 (18), 65 (27), 55 (30) and 43 (78). Anal. Calcd. for $C_{20}H_{25}O_5SN$: C, 61.36; H, 6.44. Found: C, 61.32; H 6.51.

4-Oxo-3-tosylheptanal (10aa): ν ($CHCl_3$) 2710 (CHO), 1710 (C=O), 1330 and 1140 cm^{-1} (SO_2); δ_H 0.92 (t, *J*=7.4Hz, 3H, CH_3CH_2), 1.61 (m, 2H, CH_2CH_3), 2.47 (s, 3H, CH_3Ar), 2.85 (m, 2H, CH_2C=O), 3.15 (dd, *J*=18.8, 2.9Hz, 1H, 1xCH_2CH), 3.24 (dd, *J*=18.8, 11.0Hz, 1H, 1xCH_2CH), 4.58 (dd, *J*=11.0, 2.9Hz, 1H, CHS), 7.38, 7.65 (2d, *J*=8.2Hz, 4H, ArH) and 9.58 (s, 1H, CHO); δ_C 13.3 (CH_3CH_2), 21.7 (CH_3Ar), 41.9 (CH_2CH), 46.6 (CH_2CO), 68.6 (CHS), 129.2, 129.9, 133.1, 145.9 (ArC), 196.7 (CH=O) and 200.8 (C=O); *m/z* 281 (M^+-1, 5%), 210 (25), 173 (14), 155 (25), 139 (52), 125 (13), 119 (10), 99 (17), 97 (12), 92 (20), 91 (100), 89 (13), 83 (11), 79 (10), 77 (14), 71 (63), 69 (10), 65 (37), 63 (10), 57 (14), 55 (27), 43 (39) and 41 (19).

5-Methyl-4-oxo-3-tosylhexanal (10ab): ν ($CHCl_3$) 2710 (CHO), 1720, 1700 (C=O), 1300 and 1140 cm^{-1} (SO_2); δ_H 1.13, 1.24 [2d, *J*=6.8Hz, 6H, $(CH_3)_2CH$], 2.20 (m, 1H, CHC=O), 2.45 (s, 3H, CH_3Ar), 3.10 (m, 2H, CH_2), 4.84 (d, *J*=10.5Hz, 1H, CHS), 7.37, 7.64 (2d, *J*=7.6Hz, 4H, ArH), and 9.56 (s, 1H, CHO); δ_C 17.4, 18.3 [$(CH_3)_2CH$], 21.6 (CH_3Ar), 41.6 (CH_2), 42.2 (CHC=O), 67.0 (CHS), 129.1, 129.9, 133.0, 145.8 (ArC), 196.4 (CH=O) and 204.82 (C=O); *m/z* 282 (M^+, 1%), 183 (44), 155 (27), 139 (49), 127 (11), 92 (24), 91 (100), 89 (11), 73 (21), 71 (59), 65 (33), 55 (20), 43 (65) and 41 (21).

5,5-Dimethyl-4-oxo-3-tosilhexanal (10ac): ν 2705 (CHO), 1710, 1695 (C=O), 1300 and 1135 cm^{-1} (SO_2); δ_H 1.33 [s, 9H, $(CH_3)_3C$)], 2.47 (s, 3H, CH_3Ar), 3.06 (dd, *J*=18.6, 3.9Hz, 1H, 1xCH_2), 3.16 (dd, *J*=18.6, 9.8Hz, 1H, 1xCH_2), 5.15 (dd, *J*=9.8, 3.9Hz, 1H, CHS), 7.37, 7.64 (2d, *J*=8.3Hz, 4H, ArH) and 9.54 (s, 1H, CHO); δ_C 21.7(CH_3Ar), 27.5 [$(CH_3)_3C$)], 44.4 [$(CH_3)_3C$)], 45.6 (CH_2), 63.3 (CHS), 129.6, 129.8, 133.2, 145.8 (ArC), 196.5 (CHO) and 208.7 (C=O); *m/z* 253 (M^+-C_2H_3O, 1%), 221 (10), 212 (19), 184 (12), 183 (91), 157 (14), 156 (17), 155 (16), 139 (49), 129 (13), 113 (14), 92 (22), 91 (79), 89 (12), 85 (11), 84 (12), 65 (33), 57 (100), 55 (25), 43 (27) and 41 (54).

4-Phenyl-4-oxo-3-tosylbutanal (10ad): ν ($CHCl_3$) 2710 (CHO), 1710, 1670 (C=O), 1300 and 1140 cm^{-1} (SO_2); δ_H 2.48 (s, 3H, CH_3Ar), 3.48 (m, 2H, CH_2), 5.55 (dd, *J*=10.1, 2.9Hz, 1H, CHS), 7.26-7.99 (m, 9H, ArH) and 9.65 (s, 1H, CHO); δ_C 21.6 (CH_3Ar), 42.2 (CH_2), 67.0 (CHS), 128.5, 129.2, 129.3, 129.7, 133.2, 133.8, 145.7 (ArC), 191.2 (CHO) and 196.7 (C=O); *m/z* 316 (M^+, <1%), 133 (28), 105 (100), 92 (12), 91 (36), 77 (48), 65 (18), 55 (26) and 51 (17).

4-Tosyl-2,5-octanodione (10ba): ν (Nujol) 1700 (C=O), 1300 and 1140 cm^{-1} (SO_2); δ_H 0.90 (t, *J*=7.3Hz, 3H, CH_3CH_2) 1.60 (m, 2H, CH_2CH_3), 2.10 (s, 3H, CH_3C=O), 2.45 (s, 3H, CH_3Ar), 2.79 (m, 2H, CH_2C=O), 3.00 (dd, *J*=17,9, 2.6Hz, 1H, 1xCH_2CH), 3.23 (dd, *J*=17,9, 11,2Hz, 1H, 1xCH_2CH), 4.56 (dd, *J*=11.2, 2.6Hz, 1H, CHS), 7.37 and 7.65 (2d, *J*=8,6Hz, 4H, ArH); δ_C 13.13 (CH_3CH_2), 16.37 (CH_2CH_3), 21.43 (CH_3Ar), 29.21 (CH_3C=O), 41.31 (CH_2CH), 46.50 (CH_2C=O), 69.50 (CHS), 128.94, 129,70, 133.25, 145.52 (ArC), 201.05 and 203.70 (2xC=O); *m/z* 296 (M^+, <1%), 253 (12), 183 (34), 139 (16), 97 (11), 91 (46), 71 (100), 65 (18), 55 (11) and 43 (71). Anal. Calcd. for $C_{15}H_{20}O_4S$: C, 60.7; H, 6.80. Found: C, 60.93; H 6.61.

6-Methyl-4-tosyl-2,5-heptanedione (10bb): ν (Nujol) 1695 (C=O), 1310 and 1125 cm^{-1} (SO_2); δ_H 1.12, 1.23 [2d, *J*=6.9Hz, 6H, $(CH_3)_2CH$], 2.10 (s, 3H, CH_3C=O), 2.46 (s, 3H, CH_3Ar), 2.92 (dd, *J*=18.0, 2.7Hz, 1H, 1xCH_2), 3.18 (m, 2H, 1xCH_2 and $CHCH_3$), 4.83 (dd, *J*=11.0, 2.7Hz, 1H, CHS), 7.37 and 7.64 (2d, *J*=8.1Hz, 4H, ArH); δ_C 17.4, 19.1 (2xCH_3CH), 21.6 (CH_3Ar), 29.6 (CH_3C=O), 41.1 (CH_2), 42.2

(*C*HC=O), 68.3 (CHS), 129.0, 129.8, 133.4, 145.7 (ArC), 203.5 and 205.3 (2xC=O); *m/z* 296 (M^+, <1%), 253 (21), 232 (15), 283 (73), 157 (45), 155 (18), 139 (78), 97 (38), 92 (15), 91 (90), 71 (70), 65 (29), 55 (18), 43 (100) and 41 (16). Anal. Calcd. for $C_{15}H_{20}O_4S$: C, 60.79; H, 6.80. Found: C, 60.70; H 6.94.

6,6-Dimethyl-4-tosyl-2,5-heptanedione (10bc): ν (Nujol) 1710, 1685 (C=O), 1300 and 1125 cm^{-1} (SO_2); δ_H 1.33 [s, 9H, $(CH_3)_3C$], 2.06 (s, 3H, CH_3C=O), 2.45 (s, 3H, CH_3Ar), 3.01 (dd, *J*=18.1, 3.2Hz, 1H, 1xCH_2), 3.14 (dd, *J*=18.1, 10.3Hz, 1H, 1xCH_2), 5.12 (dd, *J*=10.3, 3.2Hz, 1H, CHS), 7.36 and 7.64 (2d, *J*=8,0Hz, 4H, ArH); δ_C 21.4 (*C*H_3Ar), 27.3 (3xCH_3C), 29.1 (*C*H_3C=O), 43.8 (CH_2), 45.3 (*C*C=O), 64.3 (CHS), 129.2, 129.5, 133.3, 145.3 (ArC), 203.4 and 208.9 (2xC=O); *m/z* 295 (M^+-CH_3, <1%), 253 (14), 183 (100), 157 (38), 139 (71), 97 (24), 92 (11), 91 (60), 65 (19), 67 (33), 55 (10), 43 (42) and 41 (19). Anal. Calcd. for $C_{16}H_{22}O_4S$: C, 61.91; H, 7.14. Found: C, 61.74; H 7.36.

1-Phenyl-2-tosyl-1,4-pentanodione (10bd): ν ($CHCl_3$) 1710, 1670 (C=O), 1315 and 1150 cm^{-1} (SO_2); δ_H 2.14 (s, 3H, CH_3C=O), 2.37 (s, 3H, CH_3Ar), 3.29 (dd, *J*=18.1, 2.9Hz, 1H, 1xCH_2), 3.50 (dd, *J*=18.1, 10.7Hz, 1H, 1xCH_2), 5.52 (dd, *J*=10.7, 2.9Hz, 1H, CHS) and 7.12-8.15 (m, 9H, ArH); δ_C 21.5 (*C*H_3Ar), 29.4 (*C*H_3C=O), 41.7 (CH_2), 65.4 (CH), 128.4, 129.0, 129.1, 129.6, 132.9, 133.5, 136.5, 145.5 (ArC) 191.5 and 203.8 (2xC=O); *m/z* 330 (M^+, <1%), 266 (15), 223 (14), 158 (11), 155 (11), 133 (25), 106 (16), 105 (100), 91 (46), 77 (95), 65 (21), 55 (14), 51 (12) and 43 (43). Anal. Calcd. for $C_{18}H_{18}O_4S$: C, 65.43; H, 5.49. Found: C, 65.49; H 5.73.

N-*Phenyl-4-oxo-2-tosylpentanamide (10bf)*: ν ($CHCl_3$) 3290 (NH), 1705, 1665 (C=O), 1305 and 1145 cm^{-1} (SO_2); δ_H 2.19 (s, 3H, CH_3C=O), 2.43 (s, 3H, CH_3Ar), 2.97 (dd, *J*=17.6, 2.8Hz, 1H, 1xCH_2), 3.24 (dd, *J*=17.6, 10Hz, 1H, 1xCH_2), 4.57 (dd, *J*=10.4, 2.8Hz, 1H, CHS), 7.37 (m, 7H, ArH), 7.70 (d, *J*=8.6Hz, 2H, ArH) and 8.36 (br s, 1H, NH); δ_C 21.7 (*C*H_3Ar), 29.9 (*C*H_3C=O), 39.8 (*C*H_2C=O), 67.1 (CHS), 120.1, 125.1, 129.0, 129.1, 130.1, 132.9, 137.1, 146.1 (ArC), 160.7 (NC=O) and 203.6 (C=O); *m/z* 345 (M^+, 2%), 238 (17), 139 (12), 97 (12), 94 (16), 93 (73), 65 (37), 55 (47), 51 (10), 43 (100) and 41 (10). Anal. Calcd. for $C_{18}H_{19}O_2NS$: C, 62.59; H, 5.54. Found: C, 62.00; H 5.74.

Ethyl 4-Oxo-3-tosylpentanoate (10bg): ν ($CHCl_3$) 1715 (C=O), 1320 and 1145 cm^{-1} (SO_2); δ_H 1.11 (t, *J*=7.2Hz, 3H, C$H_3$$CH_2$), 2.22 (s, 3H, CH_3C=O), 2.47 (s, 3H, CH_3Ar), 3.23 (dd *J*=18.2, 4.1Hz, 1H, 1xCH_2CH), 3.34 (dd, *J*=18.2, 10.1Hz, 1H, 1xCH_2CH), 4.05 (q, *J*=7.2Hz, 2H, OCH_2), 4.42 (dd, *J*=18.2, 10.1Hz, 1H, CH), 7.37 and 7.75 (2d, *J*=7.2Hz, 4H, ArH); δ_C 13.6 (*C*$H_3$$CH_2$), 21.7 (*C*$H_3$Ar), 29.8 (*C*$H_3$C=O), 39.3 (*C*$H_2$C=O), 62.3 (CHS), 65.8 ($CH_2O$), 128.9, 129.7, 134.6, 145.5 (ArC), 165.1 (COO) and 203.6 (C=O); *m/z* 283 (M^+-CH_3, <1%), 234 (15), 191 (36), 157 (13), 155 (62), 150 (26), 143 (21), 139 (31), 101 (60), 97 (13), 92 (14), 91 (100), 73 (28), 65 (28), 55 (23) and 43 (84).

Preparation of Unsaturated 1,4-Dicarbonyl Compounds 11 and Lactam 13a. General Procedure. To a solution of compound **10** or **12a** (0.5 mmol) in dry CH_2Cl_2 (5 ml) at 0°C was added DBU (0,082 ml, 0,55 mmol) and 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 (3x10 ml). The ethereal layers were washed with 2N aq HCl and brine, dried (Na_2SO_4), and evaporated to yield crude compounds **11** and **13a**, which were purified by column chromatography on silica gel. Yields and physical data are include in Table 2, spectral data follow.

(E)-4-Oxo-2-heptenal (11aa)[23]: ν 2860, 2730 (CHO), 1710, 1680 (C=O), 1590 and 980 cm^{-1} (CH=C); δ_H 0.97 (t, *J*=7.3Hz, 3H, CH_3), 1.70 (sextet, *J*=7.3Hz, 2H, C$H_2$$CH_3$), 2.69 (t, *J*=7.3Hz, 2H, CH_2C=O), 6.78

(dd, *J*=16.5, 6.9Hz, 1H, C*H*CHO), 6.89 (d, *J*=16.5Hz, 1H, CHC=O) and 9.78 (d, *J*=6.9Hz, 1H, CHO); δ_C 13.6 (CH_3), 17.1 (CH_2CH_3), 43.0 (CH_2C=O), 137.3 (2xCH), 193.4 (CHO) and 200.0 (C=O); *m/z* 98 (M^+-C_2H_4, 16%), 97 (47), 84 (22), 83 (42), 56 (15), 55 (100), 54 (14), 53 (11), 43 (93), 42 (27) and 41 (99).

(E)-5,5-Dimethyl-4-oxo-2-hexenal (11ac)[24]: ν 3020, 1615, 980 (CH=C), 2730 (CHO) and 1690 cm $^{-1}$ (C=O); δ_H 1.24 [s, 9H, $(CH_3)_3C$], 6.91 (dd, *J*=15.5, 7.6Hz, 1H, C*H*CHO), 7.38 (d, *J*=15.5Hz, 1H, CHC=O) and 9.79 (d, *J*=7.6Hz, 1H, CHO); δ_C 25.7 [$(CH_3)_3C$], 43.7 [$(CH_3)_3C$], 138.3, 140.7 (CH=CH), 192.8 and 203.5 (C=O); *m/z* 140 (M^+, <1%), 84 (100), 57 (71), 55 (17) and 41 (47).

(E)-4-Oxo-4-phenyl-2-butenal (11ad)[25]: ν ($CHCl_3$) 3020, 1615, 980 (CH=C), 2730 (CHO) and 1690 cm $^{-1}$ (C=O); δ_H 6.99 (dd, *J*=15.8, 7.4Hz, 1H, C*H*CHO), 7.54 (tt, *J*=7.6, 1.3Hz, 2H, *m*-Ph), 7.66 (m, 1H, *p*-Ph), 7.71 (d, *J*= 15.8, 1H, CHC=O), 8.93 (m, 2H, *o*-Ph) and 9.89 (d, *J*=7.4Hz, 1H, CHO); δ_C 128.9, 129.0, 134.1, 136.4, 139.1, 142.0 (ArC and CH=CH), 191.1 and 192.7 (C=O); *m/z* 160 (M^+, 32%), 131 (10), 105 (91), 77(100), 74 (13), 54 (10), 53 (10), 51 (68) and 50 (33).

(E)-3-Octen-2,5-dione (11ba)[26]: ν ($CHCl_3$) 3025, 1590, 980 (CH=C) and 1665 cm^{-1} (C=O); δ_H 0.96 (t, *J*=7.4Hz, 3H, CH_3CH_2), 1.18 (m, 2H, CH_2CH_3), 2.37 (s, 3H, CH_3C=O), 2.64 (t, *J*=7.2Hz, 2H, CH_2C=O), 6.81 and 6.85 (2 deformed d, *J*=13.6Hz, 2H, CH=CH); δ_C 13.6 (CH_3CH_2), 17.2 (CH_2CH_3), 28.1 (CH_3C=O), 43.18 (CH_2C=O), 136.8, 137.2 (CH=CH), 198.5 and 200.6 (2xC=O); *m/z* 140 (M^+, <1%), 97 (65), 69 (19), 55 (19), 43 (100) and 41 (22).

(E)-6-Methyl-3-hepten-2,5-dione (11bb)[22]: ν ($CHCl_3$) 3010, 1615, 975 (CH=C), 1690 and 1670 cm^{-1} (C=O); δ_H 1.16 [d, *J*=6.9Hz, 6H, $(CH_3)_2CH$], 2.37 (s, 3H, CH_3C=O), 2.90 (m, 1H, C*H*CH_3), 6.89 and 6.95 (2 deformed d, *J*=15.9Hz, 2H, CH=CH); δ_C 19.7 [$(CH_3)_2CH$], 28.5 (CH_3C=O), 39.8 ($CHCH_3$), 135.7, 136.9 (CH=CH), 198.3 and 203.8 (2xC=O); *m/z* 140 (M^+, 3%), 98 (86), 97 (58), 84 (16), 70 (22), 69 (27), 55 (83), 54 (11), 49 (19), 43 (100), 42 (10) and 41 (31).

(E)-6,6-Dimethyl-3-hepten-2,5-dione (11bc)[29]: ν 3010, 1605, 975 (CH=C) and 1665 cm^{-1} (C=O); δ_H 1.20 [s, 9H, $(CH_3)_3C$], 2.37 (s, 3H, CH_3C=O), 6.99 and 7.32 (2d, *J*=15.5Hz, CH=CH); δ_C 21.7 [$(CH_3C)_3$], 29.1 (CH_3C=O), 43.6 (*C*C=O), 132.6, 137.1 (CH=CH), 197.8 and 204.2 (2xC=O); *m/z* 154 (M^+, <1%), 98 (100), 98 (10), 82 (15), 70 (25), 69 (11), 66 (71), 55 (38), 54 (25), 43 (77), 42 (20) and 41 (77).

(E)-1-Phenyl-2-penten-1,4-dione (11bd)[30]: ν ($CHCl_3$) 3070, 1630, 1600, 1585, 980 (CH=C) and 1660 cm^{-1} (C=O); δ_H 2.44 (s, 3H, CH_3), 7.09, 7.70 (2d, *J*=15.5Hz, 2H, CH=CHC=O), 7.52 (m, 2H, *m*-Ph), 7.64 (m, 1H, *p*-Ph) and 7.99 (m, 2H, *o*-Ph); δ_C 29.0 (CH_3), 128.8, 128.9, 133.9, 134.0, 136.7, 138.4 (CH=CH and ArC), 190.3 and 197.8 (C=O); *m/z* 174 (M^+, 11%), 159 (14), 131 (21), 105 (100), 103 (10), 77 (85), 51 (44), 50 (16) and 43 (43).

N-*Phenyl-4-oxo-2-pentenamide (11bf)*[31]: ν (KBr) 3320 (NH), 1660, 1545 (C=O), 1625, 1600 and 975 cm^{-1} (CH=C); δ_H 2.39 (s, 3H, CH_3), 6.99, 7.21 (2d, *J*=15.4Hz, 2H, CH=CHC=O), 7.19 (m, 1H, 1xArH), 7.35 (t, *J*=7.5Hz, 2H, 2xArH), 7.63 (d, *J*=7.5Hz, 2H, 2xArH) and 8.20 (br s, 1H, NH); δ_C 29.6 (CH_3), 120.1, 125.1, 129.1, 134.5, 138.9, 137.5 (CH=CH and ArC), 162.6 (NC=O) and 198.0 (C=O); *m/z* 198 (M^+, 14), 146 (60), 97 (23), 93 (100), 77 (12), 69 (18), 65 (23) and 43 (74).

Ethyl (E)-4-Oxo-2-pentenoate (11bg)[32]: ν ($CHCl_3$) 3020, 1635, 975 (HC=C), 1715 and 1690 cm^{-1} (C=O); δ_H 1.33 (t, *J*=7.1Hz, 1H, CH_3CH_2), 2.37 (s, 3H, CH_3C=O), 4.28 (q, *J*=7.1Hz, CH_2), 6.65 and 7.02 (2d, *J*=16.1Hz, 2H, HC=CH); δ_C 14.01 (CH_3), 27.97 (CH_3C=O), 61.35 (CH_2), 131.51, 139.84 (HC=CH),

165.36 (COO) and 197.53 (C=O); *m/z* 142 (M^+,13%), 127 (100), 124 (17), 99 (39), 97 (65), 71 (12), 89 (14), 55 (21) and 43 (38).

N-Phenyl-5-hydroxy-2-pyrrolinone (13a)[5b]: ν ($CHCl_3$) 3180 (OH, NH), 1680 (C=O) and 1590 cm^{-1} (O=CNH); δ_H 3.08 (br s, 1H, OH), 5.98 (br s, 1H, C*H*OH), 6.20 (d, *J*=6.0Hz, 1H, CHC=O), 7.03 (dd, *J*=6.0, 1.7Hz, 1H, C*H*CHOH), 7.19 (t, *J*=7.8Hz, 1H, *p*-Ph), 7.39 (t, J=7.8Hz, 2H, *m*-Ph) and 7.64 (d, J=7.8Hz, 2H, *o*-Ph); δ_C 84.1 (CHOH), 113.2, 121.2, 125.2, 129.2, 136.6, 144.9 (HC=CH and ArC) and 168.4 (C=O); *m/z* 176 (M^++1, 13%), 175 (M^+, 100), 146 (43), 130 (44), 128 (16), 119 (12), 118 (13), 104 (13), 93 (61), 91 (10), 77 (57), 55 (26) and 51 (15).

Preparation of Cyclic Acetals 14 and Lactols 15. General Procedure. To a solution of acetal **7a** (1 mmol) in dry THF (5 ml) was added a 1.6 M hexane solution of *n*-BuLi (0.75 ml, 1.2 mmol) at -78°C under Ar. The resulting yellow solution was stirred for 1h at the same temperature and the carbonyl compound was added (1.1 mmol). The reaction mixture was stirred overnight and was quenched with 2N aq HCl (20 ml) and extracted with ether (3x20 ml), washed with water, dried (Na_2SO_4) and solvents were removed under vacuum (15 torr) to yield crude products **14** as diasteromeric mixture which were used in the next step without further purification. To a solution of crude compound **14** (1 mmol) in THF (10 ml) was added aqueous 4N HCl (10 ml) and the resulting mixture was stirred at rt. The reaction was extracted with ether (3x20 ml), the organic layer was washed with water, dried (Na_2SO_4) and evaporated to yield crude products **15** as diasteromeric mixture which were purified by column chromatography on silica gel.

Preparation of Lactones 16. General Procedure. To a solution of compound **15a,b** (1 mmol) in CH_2Cl_2 (10 ml) at 0°C, PDC (0.56 g, 1.5 mmol) and 4Å molecular sieves were added and the reaction mixture was stirred at rt. When the reaction was complete (TLC), the reaction mixture was purified by column chromatography on silica gel to yield pure compounds **16a,b**. To a solution of compound **15c,d** (1 mmol) in acetone (5 ml) at 0°C, CrO_3 (0.67 g, 6.7 mmol) dissolved in concd. sulfuric acid (1ml) and water (5 ml) were added. The reaction mixture was stirred at rt untill complete oxidation. The solvents were removed *in vacuo*, water (20 ml) was added and extracted with ether (3x20 ml). The ethereal layer was washed with brine (20 ml), dried (Na_2SO_4) and evaporated to give γ-lactones **16c,d** as a diasteromeric mixture.

Preparation of α,ß-Butenolides 17. General Procedure. See general procedure for the preparation of compounds **11** and **13a**. These compounds have been decribed in reference 16b.

ACKNOWLEDGEMENTS

We thank DGICYT (Project PB91-0751) from the Spanish Ministerio de Educación y Ciencia (MEC) for financial support. P.B. thanks the Generalitat Valenciana for a predoctoral fellowship. We thank also the referee's comments about mechanistic considerations.

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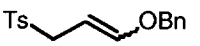
I



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(*Received in UK* 2 *November* 1994; *revised* 30 *December* 1994; *accepted* 6 *January* 1995)