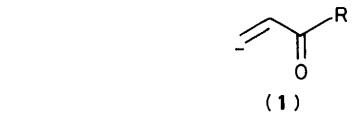
Dilithiated (*E*)-*N*-Isopropyl-3-tosylacrylamide: A New β-Acylvinyl Anion Equivalent in Organic Synthesis

Carmen Nájera * **and Miguel Yus** †
Departamento de Química Organometálica, Facultad de Química, Universidad de Oviedo, 33071 Oviedo, Spain

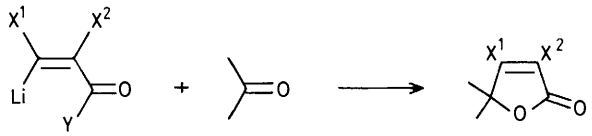
The dilithiated anion (**6**) obtained by reaction of (*E*)-*N*-isopropyl-3-tosylacrylamide with 2 equiv. of methyl-lithium at −78 °C is a new and efficient β-acylvinyl anion equivalent useful in the synthesis of substituted 3-tosyl-α,β-butenolides (**8**) by reaction with aldehydes followed by treatment with hydrochloric acid. In the absence of acid the process leads to the γ-hydroxy amide derivatives (**7**), which undergo thermal isomerization to various 1,4-dicarbonyl compounds, (**10**)—(**12′**), depending on the solvent used. The butenolides (**8**) suffer ring opening on treatment with nucleophiles such as pyrrolidine or methyl-lithium to yield the 1,4-dicarbonyl compound (**14**) or the 3-tosyl-β,γ-unsaturated acid (**15**), respectively.

One of the most important methodologies for the generation of α,β-unsaturated acyl functonality is based on the use of β-acylvinyl anion equivalents of the type (**1**).[1,2] When the precursor of this synthon is an acrylic acid derivative of the type (**2**), its reaction with carbonyl compounds leads directly to the creation of an α,β-butenolides (**3**). So, lithiated intermediates such as salts,[3–9] esters,[10–12] or amides[7,13,14] have been used for this reaction; they can be either unsubstituted[3] or substituted[4–14] by alkyl,[3,4,13] bromo,[4,5,8] alkoxy,[6,7,12,14] thioalkoxy,[6,9,12,14] or amino[10–12] groups in the α or β positions (Scheme 1).

Using the stabilizing and directing effects of the sulphonyl group in metallation reactions we have recently reported the synthesis and reactivity of (*E*)-4-lithio-4-tosylbut-3-en-2-one dimethyl ketal (**4**), a new β-acylvinyl anion equivalent derived from methyl vinyl ketone.[15,16] In the present paper we describe the preparaton of a new dianion derived from (*E*)-*N*-isopropyl-3-tosylacrylamide, which constitutes an appropriate d^3-reagent[17] for the synthesis of 3-tosyl-α,β-butenolides and 1,4-dicarbonyl compounds using the approach described in Scheme 1.



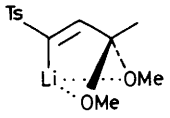
(**1**)



(**2**) (**3**)

X^1 and /or X^2 = R, Br, RO, RS, R_2N
Y = OLi, RO, RNLi, R_2N

Scheme 1.



(**4**)

Results and Discussion

The reaction of (*E*)-*N*-isopropyl-3-tosylacrylamide (**5**) (prepared from *N*-isopropylacrylamide *via* a tandem iodosulphonylation-dehydroiodination reaction)[18] with methyl-lithium–lithium bromide complex (1:2 molar ratio) at −78 °C‡ gave regio- and stereo-selectively the anion (**6**), which by treatment with different aldehydes yielded compounds (**7**). The final acidic hydrolysis of the crude compounds (**7**) using concentrated hydrochloric acid in dioxane at ambient temperature afforded the corresponding 4-substituted-3-tosyl-α,β-butenolides (**8**) (Scheme 2 and Table).

Under the above described reaction conditions, the butenolides derived from crotonaldehyde and cinnamaldehyde are the only ones to suffer partial or total isomerization, respectively, to give the more stable β,γ-butenolides[19] (**9c**) and (**9f**) (see Table).

It is noteworthy that the transformation (**6**) ⟶ (**7**) occurs with total retention of configuration. The stereochemistry of compounds (**7**) was assigned not only by their spectroscopic data but also by their capacity to form the cyclic butenolides (**8**) or (**9**). The observed result in the mentioned S_E process is in agreement with the literature data for stabilization of lithiated systems of the type (**4**)[16] by intramolecular complexation.[20–22]

When the acidic hydrolysis of compounds (**7**) was performed under reflux the corresponding γ-keto acid derivatives were obtained; even in absence of the acidic conditions we obtained the same results. Thus, the treatment of compounds (**7d**) or (**7′h**)§ with concentrated hydrochloric acid in boiling ethanol or dioxane yielded the expected esters (**10d**) and (**10′h**), or the acid (**11**), respectively. The mechanism involved in this process seems to be a thermal 1,3-migration of hydrogen [see (**13**)],¶ since the corresponding amide (**12′**) was isolated after heating compound (**7′d**)§ under neutral conditions in boiling chlorobenzene (Scheme 3).

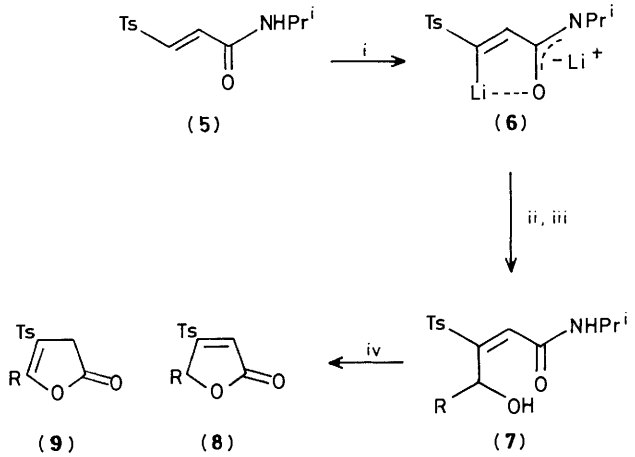
Products of type (**12′**) can also be obtained from the butenolides (**8**). Thus, the treatment of the compound (**8d**) with

† *Present address:* División de Química Orgánica, Facultad de Ciencias, Universidad de Alicante, Aptdo. 99, Alicante, Spain.

‡ Although intermediate (**6**) is stable at *ca.* −50 °C, a cleaner reaction with aldehydes takes place at −78 °C.

§ Compounds (**7′**)[23] were prepared using the same methodology as for (**7**), starting from the corresponding *N*-propylacrylamide.[18]

¶ A referee has suggested that this process probably takes place by an intermolecular process rather than through an intramolecular antarafacial mechanism. We thank the referee for this suggestion.



a; R = Et
b; R = Pr^i
c; R = (*E*)-MeCH=CH
d; R = Ph
e; R = 4-ClC_6H_4
f; R = (*E*)-PhCH=CH
g; R = PhCH(Me)

Scheme 2. *Reagents and conditions:* i, MeLi–LiBr, −78 °C; ii, RCHO, −78 to 20 °C; iii, H_2O; iv, conc. HCl–dioxane

Table. β-Hydroxyalkylacrylamides (**7**) and 4-substituted 3-tosyl-α,β-butenolides (**8**)

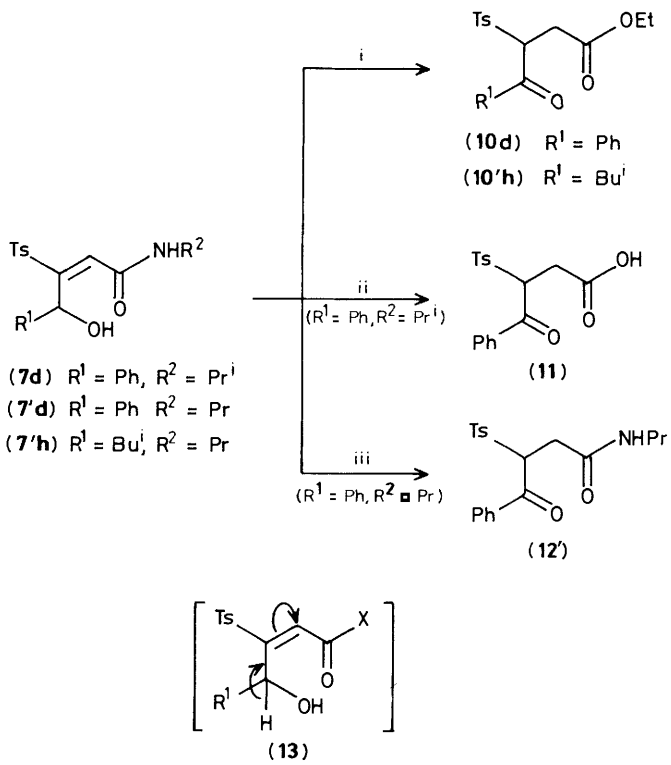
	Acrylamides (**7**)		Butenolides (**8**)	
R	No.	Yield[a] (%)	No.	Yield[a] (%)
Et	(**7a**)	88[b,c]	(**8a**)	75[b,c]
Pr^i	(**7b**)	90[b,c]	(**8b**)	85
(*E*)-MeCH=CH	(**7c**)	92[b,c]	(**8c**)	55[d]
Ph	(**7d**)	80	(**8d**)	90
4-ClC_6H_4	(**7e**)	86	(**8e**)	95[b,c]
(*E*)-PhCH=CH	(**7f**)	83	(**9f**)	88
PhCH(Me)	(**7g**)	87	(**8g**)	90

[a] Isolated yield after recrystallization based on compound (**5**). [b] Isolated crude yield based on compound (**5**). [c] This product was homogeneous (t.l.c.) and pure (300 MHz ^1H n.m.r.). [d] A 30% yield of compound (**9c**) was also obtained (300 MHz ^1H n.m.r. of the crude reaction mixture).

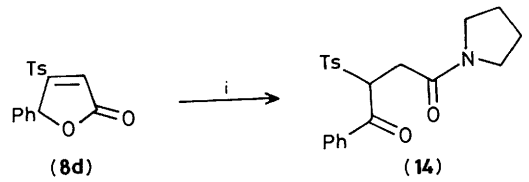
pyrrolidine in dichloromethane afforded the product (**14**) through an opening of the cyclic system together with the corresponding isomerization under the basic reaction conditions (Scheme 4). However, the use of a more powerful nucleophile such as methyl-lithium yielded the product of a Michael addition at the α position with respect to the carbonyl group followed by the corresponding β-elimination [see (**16**)]; so, starting from the butenolide (**8b**) the corresponding (*Z*/*E*)-mixture of compounds (**15**) was isolated (Scheme 5). This result contrasts with that obtained in the treatment of (*E*)-*N*-[3-tosylacryloyl]piperidine with methyl-lithium, in which an S_N type reaction takes place affording (*E*)-*N*-crotonoylpiperidine.[24]

Experimental

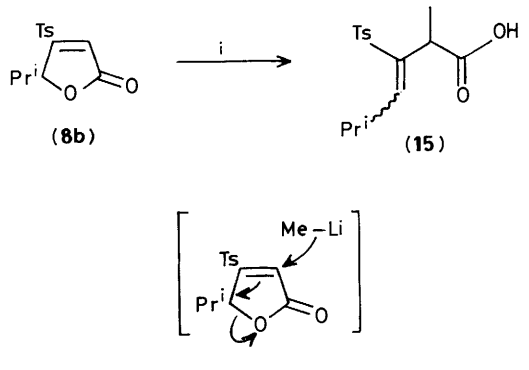
General.—M.p.s are uncorrected and were measured with a Büchi–Tottoli capillary melting point apparatus. I.r. spectra were determined with a Perkin-Elmer 577 spectrometer. ^1H and ^{13}C N.m.r. spectra were recorded on a Bruker AC-300 spectrometer using $CDCl_3$ as solvent and $SiMe_4$ as internal



Scheme 3. *Reagents and conditions:* i, conc. HCl–EtOH, reflux; ii, conc. HCl–dioxane, reflux; iii, PhCl, reflux



Scheme 4. *Reagents and conditions:* i, $(CH_2)_4NH$, CH_2Cl_2



Scheme 5. *Reagents and conditions:* i, MeLi, THF, −78 °C

standard. ^{13}C N.m.r. assignments were done on the basis of DEPT experiments. M.s. (e.i.) were recorded with a Hewlett-Packard 5987A spectrometer. Microanalyses were performed on a Perkin-Elmer 240 Elemental Analyser. T.l.c. analyses were carried out on Merck Kieselgel 60 F-254 plates (visualization by u.v.); flash column chromatography was performed on Merck Kieselgel 60 (230—400 mesh). Ether refers to diethyl ether. All reagents were of the best commercial grade available (Aldrich, Fluka, and Merck) and were used without further purification.

Ether was dried successively with anhydrous calcium chloride, sodium sulphate, sodium, and finally a K-Na (K_3Na) liquid alloy[25] under reflux, and was then distilled and stored under argon. Tetrahydrofuran (THF) was dried successively with anhydrous calcium chloride and sodium sulphate; it was then refluxed with lithium aluminium hydride, distilled, and stored under argon. Reactions which involve organolithium reagents were carried out under argon and all glassware was dried before use.

(E)-N-*Isopropyl*-3-*tosylpropenamide* (**5**).—This compound was prepared on a 50 mmol scale by one-pot iodosulphonylation-dehydro-iodination[18] of *N*-isopropylpropenamide. After work-up, the residue was treated with ethanol and the resulting white suspension filtered off and dried under reduced pressure (0.1 mmHg) to afford the title compound in 65% overall yield; m.p. 170—172 °C (from ethanol) (Found: C, 58.1; H, 6.3; N, 5.1. $C_{13}H_{17}NO_3S$ requires C, 58.40; H, 6.41; N, 5.24%); $\nu_{max.}$(Nujol) 3 300 (NH), 1 650 (C=O), 1 300, 1 140 (SO_2), and 980 cm^{-1} (CH=C); δ_H 1.15 [6 H, d, *J* 6.5 Hz, $(CH_3)_2CH$], 2.45 (3 H, s, CH_3Ar), 4.09 (1 H, m, *J* 6.5 Hz, CHN), 6.60 (1 H, d, *J* 6.5 Hz, NH), 7.04, 7.30 (2 H, 2 d, *J* 15 Hz, CH=CH), 7.37, and 7.78 (4 H, 2 d, *J* 8 Hz, ArH); δ_C 21.50 (CH_3Ar), 22.19 [$(CH_3)_2CH$], 42.16 (CHN), 128.02, 130.14, 135.85, 145.33 (ArC), 134.38, 139.38 (CH=CH), and 161.05 (C=O); *m*/*z* 269 (M^+ + 2, 2%), 267 (M^+, 35), 252 (21), 209 (69), 139 (100), and 91 (26).

Lithiation of Compound (**5**) *and Reaction with Aldehydes to give the Products* (**7**)*: General Procedure.*—An ethereal solution of methyl-lithium–lithium bromide complex (Aldrich, 2.2 mmol) was dropwise added to a solution of compound (**5**) (0.27 g, 1 mmol) in THF (5 ml) at −78 °C. Stirring was continued for 30 min at the same temperature and the corresponding aldehyde (1.2 mmol) was then added. The resulting mixture was stirred overnight the temperature being allowed to rise to 20 °C. It was then hydrolysed with water and 1M hydrochloric acid and extracted with dichloromethane. The organic layer was washed with water, dried (Na_2SO_4), and evaporated (15 mmHg) to give crude products (**7**), which were purified by recrystallization or by flash chromatography (hexane–ether as eluant). The following compounds were prepared by this method.

(E)-4-*Hydroxy*-N-*isopropyl*-3-*tosylhex*-2-*enamide* (**7a**), m.p. 145—147 °C (from hexane–$CHCl_3$) (Found: C, 58.8; H, 7.0; N, 4.2. $C_{16}H_{23}NO_4S$ requires C, 59.05; H, 7.12; N, 4.30%); $\nu_{max.}$($CDCl_3$) 3 340 (OH), 3 260 (NH), 1 640 (C=O), 1 300, and 1 140 cm^{-1} (SO_2); δ_H 0.97 (3 H, t, *J* 7 Hz, CH_3CH_2), 1.07, 1.09 [6 H, 2 d, *J* 6.5 Hz, $(CH_3)_2CH$], 1.62, 1.79 (2 H, 2 m, CH_2CH_3), 2.42 (3 H, s, CH_3Ar), 4.0 (1 H, m, *J* 6.5 Hz, CHN), 4.16 (1 H, ddd, *J* 14, 10, 3.5 Hz, CHO), 6.37 (1 H, d, *J* 10.5 Hz, OH), 7.12 (1 H, s, CHCO), 7.35, 7.76 (4 H, 2 d, *J* 8 Hz, ArH), and 7.43 (1 H, d, *J* 7.5 Hz, NH); δ_C 10.76 (CH_3CH_2), 21.57 (CH_3Ar), 21.87 [$(CH_3)CH$], 30.24 (CH_2), 42.45 (CHN), 70.63 (CHO), 128.30, 130.20, 134.84, 145.38 (ArC), 129.85, 157.34 (CH=C), and 163.45 (C=O); *m*/*z* 298 [$(M^+ + 2) - C_2H_5$, 7%], 296 ($M^+ - C_2H_5$, 100), 170 (38), 157 (26), 139 (73), 111 (42), 98 (24), 92 (28), 91 (88), 83 (32), 65 (45), 60 (34), 58 (31), 55 (30), 44 (40), 43 (37), and 41 (26).

(E)-4-*Hydroxy*-N-*isopropyl*-5-*methyl*-3-*tosylhex*-2-*enamide* (**7b**), m.p. 143—144 °C (from hexane–CCl_4) (Found: C, 59.9; H, 7.5; N, 4.0. $C_{17}H_{25}NO_4S$ requires C, 60.15; H, 7.42; N, 4.13%); $\nu_{max.}$($CDCl_3$) 3 340 (OH), 3 260 (NH), 1 660 (C=O), 1 300, and 1 150 cm^{-1} (SO_2); δ_H 0.88, 0.99 [6 H, 2 d, *J* 6.5 Hz, $(CH_3)CH$], 1.10 (6 H, d, *J* 6.5 Hz, 2 × CH_3CO), 2.11 (1 H, sextet, *J* 6.5 Hz, CHCHO), 2.42 (3 H, s, CH_3Ar), 4.0 (2 H, m, CHN and CHO), 6.21 (1 H, d, *J* 11.5 Hz, OH), 7.21 (1 H, s, CHCO), 7.25 [1 H, br s, NH(?)], 7.35, and 7.78 (4 H, 2 d, *J* 8 Hz, ArH); δ_C 18.61, 19.85, 21.59, 21.88, 21.92 (5 × CH_3), 34.25 (CHCO), 42.43 (CHN), 74.35 (CHO), 128.33, 130.16, 135.21, 145.30 (ArC), 131.11, 156.53 (CH=C), and 163.56 (C=O); *m*/*z* 339 (M^+, 2%), 296 (100), 184 (56), 157 (20), 142 (24), 139 (59), 91 (48), and 43 (23).

(E,E)-4-*Hydroxy*-N-*isopropyl*-3-*tosylhepta*-2,5-*dienamide* (**7c**), oil, R_F 0.60 [hexane–ether (1:10)]; $\nu_{max.}$($CDCl_3$) 3 360 (OH), 3 280 (NH), 1 665 (C=O), 1 630 (CH=C), 1 310, and 1 160 cm^{-1} (SO_2); δ_H 1.00, 1.02 [6 H, 2 d, *J* 6.5 Hz, $(CH_3)_2CH$], 1.46 (3 H, d, *J* 5.5 Hz, CH_3C=C), 2.34 (3 H, s, CH_3Ar), 3.93 (1 H, m, *J* 7 Hz, CHN), 4.72 (1 H, t, *J* 5.5 Hz, CHO), 5.42 (1 H, dq, *J* 15, 5.5 Hz, C=CHCH$_3$), 5.50 (1 H, dd, *J* 15, 5.5 Hz, C=CHCO), 6.77 (1 H, d, *J* 10.5 Hz, OH), 7.08 (1 H, s, CHC=O), 7.27, 7.69 (4 H, 2 d, *J* 8 Hz, ArH), and 7.48 (1 H, d, *J* 7.5 Hz, NH); δ_C 17.31, 21.41, 21.68, 21.72 (4 × CH_3), 42.26 (CHN), 69.24 (CHO), 128.38, 129.95, 134.71, 145.20 (ArC), 128.04, 129.63, 129.97, 155.49 (CH=CH, CH=C), and 163.21 (C=O); *m*/*z* 337 (M^+, 2%), 182 (100), 139 (37), 123 (34), 97 (52), 95 (40), 91 (46), 83 (23), 44 (20), 43 (33), and 41 (20).

(E)-4-*Hydroxy*-N-*isopropyl*-4-*phenyl*-3-*tosylbut*-2-*enamide* (**7d**), m.p. 160—161 °C (from hexane–CH_2Cl_2) (Found: C, 64.5; H, 6.3; N, 3.7. $C_{20}H_{23}NO_4S$ requires C, 64.32; H, 6.21; N, 3.75%); $\nu_{max.}$($CDCl_3$) 3 420 (OH), 3 350 (NH), 1 660 (C=O), 1 300, and 1 150 cm^{-1} (SO_2); δ_H 0.88, 1.02 [6 H, 2 d, *J* 6.5 Hz, $(CH_3)_2CH$], 2.40 (3 H, s, CH_3Ar), 3.86 (1 H, m, *J* 6.5 Hz, CHN), 5.58 (1 H, d, *J* 11.5 Hz, CHO), 6.80 (1 H, d, *J* 11.5 Hz, OH), 6.96 (1 H, d, *J* 7.5 Hz, NH), 7.2—7.4 (8 H, m, ArH), and 7.77 (2 H, d, *J* 8 Hz, ArH); δ_C 21.60, 21.74, 21.79 (3 × CH_3), 42.40 (CHN), 69.90 (CHO), 126.28, 127.31, 127.96, 128.42, 130.15, 131.85, 134.67, 140.84, 145.28, 156.28 (ArC, CH=C), and 163.27 (C=O); *m*/*z* 373 (M^+, 3%), 218 (100), 159 (32), 139 (24), 132 (27), 131 (71), 115 (25), 105 (38), 91 (44), 77 (31), and 58 (20)

(E)-4-(p-*Chlorophenyl*)-4-*hydroxy*-N-*isopropyl*-3-*tosylbut*-2-*enamide* (**7e**), m.p. 134—136 °C (from hexane–$CHCl_3$) (Found: C, 58.5; H, 5.3; N, 3.3. $C_{20}H_{22}ClNO_4S$ requires C, 58.89; H, 5.44; N, 3.43%); $\nu_{max.}$($CDCl_3$) 3 320 (OH), 3 270 (NH), 1 650 (C=O), 1 300, and 1 145 cm^{-1} (SO_2); δ_H 0.86, 0.99 [6 H, 2 d, *J* 6.5 Hz, $(CH_3)_2CH$], 2.37 (3 H, s, CH_3Ar), 3.82 (1 H, m, *J* 6.5 Hz, CHN), 5.52 (1 H, d, *J* 9.5 Hz, CHO), 6.93 (1 H, d, *J* 11 Hz, OH), 7.14, 7.68 (4 H, 2 d, *J* 8 Hz, $CH_3C_6H_4$), 7.16—7.30 (5 H, m, ClC_6H_4, NH), and 7.33 (1 H, s, CHCO); δ_C 21.53, 21.66, 21.70 (3 × CH_3), 42.41 (CHN), 69.30 (CHO), 127.76, 128.01, 128.31, 130.15, 132.01, 133.19, 134.47, 139.40, 145.63, 155.66 (ArC, CH=C), and 163.10 (C=O); *m*/*z* 409 (M^+ + 2, 2%), 407 (M^+, 6), 254 (34), 252 (100), 193 (31), 167 (23), 165 (58), 141 (22), 140 (22), 139 (86), 111 (22), 92 (27), 91 (88), 77 (35), 65 (43), 60 (21), 57 (40), 53 (46), 44 (39), 43 (53), and 41 (28).

(E,E)-4-*Hydroxy*-N-*isopropyl*-6-*phenyl*-3-*tosylhexa*-2,5-*dienamide* (**7f**), m.p. 158—159 °C (from hexane–CH_2Cl_2) (Found: C, 66.0; H, 6.1; N, 3.4. $C_{22}H_{25}NO_4S$ requires C, 66.14; H, 6.31; N, 3.51%); $\nu_{max.}$($CDCl_3$) 3 340 (OH), 3 270 (NH), 1 640 (C=O), 1 300, 1 145 (SO_2), and 970 cm^{-1} (CH=C); δ_H 0.98, 1.05 [6 H, 2 d, *J* 6.5 Hz, $(CH_3)_2CH$], 2.27 (3 H, s, CH_3Ar), 3.98 (1 H, m, *J* 6.5 Hz, CHN), 4.99 (1 H, dd, *J* 11, 6 Hz, CHO), 6.17 (1 H, dd, *J* 16, 6 Hz, C=CHCO), 6.32 (1 H, d, *J* 16 Hz, CH=CHCO), 6.97 (1 H, d, *J* 11 Hz, OH), 7.10—7.20 (6 H, m with s at 7.19, Ph, CHC=O), 7.22, 7.74 (4 H, 2 d, *J* 8 Hz, $CH_3C_6H_4$), and 7.35 (1 H, d, *J* 7.5 Hz, NH); *m*/*z* 399 (M^+, 2%), 244 (51), 185 (30), 159 (100), 158 (38), 157 (44), 139 (33), 131 (37), 129 (32), 128 (35), 115 (24), 103 (27), 91 (53), 77 (26), 44 (22), and 43 (39).

(E)-4-*Hydroxy*-N-*isopropyl*-5-*phenyl*-3-*tosylhex*-2-*enamide* (**7g**), m.p. 75—77 °C (from hexane–$CHCl_3$) (Found: C, 65.5; H, 6.8; N, 3.4. $C_{22}H_{27}NO_4S$ requires C, 65.81; H, 6.78; N, 3.49%); $\nu_{max.}$($CDCl_3$) 3 340 (OH), 3 260 (NH), 1 645 (C=O), 1 300, and 1 140 cm^{-1} (SO_2); δ_H 1.05, 1.09 [6 H, 2 d, *J* 6.5 Hz, $(CH_3)_2CH$], 1.32 (3 H, d, *J* 7 Hz, CH_3CCO), 2.38 (3 H, s, CH_3Ar), 3.29 (1 H, quintet, *J* 7 Hz, CHCO), 4.01 (1 H, m, *J* 7 Hz, CHN), 4.45 (1 H, dd, *J* 11, 6 Hz, CHO), 6.66 (1 H, d, *J* 11 Hz, OH), 7.1—7.3 (9 H, m with d at 7.26, *J* 8 Hz, ArH, CHC=O), and 7.65 (2 H, d, *J* 8 Hz, ArH); δ_C 15.88 (CH_3CCO), 21.57, 21.86, 22.01 [$(CH_3)_2CH$, CH_3Ar], 42.52 (CHN), 45.33 (CHCO), 74.00 (CHO), 126.44,

128.09, 128.13, 128.19, 130.16, 131.79, 135.26, 143.29, 145.15, 155.59 (ArC, CH=C), and 163.69 (C=O); *m/z* 298 [(M^+ + 2) − C_8H_9, 8%], 297 (23), 296 (100), 139 (20), and 105 (57).

Preparation of Compounds (**7'd**) *and* (**7'h**).—Compounds (**7'**) were obtained following the same procedure as for (**7**), starting from (*E*)-*N*-propyl-3-tosylpropenamide.[18]

(E)-4-*Hydroxy*-4-*phenyl*-N-*propyl*-3-*tosylbut*-2-*enamide* (**7'd**) (80% yield), m.p. 131—133 °C (decomp.; lit.,[23] 130—133 °C); $\nu_{max.}$(Nujol) 3 260 (NH, OH), 1 640 (C=O), 1 310, and 1 145 cm^{-1} (SO_2); δ_H *0.81* (3 H, t, *J* 7.5 Hz, CH_3CH_2), 1.10—1.58 (2 H, m, CH_2CH_3), 2.4 (3 H, s, CH_3Ar), 3.25 (2 H, q, *J* 7 Hz, CH_2N), 5.72 (1 H, d, *J* 11.5 Hz, CHO), 6.73 (1 H, d, *J* 11.5 Hz, OH), 6.92 (1 H, br s, NH), 7.22—7.83 (7 H, m, ArH), and 7.88 (2 H, d, *J* 8 Hz, ArH); δ_C 11.48 (CH_3CH_2), 21.47 (CH_2CH_3), 22.49 (CH_3Ar), 42.06 (CH_2N), 70.46 (CHO), 127.03, 127.98, 128.45, 129.04, 131.06, 132.48, 135.42, 141.96, 146.47, 156.97 (ArC, CH=C), and 164.98 (C=O); *m/z* 373 (M^+, 4%), 314 (18), 218 (70), 131 (71), and 91 (67).

(E)-4-*Hydroxy*-6-*methyl*-N-*propyl*-3-*tosylhept*-2-*enamide* (**7'h**) (90% yield), m.p. 114—115 °C (from hexane–$CHCl_3$) (Found: C, 60.9; H, 7.8; N, 3.8. $C_{18}H_{27}NO_4S$ requires C, 61.16; H, 7.70; N, 3.96%); $\nu_{max.}$(Nujol) 3 270 (NH, OH), 1 645 (C=O), 1 310 and 1 150 cm^{-1} (SO_2); δ_H 0.90 (9 H, m, 2 × CH_3CH, CH_3CH_2), 1.23—2.13 (5 H, m, CH_2CH_3, CH_2CH, $CHCH_3$), 2.40 (3 H, s, CH_3Ar), 3.23 (2 H, q, *J* 7 Hz, CH_2N), 4.40 (1 H, td, *J* 13.5, 3 Hz, CHO), 6.23 (1 H, d, *J* 13.5 Hz, OH), 7.2 (2 H, s, NH, CHC=O), 7.46 and 7.60 (4 H, 2 d, *J* 8 Hz, ArH); δ_C 11.37 (CH_3CH_2), 21.48, 22.11, 23.37, 24.64, 25.28 (2 × CH_3CH, CH_2CH_3, CH_3Ar, CH_2CH), 42.97 (CH_2N), 46.11 ($CHCH_2$), 68.26 (CHO), 128.93, 131.46, 136.51, 147.25 (ArC), 130.19, 159.26 (CH=C), and 166.22 (C=O); *m/z* 353 (M^+, 2%), 296 (100), 198 (23), 139 (52), 91 (34), 60 (31), 55 (20), 43 (36), and 41 (25).

Preparation of the Butenolides (**8**)*: General Procedure.*—A solution of the crude product (**7**) (1 mmol) in dioxane (5 ml) and 12M hydrochloric acid (0.5 ml) was stirred overnight at room temperature. The mixture was then extracted with dichloromethane and the organic layer was washed with saturated aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and evaporated (15 mmHg) to afford the corresponding butenolides (**8**) or (**9**); these were purified by recrystallization or by flash chromatography (hexane–ether as eluant).

4-*Ethyl*-3-*tosylbut*-2-*en*-4-*olide* (**8a**), oil, R_F 0.60 [hexane–ether (1:10)]; $\nu_{max.}$($CDCl_3$) 1 780, 1 760 (C=O), 1 330, and 1 155 cm^{-1} (SO_2); δ_H 0.80 (3 H, t, *J* 7 Hz, CH_3CH_2), 1.70 (1 H, septet, *J* 7 Hz, CH_2), 2.11 (1 H, sextet, *J* 7, 3.5 Hz, CH_2), 2.41 (3 H, s, CH_3Ar), 5.11 (1 H, ddd, *J* 7, 3.5, 2 Hz, CHO), 6.30 (1 H, d, *J* 2 Hz, CHC=O), 7.36 and 7.66 (4 H, 2 d, *J* 8 Hz, ArH); δ_C 7.78 (CH_3CH_2), 21.63 (CH_3Ar), 25.53 (CH_2), 82.28 (CHO), 125.60 (*C*HC=O), 128.49, 130.44, 134.42, 146.70 (ArC), 166.89, and 168.25 (*C*=CH, C=O); *m/z* 266 (M^+, 22%), 140 (20), 139 (67), 119 (20), 111 (100), 92 (35), 91 (87), 83 (70), 67 (22), 65 (48), 57 (26), 55 (33), 53 (22), and 39 (29).

4-*Isopropyl*-3-*tosylbut*-2-*en*-4-*olide* (**8b**), m.p. 98—100 °C (from hexane–$CHCl_3$) (Found: C, 59.7; H, 5.6. $C_{14}H_{16}O_4S$ requires C, 59.98; H, 5.75%); $\nu_{max.}$($CDCl_3$) 1 780, 1 760 (C=O), 1 330, and 1 150 cm^{-1} (SO_2); δ_H 0.67, 1.18 (6 H, 2 d, *J* 7 Hz, 2 × CH_3CH), 2.40—2.60 (4 H, m with s at 2.50, CH_3Ar, $CHCH_3$), 5.14 (1 H, t, *J* 2 Hz, CHO), 6.32 (1 H, s, CHC=O), 7.44, and 7.84 (4 H, 2 d, *J* 8 Hz, ArH); δ_C 12.75, 19.41 (2 × CH_3CH), 21.11 (CH_3Ar), 29.80 ($CHCH_3$), 85.27 (CHO), 125.48 (*C*HC=O), 128.11, 130.03, 133.96, 146.23 (ArC), 165.95, and 168.06 (*C*=CH, C=O); *m/z* 280 (M^+, 3%), 238 (100), 139 (27), 92 (31), 91 (37), 83 (25), 65 (24), 55 (20), and 43 (24).

(E)-4-*Prop*-1-*enyl*-3-*tosylbut*-2-*en*-4-*olide* (**8c**), m.p. 94—95 °C (from hexane–$CHCl_3$) (Found: C, 60.5; H, 5.0. $C_{14}H_{14}O_4S$ requires C, 60.42; H, 5.07%); $\nu_{max.}$(Nujol) 1 780, 1 750 (C=O), 1 665, 980 (CH=CH), 1 310, and 1 140 cm^{-1} (SO_2); δ_H 1.67 (3 H, dd, *J* 6.5, 2 Hz, CH_3CH), 2.49 (3 H, s, CH_3Ar), 5.00 (1 H, ddq, *J* 15, 8.5, 2 Hz, *C*HCHO), 5.51 (1 H, dd, *J* 8.5, 2 Hz, CHO), 5.99 (1 H, dq, *J* 15, 6.5 Hz, *C*HCH_3), 6.57 (1 H, d, *J* 2 Hz, CHC=O), 7.41, and 7.77 (4 H, 2 d, *J* 8 Hz, ArH); δ_C 17.66 (CH_3CH), 21.72 (CH_3Ar), 82.30 (CHO), 122.81, 125.48, 135.71 (3 × *C*H=C), 129.02, 130.17, 134.68, 146.57 (ArC), 166.68, and 168.03 (*C*=CH, C=O); *m/z* 280 (M^+ + 2, 5%), 278 (M^+, 70), 250 (32), 140 (29), 139 (89), 123 (49), 119 (65), 95 (100), 92 (33), 91 (74), 77 (45), 69 (41), 67 (23), 65 (48), 53 (26), 41 (23), and 39 (28).

(E)-4-*Prop*-1-*enyl*-3-*tosylbut*-3-*en*-4-*olide* (**9c**), oil, R_F 0.40 [hexane–ether (1:2)]; $\nu_{max.}$($CDCl_3$) 1 820 (C=O), 1 650 (CH=C), 1 325, and 1 150 cm^{-1} (SO_2); δ_H 1.93 (3 H, d, *J* 7 Hz, CH_3CH), 2.38 (3 H, s, CH_3Ar), 3.36 (2 H, s, CH_2), 6.57 (1 H, dq, *J* 15.5, 7 Hz, *C*HCH_3), 6.96 (1 H, d, *J* 15.5 Hz, CHC=O), 7.29, and 7.69 (4 H, 2 d, *J* 8 Hz, ArH); δ_C 19.00 (CH_3CH), 21.59 (CH_3Ar), 34.29 (CH_2), 116.03, 127.22, 128.82, 130.18, 130.87, 137.55, 141.09, 156.57 (ArC, CH=CH, CH=C), and 169.92 (C=O); *m/z* 280 (M^+ + 2, 4%), 278 (M^+, 32), 177 (23), 149 (100), 139 (33), 119 (27), 95 (59), 92 (21), 91 (66), 77 (32), 69 (88), 65 (50), 43 (25), 41 (46), and 39 (43).

4-*Phenyl*-3-*tosylbut*-2-*en*-4-*olide* (**8d**), m.p. 145—147 °C (from hexane–$CHCl_3$) (Found: C, 64.5; H, 4.4. $C_{17}H_{14}O_4S$ requires C, 64.95; H, 4.49%); $\nu_{max.}$(Nujol) 1 770, 1 750 (C=O), 1 330, and 1 145 cm^{-1} (SO_2); δ_H 2.37 (3 H, s, CH_3), 6.12 (1 H, s, CHO), 6.80 (1 H, s, CHC=O), and 6.90—7.40 (9 H, m, ArH); δ_C 21.57 (CH_3), 83.16 (CHO), 125.93, 127.58, 128.41, 128.79, 129.87, 131.44, 134.32, 145.96, 167.39, and 168.36 (ArC, CH=C, C=O); *m/z* 316 (M^+ + 2, 7%), 315 (M^+ + 1, 20), 314 (M^+, 100), 159 (72), 158 (25), 139 (29), 131 (75), 119 (26), 115 (47), 105 (77), 103 (27), 91 (33), 77 (50), 65 (25), and 53 (26).

4-(p-*Chlorophenyl*)-3-*tosylbut*-2-*en*-4-*olide* (**8e**), m.p. 106—107 °C (from hexane–$CHCl_3$) (Found: C, 58.2; H, 3.8. $C_{17}H_{13}ClO_4S$ requires C, 58.54; H, 3.76%); $\nu_{max.}$($CDCl_3$) 1 790, 1 760 (C=O), 1 330, 1 175, and 1 150 cm^{-1} (SO_2); δ_H 2.40 (3 H, s, CH_3), 6.09 (1 H, s, CHO), 6.81 (1 H, s, CHC=O), 6.93 (2 H, d, *J* 7 Hz, ArH), 7.13, and 7.33 (6 H, 2 d, *J* 8 Hz, ArH); δ_C 21.44 (CH_3), 81.96 (CHO), 125.95, 128.23, 128.76, 128.81, 129.80, 129.95, 134.01, 135.92, 146.17, 166.84, and 167.99 (ArC, CH=C, C=O); *m/z* 350 (M^+ + 2, 27%), 348 (M^+, 71), 193 (45), 167 (20), 165 (63), 149 (35), 141 (22), 140 (27), 139 (100), 119 (38), 111 (27), 91 (38), 65 (24), and 53 (24).

(E)-4-(2-*Phenylvinyl*)-3-*tosylbut*-3-*en*-4-*olide* (**9f**), m.p. 199—200 °C (decomp.) (from ether) (Found: C, 66.8; H, 4.7. $C_{19}H_{16}O_4S$ requires C, 67.04; H, 4.74%); $\nu_{max.}$(Nujol) 1 820 (C=O), 1 630, 960 (CH=C), 1 320, and 1 150 cm^{-1} (SO_2); δ_H 2.45 (3 H, s, CH_3), 3.50 (2 H, CH_2), 7.30—7.70 (9 H, m with 2 d at 7.38 and 7.67, *J* 16 Hz, ArH, CH=CH), and 7.80 (2 H, d, *J* 8 Hz, ArH); δ_C 21.60 (CH_3), 35.54 (CH_2), 111.42, 112.70, 127.32, 128.19, 129.01, 130.26, 130.42, 134.74, 137.42, 140.64, 145.06, 156.80 (ArC, C=C), and 169.78 (C=O); *m/z* 342 (M^+ + 2, 4%), 340 (M^+, 44), 185 (100), 184 (34), 157 (63), 156 (29), 139 (25), 131 (67), 129 (30), 128 (42), 103 (63), 91 (36), 77 (47), and 65 (20).

4-(1-*Phenylethyl*)-3-*tosylbut*-2-*en*-4-*olide* (**8g**), m.p. 159—161 °C (from hexane–$CHCl_3$) (Found: C, 66.5; H, 5.1. $C_{19}H_{18}O_4S$ requires C, 66.65; H, 5.30%); $\nu_{max.}$($CDCl_3$) 1 780, 1 760 (C=O), 1 330, 1 160, and 1 150 cm^{-1} (SO_2); δ_H 1.10 (3 H, d, *J* 7 Hz, CH_3CH), 2.50 (3 H, s, CH_3Ar), 3.65 (1 H, m, $CHCH_3$), 5.31 (1 H, t, *J* 2 Hz, CHO), 6.42 (1 H, d, *J* 2 Hz, CHC=O), 7.33 (5 H, m, Ph), 7.46, and 7.90 (4 H, 2 d, *J* 8 Hz, $CH_3C_6H_4$); δ_C 11.72 (CH_3CH), 21.52 (CH_3Ar), 40.77 ($CHCH_3$), 85.01 (CHO), 126.06, 127.08, 127.57, 128.43, 130.43, 134.21, 141.58, 146.75, 165.75, and 168.17 (ArC, CH=C, C=O); *m/z* 342 (M^+, 3%), and 105 (100).

Transformation of Compounds (**7d**) *or* (**7'd,h**) *into Products* (**10d**), (**10'h**), (**11**), *and* (**12'**)*: General Procedure.*—A solution of

the crude compound (**7**) or (**7′**) (1 mmol) in the corresponding solvent (5 ml; see Scheme 3) was refluxed for 24 h [1 h for the transformation (**7′d**) ⟶ (**12′**)]. The resulting mixture was worked up as is described for compounds (**8**), except in the case of product (**11**), which was extracted under acidic conditions. Compound (**12′**) was isolated after evaporation of the solvent. All products were purified by recrystallization or by flash chromatography (hexane–ether as eluant).

Ethyl 4-*Oxo*-4-*phenyl*-3-*tosylbutanoate* (**10b**) (80% yield), oil, R_F 0.68 [hexane–ether (1:10)]; $\nu_{max.}$($CDCl_3$) 1 710, 1 670 (C=O), 1 320, and 1 145 cm^{-1} (SO_2); δ_H 1.03 (3 H, t, *J* 7 Hz, CH_3CH_2), 2.31 (3 H, s, CH_3Ar), 3.04 (1 H, dd, *J* 17, 3.5 Hz, CH_2C=O), 3.19 (1 H, dd, *J* 17, 11 Hz, CH_2C=C), 3.94 (2 H, dq, *J* 7, 3 Hz, CH_2CH_3), 5.45 (1 H, dd, *J* 11, 3.5 Hz, CHS), 7.18 (2 H, d, *J* 8 Hz, *o*-Ph), 7.35 (2 H, t, *J* 7.5 Hz, *m*-Ph), 7.43 (1 H, t, *J* 7 Hz, *p*-Ph), 7.45, and 7.89 (4 H, 2 d, *J* 8 Hz, $CH_3C_6H_4$); δ_C 13.74 (CH_3CH_2), 21.44 (CH_3Ar), 32.80 (CH_2C=O), 61.32 (CH_2CH_3), 65.78 (CHS), 128.42, 129.04, 129.37, 129.55, 133.08, 133.63, 136.53, 145.56 (ArC), 169.52 (CO_2), and 191.35 (C=O); *m*/*z* 315 (M^+ − EtO, 4%), 105 (100), 91 (15), and 77 (15).

Ethyl 6-*Methyl*-4-*oxo*-3-*tosylheptanoate* (**10′h**) (88% yield), m.p. 85—87 °C (from hexane–CH_2Cl_2) (Found: C, 59.6; H, 7.0. $C_{17}H_{24}O_5S$ requires C, 59.98; H, 7.11%); $\nu_{max.}$($CDCl_3$) 1 720 (C=O), 1 320, and 1 145 cm^{-1} (SO_2); δ_H 0.86, 0.87 (6 H, 2 d, *J* 6.5 Hz, 2 × CH_3CH), 1.13 (3 H, t, *J* 7 Hz, CH_3CH_2), 2.09 (1 H, m, $CHCH_3$), 2.39 (3 H, s, CH_3Ar), 2.55—2.95 (4 H, m, 2 × CH_2CH), 3.99 (2 H, q, *J* 7 Hz, CH_2O), 4.46 (1 H, dd, *J* 11, 3.5 Hz, CHS), 7.29, and 7.57 (4 H, 2 d, *J* 8 Hz, ArH); δ_C 13.99 (CH_3CH_2), 21.66, 22.16, 22.39 (2 × CH_3CH, CH_3Ar), 23.6 ($CHCH_3$), 32.42 (CH_2CO_2), 53.74 (CH_2C=O), 61.46 (CH_2O), 70.39 (CHS), 129.37, 129.85, 133.04, 145.77 (ArC), 169.69 (CO_2), and 200.57 (C=O); *m*/*z* 340 (M^+, 2%), 257 (30), 256 (21), 209 (23), 183 (21), 139 (70), 91 (57), 85 (100), and 57 (35).

4-*Oxo*-4-*phenyl*-3-*tosylbutyric Acid* (**11**) (95% yield), m.p. 153—155 °C (from hexane–CH_2Cl_2) (Found: C, 61.5; H, 4.7. $C_{17}H_{16}O_5S$ requires C, 61.43; H, 4.85%); $\nu_{max.}$($CDCl_3$) 3 700—2 400 (OH), 1 710, 1 680 (C=O), 1 320, and 1 145 cm^{-1} (SO_2); δ_H 2.40 (3 H, s, CH_3), 3.13 (1 H, dd, *J* 17.5, 4 Hz, CH_2), 3.27 (1 H, dd, *J* 17.5, 10.5 Hz, CH_2), 5.46 (1 H, dd, *J* 10.5, 4 Hz, CHS), 7.25 (2 H, d, *J* 7.5 Hz, *o*-Ph), 7.42 (2 H, t, *J* 7.5 Hz, *m*-Ph), 7.50—7.60 (3 H, m with d at 7.54, *J* 8 Hz, *p*-Ph, *m*-Tol), 7.92 (2 H, d, *J* 8 Hz, *o*-Tol), and 7.0—8.0 (1 H, br s, OH); δ_C 21.60 (CH_3), 32.35 (CH_2), 65.81 (CHS), 128.57, 129.27, 129.47, 129.75, 133.00, 133.91, 136.41, 145.85 (ArC), 174.59 (CO_2), and 191.14 (C=O); *m*/*z* 268 (M^+ − SO_2, 5%), 105 (100), 91 (28), and 77 (42).

4-*Oxo*-4-*phenyl*-N-*propyl*-3-*tosylbutanamide* (**12′**) (87% yield), oil; $\nu_{max.}$($CDCl_3$) 1 680 (C=O), 1 325, and 1 155 cm^{-1} (SO_2); δ_H(80 MHz) 0.9 (3 H, t, *J* 7.5 Hz, CH_3CH_2), 1.4 (2 H, sextet, *J* 7.5 Hz, CH_2CH_3), 2.4 (3 H, s, CH_3Ar), 3.15 (4 H, m, CH_2C=O, CH_2N), 5.7 (1 H, dd, *J* 10.5, 4 Hz, CHS), 6.0 (1 H, br s, NH), and 7.15—8.15 (9 H, m, ArH); δ_C(20 MHz) 11.4 (CH_3CH_2), 22.1 (CH_3Ar), 23.4 (CH_2CH_3), 34.8 (CH_2C=O), 42.4 (CH_2N), 67.1 (CHS), 129.3, 129.9, 130.4, 130.95, 134.8, 135.45, 138.0, 146.85 (ArC), 169.0 (CON), and 194.3 (C=O); *m*/*z* 373 (M^+, 1%), 159 (20), 105 (100), and 82 (22).

Preparation of N-(4-*Oxo*-4-*phenyl*-3-*tosylbutyryl*)*pyrrolidine* (**14**).— A solution of compound (**8d**) (0.157 g, 0.5 mmol) and pyrrolidine (0.36 g, 5 mmol) in dichloromethane (5 ml) was stirred for 90 min at room temperature. The resulting solution was washed with 1M hydrochloric acid and water, dried (Na_2SO_4), and evaporated (15 mmHg). The resulting residue was purified by flash chromatography (hexane–ether) to give the title compound (0.135 g, 70%) as an oil, R_F 0.30 [hexane–ether (1:10)]; $\nu_{max.}$ 1 670, 1 630 (C=O), 1 320, and 1 145 cm^{-1} (SO_2); δ_H 1.70—2.00 (4 H, 2 m, $CH_2CH_2CH_2N$), 2.32 (3 H, s, CH_3), 3.00—3.50 (6 H, m with d at 3.10, *J* 16 Hz, 2 × CH_2N, CH_2C=O), 5.65 (1 H, dd, *J* 11, 3 Hz, CHS), 7.19 (2 H, d, *J* 8 Hz, *o*-Ph), 7.35 (2 H, t, *J* 7.5 Hz, *m*-Ph), 7.48 (1 H, t, *J* 7 Hz, *p*-Ph), 7.59, and 7.91 (4 H, 2 d, *J* 8 Hz, $CH_3C_6H_4$); δ_C 21.11 (CH_3), 23.85, 25.45 ($CH_2CH_2CH_2N$), 32.99 (CH_2C=O), 45.40, 46.11 (2 × CH_2N), 65.80 (CHS), 127.95, 128.66, 128.78, 129.24, 132.82, 133.75, 136.57, 145.01 (ArC), 166.35 (CON), and 191.58 (C=O); *m*/*z* 280 (M^+ − PhCO, 2%), 230 (21), 159 (20), 105 (73), 98 (24), 91 (53), 77 (48), 70 (100), 56 (25), and 55 (34).

Preparation of (Z/E)-2,5-*Dimethyl*-3-*tosylhex*-3-*enoic Acid* (**15**).—An ethereal solution of methyl-lithium–lithium bromide complex (0.6 mmol) was dropwise added to a solution of compound (**8d**) (0.157 g, 0.5 mmol) in THF at −78 °C under argon. The mixture was stirred for 10 min at the same temperature and then quenched with water (1 ml) and extracted with dichloromethane. The organic layer was washed with 1M hydrochloric acid, dried (Na_2SO_4), and evaporated (15 mmHg). The resulting residue was purified by flash chromatography (hexane–ether) to give the title compound (0.089 g, 60%) as an oily mixture of *Z*/*E*-isomers (1:8) (by 300 MHz ^{1}H n.m.r.); $\nu_{max.}$(neat) 3 700—2 400 (OH), 1 710 (C=O), 1 640 (CH=C), 1 310, and 1 140 cm^{-1} (SO_2); δ_H (for the major isomer) 0.93, 0.99 (6 H, 2 d, *J* 6 Hz, 2 × CH_3CHC=C), 1.17 (3 H, d, *J* 7 Hz, CH_3CHC=O), 2.35 (3 H, s, CH_3Ar), 2.44 (1 H, m, $CHCH$=C), 3.43 (1 H, q, *J* 7 Hz, CH_3CHC=O), 6.70 (1 H, d, *J* 11 Hz, $CHCH$=C), 7.24, 7.65 (4 H, 2 d, *J* 8 Hz, ArH), and 8.50 (1 H, br s, OH); δ_C (for the major isomer) 16.54, 20.65, 21.52, 21.66 (4 × CH_3), 28.75 ($CHCH$=C), 37.65 (CHC=O), 12.08, 129.70, 137.66, 144.25, 150.05, 150.88 (ArC, CH=C), and 177.29 (C=O); *m*/*z* 296 (M^+, 1%), 157 (55), 139 (27), 95 (100), 92 (23), 91 (50), 85 (23), 81 (41), 79 (24), 77 (21), 67 (36), 65 (49), 55 (49), 53 (32), 43 (79), 41 (77), and 39 (51).

Acknowledgements

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.

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Received 5th May 1988; *Paper* 8/03696I