Regio- and Stereo-selective Synthesis of β-Sulphonyl-α,β-Unsaturated Carbonyl Compounds *via* an Iodosulphonylation–Dehydroiodination Reaction

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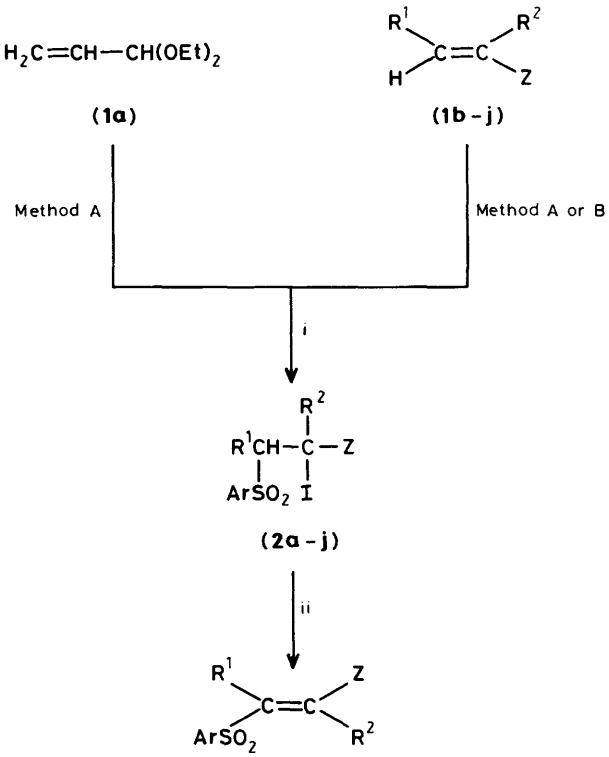
α,β-Unsaturated carbonyl compounds underwent regiospecific iodosulphonylation with toluene-*p*-sulphonyl iodide or sodium toluene-*p*-sulphinate and iodine to afford products (**2**), which were stereoselectively dehydroiodinated by triethylamine to give β-sulphonyl derivatives (**3**). The reactivity of compounds (**3**) as cationic β-acylvinyl equivalents, tested with amines or thiophenol, gave compounds (**4**) resulting from a displacement reaction.

The free radical addition of sulphonyl halides to unsaturated compounds represents a general method for the synthesis of sulphones.[1] The reaction has been studied[2] with alkenes, alkynes, dienes, and allenes; among the sulphonyl halides, iodides give the best yields under the mildest reaction conditions. Recently, we have applied the iodosulphonylation reaction of conjugated dienes, using metallic toluene-*p*-sulphinate–iodine combinations, for the preparation of dienyl and δ-functionalized allyl sulphones.[3] However, this process has not yet been studied with α,β-unsaturated carbonyl compounds, except in the case of acrylonitrile and toluene-*p*-sulphonyl iodide.[4] We now report a convenient and general synthesis of β-sulphonyl derivatives of different α,β-unsaturated carbonyl compounds by means of an iodosulphonylation–dehydroiodination process. These compounds exhibit antifungal and antibacterial activity and some of the synthetic methods used to prepare them have been the subject of several patents.[5–11] The preparation of β-sulphonyl derivatives of α,β-unsaturated carbonyl compounds includes some of the following methods: (*a*) oxidation of the corresponding β-arylthio systems;[8–10] (*b*) nucleophilic substitution of β-chlorovinyl ketones[12] or β-acylvinyl quaternary ammonium salts[13] by sodium sulphinates; (*c*) addition of sulphinic acids or their alkaline salts to alkyl propiolates;[6] (*d*) reaction of sulphinic acids or their salts with α,β-dihalogenated[7,14] or α-chloro α,β-unsaturated[14] carbonyl compounds; (*e*) sulphonylmercuriation–bromodemercuriation–dehydrobromination of α,β-unsaturated carbonyl compounds.[15] Among these, only the final procedure starts directly from α,β-unsaturated carbonyl compounds.

Results and Discussion

Iodosulphonylation–Dehydroiodination of α,β-Unsaturated Carbonyl Compounds.—When different α,β-unsaturated carbonyl systems (**1**) were treated with toluene-*p*-sulphonyl iodide (method A) or with sodium toluene-*p*-sulphinate and iodine (method B) in dichloromethane at room temperature, the corresponding addition products (**2**) (Scheme 1) were regiospecifically obtained. Both methods afforded similar yields (Table 1), the reaction time of the former (A) being shorter (*ca.* 1 day) than for the second one (B) (*ca.* 2 or 3 days) due to the more heterogeneous reaction medium in the latter procedure. Aldehydes, such as acrylaldehyde or crotonaldehyde were oxidized under iodosulphonylation conditions. However, by reaction of the acrylaldehyde diethyl acetal derivative (**1a**) with toluene-*p*-sulphonyl iodide (method A) the corresponding deprotected α-iodo-β-(*p*-tolylsulphonyl)acryladehyde (**2a**) was directly obtained.

Typical alkyl iodide reactions such as nucleophilic substitution or radical coupling (induced by tributyltin hydride in stoicheiometric[16] or catalytic[17] amounts) in the presence of acrylonitrile with compounds (**2**) failed. Thus, the treatment of compound (**2e**) with tributyltin hydride gave exclusively the corresponding reduction[18] product, ethyl 3-(*p*-tolylsulphonyl)-propionate.



	R¹	R²	Z
a;	H	H	CHO
b;	H	H	Ac
c;	Me	H	Ac
d;	H	H	CO_2H
e;	H	H	CO_2Et
f;	Me	H	CO_2Me
g;	H	Me	CO_2Me
h;	H	H	$CON(CH_2)_5$
i;	H	H	CONHPr
j;	H	H	CN

Scheme 1. *Reagents:* i, *p*-$MeC_6H_4SO_2I$ (Method A) or *p*-$MeC_6H_4SO_2NaI_2$ (Method B); ii, Et_3N

Table 1. Iodosulphonylation of electrophilic olefins

Olefin	Method[a]	Product	Reaction time (days)	Yield (%)[b]
(**1a**)	A	(**2a**)	1	68
(**1b**)	A	(**2b**)	1	87 (80)
(**1b**)	B	(**2b**)	1	71
(**1c**)	A	(**2c**)	1	62 (51)
(**1c**)	B	(**2c**)	3	56
(**1d**)	A	(**2d**)	1	80 (65)
(**1d**)	B	(**2d**)	2	40
(**1e**)	A	(**2e**)	1	64 (60)
(**1e**)	B	(**2e**)	2	62
(**1f**)	A	(**2f**)	1	66 (60)
(**1f**)	B	(**2f**)	3	42
(**1g**)	A	(**2g**)	1	59
(**1g**)	B	(**2g**)	3	79 (70)
(**1h**)	A	(**2h**)	1	67
(**1h**)	B	(**2h**)	3	74 (66)
(**1i**)	A	(**2i**)	1	77 (70)
(**1i**)	B	(**2i**)	2	77
(**1j**)	B	(**2j**)	2	50[c]

[a] A: toluene-*p*-sulphonyl iodide, B: sodium toluene-*p*-sulphinate and iodine. [b] Yield of isolated crude products. In parentheses yields after purification (see Experimental section). Based on compounds (**1**). [c] Lit.,[4] 87% yield (method A).

Table 2. Dehydration of compounds (**2**)

Iodo sulphone	Product	Reaction time	Yield (%)[a]	Stereochemistry
(**2a**)	(**3a**)	30 min	80	*E*
(**2b**)	(**3b**)	1 h	95	*E*
(**2c**)	(**3c**)	1 d	82	*E*
(**2d**)	(**3d**)	1 d	80	*E*
(**2e**)	(**3e**)	2 h	94	*E*
(**2f**)	(**3f**)	6 h	64	*E*
(**2g**)	(**3g**)	2 h	71	*E*
(**2h**)	(**3h**)	2 h	90	*E*
(**2i**)	(**3i**)	2 h	81	*E*
(**2j**)	(**3j**)	1 h	87[b]	*E*

[a] Isolated yields. Based on crude iodo sulphones (**2**). [b] Lit.[4]

However, compounds (**2**) were easily dehydroiodinated in the presence of triethylamine in dichloromethane to yield stereoselectively β-sulphonyl α,β-unsaturated carbonyl systems (**3**) (Scheme 1). This elimination process can be carried out without isolation of the iodo derivatives (**2**) by adding the base to the dichloromethane solution obtained from the iodosulphonylation reaction (Table 2). Products (**3**; $R^1 = R^2 = H$) are shown in the *E* configuration, n.m.r. results suggesting that this is thermodynamically the more stable form;[19] compounds (**3c**, **f**, **g**) were also assumed to have the *E* configuration.

The above method is a simple, direct, and general procedure for the stereoselective synthesis of β-sulphonyl α,β-unsaturated carbonyl compounds (**3**) under mild reaction conditions avoiding polymerization and starting from commercially available α,β-unsaturated systems.

Nucleophilic Substitution of Compounds (**3**).—The reactivity of compounds (**3**) as cationic β-acylvinyl equivalents has been described for phenyl β-(phenylsulphonyl)vinyl ketone with sodium azide,[20] potassium hydroxide,[21] and phenylmagnesium bromide.[21] We have tested the nucleophilic displacement of the sulphonyl group with compounds (**3b**) and (**3e**) which reacted stereospecifically with amines or thiophenol in dichloromethane at room temperature to afford compounds (**4**) (Scheme 2, Table 3).

Table 3. Nucleophilic substitution of compounds (**3**)

Compound	Nucleophile	Product	Reaction time	Yield (%)[a]
(*E*)-(**3b**)	$(CH_2)_5NH$	(*E*)-(**4a**)	5 h	82
(*E*)-(**3b**)	$PhCH_2NH_2$	(*Z*)-(**4b**)	5 h	85
(*E*)-(**3b**)	PhSH	(*E*)-(**4c**)[b]	1 d	90
(*E*)-(**3e**)	$(CH_2)_5NH$	(*E*)-(**4d**)	2 h	30

[a] Isolated yields. Based on crude products (**3**). [b] 19% of *Z*-isomer was also obtained (g.l.c. analysis).

$$p\text{-}MeC_6H_4SO_2CH{=}CHZ \xrightarrow{NuH} NuCH{=}CHZ$$
(**3b**, **e**) (**4a**—**d**)

a; Nu = $(CH_2)_5N$, Z = Ac
b; Nu = $PhCH_2NH$, Z = Ac
c; Nu = PhS, Z = Ac
d; Nu = $(CH_2)_5N$, Z = CO_2Et

Scheme 2.

The stereochemistry of products (**4**) was *E* except in the case of (**4b**) derived from benzylamine, which had a *Z* configuration owing to the intramolecular hydrogen bond.[22] Therefore, products (**3**) can be used as alternative β-acylvinylating agents to the β-chloro derivatives.[23]

Experimental

The experimental techniques and spectroscopic instrumentation employed in the course of this work were as described in ref. 3.

Iodosulphonylation of α,β-Unsaturated Carbonyl Compounds.—The following procedures are typical.

Method A. A solution of compound (**1**) (5 mmol) and toluene-*p*-sulphonyl iodide[2] [prepared by adding a solution of iodine (1.27 g, 5 mmol) in ethanol (20 ml) to a solution of sodium toluene-*p*-sulphinate monohydrate (0.98 g, 5 mmol) in water (50 ml)] in dichloromethane (30 ml) was stirred for *ca.* 1 day at room temperature. The reaction mixture was washed with aqueous sodium thiosulphate (0.1M), until decolouration of the organic layer was complete, dried (Na_2SO_4), and evaporated to provide the crude products (**2**); these were purified by recrystallization from hexane–dichloromethane.

Method B. Iodine (1.27 g, 5 mmol) was added to a suspension of compound (**1**) (5 mmol) and sodium toluene-*p*-sulphinate monohydrate (0.98 g, 5 mmol) in dichloromethane (50 mmol). The resulting mixture was stirred at room temperature (see Table 1) and worked up as described in method A. 2-*Iodo*-3-(*toluene*-p-*sulphonyl*)*propionaldehyde* (**2a**) unstable oil; $\nu_{max.}(CCl_4)$ 1 720 (C=O), 1 320, and 1 140 cm^{-1} (SO_2); $\delta_H(CDCl_3)$ 2.45 (3 H, s, Me), 3.6 (1 H, dd, *J* 15 and 5 Hz, CHS), 4.2 (1 H, dd, *J* 15 and 10 Hz, CHS), 4.85 (1 H, m, CHI), 7.45 and 7.9 (4 H, 2 d, *J* 8 Hz, ArH), and 9.2 (1 H, d, *J* 3 Hz, CHO); $\delta_C(CDCl_3)$ 14.9 (CHI), 21.2 (Me), 57.7 (CH_2), 127.4, 129.6, 134.9, 145.2 (ArC), and 188.4 (CO).

3-*Iodo*-4-(p-*tolylsulphonyl*)*butan*-2-*one* (**2b**), m.p. 90—92 °C (Found: C, 38.0; H, 3.6. $C_{11}H_{13}IO_3S$ requires C, 37.51; H, 3.72%); $\nu_{max.}$(Nujol) 1 690 (C=O), 1 310, and 1 130 cm^{-1} (SO_2); $\delta_H(CDCl_3)$ 2.45, 2.5 (6 H, 2 s, 2 × Me), 3.55 (1 H, dd, *J* 15 and 4 Hz, CHS), 4.3 (1 H, dd, *J* 15 and 12 Hz, CHS), 4.95 (1 H, dd, *J* 12 and 4 Hz, CHI), and 7.4 and 7.8 (4 H, 2d, *J* 8 Hz, ArH); $\delta_C(CDCl_3)$ 16.9 (CHI), 21.2 (*Me*Ar), 25.4 (*Me*CO), 60.0 (CH_2), 127.6, 129.7, 135.5, 145.0 (ArC), and 198.8 (CO); *m/z* 352 (M^+, 2%), 198 (30), 155 (20), 150 (45), 91 (100), 65 (50), and 43 (80).

3-*Iodo*-4-(p-*tolylsulphonyl*)*pentan*-2-*one* (**2c**), m.p. 89—91 °C (Found: C, 39.0; H, 3.9. $C_{12}H_{15}IO_3S$ requires C, 39.36; H, 4.13%); $\nu_{max.}$(Nujol) 1 700 (C=O), 1 300, and 1 130 cm^{-1} (SO_2); δ_H($CDCl_3$) 1.5 (3 H, d, *J* 7.5 Hz, MeCS), 2.45 and 2.55 (6 H, 2 s, MeCO and *Me*Ar), 3.8 (1 H, m, CHS), 5.05 (1 H, d, *J* 10 Hz, CHI), and 7.4 and 7.8 (4 H, 2d, *J* 8 Hz, ArH); δ_C($CDCl_3$) 18.3 (*Me*CH), 21.4 (*Me*Ar), 25.8 (*Me*CO), 30.0 (CHI), 60.4 (CHS), 128.9, 130.0, 134.3, 145.5 (ArC), and 199.7 (CO); *m*/*z* 366 (M^+, 2%), 239 (30), 211 (35), 155 (31), 150 (37), 139 (25), 127 (8), 91 (100), 69 (40), 65 (50), and 43 (75).

2-*Iodo*-3-(p-*tolylsulphonyl*)*propionic acid* (**2d**), m.p. 139—141 °C (decomp.) (Found: C, 33.6; H, 2.8. $C_{10}H_{11}IO_4S$ requires C, 33.91; H, 3.13%); $\nu_{max.}$(Nujol) 3 300—2 500, 1 715, 1 670 (CO_2H), 1 320, and 1 140 cm^{-1} (SO_2); δ_H($CDCl_3$) 2.4 (3 H, s, Me), 3.6 (1 H, dd, *J* 15 and 4 Hz, CHS), 4.7 (1 H, dd, *J* 15 and 12 Hz, CHS), 4.7 (1 H, dd, *J* 12 and 4 Hz, CHI), 7.4 and 7.85 (4 H, 2 d, *J* 8 Hz, ArH), and 8.7 (1 H, br s, OH); δ_C($CDCl_3$) 6.2 (CHI), 21.5 (Me), 61.5 (CH_2), 127.4, 129.6, 134.9, 145.6 (ArC), and 173.7 (CO); *m*/*z* 354 (M^+, 4%), 199 (21), 155 (43), 139 (23), 127 (15), 91 (100), and 65 (35).

Ethyl 2-*iodo*-3-(p-*tolylsulphonyl*)*propionoate* (**2e**), m.p. 70—72 °C (Found: C, 37.5; H, 3.8 $C_{12}H_{15}IO_4S$ requires C, 37.71; H, 3.96%); $\nu_{max.}$(Nujol) 1 720 (C=O), 1 320, and 1 150 cm^{-1} (SO_2); δ_H($CDCl_3$) 1.25 (3 H, t, *J* 7.5 Hz, *Me*CH_2), 2.45 (3 H, s, *Me*Ar), 3.45 (1 H, dd, *J* 15 and 4 Hz, CHS), 3.9—4.3 (3 H, m with q at 4.1, *J* 7.5 Hz, CHS and CH_2Me), 4.6 (1 H, dd, *J* 12 and 4 Hz, CHI), and 7.4 and 7.8 (4 H, 2 d, *J* 8 Hz, ArH); δ_C($CDCl_3$)7.2 (CHI), 13.7 (*Me*CH_2), 21.7 (*Me*Ar), 61.8, 62.4 (2 × CH_2), 128.5, 130.2, 136.0, 145.4 (ArC), and 169.2 (CO); *m*/*z* 382 (M^+, 7%), 227 (48), 155 (58), 139 (24), 91 (100), 65 (35), and 55 (30).

Methyl 2-*iodo*-3-(p-*tolylsulphonyl*)*butyrate* (**2f**), m.p. 96—98 °C (from ether) (Found: C, 37.4; H, 4.0. $C_{12}H_{15}IO_4S$ requires C, 37.71; H, 3.96%); $\nu_{max.}$(Nujol) 1 735 (C=O), 1 315, and 1 130 cm^{-1} (SO_2); δ_H($CDCl_3$) 1.45 (3 H, d, *J* 7.5 Hz, *Me*CH), 2.4 (3 H, s, *Me*Ar), 3.5—3.9 (4 H, m with s at 3.75, CHS and MeO), 4.65 (1 H, d, *J* 10 Hz, CHI), and 7.4 and 7.8 (4 H, 2 d, *J* 8 Hz, ArH); δ_C($CDCl_3$) 18.0 (*Me*CH), 19.3 (CHI), 21.5 (*Me*Ar), 53.4 (MeO), 61.5 (CHS), 129.0, 130.0, 133.7, 145.5 (ArC), and 169.9 (CO); *m*/*z* 382 (M^+, 2%), 227 (45), 155 (21), 100 (24), 91 (100), 69 (45), and 65 (50).

Methyl 2-*iodo*-2-*methyl*-3-(p-*tolylsulphonyl*)*propionoate* (**2g**), m.p. 129—131 °C (Found: C, 37.5; H, 3.9. $C_{12}H_{15}IO_4S$ requires C, 37.71; H, 3.96%); $\nu_{max.}$(Nujol) 1 720 (C=O), 1 310, and 1 130 cm^{-1} (SO_2); δ_H($CDCl_3$) 2.4 (6 H, s, MeCI and *Me*Ar), 3.8 and 4.0 (5 H, 2 s, MeO and CH_2S), and 7.4 and 7.8 (4 H, 2 d, *J* 8 Hz, ArH); δ_C($CDCl_3$) 21.5 (*Me*Ar), 29.3 (CI), 29.95 (*Me*CI), 53.4 (MeO), 68.7 (CH_2S), 127.7, 129.9, 137.4, 145.2 (ArC), and 170.9 (CO); *m*/*z* 382 (M^+, 1%), 255 (9), 227 (12), 199 (11), 155 (47), 127 (10), 100 (13), 91 (100), 69 (38), and 65 (30).

N-[2-*Iodo*-3-(p-*tolylsulphonyl*)*propionyl*]*piperidine* (**2h**), m.p. 93—95 °C (Found: C, 42.3; H, 4.6; N, 3.2. $C_{15}H_{20}INO_3S$ requires C, 42.76; H, 4.79; N, 3.32%); $\nu_{max.}$(Nujol) 1 630 (C=O), 1 330, and 1 130 cm^{-1} (SO_2); δ_H($CDCl_3$) 1.6, 3.4 (10 H, 2 m, 5 × CH_2), 2.4 (3 H, s, *Me*Ar), 3.6 (1 H, dd, *J* 15 and 4 Hz, CHS), 4.5 (1 H, dd, *J* 15 and 12 Hz, CHS), 5.0 (1 H, dd, *J* 12 and 4 Hz, CHI), and 7.4 and 7.8 (4 H, 2 d, *J* 8 Hz, ArH); δ_C($CDCl_3$) 6.4 (CHI), 21.2 (Me), 24.0, 24.9, 25.5, 43.4, 47.1 (5 × CH_2), 62.1 (CH_2S), 128.0, 129.3, 135.9, 145.6 (ArC), and 165.0 (CO); *m*/*z* 421 (M^+, 1%), 294 (9), 155 (8), 139 (26), 138 (100), 91 (39), 84 (62), and 55 (25).

N-*Propyl*-2-*iodo*-3-(p-*tolylsulphonyl*)*propionamide* (**2i**), m.p. 109—111 °C (from ether) (Found: C, 39.1; H, 4.5; N, 3.6. $C_{13}H_{18}INO_3S$ requires C, 39.50; H, 4.59; N, 3.54%); $\nu_{max.}$(Nujol) 3 240 (NH), 1 640 (C=O), 1 320, and 1 140 cm^{-1} (SO_2); δ_H($CDCl_3$) 0.9 (3 H, t, *J* 7.5 Hz, *Me*CH_2), 1.5 (2 H, sext., *J* 7.5 Hz, CH_2Me), 2.45 (3 H, s, *Me*Ar); 3.15 (2 H, q, *J* 7.5 Hz, CH_2N), 3.6 (1 H, dd, *J* 15 and 4 Hz, CHS), 4.4 (1 H, dd, *J* 15 and 4 Hz, CHS), 4.8 (1 H, dd, *J* 12 and 4 Hz, CHI), 6.2 (1 H, br s, NH), and 7.4 and 7.85 (4 H, 2 d, *J* 8 Hz, ArH); δ_C($CDCl_3$) 10.9 (*Me*CH_2), 11.5 (CHI), 21.5 (*Me*Ar), 22.1 (CH_2Me), 41.8 (CH_2N), 61.8 (CH_2S), 128.0, 129.9, 135.5, 145.2 (ArC), and 168.7 (CO); *m*/*z* 395 (M^+, 8%), 337 (10), 240 (20), 154 (22), 155 (30), 139 (62), 91 (90), 84 (44), 65 (34), and 55 (100).

2-*Iodo*-3-(p-*tolylsulphonyl*)*propiononitrile* (**2j**), m.p. 150—152 °C (decomp., lit.,[4] 149—152 °C); $\nu_{max.}$(Nujol) 2 240 (CN), 1 300, and 1 140 cm^{-1} (SO_2); δ_H($CDCl_3$) 2.45 (3 H, s, Me), 3.75 (1 H, d, *J* 6 Hz, CHS), 3.9 (1 H, d, *J* 9 Hz, CHS), 4.65 (1 H, dd, *J* 12 and 6 Hz, CHI), and 7.5 and 7.9 (4 H, 2 d, *J* 8 Hz, ArH); δ_C($CDCl_3$) 16.8 (CHI), 21.7 (CH_3), 62.1 (CH_2), 124.9 (CN), 128.1, 130.2, 133.7, and 140.6 (ArC); *m*/*z* 335 (M^+, 4%), 155 (71), 127 (20), 91 (100), and 65 (35).

β-(p-*Tolylsulphonyl*) α,β-*Unsaturated Compounds* (**3**). *General Procedure*.—A solution of triethylamine (1.6 ml, 10 mmol) in dichloromethane (10 ml) was slowly added to a stirred solution of crude compound (**2**) (5 mmol) in dichloromethane (30 ml) at 0 °C. The resulting solution was stirred at room temperature (see Table 2) and then washed with 1M aqueous hydrochloric acid and saturated aqueous sodium hydrogen carbonate. The organic layer was dried (Na_2SO_4) and evaporated to afford crude compounds (**3**) which were purified by recrystallization from hexane–dichloromethane or by column chromatography on silica gel (hexane–ether as eluant).

(*E*)-3-(*p*-Tolylsulphonyl)acrylaldehyde (**3a**), an oil (lit.,[24] no data reported); $\nu_{max.}$(neat) 1 690 (C=O), 1 670, 960 (CH=CH), 1 320, and 1 140 cm^{-1} (SO_2); δ_H($CDCl_3$) 2.45 (3 H, s, Me), 6.9 (1 H, dd, *J* 15 and 6 Hz, CHCO), 7.4 (3 H, m, CHS and ArH), 7.8 (2 H, d, *J* 8 Hz, ArH), and 9.8 (1 H, d, *J* 6 Hz, CHO); δ_C($CDCl_3$) 21.5 (Me), 128.4, 130.3, 135.3, 145.8 (ArC), 136.0, 148.7 (2 × CH=C), and 189.5 (CO); *m*/*z* 210 (M^+, 21%), 155 (10), 139 (88), 131 (20), 91 (100), and 65 (40).

(*E*)-3-(*p*-Tolylsulphonyl)but-3-en-2-one (**3b**), m.p. 77—79 °C (lit.,[25] no data reported); $\nu_{max.}$(Nujol) 1 700 (C=O), 1 650, 950 (CH=CH), 1 310, and 1 140 cm^{-1} (SO_2); δ_H($CDCl_3$) 2.35 (3 H, s, *Me*CO), 2.45 (3 H, s, *Me*Ar), 7.0 and 7.2 (2 H, 2 d, *J* 15 Hz, 2 × CH=C), and 7.45 and 7.9 (4 H, 2 d, *J* 8 Hz, ArH); δ_C($CDCl_3$) 21.5 (*Me*Ar), 28.6 (*Me*CO), 128.1, 131.1, 135.8, 145.8 (ArC), 136.1, 141.2 (CH=CH), and 195.9 (CO); *m*/*z* 224 (M^+, 16%), 181 (2), 145 (37), 139 (100), 91 (36), 65 (25), and 43 (40).

(*E*)-3-(*p*-Tolylsulphonyl)pent-3-en-2-one (**3c**), an oil, $\nu_{max.}$(neat) 1 700 (C=O), 1 620, 800 (CH=C), 1 310, and 1 150 cm^{-1} (SO_2); δ_H(CCl_4) 2.1 (3 H, d, *J* 2 Hz, *Me*CS), 2.3 (3 H, s, *Me*CO), 2.45 (3 H, s, *Me*Ar), 7.2 (1 H, q, *J* 2 Hz, CHCO), and 7.4 and 7.8 (4 H, 2 d, *J* 8 Hz, ArH); δ_C($CDCl_3$) 12.9 (*Me*CS), 21.3 (*Me*Ar), 31.85 (*Me*CO), 128.5, 130.1, 135.7, 145.9 (ArC), 130.4, 150.9 (CH=C), and 197.7 (CO); *m*/*z* 238 (M^+, 7%), 139 (30), 119 (15), 91 (50), 83 (100), 65 (39), and 43 (90).

(E)-3-(p-*Tolylsulphonyl*)*acrylic acid* (**3d**), m.p. 105—107 °C (Found: C, 52.5; H, 4.6. $C_{10}H_{10}O_4S$ requires C, 53.09; H, 4.46%); $\nu_{max.}$(Nujol) 3 200—2 400, 1 690 (CO_2H), 1 650, 960 (CH=CH), 1 315, and 1 140 cm^{-1} (SO_2); δ_H($CDCl_3$) 2.5 (3 H, s, *Me*Ar), 6.85, 7.45 (2 H, 2 d, *J* 18 Hz, CH=CH), 7.5 and 7.9 (4 H, 2 d, *J* 8 Hz, ArH), and 7.6 (1 H, s, OH); δ_C($CDCl_3$) 21.5 (Me), 128.1, 129.9, 135.2, 145.9 (ArC), 129.8, 144.0 (CH=CH), and 166.8 (CO); *m*/*z* 226 (M^+, 22%), 155 (12), 139 (79), 91 (100), and 65 (37).

Ethyl (E)-3-(p-*tolylsulphonyl*)*acrylate* (**3e**), m.p. 75—76 °C (Found: C, 56.9; H, 5.4. $C_{12}H_{14}O_4S$ requires C, 56.68; H, 5.55%); $\nu_{max.}$(Nujol) 1 715 (C=O), 1 625, 970 (CH=CH), 1 300, and 1 140 cm^{-1} (SO_2); δ_H(CCl_4) 1.3 (3 H, t, *J* 7.5 Hz, *Me*CH_2), 2.45 (3 H, s, *Me*Ar), 4.2 (2 H, quint., *J* 7.5 Hz, CH_2), 6.75, 7.3 (2 H, 2 d, *J* 18 Hz, CH=CH), and 7.4 and 7.85 (4 H, 2 d, *J* 8 Hz, ArH); δ_C($CDCl_3$) 14.0 (*Me*CH_2), 21.5 (*Me*Ar), 61.8 (CH_2O), 128.0, 129.9, 135.2, 145.5 (ArC), 130.2, 143.3 (CH=CH), and 163.3 (CO); *m*/*z* 254 (M^+, 9), 209 (4), 139 (100), 91 (43), and 65 (25).

Methyl (*E*)-3-(*p*-tolylsulphonyl)crotonate (**3f**), an oil,

$\nu_{max.}$(neat) 1 735 (C=O), 1 640 (CH=C), 1 320, and 1 160 cm^{-1} (SO_2); $\delta_H(CCl_4)$ 2.1 (3 H, d, *J* 2 Hz, MeCS), 2.35 (3 H, s, *Me*Ar), 3.65 (3 H, s, MeO), 6.8 (1 H, q, *J* 2 Hz, CH=C), and 7.3 and 7.7 (4 H, 2 d, *J* 8 Hz, ArH); $\delta_C(CCl_4)$ 13.6 (*Me*CS), 21.7 (*Me*Ar), 52.0 (MeO), 124.2, 154.8 (CH=C), 129.2, 130.4, 135.2, 144.8 (ArC), and 164.2 (CO); *m/z* 254 (M^+, 3%), 139 (43), 99 (100), 91 (25), 67 (22), and 59 (20).

Methyl (E)-2-*methyl*-3-(p-*tolylsulphonyl*)*acrylate* (**3g**), m.p. 53—55 °C (Found: C, 56.4; H, 5.7. $C_{12}H_{14}O_4S$ requires C, 56.68; H, 5.55%); $\nu_{max.}$(Nujol) 1 710 (C=O), 1 630 (CH=C), 1 310, and 1 140 cm^{-1} (SO_2); $\delta_H(CDCl_3)$ 2.3 (3 H, d, *J* 2 Hz, MeCCO), 2.4 (3 H, s, *Me*Ar), 3.75 (3 H, s, MeO), 7.25 (1 H, q, *J* 2 Hz, CHS), and 7.4 and 7.8 (4 H, 2 d, *J* 8 Hz, ArH); $\delta_C(CDCl_3)$ 13.4 (*Me*CCO), 21.5 (*Me*Ar), 52.7 (MeO), 127.1, 129.6, 137.1, 144.6 (ArC), 137.0, 140.2 (CH=C), and 165.3 (CO); *m/z* 254 (M^+, 6%), 222 (32), 155 (29), 139 (100), 130 (23), 119 (24), 91 (85), and 65 (37).

(E)-N-[3-(p-*Tolylsulphonyl*)*acryloyl*]*piperidine* (**3h**), m.p. 98—100 °C (from ether) (Found: C, 61.0; H, 6.3; N, 4.9. $C_{15}H_{19}NO_3S$ requires C, 61.41; H, 6.53; N, 4.77%); $\nu_{max.}$(Nujol) 1 640 (C=O), 1 310, 1 150 (SO_2), and 950 cm^{-1} (CH=CH); $\delta_H(CDCl_3)$ 1.6, 3.5 (10 H, 2 m, 5 × CH_2), 2.4 (3 H, s, *Me*Ar), 7.2 and 7.5 (2 H, 2 d, *J* 18 Hz, CH=CH), and 7.4 and 7.8 (4 H, 2 d, *J* 8 Hz, ArH); $\delta_C(CDCl_3)$ 21.3 (Me), 24.1, 25.3, 26.5, 43.1, 47.0 (5 × CH_2), 127.4, 129.6, 135.9, 144.6 (ArC), 131.2, 139.6 (CH=CH), and 160.5 (CO); *m/z* 293 (M^+, 8%), 209 (2), 132 (45), 138 (88), 92 (22), 91 (37), 84 (100), and 65 (20).

(E)-N-*Propyl*-3-(p-*tolylsulphonyl*)*acrylamide* (**3i**), m.p. 125—127 °C (from ether) (Found: C, 57.9; H, 6.5; N, 5.0. $C_{13}H_{17}NO_3S$ requires C, 58.40; H, 6.41; N, 5.24%); $\nu_{max.}$(Nujol) 3 280 (NH), 1 650 (C=O), 1 310, 1 140 (SO_2), and 980 cm^{-1} (CH=CH); $\delta_H(CDCl_3)$ 0.9 ($CDCl_3$) 0.9 (3 H, t, *J* 7.5 Hz, $MeCH_2$), 1.5 (2 H, sext., *J* 7.5 Hz, CH_2Me), 2.45 (3 H, s, *Me*Ar), 3.3 (2 H, q, *J* 7.5 Hz, CH_2N), 6.5 (1 H, br s, NH), 7.05 and 7.4 (2 H, 2 d, *J* 18 Hz, CH=CH), and 7.45 and 7.85 (4 H, 2 d, *J* 8 Hz, ArH); $\delta_C(CDCl_3)$ 11.8 ($MeCH_2$), 21.5 (*Me*Ar), 22.7 (CH_2Me), 41.8 (CH_2N), 127.7, 129.9, 135.9, 145.2 (ArC), 134.0, 139.0 (CH=CH), and 161.8 (CO); *m/z* 267 (M^+, 22%), 209 (24), 139 (100), 91 (21), and 58 (20).

(*E*)-3-(*p*-Tolylsulphonyl)acrylonitrile (**3j**), m.p. 130—132 °C (from ether) (lit.,[4] m.p. 131—133 °C); $\delta_H(CDCl_3)$ 2.4 (3 H, s, Me), 6.5 and 7.25 (2 H, 2 d, *J* 18 Hz, CH=CH), and 7.4 and 7.8 (4 H, 2 d, *J* 8 Hz, ArH);[4] $\delta_C(CDCl_3)$ 21.7 (Me), 109.5, 148.9 (CH=CH), 112.9 (CN), 127.6, 130.1, 133.9, and 146.1 (ArC); *m/z* 207 (M^+, 32%), 139 (100), 91 (82), and 65 (43).

Reaction of Compounds (**3**) *with Nucleophiles: General Procedure.*—The nucleophile (6 mmol) was added to a solution of crude compound (**3**) (5 mmol) in dichloromethane (30 ml) at room temperature. In the case of thiophenol, triethylamine (0.96 ml, 6 mmol) was also added.[26] The reaction mixture was stirred for several hours (see Table 3) and then washed with water (2 × 10 ml) or with 1M aqueous sodium hydroxide (10 ml) in the case of compound (**4c**). The organic layer was dried (Na_2SO_4) and evaporated to give compounds (**4**). Purification of compound (**4a**) was by silica gel chromatography (ether–hexane as eluant), compounds (**4b**, **d**) were distilled at reduced pressure (0.1 mmHg), and compound (**4c**) was recrystallized from hexane–ether. (E)-4-Piperidinobut-3-en-2-one (**4a**), R_F 0.15 (hexane–ether, 1:1) (lit.,[27] b.p. 156 °C/7 mmHg); $\nu_{max.}(CCl_4)$ 1 650 (C=O), 1 600, and 960 cm^{-1} (CH=CH); $\delta_H(CDCl_3)$ 1.6 and 3.2 (10 H, 2 m, 5 × CH_2), 2.1 (3 H, s, Me), and 5.1 and 7.4 (2 H, 2 d, *J* 15 Hz, 2 × CH); $\delta_C(CDCl_3)$ 23.7, 25.3, and 49.7 (5 × CH_2), 27.5 (Me), 95.0 and 151.2 (2 × CH), and 193.7 (CO); *m/z* 153 (M^+, 69%), 138 (100), 136 (58), 110 (47), 82 (34), and 43 (22).

(*Z*)-4-Benzylaminobut-3-en-2-one (**4b**), bath temperature 80 °C (lit.,[22] b.p. 116.5—117.0 °C/5 mmHg); $\nu_{max.}$(neat) 3 260 (NH) and 1 650 cm^{-1} (C=O): $\delta_H(CCl_4)$ 1.95 (3 H, s, Me), 4.3 (2 H, d, *J* 6 Hz, CH_2), 4.9 (1 H, d, *J* 7.5 Hz, CHCO), 6.5 (1 H, dd, *J* 12 and 7.5 Hz, CHN), 7.3 (5 H, s, ArH), and 10.0 (1 H, br s, NH);[22] $\delta_C(CDCl_3)$ 28.7 (Me), 51.5 (CH_2), 93.4, 151.8 (2 × CH), 126.2, 126.5, 127.7, 137.8 (ArC), and 193.4 (CO).

(*E*)-2-Phenylthiobut-3-en-2-one (**4c**), m.p. 73—75 °C (lit.,[28] no data reported); $\nu_{max.}$(Nujol) 1 645 (C=O) and 960 cm^{-1} (CH=CH); $\delta_H(CDCl_3)$ 2.2 (3 H, s, Me), 6.05, 7.8 (2 H, 2 d, *J* 18 Hz, 2 × CH), and 7.5 (5 H, s, ArH);[28] $\delta_C(CDCl_3)$ 27.0 (Me), 125.3, 146.3 (2 × CH), 129.6, 130.3, 132.8, 147.5 (ArC), and 193.3 (CO); *m/z* 178 (M^+, 82%), 163 (100), 135 (30), 109 (44), 101 (22), 91 (32), and 43 (36).

Ethyl (*E*)-3-piperidinoacrylate (**4d**), bath temperature 90 °C, $\nu_{max.}(CCl_4)$ 1 690 (C=O), 1 610, and 975 cm^{-1} (CH=CH); $\delta_H(CDCl_3)$ 1.2 (3 H, t, *J* 7.5 Hz, Me), 1.45 and 3.2 (10 H, 2 m, 5 × CH_2), 4.0 (2 H, q, *J* 7.5 Hz, CH_2Me), and 4.5 and 7.25 (2 H, 2 d, *J* 15 Hz, 2 × CH); $\delta_C(CDCl_3)$ 13.8 (Me), 22.9, 24.4, 48.5 (5 × CH_2), 56.6 (CH_2Me), 83.2, 150.1 (2 × CH), and 166.6 (CO); *m/z* 183 (M^+, 25%), 154 (100), 138 (51), and 110 (38).

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