# Palladium-catalysed Desulphonylative Vinylation of Arenesulphonyl Chlorides under Solid–Liquid Phase-transfer Conditions

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The reaction of arenesulphonyl chlorides (1a–n) with butyl acrylate (2a) in the presence of a catalytic amount of bis(benzonitrile)dichloropalladium [PdCl$_2$(PhCN)$_2$] under solid–liquid phase-transfer conditions gave the corresponding butyl (E)-3-arylprop-2-enoates (3a–n) in good yield. The alkenes (2b–g) could also be used in place of (2a).

The palladium-catalysed coupling reaction of aryl bromides or iodides with alkenes is a useful method for the preparation of styrene derivatives.[1] While aryl chlorides react only with extreme difficulty, arenediazonium salts and related compounds,[2] aroyl chlorides,[3] aryl triflates,[4] and arylazo aryl sulphones[5] have been successfully used in place of aryl halides. Recently, it was found that the reaction could also be achieved by use of arenesulphonyl chlorides, which are readily available from the corresponding sulphonic acids.[6,7] We observed that the coupling reaction of the sulphonyl chlorides with acrylate esters proceeded efficiently under solid–liquid phase-transfer conditions[8] in the presence of an appropriate quaternary ammonium salt as phase-transfer catalyst (PTC) to give the corresponding 3-arylprop-2-enoates (Scheme 1).[7] Subsequently,

ArSO$_2$Cl + CH$_2$=CHCO$_2$R $\longrightarrow$ $\underset{H}{\overset{Ar}{}}$C=C$\underset{CO_2R}{\overset{H}{}}$
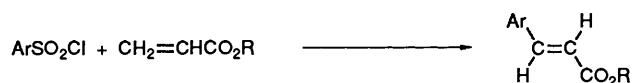
Scheme 1. *Reagents:* Pd-catalyst, K$_2$CO$_3$, xylene, and PTC.

we carried out a detailed study of the scope and limitations of the coupling reaction. The results are described herein.†

Results and Discussion

Reaction of Naphthalene-1-sulphonyl Chloride (**1a**) *with Butyl Acrylate* (**2a**).—The results for the coupling reaction of the sulphonyl chloride (**1a**) with the acrylate (**2a**) in the presence of several palladium species (2.5 mol %) in *m*-xylene at 140 °C for 4 h under nitrogen are summarised in Table 1. In a series of reactions under solid–liquid phase-transfer conditions with potassium carbonate as base in the presence of PdCl$_2$(PhCN)$_2$ with a number of quaternary ammonium chlorides as phase-transfer catalysts, the yield of butyl (E)-3-(1-naphthyl)prop-2-enoate (**3a**) was found to be remarkably influenced by the identity of the ammonium chloride employed. The efficiency order for the PTC was Bzl(Oct$_3$)NCl $\geq$ Me(Oct$_3$)NCl $\gg$ Bu$_4$NCl $\gg$ BzlEt$_3$NCl $\geq$ Et$_4$NCl, where Oct = octyl. Thus, ester (**3a**) was obtained in 95% yield when Bzl(Oct$_3$)NCl was used, indicating that the use of a PTC having high lipophilicity is essential for a high-yield coupling reaction. It should be noted that the reaction using Bzl(Oct$_3$)NCl also took place without the presence of base to give ester (**3a**) in 62% yield, whereas the use of BzlEt$_3$NCl in place of Bzl(Oct$_3$)NCl or in the absence of both the base and PTC the product yield was <10%. These results suggest that the ammonium chloride has another important function in addition to that of transferring the solid base into the liquid phase. While tertiary amines which can be completely dissolved in the solvent could be used as the base, the yield of product (**3a**) was moderate;[6] direct reaction of the sulphonyl chloride with the amines appears to compete with the

**Table 1.** Reaction of naphthalene-1-sulphonyl chloride (**1a**) with butyl acrylate (**2a**).[a]

Pd-catalyst	Base	PTC	Yield (%) of (3a)[b]
PdCl$_2$(PhCN)$_2$	K$_2$CO$_3$	Bzl(Oct$_3$)NCl	95
PdCl$_2$(PhCN)$_2$	K$_2$CO$_3$	Me(Oct$_3$)NCl	91
PdCl$_2$(PhCN)$_2$	K$_2$CO$_3$	Bu$_4$NCl	36
PdCl$_2$(PhCN)$_2$	K$_2$CO$_3$	BzlEt$_3$NCl	11
PdCl$_2$(PhCN)$_2$	K$_2$CO$_3$	Et$_4$NCl	8
PdCl$_2$(PhCN)$_2$	K$_2$CO$_3$		6
PdCl$_2$(PhCN)$_2$		Bzl(Oct$_3$)NCl	62
PdCl$_2$(PhCN)$_2$		BzlEt$_3$NCl	8
PdCl$_2$(PhCN)$_2$			10
PdCl$_2$(PhCN)$_2$	Bu$_3$N		49
PdCl$_2$(PhCN)$_2$	Oct$_3$N		45
Pd-black	K$_2$CO$_3$	Bzl(Oct$_3$)NCl	65
PdCl$_2$	K$_2$CO$_3$	Bzl(Oct$_3$)NCl	81
Pd(OAc)$_2$	K$_2$CO$_3$	Bzl(Oct$_3$)NCl	75
PdCl$_2$(PPh$_3$)$_2$	K$_2$CO$_3$	Bzl(Oct$_3$)NCl	76
Pd(PPh$_3$)$_4$	K$_2$CO$_3$	Bzl(Oct$_3$)NCl	54
PdCl$_2$(PhCN)$_2$[c]	K$_2$CO$_3$	Bzl(Oct$_3$)NCl	96
PdCl$_2$(PhCN)$_2$[d]	K$_2$CO$_3$	Bzl(Oct$_3$)NCl	83

[a] The reaction was carried out in *m*-xylene at 140 °C for 4 h under nitrogen unless otherwise noted. [(**1a**)]:[(**2a**)]:[Base]:[PTC]:[Pd] 2:5:3:0.3:0.05. [b] Yield based on initial quantity of (**1a**) charged was determined by GLC analysis. [c] Reaction in benzonitrile. [d] Reaction in *o*-dichlorobenzene.

coupling reaction. The reaction was also catalysed by a number of palladium species, Pd(OAc)$_2$, PdCl$_2$, PdCl$_2$(PhCN)$_2$, PdCl$_2$(PPh$_3$)$_2$, Pd(PPh$_3$)$_4$, and Pd-black. Among these species, PdCl$_2$(PhCN)$_2$ gave the most satisfactory results. No coupling product was detected in the absence of the catalysts. Benzonitrile and *o*-dichlorobenzene could be satisfactorily used as the solvent, but with *N,N*-dimethylformamide (DMF) the reaction was unsuccessful.

Reaction of Various Arenesulphonyl Chlorides with the Acrylate (**2a**).—Table 2 shows the results for the reaction of arenesulphonyl chlorides (**1b–n**) with (**2a**) under solid–liquid phase-transfer conditions using PdCl$_2$(PhCN)$_2$ and Bzl(Oct$_3$)NCl in *m*-xylene. The reactions of 6-substituted naphthalene-2-sulphonyl chlorides (**1d–f**) afforded the expected products (**3d–f**) in good yield as well as those with 4-substituted naphthalene-1-(**1a–c**) and 3- or 4-substituted benzene-sulphonyl

† The following relevant work has also been reported. (i) Arylation of alkenes with sodium toluenesulphinate occurs in the presence of a stoicheiometric amount of Na$_2$PdCl$_4$.[9] (ii) Ethenesulphonyl chloride reacts with styrenes *via* desulphonylation in the presence of a ruthenium complex.[10]
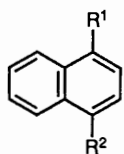
(1a) R^1 = SO$_2$Cl, R^2 = H
(1b) R^1 = SO$_2$Cl, R^2 = Me
(1c) R^1 = SO$_2$Cl, R^2 = Cl
(3a) R^1 = CH=CHCO$_2$Bu, R^2 = H
(3b) R^1 = CH=CHCO$_2$Bu, R^2 = Me
(3c) R^1 = CH=CHCO$_2$Bu, R^2 = Cl
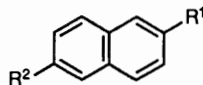
(1d) R^1 = SO$_2$Cl, R^2 = H
(1e) R^1 = SO$_2$Cl, R^2 = Me
(1f) R^1 = SO$_2$Cl, R^2 = OMe
(3d) R^1 = CH=CHCO$_2$Bu, R^2 = H
(3e) R^1 = CH=CHCO$_2$Bu, R^2 = Me
(3f) R^1 = CH=CHCO$_2$Bu, R^2 = OMe
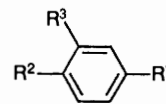
(1g) R^1 = SO$_2$Cl, R^2 = R^3 = H
(1h) R^1 = SO$_2$Cl, R^2 = OMe, R^3 = H
(1i) R^1 = SO$_2$Cl, R^2 = Me, R^3 = H
(1j) R^1 = SO$_2$Cl, R^2 = F, R^3 = H
(1k) R^1 = SO$_2$Cl, R^2 = Cl, R^3 = H
(1l) R^1 = SO$_2$Cl, R^2 = H, R^3 = Cl
(1m) R^1 = SO$_2$Cl, R^2 = Br, R^3 = H
(1n) R^1 = SO$_2$Cl, R^2 = NO$_2$, R^3 = H
(3g) R^1 = CH=CHCO$_2$Bu, R^2 = R^3 = H
(3h) R^1 = CH=CHCO$_2$Bu, R^2 = OMe, R^3 = H
(3i) R^1 = CH=CHCO$_2$Bu, R^2 = Me, R^3 = H
(3j) R^1 = CH=CHCO$_2$Bu, R^2 = F, R^3 = H
(3k) R^1 = CH=CHCO$_2$Bu, R^2 = Cl, R^3 = H
(3l) R^1 = CH=CHCO$_2$Bu, R^2 = H, R^3 = Cl
(3m) R^1 = CH=CHCO$_2$Bu, R^2 = Br, R^3 = H
(3n) R^1 = CH=CHCO$_2$Bu, R^2 = NO$_2$, R^3 = H
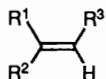
(2a) R^1 = CO$_2$Bu, R^2 = R^3 = H
(2b) R^1 = CO$_2$Et, R^2 = R^3 = H
(2c) R^1 = R^2 = R^3 = H
(2d) R^1 = Ph, R^2 = R^3 = H
(2e) R^1 = Ph, R^2 = Me, R^3 = H
(2f) R^1 = CO$_2$Bu, R^2 = Me, R^3 = H
(2g) R^1 = R^3 = CO$_2$Me, R^2 = H
(2h) R^1 = H, R^2 = R^3 = CO$_2$Me

Table 2. Reaction of arenesulphonyl chlorides (**1b–n**) with butyl acrylate (**2a**).[a]

ArSO$_2$Cl	Yield [%] of (3)[b,c]
(**1b**)	(**3b**) [58]
(**1c**)	(**3c**) [81]
(**1d**)	(**3d**) [74 (84)]
(**1e**)	(**3e**) [78 (89)]
(**1f**)	(**3f**) [80]
(**1g**)	(**3g**) [63 (63)]
(**1h**)	(**3h**) [55]
(**1i**)	(**3i**) [71 (72)]
(**1j**)	(**3j**) [59]
(**1k**)	(**3k**) [89 (90)]
(**1l**)	(**3l**) [74 (79)]
(**1m**)	(**3m**) [44]
(**1n**)	(**3n**) [86 (90)]

[a] The reaction was carried out using PdCl$_2$(PhCN)$_2$ and Bzl(Oct$_3$)NCl in *m*-xylene at 140 °C for 4 h under nitrogen. [(1)]:[(2a)]:[Base]: [PTC]:[Pd] 2:5:3:0.3:0.05. [b] Isolated yield based on initial quantity of chloride (1) charged. The value in parentheses indicates yield determined by GLC analysis. [c] Each product had exclusively the (*E*)-configuration.

chlorides (**1g–n**) to give compounds (**3a–c**) and (**3g–n**).* The esters (**3b–n**) were found to have exclusively (*E*)-configurations. Since both naphthalene-α- and -β-sulphonic acids are well known to be prepared by means of sulphonation reactions, whilst either halogenation or nitration predominantly gives the α-substituted compounds, the desulphonylative coupling reaction seems to be particularly useful for the synthesis of the naphthalene derivatives.

* It has been reported that palladium-catalysed decarbonylation of naphthalene-α-carboxaldehyde smoothly occurs to give naphthalene in good yield, but with the β-isomer no reaction is observed.[9] On the other hand, both naphthalene-α- and -β-sulphonyl chlorides undergo desulphonylation in the presence of a rhodium complex to give the corresponding chloronaphthalenes.[10]

Reaction of the Sulphonyl Chlorides (**1a**) *or* (**1d**) *with the Alkenes* (**2b–h**).—The reactions of compound (**1a**) with ethylene (**2c**) and styrene (**2d**) gave the expected products (**5**) and (**6**) (Table 3). Similarly, the alkenes (**7**) and (**8**) were also obtained
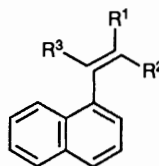
(4) R^1 = CO$_2$Et, R^2 = R^3 = H
(5) R^1 = R^2 = R^3 = H
(6) R^1 = Ph, R^2 = R^3 = H
(9) R^1 = Ph, R^2 = Me, R^3 = H
(11) R^1 = CO$_2$Bu, R^2 = Me, R^3 = H
(13) R^1 = H, R^2 = R^3 = CO$_2$Me
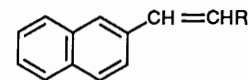
(7) R = H
(8) R = Ph
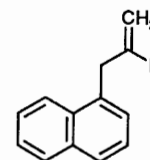
(10) R = Ph
(12) R = CO$_2$Bu

from the reactions with compound (**1d**). The reactions of compound (**1a**) with 1,1-disubstituted alkenes (**2e**) and (**2f**) afforded products (**9**) and (**11**) along with the corresponding isomers (**10**) and (**12**).[11] Reaction of compound (**1a**) with dimethyl maleate (**2g**) gave dimethyl 1-naphthylfumarate (**13**), indicating that the configuration of the alkene (**2g**) inverted during the reaction. With dimethyl fumarate (**2h**) the product yield was very low. The reaction with oct-1-ene gave a complex mixture of products.

Reaction of 4-Substituted Benzoyl Chlorides (**14**)–(**18**) *with the*

**Table 3.** Reaction of naphthalenesulphonyl chlorides (1a) and (1d) with alkenes (2b–h).[a]

$ArSO_2Cl$	Alkene	Products [Yield (%)][b]
(1a)	(2b)	(4) [88 (94)]
(1a)	(2c)	(5) [69 (72)][c]
(1a)	(2d)	(6) [92]
(1d)	(2c)	(7) [58][c]
(1d)	(2d)	(8) [78]
(1a)	(2e)	(9) [56], (10) [28]
(1a)	(2f)	(11) [71], (12) [24]
(1a)	(2g)	(13) [71]
(1a)	(2h)	(13) [4]

[a] The reaction was carried out using $PdCl_2(PhCN)_2$ and $Bzl(Oct_3)NCl$ in *m*-xylene at 140 °C for 4 h under nitrogen unless otherwise noted. [(1)]:[(2)]:[Base]:[PTC]:[Pd] 2:5:3:0.3:0.05. [b] Isolated yield based on initial quantity of chloride (1) charged. The value in parentheses indicates yield determined by GLC analysis. [c] Reaction in benzene at 160 °C under 10 atm of ethylene for 2 h (see also Experimental section).

Table 4. Reaction of 4-substituted benzoyl chlorides (14)–(18) with butyl acrylate (2a).[a]

| $ArCOCl$	Yield (%)[b] of (3)
(14)	(3g) [95]
(15)	(3h) [94]
(16)	(3i) [95]
(17)	(3k) [93]
(18)	(3n) [87]

[a] The reaction was carried out using $PdCl_2(PhCN)_2$ and $Bzl(Oct_3)NCl$ in *m*-xylene at 140 °C for 4 h under nitrogen. [ArCOCl]:[(2a)]:[Base]:[PTC]:[Pd] 2:5:3:0.3:0.05. [b] Yield based on initial quantity of aroyl chloride charged was determined by GLC analysis.
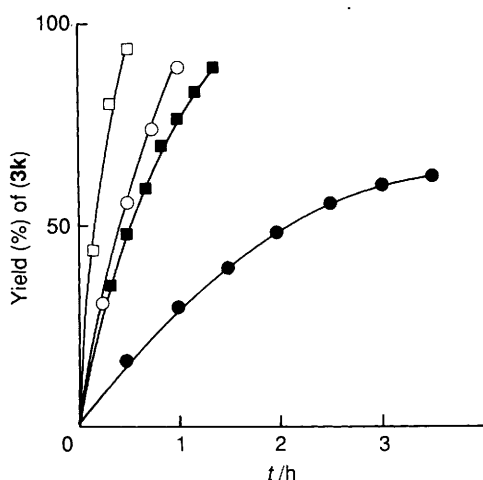
Figure. Reactions of the sulphonyl chloride (1k) and the benzoyl chloride (17) with the acrylate (2a): (1k) at 140 °C (○); (1k) at 130 °C (●); (17) at 140 °C (□); (17) at 130 °C (■).

Acrylate (2a).—Under the present reaction conditions, aroyl chlorides also reacted efficiently with alkenes *via* decarbonylation.[3] Thus, reaction of the benzoyl chlorides (14)–(18) with butyl acylate (2a) gave the corresponding coupling products (3) in high yield (Scheme 2 and Table 4).

Comparison between the Desulphonylative and Decarbonylative Coupling Reactions.—When the reaction of 4-chlorobenzenesulphonyl chloride (1k) with butyl acrylate (2a)
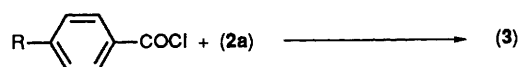
(14) R = H
(15) R = OMe
(16) R = Me
(17) R = Cl
(18) R = NO$_2$

Scheme 4. *Reagents:* $PdCl_2(PhCN)_2$, K_2CO_3, $Bzl(Oct_3)NCl$.

at 140 °C was followed periodically by GLC, it was found that the reaction was complete within 1 h to give the product (3k) in >90% yield (Figure 1). With 4-chlorobenzoyl chloride (17) in place of the sulphonyl chloride (1k) the product (3k) formed more rapidly, suggesting that the decarbonylative coupling is faster than the desulphonylative reaction. While, in the case of compound (17), a decrease in the reaction temperature to 130 °C simply decreased the rate of formation of product (3k), with the sulphonyl compound (1k) the yield of product (3k) was also reduced.

Reaction Scheme.—A probable catalytic cycle for the desulphonylative coupling reaction is illustrated in Scheme 3,

Scheme 3.
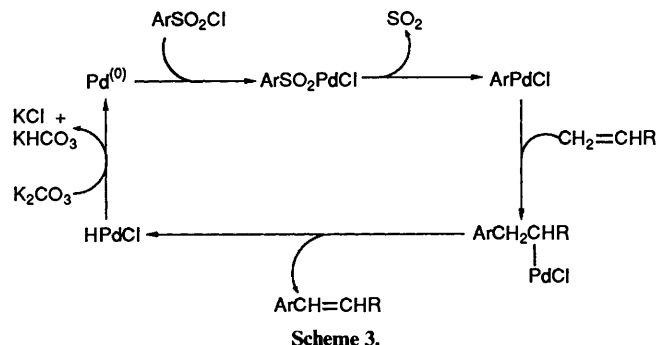
which is similar to that proposed for the reactions using aryl halides[1] and aroyl chlorides.[3] Oxidative addition of an arenesulphonyl chloride to palladium(o) species generated *in situ*, and successive loss of sulphur dioxide, gave an arylpalladium intermediate.* Subsequently, reaction with alkene followed by elimination of chlorohydridopalladium afforded the coupling product. The fact that a relatively higher temperature, compared with that for the reaction using aryl halides,[1] is required suggests that the desulphonylation is the rate-determining step, as is the decarbonylation in the reaction using aroyl chlorides.[3]† Comparison between the reactions of acid chlorides (1k) and (17) with butyl acrylate (2a) might demonstrate that the rate of desulphonylation from the arylsulphonylpalladium intermediate is slower than that of decarbonylation from the aroylpalladium species.‡ The

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* Evolution of sulphur dioxide from the reaction of compounds (1a) and (2a) was qualitatively confirmed by use of a conventional detector tube. Part of the gas might also react with the base.

† Recently, it has been reported that arenesulphonyl chlorides react with vinyl- and allyl-stannanes in the presence of a palladium complex at 65–70 °C to give sulphones, indicating that oxidative addition of the sulphonyl chlorides to the complex occurs at a relatively low temperature (S. S. Labadie, *J. Org. Chem.*, 1989, **54**, 2496).

‡ Desulphonylation reactions from the complexes $ArSO_2IrCl_2$-(CO)(PPh$_3$)$_2$ in refluxing toluene (J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, 1966, **88**, 180) and $ArSO_2PtCl(PPh_3)_2$ at 200–210 °C (C. D. Cook and G. S. Jauhal, *Can. J. Chem.*, 1967, **45**, 301) to give the corresponding arylmetal species have been reported. The ease of SO$_2$ loss is considered to be determined by the identity of both the metal and the aryl moiety.

Table 5. Physical properties of butyl 3-arylpropenoates (3)[a] and their free acids.[b]

Ester	m/z (M^+)	δ_H	M.p. (°C) of acid (lit.)
(3a)	254	0.96 (3 H, t, J 7.5 Hz), 1.16–1.92 (4 H, m) 4.24 (2 H, t, J 6.0 Hz), 6.48 (1 H, d, J 15.0 Hz), 7.06–8.26 (7 H, m), and 8.50 (1 H, d, J 15.0 Hz)	215.5–216.5[c] (209–212)[i]
(3b)	268	0.96 (3 H, t, J 7.5 Hz), 1.20–1.96 (4 H, m), 2.74 (3 H, s), 4.28 (2 H, t, J 6.0 Hz), 6.50 (1 H, d, J 15.0 Hz), 7.20–7.88 (4 H, m), 7.96–8.36 (2 H, m), and 8.52 (1 H, d, J 15.0 Hz)	223–224[d,e]
(3c)	288, 290	0.96 (3 H, t, J 7.5 Hz), 1.16–1.96 (4 H, m), 4.26 (2 H, t, J 6.0 Hz), 6.40 (1 H, d, J 15.0 Hz), 7.16–7.80 (4 H, m), 7.96–8.36 (2 H, m), and 8.32 (1 H, d, J 15.0 Hz)	259–260[c,f]
(3d)[g]	254	0.96 (3 H, t, J 7.5 Hz), 1.20–2.00 (4 H, m), 4.22 (2 H, t, J 6.0 Hz), 6.50 (1 H, d, J 15.0 Hz), and 7.36–8.05 (8 H, m)	213–213.5[c] (208–209)[ii]
(3e)[h]	268	0.96 (3 H, t, J 7.5 Hz), 1.16–1.96 (4 H, m), 2.50 (3 H, s), 4.24 (2 H, t, J 6.0 Hz), 6.50 (1 H, d, J 15.0 Hz), and 7.20–8.10 (7 H, m)	
(3f)[i]	284	0.96 (3 H, t, J 7.5 Hz), 1.20–1.92 (4 H, m), 3.92 (3 H, s), 4.24 (2 H, t, J 6.0 Hz) 6.50 (1 H, d, J 15.0 Hz), 7.08–7.30 (2 H, m), and 7.52–7.96 (5 H, m)	
(3g)	204	0.96 (3 H, t, J 7.5 Hz), 1.16–1.96 (4 H, m), 4.22 (2 H, t, J 6.0 Hz), 6.42 (1 H, d, J 15.0 Hz), 7.00–7.80 (5 H, m), and 7.66 (1 H, d, J 15.0 Hz)	132–133[c] (133.1)[iii]
(3h)	234	0.96 (3 H, t, J 7.5 Hz), 1.16–1.96 (4 H, m), 3.82 (3 H, s), 4.20 (2 H, t, J 6.0 Hz), 6.30 (1 H, d, J 15.0 Hz), 6.84 (2 H, d, J 9.0 Hz), 7.44 (2 H, d, J 9.0 Hz), and 7.62 (1 H, d, J 15.0 Hz)	170–171[j] (171.6–173.2)[iv]
(3i)	218	0.96 (3 H, t, J 7.5 Hz), 1.16–1.96 (4 H, m), 2.36 (3 H, s), 4.20 (2 H, t, J 6.0 Hz), 6.36 (1 H, d, J 15.0 Hz), 7.00–7.30 (2 H, d, J 9.0 Hz), 7.30–7.52 (2 H, d, J 9.0 Hz), and 7.68 (1 H, d, J 15.0 Hz)	199–200[c] (199–200)[v]
(3j)	222	0.96 (3 H, t, J 7.5 Hz), 1.16–1.96 (4 H, m), 4.24 (2 H, t, J 6.0 Hz), 6.34 (1 H, d, J 15.0 Hz), 7.92–7.70 (4 H, m), and 7.66 (1 H, d, J 15.0 Hz)	209–210[c] (209)[vi]
(3k)	238, 240	0.96 (3 H, t, J 7.5 Hz), 1.16–1.92 (4 H, m), 4.20 (2 H, t, J 6.0 Hz), 6.34 (1 H, d, J 15.0 Hz), 7.10–7.60 (4 H, m), and 7.60 (1 H, d, J 15.0 Hz)	248.5–249.5[j] (249)[vii]
(3l)	238, 240	0.96 (3 H, t, J 7.5 Hz), 1.16–1.92 (4 H, m), 4.22 (2 H, t, J 6.0 Hz), 6.42 (1 H, d, J 15.0 Hz), 7.10–7.55 (4 H, m), and 7.56 (1 H, d, J 15.0 Hz)	165.5–166[j] (167)[viii]
(3m)	282, 284	0.96 (3 H, t, J 7.5 Hz), 1.16–1.96 (4 H, m), 4.22 (2 H, t, J 6.0 Hz), 6.42 (1 H, d, J 15.0 Hz), and 7.20–7.84 (5 H, m)	256–257[c] (257)[ix]
(3n)[k]	249	0.96 (3 H, t, J 7.5 Hz), 1.20–2.00 (4 H, m), 4.24 (2 H, t, J 6.0 Hz), 6.56 (1 H, d, J 15.0 Hz), 7.56–7.92 (3 H, m), and 8.12–8.44 (2 H, m)	

[a] The esters were obtained as oils unless otherwise noted. [b] The acids were obtained from the corresponding butyl esters by refluxing in aq. sodium hydroxide–methanol. [c] Recrystallised from benzene. [d] Recrystallised from benzene–ethanol. [e] Found: C, 79.4; H, 5.6. $C_{14}H_{12}O_2$ requires C, 79.23; H, 5.70%. [f] Found: C, 67.1; H, 3.9; Cl, 15.3. $C_{13}H_9ClO_2$ requires C, 66.68; H, 3.88; Cl, 15.24%. [g] M.p. 66–68 °C (from hexane). [h] M.p. 87–88 °C (from hexane) (Found: C, 80.6; H, 7.4. $C_{18}H_{20}O_2$ requires C, 80.56; H, 7.51%). [i] M.p. 47–48 °C (from hexane) (Found: C, 75.7; H, 7.1. $C_{18}H_{20}O_3$ requires C, 76.03; H, 7.09%). [j] Recrystallised from ethanol. [k] M.p. 68–70 °C (from EtOH) (lit.,[x] 68–69 °C). (i) B. L. West, *J. Am. Chem. Soc.*, 1920, **42**, 1656. (ii) J. D. Fulton and R. Robinson, *J. Chem. Soc.*, 1939, 200. (iii) P. M. Gross, J. H. Saylor, and M. A. Gorman, *J. Am. Chem. Soc.*, 1933, **55**, 650. (iv) W. S. Johnson and W. E. Shelberg, *J. Am. Chem. Soc.*, 1945, **67**, 1853. (v) F. G. Baddar, L. S. El-Assal, and N. A. Doss, *J. Chem. Soc.*, 1955, 461. (vi) E. D. Bergmann, S. Berkovic, and R. Ikan, *J. Am. Chem. Soc.*, 1956, **78**, 6037. (vii) J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 1937, 1426. (viii) J. F. J. Dippy and J. E. Page, *J. Chem. Soc.*, 1938, 357. (ix) M. Reimer and E. Tobin, *J. Am. Chem. Soc.*, 1941, **63**, 2490. (x) M. Semonksy and J. Kunak, *Chem. Listy*, 1951, **45**, 156.

observation that a small decrease in the reaction temperature considerably reduced the product yield (Figure 1) would suggest that, in the arylsulphonylpalladium intermediate, another reaction other than the desulphonylation occurs at a lower temperature. Attempted isolation of by-products was unsuccessful. A PTC having high lipophilicity may effectively transfer the solid base into the liquid phase to enhance

dehydrochlorination from the chlorohydridopalladium species.[8] The fact that the reaction of compound (1a) with ester (2a) and $Bzl(Oct_3)NCl$ in the absence of base gave product (3a) in considerable yield suggests that the ammonium chloride also plays another important role, such as stabilising the intermediates by complexation in the less polar reaction medium.[1] However, details are not clear.

Experimental

^{1}H NMR spectra were obtained with a JEOL JNM-PS-100 spectrometer for $CDCl_3$ solutions. GLC-MS data were obtained with a JEOL JMS-DX-303 spectrometer. GLC analysis was carried out with a Shimadzu GC-8A gas chromatograph.

Arenesulphonyl chlorides (1b),[12] (1c),[13] (1e),[14] (1f),[15] (1j),[13] (1l),[16] and (1m)[13] and palladium complexes $PdCl_2(PhCN)_2$,[1c] $PdCl_2(PPh_3)_2$,[1c] and $Pd(PPh_3)_4$[1c] were prepared by the methods reported previously. Other starting materials were commercially available. The following experimental details may be regarded as typical in methodology and scale.

Reaction of Naphthalene-1-sulphonyl Chloride (1a) with Butyl Acrylate (2a).—A stirred mixture of the sulphonyl chloride (1a) (454 mg, 2 mmol), butyl acrylate (2a) (640 mg, 5 mmol), potassium carbonate (415 mg, 3 mmol), $PdCl_2(PhCN)_2$ (19.2 mg, 0.05 mmol), and benzyltrioctylammonium chloride (144 mg, 0.3 mmol) in *m*-xylene (4 ml) was heated at 140 °C for 4 h under nitrogen. Formation of butyl (E)-3-(1-naphthyl)prop-2-enoate (3a) (483 mg, 95%) was confirmed by GLC-MS and GLC analysis. The ester (3a) (458 mg, 90%) was also isolated by column chromatography on silica gel with benzene–hexane (1:1) as eluant.

Reaction of Naphthalene-1-sulphonyl Chloride (1a) with Ethylene (2c).—The sulphonyl chloride (1a) (454 mg, 2 mmol), potassium carbonate (415 mg, 3 mmol), $PdCl_2(PhCN)_2$ (19.2 mg, 0.05 mmol), and benzyltrioctylammonium chloride (144 mg, 0.3 mmol) was added to a 50 ml stainless steel autoclave containing benzene (10 ml). The system was then charged with ethylene (10 atm at room temperature) and was stirred at 160 °C for 2 h. Formation of 1-vinylnaphthalene (5) (222 mg, 71%) was confirmed by GLC-MS and GLC analysis. The alkene (5) (213 mg, 69%) was also isolated by column chromatography on silica gel with hexane as eluant.

Products. The physical properties of the butyl esters (3) and their free acids are summarised in Table 5. The ester (4) was an oil; m/z 226 (M^+); δ_H 1.34 (3 H, t, J 7.5 Hz), 4.30 (2 H, q, J 7.5 Hz), 6.48 (1 H, d, J 15.0 Hz), 7.24–8.36 (7 H, m), and 8.48 (1 H, d, J 15.0 Hz). The alkene (5) was an oil; m/z 154 (M^+); δ_H 5.32–5.60 (1 H, m), 5.60–5.96 (1 H, m), and 7.30–8.36 (8 H, m). The alkene (6) had m.p. 71–72 °C (from EtOH) (lit.,[18] 70–70.5 °C); m/z 230 (M^+); δ_H 6.92–8.32 (14 H, m). The alkene (7) had m.p. 65.5–66 °C (from EtOH) (lit.,[18] 65–66 °C); m/z 154 (M^+); δ_H 5.34 (1 H, d, J 10.5 Hz), 5.88 (1 H, d, J 16.5 Hz), 6.90 (1 H, dd, J 10.5 and 16.5 Hz), and 7.24–8.06 (7 H, m). The alkene (8) had m.p. 148–149 °C (lit.,[18] 145–146 °C); m/z 230 (M^+); δ_H 7.12–8.04 (14 H, m). The alkene (9) was isolated along with the isomer (10) as an oil [(9):(10) 67:33; (9) had a longer GLC retention time than (10) (silicone OV-17 column)]; (9), m/z 244 (M^+); δ_H 2.05 (3 H, s, Me); (10), m/z 244 (M^+); δ_H 4.20 (2 H, s, CH_2), 4.76 (1 H, s, vinyl), and 5.48 (1 H, s, vinyl). The alkene (11) was isolated along with the isomer (12) as an oil [(11):(12) 75:25; (11) had a longer GLC retention time than (12) (silicone OV-17 column)];

(11), m/z 268 (M^+); δ_H 1.96 (3 H, s, Me) and 8.16 (1 H, s, vinyl); (12), m/z 268 (M^+); δ_H 4.08 (2 H, s, CH_2), 5.12 (1 H, s, vinyl), and 6.20 (1 H, s, vinyl). Treatment of the mixture of isomers (11) and (12) with aq. sodium hydroxide–methanol and recrystallisation from benzene gave the free acid of (11); m.p. 151–152 °C (lit.,[19] 149–150 °C). The diester (13) had m.p. 67–68 °C (lit.,[20] 62–63 °C); m/z 270 (M^+); δ_H 3.44 (3 H, s), 3.68 (3 H, s), and 7.16–7.96 (8 H, m).

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