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SYNTHESIS OF α,β-UNSATURATED SULPHONATES VIA THE WITTIG-HORNER REACTION‡

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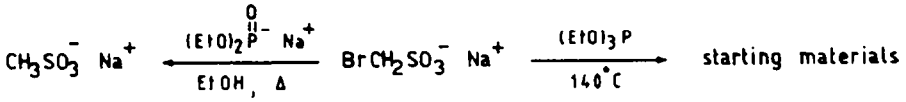
Abstract : A general and practical method of synthesis of α,β-unsaturated sulphonates (25 examples) by the Wittig-Horner reaction is described. Reactions with the salts 2 and carbonyl compounds are not very stereoselective. On the contrary, reactions with esters 1 gave high yields of (E)-α,β-unsaturated sulphonic esters.

The Wittig-Horner reaction has been applied to the synthesis of a large variety of olefinic, compounds bearing sulphide[1], sulphonium[2], sulphoxide[3] or sulphone[4] functional groups. In contrast, little attention has been paid to the preparation of α,β-unsaturated sulphonic acid derivatives by phosphonate olefination. A single paper briefly describes the Wittig-Horner reaction of aromatic aldehydes with dialkylphosphorylmethanesulphonic ester 1 prepared in four steps from isopropyl chloroacetate[5].

In a recent preliminary paper[6], we described a novel and practical approach to the salts and esters derived from diethylphosphorylmethanesulphonic acid. We also showed that these phosphonate reagents are capable of converting aldehydes and ketones into α,β-unsaturated sulphonates. We herein present this work in detail along with additional examples and some mechanistic and stereochemical discussions.

Synthesis of the Phosphonate Reagents 1 and 2 $(EtO)_2P(O)-CH_2-SO_3X$

Our initial attempts to obtain phosphonates 2 were based on the Arbuzov reaction. No reaction took place between triethylphosphite and sodium bromoethylsulphonate even at 140°C for 24 hrs (Scheme 1). The more nucleophilic diethyl phosphite anion was found to attack on bromine leading to the formation of sodium methanesulphonate. This result parallels the well-known behaviour of α-bromosulphones toward phosphines[7].

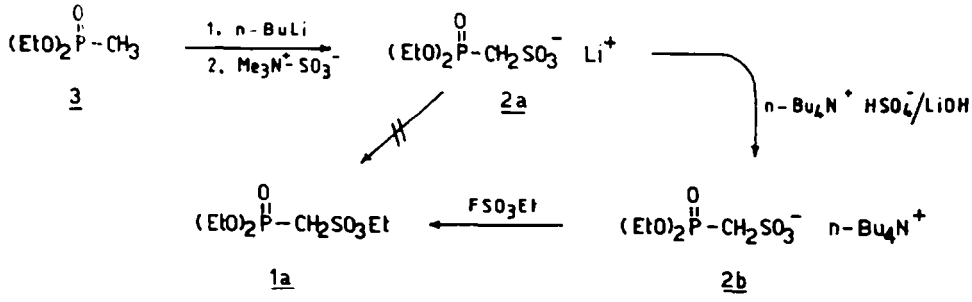


Scheme 1

Although various dialkyl methanephosphonates bearing sulphide, sulphonium, sulphoxides or sulphone groups have been reported[1-4], their oxidation to the corresponding sulphonic acid derivatives was expected to be a difficult step requiring strong oxidizing agents and leading to unselective cleavage of the two carbon sulphur bonds.

‡ This paper is dedicated to Professor Hans Wynberg on the occasion of his 65th birthday.

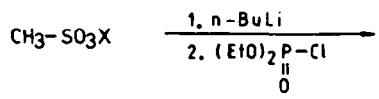
We rather examined the sulphonation of the commercially available or readily prepared[8] diethyl methanephosphonate 3. Deprotonation of 3 with n-butyl lithium (THF,-78°C) followed by sulphonation of the resulting carbanion with the trimethylamine-sulphur trioxide complex (-78°C to -10°C) yielded (64%) pure lithium diethylphosphorylmethanesulphonate 1a (Scheme 2). Owing to the greater acidity of α-hydrogens in 2a than in 3, optimum yields were obtained with 0.5 equivalent of the sulphonating agent[9]. Excess of 3 was easily recovered. Other sulphonating agents such as the pyridine or DMF-sulphur trioxide complexes gave less satisfactory results.



3 2a 1a 2b

Scheme 2

All attempts to alkylate 2a with powerful reagents such as triethyloxonium tetrafluoroborate or ethyl fluorosulphonate were unsatisfactory owing to the insolubility of the lithium salt 2a. It was thus converted into the highly hygroscopic tetrabutylammonium salt 2b (90% yield) by ion-pair extraction[10]. Compound 2b readily reacted with ethyl fluorosulphonate to give ester 1a (92% yield)[11]. Yet the most practical route toward 1a involved the phosphorylation of the anion derived from ethyl methanesulphonate (Scheme 3). The method was applied to the preparation of the isopropyl ester 1b and the tetrabutylammonium salt 2b. Esters 1a and 1b were obtained in high yields. The method did not apply well to the preparation of salt 2b owing to the difficulty to separate 2b from tetrabutylammonium methanesulphonate.

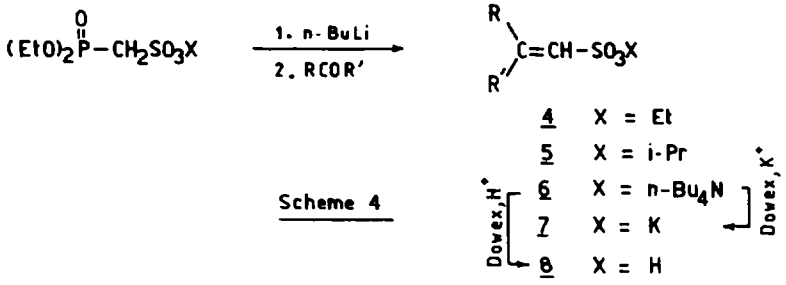


1a X = Et 95%
1b X = i-Pr 89%
2b X = n-Bu4N impure material

Scheme 3

Wittig-Horner Reactions

All four diethylphosphorylmethanesulphonates 1 and 2 were subjected to the classical conditions of the Wittig-Horner reactions (Scheme 4). Deprotonation of the well-soluble 1a,1b and 2b was readily effected in a few minutes at -78°C with n-BuLi in THF. With the less soluble lithium salt 2a, the reaction was too slow at -78°C but could be conveniently performed at -15°C in one hour. Addition of the carbonyl compound at -78°C and stirring overnight yielded unsaturated sulphonates 4 to 6. Esters 4 and 5 were easily purified by flash chromatography. Since the reaction mixture from 2a contained a mixture of hardly separable lithium salts, it was submitted to ion-pair extraction conditions[10]. The resulting tetrabutylammonium sulphonates 6 were obtained with a purity greater than 95%. They could be easily transformed into the corresponding potassium salt 7 or sulphonic acid 8 on a Dowex (50x2) cation-exchange resin (methanol-water 1:1).



Scheme 4

Table 1: Synthesis of α,β-Unsaturated Sulphonates 4, 5, 6 from 1 and 2

Entry	Phosphonate	Product	R	R'	X	Yield(%)[a]	E:Z[b]
1	1a	4a	Et	H	Et	85	74:26
2	1a	4b	i-Pr	H	Et	96	85:15
3	1a	4c	t-Bu	H	Et	94	>98:<2
4	1a	4d	p-ClC$_6$H$_4$	H	Et	99	98:2
5	1a	4e	n-Pr	H	Et	96	80:20
6	1a	4f	i-Bu	H	Et	98	78:22
7	1a	4g	o-MeOC$_6$H$_4$	H	Et	92	96:4
8	1a	4h	m-NO$_2$C$_6$H$_4$	H	Et	93	96:4
9	1a	4i	(E) PhCH=CH-	H	Et	88	93:7
10	1a	4j	-(CH$_2$)$_5$-		Et	99	-
11	1a	4k	Ph	Me	Et	25	>98:<2
12	1a	4l	i-Pr	Me	Et	traces	-
13	1b	5a	n-Pr	H	i-Pr	86	79:21
14	1b	5b	i-Bu	H	i-Pr	67	86:14
15	1b	5c	t-Bu	H	i-Pr	89	>98:<2
16	2a	6a	Et	H	n-Bu$_4$N	57	44:56
17	2b					68	40:60
18	2a	6b	i-Pr	H	n-Bu$_4$N	80	45:55
19	2b					84	35:65
20	2a	6c	t-Bu	H	n-Bu$_4$N	90	92:8
21	2b					80	70:30
22	2a	6d	p-ClC$_6$H$_4$	H	n-Bu$_4$N	77	80:20
23	2b					76	72:28
24	2a	6e	i-Pr	Me	n-Bu4N	68	48:52
25	2a	6f	Ph	Me	n-Bu4N	69	88:12
26	2a	6g	Ph	Ph	n-Bu$_4$N	61	-

(a) All reactions have been carried out on 0.3-1.0 mmole scale. Isolated yields after flash chromatography (4,5) or ion pair extraction (6).

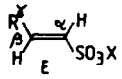
(b) Determined by ^{1}H-NMR of the crude mixture. In the reactions with 2a, ratios remained unchanged after ion-pair extraction.

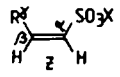
The method is quite general (Table 1). Sulphonic esters 1a-b gave excellent yields of unsaturated sulphonate esters 4 or 5 in reactions with aliphatic (entries 1,2,3,5,6,13,14 and 15), aromatic (entries 4,7 and 8) and conjugated (entry 9) aldehydes. Yields strongly dropped with hindered (entry 12) or readily enolisable (entry 11) ketones. Substantial amounts of starting ketone and condensation products were obtained indicating that for these enolisable ketones deprotonation was favoured over attack on the carbonyl group. Such behaviour had been previously observed in other Wittig-Horner reactions[1b]. With ionic sulphonates 2a-b, yields are good even with hindered (entries 20, 21 and 24) and readily enolisable (entry 25) carbonyl compounds.

Stereochemistry

α,β-unsaturated sulphonates 4-6 were obtained as mixtures of E and Z isomers. The stereochemical assignments were based on the values of coupling constants of the vicinal olefinic protons. Examination of the chemical shift of H_β in both E and Z isomers could also be used as a reliable criterion for stereochemical assignment : as a result of the anisotropic effect of the sulphonate group, the signal for H_β in the E isomer (H_β cis to SO_3X) was always found at a lower field than that in the Z isomer (Table 2).

Table 2 : Chemical Shifts δ(ppm) and Coupling Constants J(Hz) in $CDCl_3$ for some E and Z Disubstituted α,β-Unsaturated Sulphonates.



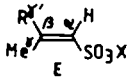


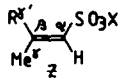
Compound	$\delta^E_{H\beta}$	$\delta^E_{H\gamma}$	$J^E_{H_\alpha H_\beta}$	$\delta^Z_{H\beta}$	$\delta^Z_{H\gamma}$	$J^Z_{H_\alpha H_\beta}$	$\Delta\delta_{H\beta}$ (a)	$\Delta\delta_{H\gamma}$ (a)
4a	6.99	2.33	15.2	6.40	2.63	11.0	0.59	-0.30
6a	6.49	1.96	15.2	5.63	2.50	11.2	0.86	-0.54
4b	6.84	2.48	15.3	6.00	3.40	(b)	0.84	-0.92
6b	6.41	2.34	15.2	5.41	3.74	11.2	1.00	-1.40
4c	6.92	-	15.4		not found		-	-
6c	6.23	-	15.4	5.29	-	12.3	0.94	-
4d	7.55	-	15.6	7.09	-	12.1	0.46	-
6d	7.20	-	15.6	6.39	-	12.7	0.81	-
4f	6.88	2.18	15.1	6.27	2.52	11.2	0.61	-0.34
5b	6.86	2.17	15.1	6.27	2.55	(b)	0.59	-0.38

(a) : $\Delta\delta=\delta^E_H-\delta^Z_H$ (ppm); (b) : Degenerated system

A similar criterion was used to establish the configuration of trisubstituted double bonds in 4k, 6e and 6f. The anisotropic effect of the sulphonate group was also observed in the allylic hydrogens (Hγ). These protons appear at lower field when they are situated on the same side of the double bond as the sulphonate group (Table 3).

Table 3 : γ-Chemical Shifts (ppm) in $CDCl_3$ for E and Z Trisubstituted Sulphonates.





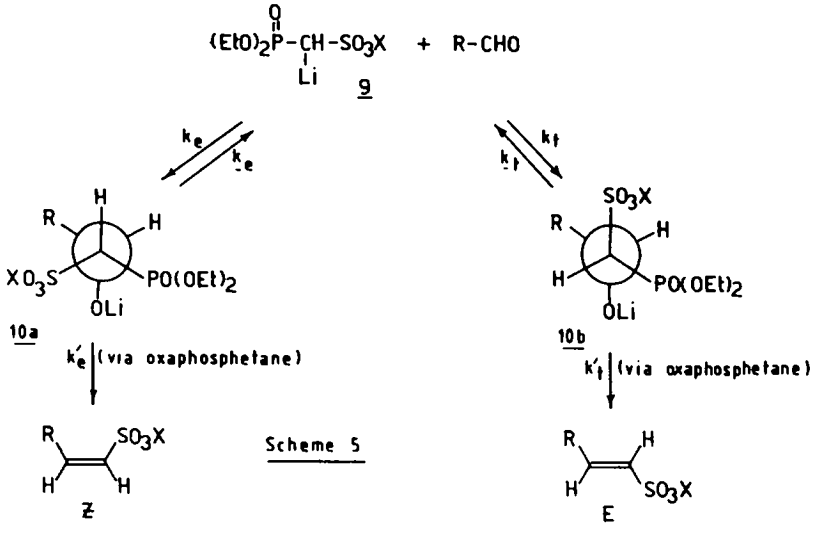
Compound	$\delta^E_{H\gamma}$	$\delta^E_{H\gamma'}$	$\delta^Z_{H\gamma}$	$\delta^Z_{H\gamma'}$	$\Delta\delta_{H\gamma}$ (a)	$\Delta\delta_{H\gamma'}$ (a)
6e	2.06	2.20	1.63	3.88	0.43	-1.68
6f	2.49	-	2.06	-	0.43	-
4k	2.54	-	not found		-	-

(a) : $\Delta\delta = \delta^E_H-\delta^Z_H$ (ppm)

The E:Z ratios were determined by ^{1}H-NMR. Compounds 4-6 were found configurationally stable under the reaction and work-up conditions. The stereoselectivity was rather insensitive to temperature or to the addition of cosolvents such as HMPA or TMEDA.

From the data of Table 1, it can been seen that greater stereoselectivities in favour of the E isomer were observed for aromatic (entries 4,7,8,11,22 and 23) or hindered (entries 3,15,20 and 21) carbonyl compounds. Much higher E-selectivities were obtained from esters 1a,b than from salts 2a,b. With 1a,b the E isomer largely predominated in all cases. This behaviour parallels that reported for the Wittig-Horner reaction leading to α,β-unsaturated sulphones.[4]

These stereochemical results can be rationalised on the basis of the well-established mechanism of the Wittig-Horner reaction[12] (Scheme 5).



Scheme 5

E:Z ratios of isomeric olefins have been shown to be determined by the degree of reversibility of the formation of the two oxyanions 10a and 10b and the rates of their decomposition. On steric grounds one should expect that threo-alkoxyde (10b) to be more stable than erythro (10a). A greater degree of reversibility of the first step must then favour the formation of the threo isomer and thus increase the E-selectivity[12].

A high degree of reversibility of the first step should be expected for aromatic carbonyl compounds which, accordingly, show a greater E-stereoselectivity. On the other hand, the reversibility of alkoxide formation (10a⇌10b) must be directly related with the stability of the reactants. In the case of the phosphonate carbanion 9, the stabilisation is due to the inductive effect of the sulphonate group which increases in the order $SO_3^-Bu_4N^+ < SO_3^-Li^+ < SO_3Et \sim SO_3i\text{-}Pr$. This accounts for greater E-selectivities observed for 1a and 1b as compared to 2a and 2b.

Cis-elimination from threo-alkoxide (10b) is expected to be faster than from the erythro isomer (10a) ($k'_t > k'_e$) because of steric interactions between the two substituents (R and SO_3X) in the incipient double bond of the transition state leading to the Z-isomer. This difference increases with the steric bulkiness of R. This explains the greater E-selectivity observed with 2,2-dimethylpropionaldehyde (R=^{t}Bu, entries 3,15,20 and 21). This factor can also contribute to the high E-stereoselectivity found in reactions with aromatic carbonyl compounds, because the conjugative stabilisation of the incipient double bond in the transition state leading to a Z olefin (steric interaction between R and SO_3X) is usually smaller than that leading to the E isomer[12a].

In conclusion, this new variation of the Wittig-Horner reaction offers a practical synthetic route toward α,β-unsaturated sulphonic acid derivatives. It is experimentally simple and allows for many structural variations.

EXPERIMENTAL

Melting points were determined on a Mettler FP1 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 297 spectrophotometer, ^{1}H-NMR spectra were determined for solutions in deuterochloroform (unless otherwise mentioned) with $SiMe_4$ as internal standard on a Varian XL 200 spectrometer. Mass spectra were recorded on a Varian MAT 44 spectrometer in the electron impact EI (70 e.v.) or chemical ionisation CI (acetone) modes. Data are reported in mass unit m/e (relative intensity). Column chromatographies were performed using Merk silicagel K-60 (230-400 mesh). All solvents were distilled before use. Dichloromethane was dried at reflux over P_2O_5. THF was dried over sodium benzophenone under argon. Ether refers to diethyl ether. Microanalysis were performed at the University of Vienna.

Lithium diethylphosphorylmethanesulphonate (2a)
A solution of diethyl methanephosphonate 3 (7.7 ml, 52.4 mmol) in 85 ml of dry THF under argon was cooled to -78°C and treated with 24.5 ml (56 mmol) of 2.3 M n-BuLi in hexane. After 40 min., Me_3N-SO_3, (4.0 g, 28.8 mmol) was added in small portions over a period of 15 min. The mixture was stirred at -78°C for 2h and slowly (~3h) allowed to warm to -10°C. The colourless solution was cooled to -20°C. Addition of acetic acid (3.5 ml, 60 mmol) lead to the immediate formation of a white pricipitate. The mixture was warmed to room temperature and the precipitate was filtered off and washed with ether. Excess of 3 could be easily recovered from the combined ether solutions. The solid was chromatographed on silicagel (CH_2Cl_2 : MeOH 7:1) to give the lithium sulphonate 2a (4.0 g, 64%) : m.p. ~220°C (sublim); Rf = 0.2 in CH_2Cl_2 : MeOH (7:1); ν_{max} (KBr) 2985, 2920, 1250, 1235, 1200, 1020-1040, 975 and 820 cm^{-1}; δ_H (CD_3OD) 1.42 (t, J=7.0Hz, 6H, OCH_2CH_3), 3.68 (d, J=17 Hz, 2H, CH_2-P) and 4.28 ppm (pseudo quintet, J = 7.0 Hz, 4H, O-CH_2-CH_3).

Tetrabutylammonium diethylphosphorylmethanesulphonate (2b)
0.95 g (4.0 mmol) of 2a, 1.36 g (4.0 mmol) of tetrabutylammonium bisulphate and 0.17g (4.0 mmol) of lithium hydroxyde monohydrate were dissolved in distilled water (30 ml) and extracted with dichloromethane (6x30 ml). The organic layers were dried ($MgSO_4$) and evaporated to afford crude sulphonate 2b as an hygroscopic syrup (1.7 g, 90%). ν_{max} (film) 2960, 2880, 1390, 1260-1220 (SO_3), 1180, 1070, 1030 (SO_3), 960, 830, 800 and 730 cm^{-1}; δ_H 1.00 (t, J=7.1 Hz, 12H, CH_3-CH_2-CH_2-CH_2N^+) 1.2-1.7 (m, 22H, CH_3CH_2-CH_2-CH_2-N^+ + CH_3-CH_2-O), 3.2-3.4 (m, 8H, -CH_2N^+), 3.5 (d, J=17.0 Hz, 2H, -P-CH_2-SO_3) and 4.22 ppm (quintet, J=7.2 Hz, 4H, CH_3-CH_2-O-P).

Ethyl diethylphosphorylmethanesulphonate (1a)
Method A : Ethylation of 2b
To a solution of 2b (6.94 g, 14.7 mmol) in 15 ml of dry dichloromethane under argon and at 0°C was added ethyl fluorosulphonate (1.8 ml, 17.6 mmol). The solution was stirred at 0°C for 60 min and at room temperature for 2h. After removal of the solvent the residue was treated with 40 ml of ether-ethyl acetate (4:1). The white solid (Bu_4N^+ FSO_3^-) was filtered off and washed with the same mixture of solvents. The combined filtrate and washing were diluted with 40 ml of ethyl acetate and washed with water (2x20 ml). The combined aqueous layers were extracted with ether:ethyl acetate 4:1 (2x20 ml) and all organic solutions were dried ($MgSO_4$) and evaporated to afford the crude sulphonate 1a. Remaining traces of tetrabutylammonium salts were removed by rapid filtration on silica gel (Et_2O:CH_2Cl_2 6/1) to yield pure sulphonate 1a (3.47g, 91%).
Method B : Phosphorylation of ethyl methanesulphonate
A solution of ethyl methanesulphonate (4.27 ml, 40.3 mmol) in 100 ml of dry THF was treated at -78°C under argon atmosphere with 2.3 M n-BuLi in hexane (19.3 ml, 44.4 mmol). After 15 min. freshly distilled ethyl chlorophosphate (3.30 ml, 22.2 mmol) was added. The solution was kept at -78°C for 30 min. and allowed to stay at -50°C for 60 min. 4.4 M NH_4Cl was added (11.0 ml, 44.4 mmol) and the mixture was warmed to room temperature. The mixture was concentrated (elimination of THF). Then the residue was diluted with 50 ml of water and extracted with dichloromethane (3x80 ml). The organic layers were dried ($MgSO_4$) and evaporated to afford a mixture of sulphonate 1a and the excess of ethyl methanesulphonate. Pure 1a (5.50g, 95%) was obtained after flash chromatography (CH_2Cl_2 : Et_2O 1/1, Rf = 0.25). The excess of ethyl methanesulphonate (2.24 g, Rf=0.6) was also recovered. Data for 1a : b.p. 120-130°C/ 0.1 mm (Lit.[5] 106-108°C/1.3 Pa). ν_{max} (film) 2990, 2915, 1480, 1440, 1340-1380 (SO_3), 1260 ($PO(OEt)_2$), 1180 (SO_3), 950-1070, 920 and 800-830 cm^{-1}; δ_H 1.35 (dt, J=0.7 and 7.1 Hz, 6H, CH_3-CH_2-O-P), 1.41 (t, J=7.1Hz, 3H, CH_3-CH_2-O) 3.71 (d, J=17.2Hz, 2H, P-CH_2-S), 4.22 (dq, J=7.1 and 8.3 Hz, 4H, P-O-CH_2CH_3) and 4.38 ppm (q, J=7.1 Hz 2H, S-O-CH_2-CH_3); m/e (CI) 261 (M^++1, 100).

Isopropyl diethylphosphorylmethanesulphonate (1b)
Sulphonate 1b was prepared by phosphorylation of isopropyl methanesulphonate following the procedure (method B) described for the synthesis of 1a. Quantities : 1.0 g (7.25 mmol) of isopropyl methanesulphonate, 20 ml of THF, 3.47 ml (7.97 mmol) of 2.3 M n-BuLi and 576 µl (4.0 mmol) of ethyl chlorophosphate. Yield : 967 mg (89%) based on ethyl chlorophosphate). Data for 1b : TLC (CH_2Cl_2 : Et_2O 1/1) Rf = 0.27; ν_{max} (film) 2990, 2880, 1460, 1360 (SO_3), 1265 (PO), 1225, 1185 (SO_3), 1100, 1020-1060, 980, 920, 890 and 810 cm^{-1}; δ_H 1.38 (t, J=7.1 Hz, 6H, CH_3-CH_2), 1.45 (d, J=6.3 Hz, 6H, CH_3-CH-), 3.74 (d, J=17.3 Hz, 2H, P-CH_2-S), 4.25 (quintet, J=7.1 Hz, 2H, CH_2-O) and 5.07 ppm (septuplet, J=6.3 Hz, 1H, -CH-CH_3); m/e (CI) 275 (M^++1, 100) and 233 (51); Found C, 34.97; H, 7.12, S, 12.15; $C_8H_{19}O_6PS$ requires C, 35.03; H, 6.98; S, 11.69.

General procedure for the preparation of ethyl vinylsulphonates 4

A solution of 1a (1.0 equiv) and ~0.5 mg of 1,10-phenantroline (used as indicator) in dry THF (1 ml per 0.25 mmol of 1a) was cooled to -78°C under argon. A solution of 2.3 n-BuLi in hexane was slowly added till a persistent orange colour appears (approximately 1.05 equiv.). Stirring was continued for 20 min. Then freshly aldehyde or ketone (~1.1 equiv.) was added. After an additional 45 min. at -78°C the solution was allowed to warm to room temperature and stirring was continued for 18h. The bulk of the solvents were evaporated and the residue was treated with water (5ml per 0.25mmol of 1a) and extracted with dichloromethane (3x5 ml per 0.25 mmol of 1a). The organic layers were dried ($MgSO_4$) and evaporated to afford crude sulphonates 4, which were purified by flash chromatography (CH_2Cl_2 or hexane : ethyl acetate 6:1 as eluents).

Ethyl 1-butenesulphonate (4a)

Quantities : 78 mg (0.30 mmol) of 1a, 140 μl (0.32 mmol) of 2.3 M n-BuLi and 24μl (0.33 mmol) of propionaldehyde. Yield : 42 mg (85%, E/Z =74/26). Data for 4a (E+Z) : ν_{max} (film) 3060, 2980, 2940, 2880, 1630 (C=C), 1460, 1340-1370 (SO_3), 1220, 1170 (SO_3), 1100, 1010, 970, 910-940, 900, 820, 780 and 690 cm^{-1}; δ_H E-isomer, 1.12 (t, J=7.4 Hz, 3H, CH_3), 1.38 (t, J=7.2Hz, 3H, CH_3-CH_2O), 2.33 (m, 2H, CH_2-CH=C), 4.17 (q, J=7.2 Hz, 2H, O-CH_2-CH_3), 6.20 (dt, J=1.7 and 15.2 Hz, 1H, C=CH-SO_3) and 6.99 ppm (dt, J=6.2 and 15.2 Hz, 1H, CH=CH-SO_3); Z-isomer, 1.10 (t, J=7.6 Hz, 3H, CH_3), 1.40 (t, J=7.1 Hz, 3H, CH_3-CH_2-O), 2.63 (d quintet, J=1.5 and 7.6 Hz, 2H, CH_2-CH=C), 4.21 (q, J=7.1 Hz, 2H, O-CH_2), 6.18 (dt, J=1.5 and 11.0 Hz, 1H, C=CH-SO_3) and 6.40 ppm (dt, J=7.7 and 11.0 Hz, 1H, CH=CH-SO_3); m/e (EI) 164 (M^+,1), 136(2) and 55(100).

Ethyl 3-methyl-1-butenesulphonate (4b)

Quantities : 172 mg (0.66 mmol) of 1a, 295 μl(0.68 mmol) of 2.3 M n-BuLi and 66 μl (0.73 mmol) of isobutyraldehyde. Yield : 113 mg (96%, E/Z = 85/15). Data for 4b (E+Z): ν_{max} (film) 3060, 2970, 2940, 2880, 1630 (C=C), 1470, 1340-1375 (SO_3), 1310, 1230, 1170 (SO_3), 1010, 920, 850, 830, and 750-780 cm^{-1}; δ_H E-isomer, 1.04 (d, J=6.8 Hz, 6H, CH_3-CH), 1.31 (t, J=7.1 Hz, 3H, OCH_2CH_3), 2.48 (m, 1H, CH-C=C), 4.1 (q, J=7.1 Hz, 2H, O-CH_2-CH_3), 6.08 (dd, J=1.5 and 15.3 Hz, 1H, C=CH-SO_3) and 6.84 ppm (dd, J=6.4 and 15.3 Hz, 1H, CH=CH-SO_3); Z-isomer, 1.00 (d, J=6.6 Hz, 6H, CH_3), 1.33 (t, J=7.1 Hz, 3H, OCH_2CH_3), 3.4 (m, 1H, CH-CH=C) and 6.0 ppm (m, 2H, CH = CH); m/e (EI) 178 (M^+, 1), 150 (5) and 69(100); Found C, 47.21; H, 7.99; S, 17.90; $C_7H_{14}O_3S$ requires C, 47.17; H, 7.92; S, 17.99.

Ethyl (E)-3,3-dimethyl-1-butenesulphonate (4c)

Quantities : 260 mg (1.0 mmol) of 1a, 470 μl (1.08 mmol) of 2.3 M n-BuLi and 114 μl (1.05 mmol) of trimethylacetaldehyde. Yield : 180 mg (94%, >98% E-isomer). Data for 4c(E): ν_{max} (film) 3060, 2960, 2910, 2880, 1625 (C=C), 1470, 1350-1375 (SO_3), 1310, 1240, 1160-1185 (SO_3), 1010, 990, 920, 850, 810, 770 and 740 cm^{-1}; δ_H 1.14 (s, 9 H, CH_3-C), 1.39 (t, J=7.1 Hz, 3H, CH_3- CH_2-O), 4.16 (q, J=7.1 Hz, 2H, O-CH_2-CH_3), 6.11 (d, J=15.4 Hz, 1H, C=CH-SO_3) and 6.92 ppm (d, J=15.4 Hz, 1H, CH=CH-SO_3); m/e (CI) 193 (M^+ + 1, 100); Found C, 50.00; H, 8.41; S, 16.71; $C_8H_{16}O_3S$ requires C, 49.97; H, 8.39; S, 16.67.

Ethyl 2-(p-chlorophenyl)vinylsulphonate (4d)

Quantities : 107 mg (0.41 mmol) of 1a, 190 μl(0.44 mmol) of 2.3 M n-BuLi and 64 mg (0.45 mmol) of p-chlorobenzaldehyde. Yield : 100 mg (99%, E/Z=98/2). Data for 4d (E+Z) : m.p. 73°C (Lit.[5] 75°C); δ_H E-isomer, 1.41 (t, J=7.1 Hz, 3H, CH_3), 4.23 (q, J=7.1 Hz, 2H, CH_2), 6.73 (d, J=15.6 Hz, 1H, C=CH-SO_3), 7.4 (m, 4H, C_6H_4) and 7.55 (d, J=15.6 Hz, 1H, CH=CH-SO_3); Z-isomer, 6.4 (d, J=12.1 Hz, 1H, CH=CH-SO_3) and 7.09 ppm (d, J=12.1 Hz, 1H, CH=CH-SO_3); m/e (EI) 248 (M^++2, 7), 246 (M^+, 20), 138 (50), 136 (100) and 75(60).

Ethyl 1-pentenesulphonate (4e)

Quantities : 185 mg (0.71 mmol of 1a, 315 μl (0.72 mmol) of 2.3 M n-BuLi and 70 μl (0.78 mmol) of butyraldehyde. Yield : 121 mg (96%, E/Z=80/20). Data for 4e (E+Z): ν_{max} (film) 3040, 2960, 2880, 1630 (C=C), 1355 (SO_3), 1195, 1170(SO_3), 1005, 970, 920 and 830 cm^{-1}; δ_H E-isomer, 0.97 (t, J=7.2 Hz, 3H, CH_3), 1.38 (t, J=7.1 Hz, 3H, CH_3-CH_2-O), 1.54 (m, 2H, CH_3CH_2-C), 2.26 (m, 2H, CH_2-CH=C), 4.20 (q, J=7.1 Hz, 2H, O-CH_2), 6.2 (dt, J=1.6 and 15.1 Hz, 1H, C=CH-SO_3) and 6.92 ppm (dt, J=6.9 and 15.1 Hz, 1H, CH=CH-SO_3); Z-isomer, 0.97 (t, J=7.2 Hz, 3H, CH_3), 1.40 (t, J=7.1 Hz, 3H, CH_3-CH_2-O), 1.54 (m, 2H, CH_3-CH_2-C), 2.60 (dq, J=1.5 and 7.6 Hz, 2H, CH_2-CH=C), 4.16(q, J=7.1 Hz, 2H, CH_2-O), 6.2 (dt, J=1.5 and 11.0 Hz, 1H, C=CHSO$_3$) and 6.40 ppm (dt, J=7.6 and 11.0 Hz, 1H, CH=CH-SO_3); m/e (CI) 179 (M^++1, 100); Found C, 47.21; H, 7.98; S, 18.05; $C_7H_{14}O_3S$ requires C, 47.17; H, 7.92; S, 17.99.

Ethyl 4-methyl-1-pentenesulphonate (4f)

Quantities : 172 mg (0.66 mmol) of 1a, 290 μl (0.67 mmol) of 2.3 M n-BuLi and 75μl (0.69 mmol) of isovaleraldehyde. Yield : 124 mg (98%, E/Z=78/22). Data for 4f (E+Z) : ν_{max} (film) 3060, 2960, 2870, 1630 (C=C), 1465, 1350 (SO_3), 1225, 1165 (SO_3), 1010, 915, 850, 825, 800 and 775 cm^{-1}; δ_H E-isomer, 0.96 (d, J=6.6 Hz, 6H, CH_3-CH), 1.38 (t, J=7.1 Hz, 3H, CH_3-CH_2-O), 1.82 (m, 1H, CH-CH_3), 2.18 (dt, J=1.3 and 7.2 Hz, 2H, CH_2-CH=C), 4.16 (q, J=7.1 Hz, 2H, CH_2-O), 6.2 (dt, J=1.3 and 15.1 Hz, 1H, C=CH-SO_3) and 6.88 ppm (dt, J=7.7 and 15.1 Hz, 1H, CH=CH-SO_3); Z-isomer, 0.97 (d, J=6.6 Hz, 6H, CH_3-CH), 1.39 (t, J=7.2 Hz, 3H, CH_3-CH_2O), 1.82 (m, 1H, CH_3-CH), 2.52 (dt, J=1.4 and 7.3 Hz, 2H, CH_2-CH=C), 4.18 (q, J=7.2 Hz, 2H, O-CH_2), 6.24 (dt, J=1.4 and 11.2 Hz, 1H, C=CH-SO_3) and 6.27 ppm (dt, J=7.7 and 11.2 Hz, 1H, CH=CH-SO_3); m/e (CI) 193 (M^++1, 100); Found C, 50.09; H, 8.42; S, 16.71; $C_8H_{16}O_3S$ requires C, 49.97; H, 8.39; S, 16.67.

Ethyl 2-(o-methoxyphenyl)vinylsulphonate (4g)
Quantities : 172 mg (0.66 mmol) of 1a, 295 µl (0.68 mmol) of 2.3 M n-BuLi and 97 mg (0.71 mmol) of o-methoxybenzaldehyde. Yield : 147 mg (92%, E/Z = 96/4). Data for 4g (E+Z): ν_{max} (film) 3060, 2980, 2840, 1615(C=C), 1600 (Ar), 1575, 1485, 1465, 1435, 1350(SO_3), 1250, 1160 (SO_3), 1005, 915, 840 and 755 cm^{-1}; δ_H E-isomer, 1.38 (t, J=7.0 Hz, 3H, CH_3-CH_2), 3.90 (s, 3H, CH_3-O), 4.21 (q, 2H, J=7.0 Hz, O-CH_2),6.95 (m, 3H, C_6H_4 and C=$CHSO_3$), 7.41 (m, 2H, C_6H_4) and 7.77 ppm (d, J=15.6 Hz, 1H, CH=CH-SO_3); Z-isomer, 1.42 (t, J=7.1 Hz, 3H, CH_3-CH_2), 3.85 (s, 3H, O-CH_3), 4.30 (q, J=7.1 Hz, 2H, CH_2-O) and 6.35 ppm (d, J=12.0 Hz, 1H, C=$CHSO_3$); m/e (EI) 242 (M^+, 30), 132 (100), 105 (95) and 77 (70); Found C, 54.61; H, 5.85; S, 13.20; $C_{11}H_{14}O_4S$ requires C, 54.53; H, 5.82; S, 13.23.

Ethyl 2-(m-nitrophenyl)vinylsulphonate (4h)
Quantities : 148 mg (0.57 mmol) of 1a, 260 µl (0.60 mmol) of 2.3 M n-BuLi and 91 mg (0.60 mmol) of m-nitrobenzaldehyde. Yield : 136 mg (93%, E/Z=96/4). Data for 4h (E+Z): m.p. 84°C, ν_{max} (CH_2Cl_2) 3060, 2980, 1640(C=C), 1525, 1350 (SO_3), 1170 (SO_3), 1000, 915, 860, 815 and 730 cm^{-1}; δ_H E-isomer, 1.43 (t, J=7.1 Hz, 3H, CH_3), 4.31 (q, J=7.1 Hz, 2H, O-CH_2),7.01 (d, J=15.6 Hz, 1H, C=CH-SO_3), 7.69 (d, J=15.6 Hz, 1H, CH=CH-SO_3), 7.70 (m, 1H, C_6H_4), 7.92 (m, 1H, C_6H_4), 8.30 (m, 1H, C_6H_4) and 8.42 ppm (m, 1H, C_6H_4); Z-isomer, 6.64 ppm (d, J=11.6 Hz, 1H, C=CH-SO_3); m/e (EI) 257 (M^+, 20), 212 (20), 149 (100) and 102 (75); Found C, 46.75; H, 4.26; N, 5.52; S, 12.64; $C_{10}H_{11}NO_5S$ requires C, 46.69; H, 4.31; N, 5.44; S, 12.46.

Ethyl 4-phenyl-1,3-butadienesulphonate (4i)
Quantities : 172 mg (0.66 mmol), 300 µl (0.69 mmol) of 2.3 M n-BuLi ard 91 µl(0.72 mmol) of trans-cinnamaldehyde. Yield : 138 mg (88%, 1E,3E/1Z,3E=93/7). Data for 4i (E+Z): ν_{max} (film) 3060, 2980, 1625 (C=C), 1590, 1450, 1350 (SO_3), 1285, 1190, 1160(SO_3), 1000, 920, 860, 825, 790, 750 and 690 cm^{-1}; δ_H 1E,3E-isomer, 1.38 (t, J=7.1 Hz, 3H, CH_3), 4.20, (q, J=7.1 Hz, 2H, CH_2), 6.33 (d, J=14.8 Hz, 1H, C=$CHSO_3$), 6.82 (dd, J=10.4 and 15.5 Hz, 1H, Ph-CH=CH), 7.00 (d, J=15.5 Hz, 1H, Ph-CH =C), 7.35 (dd, J=10.4 and 14.8 Hz, 1H, CH=CH-SO_3) and 7.3-7.5 ppm (m, 5H, C_6H_5); 1Z,3E-isomer, 6.08 ppm (d, J=11.1 Hz, C=$CHSO_3$); m/e (CI) 239 (M^++1, 100) and 161(30); Found C, 60.04; H, 5.95; S, 13.50; $C_{12}H_{14}O_3S$ requires C, 60.48, H, 5.92; S, 13.45.

Ethyl 2,2-pentamethylenevinylsulphonate (4j)
Quantities : 2.60 g (10.0 mmol) of 1a, 15 ml of THF, 4.38 ml (10.0 mmol) of 2.3 M n-BuLi and 1.08 ml (10.5 mmol) of cyclohexanone. Yield : 2.02 g (99 %). ν_{max} (film) 3060, 2960, 2860, 1630 (C=C), 1360 (SO_3), 1270, 1160-1190 (SO_3), 1130, 1100, 1010, 920, 870, 860, 830 and 780 cm^{-1}; δ_H 1.38 (t, J=7.1 Hz, 3H, CH_3), 1.65-1.74 (m, 6H,-(CH_2)$_3$-), 2.26 (t, J=5.8 Hz, 2H, CH_2-C=C- SO_3), 2.69 (t, J=5.6 Hz, 2H, CH_2-C=C-SO_3), 4.18 (q, J=7.1 Hz, 2H, CH_2-O) and 6.03 ppm (broad s, 1H, C=CH, SO_3); m/e (EI) 204 (M^+, 5), 176(30) 95(43), 79(100), and 55(55); Found C, 52.95; H, 7.98; S, 15.71; $C_9H_{16}O_3S$ requires C,52.92; H, 7.89; S, 15.70.

Ethyl 2-phenyl-1-propenesulphonate (4k)
Quantities : 260 mg (1.0 mmol) of 1a, 435 µl (1.05 mmol) of 2.3 M n-BuLi and 130 µl (1.1 mmol) of acetophenone. Yield calculated by ^{1}H-NMR of the crude mixture : 47% acetophenone, 20% 1a and 25% of 4k (>98% E-isomer). Data for 4k (E) : δ_H 1.38 (t, J=7.1 Hz, 3H, CH_3-CH_2), 2.54 (d, J=1.2 Hz, 3H, CH_3-C=C), 4.2 (q, J=7.1 Hz, 2H, CH_2), 6.50 (q, J= 1.2 Hz, 1H, C=CH-SO_3) and 7.3-7.6 ppm (m, 5H, C_6H_5).

General procedure for the preparation of isopropyl vinylsulphonates 5
Isopropyl sulphonates 5 were prepared from phosphonate 1b following the same experimental procedure previously described for ethyl sulphonates 4.

Isopropyl 1-pentenesulphonate (5a)
Quantities : 274 mg (1.0 mmol) of 1b, 435 µl (1.0 mmol) of 2.3 M nBuLi and 92 µl (1.05mmol) of butyraldehyde. Yield : 165 mg (86%, E/Z=79/21). Data for 5a (E+Z) : ν_{max} (film) 2965, 2890, 1630(C=C), 1465, 1390-1370(SO_3), 1180-1160(SO_3), 1100, 970, 920, 880, 820, 790 and 765 cm^{-1}; δ_H E-isomer, 0.96 (t, J=7.3 Hz, 3H, CH_3-CH_2), 1.38 (d, J=6.3 Hz, 6H, CH_3-CH), 1.53 (m, 2H, CH_3-CH_2), 2.26 (dq, J=1.6 and 7.0 Hz, 2H, CH_2-CH=C), 4.75 (septuplet, J=6.3 Hz, 1H, CH-O), 6.22 (dt, J=1.6 and 15.2 Hz, 1H, C=CH-SO_3) and 6.90 ppm (dt, J=6.9 and 15.2 Hz, 1H, CH=CH-SO_3) ; Z-isomer, 0.97 (t, J=7.2 Hz, 3H, CH_3-CH_2), 1.39 (d, J=6.2 Hz, 6H, CH_3-CH), 1.53 (m, 2H, CH_3-CH_2), 2.60 (m, 2H, CH_2-, CH=C), 4.80 (m, 1H, CH-O), 6.2 (m, 1H, C=CH-SO_3) and 6.34 ppm (dt, J= 7.4 and 11.0 Hz, 1H, CH=CH-SO_3); m/e (EI) 192 (M^+,5), 177(50), 133(100) and 109(70); Found C, 50.07; H, 8.42; S, 16.79; $C_8H_{16}O_3S$ required C, 49.97; H, 8.39; S, 16.68.

Isopropyl 4-methyl-1-pentenesulphonate (5b)
Quantities : 200 mg (0.73 mmol) of 1b, 317 µl (0.73 mmol of 2.3 M n-BuLi and 83 µl (0.77 mmol) of isovaleraldehyde. Yield : 149 mg (67%, E/Z = 86/14). Data for 5b (E+Z) : ν_{max} (film) 3060, 2980, 2880, 1635 (C=C), 1460, 1390, 1350-1370 (SO_3), 1140-1160 (SO_3), 1100, 980, 920, 880, 810 and 765 cm^{-1}; δ_H E-isomer, 0.95 (d, J=6.6 Hz, 6H, CH_3-CH-CH_2), 1.38 (d, J=6.3 Hz, 6H, CH_3-CH-O), 1.82 (m, 1H, CH_3-$CH$$CH_2$), 2.17 (dt, J=1.3 and 7.2 Hz, 2H, CH_2-CH=C), 4.74 (septuplet, J=6.3 Hz, 1H, O-$CH$$CH_3$), 6.22 (dt, J=1.3 and 15.0 Hz, C=CH-SO_3) and 6.86 ppm (dt, J= 7.6 and 15.0 Hz, 1H, CH=SO_3); Z-isomer, 2.52 (t, J=7.2 Hz, 2H,-CH_2-CH=C), 4.9 (m, 1H, O-CH-CH_3) and 6.34 ppm (m, 2H, CH=CH); m/e (EI) 206 (M^+,2), 164(18), 122(100) and 55(70).

Isopropyl (E)-3,3-dimethyl-1-butenesulphonate (5c)
Quantities : 200 mg (0.73 mmol) of 1b, 317 µl(0.73 mmol) of 2.3 M n-BuLi and 84 µl(0.77 mmol) of trimethylacetaldehyde. Yield : 134 mg (89%, > 98% E-isomer), ν_{max} (CH_2Cl_2) 3080, 2980, 1630(C=C), 1475, 1340, 1370-1350 (SO_3), 1190-1165 (SO_3), 1100, 990, 920, 890, 845, 815 and 775 cm^{-1}; δ_H 1.12 (s, 9H, CH_3-C), 1.38 (d, J=6.3 Hz, H, CH_3-CH-O), 4.76 (septuplet, J=6.3 Hz, 1H, CH-O), 6.11 (d, J=15.4 Hz, 1H, C=CH-SO_3) and 6.89 ppm (d, J=15.4 Hz, 1H= CH=CH-SO_3); m/e (EI) 207 (M^++1,2), 164(10), 149(12) and 83(100).

General procedure for the preparation of tetrabutylammonium vinylsulphonates 6
Method A : From phosphonate 2a :
220 µl (0.50 mmol) of 2.3 M n-BuLi was added at -40°C under argon to a supension of dry powdered 2a (100 mg, 0.42 mmol) in 2 ml of dry THF. The resulting mixture was stirred at -15°C for 60 min., then cooled to -78°C. Freshly distilled aldehyde or ketone (1.1-1.4 equiv.) was added and the resulting mixture was stirred at -78°C for 30 min. Stirring was continued at room temperature over a period of 18 h in the case of aldehydes and 40 h in the case of ketones. After removal of the solvent, the residue was dissolved in water (10 ml) and the solution washed with dichloromethane (2X6 ml) (to remove organic soluble compounds such as the excess of the carbonyl coumpound). Then, tetrabutylammonium bisulphate (142 mg, 0.42 mmol) and lithium hydroxyde monohydrate (18 mg, 0.42 mmol) were added to the aqueous phase which was extracted with dichloromethane (5x10 ml). The organic phase was dried ($MgSO_4$) and evaporated to yield the crude sulphonates 6.
Method B : From phosphonate 2b
To a solution of 2b (238 mg, 0.50 mmol) in dry THF (4 ml) was slowly added 250 µl (0.58 mmol) of 2.3 M n-BuLi at -78°C under argon atmosphere. The mixture was vigorously strirred for 20 min. and then freshly distilled aldehyde (0.58 mmol) was added. Stirring was continued for 30 min. at -78°C. The mixture was slowly warmed to room temperature. After 18 h the residue was treated with water (12 ml) and extracted successively with ethylacetate (2X6 ml) and dichloromethane (4x8ml). The dichloromethane solutions were dried ($MgSO_4$) and evaporated to yield the crude sulphonates 6. In all cases tetrabutylammonium salts 6 were obtained as highly hygroscopic syrups. These salts did not give satisfactory elemental analyses. The tetrabutylammonium cation presents the following characteristic signals in ^{1}H-NMR, δ_H ($CDCl_3$), 1.0 (t, J=7.1 Hz, 12H, CH_3), 1.2-1.7 (m, 16H, CH_3-CH_2-CH_2-CH_2-N) and 3.1-3.4 ppm (m, 8H, CH_2-N). ^{1}H— NMR data described below for compounds 6 exclusively deal with the sulphonate part.

Tetrabutylammonium 1-butenesulphonate (6a)
Method A : Yield 96 mg (57%, E/Z=44/56) from 110 mg (0.45 mmol) of 2a, 235 µl (0.54 mmol) of 2.3 M n-BuLi and 42µl (0.58 mmol) of propionaldehyde. Method B : Yield 97 mg (68%, E/Z=40/60) from 180 mg (0.38 mmol) of 2b, 190µl (0.44 mmol) of 2.3 M n-Buli and 33 µl (0.46 mmol) of propionaldehyde. Data for 6a (E+Z) : ν_{max} (film) 2980, 2880, 1630 (C=C),1490-1460, 1380, 1250-1070 (SO_3), 1030 (SO_3), 925, 890 and 730 cm^{-1}; δ_H E-isomer, 1.0 (m, 3H, CH_3), 1.96 (m, 2H, CH_2), 6.32 (dt, J=1.2 and 15.2 Hz, 1H, C=CHSO$_3$) and 6.49 ppm (dt, J=5.8 and 15.2 Hz, 1H, CH=CH-SO_3); Z-isomer, 1.0 (m, 3H, CH_3), 2.50 (m, 2H, CH_2), 5.63 (dt, J=7.3 and 11.2 Hz, 1H, CH=CH-SO_3) and 6.28 ppm (dt, J=1,7 and 11.2 Hz, 1H, C=CH-SO_3).

Tetrabutylammonium 3-methyl-1-butenesulphonate (6b).
Method A : Yield 131 mg (80%, E/Z =45/55) from 100 mg (0.42 mmol) of 2a, 220 µl (0.50 mmol) of 2.3 M n-BuLi and 53 µl (0.58 mmol) of isobutyraldehyde. Method B : Yield 181 mg (84%, E/Z = 35/65) from 295 mg (0.55 mmol) of 2b, 260 µl (0.6 mmol) of 2.3 M n-Buli and 55 µl (0.60 mmol) of isobutyraldehyde.
Data for 6b (E+Z): ν_{max} (film) 2960, 2580; 1630(C=C), 1460-1490, 1380, 1180-1220(SO_3), 1035 (SO_3), 880 and 730 cm^{-1}; δ_H E-isomer 1.15 (d, J=6.7 Hz, 6H, CH_3), 2.50 (m, 1H, CH_3-CH), 6.30 (dd, J=1.25 and 15.3 Hz, 1H, C=CH-SO_3) and 6.54 ppm (dd, J=6.4 and 15.3 Hz, 1H, CH=CH-SO_3); Z-isomer, 1.10 (d, J=6.6 Hz, 6H, CH_3), 3.6 (m, 1H, CH_3-CH), 5.70 (dd, J=10.3 and 11.2 Hz, 1H, CH=CH-SO_3) and 6.25 ppm (dd, J=0.9 and 11.2 Hz, 1H, C=CH-SO_3).

Tetrabutylammonium 3,3-dimethyl-1-1-butenesulphonate (6c).
Method A : Yield 200 mg (90%, E/Z=92/8) from 130 mg (0.55 mmol) of 2a, 290 µl (0.67 mmol) of 2.3 M n-BuLi and 78µl (0.71 mmol) of trimethylacetaldehyde. Method B : Yield 204 mg (80%, E/Z=70/30) from 300 mg (0.63 mmol) of 2b, 310 µl(0.68 mmol) of 2.3 M n-Buli and 80µl (0.73 mmol) of trimethylacetaldehyde. Data for 6c (E+Z) ν_{max} (film) 2960, 2880, 1640 (C=C), 1490-1460, 1380, 1250, 1220-1180 (SO_3), 1040 (SO_3), 970, 880 and 700 cm^{-1}; δ_H E-isomer, 1.15 (s, 9H, CH_3), 6.01 (d, J=15.4 Hz, 1H, C=CH-SO_3) and 6.23 ppm (d, J=15.4 Hz, 1H, CH=CH-SO_3); Z-isomer, 1.15 (s, 9H, CH_3), 5.29 (d, J=12.3 Hz, 1H, CH=CH-SO_3) and 5.97 ppm (d, J=12.3 Hz, 1H, CH=CH-SO_3).

Tetrabutylammonium 2-(p-chlorophenyl)vinylsulphonate (6d)
Method A : Yield 140 mg (77%, E/Z=80/20) from 95 mg (0.4 mmol) of 2a, 215 µl (0.49 mmol) of 2.3 M n-BuLi and 67 mg (0.48 mmol) of p-chlorobenzaldehyde. Method B : Yield 118 mg (76%, E/Z=72/28) from 160 mg (0.34 mmol) of 2b, 170 µl (0.39 mmol) of 2.3 M n-Buli and 63 mg (0.45 mmol) of p-chlorobenzaldehyde. Data for 6d (E+Z) : ν_{max} (film) 2960, 2880, 1590, 1480, 1380, 1240-1180 (SO_3), 1010, 800 and 680 cm^{-1}; δ_H E-isomer, 6.95 (d, J=15.6 Hz, 1H, C=CH-SO_3), 7.20 (d, J=15.6 Hz, 1H, CH=CH-SO_3) and 7.3 ppm (m, 4H, C_6H_4); Z-isomer, 6.39 (d, J=12.7 Hz, 1H, CH=CH-SO_3), 6.58 (d, J=12.7 Hz, 1H, C=CH-SO_3), 7.22 (m, 2H, C_6H_4) and 7.87 ppm (m, 2H C_6H_4).

Tetrabutylammonium 2,3-dimethyl-1-butenesulphonate (6e)
Method A : Yield 148 mg (68%, E/Z=48/52) from 128 mg (0.54 mmol) of 2a, 270 µl (0.62 mmol) of 2.3 M n-BuLi and 66 µl (0.62 mmol) of 3-methyl-2-butanone. Data for 6e (E+Z): ν_{max} (film) 2960, 2880, 1635(C=C), 1380, 1220-1170 (SO_3) , 1030 (SO_3), 880, 800 and 740 cm^{-1}; δ_H E-isomer, 1.0 (m, 6H, CH_3-CH), 2.06 (bs, 3H, CH_3-C=C), 2.20 (m, 1H, CH_3-CH), and 6.05 ppm (bs, 1H, C=CH-SO_3); Z-isomer, 1.0 (m, 6H, CH_3-CH), 1.63(bs, 3H, CH_3-C=C), 3.88 (m, 1H, CH_3-CH) and 5.94 ppm (d, J=1.2 Hz, 1H, C=CHSO$_3$).

Tetrabutylammonium 2-phenyl-1-propenesulphonate (6f)
Method A : Yield 151 mg (69%, E/Z=88/12) from 120 mg (0.50 mmol) of 2a, 250 µl (0.58 mmol) of 2.3 M n-BuLi and 64 µl(0.55 mmol) of acetophenone. Data for 6f (E+Z) : ν_{max} (film) 2960, 2870, 1485, 1230, 1200(SO_3), 1035(SO_3), 805, 755 and 700 cm^{-1}; δ_H E-isomer, 2.49 (d, J=1.3 Hz, 3H, CH_3), 6.72 (q, J=1.3 Hz, 1H, C=CHSO$_3$) and 7.2-7.5 ppm (m, 5H, C_6H_5); Z-isomer, 2.06 (d, J=1.5 Hz, 3H, CH_3), 6.49 (q, J=1.5 Hz, 1H, C=CH-SO_3) and 7.2-7.5 ppm (m, 5H, C_6H_5).

Tetrabutylammonium 2,2-diphenylvinylsulphonate (6g)
Method A : Yield 128 mg (69%) from 100 mg (0.42 mmol) of 2a, 210 µl (0.48 mmol) of 2.3 M n-BuLi and 90 mg (0.5 mmol) of benzophenone; ν_{max} (film) 2960, 2880, 1640 (C=C), 1600, 1490, 1460, 1450, 1380, 1240, 1220-1180 (SO_3), 1035 (SO_3), 810, 760 and 700 cm^{-1}; δ_H 6.8 (s, 1H, C=CHSO$_3$) and 7.2-7.6 ppm (m, 10H, C_6H_5).

Potassium 2,2-diphenylvinylsulphonate (7)
A solution of 100 mg of 6g in 2 ml of water-methanol (1:1) was passed through a column (1.5 cm wide) containing 20 ml of wet Dowex 50x2-200 K^+-form (prepared by treating Dowex 50x2-200 H^+-form with KOH 3M for 30 min. and then washed with water-methanol 1:1 to neutrality). The column was slowly eluted with 15 ml of water-methanol (1:1). After evaporation of methanol and addition of 12 ml of water the solution was extracted with dichloromethane (3X8ml) and lyophilised to afford 49 mg (82%) of crude potassium salt 7. ν_{max} (KBr) 2980, 1610, 1590, 1490, 1440, 1240, 1200 (SO_3), 1180, 1060 (SO_3) and 820 cm^{-1}; δ_H (D_2O), 6.9 (s, 1H, C=CH-SO_3) and 7.2-7.5 ppm (m, 10H, C_6H_5).

3,3-dimethyl-1-butenesulphonic acid (8)
A solution of 266 mg of 6c (E/Z = 92/8) in 2 ml of water-methanol (1:1) was passed through a column (1.5 cm wide) containing 18 ml of wet Dowex 50x2-200 H^+-form. The column was eluted with 12 ml of methanol-water (1:1) and the eluate was lyophilised giving 120 mg (100%) of hydrated 8 (E/Z=92/8). Data for 8 : ν_{max} (CH_2Cl_2), 3500-2500 (OH), 1630 (C=C), 1370 (SO_3), 1160 (SO_3) and 910 cm^{-1}. δ_H E-isomer, 1.1 (s, 9H, CH_3), 6.23 (d, J=15.4 Hz, 1H, C=CHSO$_3$), 6.78 (d, J=15.4 Hz, 1H, CH=CH-SO_3) and 11.3 ppm (bs, SO_3H + water); Z-isomer, 1.27 (s, 9H, CH_3) and 6.04 ppm (d, J=12.1 Hz, 1H, C=CH-SO_3); m/e (CI) 165 (M^++ 1, 100) and 83(40).

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