Tetrahedron 64 (2008) 11218–11223

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Pyridine and triphenylphosphine oxide activation of sulfonyl chlorides in the syntheses of (*E*) alk-1-enyl sulfones

G. Signore, C. Malanga, R. Menicagli *

Dipartimento di Chimica e Chimica Industriale, via Risorgimento 35, 56126 Pisa, Italy

ARTICLE INFO

Article history:
Received 6 June 2008
Received in revised form 4 September 2008
Accepted 18 September 2008
Available online 26 September 2008

ABSTRACT

This paper describes efficient and new approaches to (*E*) alk-1-enyl sulfones, starting from sulfonyl chloride/pyridine or sulfonyl chloride/triphenylphosphine complexes in the presence of (*E*) di-*iso*-butyl alk-1-enyl alanes.
The use of CuCl in the presence of sulfonyl chloride/pyridine complexes or pyridine in the presence of sulfonyl chloride/triphenylphosphine complexes, respectively, results in a remarkable increase in the yields and conversions.

1. Introduction

Alk-1-enyl sulfones are useful intermediates in organic synthesis, but usually do not represent final target molecules.[1–10]

Oxidation of sulfides,[11–14] metathesis,[15] addition of *C*-nucleophiles on acetylenic sulfones,[16–18] radical addition of sulfonyl halides on alkynes,[19,20] reaction of sulfonyl derivatives with vinyl organometallic reagents (Sn,[21] Zr,[22] Hg[23]), addition/elimination reactions[24,25] and Knoevenagel condensation[26–28] represent valuable synthetic approaches to these targets.

In the organometallic chemistry field, our main area of interest, it should be noted that the reactions of alk-1-enyl derivatives of Sn need the employment of transition metal catalysts.[21] On the other hand the reactions involving alk-1-enyl mercurials require unusual reaction conditions incompatible with various functional groups.[23] The alkenylzirconocenes are not commonly available.[22]

Recently alkenyl sulfoxides were easily synthesised, starting from sulfonyl chlorides and dialkyl alkenyl alanes.[29,30] It was interesting to verify if this reactivity could be exploited to the synthesis of alkenyl sulfones too.

This idea was suggested by the formation of appreciable amount of sulfones as byproducts in the synthesis of sulfoxides and by preliminary observations on the reactivity of alkenyl alanes with sulfonyl pyridinates, recently reported.[30,31]

On the basis of this data,[30,31] it was reasonable to suppose that a sulfonyl chloride/pyridine complex could represent the key intermediate in the preparation of an alkenyl sulfone.

2. Results and discussion

In a preliminary experience, a CH_2Cl_2 solution of (*E*) di-*iso*-butyl hex-1-enyl alane was slowly (30 min) added to the preformed tosyl chloride/pyridine complex, in the same solvent to give, after hydrolysis, the desired sulfone in 47% yield along with the starting sulfonyl chloride (50%) (Scheme 1).

An almost quantitative conversion (96%) and yield (90%) could be obtained by performing a faster addition (10–20 s) of the organoalane to the sulfonyl chloride/pyridine complex. The results obtained by using different dialkyl alk-1-enyl alanes are shown in Table 1. The sulfone was the only product obtained, as confirmed by the amount of sulfonyl chloride recovered after hydrolysis.

The fluctuations in the reaction yields and conversions in alkenyl sulfones could be caused by some side reactions deactivating one or both the reagents.

The slow addition of organometallic species to the sulfonyl chloride/pyridine complex (cf. entry 1, Table 2) may release pyridine that could complex the alkyl alkenyl alane, lowering its reactivity and inhibiting the reaction. Further evidence of the inhibiting effect of pyridine was obtained by NMR analyses of the reaction mixture in which the presence of pyridine/alkenyl alane complex was detected.

This hypothesis was verified performing the reaction employing pyridinated di-*iso*-butyl hex-1-enyl alane; in this case no traces of sulfone were recovered.

The addition of a pyridine complexing agent stronger than the organoalane would increase the yields. In a further experience di-*iso*-butyl 3,3-dimethylbut-1-enyl alane was reacted with tosyl chloride/pyridine complex; when a stationary conversion ($\approx$50%) was achieved, CuCl (0.5 mol) was added.

In these reaction conditions, a remarkable increase in conversion occurred, and the sulfone was recovered in satisfactory yield (70%) (Scheme 2).

* Corresponding author. Tel.: +39 050 2219281; fax: +39 050 2219260.
E-mail address: rime@dcci.unipi.it (R. Menicagli).

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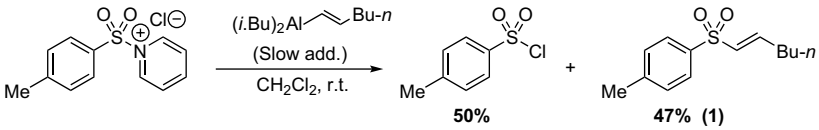
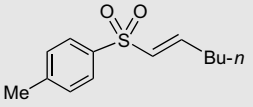
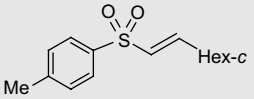
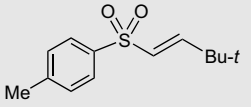
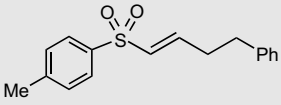
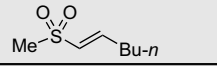
doi:10.1016/j.tet.2008.09.056



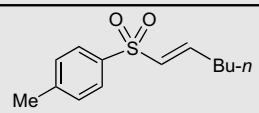
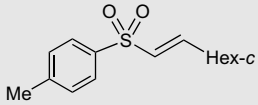
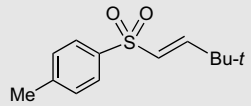
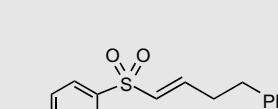
Scheme 1. Reaction of di-*iso*-butyl hex-1-enyl alane with tosyl chloride/pyridine complex.

Table 1
Reaction of dialkyl alkenyl alanes with sulfonyl chloride/pyridine complexes

Entry[a]	$(i\text{-Bu})_2$AlR	Product	Conversion[b] %	Yield[c] %
1	Bu-*n*		**1** 96	90
2	Hex-*c*		**2** 72	68
3	Bu-*t*		**3** 57	54
4	Ph		**4** 45	40
5[d]	Bu-*n*		**5** n.d.[e]	75

[a] All reactions were performed by rapid addition of the alane to a CH_2Cl_2 solution of sulfonyl chloride/pyridine complex at rt.
[b] Based on the recovered sulfonyl chloride.
[c] Calculated on the isolated, chemically pure product.
[d] Methanesulfonyl chloride was used.
[e] Work-up procedure did not allow for the recovery of the starting material.

Table 2
Effect of copper chloride on the reaction yield

Entry[a]	$(i\text{-Bu})_2$AlR	Product	Yield[b] (%)	Yield[b,c] (%)
1[d]	Bu-*n*		**1** 49	75
2	Hex-*c*		**2** 72	80
3	Bu-*t*		**3** 54	69
4	Ph		**4** 40	62

[a] All reactions were performed by rapid addition of the organoalane to the preformed TsCl/pyridine complex; the reaction was allowed to reach a stationary conversion and 0.5 equiv of copper chloride was added.
[b] GC with internal standard: *n*-nonadecane.
[c] GC after addition of CuCl.
[d] A slow addition of the organoalane was performed (cf. entry 1, Table 1).

The reaction was performed on different substrates, and the results obtained are shown in Table 2.

Increase in conversion and yield depends on the amount of copper chloride and the nature of the alkenyl chain transferred.

No traces of sulfone were obtained when the addition of CuCl was performed immediately before or after the organo alanes.

Products arising form the S–S coupling of the sulfonyl functional groups were isolated.[32,33] In these reaction conditions, the formation of R_3Al/CuCl complex promotes undesired side reactions. In our opinion the role of CuCl appears to be connected to a free pyridine-scavenging activity: during the course of the reaction, free pyridine is obtained. In order to avoid the formation of the unreactive alane/pyridinate complex, CuCl is added to subtract the pyridine and regenerate the free alane.

This behaviour seems to be confirmed by the dark blue colour solution attributable to the formation of a Cu/Py complex.

The use of a different sulfonated intermediate, such as the TsCl/$(Ph)_3PO$ complex, scarcely investigated,[34] was expected to be more effective towards organo alanes than the previously examined TsCl/Py system.

On this basis, the possibility to employ catalytic amounts of $(Ph)_3PO$ in the presence of TsCl to obtain in situ TsCl/$(Ph)_3PO$ was very intriguing.

In a first attempt (Scheme 3), TsCl was reacted with pyridinated di-*iso*-butyl hex-1-enyl alane in the presence of a catalytic amount (15%) of $(Ph)_3PO$.

Sulfone (**1**) was recovered with a partial conversion (50%) and yield (48%).

Better results were obtained when a large excess of pyridine was employed; in this case (Scheme 4) quantitative conversion of the starting TsCl and 75% yield in the desired sulfone (**1**) were obtained.

A minor amount (2 or 3 equiv) of pyridine caused a reduction in the yields (10–20%). A rationale of the mechanism is shown in the Scheme 5.

Starting from the point of view that (**B**) (Scheme 5) is unreactive[30] and (**A**) shows a different reactivity[29] towards alanes, it is possible to suppose that (**C**) represents the effective intermediate. Since the dialkyl alane chloride formed can inhibit the reaction, interacting with the Ph_3PO, the presence of pyridine in excess (15 equiv) is necessary for the formation of (**F**) restoring the free Ph_3PO.

The data obtained in the described experimental conditions, by using different substrates, are collected in Table 3.

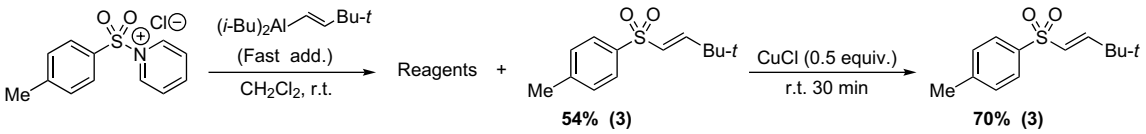
No remarkable influence of transferred chains, reaction times and yields has been observed.

The sole limitation of this procedure, compared with the previous one, is represented by the poor yield obtained when methanesulfonyl chloride is used (Table 3, entry 6).

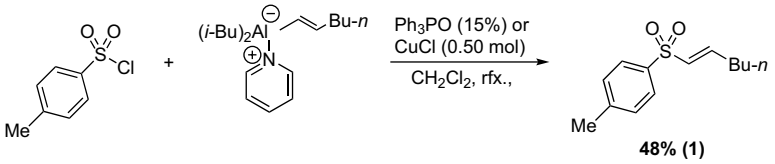
3. Conclusions

Two new methodologies for the synthesis of alkenyl sulfones are here reported; the use of sulfonyl chloride/pyridine complexes gives access to many structurally different aryl- and alkenyl sulfones.

The addition of opportune amounts of CuCl to the reaction mixture improves the yields.



Scheme 2. Increase in conversion upon addition of copper chloride.



Scheme 3. Reaction between pyridinates di-*iso*-butyl hex-1-enyl aluminium and TsCl in the presence of Ph_3PO.

Sulfonyl chloride/Ph_3PO complexes, obtained in situ from sulfonyl chlorides and catalytic amounts of Ph_3PO, are useful intermediates to obtain alkenyl sulfones in good yields (70–76%). The appreciable results obtained in this procedure represent a new synthetic approach to alkenyl sulfones and offer a new appeal towards alane chemistry.

Further studies are in progress to clarify the mechanism of the reaction.

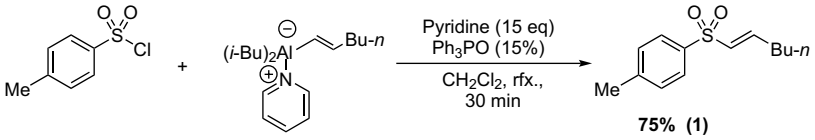
4. Experimental

4.1. General procedures and materials

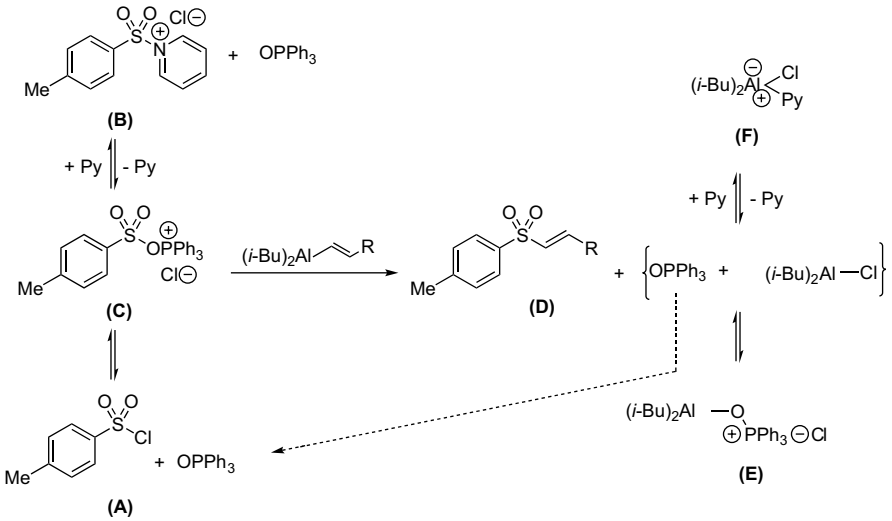
CH_2Cl_2 was refluxed on, and distilled from, P_2O_5. Di-*iso*-butyl aluminium hydride (DIBAL-H) was synthesised starting from Al(*i*-Bu)$_3$. Pyridine was purified by distillation and stored under an inert atmosphere until its use. Alkynes were distilled immediately before use. GC analyses were performed on a Perkin–Elmer 8500 instrument [ZB1 capillary column (15 m×0.25 mm), film 0.25 μm] equipped with a flame ionisation detector and a split–splitless injector, with N_2 as carrier gas. Thin layer chromatography (TLC) analyses were performed on silica gel 60 plates (Fluka) and flash chromatography purifications were carried out on silica gel 60 (Fluka, 230–400 mesh) using the eluting mixtures (v/v) reported for each case. Melting points were determined using a Kofler hot stage apparatus and are not corrected. ^1H and ^{13}C NMR (200 and 50 MHz, respectively) spectra were recorded on a Varian Gemini 200 spectrometer; all NMR data were obtained using $CDCl_3$ solutions. Chemical shifts (δ, ppm) are referred to tetramethylsilane (^1H NMR) or $CDCl_3$ (^{13}C NMR) as internal standard. Mass spectra (*m*/*z*, *I*%) were taken on a 5980 Hewlett-Packard GC instrument, equipped with an HP-5MS column (30 m×0.25 mm, film 0.25 μm) interfaced with a Hewlett-Packard 5995A instrument, with He as carrier gas. Indicated yields are reported on the isolated, chemically pure products. IR Spectra were recorded on a Perkin Elmer FT-IR, 1760X spectrophotometer.

4.2. Hydroalumination of alkynes

In a typical run, a hexane solution of DIBAL-H (1.0 mL, 1 mmol) was slowly added to a cooled (0 °C) hexane solution (25 mL) of the

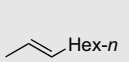
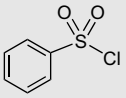
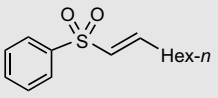
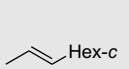
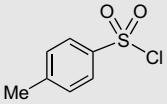
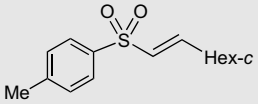
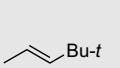
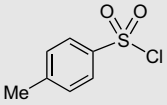
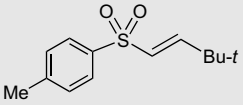
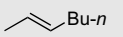
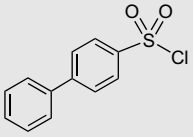
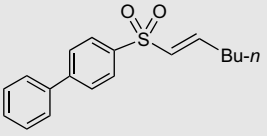
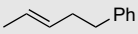
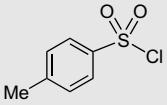
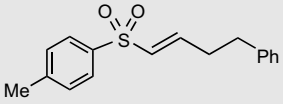
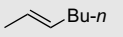
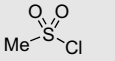
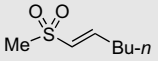
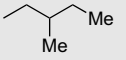
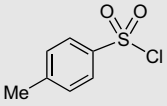
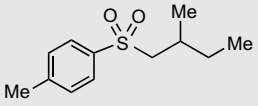


Scheme 4. Reaction between pyridinates di-*iso*-butyl hex-1-enyl aluminium and TsCl in the presence of Ph_3PO and an excess of pyridine.



Scheme 5. Proposed mechanism for the formation of (**D**).

Table 3
Reaction of pyridinated dialkyl alkenyl alanes with sulfonyl chloride

Entry[a]	$(i\text{-Bu})_2AlR$	$R'SO_2Cl$	Product		Yield[b] (%)
1				**6**	75
2				**2**	70
3				**3**	76
4				**7**	71
5				**4**	70
6				**5**	20
7[c]				**8**	63[d]

[a] All reactions were performed in CH_2Cl_2 at the reflux of the solvent, using a 20:1:0.15 pyridine/organoalane/Ph_3PO ratio.
[b] Calculated on the isolated chemically pure product.
[c] The organometallic reagent was prepared in situ starting from $AlCl_3$ and (*R*,*S*)-2-methylbutyl magnesium chloride.
[d] Maximum yield was obtained after 92 h.

suitable alkyne (1.1 mmol). The mixture was refluxed for 5 h, then cooled to room temperature. The hexane was removed in vacuo (18 mmHg), replaced with anhydrous CH_2Cl_2 (25 mL) and the solution was used without further purification.

4.3. Synthesis of alk-1-enyl sulfones using sulfonyl chloride/pyridine complexes and uncomplexed organo alanes

In a typical reaction, a three-necked flask equipped with reflux condenser, dropping funnel and magnetic stirrer was thoroughly dried and maintained under nitrogen atmosphere. The flask was charged with TsCl (380 mg, 2 mmol), CH_2Cl_2 (20 mL) and pyridine (0.16 mL, 2 mmol). The solution was stirred for 30 min and a CH_2Cl_2 solution (10 mL) of the appropriate dialkyl alk-1-enyl alane (2 mmol) was rapidly added (10 s). After stirring (4 h), the reaction mixture was hydrolysed with an aqueous solution of H_2SO_4 (1% v/v), extracted with CH_2Cl_2 and dried on anhydrous Na_2SO_4. After removal of the solvent at reduced pressure (18 mmHg), the product was further purified by flash chromatography.

4.4. Synthesis of alk-1-enyl sulfones using sulfonyl chloride/pyridine complexes and uncomplexed organo alanes in the presence of CuCl

In a typical experiment, TsCl (380 mg, 2 mmol) and CH_2Cl_2 (20 mL) were introduced under nitrogen atmosphere in a dry three-necked flask, equipped with reflux condenser, dropping funnel and magnetic stirrer. Pyridine (0.16 mL, 2 mmol) was added to the reaction mixture and the solution stirred for 30 min. The appropriate dialkyl alk-1-enyl alane (2 mmol), dissolved in CH_2Cl_2, was quickly added to the reaction mixture. The solution was stirred at room temperature until the conversion was stationary (usually overnight), and variable amounts (1–2 mmol) of CuCl were added to the reaction mixture. The blue solution was stirred at room temperature until the maximum conversion was achieved, then hydrolysed with an aqueous solution (1% v/v) of H_2SO_4. After extraction with CH_2Cl_2 the organic layer was dried (Na_2SO_4). The solvent was removed at reduced pressure (18 mmHg) and the crude product purified by flash chromatography.

4.5. Synthesis of alk-1-enyl sulfones from sulfonyl chlorides and pyridinated organo alanes in the presence of Ph_3PO

In a typical reaction, a three-necked flask equipped with a reflux condenser, a dropping funnel and a magnetic stirrer was dried and charged with 2 mmol of the appropriate organoalane in CH_2Cl_2. The solvent was removed at reduced pressure and CH_2Cl_2 (20 mL) and pyridine (0.16 mL, 2 mmol) were added to the organometallic reagent. A catalytic amount (84 mg, 0.3 mmol) of PPh_3O and TsCl (342 mg, 1.8 mmol) was added to the resulting bright yellow solution. The reaction mixture was refluxed for 1 h, cooled and hydrolysed with the addition of an aqueous solution (1% v/v) of

H_2SO_4. After extraction with CH_2Cl_2, the organic layer was dried (Na_2SO_4) and then the solvent removed at reduced pressure (18 mmHg). The product was further purified by flash chromatography.

4.6. Characterisation of the recovered sulfones

For each synthesised compound flash chromatography condition, physical state, mass spectroscopy data, ^1H and ^{13}C NMR data, IR data and elemental analysis are reported.

4.6.1. 1-((E)-Hex-1-enylsulfonyl)-4-methylbenzene (**1**)

Hexane/ethyl acetate 80:20; yellowish oil; GC–MS (*m*/*z*, *I*%): 238 ($M^{\bullet+}$,42), 223 (2), 209 (100), 157 (50), 139 (59), 91 (54), 82 (33), 67 (30); ^1H NMR 7.75 (d, *J*=7.7 Hz, 2H, *o*-Ar), 7.32 (d, *J*=7.7 Hz, 2H, *m*-Ar), 6.96 (dt, *J*=15, 6.7 Hz, 1H, SO_2–CH=*CH*–), 6.29 (dt, *J*=15 Hz, *J*′=1.5 Hz, 1H, SO_2–*CH*=CH), 2.43 (s, 3 Hz, Ar–CH_3), 2.22 (dtd, *J*=6.7 Hz, *J*′=6.7 Hz, *J*″=1.5 Hz, CH=CH–CH_2), 1.40–1.20 (m, 4H, CH_2–CH_2–CH_2–CH_3), 0.89 (t, *J*=7.3 Hz, 3H, CH_2–CH_3); ^{13}C NMR: 146.8, 144.3, 138.1 (2C), 133.2 (2C), 130.9, 127.8, 31.4, 29.9, 22.3, 21.8, 13.9; IR (cm^{-1}): 3044, 2956, 2922, 2867, 2344, 1628, 1594, 1456, 1317, 1283, 1144, 1083, 972, 833, 811, 655. Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61; O, 13.43; S, 13.45%. Found: C, 65.54; H, 7.59; S, 13.42%.

4.6.2. 1-((E)-2-Cyclohexylvinylsulfonyl)-4-methylbenzene (**2**)

Hexane/ethyl acetate 80:20; yellowish oil; GC–MS (*m*/*z*, *I*%): 264 ($M^{\bullet+}$, 11), 207 (5), 183 (24), 157 (16), 139 (26), 109 (100), 91 (33), 79 (29), 67 (53); ^1H NMR: 7.74 (d, *J*=8.1 Hz, 2H, *o*-Ar), 7.32 (d, *J*=8.1 Hz, 2H, *m*-Ar), 6.92 (dd, *J*=15.5 Hz, *J*′=6.2 Hz, 1H, SO_2–CH=*CH*–), 6.22 (dd, *J*=15.5 Hz, *J*′=1.5 Hz, 1H, SO_2–*CH*=CH–), 2.43 (s, 3H, Ar-CH_3), 2.10–2.20 (m, 1H, CH=CH–*CH*<), 1.85–1.65 (m, 5H, *c*-Hex), 1.30–1.10 (m, 5H, *c*-Hex); ^{13}C NMR: 146.1, 144.4, 138.1, 130.1(2C), 127.8(2C), 127.0, 39.1, 34.3, 28.6, 28.4, 21.8; IR (cm^{-1}): 2922, 2844, 1627, 1594, 1444, 1322, 1294, 1277, 1138, 1083, 972, 833, 811, 667, 544. Anal. Calcd for $C_{15}H_{20}O_2S$: C, 68.14; H, 7.62; O, 12.10; S, 12.13%. Found: C, 68.10; H, 7.65; S, 12.16%.

4.6.3. 1-((E)-3,3-Dimethylbut-1-enylsulfonyl)-4-methylbenzene (**3**)

Hexane/ethyl acetate 80:20; yellowish oil; GC–MS (*m*/*z*, *I*%): 238 ($M^{\bullet+}$, 3), 223 (1), 157 (8), 139 (31), 91 (20), 83 (100), 67 (16), 55 (26); ^1H NMR: 7.75 (d, *J*=8.1 Hz, 2H, *o*-Ar), 7.33 (d, *J*=8.1 Hz, 2H, *m*-Ar), 6.92 (d, *J*=15 Hz, 1H, SO_2–CH=*CH*–), 6.18 (d, *J*=15 Hz, 1H, SO_2–*CH*=CH), 2.44 (s, 3H, Ar–CH_3), 1.08 (s, 9H, C(–CH_3)$_3$); ^{13}C NMR: 146.1, 144.3, 140.1, 133.5, 130.1 (2C), 127.8 (2C), 34.3, 28.6, 21.8 (3C); IR (cm^{-1}): 2967, 2856, 2356, 1617, 1594, 1461, 1361, 1311, 1289, 1178, 1139, 1093, 978, 917, 833, 806, 756. Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61; O, 13.43; S, 13.45%. Found: C, 65.48; H, 7.64; S, 13.40%.

4.6.4. 1-((E)-4Tosylbut-3-enyl)benzene (**4**)

Hexane/ethyl acetate 80:20; white solid mp 42–45 °C; GC–MS (*m*/*z*, *I*%): 285 ($M-1^{\bullet+}$, 1), 157 (2), 130 (40), 115 (3), 91 (100), 77 (3), 65 (10); ^1H NMR: 7.95 (dt, *J*=8.4 Hz, *J*′=1.8 Hz, 2H, *o*-ArSO_2), 7.45–7.15 (m, 7H, Ar), 7.06 (dt, *J*=15.0 Hz, *J*′=6.9 Hz, 1H, SO_2–CH=*CH*–), 6.37 (dt, *J*=15.0 Hz, *J*′=1.5 Hz, 1H, SO_2–*CH*=CH–), 2.86 (t, *J*=7.0 Hz, 2H, CH_2–CH_2–Ph), 2.63 (dtd, *J*=7.0 Hz, *J*′=6.9 Hz, *J*″=1.5 Hz, 2H, CH_2–CH_2–Ph), 2.46 (s, 3H, Ar–CH_3); ^{13}C NMR: 145.4, 144.2, 140.1, 137.7, 131.4, 129.9 (2C), 128.6 (2C), 128.4 (2C), 127.6 (2C), 126.4, 33.9, 33.1, 21.6; IR (cm^{-1}): 2934, 2827, 1632, 1600, 1450, 1318, 1290, 1270, 1130, 1067, 982, 843, 801, 672, 538. Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34; O, 11.17; S, 11.20%. Found: C, 71.35; H, 6.32; S, 11.18%.

4.6.5. (E)-1-(Methylsulfonyl)hex-1-ene (**5**)

Hexane/ethyl acetate 50:50; yellowish oil; GC–MS (*m*/*z*, *I*%): 162 ($M^{\bullet+}$, 100), 143 (21), 125 (8), 111 (43), 97 (76), 83 (51), 69 (93), 55 (97), 41 (40); ^1H NMR: 7.02 (dt, *J*=14.8 Hz, *J*′=6.6 Hz, 1H, SO_2–CH=*CH*–), 6.44 (dt, *J*=14.8 Hz, *J*′=1.5 Hz, 1H, SO_2–*CH*=CH), 2.99 (s, 3H, CH_3–SO_2), 2.34 (dtd, *J*=6.6 Hz, *J*′=6.6 Hz, *J*″=1.5 Hz, 2H, SO_2–CH=CH–CH_2–), 1.60–130 (m, 4H, –CH_2–CH_2–CH_3), 0.99 (t, *J*=6.9, 3H, CH_2–CH_3); ^{13}C NMR: 149.0, 129.6, 43.1, 31.3, 29.9, 22.4, 14.0; IR (cm^{-1}): 2956, 2922, 2856, 2344, 1633, 1461, 1305, 1283, 1128, 967, 817. Anal. Calcd for $C_7H_{14}O_2S$: C, 51.82; H, 8.70; O, 19.72; S, 19.76%. Found: C, 51.79; H, 8.68; S, 19.80%.

4.6.6. 1-((E)-Oct-1-enylsulfonyl)benzene (**6**)

Hexane/ethyl acetate 80:20; yellowish oil; GC–MS (*m*/*z*, *I*%): 236 ($M^{\bullet+}$, 10), 219 (28), 207 (17), 188 (47), 149 (17), 126 (22), 124 (53), 117 (96), 110 (50), 104 (100), 91 (26), 78 (30), 69 (16), 55 (30), 41 (27); ^1H NMR: 7.70–7.40 (m, 5H, Ar), 6.62 (dt, *J*=15.4 Hz, *J*′=6.6 Hz, 1H, SO_2–CH=*CH*–), 6.23 (dt, *J*=15.4 Hz, *J*′=1.5 Hz, 1H, SO_2–*CH*=CH–), 2.22 (dtd, *J*=7.3 Hz, *J*′=7.4 Hz, *J*″=1.6 Hz, 2H, –CH=CH–CH_2), 1.50–1.20 (m, 8H, CH=CH–CH_2–(CH_2)$_4$–CH_3), 0.86 (t, *J*=6.6 Hz, 3H, CH_2–CH_3); ^{13}C NMR: 144.0, 141.3, 134.7, 130.6 (2C), 129.1 (2C), 124.2, 31.8, 31.3, 28.5, 27.8, 22.3, 13.8; IR (cm^{-1}): 3048, 2950, 2912, 2873, 2337, 1623, 1593, 1458, 1312, 1287, 1146, 978, 807. Anal. Calcd for $C_{14}H_{20}O_2S$: C, 66.63; H, 7.99; O, 12.68; S, 12.71%. Found: C, 66.61; H, 8.01; S, 12.74%.

4.6.7. 1-((E)-Hex-1-enylsulfonyl)biphenyl (**7**)

Hexane/ethyl acetate 80:20; yellowish oil; GC–MS (*m*/*z*, *I*%): 300 ($M^{\bullet+}$, 100), 271 (5), 245 (5), 217 (10), 201 (80), 169 (67), 152 (79), 141 (16); ^1H NMR: 8.05–7.95 (m, 2H, *o*-SO_2Ar), 7.85–7.80 (m, 2H, *m*-SO_2Ar), 7.75–7.65 (m, 2H, *o*-Ph), 7.60–7.50 (m, 3H, *m*+*p*-Ph), 7.11 (dt, *J*=15 Hz, *J*′=6.6 Hz, 1H, SO_2–CH=*CH*–), 6.44 (dt, *J*=15 Hz, *J*′=1.5 Hz, 1H, SO_2–*CH*=CH–), 2.34 (dtd, *J*=6.6 Hz, *J*′=7.0 Hz, *J*″=1.5 Hz, CH=CH–CH_2–), 1.60–1.30 (m, 4H, CH_2–(CH_2)$_2$–CH_3), 0.98 (t, *J*=7.0 Hz, 3H, CH_2–CH_3); ^{13}C NMR: 147.5, 146.4, 139.6, 139.5, 130.7 (2C), 129.3 (2C), 128.8 (2C), 128.3 (2C), 128.1, 127.6, 31.5, 29.9, 22.4, 14.0; IR (cm^{-1}): 3033, 2922, 2355, 1622, 1594, 1500, 1450, 1405, 1322, 1283, 1144, 1073, 956, 811, 750, 700, 657, 570, 528. Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.96; H, 6.71; O, 10.65; S, 10.67%. Found: C, 71.93; H, 6.73; S, 10.65%.

4.6.8. 1-(2-Methylbutylsulfonyl)-4-methylbenzene (**8**)

Hexane/ethyl acetate 80:20; yellowish oil; GC–MS (*m*/*z*, *I*%): 207 (2), 173 (22), 155 (72), 91 (79), 70 (100); ^1H NMR: 7.87 (d, *J*=8.0 Hz, 2H, *o*-Ar), 7.42 (d, *J*=8.0 Hz, 2H, *m*-Ar), 3.97 (dd, *J*=9.2 Hz, *J*′=6.2 Hz, 1H, SO_2–CH_2–CH), 3.88 (dd, *J*=9.2 Hz, *J*′=6.2 Hz, 1H, SO_2–CH_2–CH), 2.42 (s, 3H, Ar–CH_3), 1.40–1.30 (m, 1H, SO_2–CH_2–*CH*<), 1.30–1.20 (m, 2H, –CH–CH_2–CH_3), 0.96 (d, *J*=6.5 Hz, 3H, CH–CH_3), 0.90 (t, *J*=7.3 Hz, 3H, CH_2–CH_3); ^{13}C NMR: 130.5, 130.0 (2C), 128.1 (2C), 127.3, 75.1, 34.6, 25.7, 21.9, 16.2, 11.2; IR (cm^{-1}): 2956, 2922, 2867, 2356, 1594, 1461, 2478, 1189, 1172, 1094, 961, 844, 811, 783, 661. Anal. Calcd for: $C_{12}H_{18}O_2S$: C, 63.68; H, 8.02; O, 14.14; S, 14.17%. Found: C, 63.71; H, 8.00; S, 14.15%.

Acknowledgements

The authors thank Mr. M. Martinelli for technical assistance.

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