CAN Mediated Reaction of Aryl Sulfinates with Alkenes and Alkynes: Synthesis of Vinyl Sulfones, β-Iodovinyl Sulfones and Acetylenic Sulfones

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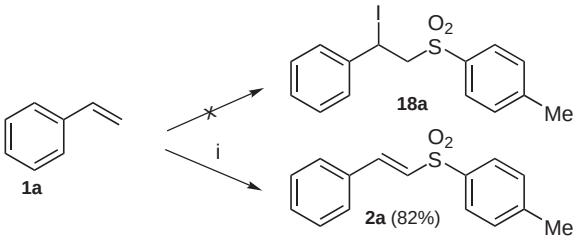
This paper is dedicated with best wishes and respectful regards to Professor Gilbert Stork.

Abstract: Cerium(IV) ammonium nitrate (CAN) mediated reaction of aryl sulfinates and sodium iodide with alkenes afforded vinyl sulfones in very good yields. Alkynes underwent similar reaction to give β-iodovinyl sulfones, which on treatment with potassium carbonate afforded the corresponding acetylenic sulfones in high yields.

Key words: cerium(IV) ammonium nitrate, sulfonylation, aryl alkenes, alkenes, acetylenes, vinyl sulfones, β-iodovinyl sulfones, acetylenic sulfones

Although cerium(IV) ammonium nitrate(CAN) has found much use in carbon-carbon bond forming reactions[1,2] the use of this reagent in carbon-heteroatom bond formation has not been studied extensively. The first report on CAN mediated carbon-heteroatom bond formation was by Trahanovsky who in 1971 observed the addition of azide to alkenes resulting in azidonitrates.[3] This reaction has been subsequently exploited in the synthesis of azidosugars which are key intermediates for aminosugars, by Lemieux et al.[4] Recently we have reported a facile CAN mediated addition of thiocyanate to styrenes[5] and indoles.[6] We have also reported the synthesis of azidocinnamates,[7] phenacylazides and phenacylthiocyanates[8] from the corresponding cinnamates and styrenes respectively. Very recently, we have observed similar CAN mediated addition of selenocyanate to styrenes.[9] In view of the success of these reactions and in the context of our recent observation of a very efficient azidoiodination,[10] we attempted the CAN mediated addition of sulfinate and iodide to alkenes with the anticipation that the reaction would lead to iodosulfones efficiently and the latter can serve as excellent precursors for vinyl sulfones. The reaction, however, proceeded to afford vinyl sulfones directly; a preliminary report of this work has been published.[11] It is noteworthy that the available methodology for vinyl sulfone synthesis mainly consists of the Horner–Emmons[12] reaction of carbonyl compounds and sulfonyl phosphoranes, the Peterson reaction,[13] and β-elimination of selenosulfones[14] or halosulfones.[15] In view of the importance of vinyl sulfones[16] as versatile intermediates in organic synthesis, the known limitations of the existing methods, and the novelty of the present work it was of interest to examine the viability of CAN mediated addition of sulfinate and iodide to alkenes as a convenient alternative to conventional vinyl sulfone syntheses. We have carried out a detailed investigation in this area and the results are presented here.

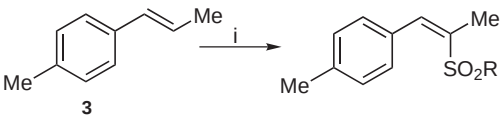
As previously reported,[11] our initial experiments involved the reaction of styrene, sodium *p*-toluenesulfinate, and sodium iodide in anhydrous acetonitrile with a solution of CAN in the same solvent under a deoxygenated atmosphere. A facile reaction occurred, but instead of the expected β-iodo sulfone, the vinyl sulfone **2a** was formed in 82% yield (Scheme 1).



Scheme 1 i. *p*-TolSO$_2$Na, NaI, CAN, anhyd CH$_3$CN, argon, r.t., 45 min.

Impressed by the efficiency of the reaction, we extended it to a number of styrenes. The reaction was found to be general and the results are summarized in Table 1.

β-Methylstyrene also showed similar reactivity as shown in Scheme 2.



Scheme 2 i. RSO$_2$Na, NaI, CAN, anhyd CH$_3$CN, argon, 0 °C, 45 min.

Preliminary investigations suggest that the sulfonylation is applicable to *n*-alkenes as well as cyclic alkenes. The reaction of oct-1-ene with *p*-toluenesulfinate in acetonitrile afforded the vinyl sulfone **4a** in 65% yield. Similar result was obtained with benzenesulfinate also and the results are shown in Scheme 3.

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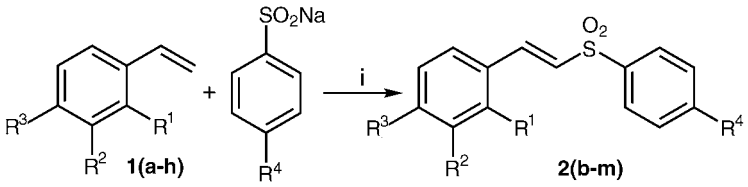
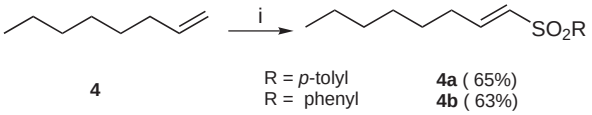
Table 1 Synthesis of Vinyl Sulfones



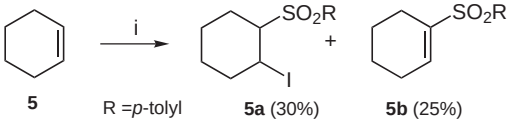
i. NaI, CAN, anhyd CH_3CN, argon, rt, 45 min

Entry	Substrate	R^1	R^2	R^3	R^4	Product	Yield (%)
1	**1a**	H	H	H	H	**2b**	76
2	**1b**	H	H	Me	Me	**2c**	83
3	**1b**	H	H	Me	H	**2d**	80
4	**1c**	H	H	Cl	Me	**2e**	88
5	**1c**	H	H	Cl	H	**2f**	85
6	**1d**	Cl	H	H	Me	**2g**	87
7	**1e**	H	NO_2	H	Me	**2h**	80
8	**1e**	H	NO_2	H	H	**2i**	81
9	**1f**	H	H	AcO	Me	**2j**	72
10	**1f**	H	H	AcO	H	**2k**	70
11	**1g**	1-naphthyl			Me	**2l**	77
12	**1h**	2-naphthyl			H	**2m**	83



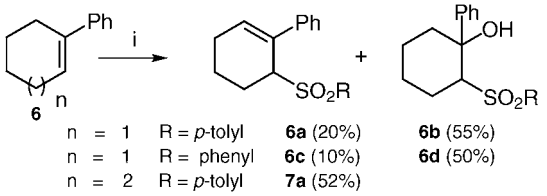
Scheme 3 i. RSO_2Na, NaI, CAN, anhyd CH_3CN, argon, 0 °C, 45 min.

Cyclohexene under similar reaction conditions afforded the vinyl sulfone **5a** along with the iodosulfone **5b** (Scheme 4).



Scheme 4 i. RSO_2Na, NaI, CAN, anhyd CH_3CN, argon, 0 °C, 45 min.

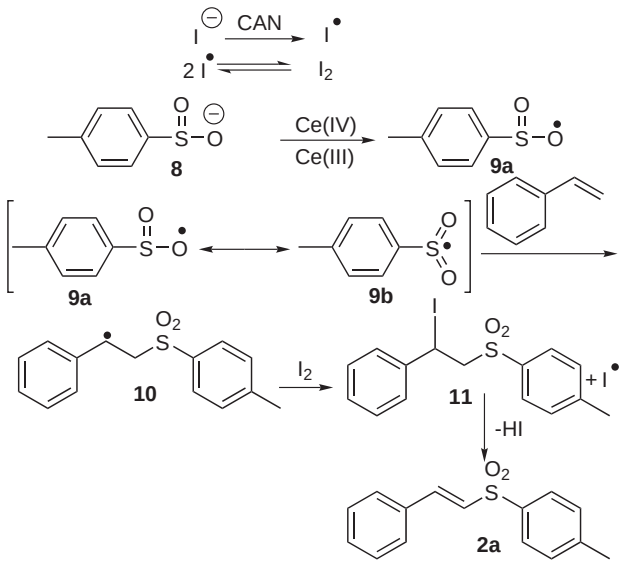
Phenylcycloalkenes, however, exhibited a different type of reactivity under similar reaction conditions (Scheme 5).



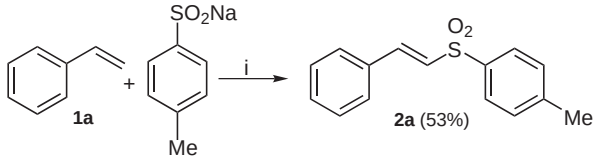
Scheme 5 i. RSO_2Na, NaI, CAN, anhyd CH_3CN, argon, 0 °C, 45 min.

Mechanistically, the formation of the vinyl sulfone **2a** can be rationalized as shown in Scheme 6. The sulfonyl radical which resonates with the oxygen centered radical generated, adds to styrene to give a benzylic radical which is trapped by molecular iodine, produced by the fast combination of two iodine radicals, to give β-iodo sulfone. Spontaneous elimination of a molecule of hydrogen iodide from this iodo sulfone would then afford the corresponding vinyl sulfone.

In order to provide support for the suggested mechanism, we carried out the reaction of styrene with sodium *p*-toluenesulfinate and iodine, which resulted in the formation of the vinyl sulfone **2a** albeit in lower yield (Scheme 7).



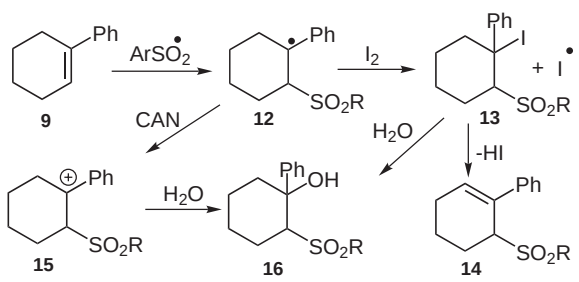
Scheme 6



Scheme 7 i. I_2, CAN, anhyd CH_3CN, r.t., 45 min.

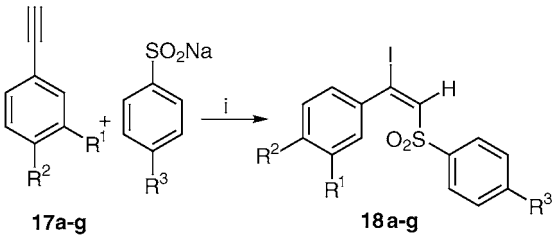
In the case of arylcycloalkenes such as **9** the initial step may also be considered to be the formation of the benzylic radical, which results from the addition of the sulfinate radical (generated by the oxidation of the sulfinate anion by CAN). This benzylic radical undergoes oxidation to the cation **15**, followed by quenching with water thus leading to the formation of **16**. Alternatively, the benzylic radical can be trapped by iodine, formed by the fast combination of iodine radicals, to form the β-iodo sulfone, which eliminates a molecule of HI to form the allyl sulfone **14** (Scheme 8). It is also likely that some of the iodo compound is undergoing solvolysis during work-up to give the alcohol **16**.

As a logical extension of this work, it was of interest to study the oxidative addition of sulfinate and iodide to alkynes. Our efforts, initiated by the reaction of phenyl acetylene with *p*-toluene sulfinate and sodium iodide in the presence of CAN in acetonitrile, afforded the β-iodovinyl sulfone in 78% yield.[17] This reaction was found to be general as attested by the results presented in Table 2.



Scheme 8

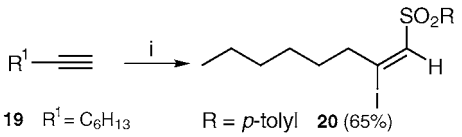
Table 2 Synthesis of β-Iodovinyl Sulfones



i. NaI, CAN, anhyd CH_3CN, argon, rt, 45 min

Entry	Substrate	R^1	R^2	R^3	Product	Yield (%)
1	**17a**	H	H	Me	**18a**	78
2	**17b**	H	H	H	**18b**	82
3	**17c**	H	Me	Me	**18c**	80
4	**17d**	H	MeO	Me	**18d**	75
5	**17e**	MeO	H	Me	**18e**	68
6	**17f**	NO_2	H	Me	**18f**	65
7	**17g**	NO_2	H	H	**18g**	62

Similarly, a normal alkyne such as 1-octyne when subjected to the usual reaction afforded the β-iodovinyl sulfone **20** as shown in Scheme 9. The product was characterized on the basis of spectroscopic data.

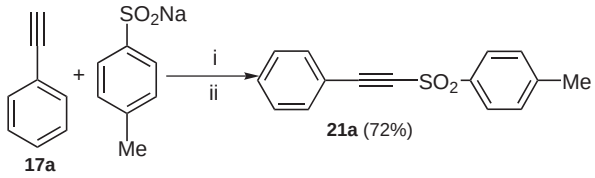


Scheme 9 i. RSO_2Na, NaI, CAN, anhyd CH_3CN, argon, r.t., 45 min.

One-pot Synthesis of Acetylenic Sulfones

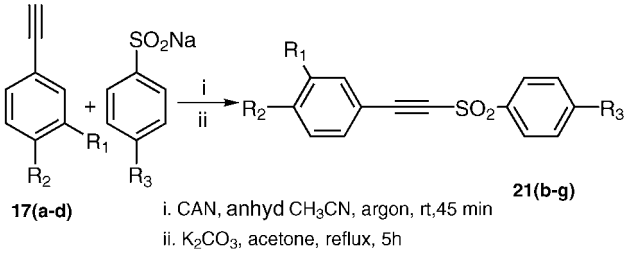
Subsequent to the synthesis of vinyl sulfones, we attempted the one pot synthesis of acetylenic sulfones.[17a,b,18] In a pilot experiment the crude product derived from the reaction between phenyl acetylene and *p*-toluenesulfinate was refluxed with potassium carbonate in anhydrous acetone for 5 hours which resulted in the formation of acetylenic sulfone **21a** in 72% yield (Scheme 10).

Similar reactions were observed with substituted phenyl acetylenes and the results are summarized in Table 3.



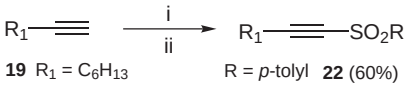
Scheme 10 i. CAN, anhyd CH_3CN, argon, r.t., 45 min. ii. K_2CO_3, acetone, reflux, 5 h.

Table 3 Synthesis of Acetylenic Sulfones



Entry	Substrate	R^1	R^2	R^3	Product	Yield (%)
1	**17b**	H	H	H	**21b**	68
2	**17c**	H	Me	Me	**21c**	75
3	**17h**	H	Me	H	**21d**	74
4	**17d**	H	MeO	Me	**21e**	75
5	**17i**	H	MeO	H	**21f**	70
6	**17e**	MeO	H	Me	**21g**	65

Similarly, 1-octyne underwent the same type of reaction as shown in Scheme 11 to afford the alkynyl sulfone **22**.



Scheme 11 i. NaI, CAN, anhyd CH_3CN, argon, rt, 45 min. ii. K_2CO_3, acetone, reflux, 5 h.

In conclusion, we have found that CAN serves as an excellent reagent for the synthesis of vinyl sulfones, β-iodovinyl sulfones and acetylenic sulfones. In view of the experimental simplicity and mild reaction conditions, the present method can be considered to be a convenient and attractive alternative to the existing methods for the synthesis of these intermediates, which are important in organic synthesis.

All reactions were carried out in oven-dried glasswares. Melting points were recorded on MEL TEMP II melting point apparatus and were uncorrected. The IR spectra were recorded on Nicolet Impact 400D FT-IR and Bomem MB series FT-IR spectrophotometers. The NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer using $CDCl_3$–CCl_4 as the solvent. Chemical shifts are reported on δ scale with TMS (^{1}H NMR) or $CDCl_3$ (^{13}C NMR) as the internal standards. Elemental analyses were carried out using Perkin-Elmer 2400 CHNS analyzer. Products were purified by gravity column chromatography on neutral alumina with hexane–EtOAc (90:10) as eluent, and all the solid compounds were recrystallized from hexane–CH_2Cl_2. CAN was purchased from Aldrich Co. and was used without further purification. Anhyd CH_3CN was used in all the experiments.

Vinyl sulfones and β-Iodovinyl Sulfones; General Procedure

A mixture of of styrene (1 mmol), sodium *p*-toluenesulfinate (1.2 mmol) and NaI (1.2 mmol) in anhyd CH_3CN (10 mL) was treated with CAN (1.37 g, 2.5 mmol) in anhyd CH_3CN (15 mL) under an argon atmosphere for 45 min. After completion of the reaction, the reaction mixture was washed with H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with sat. $Na_2S_2O_3$ soln (3 mL), brine (2 mL), and dried over anhyd Na_2SO_4. The solvent was removed in vacuo using a rotary evaporator and the residue chromatographed to afford the product.

Acetylenic Sulfones; General Procedure

To a mixture of phenylacetylene (1 mmol), sodium *p*-toluenesulfinate (1.2 mmol) and NaI (1.2 mmol) in anhyd CH_3CN (5 mL) was added a solution of CAN (2.5 mmol) in the same solvent (10 mL) under an argon atmosphere. After the completion of the reaction, the reaction mixture was extracted with CH_2Cl_2, the CH_2Cl_2 layer was separated, washed with brine (50 mL) and dried over anhyd Na_2SO_4. The residue after removing the solvent was refluxed with K_2CO_3 (2 mmol) in anhyd acetone (5 mL) for about 3 h. After the completion of the reaction, the reaction mixture was washed with H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with brine (2 mL) and dried over anhyd $Na_2S_2O_3$. The solvent was removed in vacuo using a rotary evaporator and the residue chromatographed to afford the product.

1-(4′-Methylphenylsulfonyl)-2-phenylethene (2a)[19]

Mp 119–121 °C.

1-(4′-Methylphenylsulfonyl)-2-(4′-methylphenyl)ethene (2c)[20]

Mp 154–156 °C.

1-(4′-Methylphenylsulfonyl)-2-(4′-chlorophenyl)ethene (2e)[20]

Mp 138–140 °C.

1-(4′-Methylphenylsulfonyl)-2-(2′-chlorophenyl)ethene (2g)

Mp 105–107 °C .

IR (KBr): 3058, 3027, 1647, 1611, 1592, 1491, 1465, 1323, 1299, 1145, 1089, 1029, 810, 748 cm^{-1}.

^{1}H NMR: δ = 8.03 (d, 1 H, olefinic, *J* = 15.4 Hz), 7.83 (d, 2 H, ArH, *J* = 8.1 Hz), 7.50 (d, 1 H, ArH, *J* = 7.6 Hz), 7.42 (d, 1 H, ArH, *J* = 7.7 Hz), 7.34 (d, 1 H, ArH, *J* = 8.0 Hz), 7.32–7.22 (m, 3 H, ArH), 6.86 (d, 1 H, olefinic, *J* = 15.4 Hz), 2.45 (s, 3 H, CH_3).

^{13}C NMR: δ = 144.40, 137.80, 137.59, 135.37, 131.72, 130.96, 130.63, 130.41, 130.01, 128.25, 127.99, 127.14, 21.68.

Anal. Calcd for $C_{15}H_{13}ClO_2S$: C, 61.53; H, 4.48; S, 10.95. Found: C, 62.05; H, 4.57; S, 11.13.

1-(4′-Methylphenylsulfonyl)-2-(3′-nitrophenyl)ethene (2h)[20]

Mp 142–145 °C.

1-(4′-Methylphenylsulfonyl)-2-(1-naphthyl)ethene (2l)

Mp 132–134 °C.

IR (KBr): 3063, 1613, 1310, 1155, 1088, 973, 852, 804, 744, 676, 555 cm^{-1}.

^{1}H NMR: δ = 8.47 (d, 1 H, olefinic, *J* = 15.1 Hz), 8.16 (d, 1 H, ArH, *J* = 8.1 Hz), 7.90-7.85 (m, 4 H, ArH), 7.65–7.41 (m, 5 H, ArH), 7.35

(d, 1 H, ArH, *J* = 8.0 Hz), 6.92 (d, 1 H, olefinic, *J* = 15.1 Hz), 2.44 (s, 3 H, CH_3).

^{13}C NMR: δ = 144.26, 138.92, 137.92, 133.72, 131.34, 130.18, 130.01, 129.73, 128.85, 127.89, 127.31, 126.50, 125.63, 125.28, 123.16, 21.68.

Anal. Calcd for $C_{19}H_{16}O_2S$: C, 74.00; H, 5.23; S, 10.40. Found: C, 74.36; H, 5.88; S, 10.54.

1-(4′-Methylphenylsulfonyl)-2-(4′-acetoxyphenyl)ethene (2j)
Mp 127–129 °C.

IR (KBr): 3049, 1769, 1613, 1506, 1371, 1317, 1209, 1142, 1088, 987, 919, 804, 589 cm^{-1}.

^{1}H NMR: δ = 7.80 (d, 2 H, ArH, *J* = 8.1 Hz), 7.61 (d, 1 H, olefinic, *J* = 15.4 Hz), 7.48 (d, 2 H, ArH, *J* = 8.5 Hz), 7.33 (d, 2 H, ArH, *J* = 8.0 Hz), 7.11 (d, 2 H, ArH, *J* = 8.5 Hz), 6.78 (d, 1 H, olefinic, *J* = 15.4 Hz), 2.44 (s, 3 H, $OCOCH_3$), 2.29 (s, 3 H, CH_3).

^{13}C NMR: δ = 168.50, 152.61, 144.14, 140.60, 137.83, 130.07, 129.86, 129.60, 127.88, 127.70, 122.26, 21.57, 21.00.

Anal. Calcd for $C_{17}H_{16}O_4S$: C, 64.54; H, 5.10; S, 10.14. Found: C, 64.43; H, 5.53; S, 10.22.

1-Phenylsulfonyl-2-phenylethene (2b)[19c,21]
Mp 70–71 °C.

1-Phenylsulfonyl-2-(4′-methylphenyl)ethene (2d)[20]
Mp 132–135 °C.

1-Phenylsulfonyl-2-(4′-chlorophenyl)ethene (2f)[20,21b]
Mp 129–130 °C

1-Phenylsulfonyl-2-(3′-nitrophenyl)ethene (2i)[21b]
Mp 126–128 °C.

1-Phenylsulfonyl-2-(2-naphthyl)ethene (2m)
Mp 99–101 °C.

IR (KBr): 3052, 1611, 1595, 1479, 1448, 1306, 1289, 1142, 1067, 964, 846 cm^{-1}.

^{1}H NMR: δ = 7.87–7.84 (m, 2 H, ArH), 7.73–7.64 (m, 4 H, ArH), 7.63 (d, 1 H, olefinic, *J* = 15.2 Hz), 7.45–7.34 (m, 6 H, ArH), 6.84 (d, 1 H, olefinic, *J* = 15.3 Hz).

^{13}C NMR: δ = 142.29, 140.86, 134.32, 133.14, 132.93, 130.74, 129.65, 129.18, 128.75, 128.53, 127.66, 127.60, 127.54, 127.35, 126.80, 123.33.

Anal. Calcd for $C_{18}H_{14}O_2S$: C, 73.44; H, 4.79; S, 10.89. Found: C, 73.71; H, 4.88; S, 10.83.

1-Phenylsulfonyl-2-(4′-acetoxyphenyl)ethene (2k)
Mp 126–127 °C.

IR (KBr): 3049, 1755, 1613, 1506, 1445, 1378, 1317, 1135, 1088, 1013, 973, 818, 690 cm^{-1}.

^{1}H NMR: δ = 7.94–7.92 (m, 2 H, ArH), 7.68–7.56 (m, 3 H, ArH), 7.57 (d, 1 H, olefinic, *J* = 15.1 Hz), 7.50 (d, 2 H, ArH, *J* = 8.5 Hz), 7.12 (d, 2 H, ArH, *J* = 8.5 Hz), 6.79 (d, 1 H, olefinic, *J* = 15.3 Hz), 2.30 (s, 3 H, $OCOCH_3$).

^{13}C NMR: δ = 168.53, 152.71, 141.19, 133.24, 129.66, 129.23, 127.62, 127.52, 122.29, 20.99.

1-(4′-Methylphenylsulfonyl)-1-methyl-2-(4′-methylphenyl)ethene(3a)
Mp 113–115 °C.

IR (KBr): 3036, 2982, 2928, 1600, 1445, 1303, 1155, 1108, 1081, 966, 818, 744, 663, cm^{-1}.

^{1}H NMR: δ = 7.80–7.74 (m, 3 H, ArH), 7.33–7.27 (m, 4 H, ArH, CH=C*H*), 7.20–7.15 (m, 2 H, ArH), 2.44 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 2.09 (s, 3 H, CH_3).

^{13}C NMR: δ = 143.92, 139.42, 137.01, 136.51, 131.11, 129.76, 129.71, 129.38, 128.28, 127.95, 21.64, 21.42, 13.26.

1-Phenylsulfonyl-1-methyl-2-(4′-methylphenyl)ethane (3b)[21a,22]
Mp 89–90 °C.

1-(4′-Methylphenylsulfonyl)-oct-1-ene (4a)[19b,c]
Colorless viscous liquid.

1-(Phenylsulfonyl)-oct-1-ene (4b)[20]
Colorless viscous liquid.

1-(4′-Methylphenylsulfonyl)-2-iodocyclohexane (5a) and 1-(4′-Methylphenylsulfonyl)-cyclohex-1-ene (5b)[19a,b,21b]
5a Colorless viscous liquid.

5b Colorless crystalline solid, recrystallized, mp 79–80 °C.

2-(4′-Methylphenylsulfonyl)-1-phenyl-cyclohex-1-ene (6a) and 2-(4′-Methylphenylsulfonyl)-1-hydroxyphenylcyclohexane (6b)
6a
Mp 127–130 °C.

IR (KBr): 3029, 2948, 2908, 1607, 1452, 1297, 1142, 1088, 912, 771, 730 cm–$^{-1}$.

^{1}H NMR: δ = 7.50-7.48 (m, 2 H, ArH), 7.38–7.16 (m, 2 H, ArH), 7.04–6.95 (m, 5 H, ArH), 6.21–6.20 (m, 1 H, olefinic), 4.32 (m, 1 H, $CHSO_2$), 2.82–2.77 (m, 1 H, CH_2), 2.35–2.14 (m, 3 H, CH_2), 2.30 (s, 3 H, CH_3), 1.92–1.89 (m, 1 H, CH_2), 1.87–1.76 (m, 1 H, CH_2).

^{13}C NMR :δ 143.48, 137.17, 135.07, 131.24, 129.05, 128.70, 128.04, 127.19, 126.55, 126.39, 62.78, 25.57, 23.49, 21.50, 17.45.

6b
Mp157–159 °C.

IR (KBr): 3494, 2942, 2867, 1607, 1449, 1310, 1290, 1135, 1081, 973, 746 cm^{-1}.

^{1}H NMR: δ = 7.63–7.61 (m, 2 H, ArH), 7.48 (d, 2 H, ArH, *J* = 8.1 Hz), 7.25–7.23 (m, 3 H, ArH), 7.19 (d, 2 H, ArH, *J* = 8.1 Hz), 4.33 (br s, 1 H, OH, exchangeable with D_2O), 3.60–3.55 (m, 1 H, $CHSO_2$), 2.41 (s, 3 H, CH_3), 2.33–1.35 (m, 8 H, CH_2).

^{13}C NMR: δ = 144.03, 143.76, 137.10, 129.51, 128.30, 127.84, 127.49, 127.12, 74.98, 73.49, 25.30, 24.38, 21.58, 21.33.

Anal. Calcd for $C_{19}H_{22}O_3S$: C, 69.06; H, 6.71; S, 9.70. Found: C, 69.03; H, 7.06; S, 9.65.

2-(Phenylsulfonyl)-1-phenyl-1-cyclohexene (6c) and 2-(Phenylsulfonyl)-1-hydroxy-1-phenylcyclohexane (6d)
6c
Mp 86–89 °C.

IR (KBr) 3063, 2948, 1445, 1297, 1135, 1081, 724, 697, 622 cm^{-1}.

^{1}H NMR: δ 7.50–7.47 (m, 2 H, ArH), 7.38–7.33 (m, 1 H, ArH), 7.21–7.16 (m, 2 H, ArH), 7.02–7.00 (m, 5 H, ArH), 6.22–6.21 (m, 1 H, olefinic), 4.36 (m, 1 H, $CHSO_2$), 2.85–2.80 (m, 1 H, CH_2), 2.42–2.10 (m, 3 H, CH_2), 1.95–1.89 (m, 1 H, CH_2), 1.83–1.73 (m, 1 H, CH_2).

^{13}C NMR: δ = 140.84, 140.21, 134.98, 132.67, 131.11, 128.50, 128.34, 128.02, 126.80, 126.30, 62.72, 25.47, 23.36, 17.43.

6d
Mp 131–133 °C.

IR (KBr): 3505, 3062, 2943, 2862, 1495, 1447, 1301, 1139, 1082, 1035, 971, 763, 688 cm^{-1}.

^1H NMR: δ = 7.59–7.51 (m, 5 H, ArH), 7.42–7.37 (m, 2 H, ArH), 7.25–7.21 (m, 3 H, ArH), 4.18 (br s, 1 H, OH, exchangeable with D_2O), 3.64–3.59 (m, 1 H, $CHSO_2$), 2.34–1.45 (m, 8 H, CH_2).

^{13}C NMR: δ = 143.69, 139.99, 132.94, 128.77, 128.03, 127.78, 127.50, 126.97, 74.65, 73.09, 25.01, 24.02, 21.21.

1-(4′-Methylphenylsulfonyl)-2-phenyl-cyclohept-1-ene (7a)
Mp 122–124 °C.

IR (KBr): 3029, 2921, 2861, 1600, 1452, 1317, 1290, 1142, 1088, 852, 771, 676 cm^{-1}.

^1H NMR: δ = 7.55 (d, 2 H, ArH, *J* = 8.2 Hz), 7.06–7.03 (m, 5 H, ArH), 6.93–6.90 (m, 2 H, ArH), 6.30–6.25 (m, 1 H, olefinic), 4.39–4.36 (m, 1 H, $CHSO_2$), 2.91–2.82 (m, 1 H, CH_2), 2.63–2.57 (m, 1 H, CH_2), 2.46–2.36 (m, 1 H, CH_2), 2.30 (s, 3 H, CH_3), 1.99–1.85 (m, 3 H, CH_2), 1.54–1.35 (m, 2 H, CH_2).

^{13}C NMR: δ = 144.30, 143.79, 139.05, 136.67, 135.53, 129.20, 128.69, 127.83, 126.35, 126.28, 69.65, 27.42, 26.79, 26.13, 25.55, 21.50.

Anal. Calcd for $C_{20}H_{22}O_2S$: C, 73.58; H, 6.79; S, 8.35. Found: C, 73.70; H, 6.82; S, 9.84.

1-(4′-Methylphenylsulfonyl)-2-iodo-2-phenylethene (18a)[23]
Mp 77–79 °C.

1-Phenylsulfonyl-2-iodo-2-phenylethene (18b)[24]
Colorless viscous liquid.

1-(4′-Methylphenylsulfonyl)-2-iodo-2-(4′-methylphenyl)ethene (18c)
Mp 114–116 °C.

IR (KBr): 3043, 1607, 1499, 1337, 1155, 1088, 825, 791, 744, 676 cm^{-1}.

^1H NMR: δ 7.49 (d, 2 H, ArH, *J* = 8.2 Hz), 7.28 (s, 1 H, olefinic), 7.21–7.15 (m, 4 H, ArH), 7.09 (d, 2 H, ArH, *J* = 8.1 Hz), 2.40 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3).

^{13}C NMR: δ = 144.35, 140.72, 140.09, 136.89, 129.61, 128.54, 127.92, 127.90, 114.65, 21.66, 21.50.

Anal. Calcd for $C_{16}H_{15}IO_2S$: C, 48.25; H, 3.80; S, 8.05. Found: C, 48.21; H, 3.58; S, 7.58.

1-(4′-Methylphenylsulfonyl)-2-iodo-2-(4′-methoxyphenyl)-ethene (18d)
Mp 134–136 °C.

IR (KBr): 2962, 2908, 1681, 1600, 1573, 1317, 1263, 1182, 1142, 1034, 993, 818, 764.

^1H NMR: δ = 7.49 (d, 2 H, ArH, *J* = 8.3 Hz), 7.25 (s, 1 H, olefinic), 7.23–7.18 (m, 4 H, ArH), 6.78 (d, 2 H, ArH, *J* = 8.4 Hz), 3.83 (s, 3 H, OCH_3), 2.40 (s, 3 H, CH_3).

^{13}C NMR: δ = 160.84, 144.30, 142.38, 140.40, 137.75, 131.88, 130.05, 129.62, 127.90, 113.23, 55.31, 21.66.

1-(4′-Methylphenylsulfonyl)-2-iodo-2-(3′-methoxyphenyl)-ethene (18e)
Mp 104–106 °C.

IR (KBr):3043, 2996, 1593, 1479, 1324, 1236, 1155, 1081, 818, 737, 649 cm^{-1}.

^1H NMR: δ = 7.52 (d, 2 H, ArH, *J* = 8.1 Hz), 7.33–7.32 (m, 2 H, ArH), 7.29 (s, 1 H, olefinic), 7.21 (d, 2 H, ArH, *J* = 8.0 Hz), 6.74–6.71 (m, 2 H, ArH), 3.75 (s, 3 H, OCH_3), 2.40 (s, 3 H, CH_3).

^{13}C NMR: δ = 158.30, 144.73, 142.02, 140.11, 136.66, 133.55, 130.20, 129.71, 128.40, 128.19, 117.23, 113.80, 55.51, 21.65.

1-(4′-Methylphenylsulfonyl)-2-iodo-2-(3′-nitrophenyl)ethene (18f)
Mp 156–157 °C.

IR (KBr): 3090, 3049, 1610, 1533, 1351, 1297, 1155, 1088, 912, 858, 751, 649 cm^{-1}.

^1H NMR :δ = 8.20–8.17 (m, 1 H, ArH), 7.89 (s, 1 H, ArH), 7.67–7.65 (m, 1 H, ArH), 7.58–7.49 (m, 3 H, ArH), 7.41 (s, 1 H, olefinic), 7.27–7.24 (m, 2 H, ArH), 2.41 (s, 3 H, CH_3).

^{13}C NMR: δ = 147.57, 145.26, 143.21, 141.27, 137.07, 133.55, 131.40, 130.06, 129.19, 127.89, 124.24, 122.31, 108.84, 21.63.

1-Phenylsulfonyl-2-iodo-2-(3′-nitrophenyl)ethene (18g)
Mp 117–119 °C.

IR (KBr): 3083, 3043, 1526, 1351, 1297, 1155, 1094, 912, 831, 757, 690 cm^{-1}.

^1H NMR: δ = 8.20–8.18 (m, 2 H, ArH), 7.94 (s, 1 H, ArH), 7.65–7.46 (m, 6 H, ArH), 7.42 (s, 1 H, olefinic).

^{13}C NMR: δ = 147.62, 142.78, 141.22, 140.02, 134.02, 133.52, 129.45, 129.23, 127.84, 124.36, 122.37, 109.50.

1-(4′-Methylphenylsulfonyl)-2-iodo-oct-1-ene (20)[23,24]
Colorless viscous liquid.

1-(4′-Methylphenylsulfonyl)-2-phenylethyne (21a)[23,25a]
Mp 78–79 °C.

IR (KBr): 3036, 2180, 1593, 1492, 1337, 1162, 1094, 852, 771, 697, 548 cm^{-1}.

^1H NMR: δ = 7.94 (d, 2 H, ArH, *J* = 8.1 Hz), 7.50–7.42 (m, 3 H, ArH), 7.39–7.32 (m, 4 H, ArH), 2.46 (s, 3 H, CH_3).

^{13}C NMR: δ = 145.27, 139.15, 132.72, 131.44, 130.01, 128.68, 127.56, 118.10, 92.76, 85.85, 21.77.

Anal. Calcd for $C_{15}H_{12}O_2S$: C, 70.29; H, 4.72; S, 12.51. Found: C, 70.43; H, 4.93; S, 12.60.

1-Phenylsulfonyl-2-phenylethyne (21b)[25]
Mp 68–69 °C.

1-(4′-Methylphenylsulfonyl)-2-(4′-methylphenyl)ethyne (21c)[25a]
Mp 103–105 °C.

1-Phenylsulfonyl-2-(4′-methylphenyl)ethyne (21d)
Mp 87–88 °C.

IR (KBr): 3056, 2180, 1613, 1580, 1452, 1344, 1169, 1088, 865, 811, 724 cm^{-1}.

^1H NMR: δ = 8.08–8.05 (m, 2 H, ArH), 7.67–7.56 (m, 3 H, ArH), 7.40 (d, 2 H, ArH, *J* = 8.0 Hz), 7.16 (d, 2 H, ArH, *J* = 7.9 Hz), 2.37 (s, 3 H, CH_3).

^{13}C NMR: δ = 142.26, 142.10, 133.94, 132.69, 129.42, 129.27, 127.35, 114.80, 93.90, 85.10, 21.77.

Anal. Calcd for $C_{15}H_{12}O_2S$: C, 70.29; H, 4.72; S, 12.51. Found: C, 70.33; H, 4.76; S, 12.70.

1-(4′-Methylphenylsulfonyl)-2-(4′-methoxyphenyl)ethyne (21e)
Mp 123–124 °C.

IR (KBr): 2955, 2894, 2362, 1674, 1607, 1317, 1270, 1182, 1142, 1000, 845, 771, 683 cm^{-1}.

^1H NMR: δ = 7.91 (d, 2 H, ArH, *J* = 8.2 Hz), 7.41 (d, 2 H, ArH, *J* = 8.9 Hz), 7.35 (d, 2 H, ArH, *J* = 8.0 Hz), 6.83 (d, 2 H, ArH, *J* = 8.9 Hz), 3.79 (s, 3 H, OCH_3), 2.43 (s, 3 H, CH_3).

^{13}C NMR: δ = 161.94, 144.87, 139.23, 134.40, 129.76, 127.16, 114.26, 109.36, 93.78, 84.88, 55.22, 21.52.

1-Phenylsulfonyl-2-(4′-methoxyphenyl)ethyne (21f)[25b]
Mp 103–105 °C.

1-(4′-Methylphenylsulfonyl)-2-(3′-methoxyphenyl)ethyne (21g)
Mp 129–130 °C.

IR (KBr): 2962, 2908, 1688, 1607, 1330, 1263, 1155, 1182, 1034, 993, 764 cm^{-1}.

^1H NMR: δ = 7.93 (d, 2 H, ArH, *J* = 8.0 Hz), 7.37 (d, 2 H, ArH, *J* = 8.0 Hz), 7.24 (t, 1 H, ArH, *J* = 7.8 Hz), 7.08 (d, 2 H, ArH, *J* = 7.4 Hz), 6.99 (m, 2 H, ArH), 3.77 (s, 3 H, OCH_3), 2.46 (s, 3 H, CH_3).

^{13}C NMR: δ = 159.26, 145.17, 138.95, 129.89, 129.70, 127.43, 125.07, 118.78, 118.19, 116.95, 92.57, 85.34, 55.22, 21.65.

1-(4′-Methylphenylsulfonyl)-oct-1-yne (22)
Colorless viscous liquid.

IR (neat): 2955, 2935, 2867, 1600, 1472, 1344, 1169, 1094, 818, 690, 629, 562 cm^{-1}.

^1H NMR: δ = 7.86 (d, 2 H, ArH, *J* = 8.2 Hz), 7.34 (d, 2 H, ArH, *J* = 8.1 Hz), 6.98 (s, 1 H, olefinic), 2.46 (s, 3 H, CH_3), 2.34 (t, 2 H, CH_2, *J* = 7.1 Hz), 1.59–1.49 (m, 2 H, CH_2), 1.37–1.17 (m, 6 H, CH_2), 0.88–0.83 (m, 3 H, CH_3).

^{13}C NMR: δ = 144.73, 139.38, 129.71, 127.22, 96.86, 78.56, 30.96, 28.32, 26.89, 22.27, 21.60, 18.33, 13.85.

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