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LETTERS

An efficient one-pot synthesis of vinyl sulphones via CAN mediated reaction of aryl sulphinates and alkenes[†]

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Abstract—Cerium(IV) ammonium nitrate mediated reaction of sodium arene sulphinate and sodium iodide with alkenes afforded vinyl sulphones in very good yields. © 2001 Elsevier Science Ltd. All rights reserved.

Oxidative addition of soft anions to alkenes mediated by cerium(IV) ammonium nitrate (CAN) has recently been shown to offer a practical method for carbon–heteroatom (C–N, C–S and C–Br)[1–4] bond formation. In view of the success of these reactions and the very efficient azidoiodination,[5] it was anticipated that CAN mediated addition of sulphinate and iodine to alkenes would lead to iodosulphones efficiently. In the event, a facile reaction leading to the vinyl sulphone, presumably via the expected iodosulphone, occurred. It is noteworthy that the available methodology for vinyl sulphone synthesis mainly consists of Horner–Emmons reactions of carbonyl compounds and sulphonyl phosphoranes,[6] Peterson reactions[7] and β-elimination of selenosulphones[8] or halosulphones.[9] In view of the importance of vinyl sulphones[10] as versatile intermediates in organic synthesis and the known limitations of existing methods, it was of interest to examine the above reaction as a convenient alternative to the latter.

With the stated objective, a mixture of styrene, *p*-toluene sulphinate and sodium iodide in acetonitrile was treated with a solution of CAN. A facile reaction occurred, and the vinyl sulphone **3** was formed in 82% yield (Scheme 1).[13]

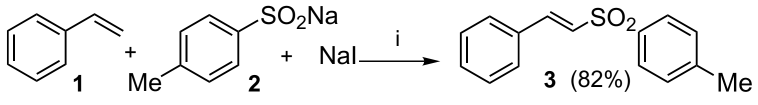
Impressed by the efficiency of the reaction we extended the studies to involve a number of aryl alkenes. The reaction was found to be general and the results are summarized in Table 1.

In addition to styrenes the reaction appears to be applicable to *n*-alkenes as illustrated in Scheme 2.

As a logical extension of this work, it was of interest to study the oxidative addition of sulphinate and iodine to alkynes. Phenylacetylene on reaction with *p*-toluene sulphinate and sodium iodide in the presence of CAN in acetonitrile afforded the iodo vinyl sulphone[11] in 78% yield (Scheme 3).

This reaction also appears to be general as attested by the results presented in Table 2.

Mechanistically, the reaction may be considered to proceed as follows. An oxygen centered radical generated by the oxidation of sulphinate with CAN resonates with a sulphonyl radical.[12] This radical 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 vinyl sulphone. Spontaneous



i. CAN, dry CH_3CN, argon, rt, 45 min

Scheme 1.

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[†] Dedicated with best wishes to Professor Dr. Rolf Gleiter on the occasion of his 65th birthday.

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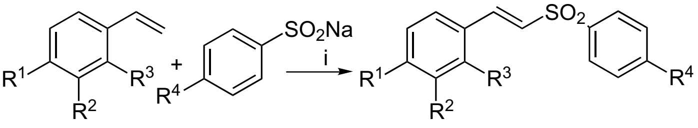
Table 1. Sulphinylation of styrenes

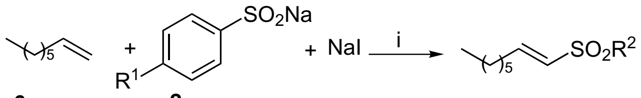


4 (a-i) **2** R^4 = Me,H **5 (a-i)**

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

Entry	Substrate	R^1	R^2	R^3	R^4	Product	Yield (%)[a]
1	**4a**	H	H	H	H	**5a**	76
2	**4b**	Me	H	H	Me	**5b**	83
3	**4c**	Me	H	H	H	**5c**	80
4	**4d**	H	NO_2	H	Me	**5d**	80
5	**4e**	Cl	H	H	Me	**5e**	88
6	**4f**	Cl	H	H	H	**5f**	85
7	**4g**	OAc	H	H	Me	**5g**	72
8	**4h**	1-Naphthyl			H	**5h**	76
9	**4i**	1-Naphthyl			Me	**5i**	70

[a] Isolated yield.

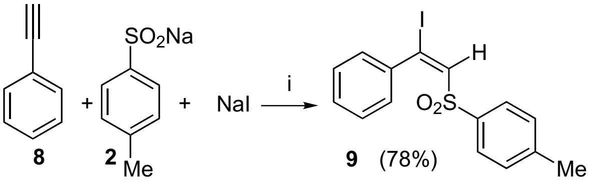


6 **2** **7**

i. CAN, dry CH_3CN, argon, rt, 45 min

R^1 = Me **2a** R^2 = phenyl **7a** (65%)
R^1 = H **2b** R^2 = tolyl **7b** (55%)

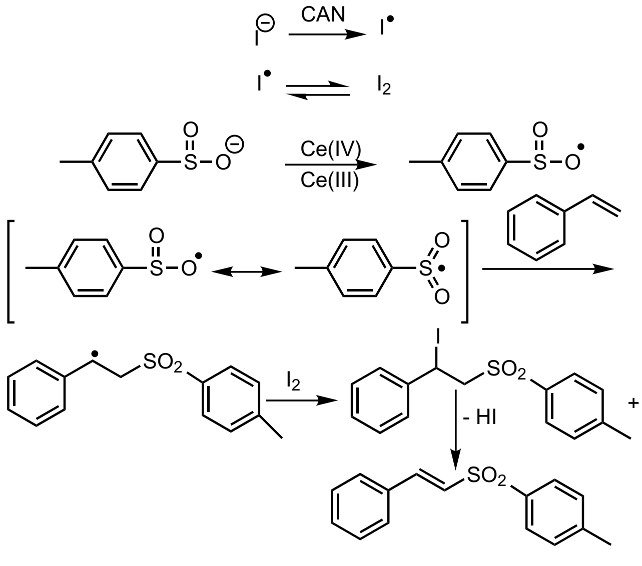
Scheme 2.



8 **2** **9** (78%)

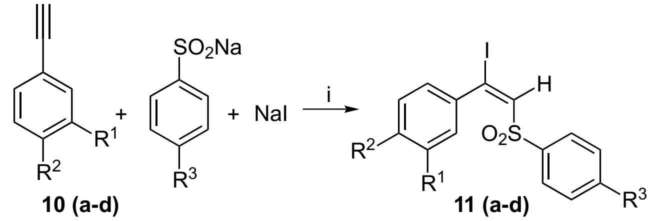
i. CAN, dry CH_3CN, argon, rt, 45 min

Scheme 3.



Scheme 4.

Table 2. Iodo-sulphinylation of acetylenes



10 (a-d) **11 (a-d)**

i. CAN, dry CH_3CN, argon, rt, 45 min

Entry	Substrate	R^1	R^2	R^3	Product	Yield (%)[a]
1	**10a**	H	Me	H	**11a**	79
2	**10b**	H	OMe	Me	**11b**	75
3	**10c**	OMe	H	H	**11c**	65
4	**10d**	NO_2	H	Me	**11d**	65

[a] Isolated yield.

elimination of a molecule of hydrogen iodide from this iodo sulphone would then afford the corresponding vinyl sulphone (Scheme 4).

In conclusion, we have devised a novel and very efficient synthesis of vinyl sulphones. The experimental simplicity and mild reaction conditions make the present one-pot reaction attractive over the other available methods.

Acknowledgements

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13. All new compounds were fully characterised.

    Typical experimental procedure and selected data for **3**: A mixture of styrene (104 mg, 1 mmol), *p*-toluene sulphinate (178 mg, 1.5 mmol) and sodium iodide (224 mg, 1.5 mmol) was taken in dry acetonitrile (12 mL) in a two necked round-bottomed flask fitted with a pressure equalising funnel containing CAN (1.260 g, 2.3 mmol) dissolved in dry acetonitrile (8 mL). Both the solutions were simultaneously bubbled with argon, which was deoxygenated by passing through Fieser's solution for 15 min. Then the CAN solution was added dropwise at room temperature and the reaction mixture was stirred vigorously under an argon atmosphere for 45 min. When the reaction was completed, the solvent was removed in vacuo, the reaction mixture was diluted with water (100 mL) and extracted using dichloromethane (4×25 mL). The combined organic extracts were washed with water, then with saturated sodium thiosulphate solution, followed by saturated brine, and finally dried over anhydrous sodium sulphate and concentrated in vacuo. Column chromatography on neutral alumina using hexane–ethyl acetate (80:20) afforded the vinyl sulphone (211 mg, 82%) as a colourless crystalline solid, which was recrystallised from dichloromethane–hexane mixture, mp 119–121°C. IR (KBr) ν_{max}: 3046, 2915, 1613, 1594, 1447, 1301, 1143, 1085, 974, 858, 810, 742, 692, 661, 536. ^{1}H NMR (300 MHz; $CDCl_3$–CCl_4 v/v 3:1) 7.82 (d, 2H, $J=8.1$ Hz, ArH), 7.64 (d, 1H, $J=15.4$ Hz, olefinic H), 7.48–7.45 (m, 2H, ArH), 7.39–7.37 (m, 3H, ArH), 7.33 (d, 2H, $J=8.1$ Hz, ArH) 6.82 (d, 1H, $J=15.4$ Hz, olefinic H), 2.44 (s, 3H, Me). ^{13}C NMR (75 MHz; $CDCl_3$–CCl_4 v/v 3:1) 144.12, 141.72, 137.89, 132.43, 130.95, 129.85, 128.95, 128.44, 127.78, 127.67, 21.53. Elemental analysis; calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46; S, 12.41. Found: C, 70.00; H, 5.60; S, 12.63. GC–MS (*m*/*z*): 258 [M$^+$] (26), 194 (13), 193 (26), 178 (19).