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Aryl radical-mediated Alkenylation of Alkyl Halides

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Dedicated to Prof. Philippe Renaud on the occasion of his 60th birthday

The free-radical alkenylation of a range of alkyl iodides with a vinyldisulfone has been carried out, leading to the desired vinylsulfone in moderate to good yields under mild conditions. The process is initiated by an aryl radical which abstracts the iodine atom from the alkyl iodide to form a C-centered radical intermediate, the addition of which onto the vinyldisulfone providing the final vinylsulfone. The aryl radical is generated *in situ* through a single-electron transfer from an electron donor-acceptor complex (EDA) formed between a diaryliodonium salt ($Ph_2I^+ \ ^-PF_6^-$) and triethylamine.

Keywords: Aryl radical • alkenylation • diaryliodonium • Electron Donor-Acceptor • vinylsulfone

Introduction

Free-radical alkenylation (also called vinylation) of alkyl halides constitutes a powerful C-C bond forming process offering an access to a wide range of olefins.[1-9] The reaction proceeds through the addition of a C-centered radical **IV**, generated from an alkyl halide precursor **I**, onto an olefinic acceptor **II**. The final unsaturated system **III** is finally obtained through β-elimination from radical intermediate **V** (Figure 1).[1,4-7] Among the broad range of alkenyl acceptors (varying the Y substituent), sulfur derivatives,[5,7,9-11] and in particular vinylsulfones,[7,11-16] have attracted the most interest due to their easy accessibility and relative innocuousness. The generation of radical precursors **IV** from alkyl halides **I** generally implies the use of tin reagents such as R_3SnSnR_3 (R=Me, nBu) to initiate the reaction. [7] In this efficient process, the released sulfonyl radical (Y = SO_2R') was shown to react with ditin, forming a new R_3Sn radical, which sustained the radical chain.[1,7-8] However, due to the perceived toxicity of tin reagents and the contamination of final products with tin residues, alternative strategies have been developed using, for instance, the Pd/light-initiated radical reactions, as recently reported by Ryu and co-workers.[17]

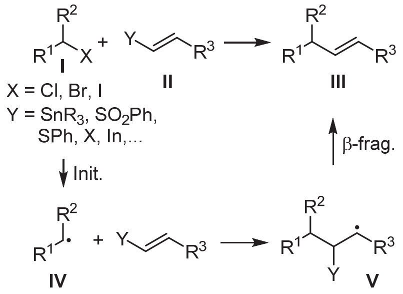


Figure 1. General free-radical alkenylation of alkyl halides.

In the course of our studies on multi-component olefin carbo-functionalization processes,[7,11] we also devised recently a radical alkenylation of alkyl iodides, in which aryl radicals, generated *in situ* from boronic acids, were used as initiators.[18] The highly reactive aryl radicals are known to abstract iodine atom from alkyl iodides with rate constant close to $k \sim 10^9 \ M^{-1} \ s^{-1}$,[19] a fast process which outperforms all other competitive processes that might occur in the reaction medium. Using this method, carbo-cyanation of olefins and addition of alkyl iodides to vinylsulfones were carried out, affording the desired nitriles and olefins respectively in moderate to good yields. Although efficient, the reaction is a non-chain process, the released $PhSO_2$ radical being unable to regenerate the aryl radical from phenylboronic acid. The generation of the aryl radical thus requires the use of an excess of t-BuON=NOt-Bu (DTBHN), a costly initiator. In the course of our search for a better source of aryl radicals, our attention was drawn by recent studies on electron donor-acceptor complexes (EDA) formed between diaryliodonium salts ($Ph_2I^+ \ ^-OTf$) and electron donors. [20-24] Such complexes were shown to provide aryl radicals upon single electron transfer (SET) under thermal or photochemical activation (Figure 2).[25-26] These diaryliodonium salts are also popular photoinitiators for commercial applications based on UV-induced cationic photopolymerizations.[21,27-29] Lakhdar and co-workers elegantly illustrated the reactivity of EDA complexes and the utility of aryl radicals for the generation of phosphynoyl radicals and their subsequent reaction with isonitriles.[23] Earlier, Chatani *et al.* described the arylation of pyrroles and the generation of aryl radicals through a charge transfer complex between a diaryliodonium salt and electron-rich pyrroles.[22] Based on these premises, we devised an efficient modification of our aryl-mediated alkenylation of alkyl iodides, based on the generation of a phenyl radical from an EDA complex resulting from the association between $Ph_2I^+,^-PF_6$ and Et_3N. A scope and limitation of the methodology is provided and a mechanism is proposed to rationalize the course of the reaction between alkyl iodides **1** and bis-sulfone **2** (Figure 2).

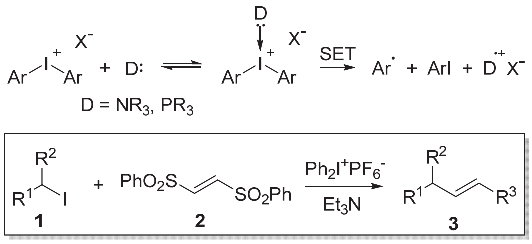
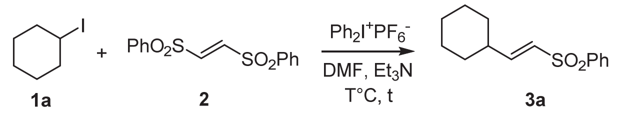


Figure 2. EDA complex and generation of aryl radicals. Application to the alkenylation of alkyl iodides.

Results and Discussion

Based on previous studies on the generation of aryl radicals from iodonium salts-amine EDA complexes, [21,23-24] we first optimized the process, using cyclohexyl iodide **1a** as an alkyl iodide model, bis-sulfone **2**, $Ph_2I^+,^-PF_6$ and Et_3N as the electron donor in DMF. Results are summarized in Table 1. The reaction was first performed at 65°C in the presence of 1.5 equiv. of $Ph_2I^+PF_6^-$, and 2 equiv. of Et_3N, leading to the formation of the expected olefin **3a** in 52% isolated yield (Table 1, entry 1). When the reaction was repeated under similar conditions but in the absence of Et_3N, **3a** was not formed, showing the importance of the amine for a smooth running of the reaction (Table 1, entry 2). The addition of a large excess of Et_3N led to a slight but not significant increase in yield (Table 1, entry 3). Under the same conditions, but under visible-light irradiation at room temperature, using blue LEDs (433 nm), the reaction led to **3a** with the same yield (Table 1, entry 4). During reactions above, we also noticed the formation of various amount of $PhSO_2Ph$ **4,** likely arising from the reaction between the released $PhSO_2$ group from bis-sulfone **2** and $Ph_2I^+,^-PF_6$,[30] indicating that a part of the iodonium reagent was consumed in undesired processes. The reaction was thus repeated using an excess of $Ph_2I^+,^-PF_6$ (3 equiv.) under thermal activation, which resulted in the formation of **3a** in a more satisfying 80% yield (Table 1, entry 5). These optimized conditions were then used in the following investigations.

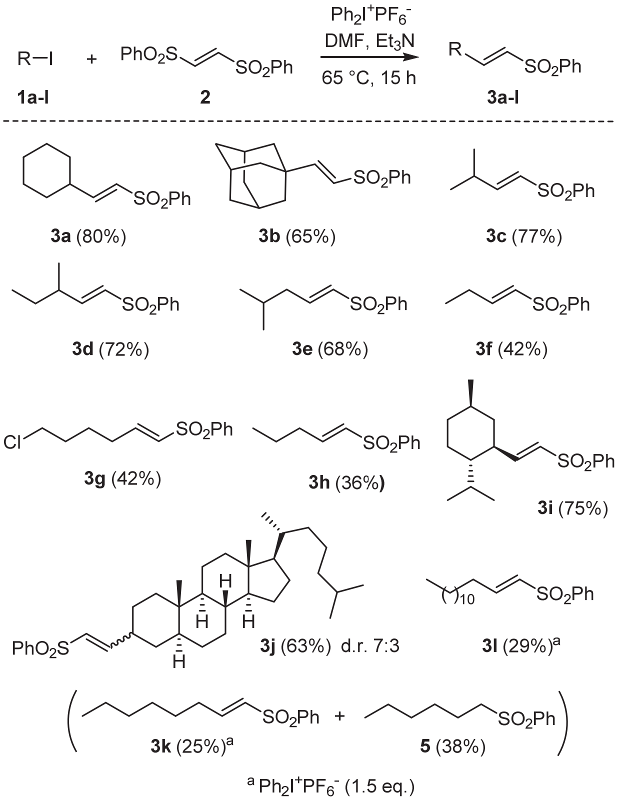
Table 1. Optimization of the alkyl iodides alkenylation process.



Entry[a]	Et3N (equiv.)	$Ph_2I^+,^-PF_6$ (equiv.)	T (°C)	t (h)	Yield[c]
1	2	1.5	65	15	52
2	-	1.5	65	24	-
3	20	1.5	65	15	56
4[b]	20	1.5	20	48	56
5	2	3.0	65	15	80

[a] The reaction was carried out using **1a** (0.5 mmol), **2** (1 mmol) in DMF in the presence of $Ph_2I^+,^-PF_6$ and Et_3N under thermal conditions. [b] The reaction was performed under visible light irradiation (blue LED (433 nm)). [c] Isolated yield.

The optimized conditions of the alkenylation reaction were then extended to several alkyl iodides **1b-l**, leading to vinylsulfones **3b-l** with moderate to good yields (Scheme 1). Alkyl radicals, whether primary, secondary or tertiary, all react effectively with bis-sulfone **2**, although with lower yields in general for the former. As mentioned before, in all reactions, $PhSO_2Ph$ **4** was also formed with yields ranging between 50-55%, but was easily discarded from the desired olefins, through silica gel chromatography. Starting from diastereomerically pure menthyl iodide **1i**, the corresponding olefin **3i** was obtained in good yield and high diastereocontrol, with the stereochemistry as shown. A 7:3 diastereomeric mixture of 3β-iodo-5α-cholestane **1j**,[31] under similar conditions led to olefin **3j** as a 75:25 mixture of diastereomers. Finally, the formation of hexylphenylsulfone **5**, along with the desired product **3k**, was also observed when starting from n-hexyl iodide **1k**. The isolation of such an alkylsulfone from primary iodide **1k** was not observed with secondary and tertiary iodides, pointing toward a S_N2 type reaction between iodide **1k** and a putative phenylsulfinate anion.[32] The presence of the latter, tentatively rationalized below, could also explain the formation of $PhSO_2Ph$ **4** through reaction with excess $Ph_2I^+,^-PF_6$ (*vide infra*).[30]



Scheme 1. $Ph_2I^+,^-PF_6$ -Et_3N mediated alkenylation of alkyl iodides.

Based on experimental evidences above, and drawing on the studies of Lakhdar and co-workers,[23] a mechanism for this radical alkenylation is proposed in Figure 3. The reaction likely begins with the association between Et_3N and $Ph_2I^+PF_6^-$, resulting in the corresponding EDA complex **A** (eq. 1). Single-electron transfer from **A** under thermal activation likely generates the required phenyl radical. Absorption of the EDA complex in the visible region also allowed its activation, and the SET process to occur using simple blue LEDs, albeit with generally lower yields and longer reaction time. The aryl radical then abstracts the iodine atom from the alkyl iodide **1** to form the alkyl radical R (eq. 2), which is trapped by the bis-sulfone **2**, affording the desired product **3** and the phenylsulfonyl radical (eq. 3).[18] It is worth noticing that reaction in the absence of alkyl iodide **1** led to only traces of addition of the phenyl radical onto bis-sulfone **2**, showing that aryl-alkenylation is not a competitive process under these conditions. As mentioned above, the formation of both $PhSO_2Ph$ **4** and the alkylsulfone **5** may be rationalized by the formation at some stage of a phenylsulfinate anion (eq. 6 and 7 respectively). A putative recombination between n-hexyl or phenyl radicals and the $PhSO_2$ radical, is unlikely considering the low concentration of these reactive radical species in the medium. Several pathways maybe envisioned to explain the formation of $PhSO_2^-$. Phenylsulfonyl radical is known for its ability to abstract allylic hydrogens to form $PhSO_2H$.[33-34] Hydrogen abstraction from vinylsulfone products **3** was ruled out due to the absence of isomerized products, including allylsulfones, in the reaction medium. However, an alternative hydrogen transfer seemed more favorable considering the presence of the $Et_3N^{+\cdot}$ radical-cation ***i*** formed in the first step (eq. 1). Recent studies indicate that the C-H bond α to nitrogen in the aminium ***i*** is significantly weakened with a BDE estimated to ~42 kcal/mol (Eq. 4).[35] Such a weak bond and the expected high concentration of the aminium ***i*** in the medium would thus allow a hydrogen atom abstraction[35-37] by the $PhSO_2$ radical, leading to iminium ***ii*** and $PhSO_2H$ (eq. 4), then to the corresponding sulfinate ***iii*** through deprotonation by excess Et_3N (eq. 5). Although we were unable to isolate diethylamine and acetaldehyde resulting from the hydrolysis of iminium ***ii*** upon work-up, this route appears reasonable to explain the presence of $PhSO_2Ph$ **4** and sulfone **5** in large amount.[38] Finally, an abstraction of the hydrogen atom from cation-radical ***i*** by the phenyl radical has been recently reported by Ryu et *al.* and may represent a competitive process, explaining the excess of iodonium salts needed in this process.[39]

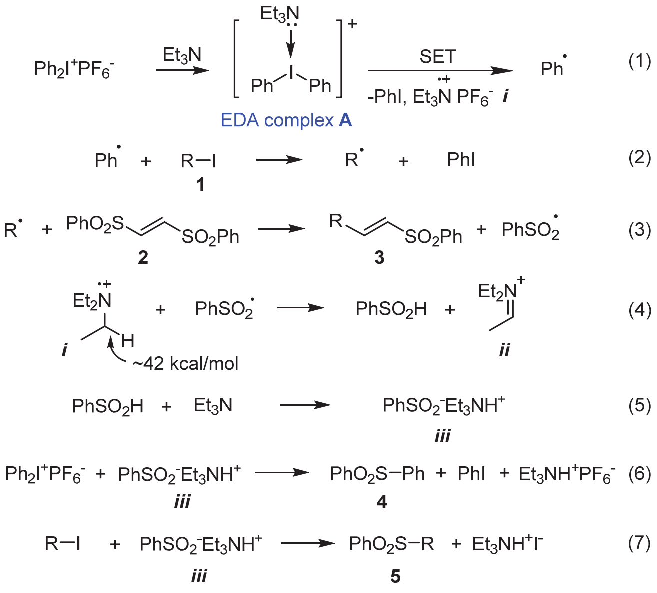


Figure 3. Mechanism of the aryl radical-mediated alkenylation of alkyl iodides.

Conclusions

In summary, we have reported a straightforward metal-free alkenylation of alkyl iodides, mediated by aryl radicals. The latter are generated through a SET process from an EDA complex formed *in situ* between a diaryliodonium salt (acceptor) and Et_3N (electron-donor). An excess of both the iodonium salt and the amine is required to reach good yields of olefins, as a portion of the iodonium salt is consumed through a side-reaction involving a phenylsulfinate, generated during the reaction. The latter may thus react with more reactive primary iodides through a S_N process, explaining the lower yields in compounds **3** in these cases, as compared to those obtained with secondary and tertiary iodides. Other sulfonyl acceptors,[7] including cyanides, oximes and alkynes, should react under these conditions, which are now studied in our laboratory and will be reported in due course.

Experimental Section

Diphenyliodonium hexafluorophosphate alkenylation of alkyl iodides - General procedure

A single-neck-round-bottomed flask was charged with the corresponding alkyl iodide **1** (0.5 mmol), the *E*-1,2-bis(phenylsulfonyl)ethylene **2** (1 mmol), the diphenyliodonium hexafluorophosphate (1.5 mmol), triethylamine (1 mmol) and DMF (0.2 M). The reaction mixture was degassed by three consecutive freeze/pump/thaw cycles. The flask was sealed under vacuum, and the reaction mixture heated at 65°C for 15 to 24 h (depending on the completion of the reaction monitored by TLC) under an argon atmosphere. The reaction was then quenched with a 0.1M HCl solution (10 mL) then extracted with CH_2Cl_2 (3x20 mL). After separation of the aqueous layer, the organic layer was saturated with brine, dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The target compound **3** was finally obtained by column chromatography using the adequate petroleum ether: ethyl acetate mixture as the eluent.

(E)-((2-cyclohexylvinyl)sulfonyl)benzene (**3a**) and Diphenylsulfone (**4**).

Synthesized according to the general procedure from iodocyclohexane **1a** (105 mg, 0.5 mmol, 1eq.), (E)-1,2-bis(phenylsulfonyl)ethene **2** (308.37 mg, 1 mmol, 2 eq.), diphenyliodonium hexafluorophosphate (640.2 mg, 1.5 mmol, 3 eq.) and triethylamine (140 µL, 1 mmol, 2 eq) in dry DMF (0.2 M, 2.5 mL). The reaction was stirred for 15 h. The crude mixture was purified by chromatography on silica gel (Pentane/EtOAc 9:1), affording **3a** (101 mg, 80%) as a colorless oil and diphenylsulfone **4** (60 mg, 55%) as a white solid. R_f = 0.43 (Pentane/EtOAc 90:10). IR (ATR) ν_{max} (cm^{-1}) = 2927, 2852, 1622, 1446, 1318, 1306, 1146, 1086, 973. ^{1}H-NMR (300 MHz, CDCl$_3$): δ (ppm) = 7.90 – 7.77 (m, 2H), 7.61 – 7.40 (m, 3H), 6.94 (dd, *J* = 15.2, 6.4 Hz, 1H), 6.24 (dd, *J* = 15.2, 1.5 Hz, 1H), 2.23 – 2.06 (m, 1H), 1.82 – 1.50 (m, 5H), 1.41 – 1.03 (m, 5H). ^{13}C-NMR (75.5 MHz, CDCl$_3$): δ (ppm) = 151.74, 140.77, 133.10, 129.15, 128.24, 127.45, 39.82, 31.21, 25.66, 25.48. HRMS (ESI): [M+H]$^+$ calculated for $C_{14}H_{19}O_2S$ 251.1100. found 251.1105. Diphenylsulfone (**4**). **R_f** = 0.38 (PE/EtOAc 90:10). IR (ATR), ν_{max} (cm^{-1}) = 3081, 3065, 1448, 1309, 1296, 1154, 761, 728, 699, 689. ^{1}H-NMR (300 MHz, CDCl$_3$): δ (ppm) = 8.08 – 7.75 (m, 4H), 7.60 – 7.40 (m, 6H). ^{13}C-NMR (75.5 MHz, CDCl$_3$): δ (ppm) = 141.52, 133.13, 129.21, 127.57. HRMS (ESI): [M+Na]$^+$ calculated for $C_{12}H_{10}O_2SNa$ 241.0293. found 241.0291.

1-((E)-2-(Phenylsulfonyl)vinyl)adamantane (**3b**).

Synthesized according to the general procedure from 1-iodoadamantane 1b (131 mg, 0.5 mmol, 1eq.), (E)-1,2-bis(phenylsulfonyl)ethene **2** (308.37 mg, 1 mmol, 2 eq.), diphenyliodonium hexafluorophosphate (640.2 mg, 1.5 mmol, 3 eq.) and triethylamine (140 µL, 1 mmol, 2 eq) in dry DMF (0.2 M, 2.5 mL). The reaction was stirred for 15 h. The crude mixture was purified by chromatography on silica gel (PE/EtOAc 9:1), affording **3b** (98.5 mg, 65%) as a colorless oil. R_f = 0.32 (PE/EtOAc 90:10). IR (ATR), ν_{max} (cm^{-1}) = 2905, 2848, 2666, 1616, 1446, 1321, 1303, 1149. ^{1}H-NMR (300 MHz, CDCl$_3$): δ (ppm) = 7.90 - 7.82 (m, 2H), 7.64 - 7.46 (m, 3H), 6.83 (d, *J* = 15.3 Hz, 1H), 6.13 (d, *J* = 15.3 Hz, 1H), 2.00 (s, 3H), 1.79 - 1.54 (m, 12H). ^{13}C-NMR (75.5 MHz, CDCl$_3$): δ (ppm) = 156.2, 141.0, 133.2, 129.3, 127.6, 126.5, 40.8, 36.4, 36.2, 27.9. HRMS (ESI): [M+H]$^+$ calculated for $C_{18}H_{23}O_2S$ 303.1413. found 303.1415.

(E)-((2-(2-Isopropyl-5-methylcyclohexyl)vinyl)sulfonyl)benzene (**3i**).

Synthesized according to the general procedure from (1S,2R,4R)-2-iodo-1-isopropyl-4- methylcyclohexane-2-iodooctane **1i** (133 mg, 0.5 mmol, 1 eq.), (E)-1,2-bis(phenylsulfonyl)ethene **2** (308.37 mg, 1 mmol, 2 eq.), diphenyliodonium hexafluorophosphate (640.2 mg, 1.5 mmol, 3 eq.) and triethylamine (140 µL, 1 mmol, 2 eq) in dry DMF (0.2 M, 2.5 mL). The reaction was stirred for 15 h. The crude mixture was purified by chromatography on silica gel (Pentane/EtOAc), affording **3h** (115 mg, 75%) as a single diastereromer and as a white solid. R_f = 0.42 (Pentane/EtOAc 95:5). IR (ATR) ν_{max} (cm^{-1}) = 2955, 2926, 1621, 1444, 1316, 1306, 1142, 828, 610, 556. ^{1}H-NMR (300 MHz, CDCl$_3$): δ (ppm) = 7.91 - 7.81 (m, 2H), 7.66 - 7.48 (m, 3H), 6.85 (dd, *J* = 15.1, 9.7 Hz, 1H), 6.27 (dd, *J* = 15.1, 0.5 Hz, 1H), 2.13 (ddd, *J* = 21.8, 10.3, 3.5 Hz, 1H), 1.81 - 1.51 (m, 5H), 1.44 - 0.90 (m, 5H), 0.87 (dd, *J* = 6.7, 1.2 Hz, 6H), 0.66 (d, *J* = 6.9 Hz, 3H). ^{13}C-NMR (75.5 MHz, CDCl$_3$): δ (ppm) = 151.7, 141.1, 133.3, 129.4, 129.3, 127.5, 47.2, 44.0, 41.2, 34.8, 32.2, 29.0, 24.2, 22.5, 21.3, 15.6. HRMS (ESI): [M+Na]$^+$ calculated for $C_{16}H_{26}O_2SNa$ 329.1546: found 329.1545.

Diphenyliodonium hexafluorophosphate mediated alkenylation of 1-iodohexane. (E)-((6-oct-1-en-1-yl)sulfonyl)benzene (**3k**) and Hexylsulfonylbenzene (**5**).

Synthesized according to the general procedure from 1-iodohexane **1k** (74 µL, 0.5 mmol, 1 eq.), (E)-1,2-bis(phenylsulfonyl)ethene **2** (308.37 mg, 1 mmol, 2 eq.), diphenyliodonium hexafluorophosphate (320 mg, 0.75 mmol, 1.5 eq.) and triethylamine (140 µL, 1 mmol, 2 eq) in dry DMF (0.2 M, 2.5 mL). The reaction was stirred for 24 h. The crude mixture was purified by chromatography on silica gel (PE/EtOAc), affording 3k (32 mg, 25%) as a colorless oil and hexylsulfonyl-benzene 5 (43 mg, 38%) as a colorless oil.

(E)-(oct-1-en-1-ylsulfonyl)benzene (**3k**). R_f = 0.45 (PE/EtOAc 95:5). IR (ATR) ν_{max} (cm^{-1}) = 2928, 2857, 1625, 1446, 1319, 1307, 1146, 1086, 821, 594. ^{1}H-NMR (300 MHz, CDCl$_3$): δ (ppm) = 7.92 – 7.81 (m, 2H), 7.66 – 7.47 (m, 3H), 6.99 (dt, *J* = 15.1, 6.8 Hz, 1H), 6.30 (dt, *J* = 15.1, 1.6 Hz, 1H), 2.28 – 2.14 (m, 2H), 1.49 – 1.40 (m, 2H), 1.31 – 1.21 (m, 6H), 0.89 – 0.81 (m, 3H). ^{13}C-NMR (75.5 MHz, CDCl$_3$): δ (ppm) = 147.34, 140.77, 133.16, 130.26, 129.18, 127.51, 31.48, 31.41, 28.66, 27.52, 22.44, 13.96. HRMS (ESI): [M+H]$^+$ calculated for $C_{14}H_{21}O_2S$ 253.1256. found 253.1260. Hexylsulfonylbenzene (**5**). R_f = 0.25 (PE/EtOAc 95:5). IR (ATR), ν_{max} (cm^{-1}) = 2931, 2859, 1447, 1305, 1146, 1086, 742, 689, 534. ^{1}H-NMR (300 MHz, CDCl$_3$): δ (ppm) = 7.95 – 7.85 (m, 2H), 7.69 – 7.50 (m, 3H), 3.18 – 2.84 (m, 2H), 1.78 – 1.61 (m, 2H), 1.43 – 1.26 (m, 2H), 1.27 – 1.23 (m, 4H), 0.87 – 0.81 (m, 3H). ^{13}C-NMR (75.5 MHz, CDCl$_3$): δ (ppm) = 139.17, 133.55, 129.19, 127.99, 56.28, 31.10, 27.89, 22.55, 22.22, 13.85. HRMS (ESI): [M+Na]$^+$calculated for $C_{12}H_{18}O_2SNa$ 249.0919. found 249.0925.

Supplementary Material

Synthetic procedures and spectroscopic data are reported in the electronic Supporting information available on the WWW under http://dx.doi.org/10.1002/MS-number.

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Author Contribution Statement

G. K. and *A. C.* contributed equally and performed the experiments and characterization of all materials. *Y. L.* and *F. R.* supervised the work and wrote the article. All authors commented on the manuscript.

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[38] As suggested by one reviewer, the $PhSO_2$ radical is also known to dimerize efficiently to afford (PhSO2)2.[33,34] The one-electron reduction of this dimer by Et3N could also provide the required sulfinate. This route should not be ruled, although we were unable to detect traces of (PhSO2)2.

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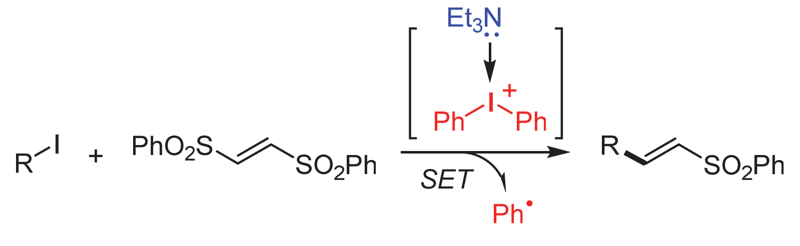

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