Preparation and Synthetic Utility of Stable 1,3-Enynyl- and 1,3-Dienyl(aryl)iodonium Salts

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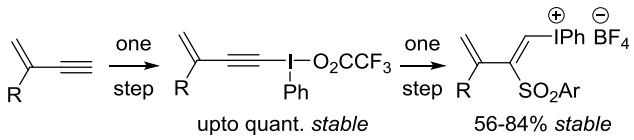


ABSTRACT: The facile synthesis of stable enynyl- and dienyl(aryl)iodonium salts is achieved from terminal enynes. An X-ray crystal structure of an example of the latter is presented. These compounds are shown to be useful in a range of transformations.

Iodonium salts are useful reagents that have found wide utility in organic synthesis.[1] The most commonly encountered are diaryliodonium salts **1** followed by alkenyl(aryl)- **2** and alkynyl(aryl)iodonium salts **3**. There are also several examples of alkyl(aryl)iodonium salts **4**. Diaryl- **1** and alkenyliodonium salts **2** exhibit similar reactivity with examples of known reactions including nucleophilic substitutions of the iodane moiety[2] and metal-catalyzed cross-couplings.[3] Alkynyliodonium salts **3** have a different reactivity profile and undergo, for example, conjugate additions[4] and cycloadditions.[5] There is also a considerable amount of research with closely related benziodoxol(on)e reagents.[6] However, despite the wealth of reactivity uncovered for these λ^3-iodanes, there is a surprising lack of different examples in the literature which limits their applicability in synthesis (Figure 1).

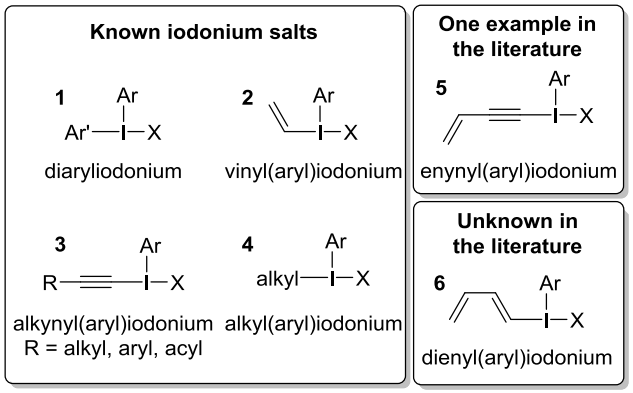


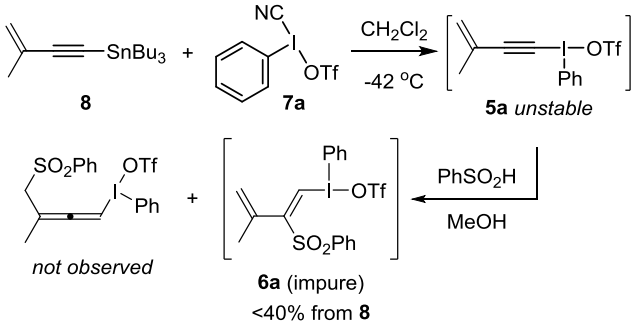
Figure 1. Known and unknown iodonium salts.

With the goal of increasing the range of iodonium salts available to synthetic chemists, we decided to target the preparation of unknown 1,3-dienyl(aryl)iodonium salts **6**. It was envisaged that these λ^3-iodanes would be useful reagents and would exhibit similar reactivities to **2**. In order to achieve this goal, we decided to first prepare the enynyl(aryl)iodonium salts **5** and convert them to the 1,3-dienyl(aryl)iodonium salts **6** by addition of a nucleophile. Just one example of an enynyl(aryl)iodonium salt **5** has been reported in the literature, by Stang and co-workers, however they stated that it was unstable.[7] Zhdankin reported one example of a related cyclic enynylbenziodoxole and did not mention any stability issues.[8]

Initially, we decided to prepare the enynyl(aryl)iodonium salts **5** by utilizing the Stang reagent **7a** as this is considered to be the mildest and most general method and was shown to be successful before in one case (*vide supra*). Enynyl stannane **8** was prepared from the terminal enyne by deprotonation with butyl lithium followed by tin-lithium exchange (Scheme 1).[9] Then, stannane **8** was treated with **7a** and the enynyl(phenyl)iodonium triflate **5a** was isolated as a solid from the reaction mixture however it decomposed within minutes at room temperature or at -20 ^{o}C. Therefore, we decided not to isolate it but to convert it directly into 1,3-dienyl(phenyl)iodonium triflate **6a** by addition of phenylsulfinic acid as this is known to be an extremely good nucleophile for similar substrates.[1g] In the event this was

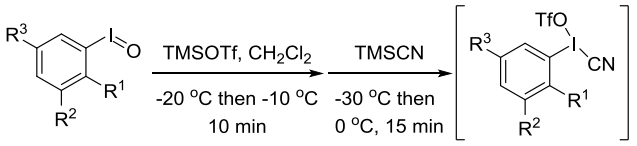
successful however a low yield (<40% from **8**) of impure **6a** was obtained. In theory, nucleophiles can add at two sites, i.e. the alkyne or the alkene, but only the product resulting from addition to the alkyne was observed.

Scheme 1. First attempt at iodonium salt formation.



We have previously reported that varying the aryl group bound to the λ^3-iodane center has a profound impact on stability and affects the yields of subsequent reactions.[10] Therefore, we decided to prepare modified Stang reagents **7b** and **7c** starting from 2-iodoanisole and 5-iodo-m-xylene respectively (Scheme 2). In the former case, the λ^3-iodane **7b** was unstable and decomposed before it could be isolated. In the latter case, an impure sample of the λ^3-iodane was isolated. We did not attempt to purify it because of concerns of stability and safety but used it in excess straight away. Subsequent work published by Studer demonstrates that electron-withdrawing substituents on the aromatic ring lead to a more stable λ^3-iodane.[11]

Scheme 2. Attempted synthesis of modified Stang reagents.

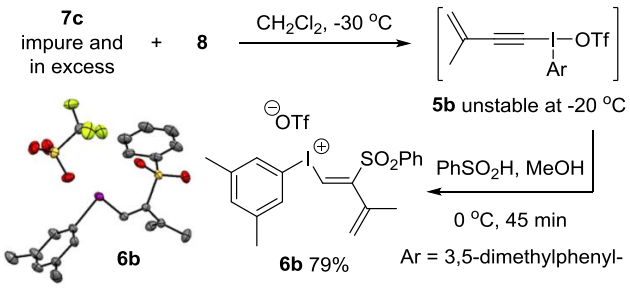


7b R^1 = OMe, R^2 = R^3 = H *decomposed*
7c R^1 = H, R^2 = R^3 = Me *impure*

Impure λ^3-iodane **7c** was combined in excess with stannane **8** and enynyl(xylyl)iodonium triflate **5b** was generated however it was unstable like **5a**. However, immediate conversion to

the 1,3-dienyl(xylyl)iodonium triflate **6b** by addition of phenylsulfinic acid was successful providing it in 79% yield from **8** (Scheme 3). Crystals suitable for X-ray crystallography were grown and analyzed.[12] Interestingly, the two alkenes are not conjugated in the solid state as they sit at approximately 72° to each other.

Scheme 3. Successful preparation of 1,3-dienyl(xylyl)iodonium triflate **6b**. X-ray crystal structure of **6b** with hydrogen atoms omitted for clarity.

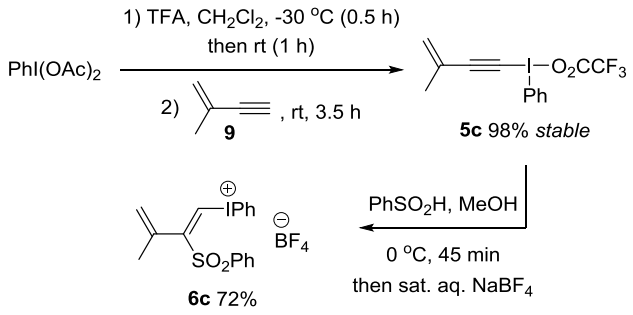


Subsequent attempts to prepare λ^3-iodane **7c** proved that its formation was very capricious and the low purities obtained were also problematic. Therefore, we decided to investigate an alternative approach to the preparation of the enynyl(aryl)iodonium salts. We have recently observed that alkynyl(phenyl)iodonium trifluoroacetates, introduced by Carroll and co-workers,[13] are particularly easy to prepare and have relatively high stability compared to salts with other counterions.[4a] Presumably, the trifluoroacetate is more closely associated with the iodine(III) centre compared to other less nucleophilic counterions, such as triflate and tetrafluoroborate, and protects it from decomposition and/or attack by errant nucleophiles. This procedure has the added advantage that the stannane does not need to be prepared as the terminal alkyne can be used directly.

Accordingly, treatment of (diacetoxyiodo)benzene with TFA followed by addition of terminal alkyne **9** provided **5c** in 98% yield (Scheme 4). Remarkably, this trifluoroacetate salt **5c** was perfectly stable at room temperature for several days. Subsequent conversion to the

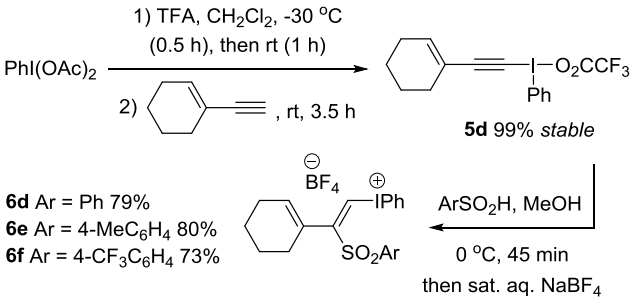
diene **6c** by addition of phenyl sulfinic acid proceeded cleanly. At this point we also switched the counterion from triflate to tetrafluoroborate to preclude any further issues with triflate.

Scheme 4. New route to stable iodonium salts.



Preparation of the stable cyclohexyl analog **5d** proceeded with 99% yield and its conversion into the three 1,3-dienyl(phenyl)iodonium trifluoroacetates **6d-f** was achieved in high yields upon addition of different aryl sulfinic acids (Scheme 5).

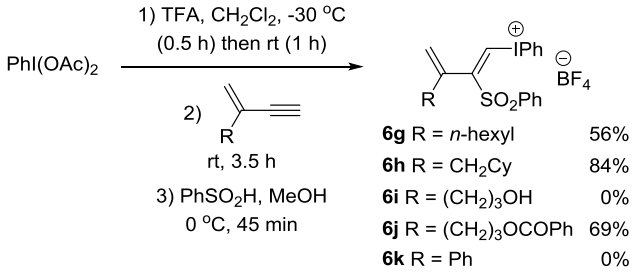
Scheme 5. General synthetic route to iodonium salts.



Next, we attempted to prepare iodonium salts from a range of enynes to investigate the reactivity and structural peculiarities. It is well known that the properties of alkynyliodonium salts varies dramatically depending on the substituent on the alkyne: for example, the direct formation of iodonium salts from terminal alkynes is successful for arylacetylenes but not alkylacetylenes. Therefore, the formation and reactivity of alkenylalkynyliodonium salts cannot be taken for granted.

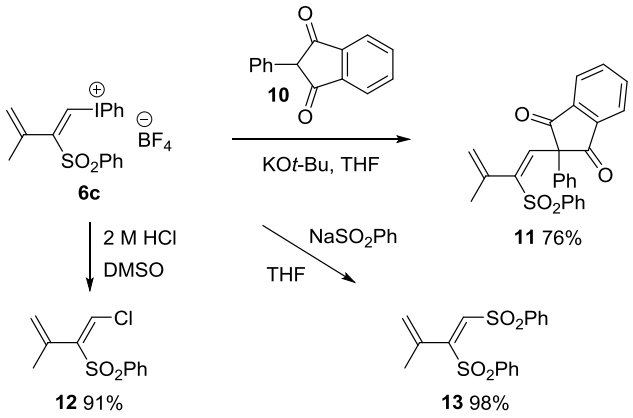
We attempted to prepare dienyliodonium tetrafluoroborates from a range of enynes following our strategy. We targeted formation of the dienes **6** so took the crude enynyliodonium trifluoroacetates **5** straight through by addition of phenylsulfinic acid (Scheme 6). The two alkyl products **6g** and **6h** were formed as expected, however the presence of a free pendent alcohol shut the reaction down and **6i** was not isolated. Protecting the alcohol as an ester permitted the reaction to proceed and **6j** was isolated in 69% yield directly from the alkyne. Preparation of phenyl analog **6k** was unsuccessful as the initial formation of the enynyliodonium trifluoroacetate did not occur.

Scheme 6. Telescoped synthesis of dienes.



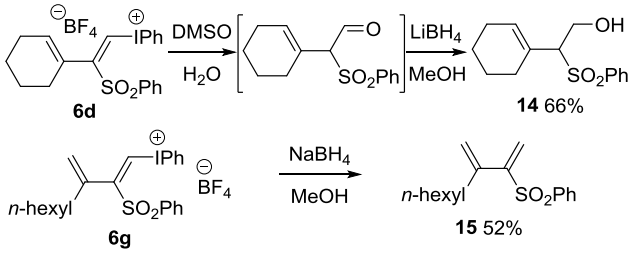
To illustrate the synthetic potential of these 1,3-dienyl(phenyl)iodonium tetrafluoroborates **6**, a range of transformations was attempted (Scheme 7). Alkylation of the enolate derived from 1,3-dicarbonyl compound **10** provided **11** in good yield without any transition metal salt being required.[14] Treatment of **6c** with 2 M HCl in DMSO provided facile access to chloride **12**.[15] Addition of sodium phenylsulfinate led to complete conversion to bis-sulfone **13**.[16]

Scheme 7. Synthetic utility of dienyliodonium salt **6c**.



In addition, solvolysis of iodonium salt **6d** with aqueous DMSO led to aldehyde formation which was reduced to alcohol **14** (Scheme 8).[15] Finally, reduction of **6g** to diene **15** was achieved with sodium borohydride in moderate yield.[17] The remainder of the mass balance in this case consisted of over-reduction products due to the activating nature of the sulfone. We did not attempt to optimize this process. Bäckvall has demonstrated the synthetic utility of several 2-(phenylsulfonyl)-1,3-dienes in Diels-Alder reactions and as electrophiles with a variety of nucleophiles.[18]

Scheme 8. Further synthetic applications of dienyliodonium salts.



In conclusion, the straightforward preparation of stable enynyl- and dienyliodonium salts has been achieved from terminal alkynes. It was found that the trifluoroacetate counterion is crucial to the formation of stable enynyliodonium salts. These λ^3-iodanes have been shown to be useful in a range of processes demonstrating their synthetic attractiveness. We envisage that these new iodonium salts will find applications in synthesis.

Experimental Section

General Procedure for the Formation of 1,3-Enynyl(phenyl)iodonium Trifluoroacetates 5. To a stirred solution of (diacetoxyiodo)benzene (3g, 9.3 mmol) in CH_2Cl_2 (60 mL) at -30 ^oC was added dropwise trifluoroacetic acid (1.4 mL, 19 mmol, 2 equiv). The mixture was stirred for 0.5 h then warmed to room temperature and stirred for 1 h. It was cooled back down to -30 ^oC and the requisite enyne (9.3 mmol, 1 equiv) was added over 10 mins and the resulting mixture was stirred in darkness at room temperature for 3.5 h. The solution was concentrated under vacuum to around 30 mL then diethyl ether (20 mL) and petroleum ether (40 mL) were added. This initiated crystallization of the product. After being placed in the freezer (-20 ^oC) for 48 h the product was filtered and dried under vacuum to provide the product **5** as a white crystalline solid.

(3-Methylbut-3-en-1-yn-1-yl)(phenyl)-λ^3-iodanyl 2,2,2-trifluoroacetate (5c). Yield: 98% (3.5 g). Mp: 40-42 ^oC. IR: 3006 (w), 1661 (s), 1185 (s), 840 (w), 738 (m). ^1H NMR ($CDCl_3$): δ 1.88 (3H, s), 5.43 (1H, s), 5.5 (1H, s), 7.50 (2H, t, J = 7.8 Hz), 7.61 (1H, t, J = 7.4 Hz), 8.11 (2H, d, J = 8.3 Hz). ^{13}C {^1H} NMR ($CDCl_3$): δ 22.1, 44.6, 105.4, 115.9 (1C, q, J = 298 Hz), 120.9, 125.4, 128.1, 132.2, 132.4 (2C), 133.7 (2C), 163.0 (1C, q, J = 37 Hz). HRMS (ESI-TOF) m/z: $[M - OCOCF_3]^+$ Calcd for $C_{11}H_{10}I$ 268.9822; Found 268.9817.

(Cyclohex-1-en-1-ylethynyl)(phenyl)-λ^3-iodanyl 2,2,2-trifluoroacetate (5d). Yield: 99% (4.0 g). Mp: 45-46 ^oC. IR: 3011 (w), 2256 (m), 1183 (s), 992 (w), 737 (s). ^1H NMR ($CDCl_3$): δ 1.48-1.67 (4H, m), 2.02-2.11 (2H, m), 2.12-2.21 (2H, m), 6.29-6.35 (1H, m), 7.46 (2H, t, J = 7.7 Hz), 7.57 (1H, t, J = 7.4 Hz), 8.08 (2H, d, J = 8.3 Hz). ^{13}C {^1H} NMR ($CDCl_3$): δ 21.3, 22.1, 26.2, 28.7, 41.6, 107.2, 115.9 (1C, q, J = 291 Hz), 119.6, 120.8, 132.0, 132.3 (2C), 133.5 (2C), 142.7, 162.9 (1C, q, J = 39 Hz). HRMS (ESI-TOF) m/z: $[M - OCOCF_3]^+$ Calcd for $C_{14}H_{14}I$ 309.0135; Found 309.0135.

General Procedure for the Conversion of 1,3-Enynyl(phenyl)iodonium Trifluoroacetates 5 into 1,3-Dienyl(phenyl)iodononium Tetrafluoroborates 6. Iodonium trifluoroacetate **5** (1.3 mmol, 1 equiv) dissolved in MeOH (5 mL) was added to a solution of arylsulfinic acid (1.4 mmol, 1.1 equiv) in MeOH (2 mL) at 0 ºC under a N_2 atmosphere. The reaction mixture was stirred for 45 minutes then poured into saturated aqueous sodium tetrafluoroborate solution (5 mL). A white precipitate was formed which was filtered off and washed with CH_2Cl_2 (2 x 8 mL). The combined organic layers were washed with water, dried over magnesium sulfate, filtered and concentrated in vacuo. The residue was a clear, colourless, viscous oil and a 1:1 mixture of diethyl ether and petroleum ether (5 + 5 mL) was added to the residue. The mixture was swirled and the solvent removed by decantation. This process was repeated until a white solid was formed. The crude solid product was recrystallized from the minimum amount of CH_2Cl_2 with slow addition of petroleum ether. Iodonium tetrafluoroborate **6** was isolated as a white crystalline solid.

(2-Methyl-1-phenylsulfonyl)allyl)(phenyl)iodonium tetrafluoroborate (6c). Yield: 72% (0.45 g). Mp: 150-152 ºC. IR: 1305 (m), 1135 (s), 1060 (s), 945 (w), 680 (m). ^{1}H NMR (DMSO-d^6): δ 1.77 (3H, s), 5.08 (1H, s), 5.25 (1H, s), 7.68 (2H, d, J = 7.8 Hz), 7.78 (2H, t, J = 7.8 Hz), 7.83 (1H, t, J = 7.4 Hz), 7.91 (1H, t, J = 7.3 Hz), 8.02 (2H, d, J = 7.5 Hz), 8.16 (1H, s), 8.38 (2H, d, J = 7.9 Hz). ^{13}C {^{1}H} NMR (DMSO-d^6): δ 24.1, 116.9, 124.1, 129.6 (2C), 131.3 (2C), 133.1 (2C), 134.2, 137.0, 137.1, 137.2 (2C), 137.6, 138.4, 147.9. HRMS (ESI-TOF) m/z: $[M - BF_4]^+$ Calcd for $C_{17}H_{16}IO_2S$ 410.991; Found 410.9901.

(Cyclohex-1-en-1-yl(phenylsulfonyl)methyl)(phenyl)iodonium tetrafluoroborate (6d). Yield: 79% (0.5 g). Mp: 156-157 ºC. IR: 1699 (s), 1417 (w), 1183 (s), 1124 (s), 720 (s). ^{1}H NMR (DMSO-d^6): δ 1.34-1.41 (4H, m), 1.87-1.91 (4H, m), 5.79 (1H, s), 7.68 (2H, d, J = 7.7 Hz), 7.73-7.88 (3H, m), 7.91 (1H, t, J = 7.5 Hz), 7.98 (2H, d, J = 7.8 Hz), 8.04 (1H, s), 8.36 (2H, d, J = 7.9 Hz). ^{13}C {^{1}H} NMR (DMSO-d^6): δ 21.7, 23.1, 26.5, 29.8, 114.9, 116.8, 129.8

(2C), 130.6 (2C), 133.2 (2C), 133.1, 134.2, 136.5, 136.9 (2C), 137.0, 137.6, 149.1. HRMS (ESI-TOF) m/z: $[M - BF_4]^+$ Calcd for $C_{20}H_{20}IO_2S$ 451.0223; Found 451.0212.

(*Z*)-(2-(Cyclohex-1-en-1-yl)-2-tosylvinyl)(phenyl)iodonium tetrafluoroborate (6e). Yield: 80% (0.19 g). Mp: 160-161 ºC. IR: 2855 (w), 1471 (w), 1038 (s), 1003 (s), 723 (s). ^{1}H NMR (DMSO-d^6): δ 1.35-1.51 (4H, m), 1.88-1.94 (4H, m), 2.48 (3H, s), 5.79 (1H, s), 7.58 (2H, d, J = 7.8 Hz), 7.67 (2H, t, J = 7.7 Hz), 7.79-7.89 (3H, m), 7.98 (1H, s), 8.36 (2H, d, J = 7.9 Hz). ^{13}C {^{1}H} NMR (DMSO-d^6): δ 22.6, 23.1, 26.5, 29.7, 114.5, 116.7, 129.8 (2C), 130.7, 131.6 (2C), 133.1 (2C), 134.1 (2C), 136.3, 137.6 (2C), 148.00, 149.3. HRMS (ESI-TOF) m/z: $[M - BF_4]^+$ Calcd for $C_{21}H_{22}IO_2S$ 465.0385; Found 465.0379.

(*Z*)-(2-(Cyclohex-1-en-1-yl)-2((4(trifluoromethyl)phenyl)sulfonyl)vinyl)(phenyl)-iodonium tetrafluoroborate (6f). Yield: 73% (0.09 g). Mp: 156-157 ºC. IR: 2935 (w), 1447 (w), 1314 (s), 1012 (s), 740 (m). ^{1}H NMR (DMSO-d^6): δ 1.30-1.40 (4H, m), 1.90-1.94 (4H, m), 5.80 (1H, s), 7.68 (2H, t, J = 7.4 Hz), 7.83 (1H, t, J = 7.5 Hz), 8.15 (3H, d, J = 7.1 Hz), 8.22 (2H, d, J = 8.3 Hz), 8.35 (2H, d, J = 8.1 Hz). ^{13}C {^{1}H} NMR (DMSO-d^6): δ 21.6, 23.1, 26.5, 29.7, 116.4, 116.8, 124.4 (1C, q, J = 274 Hz), 128.2, 128.3, 130.5, 130.9, 133.2, 134.2, 136.0 (1C, q, J = 32 Hz), 137.1, 137.5, 141.1, 148.3. HRMS (ESI-TOF) m/z: $[M - BF_4]^+$ Calcd for $C_{21}H_{19}F_3IO_2S$ 519.0097; Found 519.0098.

General Procedure for the Conversion of Enynes into 1,3-Dienyl(phenyl)iodononium Tetrafluoroborates 6. To a stirred solution of (diacetoxyiodo)benzene (0.70 g, 2.2 mmol) in CH_2Cl_2 (20 mL) at -30 ºC was added dropwise trifluoroacetic acid (0.4 mL, 4.4 mmol, 2 equiv). The mixture was stirred for 0.5 h then warmed to room temperature and stirred for 1 h. It was cooled back down to -30 ºC and the enyne (2.2 mmol, 1 equiv) added slowly. The resulting mixture was stirred in darkness at -30 ºC for 3.5 h. After which time the solvent was removed under vacuum and the residue dissolved in MeOH (5 mL). A solution of phenyl sulfinic acid (0.34 g, 2.4 mmol, and 1.1 equiv) in MeOH (2 mL) was added at 0 ºC and the

mixture was stirred for 45 minutes. This was poured into saturated aqueous sodium tetrafluoroborate solution (5 mL) and a white precipitate was formed which was filtered off and washed with CH_2Cl_2 (2 x 8 mL). The combined organic layers were washed with water (5 mL), dried over magnesium sulfate, filtered and concentrated under vacuum to provide a clear, colourless, viscous oil. A 1:1 mixture of diethyl ether and petroleum ether (5 + 5 mL) was added to the residue and the mixture was swirled. The solvent was removed by decantation. This process was repeated until a white solid was formed. The crude solid product was recrystallized from the minimum amount of CH_2Cl_2 with slow addition of petroleum ether.

(*Z*)-(3-Methylene-2-(phenylsulfonyl)non-1-en-1-yl)(phenyl)iodonium tetrafluoroborate (6g). Yield: 56% (0.68 g). Light grey solid. Mp: 140-141 ºC. IR: 2998 (w), 1446 (m), 1299 (s), 1077 (s), 624 (s). ^{1}H NMR (DMSO-*d*^{6}): δ 0.81 (3H, t, *J* = 7.2 Hz), 0.92-1.27 (8H, m), 2.08 (2H, t, *J* = 7.5 Hz), 5.11 (1H, s), 5.21 (1H, s), 7.68 (2H, t, *J* = 7.7 Hz), 7.77 (2H, t, *J* = 7.7 Hz), 7.84 (1H, t, *J* = 7.6 Hz), 7.92 (1H, t, *J* = 7.6 Hz), 8.00 (2H, d, *J* = 7.8 Hz), 8.13 (1H, s), 8.38 (2H, d, *J* = 7.7 Hz). ^{13}C {^{1}H} NMR (DMSO-*d*^{6}): δ 15.2, 23.2, 27.6, 29.1, 32.1, 36.6, 116.2, 116.9, 123.1, 129.9 (2C), 131.3 (2C), 133.2 (2C), 134.1, 136.8, 137.6 (2C), 137.5, 141.5, 148.0. HRMS (ESI-TOF) m/z: $[M - BF_4]^+$ Calcd for $C_{22}H_{26}IO_2S$ 481.0698; Found 481.0684.

2-(Cyclohexylmethyl)-1-(phenylsulfonyl)allyl)(phenyl)iodonium tetrafluoroborate (6h). Yield: 84% (1.1 g). White solid. Mp: 139-140 ºC. IR: 2999 (w), 1446 (m), 1305 (m), 627 (s). ^{1}H NMR (DMSO-*d*^{6}): δ 0.61 (2H, q, *J* = 11 Hz), 0.93-1.15 (4H, m), 1.24 (2H, d, *J* = 13 Hz), 1.40-1.60 (3H, m), 2.02 (2H, d, *J* = 6.7 Hz), 5.18 (1H, s), 5.23 (1H, s), 7.69 (2H, t, *J* = 7.8 Hz), 7.77 (2H, t, *J* = 7.8 Hz), 7.84 (1H, t, *J* = 7.4 Hz), 7.91 (1H, t, *J* = 7.4 Hz), 8.02 (2H, d, *J* = 7.5 Hz), 8.15 (1H, s), 8.37 (2H, d, *J* = 7.5 Hz). ^{13}C {^{1}H} NMR (DMSO-*d*^{6}): δ 26.7 (2C), 27.1, 33.4, 35.5 (2C), 44.3, 116.3, 117.2, 124.5, 129.8 (2C), 131.3 (2C), 133.1 (2C), 134.1,

136.9, 137.0 (2C), 137.5, 139.8, 148.0. HRMS (ESI-TOF) m/z: $[M - BF_4]^+$ Calcd for $C_{23}H_{26}IO_2S$ 493.0693; Found 493.0682.

(5-(Benzoyloxy)-2-methylene-1-(phenylsulfonyl)pentyl)(phenyl)iodonium tetrafluoroborate (6j). Yield: 84% (1.1 g). Light brown wax. IR: 3010 (w), 1708 (m), 1052 (s), 712 (s), 449 (w). ^{1}H NMR (DMSO-d^6): δ 1.63 (2H, pentet, J = 6.6 Hz), 2.27 (2H, t, J = 7.2 Hz), 4.07 (2H, t, J = 6.0 Hz), 5.10 (1H, s), 5.30 (1H, s), 7.56 (2H, t, J = 7.4 Hz), 7.64-7.72 (3H, m), 7.75 (2H, t, J = 7.4 Hz), 7.80-7.90 (2H, m), 7.92 (2H, d, J = 3.7 Hz), 8.01 (2H, d, J = 3.7 Hz), 8.23 (1H, s), 8.38 (2H, d, J = 3.7 Hz).^{13}C {^{1}H} NMR (DMSO-d^6): δ 27.0, 33.1, 65.0, 116.8, 117.0, 124.0, 130.0, 130.1 (2C), 130.4 (2C), 131.0, 131.3 (2C), 133.1 (2C), 134.2, 134.7 (2C), 136.5, 137.1, 137.6 (2C), 140.5, 147.6, 167.0. Anal. Calcd for $C_{26}H_{24}BF_4IO_4S$: C, 48.32; H, 3.74; N, 0. Found: C, 48.54; H, 3.97; N, 0.

(*E*)-2-(2,3-Dimethylbuta-1,3-dien-1-yl)-2-phenyl-1*H*-indene-1,3(2*H*)-dione (11). To a stirred solution of potassium *tert*-butoxide (13 mg, 0.12 mmol, 1.2 equiv) in THF (1.5 mL) was added 2-phenyl-1*H*-indene-1,3(2*H*)-dione **10** (26 mg, 1.2 mmol, 1.2 equiv). The mixture was stirred under a N_2 atmosphere at room temperature for 1.5 h. To this was added a solution of (2-methyl-1-(phenylsulfonyl)allyl) (phenyl)iodonium tetrafluoroborate (50 mg, 0.10 mmol, 1 equiv) in THF (1.5 mL) and the mixture was stirred for 24 h. Water was added and the mixture extracted with diethyl ether (3 x 5 mL). The combined organic layer was washed with water (5 mL) and brine (4 mL) then dried over magnesium sulfate, filtered and concentrated under vacuum. The residue was purified by flash chromatography (5:1 petroleum ether/EtOAc) which furnished **11** as a colorless oil (23 mg, 76%). IR: 2359 (s), 1221 (w), 1707 (s), 1306 (s), 528 (s). ^{1}H NMR ($CDCl_3$): δ 1.83 (3H, s), 4.99 (1H, s), 5.03 (1H, s), 6.38 (1H, s), 7.23-7.37 (3H, m), 7.44-7.52 (4H, m), 7.58 (1H, t, J = 7.4 Hz), 7.73-7.82 (4H, m), 7.99-8.03 (2H, m). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 24.3, 66.5, 121.7, 124.1, 127.8 (2C), 128.6 (2C), 128.8 (2C), 129.2, 129.8 (2C), 134.0, 135.5, 138.9 (2C), 139.2 (2C), 139.9

(2C), 140.2, 141.9, 145.8, 197.4 (2C). HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{20}NaO_4S$ 451.0975; Found 451.0974.

(*Z*)-((1-Chloro-3-methylbuta-1,3-dien-2-yl)sulfonyl)benzene (12). (2-Methyl-1-(phenylsulfonyl)allyl)(phenyl)iodonium tetrafluoroborate (0.050 g, 0.10 mmol, 1 equiv) was dissolved in DMSO (0.5 mL) at room temperature. HCl (2 N, 50 µL) was added and the mixture was stirred overnight. Brine (5 mL) was added to the mixture and the solution was shaken. This was extracted with ethyl acetate (2 x 10 mL) and washed with water (5 mL). The organic layer was dried over magnesium sulfate, filtered and concentrated under vacuum. The residue was purified by flash chromatography (20:1 petroleum ether/EtOAc) which furnished **12** as a colorless oil (0.023 g, 91%). IR: 1558 (s), 1221 (w), 1154 (s), 1120 (s), 862 (s). ^{1}H NMR ($CDCl_3$): δ 2.07 (3H, s), 4.95 (1H, s), 5.18 (1H, s), 7.65 (1H, s), 7.54 (2H, t, J = 7.7 Hz), 7.65 (1H, t, J = 7.3 Hz), 7.98 (2H, d, J = 7.7 Hz). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 23.5, 121.6, 127.6, 128.6 (2C), 129.2 (2C), 134.1, 140.1, 140.5, 148.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{12}ClO_2S$ 243.0241; Found 243.0240.

(3-Methylbut-3-ene-1,2-diyldisulfonyl)dibenzene (13). To a stirred solution of sodium benzenesulfinate (360 mg, 2.2 mmol, 1.1 equiv) in THF (5 mL) at 0 ^{o}C was added (2-methyl-1-(phenylsulfonyl)allyl)(phenyl)iodonium tetrafluoroborate (1.0 g, 2.0 mmol, 1 equiv). The mixture was stirred at 0 ^{o}C for 0.5 h then extracted with diethyl ether (2 x 10 mL). The combined organic layers were washed with water, dried over magnesium sulfate, filtered and concentrated under vacuum. The residue was washed with petroleum ether to provide **13** as a white solid (0.69 g, 98%). Mp: 160-161 ^{o}C. IR: 3068 (w), 1447 (m), 1149 (s), 1022 (w), 630 (s). ^{1}H NMR ($CDCl_3$): δ 1.91 (3H, s), 4.86 (1H, s), 5.12 (1H, s), 6.81 (1H, s), 7.51-7.63 (4H, m), 7.63-7.71 (2H, m), 8.02 (2H, d, J = 7.8 Hz), 8.05 (2H, d, J = 7.8 Hz). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 23.5, 123.1, 128.6 (2C), 129.6 (2C), 129.8 (2C), 129.9 (2C), 133.7,

134.9, 134.9, 136.1, 136.4, 139.8, 154.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}O_4S_2$ 349.0563; Found 349.0557.

2-(Cyclohex-1-en-1-yl)-2-(phenylsulfonyl)ethan-1-ol (14). (Cyclohex-1-en-1-yl(phenylsulfonyl)methyl)(phenyl)iodonium tetrafluoroborate (0.050 g, 0.10 mmol, 1 equiv) was dissolved in DMSO (0.5 mL) at room temperature. Deionized water (20 µL) was added and the mixture was stirred overnight. Water (2.5 mL) was added to the mixture and the solution was shaken. This was extracted with ethyl acetate (5 mL). The organic layer was dried over magnesium sulfate, filtered and concentrated under vacuum. The residue was dissolved in methanol (2 mL) and $LiBH_4$ (2 mg, 0.1 mmol, 1 equiv) was added in one portion. This was stirred overnight then extracted with diethyl ether (5 mL) and washed with water (5 mL). The organic layer was dried over magnesium sulfate, filtered and concentrated under vacuum. The residue was purified by flash chromatography (5:1 petroleum ether/EtOAc) which furnished **14** as a colorless oil (0.018 g, 66%). IR: 3498 (w), 2345 (s), 1456 (m), 601 (w). ^{1}H NMR ($CDCl_3$): δ 1.31-1.59 (4H, m), 1.72-1.89 (2H, m), 1.90-2.05 (2H, m), 2.79 (1H, dd, J = 9.0, 4.3 Hz), 3.69 (1H, dd, J = 8.0, 5.0 Hz), 3.90 (1H, ddd, J = 13, 9.2, 4.8 Hz), 4.30 (1H, ddd, J = 12, 8.0, 4.3 Hz), 5.36-5.38 (1H, s), 7.55 (2H, t, J = 7.5 Hz), 7.67 (1H, t, J = 7.2 Hz), 7.84 (2H, d, J = 7.5 Hz).^{13}C {^{1}H} NMR ($CDCl_3$): δ 21.9, 22.9, 25.9, 27.8, 60.6, 74.3, 128.9, 129.2 (2C), 129.5 (2C), 132.7, 134.2, 137.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{18}O_3SNa$ 289.0869; Found 289.0870.

((3-Methylenenon-1-en-2-yl)sulfonyl)benzene (15). To a stirred solution of (2-methylene-1-(phenylsulfonyl)octyl)(phenyl)iodonium tetrafluoroborate (70 mg, 0.12 mmol, 1 equiv) in methanol (5 mL) at room temperature was added sodium borohydride (0.09 g, 0.24 mmol, 2 equiv) portionwise. The mixture was heated to reflux for 1 h then cooled to room temperature. Water (3 mL) was added and the mixture was stirred for 10 min. This was extracted with CH_2Cl_2 (3 x 5 mL) and the organic layer was dried over anhydrous magnesium

sulfate, filtered and concentrated under vacuum. The residue was purified by flash chromatography (5:1 petroleum ether/EtOAc) which furnished **15** as a light brown oil (43 mg, 52%). IR: 3068 (w), 1447 (m), 1149 (s), 1022 (w), 630 (s). ^{1}H NMR ($CDCl_3$): δ 0.83 (3H, t, J = 7.3 Hz), 1.04-1.30 (8H, m), 2.16 (2H, t, J = 7.3 Hz), 5.05 (1H, s), 5.15 (1H, s), 5.83 (1H, s), 6.47 (1H, s), 7.49 (2H, t, J = 7.4 Hz), 7.58 (1H, t, J = 7.4 Hz), 7.82 (2H, d, J = 7.7 Hz). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 14.4, 22.9, 27.7, 28.9, 31.9, 36.4, 119.5, 125.3, 128.8 (2C), 129.2 (2C), 133.7, 139.4, 141.4, 151.3. HRMS (ESI-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{16}H_{26}NO_2S$ 296.1679; Found 296.1680.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc…

Copies of ^{1}H and ^{13}C NMR spectra (PDF)

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The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful to the University of Huddersfield (DJH) and the State of Libya (EZ) for funding. We thank Professor Craig Rice for obtaining the X-ray crystallographic data.

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