Azulenesulfonium and azulenebis(sulfonium) salts: Formation by interrupted Pummerer reaction and subsequent derivatisation by nucleophiles

Carlos M. López-Alled a,b, Frederick J.O. Martin a, Kuan-Yu Chen a, Gabriele Kociok-Köhnc, Tony D. James a,b, Jannis Wenkd, Simon E. Lewis a,b,*,1

a Department of Chemistry, University of Bath, Bath, BA2 7AY, UK
b Centre for Sustainable Circular Technologies, University of Bath, Bath, BA2 7AY, UK
c Centre for Sustainable Chemical Technologies, University of Bath, Bath, BA2 7AY, UK
d Department of Chemical Engineering & Water Innovation & Research Centre: WIRC @ Bath, University of Bath, Bath, BA2 7AY, UK

1 Dedicated to the memory of Prof. Jonathan M. J. Williams, mentor and friend, from whom I learned a great deal.

* Corresponding author. Department of Chemistry, University of Bath, Bath, BA2 7AY, UK
E-mail address: s.e.lewis@bath.ac.uk (S.E. Lewis).
1 © 2020 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

Abstract
Azulenes undergo either single or dual SAr reactions depending on the nature of the sulfur(IV) electrophile employed. These electrophiles are generated in situ from either sulfoxides or sulfides. The resultant cationic or dicationic azulene products can undergo further derivatisation by means of nucleophilic attack at the sulfonium z-carbon. In the case of cycloalyl azulenesulfonium salts, this leads to ring-opened azulenylsulfide products.

Keywords: Azulene Interrupted Pummerer Sulfonium

1. Introduction
Sulfonium salts, trivalent cationic sulfur(IV) species, have a rich chemistry which has seen them exploited in various applications. They are used as photoacid generators [1], for purposes including microlithography [2], initiation of polymerisation [3], optical data storage [4], and oxygen-independent photodynamic therapy [5]. In organic synthesis, sulfonium salts may be employed in cross-coupling, where they have been shown to be competent pseudohalide electrophilic coupling partners [6–12]. They have been used to enable versatile derivatisation reactions using photocatalysis [11b,c],[13–22], as well as via SAr processes and/or aryne intermediates [23,24], and via sulfuran intermediates [46,47]. Synthetic applications of sulfonium salts (and other sulfur(IV) species derived from them, such as sulfur ylides) have been reviewed [25].

Methods for preparing sulfonium salts have been reviewed [26], and include approaches such as the direct alkylation of thiols and sulfides [27]. One strategy is to employ a sulfoxide starting material in a so-called “Interrupted Pummerer” reaction [25,28,29]. As shown in Scheme 1, a sulfoxide 1 may be activated with an electrophilic activating agent 2 (commonly an acid anhydride) to give cationic intermediate 3. In a classical Pummerer reaction, intermediate 3 undergoes deprotonation at sulfur, with concomitant S–O bond cleavage to give thionium ion 4. This in turn undergoes addition of the carboxylate nucleophile to give a z-acyloxysulfide 5 as the final product. However, in the presence of a sufficiently nucleophilic additive, the reaction pathway may be “interrupted”, with nucleophilic substitution at sulfur occurring in preference to deprotonation, thereby forming sulfonium salt 6. The interrupted Pummerer reaction has been utilised in [3,3]-sigmatropic reaction cascades [30], in carbohydrate synthesis [31], and in heterocycle synthesis [32].

If an aromatic ring is sufficiently electron-rich, it may act as the nucleophile in the interrupted Pummerer reaction, by an SAr mechanism. Azulene (7), a bicyclic, non-alternant arene, fulfils this criterion. Known for its blue colour [33] and anomalous fluorescence [34], azulene has a dipole of 1.08 D, unusually high for a hydrocarbon. This may be rationalised through considerations of resonance, with the resonance structures 7–7′ shown in Scheme 2 all possessing a seven-membered ring that is itself aromatic (6π tropylium cation). It follows from these resonance structures that
the 1- and 3-positions of azulene are the most electron rich and hence the preferred sites for $S_N$Ar reactions.

Formation of a sulfonium salt by an interrupted Pummerer reaction with azulenes was first reported by Shoji, Ito, Morita and co-workers [35]. As part of our ongoing interest in the chemistry of azulene [36,48,49], we previously reported the synthesis of cyclic sulfonium salts bearing an azulene substituent. These were highly stable and applicable in cross-coupling (Scheme 3) [10]. The cross-coupling of azulenes had previously been difficult, due to instability of most azulenyl halides; this necessitated other approaches [37]. We now wish to report on the scope of the interrupted Pummerer reaction of azulenes, on a variant employing sulfide starting materials, as well as on reactions of azulenesulfonium salts other than in cross-coupling.

2. Results and discussion

2.1. Azulenebis(sulfonium) dications

Both the 1- and 3-positions of azulene are highly nucleophilic (c.f. Scheme 2), which can lead to problems of over-reaction in $S_N$Ar reactions. For example, electrophilic halogenation of azulene with $N$-halosuccinimides inevitably leads to mixtures of 1-halo- and 1,3-dihaloazulenes. In contrast, the interrupted Pummerer reaction shown in Scheme 3 provides monosubstitution product 10 cleanly, with no second $S_N$Ar reaction occurring. The introduction of a (positively charged) sulfonium substituent in 10 strongly deactivates the azulene ring towards further $S_N$Ar reactions. Nevertheless, Shoji, Ito, Morita and co-workers have previously demonstrated [35a] that a second interrupted Pummerer reaction may be induced by use of a stronger activating agent, thereby producing an azulenebis(sulfonium) dication. Specifically, use of a sulfonic acid anhydride (triflic anhydride) instead of a carboxylic acid anhydride can provide a Pummerer intermediate 12 (Scheme 4) which is electrophilic enough to react a second time with monosulfonium salts such as 13. (Use of triflic anhydride to activate DMSO for $S_N$Ar reactions with arenes was first reported by Balenková [38]).
We have employed triflic anhydride with other azulenes and sulfoxides to obtain novel azulenebis(sulfonium) dications 16–18 that have been characterised crystallographically, as shown in Table 1 and Figs. 1–3. While the procedure in Scheme 4 provides the products as their triflate salts in the first instance, a salt swap with aqueous KPF_{6} may be readily effected to give the corresponding hexafluorophosphate salts.

In order to expand further the synthetic accessibility of azulenebis(sulfonium) salts, we investigated other ways to generate reactive electrophiles such as nebis(sulfonium) salts, we investigated other ways to generate corresponding hexa-

Table 1

| Entry | Substrate | Sulfoxide | Product | Yield |
|-------|-----------|-----------|---------|-------|
| 1     | Azulene   | DMSO      | 15+2OTf | 95%   |
| 2     | Azulene   | 9         | 16+2OTf | 90%   |
| 3     | 4,6,8-Trimethylazulene | DMSO | 17+2OTf | 69%   |
| 4     | 4,6,8-Trimethylazulene | 9 | 18+2OTf | 77%   |

\(^{a}\) Reaction conditions: 14 eq. sulfoxide, 2.4 eq. Tf_{2}O, CH_{2}Cl_{2}, rt, 2 h.
\(^{b}\) Yield previously reported [35a] for this product.

Fig. 1. Structures of dications 15^{2+} - 18^{2+}.

interrupted Pummerer reactions, this is not a productive pathway for sulfides. Although acylsulfonium salts such as 21 are known species [39], they would not be expected to undergo the desired S{\text{e}}Ar process at sulfur as the acyl group is not a viable leaving group. Rather, nucleophiles reportedly effect addition/elimination at the carbonyl of 21, and/or attack on the Rʻ/R” substituents z-to sulfur. In contrast, a sulfonic acid anhydride such as 22 will activate sulfide 19 to give a disulfur species 23, in which a viable leaving group (the sulfone) is attached to the sulfonium. In this case, attack of a nucleophile at the sulfonium centre leads to S–S bond cleavage and loss of a sulfinate anion to give 24.

Reaction of arenes with electrophiles of type 23 in an S{\text{e}}Ar process was first reported by Balenkova and co-workers [40], but to date has not been reported for azulenes. At the outset it was unclear whether sulfonylsulfonium electrophiles of type 23 would be sufficiently electrophilic to react twice and form an azulenebis(sulfonium) dication (as is the case for sulfonyloxysulfonium electrophiles 12) or whether only a single S{\text{e}}Ar reaction would occur. We first attempted formation of the monosubstitution product by treating a mixture of azulene and excess 1,4-oxathiane 25 with only 1.25 eq. of triflic anhydride (Scheme 6B). This provided the expected product 26, thus demonstrating the viability of this alternative approach to the preparation of azulenesulfonium salts. The reaction was repeated with 2.2 eq. of triflic anhydride (Scheme 6B), which led to the formation of azulenesulfonium dication 27, thereby showing that sulfonylsulfonium electrophiles (23) can indeed effect a second S{\text{e}}Ar reaction on azulene. However, the yield of 27 was low, and a second product predominated, unexpected trifluoromethyl sulfoxide 28. We rationalise the formation of 28 on the basis of the sulfinate anion produced by the first S{\text{e}}Ar process reacting with triflic anhydride to produce mixed sulfonic/sulfinic anhydride 31 [41], which is itself a viable electrophile for a second S{\text{e}}Ar process that introduces the sulfoxide at the azulene 3-position (Scheme 6C). A somewhat analogous process was proposed by Gunji and co-workers to explain the unexpected formation of a sulfoxide upon the attempted sulfonylation of 2-aminoazulene [42]. The structures of 26–28 were confirmed crystallographically (Fig. 4).

We also evaluated 1,4-dithiane 33 as the sulfide in this process, for which an additional mechanistic pathway can operate. It has
been reported that cyclic bis(sulfides) can undergo electrophilic activation and transannular reaction to give disulfonium dications and this pathway operates even for 33, when the product is the highly strained bicyclo[2.2.0] dication 35. The mechanism proceeding via 35 is depicted in Scheme 7A, although both 34 and 35 would be viable electrophiles for the SEAr step and we have not attempted to determine whether this mechanism is operative or the one in Scheme 5. Regardless, these reaction conditions are able to effect either monosubstitution (Scheme 7B-C) or disubstitution (Scheme 7D), depending on stoichiometry with respect to triflic anhydride, as was the case for 1,4-oxathiane in Scheme 6. In contrast to the 1,4-oxathiane case, no sulfoxide-containing by-product was isolated from the disubstitution reaction, although its formation is mechanistically viable in this case also [42]. The structures of 37 and 39 were confirmed crystallographically (Fig. 5).

2.2. Sulfonium ring-opening

It has previously been shown that azulenyl dimethyl sulfonium salts react readily with amine nucleophiles at the methyl group, undergoing demethylation to afford the corresponding azulenyl methyl sulfides (Scheme 8A) [35]. As the azulenesulfonium salts we...
report here are all cycloalkyl structures, the corresponding transformation would effect a ring opening, as opposed to dealkylation, in these cases [44]. We applied this procedure to a selection of azulene monosulfonium and bis(sulfonium) salts, using phenylthiolate as a model nucleophile, as shown in Scheme 8B. In each instance the reaction proceeded to give products 45–50 in good to excellent yield; no chromatography was necessary. The structure of 48 was confirmed crystallographically (Fig. 6).

We also evaluated representative nitrogen nucleophiles (benzhydrylamine, potassium phthalimide) in the azulenesulfonium ring-opening process and found them to be equally competent nucleophiles (Scheme 9), giving 51–52 (Scheme 9A). In contrast, reaction with sodium ethoxide did not effect nucleophilic substitution to give 53, but instead gave a small amount of impure material tentatively assigned as homoallyl sulhide 54, which could arise from an elimination/ring-opening process (Scheme 9B).

3. Conclusions

This work describes the synthesis of cyclic azulenesulfonium and azulenebis(sulfonium) salts having diversity in both the azulene and the cyclic sulfonium motifs. Two different methods are exploited to synthesise these compounds, namely the redox-neutral interrupted Pummerer process employing sulfoxides, and the oxidative direct electrophilic activation of sulfides. Either of these processes can be made to favour either the mono- or bis(sulfonium) product, through appropriate choice of reaction stoichiometry and/or activating agent. The cyclic sulfonium salts are bench-stable, highly crystalline and readily prepared in good yield. They also undergo facile ring-opening when treated with a variety of nucleophiles, introducing a third point of diversity into the final products (Schemes 8 and 9).
4. Experimental section

4.1. General information

Reactions were carried out under an atmosphere of nitrogen unless stated otherwise. Petrol refers to petroleum ether, bp 40–60 °C. Dichloromethane was dried and degassed by passing through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system. N,N-Dimethylformamide was supplied stored under argon, over 4 Å molecular sieves; no further drying was performed. TLCs were performed using aluminium-backed plates precoated with Alugram®SIL G/UV or aluminium backed plates precoated with Alugram®ALOX N/UV 254 nm and visualised by the naked eye (for coloured azulene compounds) UV light (254 nm). Flash column chromatography was carried out using Davisil LC 60 Å silica gel (35–70 μm) purchased from Sigma Aldrich. All reagents were purchased from Sigma-Aldrich Chemical Co., Fluorochem Ltd, or Fisher Scientific Ltd.; all reagents were used as received without further purification. IR spectra were recorded on a Perkin-Elmer Spectrum 1600 FT IR spectrometer with universal ATR sampling accessory, with absorbances quoted as $\delta$ in cm$^{-1}$. NMR spectra were run on an Agilent ProPulse 500 MHz instrument or Bruker Avance 500 MHz instruments at 298 K, unless otherwise specified. In tabulated NMR data, “p” refers to a pentet/quintet, “hept” refers to a heptet, and “app” is an abbreviation of “apparent”. Capillary melting points were recorded on a Büchi 535 melting point apparatus, and are uncorrected. High resolution mass spectrometry (HRMS) was carried out using a micrOTOF ESI-TOF spectrometer coupled to an Agilent 1200 LC system for autosampling. X-ray crystallography was carried out at 150 K on a RIGAKU SuperNova, Dual, Cu at zero, EosS2 single crystal diffractometer using a microfocus sealed X-ray tube with Cu-Kα radiation $\lambda = 1.51484$ Å and a Rigaku New Xcalibur, EosS2 using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å).

4.2. General procedure A: synthesis of azulenebis(sulfonium) salts by interrupted Pummerer reaction

The required azulene (1.0 eq.) and sulfoxide (14.0 eq.) were added to a 100 mL round bottomed flask. The flask was sealed, evacuated and filled with N$_2$. 10 mL of CH$_2$Cl$_2$ was added and the reaction mixture stirred for 5 min. Triflic anhydride (2.4 eq.) was diluted in 10 mL of CH$_2$Cl$_2$, then this solution was added dropwise to the reaction flask. The reaction was stirred at room temperature for 2 h, then solvent was removed in vacuo. The crude product was dissolved in the minimum amount of CH$_2$Cl$_2$ and precipitated after addition excess of Et$_2$O. The precipitate was then recrystallised from EtOH to give the desired product.
4.2.2. (4,6,8-Trimethylazulene-1,3-diyl)bis(dimethylsulfonium) bis(trifluoromethanesulfonate) - \(17\times20\)OTf

Using General Procedure A with 4,6,8-trimethylazulene [45] (170.0 mg, 1.00 mmol), dimethylsulfoxide (0.99 mL, 14.0 mmol) and triflic anhydride (0.40 mL, 2.40 mmol) gave \(17\times20\)OTf as fluffy yellow crystals (402.4 mg, 0.68 mmol, 69%); m.p. 144–146 °C (dec.). 1H-NMR (300 MHz, Acetone-\(d_6\)) \(\delta\) 8.65 (s, 1H), 8.06 (s, 2H), 4.37–4.32 (m, 4H), 4.12–4.07 (m, 4H), 3.47 (s, 6H), 2.54–2.46 (m, 4H) ppm. 13C-NMR (126 MHz, Acetone-\(d_6\)) \(\delta\) 157.5, 154.3, 141.8, 140.5, 139.5, 110.6, 33.8, 31.8, 29.5 ppm. IR (neat): \(\nu\) = 3027, 2937, 1593 cm\(^{-1}\). HRMS (ESI\(+\)) m/z calculated for \(C_{17}H_{24}S_2^{2+}\) \([M+2]^{+}\) 146.0654, found 146.0647.

4.2.3. 1,1’-(4,6,8-trimethylazulene-1,3-diyl)bis(tetrahydro-1H-thiophen-1-ium) bis(trifluoromethanesulfonate) - \(18\times20\)OTf

Using General Procedure A with 4,6,8-trimethylazulene [45] (170.0 mg, 1.00 mmol), tetrahydrothiophene-S-oxide (1.26 mL, 14.0 mmol) and triflic anhydride (0.40 mL, 2.40 mmol) gave \(18\times20\)OTf as orange crystals (492.5 mg, 0.77 mmol, 77%); m.p. 126–129 °C (dec.). 1H-NMR (500 MHz, Acetone-\(d_6\)) \(\delta\) 8.65 (s, 1H), 8.06 (s, 2H), 4.37–4.32 (m, 4H), 4.12–4.07 (m, 4H), 3.47 (s, 6H), 2.90–2.83 (m, 4H), 2.85 (s, 3H), 2.54–2.46 (m, 4H) ppm. 13C-NMR (126 MHz, Acetone-\(d_6\)) \(\delta\) 156.5, 153.3, 141.5, 139.5, 137.9, 110.2, 52.6, 31.5, 30.1, 28.5 ppm. IR: \(\nu\) = 3015, 2982, 1696, 1589 cm\(^{-1}\). HRMS (ESI\(+\)) m/z calculated for \(C_{21}H_{28}S_2^{2+}\) 302.1469, found 302.1465.

4.3. General Procedure B: synthesis of azulenesulfonium or azulenebis(sulfonium) salts by electrophilic activation of a sulfide

The required sulfide and azulene were dissolved in CH\(_2\)Cl\(_2\) under a nitrogen atmosphere and cooled to –78 °C in an acetone/dry ice bath. The required quantity of triflic anhydride was dissolved in 5 mL of dry CH\(_2\)Cl\(_2\) and added dropwise to the reaction mixture. After vigorous stirring for the specified period, the reaction mixture was allowed to warm to room temperature, then worked up as specified.

4.3.1. 4-(Azulen-1-yl)-1,4-oxathian-4-ium trifluoromethanesulfonate - \(26\times0\)OTf

General Procedure B was used, with azulene \(7\) (100 mg, 0.78 mmol, 1.0 eq.), 1,4-oxathiane \(25\) (0.40 mL, 4.29 mmol, 5.5 eq.) and triflic anhydride (0.16 mL, 0.98 mmol, 125 eq.) in 15 mL of CH\(_2\)Cl\(_2\). Reaction time 1 h. The reaction mixture was concentrated under reduced pressure until 2/3 of the solvent was removed, then...
Et2O (20 mL) was added, forming a precipitate. This was filtered and recrystallised from EtOAc/Et2O to give 26/C15OTf as a red solid (215 mg, 73%). m.p. 259–261 °C (dec.).1H-NMR (500 MHz, Acetonitrile-d3) δ 8.88 (d, J = 9.9 Hz, 1H), 8.80 (d, J = 9.6 Hz, 1H), 8.47 (d, J = 4.5 Hz, 1H), 8.17 (app t, J = 9.9 Hz, 1H), 7.88 (app t, J = 9.9 Hz, 1H), 7.83 (app t, J = 9.8 Hz, 1H), 7.73 (d, J = 4.6 Hz, 1H), 4.47 (app dt, J = 14.0, 3.2 Hz, 2H), 4.05 (ddd, J = 13.6, 11.3, 1.5 Hz, 2H), 3.82 (ddd, J = 12.6, 11.1, 3.4 Hz, 2H), 3.62 (dd, J = 12.7, 2.5 Hz, 2H) ppm. 13C-

**Scheme 8.** Ring opening of cycloalkyl sulfonium salts by a thiolate nucleophile.

**Fig. 6.** Solid state structures of 48. Ellipsoids are represented at 50% probability. H atoms are shown as spheres of arbitrary radius. CCDC 2007955.
NMR (126 MHz, Acetonitrile-$d_3$) $\delta$ 145.6, 143.5, 143.1, 142.2, 137.0, 136.7, 130.6, 130.1, 122.0, 100.7, 66.1, 43.1 ppm. IR (neat): v = 3082, 2995, 2962, 1586 cm$^{-1}$. HRMS (ESI+) calc'd for [C$_{14}$H$_{6}$SO$_3$]$^+$ 2310838; found 2310844.

4.3.2. 11.1'-Azulene-1,3-diylbis(1,4-oxathian-4-ium) bis(hexafluorophosphate) - 27•2PF$_6$ and 4-(3-((Trifluoromethyl)sulfinyl)azulen-1-yl)-1,4-oxathian-4-ium hexafluorophosphate - 28•2PF$_6$

General Procedure B was used, with azulene 7 (110 mg, 0.86 mmol, 1.0 eq.), 1,4-oxathiane 25 (112 mg, 12 mmol, 14 eq.) and triflic anhydride (0.32 mL, 1.88 mmol, 2.2 eq.) in 15 mL of CH$_2$Cl$_2$. Reaction time 1 h. The reaction mixture was poured into Et$_2$O (100 mL) and washed with water (3 × 100 mL). The combined aqueous phases were collected and washed with Et$_2$O (3 × 20 mL). After this, KPF$_6$ (2.00 g, 10.84 mmol, 10.0 eq.) was added to the aqueous phase, and an orange precipitate formed. This was filtered off. The aqueous filtrate was then extracted with EtOAc (2 × 50 mL). The combined EtOAc phases were dried over Na$_2$SO$_4$ and filtered; the filtrate was concentrated under reduced pressure.

The crude product was recrystallized from EtOAc/Et$_2$O to give 37•2PF$_6$ as a red solid (82 mg, 54%). m.p. 212–218 °C. $^1$H-NMR (500 MHz, Acetonitrile-$d_3$) $\delta$ 8.84 (d, J = 9.9 Hz, 1H), 8.80 (d, J = 9.7 Hz, 1H), 8.47 (d, J = 4.6 Hz, 1H), 8.17 (app t, J = 9.9 Hz, 1H), 7.87 (app t, J = 9.9 Hz, 1H), 7.82 (app t, J = 9.8 Hz, 1H), 7.72 (d, J = 4.6 Hz, 1H), 3.96 (dd, J = 12.5, 4.1, 2.4 Hz, 2H), 3.88–3.84 (m, 4H), 3.45 (ddd, J = 16.1, 11.7, 2.0 Hz, 2H), 3.28–3.23 (m, 2H) ppm. $^{13}$C-NMR (126 MHz, Acetonitrile-$d_3$) $\delta$ 145.4, 143.3, 143.1, 142.1, 137.2, 136.7, 130.6, 130.0, 122.0, 100.9, 45.7, 27.2 ppm. IR (neat): v = 1548 cm$^{-1}$. HRMS (ESI+) calc'd for [C$_{14}$H$_{12}$F$_2$S$_2$]$^+$ 247.0610; found 247.0600.

4.3.4. 1-(5-Isopropyl-3,8-dimethylazulen-1-yl)-1,4-dithian-1-ium hexafluorophosphate - 39•2PF$_6$

General Procedure B was used, with guaiazulene 38 (100 mg, 0.50 mmol, 1.0 eq.), 1,4-dithiane 33 (222 mg, 1.84 mmol, 3.7 eq.) and triflic anhydride (0.17 mL, 0.61 mmol, 1.2 eq.) in 5 mL of CH$_2$Cl$_2$. Reaction time 15 min. The reaction mixture was poured into Et$_2$O (100 mL) and washed with water (3 × 100 mL). The combined aqueous phases were collected and washed with Et$_2$O (3 × 20 mL). After this, KPF$_6$ (1.50 g, 8.0 mmol, 16 eq.) was added to the aqueous phase. The aqueous phase was then extracted with EtOAc (3 × 25 mL). The combined EtOAc phases were dried over Na$_2$SO$_4$ and filtered; the filtrate was concentrated under reduced pressure. The crude product was recrystallized from EtOAc/Et$_2$O to give 39•2PF$_6$ as a pink solid (103 mg, 44%). m.p. 137–139 °C. $^1$H-NMR (500 MHz, Acetonitrile-$d_3$) $\delta$ 8.56 (d, J = 2.2 Hz, 1H), 8.18 (s, 1H), 7.93 (dd, J = 10.8, 2.1 Hz, 1H), 7.63 (d, J = 10.8 Hz, 1H), 7.39–3.83 (m, 4H), 3.45 (ddd, J = 14.6, 11.7, 2.3 Hz, 2H), 3.27 (hept, J = 7.0 Hz, 1H), 3.23–3.17 (m, 2H), 3.19 (s, 3H), 2.66 (s, 3H), 1.39 (d, J = 6.9 Hz, 6H) ppm. $^{13}$C-NMR (126 MHz, Acetonitrile-$d_3$) $\delta$ 149.7, 148.3, 143.1, 140.7, 140.0, 138.8, 136.6, 135.2, 130.1, 97.4, 47.7, 38.8, 29.2, 27.7, 24.6, 13.2 ppm. IR (neat): v = 3046, 2960, 2922, 1578 cm$^{-1}$. HRMS (ESI+) calc'd for [C$_{14}$H$_{12}$F$_2$S$_2$]$^+$ 3171392; found 3171523.

4.3.5. 11.1’-Azulene-1,3-diylbis(1,4-dithian-1-ium) bis(hexafluorophosphate) - 40•2PF$_6$

General Procedure B was used, with azulene 7 (140 mg, 1.09 mmol, 1.0 eq.), 1,4-dithiane 33 (1.83 g, 15.3 mmol, 14 eq.) and triflic anhydride (0.41 mL, 2.40 mmol, 2.2 eq.) in 15 mL of CH$_2$Cl$_2$. Reaction time 40 min. The reaction mixture was poured into Et$_2$O (100 mL) and washed with water (3 × 100 mL). The combined aqueous phases were collected and washed with Et$_2$O (3 × 20 mL). After this, KPF$_6$ (2.00 g, 10.84 mmol, 10.0 eq.) was added to the aqueous phase, and an orange precipitate formed. This was filtered off, and the precipitate was recrystallized from EtOAc/Et$_2$O to give 40•2PF$_6$ as an orange solid (373 mg, 52%). m.p. 189–191 °C (dec.). $^1$H-NMR (500 MHz, Acetonitrile-$d_3$) $\delta$ 9.12 (s, 1H), 9.10 (d, J = 9.4 Hz, 2H), 8.56 (t, J = 10.0 Hz, 1H), 8.28 (app t, J = 10.1 Hz, 2H), 4.05–3.98 (m, 8H), 3.49 (ddd, J = 15.9, 9.7, 4.1 Hz, 4H), 3.36–3.31 (m, 4H) ppm.
13C-NMR (126 MHz, Acetonitrile-\(d_3\)) \(\delta\) 147.4, 144.8, 140.8, 140.1, 134.8, 106.1, 45.7, 27.0 ppm. IR (neat): \(\nu\) = 2952, 1583 cm\(^{-1}\). HRMS (ESI-) calcld for [C\(_{49}\)H\(_{42}\)S\(_2\)Na\(^+\)] \(\delta\) 183.0297; found 183.0288.

### 4.4. General procedure C: nucleophilic ring-opening of cyclic sulfonium salts

The required sulfonium salt and nucleophile were added to a 50 mL round bottom flask with a magnetic stir bar. The flask was evacuated and filled with \(N_2\) gas. 5 mL of DMF was added to the flask and the reaction mixture was stirred at the specified temperature for the specified time. The reaction mixture was diluted with diethyl ether (30 mL), and washed with water (20 mL) and 5% LiCl(aq) solution (30 mL). The organic layer was dried over MgSO\(_4\) and filtered. The filtrate was concentrated in vacuo and if necessary, the crude product was purified as indicated.

#### 4.4.1. Azulen-1-yl[4-(phenylthio)butyl]sulfide - 45

**General Procedure C** was used, with azulen-1-yl(2-((2-(phenylthio)ethyl)thio)ethyl)sulfide - 49

#### 4.4.4. Azulen-1-yl[2-(2-(phenylthio)ethyl)thio]ethyl)sulfide - 48

**General Procedure C** was used, with azulen-1-yl(2-((2-(phenylthio)ethyl)thio)ethyl)sulfide - 49

#### 4.4.5. (5-Isopropyl-3,8-dimethylazulen-1-yl)(2-((2-phenylthio)ethyl)thio)ethyl)sulfide - 50

**General Procedure C** was used, with azulen-1-yl(2-((2-(phenylthio)ethyl)thio)ethyl)sulfide - 50

#### 4.4.6. 1,3-Bis(2-((2-phenylthio)ethyl)thio)ethyl)thio)azulene - 51

**General Procedure C** was used, with azulen-1-yl(2-((2-(phenylthio)ethyl)thio)ethyl)sulfide - 51

#### 4.4.7. 4-(4-(4,6,8-trimethylazulen-1-yl)thio)butyl)sulfide - 46

**General Procedure C** was used, with azulen-1-yl(2-((2-(phenylthio)ethyl)thio)ethyl)sulfide - 48

#### 4.4.8. 2-(4-phenylthio)butyl)thio)azulene - 52

**General Procedure C** was used, with azulen-1-yl(2-((2-(phenylthio)ethyl)thio)ethyl)sulfide - 52

#### 4.4.9. Azulen-1-yl[2-(2-(phenylthio)ethyl)thio]ethyl)sulfide - 49

**General Procedure C** was used, with azulen-1-yl(2-((2-(phenylthio)ethyl)thio)ethyl)sulfide - 49

#### 4.4.10. Azulen-1-yl(2-((2-(phenylthio)ethyl)thio)ethyl)sulfide - 50

**General Procedure C** was used, with azulen-1-yl(2-((2-(phenylthio)ethyl)thio)ethyl)sulfide - 50

#### 4.4.11. Azulen-1-yl(2-((2-(phenylthio)ethyl)thio)ethyl)sulfide - 51

**General Procedure C** was used, with azulen-1-yl(2-((2-(phenylthio)ethyl)thio)ethyl)sulfide - 51

#### 4.4.12. Azulen-1-yl(2-((2-(phenylthio)ethyl)thio)ethyl)sulfide - 52

**General Procedure C** was used, with azulen-1-yl(2-((2-(phenylthio)ethyl)thio)ethyl)sulfide - 52
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We are grateful for PhD funding to C.M.-L.A. from the EU Horizon 2020 research and innovation programme under grant agreement H2020-MSCA-CO-FUND, #665992. The Centre for Sustainable Chemical Technologies is supported by EPSRC under grant EP/L016354/1. T.D.J. thanks the Royal Society for a Wolfson Research Merit Award. The British-Spanish Society and Plastic Energy are thanked for a 2017 Scholarship to C. M. L.-A. NMR and X-ray crystallography facilities were provided through the Materials and Chemical Characterization (MC2) Facility at the University of Bath.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2020.131700.

References

[1] (For reviews, see:) (a) J.V.J. Crivello, Photopolym. Sci. Technol. 22 (2009) 357–582; (b) J.V.J. Crivello, Photopolym. Sci. Technol. 21 (2008) 493–497.
[2] (a) A. Dovas, P. Argitis, K. Misiakos, D. Dimotikali, P.S. Petrou, S.E. Kakabakos, Adv. Synth. Catal. 355 (2013) 13744–13748.
[3] (a) R. Xia, J.-P. Malval, M. Jin, A. Spangenberg, D. Wan, H. Pu, T. Vergote, Adv. Synth. Catal. 355 (2013) 7312–7323.
[4] (a) A. Douvas, P. Argitis, K. Misiakos, D. Dimotikali, P.S. Petrou, S.E. Kakabakos, Adv. Synth. Catal. 355 (2013) 13744–13748.
[5] (a) J.-N. Zhao, M. Kayumov, D.-Y. Wang, A. Zhang, Angew. Chem. Int. Ed. 59 (2020) 1452–1456.
[6] (a) M.H. Aukland, M. Marder, Science 296 (2002) 1106–1109.
[7] (a) M. Siauclis, A. West, G.J.P. Perry, D.J. Procter, Nat. Chem. 5 (2013) 4308–4313.
[8] (a) S.-M. Wang, H.-X. Song, X.-Y. Wang, N. Liu, H.-L. Qin, C.-P. Zhang, Chem. Commun. 24 (2008) 2219–2221.
[9] (a) F. Zhou, Y. Cheng, X.-P. Liu, J.-R. Chen, J. Chem. 55 (2019) 3117–3120.
[10] (a) J.N. Zhao, M. Kayumov, D.-Y. Wang, A. Zhang, Angew. Chem. Int. Ed. 59 (2020) 7303–7306.
[11] (a) A. Douvas, P. Argitis, K. Misiakos, D. Dimotikali, P.S. Petrou, S.E. Kakabakos, Adv. Synth. Catal. 355 (2013) 13744–13748.
[12] (a) A.J. Eberhart, J.E. Imbriglio, D.J. Procter, Org. Lett. 13 (2011) 5882–5885.
