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Reactivity of α -diazo sulfonium salts: rhodium-catalysed ring expansion of indenenes to naphthalenes†

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In the presence of catalytic amounts of the paddlewheel dirhodium complex $\text{Rh}_2(\text{esp})_2$, α -diazo dibenzothiophenium salts generate highly electrophilic Rh-coordinated carbenes, which evolve differently depending on their substitution pattern. Keto-moieties directly attached to the azomethinic carbon promote carbene insertion into one of the adjacent C–S bonds, giving rise to highly electrophilic dibenzothiopyrylium salts. This intramolecular pathway is not operative when the carbene carbon bears ester or trifluoromethyl substituents; in fact, these species react with olefins delivering easy to handle cyclopropyl-substituted sulfonium salts. When indenenes are the olefins of choice, the initially formed cyclopropyl rings smoothly open with concomitant departure of dibenzothiophene, enabling access to a series of 2-functionalized naphthalenes.

Introduction

Arguably, the most prominent feature of sulfonium salts when compared with hypervalent I(III)-reagents of analogous structure is their enhanced thermal stability.^{1,2} This property ultimately makes these species practical reagents for synthesis³ because: (i) it facilitates their handling even in large-scale;⁴ (ii) allows expedition of purifications, often through traditional chromatographic techniques,⁵ and importantly, (iii) it enables functional group manipulations to be carried out on these reagents after incorporation of the sulfonium moiety into their structures.⁶ This robustness is particularly manifested when the sulfonium salt bears other sensitive functional groups, and has recently been exploited for the design of sulfur-based reagents with no parallelism in the realm of hypervalent iodine species.⁷

Recently, Suero and co-workers reported the Rh-catalysed formation of cyclopropyl-I(III) intermediates **A** by reaction of α -diazoidonium salts with olefins.^{8,9} Such species smoothly evolve, even at temperatures as low as -50°C , to synthetically useful allylic cations **B** via scission of their distal C–C bond with concomitant elimination of the iodine moiety (Scheme 1A). Due to this intrinsic reactivity, cyclopropyl-substituted iodonium salts have eluded systematic isolation and, in fact, compound **C** is the only member of the series that has been characterized (Scheme 1B).⁸ Contrarily, cyclopropyl-substituted sulfonium

salts like **D** are relatively easy to handle, and have been utilized since decades for the synthesis of cyclobutanones (Scheme 1C);¹⁰ yet, their structural variability remains quite narrow. Since neither **D** or a structural derivative has been synthesized following an analogous [2 + 1] disconnection, nor their electrocyclic ring-opening has been studied, we decided to tackle both aspects.

Herein, we describe the synthesis of a series of new α -diazo-sulfonium salts and their transformation into the corresponding cyclopropyl-derivatives through the Rh-catalyzed addition of



Scheme 1 (A) Reactivity of cyclopropyl-I(III) reagents; (B) only characterized cyclopropyl-substituted λ^3 -iodane; (C) classical synthesis of cyclopropyl-substituted sulfonium salts; (D) and (E) new synthesis of cyclopropyl-substituted sulfonium salts and reactivity studies.

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sulfoniocarbene moieties to olefins.¹¹ This new route significantly expands the available structural diversity for cyclopropyl-substituted sulfonium salts, which are all isolated as crystalline materials after column chromatography. Subsequently, making use of the thermodynamically favored electrocyclic ring opening of the salts derived from indene, a protocol is implemented for the transformations of such compounds into 2-substituted naphthalenes (Scheme 1D and E).¹²

Results and discussion

Synthesis and structure of α -diazosulfonium salts

Our initial efforts were focused on the synthesis of parent sulfonium salts **1a–f**, all non-reported compounds that share the dibenzothiophene platform and an electron withdrawing group embedding the azomethine carbon. Compounds **1a–h** were prepared without exception by reaction of the corresponding diazo compounds with *in situ* generated sulfurane **2**.¹³ The reaction took place in moderate to good yields, and compounds **1a–g** were isolated as pale-yellow crystalline solids (Scheme 2). Previously reported compounds **1h** and **1i** were included in this study for completeness.^{13b}

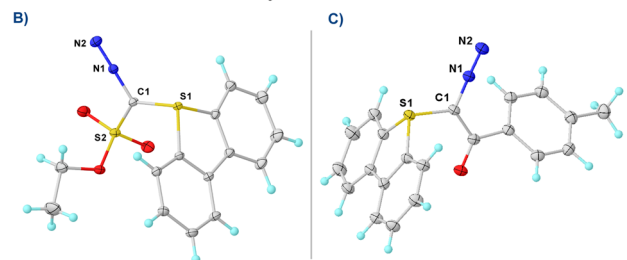
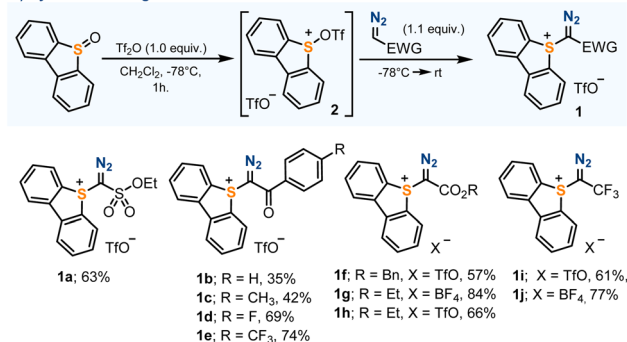
The molecular structures of **1a–f** have been determined by X-ray diffraction, confirming the expected connectivity (Scheme 2B and C and the ESI[†]). The central sulfur atom (S1) adopts for all compounds a trigonal-pyramidal coordination environment, with the sum of the bond angles around this atom falling within a narrow range (303.8–305.0°). The S1–C1 bond distances are the typical ones for S–C(sp²) single bonds (1.728–1.742 Å), and

the C1–N1 lengths (1.338–1.331 Å) are identical, within the experimental error, to those found in non-charged diazo compounds.¹⁴ Salts **1a–f** were also studied by simultaneous differential scanning calorimetry-thermogravimetric analysis (DSC-TGA). Sharp exothermic events were detected for all compounds, which start at 80–90 °C and lead to energy releases ranking between 332 J g⁻¹ (for **1a**) and 485 J g⁻¹ (for **1c**); however, on the basis of the Yoshida correlation, they are not expected to be explosive or impact sensitive.¹⁵ The heat release events observed are coupled with acute mass losses that are probably related to the decomposition of the diazo unit.

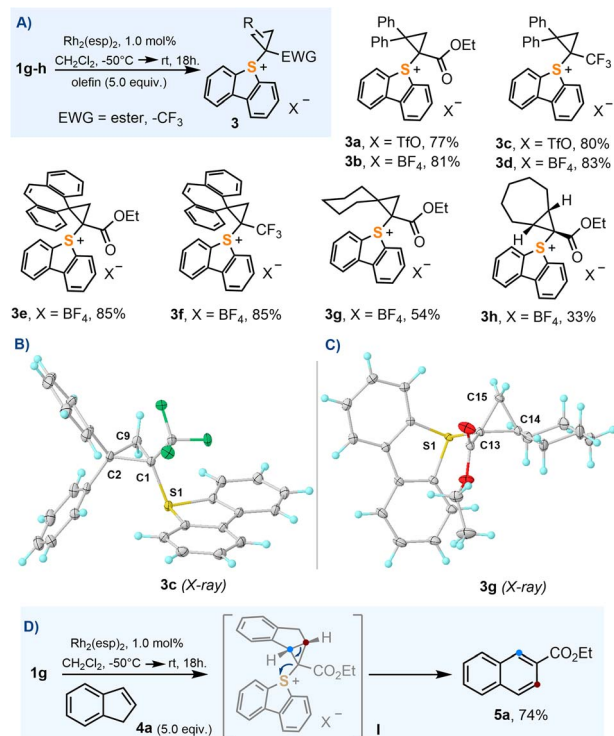
Synthesis of cyclopropyl-substituted sulfonium salts

In order to evaluate the utility of **1a–j** as cyclopropanation reagents, **1g–h** were used as model compounds and the reaction conditions optimized by Suero for I(III)-species were employed (Rh₂(esp)₂, 1 mol%; CH₂Cl₂, -50 °C → r.t.; olefin, 5.0 equiv.).⁸ The cyclopropanation reaction works particularly well for 1,1-disubstituted olefins **3a–g**; cycloheptene also delivers the expected cyclopropane product **3h**, albeit in moderate yield (Scheme 3A). In contrast to their I(III) analogues,¹⁶ sulfonium salts **3a–h** are all bench stable crystalline materials that can be stored without any precaution for months. Scheme 3B and C

A) Synthesis of 1a–g



Scheme 2 (A) Synthesis of α -diazosulfonium salts; (B) and (C) molecular structures in the solid state of compounds **1a** and **1c**, respectively. Anisotropic displacements shown at the 50% probability level. Triflate anions and solvent molecules omitted for clarity. Selected bond lengths [Å]: **1a**: S1–C1, 1.728(1); C1–N1, 1.333(1); N1–N2, 1.113(1); **1c**: S1–C1, 1.742(2); C1–N1, 1.339(2); N1–N2, 1.117(2).



Scheme 3 (A) Synthesis of cyclopropyl-substituted sulfonium salts; (B) and (C) molecular structures in the solid state of compounds **3c** and **3g**, respectively. Anisotropic displacements shown at the 50% probability level. Solvent molecules and anions omitted for clarity. Selected bond lengths [Å]: **3c**: S1–C1, 1.793(1); C1–C2, 1.520(1); C1–C9, 1.545(1); C2–C9, 1.500(2); **3g**: S1–C13, 1.785(1); C13–C15, 1.522(1); C13–C14, 1.529(1); C14–C15, 1.522(1); (D) indene ring expansion to naphthalene **5a**.



functionalities on the final naphthalene (**5s** and **5t**, respectively). However, when the indene substrate bears substituents in the 2-position, no naphthalene is observed; instead, the dimeric structures **9** are isolated (Scheme 5B).

The formation of naphthalenes **5a–t** surely involves cyclopropanation and electrocyclic ring opening, as previously reported for similar carbon-atom insertion reactions.^{19j} However, we believe that no cyclopropane is involved in the formation of

9. Probably, once intermediate **III** is formed, the regeneration of the original indene olefin is primed by deprotonation. This is followed by a protodemetalation step to deliver sulfonium salt **IV**, subsequent nucleophilic attack of a second equivalent of indene to form carbocation **V**, and final deprotonation.

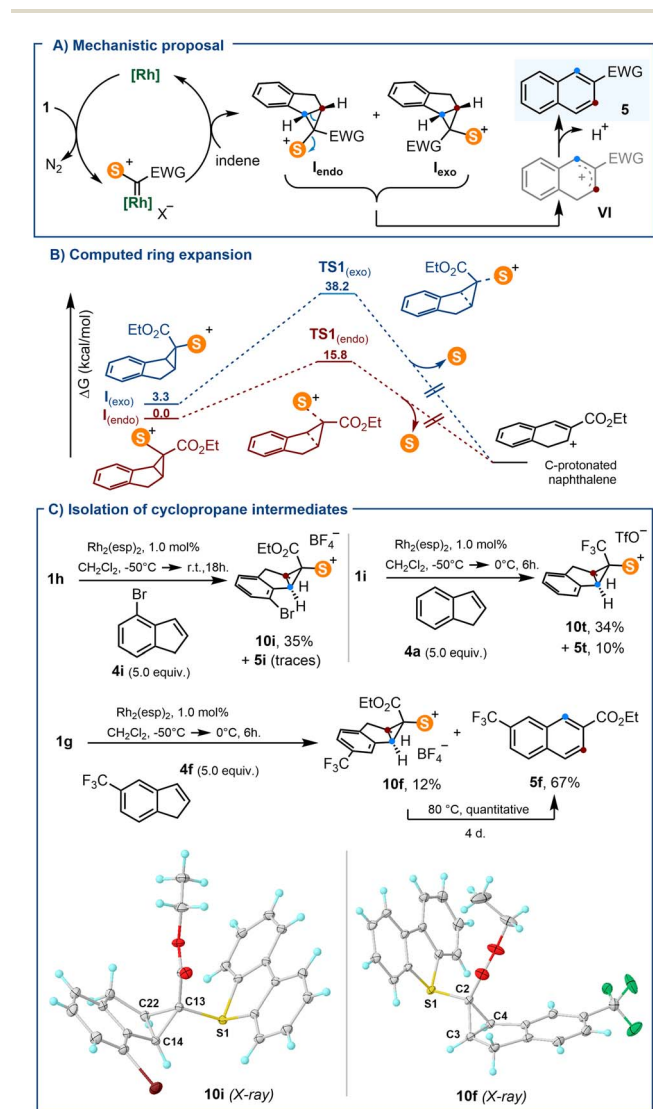
Because carbenes derived from **1a–g** contain two different substituents, the cyclopropanation of indenes with such species is expected to produce a mixture of diastereomeric cyclopropanes that are not likely to open at the same speed (**I_{endo}** and **I_{exo}**; Scheme 6A). This made us hypothesize that the geometric bias of **I_{exo}** against undergoing disrotatory ring opening might facilitate its detection or even its isolation, at least for some of the substrates employed.²¹

DFT calculations at the B3LYP-D3/def2-TZVP level provide a more quantitative perspective to that hypothesis.²² Transition states for naphthalene formation were found from both **I_{endo}** and **I_{exo}**; but, the barrier for the electrocyclic ring opening through **TS1_{exo}** is predicted to be significantly higher (34.8 kcal mol⁻¹) than that proceeding *via* **TS1_{endo}** (15.8 kcal mol⁻¹) (Scheme 6B). This is accompanied by a greater degree of C–S bond breaking, and lesser degree of cyclopropane C–C bond cleavage for the unfavoured **TS1_{exo}** (S–C, 2.270 Å vs. 2.792 Å; for **TS1_{endo}** and **TS1_{exo}**, respectively; C–C, 1.918 Å vs. 1.749 Å; for **TS1_{endo}** and **TS1_{exo}**, respectively). Jointly, these values justify the reluctance of **I_{exo}** to ring open, and suggest that when formed, **I_{exo}** should be observable.

Hence, we carefully re-checked the ¹H NMR spectra for all crude reactions leading to the formation of **5a–t**, and gratifyingly found that signals attributable to cyclopropane species were present in three cases (for **5f**, **5i** and **5t**). These assays were subsequently repeated and submitted to careful column chromatography allowing the isolation, albeit in reduced yields, of **10i**, **10f** and **10t**, the respective *exo*-cyclopropane salts (Scheme 6C). The connectivity of such species has been unambiguously confirmed by X-ray diffraction analysis (Scheme 6C and ESI[†]). It is of note that these sulfonium salts are quantitatively transformed into the corresponding naphthalenes when gently heated in acetonitrile for several days. Finally, the isolation of naphthalene **5a** when indene **4u** is used as the substrate further suggests the involvement of cationic intermediate **VI**, which evolves either *via* deprotonation, or alternatively, *via* competitive de-allylation (Scheme 6D). Compound **12** is surely formed by acid promoted cyclisation of non-observed **11**.

Conclusions

A Rh-catalysed ring expansion that enables the transformation of indenes into naphthalenes has been developed. Key for the method is the use of α -diazo sulfonium salts, which act as remarkably stable carbyne equivalents. Mechanistically, the reaction proceeds *via* initial Rh-catalysed transfer of a sulfonio-carbene unit to olefins, delivering the corresponding cyclopropanes. Subsequent electrocyclic opening of the three-membered ring with concomitant elimination of dibenzothiophene delivers the final naphthalene products. All sulfonium reagents involved can be easily handled, the conditions employed are quite mild, and the functional group tolerance is remarkable. This makes us



Scheme 6 (A) Proposed reaction mechanism; (B) computed Gibbs free energy for the indene ring expansion at the uB3LYP-D3 level; (C) isolation of *exo*-substituted cyclopropyl sulfonium salts, and molecular structures in the solid state of compounds **10i** and **10t**. Anisotropic displacements shown at the 50% probability level. Solvent molecules and anions omitted for clarity. Selected bond lengths [Å]: **10i**: S1–C13, 1.805(1); C13–C14, 1.527(2); C13–C22, 1.513(2); C14–C22, 1.521(2); **10f**: S1–C2, 1.795(1); C2–C3, 1.523(2); C2–C4, 1.527(2); C3–C4, 1.517(1); (D) partial de-allylation of **4u**.



anticipate a broad range of future applications for α -diazo sulfonium salts in the area of skeletal editing.

Data availability

All data associated with this article are available from ESI.†

Author contributions

S. T. and M. A. conceived and directed the project and designed the experiments. S. T. and T.-H. W. performed all of the experiments and analysed their results. C. G. carried out the crystallographic studies and calculations. S. T. and M. A. prepared the manuscript.

Conflicts of interest

There are no conflicts to declare.

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