First successful $[4^+ + 2]$-type polar cycloadditions of 2-benzothiopyrylium salt with dienes

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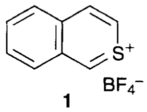
2-Benzothiopyrylium salt 1 reacted *via* a $[4^+ + 2]$-type polar cycloaddition with dienes 2 in the presence of methanol to afford benzo-fused bicyclo[2.2.2] compounds 5, while in the absence of methanol cycloaddition of 1 with 2,3-dimethylbuta-1,3-diene 2a afforded a novel benzo-fused tricyclic compound 4a, whose structure has been confirmed by X-ray crystallography.

We recently reported that novel $[2^+ + 4]$-type polar cycloadditions of 2-benzothiopyrylium salts with a variety of conjugated dienes affording benzo-fused bicyclic sulfonium adducts indicated that 2-benzothiopyrylium ions can act as electron-poor dienophiles.[1] In the course of our studies on the polar cycloaddition of benzothiopyrylium salts, we have found that 2-benzothiopyrylium salts can also act as electron-poor dienes. This communication describes the first examples of $[4^+ + 2]$-type polar cycloadditions of 2-benzothiopyrylium salt **1** with some 1,3-dienes to afford benzo-fused bicyclo[2.2.2] compounds by the trapping of intermediary thienium ion-containing cycloadducts with methanol.

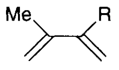
Stirring a mixture of 2-benzothiopyrylium salt **1** and 2,3-dimethylbuta-1,3-diene **2a** in dry 1,2-dichloroethane at room temperature for 3 h afforded a 32% yield of the benzo-fused tricyclic compound **4a**,† mp 102.5–104 °C, as colourless prisms (from EtOH). The structure of compound **4a** was assigned on the basis of spectral results, and the structure was confirmed by an X-ray crystal structure determination,‡ illustrated in Fig. 1.

The formation of compound **4a** is particularly interesting from a mechanistic point of view, because our previous studies revealed that the same reaction afforded a novel $[2^+ + 4]$-type polar cycloaddition product **3a** in high yield when dry diethyl ether was added to the reaction mixture after 10 min reaction time to isolate the sulfonium salt adduct.[1] Taking account of the above observation, it is suggested that the cycloadduct **3a** is an intermediate for compound **4a**. In fact, when a solution of the adduct **3a** in 1,2-dichloroethane was stirred for 3 h at room temperature, compound **4a** was formed in 65% yield.

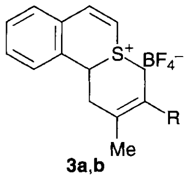
In order to elucidate the mechanism of the formation of compound **4a**, we next carried out the above cycloaddition in the presence of methanol as this is a solvent which is expected to act as a nucleophile for trapping the reactive intermediate generated during the reaction. Treatment of the salt **1** with 2,3-dimethylbuta-1,3-diene **2a** in 1,2-dichloroethane in the presence of 5 equiv. of dry methanol afforded the benzo-fused bicyclic compound **5a** (36%) in addition to compound **4a** (10%). Compound **5a** is believed to be a $[4^+ + 2]$-type cycloadduct between 2-benzothiopyrylium salt **1** as an electron-poor diene and 1,3-diene as an electron-rich alkene. The same reaction performed in dry methanol also yielded compound **5a** (29%) along with compounds **6a** (38%) and **7a** (9%), the latter compound as an inseparable mixture of diastereoisomers. Furthermore, the $[2^+ + 4]$-type cycloadduct **3a** was also stirred in dry methanol for 2 h at room temperature to afford compounds **4a** (23%), **5a** (26%) and **6a** (29%). When refluxing in dry methanol, the cycloadduct **3a** was also converted into **5a** (35%) and **6a** (20%). Similar behaviour was observed in the cycloaddition of the salt **1** with isoprene **2b**. However, this cycloaddition did not give the benzo-fused tricyclic compound corresponding to compound **4a**, but only undetermined complex mixtures, when the reaction was performed without nucleophiles. This result suggests that a presumed intermediate from the above reaction with isoprene does not undergo the subsequent reaction leading to the tricyclic compound, probably due to its unstable structure. Cycloaddition of the salt **1** with isoprene **2b** in the presence of dry methanol proceeded regiospecifically to afford the $[4^+ + 2]$-type cycloadduct **5b** in 46% yield. A $[2^+ + 4]$-type cycloadduct **3b** also afforded the compound **5b** in 31% yield under similar conditions.



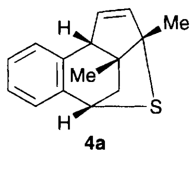
1



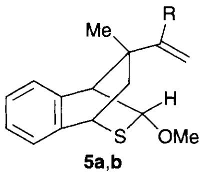
2a R = Me
b R = H



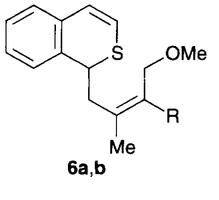
3a,b



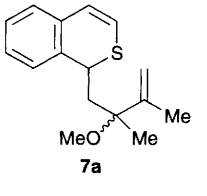
4a



5a,b



6a,b



7a

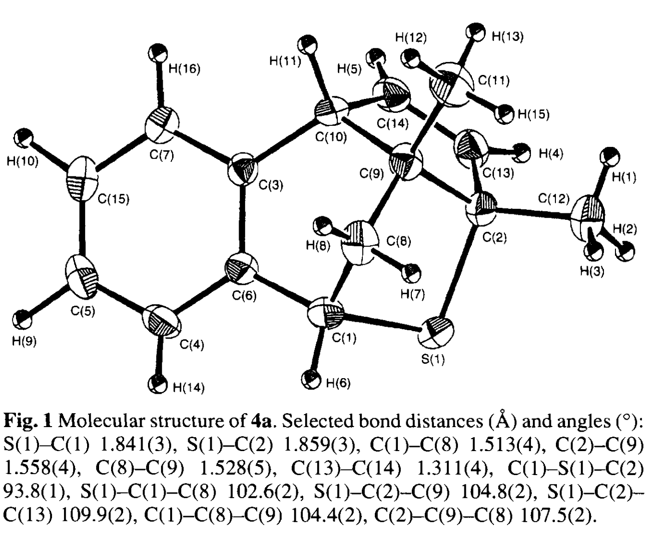
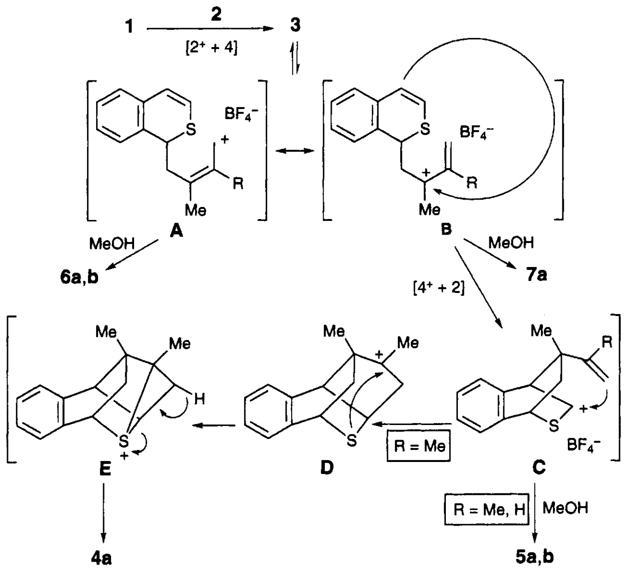


Fig. 1 Molecular structure of **4a**. Selected bond distances (Å) and angles (°): S(1)–C(1) 1.841(3), S(1)–C(2) 1.859(3), C(1)–C(8) 1.513(4), C(2)–C(9) 1.558(4), C(8)–C(9) 1.528(5), C(13)–C(14) 1.311(4), C(1)–S(1)–C(2) 93.8(1), S(1)–C(1)–C(8) 102.6(2), S(1)–C(2)–C(9) 104.8(2), S(1)–C(2)–C(13) 109.9(2), C(1)–C(8)–C(9) 104.4(2), C(2)–C(9)–C(8) 107.5(2).

A plausible mechanism for the cycloaddition of the salt **1** with buta-1,3-dienes **2** affording [4^+ + 2]-type cycloadducts **4** and **5** is depicted in Scheme 1. Rapid [2^+ + 4]-type polar cycloaddition between the salt **1** and 1,3-dienes affords the isolable cycloadduct **3**. Cycloadduct **3** in solution easily reaches equilibrium with the intermediate **A** *via* cleavage of the C–S bond. The intermediate **A** and its resonance form **B** are trapped with methanol to afford **6a,b** and **7a**, respectively. The intermediate **B** cyclises to the 4-position of thiopyran ring *via* a [4^+ + 2]-type cycloaddition as reported in the well-known Bradhser reaction of isoquinolinium salt[2] to give the thienium ion intermediate **C**, which is then attacked by methanol affording compounds **5a** and **5b**. On the other hand, in the absence of any nucleophiles, when R is a methyl group in the intermediate **C**, the alkenic moiety attacks the thienium ion carbon atom to lead to the relatively stable tertiary carbonium ion intermediate **D**. The sulfur atom of intermediate **D** then undergoes an intramolecular attack on the carbonium ion to give the four-membered sulfonium ion intermediate **E**, which then degrades by the loss of a proton along with concomitant C–S bond cleavage to furnish the compound **4a**.



Scheme 1

Footnotes

† Satisfactory analytical and spectral data were obtained for all new compounds.

‡ *Crystal data* for **4a**: $C_{15}H_{16}S$, orthorhombic, a = 11.339(2), b = 28.622(4), c = 7.500(5) Å, space group $Iba2$ (No. 45), V = 2434(2) Å^3, Z = 8, D_c = 1.246 g cm^{-3}, crystal dimensions 0.50 × 0.30 × 0.50 mm, μ(Mo-Kα) = 2.24 cm^{-1}; diffractometer: Rigaku AFC5R, radiation: Mo-Kα (λ = 0.71069 Å), scan range: 47.04 < 2θ < 49.68°, scan type: ω–2θ standard reflection: 3 standards, 150 reflections; independent reflection: 1285; R = 0.034, R_w = 0.043, GOF: 1.79. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and reference no. 182/209.

References

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