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Reactions of acetylenes, possessing bulky alkyl substituents, with S_2Cl_2. Unexpected formation of α-oxothioketones, thiirene 1-oxides, and 1,2-dithietes

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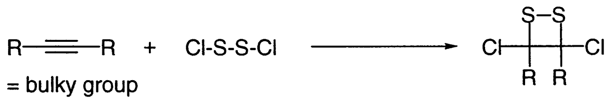
Abstract

The reaction of di-*t*-butylacetylene with S_2Cl_2, followed by purification with silica-gel column chromatography, gave 2,2,5,5-tetramethyl-4-oxo-3-hexanethione (**4a**) (37%) and 2,3-di-*t*-butylthiirene 1-oxide (**5a**) (10%), which were formed by hydrolysis of the initial product, 2,3-di-*t*-butyl-2,3-dichloroepisulfide (**3a**). The same work-up of the reaction mixture of di(1-adamantyl)acetylene with S_2Cl_2 provided 2-oxoethanethione (**4b**) (4–33%), thiirene 1-oxide (**5b**) (8–27%) and 1,2-dithiete (**9b**) (3–21%). The reaction of 2,2,5,5,6,6,9,9-octamethyl-3,7-decadiyne (**1c**) with S_2Cl_2 furnished a 4*H*,5*H*-thiepin (**12**) as the sole product in 99% yield. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: α-oxothioketone; thiirene 1-oxide; 1,2-dithiete; 4*H*,5*H*-thiepin; episulfide.

In our continuing interest in the chemistry of small ring compounds containing two sulfur atoms in the ring, such as dithiiranes[1,2] and 1,2-dithietes,[1,3] we have now turned our attention to the preparation of 1,2-dithietanes[1,4] by reactions of acetylenes (**1**), carrying two bulky alkyl substituents, with S_2Cl_2. We expected that the addition of S_2Cl_2 to **1**, which is followed by intramolecular addition, would lead to the formation of 1,2-dithietanes (**2**). The reaction, though it failed to give the expected **2**, furnished rather surprising products such as α-oxothioketones, thiirene 1-oxides and 1,2-dithietes. The formation of these unexpected products is the topic of the present paper.



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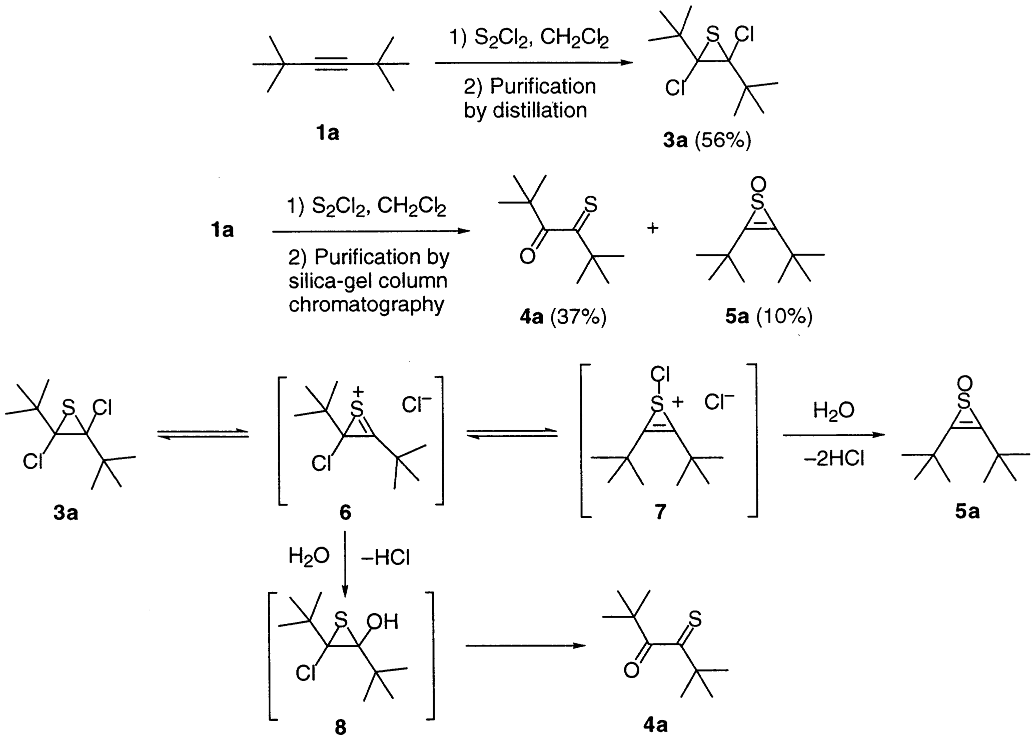
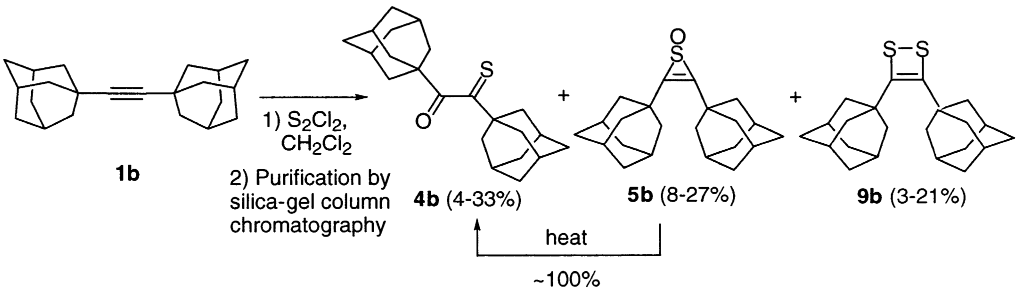
When di-*t*-butylacetylene (**1a**) was treated with an equimolar amount of S_2Cl_2 in CH_2Cl_2 at room temperature for 2 h and the resulting mixture was distilled directly, 2,3-di-*t*-butyl-2,3-dichloroepisulfide (**3a**)[5] was isolated in 56% yield. Meanwhile, interestingly, when the reaction mixture was purified by silica-gel column chromatography, 2,2,5,5-tetramethyl-4-oxo-3-hexanethione (**4a**)[6] and 2,3-di-*t*-butylthiirene 1-oxide (**5a**)[6] were obtained in 37 and 10% yields, respectively, with the sacrifice of **3a**. A separate experiment showed that **3a** is hydrolyzed to give **4a** (43%) and **5a** (29%) during purification by silica-gel column chromatography, thus revealing that **3a** is the precursor of **4a** and **5a**. The mechanism of this interesting hydrolysis would involve an equilibrium between **3a**, carbocation (**6**) and episulfonium ion (**7**). The addition of water to **6** would produce **4a** through **8**, while the usual hydrolysis of the chloro-substituted sulfonium ion **7** would result in the formation of **5a**.

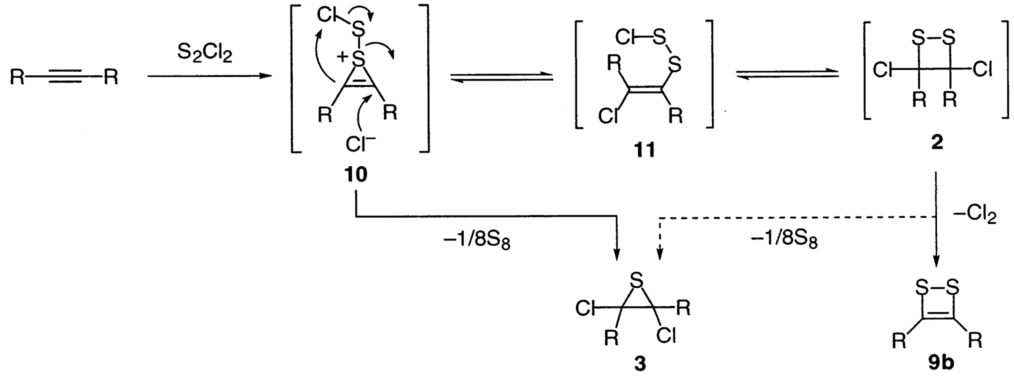


Reaction of di(1-adamantyl)acetylene (**1b**) with S_2Cl_2 in CH_2Cl_2 was examined by varying molar ratio, reaction temperature, reaction time and quenching methods of the reaction. Purification of the resulting mixtures of 1:1 molar reaction by silica-gel column chromatography furnished 3,4-di(1-adamantyl)-1,2-dithiete (**9b**)[3a,b] in 3–21% yield, in addition to 1,2-di(1-adamantyl)-2-thioxoethanone (**4b**)[5] (4–33%) and 2,3-di(1-adamantyl)thiirene 1-oxide (**5b**)[5] (8–27%), with recovery of **1b** in 3–35% yield. Compounds **4b** and **5b** correspond to **4a** and **5a**, respectively, products from the acetylene **1a**. The thiirene 1-oxide **5b** rearranged to **4b** quantitatively when heated above its melting point; the same rearrangement of **5a** to **4a** took place in refluxing toluene.



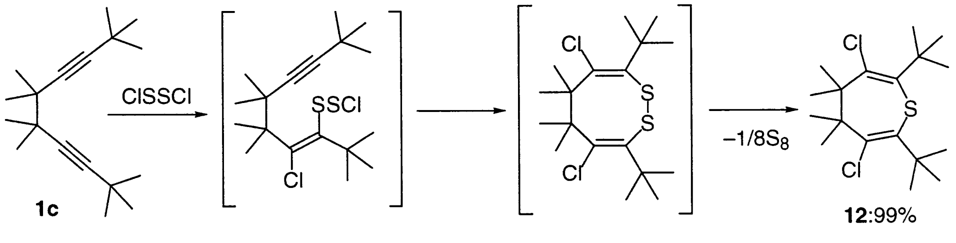
Thiirene 1-oxides are compounds of much interest in their own light. Only a few thiirene 1-oxides are known to date, and their chemistry has been investigated in some detail.[7] The formation of thiirene 1-oxides **5a** and **5b** is, therefore, the most important feature of the above two reactions. Easy accessibility of the starting materials **1a** and **1b**[8] makes up for the low yields of **5a** and **5b**.

The following give the most probable explanation as to how episulfides **3** (precursors of **4a**,**b** and **5a**,**b**) and 1,2-dithiete **9b** were formed. Addition of S_2Cl_2 to acetylenes would produce thiirenium ion intermediates (**10**) initially, which undergo two competitive reactions. One is the reorganization that leads to episulfides **3** with loss of sulfur, and the other is the completion of the addition of S_2Cl_2 that produces adducts **11**. Intramolecular addition of **11** would then provide 1,2-dithietanes **2**, whose formation was expected initially. The thermal instability of 1,2-dithientanes is notable,[1] and thus **2** decomposes to give the highly stable 1,2-dithiete **9b**[3a,b] with dechlorination. Though less probable, episulfides **3** also might form from **2** by loss of sulfur.



Diarylacetylenes, such as diphenyl-, di(*p*-anisyl)-, and di(2-thienyl)acetylenes, did not give any products corresponding to **4**, **5** and **9b** on reactions with S_2Cl_2.[9]

Incidentally, a highly congested diacetylene (**1c**),[3b] on reaction with 2.2 molar amounts of S_2Cl_2, provided a 4*H*,5*H*-thiepin (**12**)[5] quantitatively.[10] The most straightforward explanation for the formation of **12** is shown below.



Acknowledgements

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5. Relevant data for new compounds. **3a**: bp 72°C/5 mmHg; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.39 (s); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 29.6, 44.7, 85.6; stereochemistry is unknown, though probably *trans*. **4b**: red–purple needles; mp 100–103°C ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.71–1.72 (12H, m), 1.93–1.94 (3H, m), 2.01–2.06 (15H, m); ^{13}C NMR ($CDCl_3$, 100.6 MHz) $\delta = 28.0$, 28.4, 36.1, 36.3, 39.8, 42.0, 44.3, 53.6, 211.3, 269.4. **5a**: viscous oil (solidifies in a refrigerator); IR 1080 cm^{-1} (SO); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.40 (s); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 29.0, 32.9, 145.1. **5b**: mp 162–167°C (dec); IR 1071 cm^{-1} (SO); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.78 (12H, broad s), 1.97–2.01 (6H, m), 2.08–2.10 (12H, m); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 27.7, 34.5, 36.0, 40.9, 143.8. **12**: mp 75.0–75.5°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.22 (s, 12H), 1.35 (s, 18H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 22.6, 29.5, 40.3, 55.6, 127.5, 139.3.
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9. Di(*p*-anisyl)acetylene gave a complex mixture, while diphenylacetylene and di(*2*-thienyl)acetylene were recovered unchanged in good yields.
10. The use of 1.1 molar amounts of S_2Cl_2 also gave **12** in 80% yield with 17% yield of recovered **1c**.