Pergamon

Tetrahedron Letters 39 (1998) 4813–4816

TETRAHEDRON
LETTERS

In Search for Thioketene *S*-oxide. A Vinyl Sulfoxide to Sulfine Rearrangement

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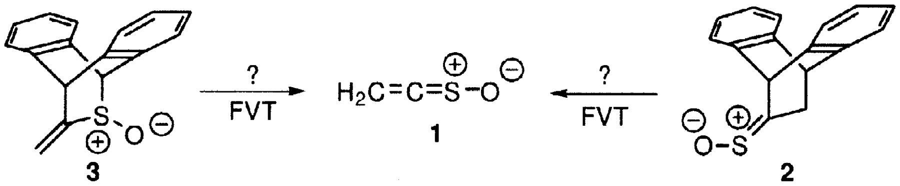
Received 3 April 1998; accepted 27 April 1998

Abstract: Two approaches to thioketene *S*-oxide have been tested. This reactive heterocumulene was tentatively characterized by low temperature IR spectroscopy. In the course of this study, an unexpected vinyl sulfoxide to sulfine rearrangement was observed. © 1998 Elsevier Science Ltd. All rights reserved.

Only few examples of sterically stabilized thioketene *S*-oxides have been reported until now.[1] Pursuing our study of simple reactive sulfines,[2,3] we present here our attempts to obtain the parent compound **1**. This simple heterocumulene being expected to be very reactive, we decided to use flash vacuum thermolysis (FVT) coupled with low temperature IR spectroscopy to detect it. Two types of retro Diels-Alder (rDA) precursors were designed : compound **2** from which the loss of anthracene would generate the C=C double bond, and compound **3** from which the rDA reaction would give the C=S double bond.



We prepared the ethanoanthracenic sulfine **2** by oxidation with MCPBA of the known thioketone **4**.[4] Both the isomers **2*Z*** and **2*E*** were observed. However, the *E/Z* ratio (determined by NMR)[5] was not reproductible, varying from one experiment to another from 1/2 to the nearly exclusive formation of **2*E***. Compound **2** was thermolysed[6] at 625°C. The heavy products resulting from the thermolysis condensed at the oven exit. Volatile products were trapped on a NaCl plate at -196°C and analyzed by IR. The heavy products consist of a mixture of anthracene (40%), resulting from the rDA reaction, and the known ketone **5**[7] (60%), resulting from desulfurization of **2**.[8] In the IR spectrum of the volatile products, two bands at 1700 cm^{-1} and

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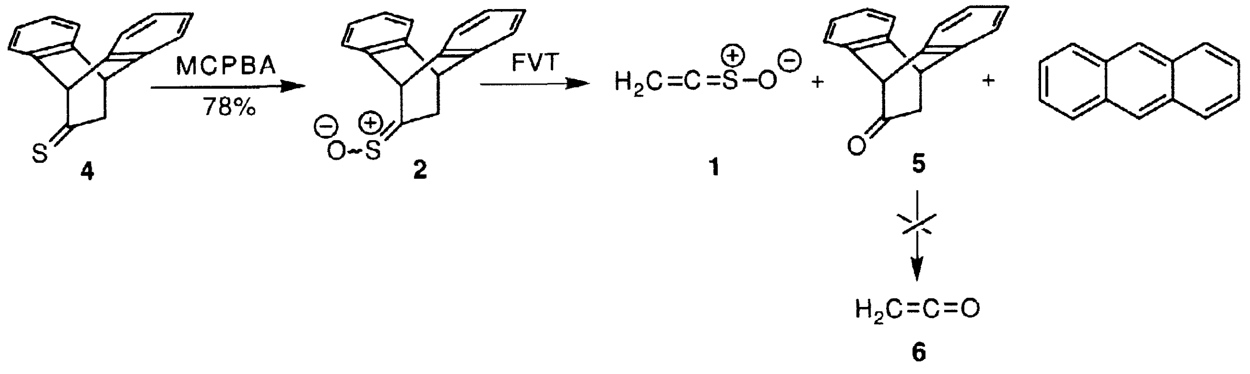
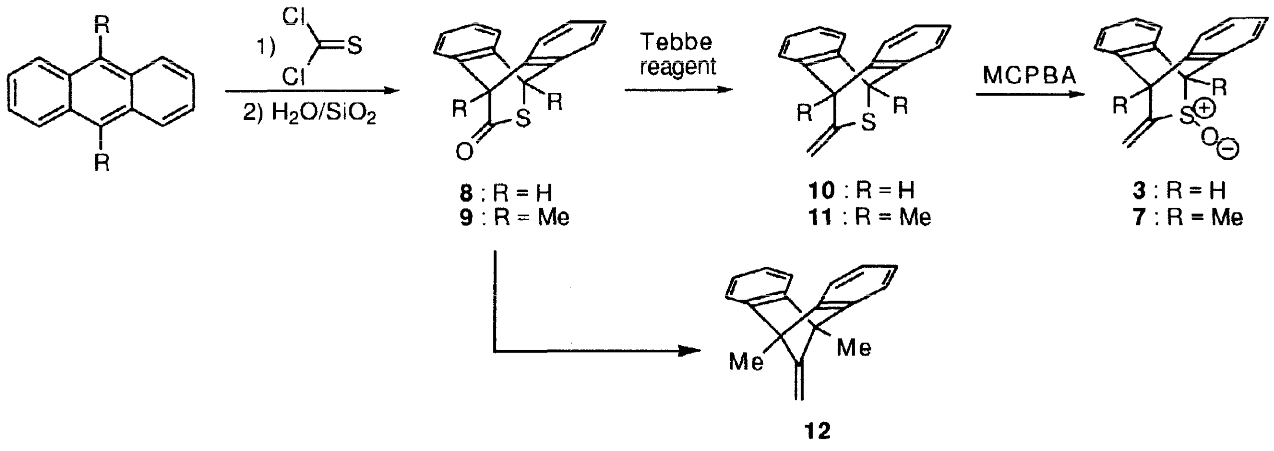
PII: S0040-4039(98)00914-9

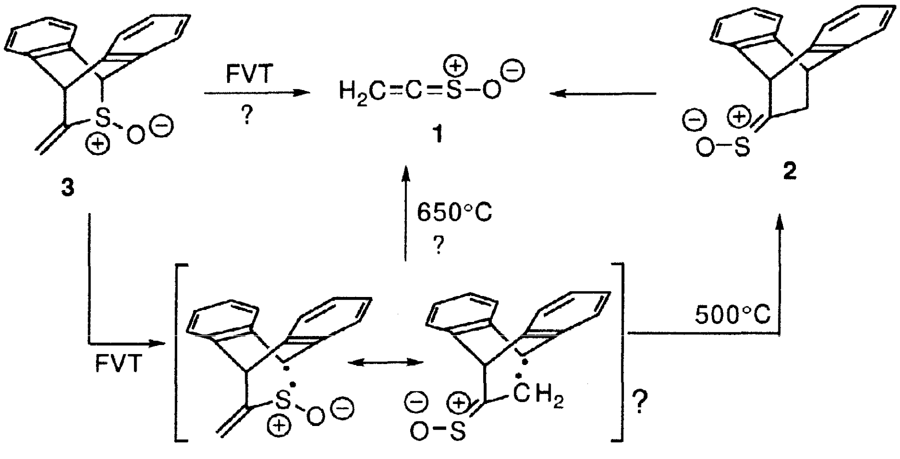
1148 cm^{-1} were tentatively attributed respectively to the $\upsilon_{C=C=S}$ and $\upsilon_{S=O}$ vibrations of **1**. No band corresponding to ketene **6** was observed. This is in agreement with previous results indicating that **2** was not a good precursor for $H_2C=C=O$.[9]



It is clear from these results that loss of sulfur from **2** largely competes with the desired rDA reaction. 11-Thia-9,10-ethanoanthracenes readily undergoing rDA cleavage,[2] we expected that **3** could be a better precursor for **1**. Furthermore, the substitution on positions 9 and 10 of such compounds generally facilitating the rDA reaction, we also tried to prepare the dimethylated analogue **7**. The general synthesis planned for compounds **3** and **7** started from the adducts of anthracene and dimethylanthracene with thiophosgene. The hydrolysis of these adducts by wet silica would give thiolactones **8** and **9** which upon treatment by Tebbe reagent should give ethylenic sulfides **10** and **11**. In a final step, we expected to obtain the needed sulfoxides **3** and **7** by oxidation of these sulfides. When dimethylanthracene was used, thiolactone **9** was obtained in good yield (74%). Unfortunately, treatment of **9** with Tebbe reagent[10] did not give the expected sulfide **11** but the methanoanthracene derivative **12**[11] in 70% yield.[12,13] At the present time, we cannot give the mechanism of this rearrangement. When anthracene was used, **8** was obtained in 40% yield (two steps, following the procedure described by Allgeier *et al.*[14]). Treatment of thiolactone **8** by Tebbe reagent gave the sulfide **10** in 25% yield. In this case, even though the yield was low, no methanoanthracenic compound was detected. Oxidation of **10** with MCPBA gave the sulfoxide **3** (yield = 50%).[15]

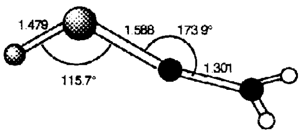


The thermolysis of **3** was effected at 500°C. In these conditions, the ^{1}H NMR spectrum of the heavy products that condensed immediately at the oven exit displayed signals at 2.9 (d, J = 2.5 Hz), 4.6 (t, J = 2.5 Hz), 5.3 (s) and 7-7.5 (m). These data were in agreement with structure **2*E*** and showed that, surprisingly, the sulfoxide **3** rearranged into sulfine **2**. To the best of our knowledge, such transformation of a vinyl sulfoxide into a sulfine has been observed until now only during thio-Claisen rearrangements.[16] This is the first reported vinyl sulfoxide to sulfine rearrangement which does not involve a [3,3] sigmatropy. It probably arises from the homolytic cleavage of the dibenzylic C-S bond, followed by recyclisation on the reverse side.



When **3** was thermolyzed at higher temperature (650°C), the IR spectrum of the volatile products recorded at -196°C showed the bands already obtained from the thermolysis of **2**. Furthermore, a band observed at 2040 cm^{-1} was tentatively attributed to the acetylenic compound H-C≡C-S-O-H (for H-C≡C-S-H, $\nu_{C\equiv C}$ = 2065 cm^{-1})[17] which could result from a proton migration from carbon to oxygen. It is not clear in this case whether the intermediate diradical cyclized into **2** which was then cleaved to **1**, or that the diradical was directly cleaved into anthracene and **1** (stepwise retro-Diels-Alder reaction).[18]

Theoretical calculations have been performed to confirm the attribution of the observed IR bands to compound **1**. Calculations were run at the B3LYP/6-311+G level[19] for **1** and the previously known thiokene ($H_2C=C=S$).[17] The results obtained for **1** are summarized in the following table.



υ	**Calculated values (cm^{-1}) (unscaled)**	**Experimental values (cm^{-1})**
$\upsilon_{C=S}$	791.2	735
υ_{SO}	1127.7	1040
$\upsilon_{C=C}$	1811.8	1700

Calculated values are higher than the experimental ones. However, such a discrepancy was also observed for thioketene. The calculated $\upsilon_{C=C}$ frequency for thioketene was 1814.7 cm^{-1} whereas the experimental value is 1755 cm^{-1}.[17] Taking into account this scaling factor, the calculated results obtained for thioketene *S*-oxide **1** are in acceptable agreement with the experimental data. However, further experiments remain to be undertaken to definitely confirm the observation of **1**.

Acknowlegement : We thank Prof. Roger Arnaud for the theoretical calculations.

References and notes

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5. **2** : IR(KBr) : 1041 cm^{-1} (υ_{SO}). ^{1}H NMR (250MHz) ; CDCl$_3$) **2(*E*)** : 2.9 (d, J = 2.5 Hz, CH$_2$), 4.6 (t, J = 2.5 Hz, CH), 5.3 (s, CH), 7-7.5 (m, ArH) ; **2(*Z*)** : 2.75 (d, J = 2.5 Hz, CH$_2$), 4.6 (t, J = 2.5 Hz, CH), 6.46 (s, CH), 7-7.5 (m, ArH).
6. Oven, l = 20 cm, i.d. = 1.6 cm, P = 10^{-5} hPa. For an overview of the uses of FVT in organic synthesis, see : *Gas phase reactions in organic synthesis*, Y. Vallée, Ed., Gordon and Breach Science Publishers, Amsterdam, **1997**.
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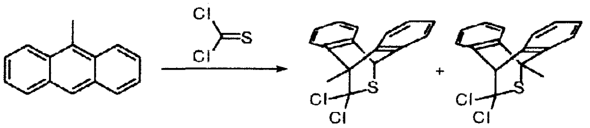
12. **9** : ^{13}C NMR (75 MHz ; CDCl$_3$) : 13.41, 17.22, 53.08, 61.39, 119.90, 123.28, 126.53, 127.00, 141.76, 144.90, 206.49 . ^{1}H NMR (300MHz) ; CDCl$_3$) : 2.14 (s, CH$_3$), 2.34 (s, CH$_3$), 7.2-7.5 (m, ArH). **12** : ^{13}C NMR (75 MHz ; CDCl$_3$) : 9.07, 54.56, 84.79, 118.56, 125.09, 151.70, 178.37 . ^{1}H NMR (300MHz ; CDCl$_3$) : 2.04 (s, 2CH$_3$), 4.43 (s, =CH$_2$), 7.0-7.3 (m, ArH).
13. We also tried methylanthracene as the diene. Cycloaddition gave the dichlorosulfide **13** as a mixture of two regioisomers (**13a**/**13b** : 25/75 : determined by ^{1}H NMR) whereas Allgeier *et al.*[14] mentioned a total regiospecificity for this reaction :



13a 13b

13a : ^{1}H NMR (300MHz ; CDCl$_3$) : 2.25 (s, CH$_3$), 5.25 (s, H$_{10}$), 7.2-7.6 (m, ArH). **13b** : ^{1}H NMR (300MHz ; CDCl$_3$) : 2.48 (s, CH$_3$), 5.19 (s, H$_9$), 7.2-7.6 (m, ArH).

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15. **8** : IR(KBr) : 1690 cm^{-1} (υ_{CO}). ^{13}C NMR (75 MHz ; CDCl$_3$) : 52.06, 65.32, 120.00, 126.04, 126.82, 127.40, 138.27, 141.57, 203.62 (C=O) .^{1}H NMR (300MHz ; CDCl$_3$) : 5.21 (s, H$_9$), 5.57 (s, H$_{10}$), 7-7.5 (m, ArH). **10** : ^{13}C NMR (75 MHz ; CDCl$_3$) : 49.07, 56.97, 104.40, 122.24, 124.36, 126.52, 126.62, 141.54 . ^{1}H NMR (300MHz ; CDCl$_3$) : 4.81 (s, H$_9$), 5.12 (s, =CH), 5.26 (s, =CH), 5.43 (s, H$_{10}$), 7.1-7.6 (m, ArH). **3** : IR (CH$_2$Cl$_2$) : 1048 cm^{-1} (υ_{SO}). ^{13}C NMR (75 MHz ; CDCl$_3$) : 52.77, 67.07, 120.03, 124.30, 124.41, 127.52, 127.68, 128.46, 128.68, 129.07, 131.40 . ^{1}H NMR (300MHz ; CDCl$_3$) : 5.08 (s, H$_9$), 5.69 (s, =CH), 5.77 (s, =CH), 5.90 (s, H$_{10}$), 7.3-7.6 (m, ArH).
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18. However, the observation of H-C≡C-S-O-H during the thermolysis of **3** but not during the thermolysis of **2**, and the formation of ketone **5** by FVT of **2** but not by FVT of **3**, suggest that **2** might not be an intermediate in the reaction pathway from **3** to **1**.
19. Recent calculations have been performed on the simplest sulfine $H_2C=S^+-O^-$ and showed that a large basis set has to be used for the geometry optimization in order to feet the experimental data. See : Ruttink, P.J.A.; Burgers, P.C.; Francis, J.T.K. *J. Chem. Phys.*, **1996**, *100*, 9694-9697.