

Dimethylsulfonium fluoren-9-ide: solution structure and dynamic behaviour of a semi-stabilised sulfonium ylide

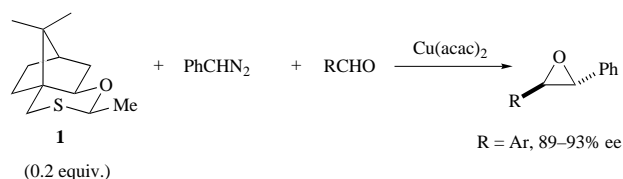
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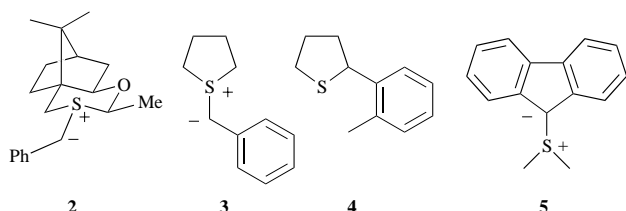
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The semi-stabilised ylide, dimethylsulfonium fluoren-9-ide, has been studied by variable temperature NMR and found to adopt a conformation in which the filled orbital on carbon is perpendicular to the lone pair on sulfur. The rotational barrier (ΔG^\ddagger) around the ylide C–S bond is found to be $42.0 \pm 1.0 \text{ kJ mol}^{-1}$.

There is considerable contemporary interest in the reaction of chiral sulfonium ylides with aldehydes to furnish non-racemic epoxides.¹ We have developed a catalytic version of this reaction^{2,3} and found that sulfide **1** gave epoxides in good yield and with high enantioselectivity (Scheme 1).⁴ Indeed, this process is



now a viable alternative to asymmetric epoxidation of unfunctionalised alkenes. In order to understand the origin of this enantioselectivity we needed more information on both the structure and dynamic behaviour of the sulfonium ylide **2**. However, the structure and dynamic behaviour of only highly stabilised ylides have been studied to date, none of which react with aldehydes to give epoxides.^{5–10} We therefore embarked on a study of less stabilised ylides¹¹ and ones that more closely resembled ylide **2**. We initially attempted to carry out detailed



studies on the model ylide **3**† but were unable to obtain any useful information due to its propensity to undergo ylide equilibration and rearrangement furnishing sulfide **4**.^{12,13} In contrast, ylide **5**¹⁴ was sufficiently stable and so a detailed analysis of its structure and dynamic behaviour was carried out by variable temperature NMR. Ylide **5** was prepared by deprotonating the corresponding perchlorate salt at -78°C with lithium bis(trimethylsilyl)amide (LiHMDS) in $[\text{C}_6\text{H}_6]$ THF (conc. approx. 0.2 M).

Temperature dependent ^1H NMR spectra of ylide **5** are shown in Fig. 1; ^{13}C NMR spectra are shown in Fig. 2 (aromatic region only in both cases); chemical shift data are listed in Table

† The study of the dynamic behaviour of ylide **3** is complicated as it can undergo ring inversion and has two bond rotations ($\text{C}-\text{S}^+$, $\text{C}-\text{Ph}$) some or all of which may be frozen at low temperature. In contrast ylide **5** has only one bond rotation ($\text{C}-\text{S}^+$) that may be frozen.

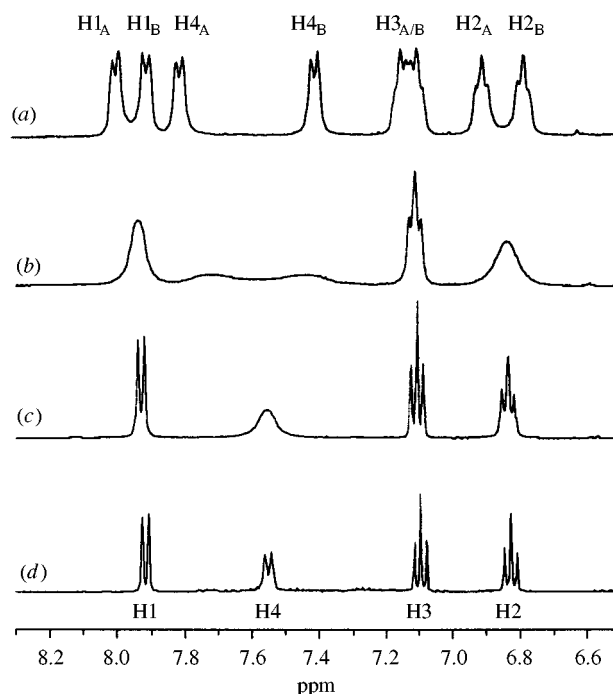
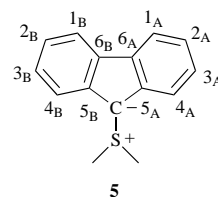


Fig. 1 ^1H NMR of **5** in $[\text{C}_6\text{H}_6]$ THF at (a) -83°C , (b) -59°C , (c) -37°C , (d) -13°C

^1H NMR) and in Table 2 (^{13}C NMR). Signal assignment in the proton and carbon NMR spectra was achieved by means of a COSY spectrum and an inverse C,H shift correlated spectrum which were recorded at -83°C . The quaternary carbons C6 and C5 appeared as small broad signals at -13°C due to the large difference in frequency between the A and B peaks at low temperature and because rotation about the C–S ylide bond was not completely free at this temperature.



At -83°C , the signals of all aromatic protons and carbons were split, indicating that the rotation around the C–S bond was frozen. However, the methyl signals were not split and remained as a sharp singlet. The four possible structures of the

sulfonium ylide are shown below.‡ Ylides **5A/5C** have a plane of symmetry which would render the two aromatic rings equivalent and so cannot represent the low temperature structure of **5**. **5D** is incompatible with the observed spectra as the methyl groups of **5D** should be non-equivalent§ (sulfur ylides are configurationally stable at low temperature and do not readily invert¹⁵). In fact only ylide **5B** is compatible with the spectra observed: the two aromatic rings are non-equivalent and the methyl groups are equivalent. Thus, the ylide carbon is sp^2

‡ The sulfur atom of a sulfonium ylide is sp^3 hybridised and is configurationally stable at low temperature.¹⁵

§ The equivalence of the methyl groups indicate that there is a plane of symmetry bisecting the Me–S–Me group and this could arise from rapid inversion of the sp^3 C of the ylide of **5D** followed by rapid rotation of the Me–S–Me group into the more stable staggered conformation. However, an sp^3 hybridised C of the ylide is less likely than an sp^2 hybridised C ylide as a p orbital on the carbon bearing ylide can conjugate with the two aromatic rings, and indeed forms a third aromatic ring.

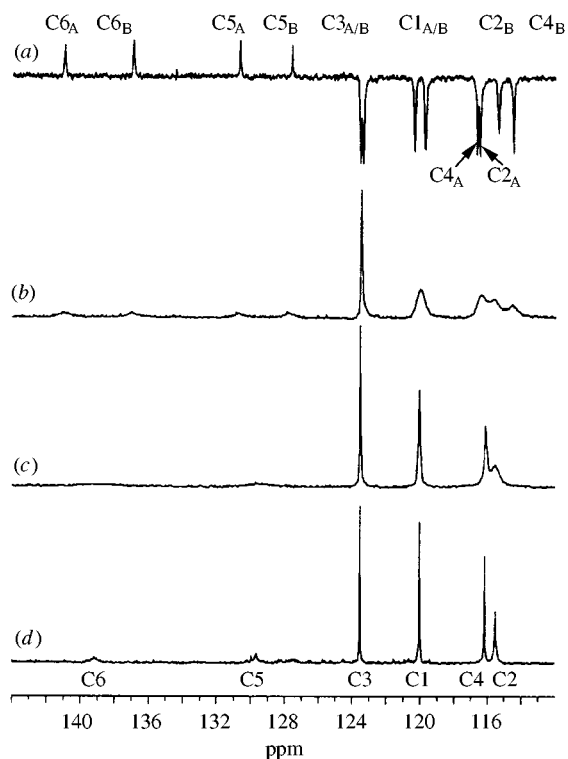
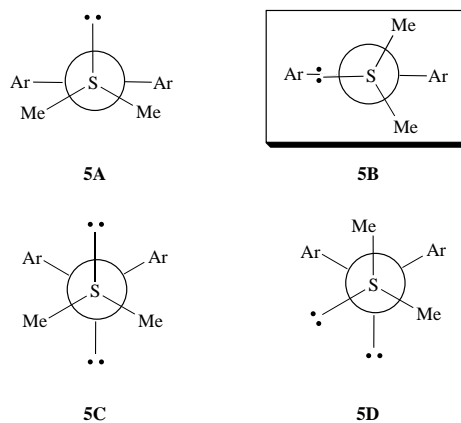


Fig. 2 ^{13}C NMR of **5** in $[\text{}^2\text{H}_8]\text{THF}$ at (a) -83°C , (b) -59°C , (c) -37°C , (d) -13°C

Table 1 ^1H NMR chemical shifts of dimethylsulfonium fluorenyl ylide **5** in $[\text{}^2\text{H}_8]\text{THF}$ ($c \approx 0.2$ M; atomic labelling see text)

$T/^\circ\text{C}$	H1 _A	H1 _B	H4 _A	H4 _B	H3 _A	H3 _B	H2 _A	H2 _B	C-Me
-83	7.99	7.90	7.80	7.40	7.14	7.09	6.90	6.78	2.99
-59	7.92	7.70	7.43	7.09	6.82	2.95			
-37	7.92	7.54	7.09	6.82	2.94				
-13	7.92	7.55	7.09	6.83	2.99				
25 ^a	8.05	7.83	7.64	7.51	2.61				

^a In $[\text{}^2\text{H}_8]\text{DMSO}$

Table 2 ^{13}C NMR chemical shifts of dimethylsulfonium fluorenyl ylide **5** in $[\text{}^2\text{H}_8]\text{THF}$ ($c \approx 0.2$ M; atomic labels see text)

$T/^\circ\text{C}$	C6 _A	C6 _B	C5 _A	C5 _B	C3 _A	C3 _B	C1 _A	C1 _B	C4 _A	C4 _B	C2 _A	C2 _B	C _{ylide}	C-Me
-83	141.0	136.9	130.7	127.6	123.3	123.5	120.3	119.7	116.6	114.5	116.4	115.3	58.7	29.2
-59	141.0	137.0	130.9	127.9	123.5	120.0	116.4	114.5	116.4	115.6	116.4	115.6	58.5	29.5
-37		139.0	129.6	123.5	120.0	116.1	115.5	58.3	29.7					
-13		139.2	129.7	123.5	120.0	116.1	115.5	58.1	30.0					
25 ^a		141.4	134.9	130.9	128.6	126.5	121.5	54.7	21.6					

^a In $[\text{}^2\text{H}_8]\text{DMSO}$.

hybridised and the sulfur atom is sp^3 hybridised with the lone pair perpendicular to the filled p orbital on carbon. This conformation is presumably favoured to minimise electronic repulsions. The perpendicular orientation of the lone pair orbital on sulfur and the filled p orbital on carbon has also been observed in X-ray crystal structures^{16,17} and NMR studies^{5,7,8,10,18} of highly stabilised sulfur ylides. Computational studies of simple sulfonium ylides have also shown that the conformation in which the sulfur lone pair is perpendicular to the filled orbital on carbon is energetically favoured.^{19,20}

We also wanted to determine the rotational barrier about the ylide C–S bond for which an additional spectrum at -70°C was taken. Line shape analysis of the spectra then afforded the rate constants, k and free activation enthalpy (ΔG^\ddagger) of rotation about the ylide C–S bond (Table 3).²¹ As expected, k increased with increasing temperature. On average, a value of $\Delta G^\ddagger = 42.0 \pm 1.0$ kJ mol⁻¹ was found which appeared to be largely independent of temperature. *Ab initio* calculations on the non-stabilised ylide $\text{Me}_2\text{S}=\text{CH}_2$ have given widely different values for the rotational barrier about the C–S ylide bond; $\Delta G^\ddagger = 46.0$ kJ mol⁻¹ in one calculation¹⁹ and $\Delta G^\ddagger = 88.7$ kJ mol⁻¹ in another.²⁰ For an α -carbonyl stabilised ylide, a rotational barrier of $\Delta G^\ddagger(298) = 59.8$ kJ mol⁻¹ was determined by NMR spectroscopy¹⁰ which is somewhat higher than the barrier observed for **5**. However, different ylides would be expected to show different barriers to rotation as ΔG^\ddagger will be influenced by both electronic and steric variations around the C–S bond of the substrate.

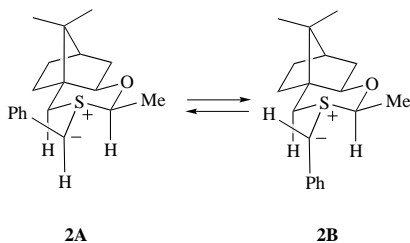
Due to the small temperature range of only 24 K in which the signals were broadened, we were unable to get enough data to obtain reliable values for the activation enthalpy ΔH^\ddagger and the activation entropy ΔS^\ddagger of the ylide C–S bond rotation. However, as ΔG^\ddagger did not change significantly with temperature, we assume that the activation entropy is approximately zero. This assumption is reasonable because changes in solvation or conformational reorganisations within the carbon skeleton of the fluorenyl moiety probably play only a minor role compared to the electron pair–electron pair repulsion.

In conclusion, we have found that semi-stabilised sulfur ylides adopt a conformation in which the filled orbital on carbon is perpendicular to the lone pair on sulfur. When applied to sulfide **1** this conclusion implies that the corresponding benzyl sulfonium ylides have structures **2A** and **2B**. The small

Table 3 Rate constant k and free activation enthalpy ΔG^\ddagger for the $^-C-S^+$ bond rotation of ylide **5** at different temperatures

Entry	$T/^\circ C$	T/K	k/s^{-1}	$\Delta G^\ddagger/kJ\ mol^{-1}$
1	-83	190	13.5 ± 2.0	41.7 ± 0.5
2	-70	203	58.5 ± 12.0	42.2 ± 1.0
3	-59	214	180.3 ± 30.0	42.6 ± 1.0

rotational barrier around the ylide C-S bond found in **5** ($\Delta G^\ddagger = 42.0 \pm 1.0\ kJ\ mol^{-1}$) suggests that **2A** and **2B** are in rapid equilibrium at room temperature. The enantioselectivity in epoxidation with sulfide **1** will therefore be determined by the equilibrium constant, relative rates of reaction and face selectivities of **2A** and **2B**.



Experimental

Low temperature 1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz instrument [spectral frequencies 400 MHz (1H) and 100 MHz (^{13}C)]. All spectra were measured in $[^2H_8]THF$ and referenced to the $THF-OCH_2$ signal ($\delta_H = 3.58$; $\delta_C = 67.4$). J values are given in Hz. Accurate temperature readings ($\pm 2\ K$) were obtained from the spectra of a methanol sample. In order to determine the activation parameters of the ylide C-S bond rotation, the carbon spectra were reprocessed without window function ($LB = 0$) and with zero filling by a factor of 4.

Dimethyl (fluoren-9-yl)sulfonium perchlorate

Sodium perchlorate (1.22 g, 10 mmol), fluoren-9-yl bromide (2.45 g, 10 mmol) and dimethyl sulfide (0.73 ml, 10 mmol) were dissolved in 30 ml of acetone and stirred overnight. The precipitated sodium bromide was filtered off. Addition of light petroleum (bp 40–65 $^\circ C$; 100–200 ml) to the acetone solution then afforded 1.01 g (3.1 mmol, 31%) of the required salt as a colourless, slightly hygroscopic, light sensitive precipitate, mp 163–166 $^\circ C$; $\nu_{max}(KBr-disc)/cm^{-1}$ 3023, 1454, 1427, 1412, 1145, 1087, 740, 623; $\delta_H(250\ MHz; [^2H_6]DMSO)$ 8.05 (2H, d, J 7.6, Ar), 7.83 (2H, d, J 7.6, Ar), 7.64 (2H, t, J 7.6, Ar), 7.51 (2H, t, J 7.6, Ar), 6.14 (1H, s, CH), 2.61 (6H, s, CH_3); $\delta_C(63\ MHz; [^2H_6]DMSO)$ 141.4, 134.9, 130.9, 128.6, 126.5, 121.5, 54.7, 21.6; m/z (positive FAB) 227 (M^+ , cation, 100%) and 165 (99) (Found: M^+ , cation, 227.0889. $C_{15}H_{15}S^+$ requires M , 227.0894); m/z (negative FAB) 99 (M^- , anion, 100%) (Found: M^- , anion, 98.9494. ClO_4^- requires M , 98.9485). Recrystallisation of an analytical sample from methanol led to an identical 1H -NMR spectrum but raised the melting point to 166–168 $^\circ C$ (decomp.).

Preparation of an NMR sample of dimethylsulfonium fluoren-9-ide **5**

A flame-dried 10 ml nitrogen flask equipped with a septum and a stirrer bar was filled with argon. A solution of LiHMDS (1.0 M in THF; 0.24 ml, 0.24 mmol) was added and evaporated to dryness in high vacuum. The flask was filled with argon, the

base was dissolved in 0.9 ml of $[^2H_8]THF$, and the resulting solution cooled to $-78\ ^\circ C$ under argon. To this was added 65.2 mg (0.2 mmol) of dimethyl fluoren-9-ylsulfonium perchlorate in one portion. During the addition, a stream of argon was allowed to flow through the flask. After 60 min, a brown-yellow, slightly cloudy solution had formed which was syringed into a dried, Ar-purged NMR-tube that was precooled to $-78\ ^\circ C$. The NMR-tube was stoppered with a small septum and sealed with parafilm. It was kept at $-78\ ^\circ C$ until the measurements were carried out. 1H and ^{13}C NMR measurements were carried out at $-83\ ^\circ C$ (190 K), $-59\ ^\circ C$ (214 K), $-37\ ^\circ C$ (236 K) and $-13\ ^\circ C$ (260 K). A COSY and a C,H shift-correlated spectrum (HMQC) were also recorded at $-83\ ^\circ C$. A dilute sample was prepared from 62.6 mg (0.1 mmol) of the salt and 0.12 mmol of LiHMDS in 1.2 ml of $[^2H_8]THF$. ^{13}C -NMR spectra were recorded at $-82\ ^\circ C$ (191 K) and $-70\ ^\circ C$ (203 K).

Acknowledgements

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