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Formation of Bifluorenylidene from 9-Mercaptofluorene via a Sulfide Autoxidation-Anionic Autoxidation-Elimination Sequence

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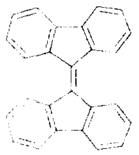
Abstract: Bifluorenylidene **1** was formed quantitatively when 9-mercaptofluorene **3** was treated with base and exposed to air. The initial step was established to be an intermolecular autoxidation of sulphide ion to form the disulphide **6**. An intramolecular autoxidation of the dianion **8** derived from **6** was expected to afford a 1,2-dithietane derivative **9** which eliminated sulphur to give bifluorenylidene **1**.

Bifluorenylidene **1** was known to be a product formed during basic treatment of 9-bromofluorene **2**.[1] It was proposed that the formation of **1** from **2** can proceed by two possible mechanisms: a bimolecular displacement as detailed by Bethell[2] in the reaction of **2** with potassium *t*-butoxide in *t*-butanol or a carbene formation involving α-elimination as supported by kinetic studies of reactions of the 4-nitrobenzyl series.[3] These mechanisms were also suggested in other reports[4] for the formation of bifluorenylidene **1** from 9-halofluorenes without compelling evidence for either. In our attempts to convert 9-mercaptofluorene **3** to its methyl sulfide **4**,[5] bifluorenylidene **1** was sometimes isolated as a side product in varied amounts. This would suggest that **1** could in fact be formed by a "dimerization" of 9-mercaptofluorene **3**.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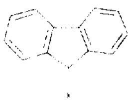
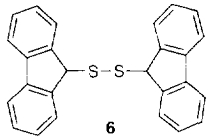

2 X = Br
3 X = SH
4 X = SMe
5 X = S⁻K⁺



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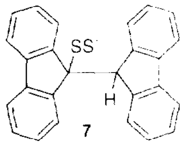
Treatment of **3** with potassium hydroxide in thoroughly degassed THF for 24 h afforded only trace amount of bifluorenylidene **1** based on TLC analysis. Repeating the reaction with exposure to air, however, resulted in an almost quantitative yield of **1** within 1 h. The presence of oxygen thus seemed to be responsible for the formation of **1** in these reactions.

Attempts in carrying out the reaction in the presence of an olefin (cyclohexene, *trans*-stilbene) failed to give any addition product. Bifuorenylidene **1** was the only product isolated. Thus formation of **1** from dimerization of a carbene was ruled out. The carbene derived from the sulphide ion **5** would require the elimination of a sulphide dianion (S^{2-}). To our knowledge no such similar reactions have been reported.

Another reaction was then monitored qualitatively by TLC and interrupted after *ca.* 15 min. A minor amount of a third compound (10%) in addition to **1** and **3** could be isolated. Its mass spectrum showed a weak molecular ion at *m/z* 394 with the base peak at *m/z* 196 indicating a facile symmetrical fragmentation and the loss of 9H. This observation is clearly consistent with the structure of the disulphide

6, mp 168-170 °C (lit.[5] 169-170 °C). A minor amount of a fourth compound (3%) was also obtained. In its mass spectrum, a molecular ion at *m/z* 180 was observed as the base peak with a ready loss of a CO to give a strong peak at *m/z* 152. This corresponded to fluorenone further confirming that autoxidation of **3** and/or **5** had occurred. Autoxidation of organic sulphide ions is well documented.[7] Thus dimerization of the sulphide ion **5** to afford **6** in the presence of oxygen is not surprising. The subsequent conversion of **6** to **1** is, however, of special interest.



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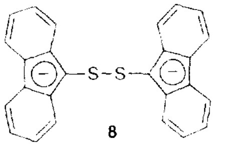

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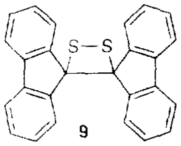

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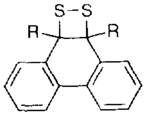

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Many examples of the Wittig rearrangement of a thiacyclophane to a ring-contracted cyclophane have been reported.[8] Although there is no reported precedence, a novel Wittig rearrangement of the disulphide **6** to give **7** followed by an elimination of HSS^- might lead to the formation of **1**. Treating the disulphide **6** with base in thoroughly degassed THF, however, gave only trace amount of **1** after 24 h. On the other hand, a similar reaction with exposure to air resulted in a quantitative yield of **1** within 30 min. The above results clearly indicate that the conversion of **6** to **1** was unikely to involve a Wittig rearrangement but a mechanism dependent again on the presence of oxygen

An alternative route is an intramolecular autoxidation of the two cyclopentadienide anions (*i.e.* **8**) derived from **6** to form a carbon-carbon bond. Autoxidation (dimerization) of organic anions is also documented.[9] Formation of the cyclic disulphide **9** followed by elimination of S_2 would then afford the bifluorenyl **1**. 1,2-Dithietane is expected to be highly strained and its derivatives **10**[10] and several related systems[11] have in fact been postulated as unstable intermediates en route to the corresponding olefins. The relative instability of these cyclic disulphides has been attributed to the expected destabilizing repulsion between lone pairs of electrons on adjacent sulphur atoms[12] and to thermochemical factors.[11a] Although our attempt in the isolation of the cyclic disulphide **9** was unsuccessful, the autoxidation-elimination sequence going from **6** to **1** via **9** is believed to be the reaction mechanism involved.

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