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BIS(ARYLSULPHONYL)ACETYLENES

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Summary: Hitherto unknown bis(arylsulphonyl)acetylenes **1** have been prepared via dimethyldioxirane oxidation of the corresponding sulphide; the acetylenes exhibit high reactivity in Diels-Alder and Michael reactions.

Two arylsulphonyl groups may activate simple molecular units such as methane,[1] methylene,[2] ethylene,[3] propene,[4] and butadiene,[5] giving rise to very useful reagents. Bis(arylsulphonyl)acetylenes, however, have not been reported as yet,[6] despite the fact that acetylenes substituted with two electron-withdrawing groups, such as dimethyl acetylenedicarboxylate[7] and dicyanoacetylene[8] and others[9] have been used for the preparation of several important molecules.[10] We report here the first synthesis of the hitherto unknown bis(arylsulphonyl)acetylenes **1a** and **1b**[6] which, by virtue of the two arylsulphonyl groups, exhibit high reactivity and wide versatility of manipulation of the products.

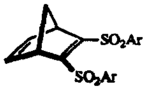
Oxidation of bis(arylthio)acetylenes **2a** and **2b**[11] at 20 °C with an acetone solution of dimethyldioxirane,[12] affords a solution of the bis(arylsulphonyl)acetylene **1a** and **1b**. Many attempts to oxidize **2a** and **2b** with peracids or metal oxides over a large range of temperatures were unsuccesful and, in all cases, only a 10 - 30% of bis(arysulphonyl)methane was obtained.

$ArSO_2C\equiv CSO_2Ar$ **1a,b**

$ArSC\equiv CSAr$ **2a,b**

a Ar = Ph
b Ar = Tol

The acetylenes **1** are highly reactive, but unstable at room temperature and decompose in a few hours. Therefore the reactions of **1a** and **1b** have been carried out without isolation of the reagents by adding the substrates in slight excess directly to the acetone solutions. Cyclopentadiene, 1,3-cyclohexadiene and anthracene furnish the corresponding [4+2] adducts **3**, **4**, **5** in yields up to 65-75%.[13] It is worth mentioning that the formation of **3** and **4** takes place nearly instantly at room temperature, whereas anthracene reacts in about 2 hours to give the adduct **5**. The yields reported were obtained when the dienes were added to the acetone solution of **2a** and **2b** and a four-fold excess of dioxirane at the time corresponding to the maximum concentrations of **1a** (ca. 1 h) and of **1b** (ca. 3 h) at 20 °C. These reaction times were determined by adding, at regular intervals, 1,3-cyclohexadiene, under standard conditions, to the solution of **2a** or **2b** and the oxidant, sampling the reaction mixture and determining the amount of **4** by quantitative GC-MS analysis using $C_{13}H_{28}$ as internal standard. When cyclopentadiene is added to the oxidative solution of **1a** or **1b** at shorter times, **3** is obtained in low yield along with adducts **6** and **7**; also at longer oxidation times, poor yields of **3** are obtained because of decomposition of **1a** or **1b**.



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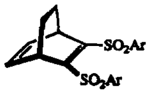

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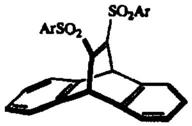

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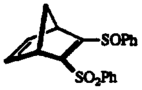

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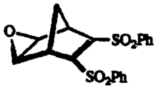

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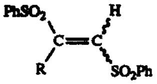

8 (R = OMe)
9 (R = SPh)

Under standard conditions **1a** and **1b** react with mild nucleophiles such as methanol and thiophenol to give the expected Michael adducts **8** and **9** in 50-60% yield. These adducts have been characterized by proton NMR and mass spectrometry and they appear as a mixture of the two geometric isomers.

In conclusion, we have shown that bis(arylsulphonyl)acetylenes can be obtained by the oxidation of the corresponding sulfides, exclusively with the strictly neutral oxidant like dimethyldioxirane and that they are highly reactive, thus rationalizing the failure of many other attempts to obtain these valuable reagents. Acetylenes **1a** and **1b** will be useful for the preparation of compounds of general structure **3**, which had previously been obtained via a more complex synthetic procedure.

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