Unusual Displacements accompanying Anionic Additions to Conjugated Enynes

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Reaction of sodium benzenesulphinate with 1,2-di(4-chlorobenzenesulphonyl)hex-2-en-4-yne affords not only the regiospecific addition of the nucleophile at C(5) but also effects concomitant vinylic and allylic displacements at C(1) and (2).

Additions to conjugated enynes have been studied extensively.[1–4] None of the studies has been concerned with additions to enynes incorporating a vinyl sulphone. We report herein unusual nucleophilic displacements of vinylic and allylic sulphone functions accompanying regiospecific addition of benzene sulphinate as a nucleophile. The enynes **1**, **2** and **3** were synthesized[5] as reported.

Sodium benzenesulphinate **4** was added at ambient temperature to all three enynes (in separate reactions) using dimethylformamide (DMF) as solvent. All reactions were complete within 20 min. Surprisingly, the trisulphone **5** was a common product from all three reactions. In addition to **5**, the enynes **1** and **2** also gave the trisulphones **6** and **7** (Scheme 1). Table 1 shows the physical and spectral characteristics of the compounds **1–3** and **5–7**.

The structure of **5** was confirmed by independent synthesis starting from 1,6-di(benzenesulphonyl)hexa-2-4-diyne; the regiospecificity of additions to this diyne and the borohydride reduction thereof have been described elsewhere.[6]

The formation of **6** and **7** reveals that the displacement of the allylic sulphone at C(1) precedes the displacement of the vinylic sulphone. However, the displacement of the allylic sulphone even precedes the addition of the sulphinate at C(5). This we have shown by interrupting the addition of **4** to **1** before completion and examining the mixture for the unchanged enyne. Compound **8** was isolated from the reaction mixture confirming our expectation stated above.

The displacement of the vinylic sulphone occurs subsequent to the formation of **6** and **7**. This is readily proven by the fact that both **6** and **7** can be converted to **5** by further reaction with sodium benzenesulphinate. Interestingly, such conversions of **6** and **7** into **5** are not quantitative but they attain an equilibrium[7]† wherein the ratio of **6**:**5** and **7**:**5** is a constant 3:1. An explanation for the feature might be found in the following possibility. The trisulphones **6** and **7** can undergo addition of **4** at either end of the diene system *viz.* C(2) or C(5). Of these two possibilities, only the former can lead to a change in structure. Even then, ejection of the aryl sulphonyl *vs.* the benzenesulphonyl moiety would determine the extent of formation of **5**. The appropriate intermediates are **9** and **10**.

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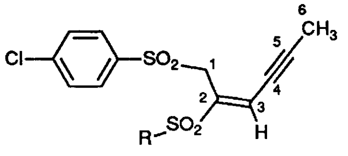
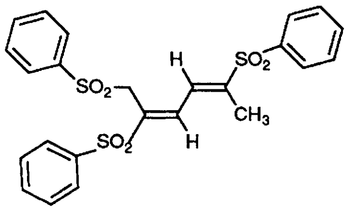
† Even with a fivefold excess of sodium benzenesulphinate, the results remained the same.



1 R = p-ClC$_6$H$_4$
2 R = p-BrC$_6$H$_4$
3 R = Ph



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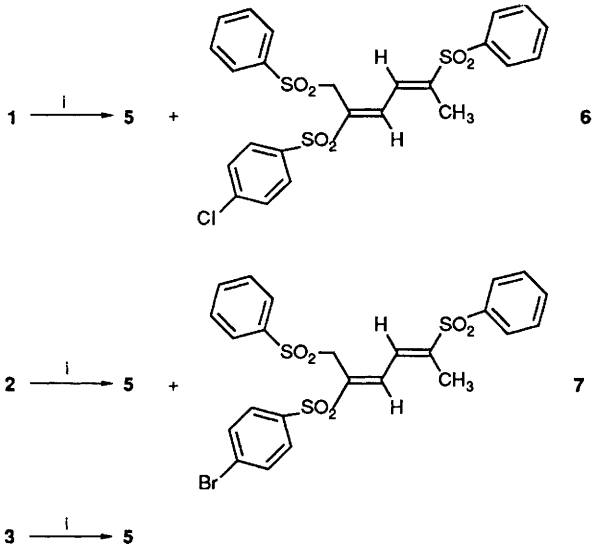
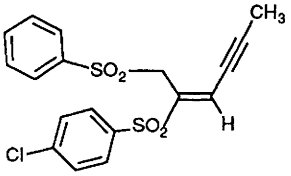


Scheme 1 *Reagents and conditions*: i, excess PhSO$_2$Na (**4**), DMF at room temperature



8

Thus, incorporation of the vinyl sulphone moiety into an enyne such as in **1**, **2** and **3** not only ensures a regiospecific addition but also effects hitherto unreported modes of displacement of a vinylic sulphone through an elimination–addition pathway. The location of the aryl sulphone moieties at the termini of the conjugated diene provides an electron-deficient diene of some synthetic value. It also raises the prospect of displacing either sulphone by other nucleophiles. These possibilities are currently under study.‡

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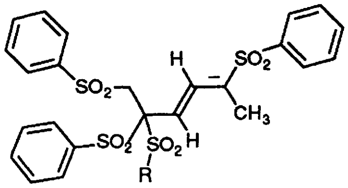

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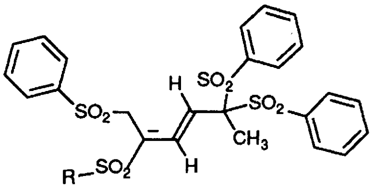

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Table 1 The physical and spectroscopic characteristics of compounds **1**–**3** and **5**–**7**

Compound	M.P./°C	IR (KBr)/cm^{-1}	^{1}H NMR (CDCl$_3$), δ (ppm)
1	131–132	3085, 2939, 2913, 2214 1583, 1322 s, 1147 vs, 1088 vs, 1013, 767	7.81 (d, 2H), 7.65 (d, 2H), 7.53 (d, 2H), 7.48 (d, 2H), 6.96 (q, 1H), 4.34 (d, 2H), 2.01 (d, 3H)
2	135–136	3092, 2980, 2929, 2216, 1574, 1329 s, 1148 vs, 1087 s, 1010, 751	7.73–7.70 (q, 4H), 7.65 (d, 2H), 7.49 (d, 2H), 6.97 (q, 1H), 4.37 (s, 2H), 1.99 (d, 3H)
3	114–115	3091, 2960, 2913, 2213, 1582, 1330 vs, 1314 s, 1147 vs, 1087 s, 1014, 740	7.86 (d, 2H), 7.68–7.45 (m, 7H), 6.94 (q, 1H), 4.33 (s, 2H), 2.01 (d, 3H)
5	199–200	3065, 2929, 1584, 1447 s, 1301 vs, 1150 vs, 1084 s, 898, 729 s, 586 s	7.95 (d, 2H), 7.86 (t, 3H), 7.74–7.53 (m, 12H), 4.35 (s, 2H), 2.11 (s, 3H)
6	198–199	3062, 2921, 2850, 1584, 1447, 1324 vs, 1301 vs, 1152 vs, 1083 s, 899, 726 s, 616 s	7.94 (d, 2H), 7.85 (t, 3H), 7.73–7.52 (m, 11H), 4.36 (s, 2H), 2.12 (s, 3H)
7	194–195	3065, 2929, 1584, 1447, 1322 vs, 1301 vs, 1151 vs, 1084 s, 899, 729 s, 586 s	7.94 (d, 2H), 7.86 (d, 2H), 7.76–7.52 (m, 12H), 4.37 (s, 2H), 2.12 (s, 3H)

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7 The *E,E* geometry for **5**, **6** and **7** are assigned on the basis of earlier established evidence. See B. S. Thyagarajan, B. F. Wood and J. A. Glowienka, *Phosphorus and Sulfur*, 1986, **26**, 275.

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‡ All new compounds in this study gave excellent elemental analyses, NMR, IR spectroscopic and mass spectrometric data.