## Additions of Sulphonyl Iodides to Acetylenes and Allenes

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Although free-radical additions of sulphonyl halides to olefins have been investigated,1-3 similar additions to acetylenes have received little attention,4 and there are no reports of such additions to allenes. We now report a method for preparing  $\alpha\beta$ -unsaturated- $\beta$ -iodosulphones by the addition of toluene-p-sulphonyl iodide to acetylenes, as well as the first instance of the addition of a sulphonyl halide to an allene.

Equimolar amounts of the acetylene and toluene-psulphonyl iodide (1-6 hr., anhydrous Et<sub>2</sub>O, 250 w heat lamp ca. 2 ft. away) gave excellent yields of 1:1 adducts.

$$R^{1}C:CR^{2} + Me$$
 $SO_{2}I \longrightarrow R^{2}IC:CR^{2}\cdot O_{2}S \longrightarrow Me$ 
 $(II)$ 

The stereochemistry of (II) has not been proven rigorously, but spectral evidence indicates that the sulphonyl iodide adds in a trans-manner. The products from various acetylenes are listed in the Table. All adducts have

Products (II) from the addition of toluene-p-sulphonyl iodide to acetylenes

| $\mathbb{R}^1$ |                                  |      |  | $\mathbb{R}^2$      | M.p.          | Yield (%) |
|----------------|----------------------------------|------|--|---------------------|---------------|-----------|
| (a)            | Ph                               |      |  | H                   | 8384          | 87        |
| (b)            | $\operatorname{Bu}^{\mathbf{t}}$ |      |  | H                   | 70-105*       | 84        |
| (c)            | cyclo-C                          | 6H11 |  | H                   | 108.5 - 109.5 | 64        |
| (d)            | PhCO                             |      |  | Н                   | 160 - 161     | 83        |
| (e)            | Et                               |      |  | $\operatorname{Et}$ | 6667          | 84        |
| (f)            | Ph                               |      |  | Cl                  | 149 - 150     | 79        |
| (g)            | Ph                               |      |  | Ph                  | 192193        | 35        |

\* This is the only case where both the cis- and trans-isomers were obtained. They were partially separated by sublimation. elemental compositions and i.r. and n.m.r. spectra consistent with the suggested structures. Adducts (IIa--c) have been dehydrohalogenated under relatively mild conditions to give the corresponding acetylenic sulphones in good yields.

Toluene-p-sulphonyl iodide also reacts extremely rapidly with allenes. Under the same conditions as employed with the acetylenes, phenylpropadiene and penta-2,3-diene gave 80% and 45%, respectively of 1:1 adducts. Propa-1,2diene also gives a 1:1 adduct (31%), as well as a smaller amount (13%) of a product the elemental analysis of which was consistent with the molecular formula for C17H18S2O4. Spectral evidence suggests the following structure for this compound:

$$\begin{array}{c} \text{CH}_2\text{-}\text{O}_2\text{S} \\ \text{O}_2\text{S} \\ \end{array} \begin{array}{c} \text{Me} \\ \text{(III)} \end{array}$$

From elemental analysis and spectral considerations, the 1:1 adducts have been assigned the structure:

$$R^{1}\text{CH:CI-CHR$^{2}$-O$_{2}$S} \\ \boxed{\hspace{1cm}} \text{Me} \qquad \begin{array}{ll} (\text{IVa}) & R^{1} = \text{Ph}, R^{2} = \text{H} \\ (\text{IVb}) & R^{1} = R^{2} = \text{Me} \\ (\text{IVc}) & R^{1} = R^{2} = \text{H} \end{array}$$

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