Additions of Sulphonyl Iodides to Acetylenes and Allenes

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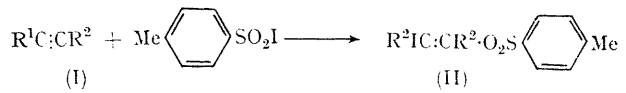
ALTHOUGH free-radical additions of sulphonyl halides to olefins have been investigated,[1-3] similar additions to acetylenes have received little attention,[4] and there are no reports of such additions to allenes. We now report a method for preparing $\alpha\beta$-unsaturated-β-iodosulphones by the 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-*p*-sulphonyl iodide (1—6 hr., anhydrous Et_2O, 250 w heat lamp *ca.* 2 ft. away) gave excellent yields of 1 : 1 adducts.



(I) (II)

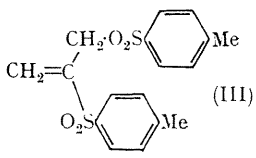
The stereochemistry of (II) has not been proven rigorously, but spectral evidence indicates that the sulphonyl iodide adds in a *trans*-manner. The products from various acetylenes are listed in the Table. All adducts have elemental compositions and i.r. and n.m.r. spectra consistent with the suggested structures. Adducts (IIa—c) have been dehydrohalogenated under relatively mild conditions[5] to give the corresponding acetylenic sulphones in good yields.

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

	R^1	R^2	M.p.	Yield (%)
(a)	Ph	H	83—84	87
(b)	Bu^t	H	70—105*	84
(c)	cyclo-C_6H_{11}	H	108·5—109·5	64
(d)	PhCO	H	160—161	83
(e)	Et	Et	66—67	84
(f)	Ph	Cl	149—150	79
(g)	Ph	Ph	192—193	35

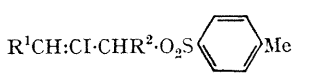
* This is the only case where both the *cis*- and *trans*-isomers were obtained. They were partially separated by sublimation.

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-1,2-diene 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 $C_{17}H_{18}S_2O_4$. Spectral evidence suggests the following structure for this compound:



(III)

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



(IVa) R^1=Ph, R^2=H
(IVb) R^1=R^2=Me
(IVc) R^1=R^2=H

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