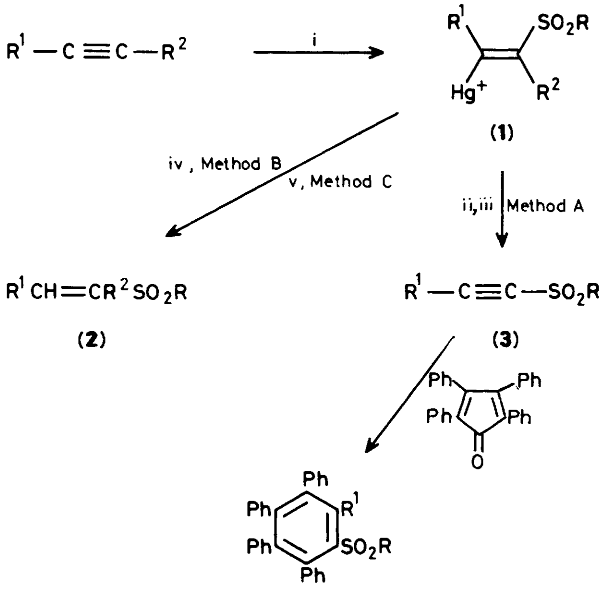
Sulphonomercuriation Route to Vinyl and Ethynyl Sulphones

Perumal Rajakumar* and Arunachalam Kannan

Department of Organic Chemistry, University of Madras, Guindy Campus, Madras 600 025, India

Ethynyl sulphones were obtained from the reaction of substituted acetylenes with mercury(II) chloride and sodium benzenesulphinate followed by oxidative demercuriation.

Dimethyl acetylenedicarboxylate (1 equiv.), mercury(II) chloride (1.25 equiv.), and sodium benzenesulphinate (1.25 equiv.) were vigorously stirred in water for 40 h at room temperature. The sulphonyl mercury(II) complex (**1**), when demercuriated with NaOH/dioxane,[1] gave a colourless solid (42%), m.p. 210 °C, the i.r. spectrum of which did not show a $-C\equiv C-$ band. Its n.m.r. spectrum showed a highly deshielded olefinic proton as a singlet at δ 6.7, and four methoxy signals at δ 3.4, 3.5, 3.36, and 3.33, indicating that the structure of the product could reasonably be assigned as *E*- and *Z*-(**2**).



Scheme 1. *Reagents:* i, $HgCl_2$, RSO_2Na, 40 h, room temp.; ii, Br_2, benzene, 2 h, room temp.; iii, NEt_3 (3 equiv.), 20 h, room temp.; iv, 50% NaOH/dioxane, room temp.; v, conc. H_2SO_4.

Table 1. Preparation of the sulphones (**2**) and (**3**).

R	R^1	R^2	Method, product	Yield (%)
Ph	CO_2Me	CO_2Me	A, (**3**)	45
Ph	CO_2Me	CO_2Me	B, (**2**)	42
Ph	CO_2Me	CO_2Me	C, (**2**)	64[a]
Ph	CO_2Bu^t	CO_2Bu^t	A, (**3**)	35
Ph	CO_2Bu^t	CO_2Bu^t	B, (**2**)	40
Ph	CO_2Bu^t	CO_2Bu^t	C, (**2**)	58[a]
Ph	Ph	H	A, (**3**)	42
Ph	Ph	H	B, (**2**)	45
Ph	CH_2OCOPh	CH_2OCOPh	B, (**2**)	60
p-MeC_6H_4	CO_2Me	CO_2Me	A, (**3**)	32
p-MeC_6H_4	CO_2Me	CH_2Me	B, (**2**)	34
p-MeC_6H_4	CO_2Bu^t	CO_2Bu^t	B, (**2**)	30

[a] Includes some insoluble materials.

Oxidative demercuriation of (**1**) with bromine (1 equiv.) and triethylamine (3 equiv.) in benzene afforded a colourless solid (45%, m.p. 145 °C) after chromatography on silica with benzene–light petroleum (2:3) as eluant. The n.m.r. spectrum of this product (**3**) displayed an OMe singlet at δ 3.8, in addition to an aromatic multiplet. The formation of (**3**) could be explained by triethylamine-catalysed decarboxylative demercuriation. Further demercuriation of (**1**) with conc. H_2SO_4 afforded (**2**).

The applicability of this synthetic route was explored with di-t-butyl acetylenedicarboxylate and phenylacetylene (Table 1). It failed with diphenylacetylene, bromoacetylene, but-2-yne-1,4-diol, and monopotassium acetylenedicarboxylate.

The facile reactivity of (**3**) in cycloaddition was tested with tetraphenylcyclopentadienone, which took place in benzene in the presence of $AlCl_3$ at room temperature.

Received, 5th August 1988; Com. 8/03219J

References

1 W. Sas, *J. Chem. Soc., Chem. Commun.*, 1984, 862, and references therein.