

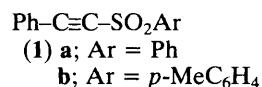
Thermal and Photochemical Addition of Phenyl(arylsulphonyl)acetylenes to Alkenes

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Phenyl(arylsulphonyl)acetylenes add thermally or photochemically to alkenes to afford stereospecifically *trans* products which are formal adducts of the two fragments derived from homolytic cleavage of the carbon-sulphur bond.

In connection with our interest in the cycloaddition of unsaturated sulphones¹ we investigated the reaction of phenyl(arylsulphonyl)acetylenes (**1**) with alkenes. Instead of the expected [2 + 2] or rearranged cycloadducts,² we have obtained products which are formally derived from homolytic cleavage of the carbon-sulphur bond of the acetylene and subsequent addition of the resulting fragments to the double bond.

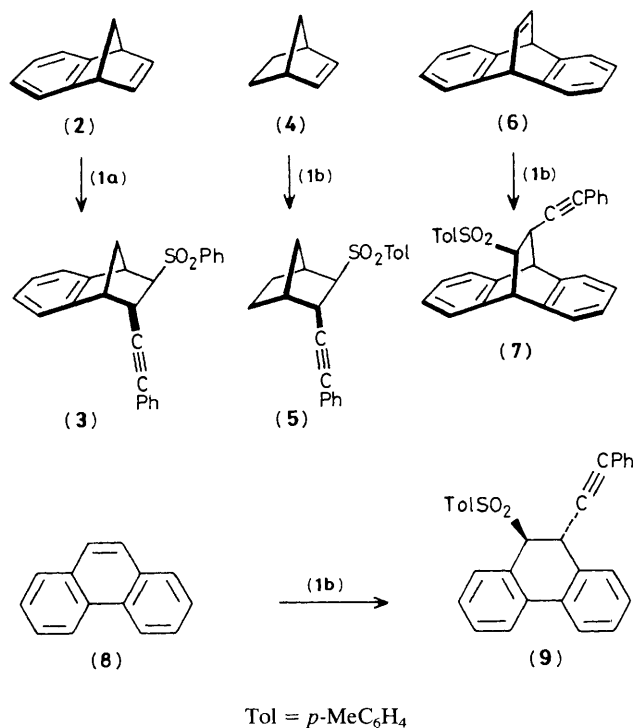


For example, thermal reaction of benzonorbornadiene (**2**) with the acetylene (**1a**) (sealed tube, under argon, 100—

110 °C, 2—3 h, neat) afforded the adduct (**3**) (52% yield, † m.p. 136—137 °C from CH₂Cl₂-Et₂O) whose structure was assigned by standard spectroscopic methods and confirmed by X-ray crystallography. ‡ The same reaction can also be brought about photochemically (sunlight, *ca.* 0.1 M in degassed acetonitrile or chloroform solution, 2—7 days, *ca.* 50% yield †). The photochemical process has advantages over the thermal reaction as, at partial conversion (*ca.* 50%), many

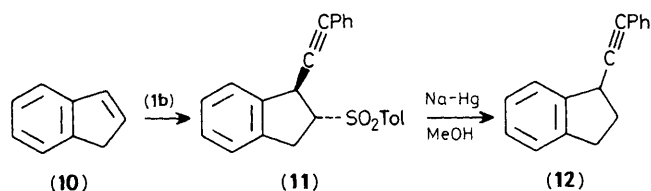
† Yields are based on recovered starting material. General conversion range for thermal processes 70—90%, photochemical 50—70%.

‡ The X-ray structure determination was performed by Dr. G. Valle and details will be published elsewhere.



side reactions from thermal decomposition of the reagents³ are minimized.

The reaction appears to be of wide scope. Norbornene (**4**) affords with (**1b**) product (**5**) (thermal process, 40% yield, † m.p. 149–150 °C from MeOH), whose structure was assigned on the basis of spectral data and the *X*-ray analysis of (**3**). Similarly, compound (**7**) was obtained from (**1b**) and (**6**) (thermal, 85% yield, † m.p. 194–195 °C from MeOH) and (**9**) from (**1b**) and (**8**) (photochemical, 65% yield, † m.p. 197–198 °C from CH₂Cl₂–light petroleum), structure assignments being based on spectral data. The regiochemistry of the adduct (**11**) between (**1b**) and indene (**10**) (thermal, 50% yield, † m.p. 137–138.5 °C from CH₂Cl₂–light petroleum) was determined by analysis of the product derived by sodium amalgam



reduction (4%, NaH₂PO₄ buffered MeOH), whose spectral data were consistent only with the hydrocarbon structure (**12**). The preparation of the acetylene (**12**) is an example of the synthetic potential of the adducts.⁴

While other aryl(arylsulphonyl)acetylenes show similar reactivity, the unsubstituted tolylsulphonylacetylene or 1-tolylsulphonylpropyne either does not react, or gives different products under these thermal or photochemical conditions. This observation and the recently reported behaviour of the acetylene (**1a**) with Grignard reagents⁵ suggest that the reactions may proceed through a charge transfer or electron transfer process, and that the intermediate radical ion pair is sufficiently stable only with aromatic substrates such as those derived from (**1**). The reactions of (**1**) with alkenes so far studied show a similarity to the reactivity of sulphonyl halides towards similar substrates.⁶

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