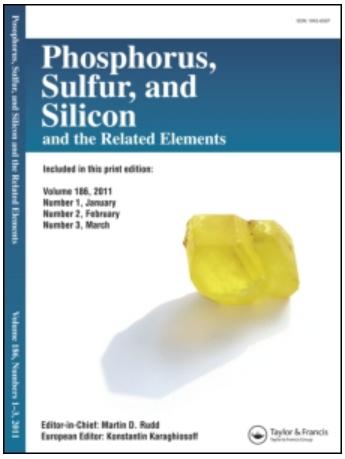

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ADDITION AND SUBSTITUTION REACTIONS OF ACETYLENIC AND ETHYLENIC SULPHONES WITH CUPRATES

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ADDITION AND SUBSTITUTION REACTIONS OF ACETYLENIC AND ETHYLENIC SULPHONES WITH CUPRATES.

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Synthetic, mechanistic, and stereochemical aspects of the reactions of cuprates with various systems are being investigated in these laboratories[1]. The series of substrates includes several sulphonyl-activated compounds.

The stereochemical course of addition of lithium dialkyl- and diphenyl-cuprates to phenylsulphonylacetylene in ether follows predominantly a syn-pathway leading to trans olefins:

$$Ph\text{-}SO_2\text{-}C{\equiv}CH \xrightarrow[ii)\ H^+]{i)\ R_2CuLi} \underline{trans}\text{-}Ph\text{-}SO_2\text{-}CH{=}CH\text{-}R$$

A procedure has been devised which affords a double-addition of organometallic reagents without isolation of the mono-addition product according to the scheme:

$$Ph\text{-}SO_2\text{-}C{\equiv}CH \xrightarrow[ii)\ ArSH]{i)\ R_2CuLi} Ph\text{-}SO_2\text{-}CH{=}CH\text{-}R \xrightarrow[iv)\ H^+]{iii)\ RLi} Ph\text{-}SO_2\text{-}CH_2\text{-}CH(R)_2$$

cis- and trans-1-halogeno-2-phenylsulphonylethylenes react with cuprates giving substitution and reduction products:

$$Ph\text{-}SO_2\text{-}CH{=}CH\text{-}X \xrightarrow{R_2CuLi} Ph\text{-}SO_2\text{-}CH{=}CH\text{-}R + Ph\text{-}SO_2\text{-}CH{=}CH_2$$

X=Br,Cl,F

The stereochemical course of the substitution reaction, which is influenced by the nature of halogen[1], has been found to depend also upon the nature of the cuprate. The degree of stereospecificity decreases on going from dimethyl- to di-n-butyl-, di-sec-butyl-, and diphenyl-cuprates.

Post-addition to the product of substitution is observed when an excess of cuprate is used.

The reductive dehalogenation becomes an important competitor only in some cases. Deuterium labelling experiments show that the process follows a retention pathway.

1) C.V.Maffeo, G.Marchese, F.Naso, and L.Ronzini.
J.Chem.Soc.Perkin I, 000,1978.