Substitution of Allylic Sulphides of Benzothiazole-2-thiol with Organomagnesium Compounds in the Presence of Copper(I) Iodide. A Regioselective Synthesis of Olefins[1]

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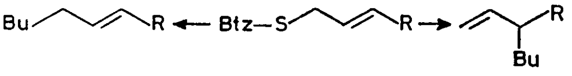
Summary Primary allylic sulphides of benzothiazole-2-thiol react with butylmagnesium bromide in the presence of copper(I) iodide to yield, depending on the solvent, olefins with or without allylic rearrangement.

ALKYLATION of allylic substrates by copper(I) reagents is of special interest since the alternative S_N2 or S_N2' mechanisms that are possible may be influenced by several factors.[2] We report now the use of a novel leaving group which has allowed us to govern the regioselectivity of the alkylation of the primary allylic substrates (A)—(C) by changing the reaction medium. Primary allylic sulphides derived from benzothiazole-2-thiol† (1) react easily with organomagnesium compounds in the presence of copper(I) iodide to give the alkenes (2) or (3) in high yields (Table).



(3) **(1)** **(2)**

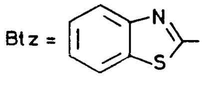
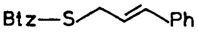


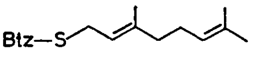
TABLE. Reaction of allyl sulphides of benzothiazole-2-thiol with butylmagnesium bromide in the presence of copper(I) iodide

Sub-strate	Solvent	(2)	:	(3)	Yield (2) + (3) /%[c]
(A)	Ether	97	:	3	81
	THF–ether (2:1)	5	:	95[a]	83
(B)	Ether	95	:	5	80
	THF–ether (2:1)	5	:	95[b]	90
	THF	70	:	30	
	THF–ether (2:1)[d]	25	:	75	70
(C)	Ether	—		—	65[e]

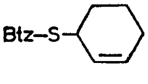
[a] Only the *E* isomer is obtained. [b] Configuration of the product is assumed to be *E* since the double bond geometry should not be affected by the substitution. [c] Yield of isolated product. All the olefins gave satisfactory n.m.r. and i.r. spectra. [d] With 4 mol equiv. of Bu_2CuLi. [e] 2-Butylcyclohexene is obtained.



(A)



(B)



(C)

The regioselectivity of these reactions is strongly influenced by the reaction medium. With ether as solvent allylic rearrangement was almost completely predominant,

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† These sulphides were synthesized in 70—80% yield according to the procedure of L. E. Overman, J. Smoot, and J. D. Overman, *Synthesis*, 1974, 59.

while in tetrahydrofuran (THF)–ether (2:1, v/v) the substitution product on the α-carbon linked to the sulphur predominated with retention of the stereochemistry of the double bond. In these substitutions the regioselectivity decreases in both solvents if lithium dibutylcuprate is used as the nucleophile. The following procedure for the synthesis of 3-phenylhept-1-ene is typical. An ethereal solution of Bu^nMgBr (0·6 M; 10 ml; 4 mol.equiv.) was added to a stirred suspension of CuI (0·55 g, 2 mol. equiv.) in diethyl ether (10 ml) at −30 °C under N_2. The mixture was stirred for 10—20 min and cinnamyl sulphide (0·45 g, 1 mol. equiv.) in diethyl ether (10 ml) was added dropwise at −30 °C. The mixture was allowed to warm to room temperature, and was then evaporated under reduced pressure to afford a residue which was extracted with pentane to yield the almost pure olefin. Alternatively the residue may be chromatographed using pentane as eluant through a short column of silica gel to yield 0·21 g (81%) of the olefin contaminated by 3% of (*E*)-1-phenylhept-1-ene (g.l.c. with 10% S.P. 2100 on 100—120 Supelcoport).

Irrespective of the mechanism of these alkylations, to our knowledge this is the first example of regioselective α- or γ-alkylation of primary allylic substrates which can be governed by changing the reaction medium.

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[1] Taken in part from the thesis of P. Barsanti, Università di Bari, 1978.

[2] G. H. Posner, *Org. Reactions*, 1975, **22**, 253; R. J. Anderson, C. A. Henrick, and J. B. Siddall, *J. Amer. Chem. Soc.*, 1970, **92**, 735; G. Fouquet and M. Schlosser, *Angew. Chem. Internat. Edn.*, 1974, **13**, 82; A. Commeçon, M. Bourgain, M. Delaumeny, J. F. Normant, and J. Villieras, *Tetrahedron Letters*, 1975, 3837; J. Levisalles, M. Rudler-Chauvin, and H. Rudler, *J. Organometallic Chem.*, 1977, **136**, 103.