Regio- and Stereo-selective γ-Substitution of Allylic Sulphoxides and Sulphones with Lithium Dialkylcuprates. A New Synthesis of Trisubstituted Olefins

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Summary A new regio- and stereo-selective γ-substitution of allylic sulphoxides and sulphones with lithium dialkylcuprates providing a promising new method for the preparation of trisubstituted olefins in particular is described.

THE regio- and stereo-selective desulphurizative substitution of sulphur-containing allylic substrates provides a new method for carbon–carbon bond formation.[1] This communication describes a new γ-substitution of allylic sulphoxides (**1**) and sulphones (**2**) with lithium dialkylcuprates (R_2CuLi) as a promising new general method for the regio- and stereo-selective synthesis of trisubstituted olefins (**3**) in particular.

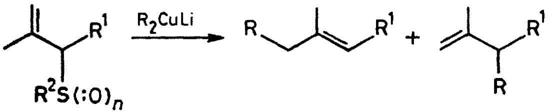
Secondary allylic sulphoxides (**1**) and sulphones (**2**), derived from the corresponding allylic sulphides which

TABLE. Reaction of allylic sulphoxides (**1**) and sulphones (**2**) with R_2CuLi [reaction (1)].

R^1	$R^2S(:O)_n$	R	Yield[a]/%	Product ratio (**3**) : (**4**)	 *E*-(**3**) : *Z*-(**3**)
$-[CH_2]_2\overset{\ulcorner}{C}(Me)-O-[CH_2]_2-\overset{\urcorner}{O}$	PhS(:O)	Me	69	91:9	79:21
		Bu^n	70	95:5	82:18
,,	$PhS(:O)_2$	Me	74	95:5	93:7
		Bu^n	73	98:2	92:8
$-CH_2Ph$	PhS(:O)	Me	65	94:6	—[c]
		Bu^n	75	95:5	93:7
,,	$PhS(:O)_2$	Me	63	95:5	—[c]
		Bu^n	89	92:8	86:14
$-[CH_2]_2C(Me)=CHCH_2OCH_2Ph$	PhS(:O)	Me	71	90:10	78:22
		Me	52[b]	87:13	
		Bu^n	75	97:3	87:13
,,	MeS(:O)	Me	22	91:9	
,,	$PhS(:O)_2$	Me	85	95:5	85:15
		Bu^n	73	97:3	86:14
,,	$MeS(:O)_2$	Me	52	88:12	
$-CH_2OCH_2Ph$	PhS(:O)	Me	53	86:14	57:43
,,	$PhS(:O)_2$	Me	26	83:17	66:34

[a] The reaction was carried out at -20 °C unless otherwise stated. [b] Carried out at -40 °C. [c] The γ-product showed a single g.l.c. peak and the *E*/*Z* ratio was not determined.

were easily prepared in high yield from *gem*-dimethyl olefins by our recently developed method,[2] react at low temperature with lithium dialkylcuprates to give the sulphur-free olefins (**3**) and (**4**) selectively. The Table indicates the scope of this reaction. In no case could the mixture of γ- and α-products and *E*- and *Z*-isomers of the γ-product (**3**) be separated by the usual column chromatography on silica gel. The regio- and stereo-isomeric ratios were determined by n.m.r. spectroscopy, g.l.c., and g.c.–m.s. analysis. The authentic *E*-olefins (**3**) were prepared stereoselectively by treatment of the corresponding allylic acetates with lithium dialkylcuprates.[3] Reactions of other allylic sulphoxides (**1**) and sulphones (**2**) gave analogous results as shown in the Table; regio- and stereo-selective substitution occurred and gave γ- and *E*-(**3**) predominantly.



(1)

(1) $n = 1$

(2) $n = 2$

(3) γ-Product

(4) α-Product

The following procedure for the preparation of *E*-1-phenyl-3-methyloct-2-ene is representative of the regio- and stereo-selective γ-substitution. To an ethereal solution of lithium di-n-butylcuprate (1 mmol; 4 ml) a solution of 2-methyl-3-phenylsulphinyl-4-phenylbut-1-ene (0·2 mmol) in ether (0·5 ml) was added dropwise at −20 °C under argon. The mixture was stirred for 30 min at −20 °C and then gradually warmed up to room temperature. After quenching of the reaction with water, workup of the reaction mixture in the usual manner gave an oil which was submitted to column chromatography on silica gel (hexane) to afford a t.l.c.-pure fraction (75%). In this case, n.m.r. and g.l.c. analysis of the products gave the ratios 95:5 for (**3**):(**4**) and 93:7 for *E*-(**3**):*Z*-(**3**).

This regio- and stereo-selective γ-substitution of allylic sulphoxides and sulphones provides a new method for the preparation of trisubstituted olefins. In addition the arylsulphinyl and sulphonyl groups may now be used as suitable leaving group in substitution reactions with organocopper reagents.[4]

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