A Novel Stereoselective Route to *cis*-Olefins *via* Addition of Vinyl Cuprates to αβ-Unsaturated Sulphones and Subsequent Desulphonylation

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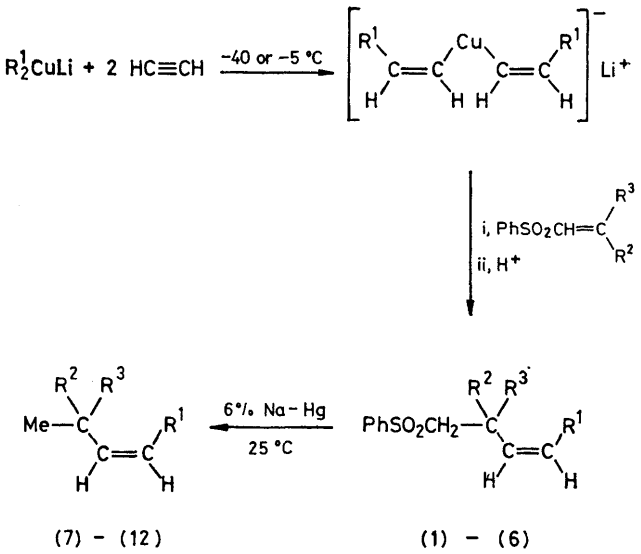
Summary Dialkenylcuprates, generated by addition of dialkylcuprates to acetylene, react with αβ-unsaturated sulphones to give *cis*-γδ-unsaturated sulphones which can be easily desulphonylated with retention of the double-bond configuration.

STEREOSELECTIVE synthesis of olefins represents a classical challenge to organic chemists.[1] In recent years the use of copper(I) reagents has provided routes to such compounds.[2] There is particular interest in the unsaturated organometallic species which can be generated by addition of cuprates or similar reagents to acetylenes.[3] We now report that during our work on the reactions of sulphur compounds with copper(I) reagents,[4] we have found that *cis*-dialkenylcuprates generated by Normant's method[3d] can be added to αβ-unsaturated sulphones to give products in which the *cis*-geometry of the cuprate alkenyl substituents is maintained. Furthermore, the resulting γδ-unsaturated sulphones can be easily desulphonylated[5] with retention of configuration (Scheme).

TABLE. Yields of γδ-unsaturated sulphones (**1**)—(**6**) and olefins (**7**)—(**12**).[a]

R^1	R^2	R^3	γδ-Unsaturated sulphone[b]	Yield[c]/%	Olefin[b,d]	Yield[e]/%
Bu^n	Me	H	(**1**)[f,g,h]	80	(**7**)	98
Bu^s	Me	H	(**2**)[f,i,j]	85	(**8**)	95
Bu^n	Me	Me	(**3**)[j,k,l]	85	(**9**)	83
Bu^n	Ph	H	(**4**)[j,k,m,n]	85	(**10**)	83
Bu^s	Ph	H	(**5**)[f,i,j]	80	(**11**)	87
Bu^t	H	H	(**6**)[f,h,l]	87	(**12**)	82

[a] The starting dialkylcuprates (R^1_2CuLi), unless otherwise indicated, were prepared from Me_2S·CuBr complex and a salt-free solution of R^1Li (*cf.* ref. 6). The concentrations of reagents ranged between 2·5 and 4·5 × 10^{-2} M. [b] All new compounds reported herein exhibited ^{1}H n.m.r. spectroscopic properties consistent with their structures and gave satisfactory elemental analysis and/or molecular-weight determinations (mass spectrometry). [c] Isolated yields. [d] Desulphonylation was performed at 25 °C. [e] Yields determined by g.l.c. [f] At −40 °C. [g] Reaction time 0·5 h. [h] Et_2O–Me_2S (60 : 40) as solvent. Stereoselectivity was lower (97—98%) if Et_2O was the only solvent. [i] Reaction time 1·5 h. [j] Et_2O as solvent. [k] At −5 °C. [l] Reaction time 1 h. [m] Reaction time 2·5 h. [n] Starting cuprate (R^1_2CuLi) prepared from CuI and R^1Li.



SCHEME

Starting with di-n-butyl-, di-s-butyl- or di-t-butylcuprates and acetylene, the resulting dialkenylcuprates were allowed to react with various sulphones to generate compounds (**1**)—(**6**). These were isolated and subjected to reductive desulphonylation[5] to give the final olefins (**7**)—(**12**). The overall yields of this novel olefin synthesis were in the range 70—80% (Table).

The configurations of the γδ-unsaturated sulphones and of the final olefins were established by ^{1}H n.m.r. spectroscopy† and no *trans*-isomer was detected. Furthermore, in the case of compounds (**7**), (**10**), and (**12**) the availability of the *trans*-isomers allowed us to perform a careful g.l.c. analysis of the isomeric purity. As a result, it was found that the degree of stereoselectivity was higher than 99%. Therefore, it appears that the novel procedure described here represents a valid synthetic tool.

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† The spectra were analysed with the aid of a modified[7] LAOCOON 3 program.

[1] For reviews of olefin synthesis see: J. Reucroft and P. G. Sammes, *Quart. Rev. Chem. Soc.*, 1971, **25**, 135; D. J. Faulkner, *Synthesis*, 1971, 175; A. S. Arora and I. K. Ugi in 'Methoden der Organischen Chemie (Houben–Weyl),' Vol. V/1b, 4th edn., ed. E. Muller, G. Thieme Verlag, Stuttgart, 1972, pp. 728—945.

[2] For reviews see: J. F. Normant, 'Organocopper Reagents in Organic Synthesis,' in 'New Applications of Organometallic Reagents in Organic Synthesis,' ed. D. Seyferth, Elsevier, Amsterdam, 1976, p. 219; G. H. Posner, *Org. React.*, 1972, **19**, 1; 1975, **22**, 253; F. Naso, *Chim. Ind. (Milan)*, 1979, **61**, 473.

[3] (a) A. Commerçon, J. F. Normant, and J. Villieras, *Tetrahedron*, 1980, **36**, 1215; (b) A. Alexakis, G. Cahiez, and J. F. Normant, *ibid.*, p. 1961; (c) *Synthesis*, 1979, 826; (d) *J. Organomet. Chem.*, 1979, **177**, 293; (e) H. Westmijze, H. Kleijn, and P. Vermeer, *Tetrahedron Lett.*, 1977, 2023; (f) A. Marfat, P. R. McGuirk, and P. Helquist, *J. Org. Chem.*, 1979, **44**, 1345, 3888.

[4] C. V. Maffeo, G. Marchese, F. Naso, and L. Ronzini, *J. Chem. Soc., Perkin Trans.* 1, 1979, 92; V. Fiandanese, G. Marchese, and F. Naso, *J. Organomet. Chem.*, 1978, **160**, C13; *Tetrahedron Lett.*, 1978, 5131; P. Barsanti, V. Calò, L. Lopez, G. Marchese, F. Naso, and G. Pesce, *J. Chem. Soc., Chem. Commun.*, 1978, 1085.

[5] M. Julia and D. Uguen, *Bull. Soc. Chim. Fr.*, 1976, 513.

[6] H. O. House, C. Y. Chu, J. M. Wilkins, and M. J. Umen, *J. Org. Chem.*, 1975, **40**, 1460.

[7] S. Castellano and A. Bothner-By, *J. Chem. Phys.*, 1964, **41**, 3863; M. Attimonelli and O. Sciacovelli, *Org. Magn. Reson.*, 1980, **13**, 277.