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SELENOSULFONATION OF ACETYLENES. SUBSTITUTION REACTIONS OF β-(PHENYLSELENO)VINYL SULFONES WITH ORGANOCUPRATES

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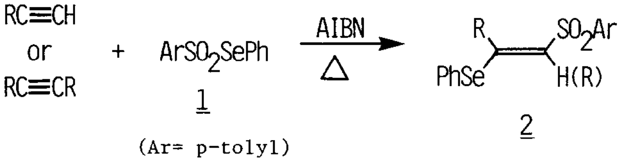
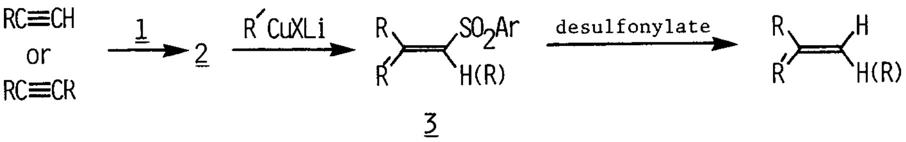
Abstract: β-(Phenylseleno)vinyl sulfones are readily available from the selenosulfonation of acetylenes and undergo efficient, stereoselective substitution of the phenylseleno moiety by the alkyl group of alkyl (phenylseleno)cuprates.

The free-radical additions of Se-phenyl p-tolueneselenosulfonate (1)[1] to terminal or disubstituted acetylenes afford β-(phenylseleno)vinyl sulfones 2 in generally excellent yield and in a highly regio- and stereoselective fashion[2,3], as shown below. These compounds can in turn be converted to other useful products such as acetylenic[2a,2b,3] or allenic[2c] sulfones, β-keto sulfones[2b] and derivatives of the latter[2b].



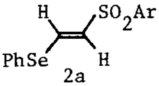
We now describe the reactions of adducts 2 with organocuprate reagents[4,5], which effect the stereoselective substitution of the phenylseleno moiety by the cuprate alkyl group. This process thus permits the efficient conversion of an acetylene to a vinyl sulfone 3 of fixed geometry, via the corresponding selenosulfonation adduct 2. Vinyl sulfones 3 are themselves of value in Diels-Alder reactions, as Michael acceptors and in other applications[6]. Furthermore, it has been previously demonstrated that vinyl sulfones can be reductively desulfonylated to olefins[7], in some cases stereoselectively[7a,7b]. Consequently, the overall alkylation of acetylenes in the 2-position is achieved by the sequence of selenosulfonation, treatment with the appropriate organocuprate, and desulfonylation as shown below. This is particularly expedient as it is generally less facile to introduce alkyl substituents into the 2-position than at the terminus of 1-alkynes.



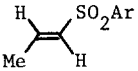
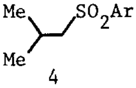
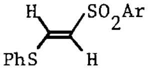
Our preliminary experiments commenced with a comparison of the reactions of various methyl cuprate reagents with adduct 2a (R = H). The results appear in Table 1. With Me_2CuLi, the desired vinyl sulfone 3a reacted further by conjugate addition to produce the saturated sulfone 4 as a byproduct. In order to suppress the formation of 4, we examined the use of the mixed cuprates MeCu(CN)Li and MeCu(SPh)Li. The cyanocuprate afforded a reasonable yield of 3a, but failed to convert substituted adducts 2 (where R ≠ H) to their corresponding vinyl sulfones 3. Interestingly, the thiocuprate preferentially transferred the PhS group[8].

The erratic nature of the results obtained with the above conventional cuprates prompted us to investigate the use of reagents of general structure R′Cu(SePh)Li[9], which to our knowledge have not been previously reported. These species are readily generated in situ when Cu(SePh)[10] is treated with an equimolar amount of the required alkyllithium in THF at 0° for 15-30 min. We were gratified to obtain 3a in 90% yield, unaccompanied by 4, from the reaction of MeCu(SePh)Li with 2a.

Table 1

Reactions of  with Organocuprates

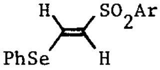
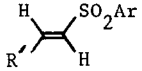
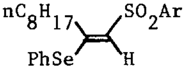
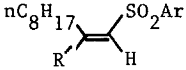
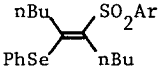
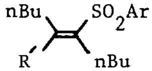
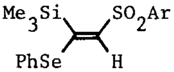
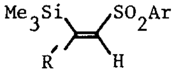
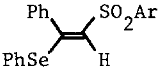
2a

Organocuprate (equivalents)	Conditions	Products (% Yield)
Me_2CuLi (1.1)	0°, Et_2O, 2 h	 3a (68%) +  4 (20%)
MeCu(CN)Li (1.2)	-23°, THF, 2.5 h	3a (74%)
MeCu(SPh)Li (1.2)	-23°, THF, 1 h	 (55%) + 3a (31%)
MeCu(SePh)Li (1.2)	0°, THF, 2 h	3a (90%)

The reactions of other alkyl (phenylseleno)cuprates with several mono- and disubstituted adducts 2 also proved successful and the results are summarized in Table 2. The method is applicable to relatively hindered systems, where the presence of HMPA is beneficial. Conjugate addition to the products 3 was not observed even with excess reagent and prolonged reaction times. The selenocuprates are stable enough to use at room temperature. In each case the products were isolated as pure geometrical isomers, presumably with retention of configuration at the vinylic carbon atom[11]. Workup consisted of treatment with aqueous NH_4Cl, filtration through Celite and chromatography on silica-gel[12]. One instance of anomalous behaviour was observed with adduct 2e (Table 2), which underwent elimination of the selenosulfonate 1 to provide phenylacetylene as the principal product.

Table 2

Reactions of β-(Phenylseleno)vinyl Sulfones 2 with R′Cu(SePh)Li

Starting material	Product	Selenocuprate		Conditions[a]	Yield[b] (%)
		R′	equivs.		
 2a		Me	1.2	0°, 2h	90%
		n-Bu	1.2	0°, 0.5h	75%
		t-Bu	2.5	RT, 3h	84%
 2b		Me	1.2	0°, 3h	86%
		n-Bu	1.2	0°, 2h	62%
 2c		Me	2.6	RT, 20h	92%
		n-Bu	2.6	RT, 19h	80%
		sec-Bu	2.5	RT, 16h[c]	76%
 2d		Me	2.6	RT, 17h	56%
 2e	$PhC\equiv CH$[d]	n-Bu	2.6	RT, 14h	76%[e]

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a) All reactions were performed in THF solution; RT = room temperature. b) Isolated yield unless otherwise indicated. All products were identified by their IR, NMR and mass spectra; yields refer to products of > 97% purity (GC). All new compounds gave satisfactory elemental analyses. c) HMPA (ca. 10%) was added to the reaction mixture. d) This was also the principal product with Me_2CuLi. e) Determined by GC analysis with an internal standard.

Acknowledgements

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References and Notes

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2. a) T.G. Back and S. Collins, Tetrahedron Lett., 22, 5111 (1981). b) T.G. Back, S. Collins and R.G. Kerr, J. Org. Chem., 48, 3077 (1983). c) T.G. Back, S. Collins, U. Gokhale and K.-W. Law, ibid., 48, 4776 (1983).
3. T. Miura and M. Kobayashi, J. Chem. Soc., Chem. Commun., 438 (1982).
4. For reviews of organocuprate reagents see: a) G.H. Posner, Org. React., 19, 1 (1972). b) G.H. Posner, ibid., 22, 253 (1975).
5. The coupling of organocopper reagents with β-iodovinyl sulfones has been reported: W.E. Truce, A.W. Borel and P.J. Marek, J. Org. Chem., 41, 401 (1976).
6. For reviews see: a) W.E. Truce, T.C. Klingler and W.W. Brand, in «Organic Chemistry of Sulfur», Ed. S. Oae, Plenum Press, New York, 1977, chapter 10. b) P.D. Magnus, Tetrahedron, 33, 2019 (1977).
7. See inter alia: a) V. Pascali and A. Umani-Ronchi, J. Chem. Soc., Chem. Commun., 351 (1973). b) J. Bremner, M. Julia, M. Launay and J.-P. Stacino, Tetrahedron Lett., 23, 3265 (1982). c) D. Savoia, C. Trombini and A. Umani-Ronchi, J. Chem. Soc., Perkin Trans. 1, 123 (1977). d) M. Ochiai, T. Ukita and E. Fujita, J. Chem. Soc., Chem. Commun., 619 (1983).
8. Preferential transfer of the phenylthio group has also been reported in the reactions of this cuprate with β-halo enones: E. Piers, K.F. Cheng and I. Nagakura, Can. J. Chem., 60, 1256 (1982).
9. Although this structure reflects the stoichiometry employed in the preparation of these reagents, we cannot rule out the possibility that higher-order cuprate species are formed under these conditions.
10. This reagent is prepared by refluxing cuprous oxide with benzeneselenol in ethanol for ca. 24 h.
11. The configurations of the products 3 derived from adduct 2a are easily established as being E as the vinylic hydrogens exhibit J = ca. 15 Hz. The other stereochemical assignments shown in Table 2 are somewhat tentative at the present time.
12. Typical procedure: Preparation of 3b (R'= Me). Methyllithium (1.2 mmol) was added to Cu(SePh) (1.2 mmol) in 3 mL of dry THF under N_2 at 0°. After 15 min, adduct 2b (1.0 mmol) in 2 mL of THF was introduced by syringe and stirring was continued for 3 h at 0°. The reaction was quenched with NH_4Cl solution, the mixture was diluted with ether, filtered through Celite, washed with NaCl solution, dried and evaporated. Chromatography over silica-gel (benzene eluant) afforded 86% of the product as a clear oil of 97% purity (GC): bp (Kugelrohr) 120°/0.03 mm; NMR δ 7.8-7.3 (m, 4H), 6.16 (unresolved s, 1H), 2.56 (t, J= 7 Hz, 2H), 2.43 (s, 3H), 1.85 (d, J= 1.3 Hz, 3H), 1.2 (m, 12H), 0.89 (t, J= 6 Hz, 3H); IR (film) 1615, 1600, 1308, 1152 cm^{-1}; m/e 308 (M^+); C,H,S analysis within ± 0.25%.

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