Tetrahedron Letters,Vol.30,No.47,pp 6481-6482,1989
Printed in Great Britain

0040-4039/89 $3.00 + .00
Pergamon Press plc

A NEW PREPARATION OF 3-SUBSTITUTED 2-(p-TOLUENESULFONYL)-1,3-DIENES

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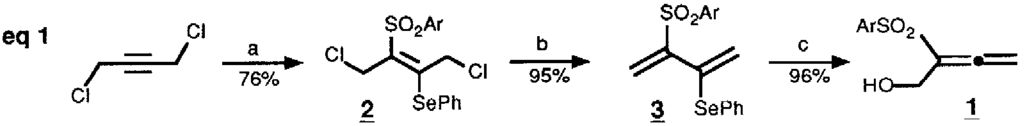
Summary: The title compounds were prepared by addition-elimination reactions of 2-(p-toluenesulfonyl)-2,3-butadien-1-ol. The latter was readily obtained from 1,4-dichloro-2-butyne by selenosulfonation, reductive elimination of chlorine and [2,3] sigmatropic rearrangement of the corresponding selenoxide.

Several recent studies of 2-arylsulfonyl-1,3-dienes have demonstrated their synthetic utility. For example, they display dual electron demand in [4+2] cycloadditions,[1] undergo nucleophilic addition and substitution reactions[1a] and produce useful epoxide derivatives.[2] Although several efficient methods for the preparation of 2-arylsulfonyl-1,3-dienes have been reported,[3] most afford products that contain substituents in only the 1- or 4-positions. We now report a method for the preparation of the corresponding 3-substituted derivatives from the sulfonylallene 1.

Sulfonylallene 1 was conveniently prepared by the method shown in eq 1. Free-radical selenosulfonation[4] of 1,4-dichloro-2-butyne afforded the adduct 2. Reductive elimination of 2 produced the sulfonyldiene 3, which underwent [2,3] sigmatropic rearrangement[5] to 1 upon oxidation to the corresponding selenoxide, followed by an aqueous workup.[6]



a) $ArSO_2SePh$ (Ar= p-tolyl), C_6H_6, AIBN, Δ b) NaI, acetone, Δ c) MCPBA, $CHCl_3$, R.T., 5 min; then K_2CO_3-H_2O

Sulfonylallene 1 reacted with organocuprates to furnish the crude addition products 4, which eliminated when treated with with mesyl chloride and triethylamine to afford the desired 3-alkyl substituted 2-(p-toluenesulfonyl)-1,3-dienes 5a-5e.[7] Alternatively, the acetoxy and chloro derivatives 5f and 5g were obtained by the reaction of 1 with acetic anhydride and triethylamine, or with thionyl chloride, respectively. The results are summarized in eq 2 and Table 1.

These results show that the readily available sulfonyl allene 1 provides convenient access to various 3-substituted 2-(p-toluenesulfonyl)-1,3-dienes 5. The phenylseleno-substituted diene 3 is also a member of this class and further investigations of its properties are in progress.

Acknowledgement: We thank the Natural Sciences and Engineering Research Council of Canada for financial support and for a Summer Studentship to E.K.Y.L.

eq 2

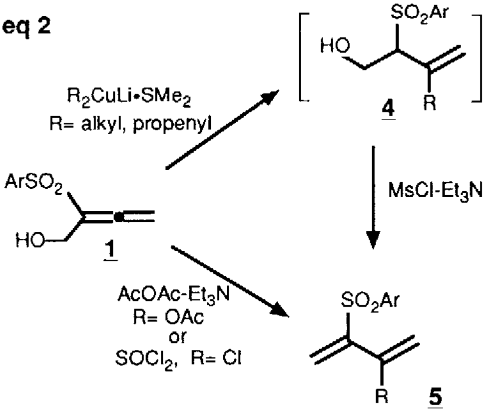


Table 1. Preparation of 2-Sulfonyl-1,3-dienes

Product[a]	R	Method[b]	Yield (%)[c]
5a	Me	A	73
5b	n-Bu	A	72
5c	sec-Bu	A	55
5d	t-Bu	A[d]	52
5e	CH=CHMe	A[e]	63
5f	OAc	B	57
5g	Cl	C	54

a) All products were characterized by IR, NMR and mass spectroscopy; all new compounds gave satisfactory analyses or high resolution mass spectra. b) Method A: see reference 7 for a typical procedure. Method B: excess AcOAc-Et$_3$N in CH$_2$Cl$_2$, 0°C, 24 h. Method C: excess SOCl$_2$-C$_6$H$_6$, Δ, 6 h. c) Isolated yields are reported. d) DBN was employed in the elimination step instead of Et$_3$N. e) The product was a 10:1 mixture of E,Z-isomers that could not be separated.

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6. Compound 1: mp 65-66°C; IR: 3500, 1968 cm^{-1}; ^{1}H-NMR: δ 5.45 (t, J= 1.8 Hz, 2 H), 4.36 (t, J= 1.8 Hz, 2 H); CHS analysis ± 0.2%.
7. Typical procedure (compound 5a): A THF solution of 1 (0.58 mmol) was added to 0.87 mmol of Me$_2$CuLi•SMe$_2$ in THF at -78°C. After 0.5 h at -78°C, the mixture was washed with water, dried (MgSO$_4$), evaporated, and stirred for 2 h with 1 mL of Et$_3$N and 0.2 mL of mesyl chloride in benzene. The mixture was evaporated in vacuo and purified by flash chromatography (elution with 15% ethyl acetate-hexane) to afford 73% of 5a as an oil with IR: 1597, 1312, 1302, 1158, 1127 cm^{-1}; ^{1}H-NMR: olefinic signals at δ 6.45, 5.90, 5.33, 5.13 and MeC=C at δ 1.88; exact mass calculated for C$_{12}$H$_{14}$O$_2$S: 222.0715. Found: 222.0703.

(Received in USA 24 August 1989)