Pergamon

Tetrahedron Letters, Vol. 37, No. 24, pp. 4161-4164, 1996

0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)00784-8

A REGIOSELECTIVE ADDITION REACTION OF A SULFONYL RADICAL TO CONJUGATE ENYNESULFONES: A CONVENIENT SYNTHESIS OF 1,4-BIS(ARYLSULFONYL)-1,3-BUTADIENE

Mitsuhiro Yoshimatsu,*[a] Mitsumasa Hayashi,[a] Genzoh Tanabe,[b] and Osamu Muraoka[b]

[a]Department of Chemistry, Faculty of Education, Gifu University, Yanagido, Gifu 501-11, Japan
[b]Kinki University, Faculty of Pharmaceutical Sciences, 3-4-1, Kowakae, Higashi-osaka, Osaka 577, Japan

Abstract: *p*-Tolyl benzeneselenosulfonate regioselectively added to the conjugate enynesulfones **1-9** gave *(1E, 3E)*-1,4-bis(arylsulfonyl)-1,3-butadienes **10-17**, which were converted to the 4-hetero atom-substituted-1-phenylsulfonyl-1,3-butadienes **18**, **21** and **22**. Copyright © 1996 Elsevier Science Ltd

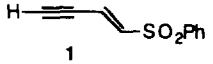
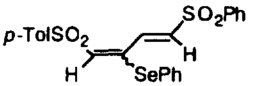
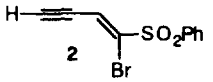
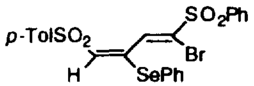
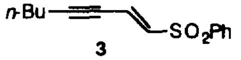
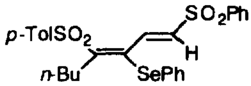
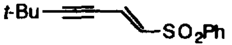
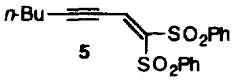
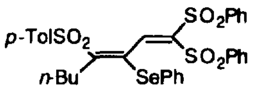
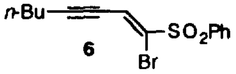
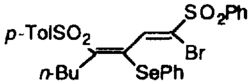
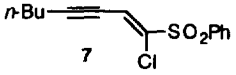
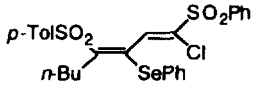
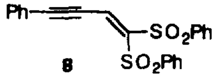
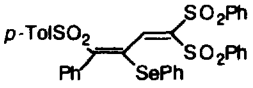
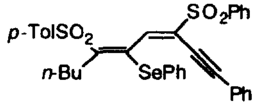
Sulfonyl substituted 1,3-butadienes have recently attracted considerable attention as useful synthetic intermediates.[1] Padwa *et al.* demonstrated the use of 1,3-[2] and 2,3-bis(phenylsulfonyl)-1,3-butadienes[3] as versatile building blocks in organic chemistry *via* reactions such as [4+2]-cycloadditions and 1,3-dipolar cycloadditions.[4] However, the preparation of 1,4-bis(sulfonyl)-1,3-butadienes[5] is quite limited although there have been a few reports on the subject, which includes the double [2,3]-sigmatropic rearrangement of β-phenylsulfenyl propargylic alcohols and subsequent oxidation[6] which gave α,β-unsaturated phenylsulfonyl ketones in some substrates. Therefore, it could not be considered a general synthetic method for 1,4-bis(arylsulfonyl)-1,3-butadienes.

Recently, we reported the syntheses and reactions of conjugate enynesulfones.[7] If the sulfonyl radical is regioselectively added to the enynesulfones, this novel method will be useful and convenient for the preparation of 1,4-bis(arylsulfonyl)-1,3-butadienes. Krause *et al.* reported that the addition reactions of organo cuprates to enyne compounds[8] underwent 1,6-addition to give substituted butadienes. We were interested as whether the radical addition reactions for the conjugate enynesulfones may occur at an acetylenic or olefinic carbon. Now we report a sulfonyl radical addition to enynesulfones; a general synthetic method for 1,4-bis(arylsulfonyl)-1,3-butadienes.

The conjugate enynesulfones were prepared according to our previous report.[7] The enynesulfone **1** reacted with *p*-tolyl benzeneselenosulfonate/AIBN[9] to give *(1Z, 3E)*- and *(1E, 3E)*-2-phenylseleno-1,3-butadiene **10** in 79% yield (*(1Z, 3E)*:*(1E, 3E)*=6:1) (Table 1, entry 1).[10] The stereochemistry of the product **10** was established by the difference nuclear Overhauser effect (DNOE) enhancement between the 2-olefinic proton and the aromatic *ortho* proton of a *p*-toluenesulfonyl group. Irradiation of the 2-olefinic proton of a minor isomer *(1E, 3E)*-**10** increased the intensity of the 4-olefinic proton. The $CDCl_3$ solution of **10** (*(1Z, 3E)*:*(1E, 3E)*=6:1) stood at room temperature overnight gave a mixture of **10** (*(1Z, 3E)*:*(1E, 3E)*=1:1.3). This result shows that the *(1E, 3E)*-isomer is thermodynamically more stable than the other isomer. α-Bromoenynesulfone **2** and **6** also exclusively gave *(1E, 3Z)*-1-bromo-1,4-bis(arylsulfonyl)-1,3-butadienes **11** and *(1E, 3E)*-**14** (Entries 2 and 6). *n*-Bu-substituted enynesulfone **3** afforded 1,3-butadiene **12** (Entry 3); however, the *t*-Bu-derivative **4** gave a complex mixture. 1,1-Bis(phenylsulfonyl)enyne **5** and **8** gave 1,1,4-

tri(arylsulfonyl)-1,3-butadienes **13** and **16** in high yields. The conjugate *(Z)*-enediynesulfone **9** did not give an aromatized product[11] but did regioselectively produce the conjugate dienyne compound **17** (Entry 9), because of the contribution of the propargyl radical **24** stabilized by the sulfonyl group compared to that of **26**.[12] The stereochemistries for other products were also determined by DNOE experiments.

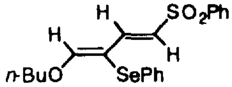
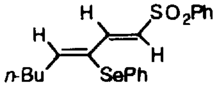
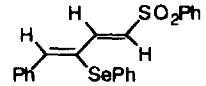
Table 1 Reactions of enyne sulfones with selenosulfonate

Entry	Enyne sulfone	Products (% yields)	
1	 **1**		**10** (79)*1
2	 **2**		**11** (96)
3	 **3**		**12** (72)
4	 **4**		
5	 **5**		**13** (75)
6	 **6**		**14** (quant.)
7	 **7**		**15** (90)
8	 **8**		**16** (quant.)
9	 **9**		**17** (72)

*1 The isomer ratio of **10** is *1Z:1E*=6:1.

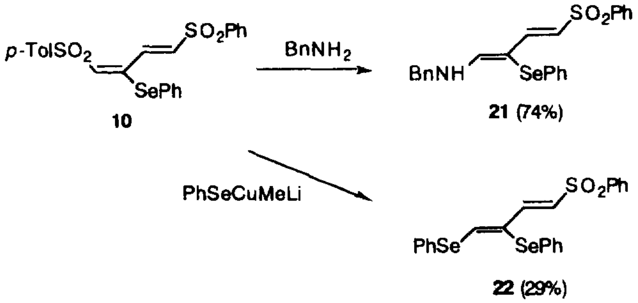
Recently, Takei and Hevesi reported the Ni-catalyzed coupling reactions of vinyl selenides and Grignard reagents.[13] If the phenylseleno group of these dienes is converted to an alkyl or aryl group by the coupling reaction, the reaction can be proposed as a general synthetic method for 3-alkyl- or 3-aryl-1,4-bis(arylsulfonyl)-1,3-butadienes. In order to clarify the reactivity of these new 1,4-bis(arylsulfonyl)-1,3-butadienes,[2] we performed several reactions. The coupling reaction of **10** and *n*-BuMgBr/$NiCl_2(PPh_3)_2$/DME gave 4-*n*-butoxy-3-phenylseleno-1-phenylsufonyl-1,3-butadiene **18** in 77% yield. The structure assignment was confirmed by MS and ^1H NMR spectra. The MS spectrum shows the molecular ion peak at *m/z* 422 ($C_{20}H_{22}O_3SSe$). The ^1H NMR spectrum exhibited the methylene protons adjacent to an oxygen at δ 4.07 ppm. $Ni(C_5H_7O_2)_2$/DME also gave the *(1E, 3E)*-*n*-BuO-substituted diene **18** in good yield. The coupling reaction of **10** under an Ar atmosphere afforded the 4-*n*-Bu-substituted 1,3-diene **19** in 68% yield. Grignard reagents are reported to react with oxygen and form alkoxy radicals or alkoxides.[14] Therefore, the alkoxy intermediates, which would be formed by the reaction of *n*-BuMgBr and oxygen, undergo the addition to the dienyl sulfone **10** followed by elimination to give the alkoxy diene **18**.[6] We also examined the reaction of **10** and PhMgBr/$NiCl_2(PPh_3)_2$/DME under an Ar atmosphere to give *(1Z, 3E)*-1-phenyl-2-phenylseleno-4-phenylsulfonyl-1,3-butadiene (**20**) in 74% yield.

Table 2 Ni-Catalyzed coupling reactions of dienyl sulfone 10

Entry	Conditions	Products (% yields)	
1	*n*-BuMgBr/$NiCl_2(PPh_3)_2$/DME		**18** (77)
2	*n*-BuMgBr/$Ni(C_5H_7O_2)_2$/DME	**18** (82)	
3	*n*-BuMgBr/$NiCl_2(PPh_3)_2$/DME/Ar		**19** (68)
4	PhMgBr/$NiCl_2(PPh_3)_2$/DME/Ar		**20** (74)

Furthermore, we performed the reaction of diene **10** with benzylamine. 1-Benzylamino-2-phenylseleno-4-phenylsulfonyl-1,3-butadiene (**21**) was obtained in 74% yield. The stereochemistry was established by a single X-ray analysis.[15] Product **21** has been reported to undergo [4+2]-cycloadditions through the reaction with acrolein.[16]

Back and co-workers reported the regioselective alkylation of β-seleno vinyl sulfones by PhSeCuMeLi.[17] However, the reaction of dienyl sulfone **10** with PhSeCuMeLi gave bis(phenylseleno)-1,3-butadiene **22** in 29% yield. This result shows that the carbon at the 1-position of the 1,4-bis(arylsulfonyl)-2-phenylseleno-1,3-butadiene derivatives first reacts with the hetero-nucleophiles to give 1-heteroatom-substituted 4-sulfonyl-1,3-butadienes.



Scheme 1

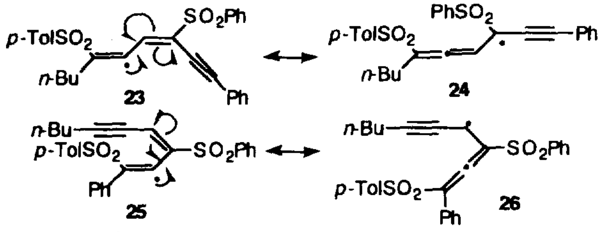
We are now examining the [4+2]- and 1,3-dipolar cycloaddition reactions of the 1,4-bis(arylsulfonyl)-1,3-butadienes. These results will be reported elsewhere.

Acknowledgements

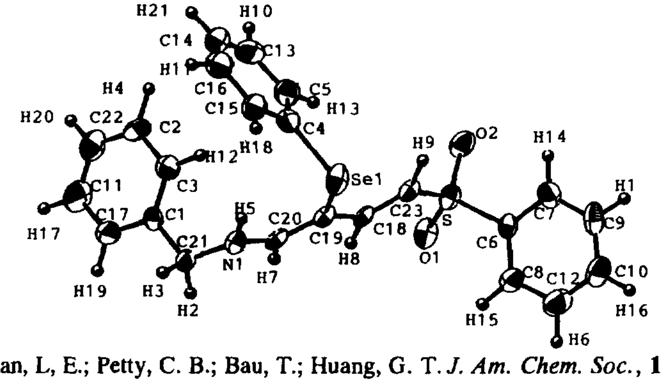
The support of a part of this work by the Ministry of Education, Science and Culture, Japan, is gratefully acknowledged.

REFERENCES AND NOTES

1. Padwa, A.; Murphree, S. S. *Org. Prep. Proced. Int.* **1991**, 23, 545-568. *The Chemistry of Sulfones and Sulfoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; Willey: Chichester, **1988**; pp 1-1210. Fuchs, P. L.; Braish, T. F. *Chem. Rev.*, **1986**, 86, 903-917.
2. Padwa, A.; Harrison, B.; Murphree, S. S.; Yeske, P. E. *J. Org. Chem.*, **1989**, 54, 4232-4235.
3. Padwa, A.; Gareau, Y.; Harrison, B.; Norman, B. H. *J. Org. Chem.*, **1991**, 56, 2713-2720. Padwa, A.; Norman, B. H. *Tetrahedron Lett.*, **1988**, 29, 3041-3044; *J. Org. Chem.*, **1990**, 55, 4801-4807.
4. Padwa, A.; Norman, B. H. *Tetrahedron Lett.*, **1988**, 29, 2417-2420.
5. Gaoni, Y. *Tetrahedron Lett.*, **1977**, 4521-4524. Krug, R. C.; Rigney, J. A.; Tichelaar, G. R. *J. Org. Chem.*, **1962**, 27, 1305-1309.
6. Wang, X.; Ni, Z.; Lu, X.; Hollis, A.; Banks, H.; Rodriguez, A.; Padwa, A. *J. Org. Chem.*, **1993**, 58, 5377-5385. Ni, Z; Wang, X.; Rodriguez, A.; Padwa, A. *Tetrahedron Lett.*, **1992**, 33, 7303-7306. Jeganathan, S.; Okamura, W. H. *Tetrahedron Lett.*, **1982**, 23, 4763-4764.
7. Yoshimatsu, M.; Kawahigashi, M.; Shimizu, H.; Kataoka, T. *J. Chem. Soc., Chem. Commun.*, **1995**, 583-584.
8. Hohmann, M.; Krause, N. *Chem. Ber.*, **1995**, 128, 851-860.
9. Back, T. G.; Collins, S.; Kerr, R. G. *J. Org. Chem.*, **1983**, 48, 3077-3084.
   Liw, H.-S.; Coghlan, M. J.; Paquette, L. A. Org. Synth., Coll. Vol.VIII, 1993, 543-546.
10. **10**:*(1Z, 3E)*- and *(1E, 3E)*-2-Phenylseleno-4-phenylsulfonyl-1-*p*-toluenesulfonyl-1,3-butadiene: mp 143-145 °C; IR (KBr, cm^{-1}) 1310, 1140 (SO_2); ^1H NMR (270 MHz, $CDCl_3$) δ 2.42 (s, *1Z*-CH_3), 2.43 (s, *1E*-CH_3), 6.10 (brs, *1E*-olefinic H), 6.11 (d, *J*=2 Hz, *1Z*-olefinic H), 6.45 (d, *J*=15 Hz, *1E*-olefinic H), 6.90 (d, *J*=15 Hz, *1Z*-olefinic H), 7.27-7.49 (m, ArH), 7.55-7.70 (m, ArH), 7.91-7.95 (m, ArH), 8.32 (brd, *J*=15 Hz, *1E*-olefinic H), 8.34 (dd, *J*=2 and 15 Hz, *1Z*-olefinic H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 21.52 (q), 127.28 (d), 128.07 (d), 129.40 (d), 130.05 (d), 130.19 (d), 130.28 (d), 131.20 (d), 133.86 (d), 135.27 (d), 135.91 (d), 136.48 (d), 144.75 (s); MS m/z 504 (M^+); Anal. Calcd for $C_{23}H_{20}O_4S_2Se$: C, 54.87; H, 4.00. Found: C, 54.70; H, 3.98.
11. Grissom, J. W.; Gunawardena, G. U. *Tetrahedron Lett.*, **1995**, 36, 4951-4954.
12.



13. Kosugi, K.; Takei, H. *Tetrahedron Lett.*, **1980**, 21, 87-90. Hevesi, L.; Hermans, B.; Allard, C. *Tetrahedron Lett.*, **1994**, 35, 6729-6732.
14. Walling, C; Buckler, S. A. *J. Am. Chem. Soc.*, **1955**, 77, 6032. Hock, H.; Ernst, F. *Chem. Ber.*, **1959**, 92, 2716.
15. Perspective ORTEP drawing of *(1E, 3E)*-1-benzylamino-2-phenylseleno-4-phenylsulfonyl-1,3-butadiene (**21**).



16. Overman, L, E.; Petty, C. B.; Bau, T.; Huang, G. T. *J. Am. Chem. Soc.*, **1983**, 105, 6335-6337.
17. Back, T. G.; Collins, S.; Krishna, M. V.; Law, K. W. *J. Org. Chem.*, **1987**, 52, 4258-4264.

(*Received in Japan* 11 *March* 1996; *accepted* 24 *April* 1996)