ChemComm

# The synthesis of ethenyl bifunctional reagents containing a sulfone moiety and zirconium by the abnormal addition of $Cp_2Zr(H)Cl$ to internal acetylenic sulfones

**Xian Huang* and De-Hui Duan**

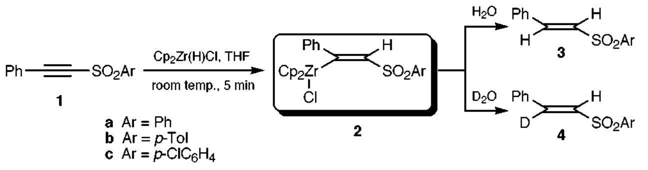
*Department of Chemistry, Zhejiang University (Xixi Campus), Hangzhou Zhejiang 310028, P.R. China.*
*E-mail: Huangx@mail.hz.zj.cn*

*Received (in Cambridge, UK) 9th June 1999, Accepted 27th July 1999*

**Ethenyl bifunctional reagents containing a sulfone moiety and zirconium are prepared by the abnormal addition of $Cp_2Zr(H)Cl$ to internal acetylenic sulfones.**

Acetylenic sulfones have been used extensively in organic synthesis as activated acetylene equivalents. They can take part in cycloadditions,[1] Michael additions[2] and alkylative desulfonylation reactions.[3] Surprisingly, little attention has been paid to their hydrometalation reactions. On the other hand, *via* the hydrozirconation of alkynes, many bifunctional ethenyl reagents have been synthesized containing elements such as selenium and zirconium,[4] tellurium and zirconium,[5] silicon and zirconium,[6] tin and zirconium,[7] zinc and zirconium[8] and boron and zirconium.[9] Apparently, no efforts have been focused on the bifunctional ethenyl reagent containing sulfur and zirconium. We now report that we have successfully synthesized sulfonyl-substituted alkenylzirconocene compounds *via* the hydrozirconation of internal acetylenic sulfones. Unexpectedly, the products of *anti*-addition of $Cp_2Zr(H)Cl$ to the acetylene are observed.

Phenylacetylenic sulfones **1a–c** were synthesized in good yields according to the method of Suzuki.[10] Hydrozirconation of the acetylenic sulfones with 1.2 equiv. of $Cp_2Zr(H)Cl$ in THF for 5 min at room temperature gave a clear yellow solution. Unique *E*-vinyl sulfones **3a–c** or *E*-β-deuterovinyl sulfones **4a–c** were obtained respectively after hydrolysis or deuterolysis (Scheme 1 and Table 1).† The *E*-olefin geometry was verified by the coupling constant ($^3J_{HH}$ = 15.4 Hz) of the vicinal olefinic protons. In addition, the product melting points are also identical to those previously reported.[11] The olefinic proton of every deuterovinyl sulfone presents a single peak at $\delta$ 6.84, which shows that the deuterium atom must be attached to the β-position of the sulfonyl group. Thus the (*Z*)-β-sulfonylalkenylzirconocene compounds **2** are produced in the hydrozirconation reaction (Scheme 1).



Scheme 1

**Table 1** Yields and melting points for **3a–c** and **4a–c**

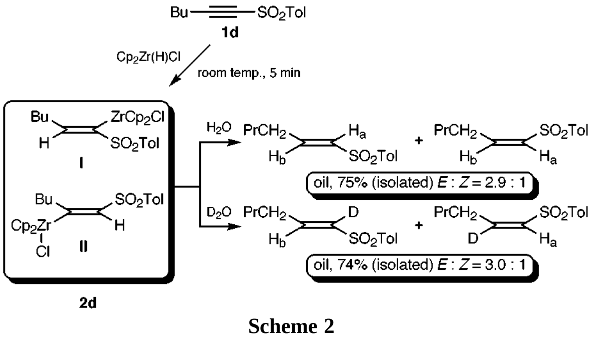
| Compound | Ar | Yield (%)[a] | Mp/°C |
|---|---|---|---|
| **3a** | Ph | 72 | 74.5–75.5 |
| **3b** | *p*-Tol | 69 | 126–121 |
| **3c** | *p*-$ClC_6H_4$ | 70 | 82–84 |
| **4a** | Ph | 70 | 73.5–75 |
| **4b** | *p*-Tol | 73 | 118–120 |
| **4c** | *p*-$ClC_6H_4$ | 68 | 82–83 |

[a] Yields of pure compounds.

Hex-1-ynyl *p*-tolyl sulfone was synthesized in two steps according to the method of Truce.[12] After hydrozirconation–hydrolysis, a mixture of *E* and *Z* vinyl sulfones ($E:Z$ = 2.9 : 1) was obtained (Scheme 2). Its $^1H$ NMR spectrum (300 MHz) exhibits a doublet of triplets at $\delta$ 6.97 (*E*-$H_b$, *J* 15.1, 6.8 Hz) and multiple peaks at $\delta$ 6.20–6.32 [including *E*-$H_a$, (dt, *J* 15.1, 1.4 Hz) and *Z*-$H_a$ + $H_b$ ($ABX_2$ system, $J_{AB}$ 11.1 Hz, $J_{AX}$ 6.5 Hz)]. Further proof is also provided by the $^1H$ NMR signals for two kinds of methylenic protons [$\delta$ 2.67 (q, 0.52 H, *J* 7.7, 6.5 Hz, *Z*-$CH_2$) and 2.25 (dq, 1.48 H, *J* 7.4, 6.8, 1.4 Hz, *E*-$CH_2$)]. The proportion of the $E:Z$ mixture was estimated *via* the integral areas of the two kinds of methylenic protons. After the parallel experiment of hydrozirconation–deuterolysis, a mixture of two regio- and stereo-isomers ($E:Z$ = 3 : 1 by $^1H$ NMR) was obtained (Scheme 2). Its $^1H$ NMR spectrum exhibits a triplet at $\delta$ 6.97 (*E*-$H_b$), a single peak at $\delta$ 6.26 (*Z*-$H_a$), a triplet at $\delta$ 2.68 (*Z*-$CH_2$) and a quartet at $\delta$ 2.25 (*E*-$CH_2$). These results show that two types of alkenylzirconocene compounds **2d** (**I** and **II**) are generated in the hydrozirconation reaction.

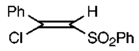
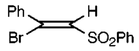
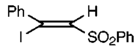
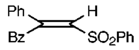
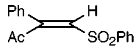
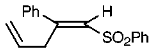
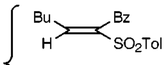
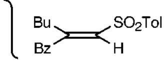
Compounds **2** were reacted with various electrophiles (Table 2). NCS, NBS and $I_2$ (2.5 equiv.) reacted with **2a** to give β-halo vinyl sulfones. Using the method, we can access *Z*-β-halo vinyl sulfones, whose configurations were identified by comparisons with authoritative data.[13] Thus this approach complements the addition of sulfonyl halides to acetylenes, which provides either an *E* and *Z* mixture[13] or only the *E* isomer.[12] Carbon–carbon bond formation also occurred readily with various carbon electrophiles. Reactions with carboxylic acid chlorides afforded (*Z*)-β-sulfonyl α,β-unsaturated ketones. The cross-coupling with allyl bromide provided (*E*)-penta-1,4-dienyl sulfone. Their configurations were affirmed by H–H 2D NOSEY spectra (300 MHz). As is expected, the reaction of **2d** with BzCl afforded two isomers.

There are some regiochemical and stereochemical issues associated with the addition of $Cp_2Zr(H)Cl$ across unsymmetrical acetylenic sulfones. Based on the different substituents (Bu or Ph) on the acetylene bond, $\alpha$- (major) or β-sulfonyl alkenylzirconocene compounds are obtained respectively. The different regiochemistry could be ascribable to the dissimilarity of the polarizing ability of the two groups to the C≡C triple bond and the long-distance π,π-interaction of the phenyl and bicyclopentadienyl groups.



Scheme 2

**Table 2** Reaction of **2a** and **2d** with electrophiles

| **2** | E–X | Product | Isolated yield (%) |
|---|---|---|---|
| **2a** | NCS |  | 57 |
| **2a** | NBS |  | 63 |
| **2a** | $I_2$ |  | 56 |
| **2a** | BzCl[a] |  | 65 |
| **2a** | AcCl[a] |  | 70 |
| **2a** | $H_2C{=}CHCH_2Br$[b] |  | 51 |
| **2d** | BzCl[a] |  | 45 |
|  |  |  | 28 |

[a] Reaction conditions: CuBr (0.5 equiv.), acid chlorides (1.05 equiv.), THF, 25 °C, 2 h. [b] Reaction conditions: $Pd(PPh_3)_4$ (5 mol%), allyl bromide (1.05 equiv.), 40 °C, 3 h.

In conclusion, bifunctional ethenyl reagents containing sulfone and zirconium moieties are prepared by the abnormal addition of $Cp_2Zr(H)Cl$ to internal acetylenic sulfones. The addition reactions usually generate vinyl sulfone compounds, which can be exploited for further synthetic elaboration.[14] Currently a more thorough study is being carried out in our laboratory.

Project 29772007 is supported by the National Natural Science Foundation of China; this work is also supported by the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Academia Sinica.

## Notes and references

†All new compounds were characterized *via* IR, $^1$H NMR (300 MHz), EI-MS and elemental analysis.

1 D. F. Huang and T. Y. Shen, *Tetrahedron Lett.*, 1993, **34**, 4477; D. J. Hlasta and J. H. Ackerman, *J. Org. Chem.*, 1994, **59**, 6184.
2 W. E. Truce and B. W. Onken, *J. Org. Chem.*, 1975, **40**, 3200; V. Fiandanese, G. Marchese and F. Naso, *Tetrahedron Lett.*, 1978, 5131.
3 J. J. Eisch, B. Shafii, J. D. Odom and A. L. Rheingold, *J. Am. Chem. Soc.*, 1990, **112**, 1847; E. J. Corey, P. Da Silva Jardine and T. Mohri, *Tetrahedron Lett.*, 1988, **29**, 6409.
4 L. S. Zhu, Z. Z. Huang and X. Huang, *J. Chem. Res. (S)*, 1996, 112; M. J. Dabdoub, M. L. Begnini and P. G. Guerrero Jr., *Tetrahedron*, 1998, **54**, 2371.
5 J. W. Sung, W. B. Jang and D. Y. Oh, *Tetrahedron Lett.*, 1996, **37**, 7537.
6 I. Hyla-Kryspin, R. Gleiter, C. Kruger, R. Zwettler and G. Erker, *Organometallics*, 1990, **9**, 517.
7 B. H. Lipshutz, R. Keil and J. C. Barton, *Tetrahedron Lett.*, 1992, **33**, 5861.
8 C. E. Tucker and P. Knochel, *J. Am. Chem. Soc.*, 1991, **113**, 9888.
9 L. Deloux, E. Skrzypczak-Janjkun, B. V. Cheesman and M. Srebnik, *J. Am. Chem. Soc.*, 1994, **116**, 10302.
10 H. Suzuki and H. Abe, *Tetrahedron Lett.*, 1996, **37**, 3717.
11 G. Cardillo, D. Savoia and A. Umani-Ronchi, *Synthesis*, 1975, 453; L. K. Liu, Y. Chi and K. Y. Jen, *J. Org. Chem.*, 1980, **45**, 406; G. H. Posner and D. J. Brunelle, *J. Org. Chem.*, 1972, **37**, 3547.
12 W. E. Truce and G. C. Wolf, *J. Org. Chem.*, 1971, **36**, 1727.
13 Y. Amiel, *J. Org. Chem.*, 1971, **36**, 3691; 1974, **39**, 3867.
14 N. S. Simpkins, *Tetrahedron*, 1990, **46**, 6951.

*Communication 9/04620H*