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

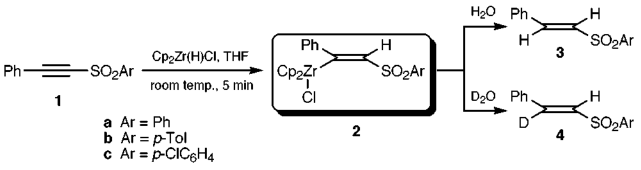
Department of Chemistry, Zhejiang University (Xixi Campus), Hangzhou Zhejiang 310028, P.R. China.
E-mail: Huangx@mail.hz.zj.cn

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 δ 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**

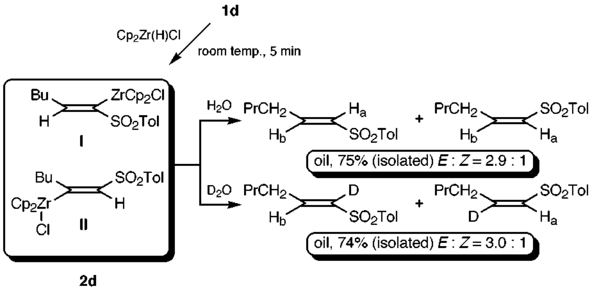
Compound	Ar	Yield (%)[a]	Mp/°C
3a	Ph	72	74.5–75.5
3b	*p*-Tol	69	126–121
3c	*p*-ClC_6H_4	70	82–84
4a	Ph	70	73.5–75
4b	*p*-Tol	73	118–120
4c	*p*-ClC_6H_4	68	82–83

[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 δ 6.97 (*E*-H_b, *J* 15.1, 6.8 Hz) and multiple peaks at δ 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 [δ 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 δ 6.97 (*E*-H_b), a single peak at δ 6.26 (*Z*-H_a), a triplet at δ 2.68 (*Z*-CH_2) and a quartet at δ 2.25 (*E*-CH_2). These results show that two types of alkenylzirconocene compounds **2d** (**I** and **II**) are generated in the hydrozirconation reaction.

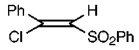
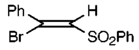
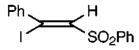
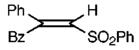
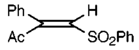
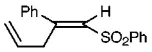
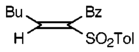
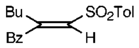
Compounds **2** were reacted with various electrophiles (Table 2). NCS, NBS and I_2 (2.5 equiv.) reacted with **2a** to give β-halo vinyl sulfones. Using the method, we can access *Z*-β-halo vinyl sulfones, whose configurations were identified by comparisons with authoritative data.[13] Thus this approach 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, α- (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, ^1H 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