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Solvent-free synthesis of ferrocenylethene derivatives

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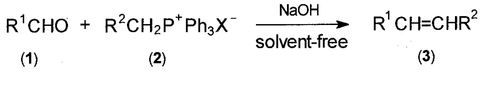
Abstract

Herein, we report a fast, mild, efficient and simple Wittig reaction in a dry state to get ferrocenylethene derivatives. The *Z* and *E* isomers can be separated by chromatography and many isomers are characterized for the first time. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Wittig reaction; Ferrocenylethene derivative; Solvent-free reaction; *Z*,*E*-separation

1. Introduction

Considerable work has been done to synthesize new materials with large second-order non-linear optical features because of their potential use in optical devices for information processing [1,2]. It is now well known that molecules possessing extensively conjugated π-electron systems exhibit large non-linear optical properties. Organometallic structures are an interesting class of potentially nonlinear molecular blocks [3,4]. Molecules with π donor-acceptor interactions, like ferrocenylethene derivatives, are examples of those structures, and may serve as monomers for ferrocene containing polymers, which may offer a variety of potential applications such as photoactivate semiconductors [5]. Many synthetic methods for ferrocenylethene derivatives have been developed. They can be summarized to three kinds: the first is based on Wittig reaction of formylferrocene with ylides or (ferrocenylmethyl) triphenylphosphonium iodide with aldehydes [6–9]; the second is based on Heck reaction of ferrocenylethene with various halides [2,10]; the third is McMurry coupling of formylferrocene with other aldehydes [11]. But all those methods bear some disadvantages, such as long reaction time, high temperature, onerous operation, expensive reagents and low yield. The solvent-free reaction has drawn great attention in recent years [12], and has been proved to have many advantages: reduced pollution, low costs, and simplicity in process and handling. This prompted us to apply this method to the synthesis of vinylferrocene derivatives by the Wittig reaction. It should be pointed out that the Wittig reaction has not been applied in dry state syntheses so far. Our work shows that the vinylferrocene derivatives can be synthesized efficiently by the Wittig reaction in solvent-free conditions



$$\underset{(1)}{R^1CHO} + \underset{(2)}{R^2CH_2P^+Ph_3X^-} \xrightarrow[\text{solvent-free}]{\text{NaOH}} \underset{(3)}{R^1CH{=}CHR^2}$$

Scheme 1.

2. Results and discussion

The vinylferrocene derivatives could be obtained from aldehyde and phosphonium salt as shown in Scheme 1.

All products were characterized with ^{1}H-NMR, MS, IR and melting points. The results are listed in Table 1 and in the experimental part.

W.M. Horspool reported that triphenylbenzylphosphonium halide reacts with formylferrocene in dimethylsulfoxide catalyzed by sodium hydride under nitrogen to get 1-ferrocenyl-2-phenylethylene in 70% yield [8], but according to our operation method in the

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Table 1
The results of solvent-free Wittig reactions (Scheme 1)

Entry	Product	R^1	R^2	X	Temperature (°C)	Time (min)	Conversion (%) [a]	Z/E [b]	Melting point of Z-isomer (°C)	Melting point of E-isomer (°C)	
										Found	Literature
1	**3a**	Fc	C_6H_5	Cl	r.t.	5	95	1/4	Oil [d]	122–124	120–122[13]
2	**3b**	C_6H_5	Fc	I	65	30	87	1/2	Oil [d]	122–124	120–122[13]
3	**3c**	Fc	p-Cl–C_6H_4	Br	r.t.	10	83	2/3	50 ~ 51 [d]	158–160	152–155[14]
4	**3d**	Fc	p-Br–C_6H_4	Br	r.t.	10	80	1/3	64 ~ 65 [d]	145–147	– [d]
5	**3e**	Fc	m-NO_2–C_6H_4	Br	r.t.	7	93	1/7	67 ~ 68 [d]	150–152	151–152[14]
6	**3f**	Fc	C_6H_5–CO–	Br	65	240	71	– [c]	–	124–126	136–137[13]
7	**3g**	Fc	p-Br–C_6H_4–CO–	Br	65	240	63	– [c]	–	187–189	– [d]
8	**3h**	Fc	H	Br	r.t.	1	62	–	–	46–47	51–52[13]
9	**3i**	p-Fc-–C_6H_4	C_6H_5	Cl	r.t.	4	100	1/6	94–95 [d]	228–229	– [d]
10	**3j**	p-MeO–C_6H_4	Fc	I	65	30	83	1/10	32–34 [d]	120–121	121–126[14]
11	**3k**	Fc	Fc	I	65	60	91	– [c]	–	263–265	265–267[13]

[a] Conversion, based on the aldehyde.

[b] Ratio of separated isomer.

[c] No Z-isomer observed.

[d] New compounds.

dry state 95% (Entry 1) and 87% (Entry 2) yields have been obtained easily. P.L. Pauson obtained *trans*-1,2-diferrocenylethylene in 73% yield by the reaction of formylferrocene with sodium diphenylphosphinite [7], which we obtained in 91% yield as compared with their result.

From the ^{1}H-NMR spectra of all the products, the coupling constants of the two protons on the double bond manifested the configuration. The characteristic coupling constant of the Z-isomer is about 12 Hz, and that of the E-isomer is about 16 Hz. It can be seen from our results that the main products are E-isomers, which is in accordance with theoretical calculation [15]. It is notable that **3a** and **3b** are the same compound, but their ratio of Z/E is different due to the diversity of the materials used. When FcCHO and $PhCH_2P^+Ph_3Cl^-$ are used as materials, the conversion is increased from 87% to 95% and the selectivity forming E-isomer is also increased (the ratio of Z/E changes from 1/2 to 1/4) as compared with those obtained from PhCHO and $FcCH_2P^+Ph_3I^-$. It is also found that reactions forming **3f** and **3g** were slower than other analogs and the yields are rather lower than obtained from aldol condensation that we had performed before [16]. Maybe, the methylene is stabilized by the carbonyl adjacent to it and then has a lower reactivity.

It is obvious, that the solvent-free Wittig reaction not only is a fast, mild, efficient and simple method to prepare vinylferrocene derivatives, but also is an effective way to obtain the E-products.

3. Experimental

^{1}H-NMR spectra were obtained on a FC-80 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. Mass spectra were obtained on a ZAB-HS mass spectrometer by fast atom bombardment (FAB, MASPECII data base). IR spectra were recorded in KBr on a Nicolet 1795X FT-IR spectrophotometer. The melting points reported here were uncorrected.

FcCHO and p-Fc-C_6H_4CHO were prepared by literature methods [6,17]. Other aldehydes were commercially available chemicals.

3.1. Preparation of phosphonium salts

(Ferrocenylmethyl)triphenylphosphonium iodide was prepared according to reported method [7]. Methyltriphenylphosphonium bromide was obtained from methyl bromide bubbling through a solution of triphenylphosphine in benzene. Other phosphonium salts were prepared by K. Friedrich's method [18].

3.2. General procedure for preparation of ferrocenylethene derivatives

3.2.1. Method A (for reactions at room temperature)

In a typical experiment, a mixture of formylferrocene (**la**) (1 mmol, 0.214 g), triphenylbenzylphosphonium chloride (**2a**) (1.1 mmol, 0.427 g) and NaOH (1.5 mmol, 0.06 g) was throughly ground with a pestle in an open mortar at room temperature (r.t.) under atmosphere. The reaction mixture was ground for 5 min until the reaction was complete by TLC monitoring, then extracted in dichloromethane (20 ml × 3). The extracts were combined and dried with anhydrous $NaSO_4$. After filtration, the solvent was removed under vacuum to give crude product. The residue was chromatographed on silica gel using petroleum ether as eluent. The product from the first band was a yellow oily liquid (0.055 g), which is Z-ferrocenyl-2-phenylethylene and that from the second band was yellow crystals (0.219 g), which is E-ferrocenyl-2-phenylethylene, m.p. 122–124°C (120–122°C in the literature, [13]).

3.2.2. Method B (for reactions at 65°C)

In case of heating, aldehyde ylide and NaOH were mixed and thoroughly ground in an open mortar at r.t. After keeping the mixture at 65°C in an oven for about 40–50 min., it was ground again for 1–2 min. These operations were repeated until the reaction was complete by TLC monitoring. The mixture was cooled to r.t., then extracted and isolated as in method A.

*3.2.3. **3a**, **3b**: 1-ferrocenyl-2-phenylethylene*

(Z)-isomer, ^{1}H-NMR (δ, ppm): 4.07 (s, 5H, Cp-ring), 4.26 (s, 2H, Cp-ring), 4.41 (s, 2H, Cp-ring), 6.22–6.58 (dd, 2H, C=C, $J = 12.5$ Hz), 7.31 (s, 5H, Ar); MS m/z (%): 288 (87); IR (KBr, cm^{-1}): $\nu_{C=C-H} = 3001$, $\nu_{C=C} = 1620$, $\omega_{C=C-H} = 670$.

(E)-isomer, ^{1}H-NMR (δ, ppm): 4.17 (s, 5H, Cp-ring), 4.31 (s, 2H, Cp-ring), 4.78 (s, 2H, Cp-ring), 6.58–7.03 (dd, 2H, C=C, $J = 16.3$ Hz), 7.42 (s, 5H, Ar); MS m/z (%): 288 (90); IR (KBr, cm^{-1}): $\nu_{C=C-H} = 3005$, $\nu_{C=C} = 1627$, $\omega_{C=C-H} = 960$.

*3.2.4. **3c**: 1-ferrocenyl-2-(4-chloro-phenyl)ethylene*

(Z)-isomer, ^{1}H-NMR (δ, ppm): 4.16 (s, 5H, Cp-ring), 4.32 (s, 2H, Cp-ring), 4.53 (s, 2H, Cp-ring), 6.34–6.70 (dd, 2H, C=C, $J = 12.1$ Hz), 7.38 (s, 4H, Ar); MS m/z (%): 324 (24), 322 (73); IR (KBr, cm^{-1}): $\nu_{C=C-H} = 3024$, $\nu_{C=C} = 1620$, $\omega_{C=C-H} = 705$.

(E)-isomer, ^{1}H-NMR (δ, ppm): 4.24 (s, 5H, Cp-ring), 4.42 (s, 2H, Cp-ring), 4.58 (s, 2H, Cp-ring), 6.46–6.97 (dd, 2H, C=C, $J = 16.4$ Hz), 7.32 (s, 4H, Ar); MS m/z (%): 324 (31), 322 (90); IR (KBr, cm^{-1}): $\nu_{C=C-H} = 3020$, $\nu_{C=C} = 1625$, $\omega_{C=C-H} = 963$.

3.2.5. ***3d****: 1-ferrocenyl-2-(4-bromo-phenyl)ethylene*

(*Z*)-isomer, ^{1}H-NMR (δ, ppm): 4.14 (s, 5H, Cp-ring), 4.20 (s, 2H, Cp-ring), 4.43 (s, 2H, Cp-ring), 6.28–6.54 (dd, 2H, C=C, $J = 12.0$ Hz), 7.17–7.49 (q, 4H, Ar); MS *m*/*z* (%): 368 (81), 366 (83); IR (KBr, cm^{-1}): $\nu_{\mathrm{C=C-H}} = 3017$, $\nu_{\mathrm{C=C}} = 1622$, $\omega_{\mathrm{C=C-H}} = 711$.

(*E*)-isomer, ^{1}H-NMR (δ, ppm): 4.17 (s, 5H, Cp-ring), 4.34 (s, 2H, Cp-ring), 4.49 (s, 2H, Cp-ring), 6.51–7.02 (dd, 2H, C=C, $J = 16.4$ Hz), 7.23–7.42 (q, 4H, Ar); MS *m*/*z* (%): 368 (87), 366 (84); IR (KBr, cm^{-1}): $\nu_{\mathrm{C=C-H}} = 3022$, $\nu_{\mathrm{C=C}} = 1625$, $\omega_{\mathrm{C=C-H}} = 965$.

3.2.6. ***3e****: 1-ferrocenyl-2-(3-nitro-phenyl)ethylene*

(*Z*)-isomer, ^{1}H-NMR (δ, ppm): 4.15 (s, 5H, Cp-ring), 4.33 (s, 2H, Cp-ring), 4.50 (s, 2H, Cp-ring), 6.44–6.80 (dd, 2H, C=C, $J = 11.8$ Hz), 7.33–8.08 (m, 4H, Ar); MS *m*/*z* (%): 333 (98); IR (KBr, cm^{-1}) $\nu_{\mathrm{C=C-H}} = 3079$, $\nu_{\mathrm{C=C}} = 1629$, $\omega_{\mathrm{C=C-H}} = 732$.

(*E*)-isomer, ^{1}H-NMR (δ, ppm): 4.18 (s, 5H, Cp-ring), 4.36 (s, 2H, Cp-ring), 4.52 (s, 2H, Cp-ring), 6.60–7.18 (dd, 2H, C=C, $J = 16.2$ Hz), 7.37–8.29 (m, 4H, Ar); MS *m*/*z* (%): 333 (29); IR (KBr, cm^{-1}) $\nu_{\mathrm{C=C-H}} = 3088$, $\nu_{\mathrm{C=C}} = 1632$, $\omega_{\mathrm{C=C-H}} = 961$.

3.2.7. ***3f****: 1-phenyl-3-ferrocenylprop-2-en-1-one*

^{1}H-NMR (δ, ppm): 4.20 (s, 5H, Cp-ring), 4.39 (s, 2H, Cp-ring), 4.60 (s, 2H, Cp-ring), 7.02–7.25 (br, 2H, C=C), 7.81–7.97 (br, 5H, Ar); MS *m*/*z* (%): 316 (61); IR (KBr, cm^{-1}): $\nu_{\mathrm{C=O}} = 1656$, $\nu_{\mathrm{C=C}} = 1597$.

3.2.8. ***3g****: 1-(4-bromophenyl)-3-ferrocenylprop-2-en-1-one*

^{1}H-NMR (δ, ppm): 4.12 (s, 5H, Cp-ring), 4.40 (s, 2H, Cp-ring), 4.55 (s, 2H, Cp-ring), 7.25–8.05 (m, 6H, C=C and Ar); MS *m*/*z* (%): 394 (61), 396 (53); IR (KBr, cm^{-1}): $\nu_{\mathrm{C=O}} = 1660$, $\nu_{\mathrm{C=C}} = 1589$

3.2.9. ***3h****: Vinylferrocene*

^{1}H-NMR (δ, ppm): 4.13 (s, 5H, Cp-ring), 4.23 (s, 2H, Cp-ring), 4.38 (s, 2H, Cp-ring), 4.97–5.12 (q, 1H, (*Z*)-FcC=CH, $^{3}J_{Z} = 10.6$ Hz, $^{2}J = 1.6$ Hz), 5.23–5.47 (q, 1H, (*E*)-FcC=CH, $^{3}J_{E} = 17.5$ Hz, $^{3}J = 1.6$ Hz), 6.31–6.66 (q, 1H, FcCH=C, $^{3}J_{E} = 17.5$ Hz, $^{3}J_{Z} = 10.6$ Hz), MS *m*/*z* (%): 212 (100); IR (KBr, cm^{-1}): $\nu_{\mathrm{C=C-H}} = 3080$, $\nu_{\mathrm{C=C}} = 1650$.

3.2.10. ***3i****: 1-(4-ferrocenylphenyl)-2-phenylethylene*

(*Z*)-isomer, ^{1}H-NMR (δ, ppm): 4.11 (s, 5H, Cp-ring), 4.40 (s, 2H, Cp-ring), 4.72 (s, 2H, Cp-ring), 6.34–6.69 (q, 2H, C=C, $J = 12.3$ Hz), 7.11–7.39 (m, 5H, Ar); MS *m*/*z* (%): 364 (87); IR (KBr, cm^{-1}) $\nu_{\mathrm{C=C-H}} = 2922$, $\nu_{\mathrm{C=C}} = 1650$, $\omega_{\mathrm{C=C-H}} = 702$.

(*E*)-isomer, ^{1}H-NMR (δ, ppm): 4.09 (s, 5H, Cp-ring), 4.38 (s, 2H, Cp-ring), 4.71 (s, 2H, Cp-ring), 7.13 (s, 2H, C=C), 7.32–7.59 (m, 5H, Ar); MS *m*/*z* (%): 364 (73); IR (KBr, cm^{-1}) $\nu_{\mathrm{C=C-H}} = 2922$, $\nu_{\mathrm{C=C}} = 1650$, $\omega_{\mathrm{C=C-H}} = 965$.

3.2.11. ***3j****: 1-ferrocenyl-2-(4-methoxyphenyl)ethylene*

(*Z*)-isomer, ^{1}H-NMR (δ, ppm): 3.64 (s, 3H, OCH_3) 4.14 (s, 5H, Cp-ring), 4.36 (s, 2H, Cp-ring), 4.53 (s, 2H, Cp-ring), 6.16–6.51 (dd, 2H, C=C, $J = 11.9$ Hz), 6.68–7.43 (m, 4H, Ar); MS *m*/*z* (%): 318 (100); IR (KBr, cm^{-1}): $\nu_{\mathrm{C=C-H}} = 3019$, $\nu_{\mathrm{C=C}} = 1621$, $\omega_{\mathrm{C=C-H}} = 682$.

(*E*)-isomer, ^{1}H-NMR (δ, ppm): 3.57 (s, 3H, OCH_3) 4.17 (s, 5H, Cp-ring), 4.32 (s, 2H, Cp-ring), 4.55 (s, 2H, Cp-ring), 6.60–6.92 (dd, 2H, C=C, $J = 16.0$ Hz), 7.13–7.50 (m, 4H, Ar); MS *m*/*z* (%): 318 (31); IR (KBr, cm^{-1}): $\nu_{\mathrm{C=C-H}} = 3020$, $\nu_{\mathrm{C=C}} = 1617$, $\omega_{\mathrm{C=C-H}} = 965$.

3.2.12. ***3k****: 1,2-diferrocenylethylene*

(*E*)-isomer, ^{1}H-NMR (δ, ppm): 4.12 (s, 5H, Cp-ring), 4.17 (s, 5H, Cp-ring), 4.31–4.55 (br, 8H, Cp-ring), 6.23–6.51 (dd, 2H, C=C, $J = 16.0$ Hz); MS *m*/*z* (%): 396 (45); IR (KBr, cm^{-1}): $\nu_{\mathrm{C=C-H}} = 3028$, $\nu_{\mathrm{C=C}} = 1629$, $\omega_{\mathrm{C=C-H}} = 960$.

References

[1] D.F. Eaton, Science 253 (1991) 281.
[2] B. Konig, H. Zieg, P. Bubenitschek, P.O. Jones, Chem. Ber. 127 (1994) 1181.
[3] G. Saswati, S. Marek, P.N. Paras, T.J. Joseph, J. Phys. Chem. 94 (1990) 2847.
[4] Y. Qian, Y.M. Sun, J.Z. Liu, J.Y. Wu, F.M. Li, Chin. J. Lasers A25 (1998) 231.
[5] R. Gooding, C.P. Lillya, C.W. Chiene, J. Chem. Soc. Chem. Commun. (1983) 151.
[6] J.M. Osgerby, P.L. Pauson, J. Chem. Soc. (1961) 4604.
[7] P.L. Pauson, W.E. Watts, J. Chem. Soc. (1963) 2990.
[8] W.M. Horspool, Can. J. Chem. 46 (1968) 3453.
[9] X.Z. You, H.S. Sun, X. Peng, C.Y. Yue, C. Li, H.Y. Wu, Inorg. Chim. Acta 234 (1995) 139.
[10] T. Jeffery, Tetrahedron Lett. 31 (1990) 6641.
[11] S. El-tamany, F.W. Raulfs, H. Hopf, Angew. Chem. Int. Ed. Engl. 22 (1983) 633.
[12] K. Tanaka, F. Toda, Chem. Rev. 100 (2000) 1025.
[13] J. Buckingham, Dictionary of Organometallic Compounds, Chapman and Hall, London, 1984.
[14] S. Toma, A. Gaplovsky, P. Elecko, Chem. Pap. 39 (1985) 115.
[15] H. Yamataka, S. Nagase, J. Am. Chem. Soc. 120 (1998) 7530.
[16] W.Y. Liu, Q.H. Xu, Y.X. Ma, Synth. Commun, in press.
[17] S.T. Shi, X.Z. Song, E.Z. Li, Kexue Tongbao (China) (1965) 78.
[18] K. Friedrich, H.O. Henning, Chem. Ber. 92 (1959) 2756.