This article was downloaded by: [Columbia University] On: 04 February 2015, At: 19:48 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



# Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

## The Wittig Reaction of Stable Ylide with Aldehyde Under Microwave Irradiation: Synthesis of Ethyl Cinnamates

Caiding Xu  $^{\rm a}$  , Guoying Chen  $^{\rm a}$  , Chong Fu  $^{\rm a}$  & Xian Huang  $^{\rm a}$ 

<sup>a</sup> Department of Chemistry , Hangzhou University Zhejiang , 310028, People'h;s Republic of China Published online: 23 Sep 2006.

To cite this article: Caiding Xu , Guoying Chen , Chong Fu & Xian Huang (1995) The Wittig Reaction of Stable Ylide with Aldehyde Under Microwave Irradiation: Synthesis of Ethyl Cinnamates, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 25:15, 2229-2233, DOI: 10.1080/00397919508011778

To link to this article: http://dx.doi.org/10.1080/00397919508011778

### PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and

are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

### THE WITTIG REACTION OF STABLE YLIDE WITH ALDEHYDE UNDER MICROWAVE IRRADIATION: SYNTHESIS OF ETHYL CINNAMATES

Caiding Xu, Guoying Chen, Chong Fu and Xian Huang \*

Department of Chemistry, Hangzhou University Zhejiang 310028, People's Republic of China

ABSTRACT: The Wittig reaction of stable ylide, triphenylcarbethoxymethylene phosphorane, with aldehydes was performed within 5-6 minutes under microwave irradiation. Remarkable rate enhancements and dramatic reductions of reaction times have been observed. Thus, the Wittig reaction of stable ylide with aldehyde is optimized.

Microwave heating had been used in chemical laboratories for a variety of purposes such as moisture analysis<sup>1</sup>, the wet ashing procedures of biological and geological materials<sup>2</sup>, regeneration of activated carbon<sup>3</sup>, and the preparation of activated carbon from carbonaceous materials<sup>4</sup>. But the start of the explosion of activity in the application of microwave heating in organic synthesis was ignited in 1986 by the pioneering papers by Gedye<sup>5</sup> and by Majetich<sup>6</sup> and their co-workers.

Recent research has demonstrated that organic reactions can be conducted safely in commercial microwave ovens with remarkable rate enhancements and dramatic reductions of reaction times than by conventional heating, and this new technique had been used to promote the Diels-Alder, Claisen, Ene reactions<sup>6,7</sup>, and also dehydration and nucleophilic substitute reactions<sup>5,8</sup>. But there is no report on the application of microwave irradiation for the Wittig reactions. As well known, the Wittig reaction of stable ylide can only proceed in a slow rate by the conventional method<sup>9,10</sup>, for example, two days' stirring of triphenylcarbethoxymethylene phosphorane and benzaldehyde in ethanol gave 77% yield of ethyl cinnamate. Our interest in taking advantage of this time-saving microwave heating led us to reinvestigate the Wittig reaction of stable ylide, triphenylcarbethoxymethylene phosphorane, with aldehydes. The experiment results show that, using microwave heating for five to six minutes, this Wittig reaction can be completed in 82 - 96% yields, and only transform products are obtained.

$$ArCHO + Ph_{3}P = CHCOOCH_{2}CH_{3} \xrightarrow{\text{Microwave}, 5-6 \text{min.}}_{\text{Silica gel}} ArCH = CHCOOCH_{2}CH_{3}$$

$$1 \qquad 2 \qquad 3$$

$$3a_{:} Ar = C_{6}H_{5}, \qquad 3b_{:} Ar = 3 - CH_{3}C_{6}H_{4}, \qquad 3c_{:} Ar = 4 - NO_{2}C_{6}H_{4}, \qquad 3d_{:} Ar = 3 - BrC_{6}H_{4}, \qquad 3e_{:} Ar = 3 - NO_{2}C_{6}H_{4}, \qquad 3f_{:} Ar = 4 - BrC_{6}H_{4}, \qquad 3g_{:} Ar = 4 - ClC_{6}H_{4}$$

Aldehyde	Time(min.	) Product <sup>a</sup>	Yield <sup>b</sup> , %
C <sub>6</sub> H₅CHO	5	$C_6H_5CH = CHCOOC_2H_5$	85
3-CH₃C <sub>6</sub> H₄CHO	6	3-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH=CHCOOC <sub>2</sub> H <sub>5</sub>	95
4-NO₂C <sub>6</sub> H₄CHO	5	$4-NO_2C_6H_4CH=CHCOOC_2H_5$	89
3-BrC₅H₄CHO	6	$3-BrC_6H_4CH = CHCOOC_2H_5$	96
3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	6	$3-NO_2C_6H_4CH=CHCOOC_2H_5$	82
4-BrC <sub>6</sub> H <sub>4</sub> CHO	6	$4-BrC_{6}H_{4}CH=CHCOOC_{2}H_{5}$	91
4-ClC₅H₄CHO	6	$4-ClC_6H_4CH=CHCOOC_2H_5$	82

Table 1. The Wittig Reaction of TriphenylcarbethoxymethylenePhosphorane With Aldehydes.

a. Only trans-form products were observed, which were identified spectroscopically and also by comparison with known compounds.

b. Yield of isolated product.

Typical Procedure: A mixture of triphenylcarbethoxymethylenephosphorane(1mmol), benzaldehyde(1mmol), and silica gel 200-300mesh(2g) was introduced into the domestic microwave oven in an open container, microwave irradiation was carried out at an output of about 400w for 5 minutes. Then 30ml of methylene dichloride was added into the cooled mixture, the extract was concentrated and chromatographed to give an almost colorless oily liquid, ethyl cinnamate (150mg, 85% yield).

3a, Ethyl cinnamate, oil(lit. <sup>11</sup> b. p. 271°C, m. p. 6-10°C) C<sub>11</sub>H<sub>12</sub>O<sub>2</sub>, <sup>1</sup>H NMR(CDCl<sub>3</sub>)  $\delta$ (ppm): 1. 30(t, J=7Hz, 3H, CH<sub>3</sub>), 4. 18(q, J=7Hz, 2H, CH<sub>2</sub>), 6. 33(d, J=15. 6Hz, 1H), 7. 35(m, 5H, ArH), 7. 73(d, J=15. 6Hz, 1H).

3b, m – Methyl ethyl cinnamate, oil,  $C_{12}H_{14}O_2$ , <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 1. 27(t, J = 6. 4Hz, 3H, CH<sub>3</sub>), 2. 28(s, 3H,  $CH_3$ ), 4. 21(q, J=6. 4Hz, 2H,  $CH_2$ ), 6. 37(d, J=16Hz, 1H), 7. 30 (m, 4H, ArH), 7. 63(d, J=16Hz, 1H).

3c, p-Nitro ethyl cinnamate, m. p.  $140-141^{\circ}C$  (lit. <sup>12</sup> 141-142°C), C<sub>11</sub>H<sub>11</sub>NO<sub>4</sub>, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 1. 33(t,J=7. 6 Hz, 3H,CH<sub>3</sub>), 4. 25(q,J=7. 6Hz, 2H,CH<sub>2</sub>), 6. 50(d,J=16. 0Hz, 1H), 7. 70(d,J=16. 0Hz, 1H), 7. 66, 8. 25(dd, J=8. 6Hz, 4H, ArH).

3d, m-Bromo ethyl cinnamate, oil,  $C_{11}H_{11}BrO_2$ , <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 1.30(t,J=7.0Hz,3H,CH<sub>3</sub>), 4.25(q,J=7.0 Hz,2H,CH<sub>2</sub>), 6.36(d,J=16.0Hz,1H), 7.53(m,4H,ArH), J= 7.82(d,J=16.0Hz,1H).

3e, m-Nitro ethyl cinnamate, m. p.  $77 - 79^{\circ}C(\text{lit.}^{13} 78 - 79^{\circ}C)$ ,  $C_{11}H_{11}NO_4$ , 'H NMR(CDCl<sub>3</sub>)  $\delta(\text{ppm})$ : 1. 33(t, J=6. 4Hz, 3H, CH<sub>3</sub>), 4. 30(q, J=6. 4Hz, 2H, CH<sub>2</sub>), 6. 23(d, J=16. 0Hz, 1H), 7. 72(d, J=16. 0Hz, 1H), 7. 60-8. 40(m. 4H, ArH).

3f, p-Bromo ethyl cinnamate, oil(lit. <sup>14</sup> b. p.  $_{15}150^{\circ}$ C), C $_{11}H_{11}$ BrO<sub>2</sub>, <sup>1</sup>H NMR(CDCl<sub>3</sub>)  $\delta$ (ppm): 1. 27(t, J=6. 4Hz, 3H, CH<sub>3</sub>), 4. 21(q, J=6. 4Hz, 2H, CH<sub>2</sub>), 6. 33(d, J=16. 4Hz, 1H), 7. 33(s, 4H, ArH), 7. 58(d, J=16. 4Hz, 1H).

3g, p-Chloro ethyl cinnamate, oil(lit. <sup>15</sup> b. p.  $_{16}166^{\circ}$ C), C $_{11}H_{11}$ ClO<sub>2</sub>, <sup>1</sup> H NMR(CDCl<sub>3</sub>)  $\delta$ (ppm): 1.28(t,J=6.8Hz,3H,CH<sub>3</sub>), 4.22(q,J=6.8Hz,2H, CH<sub>2</sub>), 6.35(d,J=16.0Hz,1H), 7.30, 7.48(dd,J=8Hz,4H,ArH), 7.58(d,J=16.0Hz,1H).

Acknowledgement: This research was supported by the Natural Science Foundation of Zhejiang Province and by the Education Committee of Zhejiang Province.

#### REFERENCES

1. Hesek, J. A., Williams, R. C., Anal. Chem., 1974, 46, 1160.

2. Abu-Samra, A., Morris, J. S., Koirtyohann, S. R., Anal. Chem., 1975, 47, 1475; Cooley, T. N., Martin, D. F., Quincel, R. F., J. Environ. Sci. Health, 1977, A12, 15; Fischer, L. B., Anal. Chem., 1986, 58, 261.

- Katsuta, A., Japan. Kokai JP 51027893(1976); Chem. Abstr., 1977, 87, 70374v.
- Mukai, A., Tanaka, M., Ikeda, A., Japan. Kokai JP 51037890 (1976); Chem. Abstr., 1976, 85, 35167s.
- Gedye, R. J., Smith, F., Westaway, K., Ali, H., Baldisera, L., Laberge, L., Rousell, J., Tetrahedron Lett., 1986, 27, 279.
- 6. Giguere, R. J., Bray, T. L., Duncan, S. M., Majetich, G., Tetra hedron Lett., 1986, 27, 4945.
- 7. Giguere, R. J., Namen, A. M., Lopez, B., Arepally, A., Romos, D. E., Majetich, G., Defauw, J., Tetrahedron Lett., 1987, 28, 6553.
- 8. Giguere, R. J., "Organic Synthesis: Theory and Application", Vol. 1, p103, JAI Press Inc., Greenwich, CT, 1989.
- 9. Wittig, G. and Haag, W., Chem. Ber., 1955, 88, 1654.
- Kucherov, Kovalev, Nazarova and Yanovskaya, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1960, 1512; Chem. Abstr., 1961, 55, 1420b.
- The Merck Index, 11th Ed., Merck & Co. Inc., Rahway, New Jersey, 1989.
- 12. Beilstein, 9, 607.
- 13. Beilstein, 9, 606.
- 14. Beilstein, 9, I, 397.
- 15. Beilstein, 9, I, 396.

(Received in the UK 18 October 1994)