Tetrahedron Letters Vol. 21, pp 3595 - 3598
©Pergamon Press Ltd. 1980. Printed in Great Britain

0040-4039/80/0908-3595$02.00/0

STEREOSELECTIVE SYNTHESIS OF VINYLPHOSPHONATE

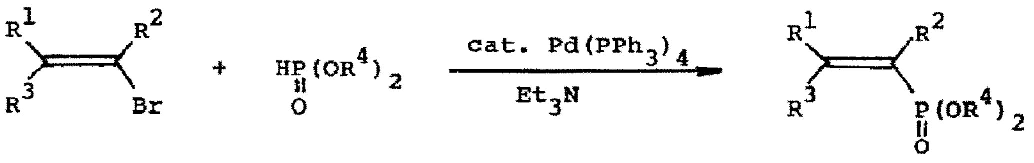
Toshikazu Hirao,* Toshio Masunaga, Yoshiki Ohshiro, and Toshio Agawa
Department of Petroleum Chemistry, Faculty of Engineering, Osaka University
Yamadakami, Suita, Osaka 565, Japan

Summary: Dialkyl vinylphosphonate is stereoselectively prepared by palladium-catalyzed reaction of vinyl bromide with dialkyl phosphite.

Vinylphosphonates are not easily obtainable compounds by using Arbuzov-Michaelis reaction. Only few methods have been explored for the preparation of vinylphosphonates,1) and most of the products have an E-form. One of these methods involves direct reaction of vinyl bromides with trialkyl phosphites in the presence of nickel halides at a high temperature.1g) The conversion of thi reaction, however, was low and the stereochemistry of the products has not bee clarified.

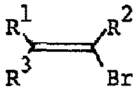
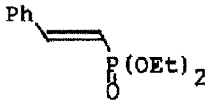
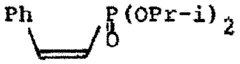
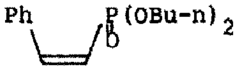
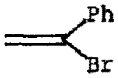
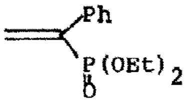
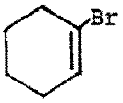
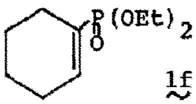
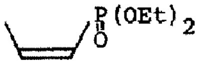
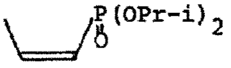
In the preceding paper,2) we reported palladium-catalyzed synthesis of arylphosphonates as a new route to the formation of carbon-phosphorus bond. In an extension of this work, we found that this reaction could be applied to stereoselective syntheses of vinylphosphonates.

Vinyl bromides reacted with dialkyl phosphite in the presence of a cataly amount of tetrakis(triphenylphosphine)palladium to afford dialkyl vinylphosphonates in good yields.



1

Table Preparation of Dialkyl Vinylphosphonates

Run		$HP(O)(OR^4)_2$ R^4	Reaction a) Time (h)	Product	Yield (%)
1		Et	0.2	 b) **1a**	93
2		Et	1.5	 c) **1b**	91
3		i-Pr	12	 c) **1c**	81
4		n-Bu	1.5	 c) **1d**	92
5		Et	30	 **1e**	66
6		Et	9	 **1f**	69
7	 d)	Et	1.5	 c) **1g**	98
8	 d)	i-Pr	6	 c) **1h**	92

a) Reaction temperature; 90°C.

b) Formation of no Z-isomer was observed in an nmr spectrum.

c) No E-isomer was detected in an nmr spectrum.

d) Reaction was carried out by mixing 4.8 mmol of cis-1-bromo-1-propene, 4.0 mmol of dialkyl phosphite, 4.0 mmol of triethylamine, and $Pd(PPh_3)_4$ (0.2 mmol) in toluene (1 ml) at 90°C. Yields were based on the starting dialkyl phosphite.

To a stirring mixture of dialkyl phosphite (4.4 mmol) and triethylamine (4.4 mmol) in the presence of $Pd(PPh_3)_4$ (0.2 mmol), vinyl bromide (4.0 mmol) was added under nitrogen atmosphere. The resultant mixture was stirred at 90°C for 0.2-30 h. After removal of $Et_3N \cdot HBr$, the vinylphosphonate **1** was isolated by column chromatography on silica gel or distillation *in vacuo*. The structure of the vinylphosphonate **1** was identified by ir, nmr, and mass spectra.$^{3)}$ Results ar summarized in Table.

(E)- and (Z)-β-bromostyrenes gave (E)- and (Z)-styrylphosphonates in 93% ar 91% yields, respectively, without any contamination of the isomer (runs 1 and 2) Diisopropyl (Z)-1-propenylphosphonate was also obtained in a high yield, and thi method provides an effective route to the synthesis of phosphonomycin$^{4)}$ (run 8).

The present phosphonation has the apparent advantage on the yield and selectivity for the synthesis of vinylphosphonates. Vinylpalladium,$^{5)}$ being thought to be the key intermediate, is subjected to the attack of dialkyl phosphite resulting in the formation of dialkyl vinylphosphonate. Triethylamine may activate dialkyl phosphite besides regeneration of palladium(0) species, which is available to the reaction cycle. Further works on this palladium-catalyzed phosphonation are in progress.

References and Notes

1) a) G. M. Kosolapoff and I. F. McCullough, *J. Am. Chem. Soc*., **73**, 855 (1951).
   b) L. N. Mashljakovskiǐ, B. I. Ionin, I. S. Okhrimenko and A. A. Petrov, *Zh. Obshch. Khim*., **37**, 1307 (1967).
   c) B. I. Ionin and A. A. Petrov, *ibid*., **33**, 432 (1963).
   d) G. L. Kenyon and F. H. Westheimer, *J. Am. Chem. Soc*., **88**, 3557 (1966).
   e) A. M. Aguiar and D. Daigle, *J. Org. Chem*., **30**, 2826 (1965).
   f) A. A. Petrov, B. I. Ionin and V. M. Ignatyev, *Tetrahedron Lett*., 15 (1968)
   g) P. Tavs and H. Weitkamp, *Tetrahedron*, **26**, 5529 (1970).
2) T. Hirao, T. Masunaga, Y. Ohshiro and T. Agawa, to be published.
3) **1b**: ir (neat) 1600, 1235, 1050-1020, 955 cm^{-1}; nmr ($CDCl_3$ with TMS) δ1.12 (t, 6H, J=7.0 Hz), 3.98 (dq, 4H, J=7.0 Hz), 5.78 (dd, 1H, J_1=14.0 Hz, J_2=14.9 Hz)

6.70-7.90 (m, 5+1H); m/e 240 (M^+).

1f: ir (neat) 1635, 1245, 1060-1030, 960 cm^{-1}; nmr ($CDCl_3$ with TMS) δ1.20 (6H, J=7.0 Hz), 1.50-2.47 (m, 8H), 4.06 (dq, 4H, J=7.0 Hz), 6.47-7.03 (m, 1H m/e 218 (M^+).

The structures of the other vinylphosphonates were supported by comparison their ir and nmr spectra with those of the authentic samples.[1)]

4) H. L. Slates and N. L. Wendler, Chem. & Ind., 430 (1978). E. J. Glamkowski, G. Gal, R. Purick, A. J. Devidson and M. Sletzinger, J. O Chem., **35**, 3510 (1970).

5) S.-I. Murahashi, M. Yamamura, K. Yanagisawa, N. Mita and K. Kondo, ibid., 2408 (1979), and references therein.

(Received in Japan 2 June 1980)