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A Highly Stereoselective Synthesis of α -Carbethoxy- α,β -unsaturated Phosphonates Mediated by Tri-*n*-Butylarsine

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**A HIGHLY STEREOSELECTIVE SYNTHESIS OF α -CARBETHOXY-
 α,β -UNSATURATED PHOSPHONATES MEDIATED BY TRI-*n*-BUTYLARSINE**

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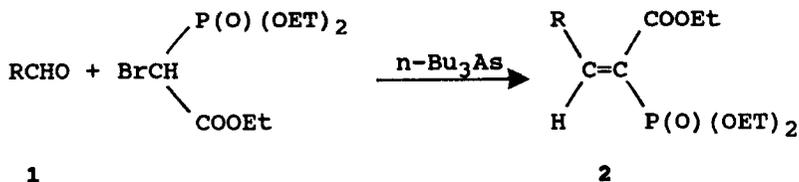
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ABSTRACT: A highly stereoselective synthesis of α -carbethoxy- α,β -unsaturated phosphonates in 71-92% yield mediated by tri-*n*-butylarsine under neutral condition is described.

Phosphonic acids and their derivatives have attracted considerable interest because many of them exhibit a variety of significant biological activities.¹ Vinyl phosphonates bearing electron-withdrawing substituents are useful intermediates in organic synthesis, particularly in the synthesis of heterocyclic compounds.² The general method for their preparation was a condensation method which gave low yields^{3a} and a base or acid had to be used as catalyst.³ Furthermore, no stereochemical results on the outcome of this condensation were

reported. In our continuing investigation of halophilic reactions of tri-n-butylarsine and its application in organic synthesis,⁴ we now wish to report a highly stereoselective synthesis of α -carbethoxy- α,β -unsaturated phosphonates mediated by tri-n-butylarsine under neutral condition in 71-92% yield.

The reaction is shown as follows:



The results are summarized in Table 1.

This method for the synthesis of the title compounds is quite convenient, employs neutral conditions and the reaction gave exclusively E-isomer (¹H-NMR).⁵ Thus this methodology has several advantages over the reported methods. It is particularly suitable to base or acid sensitive substrates, because it does not need base or acid. Also the reaction is stereoselective.

EXPERIMENTAL

All boiling points and melting points are reported uncorrected. The Infrared spectra of solid products was

Table 1. Preparation of α -Carbethoxy- α, β -Unsaturated Phosphonates

Compound	R	Condition		Yield ^a (%)
		Temp./°C	Time/h	
2a	C ₆ H ₅	70	13	71
2b	4-NO ₂ C ₆ H ₄	70	5	85
2c	4-ClC ₆ H ₄	70	16	85
2d	2-ClC ₆ H ₄	70	14	85
2e	4-CH ₃ C ₆ H ₄	70	13	62
2f	C ₆ H ₅ CH=CH	70	25	92

Isolated yields.

obtained as KCl disks and of liquid products as films using a Shimadzu IR-440 spectrometer. NMR spectra (chemical shifts in ppm from TMS) were obtained on a Varian EM-360 spectrometer at 60 MHz or an XL-200 spectrometer at 200 MHz.

General procedure:

Tri-n-butylarsine (2 mmol) was injected dropwise and slowly into a suspension of aldehyde (2 mmol) and ethyl (α -diethoxyphosphoryl) bromoacetate (2 mmol) under nitro-

gen. The stirred mixture was heated for several hours (see Table 1). After the disappearance of the aldehyde, chromatography on silica gel eluting with light petroleum ether (bp 60-90°C)-ethyl acetate (85:15) gave the product 2.

E-1-Carbethoxy-1-diethoxyphosphoryl-2-phenyl ethene (2a):

2a was obtained in 71% yield, b.p. 150-153°C/0.4 mmHg [Lit. 154-158°C/0.35 mmHg^{3a}]. IR(film): 1720(s), 1610(s), 1390(s), 1250(s), 1020(s) cm⁻¹. ¹H NMR (CDCl₃/TMS): δ 1.15-1.50(m, 9H); 3.90-4.40(m, 6H); 7.42(s, 5H); 7.53(d, 1H, J=24Hz) ppm.

E-1-Carbethoxy-1-diethoxyphosphoryl-2-(4-nitrophenyl) ethene (2b):

2b was obtained in 85% yield, m.p. 58-60°C [Lit. 59-61°C^{3b}]. IR(KCl): 1715(s), 1600(s), 1520(s), 1240(s), 1040(s) cm⁻¹. ¹H NMR(CDCl₃/TMS): δ 1.10-1.60(m, 9H); 3.90-4.40(m, 6H); 7.50(d, 1H, J=23.5Hz); 7.63(d, 2H, J=9Hz); 8.20(d, 2H, J=9Hz) ppm.

E-1-Carbethoxy-1-diethoxyphosphoryl-2-(4-chlorophenyl) ethene (2c):

2c was obtained in 85% yield, b.p. 179-182°C/0.4 mmHg [Lit. 182°C/0.4 mmHg^{3a}]. IR(film): 1720(s), 1600(s), 1490(s), 1250(s), 1020(s) cm⁻¹. ¹H NMR(CDCl₃/TMS): δ 1.10-1.45(m, 9H); 3.95-4.30(m, 6H); 7.40(s, 4H); 7.45(d, 1H, J=24Hz) ppm.

E-1-Carbethoxy-1-diethoxyphosphoryl-2-(2-Chlorophenyl) ethene (2d):

2d was obtained in 85% yield, b.p. 148-151°C/0.4 mmHg [Lit. 139°C/0.15 mmHg^{3b}]. IR(film): 1725(s), 1610(s), 1470(s), 1250(s), 1010(s) cm⁻¹. ¹H NMR(CDCl₃/TMS): δ 1.10-1.45(m, 9H); 3.90-4.30(m, 6H); 7.20-7.35(m, 4H); 7.67(d, 1H, J=24Hz) ppm.

E-1-Carbethoxy-1-diethoxyphosphoryl-2-(4-methylphenyl) ethene (2e):

2e was obtained in 62% yield, b.p. 173-175°C/0.4 mmHg [Lit. 162°C/0.15 mmHg^{3a}]. IR(film): 1720(s), 1605(s), 1250(s), 1020(s) cm⁻¹. ¹H NMR(CDCl₃/TMS): δ 1.10-1.50(m, 9H); 2.30(s, 3H); 3.86-4.30(m, 6H); 7.08(d, 2H, J=8.5Hz); 7.25(d, 2H, J=8.5Hz); 7.40(d, 1H, J=24Hz) ppm.

E,E-1-Carbethoxy-1-diethoxyphosphoryl-4-phenyl-1,3-butadiene (2f):

2f was obtained in 92% yield, b.p. 182-184°C/4 mmHg [Lit. 178-179°C/0.32 mmHg⁶]. IR(film): 1705(s), 1620(s), 1260(s), 1170(s) cm⁻¹. ¹H NMR(CDCl₃/TMS): δ 1.10-1.45(m, 9H); 3.90-4.25(m, 6H); 7.10-7.85(m, 8H) ppm.

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