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Unexpected Lack of Stereoselectivity in the Horner–Wadsworth–Emmons Reaction when Applied to the Synthesis of (*E*)- and (*Z*)-Methyl α-Arylcinnamates

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A facile synthetic route to chloroaromatic derivatives of (*E*)- and (*Z*)-methyl α-arylcinnamates (methyl 2,3-diarylpropenoates) is described. The reaction proceeded with good to excellent yields in all cases and separation of the *E* and *Z* isomers was easily achieved. The Horner–Wadsworth–Emmons reaction of phosphonates **2** with aromatic aldehydes afforded mixtures of *E* and *Z* isomers in approximately 1:1 ratios, except for the more *E*-biased product mixtures of 3:1, obtained when **2** was reacted with 2,6-dichlorobenzaldehyde. The high proportion of the *Z* isomers in the former systems was unexpected considering results reported for similar systems. An explanation based on the combined contributions of both steric and electronic factors is suggested for this lack of stereoselectivity.

In the context of recent work we required pure *E* and *Z* isomers of methyl α-arylcinnamates **3**, in considerable amounts. Surprisingly, we found that the *Z* isomers have barely been described in the literature[1] and, apparently no systematic investigation exists on the synthesis of such compounds. The corresponding α-arylcinnamic acids are the most obvious precursors and these are obtainable in fair to good yield with the Perkin reaction.[1–4] However, this reaction preferentially affords acids of *E* configuration, rendering it unattractive for our purposes.

More recent results have been reported for the preparation of the α-phenylcinnamic acid by the Horner–Wadsworth–Emmons (HWE) reaction in a completely *E*-stereoselective fashion.[5,6] In view of this, it was surprising to encounter a total lack of stereoselectivity when we attempted to use this reaction to synthesize the methyl α-phenylcinnamate **3a** directly. This unexpected stereochemical outcome prompted us to investigate the HWE reaction further. Here we report on the direct synthesis of *E*/*Z* mixtures of various methyl α-arylcinnamates **3** by the HWE reaction. A possible explanation for the observed lack of stereoselectivity is also discussed.

Results and discussion

Synthesis and structure. The α-bromo esters **1** were conveniently prepared in a one-pot procedure, which entailed conversion of the corresponding arylacetic acids into the acid chlorides, brominating these, preferably with *N*-bromosuccinimide,[7,8] and pouring the resulting solutions into cold methanol. The ensuing Michaelis–Arbusov reaction[9] furnished the methyl dimethoxyphosphoryl (aryl)acetates **2**. Owing to competitive formation of dimethyl methylphosphonate [$(MeO)_2P(O)CH_3$], treatment of **1** with 1.6 equiv. of trimethyl phosphite was necessary in order to obtain high yields of **2**. The isolated amount of dimethyl methylphosphonate was approximately concordant with the excess of trimethyl phosphite. The reaction of phosphonates **2** with aldehydes to form the α-arylcinnamic esters **3** was performed under various reaction conditions in order to optimize the yield and affect the *E*/*Z* ratio. The best yield was obtained by stirring the reactants at ambient temperature with sodium methoxide in methanol. This afforded the esters **3** in 60–90% yield and the *E*/*Z* ratios were always close to 1:1, except for compounds **3d** and **3h**, where the *E*/*Z* ratios were 3:1. Stereochemical data for this reaction are summarized in Table 1. All attempts to enhance the stereoselectivity in either direction by changing the reaction conditions were fruitless; other reaction conditions (bases, solvents, temperatures) resulted in similar *E*/*Z* mixtures, but with considerably diminished yield (less than 35%). For example, the most *Z*-biased isomer ratio for **3a** was an *E*/*Z* ratio of 40:60, obtained when using sodium hydride in DME, but the yield was only 30%.

The methyl α-arylcinnamates **3** were characterized on the basis of spectroscopic evidence (UV, IR, GC–MS, ^1H NMR, ^{13}C NMR). The structural assignments are

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Table 1. Yields and *E*/*Z* ratios for the preparation of methyl 2,3-diarylpropenoates **3**.

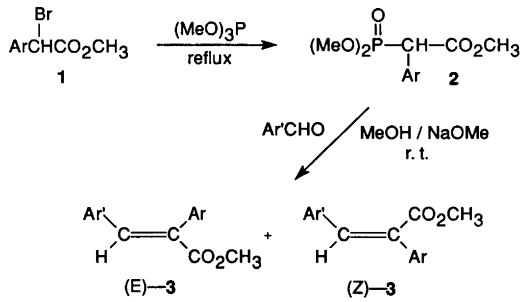
	Ar	Ar′	Yield (%)[a]	*E*/*Z* ratio[b]
3a	C_6H_5	C_6H_5	88	55/45
3b	C_6H_5	4-ClC_6H_4	63	50/50
3c	C_6H_5	2,4-$Cl_2C_6H_3$	62	61/39
3d	C_6H_5	2,6-$Cl_2C_6H_3$	61	77/23
3e	4-ClC_6H_4	C_6H_5	83	56/44
3f	4-ClC_6H_4	4-ClC_6H_4	70	52/48
3g	4-ClC_6H_4	2,4-$Cl_2C_6H_3$	82	63/37
3h	4-ClC_6H_4	2,6-$Cl_2C_6H_3$	85	73/27

[a] Yield of *E*/*Z* mixtures, purified by column chromatography. [b] Determined by ^{1}H NMR analyses of purified mixtures.

based on the ^{1}H NMR chemical shifts of the olefinic protons (β-protons). Only the olefinic protons of the *E* isomers are subjected to the anisotropy of the carbonyl group, thereby causing a downfield shift of their signals relative to those of the *Z* isomers:[10,11] the *E* isomer olefinic signals appeared at δ = 7.7–8.0,[1,5,6] whereas those of the *Z* isomers appeared at δ = 7.0–7.2. This difference in chemical shift was utilized to determine *E*/*Z* ratios in the product mixtures. The preparative separations were effected on a silica gel column with dichloromethane–hexane (60:40) as the mobile phase.

A characteristic feature of the mass spectra of **3a**, **b**, **e** was the base peak at *m*/*z* 178, possibly a phenanthrene moiety.[12] The remaining **3** all possess two or more chlorine atoms and displayed a peak at *m*/*z* 176.

Synthetic limitations. In order to evaluate further the synthetic utility of the reaction sequence, illustrated in Scheme 1, we also tested 2,4-dichlorophenylacetic acid and 4-nitrophenylacetic acid as starting materials. Both acids gave the corresponding α-bromo esters **1** in good yields, but the subsequent Michaelis–Arbuzov reaction with trimethyl phosphite was unsuccessful. As mentioned

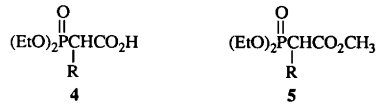


3a: Ar = C_6H_5; Ar′ = C_6H_5
3b: Ar = C_6H_5; Ar′ = 4-ClC_6H_4
3c: Ar = C_6H_5; Ar′ = 2,4-$Cl_2C_6H_3$
3d: Ar = C_6H_5; Ar′ = 2,6-$Cl_2C_6H_3$
3e: Ar = 4-ClC_6H_4; Ar′ = C_6H_5
3f: Ar = 4-ClC_6H_4; Ar′ = 4-ClC_6H_4
3g: Ar = 4-ClC_6H_4; Ar′ = 2,4-$Cl_2C_6H_3$
3h: Ar = 4-ClC_6H_4; Ar′ = 2,6-$Cl_2C_6H_3$

Scheme 1.

earlier, the phenyl and 4-chlorophenyl derivatives (**1**, Ar = phenyl and 4-chlorophenyl) reacted to form **2** in the presence of an excess of trimethyl phosphite, but with the 2,4-dichlorophenyl derivative the phosphonate **2** was formed in very poor yield, and with the 4-nitrophenyl derivative the reaction resulted in tar formation, even when the reaction temperature was lowered to 0°C. The nitro group is known to react with trimethyl phosphite and this reaction obviously precedes the substitution reaction.[13] The Michaelis–Arbuzov reaction is confined to halides capable of reacting in displacement reactions by an S_N2 mechanism.[9] In view of this it is not surprising that the substrates **1** react with reluctance. Our synthetic aim to introduce the phosphoryl moiety either as an electrophile (diethyl chlorophosphate)[14,15] or as a nucleophile (diethyl phosphite conjugate base)[5] has been unsuccessful to date.

Stereochemical outcome. The stereochemical data in Table 1 reveal that the amount of (*Z*)-**3** formed in each case, was substantially higher than could be expected on the basis of the exclusively *E*-selective reaction between the dianion of **4** (R = Ph) and benzaldehyde.[5,6] Moreover, all HWE reactions known to us of **4** (R = H, alkyl)[5,6] or **5** (R = H, alkyl)[16–18] with *aromatic* aldehydes, produced cinnamic derivatives in *E*/*Z* ratios ranging from 9:1 to 100:1.[19]



The HWE reaction became less *E*-selective only when steric bulk was increased in the phosphono reagent (**4** or **5** with R = long alkyl chains)[5,6,18,20] and, especially, if the aldehyde substrate was an α-branched aliphatic aldehyde.[16–18,21] Notable at this point is the development of bis(2,2,2-trifluoroethyl) phosphonates: a variant of the HWE reaction reported to afford high levels of *Z* selectivity for both aliphatic and aromatic aldehydes.[18,22–24] As of yet, this method has not been of advantage to us owing to difficulties in the preparation of the pertinent phosphonate reagents. Except for the bis(2,2,2-trifluoroethyl) phosphonates, the results reported here are, presumably, the first examples where the standard HWE reaction with *aromatic* aldehydes exhibits little or no preference for (*E*)-cinnamates.

To gain insight into the steric restraints evident in **3**,[25–27] it is worth noting that only the (*E*)-acids undergo conventional esterification (methanol–acid–reflux), whereas the conversion of (*Z*)-acids into their methyl esters has been effected by reacting the acids with diazomethane.[1] The failure of the (*Z*)-acids to undergo esterification with methanol under acidic conditions can be reasonably attributed to steric crowding in the tetrahedral intermediate, postulated for the esterification of a carboxylic acid with alcohol. The reaction with diazomethane proceeds by a completely different

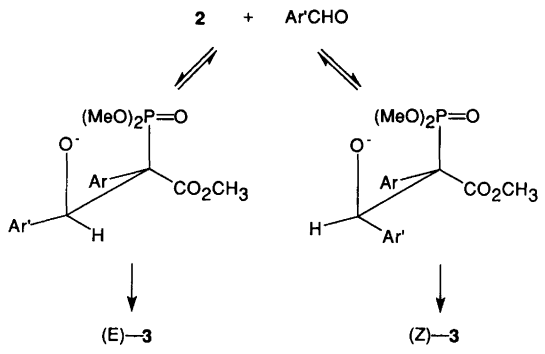
mechanism, not involving this intermediate.[28,29] This finds support in our observation, that the (*Z*)-**3** esters are resistant to hydrolysis, whereas the (*E*)-**3** esters undergo hydrolysis with ease.

To test the stability of the products **3** under the reaction conditions, an isolated isomer, either (*E*)-**3** or (*Z*)-**3**, was stirred in methanol at room temperature. No detectable *E*/*Z* isomerization was observed, even when stirring was conducted in the presence of sodium methoxide, sulfuric acid or a Lewis acid (BF_3 or $FeCl_3$).

The stereochemical outcome of the HWE reaction emanates from a combination of stereoselectivity in the initial condensation step and, perhaps, reversibility of intermediates (Scheme 2).[18] Enhanced *Z* selectivity has thus been attributed to an increase in the rate of the elimination step, relative to equilibration of the β-oxidophosphonate intermediate formed in the preceding step.[21,30,31]

The results presented here are primarily to be compared with results obtained for the reaction of **4** (R = Ph) with benzaldehyde. The observed *E*-selectivity for the reaction of **4** with benzaldehyde has been reasonably explained as being due to steric retardation of the elimination step.[5,6,20] By comparison, for the similar reaction with **2** the observed lack of stereoselectivity implies a decrease in reversibility of the reaction, indicating that the methoxycarbonyl group behaves as if it were smaller than the carboxylate moiety with its counterion and associated solvent shell.

In addition to steric factors, the rate of the elimination step may possibly be affected by electronic factors[18] and it is worth noting in this context that in (*Z*)-**3** the aromatic rings are in a *trans* position to each other, whereas in (*E*)-**3** the β-aromatic ring is positioned *trans* to the ester group. This may be of importance considering that the π-conjugation is more extensive in *trans*-stilbene than in (*E*)-methyl cinnamate, as concluded from their absorption spectra.[32] Consequently, for the formation of **3** it seems difficult, pending further evidence, to exclude conjugational participation in an elimination step, possibly with a product-like transition state.[20] In other words, the effective size of the methoxycarbonyl group makes possible increased participation of both aromatic rings in the elimination step, and this results in a decrease in reversibility of the reaction, which in turn leads to an increased amount of (*Z*)-**3** formed. Furthermore, the formation of the *Z* isomer appears to be sensitive towards substituents on the aromatic aldehyde, presumably due to steric crowding in the β-oxidophosphonate intermediate. For example when the reacting aldehyde is 2,4-dichlorobenzaldehyde (Scheme 2, Ar′ = 2,4-dichlorophenyl) only a small increase in the amount of the *E* isomer is observed. In this case the aromatic aldehyde has a chlorine atom in an *ortho* position, the steric impact of which is probably small because it can be directed away from the methoxycarbonyl group. This is not possible if both *ortho* positions of the reacting aromatic aldehyde are occupied by chlorine atoms, as in the formation of **3d** and **3h** (Scheme 2, Ar′ = 2,6-dichlorophenyl). Accordingly, an alteration of the *E*/*Z* ratio from 1:1 to 3:1 is observed, strongly indicating this change in ratio to be mainly steric in nature. Substituting only the *para* positions with chlorine atoms, as in **3b**, **3e** and **3f**, did not affect the product ratios in a noticeable way.



Scheme 2.

In summary we have demonstrated that the methyl α-arylcinnamates **3** are easily prepared by the HWE reaction, but difficulties in the preparation of the phosphonate precursors **2** limit the usefulness of the reaction sequence to some extent. The reaction exhibited unusual lack of stereoselectivity, hitherto unknown for this reaction with *aromatic* aldehydes as substrates. The unexpectedly large amount of the *Z* isomer in the product mixtures can be reasonably accounted for by assuming that the formation of these isomers is facilitated by extensive conjugational participation of both aromatic rings in the transition state of the final elimination step.

Experimental

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 250P spectrometer using $CDCl_3$ as the solvent. IR spectra were obtained on a Perkin-Elmer Model 283 spectrophotometer. Mass spectra were measured on a Hewlett Packard 5971A GC/MS instrument at the Environmental and Food Agency in Iceland. UV spectra were recorded on a Perkin-Elmer Lambda 17 UV/VIS spectrophotometer. Elemental analyses were carried out at the Schwarzkopf Microanalytical Laboratory, New York, USA, and on a Model 1106 Carlo Erba microanalyzer at the University of Iceland. Melting points (m.p.) were obtained on a Büchi 520 melting point apparatus and are uncorrected. Distillation of small amounts was effected by a bulb-to-bulb distillation in a Büchi Kugelrohr oven, Model GKR-50 (only external or oven temperature reported). TLC was performed on silica gel 60 F_{254} (Merck). Preparative HPLC separations were performed on an instrument from Waters, Model Prep-LC 500A.

General procedure for the preparation of trimethyl α-aryl (phosphono)acetates **2**. A mixture of methyl 2-bromo (aryl)acetate **1** (0.052 mol; **CAUTION**: potent lachrymators) and trimethyl phosphite (10.4 g, 0.084 mol) was

heated at reflux until the evolution of methyl bromide had ceased (0.5–1 h). The reaction could also be monitored by TLC (hexane–EtOAc 7:3). The cooled mixture was subjected to Kugelrohr distillation and afforded **2** as colorless oils. The side-product dimethyl methylphosphonate distilled at 80–100°C/0.01 Torr. Worthy of note is the unusually large coupling constant $^2J_{HP}$ displayed in the ^{1}H NMR spectra of compounds **2**; furthermore the ^{13}C NMR spectra of **2** revealed that the phosphorus coupled with all carbons, except the methoxy carbon attached to the carbonyl group ($COOCH_3$).[33]

Methyl dimethoxyphosphoryl(phenyl)acetate (**2**, *Ar = phenyl)*. Yield: 85%, b.p. 155–165°C/0.01 Torr. IR (neat) 1740, 1600 cm^{-1}. ^{1}H NMR: δ 3.59 (3 H, d, *J* 10.9 Hz, P–O–CH_3), 3.65 (3 H, d, *J* 10.9 Hz, P–O–CH_3), 3.68 (3 H, s, $COOCH_3$), 4.23 (1 H, d, *J* 23.5 Hz, H–C–P), 7.20–7.45 (5 H, m). ^{13}C NMR: δ 51.36 (J_{PC} 136.2 Hz), 52.69 (q), 53.47 (J_{PC} 7.1 Hz), 53.84 (J_{PC} 6.6 Hz), 127.94 (J_{PC} 3.0 Hz), 128.47 (J_{PC} 2.5 Hz), 129.34 (J_{PC} 6.4 Hz), 130.36 (J_{PC} 8.5 Hz), 167.75 (J_{PC} 3.1 Hz).

Methyl dimethoxyphosphoryl(4-chlorophenyl)acetate (**2**, *Ar = 4-chlorophenyl)*. Yield: 79%, b.p. 160–170°C/0.01 Torr. IR (neat) 1740, 1590 cm^{-1}. ^{1}H NMR: δ 3.61 (3 H, d, *J* 11.0 Hz, P–O–CH_3), 3.66 (3 H, d, *J* 11.0 Hz, P–O–CH_3), 3.69 (3 H, s, $COOCH_3$), 4.19 (1 H, d, *J* 23.8 Hz, H–C–P), 7.22–7.40 (4 H, m). ^{13}C NMR: δ 50.70 (J_{PC} 135.6 Hz), 52.86 (q), 53.57 (J_{PC} 7.2 Hz), 53.89 (J_{PC} 6.7 Hz), 128.66 (J_{PC} 2.5 Hz), 129.02 (J_{PC} 8.7 Hz), 130.75 (J_{PC} 6.4 Hz), 134.06 (J_{PC} 3.6 Hz), 167.48 (J_{PC} 3.6 Hz).

*General procedure for the preparation of (*E*)- and (Z)-methyl 2,3-diarylpropenoates* **3**. Methyl dimethoxyphosphoryl(aryl)acetate **2** (3.9 mmol) was added to a solution of sodium methoxide (4.3 mmol) in methanol (10 ml) and stirred at ambient temperature for 0.5 h. The aromatic aldehyde (4.3 mmol) was then added to this solution over a period of 1–2 min. The resulting mixture was stirred at ambient temperature overnight, after which the methanol was removed *in vacuo*. The residue was filtered through a short column of silica gel (elution with CH_2Cl_2–hexane 7:3) to afford a mixture of the *E* and *Z* isomers. The separation of the isomers was then effected by preparative HPLC using CH_2Cl_2–hexane (60:40) as the mobile phase. The products are listed in Table 1. Given below are representative examples of spectroscopic data for selected compounds.

Methyl 2,3-diphenylpropenoate (**3a**). Yield 88%. *E/Z* Ratio: 55/45.

E-isomer: m.p. 75–76°C (EtOH–H_2O). Anal. $C_{16}H_{14}O_2$: C, H. MS [IP 70 eV; *m/z* (% rel. int.)]: 238 (M^+, 48), 176 (18), 178 (100), 152 (16), 121 (26). ^{1}H NMR: δ 3.80 (3 H, s), 7.87 (1 H, s), 7.03–7.41 (10 H, m). ^{13}C NMR: δ 52.3 (CH_3), 127.8 (CH), 128.1 (CH, 2 C), 128.6 (CH, 2 C), 129.0 (CH), 129.7 (CH, 2 C), 130.6 (CH, 2 C), 132.4 (C), 134.5 (C), 135.8 (C), 140.5 (CH), 168.3 (C). IR (KBr): 1705, 1625, 1495 cm^{-1}. UV [methanol (log ε)]: λ_{max} 283 nm (4.16).

Z-isomer: pale yellow oil. MS [IP 70 eV; *m/z* (% rel. int.)]: 238 (M^+, 33), 176 (23), 178 (100), 152 (25), 121 (37). ^{1}H NMR: δ 3.82 (3 H, s), 7.10 (1 H, s), 7.34–7.54 (10 H, m). ^{13}C NMR: δ 52.1 (CH_3), 126.3 (CH, 2 C), 128.1 (CH, 2 C), 128.2 (CH, 2 C), 128.4 (CH, 2 C), 128.6 (CH, 2 C), 131.4 (CH), 134.8 (C), 135.5 (C), 136.7 (C), 169.9 (C). IR (neat): 1725, 1600, 1495 cm^{-1}. UV [methanol (log ε)]: λ_{max} 286 nm (4.32).

Methyl 2,3-bis(4-chlorophenyl)propenoate (**3f**). Yield 70%. *E/Z* Ratio: 52/48.

E-isomer: m.p. 82–84°C (EtOH–H_2O). Anal. $C_{16}H_{12}Cl_2O_2$: C, H. MS [IP 70 eV; *m/z* (% rel. int.)]: 306/308/310 (M^+, 75/46/5), 247 (27), 212 (72), 176 (62), 155 (100). ^{1}H NMR: δ 3.80 (3 H, s), 7.80 (1 H, s), 6.96–7.37 (8 H, m). ^{13}C NMR: δ 52.5 (CH_3), 128.6 (CH, 2 C), 129.0 (CH, 2 C), 131.2 (CH, 2 C), 131.6 (CH, 2 C), 131.8 (C), 132.7 (C), 133.8 (C), 134.1 (C), 135.2 (C), 139.6 (CH), 167.6 (C). IR (KBr): 1710, 1620, 1595 cm^{-1}. UV [methanol (log ε)]: λ_{max} 288 nm (4.16).

Z-isomer: m.p. 76–77°C (EtOH–H_2O). Anal. $C_{16}H_{12}Cl_2O_2$: C, H. MS [IP 70 eV; *m/z* (% rel. int.)]: 306/308/310 (M^+, 65/49/4), 247 (29), 207 (24), 176 (44), 155 (100). ^{1}H NMR: δ 3.78 (3 H, s), 6.95 (1 H, s), 7.25–7.40 (8 H, m). ^{13}C NMR: δ 52.4 (CH_3), 127.8 (CH, 2 C), 128.8 (CH, 2 C), 129.0 (CH, 2 C), 129.5 (CH, 2 C), 130.8 (CH), 133.9 (C), 134.3 (C), 134.4 (C), 134.5 (C), 135.1 (C), 169.4 (C). IR (KBr): 1710, 1595 cm^{-1}. UV [methanol (log ε)]: λ_{max} 295 nm (4.28).

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