Phosphonate Modification for a Highly (*Z*)-Selective Synthesis of Unsaturated Esters by Horner–Wadsworth–Emmons Olefination

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The Horner–Wadsworth–Emmons (HWE) reaction of various ethyl diarylphosphonoacetates with benzaldehyde, cyclohexane carboxaldehyde and octanal is reported. Selectivities of up to 98 % at –78 °C are obtained with the three substrates. Among all the phosphonates prepared, the reagent based on 2-*tert*-butylphenol proved to be especially efficient, with *Z*/*E* ratios close to 95:5 at 0 °C. It appears thus to be the reagent of choice for the (*Z*)-selective HWE reaction with both aromatic and aliphatic aldehydes.

Introduction

The Horner–Wadsworth–Emmons (HWE) reaction is a variant of the Wittig reaction that possesses a number of significant advantages: not only is the work-up greatly facilitated since the phosphate salt formed is water soluble, but the reactivity of HWE reagents allows them to effect transformations that are either difficult or impossible using the analogous Wittig ylides. This reaction, which usually proceeds smoothly and under mild conditions with phosphonates bearing stabilising substituents, typically leads to the more stable (*E*)-disubstituted olefins.[1] As it is highly desirable to be able to prepare the (*E*)- or (*Z*)-isomer at will, Still,[2] in 1983, and Ando,[3,4] in 1995, developed two (*Z*)-selective reagents, namely methyl bis(trifluoroethyl)phosphonoacetate (**1**) and ethyl diphenylphosphonoacetate (**2**), respectively (Figure 1).[5] However, the conditions required to obtain high *Z*/*E* ratios were fairly stringent and usually implied working at low temperatures.[6] The aim of this study was to establish an efficient and scalable protocol for the (*Z*)-selective olefination of aldehydes and to reinvestigate and modulate the Still/Ando procedures. By using Still's reagent, it has already been shown that it is possible to work at 0 °C in the presence of K_2CO_3 and 10 mol-% 18-C-6 with selectivities of up to 98%.[7] However, these conditions are effective essentially only with aromatic aldehydes. This article reports on how to achieve high product selectivities under mild reaction conditions with phosphonates based upon phenols and both aromatic and aliphatic aldehydes.

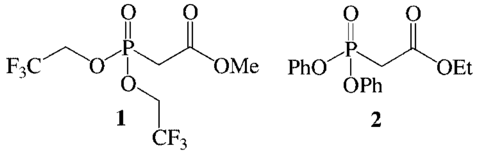

Figure 1. Phosphonates developed by Still and Ando.

Results and Discussion

With the objective of reaching selectivities of over 90% at 0 °C with a broad range of aldehydes, we decided to take advantage of the large availability of phenols to prepare a series of phosphonates bearing *ortho* electron-withdrawing, electron-donating and sterically bulky groups. They were synthesized by an Arbusov reaction of ethyl bromoacetate with mixed phosphites $P(OEt)(OAr)_2$ obtained from ethyl dichlorophosphite (Figure 2).

The yields and purities of the phosphites and phosphonates thus prepared are collected in Table 1.

The crude phosphites were generally of good purity (close to 90% by ^{31}P NMR spectroscopy) but simple filtration through a pad of basic alumina enabled this to be increased further to 98% by the removal of acidic impurities [excess phenol and HP(O)(OR)(OR′)].[8] The phosphonates obtained after the Arbusov reaction with ethyl bromoacetate were pure enough to be used without any further treatment.

All the structures were then tested in the HWE reaction with benzaldehyde, cyclohexane carboxaldehyde and *n*-octanal as representatives of aromatic and aliphatic aldehydes. The initial experiments were carried out in THF as the solvent and NaI/TMG (tetramethyl guanidine) as the basic system (Figure 3).[9]

The selectivities [$S = Z/(Z + E) \times 100$] and 5 h aldehyde conversions [Conv. (%)] both at –78 °C and 0 °C are given

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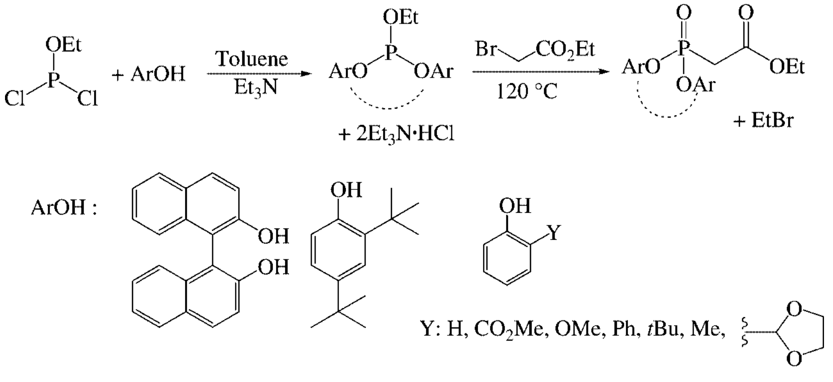

Figure 2. Synthesis of phosphonates **2**–**10**.

Table 1. Phosphite and phosphonate yields and purities.[a]

Entry	Phenol	Phosphite			Phosphonate	
		Yield [%]	Purity [mol-%]		Yield [%] (time)	Purity [mol-%]
1	Y = H	85	98	**2**	75 (24 h)	98
2	Y = CO_2Me	79	98	**3**	91 (24 h)	98
3	Y = $CH(OCH_2)_2$	87	90	**4**	84 (6 h)	90
4	Y = OMe	86	98	**5**	92 (1 h)	98
5	Y = Ph	92	98	**6**	92 (24 h)	98
6	Binol	89	98	**7**	82 (24 h)	98
7	Y = Me	92	98	**8**	93 (24 h)	98
8	Y = *t*Bu	94	98	**9**	91 (30 h)	98
9	2,4-di-*t*Bu-phenol	80	98	**10**	88 (30 h)	98

[a] See the Experimental Section for further details.

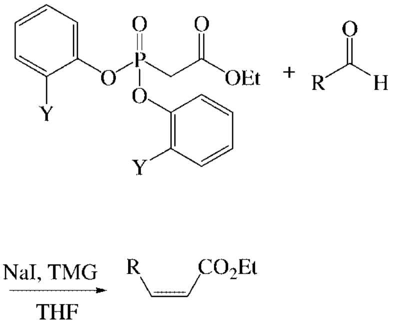

Figure 3. Initial HWE experiments.

below. The phosphonates have been ranked by selectivities observed first at –78 °C and then at 0 °C.

Reaction with Benzaldehyde

We were pleased to obtain selectivities of over 95% with Y = OMe, CO_2Me, Ph and *t*Bu at –78 °C (Table 2). This indicates that the reaction is not very sensitive to electronic effects. We were even quite surprised to obtain close to 98% (*Z*)-selectivity with guaiacol, as Ando has reported only moderate *Z*/*E* ratios with the same phosphonate using Triton B as the base.[4a] We will see hereafter that there is a noticeable salt effect with this structure. With Y = CO_2Me, low conversions were always obtained. In fact, we observed the release of large amounts of methyl salicylate in the reaction mixture, which indicates the instability of the phosphonate or its anion in the reaction conditions. The other structures led to selectivities close to 90% at –78 °C, except Y = Me, which was less selective. Concerning the reaction kinetics, conversions of over 85% were always obtained at 0 °C after 5 h. At this temperature, only the phosphonates with OMe and ketal substituents gave close to 90% (*Z*)-selectivity.

Table 2. Reaction of phosphonates with benzaldehyde under NaI/TMG conditions.[a]

Entry	Phenol	*T* = –78 °C		*T* = 0 °C	
		S	Conv.	*S*	Conv.
1	Y = OMe	98	75	89	97
2	Y = CO_2Me	98	50	–	–
3	Y = Ph	95	98	83	98
4	Y = *t*Bu	95	75	82	100
5	Y = ketal	92	70	89	85
6	Y = H	89	98	78	92
7	Binol	89	90	77	85
8	Y = Me	82	100	69	100
9	2,4-di-*t*Bu-phenol	–	–	81	95

[a] See the Experimental Section for further details; *S*: selecticity.

Reaction with Cyclohexane Carboxaldehyde

Selectivities close to 90% and even higher were obtained with all the phosphonates at –78 °C (Table 3). 2-*tert*-Butylphenol led to the best result with a 98:2 *Z*/*E* ratio. The phosphonates based upon 2-Ph, 2-Me, 2-CO_2Me phenols and binol were less selective, with ratios close to 95:5. As already mentioned, Y = CO_2Me gave low conversion. With both *t*Bu and ketal substituents, the reaction was slow at –78 °C, and increasing the temperature to 0 °C caused a marked enhancement of the conversions. The most remarkable results were obtained with 2-*t*Bu and 2,4-di-*t*Bu-phenols with 95% *Z*-selectivity at 0 °C. The corresponding phosphonates are thus as selective at 0 °C as the others at –78 °C (!).

Table 3. Reaction of phosphonates with cyclohexane carboxaldehyde under NaI/TMG conditions.[a]

Entry	Phenol	*T* = –78 °C		*T* = 0 °C	
		S	Conv.	*S*	Conv.
1	Y = *t*Bu	98	70	95	100
2	Y = Ph	95	94	91	97
3	Y = Me	95	98	89	100
4	Binol	95	75	86	86
5	Y = CO_2Me	95	40	–	–
6	Y = OMe	93	90	–	–
7	Y = ketal	91	50	85	81
8	Y = H	90	95	87	95
9	2,4-di-*t*Bu-phenol	–	–	94	93

[a] See the Experimental Section for further details.

Reaction with *n*-Octanal

We observed similar tendencies here to the reaction with cyclohexane carboxaldehyde. *Z*/*E* ratios of over 90:10 were obtained at –78 °C (Table 4). 2-*t*Bu-phenol led again to the best result, with a selectivity of 98%. The phosphonates based on 2-Ph and 2-CO_2Me phenols were then close to 95% (*Z*)-selective, with low conversion for the latter. Here again, 2-*t*Bu and 2,4-di-*t*Bu substituents proved to be also efficient at 0 °C, with a 92:8 *Z*/*E* ratio.

Table 4. Reaction of phosphonates with *n*-octanal under NaI/TMG conditions.[a]

Entry	Phenol	*T* = –78 °C		*T* = 0 °C	
		S	Conv.	*S*	Conv.
1	Y = *t*Bu	98	94	92	100
2	Y = Ph	96	89	89	98
3	Y = CO_2Me	95	65	–	–
4	Y = Me	93	100	85	100
5	Y = ketal	92	80	85	88
6	Y = OMe	92	95	–	–
7	Y = H	91	98	83	100
8	Binol	90	88	79	90
9	2,4-di-*t*Bu-phenol	–	–	91	95

[a] See the Experimental Section for further details.

From these preliminary results, the phosphonates based on guaiacol (**5**) and 2-*tert*-butylphenol (**9**) seem to be candidates of choice for benzaldehyde and cyclohexane carboxaldehyde/octanal, respectively. However, intrigued by the good results obtained with **5**, we decided to look at the effect of NaI. As described by Pihko et al.,[10] we also observed that adding an excess of sodium ions caused an increase in the selectivities (Table 5).

Table 5. NaI effect with the phosphonate based on guaiacol **5** and TMG as the base.[a]

Entry	Aldehyde	NaI [equiv.]	Temp. [°C]	S
1	PhCHO	1.3	0	89
2	PhCHO	2.2	0	93
3	PhCHO	5	0	93
4	CyCHO	1.3	–78	93
5	CyCHO	2.2	–78	97
6	CyCHO	5	–78	98
7	CyCHO	5	0	92
8	*n*-octanal	1.3	–78	92
9	*n*-octanal	2.2	–78	96
10	*n*-octanal	5	–78	96
11	*n*-octanal	5	0	90

[a] See the Experimental Section for further details.

As the reaction with benzaldehyde was highly selective at –78 °C, the additive effect was studied at 0 °C. We observed an increase from 89% to 93% (*Z*)-selectivity on going from 1.3 to 2.2 equivalents of NaI. Adding more NaI had no noticeable effect. With cyclohexane carboxaldehyde, the selectivity increased from 93 to 97–98% on going from 1.3 to 2–5 equivalents at –78 °C, and working with five equivalents at 0 °C led to a 92:8 *Z*/*E* ratio. Finally, the same increase was also observed with octanal: from 92 to 96% at –78 °C and 90% (*Z*)-selectivity at 0 °C with five equivalents of NaI.

As this effect was much less pronounced and even not observed with most of the other structures, we think it is directly due to the methoxy group in the *ortho* position. However, these observations, although interesting from the selectivity point of view, do not really lead to any simplification of the protocol.

As Ando has already shown that the phosphonate based upon *o*-cresol is the reagent of choice both with aliphatic aldehydes using NaH and aromatic aldehydes using Triton B as bases, we then tested **9** with other basic systems to evaluate the cation influence. The first experiments were carried out with sodium hexamethyldisilazide (NaHMDS) and KHMDS in THF (Table 6). These results show that the selectivity is not sensitive to the strength of the base, as NaHMDS and NaI/TMG led to the same *Z*/*E* ratios (entries 2 and 3, 6 and 7, and 10 and 11). The selectivity is

Table 6. Cation effect with the phosphonate based on 2-*tert*-butylphenol (**9**).[a]

Entry	Aldehyde	Conditions	*S*	Conv.
1	PhCHO	NaI-TMG/–78 °C/17 h	95	100
2	PhCHO	NaI-TMG/0 °C/1 h	81	100
3	PhCHO	NaHMDS/0 °C/1 h	81	100
4	PhCHO	KHMDS/0 °C/1 h	93	100
5	CyCHO	NaI-TMG/–78 °C/17 h	98	100
6	CyCHO	NaI-TMG/0 °C/1 h	95	100
7	CyCHO	NaHMDS/0 °C/1 h	95	97
8	CyCHO	KHMDS/0 °C/1 h	94	97
9	octanal	NaI-TMG/–78 °C/17 h	98	100
10	octanal	NaI-TMG/0 °C/1 h	92	100
11	octanal	NaHMDS/0 °C/1 h	93	99
12	octanal	KHMDS/0 °C/1 h	93	98

[a] See the Experimental Section for further details.

rather influenced by the cation: with benzaldehyde, it increased from 81 to 93% on going from Na^+ to K^+ at 0 °C. With the other aldehydes Na^+ and K^+ gave similar selectivities. This difference can be explained by the fact that the reaction is more prone to reversibility with benzaldehyde due to the phenyl group being electron withdrawing. The potassium cation causes an increase in the rate of the elimination step and thus helps to maintain a high level of (*Z*)-stereoselection.

Conclusions

This study clearly indicates that the phosphonate based upon 2-*tert*-butylphenol is a reagent of choice for the (*Z*)-selective HWE reaction both with aromatic and aliphatic aldehydes. *Z*/*E* ratios close to 95:5 have indeed been obtained with the two kinds of substrate at 0 °C. Further development in order to design a scalable process will be reported in due course.

Experimental Section

General Remarks: NMR spectra were recorded from $CDCl_3$ solutions at 300 K with a Bruker AMX 300 (300 MHz) spectrometer. The GC analyses were performed with a Varian 3400Cx apparatus equipped with a SGE BPX5 (764) 25 m × 0.53 mm × 1 μm column and FID detector. He was used as the vector gas (5 mL min^{-1}) and N_2 as make-up (25 mL min^{-1}). Program: 80 °C (4 min) → 170 °C (rate: 7 °C min^{-1}) → 300 °C (4 min; rate: 30 °C min^{-1}). The retention times of the analyzed compounds under these conditions are given in Table 7.

Table 7. Retention times of the analyzed compounds.

Compound	t_R [min]
PhCHO	5.1
CyCHO	4.4
Octanal	5.7
Ph-CH=CH-CO_2Et [(*Z*)-isomer]	14.1
Ph-CH=CH-CO_2Et [(*E*)-isomer]	15.6
Cy-CH=CH-CO_2Et [(*Z*)-isomer]	12.6
Cy-CH=CH-CO_2Et [(*E*)-isomer]	14.4
n-C_7H_{15}-CH=CH-CO_2Et [(*Z*)-isomer]	13.9
n-C_7H_{15}-CH=CH-CO_2Et [(*E*)-isomer]	15.0

Authentic samples were either commercially available (ethyl *trans*-cinnamate and ethyl *trans*-2-decenoate) or were prepared according to well known procedures.[4a]

Synthesis of Phosphonates 2–10. General Procedure: The appropriate substituted phenol (0.130 mol, 1.95 equiv.) and triethylamine (14 g, 0.137 mol, 2.05 equiv.) were mixed in toluene (100 mL) and cooled to 0 °C. Ethyldichlorophosphite (10 g, 0.067 mol, 1 equiv.) in diethyl ether (40 mL) was then added slowly in order to maintain the temperature below 5 °C. After 30 min at 0 °C, the mixture was left to warm to room temperature. Three hours later the salts were filtered and washed twice with toluene (2 × 50 mL). The organic phase was then passed through a pad of basic alumina and the solvent was removed under reduced pressure. This phosphite (48.0 mmol, 1 equiv.) was added over 1 h to ethyl bromoacetate (12.3 g, 72.4 mmol, 1.51 equiv.) at 120 °C. After reaction completion (^{31}P NMR monitoring), the mixture was heated to remove excess ethyl bromoacetate under reduced pressure and the phosphonate thus obtained was used without further purification.

Phosphonate 3: Pale-yellow oil. Yield: 73% (from PCl_2OEt). ^{1}H NMR ($CDCl_3$): δ = 1.06 (t, *J* = 7.4 Hz, 3 H), 3.47 (d, *J* = 22.2 Hz, 2 H), 3.79 (s, 6 H), 4.04 (q, *J* = 7.4 Hz, 2 H), 7.17 (tt, *J* = 7.7, *J* = 1.3 Hz, 2 H), 7.26 (dt, *J* = 8.5, *J* = 1.3 Hz, 2 H), 7.36 (td, *J* = 8.5, *J* = 1.6 Hz, 2 H), 7.81 (broad d, *J* = 7.7 Hz, 2 H) ppm. ^{31}P NMR ($CDCl_3$): δ = 14.1 ppm. $C_{20}H_{21}O_9P$ (436.4): calcd. C 55.05, H 4.85, P 7.10; found C 55.37, H 4.92, P 6.83.

Phosphonate 4: Pale-yellow oil. 2-(1,3-Dioxolan-2-yl)phenol was prepared according to an already described procedure.[11] Yield: 73% (from PCl_2OEt). ^{1}H NMR ($CDCl_3$): δ = 1.15 (t, *J* = 7.15 Hz, 3 H), 3.33 (d, *J* = 21.7 Hz, 2 H), 3.93–4.02 (m, 8 H), 4.10 (q, *J* = 7.15 Hz, 2 H), 6.05 (s, 2 H), 7.13 (broad t, *J* = 7.7 Hz, 2 H), 7.24 (td, *J* = 7.4, *J* = 1.6 Hz, 2 H), 7.34 (dt, *J* = 8.2, *J* = 1.3 Hz, 2 H), 7.51 (dt, *J* = 7.7, *J* = 1.3 Hz, 2 H). ^{31}P NMR ($CDCl_3$): δ = 13.7 ppm. $C_{22}H_{25}O_9P$ (464.4): calcd. C 56.90, H 5.43, P 6.67; found C 56.50, H 5.50, P 6.50.

Phosphonate 6: Colourless oil. Yield: 85% (from PCl_2OEt). ^{1}H NMR ($CDCl_3$): δ = 1.00 (t, *J* = 7.15 Hz, 3 H), 2.41 (d, *J* = 21.7 Hz, 2 H), 3.89 (q, *J* = 7.15 Hz, 2 H), 7.18–7.27 (m, 18 H). ^{13}C NMR ($CDCl_3$): δ = 13.8 (s, CH_3), 34.1 (d, *J* = 138.6 Hz, PCH_2), 61.6 (s, CH_2), 121.3 (d, *J* = 2.7 Hz, 2 CH_{arom}), 125.5 (d, *J* = 1.0 Hz, 2 CH_{arom}), 127.3 (s, 2 CH_{arom}), 128.1 (s, 4 CH_{arom}), 128.6 (d, *J* = 1.3 Hz, 2 CH_{arom}), 129.3 (s, 4 CH_{arom}), 131.1 (s, 2 CH_{arom}), 133.6 (d, *J* = 5.9 Hz, 2 C_{arom}), 137.1 (s, 2 C_{arom}), 147.1 (d, *J* = 8.9 Hz, 2 C_{arom}), 164.2 (d, *J* = 6.2 Hz, C=O) ppm. ^{31}P NMR ($CDCl_3$): δ = 12.7 ppm. $C_{28}H_{25}O_5P$ (472.5): calcd. C 71.18, H 5.33, P 6.56; found C 71.23, H 5.59, P 6.58.

Phosphonate 9: White solid. Yield: 85% (from PCl_2OEt). M.p.: 90 °C. ^{1}H NMR ($CDCl_3$): δ = 1.08 (t, *J* = 7.15 Hz, 3 H), 1.30 (s, 18 H), 3.29 (d, *J* = 21.7 Hz, 2 H), 4.05 (q, *J* = 7.15 Hz, 2 H), 7.02–7.07 (m, 4 H), 7.29 (dt, *J* = 7.7, *J* = 1.6 Hz, 2 H), 7.61 (dt, *J* = 7.9, *J* = 1.1 Hz, 2 H). ^{31}P NMR ($CDCl_3$): δ = 10.4 ppm. $C_{24}H_{33}O_5P$ (432.5): calcd. C 66.65, H 7.69, P 7.16; found C 66.40, H 7.80, P 7.10

Phosphonate 10: Colourless oil. Yield: 70% (from PCl_2OEt). ^{1}H NMR ($CDCl_3$): δ = 1.07 (t, *J* = 7.15 Hz, 3 H), 1.22 (s, 18 H), 1.32 (s, 18 H), 3.26 (d, *J* = 21.4 Hz, 2 H), 4.04 (q, *J* = 7.15 Hz, 2 H), 7.07 (dd, *J* = 8.8, *J* = 2.4 Hz, 2 H), 7.30 (t, *J* = 2.2 Hz, 2 H), 7.49 (dd, *J* = 8.5, *J* = 1.1 Hz, 2 H). ^{31}P NMR ($CDCl_3$): δ = 10.3 ppm. $C_{32}H_{49}O_5P$ (544.7): calcd. C 70.56, H 9.07, P 5.69; found C 70.20, H 9.10, P 5.80.

HWE Reaction With NaI/TMG. General Procedure: The appropriate phosphonoacetate (0.50 mmol, 1.1 equiv.) and NaI (89 mg, 0.59 mmol, 1.3 equiv.) were dissolved in anhydrous THF (10 mL). The mixture was then cooled to 0 °C and TMG (70 μL, 0.55 mmol, 1.2 equiv.) was added. The mixture was further stirred for 30 min before the aldehyde addition (0.45 mmol, 1 equiv.). For reaction at –78 °C, the mixture was first cooled to –78 °C and stirred for 30 min before the aldehyde addition (0.45 mmol, 1 equiv.). The reaction was then monitored by gas chromatography for the selectivity and conversion determination after quenching aliquots with saturated ammonium chloride and extracting the mixture with toluene.

HWE Reaction With Na/KHMDS. General Procedure: Phosphonate **9** (216 mg, 0.5 mmol, 1.1 equiv.) was first dissolved in anhydrous THF (10 mL). The mixture was then cooled to 0 °C and a solution of NaHMDS (1 M solution in THF, 0.47 mmol, 1.05 equiv.) or KHMDS (0.5 M solution in toluene, 0.47 mmol, 1.05 equiv.) was added. The mixture was stirred for a further

10 min before the aldehyde addition (0.45 mmol, 1 equiv.). The reaction was then monitored by gas chromatography for the selectivity and conversion determination after quenching aliquots with saturated ammonium chloride and extracting the mixture with toluene.

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[6] The phosphonate based on 2,4-difluorophenol described by Motoyoshiya et al. (ref. 4e–4f) was the only one reported to date leading to selectivities over 92% at 0 °C with various aldehydes.

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[8] This purification could not be performed with the ketal as the phosphite remained adsorbed on alumina.

[9] Ando has shown that NaI/DBU is an effective combination, especially with aliphatic aldehydes. In a preliminary screening, we have seen that TMG and DBU lead to the same results and that NaI/TMG also gives promising selectivities with benzaldehyde.

[10] During this work, an article entitled “Excess sodium ions improve (*Z*)-selectivity in Horner–Wadsworth–Emmons olefinations with the Ando phosphonate” was published: P. M. Pihko, T. M. Salo, *Tetrahedron Lett.* **2003**, *44*, 4361–4364.

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