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$P(RNCH_2CH_2)_3N$: an efficient promoter for the direct synthesis of *E*-α,β-unsaturated esters

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Abstract—Upon reacting ethyl acetate or methyl propionate with a variety of aromatic aldehydes in the presence of 1.06–1.2 equiv. of the pro-azaphosphatranes, $P(MeNCH_2CH_2)_3N$, $P(i\text{-}PrNCH_2CH_2)_3N$ or $[P(i\text{-}PrNCH_2CH_2)_2(NHCH_2CH_2)N$ at 40–50°C for 2–6 h in isobutyronitrile, the corresponding α,β-unsaturated esters were formed as the only products. Ethyl acetate reacts with aldehydes to form exclusively *E*-isomers while the higher homologue methyl propionate gives rise to a mixture of *E* and *Z* isomers with the former as the major product. When used as the solvent, methyl propionate selectively forms the *E*-α,β-unsaturated ester. The reaction is not as successful for the preparation of α,β-unsaturated ketones.

1. Introduction

The currently most commonly used strategy for the preparation of α,β-unsaturated esters is the Wittig reaction and its modifications devised by Horner et al.[1] Although these reactions are widely used, their major drawback is the need for the preparation of intermediates of the type $[Ph_3PCH_2R]^+X^-$ and $(EtO)_2P(O)CH_2CO_2R$ from the corresponding halogenated reagents.[2–5] Several organometallic catalysts such as $RuCl_2(PPh_3)_3$,[6] $ReOCl_3(PPh_3)_3$,[7,8] $Sn(OSO_2CF_3)_2$,[5] and Bu_3Sb[9] have also been employed to convert aldehydes into α,β-unsaturated esters. However, the use of heavy metal catalysts introduces environmental concerns and these procedures rarely produce a single isomer.[5–9] Other variations of the Wittig approach that have been employed include the reaction of ylides on silica gel under microwave conditions,[10] the use of pentacoordinate spirophosphoranes,[2] and the use of activated alumina[11] to promote coupling between the Wittig reagent and the aldehyde, to name but a few. These approaches proceed with moderate to high yields, but they require prior preparation of the intermediates and they rarely produce a single isomer.

Peterson olefination[12] has also been used for the synthesis of disubstituted *E*-α,β-unsaturated esters. However, most of the variations of this reaction require elevated temperatures and they provide only modest yields.[13] Although the Wittig reaction and its Peterson and Julia-Lithgoe[14] modifications are very useful for preparing disubstituted *E*-α,β-unsaturated esters, their general failure in inducing good stereoselectivity in the preparation of trisubstituted α,β-unsaturated esters has remained a major draw-back.[15] 1-Alkoxycarbonylalkylidenetriphenylarsoranes[16] have been employed to address the stereoselectivity problem in the formation of trisubstituted *E*-α,β-unsaturated esters. Although this strategy is successful in producing the *E*-trisubstituted α,β-unsaturated esters in 64–95% yield, the toxicity of arsenic compounds makes this methodology less attractive.

In recent years, several transition metal compounds have been used in the preparation of *E*-α,β-trisubstituted unsaturated esters. These include the reaction of iodobenzene with methyl methacrylate in the presence of $NaHCO_3$, $PdCl_2$, and PEG-800 in DMF at 120°C for 6 h to afford the *E*-esters in moderate yields;[17] a Pd-catalyzed Heck[18] reaction, and the use of alkenyl and aryl boronic acids in a Pd-catalyzed transformation.[19] The toxicity of DMF and the high temperature required in the PEG-800 reaction is disadvantageous, however. The aforementioned Pd-catalyzed reactions also lead to mixtures of products and require long reaction times (up to 24 h). A reported process using aryl iodides and acrylates also requires a relatively high temperature (130°C), the presence of platinum complexes and a reaction time of 24 h to afford moderate conversions (26–90%) and selectivities (40–95%).[20] Very recently, β(*tertiary*-butyl diphenylsilyl)aldehydes and ketones have been reacted with organolithium and Grignard reagents to give the corresponding β-hydroxy silane derivatives which were then allowed to undergo silanol elimination in the

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Table 1. The reaction of benzaldehyde with ethyl acetate in different solvents and at various temperatures for 6 h in the presence of 20 mol% of **1b**

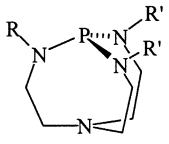
Solvent	*T* (°C)	% Conversion[a] to ethyl cinnamate	% Starting material (**3a**)[b]
Isobutyronitrile	40	22	0
THF	40	0	100
Benzene	40	<1	100
Ether	30	0	100
Ethyl acetate	40	28	43 (28)[c]
Acetonitrile	40	20	13 (66)[d]
Pentane	30	<1	>99
Isobutyronitrile	30	15	85
Isobutyronitrile	50	24	76
Ethyl acetate	50	36	42 (22)[c]

[a] Based on the aldehyde as estimated by ^{1}H NMR integration.
[b] The quantities in parentheses represent side products as estimated by ^{1}H NMR integration.
[c] Conversion to β-hydroxy ester as estimated by ^{1}H NMR integration.
[d] Conversion to β-hydroxy nitrile as estimated by ^{1}H NMR integration.

presence of KH or BF_3 to afford *E*- or *Z*-olefins with a high degree of stereocontrol.[21] The procedure includes a total of five steps, the first of which involves the use of an environmentally unfriendly organocuprate reagent.

Another class of related compounds is α,β-unsaturated acids which have traditionally been prepared through the Perkin reaction.[22] In this process, an aromatic aldehyde is reacted with an acid anhydride in the presence of a base, often the salt of the acid whose anhydride is the reactant.[22a,b] Other variations of the Perkin reaction include the use of phosphorus oxychloride[22c] and triethyl amine.[24] However, this reaction affords low to modest yields and requires high temperatures.

Since our first report of the pro-azaphosphatrane **1a**,[23] the efficacy of this compound as a catalyst or promoter for a variety of reactions has been demonstrated in a series of reports from our laboratories.[24–33] The more basic analogues **1b**[25] and **1c**[26] have been shown to be even more effective in some of our more recent studies[28,30] as well as in the present one. On the other hand, **1b** has proven to be advantageous in reactions requiring longer reaction times, such as the synthesis of homoallylic alcohols via the alkylation of aldehydes,[27] wherein both **1a** and **1c** failed to effect better conversions.

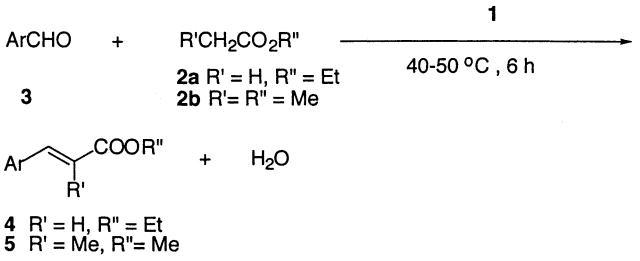


1a: R = R' = Me
1b: R = R' = *i*-Pr
1c: R = H, R' = *i*-Pr

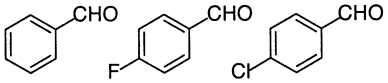
We report here that bases of type **1** also efficiently deprotonate ethyl acetate to afford enolates that add to aldehydes to produce the corresponding *E*-α,β-unsaturated esters. We also report the promotion by **1b** of the direct condensation of aromatic aldehydes and methyl propionate to form the trisubstituted *E*-methyl acrylate as the sole product. To our knowledge, this is the first report in which important transformations of this type have been effected directly by a nonionic base.

2. Results and discussion

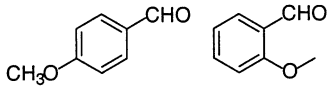
Because of the broad range of reactions catalyzed by compounds of type **1**,[23–33] we believed that such bases might be capable of deprotonating ethyl acetate (**2a**) and that the resulting enolate would add to aldehydes to produce β-hydroxy esters that would then undergo dehydration to afford the corresponding α,β-unsaturated esters (Eq. 1)



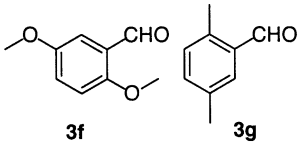
(1)



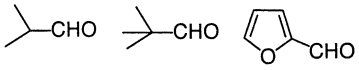
3a **3b** **3c**



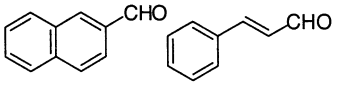
3d **3e**



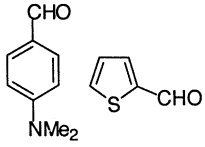
3f **3g**



3h **3i** **3j**



3k **3l**



3m **3n**

We were disappointed, however, when only the starting aldehyde **3a** was recovered in reactions in which benzaldehyde (**3a**) was reacted with ethyl acetate (**2a**) at 30–40°C using 20 mol% of **1b** in the presence of THF for 6 h. Reactions in ether, benzene, and pentane gave similar results (Table 1). Although the reaction in ethyl acetate (**2a**) was encouraging (28% conversion to the desired product), we were disappointed to observe an overall 56% conversion to

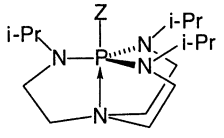
Table 2. The reaction of esters with aldehydes in the presence of 1.06 equiv. of **1a–c**

Starting materials	Base	T (°C)/time (h)	% Yield[a] (E/Z)[b] of product
3a+**2a**	**1b**	40/2	96 (100:0)
3a+**2b**	**1b**	40/2	91 (10:1)
3c+**2a**	**1b**	40/2	95 (100:0)
3c+**2b**	**1b**	40/2	93 (9:1)
3d+**2a**	**1b**	40/6	73(5:3)
3d+**2b**	**1b**	50/6	40 (1:1)
3h+**2a**	**1b**	30/2	0[c]
3i+**2a**	**1b**	30/2	0[c]
3l+**2a**	**1b**	40/2	67 (100:0)
3m+**2a**	**1b**	40/6	0
3a+**2a**	**1a**	40/2	83 (100:0)
3a+**2a**	**1c**	40/2	94 (100:0)
3d+**2a**	**1a**	40/2	61 (2:1)
3d+**2a**	**1c**	40/2	75(9:4)

The reactions were carried out in isobutyronitrile as solvent.
[a] Isolated yield.
[b] Determined by ^{1}H NMR integration.
[c] None of the starting aldehyde was observed in the reaction mixture.

a 1:1 mixture of the desired product and the intermediate β-hydroxy ester. Upon extending the reaction time to 12 h, the product mixture consisted of 37% of the desired product and 13% of the intermediate alcohol. By contrast, a reaction monitored by ^{31}P NMR spectroscopy indicated that the base (**1b**) was completely converted to **1b**H$^+$ after 4 h at 40°C.

Since the α-methyl group protons in ethyl acetate are more acidic than the hydrogens in acetonitrile by about three-fold,[34] we thought that perhaps the preferential deprotonation of the ester in acetonitrile might favor α,β-unsaturated ester formation. Experimentally, however, the reaction of **3a** with **2a** in acetonitrile in the presence of **1b** gave the β-hydroxy nitrile (66% conversion) as the major product (Table 1) while showing only a 20% conversion to the desired α,β-unsaturated ester as estimated by ^{1}H NMR integration. Therefore we elected to try *iso*-butyronitrile (also a polar nitrile) as the solvent, since its addition to aldehydes would be less favored (see later) because of its greater steric hindrance. At the same time, we expected to maintain the strong basicity of the pro-azaphosphatranes[25,35] (pK_a~33.6 for **1a** in acetonitrile[35c]) by using an analogous nitrile solvent. A perhaps more convincing reason to use a nitrile solvent was our observation that the protonation of **1b** is not detectable by ^{31}P NMR analysis in neat dry methyl ethyl ketone/dry C_6D_6 or in dry acid-free ethyl acetate/dry C_6D_6 at room temperature up to 40°C for 1 h. On the other hand a solution of 60 mg of **1b** in 0.75 mL of a 1:1 mixture of dry CD_3CN and methyl ethyl ketone instantaneously formed **1b**, **1b**H$^+$, and **1b**D$^+$ in a ratio of 76:7:17 as shown by ^{1}H NMR spectroscopy.



	Z
1bH$^+$	H
1bD$^+$	D

A comparable ratio (81:5:14) was observed under similar conditions for a 1:1 mixture of dry CD_3CN and ethyl acetate. These observations are consistent with a higher basicity of **1b** in acetonitrile, and/or prior deprotonation of acetonitrile by **1b** with subsequent deprotonation of the ester or ketone by the $^-CH_2CN$ ion that is produced. In a similar way, we found that a solution of **1b** in a 1:1 mixture of *iso*-butyronitrile and ethyl acetate led to the formation of **1b** and **1b**H$^+$ in a ratio of 84:16 in about 20 min. These experiments indicate either a stronger basicity of **1b** in this mixed solvent medium than in neat ethyl acetate, or that a proton transfer equilibrium is reached more rapidly via the $^-CH_2CN$ or $^-C(Me_2)CN$ ion. In a competitive study, we found that only addition of $^-CH_2CN$ to **3a** occurred in the presence of a 1:1 mixture of CH_3CN and Me_2CHCN. Furthermore, we had already established that acetonitrile reacts quantitatively with aldehydes in 2.5–4 h to form α,β-unsaturated nitriles,[28] glutaronitriles or β-hydroxynitriles.[30] In contrast, less than 10% addition of *iso*-butyronitrile to benzaldehyde (**3a**) occurs over 6 h under identical conditions to form the corresponding β-hydroxy nitrile.

The reaction of **3a** with ethyl acetate in the presence of *iso*-butyronitrile and 20 mol% of **1b** resulted in only a 22% conversion as estimated by ^{1}H NMR integration, and we attributed this to the stoichiometric nature of the reaction imposed by the inability of both OH^- and the secondary β-alkoxy anion to deprotonate the azaphosphatrane cation **1b**H$^+$ appreciably.[25] When the reaction of benzaldehyde (**3a**) with ethyl acetate was repeated in the presence of 1.06 equiv. of **1b**, a 96% yield of ethyl *E*-cinnamate was obtained as the only product (Table 2). The reaction of *p*-anisaldehyde (**3d**) proceeded in 73% yield (84% conversion) while *p*-dimethylamino benzaldehyde (**3m**) did not react under these conditions (Table 2). The inability of *p*-dimethylaminobenzaldehyde to react under our conditions is in accord with our previous experience with this substrate in the attempted synthesis of its corresponding β-hydroxy nitrile.[29] The reaction of *p*-chlorobenzaldehyde (**3c**) on the other hand produced the corresponding α,β-unsaturated ester in excellent yield (Table 2). The reaction of methyl propionate (**2b**) was found to be less stereoselective, although the major product was the *E*-isomer (Table 2). Table 2 also shows that both **1b** and **1c** are efficient bases for the preparation of unsaturated esters, but that probably because of its somewhat lower basicity,[24] **1a** is less efficient.

The production of some *Z*-olefin from **3d** and the low conversion of **3l** (although comparable with recently reported results[5–8]) was rather disappointing, spurring us to seek alternative conditions under which higher selectivities could be realized. We subsequently observed that the use of ethyl acetate as the solvent, although producing a mixture of the corresponding *E*-α,β-unsaturated ester and β-hydroxy ester (Table 1), failed to produce detectable amounts of the *Z*-isomer. When an acid-free sample of ethyl acetate was used as the solvent, the conversions using 0.2 and 0.5 mol equiv. of **1b** in separate reactions were found to be 30 and 79%, respectively, in 6 h at 50°C (Table 3). With 1.2 equiv. of **1b**, however, the conversion was quantitative over 6 h at 50°C (Table 3). This table also shows that neither **1a** nor **1c** efficiently promotes the preparation of the *E*-α,β-unsaturated esters in ethyl acetate. Lower yields with **1c** are attributed to the requirement for elevated temperatures at which this base is relatively unstable with respect to oligomerization[26] compared with

Table 3. Reactions of ethyl acetate (**2a**) with aldehydes in the presence of bases **1a–c**

Aldehyde	Base	*T* (°C)/time (h)	% Yield[a] of *E*-product
3a	**1b**[b]	50/6	30
3a	**1b**[c]	50/6	73
3a	**1b**	50/6	96
3b	**1b**	50/6	95
3c	**1b**	50/6	98
3d	**1b**	50/6	60
3e	**1b**	50/6	91
3f	**1b**	50/6	82
3g	**1b**	50/6	95
3h	**1b**	30/4[d]	0
3i	**1b**	30/4[d]	0
3j	**1b**	50/6	96
3k	**1b**	50/6	96
3l	**1b**	50/6	88
3m	**1b**	50/18	0
3n	**1b**	50/6	98
3c	**1a**	40/12	(89)[e]
3c	**1c**	40/12	(82)[e]
3d	**1a**	40/12	(50)[e]
3d	**1c**	40/12	(55)[e]

The amount of **1** used was 1.06 equiv. unless stated otherwise.
[a] Isolated yield after column chromatography.
[b] The amount of **1b** used was 0.2 equiv.
[c] The amount of **1b** used was 0.5 equiv.
[d] All the aldehydes were consumed after 4 h with no detectable formation of the expected unsaturated esters.
[e] Conversion as estimated by ^{1}H NMR spectroscopic integration.

1b, while lower yields with **1a** are attributable to its lower basicity.

The efficacy of our methodology is demonstrated by the high yields and selectivities compared with those reported by Kayser et al.[36] (36–95% yields, 100:0–70:30 *E*/*Z* ratios), Fujimura et al. (85–92% yields, >99:1–90:10 *E*/*Z* ratios)[6] and Sano et al.[5] (29–100% yields, 100:0–6:94 *E*/*Z* ratios). The reactions of the aliphatic aldehydes **3i** and **3h** produced none of the expected unsaturated ester, and no starting material is either recovered or observed in a ^{1}H NMR-monitored reaction after 4 h. The unpredictable reactivity of **3h** is not surprising and is in accord with our previous findings,[28,29] but the inability of **3i** to afford the desired unsaturated ester is unexpected. However, in another study, we found that γ-alkyl and γ,γ-dialkyl substituted α,β-unsaturated nitriles are able to dimerize and oligomerize in the presence of bases of type **1**.[29] In the reactions of the two substrates **3h** and **3i**, we observed that like ethyl *E*-crotonate,[6] they oligomerize in the presence of **1b**. Perhaps, the corresponding α,β-unsaturated ester produced oligomerizes upon formation. Although **3f** is somewhat sterically hindered and also experiences reduced reactivity because of possible resonance with the *o*-methoxy group, the desired unsaturated ester is produced in 82% yield.

Table 4. The reaction of methyl propionate **2b** with aldehydes in the presence of 1.2 equiv. of **1b**

Substrate	*T* (°C)/time (h)	% Yield of *E*-product
3a	50/6	93
3b	50/6	93[a]
3c	50/6	95
3d	50/6	68
3e	50/6	87
3f	50/6	88
3g	50/6	76
3h	40/4	0
3i	40/4	0
3j	50/6	83
3k	50/6	91
3l	50/6	64[a]
3m	50/18	0
3n	50/6	98

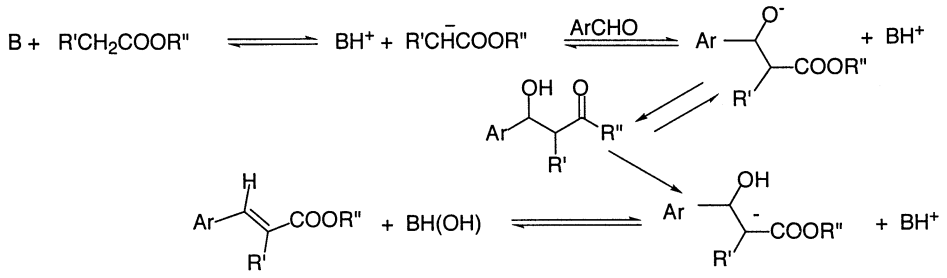
[a] A trace amount of the *Z*-isomer was observed but was not separated from the major *E*-isomer.

Motivated by these results, we explored the selectivity of reaction (1) for the synthesis of trisubstituted α,β-unsaturated esters. In the presence of 1.06 equiv. of **1b** at 50°C, benzaldehyde (**3a**) reacted with **2b** in 6 h to provide a 95% conversion to the corresponding trisubstituted α,β-unsaturated ester as the sole product as shown by TLC, ^{1}H and ^{13}C NMR analyses. In the presence of 1.2 equiv. of **1b** the reaction was quantitative. The reactions of 4-fluorobenzaldehyde (**3b**) or 4-chlorobenzaldehyde (**3c**) with methyl propionate (**2b**) at 50°C for 6 h were quantitative and afforded single products as well. Comparison of the ^{1}H NMR spectra of these products to those reported in the literature[36] showed that we obtained the *E*-isomer[36,37] of the expected esters with excellent selectivity. All disubstituted olefins were found to have vinylic coupling constants of 16–20 Hz typical of *trans* double bonds, while the trisubstituted alkenes showed a broad singlet or doublets with J=1–2 Hz in the region 7.5–8.0 ppm. It is worth mentioning that *Z*-trisubstituted olefins of this type display a broad singlet in the region 6.50–7.00 ppm. We therefore repeated the reaction for a variety of aldehydes and the results of these experiments are shown in Table 4. This table shows that in addition to excellent selectivity, the isolated yields range from very good to excellent with the exception of *p*-anisaldehyde (**3d**) which gave a moderate yield, and *p*-dimethyaminobenzaldehyde (**3m**) which does not react under our conditions. The use of molecular sieves in these reactions proved fruitless. An important advantage of our methodology is also evident from the high conversions and isolated yields obtained in the reaction of **2b** with the sterically hindered aldehydes **3e** and **3g** to form the corresponding new trisubstituted *E*-α,β-unsaturated esters.

The proposed pathway of this reaction shown in Scheme 1 is initiated with a pre-equilibrium that lies far to the left. Since the α-protons of ketones are more acidic than those of esters,[32] we expected bases of type **1** to catalyze a cross-aldol condensation between ketones and aldehydes. Because of the sterically hindered nature of the pro-azaphosphatranes, we believed they would be able to regioselectively deprotonate the less hindered methyl protons in methyl ethyl ketone. However, in the presence of Me_2CHCN, ether or THF as the solvent, the reaction mixture utilizing either **1a** or **1b** did not afford consistent formation of the expected unsaturated ketone PhCH═CHCOEt.

3. Conclusions

We have shown that the pro-azaphosphatrane **1b** is an efficient base for the direct synthesis of α,β-unsaturated



Scheme 1.

esters from the corresponding aldehydes and esters in excellent *E*-stereoselectivity. This reaction can be carried out in isobutyronitrile as a solvent or in the presence of excess dry acid-free ester as the reactant and solvent. The reaction of methyl propionate with aldehydes gives the corresponding trisubstituted α,β-unsaturated esters with excellent *E*-selectivity. Since the base can be efficiently recovered for recycling (see Section 4) the only waste product in reaction (1) is water.

4. Experimental

All reactions were carried out under nitrogen. The esters (ethyl acetate and methyl propionate) were purchased from Aldrich Chemical Company and were dried according to standard procedures[38] and then stored under nitrogen over 4 Å molecular sieves. The bases **1a**–**1c** were prepared according to previously reported methods.[23–25]

4.1. Procedure for the preparation of α,β-unsaturated esters in isobutyronitrile

In a typical experiment, 2.00 mmol of the aldehyde was dissolved in isobutyronitrile (2.0 mL) in a small flask preflushed with nitrogen. A solution of 2.10 mmol of **1** (449 mg of **1a**, 636 mg of **1b** or 547 mg of **1c**) in 1.0 mL of isobutyronitrile was then prepared in another flask under nitrogen. To this solution was added 2.1 mmol of the ester (ethyl acetate or methyl propionate). This solution was then added to the solution of the aldehyde and stirring was continued while the mixture was warmed under the conditions stated in Table 2. At the end of the reaction time the reaction mixture was allowed to cool to room temperature. The crude reaction mixture was then loaded onto a small silica gel column and column filtered with 100% ether. The crude product was purified when necessary by fractionation on a silica gel column using an eluent system consisting of hexane and ethyl acetate. The esters eluted with 30% EtOAc in hexane. The esters from **3f**, **3l**, **3n** did not separate well with the ethyl acetate/hexanes eluent system and were thus eluted with a hexanes/ethyl ether solvent system, eluting at 40% ether in hexanes.

4.2. Procedure for the preparation of α,β-unsaturated esters in ethyl acetate

In a typical experiment 2.10 mmol of **1** (449 mg of **1a**, 636 mg of **1b** or 547 mg of **1c**) was dissolved in dry ethyl acetate (2.0 mL) in a small flask preflushed with nitrogen. The solution was warmed at 50°C for 2 min. To this solution was added 2.00 mmol of the aldehyde and then the mixture was stirred for 6 h at 50°C. After cooling the reaction mixture to room temperature, the crude product was loaded onto a small silica gel column and column filtered with 100% ethyl ether. When necessary, purification was achieved as detailed above.

4.3. Procedure for the preparation of α,β-unsaturated esters in methyl propionate

In a typical experiment 2.40 mmol of **1b** (720 mg) was dissolved in dry methyl propionate (2.0 mL) in a small flask preflushed with nitrogen. The solution was warmed at 50°C for 2 min. To this solution was added 2.00 mmol of the aldehyde and then the mixture was stirred for 6 h. The process was continued as stated above for ethyl actetate.

4.4. Catalyst recovery

After the reaction times given in Tables 2–4, the solvent was removed under reduced pressure and then the mixture was dissolved in the least amount of water and extracted with 5×20 mL portions of ether. The ether extracts were dried over anhydrous potassium carbonate and the solvent was removed under reduced pressure to afford the crude ester. The aqueous layer was then treated with 5 mL of 1.0 M HCl and extracted with 4×10 mL portions of methylene chloride. The combined extracts were dried over anhydrous magnesium sulfate followed by removal of the solvent under reduced pressure affording the protonated base in 81% yield. This base hydrochloride can be deprotonated according to our previously published methods.[23–25] The yields of the α,β-unsaturated esters obtained by this workup procedure are slightly lower (by about 5%) than those obtained by the column filtration method given above.

4.5. Supporting information

^{1}H and ^{13}C NMR data and mass spectral molecular weights is available upon request.

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References

1. Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863 and references therein.
2. Kojima, S.; Takagi, R.; Akiba, K. *J. Am. Chem. Soc.* **1997**, *119*, 5970.
3. Ando, K. *J. Org. Chem.* **1997**, *62*, 1934.
4. Mouloungui, Z.; Elmestour, R.; Delmas, M.; Gaset, A. *Tetrahedron* **1992**, *48*, 2119.
5. Sano, S.; Yokoyama, K.; Fukushima, M.; Yagi, T.; Nagao, Y. *Chem. Commun.* **1997**, 559.
6. Fujimura, O.; Honoma, T. *Tetrahedron Lett.* **1998**, *39*, 625.
7. Ledord, B. E.; Carreira, E. M. *Tetrahedron Lett.* **1997**, *38*, 8125.
8. Herrmann, W. A.; Wang, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1641.
9. Lao, Y.; Huang, Y. *Tetrahedron Lett.* **1990**, *31*, 5897.
10. Xu, C.; Chen, G.; Fu, C.; Huang, X. *Synth. Commun.* **1995**, *25*, 2229.
11. Dhavale, D. D.; Sindkhedkar, M. D.; Mali, R. S. *J. Chem. Res. (Synopsis)* **1995**, 414.
12. (a) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780. (b) Bellassoued, M.; Majidi, A. *J. Org. Chem.* **1993**, *58*, 2517 and references cited therein. For reviews, see: (c) Ager, D. J. *Synthesis* **1984**, 384 and Ager, D. *J. Org. React.*, **1990**, *38*, 1.
13. Bellassoued, M.; Ozanne, N. *J. Org. Chem.* **1995**, *60*, 6582 and references therein.
14. For recent references see: (a) Markó, I. E.; Murphy, F.; Dolan, S. *Tetrahedron Lett.* **1996**, *37*, 2089. (b) Keck, G. E.; Savin, K. A.; Weglarz, M. A. *J. Org. Chem.* **1995**, *60*, 3194. For a recent review see: (c) Breit, B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 453 and references therein.
15. For recent references see: (a) Rossi, R.; Carpita, A.; Cossi, P. *Tetrahedron* **1992**, *48*, 8801. (b) Bellina, F.; Carpita, A.; De'Santis, M.; Rossi, R. *Tetrahedron* **1994**, *41*, 12029. (c) Satoh, T.; Yamada, N.; Asano, T. *Tetrahedron Lett.* **1998**, *39*, 6935.
16. Castells, J.; Lopez-Calahorra, F.; Yu, Z. *Tetrahedron* **1994**, *50*, 13765.
17. Ruhong, K.; Jianrong, H. *Huaxue Shiji* **1997**, *19*, 308 *Chem. Abstr.*, **1997**, *127*, 331257..
18. Beller, M.; Riermeier, T. *Tetrahedron Lett.* **1996**, *37*, 6535.
19. Cho, C. S.; Uemura, S. *J. Organomet. Chem.* **1994**, *465*, 85.
20. Kelkar, A. A. *Tetrahedron Lett.* **1996**, *37*, 8917.
21. Barbero, A.; Blanco, Y.; Garcia, C.; Pulidao, F. J. *Synthesis* **2000**, *9*, 1223.
22. (a) Somarekharan, K. N.; Kiefer, E. I. *Indian J. Chem. Sect. B* **1988**, *27*, 29. (b) Poonia, N. S.; Sen, S.; Prowal, P. K.; Jayakummar, A. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3338. (c) Simonyan, A. V. *Pharm. Chem. J.* **1999**, *33*, 158 (English translation).
23. Schmidt, H.; Lensink, C.; Xi, S. K.; Verkade, J. G. Z. *Anorg. Allg. Chem.* **1989**, *578*, 75.
24. (a) Tang, J.-S.; Verkade, J. G. US Patent 5,260,436, 1993; *Chem. Abstr.*, **1994**, *120*, 218836. (b) Tang, J.-S.; Verkade, J. G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 896. (c) Tang, J.-S.; Verkade, J. G. US Patent 5367084; *Chem Abstr.*, **1995**, *123*, 83101. (d) Tang, J.-S.; Verkade, J. G. US Patent 5554746, 1996; *Chem. Abstr.*, **1997**, *127*, 307251. (e) Tang, J.-S.; Verkade, J. G. *J. Org. Chem.* **1994**, *59*, 7793. (f) Arumugam, S.; McLeod, D.; Verkade, J. G. *J. Org. Chem.* **1997**, *62*, 4827.
25. Wroblewski, A.; Pinkas, J.; Verkade, J. G. *Main Group Chem.* **1995**, *1*, 69.
26 D'Sa, B.; Verkade, J. G. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1997**, *123*, 301.
27. Wang, Z.; Kisanga, P.; Verkade, J. *J. Org. Chem.* **2000**, *64*, 6459.
28. D'Sa, B.; Kisanga, P.; Verkade, J. *J. Org. Chem.* **1998**, *63*, 3691.
29. Kisanga, P.; D'Sa, B.; Verkade, J. *J. Org. Chem.* **1998**, *63*, 10057.
30. Kisanga, P.; McLeod, D.; D'Sa, B.; Verkade, J. *J. Org. Chem.* **1999**, *64*, 3090.
31. Kisanga, P.; Verkade, J. *J. Org. Chem.* **1999**, *64*, 4298.
32. (a) D'Sa, B.; Verkade, J. G. *J. Am. Chem. Soc.* **1996**, *118*, 832. (b) D'Sa, B.; Verkade, J. G. *J. Org. Chem.* **1996**, *61*, 2963.
33. Ilankumaran, P.; Verkade, J. G. *J. Org. Chem.* **1999**, *64*, 3086.
34. Schwesinger, R.; Schlemper, H.; Hasenfratz, C.; Willaredt, J.; Dambacher, T.; Breuer, T.; Ottaway, C.; Fletschinger, M.; Boele, J.; Fritz, H.; Putzas, D.; Rotter, H. W.; Bordwell, F. G.; Satish, A. V.; Ji, G.-Z.; Peters, E.-M.; Peters, K.; von Schnering, H. G.; Walz, L. *Liebigs Ann.* **1996**, 1055.
35. (a) Laramay, M. A. H.; Verkade, J. G. *Anorg. Allg. Chem.* **1991**, *605*, 163. (b) Arnett, E. M.; Small, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 808. (c) Kisanga, P.; Verkade, J. G.; Schwesinger, R. *J. Org. Chem.* **2000**, *65*, 5431.
36. Kayser, M. M.; Zhu, J.; Hooper, D. L. *Can. J. Chem.* **1997**, *75*, 1315.
37. (a) Miyata, O.; Shinada, T.; Ninomiya, I.; Naito, T. *Synthesis* **1990**, 1123. (b) Heerdan, S.; Bezuidenhoudt, B. C. B.; Ferreira, D. *Tetrahedron* **1996**, *52*, 12313.
38. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; 3rd ed.; Permagon: New York, 1988 p 175.