On the stereochemistry of the Horner—Emmons reaction between 3-functionally substituted 2-methyl-2-propenylphosphonates and aliphatic aldehydes

7*. Quaternary ammonium phase transfer catalysts in a stereoselective synthesis of esters of 3-methyl-2*E*,4*E*-alkadienoic acids

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The reaction of diethyl 3-ethoxycarbonyl-2-methyl-2-propenylphosphonate (**1a**) with 3-methylbutanal (**2**) in heterogeneous MOH (solid)—benzene systems in the presence of 5—10 mol.% of benzyltriethylammonium chloride (BTEAC) gives the reaction product (**3**) with a higher, for M = K, or lower, for M = Li, ratio of 2*E*,4*E*- and 2*Z*,4*E*-stereoisomers than that observed in the absence of BTEAC. Tetrabutylammonium bromide (TBAB) as a catalyst of the reaction **1a** + **2** → **3** in the system KOH (solid)—wet benzene leads to a higher [2*E*,4*E*-**3**]:[2*Z*,4*E*-**3**] ratio than BTEAC; this ratio grows from 44:56 without TBAB to 80:20 at 100 mol.% of TBAB. In the latter case the stereochemical outcome of the reaction is similar to that obtained when tetrabutylammonium hydroxide in dry benzene is used as the deprotonating agent. The corresponding diisopropyl phosphonate (**1b**) and 3,7-dimethyloctanal (**4a**) interact in the system KOH (solid)—wet benzene—TBAB to give hydroprene (**5**) containing 88 % of the 2*E*,4*E*-isomer (**5a**) while in the case of 1 equiv. of [(*n*-Bu_4)N]OH in dry benzene the content of **5a** is 92 %. Diisopropyl 3-isopropoxycarbonyl-2-methyl-2-propenylphosphonate (**1c**) and 7-methoxy-3,7-dimethyloctanal (**4b**) under either of these conditions afford methoprene (**6**) containing 93 % of the 2*E*,4*E*-isomer.

Key words: heterogeneous systems; tetraalkylammonium halides; concentration effect; the effect of water; tetrabutylammonium hydroxide; hydroprene; methoprene.

In previous reports[2—6] we have considered the influence of various factors on the stereoselectivity of the Horner—Emmons reaction of diethyl 3-ethoxycarbonyl-2-methyl-2-propenylphosphonate (**1a**) and its analogs with 3-methylbutanal (**2**) and its analogs under conditions of phase transfer catalysis (PTC).

$$(EtO)_2P(O)CH_2CMe{=}CHCO_2Et + Me_2CHCH_2CHO + OH^- \longrightarrow$$
$$\textbf{1a} \qquad\qquad \textbf{2} \qquad\qquad (1)$$
$$\longrightarrow Me_2CHCH_2CH{=}CH{-}CMe{=}CHCO_2Et + {}^-O_2P(OEt)_2 + H_2O$$
$$\textbf{3a}\ (2E,4E)$$
$$\textbf{3b}\ (2Z,4E)$$

As has been shown in the preceding communication,[1] the addition of crown ethers to a heterogeneous MOH(solid)—benzene system (M = Na, K) leads to a substantial increase in the ratio of the 2*E*,4*E*- to the 2*Z*,4*E*-stereoisomer of ethyl 3,7-dimethyl-2,4-octadienoate (**3a** and **3b**, respectively), the isomer **3a** becoming the predominant reaction product. It was also found in the same work that in the (homogeneous in appearance) tetraalkylammonium hydroxide (QOH)—benzene system, when the deprotonating agent QOH was present in the stoichiometric amount, the **3a**:**3b** ratio in the reaction product was considerably higher than with the use of MOH in the absence of crown ethers and sometimes even somewhat higher than that in the presence of the latter.

In this work we have studied the effect of another type of PTC, quaternary ammonium halides (QHal), on the stereochemical route of the reaction. First, we studied the effect of the addition of 10 mol.% of benzyltriethylammonium chloride (BTEAC) on the stereochemistry of the reaction **1a** + **2** → **3a** + **3b** carried out in the KOH(solid)—benzene or LiOH

* Part 6, see ref. 1.

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Table 1. Dynamics of the *E*/*Z* isomeric ratio in the starting phosphonate **1a**, and of the 2*E*,4*E*/2*Z*,4*E* ratio in the resulting ethyl dienoate **3** in the presence of 10 mol.% of benzyltriethylammonium chloride (BTEAC) in a heterogeneous MOH(solid)—benzene system

Time /min	KOH		LiOH	
	E-**1a** : *Z*-**1a**	**3a** : **3b**	*E*-**1a** : *Z*-**1a**	**3a** : **3b**
0	56:44		56:44	
1	50:50		56:44	
2	46:54		56:44	
5	39:61		55:45	
10	39:61	56:44	50:50	
15	38:62	56:44	55:45	
30	38:62	58:42	44:56	
60	39:61	57:43	44:56	
120	37:63	57:43	38:62	78:22
240	36:64	58:42	36:64	72:28
480	38:62	58:42	34:66	70:30
1440	—	—	34:66	60:40
2880	—	—	34:66	60:40

Note. The [**1a**]:[**2**]:[MOH]:[QHal] ratios were in both cases 0.33:0.33:0.66:0.033 *M* at 22 °C. The volume of the solvent was 30 mL.

(solid)—benzene system, as well as on the dynamics of the establishment of the stationary equilibrium between *E* and *Z* isomers of phosphonate **1a** (Table 1). The *E*-**1a**:*Z*-**1a** ratio in the starting **1a** was 56:44; it is known[1–8] that this ratio exerts practically no effect on the stereochemical outcome of the reaction.

As Table 1 indicates, the addition of BTEAC to the KOH—benzene system results in the fast establishment of the equilibrium between *E*-**1a** and *Z*-**1a** and in rapid formation and accumulation of the reaction products, their ratio remaining practically constant. However, the prevalence of **3a** over **3b** is less than when 18-crown-6 ether is used instead of BTEAC (*cf.* ref. 1). In the LiOH—benzene system the addition of 10 mol.% of BTEAC does not cause the fast establishment of the *E*-**1a**, *Z*-**1a** equilibrium, and the **3a**:**3b** ratio in the slowly accumulating reaction product is maximum at the beginning and then steadily decreases to the stationary equilibrium value. The course of the reaction and the resulting ratio of the stereoisomers in the reaction product almost do not differ from those for the LiOH—benzene system in the absence of a PT-catalyst. In particular, the lag-period in the establishment of the *E*-**1a**:*Z*-**1a** and **3a**:**3b** equilibrium ratios is the same as in the absence of BTEAC. The results obtained can be explained by the assumption that the reaction proceeds by two concurrent pathways: with and without involvement of QHal.

Since an increase in the radius of the tetraalkylammonium cation Q^+ has been shown to result in an increase in the **3a**:**3b** ratio in the QOH—benzene system,[1] we have used tetrabutylammonium bromide (TBAB) instead of BTEAC. In fact, the **3a**:**3b** ratio in the KOH(solid)—benzene system increased noticeably on the replacement of BTEAC by TBAB (Table 2). It should be noted that in the latter case the reaction proceeds efficiently in the presence of a small amount of water (~0.1 mL) in addition to the equilibrium amount present in wet benzene. We suppose that with this amount of water added to the system the bulk of the KOH exists as a solid phase, while a small amount of a saturated aqueous KOH solution ("a liquid microphase") facilitates the necessary cation exchange at the interphase boundary. When the system KOH(solid)—dry benzene—TBAB is used, the catalytic effect of TBAB affects neither the **3a**:**3b** ratio nor the overall rate of the process.*

Table 2. Effect of the addition of 1 equiv. of QHal on the stationary equilibrium *E*-**1a** ⇌ *Z*-**1a** and on the final **3a**:**3b** ratio in the KOH (solid)—benzene system

QHal	*E*-**1a** : *Z*-**1a**	**3a** : **3b**
—	36:64	44:56
BTEAC	38:62	65:35
TBAB	40:60	80:20*

Note. Benzene was saturated with water at 22 °C, 0.3—0.5 vol.% of additional water was present in the system.
* For the homogeneous system $[(n\text{-Bu})_4\text{N}]\text{OH}$ (1 equiv.) + **1a** + **2** in dry benzene at 22 °C the **3a**:**3b** ratio was found to be 86:14 (see ref. 1).

A comparison of the data of Table 2 concerning TBAB with the results obtained using the seemingly homogeneous tetrabutylammonium hydroxide—benzene system indicates that conversion **1a** + **2** → **3** under conditions similar to those for the extraction of ion pairs (*cf.* ref. 10) proceeds predominantly according to the pathway involving the effective formation of $[(n\text{-Bu})_4\text{N}]\text{OH}$ from $[(n\text{-Bu})_4\text{N}]\text{Br}$ and KOH.

In order to determine the optimal amount of TBAB which would provide the highest **3a**:**3b** ratio we examined the dependence of this ratio on the concentration of TBAB in the KOH—benzene system. We found that an increase in the amount of TBAB from 2.5 to 25 mol. % (relative to KOH) leads to a gradual increase in the content of **3a** in the reaction products from 63 % to 75 %. The highest stereoselectivity (**3a**:**3b** = 80:20) is only attained at equimolar amounts of KOH and TBAB, i.e., under conditions resembling those for the extraction of ion pairs. However, the overall rate of the process, which increases drastically with the introduction of even 2.5 mol.% TBAB to the heterogeneous system, is practically not changed with its further addi-

* Judging by the solubility of TBAB in hexane and toluene at 20 °C, which is 0.0 g and 0.3 g in 100 mL of the solvent, respectively,[9] the solubility of TBAB in benzene is ≤ 1 mmol L^{-1}. With such solubility in the absence of water a dense layer of chemisorbed QHal is likely to form on the surface of the solid base and to hamper the deprotonation of the phosphonate.

Table 3. The effect of the conditions of the reaction of aldehyde **4a** or **4b** with phosphonate **1b** or **1c** on the yield and the stereoisomeric composition of the resulting **5** or **6**

Run	X in **4**	R in **1**	Reaction conditions	Products (overall yield, %)	2*E*,4*E*: 2*Z*,4*E*
1	H	H	solid KOH (2 equiv.)—PhH	**5a** + **5b** (60)	45:55
2	H	H	solid KOH (2 equiv.)—PhH—[(*n*-Bu)$_4$N]Br (2 equiv.)	**5a** + **5b** (70)	88:12
3	H	H	[(*n*-Bu)$_4$N]OH (1 equiv.)—PhH	**5a** + **5b** (76)	92:8
4	MeO	Me	solid KOH (2 equiv.)—PhH	**6a** + **6b** (61)	30:70
5	MeO	Me	solid KOH (2 equiv.)—PhH—[(*n*-Bu)$_4$N]Br (0.1 equiv.)	**6a** + **6b** (74)	75:25
6	MeO	Me	solid KOH (2 equiv.)—PhH—[(*n*-Bu)$_4$N]Br (2 equiv.)	**6a** + **6b** (85)	93:7
7	MeO	Me	solid KOH (2 equiv.)—PhH—[(BnNEt$_3$]Cl (2 equiv.)	**6a** + **6b** (71)	80:20
8	MeO	Me	solid KOH (2 equiv.)—PhH—PhH—Catamine AB (2 equiv.)*	**6a** + **6b** (83)	80:20
9	MeO	Me	[(*n*-Bu)$_4$N]OH (1 equiv.)—PhH	**6a** + **6b** (96)	93:7
10	MeO	Me	[(*n*-Bu)$_4$N]OH (1 equiv.)—DMSO	**6a** + **6b** (95)	92:8

Note. In runs 2, 6, 7, 8 (extraction of ion pairs) ~0.5 vol.% of water was added to the system, in addition to that present in the water-saturated benzene.

*Catamine AB is a mixture of quaternary ammonium chlorides of the composition {Alk—NMe$_2$—Bn}Cl, where Alk is C$_{10}$—C$_{18}$.

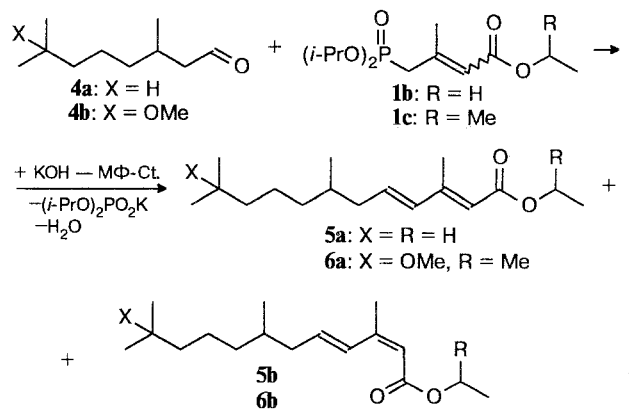
tion: in the absence of TBAB the reaction is complete in 24 h, while in the presence of 2.5—100 mol.% of TBAB it is finished in 2.5—3 h. The effect of the TBAB concentration on the stereoselectivity of olefination is in contrast to the previously observed[6] fact that an increase in the amount of 18-crown-6 ether added to the system from 10 to 100 mol.%, in relation to **1a** and **2**, does not change the **3a**:**3b** ratio in the KOH(solid)—benzene system.

The above mentioned regularities were confirmed as well in the reactions of the analogs of the ester **1a** with 3,7-dimethyloctanal (**4a**) and 7-methoxy-3,7-dimethyloctanal (**4b**) which afforded hydroprene (**5**) and methoprene (**6**), respectively, highly effective analogs of the insect juvenile hormone.

It is known[11] that among the four possible geometric isomers of hydroprene and methoprene the 2*E*,4*E*-isomers possess the highest morphogenetic activity. However, the stereospecific synthesis of these isomers is cumbersome and involves the use of organometallic compounds,[11—13] and can therefore be employed for preparation of only small amounts of standard samples. The alternative syntheses are β-methylglutaconate[14—17] and phosphonate[18—22] methods, in which the aldehyde C$_{10}$-component, **4a** or **4b**, is treated with a complementary (C$_6$ or C$_5$) ω-alkoxycarbonyl component, and then the product of the non-stereoselective olefination is converted in a number of steps (including separation of stereoisomers by crystallization) to the desired product containing ~90—92 % of the 2*E*,4*E*-isomer and 6—8 % of the 2*Z*,4*E*-isomer which has low biological activity. These methods are better for the industrial production of both juvenoids, but they are also laborious, multistep, and, as a consequence, the overall yield of the final product is low.

Since the condensation of aldehyde **4a** or **4b** with diisopropyl 3-ethoxycarbonyl-2-methyl-2-propenylphosphonate (**1b**) or 3-isopropoxycarbonyl-2-methyl-2-propenylphosphonate (**1c**), respectively, under PTC conditions yields **5** or **6** directly in a high yield and with ~85 % content of the biologically active 2*E*,4*E*-isomer (**5a** or **6a**, respectively) as a binary mixture with the corresponding 2*Z*,4*E*-isomer (**5b** or **6b**),[23,24] we decided to examine the possibility of further increasing the stereoselectivity of this reaction. Our experiments were based on a heterogeneous KOH(solid)—an aprotic organic solvent—PT-catalyst system, which combines the availability of the base and minimum risk of hydrolysis of **5** and **6** formed.

Taking into account the suggestion[18—20] that the reactions **1b** + **4a** and **1c** + **4b** could be carried out in benzene in the presence of NaOH, we carried out both reactions in the KOH(solid)—benzene system at 22 °C without a PT-catalyst. The yield of the binary mixture of stereoisomers **5a** + **5b** or **6a** + **6b** did not exceed 60 or 61 %, respectively, under the optimal conditions, and the 2*Z*,4*E*-isomers predominated in both cases in their binary mixtures with the 2*E*,4*E*-isomers (Table 3, runs 1 and 4)*.



* Similar stereoselectivity (2*Z*,4*E* > 2*E*,4*E*) was observed in the reaction of 3-methylbutanal with phosphonate **1a** in the same system (*cf.* ref. 2—6).

On the other hand, our data concerning the effect of the nature of the cation of the base on the stereochemistry of the Horner—Emmons reaction between the aldehyde **2** and phosphonate **1a** indicated that the application of tetraalkylammonium hydroxides[1] or equimolar amounts of an alkali metal hydroxide and tetraalkylammonium halide would be promising in the preparation of esters **5** and **6** with a high content of the required 2*E*,4*E*-isomer.

Actually, when the interaction between **4a** and **1b** or between **4b** and **1c** was carried out in the heterogeneous KOH(solid)—wet benzene—[(*n*-Bu)$_4$N]Br system, the overall yield of binary mixtures of stereoisomeric dienoates (**5a** + **5b**) or (**6a** + **6b**) was considerably higher, and the ratio of the isomers changed in favor of the 2*E*,4*E*-isomer (Table 3, runs 2 and 6). With equimolar amounts of KOH and the PT-catalyst and with the addition of a small amount of water to the system, the fraction of the 2*E*,4*E*-isomer of hydroprene was 88 % and that of methoprene was 93 % (Q = [(*n*-Bu)$_4$N]$^+$). When BTEAC or a commercial mixture of benzyl(*n*/*s*-alkyl)dimethylammonium chlorides, alkyl groups ranging from $C_{10}H_{21}$ to $C_{18}H_{37}$ (Catamine AB), was used as the PT-catalyst instead of TBAB, the stereoselectivity of the reaction decreased (*cf.* runs 6, 7, and 8, Table 3). This result is in agreement with the previously noted[1] dependence of the 2*E*,4*E*-selectivity of olefination on the effective radius of the cation Q$^+$ in the ion pair. Although the cations in BTEAC and in Catamine AB contain bulky groups (Bn and C_{10}—C_{18} alkyl), one can suggest that in the deprotonation of phosphonates **1b** and **1c** with QOH, as well as in the formation of ion pairs of Q$^+$ with *E*- and *Z*-isomers of the phosphonate carbanion, the partners approach each other from the least hindered side, and, as a consequence, BTEAC and Catamine AB are approximately equivalent to the tetraethylammonium cation. Therefore, the effective radius of the symmetrical [(*n*-Bu)$_4$N]$^+$ ion is greater than those of the cations in BTEAC and Catamine AB, and the **6a**:**6b** ratio is correspondingly higher as well.

As one would expect, the highest preparative yields of hydroprene and methoprene with the optimal **5a**:**5b** and **6a**:**6b** ratios were achieved when the reactions **4a** + **1b** → **5** and **4b** + **1c** → **6** were carried out in a seemingly homogeneous (possibly, micellar) system that contained the stoichiometric amount of [(*n*-Bu)$_4$N]OH in dry benzene. The reaction **4b** + **1c** → **6** in DMSO under the action of 1 equiv. of [(*n*-Bu)$_4$N]OH led to a comparable result (see Table 3, runs 9 and 10).

Thus, the use of an equimolar amount of higher tetraalkylammonium hydroxide in an aprotic organic solvent appears to be the shortest method for preparation of methoprene, hydroprene, and other derivatives of 3-methyl-2,4-alkadienoic acids with a high (up to 90 %) content of the 2*E*,4*E*-stereoisomer. Some of the inconvenience caused by the difficulties in preparing individual [R$_4$N]OH and their solutions in nonpolar solvents can easily be remedied by replacing these bases with a KOH—[R$_4$N]Hal combination, and carring out the reaction of aldehydes with type **1a**—**c** phosphonates in a wet hydrophobic solvent.

Experimental

The monitoring of the course of the reaction and control of the isomeric composition of the products was performed by GLC (a LKhM-80 instrument with a flame ionization detector equipped with a 1.5×0.003 m glass column packed with 5 % SE-30 or OV-17 on Chromaton N-AW-DMCS, using nitrogen as the carrier gas). ^{1}H NMR spectra were recorded on a Bruker WM-250 instrument (250 MHz) in $CDCl_3$.

The starting phosphonates 1a—c were prepared according to the known procedure.[25]

Interaction of phosphonate 1a with aldehyde 2 was carried out as described in ref. 1 except that the corresponding amounts of QHal were added. In the case of equimolar amounts of QHal, the reaction was carried out in the presence of a catalytic amount of water (0.3—0.5 vol.%).

The control of the reaction stereochemistry, sampling, and the workup of the samples prior to the analysis were carried out as described in ref. 1.

Preparation of hydroprene 5 and methoprene 6 (general procedure). To a stirred solution of 10 mmol of phosphonate **1b** or **1c**, 1.12 g of powdered KOH, 20 mmol of quaternary ammonium salt, and 0.1—0.15 mL of water in 30 mL of benzene were added dropwise. Then a solution of 10 mmol of aldehyde **4a** or **4b** in 2 mL of benzene was added at 20—22 °C, and the mixture was stirred for 2—3 h. When the reaction was over (according to GLC), the reaction mixture was poured onto 50 mL of ice-water and quickly extracted with benzene (3×30 mL). The combined organic extracts were washed with water (2×50 mL) and dried with $MgSO_4$. The solvent was evaporated and the residue was distilled *in vacuo* to yield **5** or **6**.

Hydroprene 5: b.p. 99—101 °C (0.1 Torr), n_D^{20} 1.4815. ^{1}H NMR, δ: 0.85 (d, *J* = 6 Hz, 9 H, 3 CH_3); 1.2 (t, *J* = 7 Hz, 3 H, CH_3); 0.99—1.78 (m, 10 H, 4 CH_2, 2 CH); 1.94 and 2.22 (both d, *J* = 1.5 Hz, 3 H, CH_3CH=); 4.07 (q, *J* = 7 Hz, 2 H, CH_2O); 5.5 (s, ~0.1 H, H-2); 5.6 (s, ~0.9 H, H-2); 6.05 (m, ~1.9 H, H-4 and H-5); 7.6 (d, *J* = 16 Hz, ~0.1 H, H-4).

Methoprene 6: b.p. 144—146 °C (0.5 Torr), n_D^{20} 1.4835. ^{1}H NMR, δ: 0.89 (d, *J* = 6 Hz, 3 H, CH_3); 1.08 (s, 6 H, 2 CH_3); 1.26 (d, *J* = 7 Hz, 6 H, 3 CH_3);1.4—2.0 (m, 9 H, 4 CH_2, CH); 1.9 and 2.2 (both d, *J* = 1.5 Hz, 3 H, CH_3C=); 4.9 (hp, *J* = 7 Hz, 1 H, $CHMe_2$); 5.5 (s, ~0.1 H, H-2); 5.57 (s, ~0.9 H, H-2); 6.0 (m, ~1.9 H, H-4 and H-5); 7.6 (d, *J* = 16 Hz, ~0.1 H, H-4).

The modification of the reaction in the absence of PT-catalyst was carried out as described above without the addition of the quaternary ammonium salt and water.

The modification with catalytic amounts of PT-catalyst was carried out as described above in the presence of 1 mmol of QHal and without water.

The modification with the quaternary ammonium hydroxide was carried out as described above in the presence of a solution of 10 mmol of [(*n*-Bu$_4$)N]OH in benzene or DMSO. This solution was prepared by the azeotropic distillation of MeOH from a mixture of a 25 % methanolic solution of [(*n*-Bu)$_4$N]OH with benzene (or DMSO) carried out on a rotary evaporator at 35—40 °C (40 Torr). With the repeated addition of benzene to the residue and the subsequent concentration of the mixture the initially heterogeneous system was transformed into a seemingly homogeneous liquid that was then used in the synthesis.

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Complexes of crown ethers with perfluorocarboxylic acids and their thermal decarboxylation

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Crown ethers form strong proton-acceptor complexes with CF_3COOH or C_4F_9COOH that undergo thermal decarboxylation at 200—260 °C which results in 60—80 % of CF_3H or C_4F_9H (including up to 20 % of a mixture of C_4F_8). Critical parameters of the process were determined in relation to the temperature and amount of crown ether. The relative activities of different crown ethers in decarboxylation were also established. A scheme is proposed that explains the effect of the structure of crown ethers on this reaction. The data obtained substantiate the view that the "topological correspondence" concept is insufficient to explain the ability of crown ethers to form complexes with cations.

Key words: crown ethers, perfluorocarboxylic acids, proton-accepting complexes, thermal decarboxylation, perfluorocarbanions.

Proton coordination with crown ethers (CE) has been established by different methods. The reason for the drastic increase in the conductivity of solutions of CF_3COOH (**1**) in dichloroethane upon addition of

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