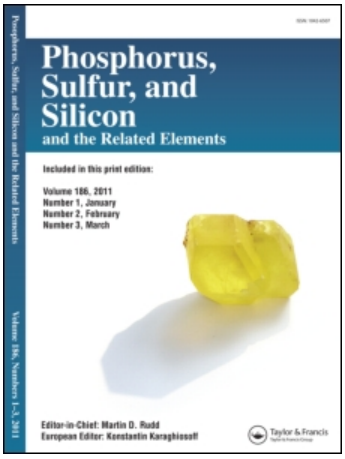

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OLEFIN FORMATION VIA *N,N,N',N'*-TETRAMETHYLDIAMIDES OF 1,2-DIARYL-2-HYDROXYETHANEPHOSPHONIC ACIDS IN ACIDIC MEDIA

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The olefin formation via the erythro-*N,N,N'N'*-tetramethyldiamides of 1,2-diaryl-2-hydroxyethanephosphonic acids **3, 4** in the presence of aqueous hydrochloric acid proceeds not stereospecifically, while in ethanolic solution of hydrochloric acid (Z)-stereospecific olefin formation predominantly takes place. The mechanism of the elimination process is discussed.

INTRODUCTION

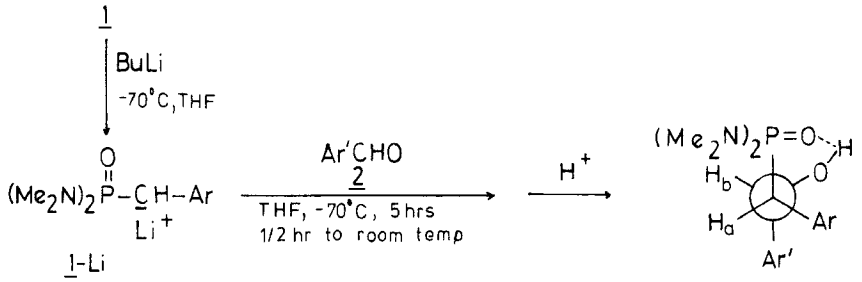
(Z)-Alkenes with high diastereomeric purity have been obtained very often by the two-stage reaction of Horner–Emmons. The first stage consists in the erythro-stereoselective addition of phosphine oxide[1,2] or phosphonamide[3,4] carbanions to carbonyl compounds and in the second stage the isolated intermediate stereospecifically (termally,[5] or in the presence of a strong base[1,2]) is cleaved. The high temperature required in the stage of elimination is a shortcoming in thermal olefination. It is partly avoided by the cleavage of the sodium salts of the phosphineoxide intermediates;[1,2] however the stereoselectivity is lost, when Ar or some other conjugating group are in the α-position to the P=O group. This is probably due to the existence of an equilibrium between the adducts and the initial reactants.[2]

The olefination via phosphonate intermediates in acid medium has not been studied profoundly.[3,6] It is shown that adducts obtained from phosphonate carbanions and N-benzoylketimines form alkenes in high yields[6] by heating with concentrated hydrochloric acid. But the clevage of tetramethyldiamides of 1,2-diphenyl-2-hydroxyethanephosphonic acid does not proceed stereospecifically[3] when heated under analogous conditions.

RESULTS

In the present work we report our results of further investigation on olefination of β-hydroxyphosphonamide adducts in acid medium. For this purpose a series of erythro-β-hydroxyphosphonamide adducts **3, 4** was used, obtained by addition of

lithium-*N,N,N',N'*-tetramethyldiamides of arylmethanephosphonic acids **1**-Li to aldehydes **2** in THF at −70°C[3,4] according to Scheme 1:



1a, 3 Ar = C_6H_5

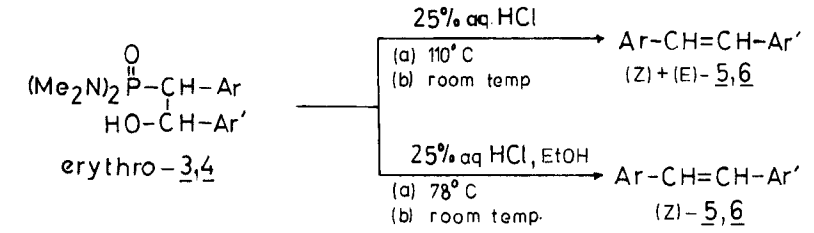
1b, 4 Ar = C_6H_4-Cl-(4)

2	Ar'
a	C_6H_5
b	C_6H_4-F-(4)
c	C_6H_4-F-(2)
d	C_6H_4-OCH_3-(4)
e	C_6H_4-OCH_3-(2)
f	C_6H_4-NO_2-(4)
g	C_6H_4-CH_3-(4)

SCHEME 1

The new synthesized adducts **3f** and **3g** were characterized by element analysis, IR and ^{1}H-NMR. Erythro-**3f** was isolated by double recrystallization of the crude product containing the two diastereomeres in a ratio erythro : threo = 2:3.

The adducts **3b–g** were treated as the adduct **3a**[3] by heating, **3**, respectively **4** with an excess of 25% hydrochloric acid for 1 hour at 110°C (see Scheme 2). We found that in all cases the reaction proceeds non-stereospecifically but with high yields (77–100%) forming mixtures of (Z)- and (E)-alkenes (Table I). When the



5: Ar = C_6H_5

6: Ar = C_6H_4-Cl-(4)

SCHEME 2

TABLE I

Yields and (Z)/(E) ratio of the olefins **5, 6** (ArCH=CHAr'), obtained from the erythro-**3, 4** in the presence of aqueous hydrochloric acid

			110°C (a)		Room temp. (b)	
No.	Ar	Ar'	Yield %	(Z)/(E)	Yield %	(Z)/(E)
5a	C_6H_5	C_6H_5	77	35/65	63	40/60
5b	C_6H_5	C_6H_4—F-(4)	99	60/40	44	60/40
5c	C_6H_5	C_6H_4—F-(2)	80	10/90		
5d	C_6H_5	C_6H_4—OCH_3-(4)	92	10/90		
5e	C_6H_5	C_6H_4—OCH_3-(2)	99	52/48		
6a	C_6H_4—Cl-(4)	C_6H_5	84	12/88		
6c	C_6H_4—Cl-(4)	C_6H_4—F-(2)			28	30/70
6d	C_6H_4—Cl-(4)	C_6H_4—OCH_3-(4)	99	25/75		
6e	C_6H_4—Cl-(4)	C_6H_4—OCH_3-(2)	98	32/68	51*	31/69

* The quantity of the unreacted adduct **4e** is 34%.

reaction temperature is reduced to room temperature the ratio (Z):(E) of the stilbenes **5a**, **5b**, **6c** and **6e** is practically not changed, but their yield is considerably reduced.

In all cases (exception **4e**) small quantities of unchanged starting material were isolated, indicating that side reactions probably take place.

With the aim to suppress the side reactions, the erythro-adducts **3, 4** were decomposed in ethanol in the presence of hydrochloric acid at room temperature or at reflux of the reaction mixture. In this case practically pure (Z)-alkenes were obtained, with the exception of **4c** at room temperature and **4d** at 78°C (Scheme 2, Table II).

TABLE II

Yields and (Z)/(E) ratio of the olefins **5, 6** (ArCh=CHAr'), obtained from the adducts erythro-**3, 4** in ethanolic solution of hydrochloric acid

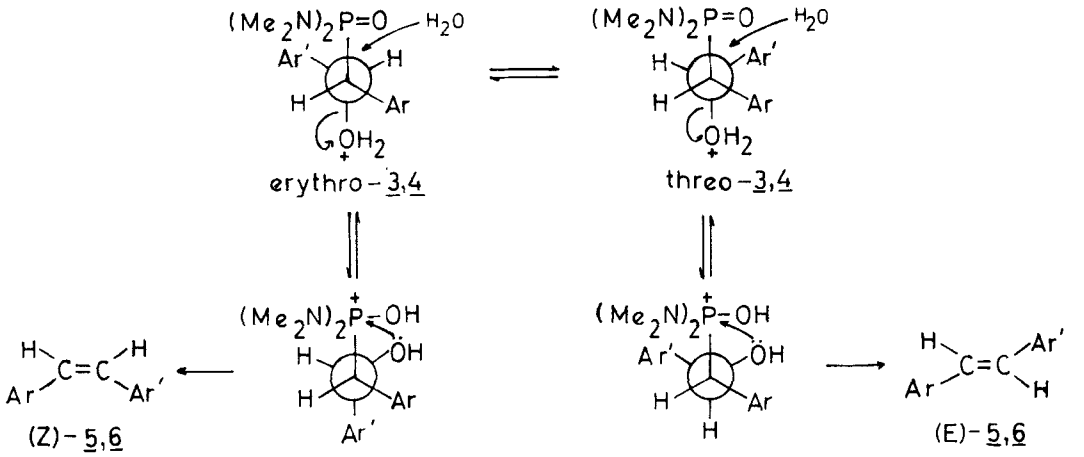
			78°C		Room temp.	
NO.	Ar	Ar'	Yield %	(Z)/(E)	Yield %	(Z)/(E)
5a	C_6H_5	C_6H_5	76	99/1*	74	99/1
5b	C_6H_5	C_6H_4—F-(4)			50	99/1
5e	C_6H_5	C_6H_4—OCH_3-(2)	99	99/1		
5g	C_6H_5	C_6H_4—CH_3-(4)	99	99/1	85	99/1
6b	C_6H_4—Cl-(4)	C_6H_4—F-(4)			50	99/1
6c	C_6H_4—Cl-(4)	C_6H_4—F-(2)			60	70/30
6d	C_6H_4—Cl-(4)	C_6H_4—OCH_3(4)	99	47/53		
6e	C_6H_4—Cl-(4)	C_6H_4—OCH_3-(2)	80	80/20	70	95/5

* Traces of (E)-**5, 6** only the tlc.

DISCUSSION

Experiments in the Presence of 25% Hydrochloric Acid

The higher part of (E)-stilbenes,obtained both at high and at room temperature (see Table I) can be explained with the preliminary epimerization of erythro-**3, 4**



SCHEME 3

to threo-**3**, **4** and a subsequent faster elimination of the threo-isomers (Scheme 3);

The high yield of the (E)-olefine starting with erythro-**3c** and **3d** could perhaps be explained with the specific influence of the fluorine atom, in the case of **3c** (Figure 1) or with the resonance stabilization of the obtained carbanion via the 4-CH_3O-group, in the case of **3d**.

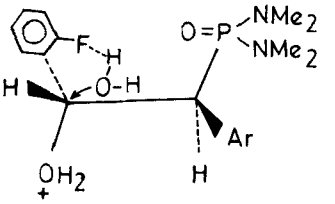
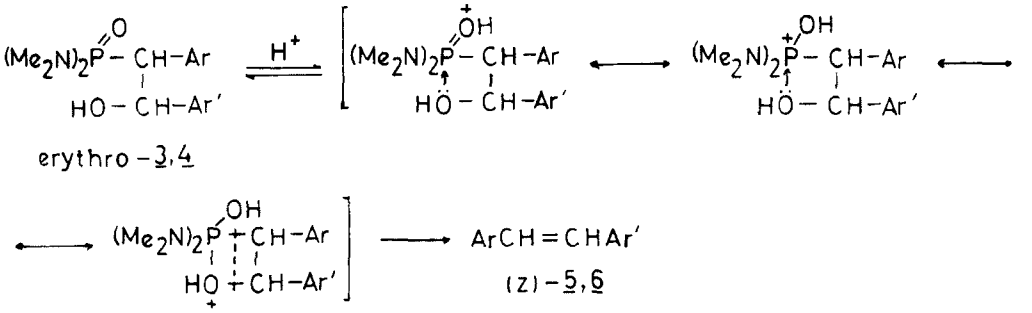


FIGURE 1

Experiments in Ethanolic Solution of Hydrochloric Acid

The (Z)-stereospecific cleavage of erythro-**3**, **4** probably proceeds as syn-elimination via cyclic intermediate. In this case the acid probably increases the electrophility of the phosphorus atom (Scheme 4).



SCHEME 4

This mechanism for the olefination in ethanol is in accordance wiht the data of our preliminary experiments on the kinetics of the reaction, which will be published latter.

It was experimentally proved that the direct isomerisation (Z)-stilbene→(E)-stilbene as well as (E)-stilbene→(Z)-stilbene does not take place in the presence of 25% hydrochloric acid (see Experimental).

EXPERIMENTAL

The ^{1}H-NMR spectra of the adducts **3, 4**, as well as of the olefins **5, 6** were recorded on TESLA-BS-487 spectrometer and in some cases on JEOL-JNM-100 spectrometer with TMS as internal standard, using $CDCl_3$ or CCl_4 as solvent. The olefins were purified by chromatography on Al_2O_3 with hexane. The (Z)/(E) ratio is determined by gas chromatography (8% PEGA Chromosorb P/NAW "Perkin–Elmer" SIGMA-3B apparatus) or by ^{1}H-NMR spectra. The qualitative TLC investigations were carried out on silicagel F_{254} (aluminium sheets "Merck") using ethylacetate-hexane 2:1 as a mobile phase (for adducts), hexane or hexane-ether 10:1 (for olefins).

Conversion of the erythro-N,N,N',N'-tetramethyldiamides of 1,2-diaryl-2-hydroxyethanephosphonic acids **3, 4** *in the presence of hydrochloric acid.* General procedure 1. 0.4 ml 25% hydrochloric acid is added to erythro-**3, 4** (1 mmol), the stirred heterogeneous mass is heated at 110°C for 1 hr (a), or the stirring continued for 1 hr at room temperature (b). The mixture is hydrolyzed with 10% aqueous solution of Na_2CO_3 (to pH = 9), 15 ml ether is added, the water layer is extracted with ether (2 × 10 ml), the combined ether solutions are washed with water (2 × 2 ml) and dried over anhydrous $MgSO_4$. After evaporation of the solvent the crude reaction products **5, 6** were investigated by tlc, ^{1}H-NMR and gas chromatography.

Conversion of the erythro-N,N,N',N'-tetramethyldiamides of 1,2-diaryl-2-hydroxyethanephosphonic acids **3, 4** *in ethanolic solution of hydrochloric acid.* General procedure 2. 0.1 ml concentrated hydrochloric acid is added to a solution of 1 mmol erythro-**3, 4** in 10 ml anhydrous ethanol and the stirred mixture is refluxed 1 hr (a), or the stirring continued for 3 hrs at room temperature (b). The solvent is evaporated in vacuum and 3 ml 10% aqueous solution of Na_2Co_3 is added, the water layer is extracted with ether (3 × 10 ml), the combined organic solutions are washed with water (2 × 2 ml) and dried over anhydrous $MgSO_4$. The solvent is evaporated in vacuum and the crude products were studied by tlc, gas chromatography and spectroscopy (UV and ^{1}H-NMR).

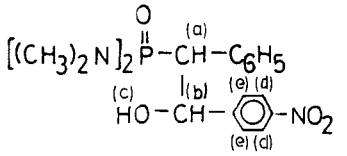
*Thermal olefination of the adduct threo-***3f** *into olefin* **5f**. A mixture of 0.372 g (1 mmol) **3f** (threo, m.p. 126–128°C), 1.1 g silicagel and 4 ml toluene is refluxed with stirring 5 hrs. After cooling 10 ml ether are added, the mixture is filtered off and washed with ether (2 × 15 ml), the combined filtrates washed with water (2 × 4 ml) and dried over $MgSO_4$. After evaporation of the solvents in vacuum 0.127 g (56%) (E)-1-phenyl-2-(4-nitrophenyl)-ethene **5f** was obtained wth m.p. 155–156°C. After recrystallization from $CHCl_3$ m.p. 157–158°C. Lit.[7]: m.p. 158°C.

Synthesis of N,N,N',N'-tetramethyldiamides of 1,2-diaryl-2-hydroxy-ethanephosphonic acids **3, 4**. The synthesis of the adducts **3, 4** was performed according ref.[3], method A and B.

N,N,N'N'-Tetramethyliamide of 1-phenyl-2-(4-methylphenyl)-2-hydroxyethanephosphonic acid **3g**. The reaction between 2.30 g (10 mmol) **1a**, 6.60 ml butyllithium (1.6 M solution in hexane) and 1.20 g (10 mmol) 4-methylbenzaldehyde **2g** in 20 ml THF as described in Reference 3, method B, gave after washing with ether/hexane 1:3 1.57 g (45%) erythro-**3g**, m.p. 108–9°C. $C_{17}H_{27}N_2O_2P$ (346.4) Calc.%: C, 58.87; H, 7.79; N, 8.08. Found%: C, 58.91; H, 7.82; N, 8.10. ^{1}H-NMR ($CDCl_3$): δ 2.38 (s, 3H, CH_3); 2.40 (d, $^3J_{PH} = 8$ Hz) and 2.85 (d, $^3J_{PH} = 9$ Hz, NCH_3, 12H); 3.40 (d, $^2J_{H_aP} = 15.5$ Hz, 1H, H_a); 5.46 (d, $^3J_{H_bP} = 6$ Hz, 1H, H_b), 5.60 (s, 1H, OH); 7.06 (m, 9H, Ph).

N,N,N',N'-Tetramethyldiamide of 1-phenyl-2-(4-nitrophenyl)-2-hydroxyethanephosphonic acid **3f**. The reaction of 2.30 g (10 mmol) **1a**, 6.60 ml butyllithium (1.6 M solution in hexane) and 1.20 g (10 mmol) 4-nitrobenzaldehyde **2f** in 20 ml THF as described in Reference 3, methode B, gave 1.70 g (66%) mixture of erythro and threo diastereoisomers. Erythro/threo = 2:3 (determined by ^{1}H-NMR, the signal for OH group $\delta = 6.46$ for threo **3f** and 6.02 for erythro **3f** being used). After two recrystalizations from ethylacetate the pure theo −**3f** m.p. 126–128°C, is obtained.

With the same reactants but using methode A (Reference 3), 2.01 g (78%) mixture of erythro **3f**/thereo **3f** = 23:77 (determined by ^{1}H-NMR) was obtained. $C_{16}H_{24}N_3O_4P$ (377.3) Calc.%: C, 50.89; H, 6.36; N, 11.13; Found %: C, 50.56; H, 6.31; N, 11.50.



^{1}H NMR ($CDCl_3$) Thero-**3f**: δ 2.31 (d, $^3J_{PH}$ = 9 Hz) and 2.71 (d, $^3J_{PH}$ = 10 Hz, NCH_3, 12H); 3.60 (dd, $^3J_{H_aH_b}$ = 9 Hz, $^2J_{H_aP}$ = 12 Hz, 1H, H_a); 5.41 (dd, $^3J_{H_bP}$ = 9 Hz, $^3J_{H_bH_c}$ = 2 Hz, 1H, H_b); 6.46 (s, 1H, H_c); 7.21 (m, 7H, Ph and H_e); 8.00 (d, $^3J_{H_eH_d}$ = 8 Hz, 2H, H_d). Erythro-**3f**: δ 2.25 (d, $^3J_{PH}$ = 8 Hz) and 2.87 (d, $^3J_{PH}$ = 9 Hz, NCH_3, 12H); 3.26 (d, $^2J_{PH_a}$ = 16 Hz, 1H, H_a); 5.37 (d, $^3J_{PH_b}$ = 4 HZ, 1H, H_b); 6.02 (s, 1H, H_c); 7.20 (m, 7H, Ph, H_e); 8.00 (d, $^3J_{H_eH_d}$ = 8 Hz, 2H, H_d).

Attempt to isomerize (E)-stilbene into (Z)-stilbene in the presence of hydrochloric acid.

A mixture of 0.197 g (10 mmol) (E)-**5a** and 0.4 ml 25% hydrochloric acid was heated 1 hr at 110°C. After treatment according the general procedure 1 0.185 g (94%) unchanged (E)-**5a** was isolated, m.p. 124–125°C, UV (ethanol) 296 nm.[8]

In analogous experiments with (Z)-**5a** as well as with (Z)-**5e** the corresponding unchanged (Z)-olefins were isolated with quantitative yields; UV (Z)-**5a** 275 nm (methanol),[9] (Z)-**5e** 273 nm (95% ethanol).[8]

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