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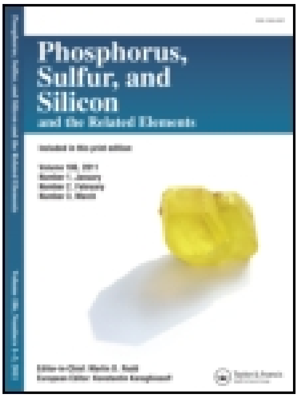

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Wittig Reaction: Role of Steric Effects in Explaining the Prevalent Formation of Z Olefin from Nonstabilized Ylides

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WITTIG REACTION: ROLE OF STERIC EFFECTS IN EXPLAINING THE PREVALENT FORMATION OF *Z* OLEFIN FROM NONSTABILIZED YLIDES

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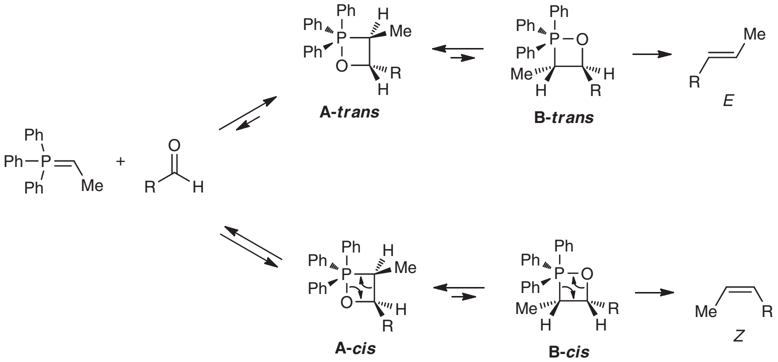
GRAPHICAL ABSTRACT



Abstract *For understanding the mechanism involved in the Wittig reaction, it is important to know the factors which influence the stability of 1,2-oxaphosphetane intermediates with pentacoordinate phosphorus; in these intermediates, the steric factor plays a predominant role. Studying the Wittig reaction between nonstabilized ylides and different aldehydes, we noted that the stereochemical outcome driving toward Z-olefin formation was influenced only by different steric factors. The proposed mechanism differs from those previously reported because it underlines the fundamental role of the two cis/trans oxaphosphetane intermediates with the oxygen atom in equatorial position.*

Keywords Oxaphosphetanes; phosphorylation; ^{31}P NMR spectroscopy; *E*-olefin; *Z*-olefin

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INTRODUCTION

Since its discovery about 60 years ago,[1] the Wittig reaction plays a central role in organic synthesis due to its ability to form a carbon–carbon double bond with high positional selectivity, relatively high chemoselectivity, and due to the possibility to be conducted in many cases with reliable and high stereocontrol.[2]

Originally, little attention was paid to stereochemistry since several olefins were obtained as *E*/*Z* mixtures, suggesting that the reaction might not be generally stereoselective. However, it was soon discovered that the type of ylide and the reaction conditions could play a key role in determining the stereochemistry of the reaction. For example, nonstabilized phosphorus ylides react with aldehydes to give mainly *Z* alkenes, except under special conditions,[3] and stabilized ylides give predominantly *E* alkenes, but semistabilized ylides generally give a mixture of *E*/*Z* alkenes with a relative ratio of around 50:50. For these reasons, the mechanism has been the subject of extensive experimental[4] and theoretical[5a] investigations, and has been comprehensively reviewed.[4,5b]

The studies have shown that the Wittig reaction is influenced by many factors: type of ylide (stabilized, nonstabilized, or semistabilized), substituents at the phosphorus atom, presence of lithium salts, solvent, temperature,[2b,2c,6] and concentration.[7e] Because it is now demonstrated[2a,7] without any doubt that, 1,2-oxaphosphetanes are central intermediates in the Wittig reaction, for better understanding of the mechanism involved in this reaction it is of fundamental importance to consider the chemistry of pentacoordinated phosphorus compounds, focusing in particular on all the factors, that influence the stability of cyclic intermediates containing a pentacoordinated phosphorus atom with a trigonal bipyramidal arrangement of the substituents.

A general rule that explains the stereoselectivity of the Wittig reaction has been difficult to formulate so far, because the large number of data reported in important contributions[2a] are often in apparent contrast. We think that this is due to the different reaction conditions used, and to the fact, that the Wittig reaction has been studied as a simple cycloaddition reaction between the ylide and the carbonyl group. Instead, we think that it is of crucial importance to analyze all the factors that determine the stability of the four-membered cyclic phosphorane intermediates, the so-called “1,2-oxaphosphetanes” (2,2,2-trisubstituted-1,2-λ^5-oxaphosphetanes) depicted in Scheme 1. Considerable information is now available[8] on the factors, which affect the stability of such trigonal bipyramidal phosphorane derivatives and control the process of ligand reorganization within them. Two factors turn out to be important in this connection: (a) the preference of electronegative groups for the apical positions and (b) the preference of a small ring for an apical–equatorial arrangement. In addition, the final stereochemistry of the reaction, in which trigonal bipyramidal phosphorane intermediates are involved, is strongly dependent on the steric interactions.

For the last 40 years, our group has been engaged in studies of reactions, in which cyclic pentacoordinated phosphorus compounds are involved as intermediates and so as to determine the different stereochemical results. In one case, we have demonstrated[9a] that the high stereoselectivity observed was due to different decomposition rates of two *cis*/*trans* cyclic isomeric trigonal bipyramidal phosphorane intermediates, which were in equilibrium with each other. In another case,[9b] we have observed that *cis* hexacoordinated phosphorane intermediates, being less stable than the *trans* isomers, immediately collapse determining a stereoselective reaction. The high decomposition rate of the *cis* pentacoordinate intermediate, caused by its major sterical overcrowding, accounts for the high stereoselective formation of the final product. In addition, Vedejs et al.[2d,10b,c] observed that

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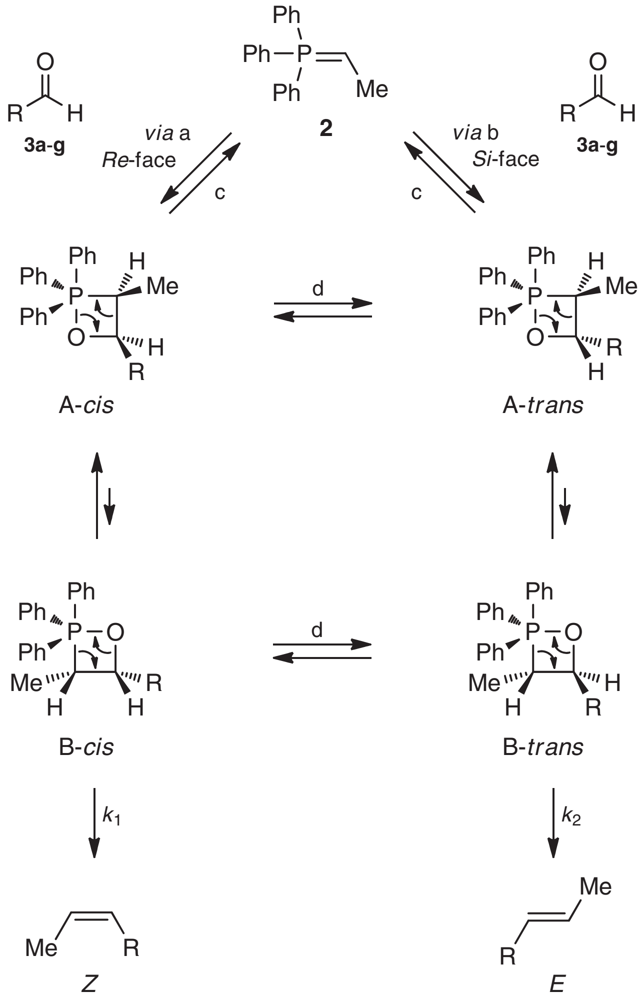

Scheme 1

the *cis*-isomer of oxaphosphetanes derived from nonstabilized ylides decompose faster than the *trans*-isomers.

For this reason, we started a study on the Wittig reaction between nonstabilized triphenylphosphonium ylides and different aldehydes. In this manner, only the steric effect should influence the different stereochemical results. In other words, this should allow as to determine, if the high sterical overcrowding in the oxaphosphetane intermediates alone will influence and consequently explain the high stereoselective formation of *Z* alkenes.

RESULTS AND DISCUSSION

In the case of nonstabilized ylides the reaction mechanism is qualitatively outlined in Scheme 1. This mechanism is in line with several previous important studies.[7]

The first step is a cycloaddition of the carbonyl group to the ylide to give pentacoordinate oxaphosphetane intermediates with trigonal bipyramidal structures. It is reported that such oxaphosphetane intermediates derived from aromatic aldehydes are formed reversibly, giving a retro-Wittig reaction.[7a,c] In addition, Reitz and Maryanoff[10a] reported that also the intermediates derived from aliphatic aldehydes and triphenylphosphonium ylides are reversibly formed. In other words, interconversion of oxaphosphetanes with the starting products might occur.

This reversibility was in part not accepted by Vedejs and Peterson,[2d] however. In fact, he suggests: (a) oxaphosphetanes derived from unbranched aliphatic aldehydes do not undergo the reverse reaction unless anionic substituents as well as lithium salts are present; (b) oxaphosphetanes derived from aromatic aldehydes can partially undergo the reverse reaction, depending on the substituents at phosphorus and the availability of electrophilic catalyst. In the triphenylphosphonium series, a catalyst such as lithium ions is required, in the trialkylphosphonium series, however, the reverse reaction appears to take place spontaneously.

In the absence of a retro-Wittig reaction, however, it is possible to achieve equilibration of the oxaphosphetanes following different pathways.[2d] For example, Bestmann[6c] has suggested that oxaphosphetane intermediates could open to give zwitterionic forms (Figure 1), which are free to rotate before giving the products. Alternatively, a *cis*/*trans* equilibration of oxaphosphetanes by proton transfer might be catalyzed by a base.

It is well known over the last 40 years that, when it possible, the formation of a cycle around a pentacoordinate phosphorus atom is favored 10-fold[6–8] with respect to the formation of acyclic intermediates.[11] Consequently, the formation of a cyclic pentacoordinated phosphorus intermediate should be strongly favored over any other type of possible intermediate. In other words, the attack of the ylidic carbon atom on the carbonyl carbon

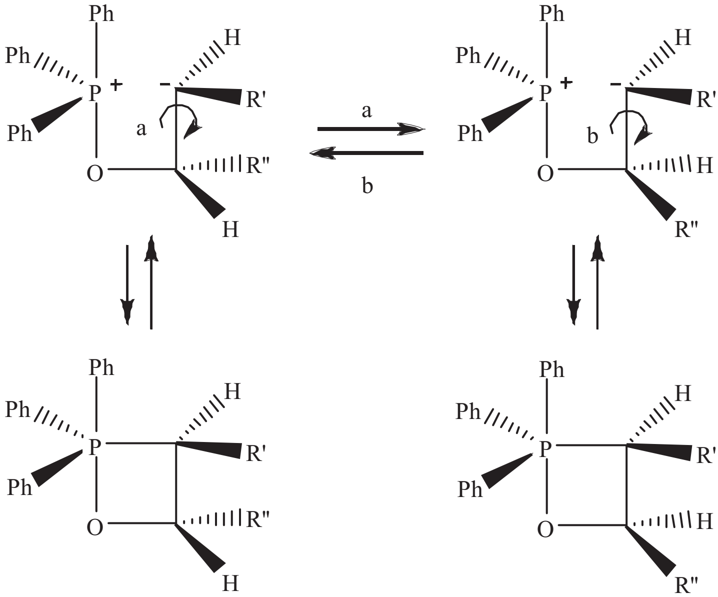

Figure 1 Possible equilibration through zwitterionic forms.

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atom with formation of a cyclic oxaphosphetane is favored by a factor 10^{6-8} over any other nucleophilic attack.[11]

The stereochemical outcome of the reaction can be explained by the rules that govern the geometry of pentacoordinate species. The most favorite geometry for a pentacoordinate species is the trigonal bipyramidal arrangement. The relative position of the substituents in pentacoordinate compounds depends on their respective steric demand and apicophilicity. (Apicophilicity is the relative preference of substituents to occupy the apical positions as opposed to the equatorial positions in trigonal bipyramidal structures: a large number of experimental results and theoretical calculations have indicated a general propensity of electronegative substituents to prefer the apical positions, while bulky ligands prefer the equatorial positions. The five-membered rings are unable, for reasons of strain, to occupy the diequatorial position of the trigonal bipyramid.)

Keeping in mind these considerations and that the carbonyl compound can react with the ylide in two ways (Scheme 1, via *a* or via *b*), we assume, that in the first step the reaction results in the formation of two pentacoordinate intermediates with trigonal bipyramidal structures – **A-*cis*** and **A-*trans*** –, which have the oxygen atom in apical position. This assumption is based on the fact, that in nucleophilic substitution reactions at phosphorus involving a pentacoordinate intermediate the attacking nucleophile and leaving group both occupy apical positions.[8c] It is also known that the cleavage of the leaving group occurs first.

To react to the final alkenes, the intermediates **A** must complete a pseudorotation to give two new pentacoordinate species **B-*cis*** and **B-*trans*** with the oxygen atom in equatorial position and the P–C bond in apical position. (Sufficiently long-lived pentacoordinated intermediates can undergo stereomutation or positional interchange of the substituents at pentacoordinated phosphorus by a Turnstile rotation (TR)[8h] or a resultwise equivalent Berry pseudorotation (BPR)[8h] that are sometime very rapid processes; in the permutational process, only conformers with apical–equatorial rings are considered to participate. Moreover, both the nucleophilic attack at the phosphorus atom and the breakup of the pentacoordinate always occurs in apical position.) Since the oxygen atom prefers to be in apical position, species **B** are generally more disfavored than species **A**, if intermediate **B** is not stabilized by other species such as metal ions. In addition, in these species **B** the equatorial position of the oxygen atom maximizes its back-bonding donation, thus favoring the decomposition to alkene and triphenylphosphine oxide. The driving force of this decomposition is given by the propensity of the oxygen atom to form a double bond with the phosphorus atom.

Stereoselection is driven by the irreversible decomposition of the intermediates **B**, which have a different rate of decomposition[10] due to their different stability. In fact, the isomer **B-*cis*** is more unstable because of the greater steric hindrance and decomposes to form the *Z* olefin much faster as compared to the pentacoordinate intermediate **B-*trans*** which forms the *E* olefin. This rapid decomposition of the pentacoordinate intermediate **B-*cis*** ($k_1 \gg k_2$) shifts the possible equilibrium between **B-*cis*** and **B-*trans***, thus increasing the quantity of the *Z* olefin.

In order to verify the above mechanism and to better understand the outcome of the Wittig reaction, we studied the influence of the steric hindrance of the carbonyl compound. In particular, we have studied the reaction using the nonstabilized ylide **2** with aldehydes **3a**–**g**, characterized by different steric hindrance (Scheme 2).

Olefins **4a**–**g** have been obtained in different *E*/*Z* ratios by reaction of triphenylethylphosphonium bromide **1** and potassium *tert*-butylate, which first give the ethylidene triphenylphosphorane **2**, followed by addition of the aldehydes **3a**–**g**, (Scheme 2). The

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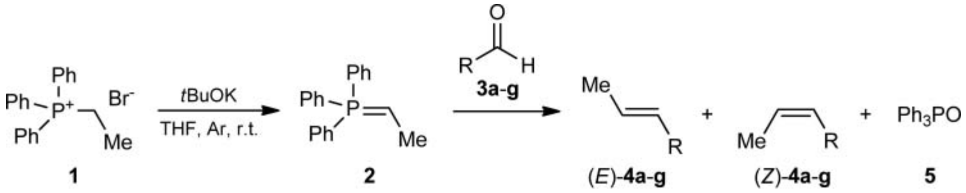

R = Ph (**a**), *o*-Tol (**b**), Mes (**c**), 1-naphthyl (**d**), 9-anthracenyl (**e**), CH_2Ph (**f**), pentyl (**g**)

Scheme 2

isomeric ratio was determined by gas chromatography-mass spectrometry (GC–MS) of the reaction mixture without purification. The isomeric ratios are reported in Table 1.

As shown in Table 1, variation of steric hindrance of the aldehyde gives a variation of the *E*/*Z*ratio in the final products.

These results could be explained by comparing the structure of the pentacoordinate intermediates, such as **A** and **B**, formed during the course of the reaction. In particular, using benzaldehyde **3a**, the corresponding pentacoordinate intermediate **B-*cis*** (Scheme 3), is more unstable than the *trans* one and it decomposes immediately after its formation ($k_1 \gg k_2$), shifting the equilibrium to finally account for the great predominance of the *Z* olefin.

In the reaction with *o*-tolyl aldehyde (**3b**) the overcrowding in the pentacoordinate intermediates is slightly greater than that found in the reaction with benzaldehyde, resulting in a small increase of the *E*/*Z* ratio (16:84) in favor of *Z* olefin. In the case of benzyl aldehyde (entry 6) the overcrowding in the pentacoordinates species is stronger than in case of the reaction with benzaldehyde, resulting in a further increase of the *E*/*Z* ratio (10:90). This increase of the ratio is probably due to the greater instability of the oxaphosphetanes, due to the fact that the benzyl group in the aldehyde moiety (in the case of phenyl acetaldehyde) is free to rotate and might give a repulsion with the phenyl groups bonded to the phosphorus atom of the pentacoordinated species.

These same considerations apply for all reactions with other aldehydes in which we always have the prevalence of *Z* olefin.

Table 1 Wittig reactions of nonstabilized ylide **2** with different hindered aldehydes

Entry	Aldehyde (R)	Products	*E*/*Z* ratio[a]
1	**3a** (Ph)	**4a** ($E + Z$)	18:82
2	**3b** (*o*-Tol)	**4b** ($E + Z$)	16:84
3	**3c** (Mes)	**4c** ($E + Z$)	48:52
4	**3d** (1-naphthyl)	**4d** ($E + Z$)	15:85
5	**3e** (9-anthracenyl)	**4e** ($E + Z$)	49:51
6	**3f** (CH_2Ph)	**4f** ($E + Z$)	10:90
7	**3g** (pentyl)	**4g** ($E + Z$)	13:87
8[b]	**3a** (Ph)	**4a** ($E + Z$)	11:89
9[b]	**3c** (*o*-Tol)	**4c** ($E + Z$)	33:67

[a] *E*/*Z* ratio determined by GC–MS.

[b] The reaction is carried out at 0 °C. All the other reactions are carried out at room temperature.

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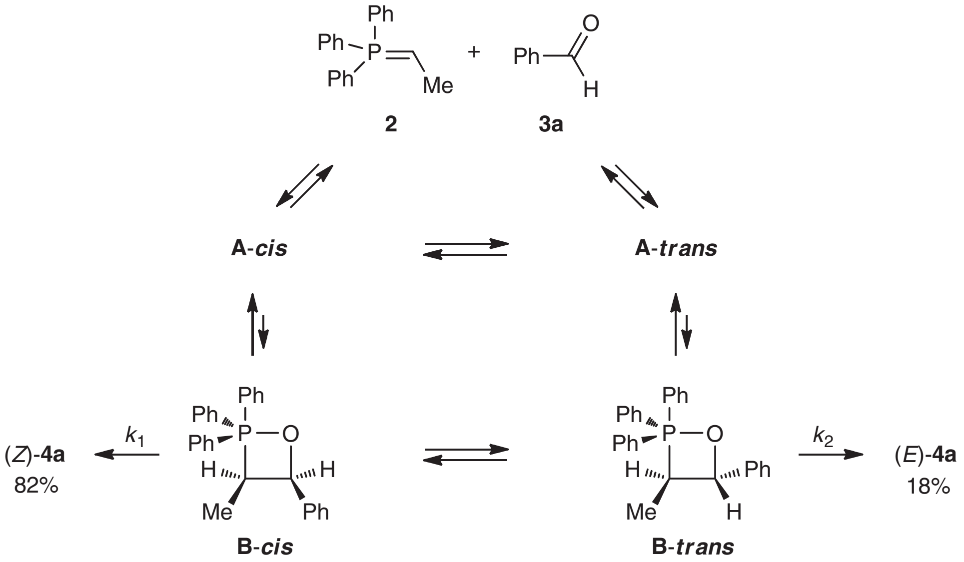
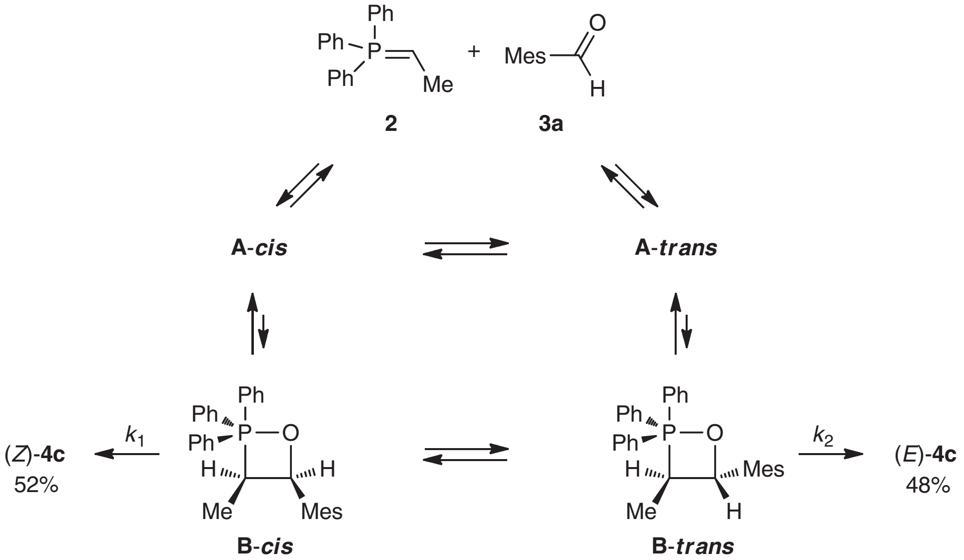


Scheme 3

On the contrary, when a more hindered compound as mesityl aldehyde (**3c**) is used (Scheme 4) the overcrowding on the pentacoordinated intermediate becomes very high, both for the *cis* and the *trans* intermediates, which probably decompose with similar rate ($k_1 \sim k_2$), resulting in a drastic increase of the *E*/*Z* ratio (48:52).

It should be noted that the ratio *E*/*Z* is also depending on the reaction temperature. In fact, when we carried out the reaction with **3a** at 0 °C (Table 1, entry 8) we obtained an



Scheme 4

E/*Z* ratio of 11:89, while at room temperature the ratio was 18:82, confirming again that oxaphosphetane **B-*cis*** is more instable as compared to the *trans* isomer.

Variable Temperature ^{31}P NMR Study

To complete this investigation, we have carried out ^{31}P NMR spectroscopy study in order to observe the *cis* and *trans* oxaphosphetane intermediates of the above reaction between nonstabilized phosphorus ylide and aldehydes.

A typical experiment was carried out with ethyltriphenylphosphonium bromide (**1**) under argon. The salt **1**, suspended in dry tetrahydrofuran (THF), was treated with potassium *tert*-butylate at 25 °C to generate the ylide, evidenced in the ^{31}P NMR spectrum by a sharp singlet at 15.1 ppm. Addition of an equimolar amount of benzaldehyde to the above reaction mixture directly in the NMR tube at −78 °C produced a spectrum with two signals in the region of pentacoordinate species at −60.5 ppm (probably *cis*-oxaphosphetane in the form **A**) and at −60.7 ppm (probably *trans*-oxaphosphetane in the form **A**). The assignment of the signals for the *cis*- and *trans*-oxaphosphetane is based on the results reported by Maryanoff,[7c] who has demonstrated by chemical arguments that the signal at lower field corresponds to the *cis*-oxaphosphetane and the signal at higher field to the *trans* isomer.

When the temperature of the NMR probe was increased to −30 °C a new singlet appeared at 29.3 ppm due to the formation of triphenylphosphine oxide. The signals of the two oxaphosphetanes became very broad and gradually disappeared concomitantly with the appearance of the signal for triphenylphosphine oxide. When the reaction was complete at 25 °C the ratio between *E*/*Z* olefins was 13:87, which did not correspond to the original ratio of *trans*/*cis* oxaphosphetanes (91:9). This suggests a possible equilibrium process between oxaphosphetanes.

The low temperature experiments have been performed also for aldehydes **3b** and **3c**. In the reaction with the aldehyde **3b** the ^{31}P NMR spectrum showed the presence of two peaks at −61.1 ppm and −61.8 ppm in an integral ratio of 10:90, which are attributed (in analogy to the reaction with benzaldehyde **3a**) to the corresponding *cis* and *trans* oxaphosphetanes. In this case at the end of the reaction the ratio between *E*/*Z* olefins was 16:84.

In the reaction with the aldehyde **3c** the ^{31}P NMR spectrum showed the presence of two peaks at −61.6 ppm and −62.0 ppm in a ratio of 27:73, respectively, which were assigned (in analogy to the reaction with benzaldehyde **3a**) to the corresponding *cis* and *trans* oxaphosphetanes. When the reaction was carried out at room temperature the ratio between *E*/*Z* olefins was 48:52.

All data confirm again an oxaphosphetane equilibration, which could arise from a possible retro-Wittig reaction or by the occurrence of other processes.

In order to demonstrate if in our cases the retro-Wittig reaction may occur, we have carried out some crossover experiments, performing first the reaction with benzaldehyde and subsequently adding another aldehyde. However, in these experiments no significant amounts of crossover products (mixture of alkenes) were observed.

The oxaphosphetane equilibration observed might also be explained by formation of zwitterionic rotamers (see Figure 1), by a proton transfer catalyzed by a base or by other hitherto unknown processes.

Thus in the case of nonstabilized ylides, we will always obtain the prevalence of the *Z* olefin, because a *cis*-oxaphosphetane is much more unstable than the *trans* isomer as demonstrated by Vedejs et al.[10b,c] The *E*/*Z* ratio in these cases depends only on the

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different steric hindrance, which is very crucial in pentacoordinated compounds causing the instability of these hypervalent species.

CONCLUSIONS

In conclusion, studying the Wittig reaction with a nonstabilized ylide (ethylidene triphenylphosphorane) while maintaining the reaction conditions unaltered and changing only the aldehyde component, we have experimentally shown that the prevailing stereochemical outcome toward the *Z* olefin is influenced only by different steric factors or different overcrowding in the oxaphosphetane intermediates. Likely, the observed oxaphosphetanes undergo some equilibration at a rate competitive with the rate of decomposition. It should be noted that the proposed mechanism differs from the previously reported mechanisms, because it puts in evidence the key role of the four different oxaphosphetane intermediates **A** (*cis* and *trans*) and **B** (*cis* and *trans*), in which oxaphosphetane **B** is fundamental for the formation of the final products. The instability of oxaphosphetane type **B** depends on steric effects and in the *cis* isomer the overcrowding of the groups around to the phosphorus atom is always superior with respect to the *trans* isomer. For this reason, the instability of the *cis* isomer is always greater than that of the *trans* isomer.

EXPERIMENTAL

General Experimental Details

^{31}P NMR spectra were recorded with a Varian Mercury 400 or with an Inova 600 spectrometer operating at 161.89 MHz and 242.77 MHz, respectively. Chemical shifts are referenced to external 85% H_3PO_4. J values are given in Hz. The GC–MS analyses were performed with a gas chromatograph equipped with a (5%-phenyl)-ethylpolysiloxane column (30 m length, 0.250 mm i.d., 0.25 μm thickness), interfaced to a quadrupole mass detector. Mass spectra were recorded at an ionization voltage of 70 eV in the electron-impact (EI) mode.

THF was distilled from sodium/benzophenone ketyl and all solvents were purified appropriately and degassed immediately prior to use. Air and moisture sensitive solutions and reagents were handled in dried apparatus under dry argon using standard Schlenk techniques. The identities of the alkenes **(*Z*)-4a** and **(*E*)-4a** (analyzed as crude reaction mixtures) were authenticated by GC–MS by comparison to the retention time of pure commercial sample of the two isomers and by ^{1}H NMR spectroscopy of the crude reaction mixture. For the other compounds (**4b–g**) identification was made by GC–MS and by similarity with compound **4a** and also keeping in mind that under our conditions the major isomers should be *Z* as reported in several articles. The *E*/*Z* ratios were determined by GC–MS. All compounds synthesized are known in literature.[13–19]

Wittig Reaction: General Procedure

Potassium *tert*-butylate (89.6 mg, 0.8 mmol) was added to a mixture of triphenylethyl phosphonium bromide (300 mg, 0.8 mmol) in dry THF (3 mL) at room temperature. The color of the mixture became orange. After 5 min 1 eq. of the corresponding aldehyde (0.8 mmol) was added. The reaction became instantly white. The reaction course was monitored by GC–MS.

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(1Z)-prop-1-en-1-ylbenzene (Z)-4a: major product. MS (70 eV, EI): m/z (%) = 118 (M^+, 71), 117 (100), 115 (41), 103 (9), 91 (31), 77 (7), 63 (7), 51 (7).

(1*E*)-prop-1-en-1-ylbenzene (*E*)-4a: minor product. MS (70 eV, EI): m/z (%) = 118 (M^+, 70), 117 (100), 115 (40), 103 (9), 91 (30), 77 (7), 65 (9), 51 (9).

1-methyl-2-[(1Z)-prop-1-en-1-yl]benzene (Z)-4b: major product. MS (70 eV, EI): m/z (%) = 132 (M^+, 63), 117 (100), 115 (50), 105 (5), 91 (26), 77 (8), 65 (8), 51 (6).

1-methyl-2-[(1*E*)-prop-1-en-1-yl]benzene (*E*)-4b: minor product. MS (70 eV, EI): m/z (%) = 132 (M^+, 61), 117 (100), 115 (47), 105 (12), 91 (26), 77 (9), 65 (10), 51 (7).

1,3,5-trimethyl-2-[(1Z)-prop-1-en-1-yl]benzene (Z)-4c: major product. MS (70 eV, EI): m/z (%) = 160 (M^+, 58), 145 (100), 128 (26), 115 (20), 105 (12), 91 (11), 77 (8).

1,3,5-trimethyl-2-[(1*E*)-prop-1-en-1-yl]benzene (*E*)-4c: minor product. MS (70 eV, EI): m/z (%) = 160 (M^+, 67), 145 (100), 128 (23), 115 (17), 105 (11), 91 (9), 77 (6).

1-[(1Z)-prop-1-en-1-yl]naphthalene (Z)-4d: major product. MS (70 eV, EI): m/z (%) = 168 (M^+, 49), 153 (100), 139 (8), 128 (4), 115 (10), 83 (5), 76 (3).

1-[(1*E*)-prop-1-en-1-yl]naphthalene (*E*)-4d: minor product. MS (70 eV, EI): m/z (%) = 168 (M^+, 51), 153 (100), 139 (6), 128 (5), 115 (11), 83 (9), 76 (4).

9-[(1Z)-prop-1-en-1-yl]anthracene (Z)-4e: major product. MS (70 eV, EI): m/z (%) = 218 (M^+, 75), 203 (100), 189 (11), 108 (9), 101 (14).

9-[(1*E*)-prop-1-en-1-yl]anthracene (*E*)-4e: minor product. MS (70 eV, EI): m/z (%) = 218 (M^+, 76), 203 (100), 189 (10), 108 (9), 101 (12).

(2Z)-but-2-en-1-ylbenzene (Z)-4f: major product. MS (70 eV, EI): m/z (%) = 132 (M^+, 56), 117 (100), 115 (42), 91 (40), 78 (9), 65 (11), 51 (9).

(2*E*)-but-2-en-1-ylbenzene (*E*)-4f: minor product. MS (70 eV, EI): m/z (%) = 132 (M^+, 51), 117 (100), 115 (44), 104 (4), 91 (37), 77 (12), 65 (13), 51 (12).

(2Z)-oct-2-ene (Z)-4g: major product. MS (70 eV, EI): m/z (%) = 112 (M^+, 49), 83 (26), 70 (56), 55 (100).

(2*E*)-oct-2-ene (*E*)-4g: minor product. MS (70 eV, EI): m/z (%) = 112 (M^+, 32), 83 (19), 70 (45), 55 (100).

Variable Temperature ^{31}P NMR Experiments

Typical Procedure. Potassium *tert*-butylate (8.96 mg, 0.08 mmol) was added, at room temperature and under argon atmosphere to a mixture of triphenylethyl phosphonium bromide (**1**, 30 mg, 0.08 mmol) in dry THF (2 mL). When the color of the mixture became orange, indicating the formation of the ylide **2**, the mixture was transferred into an NMR tube and cooled at −78 °C. The ^{31}P NMR spectrum of the ylide was recorded at this temperature ($\delta = 15.1$ ppm). Then 1 eq. of **3a** was quickly added and the ^{31}P NMR spectrum of the reaction mixture was recorded. Two new signals appeared in the spectrum, at −60.5 ppm and −60.7 ppm that integrated 9:91, respectively. On raising the temperature of the probe to +25 °C (in about 20 min), the signals of the oxaphosphetanes gradually disappeared and a new singlet appeared at +29.3 ppm (it began to appear at about −30 °C) due to the formation of triphenylphosphine oxide. The GC–MS analysis of this final reaction mixture showed the presence of the *E*-**4a**/*Z*-**4a** olefins in 18:82 ratio.

In another experiment after the formation of ylide **2** the reaction mixture was cooled to −78 °C and aldehyde **3a** was added. The reaction mixture was allowed to warm up to room temperature (5 h). After this, due to very slow increase in the temperature of the system the final *E*/*Z* ratio of products **4a** was 13:87.

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The same experiment was performed also with the aldehydes **3b** and **3c** (data are reported in the main text).

Crossover Experiments

Potassium *tert*-butylate (89.6 mg, 0.8 mmol) was added at room temperature and under argon atmosphere to a mixture of triphenylethyl phosphonium bromide (**1**, 300 mg, 0.8 mmol) in dry THF (3 mL). When the color of the mixture became orange indicating the formation of the ylide **2**, the mixture was cooled to −78 °C. Then 1 eq. of **3a** was added upon which the color of the solution disappeared. After 10 min the second aldehyde (**3b** or **3c**) was added (1 eq.) and the reaction was slowly warmed to room temperature. The reaction mixture was analyzed by GC–MS. The GC–MS chromatogram from the reaction with aldehydes **3a** and **3c** showed only the products derived from the first aldehyde. In the reaction with aldehydes **3a** and **3b** a signal of very low intensity, almost 1%, for the crossover reaction product was detected. This small amount probably derives from the incomplete disappearance of the starting ylide.

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