

Wittig reactions of moderate ylides with heteroaryl substituents at the phosphorus atom

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Abstract—The influence of various heteroaryl substituents at the phosphorus atom to the stereoselectivity of Wittig reactions of allylic and benzylic ylides has been studied. In the case of nitrogen bearing heteroaromatic ligands at the phosphorous atom of benzyliidenephosphoranes high *E*-alkene selectivity's of up to 90:10 could be observed. NMR spectroscopic investigations revealed that substituents at the phosphorus have influences on the reactivity of ylides as well as the stability of reaction intermediates. Indications for chelation of lithium ions with ylides could also be detected and will be discussed in this article.

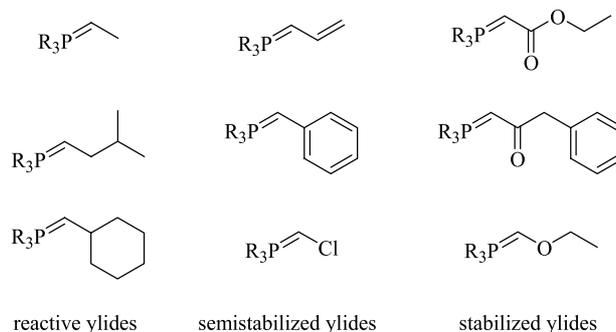
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1. Introduction

The Wittig reaction (Scheme 1) is known for more than 50 years and belongs to the most important carbon–carbon double bond forming reactions in organic chemistry¹ and is also used in large scale in industry.²

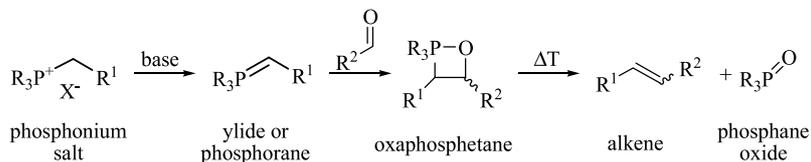
The popularity of the Wittig reaction is mainly due to the regioselective formation of the double bond at the position of the former carbonyl group and the possibility to control the stereoselectivity by applying special reaction conditions.³ The reaction conditions needed for maximum *Z*- or *E*-alkene selectivity's are strongly dependent on the nature of the ylide used (Scheme 2).

For unstabilized, so called 'reactive ylides', the selective formation of *Z*-alkenes is possible by applying 'salt free' reaction conditions.^{4,5} Salt free means performing the reactions in the absence of lithium ions, although other cations (e.g., Na⁺ or K⁺) can be present. In the presence of lithium ions most often reduced alkene selectivity's are



Scheme 2. Examples for different classes of phosphorus ylides.

observed. The negative influence of lithium ions on the stereochemistry of Wittig reactions is concentration dependent⁶ and is attributed to the fact, that lithium salts are at least partially soluble in many organic solvents. Solvated Li⁺ is able to complex the carbonyl compound, which then reacts faster with the ylide. This catalysed pathway of the Wittig reaction is rather unspecific, explaining the reduced selectivity's in the presence of Li⁺.



Scheme 1. General overview of the Wittig reaction.

Keywords: Wittig reactions; NMR spectroscopy; Ylides; Configuration; Low-temperature chemistry.

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The selective formation of *E*-alkenes in the case of reactive ylides is possible using the Schlosser methodology.⁷ For stabilized ylides the selective formation of *E*-alkenes is achieved using phosphorus ylides⁸ or PO-ylides within the Horner–Wadsworth–Emmons reaction.⁹ *Z*-Alkene selective variants of the Horner–Wadsworth–Emmons reaction with stabilized ylides are also known, for example, the Ando-methodology¹⁰ or the Still–Gennari-variant.¹¹ Despite these traditional and well established methods for the selective formation of alkenes using reactive and stabilized ylides, there is still a considerable lack of efficient methods for the selective formation of alkenes in the case of moderate or semistabilized ylides. Schlosser reported a *Z*-alkene selective variant of the Wittig reaction for moderate ylides using ‘methoxymethoxy-armed’ ylides.^{3,12} However, the yields are below 50% in many cases due to the steric demand of the 2-methoxymethoxyphenyl groups. The *E*-alkene selective formation of alkenes in the case of moderate ylides has been reported in some cases.^{13,14,15}

We were interested in the influence of heteroaromatic substituents at the phosphorus center on stereochemistry and reaction mechanism of Wittig reactions. Previously we reported that reactive ylides bearing 2-furyl substituents at the phosphorus atom react with greatly enhanced *Z*-alkene selectivity's.¹⁶ 2-Pyridyl substituents also increase the *Z*-alkene ratio.¹⁷

Encouraged by this observation we wanted to test, if those and other heteroaromatic substituents have similar effects of increased alkene selectivity in Wittig reactions of moderate ylides.

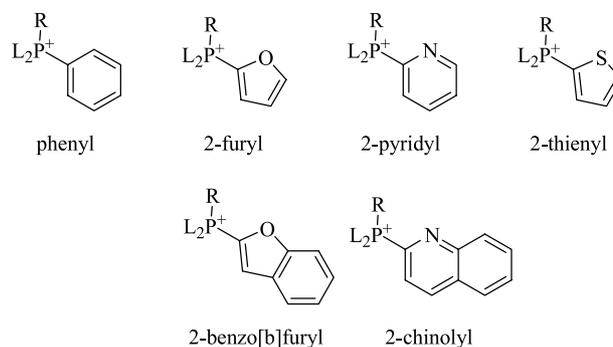
Here we want to report our investigations of the influence of a number of different heteroaromatic substituents at the phosphorus to selectivity and yield of Wittig reactions with moderate ylides. The preparative results will be analysed by means of NMR spectroscopy.

2. Results and discussion

For our studies we chose the well investigated Wittig reaction of benzaldehyde with allylidetriphenylphosphorane or benzylidetriphenylphosphorane in THF. For deprotonation of the corresponding phosphonium salts either NaHMDS or *n*-BuLi was used. We investigated the influence of the heteroaromatic systems at phosphorus by replacing one or all three standard phenyl substituents by

different heteroaromatic systems. The phosphonium salts bearing heteroaromatic substituents at phosphorus are accessible in two to three steps with an overall yield in the range of 50%.

The following heteroaromatic systems have been implemented in phosphonium salts (Scheme 3).



Scheme 3. Overview over the heteroaromatic substituents tested. R denotes allyl or benzyl groups, L represents either a phenyl substituent or a heteroaryl system.

The Wittig reactions with these heteroaromatic systems were repeated two to three times to get reliable results. In the following sections the experimental results of our investigations will be presented, divided in two parts, for the allylic and benzylic Wittig reaction, respectively.

2.1. Results of allylic Wittig reactions

The Wittig reaction of allylidetriphenylphosphorane with benzaldehyde is well investigated and results were published by a number of different authors.^{18,19,20,21} The reported yields vary from 58 to 95% and the stereochemical outcome spread from 44:56 *Z*:*E* to 75:25 *Z*:*E*. The results of our investigations concerning Wittig reactions between allylic ylides bearing heteroaromatic systems and benzaldehyde are presented in Table 1.

The standard reaction with three phenyl substituents at the phosphorus atom is indeed rather unspecific yielding *Z*:*E*-alkene ratios of 55:45 and 73:27 with *n*-BuLi and NaHMDS as base, respectively. The introduction of different heteroaromatic substituents has only minor influences of the stereochemical outcome of allylic Wittig reactions. Interestingly, Wittig reactions with one 2-pyridyl ring at

Table 1. Yield and stereochemical results of Wittig reactions in THF using allylideneheteroaryl-phenylphosphoranes and benzaldehyde with either NaHMDS or *n*-BuLi as base

Compound	<i>n</i> -BuLi		NaHMDS	
	<i>Z</i> : <i>E</i> ^a	Yield (%) ^b	<i>Z</i> : <i>E</i>	Yield (%)
AllylideneP ⁺ Ph ₃	55:45	63	73:27	68
AllylideneP ⁺ (2-thienyl)Ph ₂	66:34	68	74:26	46
AllylideneP ⁺ (2-furyl)Ph ₂	70:30	59	75:25	50
AllylideneP ⁺ (2-furyl) ₃	66:34	63	67:33	68
AllylideneP ⁺ (benzo[<i>b</i>]furyl)Ph ₂	61:39	33	63:37	62
AllylideneP ⁺ (2-pyridyl)Ph ₂	37:63	32	44:56	12
AllylideneP ⁺ (2-pyridyl) ₃	66:34	19	54:46	20

^a *Z*:*E* ratios were determined on isolated products using NMR-spectroscopy and GC.

^b All yields were determined on isolated products.

Table 2. Yield and stereochemical results of Wittig reactions in THF using benzyldieneheteroaryl-phenylphosphoranes and benzaldehyde with either NaHMDS or *n*-BuLi as base

Compound	<i>n</i> -BuLi		NaHMDS	
	<i>Z</i> : <i>E</i> ^a	Yield (%) ^b	<i>Z</i> : <i>E</i>	Yield (%)
BenzyldieneP ⁺ Ph ₃	65:35	66	61:39	81
BenzyldieneP ⁺ (2-thienyl)Ph ₂	79:21	89	53:47	91
BenzyldieneP ⁺ (2-furyl)Ph ₂	67:33	82	42:58	65
BenzyldieneP ⁺ (2-furyl) ₃	69:31	92	51:49	92
BenzyldieneP ⁺ (benzo[<i>b</i>]furyl)Ph ₂	55:45	85	30:70	81
BenzyldieneP ⁺ (benzo[<i>b</i>]furyl) ₃	46:54	87	32:68	86
BenzyldieneP ⁺ (2-pyridyl)Ph ₂	40:60	79	14:86	85
BenzyldieneP ⁺ (2-pyridyl) ₃	49:51	65	51:49	69
BenzyldieneP ⁺ (2-chinolyl)Ph ₂	24:76	58	11:89	84

^a *Z*:*E* ratios were determined on isolated product using NMR-spectroscopy and GC.

^b All yields were determined on isolated products.

phosphorus yield a slight excess of the *E*-alkene in contrast to the standard reaction. The yield of this Wittig reaction drops from above 60% to less than 20% with nitrogen bearing ligands present in the phosphonium salt. In these cases a side product could be isolated, which is formed via γ -substitution of the allylic ylides.¹⁹

It has to be summarized that the introduced heteroaromatic substituents at phosphorus had not the anticipated influences on Wittig reactions of allylic ylides. Instead of increased stereoselectivity only minor influences on the stereochemistry of Wittig reactions could be observed. The decreased yield in some cases could be attributed to a concurrence reaction of allylic ylides.

2.2. Results of benzylic Wittig reactions

The Wittig reaction of benzyldienetriphenylphosphorane with benzaldehyde is extraordinary well investigated and many results have been published in literature.^{19,22,23,24,25,26} The *Z*:*E* alkene ratios reported vary from of 68:32 to 47:53 with a yield typically above 90%. Our results for Wittig reactions between different benzyldienephosphoranes and benzaldehyde are shown in Table 2.

Our results for the standard reaction with three phenyl groups at phosphorus are in accordance with reported values in literature and proof that this reaction is unspecific. Only a slight preference for the *Z*-alkene could be observed. Introduction of heteroaromatic systems changes the stereochemical results of this Wittig reaction fundamentally. In most cases with NaHMDS as base the *E*-alkene gets the preferred product. With one 2-pyridyl or one 2-chinolyl group present, the *E*-alkene is even formed in ratios of almost 90:10. With *n*-BuLi as base the tendency to form the *E*-alkene is also present, although to a lesser extent. The yield remains in the order of 80% in most cases.

Heteroaromatic substituents at the phosphorus atom have at least in benzylic Wittig reactions significant influences on the stereoselectivity. Often an inversion of the stereoselectivity is obtained, leading to high *E*-alkene selectivity's in two cases. The origin of these influences was unknown at this point and numerous NMR experiments were initiated to clarify the role of those heteroaryl groups at phosphorus.

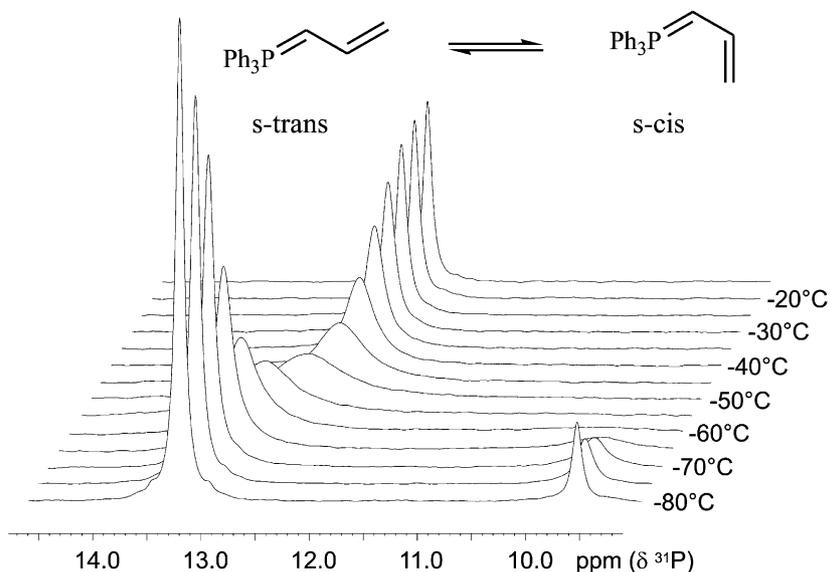
2.3. NMR investigations

We rationalized three kinds of possible influences of the different heteroaryl groups at phosphorus on the stereochemistry of the investigated Wittig reactions.

- Steric influences
- Chelation of metal ions with ylides
- Electronic influences on ylide reactivity

The stereoselectivity of benzylic Wittig reactions was changed the most, when one 2-chinolyl group was present in the ylide. The question arose, if this influence is due to the increased steric demand of the 2-chinolyl group in comparison to the phenyl substituent. We therefore prepared a 2-naphthyl group bearing ylide. The 2-naphthyl group has almost the same steric demand as the 2-chinolyl group, but lacks the heteroatom. The Wittig reaction of benzyldiene(2-naphthyl)diphenylphosphorane with benzaldehyde yielded *Z*:*E*-alkene ratios of 73:27 with *n*-BuLi as base and 67:33 with NaHMDS. These values are almost identical to the results of the similar Wittig reaction with three phenyl groups at phosphorus presented in Table 2 (entry 1). Furthermore, the stereochemistry of benzylic Wittig reactions is similar with one or three benzo[*b*]furyl groups at phosphorus (Table 2, entries 5 and 6). We therefore rule out any significant steric influence of the investigated heteroaromatic systems on the stereo selectivity of the presented Wittig reactions with benzylic ylides.

Another possible influence on stereochemistry of Wittig reactions might be the chelation of solvated metal ions between the carbanion site and the heteroatom of the heteroarylsubstituent. Such chelated species might possess a preferred conformation in the transition state of the Wittig reaction, which could be an explanation for the selective formation of one alkene.¹⁷ To investigate the possible presence of such species we switched our attention to allylic ylides. Although the stereo selectivity of Wittig reactions with allylic ylides was rather unaffected by heteroaromatic systems, these species in contrast to benzylic ylides showed dynamic behaviour at different temperatures. This circumstance allowed NMR studies concerning chelation. In Scheme 4 ³¹P NMR spectra of allyldienetriphenylphosphorane in THF are shown, which were recorded at



Scheme 4. ^{31}P NMR spectra of allylidetriphenylphosphorane at different temperatures.

different temperatures between -80 and -15 °C. The ylide has been prepared using NaHMDS as base.

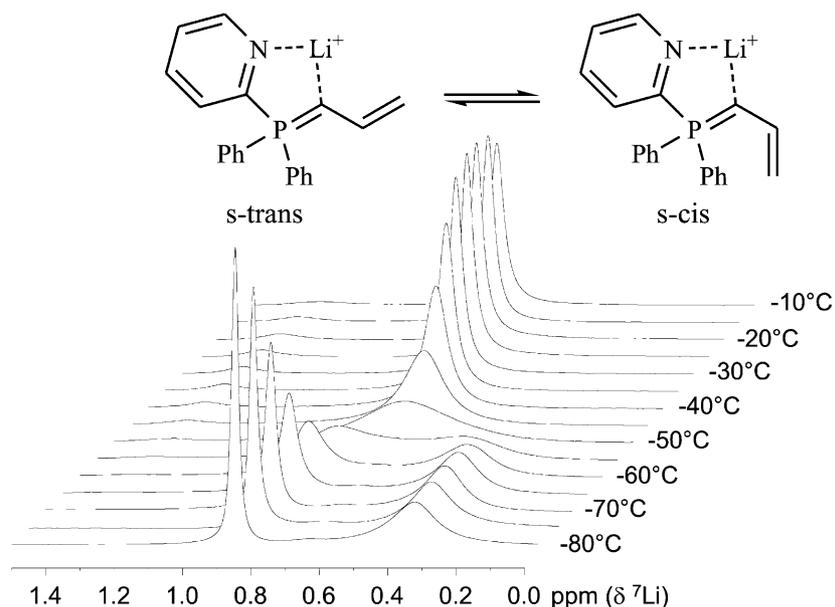
At higher temperatures one sharp signal represents the phosphorus ylide. At temperatures below -50 °C two different conformers are present in the solution. The coalescence temperature for this dynamic and reversible process is at -50 °C. The calculated free activation enthalpy is 40.8 kJ/mol.²⁷ To the best of our knowledge such dynamic behaviour of allylidene phosphoranes has so far not been described in literature.

In **Scheme 5** ^7Li NMR spectra of allylidene(2-pyridyl)-diphenylphosphorane are shown, which were recorded at temperatures between -80 and -10 °C. This ylide was prepared using *n*-BuLi as base.

Again a dynamic interconversion of the two conformers

could be detected, the coalescence temperature lies also at -50 °C. It has to be stressed, that here the dynamic process has been detected via ^7Li NMR spectra, although the lithium ions are not covalently bound to the phosphorus ylide. This result therefore is a strong indication for the presence of lithium–ylide complexes, which have been postulated above. The two different ^7Li NMR-signals at lower temperatures do not represent different lithiated species, since the same splitting can be observed in **Scheme 4**, where no ^7Li -ions were present. Unfortunately, numerous other methods, including several HOESY experiments^{28,29,30} and the detection of ^{15}N -chemical shifts in possibly chelated structures, failed to provide any further evidence for the existence of such lithium–ylide complexes.

Nevertheless it has to be concluded, that these investigations give a clear indication for the presence of lithium ion–ylide chelate complexes, since the conformational changes in the



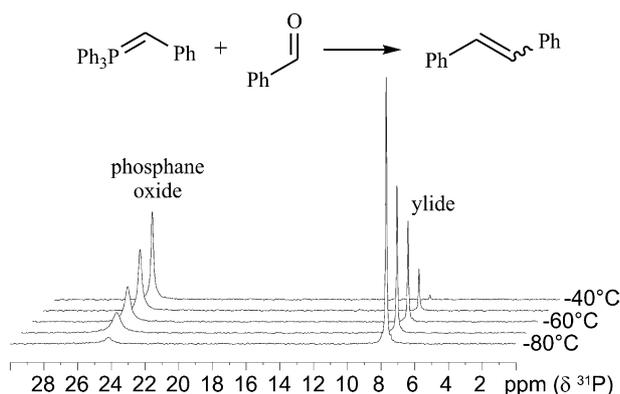
Scheme 5. ^7Li NMR spectra of allylidene(2-pyridyl)diphenylphosphorane at different temperatures.

ylide structure can be detected via ^{31}P NMR spectroscopy as well as ^7Li NMR.

Finally, we wanted to investigate the possible influence of heteroaryl groups at phosphorus on ylide reactivity. Again NMR is the most valuable tool for this purpose. Different phosphorus ylides bearing heteroaromatic substituents were prepared in NMR tubes. All ylides were prepared using the base NaHMDS, since the highest stereoselectivity's could be observed in this case. Furthermore, with the base *n*-BuLi often several peaks are observed for one species, which are broadened at lower temperatures, most likely due to the formation of different lithiated species. The Wittig reaction was started by adding 1.5 equiv of benzaldehyde at low temperatures. The reaction was then monitored with ^{31}P NMR spectra at temperatures between $-80\text{ }^\circ\text{C}$ and room temperature. For these experiments we switched our attention back to benzylic ylides, since they were generally more influenced by heteroaryl substituents than allylic ylides.

First of all we investigated the standard reaction with benzylidenetriphenylphosphorane and benzaldehyde in THF. The reaction was started by addition of the benzaldehyde at $-80\text{ }^\circ\text{C}$ and after that the NMR tube was put into the NMR spectrometer, which was precooled to $-80\text{ }^\circ\text{C}$. The first ^{31}P NMR spectrum could be recorded ca. 1 min after addition of the benzaldehyde. In the first spectrum a sharp signal at 8 ppm was detected representing the phosphorus ylide. At 24 ppm a signal slowly arose, corresponding to the phosphane oxide. Since, here moderate ylides are under investigation, the reaction from the ylide to the phosphane oxide is rather slow at low temperatures of $-80\text{ }^\circ\text{C}$. No oxaphosphetane species could be detected in the expected chemical shift range, in accordance with earlier investigations concerning benzylic Wittig reactions.³¹ As expected, the reaction was slow at $-80\text{ }^\circ\text{C}$. After 20 min ca. 45% of the ylide had reacted to phosphane oxide and alkene. After that point the reaction rate dramatically decreased, so that no further decay of the ylide signal could be detected at $-80\text{ }^\circ\text{C}$. The reaction mixture had to be warmed to $-70\text{ }^\circ\text{C}$ in order to let the reaction proceed any further. The progress of the reaction at temperatures between -80 and $-40\text{ }^\circ\text{C}$ is shown in Scheme 6.

Each spectrum was recorded after 5 min at the temperature

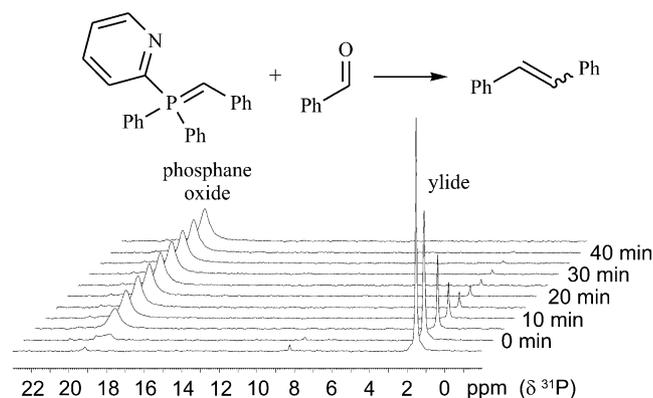


Scheme 6. Progress of the Wittig reaction between benzylidenetriphenylphosphorane and benzaldehyde.

denoted in Scheme 6. The temperature was kept for 20 min and then warmed further. At a temperature of $-40\text{ }^\circ\text{C}$ the reaction was finished. All the ylide had been reacted into alkene and phosphane oxide.

In conclusion, the standard benzylic Wittig reaction with three phenyl rings at the phosphorus atom proceeds at temperatures between -80 and $-40\text{ }^\circ\text{C}$. At very low temperatures of $-80\text{ }^\circ\text{C}$ the reaction gets very slow, after 50% of the starting material is consumed. The mixture had to be warmed, to let the reaction proceed further. This might be an explanation, why Wittig reactions of moderate ylides are rather unspecific, since the reaction takes place over a temperature span of $40\text{ }^\circ\text{C}$. Different thermal influences act to the transition state of the reaction, yielding different alkene ratios at each temperature. These different alkene ratios add to a rather unspecific overall reaction.

The highest *E*-alkene selectivity for benzylic Wittig reactions could be observed, when one 2-pyridyl substituent was bound to the phosphorus atom. This reaction was also monitored by ^{31}P NMR spectroscopy. The result of this experiment is shown in Scheme 7.



Scheme 7. Progress of the Wittig reaction between benzylidene(2-pyridyl)diphenylphosphorane and benzaldehyde.

All shown spectra were recorded at a temperature of $-80\text{ }^\circ\text{C}$. Again no oxaphosphetane species could be detected. More importantly, the reaction is finished after 40 min at $-80\text{ }^\circ\text{C}$. The introduction of one 2-pyridyl substituent thus greatly increases the ylide reactivity. This might explain the high alkene selectivity in this reaction. The reaction proceeds completely at low temperatures, therefore a change of temperature does not lower the alkene selectivity. However, unexplained remains the fact, that the *E*-alkene is the preferred product, which is formed with an excess of almost 90:10 in this reaction.

Finally, we want to present the effect, which 2-furyl substituents have in this benzylic Wittig reaction. In Scheme 8 ^{31}P NMR spectra of the Wittig reaction between benzylidenetris-(2-furyl)phosphorane and benzaldehyde are shown.

Like in the standard case with three phenyl rings at phosphorus, the reaction mixture has to be warmed to let the reaction proceed. But in contrast to the case above, here

3. Conclusion

This work investigated the influence of heteroaryl substituents at phosphorus on the stereochemistry of Wittig reactions of moderate ylides. With standard phenyl ligands at phosphorus Wittig reactions of allylic and benzylic ylides are rather unspecific. While the introduction of heteroaryl substituents does not significantly change the stereochemistry of allylic Wittig reactions, the situation is different with benzylic Wittig reactions. With the introduction of heteroaryl substituents the *E*-alkene gets the predominant product in most reactions. With one nitrogen containing heteroaromatic substituent the *E*-alkene selectivity almost reaches 90:10.

The reasons for these influences have been investigated by three different approaches. First, steric interactions of the heteroaromatic systems can be ruled out, since the stereochemistry of benzylic Wittig reactions is not changed if one phenyl or one bigger naphthyl ligand is present. Second, we investigated the possibility of a metal ion chelation with ylides. We observed a conformational equilibrium for allylic ylides in ^{31}P NMR as well as ^7Li NMR spectra, indicating some kind of contact between both nuclei. The third investigation concerned the influence of heteroaryl substituents on ylide reactivity. We could show, that one 2-pyridyl substituent greatly increases the reactivity of benzylic ylides, so that the Wittig reaction proceeds completely at very low temperatures. This circumstance favours high alkene selectivity's. We could show, that 2-furyl substituents greatly increase the stability of oxaphosphetane intermediates. The reasons for this stabilization and the unusual values of ^{31}P NMR chemical shift will be discussed elsewhere.

4. Experimental

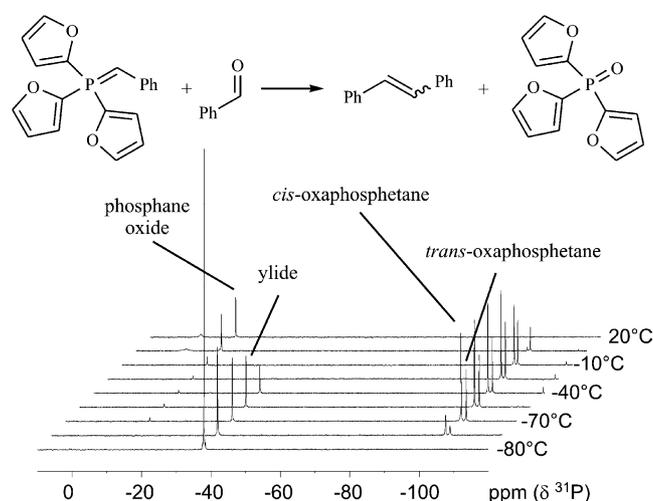
4.1. General remarks

All reactions were carried out with exclusion of air and moisture. THF was dried over sodium/benzophenone and freshly distilled prior to use. Benzaldehyde was also distilled. All other reagents were bought from commercial sources and were used without further purification.

NMR spectra were recorded with a Bruker DRX 400 spectrometer in CDCl_3 , with TMS as internal shift reference. ^{31}P - and ^7Li NMR spectra were calibrated according to the Ξ -scale, in which nitromethane is at 0 ppm.³² NMR investigations of Wittig reactions were performed in $[\text{D}_8]\text{THF}$, shifts being referred to traces of undeuterated solvent. High resolution mass spectra were recorded with a Bruker FT-ICR-MS apex II with ESI technique.

4.2. Synthesis of phosphanes

Phosphanes with 2-furyl, 2-thienyl or 2-benzo[*b*]furyl substituents were prepared according to a procedure described by Allen et al.³³ 2-Pyridyl bearing phosphanes were prepared by a procedure starting from 2-bromopyridine.³⁴ Phosphanes with 2-chinoly substituents were



Scheme 8. Progress of the Wittig reaction between benzylidenebis(2-furyl)phosphorane and benzaldehyde at $-80\text{ }^\circ\text{C}$.

we were able to detect oxaphosphetane intermediates. They are formed by the reaction of benzaldehyde with the ylide and remain stable until ca. $-20\text{ }^\circ\text{C}$. This is the first time well characterized oxaphosphetane signals can be observed in the case of benzylic Wittig reactions. Furthermore, the two isomers *cis* and *trans* could be resolved in the chemical shift region of -100 ppm . The two peaks were assigned to the *cis*- and *trans*-oxaphosphetane taking into account, that the *cis*-oxaphosphetane is less stable than the *trans*-isomer.³¹ This explains why at $5\text{ }^\circ\text{C}$ the signal for the *cis*-isomer is almost gone, whereas still significant amounts of the *trans*-oxaphosphetane are present. In the Wittig reaction of benzylidene-(2-furyl)diphenylphosphorane, where only one 2-furyl ring is present, also oxaphosphetanes could be observed. However, in this case, only one signal was resolved for the two oxaphosphetane species. Furthermore, the oxaphosphetanes were only semistable in this case. They were formed up to a maximum concentration, which remained constant until the beginning of decomposition at $-10\text{ }^\circ\text{C}$. We can conclude that 2-furyl substituents stabilize oxaphosphetane intermediates and the amount of stabilization is higher the more 2-furyl rings are present within the phosphorane. Additionally 2-furyl systems have a dramatic shielding effect on the phosphorus nucleus. These two effects have been observed previously for reactive ylides.¹⁶ In the case of reactive ylides the stabilization of oxaphosphetanes was strong enough that these intermediates could be isolated at ambient temperatures allowing the recording of a crystal structure.

In summary we could show, that heteroarylsubstituents at the phosphorus nucleus change the reactivity of phosphorus ylides, which has consequences for the reaction intermediates and most important for the observed alkene ratio. 2-Pyridyl substituents increase the ylide reactivity so, that the Wittig reaction is finished in less than 1 h at $-80\text{ }^\circ\text{C}$. This results in a high *E*-alkene selectivity. In contrast 2-furyl substituents increase the stability of reaction intermediates, allowing for the first time the detection of oxaphosphetanes in the case of moderate ylides, which are stable until $-20\text{ }^\circ\text{C}$.

prepared by the same procedure, however 2-bromochinolin is not commercially available and had to be synthesised.³⁵

4.3. Synthesis of phosphonium salts

One equivalent phosphane was dissolved in toluene and stirred with 2 equiv allyl bromide or benzyl bromide at temperatures of 80 °C until a white precipitate had formed. If this method was unsuccessful, the reaction was performed in neat allyl bromide or benzyl bromide. The precipitate was filtered off, washed and dried. If necessary recrystallisation was performed in ethanol/ethyl acetate.

4.4. Wittig reactions

Wittig reactions were performed as described previously.¹⁶

4.4.1. Allyl(2-thienyl)diphenylphosphonium bromide. Yield 78%; mp 178–182 °C. ³¹P NMR (CDCl₃): δ = 16.7. MS (FAB): *m/z* = 389.0 and 387.0 (1:1).

4.4.2. Allyl(2-furyl)diphenylphosphonium bromide. Yield 88%; mp 180–185 °C. ³¹P NMR (CDCl₃): δ = 11.4. HR-MS: *m/z* = 293.10874 [C₁₉H₁₈OP⁺], Calcd 293.10898.

4.4.3. Allyltris(2-furyl)phosphonium bromide. Yield 45%; mp 153–157 °C. ³¹P NMR (CDCl₃): δ = -14.3. HR-MS: *m/z* = 273.06735 [C₁₅H₁₄O₃P⁺], Calcd 273.06751.

4.4.4. Allyl(2-benzo[*b*]furyl)diphenylphosphonium bromide. Yield 76%; mp 152–156 °C. ³¹P NMR (CDCl₃): δ = 12.8. HR-MS: *m/z* = 343.12465 [C₂₃H₂₀OP⁺], Calcd 343.12463.

4.4.5. Allyl(2-pyridyl)diphenylphosphonium bromide. Yield 78%; mp 187–190 °C. ³¹P NMR (CDCl₃): δ = 17.0. HR-MS: *m/z* = 304.12452 [C₂₀H₁₉NP⁺], Calcd 304.12496.

4.4.6. Allyltris(2-pyridyl)phosphonium bromide. Yield 83%; mp 106–110 °C. ³¹P NMR (CDCl₃): δ = 9.8. HR-MS: *m/z* = 306.11548 [C₁₈H₁₇N₃P⁺], Calcd 306.11546.

4.4.7. Benzyl(2-thienyl)diphenylphosphonium bromide. Yield 89%; mp > 260 °C. ³¹P NMR (CDCl₃): δ = 18.4. MS (FAB): *m/z* = 439.3.

4.4.8. Benzyl(2-furyl)diphenylphosphonium bromide. Yield 84%; mp 260–263 °C. ³¹P NMR (CDCl₃): δ = 13.2. HR-MS: *m/z* = 343.12403 [C₂₃H₂₀OP⁺], Calcd 343.12463.

4.4.9. Benzyltris(2-furyl)phosphonium bromide. Yield 90%; mp 218–220 °C. ³¹P NMR (CDCl₃): δ = -12.7. HR-MS: *m/z* = 323.08282 [C₁₉H₁₆O₃P⁺], Calcd 323.08316.

4.4.10. Benzyl(benzo[*b*]furyl)diphenylphosphonium bromide. Yield 98%; mp 165–168 °C. ³¹P NMR (CDCl₃): δ = 14.5. HR-MS: *m/z* = 393.140347 [C₂₇H₂₂OP⁺], Calcd 393.14028.

4.4.11. Benzyltris(benzo[*b*]furyl)phosphonium bromide. Yield 83%; mp 180–185 °C. ³¹P NMR (CDCl₃): δ = -6.8. HR-MS: *m/z* = 473.1303 [C₃₁H₂₂O₃P⁺], Calcd 473.13011.

4.4.12. Benzyl(2-chinoly)diphenylphosphonium bromide. Yield 61%; mp ca. 265 °C. ³¹P NMR (CDCl₃): δ = 19.5. HR-MS: *m/z* = 404.15630 [C₂₈H₂₃NP⁺], Calcd 404.15626.

4.4.13. Benzyl(2-pyridyl)diphenylphosphonium bromide. Yield 89%; mp 217–220 °C. ³¹P NMR (CDCl₃): δ = 19.6. HR-MS: *m/z* = 354.14010 [C₂₄H₂₁NP⁺], Calcd 354.14061.

4.4.14. Benzyltris(2-pyridyl)phosphonium bromide. Yield 54%; ³¹P NMR (CDCl₃): δ = 9.8. HR-MS: *m/z* = 356.13122 [C₂₂H₁₉N₃P⁺], Calcd 356.13111.

4.4.15. Benzyl(2-naphthyl)diphenylphosphonium bromide. Yield 71%; mp 253–255 °C. ³¹P NMR (CDCl₃): δ = 23.4. HR-MS: *m/z* = 403.16108 [C₂₉H₂₄P⁺], Calcd 403.16101.

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