Synthetic Applications of Metalated Phosphonium Ylides

Henri-Jean Cristau

Laboratoire de Chimie Organique E.N.S.C.M., URA No. 458 du C.N.R.S., 8, rue de l'Ecole Normale, 34053 Montpellier Cedex 1, France

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I. Introduction

"Metalated phosphonium ylides"[1] and "phosphonium ylide anions"[2a] can correspond to various kinds of structures, such as **4**–**6**, which can be unambiguously and individually named by simple extension of the original definition given as early as 1944 by Wittig[3,4] for the term "ylide" (after the German "ylid"). On this basis they can be clearly distinguished from each other and from other phosphonium ylides without metal, such as **1**–**3** (Figure 1).

According to this definition,[3] the "onium ylide" denotes a species with a carbon group, indicated by the suffix "yl" (from the radical "alkyl"), bearing a negative charge (corresponding to a heteropolar bond), indicated by the suffix "ide" (by analogy with acetylide), located on carbon directly linked to a heteroatom bearing a positive charge (onium). By extension of this definition we suggest, for instance, for compound **4** the term lithium phosphonium "diylide", indicating the presence of two alkyl groups each bearing one negative charge. Similarly, for compound **6** the term lithium phosphonium "yldiide" indicates the presence of one alkyl group bearing two negative charges.

Apart from its generality, one of the main advantages of this formal definition is that it avoids all speculation as to the actual structure (metallotropic, covalent/ionic, or monomeric/polymeric structures, etc.) which would be inherent in a more detailed definition.

Henri-Jean Cristau was born in 1942 in Narbonne, France. In 1965, he graduated from the E.N.S.C. Montpellier and joined the C.N.R.S. He prepared his doctoral work in Heidelberg (1965–1969) under the supervision of Professor G. Wittig and obtained his Ph.D. degree from Montpellier University in 1970. As C.N.R.S. researcher he joined Professor H. Christol in Montpellier and became "Maître de Recherche" in 1975. Since 1988, he has been a professor at the E.N.S.C.M. His research is focused on organophosphorus chemistry and the applications of organophosphorus compounds, particularly on new synthetic reagents and methodologies.

Further extension of the definition would lead to "diazadiylide" for compound **10** and to "azayldiide" for compound **12** in the case of aminophosphonium ylides (Figure 2).

Several reviews have been devoted to the interesting subject of coordination chemistry of metalated ylides.[1,19–22] This review however will focus more specifically on recent developments in the use of lithium phosphonium diylides **4** and **10** and of lithium and phosphonium yldiides **6** and **12** in organic synthesis.

II. Lithium Phosphonium Yldiides

At the end of the 1960s, in the search for an operational reversal to the standard preparation of the "betaine ylides",[23] Schlosser attempted the preparation of phosphonium α-lithioalkylides[24,25] (**13**). However, in spite of positive deuterium–hydrogen exchange experiments, the reaction mixture remained complex.

In 1982, Corey and Kang[10] reported the preparation and reactivity of lithium triphenylphosphonium methyldiide (**14**) by direct lithiation of the phosphonium methylide **15** (Scheme 1). Even though this preparation was later confirmed and more precisely described, with slight experimental changes, by the same authors,[26] it still appears to be in contradiction with the results of Schlosser and co-workers,[11,27,28] which show that in the same conditions a nearly quantitative *o*-lithiation of the monoylide **16** takes place to give the lithiated compound **17**, whose evolution does not afford the yldiide **14**.

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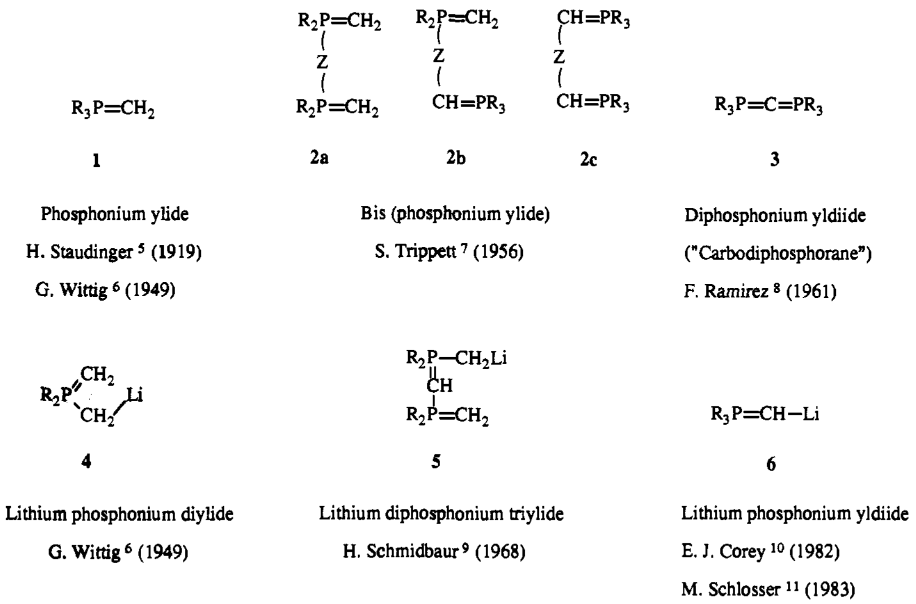


Figure 1. Parent structures[12] of various kinds of phosphonium ylides.

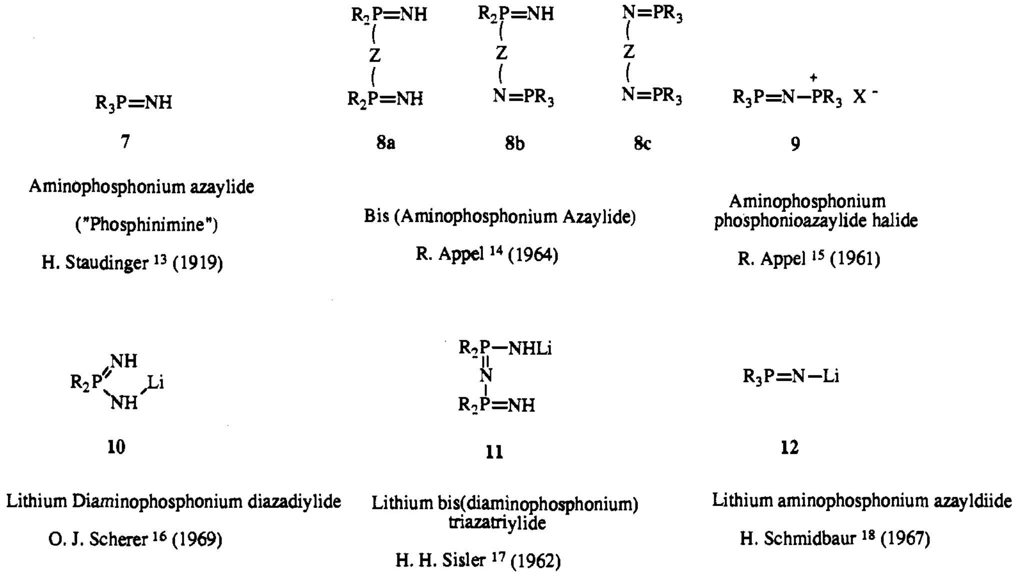
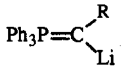


Figure 2. Parent structures[12] of various kinds of aminophosphonium azaylides.

However both research teams endorse another method for preparing orange-red yldiide 14 (Scheme 1), not described in the first publication,[10] using (bromomethyl)phosphonium bromide 18.

According to Corey,[10,26] yldiide 14 in comparison to the corresponding monoylide 16 exhibits an enhanced reactivity toward a sterically hindered ketone, such as fenchone 19, or toward an epoxide such as cyclopentene oxide 21 (Scheme 2). As expected with an excess of aldehydes 23, yldiide 14 affords the *trans*-allylic alcohols 24, through the *in situ* formation of the corresponding "betaine ylides".


$Ph_3P{=}C(R)Li$

13

$Ph_3P{=}CH{-}Li$

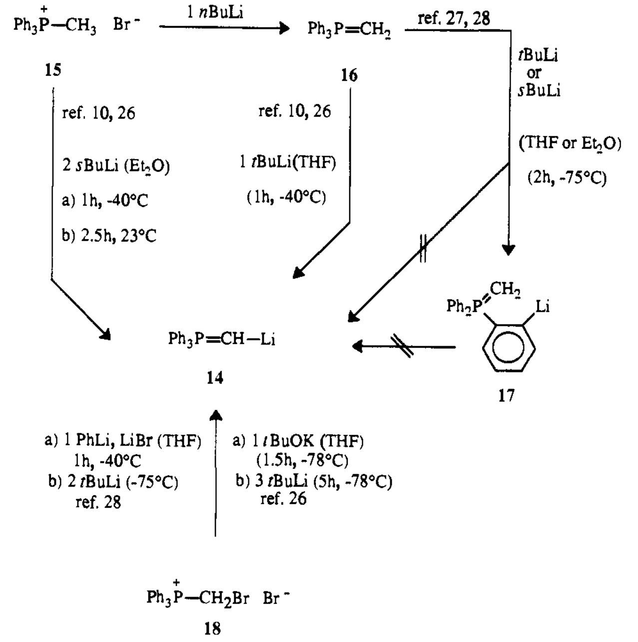
14

The high reactivity of yldiide 14 has been theoretically investigated[29] using *ab initio* SCF-MO calculations on the parent structures $H_3P{=}CHLi$ and H_3PCH^-, indicating a contact ion pair chemistry for 14 and a correlation between the enhancement of reactivity, particularly with overcrowded ketones, with the lower steric hindrance of the yldiide 14 in comparison to the ylide 16.

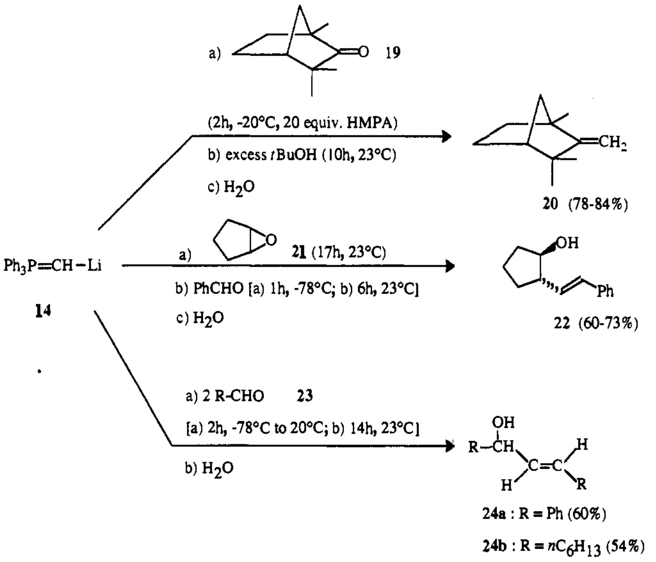
However, concerning the synthetic potential of the yldiides, it must be pointed out that Schlosser[11] predicts a limited role for "α-lithio ylides", since they do not represent a breakthrough in classical ylide chemistry: (i) in *trans*-selective or "SCOOPY" Wittig reactions the conventional preparation of the "betaine-ylide" intermediates is generally superior to the "α-lithio ylide" approach; (ii) the overcrowded ketone olefination can also be performed using a Wittig–Horner sequence with a PO ylide; (iii) ordinary ylides react smoothly with most oxiranes provided soluble lithium salts are present.

With regard to the lack of further publications on these reagents during the last few years (with the exception of one experiment which failed to give the corresponding "betaine ylide" [30]), this prediction seems, at least temporarily, to be verified.

Scheme 1. Preparation of the Lithium Triphenylphosphonium Methyldiide (14)



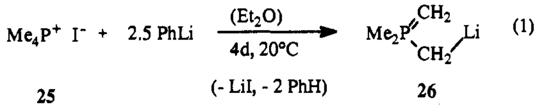
Scheme 2. Reactivity of the Lithium Triphenylphosphonium Methyldiide (14)[10,26]



III. Lithium Phosphonium Diylides

A. Preparations and Structural Characteristics

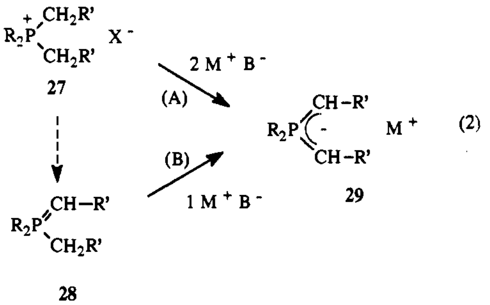
The various procedures used to prepare alkali metal and phosphonium diylides are similar to those of Wittig and Rieber,[6] who described the first example of lithium phosphonium diylide 26 in ethereal solution (eq 1).



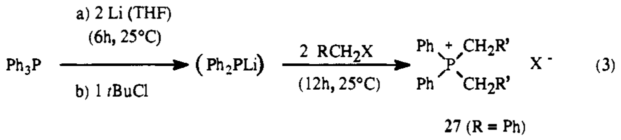
Most of the work to isolate and characterize alkali metals phosphonium diylides was done in the 1980s (Table 1), using either the direct addition of two base equivalents to dialkylphosphonium salt 27 (method A) or the addition of one base equivalent to the corresponding monoylide 28 (method B) (eq 2).

Table 1. Preparation of Alkali Metal Phosphonium Diylides 29 (eq 2)

R	R′	BM	method	yield (%)	color of the crystals	ref
Me	H	$nBuLi$	B	99	yellow	9
Et	H	$nBuLi$	B	81		9
Me	Ph	$tBuLi$	B	89	orange	31
Ph	Ph	$tBuLi$	B	90	orange	32
$PhCH_2$	Ph	$tBuLi$	B	94	yellow	32
Me	Ph	NH_2Na	B	94	yellow	32
Ph	Ph	NH_2Na	B	89	orange	32
$PhCH_2$	Ph	NH_2Na	B	94	orange	32
Me	Ph	HK	B	92	yellow	32
Ph	H	$nBuLi$	A	91	white	33
Ph; Me	H	MeLi	A	81	white	33
Me	H	PhLi	A		yellow	6
Me; tBu	H	MeLi	A		white	34
Ph	Ph	$nBuLi$	A			35

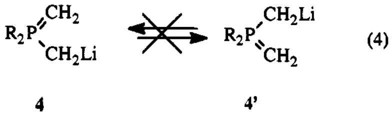


For the preparation of the necessary starting dialkylphosphonium salts 27 (R = Ph), a general one-pot procedure has been developed,[36] extending a previous example (R′ = Ph)[37] corresponding to the double alkylation of lithium diphenylphosphide generated from triphenylphosphine (eq 3).



R : Alkyl	X : I	(80-95 %)
R : Aryl, Alkenyl	X : Br	(75-85 %)
R : COR, CO_2R, CN, CO_2Na	X : Cl	(70-80 %)

Concerning the structure of alkali metal phosphonium diylides, an initial ^1H NMR study[9] on the two diylides 4a (R = Me) and 4b (R = Et), obtained in "salt free" solutions, showed: (i) a full equivalence of the two methylenic groups in each diylide, between −30 °C and +25 °C (no metallotropic equilibrium (eq 4) could be observed); (ii) an almost certain sp^3-character for the methylenic groups according to their coupling constant values and signs.

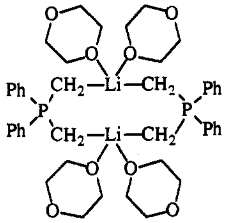


These results are corroborated by the single-crystal X-ray analysis of the compound 4c (R = Ph)[38] (Table 2), which shows a dimeric structure, with two dioxane molecules coordinated to each lithium atom (Figure 3).

The P–CH_2 bond length (1.71 Å) for diylide 4c is between those of the corresponding phosphonium salt

Table 2. Structural Characteristics[38] of the Lithium Diphenylphosphonium Dimethylide 4c

bond length (Å)		bond angles (deg)	
P-CH$_2$	1.71	Ph-P-Ph	99.7
C-Li	2.175	CH$_2$-Li-CH$_2$	127.2
P-Ph	1.84	CH$_2$-P-CH$_2$	113.6
C-H (CH$_2$Li)	0.91	CH$_2$-P-Ph	105.4; 116.3
		Li-CH$_2$-P	122
		Li-C-H	105



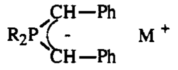
4c

Figure 3. Single-crystal X-ray analysis[38] of lithium diphenylphosphonium dimethylide 4c.

(1.80 Å) and monoylide (1.66 Å); this value reflects therefore a true ylide character. Furthermore, the Li–C bond length (2.17 Å) lies in the range of bond lengths corresponding to the normal organolithium compounds (2.1–2.4 Å),[39] indicating a strong nucleophilic character for this bond.

It is noteworthy that a theoretical study[40] of the lithium phosphonium dimethylide, $H_2P(CH_2)_2Li$, gives the P–C bond lengths between 1.70 and 1.75 Å and a C–P–C bond angle between 116° and 134°, in rough agreement with the X-ray analysis data.

Other X-ray analysis and NMR studies of alkali metal phosphonium dibenzylides (30) give similar results.[32]



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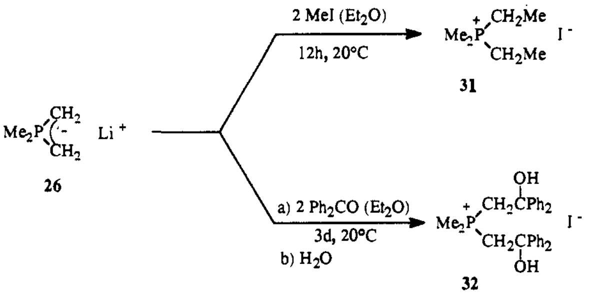
(R = Me, Ph, CH$_2$Ph) (M = Li, Na, K)

B. Reactivity of Diylides toward Aldehydes and Ketones

The first diylide reactivity studies were described, in 1949 by Wittig,[6] who demonstrated the structure of lithium dimethylphosphonium dimethylide (26), by isolating the corresponding dimethylation 31 and dihydroxyalkylation 32 products (eq 5).



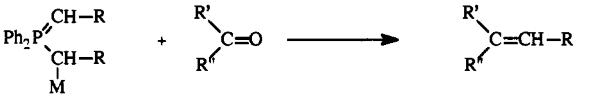
(5)

It is interesting to note that the reaction with benzophenone, probably owing to the alkyl substituents of the phosphorus, did not afford the carbonyl olefination into the 1,1-diphenylethylene: the "Wittig reaction" was described four years later, using the phosphonium monoylide.[41]

Apart from one report on olefination of cyclohexanone with transition metal (Ti, Sc, V) complexes of diphenylphosphonium dimethylide,[33] the use of diylides as reagents for organic synthesis was not investigated until 1987, when we carried out our first studies.[42–45]

In addition to the possibility of changing their reactivity by exchanging the associated metal, a determining reason for our initial interest in the diylides 34 was the expectation[42] that they would exhibit a strong nucleophilicity, higher than that of corresponding monoylides 33, indeed even higher than that of the corresponding α-phosphoryl carbanion 35, because the empty phosphorus orbitals, already engaged in the first ylidic bond, are less available for stabilizing the second carbanionic center.

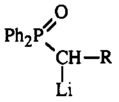
The comparison of "monoylide *versus* diylide" reactivity toward aldehydes and ketones (eq 6), completed later by the results of McKenna and Walker,[44–47] corroborates this expectation [Table 3; see particularly entries 2m/2d (unstabilized ylides), 7m/7d (semistabilized ylides), and 10m/10d (stabilized ylides)].



(6)

33 M = H

34 M = Li



35

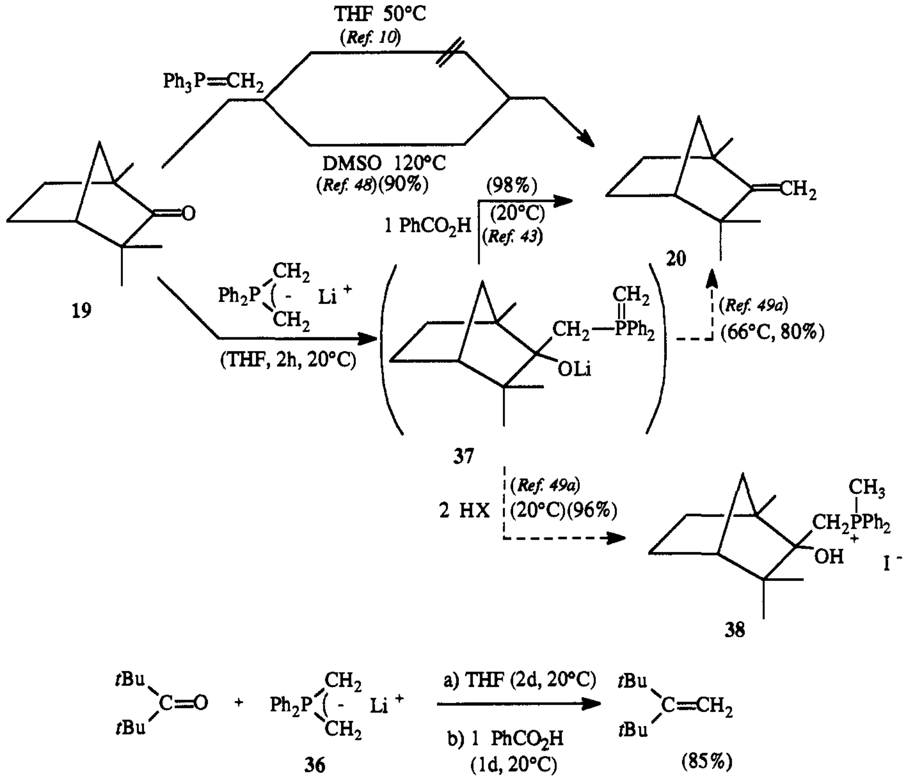
This strong nucleophilicity is further supported by the easy olefination of sterically hindered ketones such as L-fenchone (98%) or di-*tert*-butyl ketone (85%)[43,49a] (Scheme 3) which do not react easily with monoylides.[10,48]

Evolution of the intermediate metalated betaine 37 (which can also be quantitatively trapped by treatment with an excess of acid) can be facilitated at room temperature by selective monoprotonation of the carbanionic center with 1 equiv of acid (Scheme 3), resulting as expected[42] in an increase of the electrophilic character of the phosphorus.

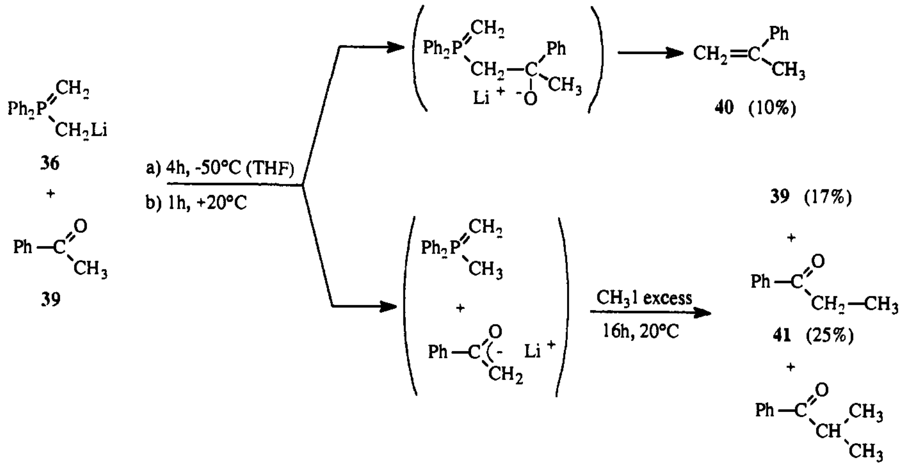
By contrast to the monoylide behavior,[41b] in the reaction of *unstabilized* diylide 36 with an enolizable ketone such as acetophenone 39, normal olefination is only a minor process (10%); the main reaction corresponds to enolization and is proved by trapping the enolate with methyl iodide into the ketones 41 and 42 (48%)[49b] (Scheme 4).

Such enolization does not seem to take place with semistabilized[46] or stabilized[47] diylides. However minor enolization was observed out in the reaction of acetophenone with a semistabilized diylide,[49c] while no enolization was observed with unstabilized diylides.[30] Neither of these last two results have been exactly described from an experimental point of view, and are not in accordance with other results. This discrepancy may be connected with the exact reaction conditions. A more systematic investigation would be necessary to elucidate this point.

Scheme 3



Scheme 4



However, in all cases of aldehydes, no enolization seems to take place, probably due to the higher electrophilicity of the carbonyl function.

Another kind of secondary reaction, unusual with phosphonium monoylides but encountered with α-phosphoryl carbanions,[50,51] is the Michael addition occurring in the reaction of phosphonium dimethylide **36** with an α,β-unsaturated ketone such as the chalcone **43a**, but not with the methyl vinyl ketone **43b**[49d] (Scheme 5).

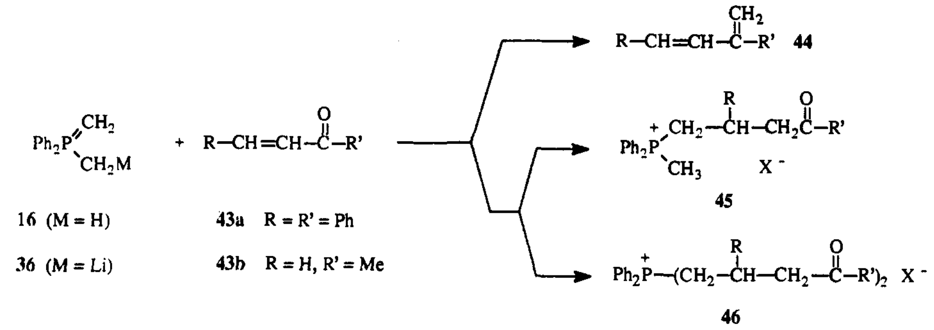
The stereochemical results of the olefination reaction of aldehydes with diylides depend on the molecular ratio (1/1 or 1/2) used between diylides and aldehydes.

For the equimolecular ratio 1/1, the results are summarized in Table 3 and normally show (except entries 3 and 11) an increase in the *E* selectivity compared to the reactions of the corresponding monoylides. A possible explanation for this *E* selectivity may be a Schlosser-type equilibration[52] of the diastereoisomeric intermediates, favored by an intramolecular α/α' proton transfer (Scheme 6), or a Maryanoff's anionic group effect,[53,54] or further an ate complex mechanism suggested more recently by McKenna and Walker[30] (Scheme 7).

This last suggestion seems to be corroborated by the isolation of 0.5 mol of the phosphinate anion together with 0.5 mol of the unreacted diylide,[30] but refuted by the isolation of *ca.* 0.6 mol of methyldiphenylphosphine oxide in the olefination of benzophenone.[49e] Nevertheless, in this hypothesis, no indication is given about the origin of the diastereoselection between the six possible diastereoisomeric ate complexes, leading to a higher *E* stereoselectivity.

For the molar ratio 1/2 (diylide/carbonyl compound) the results summarized in the Table 4 show: (i) that a second olefination can occur involving either the resulting phosphoryl-stabilized anion in a classical

Scheme 5



Reagent	M	R	R'	Yields (%)		
				44	45	46
16	H	Ph	Ph	67	-	-
36	Li	Ph	Ph	5 <	35	31
36	Li	H	Me	56	-	-

Table 3. Comparison of Reactivity "Monoylide *versus* Diylide" toward Aldehydes and Ketones (Eq 6)

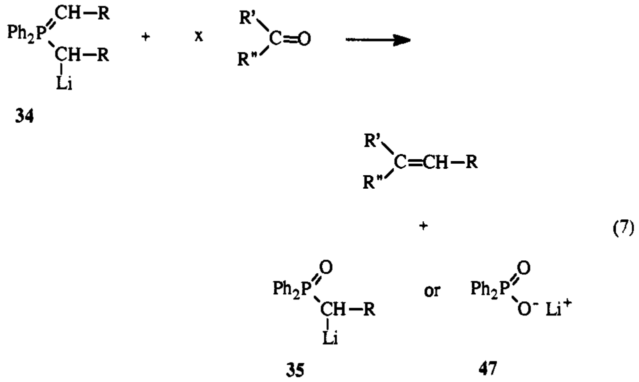
entry[a]	R	M	R′	R″	yield (%)	Z/E	Ref.
1m	H	H	Ph	Ph	75		43
1d	H	Li	Ph	Ph	63 (+23)[b]		43
2m	Et	H	C_6H_{13}	H	10	98/2	43
2d	Et	Li	C_6H_{13}	H	98	40/60	43
3m	Ph	H	C_6H_{13}	H	95	10/90	43
3d	Ph	Li	C_6H_{13}	H	95	25/75	43
4m	Ph	H	C_5H_{11}	H	85	15/85	35
4d	Ph	Li	C_5H_{11}	H	91	5/95	35
5m	Ph	H	Ph	H	98	15/85	43
5d	Ph	Li	Ph	H	98	5/95	43
6m	Ph	H	Ph	H	87	15/85	46
6d	Ph	Li	Ph	H	96	15/85	46
7m	Ph	H	Ph	Ph	45		43
7d	Ph	Li	Ph	Ph	80		43
8m	CO_2Me	H	*i*Pr	H	94	8/92	47
8d	CO_2Me	Li	*i*Pr	H	94	0/100	47
9m	CO_2Me	H	Ph	H	80	13/87	47
9d	CO_2Me	Li	Ph	H	95	2/98	47
10m	CO_2Me	H	Me	Me	10		47
10d	CO_2Me	Li	Me	Me	43		47
11m	CN	H	Me	H	49	51/49	47
11d	CN	Li	Me	H	55	56/44	47
12m	CN	H	$-(CH_2)_5-$		81		47
12d	CN	Li	$-(CH_2)_5-$		91		47

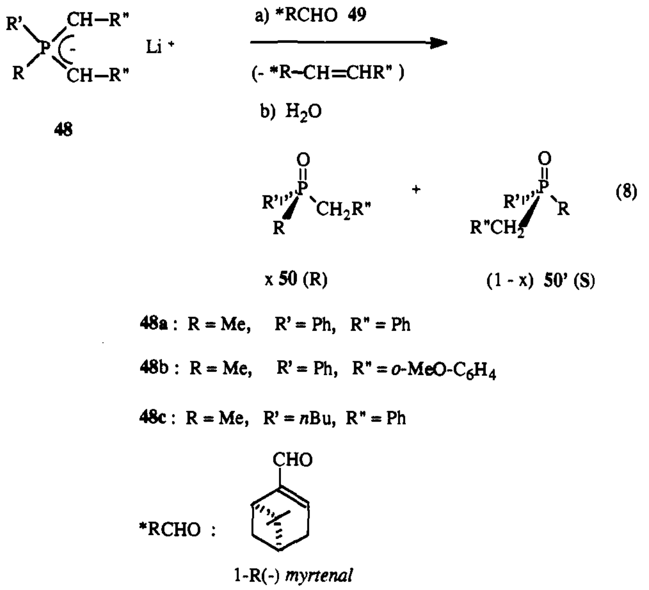
[a] m = monoylide; d = diylide. [b] The corresponding β-hydroxyalkylphosphonium salt (23%) is isolated demonstrating that in this experiment the decomposition of the intermediate metallated betaine adduct is slow.

Wittig–Horner reaction, or the intermediate metalated oxyphosphetane; (ii) that the second olefination is also highly *E* stereoselective since there is a slight increase in the *E* stereoselectivity normally observed (except for the entries 2a/2b and 6a/6b).

With regard to the stereoselectivity in the olefin formation, it is interesting to notice the extension of the chemistry of the phosphonium diylides to the analogous arsonium diylides which give similar results in the olefination of aldehydes, even with an *E*/*Z* ratio higher than 99/1.[35]

Another point of view for the stereochemistry of the reaction of the diylides with aldehydes or ketones concerns the phosphonium transformation. When the residual substituents on the phosphorus are unlike, the phosphonium diylide **48** is a prochiral substrate: the reaction with 1 equiv of a chiral aldehyde **49** (or ketone) can afford an optically active phosphine oxide **50** through asymmetric synthesis (eq 8).





The reaction was performed for the diylides **48a–c** with various chiral carbonyl substrates,[49f] but the

Scheme 6

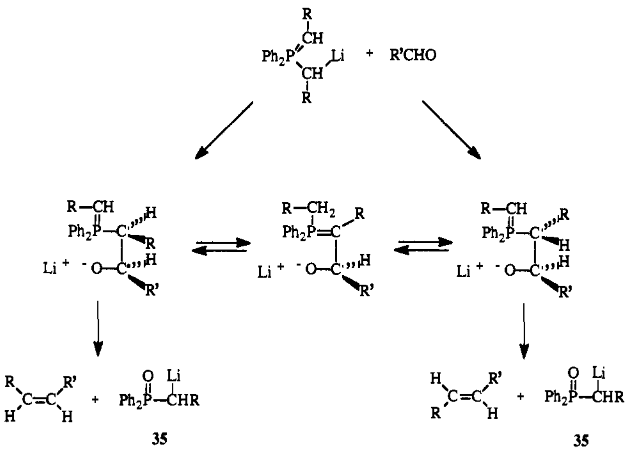


Table 4. Comparison of Reactivity of Diylides toward 1 *or* 2 Equiv of Aldehyde or Ketone (eq 7)

entry	R	x^a	R′	R″	yield (%)^b	Z/E	ref
1a	Ph	1	Ph	H	96	15/85	46^c
1b	Ph	2	Ph	H	144	6/94	46^c
2a	Ph	1	Ph	H	92	12/88	47^d
2b	Ph	2	Ph	H	176	18/82	47^d
3a	Ph	1	nC$_5$H$_{11}$	H	91	5/95	35^e
3b	Ph	2	nC$_5$H$_{11}$	H	152	4/96	35^e
4a	CO$_2$Me	1	Me	Me	43		47^c
4b	CO$_2$Me	2	Me	Me	61		47^c
5a	CO$_2$Me	1	Ph	Me	95	2/98	47^c
5b	CO$_2$Me	2	Ph	Me	120	1/99	47^c
6a	CO$_2$Me	1	iPr	H	94	0/100	47^c
6b	CO$_2$Me	2	iPr	H	200	2/98	47^c
7a	CN	1	-(CH$_2$)$_5$-		91		47^c
7b	CN	2	-(CH$_2$)$_5$-		171		47^c
8a	CN	1	Me	H	55	56/44	47^c
8b	CN	2	Me	H	80	50/50	47^c

[a] Molar ratio of aldehyde or ketone to diylide. [b] Calculated as molar ratio between the alkene formed and the initial diylide. [c] THF, + 20 °C. [d] THF, -98 °C. [e] THF/HMPA (85/15:v/v), -78 °C.

best enantiomeric excesses, obtained with [1-R(−)]-myrtenal, were not higher than 12% (corresponding to the quantitative formation of the corresponding phosphine oxide, with the S(−) compound **50′a** as the major enantiomer) and were not improved (ee = 7%) by partial kinetic resolution (51% transformation of the starting compounds).

Nevertheless, with a more effective chiral inductor, it might be possible to use this approach to synthesize optically active phosphine oxides, normally obtained by less straightforward methods.[56–58]

C. Reactivity of Diylides toward Other Electrophiles

Owing to the strong stabilization of their carbanionic part by the positive phosphorus counterpart, phosphonium monoylides exhibit a moderate nucleophilicity which restricts most of their reactivity to aldehydes and ketones. On the one hand this behavior is favorable to the chemoselectivity of the Wittig reagents and contributes to their success in the synthesis of elaborated structures, but on the other it sets limits to their use in organic synthesis as a tool for function interconversion. In this respect, phosphonium diylides have a higher nucleophilicity and therefore a more widespread field of applications.

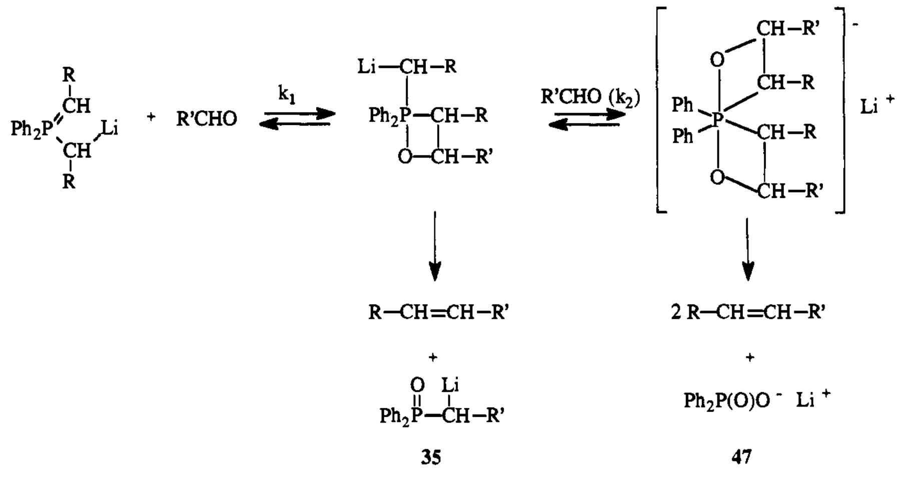
1. Reactivity of Diylides toward Derivatives of Carboxylic Acids

With esters of carboxylic acids[2c] **52**, phosphonium monoylides **51** generally react under drastic conditions or with "activated" esters and give moderate yields of products **53** and **54** corresponding either to the carbonyl olefination of the ester or to the acylation of the ylide (Scheme 8).[59] For intermolecular reaction, the nature of the products depends on the stabilization of the monoylide: generally, with nonstabilized ylides, the major reaction is the acylation[41b,60,61] but with the stabilized or semistabilized ylides olefination is preponderant.[61,62] Intramolecular reactions have also been intensively investigated: in the same general way, nonstabilized ylides **55** afford the corresponding cyclic β-keto ylides **56** as a result of the acylation process,[63,64] and the stabilized or semistabilized ylides **57** lead mostly to oxygenated heterocycles **58**.[65–67]

With an aromatic ester such as ethyl benzoate (**59**), the nonstabilized and semistabilized diylides **34** react more easily than the corresponding monoylides **33**, and the reaction affords only benzoylation product **60** (eq 9, Table 5, entries 1–4).

However, with an aliphatic ester such as ethyl acetate (entry 5), the acylation reaction is only a minor process as compared to the predominant enolization. Also with an α,β-unsaturated ester such as ethyl cinnamate (entry 6), the acylation, although the main reaction (47%), takes place in parallel to a secondary reaction (18%)

Scheme 7



Scheme 8. Reactivity of Monoylides toward Esters

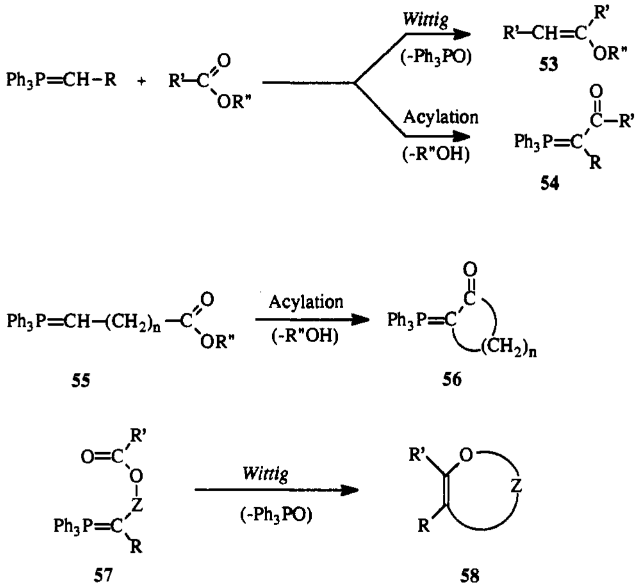
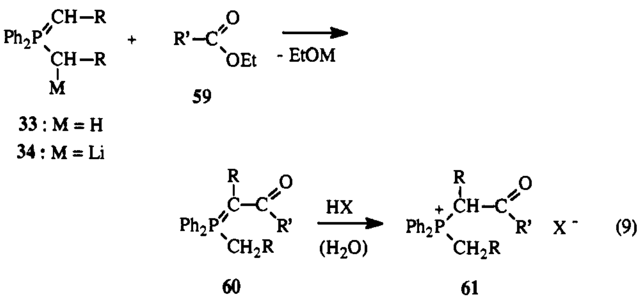


Table 5. Reaction of Ylides 33 or 34 with Esters 59 (Eq 9)

entry	R	M	R′	conditions	yields 61 (%)	ref
1	H	H	Ph	10 h, +20 °C	23	49f
2	H	Li	Ph	2 h, -76 °C	60	49f
3	H	Li	Ph	2 h, -20 °C	98	44,49f
4	Ph	Li	Ph	2 h, +20 °C	98	42, 49f
5	H	Li	Me	5 h, -50 °C	5	49f
6	H	Li	PhCH=CH—	2 h, -55 °C 13 h, +20 °C	47	44

corresponding to the 1,4-addition of the ylide on the activated C=C double bond.



From the synthetic point of view, the easy acylation of diylides with nonenolizable esters was particularly suited to carbonic acid derivatives 62.[68,69] Lithium diphenylphosphonium dimethylide (36) readily attacks at room temperature the cyclic carbonates **62a,b**, carbamate **62c**, and thiocarbamate **62d** to afford the corresponding "pseudo-acylation" products **63** as a result of a ring-opening step followed by an intramolecular proton transfer. The functional stabilized monoylides **63** can be trapped by acidolysis into the corresponding phosphonium salts **64**, but they can also be used *in situ* as carbonyl olefination reagents for aldehydes, affording a new one-pot procedure for the *E* stereoselective synthesis of α,β-unsaturated esters **65** (Y = O) and amides **65** (Y = NR) bearing a free ω-hydroxyl or ω-thiol group. (The latter can give intramolecularly a pseudo-Michael reaction to afford a sulfur heterocycle, Scheme 9).

With carboxamides **66**, reactions of monoylides are very similar to reactions with esters: both acylation and Wittig olefination can occur (Scheme 10).[2d]

The course of the reaction is not easy to predict, although some general indications can be pointed out. On the one hand, acylation seems to be favored by the good leaving amino groups (aziridine,[70] imidazole[71]); on the other hand, the Wittig olefination can preferentially occur in the intramolecular reactions,[72-75] with activated amides (such as oxamic esters[76] or perfluorinated amides[77]), with amides which have a poor leaving group[78] and with imides.[59]

Diylide **36** reacts spontaneously with *N,N*-dimethylbenzamide (**67**, Scheme 11) to yield only 20% of the Wittig reaction product **70**, the major product (80%) being the benzoylated ylide **71** (Table 6, entry 1).[44]

In comparison to the monoylide behavior, it is likely that the evolution of the intermediate adduct **68** is (i) favored for the acylation pathway *b* with the electrophilic assistance of the lithium cation for the cleavage of the amino group and (ii) disfavored for the Wittig pathway *a* by the lowering of the phosphorus positive charge induced by the remaining ylide moiety on the phosphorus. This explanation is in accordance with the 76% Wittig olefination produced when the lithium is exchanged with an hydrogen by monoprotonation of the adduct **68** at low temperature (Table 6, entry 2). In this case, the evolution parallels the reaction of monoylides to afford mainly the enamine **70**. It is also the result of the reaction with *N,N*-dimethylformamide (entry 3).

It is significant that the reaction of amides with diylides is much easier than with the corresponding monoylides: for example, the monoylide **33** (R = H) does not react at all with the *N,N*-dimethylbenzamide after 2 days at room temperature.

The reaction of nonenolizable amides **67** (R = Ph, H) with diylides takes place first through addition to the carbonyl group and, owing to the selective monoprotonation of the intermediate adduct **68**, can be directed toward the Wittig olefination. But, just as with esters, enolization is the main reaction (60%) with *N,N*-diethylacetamide, and also the 1,4-addition (80%) with *N,N*-diethylcinnamide.[44]

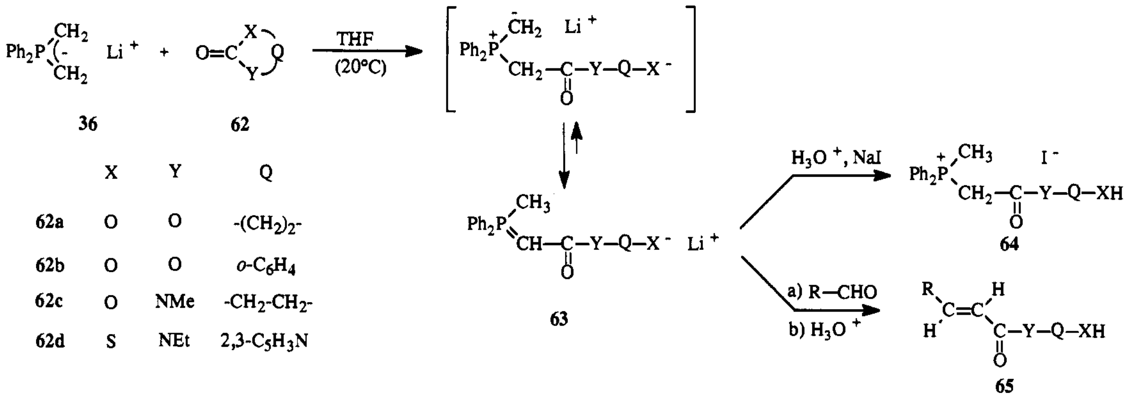
2. Reactivity of Diylides toward Derivatives of Carbonic Anhydride

In the reaction of monoylides with isocyanates **73**, the conditions and products depend on the presence or absence of at least one hydrogen on the ylidic carbon: (i) the disubstituted monoylides **72** afford, at high temperature, the corresponding ketenimines **74** by a Wittig-type olefination (eq 10)[79-81] and (ii) nonsubstituted or monosubstituted monoylides **51** condense, at moderate temperature, to produce stabilized ylides **75** (eq 11).[82,83]

As far as carbodiimides **76** are concerned, even if the reaction of monoylides with diphenylcarbodiimide is known, no reaction is detected for DCC due to a lack of activation (eq 12).[84,85]

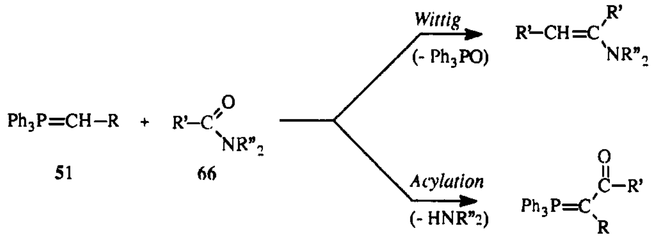
Nonstabilized as well as semistabilized diylides **34** react with the phenyl isocyanate **73** (R′ = Ph) and the dicyclohexylcarbodiimide **76** (R′ = c-Hex) in a pseudo-acylation way (Scheme 12): the first addition step gives the corresponding adducts **78** which are transformed

Scheme 9. Reaction of Diylide 36 with Carbonic Acid Derivatives



	X	Y	Q
62a	O	O	-(CH$_2$)$_2$-
62b	O	O	o-C$_6$H$_4$
62c	O	NMe	-CH$_2$-CH$_2$-
62d	S	NEt	2,3-C$_5$H$_3$N

Scheme 10. Reactivity of Monoylides toward Amides



Scheme 11

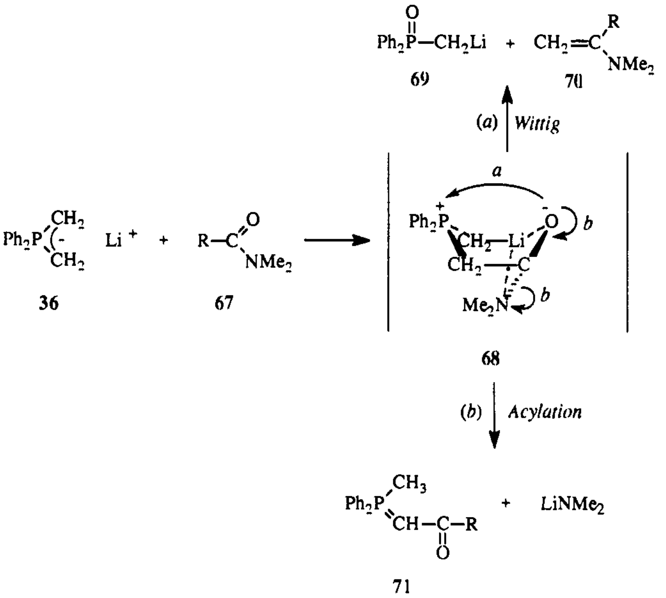
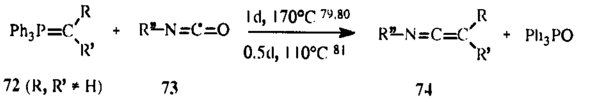


Table 6. Reactions of Diylide 36 with *N,N*-Dimethylcarboxamides 67 (Scheme 11)

entry	R	conditions	70 (%) *Wittig*	71 (%) *Acylation*
1	Ph	(a) 2 h, -55 °C (b) 13 h, +20 °C	20	80
2	Ph	(a) 4 h, -55 °C (b) 1 PhCO$_2$H, (-55 °C) (c) 16 h, +20 °C	76	18
3	H	(a) 4 h, -55 °C (b) 1 PhCO$_2$H, (-55 °C) (c) 16 h, +20 °C	60	

into pseudo-acylated monoylides 78′ by an intramolecular transylidation process. The intermediate adducts 78′, which can be trapped into the corresponding phosphonium salts 79 by acidolysis, are nonstabilized monoylides, bearing a metalated α-function. They can be used *in situ* as Wittig reagents in a one-pot procedure with aldehydes as well as ketones: the corresponding α,β-unsaturated N-substituted amides 80 (X = O) and amidines 80 (X = NR′) are obtained in moderate to good yields and high *E* stereoselectivity (Scheme 12).[68,86]



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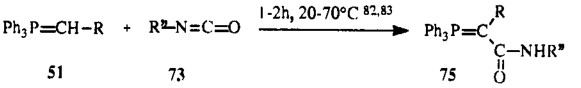
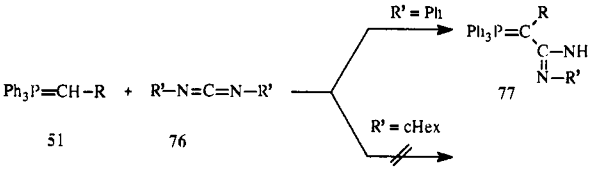
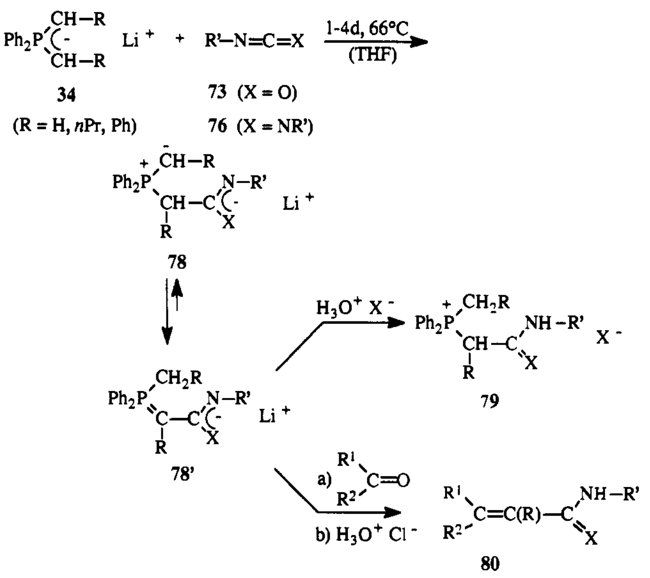


(11)



(12)

Scheme 12

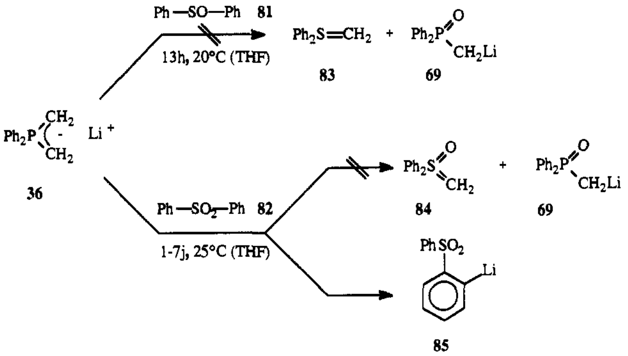


3. Reactivity of Diylides toward Sulfur Electrophiles

Until now, apart from a few examples,[2d] the reactivity of phosphonium monoylides toward sulfur electrophiles has not really been investigated.

Owing to the high nucleophilicity of the phosphonium diylides, it was expected that they would react with such heteroatomic electrophiles. In practice the first

Scheme 13



results were disappointing: at room temperature the lithium diphenylphosphonium dimethylide (**36**) did not appear to react with the diphenyl sulfoxide **81** and there only were indications of an *ortho* metalation process on the phenyl ring of the diphenyl sulfone **82** (Scheme 13).[87]

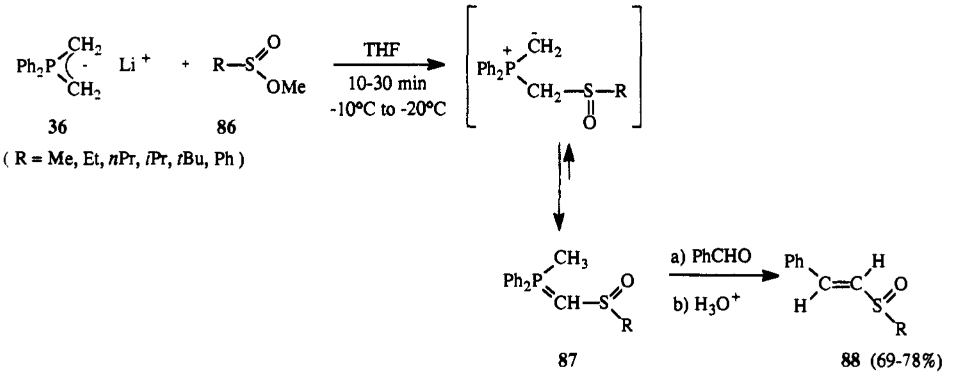
With methyl sulfinates **86**, however, and in a similar way to acylation by the carboxylic esters, a sulfinylation reaction of diylide **36** took place easily at room temperature to give the corresponding stabilized monoylides **87**, which can react as Wittig olefination reagents for the benzaldehyde. Starting with the methyl aryl- or alkylsulfinates, this reaction affords a new one-pot synthesis of the vinylic sulfoxides **88** obtained with a high *E* stereoselectivity (usually $E/Z > 96/4$) (Scheme 14).[68,88]

From the stereoselectivity point of view, this synthesis appears to be superior to the analogous Horner reactions involving α-phosphoryl sulfoxides which afford mixtures of *E* and *Z* isomers.[89,90] It is also interesting to point out that the analogous reaction of the phosphonium monoylide **16** with sulfinates led to the same α,β-unsaturated sulfoxides **88**, but with a much lower yield (ca. 40%) as a result of a transylidation process involving the loss of half the initial ylide.[68] Further, it is noteworthy that, in contrast to the reaction with the aliphatic carboxylic esters, the reaction of the diylide **36** with alkyl sulfinates does not afford the enolization of the substrate but the normal sulfinylation of the diylide.

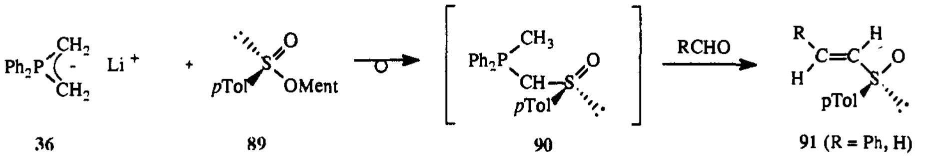
An interesting development for this synthesis of vinylic sulfoxides concerns the possibility of obtaining the chiral compounds with a high enantiomeric purity: for instance, the reaction of diylide **36** with the optically pure menthyl sulfinate **89** followed by the *in situ* Wittig reaction with benzaldehyde leads to the chiral (E)-styryl sulfoxide **91** with an enantiomeric excess higher than 95% corresponding to a full inversion of configuration at the sulfur atom (Scheme 15).[68,88]

With sulfonates **92** the diylide **36** reacts differently according to the leaving group on the sulfur atom: the aryl tosylate **92** (R = Ph) reacts, similarly to alkyl sulfinates, through nucleophilic substitution at the electrophilic sulfur atom, and affords the possibility of a one-pot (fully *E* stereoselective) synthesis for the α,β-unsaturated sulfone **94**. However alkyl tosylate **92** (R = Me) reacts, through a nucleophilic substitution at the electrophilic carbon atom, as an alkylating agent for the diylide **36** (Scheme 16).[87] In the same way,

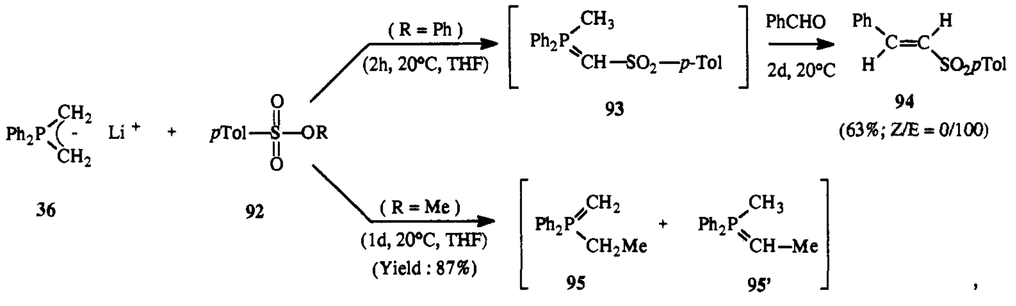
Scheme 14. Reaction of Diylide 36 with Sulfinates 86



Scheme 15



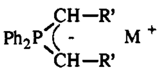
Scheme 16

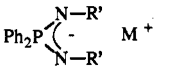


alkylation also takes place easily on the ylidic position of the diylide **36** reacting with dimethyl sulfate.

IV. Lithium Diaminophosphonium Diazadiylides

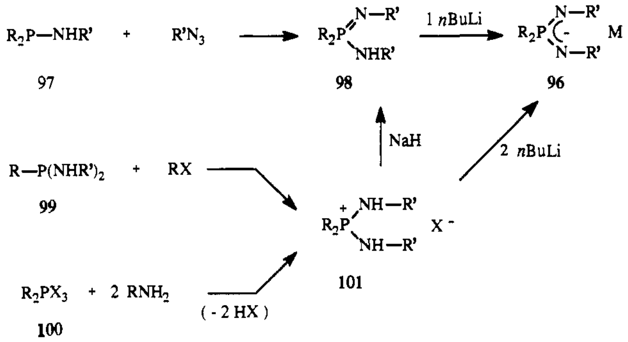
For diazadiylides **96**, which are isoelectronic structures for the diylides **29**, some attention has been devoted to silylated structures (R′ = $SiMe_3$),[91–94] but we focus here more specifically on alkyl or aryl N-substituents.


29

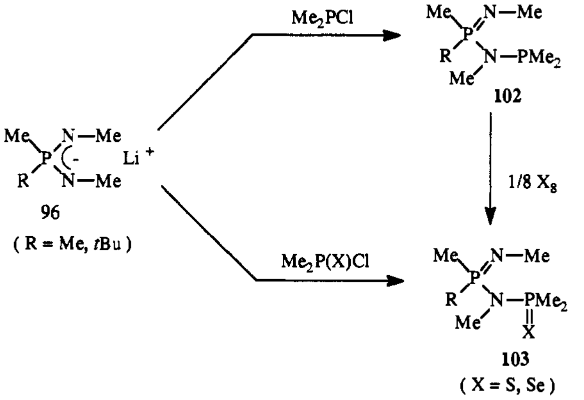

96

Diazadiylides **96** are generally obtained either by monodeprotonation[16,95,96] of azaylides **98** (also called phosphinimines (phosphine imides) or monophosphazenes or iminophosphoranes),[2e] which are usually obtained from aminophosphines **97** by a Staudinger reaction[2f,97,98] with an azide,[16,95,96] or by double deprotonation of diaminophosphonium salts **101**,[42b,99,100] generally prepared by alkylation of diaminophosphines **99**[99] or double aminolysis of trihalophosphoranes **100**[101] (Scheme 17).

Scheme 17. Preparations of Diazadiylides 96



Scheme 18



In the solid state, the N,N′-unsubstituted diazadiylide **96** (R = tBu, R′ = H) is an oligomeric species in which the lithium atom occupies a symmetric position with regard to the nitrogen atom.[16] But, for N-substituted diazadiylide the structure **96** is trimeric (R′ = Me)[16] or dimeric (R′ = $SiMe_3$).[93]

Apart from the N-silylated derivatives,[93,94] diazadiylides **96** have been only investigated toward monochlorophosphines or the corresponding thiono- or selenophosphinic acid chlorides (Scheme 18).[99]

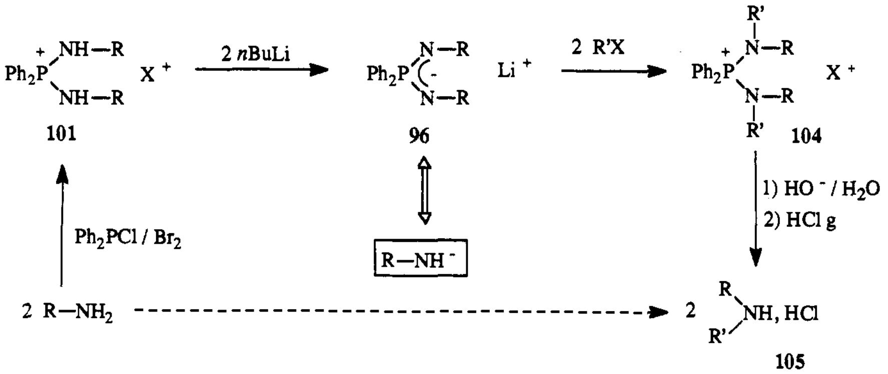
The selective N-mono or N,N′-dialkylation of diylides **96** has been achieved with activated alkylating agents, such as benzyl, allyl, or propargyl tosylates.[102a] The corresponding diaminophosphonium salts **104** can be cleaved to give 2 equiv of the secondary amines chlorhydrates **105** after an alkaline hydrolysis step followed *in situ* by acidolysis of the resulting phosphinamide (Scheme 19).[102b]

According to this scheme, diazadiylides react as synthetic equivalents of the synthon RNH^-. In comparison with other nucleophilic phosphorus aminating agents,[103–109] they can present somes advantages owing on the one hand to their higher reactivity [pK_{a_1} and pK_{a_2} values are estimated respectively at 14.9 and 30.6 for the diaminophosphonium salt **101** (R = Ph, R′ = nBu)][102c] and on the other to the presence of two reactive nitrogen atoms in the same moiety, which should facilitate the selective N-monoalkylation of cyclic phosphonium salts **101** obtained from diamines.

V. Lithium Aminophosphonium Azadiylides

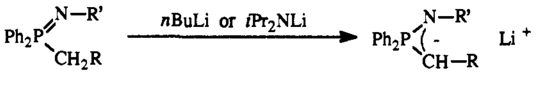
Lithium aminophosphonium azadiylides **107** are mixed diylides, in which the ylidic positions are located both on the nitrogen and carbon atoms situated α to the phosphorus. They are obtained by deprotonation of N-substituted alkyldiphenylphosphinimines **106** with organolithium reagents or with lithium amides (eq 13).[110,111] A cyclic azadiylide, derived from diazaphosphole, has also be obtained in the reaction of lithium di-*tert*-butylphosphide with 2 equiv of benzonitrile.[112]

Scheme 19



(R = nBu, $PhCH_2$, Ph)

(R′ = $PhCH_2$, CH_2=CH-CH_2, Me-CH=CH-CH_2, Me—C≡C—CH_2)

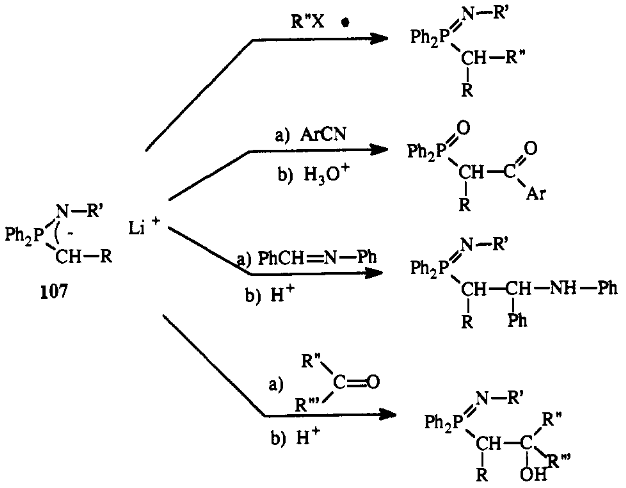


(13)

106 107

Reflecting probably the difference in nucleophilicity between the two ylidic positions, all the reactions described with various electrophiles occur at the carbon center: alkylation,[110,111] acylation,[110,113] as well as α-aminoalkylation[114] or α-hydroxyalkylation[111,115] (Scheme 20).

Scheme 20



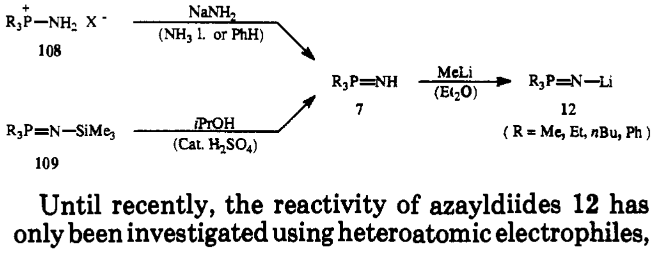
In the reaction with aldehydes[115] or ketones[111] it must be pointed out that the Wittig reaction does not occur and the betaine adduct can be trapped by selective protonation or silylation of the oxygen anionic center. In the betaine adduct, oxygen transfer to phosphorus, resulting in alkene formation, does not take place probably because of the low positive charge on the phosphorus due to the +M effect of the nitrogen atom of the imino group. The stability of intermediate betaine can be compared here with that of analogous adducts, such as **37** formed by carbon diylides **29**; but, in this case, the evolution into alkene does not appear to be facilitated by a selective monoprotonation of the second ylidic center, the nitrogen atom.

VI. Lithium Aminophosphonium Azayldiides

Lithium aminophosphonium azayldiides **12**, which can also be considered as N-lithiated phosphinimines, are isoelectronic structures for the yldiides **6**.

They were initially prepared by Schmidbaur,[18] by direct metalation of the corresponding N-unsubstituted azaylides **7**,[116,117] which can be obtained either from the aminophosphonium salts **108**[117-120] or from the N-silylated phosphinimines **109**[121] (Scheme 21).

Scheme 21



Until recently, the reactivity of azayldiides **12** has only been investigated using heteroatomic electrophiles, to give the corresponding N-substituted azaylides **110** (eq 14).[18,122-126]

$$R_3P{=}N{-}Li \ + \ R'_nECl \longrightarrow R_3P{=}N{-}ER'_n \qquad (14)$$

110

E = P, As (n = 2) [123]

E = Si, Ge, Sn (n = 3) [123, 124]

Comparing the nitrogen analog **112** to the yldiide **14**, the corresponding aminophosphonium salt **111** can easily be prepared in solution form and submitted to a double deprotonation with 2 equiv of n-butyllithium (eq 15).[45,127] In THF solution the reagent **14** appears to exist as a cyclic trimer.[127]

$$Ph_3P \xrightarrow[b)\ NH_3\ (g)]{a)\ Br_2\ (MeCN)}$$

$$Ph_3\overset{+}{P}{-}NH_2\ Br^- \xrightarrow[(THF)]{2\ nBuLi} Ph_3P{=}N{-}Li \qquad (15)$$

111 **112**

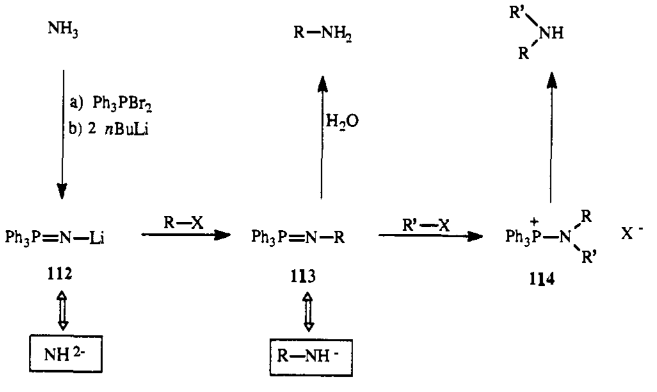
Azayldiide **112** reacts toward alkylating agents as a synthetic equivalent of dimetalated ammonia: it affords a new synthetic approach to primary and secondary amines, resulting from the hydrolysis of the N-monoalkylated phosphinimines **113** or N-dialkylated aminophosphonium salts **114** (Scheme 22).[127]

The process can also be applied, even with moderate yields, to mono- or dialkylation by α-bromo esters, thus providing a method of preparing amino acids.[68,128]

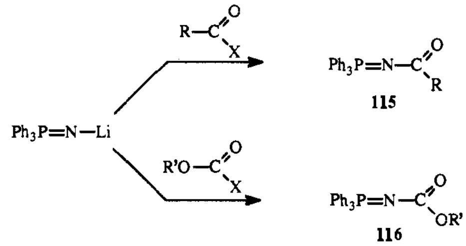
Similarly, owing to its high nucleophilicity, the azayldiide **112** can be readily acylated not only with acyl chlorides or acid anhydrides, but also with esters or carbonates to give the corresponding N-acyl phosphinimines **115** and **116** (Scheme 23).[129]

Reactions of azayldiide **112** take place easily and without any transyluration process with various

Scheme 22



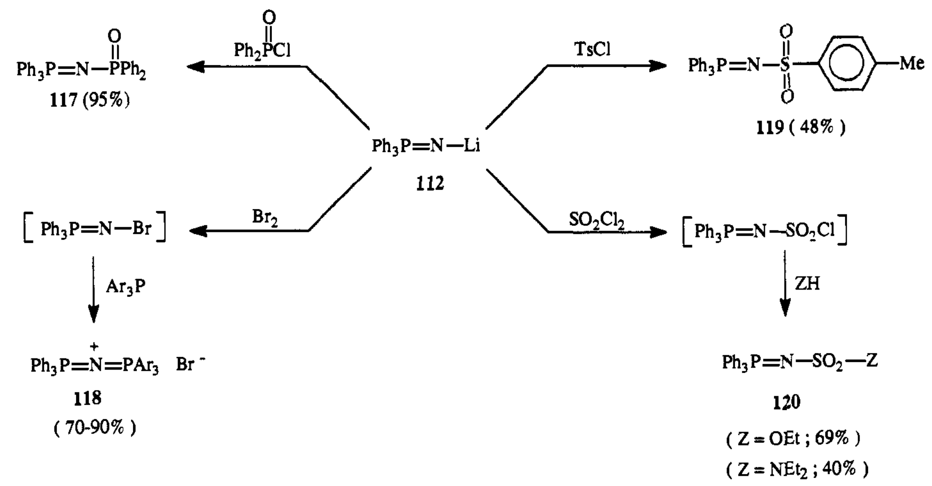
Scheme 23



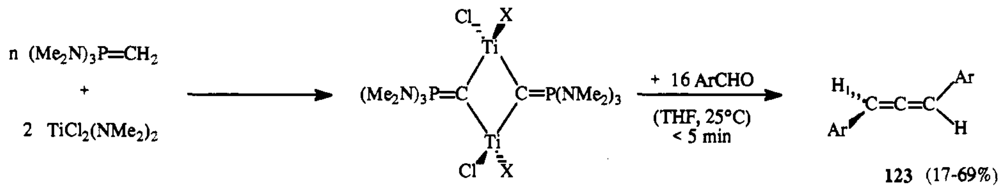
R = Me, CCl₃, CF₃, Ph X = Cl, OAc, OEt

R' = Me, Et, CH₂Ph, Ph X = Cl, OPh

Scheme 24



Scheme 25



121 X = NMe2 (n = 3)
122 X = Cl (n = 2)

heteroatomic electrophiles to give an easy one-pot preparation for a large range of N-substituted phosphinimines which are valuable precursors in phosphorus or sulfur chemistry (Scheme 24).[128]

VII. Concluding Remarks

The previously mentioned applications illustrate the worth of metalated phosphonium ylides as reagents for organic synthesis, in particular for their ability to react with poor electrophiles due to their high nucleophilicity. Yldiides are, if only for the present, mainly restricted to the parent structure **14**.

Diylides **34** have more scope and could be further developed to (i) better investigate the mechanism and stereoselectivity of carbonyl olefination with aldehydes and ketones, (ii) find new synthetic applications with other electrophiles, and (iii) determine the influence of other associated metals, particularly transition metals, on the reactivity of the diylide moiety.

At present the main interest of diazadiylides **96** is possibly for the synthesis of polyamines and functional amines, but it is probable that in the future they will be used in heterocycle synthesis by specific intramolecular reaction, following an aza-Wittig imination reaction.

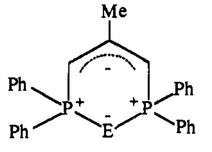
Finally, azayldiides, mainly compound **112**, are promising nucleophilic aminating agents, which could also be transformed into chirality-inducing reagents by using a chiral phosphonio group.

However, as already pointed out with diylides **34**, the potentially most fruitful developments for metalated phosphonium ylides in organic synthesis will probably concern changing of lithium by other cationic counterparts, in particular transition metals.

Recently, such possibilities of development have been illustrated by the synthesis of complexes of titanium with bridging ylide ligands corresponding to structures **121** and **122** (which actually could be considered as dimeric yltriides) (Scheme 25).[130]

These complexes have found interesting applications as "carbon atom" synthons, particularly for the selective synthesis of allenes **123** by condensation *in situ* with 2 equiv of aromatic aldehydes.[130,131]

At last, another promising area for further developments of the metalated phosphonium ylides probably will be found in the synthetic use of diylides or yldiides containing heteroatoms such as B, P, As, etc., as anionic centers bound to the phosphonio group. Some recent articles of the Schmidbaur's group concern the synthesis and structural study of such cyclic compounds **124** and could open very new synthetic applications.



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(E = CH, N, BH2, P, As)

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IX. References and Notes

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(3) Wittig, G.; Felletschin, G. *Justus Liebigs Ann. Chem.* **1944**, *555*, 133. More exactly, the name "phosph*onium* ylide" should be transformed to "phosph*onio* ylide" [for instance, "triphenylphosphonio methylide" in the case of compound 1, R − Ph], in order to take into account the fact that the "alkylide" group is the fourth substituent of the phosphonium entity. But, owing to accepted procedure,[2b] we will continue to use the term phosphonium instead of phosphonio.
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