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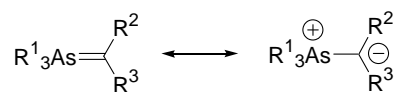
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Arsonium Ylides in Organic Synthesis

Helen Song He, Cecilia Wan Ying Chung, Tracy Yuen Sze But
and Patrick H. Toy*

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Arsonium Ylides in Organic Synthesis

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Abstract—Arsonium ylides are versatile reagents in organic synthesis. They exhibit greater nucleophilicity than do the corresponding triphenylphosphonium ylides and can thus participate in a wider range of reactions. The uses of these ylides in the context of organic synthesis are reviewed here. © 2004 Elsevier Science. All rights reserved

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1. Introduction

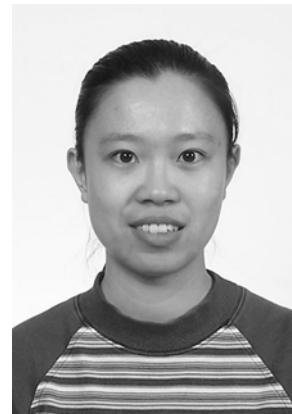
In the field of organic synthesis, organoarsines have found wide application. They, especially triphenylarsine (**1**),¹ have been found to be useful as a metal ligand in a range of palladium-catalyzed cross-coupling reactions between organohalides and organostannanes² or organoboronic acids.³ They can also be used for the preparation of arsonium ylides (alkylidene arsonanes) that are more nucleophilic than their phosphonium counterparts.⁴ Since the preparation and use of arsonium ylides in the context of organic synthesis was last comprehensively reviewed in 1987,⁵⁻⁷ the present review

covers this subject in the literature from 1987 through to early 2004.

Of the many organoarsine compounds that are useful for the preparation of arsonium ylides,⁵ **1** is currently used almost exclusively since it is commercially available in high purity as a non-volatile crystalline solid. Arsonium ylides prepared from **1** and other organoarsines are stronger nucleophiles than are the corresponding phosphonium ylides because the zwitterionic resonance form makes a larger contribution in them (Figure 1). This has been established by a variety of methods, including X-ray crystallography,⁸ and IR,⁹ and NMR¹⁰ spectroscopy. The increase in negative charge density on the carbon center of arsonium ylides as compared to

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Helen Song He received her B.S. degree in chemistry from Jilin University in 1999 and her M.S. degree in chemistry from Nankai University under the supervision of Professor Yu Liu in 2002. She is currently pursuing her Ph.D. degree in Prof. Toy's group at the University of Hong Kong. Her research is directed towards the development of polymer-supported arsines and phosphines.



Cecilia Wan Ying Chung was born in Hong Kong, People's Republic of China. She received her B.Sc. degree from the University of Hong Kong in 2002. The following year she started her doctoral studies under the supervision of Prof. Toy. Her research is focused on the development of new polymeric reagents and catalysts for organic synthesis.

Tracy Yuen Sze But received her B.Sc. degree in chemistry from the University of Hong Kong in 2004. She is currently working as a research assistant in Prof. Toy's research group investigating multi-polymer oxidation reactions.

phosphonium ylides accounts for the dramatically different observed reactivity of these two classes of ylides. Thus, in this review, we try to highlight examples where the use of the arsonium ylides broadens the range of chemistry possible with phosphonium ylides or improves the reaction selectivity.

For convenience, the ylides described in this review are tabulated in Table 1, along with the literature citations describing their use. They are designated (AA)-(DZ) and when important, their corresponding precursors are designated (AA')-(DZ'), respectively. It should be noted again that they are almost exclusively prepared from **1**.

Figure 1. Resonance structures of arsonium and phosphonium ylides.

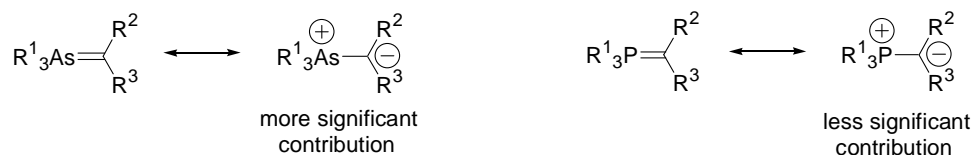
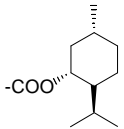
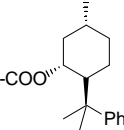
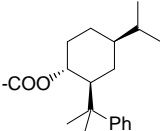




Table 1. Structure of triphenylarsonium ylides (AA)-(DZ).

Ylide	^a R ¹	R ²	R ³	References
AA	-Ph	-H	-H	31, 33, 35, 54, 69, 70, 78, 87
AB	-Ph	-H	-CH ₃	33
AC	-Ph	-H	- <i>n</i> -Bu	33
AD	-Ph	-H	-CH ₂ CH ₂ Br	15
AE	-Ph	-H	-CH ₂ CH-(<i>O</i> - <i>i</i> -Pr) ₂	11, 73
AF	-Ph	-H	-CH ₂ OH	75
AG	-Ph	-H	-CH ₂ CH=CHCH ₂ CH(OEt) ₂	74
AH	-Ph	-H	-CH=CH ₂	15, 37, 38, 81, 88
AI	-Ph	-H	-CH=CHMe	88
AJ	-Ph	-H	-CH=CHPh	88
AK	-Ph	-H	-CH=CHCH ₂ OH	76, 80
AL	-Ph	-H	-CH=CHCHO	65
AM	-Ph	-H	-CH=CHSiMe ₃	88
AN	-Ph	-H	-CH=CHCO ₂ Me	15, 92, 93
AO	-Ph	-H	-CH=CHCO ₂ Et	63, 64
AP	-Ph	-H	-CH=CMe ₂	79
AQ	-Ph	-H	-CH=CHC ₆ F ₅	38
AR	-Ph	-H	-C(CH ₃)=CH ₂	103
AS	-Ph	-H	-C(CH ₃)=CHCO ₂ Me	62
AT	-Ph	-H	-(CF ₃)C=CMe ₂	69, 70, 87
AU	-Ph	-H	(F ₃ C)C=C	69, 70, 87
AV	-Ph	-H	-(C ₂ F ₅)C=CMe ₂	87
AW	-Ph	-H	(C ₂ F ₅)C=C	87
AX	-Ph	-H	-C(OAc)=CHCO ₂ Me	15
AY	-Ph	-H	-CCSi(CH ₃) ₃	39, 71, 72, 85, 86
AZ	-Ph	-H	-Ph	15, 88
BA	-Ph	-H	-C ₆ H ₄ - <i>p</i> -OMe	30, 99-102
BB	-Ph	-H	-C ₆ F ₅	31, 32, 54
BC	-Ph	-H	-CHO	40, 41, 66

Tetrahedron

Table 1. Continued

Ylide	^a R ¹	R ²	R ³	References
BD	-Ph	-H	-COMe	15, 21, 23, 24, 29, 30, 50, 89
BE	-Ph	-H	-CO- <i>i</i> -Pr	42, 43, 45-47
BF	-Ph	-H	-CO- <i>n</i> -C ₅ H ₁₁	42
BG	-Ph	-H	-COCH ₂ CO ₂ Me	15, 94
BH	-Ph	-H	-COCH ₂ CO ₂ Et	15, 94
BI	-Ph	-H	-COCH ₂ CO ₂ - <i>i</i> -Pr	94
BJ	-Ph	-H	-COPh	15, 21-24, 27, 29, 30, 97, 98
BK	-Ph	-H	-COC ₆ H ₄ - <i>p</i> -Cl	23
BL	-Ph	-H	-COC ₆ H ₄ - <i>p</i> -Br	23
BM	-Ph	-H	-COC ₆ H ₄ - <i>p</i> -NO ₂	95, 96
BN	-Ph	-H	-COC(OH)Me ₂	44
BO	-Ph	-H	-CO ₂ Me	15, 21-23, 25, 29, 30, 50, 55, 57, 90, 91
BP	-Ph	-H	-CO ₂ Et	14, 15, 21, 25, 58
BQ	-Ph	-H	-CO ₂ - <i>t</i> -Bu	15
BR	-Ph	-H		17
BS	-Ph	-H		17
BT	-Ph	-H		59
BU	-Ph	-H	-CONH- <i>t</i> -Bu	68
BV	-Ph	-H	-CON 	67
BW	-Ph	-H	-CN	15, 21, 28, 30, 50, 61
BX	-Ph	-H	-OTf	82
BY	-Ph	-H	-SPh	77
BZ	-Ph	-	=CMe ₂	16
CA	-Ph	-		16
CB	-Ph	-Me	-(CH ₂) ₄ CH ₃	33
CC	-Ph	-Me	-CH=CHOSi- <i>i</i> -Pr ₃	26
CD	-Ph	-Me	-CO ₂ Et	14
CE	-Ph	-Et	-CO ₂ Et	14
CF	-Ph	- <i>n</i> -Pr	-CO ₂ Et	14
CG	-Ph	- <i>n</i> -Bu	-CH=CHOSi- <i>i</i> -Pr ₃	26
CH	-Ph	- <i>n</i> -Bu	-CO ₂ Et	14
CI	-Ph	- <i>n</i> -C ₆ H ₁₃	-CH=CHOSi- <i>i</i> -Pr ₃	26
CJ	-Ph	- <i>n</i> -C ₁₁ H ₂₃	-CO ₂ Me	14
CK	-Ph	-CH=CHCOPh	-CO ₂ Me	27
CL	-Ph	-CH=CHCOPh	-CO ₂ Et	27

Tetrahedron

Table 1. Continued

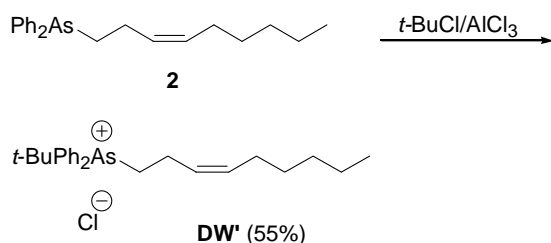
Ylide	^a R ¹	R ²	R ³	References
CM	-Ph		-CO ₂ Et	28
CN	-Ph		-CN	28
CO	-Ph	-COMe	-COMe	19, 21
CP	-Ph	-COMe	-CO- <i>n</i> -C ₅ H ₁₁	21
CQ	-Ph	-COMe	-COPh	21
CR	-Ph	-COMe	-CO ₂ Me	21
CS	-Ph	-COMe	-CO ₂ Et	21
CT	-Ph	-COMe	-CN	21
CU	-Ph	-CO- <i>n</i> -C ₅ H ₁₁	-CO ₂ Me	21
CV	-Ph	-CO- <i>n</i> -C ₅ H ₁₁	-CO ₂ Et	21
CW	-Ph	-CO- <i>n</i> -C ₅ H ₁₁	-CN	21
CX	-Ph	-COPh	-CH=CHCO ₂ Me	27
CY	-Ph	-COPh	-CH=CHCO ₂ Et	27
CZ	-Ph	-COPh	-CO ₂ Me	21
DA	-Ph	-COPh	-CO ₂ Et	21
DB	-Ph	-SPh	-COMe	24
DC	-Ph	-SPh	-COPh	24
DD	-Ph	-SPh	-CO ₂ Me	25, 56c
DE	-Ph	-SPh	-CO ₂ Et	25, 56c
DF	-Ph	-SC ₆ H ₄ - <i>p</i> -Me	-CO ₂ Me	25
DG	-Ph	-SC ₆ H ₄ - <i>p</i> -Me	-CO ₂ Et	25
DH	-Ph	-SePh	-COMe	22b, 23
DI	-Ph	-SePh	-COPh	22b, 23
DJ	-Ph	-SePh	-COC ₆ H ₄ - <i>p</i> -Cl	23
DK	-Ph	-SePh	-COC ₆ H ₄ - <i>p</i> -Br	22a, 23
DL	-Ph	-SePh	-CO ₂ Me	22a, 23, 56a, 56b
DM	-Ph	-SePh	-CN	61
DN	-Ph	-I	-C ₆ H ₄ - <i>p</i> -NO ₂	34
DO	-Ph	-I	-COMe	50
DP	-Ph	-I	-CO ₂ Me	50
DQ	-Ph	-I	-CN	50
DR	-Ph	-IPh	-CO ₂ Me	25
DS	-Ph	-IPh	-CO ₂ Et	25, 53
DT	-Ph	-HgCl	-C ₆ H ₄ - <i>p</i> -COMe	103
DU	- <i>n</i> -Bu	-H	-CO ₂ Me	48
DV	- <i>n</i> -Bu	-H	-COPh	48
DW	<i>t</i> -BuPh ₂ As	-H	-CH ₂ CH=CH- <i>n</i> -C ₅ H ₁₁	11
DX	BnPh ₂ As	-H	-Ph	12
DY	Ph ₂ As(CH ₂) ₂ OH	-H	-Ph	13
DZ		-H	-CO ₂ Me	60

^aexcept for arsonium ylides (DW)-(DZ).

2. Synthesis of Arsonium Salts and Ylides

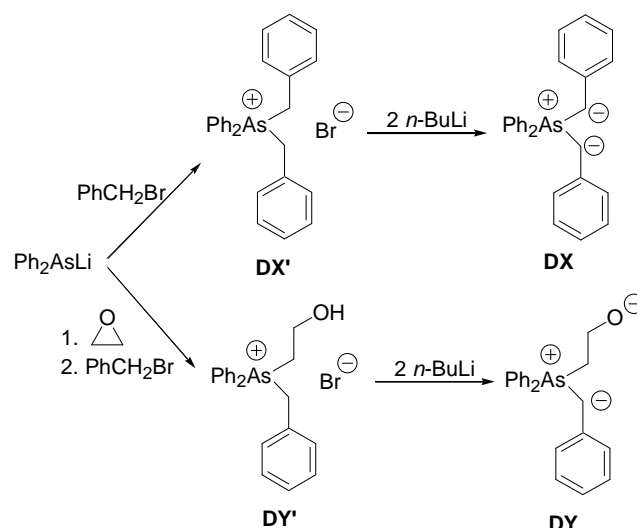
In the review by Lloyd et al., the methods for the preparation of arsonium ylides that were available at that time were summarized, along with the mechanisms for their formation.⁵ These methods include: (1) deprotonation of an arsonium salt, (2) methods involving arsine dihalides, arsine oxides, or diazo compounds, (3) transylidation and (4) reverse Wittig processes. It was noted that the salt method, in which an arsonium salt (obtained by the reaction of an organosulfonate or halide with a tertiary arsine) is treated with a suitable base to provide the ylide, has been the most widely used for arsonium ylide generation in recent years. This remains the case and most of the ylides covered in this review were prepared from a corresponding salt. As noted previously, when it is necessary to mention the precursor for ylide **X** in this review, it is designated as **X'**. Furthermore, factors regarding arsonium ylide stability and basicity were also discussed in the previous review and are therefore not covered again here. Below are some of the more recent and important advances in the synthesis of arsonium salts and ylides.

A variation for arsonium salt synthesis has been reported by Mioskowski et al. that utilizes *t*-butyl chloride and aluminum chloride. They prepared **DW'** from the alkylidiphenylarsine **2** as an intermediate in their synthesis of (\pm)-hepoxilin A₃ (Scheme 1).¹¹ In this synthesis, the use of an arsonium ylide was essential because it was used to convert an aldehyde group into an epoxide moiety in the penultimate step of the synthesis.



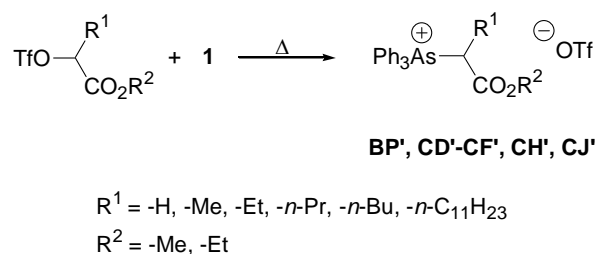
Scheme 1

At approximately the same time, this group also reported the synthesis of ylide **DX**,¹² which they described as the first ylide-anion, together with β -oxido benzyl ylide **DY**¹³ (Scheme 2). Lithium diphenylarsenide, which was freshly prepared from **1** and lithium in THF, was reacted with benzyl bromide or ethylene oxide followed by benzyl bromide to afford **DX'** and **DY'**, respectively. The ylides **DX** and **DY** were obtained by the addition of two equivalents of *n*-BuLi to the corresponding salt in THF or in a mixture of THF and HMPA (85/15) at -20 °C. When condensed with aldehydes such as hexanal, these ylides afforded *trans*-alkenes with a very high stereoselectivity (> 99:1) that was greater than that observed with the corresponding phosphonium ylides.



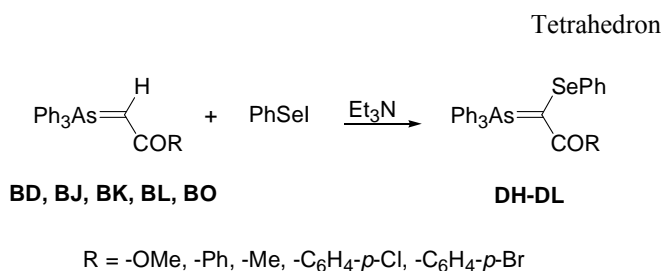
Scheme 2

In order to obtain higher homologues of alkoxy carbonyl-methylenetriphenylarsonium ylides, Castells et al. reported the synthesis of arsonium triflate salts **BP'**, **CD'-CF'**, **CH'** and **CJ'** (Scheme 3).¹⁴ They noted that it was necessary to use the more reactive triflate alkylating reagents since the corresponding bromides were ineffective in reacting with **1**, due to its low nucleophilicity. The authors also noted that the use of the triflates carries the added advantage that the lower nucleophilicity of the triflate anion compared to the bromide anion minimizes undesired ester cleavage and decarboxylation of the salts.



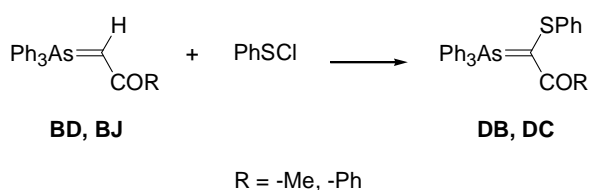
Scheme 3

Another improvement in arsonium salt synthesis was reported by Moorhoff when he described an easy and rapid method for their preparation in high yield and purity.¹⁵ This procedure involves heating **1** with an alkylating reagent as a melt between 80-110 °C. This method allows the alkylation reaction to proceed much more rapidly than when a solvent is used. By heating the binary mixture of an alkylating reagent and **1**, a wide range of arsonium salts could be isolated in 77-99% yield after simply washing the product with petroleum ether (Scheme 4).



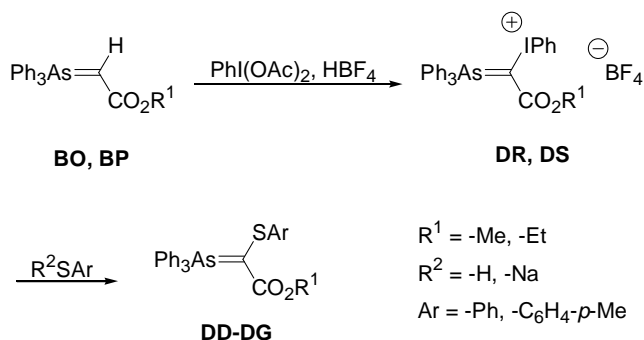
Scheme 9

Similarly, ylides functionalized with arylthio groups at the α -position can play important roles in synthesis. Thus, Huang and co-workers have also reported the synthesis of α -phenylthioacrylmethylene arsonium ylides **DB** and **DC** from **BD** and **BJ**, respectively (Scheme 10).²⁴ The method used to prepare these ylides was similar to that used to prepare the selenium-functionalized ylides.



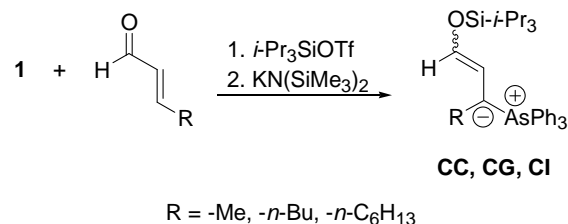
Scheme 10

Most recently, this group has synthesized mixed iodonium-arsonium ylides, and developed a novel method for the synthesis of α -thio- and α -selenoarsonium ylides via a substitution reaction, instead of the usual addition/elimination method (Scheme 11).²⁵ Treatment of the ylides **BO** or **BP** with iodosobenzene diacetate and tetrafluoroboric acid afforded the ylides **DR** and **DS**, respectively. These, in turn, were converted into the ylides **DD-DG** upon reaction with both arylthiols and their sodium salts.



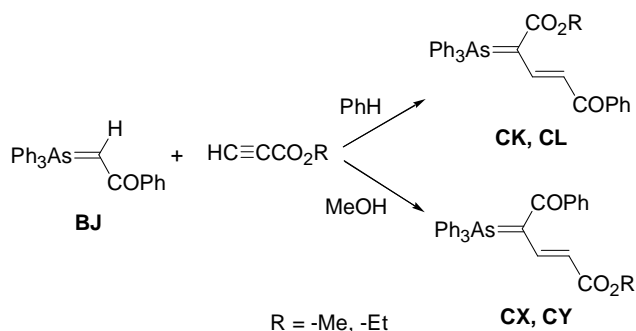
Scheme 11

Kim and Kim have reported a successful attempt to generate the arsonium ylides **CC**, **CG**, and **CI**, containing triisopropylsilyl enol ether groups, from α,β -enals (Scheme 12).²⁶ The analogous arsoniosilylation of α,β -enones was, however, unsuccessful due to the instability of the formed arsonium ylides and the formation of diene enol ethers.



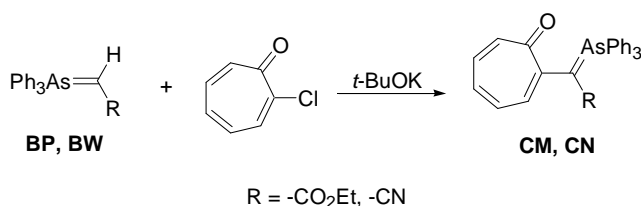
Scheme 12

Aitken et al. have examined the reactions of **BJ** with methyl and ethyl propiolate.²⁷ These reactions proceeded readily to afford 1:1 adducts in moderate yield, where the structure of the product was dependent upon the solvent used (Scheme 13). In benzene, the ylides **CK** and **CL** were formed, while, in methanol, **CX** and **CY** were produced.



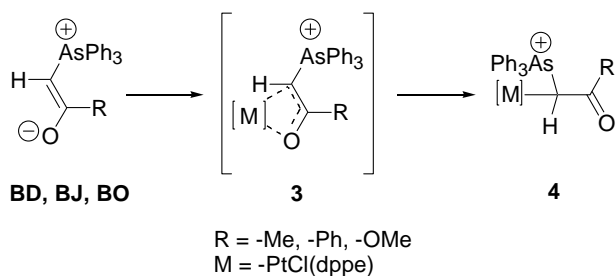
Scheme 13

Mitsumoto and Nitta have recently prepared the first stable arsonium ylide derivatives bearing cyclohepta-2,4,6-trienyl and electron-withdrawing CO₂Et and CN groups (**CM** and **CN**) in low yield from **BP** and **BW**, respectively (Scheme 14).²⁸ These ylides did not undergo hydrolysis, even under acidic conditions. X-ray analysis revealed that the distances between the arsenic and oxygen atoms 2.31 Å for **CM**, 2.39 Å for **CN**) were well below the sum of the van der Waals radii (3.37 Å) for these atoms and, thus, there was appreciable bonding between them.



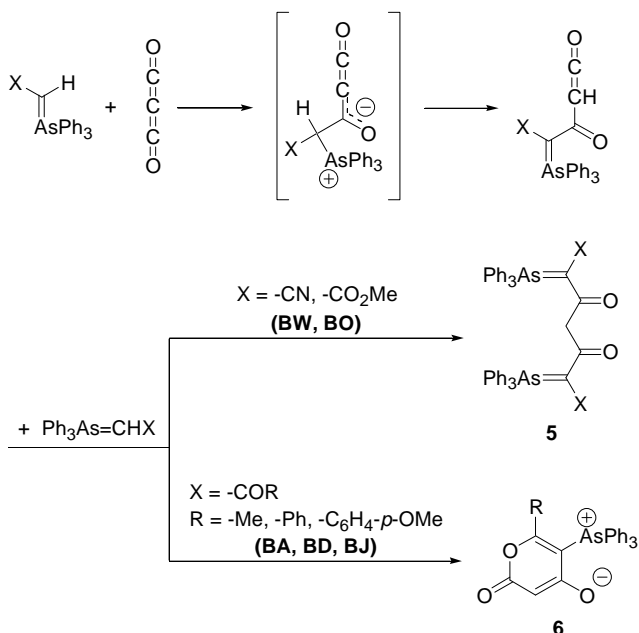
Scheme 14

Facchin et al. reported that the reaction of [PtCl(dppe)]₂[BF₄]₂ (dppe = 1,2-bis(diphenylphosphino)ethane) with the ylides **BD**, **BJ**, and **BO** led to novel platinum(II) complexes **3** in which the carbonyl-stabilized arsonium ylides were coordinated to the metal center via the carbonyl oxygen atom. These derivatives were not stable in chlorinated solvents and slowly underwent isomerization to their C-coordinated analogues **4** (Scheme 15).²⁹



Scheme 15

Pandolfo et al. have described the reaction of carbon suboxide with a series of stabilized triphenylarsoranes (**BA**, **BD**, **BJ**, **BO**, and **BW**) to yield two different kinds of compounds (Scheme 16).³⁰ When X = CN, or CO₂Me, the reaction proceeded to form 2:1 (ylide:C₃O₂) adducts, such as open-chain malonyl bis-ylidic compounds **5**. When X = COMe, COPh, or COC₆H₄-*p*-OMe, only 1:1 cyclic zwitterionic adducts **6** were obtained.



Scheme 16

3. Synthetic Applications of Arsonium Ylides

Due to the increased zwitterionic nature of the As-C bond in these ylides, compared to the corresponding phosphonium ylides, arsonium ylides are stronger nucleophiles and they participate in a wide range of addition and substitution reactions, most of which involve electrophilic carbonyl compounds.

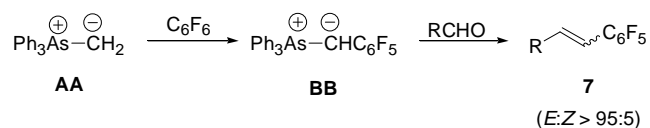
3.1. Alkene synthesis

As with their phosphonium counterparts, arsonium ylides can add to aldehydes and ketones in Wittig reactions to

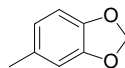
form alkenes that are accompanied by the formation of an arsine oxide.

3.1.1. Unconjugated alkene synthesis

Shen and Qiu have reported that reaction of the ylide **BB**, generated *in situ* by the reaction of **AA** with hexafluorobenzene, with a wide range of aromatic aldehydes afforded good to excellent yields (83-94%) of pentafluorophenylalkenes **7** (Scheme 17).³¹ The authors reported that most products were formed with a predominantly *E* stereochemistry and that even the worst case afforded an *E:Z* ratio of 95:5.

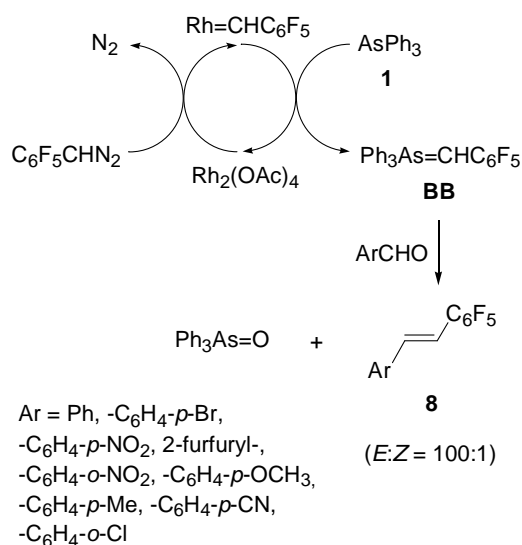


R = -Ph, -CH=CHPh, -C₆H₄-*o*-Cl, -C₆H₄-*p*-Cl, -C₆H₄-*p*-F, -C₆H₄-*p*-NO₂, -C₆H₄-2,4-Cl₂, -C₆H₄-*p*-Br, -C₆H₄-*p*-Me,



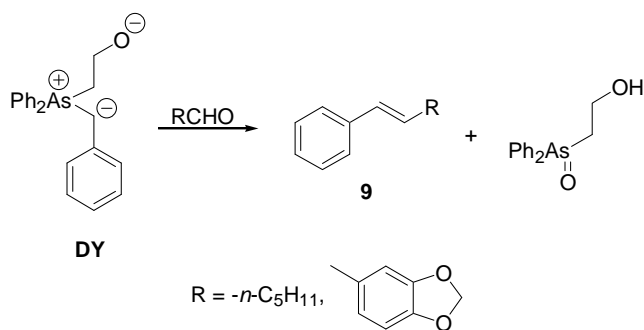
Scheme 17

More recently, Zhu et al. described a novel and straightforward method using **BB** for the synthesis of pure *trans*-pentafluorophenylalkenes **8** from aromatic aldehydes in moderate to good yields in a one-pot reaction.³² This procedure uses Rh₂(OAc)₄ as a catalyst for diazo transfer. Considering that the diazo compounds are generated from tosylhydrazone salts, which are, in turn, prepared from aldehydes, this is reported to be the first example of the net coupling of two different aldehydes to form pure *trans*-alkenes (Scheme 18).



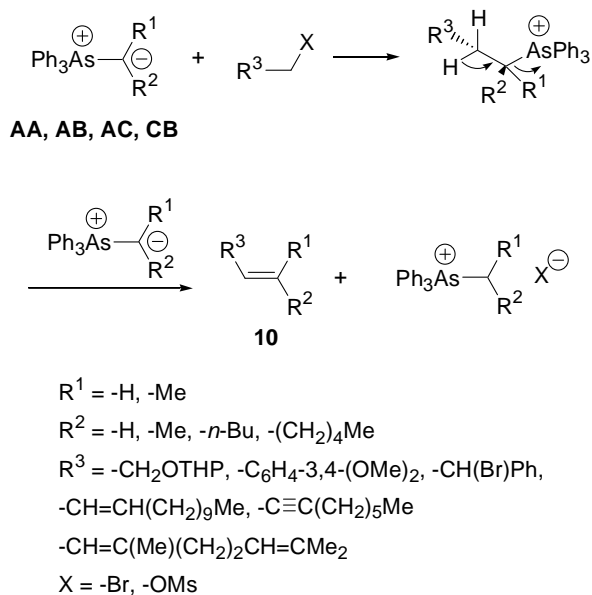
Scheme 18

Mioskowski et al. investigated the bisbenzyl ylide-anion **DX** (Scheme 2) in an attempt to improve the stereoselectivity of the reaction between hexanal and the corresponding phosphonium ylide. In a THF/HMPA (85/15) solvent mixture, alkene formation was observed in high yields, with *E:Z* ratios of > 99:1 being achieved.¹² Later, they reported that the ylide **DY**, under the same reaction conditions, afforded exclusively the *E*-isomer of **9** (Scheme 19).¹³



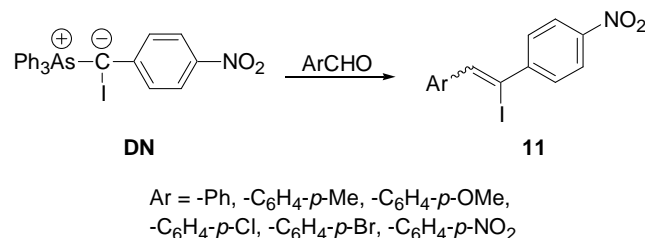
Scheme 19

Mioskowski et al. also reported the straightforward olefination of activated halides and mesylates using non-stabilized alkyltriphenylarsonium ylides (**AA**, **AB**, **AC**, and **CB**) to afford the alkenes **10** (Scheme 20).³³ The semi-stabilized ylide **AZ** and the stabilized ylide **BP** were also examined in this reaction, but no olefin formation was observed. The mechanism for this process is proposed to involve nucleophilic substitution of the activated halide or mesylate by the ylide, followed by deprotonation and elimination of the formed arsonium salt to afford the product alkene. A variety of allylic and benzylic alkyl halides and mesylates were converted into the corresponding olefins.



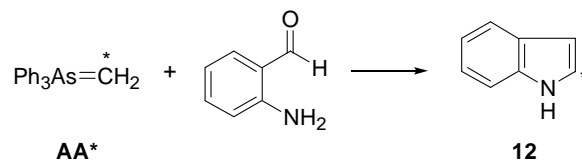
Scheme 20

Vinyl halides are important intermediates in organic synthesis that can be used in a variety of metal-catalyzed coupling reactions. Huang et al. synthesized such α -iodo-substituted alkenes **11** using a semi-stabilized ylide **DN** (Scheme 21).³⁴ These reactions afforded *E:Z* ratios ranging from 34:66 to 67:33.



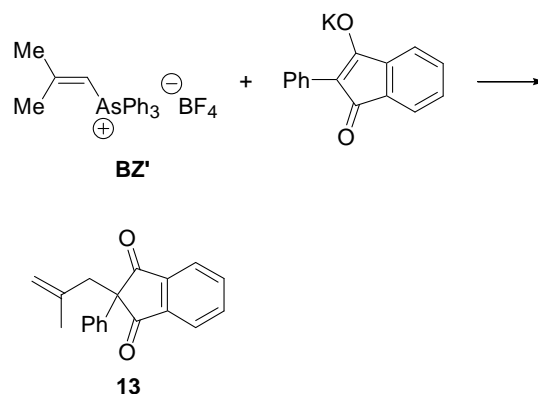
Scheme 21

In the area of labeled-compound synthesis, Zessin et al. have reported ¹¹C-labeled **AA*** and used here this in a one-pot synthesis of indole **12** (Scheme 22).³⁵ They reported that a THF/DMSO solvent mixture afforded the highest yields with **AA***.



Scheme 22

In terms of using arsonium salts as reagents, Ochiai et al. reported that arsonium tetrafluoroborate **BZ'** is an effective alkylating reagent for the synthesis of **13** (Scheme 23).¹⁶ As mentioned previously, **BZ'** was prepared by base-induced reductive α -elimination of an iodonium salt, followed by nucleophilic trapping with **1** (Scheme 5).

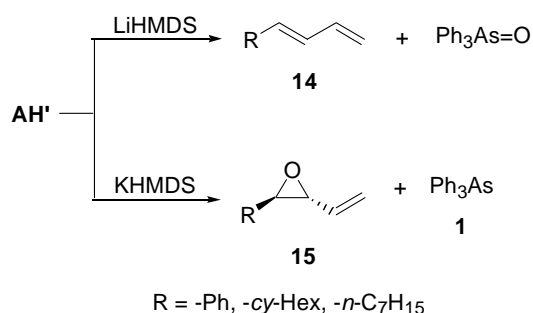


Scheme 23

3.1.2. 1,3-Diene synthesis

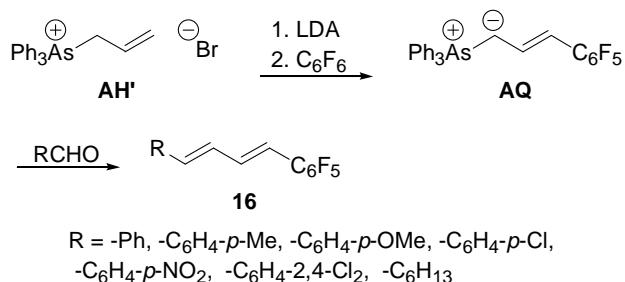
It was known that the reaction of semi-stabilized arsonium ylides with carbonyl compounds results in a mixture of olefin and epoxide products.³⁶ Hsi and Koreeda reported

that the selectivity for the formation of either olefins **14** or epoxides **15** was dependent upon the choice of base used for the generation of the arsonium ylide **AH** (Scheme 24).³⁷ Deprotonation of **AH'** with either LiHMDS or KHMDS, followed by the addition of the aldehyde, resulted in virtually exclusive olefin **14** or epoxide **15**, respectively.



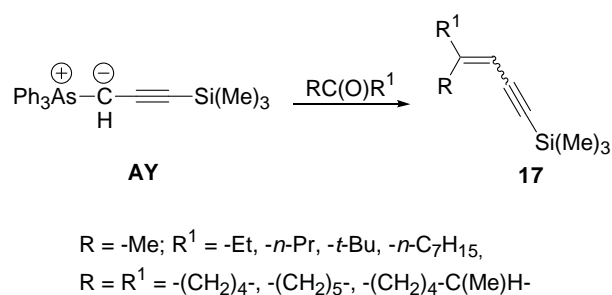
Scheme 24

Shen and Wang reported a highly stereoselective synthesis of substituted 1-pentafluorophenyl-1,3-dienes using an arsonium ylide (Scheme 25).³⁸ Ylide **AH**, generated from the corresponding arsonium salt and lithium diisopropylamide, was first reacted with hexafluorobenzene to afford **AQ**. This was subsequently reacted with aldehydes to afford substituted 1,3-dienes **16** with *1E,3E* selectivity in 80-96 % yield.



Scheme 25

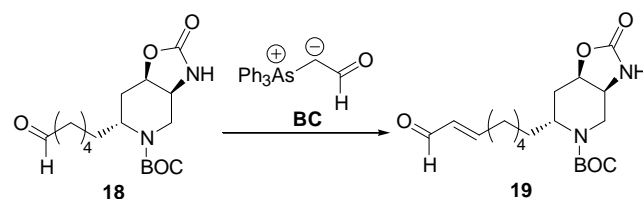
Shen and Liao described the synthesis of a series of terminal trimethylsilyl enynes **17** using a silylated ylide **AY** (Scheme 26).³⁹ The isolated yields ranged from 72-100%, but only modest stereoselectivity was observed for most cases. Only when a bulky *t*-butyl group was adjacent to the carbonyl group was the *E*-alkene formed exclusively. The authors also reported that the addition of **AY** to ketones afforded higher isolated yields of **17** than were obtained using the corresponding phosphorous ylide.



Scheme 26

3.1.3. α,β -Alkenal synthesis

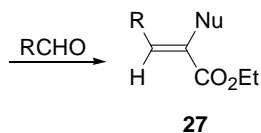
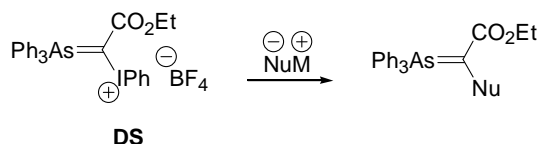
Huang et al. first described the facile formyl olefination of aldehydes by means of formylmethyltriphenylarsonium bromide **BC'** and they reported that the use of an arsonium ylide allowed the reaction to occur under much milder conditions than with the corresponding phosphorous ylide.⁴⁰ Ma and Sun used this method in the synthesis of an intermediate of pseudodistomin B triacetate.⁴¹ Treatment of aldehyde **18** with **BC** afforded the desired formyl-olefination product **19** in 73% yield (Scheme 27).



Scheme 27

3.1.4. α,β -Alkenone synthesis

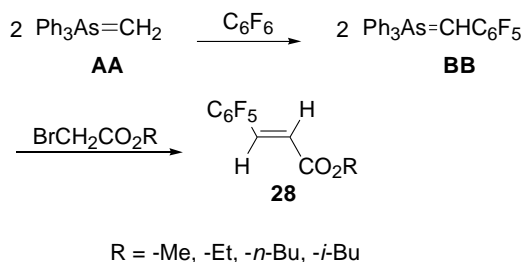
Huang et al. reported an efficient and highly stereoselective synthesis of (*E*)- α -enones by the reaction of aldehydes with arsonium bromides **BE'** and **BF'** (not shown) and potassium carbonate with a trace of water at room temperature.⁴² Using this method, the key intermediate **21** for the synthesis of brassinosteroid was prepared from the aldehyde **20** (Scheme 28). This procedure was also useful in the synthesis of prostaglandin intermediates. The simplicity of this procedure, the mildness of the reaction conditions, the high stereoselectivity, and the good yields have combined to make this method a convenient approach to (*E*)- α -enones from aldehydes. Thus, it has been used for the synthesis of intermediates of brassinolide,⁴³ yingzhaosu A,⁴⁴ polyhydroxysterols,^{45,46} and HIV protease inhibitors.⁴⁷



NuM = Me₄NCl, *n*-Bu₄NBr, *n*-Bu₄NCl, *n*-Bu₄NI, PhSK, 4-MePhSK, PhSeNa
 R = -C₆H₄-*p*-Cl, -Ph, -C₆H₄-*p*-Me, -C₆H₄-*p*-NO₂, -C₆H₄-*p*-F

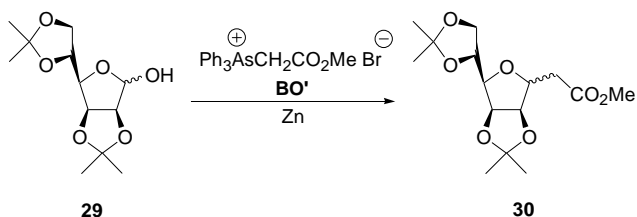
Scheme 32

Shen et al. reported a one-pot synthesis of fluorinated α,β -unsaturated esters. Ylide **BB**, generated *in situ* from **AA** and hexafluorobenzene, was reacted with bromoacetates to afford selectively the *E*-isomer of the fluorinated enoates **28** in 94-99% yield (Scheme 33).⁵⁴



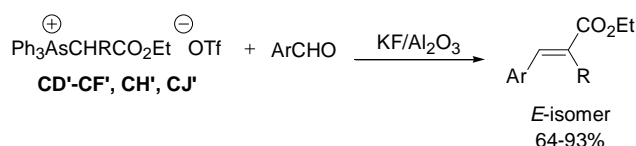
Scheme 33

Demilly et al. reported that the reaction of the arsenic ylide **BO** with a pyranose (not shown) and furanose carbohydrate **29** led mainly to the *E*-alkene derivatives. Furthermore, reaction of the corresponding arsonium salt **BO'**, in the presence of zinc, directly afforded C-glycoside **30** in 95% yield as a 2.5:1 mixture of the β and α anomers (Scheme 34).⁵⁵

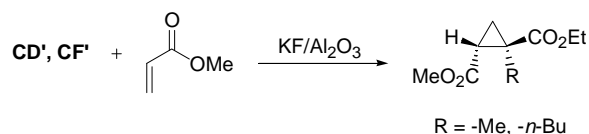
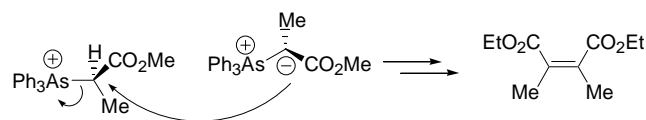


Scheme 34

Castells et al. studied the higher homologues of **BO** and **BP**. These ylides (**CD-CF**, **CH**, and **CJ**) reacted with aromatic aldehydes to afford good to excellent yields of the *E*-alkenes and afforded synthetically interesting "coupling" and cyclopropanation products upon reaction with poor electrophiles and methyl acrylate, respectively (Scheme 35).¹⁴

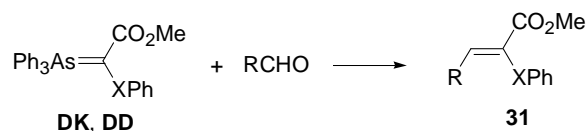


R = -Me, -Et, -*n*-Bu, -*n*-C₁₁H₂₃
 Ar = 2-furyl, -Ph, -C₆H₄-*p*-OMe, -C₆H₄-*p*-Cl



Scheme 35

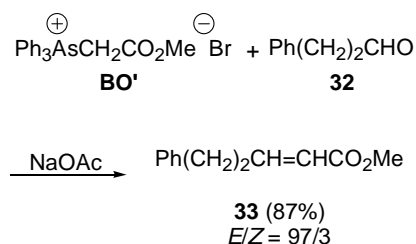
Huang et al. explored the synthesis of α -phenylseleno- and α -phenylthio-substituted enoates.^{22a,56} Since Wittig reactions do not occur with α -electron-withdrawing group-substituted α -selenophosphonium ylides, the corresponding arsonium ylides, with their expected higher reactivity, were examined. α -Seleno **DK** (or thio **DD**) arsonium ylide reacted with aldehydes to afford *Z*- α -phenylseleno-(or thio)- α,β -unsaturated esters **31** in high yields with good stereoselectivity (Scheme 36).



X = -Se, -S
 R = -CH₂(CH₂)₆Me, -CH₂CHMe₂, -CH=CHMe, -Ph, -CH=CHPh, -C₆H₄-*p*-Me, -C₆H₄-*p*-Cl, -C₆H₄-*p*-NO₂

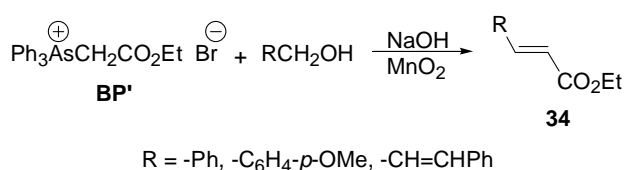
Scheme 36

Hon and Lee recently reported that the salt **BO'** could undergo a Wittig reaction with aldehyde **32** to afford the conjugated ester **33** in good yield in the presence of sodium acetate (Scheme 37).⁵⁷ The reactivity of **BO'** was found to be dependent upon the counteranion, with the following trend being observed: *p*-TsO⁻, Br⁻ \ll CF₃CO₂⁻ \ll ClCH₂CO₂⁻ $<$ PhCO₂⁻, HCO₂⁻, MeCO₂⁻. Furthermore, they reported that the proton-coupled ¹³C NMR splitting patterns of the α -methylene groups of the salts provided valuable information to predict their reactivity.



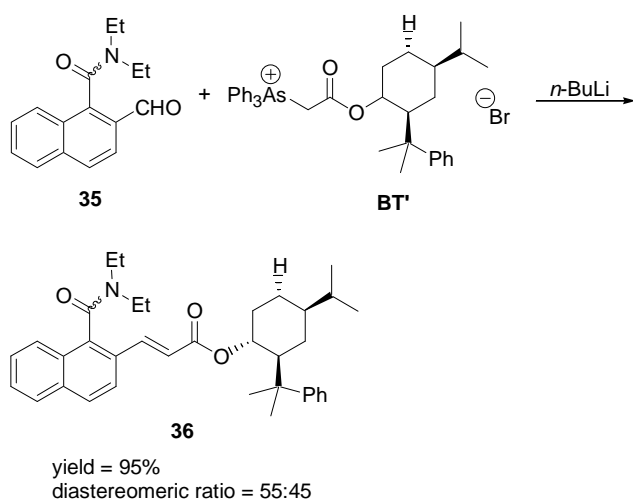
Scheme 37

More recently, a stereoselective synthesis of (*E*)- α,β -unsaturated esters **34** by a tandem deprotonation-oxidation-Wittig reaction process using the arsonium salt **BP'** was reported.⁵⁸ A mixture of **BP'**, alcohol, sodium hydroxide, and manganese dioxide afforded the *E*-enoates **34** in 73–95% yield (Scheme 38).



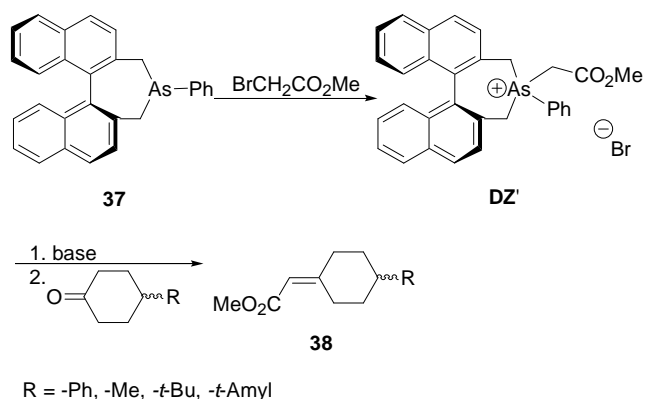
Scheme 38

The first asymmetric Wittig reaction involving a chiral arsonium ylide was recently described by Dai and Lau.¹⁷ They investigated the atroposelective olefination of axially chiral *N,N*-dialkyl 2-formyl-1-naphthamides such as **35** with the chiral auxiliary-derived stable arsonium ylide **BT'**.⁵⁹ It was found that olefination could be carried out at low temperature (-60 °C) to give the *E*-alkenes **36** in excellent yield (Scheme 39). The effects of metal counterions and solvents on the diastereoselectivity were investigated. They reported that the diastereoselectivity decreased in the following order: Li > Na > K \approx Mg > Zn. Moreover, polar solvents gave better results than non-polar solvents, such as toluene.



Scheme 39

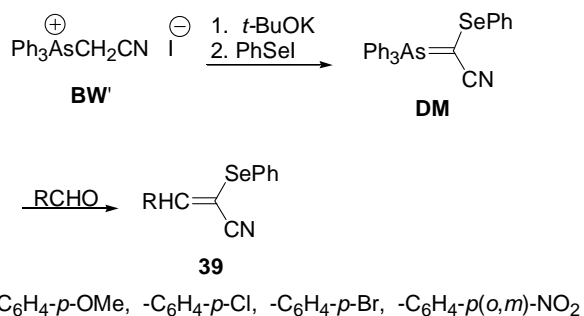
Dai et al. next studied a chiral arsine **37** that was synthesized from *C*₂-symmetric (*S*)-(-)-1,1'-bi-2-naphthol in three steps. It was employed in the enantioselective olefination of 4-substituted cyclohexanones via the stabilized ylide **DZ** generated *in situ*. Enantiomeric excesses of greater than 40% were obtained (Scheme 40).⁶⁰ Moreover, a reversal in the stereochemistry of the product **38** was observed simply by changing the counteraction of the base from lithium to potassium.



Scheme 40

3.1.6. α,β -Alkenitrile synthesis

α -Phenylseleno- α,β -unsaturated nitriles **39** have been prepared by Huang et al.⁶¹ The salt **BW'** was treated sequentially with base and phenylselenenyl iodide to produce ylide **DM**, which was found to be very unstable in air and water. Thus, after filtration under nitrogen, **DM** was used directly in Wittig reactions with aromatic aldehydes to afford the nitriles **39** in good yields (Scheme 41).

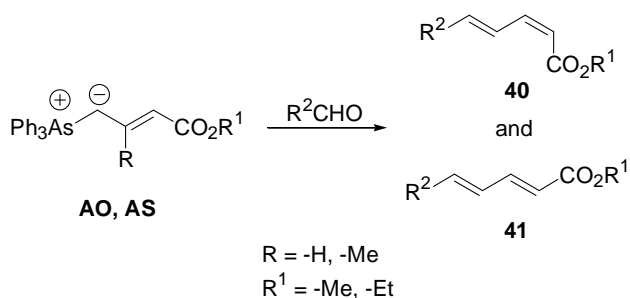


Scheme 41

3.1.7. 2,4-Diene carbonyl compound synthesis

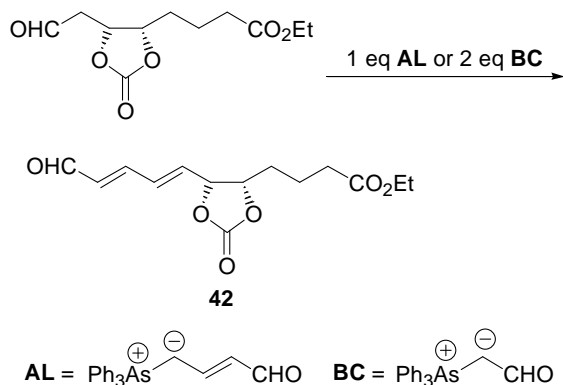
Huang et al. reported the use of the highly reactive arsorane **AS** as an isoprenoid reagent to synthesize abscisic acid ester analogs.⁶² This method gave only two isomeric products **40**, and **41**, while the corresponding phosphonium ylide afforded four geometric isomers (Scheme 42). Li et al. used a similar strategy in the synthesis of pear ester with

ylide **AO**.⁶³ Finally, Lu and Zhou used this method in the synthesis of (+)-azimic acid.⁶⁴



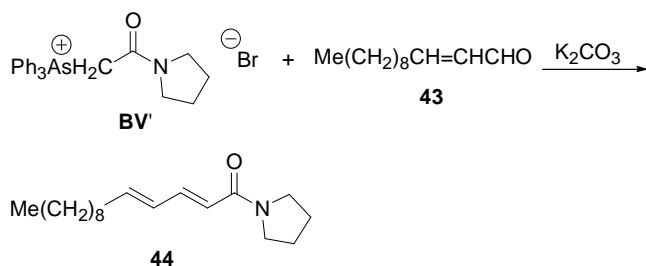
Scheme 42

Gravier-Pelletier et al. and Wu et al. independently reported the synthesis of lipoxin A_4 and B_4 intermediate **42** using arsonium ylides (Scheme 43).^{65,66} The addition of either two equivalents of **BC** or one equivalent of **AL** afforded the conjugated aldehyde **42**, which, in turn, could be processed into the lipoxins.



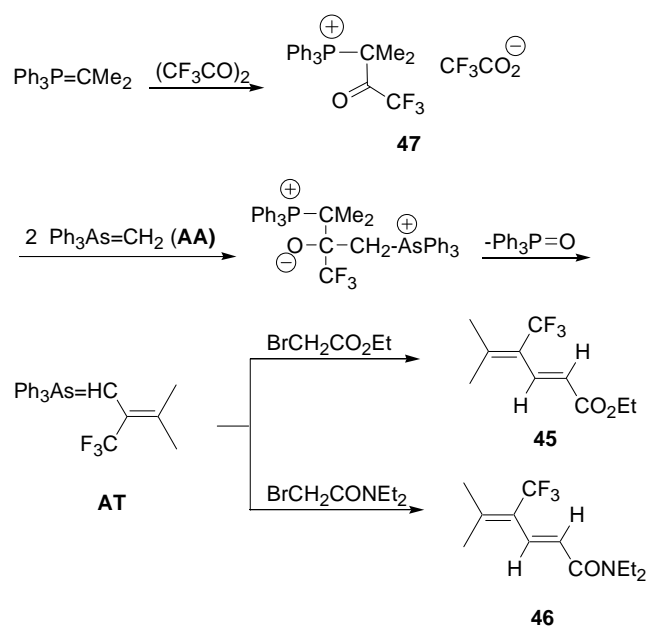
Scheme 43

Huang et al. reported a simple procedure for the synthesis of unsaturated amides.⁶⁷ Arsonium bromide **BV'** was treated with base and unsaturated aldehyde **43** to afford Achillea amide **44** (Scheme 44) and trichonine. Subsequently, Shi et al. applied the same methodology by using **BU'** to give unsaturated isobutylamides with high stereoselectivity.⁶⁸



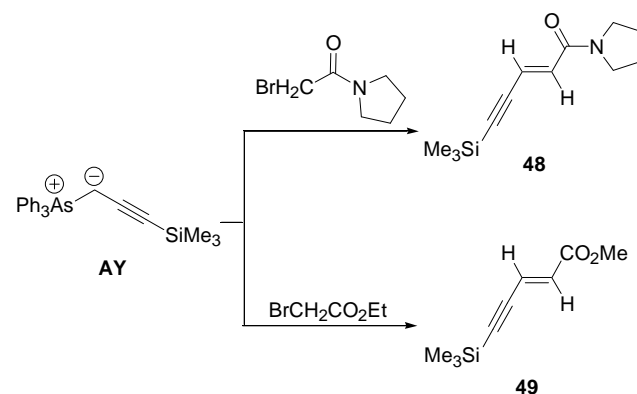
Scheme 44

Shen et al. described a double elimination of arsonium salts and the application of this methodology to this synthesis of 4-trifluoromethyl-2,4-dienyl carboxylate **45**⁶⁹ and 4-trifluoromethyl-2,4-dienamide **46** (Scheme 45).⁷⁰ Phosphoranes, generated from the corresponding phosphonium salts and phenyllithium in THF, were acylated by the addition of trifluoroacetic anhydride to give the β -oxophosphonium salt **47**. This was treated with two equivalents of **AA** to effect addition, deprotonation and elimination of triphenylphosphine oxide, to afford ylide **AT**. Without isolation, ylide **AT** was treated with α -bromoacetamides and α -bromoacetic esters to give **45** and **46**, respectively, in good yield.



Scheme 45

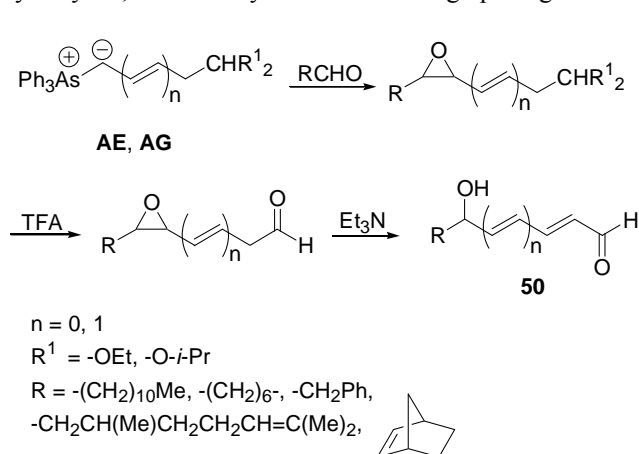
Subsequently, this group described the synthesis of a silylated 2,4-enynyl amide **48**,⁷¹ and carboxylate **49**⁷² by the reaction of ylide **AY** with α -bromoacetamide and α -bromoacetate, respectively, in moderate yield and high stereoselectivity (Scheme 46).



Scheme 46

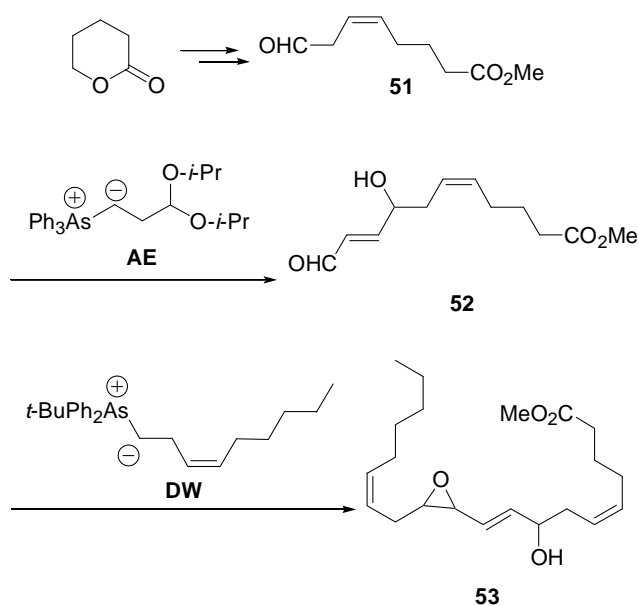
3.2. Heterocycle synthesis

Mioskowski et al. reported ylides **AE**⁷³ and **AG**⁷⁴ as β -formyl vinyl anion and δ -formyl butadienyl anion equivalents, respectively. Using these ylides, a variety of aldehydes could be homologated by three or five carbons to form the corresponding hydroxyl enals **50** under very mild conditions through a three-step sequence (Scheme 47). The initially formed acetal-containing epoxide is first hydrolyzed, followed by base-induced ring opening.



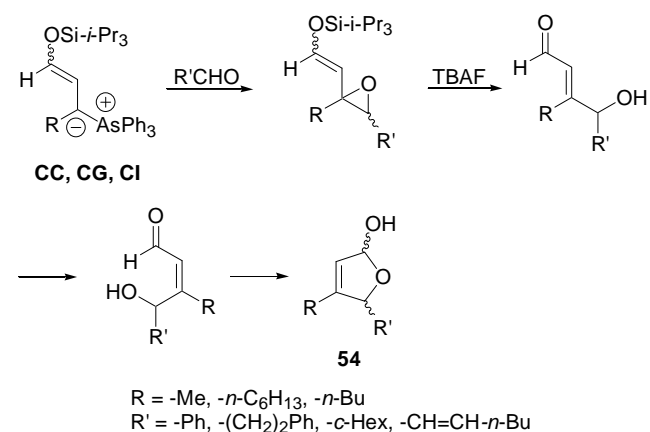
Scheme 47

This group prepared (\pm)-hepoxilin A₃ from 1-heptyne and δ -valerolactone utilizing ylides **AE** and **DW**.¹¹ δ -Valerolactone was transformed into β,γ -unsaturated aldehyde **51**, which was subsequently converted into γ -hydroxy-enal **52** by using ylide **AE**. Coupling of **52** with the ylide of **DW** afforded **53**, the methyl ester of hepoxilin A₃, which could in turn be converted into the desired product (Scheme 48).



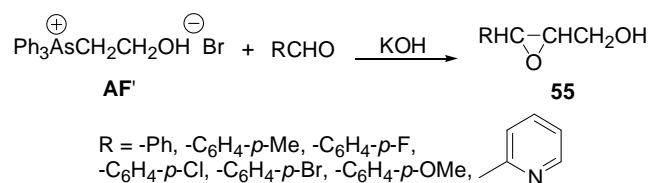
Scheme 48

As mentioned previously, Kim and Kim studied the arsoniosilylation reactions of α,β -unsaturated ketones and aldehydes (Scheme 49).²⁶ It was found that the reaction occurred at low temperature (-78°C). The authors also studied the possibility of arsonium ylides functioning as α,β -formyl vinyl anion equivalents. They observed that the reaction of ylides **CC**, **CG**, and **CI** with aldehydes in THF at -78°C , followed by the addition of TBAF, afforded the lactols **54**.



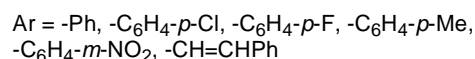
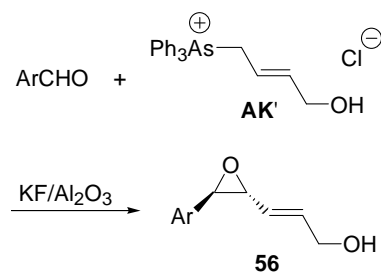
Scheme 49

Shi et al. synthesized 2,3-epoxy-3-arylpropanols in one step using β -hydroxyethyltriphenylarsonium bromide **AF'**.⁷⁵ In the presence of the strong base KOH, 2,3-epoxy-3-arylpropanols **55** were formed in good yield under phase-transfer conditions (Scheme 50).



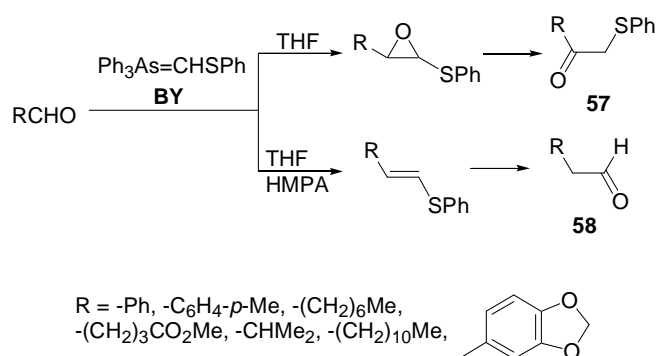
Scheme 50

This same group applied a one-pot procedure using the salt **AK'** to prepare 5-aryl- and 5-(2-styrenyl)-4,5-trans-epoxy-2E-penten-1-ols **56**.⁷⁶ In all reported examples, the epoxide ring was generated with *trans* stereochemistry (Scheme 51).



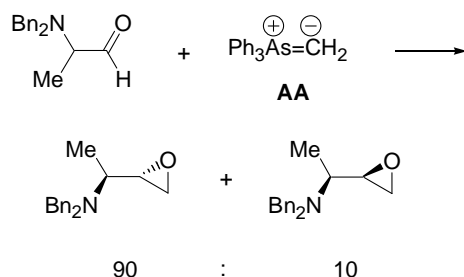
Scheme 51

Mioskowski et al. observed that the ylide **BY** reacted with aldehydes to afford exclusively α -thiophenoxyepoxides in THF and phenylthioenol ethers in THF/HMPA mixtures.⁷⁷ The former adducts were readily transformed into α -thiophenoxy carbonyl compounds **57** and the latter into one-carbon homologated aldehydes **58** (Scheme 52).



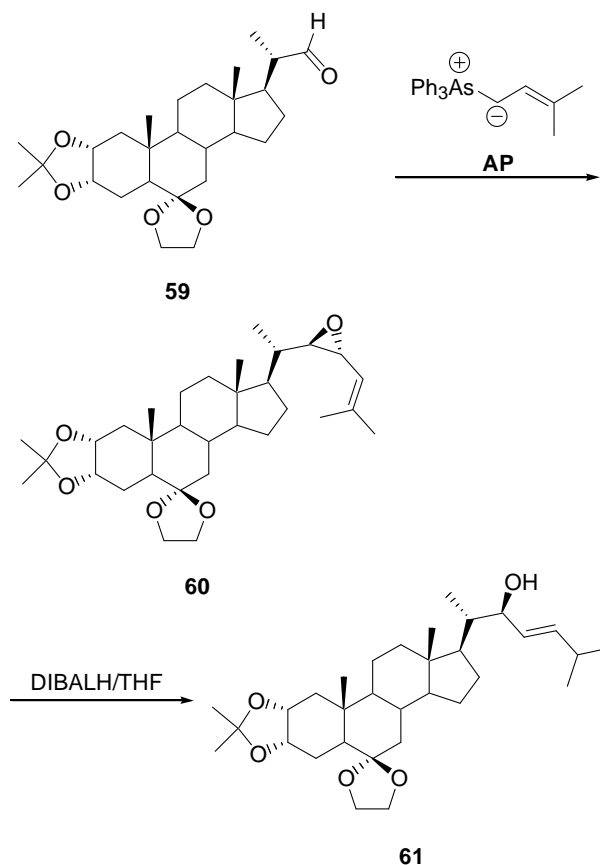
Scheme 52

Reetz et al. reported that the addition of the arsonium ylide **AA** to protected α -amino aldehydes formed the corresponding epoxides with greater stereoselectivity than did the corresponding phosphonium ylide (Scheme 53).⁷⁸



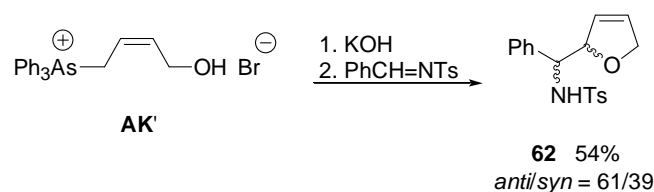
Scheme 53

In another example of the use of an arsonium ylide as a vinyl anion equivalent, Werner et al. used ylide **AP** to convert aldehyde **59** into epoxide **60**.⁷⁹ Subsequent reduction of **60** with DIBALH afforded the allylic alcohol **61**, which was a key synthetic intermediate of castasterone and its analogues (Scheme 54).



Scheme 54

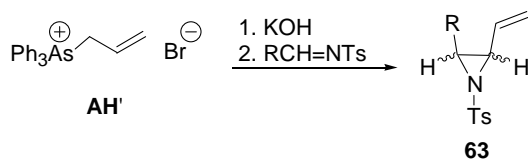
Deng et al. reported that, when the *cis*-alkene-containing ylide **AK** was reacted with *N*-sulfonylimines, 2,5-dihydrofurans such as **62** were obtained instead of the expected aziridines (Scheme 55).⁸⁰ This reaction was found to be general for a range of aryl aldehydes. Thus, **AK** may be formally regarded as an equivalent of the 2,5-dihydrofuran anion. The authors also note that, when the corresponding *trans*-alkene-containing ylide is used, the expected aziridine is formed.



Scheme 55

This group has also reported a successful aziridine synthesis using ylide **AH** generated *in situ*. The precursor salt **AH'** was found to react with aromatic, heteroaromatic, and α,β -unsaturated *N*-sulfonylimines under solid-liquid phase-transfer conditions in the presence of KOH at room temperature to produce the vinylaziridines **63** in a matter of minutes (Scheme 56).⁸¹

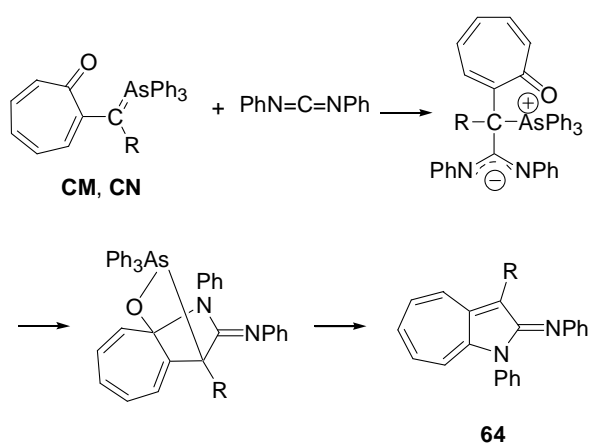
Tetrahedron



R = -Ph, -C₆H₄-*p*-Cl, -C₆H₄-*o*-OMe, α -naphthyl

Scheme 56

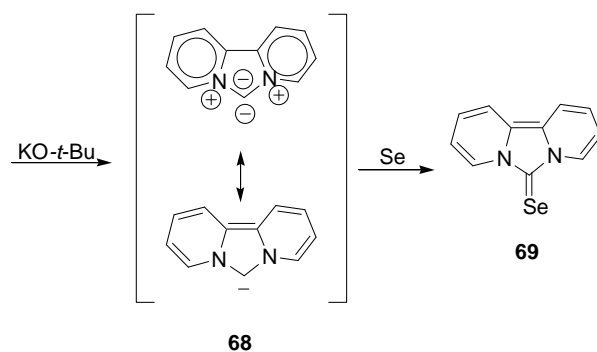
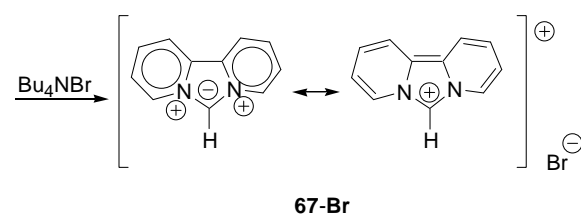
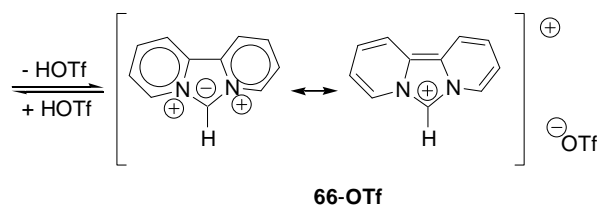
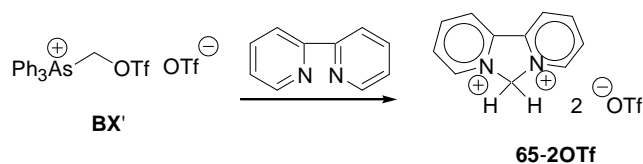
Mitsumoto and Nitta reacted the stable arsonium ylides **CM**, and **CN** with heterocumulenes such as carbon disulfide, phenyl isothiocyanate, diphenylcarbodiimide and phenyl isocyanate in Wittig-type reactions that were followed by electrocyclization or formal [8+2]-type cycloaddition reactions (Scheme 57). Subsequent elimination of triphenylarsine sulfide or oxide afforded 2*H*-cyclohepta[*b*]furan-2-thione, its imine, 2-phenylimino-2*H*-cyclohepta[*b*]pyrrole **64** or 2*H*-cyclohepta[*b*]furan-2-one. Furthermore, the reactions with dimethyl acetylenedicarboxylate afforded azulene derivatives.²⁸



R = -CO₂Et, -CN

Scheme 57

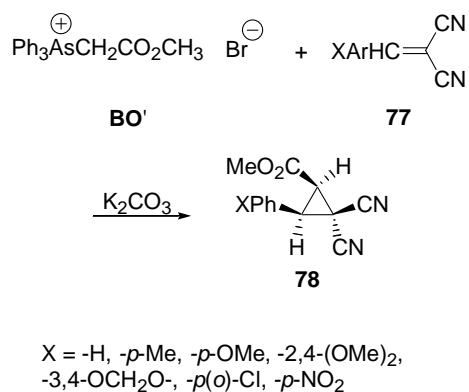
Weiss et al. used the salt **BX'** to generate a formal 1:1 complex between 2,2'-bipyridine and singlet carbon (Scheme 58).⁸² The salt reacted with 2,2'-bipyridine to provide a cyclic bis(onio)-substituted salt **65-2OTf**, a bis(azonia) analogue of fluorene. Under these reaction conditions, this C-H-acidic compound was converted into salt **66-OTf** with excess 2,2'-bipyridine and isolated as the salt **67-Br** after anion exchange. In the presence of KO-*t*-Bu, this salt was deprotonated to afford **68**, that was stable for several hours at low temperature and which could be trapped in high yields by a number of electrophiles,⁸³ e.g. reaction with selenium led to the chalcogenone **69**.



Scheme 58

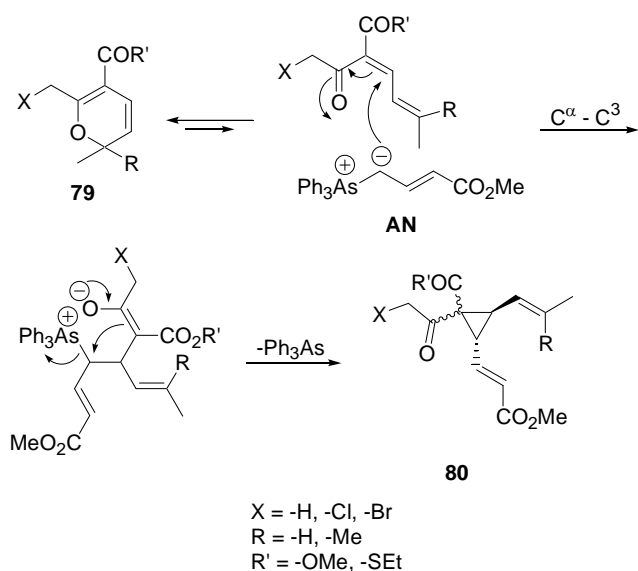
3.3. Carbocycle synthesis

Silylcyclopropanes are useful intermediates in organic synthesis since they are capable of undergoing many synthetic transformations.⁸⁴ In this regard, Shen and Liao prepared **AY**, which, when treated with enones, afforded the trimethylsilylethynylcyclopropanes **70** in 96-100% yield with high stereoselectivity (Scheme 59).⁸⁵ Addition of methanol removed the silyl groups and afforded the terminal acetylenes **71** in a one-pot procedure in excellent yields (95-96%).⁸⁶



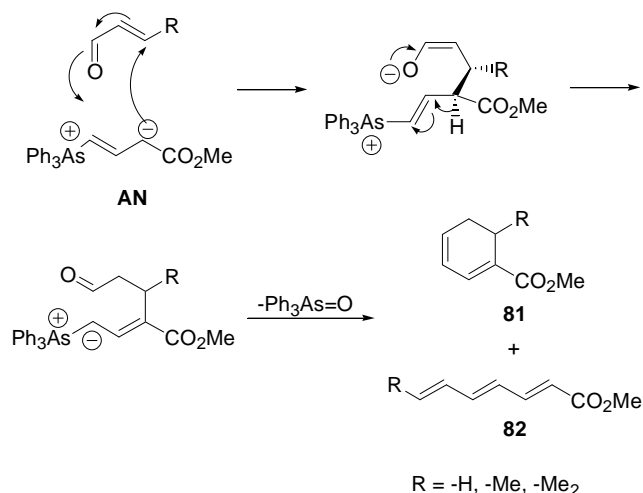
Scheme 63

Moorhoff investigated the reaction of the ylide **AN** with substituted *2H*-pyran-5-carboxylates **79**,⁹² which undergo reversible electrocyclic ring opening to form the ketodienes, making these compounds subject to conjugate addition. Thus, **79** reacted with **AN** to afford a mixture of the diastereomeric *trans*-2,3-divinylcyclopropanecarboxylates **80** (Scheme 64).



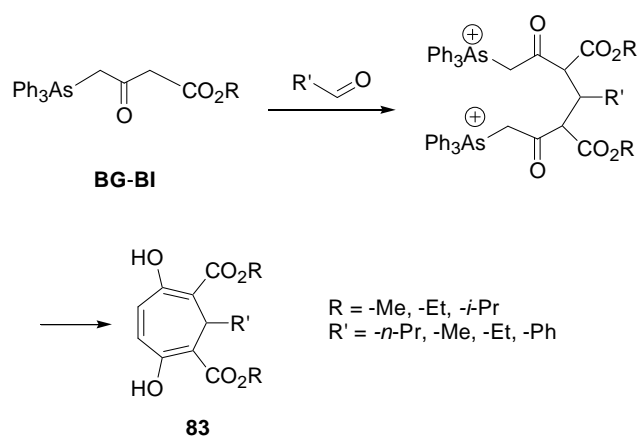
Scheme 64

Moorhoff also reacted **AN** with conjugated carbonyl compounds. The initial addition was followed by an intramolecular Wittig condensation to form the 1,3-cyclohexadiene-1-carboxylates **81** and/or acyclic trienes **82** (Scheme 65).⁹³ It was reported that the yields using **AN** were much higher than when the corresponding phosphonium ylide was used. The reaction of **AN** and ethyl 2-cyano-5-methyl-2,4-hexadienoate, however, gave a mixture of two diastereomeric *trans*-bisvinylcyclopropanecarboxylates in a reaction similar to that described in Scheme 64.



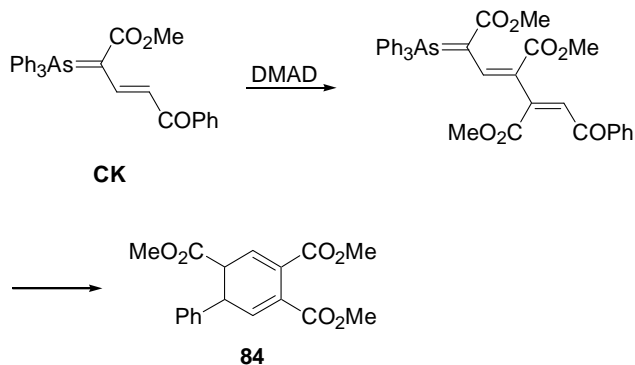
Scheme 65

Moorhoff reported a useful synthetic method for the preparation of 2-substituted 4,7-dihydroxy-cyclohepta-3,5,7-triene-1,3-dicarboxylates **83** (Scheme 66).⁹⁴ Two equivalents of an appropriate ylide (**BG-BI**) were treated with one equivalent of aldehyde to afford the desired product.



Scheme 66

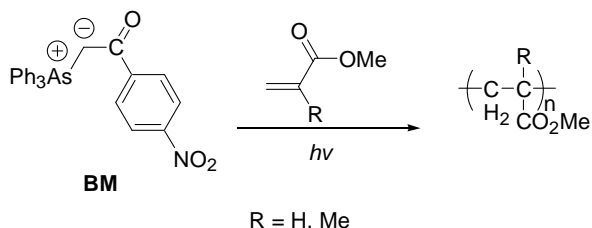
Aitken et al. examined the reaction between the β,γ -unsaturated arsonium ylide **CK** and DMAD and found that it proceeded with net insertion of the alkyne into the $\text{C}=\text{C}$ double bond (Scheme 67).²⁷ Spontaneous intramolecular cyclisation of this adduct afforded the tetrasubstituted 1,3-cyclohexadiene derivative **84**.



Scheme 67

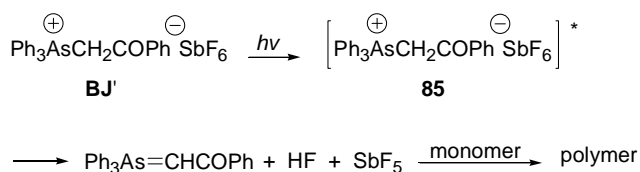
3.4. Polymerization reactions

Mishra and Mathur studied the photo-initiating ability of triphenylarsonium-*p*-nitrophenacylide **BM** in the polymerization of methyl acrylate⁹⁵ and methyl methacrylate (Scheme 68).⁹⁶ They reported that the polymerization proceeded with low conversion when the reaction mixture was illuminated by visible light. Kinetic data and ESR spectroscopy confirmed that the photopolymerization initiated by **BM** proceeded via a radical mechanism. It was proposed that the origin of the radical initiator is from homolysis of one of the phenyl C-As bonds.



Scheme 68

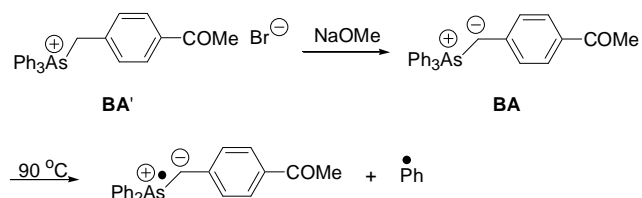
Abu-Abdoun and Ali reported the cationic photopolymerization of *p*-methylstyrene⁹⁷ and cyclohexene oxide⁹⁸ initiated by the phenacyltriphenylarsonium salt **BJ'**. The mechanism of this polymerization process was proposed to proceed via dissociation of the excited state **85** (Scheme 69). The efficiency of initiation, and hence conversion, was dependent upon the nature of the anion, e.g. SbF_6^- afforded the best conversion.



Scheme 69

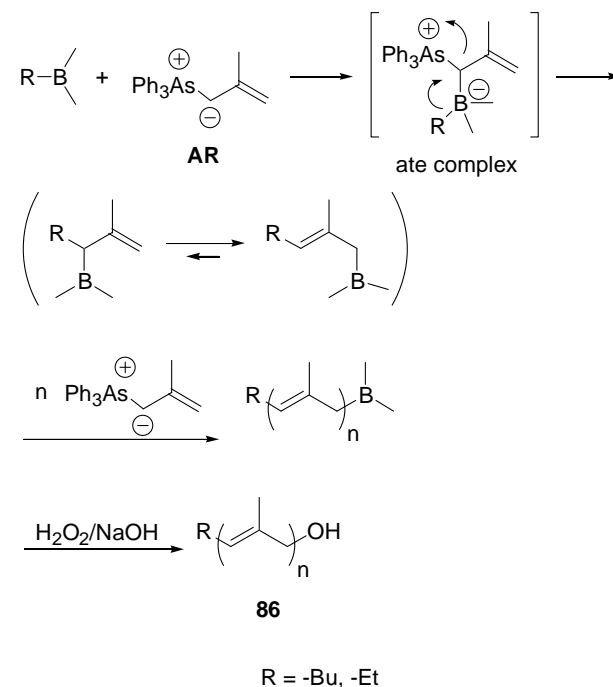
Srivastava et al. have reported a series of polymerizations using the *p*-acetylbenzylidenetriphenylarsonium ylide **BA** as the initiator. These include the terpolymerization of styrene, acrylonitrile and copper acrylate,⁹⁹ the synthesis of

arsenic-containing syndiotactic polymethyl methacrylate,¹⁰⁰ the generation of alternating copolymers containing styrene and citronellol sequences,¹⁰¹ and vinyl acetate radical polymerization.¹⁰² As before, the initiation step was proposed to be the decomposition of **BA** to generate a phenyl radical (Scheme 70).



Scheme 70

More recently, Mioskowski et al. developed a method that provided successive elongation by three carbon atoms using methallyltriphenylarsonium ylide **AR** as the monomer in a boron-catalyzed process.¹⁰³ In the product oligomers **86**, methyl-substituted double bonds were separated by one methylene group, which allowed the preparation of cyclic ketones (Scheme 71).



Scheme 71

4. Conclusions

A variety of arsonium ylides have been investigated in a number of laboratories and significant progress has been made regarding their application in organic synthesis. These ylides have proven to be a very effective reagents for converting carbonyl compounds into olefins and epoxides. These reactions are very useful synthetically, especially in

the synthesis of biologically active natural products. As shown, diverse functional groups such as enynyl, trifluoromethyl, and organoselenium groups can be introduced using arsonium ylides. In addition, such ylides have also been used in the stereoselective synthesis of cyclopropane derivatives, which can easily be converted into other diverse and useful building blocks.

Arsonium ylides are more reactive nucleophilic reagents than their phosphonium counterparts and their use in organic synthesis is marked by mild reaction conditions and high stereoselectivity and yield. Furthermore, they often possess reactivity associated with sulfonium and sulfoxonium ylides in that they can add to C-O and C-C double bonds to form epoxides and cyclopropane rings, respectively.

Along with the previously mentioned recent development of catalytic applications of arsonium ylides, the use of supported arsines for the immobilization of such ylides should further enhance their utility, since such recoverable arsines will also reduce toxicity and environmental concerns. In this regard, arsines have been reported attached to both polystyrene¹⁰⁴ and silica,¹⁰⁵ and it should be interesting to see if these materials become useful platforms for expanding the range of applications for which arsonium ylides are useful.

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References

- Huang, Y.-Z.; Shi, L.-L.; Zhou, Z.-L. Triphenylarsine. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: **1995**; p 5339-5342.
- Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585-9595.
- Faust, R.; Göbel, B. *J. Prakt. Chem.* **1998**, *340*, 90-93.
- Huang, Y.-Z.; Shen, Y.-C. *Adv. Organomet. Chem.* **1982**, *20*, 115-157.
- Lloyd, D.; Gosney, I.; Ormiston, R. A. *Chem. Soc. Rev.* **1987**, *16*, 45-74.
- For an interesting personal account describing one scientist's professional journey that includes a section regarding the early development of arsonium ylides in organic synthesis, see: Huang, Y.-Z. *Rev. Heteroat. Chem.* **1995**, *12*, 1-21.
- For a review comparing the reactivities of phosphonium and arsonium ylides of γ -acetoacetate-, γ -crotonate- and related compounds, see: Moorhoff, C. M. *Recent Res. Devel. Org. Chem.* **2000**, *4*, 239-259.
- Shao, M.-C.; Jin, X.-L.; Tang, Y.-Q.; Huang, Q.-C.; Huang, Y.-Z. *Tetrahedron Lett.* **1982**, *23*, 5343-5346.
- (a) Nesmeyanov, N. A.; Mikulshina, V. V.; Reutov, O. A. *J. Organomet. Chem.* **1968**, *13*, 263-265. (b) Gosney, I.; Lloyd, D. *Tetrahedron* **1973**, *29*, 1697-1710.
- Ernstbrunner, E. E.; Lloyd, D. *Chem. Ind. (London)* **1971**, 1332.
- Chabert, P.; Mioskowski, C.; Falck, J. R. *Tetrahedron Lett.* **1989**, *30*, 2545-2548.
- Boubia, B.; Mioskowski, C.; Bellamy, F. *Tetrahedron Lett.* **1989**, *30*, 5263-5266.
- Boubia, B.; Mann, A.; Bellamy, F. D.; Mioskowski, C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1454-1456.
- Castells, J.; López-Calahorra, F.; Yu, Z.-R. *Tetrahedron* **1994**, *50*, 13765-13774.
- Moorhoff, C. M. *Synth. Commun.* **1998**, *28*, 2925-2935.
- Ochiai, M.; Sueda, T.; Noda, R.; Shiro, M. *J. Org. Chem.* **1999**, *64*, 8563-8567.
- Dai, W.-M.; Wu, J.-L.; Huang, X. *Tetrahedron: Asymmetry* **1997**, *8*, 1979-1982.
- (a) Hadjiarapoglou, L.; Varvoglis, A. *Synthesis* **1988**, 913-915. (b) Hood, J. N. C.; Lloyd, D.; MacDonald, W. A.; Shepherd, T. M. *Tetrahedron* **1982**, *38*, 3355-3358.
- Suzuki, H.; Murafuji, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 950-951.
- (a) Kendurkar, P. S.; Tewari, R. S. *J. Organomet. Chem.* **1973**, *60*, 247-254. (b) Bansal, R. K.; Bhagchandani, G. *J. Prakt. Chem.* **1981**, *323*, 49-54.
- Deng, G.-S.; Huang, Z.-Z.; Yu, X.-C.; Huang, X. *Synth. Commun.* **2000**, *30*, 2487-2495.
- (a) Huang, Z.-Z.; Huang, X.; Huang, Y.-Z. *J. Organomet. Chem.* **1995**, *490*, C23-C26. (b) Huang, Z.-Z.; Huang, X.; Huang, Y.-Z. *J. Chem. Soc., Perkin Trans. 1* **1995**, 95-96.
- Deng, G.-S.; Huang, Z.-Z.; Huang, X. *Chin. Chem. Lett.* **2000**, *11*, 293-294.
- Deng, G.-S.; Huang, Z.-Z.; Yu, X.-C.; Huang, X. *J. Chem. Res., Synop.* **1999**, 144-145.
- (a) Deng, G.-S. *J. Chem. Res., Synop.* **2002**, 558-559. (b) Huang, Z.-Z.; Yu, X.-C.; Huang, X. *J. Org. Chem.* **2002**, *67*, 8261-8264.
- Kim, S.; Kim, Y. G. *Tetrahedron Lett.* **1991**, *32*, 2913-2916.
- Aitken, R. A.; Blake, A. J.; Gosney, I.; Gould, R. O.; Lloyd, D.; Ormiston, R. A. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1801-1805.
- Mitsumoto, Y.; Nitta, M. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2268-2274.
- (a) Facchin, G.; Zanotto, L.; Seraglia, R.; Traldi, P. *Org. Mass Spectrom.* **1992**, *27*, 1181-1186. (b) Facchin, G.; Zanotto, L.; Bertani, R.; Canovese, L.; Uguagliati, P. *J. Chem. Soc., Dalton Trans.* **1993**, 2871-2874. (c) Belluco, U.; Michelin, R. A.; Mozzon, M.; Bertani, R.; Facchin, G.; Zanotto, L.; Pandolfo, L. *J. Organomet. Chem.* **1998**, *557*, 37-68.
- Pandolfo, L.; Bertani, R.; Facchin, G.; Zanotto, L.; Ganis, P.; Valle, G.; Seraglia, R. *Inorg. Chim. Acta* **1995**, *237*, 27-35.
- Shen, Y.-C.; Qiu, W.-M. *Synthesis* **1987**, 65-66.
- Zhu, S.-F.; Liao, Y.-X.; Zhu, S.-Z. *Org. Lett.* **2004**, *6*, 377-380.
- Seyer, A.; Alcaraz, L.; Mioskowski, C. *Tetrahedron Lett.* **1997**, *38*, 7871-7874.
- Huang, Z.-Z.; Lan, G.-C.; Huang, X. *Synth. Commun.* **1998**, *28*, 633-637.
- Zessin, J.; Steinbach, J.; Johannsen, B. *J. Labelled Compd. Radiopharm.* **1999**, *42*, 725-736.
- Johnson, A. W.; Martin, J. O. *Chem. Ind. (London)* **1965**, 1726-1727.
- Hsi, J. D.; Koreeda, M. *J. Org. Chem.* **1989**, *54*, 3229-3231.
- Shen, Y.-C.; Wang, T.-L. *J. Fluorine Chem.* **1997**, *82*, 139-141.
- Shen, Y.-C.; Liao, Q.-M. *J. Organomet. Chem.* **1988**, *346*, 181-184.

40. (a) Huang, Y.-Z.; Shi, L.-L.; Yang, J.-H. *Tetrahedron Lett.* **1985**, *26*, 6447-6448. (b) Huang, Y.-Z.; Shi, L.-L.; Yang, J.-H. *J. Org. Chem.* **1987**, *52*, 3558-3560.
41. Ma, D.-W.; Sun, H.-Y. *J. Org. Chem.* **2000**, *65*, 6009-6016.
42. Huang, Y.-Z.; Shi, L.-L.; Li, S.-W. *Synthesis* **1988**, 975-977.
43. (a) Zhou, W.-S.; Jiang, B.; Pan, X.-F. *J. Chem. Soc., Chem. Commun.* **1989**, 612-614. (b) Zhou, W.-S.; Jiang, B.; Pan, X.-F. *Tetrahedron* **1990**, *46*, 3173-3188.
44. Xu, X.-X.; Zhu, J.; Huang, D.-Z.; Zhou, W.-S. *Tetrahedron Lett.* **1991**, *32*, 5785-5788.
45. (a) Cui, J.-G.; Zeng, L.-M.; Su, J.-Y.; Lu, W.-G. *Steroids* **2001**, *66*, 33-38. (b) Cui, J.-G.; Lin, C.-W.; Zeng, L.-M.; Su, J.-Y. *Steroids* **2002**, *67*, 1015-1019.
46. Corey, E. J.; Grogan, M. J. *Tetrahedron Lett.* **1998**, *39*, 9355-9356.
47. Hagen, S. E.; Domagala, J.; Gajda, C.; Lovdahl, M.; Tait, B. D.; Wise, E.; Holler, T.; Hupe, D.; Nouhan, C.; Urumov, A.; Zeikus, G.; Zeikus, E.; Lunney, E. A.; Pavlovsky, A.; Gracheck, S. J.; Saunders, J.; VanderRoest, S.; Brodfuehrer, J. *J. Med. Chem.* **2001**, *44*, 2319-2332.
48. Shi, L.-L.; Wang, W.-B.; Wang, Y.-C.; Huang, Y.-Z. *J. Org. Chem.* **1989**, *54*, 2027-2028.
49. For a report regarding a related catalytic Wittig reaction involving a poly(ethylene glycol)-supported teluride, see: Huang, Z.-Z.; Ye, S.; Xia, W.; Yu, Y.-H.; Tang, Y. *J. Org. Chem.* **2002**, *67*, 3096-3103.
50. Huang, Y.-Z.; Shi, L.-L.; Li, S.-W.; Huang, R. *Synth. Commun.* **1989**, *19*, 2639-2646.
51. Chenault, J.; Dupin, J. E. *Synthesis* **1987**, 498-499.
52. Huang, Z.-Z.; Wu, L.-L.; Zhu, L.-S.; Huang, X. *Synth. Commun.* **1996**, *26*, 677-682.
53. Huang, Z.-Z.; Yu, X.-C.; Huang, X. *Tetrahedron Lett.* **2002**, *43*, 6823-6825.
54. Shen, Y.-C.; Xiang, Y.-J. *Synth. Commun.* **1991**, *21*, 1403-1408.
55. Dheilly, L.; Lièvre, C.; Fréchou, C.; Demailly, G. *Tetrahedron Lett.* **1993**, *34*, 5895-5898.
56. (a) Huang, Z.-Z.; Huang, X.; Huang, Y.-Z. *J. Chem. Res., Synop.* **1995**, 206-207. (b) Huang, Z.-Z.; Huang, X.; Huang, Y.-Z. *Tetrahedron Lett.* **1995**, *36*, 425-426. (c) Deng, G.-S.; Huang, Z.-Z.; Huang, X. *Chin. Chem. Lett.* **2003**, *14*, 3-5.
57. Hon, Y.-S.; Lee, C.-F. *Tetrahedron* **2000**, *56*, 7893-7902.
58. Sun, R.-J.; Jiang, H.; Huang, Z.-Z. *Chin. Chem. Lett.* **2003**, *14*, 243-244.
59. Dai, W.-M.; Lau, C. W. *Tetrahedron Lett.* **2001**, *42*, 2541-2544.
60. Dai, W.-M.; Wu, A.-X.; Wu, H.-F. *Tetrahedron: Asymmetry* **2002**, *13*, 2187-2191.
61. (a) Deng, G.-S.; Huang, Z.-Z.; Huang, X. *Org. Prep. Proced. Int.* **1999**, *31*, 453-456. (b) Deng, G.-S.; Huang, Z.-Z.; Huang, X. *Synth. Commun.* **2002**, *32*, 1775-1780.
62. Shi, L.-L.; Xiao, W.-J.; Wen, X.-Q.; Huang, Y.-Z. *Synthesis* **1987**, 370-371.
63. Li, Z.-M.; Wang, T.-S.; Zhang, D.-K.; Gao, Z.-H. *Synth. Commun.* **1989**, *19*, 91-96.
64. Lu, Z.-H.; Zhou, W.-S. *Tetrahedron* **1993**, *49*, 4659-4664.
65. Gravier-Pelletier, C.; Dumas, J.; Le Merrer, Y.; Depezay, J. C. *Tetrahedron Lett.* **1991**, *32*, 1165-1168.
66. Peng, Z.-H.; Li, Y.-L.; Wu, W.-L.; Liu, C.-X.; Wu, Y.-L. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1057-1066.
67. Huang, Y.-Z.; Shi, L.-L.; Yang, J.-H.; Zhang, J.-T. *Tetrahedron Lett.* **1987**, *28*, 2159-2162.
68. Shi, L.-L.; Yang, J.-H.; Wen, X.-Q.; Huang, Y.-Z. *Tetrahedron Lett.* **1988**, *29*, 3949-3950.
69. Shen, Y.-C.; Xiang, Y.-J. *Tetrahedron Lett.* **1990**, *31*, 2305-2306.
70. Shen, Y.-C.; Xiang, Y.-J. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2493-2494.
71. Shen, Y.-C.; Xiang, Y.-J. *Synth. Commun.* **1991**, *21*, 1991-1998.
72. Shen, Y.-C.; Xiang, Y.-J. *Heteroat. Chem.* **1992**, *3*, 547-549.
73. Chabert, P.; Ousset, J. B.; Mioskowski, C. *Tetrahedron Lett.* **1989**, *30*, 179-182.
74. Chabert, P.; Mioskowski, C. *Tetrahedron Lett.* **1989**, *30*, 6031-6034.
75. Shi, L.-L.; Wang, W.-B.; Huang, Y.-Z. *Tetrahedron Lett.* **1988**, *29*, 5295-5296.
76. Wang, W.-B.; Shi, L.-L.; Li, Z.-Q.; Huang, Y.-Z. *Tetrahedron Lett.* **1991**, *32*, 3999-4000.
77. Boubia, B.; Mioskowski, C.; Manna, S.; Falck, J. R. *Tetrahedron Lett.* **1989**, *30*, 6023-6026.
78. Reetz, M. T.; Binder, J. *Tetrahedron Lett.* **1989**, *30*, 5425-5428.
79. Werner, F.; Parmentier, G.; Luu, B.; Dinan, L. *Tetrahedron* **1996**, *52*, 5525-5532.
80. Deng, W.-P.; Li, A.-H.; Dai, L.-X.; Hou, X.-L. *Tetrahedron* **2000**, *56*, 2967-2974.
81. Li, A.-H.; Dai, L.-X.; Hou, X.-L.; Chen, M.-B. *J. Org. Chem.* **1996**, *61*, 4641-4648.
82. Weiss, R.; Reichel, S.; Handke, M.; Hampel, F. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 344-347.
83. Reichel, S. Dissertation, Universität Erlangen-Nürnberg, in **1998**.
84. Paquette, L. A. *Isr. J. Chem.* **1981**, *21*, 128-134.
85. Shen, Y.-C.; Liao, Q.-M. *Synthesis* **1988**, 321-323.
86. Shen, Y.-C.; Liao, Q.-M. *J. Organomet. Chem.* **1989**, *371*, 31-34.
87. Shen, Y.-C.; Xiang, Y.-J. *J. Chem. Res., Synop.* **1994**, 198-199.
88. Tang, Y.; Huang, Y.-Z.; Dai, L.-X.; Sun, J.; Xia, W. *J. Org. Chem.* **1997**, *62*, 954-959.
89. Cao, W.-G.; Ding, W.-Y.; Chen, Y.-L.; Gao, J.-S. *Synth. Commun.* **2000**, *30*, 4523-4530.
90. Chen, Y.-L.; Ding, W.-Y.; Cao, W.-G.; Lu, C. *Synth. Commun.* **2002**, *32*, 1953-1960.
91. Ren, Z.-J.; Ding, W.-Y.; Cao, W.-G.; Wang, S.-H.; Huang, Z.-J. *Synth. Commun.* **2002**, *32*, 3143-3148.
92. (a) Moorhoff, C. M. *Tetrahedron Lett.* **1996**, *37*, 9349-9352. (b) Moorhoff, C. M. *J. Chem. Res., Synop.* **1997**, 130-131.
93. Moorhoff, C. M. *Synlett* **1997**, 126-128.
94. (a) Moorhoff, C. M. *Tetrahedron Lett.* **1997**, *38*, 4157-4160. (b) Moorhoff, C. M. *Heteroat. Chem.* **1998**, *9*, 411-418.
95. Mishra, A.; Mathur, G. N. *Polym. Commun.* **1990**, *31*, 378-379.
96. Mishra, A.; Mathur, G. N. *Acta Polym.* **1990**, *41*, 185-187.
97. Abu-Abdoun, I. I.; Aale-Ali *Eur. Polym. J.* **1993**, *29*, 1439-1443.
98. Abu-Abdoun, I. I.; Aale-Ali *Eur. Polym. J.* **1993**, *29*, 1445-1450.
99. Shukla, P.; Srivastava, A. K. *Polym. Int.* **1996**, *41*, 407-412.
100. Kaur, M.; Srivastava, A. K. *J. Photochem. Photobio., A: Chem.* **1998**, *119*, 67-72.
101. Srivastava, A. K.; Pandey, P. *Polym. Int.* **2001**, *50*, 937-945.
102. (a) Daniel, N.; Srivastava, A. K. *Eur. Polym. J.* **2001**, *37*, 2313-2318. (b) Daniel, N.; Srivastava, A. K. *Adv. Polym. Technol.* **2002**, *21*, 108-115.
103. Goddard, J.-P.; Lixon, P.; Le Gall, T.; Mioskowski, C. *J. Am. Chem. Soc.* **2003**, *125*, 9242-9243.
104. (a) Smith, C. P.; Temme, G. H. *J. Org. Chem.* **1983**, *48*, 4681-4685. (b) Steiner, U. B.; Caseri, W. R.; Suter, U. W. *Langmuir* **1998**, *14*, 347-351.
105. Cai, M.; Huang, Y.; Zhao, H.; Song, C. *React. Funct. Polym.* **2004**, *59*, 81-86.

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