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## Arsonium ylides in organic synthesis

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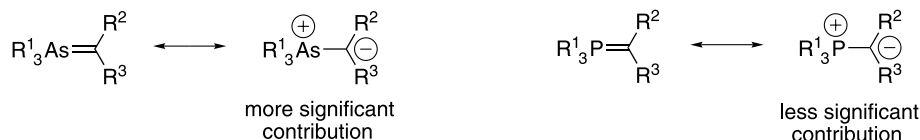
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### 1. Introduction

In the field of organic synthesis, organoarsines have found wide application. They, especially triphenylarsine (**1**),<sup>1</sup> have been found to be useful as a metal ligand in a range of palladium-catalyzed cross-coupling reactions between organohalides and organostannanes<sup>2</sup> or organoboronic acids.<sup>3</sup> They can also be used for the preparation of arsonium ylides (alkylidene arsonanes) that are more nucleo-

philic than their phosphonium counterparts.<sup>4</sup> Since the preparation and use of arsonium ylides in the context of organic synthesis was last comprehensively reviewed in 1987,<sup>5–7</sup> the present review covers this subject in the literature from 1987 through to early 2004.

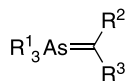
Of the many organoarsine compounds that are useful for the preparation of arsonium ylides,<sup>5</sup> **1** is currently used almost exclusively since it is commercially available in high purity



**Figure 1.** Resonance structures of arsonium and phosphonium ylides.

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



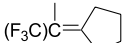
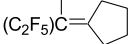
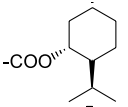
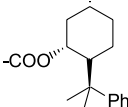
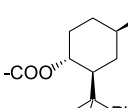
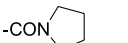



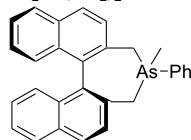
Ylide	R <sup>1a</sup>	R <sup>2</sup>	R <sup>3</sup>	References
AA	–Ph	–H	–H	31,33,35,54,69,70,78,87
AB	–Ph	–H	–CH <sub>3</sub>	33
AC	–Ph	–H	– <i>n</i> -Bu	33
AD	–Ph	–H	–CH <sub>2</sub> CH <sub>2</sub> Br	15
AE	–Ph	–H	–CH <sub>2</sub> CH–( <i>O</i> - <i>i</i> -Pr) <sub>2</sub>	11,73
AF	–Ph	–H	–CH <sub>2</sub> OH	75
AG	–Ph	–H	–CH=CHCH <sub>2</sub> CH(OEt) <sub>2</sub>	74
AH	–Ph	–H	–CH=CH <sub>2</sub>	15,37,38,81,88
AI	–Ph	–H	–CH=CHMe	88
AJ	–Ph	–H	–CH=CHPh	88
AK	–Ph	–H	–CH=CHCH <sub>2</sub> OH	76,80
AL	–Ph	–H	–CH=CHCHO	65
AM	–Ph	–H	–CH=CHSiMe <sub>3</sub>	88
AN	–Ph	–H	–CH=CHCO <sub>2</sub> Me	15,92,93
AO	–Ph	–H	–CH=CHCO <sub>2</sub> Et	63,64
AP	–Ph	–H	–CH=CMe <sub>2</sub>	79
AQ	–Ph	–H	–CH=CHC <sub>6</sub> F <sub>5</sub>	38
AR	–Ph	–H	–C(CH <sub>3</sub> )=CH <sub>2</sub>	103
AS	–Ph	–H	–C(CH <sub>3</sub> )=CHCO <sub>2</sub> Me	62
AT	–Ph	–H	–(CF <sub>3</sub> )C=CMe <sub>2</sub>	69,70,87
AU	–Ph	–H		69,70,87
AV	–Ph	–H	–(C <sub>2</sub> F <sub>5</sub> )C=CMe <sub>2</sub>	87
AW	–Ph	–H		87
AX	–Ph	–H	–C(OAc)=CHCO <sub>2</sub> Me	15
AY	–Ph	–H	–CCSi(CH <sub>3</sub> ) <sub>3</sub>	39,71,72,85,86
AZ	–Ph	–H	–Ph	15,88
BA	–Ph	–H	–C <sub>6</sub> H <sub>4</sub> - <i>p</i> -OMe	30,99–102
BB	–Ph	–H	–C <sub>6</sub> F <sub>5</sub>	31,32,54
BC	–Ph	–H	–CHO	40,41,66
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 <sub>5</sub> H <sub>11</sub>	42
BG	–Ph	–H	–COCH <sub>2</sub> CO <sub>2</sub> Me	15,94
BH	–Ph	–H	–COCH <sub>2</sub> CO <sub>2</sub> Et	15,94
BI	–Ph	–H	–COCH <sub>2</sub> CO <sub>2</sub> - <i>i</i> -Pr	94
BJ	–Ph	–H	–COPh	15,21–24,27,29,30,97,98
BK	–Ph	–H	–COC <sub>6</sub> H <sub>4</sub> - <i>p</i> -Cl	23
BL	–Ph	–H	–COC <sub>6</sub> H <sub>4</sub> - <i>p</i> -Br	23
BM	–Ph	–H	–COC <sub>6</sub> H <sub>4</sub> - <i>p</i> -NO <sub>2</sub>	95,96
BN	–Ph	–H	–COC(OH)Me <sub>2</sub>	44
BO	–Ph	–H	–CO <sub>2</sub> Me	15,21–23,25,29,30,50,55,57,90,91
BP	–Ph	–H	–CO <sub>2</sub> Et	14,15,21,25,28,58
BQ	–Ph	–H	–CO <sub>2</sub> - <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

Table 1 (continued)

Ylide	R <sup>1a</sup>	R <sup>2</sup>	R <sup>3</sup>	References
BY	–Ph	–H	–SPh	77
BZ	–Ph	—	=CMe <sub>2</sub>	16
CA	–Ph	—		16
CB	–Ph	–Me	–(CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	33
CC	–Ph	–Me	–CH=CHOSi- <i>i</i> -Pr <sub>3</sub>	26
CD	–Ph	–Me	–CO <sub>2</sub> Et	14
CE	–Ph	–Et	–CO <sub>2</sub> Et	14
CF	–Ph	– <i>n</i> -Pr	–CO <sub>2</sub> Et	14
CG	–Ph	– <i>n</i> -Bu	–CH=CHOSi- <i>i</i> -Pr <sub>3</sub>	26
CH	–Ph	– <i>n</i> -Bu	–CO <sub>2</sub> Et	14
CI	–Ph	– <i>n</i> -C <sub>6</sub> H <sub>13</sub>	–CH=CHOSi- <i>i</i> -Pr <sub>3</sub>	26
CJ	–Ph	– <i>n</i> -C <sub>11</sub> H <sub>23</sub>	–CO <sub>2</sub> Me	14
CK	–Ph	–CH=CHCOPh	–CO <sub>2</sub> Me	27
CL	–Ph	–CH=CHCOPh	–CO <sub>2</sub> Et	27
CM	–Ph		–CO <sub>2</sub> Et	28
CN	–Ph		–CN	28
CO	–Ph	–COMe	–COMe	19,21
CP	–Ph	–COMe	–CO- <i>n</i> -C <sub>5</sub> H <sub>11</sub>	21
CQ	–Ph	–COMe	–COPh	21
CR	–Ph	–COMe	–CO <sub>2</sub> Me	21
CS	–Ph	–COMe	–CO <sub>2</sub> Et	21
CT	–Ph	–COMe	–CN	21
CU	–Ph	–CO- <i>n</i> -C <sub>5</sub> H <sub>11</sub>	–CO <sub>2</sub> Me	21
CV	–Ph	–CO- <i>n</i> -C <sub>5</sub> H <sub>11</sub>	–CO <sub>2</sub> Et	21
CW	–Ph	–CO- <i>n</i> -C <sub>5</sub> H <sub>11</sub>	–CN	21
CX	–Ph	–COPh	–CH=CHCO <sub>2</sub> Me	27
CY	–Ph	–COPh	–CH=CHCO <sub>2</sub> Et	27
CZ	–Ph	–COPh	–CO <sub>2</sub> Me	21
DA	–Ph	–COPh	–CO <sub>2</sub> Et	21
DB	–Ph	–SPh	–COMe	24
DC	–Ph	–SPh	–COPh	24
DD	–Ph	–SPh	–CO <sub>2</sub> Me	25,56c
DE	–Ph	–SPh	–CO <sub>2</sub> Et	25,56c
DF	–Ph	–SC <sub>6</sub> H <sub>4</sub> - <i>p</i> -Me	–CO <sub>2</sub> Me	25
DG	–Ph	–SC <sub>6</sub> H <sub>4</sub> - <i>p</i> -Me	–CO <sub>2</sub> Et	25
DH	–Ph	–SePh	–COMe	22b,23
DI	–Ph	–SePh	–COPh	22b,23
DJ	–Ph	–SePh	–COC <sub>6</sub> H <sub>4</sub> - <i>p</i> -Cl	23
DK	–Ph	–SePh	–COC <sub>6</sub> H <sub>4</sub> - <i>p</i> -Br	22a,23
DL	–Ph	–SePh	–CO <sub>2</sub> Me	22a,23,56a,b
DM	–Ph	–SePh	–CN	61
DN	–Ph	–I	–C <sub>6</sub> H <sub>4</sub> - <i>p</i> -NO <sub>2</sub>	34
DO	–Ph	–I	–COMe	50
DP	–Ph	–I	–CO <sub>2</sub> Me	50
DQ	–Ph	–I	–CN	50
DR	–Ph	–IPh	–CO <sub>2</sub> Me	25
DS	–Ph	–IPh	–CO <sub>2</sub> Et	25,53
DT	–Ph	–HgCl	–C <sub>6</sub> H <sub>4</sub> - <i>p</i> -COMe	103
DU	– <i>n</i> -Bu	–H	–CO <sub>2</sub> Me	48
DV	– <i>n</i> -Bu	–H	–COPh	48
DW	<i>t</i> -BuPh <sub>2</sub> As	–H	–CH <sub>2</sub> CH=CH- <i>n</i> -C <sub>5</sub> H <sub>11</sub>	11
DX	BnPh <sub>2</sub> As	–H	–Ph	12
DY	Ph <sub>2</sub> As(CH <sub>2</sub> ) <sub>2</sub> OH	–H	–Ph	13
DZ		–H	–CO <sub>2</sub> Me	60

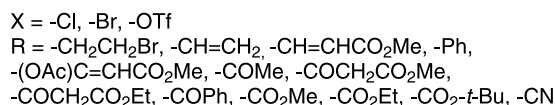
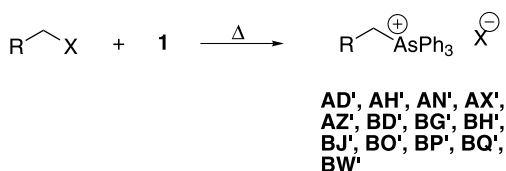
<sup>a</sup> Except for arsonium ylides (DW)–(DZ).

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 (Fig. 1). This has been established by a variety of methods, including X-ray crystallography,<sup>8</sup> and IR,<sup>9</sup> and NMR<sup>10</sup> spectroscopy. The increase in negative charge density on the carbon center of arsonium ylides as compared

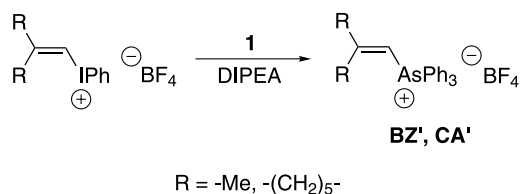


could be isolated in 77–99% yield after simply washing the product with petroleum ether (Scheme 4).



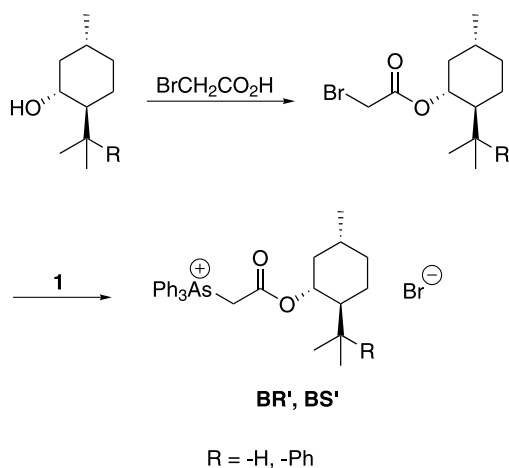
Scheme 4.

Another method for arsonium salt synthesis was reported by Ochiai et al. where 1-alkenyl triphenylarsonium tetrafluoroborate salts **BZ'** and **CA'** could be prepared via an onium transfer reaction of alkenyl(phenyl)iodonium tetrafluoroborate salts under mild conditions. This reaction occurs via a base-induced  $\alpha$ -elimination/nucleophilic trapping mechanism (Scheme 5).<sup>16</sup> The authors report that this method is general and that the analogous phosphorous, antimony, sulphur, selenium and tellurium salts can all be prepared in this manner.



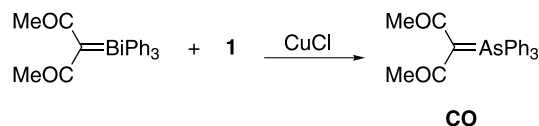
Scheme 5.

The asymmetric Wittig reaction using chiral arsonium ylides has been described by Dai et al. Thus, they reported the first synthesis of chiral arsonium salts **BR'** and **BS'**, which were obtained from **1** and chiral menthol-derived esters (Scheme 6).<sup>17</sup> The stereoselectivity achieved with the chiral ylides derived from these salts will be discussed later.



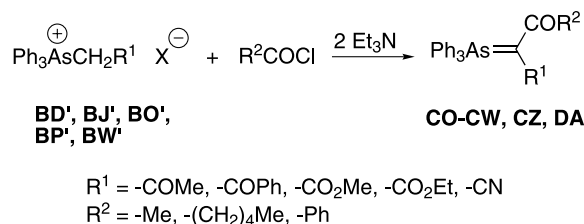
Scheme 6.

While the formation of arsonium ylides by the thermal decomposition of iodonium ylides was known,<sup>18</sup> Suzuki and Murafuji reported the first example of transylidation of a bismuthonium ylide with **1** in the presence of a copper(I) salt catalyst in benzene at room temperature to form the arsonium ylide **CO** in moderate yields (Scheme 7).<sup>19</sup> The authors note that this transylidation reaction also works with methyl sulfide, but fails with triphenylphosphine in one case and with triphenylantimony in both cases examined.



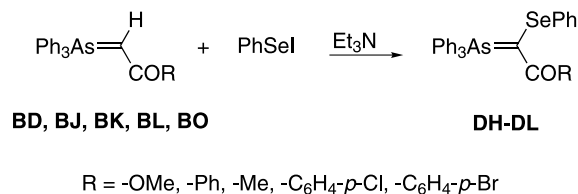
Scheme 7.

Huang et al. reported that, compared to the typical method for the preparation of  $\alpha$ -acyl arsonium ylides, e.g. transylidation reactions,<sup>20</sup> the direct treatment of arsonium salts with an acid chloride in the presence of 2 equiv of triethylamine is a more efficient procedure, since the formation of undesired side-products is avoided (Scheme 8).<sup>21</sup> It was observed that, when R<sup>1</sup> was an electron-withdrawing group such as alkoxyacyl, cyano, or acyl, the arsonium ylides **CO–CW**, **CZ**, and **DA** were formed in moderate to good yield. It was proposed that the salt is deprotonated to form an ylide that is, in turn, acylated and deprotonated to furnish the end product.



Scheme 8.

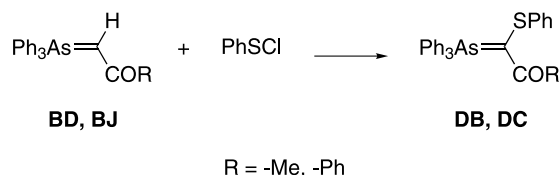
Organoselenium compounds have begun to play an ever more important role in organic synthesis and, in this regard, Huang et al. reported the first example of  $\alpha$ -organoseleno arsonium ylides.<sup>22</sup> These compounds were prepared by treating  $\alpha$ -unfunctionalized arsonium ylides with phenylselenenyl iodide. They later reported an improvement of this method, when it was observed that the presence of a weak base such as triethylamine afforded excellent yields (80–90%) of the ylides **DH–DL** (Scheme 9).<sup>23</sup>



Scheme 9.

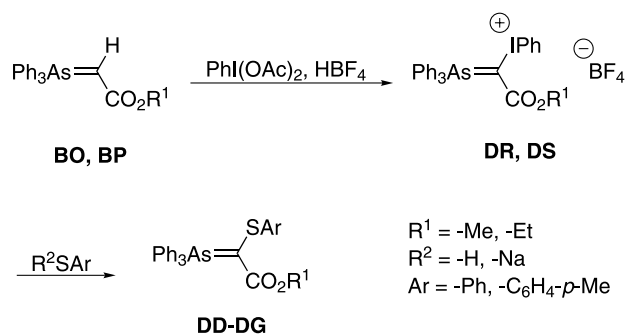
Similarly, ylides functionalized with arylthio groups at the  $\alpha$ -position can play important roles in synthesis. Thus,

Huang and co-workers have also reported the synthesis of  $\alpha$ -phenylthioacrylyl arsonium ylides **DB** and **DC** from **BD** and **BJ**, respectively (Scheme 10).<sup>24</sup> The method used to prepare these ylides was similar to that used to prepare the selenium-functionalized ylides.



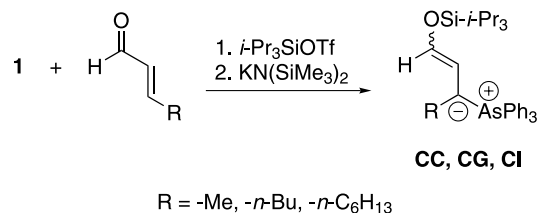
Scheme 10.

Most recently, this group has synthesized mixed iodonium–arsonium ylides, and developed a novel method for the synthesis of  $\alpha$ -thio- and  $\alpha$ -selenoarsonium ylides via a substitution reaction, instead of the usual addition/elimination method (Scheme 11).<sup>25</sup> 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.



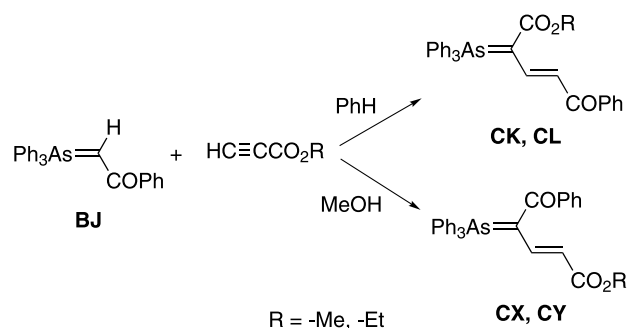
Scheme 11.

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



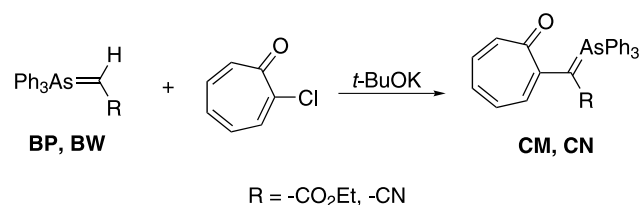
Scheme 12.

Aitken et al. have examined the reactions of **BJ** with methyl and ethyl propiolate.<sup>27</sup> 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.



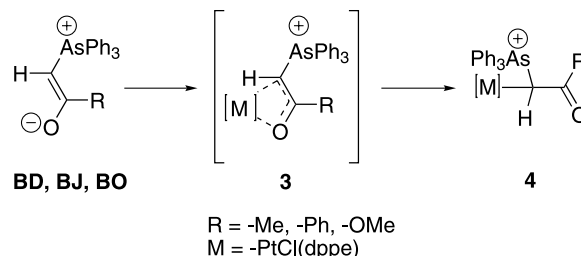
Scheme 13.

Mitsumoto and Nitta have recently prepared the first stable arsonium ylide derivatives bearing cyclohepta-2,4,6-trienyl and electron-withdrawing CO<sub>2</sub>Et and CN groups (**CM** and **CN**) in low yield from **BP** and **BW**, respectively (Scheme 14).<sup>28</sup> 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.



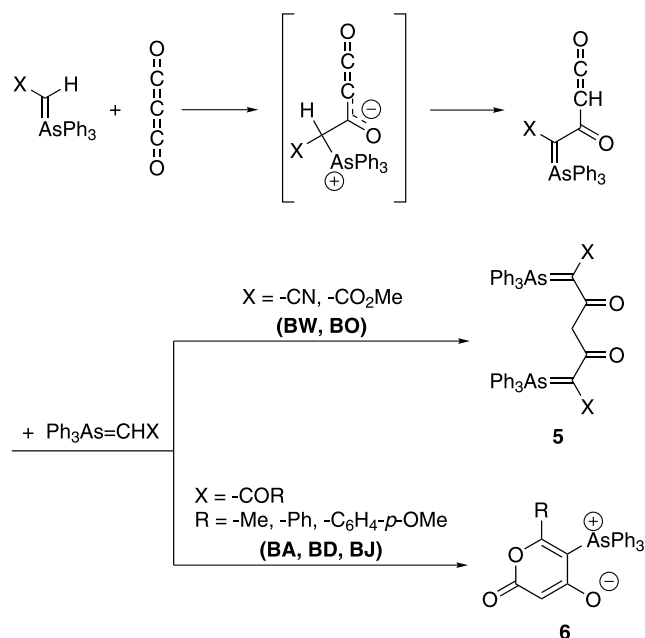
Scheme 14.

Facchin et al. reported that the reaction of [PtCl(dppe)]<sub>2</sub>[BF<sub>4</sub>]<sub>2</sub> (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).<sup>29</sup>



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).<sup>30</sup> When X = CN, or CO<sub>2</sub>Me, the reaction proceeded to form 2:1 (ylide/C<sub>3</sub>O<sub>2</sub>) adducts, such as open-chain malonyl bis-ylidic compounds **5**. When X = COMe, COPh, or COC<sub>6</sub>H<sub>4</sub>-*p*-OMe, only 1:1 cyclic zwitterionic adducts **6** were obtained.



Scheme 16.

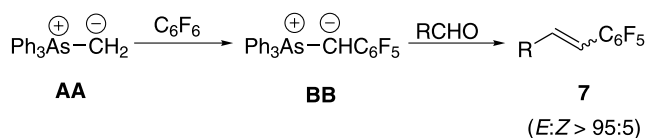
### 3. Synthetic applications of arsonium ylides

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.

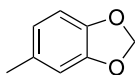
#### 3.1. Alkene synthesis

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).<sup>31</sup> 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.

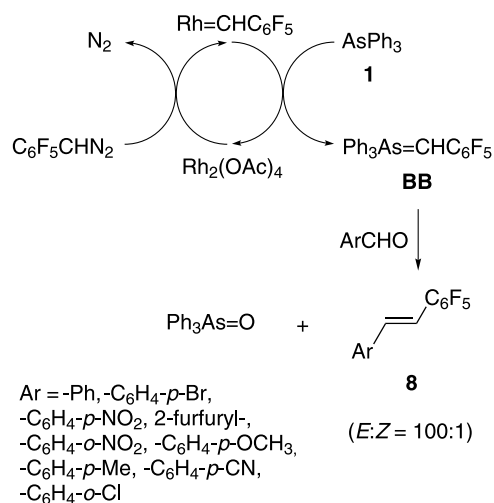


R = -Ph, -CH=CHPh, -C<sub>6</sub>H<sub>4</sub>-*o*-Cl, -C<sub>6</sub>H<sub>4</sub>-*p*-Cl, -C<sub>6</sub>H<sub>4</sub>-*p*-F, -C<sub>6</sub>H<sub>4</sub>-*p*-NO<sub>2</sub>, -C<sub>6</sub>H<sub>3</sub>-2,4-Cl<sub>2</sub>, -C<sub>6</sub>H<sub>4</sub>-*p*-Br, -C<sub>6</sub>H<sub>4</sub>-*p*-Me,



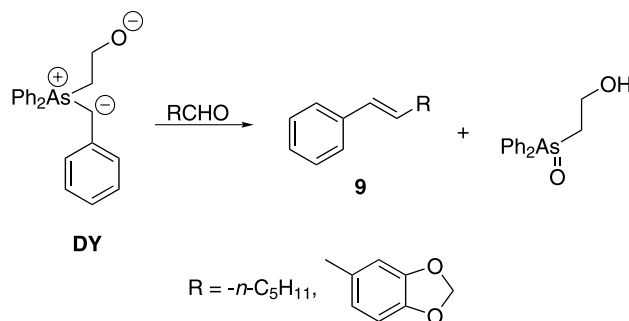
Scheme 17.

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.<sup>32</sup> This procedure uses Rh<sub>2</sub>(OAc)<sub>4</sub> 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).



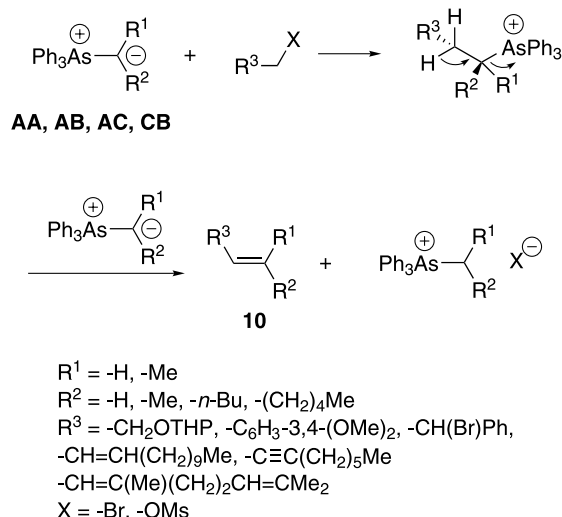
Scheme 18.

Mioskowski et al. investigated the bisbenzyl ylide-anion **DX** (Scheme 2) in an attempt to improve the stereo-selectivity 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.<sup>12</sup> Later, they reported that the ylide **DY**, under the same reaction conditions, afforded exclusively the *E*-isomer of **9** (Scheme 19).<sup>13</sup>



Scheme 19.

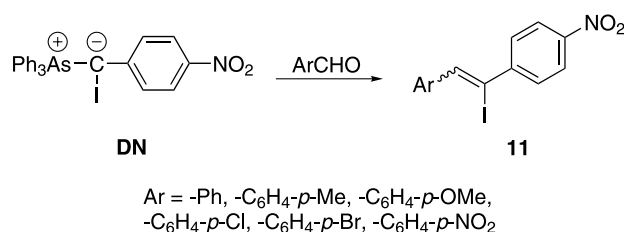
Mioskowski et al. also reported the straightforward olefination of activated halides and mesylates using non-stabilized alkyltriphenylarsonium ylides (**AA**, **AB**, **AC**, and **CB**) to afford the alkenes **10** (Scheme 20).<sup>33</sup> The semi-stabilized ylide **AZ** and the stabilized ylide **BP** 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



Scheme 20.

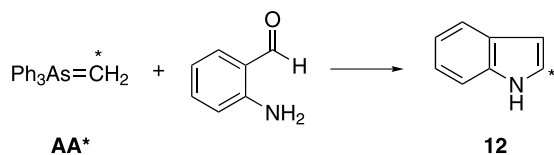
by the ylide, followed by deprotonation and elimination of the formed arsonium salt to afford the product alkene. A variety of allylic and benzylic alkyl halides and mesylates were converted into the corresponding olefins.

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  $\alpha$ -iodo-substituted alkenes **11** using a semi-stabilized ylide **DN** (Scheme 21).<sup>34</sup> These reactions afforded *E/Z* ratios ranging from 34:66 to 67:33.



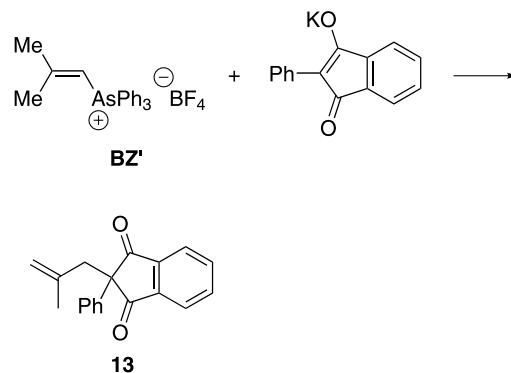
Scheme 21.

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



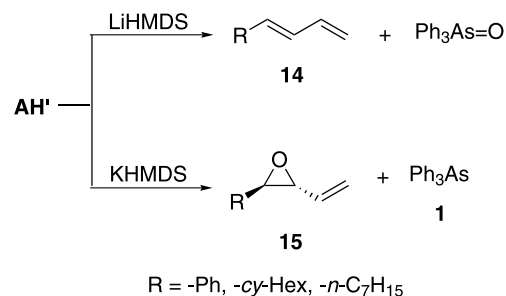
Scheme 22.

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).<sup>16</sup> As mentioned previously, **BZ'** was prepared by base-induced reductive  $\alpha$ -elimination of an iodonium salt, followed by nucleophilic trapping with **1** (Scheme 5).



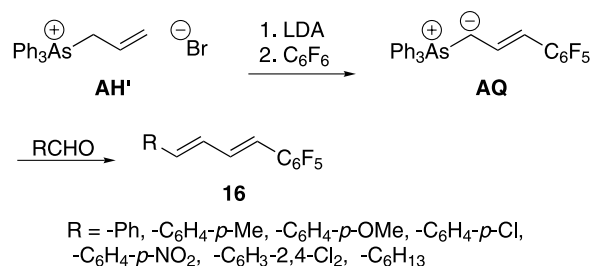
Scheme 23.

**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.<sup>36</sup> 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).<sup>37</sup> 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.

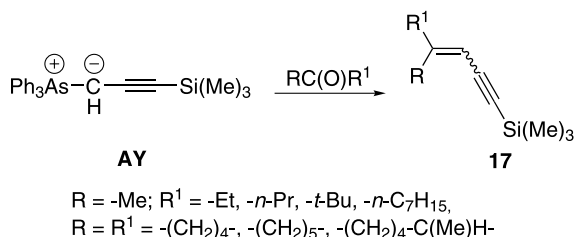
Shen and Wang reported a highly stereoselective synthesis of substituted 1-pentafluorophenyl-1,3-dienes using an arsonium ylide (Scheme 25).<sup>38</sup> Ylide **AH'**, generated from the corresponding arsonium salt and lithium diisopropylamide, was first reacted with hexafluorobenzene to afford **AQ**.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



Scheme 25.

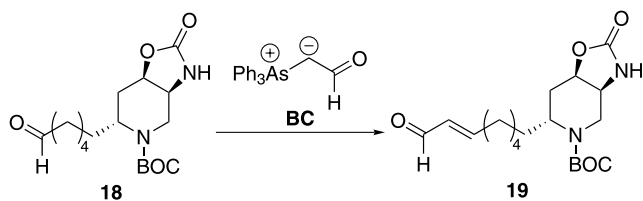
Shen and Liao described the synthesis of a series of terminal trimethylsilyl enynes **17** using a silylated ylide **AY**

(Scheme 26).<sup>39</sup> The isolated yields ranged from 72 to 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.



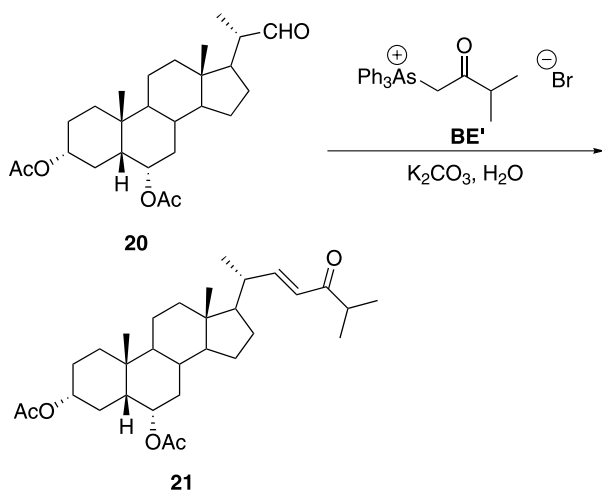
Scheme 26.

**3.1.3.  $\alpha,\beta$ -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 more milder conditions than with the corresponding phosphorous ylide.<sup>40</sup> Ma and Sun used this method in the synthesis of an intermediate of pseudodistomin B triacetate.<sup>41</sup> Treatment of aldehyde **18** with **BC** afforded the desired formyl-olefination product **19** in 73% yield (Scheme 27).



Scheme 27.

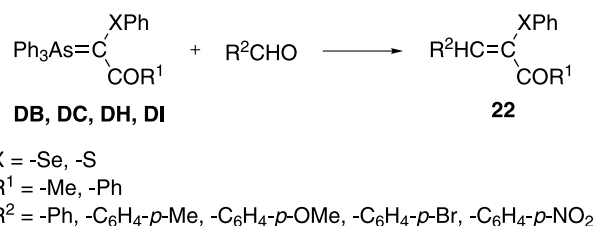
**3.1.4.  $\alpha,\beta$ -Alkenone synthesis.** Huang et al. reported an efficient and highly stereoselective synthesis of (*E*)- $\alpha$ -enones by the reaction of aldehydes with arsonium bromides



Scheme 28.

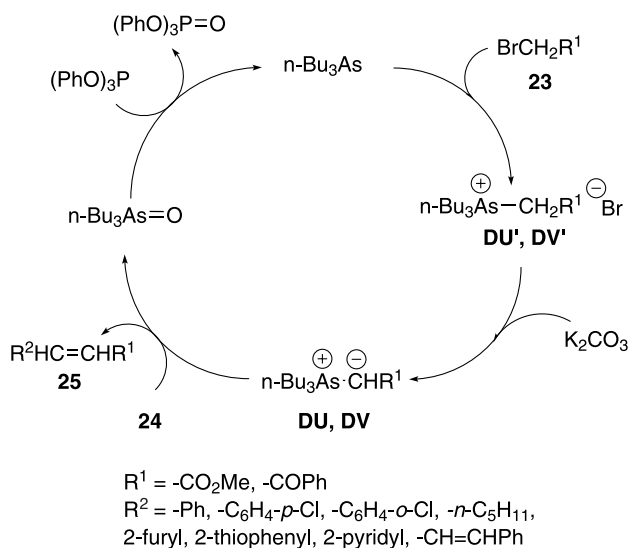
**BE'** and **BF'** (not shown) and potassium carbonate with a trace of water at room temperature.<sup>42</sup> Using this method, the key intermediate **21** for the synthesis of brassinosteroid was prepared from the aldehyde **20** (Scheme 28). This procedure was also useful in the synthesis of prostaglandin 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*)- $\alpha$ -enones from aldehydes. Thus, it has been used for the synthesis of intermediates of brassinolide,<sup>43</sup> yingzhaosu A,<sup>44</sup> polyhydroxysterols,<sup>45,46</sup> and HIV protease inhibitors.<sup>47</sup>

$\alpha$ -Phenylselenenyl-<sup>22b</sup> and  $\alpha$ -phenylthioenones<sup>24</sup> **22** were obtained from the stable  $\alpha$ -phenylselenenyl and  $\alpha$ -phenylthioenones ylides **DB**, **DC**, **DH**, and **DI**. These olefination reactions showed good stereoselectivity and provided products with predominantly *Z* stereochemistry (Scheme 29).



Scheme 29.

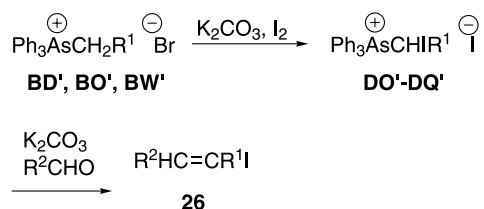
Shi et al. used arsonium ylides in the first reported example of a catalytic Wittig-type reaction.<sup>48,49</sup> Tri-*n*-butylarsine was reacted with bromo compounds **23** to form arsonium salts **DU'** or **DV'**, which, in the presence of potassium carbonate, generated the corresponding ylides **DU** and **DV** in situ. The ylide reacted rapidly with aldehyde **24** to afford the desired olefin **25**, and tri-*n*-butylarsine was regenerated by the reduction of tri-*n*-butylarsine oxide with triphenyl phosphite (Scheme 30).



Scheme 30.

**3.1.5.  $\alpha,\beta$ -Alkenoate synthesis.**  $\alpha$ -Halo- $\alpha,\beta$ -unsaturated compounds are useful intermediates in organic synthesis.

Huang et al. reported that  $\alpha$ -iodo-unsaturated esters, ketones and nitriles **26** could be synthesized under mild conditions using readily available arsonium salts in a one-pot procedure (Scheme 31).<sup>50</sup> It was noteworthy that the weak base, potassium carbonate, did not effect the elimination of an  $\alpha$ -iodo- $\alpha,\beta$ -unsaturated ester, although Chenault et al. pointed out that this was a possibility.<sup>51</sup> Later,  $\alpha$ -bromo-unsaturated esters were also prepared directly using an arsonium ylide with bromine in an analogous one-pot reaction.<sup>52</sup>

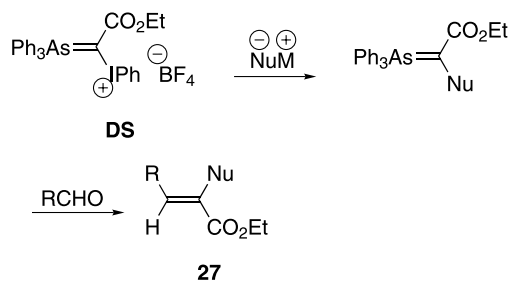


R<sup>1</sup> = -CO<sub>2</sub>Me, -COMe, -CN

R<sup>2</sup> = -Ph, -C<sub>6</sub>H<sub>4</sub>-*p*-NO<sub>2</sub>, -C<sub>6</sub>H<sub>4</sub>-*p*-Cl, -C<sub>6</sub>H<sub>4</sub>-*p*-OMe, -CH=CHPh

Scheme 31.

Huang et al. also reported another method for making  $\alpha$ -halo- $\alpha,\beta$ -unsaturated esters.<sup>25b,53</sup> An  $\alpha$ -hypervalent iodo-functionalized arsonium ylide **DS** could be used as an umpolung ylide in a nucleophilic substitution reaction and then proceed in a Wittig reaction with an aldehyde to afford (*Z*)- $\alpha$ -heteroatom- $\alpha,\beta$ -unsaturated esters **27**, stereoselectively, in moderate to excellent yields (60–97%) (Scheme 32).

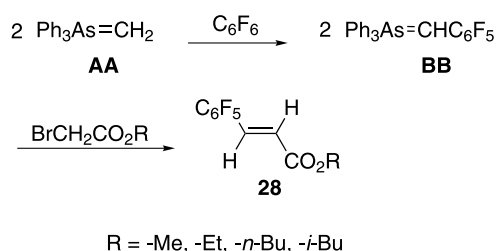


NuM = Me<sub>4</sub>NCl, *n*-Bu<sub>4</sub>NBr, *n*-Bu<sub>4</sub>NCl, *n*-Bu<sub>4</sub>NI, PhSK, 4-MePhSK, PhSeNa

R = -C<sub>6</sub>H<sub>4</sub>-*p*-Cl, -Ph, -C<sub>6</sub>H<sub>4</sub>-*p*-Me, -C<sub>6</sub>H<sub>4</sub>-*p*-NO<sub>2</sub>, -C<sub>6</sub>H<sub>4</sub>-*p*-F

Scheme 32.

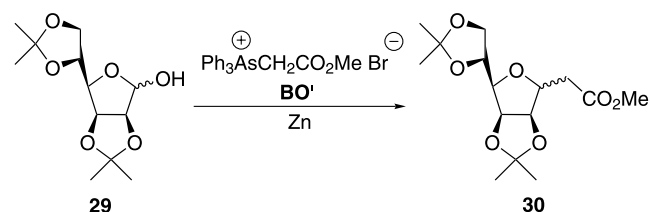
Shen et al. reported a one-pot synthesis of fluorinated  $\alpha,\beta$ -unsaturated esters. Ylide **BB**, generated in situ from **AA** and hexafluorobenzene, was reacted with bromoacetates to



Scheme 33.

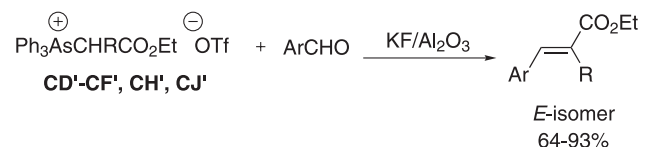
afford selectively the *E*-isomer of the fluorinated enoates **28** in 94–99% yield (Scheme 33).<sup>54</sup>

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  $\beta$  and  $\alpha$  anomers (Scheme 34).<sup>55</sup>



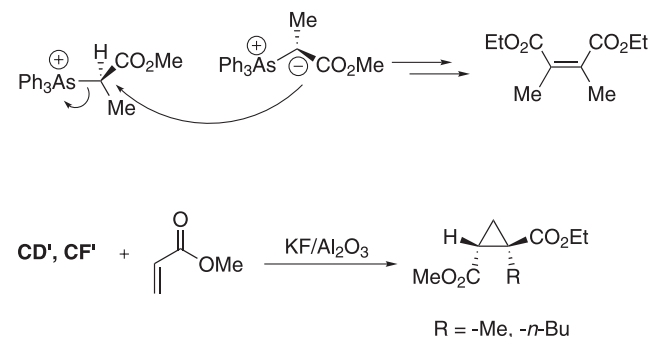
Scheme 34.

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).<sup>14</sup>



R = -Me, -Et, -*n*-Bu, -*n*-C<sub>11</sub>H<sub>23</sub>

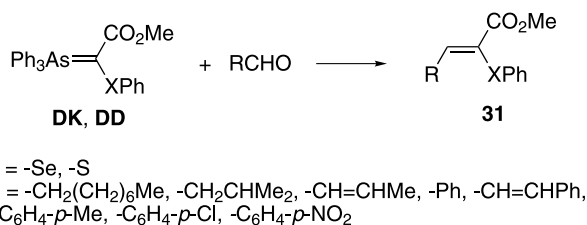
Ar = 2-furyl, -Ph, -C<sub>6</sub>H<sub>4</sub>-*p*-OMe, -C<sub>6</sub>H<sub>4</sub>-*p*-Cl



Scheme 35.

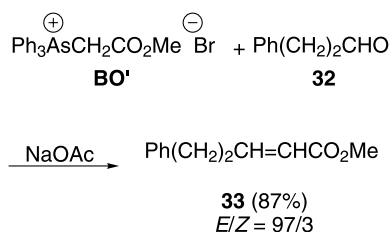
Huang et al. explored the synthesis of  $\alpha$ -phenylseleno- and  $\alpha$ -phenylthio-substituted enoates.<sup>22a,56</sup> Since Wittig reactions do not occur with  $\alpha$ -electron-withdrawing group-substituted  $\alpha$ -selenophosphonium ylides, the corresponding arsonium ylides, with their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

Hon and Lee recently reported that the salt **BO'** could



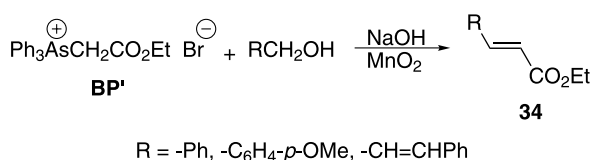
## Scheme 36.

undergo a Wittig reaction with aldehyde **32** to afford the conjugated ester **33** in good yield in the presence of sodium acetate (Scheme 37).<sup>57</sup> The reactivity of **BO'** was found to be dependent upon the counteranion, with the following trend being observed:  $p\text{-TsO}^-$ ,  $\text{Br}^- \ll \text{CF}_3\text{CO}_2^- \ll \text{ClCH}_2\text{-CO}_2^- < \text{PhCO}_2^-, \text{HCO}_2^-, \text{MeCO}_2^-$ . Furthermore, they reported that the proton-coupled <sup>13</sup>C NMR splitting patterns of the  $\alpha$ -methylene groups of the salts provided valuable information to predict their reactivity.



## Scheme 37.

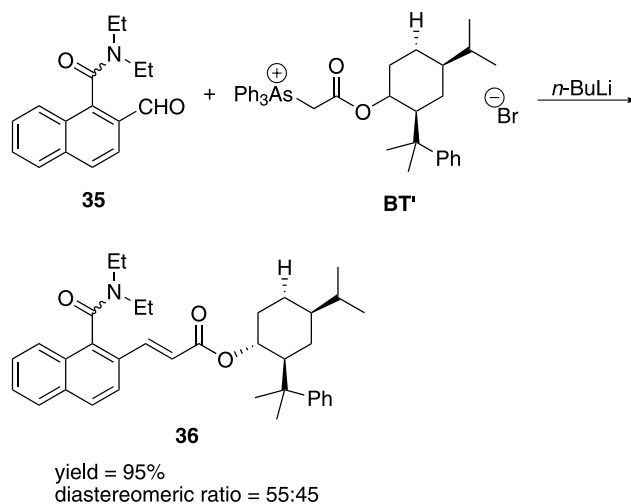
More recently, a stereoselective synthesis of (*E*)- $\alpha,\beta$ -unsaturated esters **34** by a tandem deprotonation-oxidation-Wittig reaction process using the arsonium salt **BP'** was reported.<sup>58</sup> A mixture of **BP'**, alcohol, sodium hydroxide, and manganese dioxide afforded the *E*-enoates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



## Scheme 38.

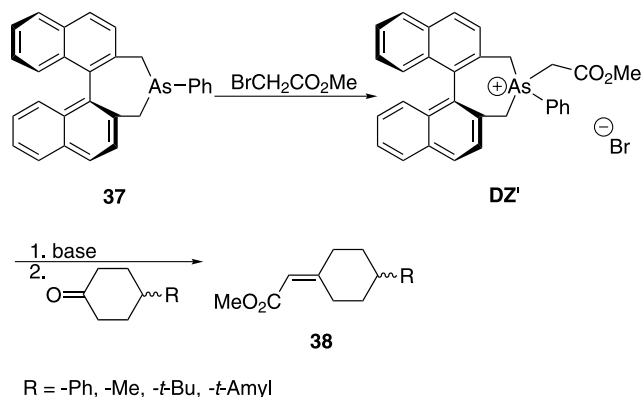
The first asymmetric Wittig reaction involving a chiral arsonium ylide was recently described by Dai and Lau.<sup>17</sup> They investigated the atroposelective olefination of axially chiral *N,N*-dialkyl 2-formyl-1-naphthamides such as **35** with the chiral auxiliary-derived stable arsonium ylide **BT'**.<sup>59</sup> It was found that olefination could be carried out at low temperature ( $-60^\circ\text{C}$ ) 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:  $\text{Li} > \text{Na} > \text{K} \approx \text{Mg} > \text{Zn}$ . Moreover, polar solvents gave better results than non-polar solvents, such as toluene.

Dai et al. next studied a chiral arsine **37** that was synthesized from *C*<sub>2</sub>-symmetric (*S*)-(-)-1,1'-bi-2-naphthol in three



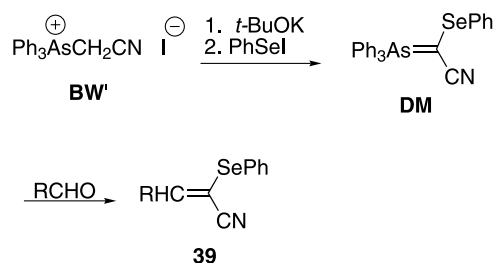
## Scheme 39.

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).<sup>60</sup> Moreover, a reversal in the stereochemistry of the product **38** was observed simply by changing the counteranion of the base from lithium to potassium.



## Scheme 40.

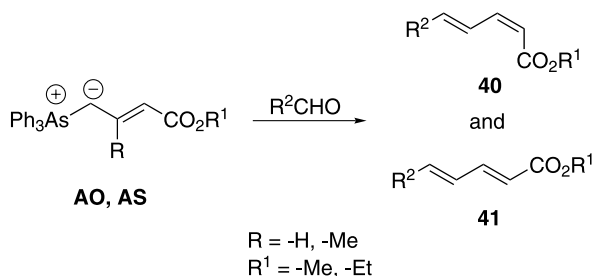
**3.1.6.  $\alpha,\beta$ -Alkenitrile synthesis.**  $\alpha$ -Phenylseleno- $\alpha,\beta$ -unsaturated nitriles **39** have been prepared by Huang et al.<sup>61</sup> The salt **BW'** was treated sequentially with base and phenylselenenyl iodide to produce ylide **DM**, which was found to be very unstable in air and water. Thus, after filtration under nitrogen, **DM** was used directly in Wittig reactions with



## Scheme 41.

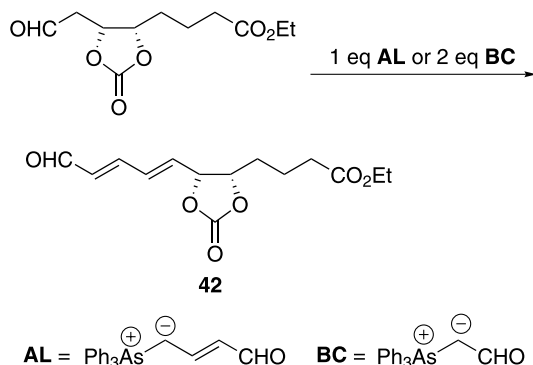
aromatic aldehydes to afford the nitriles **39** in good yields (Scheme 41).

**3.1.7. 2,4-Diene carbonyl compound synthesis.** Huang et al. reported the use of the highly reactive arsonane **AS** as an isoprenoid reagent to synthesize abscisic acid ester analogs. <sup>62</sup> 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**. <sup>63</sup> Finally, Lu and Zhou used this method in the synthesis of (+)-azimic acid. <sup>64</sup>



Scheme 42.

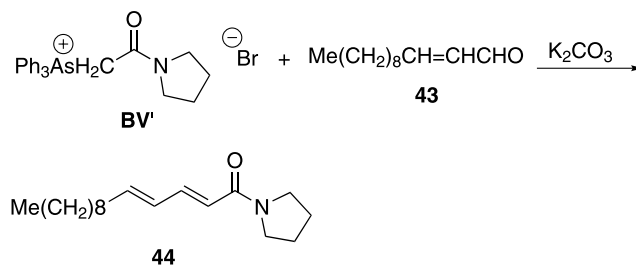
Gravier-Pelletier et al. and Wu et al. independently reported the synthesis of lipoxin A<sub>4</sub> and B<sub>4</sub> intermediate **42** using arsonium ylides (Scheme 43). <sup>65,66</sup> The addition of either 2 equiv of **BC** or 1 equiv of **AL** afforded the conjugated aldehyde **42**, which, in turn, could be processed into the lipoxins.



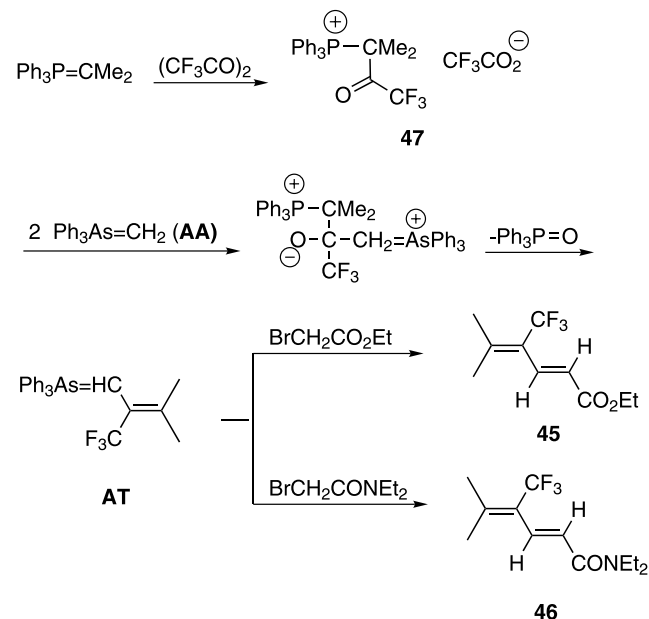
Scheme 43.

Huang et al. reported a simple procedure for the synthesis of unsaturated amides. <sup>67</sup> 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. <sup>68</sup>

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** <sup>69</sup> and 4-trifluoromethyl-2,4-dienamide **46** (Scheme 45). <sup>70</sup> Phosphoranes, generated from the corresponding phosphonium salts and phenyllithium in THF, were acylated by the addition of trifluoroacetic anhydride to give the  $\beta$ -oxophosphonium salt **47**. This was treated with 2 equiv of **AA** to effect addition,



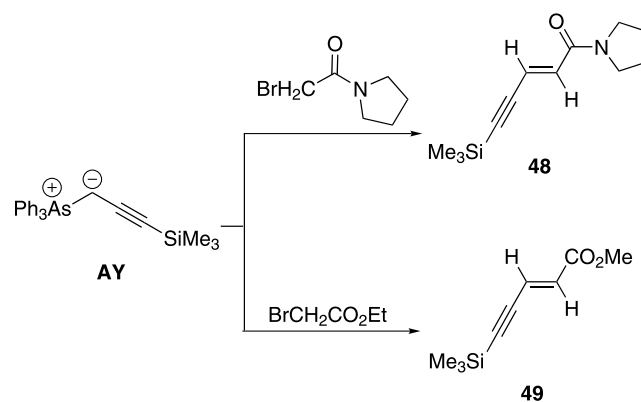
Scheme 44.



Scheme 45.

deprotonation and elimination of triphenylphosphine oxide, to afford ylide **AT**. Without isolation, ylide **AT** was treated with  $\alpha$ -bromoacetamides and  $\alpha$ -bromoacetic esters to give **45** and **46**, respectively, in good yield.

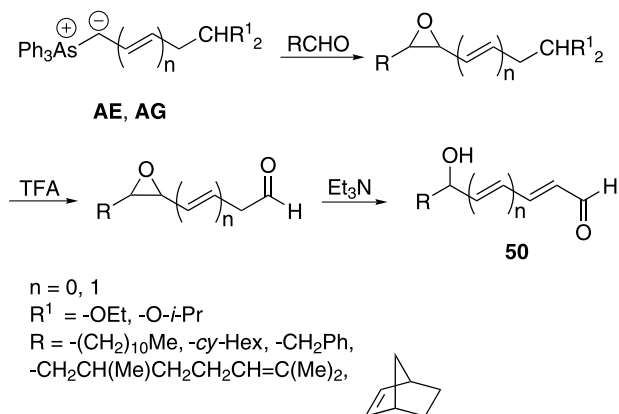
Subsequently, this group described the synthesis of a silylated 2,4-enynyl amide **48**, <sup>71</sup> and carboxylate **49** <sup>72</sup> by the reaction of ylide **AY** with  $\alpha$ -bromoacetamide and  $\alpha$ -bromoacetate, respectively, in moderate yield and high stereoselectivity (Scheme 46).



Scheme 46.

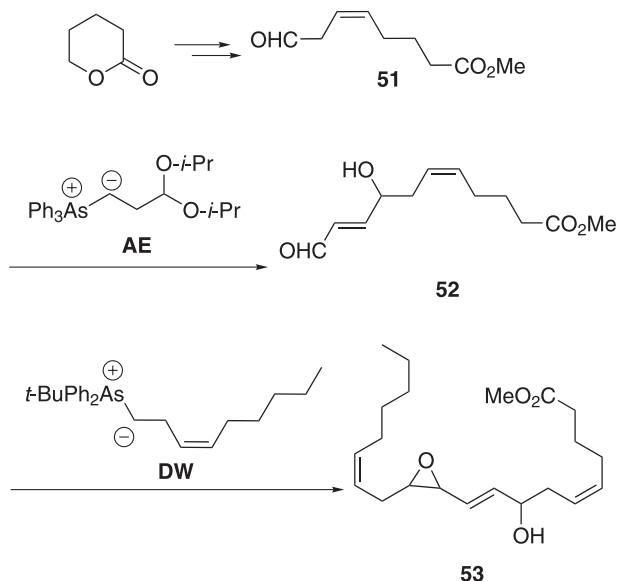
### 3.2. Heterocycle synthesis

Mioskowski et al. reported ylides **AE**<sup>73</sup> and **AG**<sup>74</sup> as  $\beta$ -formyl vinyl anion and  $\delta$ -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.



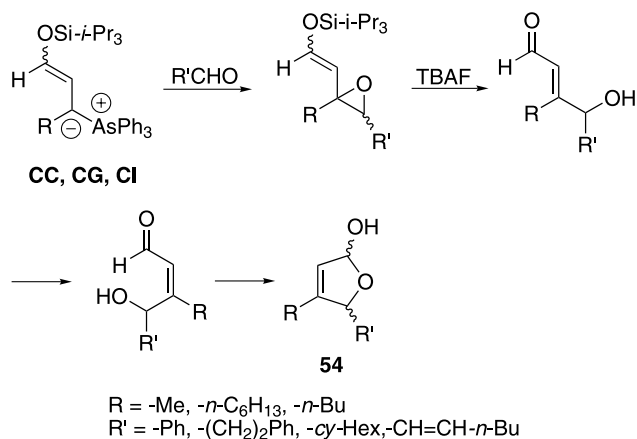
Scheme 47.

This group prepared ( $\pm$ )-hepoxilin A<sub>3</sub> from 1-heptyne and  $\delta$ -valerolactone utilizing ylides **AE** and **DW**.<sup>11</sup>  $\delta$ -Valerolactone was transformed into  $\beta,\gamma$ -unsaturated aldehyde **51**, which was subsequently converted into  $\gamma$ -hydroxy-enal **52** by using ylide **AE**. Coupling of **52** with the ylide of **DW** afforded **53**, the methyl ester of hepoxilin A<sub>3</sub>, which could in turn be converted into the desired product (Scheme 48).



Scheme 48.

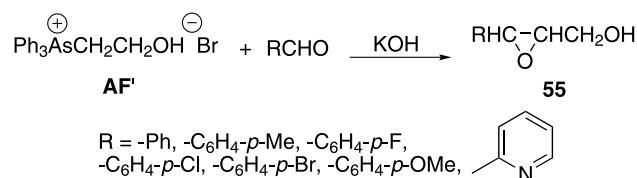
As mentioned previously, Kim and Kim studied the arsoniosilylation reactions of  $\alpha,\beta$ -unsaturated ketones and aldehydes (Scheme 49).<sup>26</sup> It was found that the reaction occurred at low temperature ( $-78^\circ\text{C}$ ). The authors also



Scheme 49.

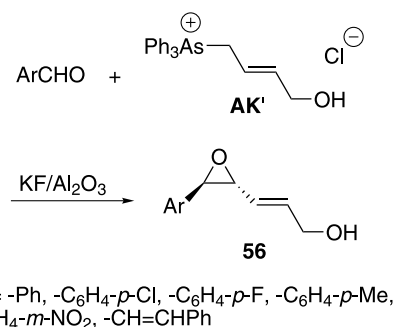
studied the possibility of arsonium ylides functioning as  $\alpha,\beta$ -formyl vinyl anion equivalents. They observed that the reaction of ylides **CC**, **CG**, and **CI** with aldehydes in THF at  $-78^\circ\text{C}$ , followed by the addition of TBAF, afforded the lactols **54**.

Shi et al. synthesized 2,3-epoxy-3-arylpropanols in one step using  $\beta$ -hydroxyethyltriphenylarsonium bromide **AF'**.<sup>75</sup> 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.

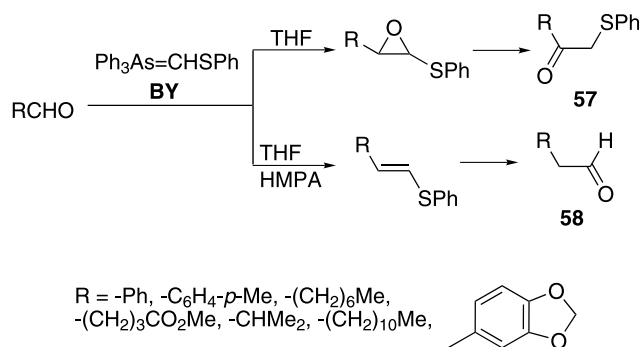
This same group applied a one-pot procedure using the salt **AK'** to prepare 5-aryl- and 5-(2-styrenyl)-4,5-*trans*-epoxy-2*E*-penten-1-ols **56**.<sup>76</sup> In all reported examples, the epoxide ring was generated with *trans* stereochemistry (Scheme 51).



Scheme 51.

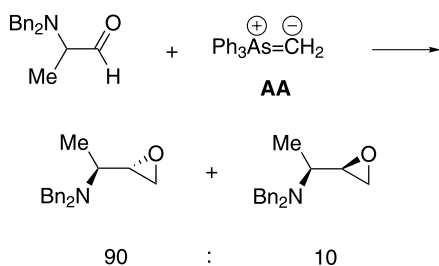
Mioskowski et al. observed that the ylide **BY** reacted with aldehydes to afford exclusively  $\alpha$ -thiophenoxyepoxides in THF and phenylthioenol ethers in THF/HMPA mixtures.<sup>77</sup> The former adducts were readily transformed into

$\alpha$ -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  $\alpha$ -amino aldehydes formed the corresponding epoxides with greater stereoselectivity than did the corresponding phosphonium ylide (Scheme 53).<sup>78</sup>



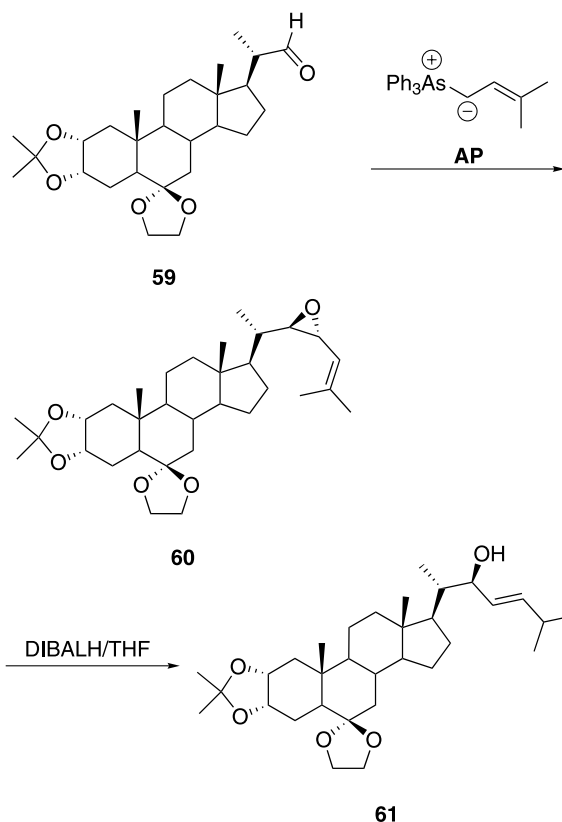
Scheme 53.

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**.<sup>79</sup> Subsequent reduction of **60** with DIBALH afforded the allylic alcohol **61**, which was a key synthetic intermediate of castasterone and its analogues (Scheme 54).

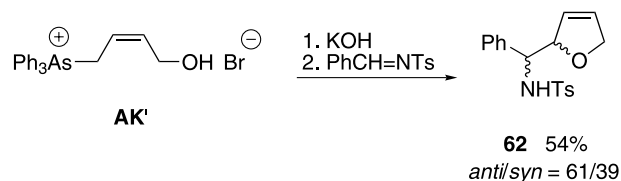
Deng et al. reported that, when the *cis*-alkene-containing ylide **AK** was reacted with *N*-sulfonylimines, 2,5-dihydrofurans such as **62** were obtained instead of the expected aziridines (Scheme 55).<sup>80</sup> This reaction was found to be general for a range of aryl aldehydes. Thus, **AK** may 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.

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  $\alpha,\beta$ -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).<sup>81</sup>

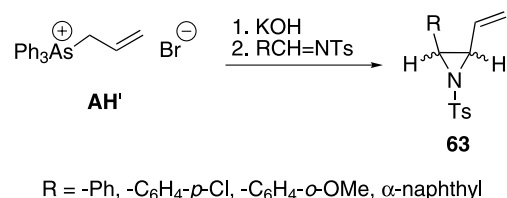
Mitsumoto and Nitta reacted the stable arsonium ylides **CM**, and **CN** with heterocumulenes such as carbon disulfide, phenyl isothiocyanate, diphenylcarbodiimide and



Scheme 54.



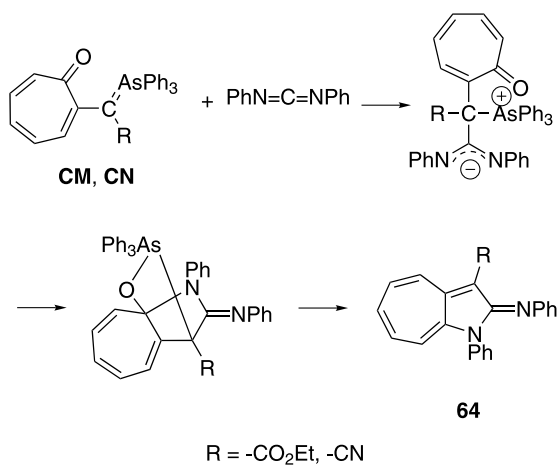
Scheme 55.



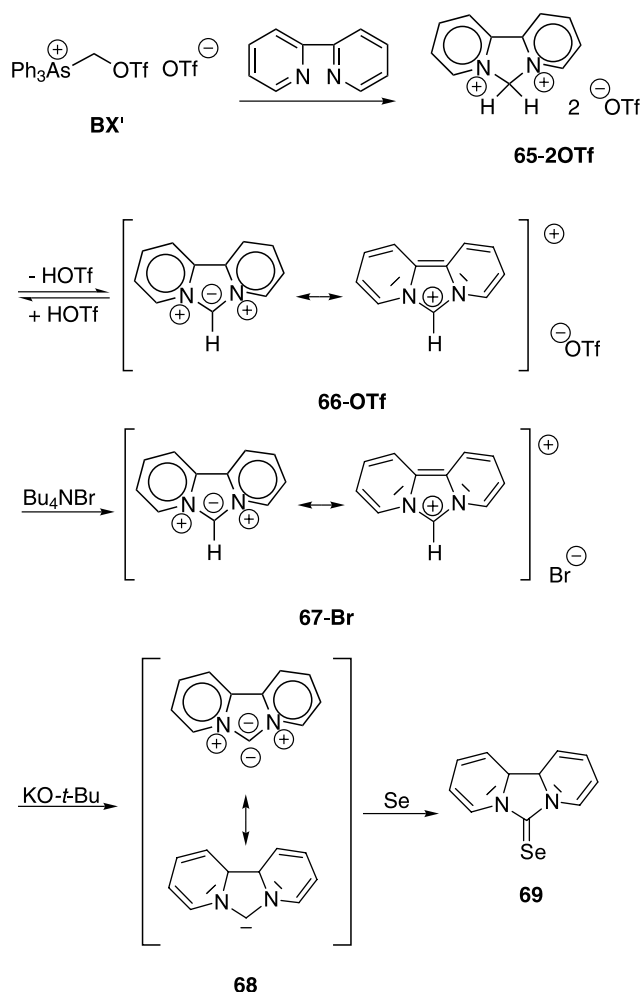
Scheme 56.

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.<sup>28</sup>

Weiss et al. used the salt **BX'** to generate a formal 1:1 complex between 2,2'-bipyridine and singlet carbon (Scheme 58).<sup>82</sup> The salt reacted with 2,2'-bipyridine to



Scheme 57.



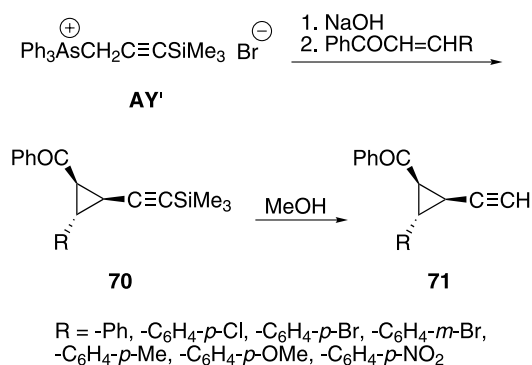
Scheme 58.

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,<sup>83</sup> e.g. reaction with selenium led to the chalcogenone **69**.

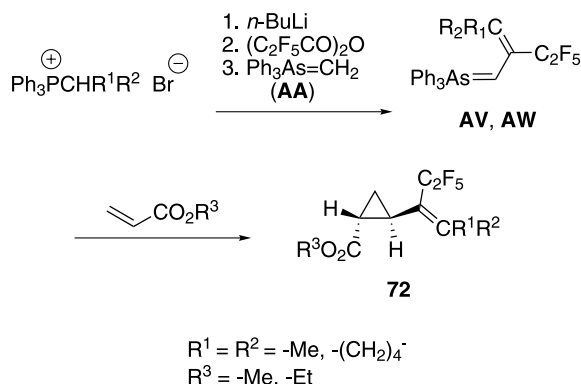
### 3.3. Carbocycle synthesis

Silylcyclopropanes are useful intermediates in organic synthesis since they are capable of undergoing many synthetic transformations.<sup>84</sup> 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).<sup>85</sup> Addition of methanol removed the silyl groups and afforded the terminal acetylenes **71** in a one-pot procedure in excellent yields (95–96%).<sup>86</sup>



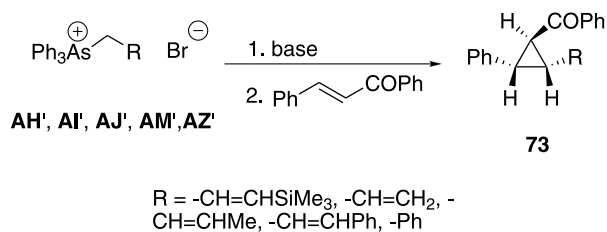
Scheme 59.

This group also reported the preparation of *trans*-perfluoroalkylated vinylcyclopropanes in a one-pot procedure.<sup>87</sup> Arsoranes **AV**, and **AW**, generated from the corresponding phosphonium salts via transylidation reactions, were reacted with vinyl esters to give the vinylcyclopropanes **72** in 43–62% yield (Scheme 60). These reactions were highly stereoselective and *trans*-isomers were obtained exclusively, on the basis of their NMR spectra.



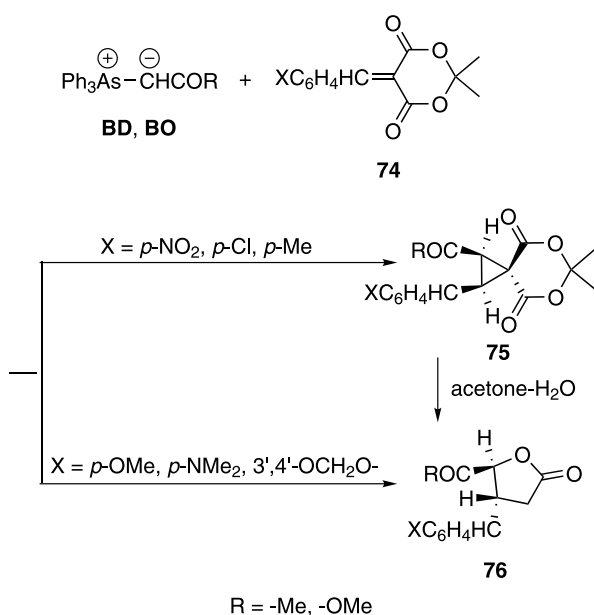
Scheme 60.

Huang et al. compared the stereoselectivity of arsonium ylides with the corresponding telluronium ylides in cyclopropanation reactions.<sup>88</sup> They reported that semi-stabilized allylic arsonium ylides reacted smoothly with enones to afford the *cis*-2-vinyl-*trans*-3-substituted cyclopropyl ketones **73** in high yields (Scheme 61). On the other hand, the telluronium ylides afforded the *trans*-2-vinyl-*trans*-3-substituted cyclopropyl ketones.



Scheme 61.

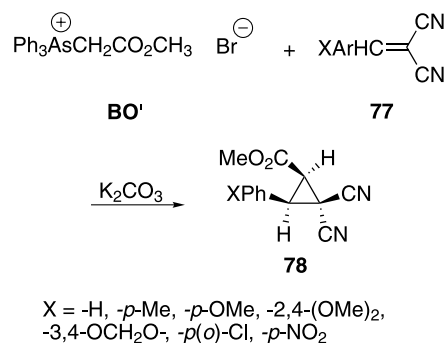
Recently, Cao et al. reported that the arsoranes **BD**<sup>89</sup> and **BO**<sup>90</sup> reacted with 2,2-dimethyl-1,3-dioxane-5-substituted-benzylidene-4,6-diones **74** to give *cis*-1,2-cyclopropane derivatives **75** or  $\beta,\gamma$ -*trans*-disubstituted- $\gamma$ -butyrolactones **76**. If the phenyl group in **74** contained a *p*-NO<sub>2</sub>, *p*-Cl or *p*-Me substituent, the *cis*-cyclopropane derivatives **75** were obtained (Scheme 62). When the phenyl group contained a strongly electron-donating substituent such as a methoxy group, a  $\beta,\gamma$ -*trans*-disubstituted- $\gamma$ -butyrolactone was formed. In the case with **BO**, it was also reported that all of the cyclopropane derivatives **75** could be transformed into the butyrolactones **76** by heating in acetone-water.



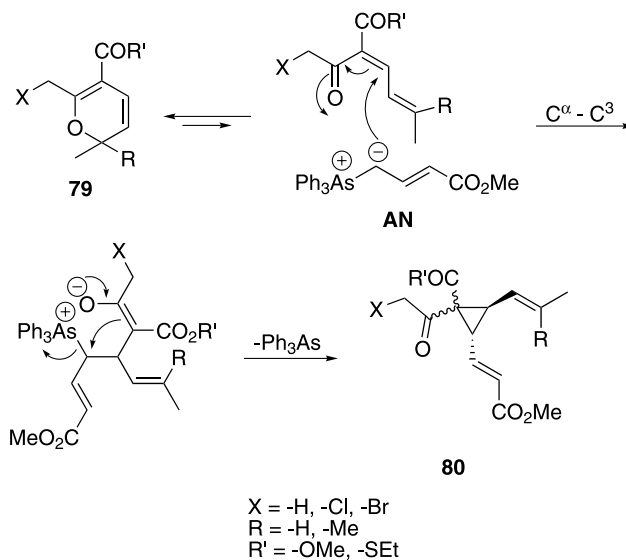
Scheme 62.

Recently Ren et al. have used a similar route for the preparation of 1-carbomethoxy-2-aryl-3,3-dicyanocyclopropanes **78** through the reaction of **77** with the ylide **BO**.<sup>91</sup> When the arylidenemalononitrile **77** was employed as the substrate, cyclopropane derivatives were the sole product (Scheme 63).

Moorhoff investigated the reaction of the ylide **AN** with substituted 2*H*-pyran-5-carboxylates **79**,<sup>92</sup> 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).

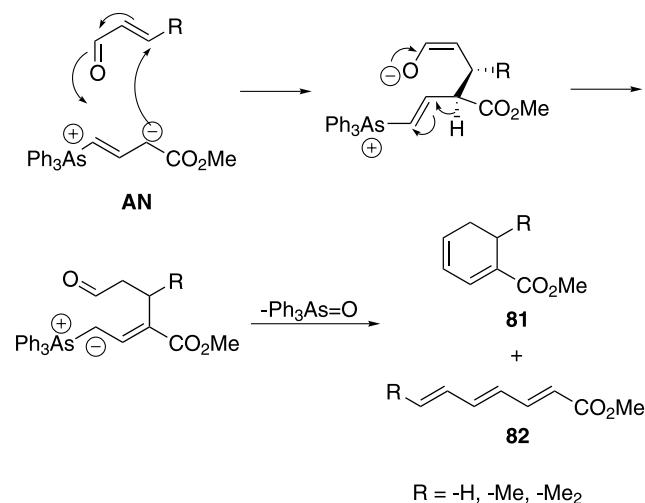


Scheme 63.



Scheme 64.

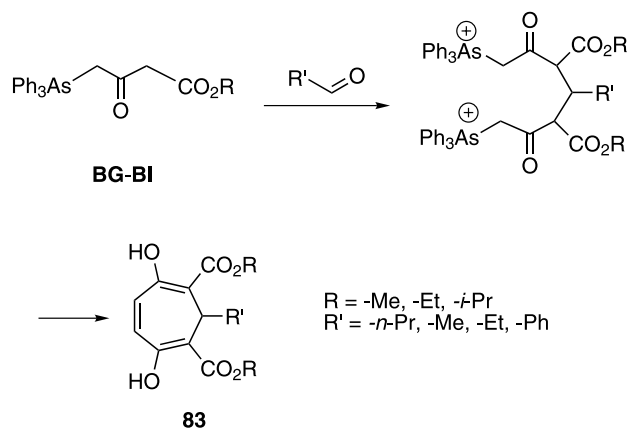
Moorhoff also reacted **AN** with conjugated carbonyl compounds. The initial addition was followed by an intramolecular Wittig condensation to form the 1,3-cyclohexadiene-1-carboxylates **81** and/or acyclic trienes **82** (Scheme 65).<sup>93</sup> It was reported that the yields using **AN** were much higher than when the corresponding



Scheme 65.

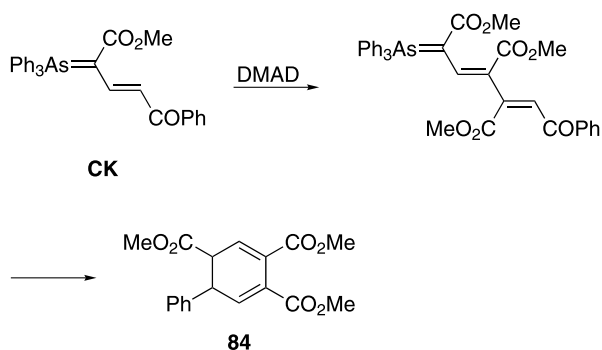
phosphonium ylide was used. The reaction of **AN** and ethyl 2-cyano-5-methyl-2,4-hexadienoate, however, gave a mixture of two diastereomeric *trans*-bisvinylcyclopropane-carboxylates in a reaction similar to that described in Scheme 64.

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).<sup>94</sup> Two equivalents of an appropriate ylide (**BG–BI**) were treated with 1 equiv of aldehyde to afford the desired product.



Scheme 66.

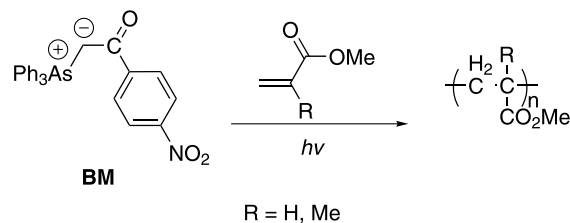
Aitken et al. examined the reaction between the β,γ-unsaturated arsonium ylide **CK** and DMAD and found that it proceeded with net insertion of the alkyne into the C=C double bond (Scheme 67).<sup>27</sup> Spontaneous intramolecular cyclisation of this adduct afforded the tetrasubstituted 1,3-cyclohexadiene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



Scheme 67.

### 3.4. Polymerization reactions

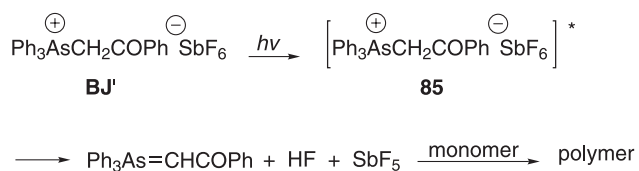
Mishra and Mathur studied the photo-initiating ability of triphenylarsonium-*p*-nitrophenacylide **BM** in the polymerization of methyl acrylate<sup>95</sup> and methyl methacrylate (Scheme 68).<sup>96</sup> They reported that the polymerization proceeded with low conversion when the reaction mixture was illuminated by visible light. Kinetic data and ESR spectroscopy confirmed that the photo-polymerization initiated by **BM** proceeded via a radical mechanism. It was



Scheme 68.

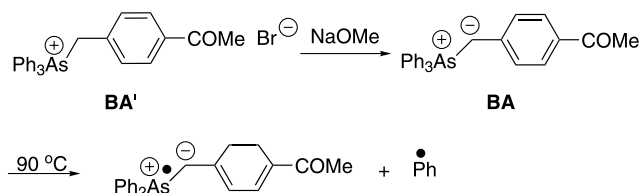
proposed that the origin of the radical initiator is from homolysis of one of the phenyl C–As bonds.

Abu-Abdoun and Ali reported the cationic photopolymerization of *p*-methylstyrene<sup>97</sup> and cyclohexene oxide<sup>98</sup> 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<sub>6</sub><sup>−</sup> afforded the best conversion.



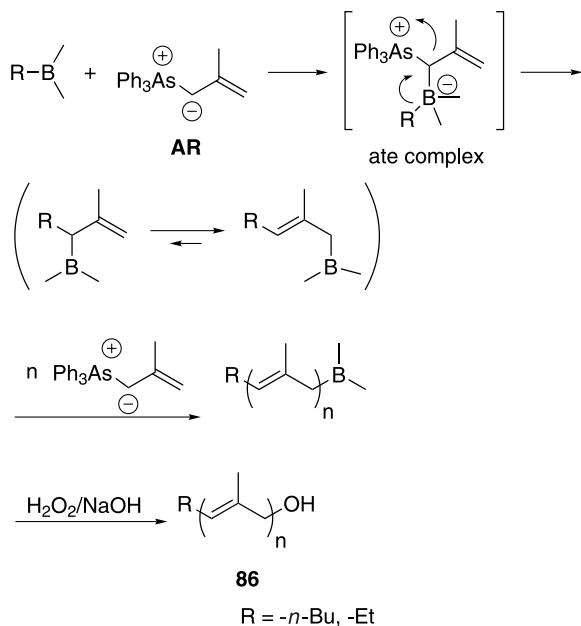
Scheme 69.

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,<sup>99</sup> the synthesis of arsenic-containing syndiotactic polymethyl methacrylate,<sup>100</sup> the generation of alternating copolymers containing styrene and citronellol sequences,<sup>101</sup> and vinyl acetate radical polymerization.<sup>102</sup> 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.<sup>103</sup> 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 polystyrene<sup>104</sup> and silica,<sup>105</sup> 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.

#### Acknowledgements

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Kong Special Administrative Region, P. R. of China (Projects HKU 7112/02P and HKU 7027/03P).

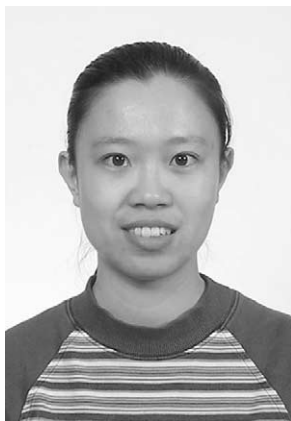
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