Arsonium Ylides (with some mention also of Arsinimines, Stibonium and Bismuthonium Ylides)

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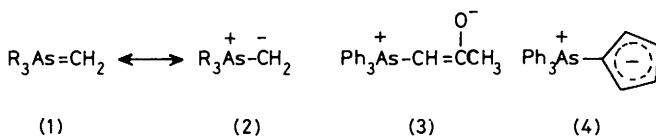DEPARTMENT OF CHEMISTRY, UNIVERSITY OF EDINBURGH,
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1 Introduction

Whereas much information has been published about phosphonium ylides, relatively little attention has been paid to arsonium ylides. There may be a psychological barrier in that for centuries the word arsenic has been associated with poisoning. In the case of triarylarsonium ylides, which are those most commonly used, there are no problems of this sort in their normal handling, but it must be emphasized that great care must be taken in handling alkylarsines and in these cases efficient fume-chambers are a necessity.

Arsonium ylides are relatively easy to prepare, and are of particular interest in that they are more reactive than analogous phosphonium or sulphonium ylides in the Wittig reaction, in which they may provide alkenes or epoxides, the type of product depending on the nature of the substituents on both the ylidic carbon atom and the arsenic atom, and also to some extent on the solvent used.

2 Structure of Arsonium Ylides

Arsonium ylides may be represented as hybrids of pentacovalent arsenic (1) and dipolar (2) structures. For convenience, in this review ylides will commonly be represented by covalent structures such as (1) but the dipolar contribution to such structures must be taken as understood.

$$R_3As{=}CH_2 \longleftrightarrow R_3\overset{+}{As}{-}\overset{-}{C}H_2 \qquad Ph_3\overset{+}{As}{-}CH{=}\overset{O^-}{\underset{|}{C}}CH_3 \qquad Ph_3\overset{+}{As}$$

$$(1) \qquad\qquad (2) \qquad\qquad (3) \qquad\qquad (4)$$

If electron-withdrawing centres are conjugated with the ylidic carbon atom, further dipolar structures, such as (3) and (4) may make major contributions to the overall structure. Delocalization of the negative charge in this way frequently leads to the ylides being isolable. Such ylides are commonly described as *stable* ylides; in this context stable is, in effect, usually synonomous with isolable. Many ylides are not, however, isolable, because of their high reactivity, in particular their very ready

hydrolysis. In this article such ylides will be called *reactive* ylides. Some other ylides, notably benzylylides, have reactivity intermediate between those ylides which are obviously *stable* or obviously *reactive*. In this article they will be termed *semi-stabilized.*

Experimental evidence suggests that arsonium ylides are more dipolar than their phosphonium and sulphonium analogues.

This is shown, for example, by dipole moment measurements on a series of tetraphenylcyclopentadienylides. The moments for the diphenylsulphonium, triphenylphosphonium, and triphenylarsonium derivatives are, respectively, 6.69, 7.75, 8.32 D.[1] Similarly triphenylarsonium fluorenylide has been shown to be more polar than its triphenylphosphonium analogue.[2]

Infra-red spectra of a number of stable arsonium ylides indicate their polarity and show that the negative charge is sited appreciably in the stabilizing substituent group.[3-5] The stretching frequencies associated with β-carbonyl ($1505—1525 \text{ cm}^{-1}$) or β-cyano substituents ($2105—2170 \text{ cm}^{-1}$) are significantly lower than those observed for analogous phosphonium ylides, in keeping with the greater polarity of the arsonium ylides.

Analysis of the ^{1}H-n.m.r. spectra of a series of cyclopentadienylides similarly indicates that the triphenylarsonium ylide is more polar and has greater delocalization of negative charge in the five-membered ring than its phosphonium or sulphonium analogues.[6]

Comparative studies of ^{13}C-n.m.r. spectra of phosphonium and arsonium ylides also suggest more covalent bonding in the former.[7,8] When methyltriphenyl- or tetramethyl-arsonium halides were converted into, respectively, triphenyl- or trimethyl-arsonium methylides there was only a small change in the CH coupling constant at the carbon atom undergoing deprotonation, whereas in the corresponding phosphorus system J_{CH} was greatly increased on deprotonation. This was taken to show that in the case of arsenic the bonding of the relevant carbon atom remained virtually unchanged, indicating a pseudo-tetrahedral geometry (5), in contrast to the case of phosphorus, when deprotonation causes an effective sp^3 to sp^2 rehybridization of the ylidic carbon atom (6). Introduction of silyl groups at the ylidic carbon atom causes a flattening of that atom[8] to a more planar structure. In arsonium acylylides the structure of the ylidic carbon atom appears to be planar.[9]

The ^{13}C-n.m.r. spectra of a series of triphenylarsonium *p*-substituted aroylylides indicated a high electron density on the ylidic carbon atom.[10] The chemical shifts

[1] H. Lumbroso, D. Lloyd, and G. S. Harris, *C.R. Seances Acad. Sci.*, 1974, **C278**, 219.

[2] A. W. Johnson and J. O. Martin. *Chem. Ind. (London)*, 1965, 1726.

[3] N. A. Nesmeyanov, V. V. Mikulshin, and O. A. Reutov, *J. Organomet. Chem.*, 1968, **13**, 263.

[4] A. J. Dale and P. Frøyen, *Acta Chem. Scand.*, 1970, **24**, 3772.

[5] I. Gosney and D. Lloyd. *Tetrahedron*, 1973, **29**, 1697.

[6] E. E. Ernstbrunner and D. Lloyd, *Chem. Ind. (London)*, 1971, 1332.

[7] Y. Yamomoto and H. Schmidbaur, *J. Chem. Soc., Chem. Commun.*, 1975, 668; H. Schmidbaur, W. Richter, W. Wolf, and F. H. Köhler, *Chem. Ber.*, 1975, **108**, 2649.

[8] H. Schmidbaur, W. Richter, W. Wolf, and F. H. Köhler, *Chem. Ber.*, 1975, **108**, 2649.

[9] G. Fronza, P. Bravo, and C. Ticozzi, *J. Organomet. Chem.*, 1978, **157**, 299.

[10] P. Frøyen and D. G. Morris, *Acta Chem. Scand., Ser. B*, 1976, **30**, 435.
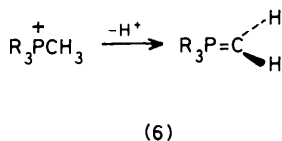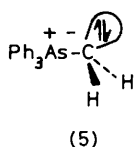
for the ylidic carbon atoms, but not those for the carbonyl carbon atoms, showed a correlation with the electronic character of the *p*-substituent.[10]

The difference between arsonium and phosphonium ylides is commonly ascribed to less efficient $p\pi$–$d\pi$ overlap between the C-sp^2 orbitals and the larger and more diffuse $4d$ orbitals of arsenic, and to decreased electrostatic interaction across the ylide bond, but it is probable that these are not the only factors involved.

The P.E. spectra of trimethylarsonium methylide and its phosphorus analogue have been recorded and CNDO/2 calculations have been carried out.[11] Results are in accord with a raising of the HOMO levels for the arsenic ylide compared to the phosphorus analogue, thereby lowering the d-population and the ylide bond order, and increasing the charge on the ylidic carbon atom.

(7)
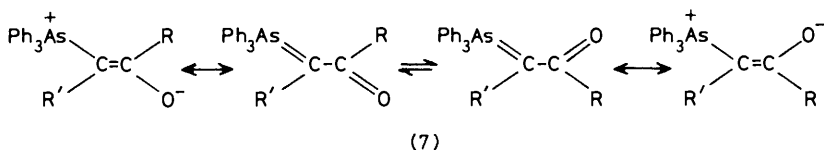
A. Conformation.—There has been an amount of study of the conformational mobility of β-carbonyl ylides (7). When R was a methoxy group separate signals for *Z* and *E* isomers (with respect to the AsC=CO bond) were observable; coalescence occurred at higher temperatures.[12] The *Z* configuration is strongly favoured, presumably because of coulombic interaction between As$^+$ and O$^-$, but less so than in the case of phosphorus ylides. It was suggested that phosphorus orbitals overlap with the oxygen 2*p*-orbitals more effectively than do the more diffuse arsenic orbitals, giving rise to a P–O interaction that is more bonding than the As–O interaction.[12] In that case stronger contraction of the arsenic orbitals should lead to stronger bonding, and this is supported by the observation that the *Z–E* ratio is higher when $R^1 = CN$ than when $R^1 = H$ or Ph.[12] Similar variation of spectra with temperature was observed when R = SEt.[13]

When R was an alkyl or aryl group no such temperature dependence was observed.[4] This can be rationalized in terms of a higher negative charge on a keto oxygen compared to an ester oxygen, leading to stronger coulombic interaction in the keto case and a freezing of the ylide into a *Z* structure. Some broadening of the

[11] H. Starzewski, W. Richter, and H. Schmidbauer, *Chem. Ber.*, 1976, **109**, 473.

[12] A. J. Dale and P. Frøyen, *Acta Chem. Scand.*, 1971, **25**, 1452.

[13] H. J. Bestmann and R. K. Bansal, *Tetrahedron Lett.*, 1981, 3839.

methine signal was observed in the spectrum of the benzoylylide (7; R = Ph, R^1 = H), but this was attributed to a protolytic exchange reaction.[14]


(8)
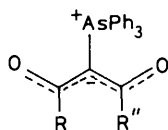
In the case of β,β'-dicarbonyl substituted ylides (7, R^1 = COR″) the situation is more complex but in nearly all cases n.m.r. spectra suggest that the molecule exists as the Z,Z-isomer (8).[5] Exceptions may arise if the acyl group is stabilized in an alternative configuration by intramolecular hydrogen bonding.[5]
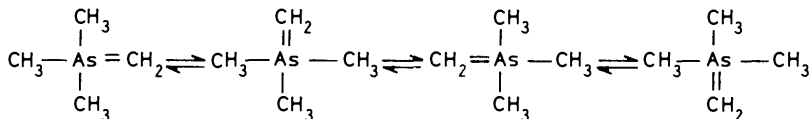
(9)

The [1]H-n.m.r. spectrum of trimethylarsonium methylide (9) is of some interest.[15] At room temperature the expected two singlets are observed, at chemical shifts which indicate a considerable dipolar contribution to the structure of the ylide. At higher temperatures there is considerable line broadening of both signals; a coalescence temperature could not be attained because of the onset of thermal decomposition. This broadening was attributed to fast proton exchange among the groups on arsenic as shown in (9). Significantly, addition of trace amounts of a protic acid caused coalescence at room temperature, by catalysis of the proton exchange.
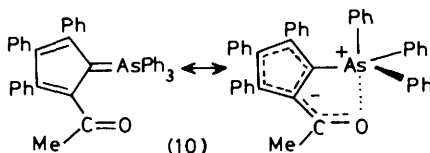
(10)

B. X-Ray Structure Determination.—Examination of a number of stable arsonium acylylides[16–18] and cyclopentadienylides[19–21] shows that the ylidic bond has a

[14] A. W. Johnson and H. Schubert, *J. Org. Chem.*, 1970, **35**, 2678.

[15] H. Schmidbaur and W. Tronich, *Inorg. Chem.*, 1968, **7**, 168.

[16] Meicheng Shao, Xianglin Jin, Yougi Tang, Qichen Huang, and Yaozeng Huang, *Tetrahedron Lett.*, 1982, 5343.

[17] Fan Zhao-chang and Shen Yang-Chang, *Acta Chim. Sinica*, 1984, **42**, 759; Xia Zong-Xiang and Zhang Zhi-ming, *Acta Chim. Sinica (Engl. Trans.)*, 1983, **41**, 148.

[18] G. Ferguson, I. Gosney, D. Lloyd, and B. L. Ruhl. *J. Chem. Res.*, 1987, submitted.

[19] G. Ferguson, D. F. Rendle, D. Lloyd, and M. I. C. Singer, *J. Chem. Soc., Chem. Commun.*, 1971, 1647.
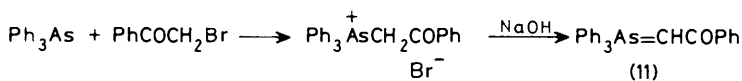
[20] G. Ferguson and D. F. Rendle, *J. Chem. Soc., Dalton Trans.*, 1975, 1284.

[21] G. Ferguson and D. F. Rendle. *J. Chem. Soc., Dalton Trans.*, 1976, 171.

length ($\sim$1.86—1.88 Å) intermediate between the sums of the covalent radii of singly bonded and doubly bonded carbon and arsenic, indicating an appreciable amount of single-bond character and consequently of dipolar character. It is also evident that the negative charge is spread from the ylidic carbon atom into the substituent acyl or cyclopentadienyl groups. The configurations of the acylylides with the oxygen atoms directed towards the arsenic atoms is also confirmed. This is especially noticeable in the case of ylide (10) wherein there is evidently strong interaction between the oxygen and arsenic atoms and the latter atom is distorted from a tetrahedral-type geometry towards a trigonal bipyramid configuration with the oxygen atom at one of the vertices.[19,20] That this interaction is also important in solution is evident from the lower dipole moment;[1] dipole moment measurements also confirm that other acylylides take up similar conformations.[22]

3 Preparation of Arsonium Ylides

The first account of the preparation of an arsonium ylide (11) was given more than eighty years ago (Scheme 1),[23] although the correct ylide structure for the product was not provided for nearly half a century.[24] This is an example of the 'salt method' for the preparation of ylides.

$$Ph_3As + PhCOCH_2Br \longrightarrow \overset{+}{Ph_3}AsCH_2COPh \underset{Br^-}{\overset{NaOH}{\longrightarrow}} Ph_3As=CHCOPh$$

(11)

Scheme 1

A. Salt Method.—In the salt method an arsonium salt, usually obtained by reaction of a halogeno compound with an arsine, is treated with a suitable base to provide the ylide. Stable ylides are frequently made and isolated by using aqueous alkali. Reactive ylides need anhydrous conditions and the use of a suitable strong base, and are used *in situ*. Thus triphenylarsonium methylide (12) has been prepared in solution;[25–28] it was isolated by using as base sodamide in tetrahydrofuran under an atmosphere of nitrogen.[7] Trimethylarsonium methylide (13) has been made indirectly, by desilylation of the trimethylsilylmethylide (14) with trimethylsilanol.[15] Ylide (14) was itself made by the salt method from chloromethyltrimethylsilane.[29]

$$Ph_3As=CH_2 \qquad Me_3As=CH_2 \qquad Me_3As=CHSiMe_3$$

(12) (13) (14)
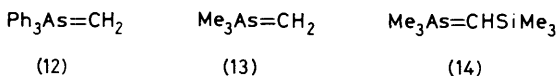
[22] H. Lumbroso, D. M. Bertin, and P. Frøyen, *Bull. Soc. Chim. Fr.*, 1974, 819.
[23] A. Michaelis, *Liebigs Ann. Chem.*, 1902, **321**, 174.
[24] F. Krohnke, *Chem. Ber.*, 1950, **83**, 291.
[25] S. O. Grim and D. Seyferth, *Chem. Ind. (London)*, 1959, 849.
[26] M. C. Henry and G. Wittig, *J. Am. Chem. Soc.*, 1960, **82**, 563.
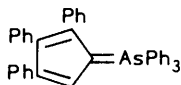[27] D. Seyferth and H. M. Cohen, *J. Inorg. Nucl. Chem.*, 1961, **20**, 73.
[28] S. Trippett and M. A. Walker, *J. Chem. Soc. C*, 1971, 1114.
[29] N. E. Miller, *Inorg. Chem.*, 1965, **4**, 1458.

A variety of stable arsonium ylides (15) wherein COX represents a ketone, ester, or amide function, has been prepared by the salt method[3,4,30-39] as have arsonium cyclopentadienylides (16)[40] and fluorenylides.[41-43]
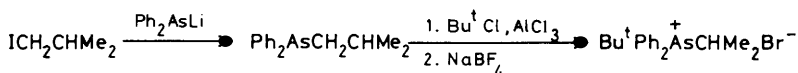
$$R_3As=CR'COX$$
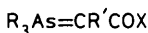
(15)

(16)

A phenyl group attached to the ylidic carbon atom has a smaller stabilizing effect and a number of examples of such semi-stabilized ylides have been prepared by the salt method.[44-46]

A publication[47] discussing the uses of reactive arsonium ylides for the stereospecific preparation of epoxides draws attention to the fact that arsonium salts are less readily prepared than phosphonium salts because of the poorer nucleophilicity of arsenic compared to phosphorus, and suggests methods for obtaining them. Primary salts were made from alkyl triflates, while α-branched salts were prepared from alkyldiphenylarsines, obtained from iodo-compounds as, for example, in Scheme 2. Reaction of alkyl halides with arsines to form arsonium salts is also promoted by the presence of silver tetrafluoroborate.[48]

Variants of the salt method include the use of 1,3-dihalogeno compounds, which

$$ICH_2CHMe_2 \xrightarrow{Ph_2AsLi} Ph_2AsCH_2CHMe_2 \xrightarrow[\text{2. NaBF}_4]{\text{1. Bu}^t Cl, AlCl_3} Bu^t Ph_2\overset{+}{As}CHMe_2Br^-$$

Scheme 2

[30] G. Asknes and J. Songstad. *Acta Chem. Scand.*, 1964, **18**, 655.

[31] N. A. Nesmeyanov, V. V. Pravdina, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, 1964, **155**, 1364; *Proc. Acad. Sci. USSR*, 1964, **155**, 424.

[32] N. A. Nesmeyanov, V. V. Pravdina, and O. A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, 1474; *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1965, 1434.

[33] Y. T. Huang, W. Y. Ting, and H. S. Sheng, *Acta Chim. Sinica*, 1965, **31**, 38.

[34] K. Isslieb and R. Lindner, *Liebigs Ann. Chem.*, 1967, **707**, 120.

[35] A. W. Johnson and R. T. Amel, *Can. J. Chem.*, 1968, **46**, 461.

[36] P. Frøyen, *Acta Chem. Scand.*, 1971, **25**, 2541.

[37] R. S. Tewari and K. C. Gupta, *Indian J. Chem., Sect. B*, 1979, 17, 637.

[38] Y. T. Huang, Y. C. Shen, J. J. Ma, and Y. K. Xin, *Acta Chim. Sinica*, 1980, **38**, 185.

[39] R. K. Bansal and G. Bhagchandani, *J. Prakt. Chem.*, 1981, **323**, 49.

[40] D. Lloyd and M. I. C. Singer, *J. Chem. Soc. C*, 1971, 2941.

[41] G. Wittig and H. Laib, *Liebigs Ann. Chem.*, 1953, **580**, 57.

[42] A. W. Johnson, *J. Org. Chem.*, 1960, **25**, 183.

[43] R. S. Tewari and K. C. Gupta, *Indian J. Chem., Sect. B*, 1978, **16**, 623.

[44] P. S. Kendurkar and R. S. Tewari, *J. Organomet. Chem.*, 1973, **60**, 247; 1975, **85**, 173; N. Kumari, P. S. Kendurkar, and R. S. Tewari, *ibid.*, 1975, **96**, 237.

[45] P. S. Kendurkar and R. S. Tewari, *J. Organomet. Chem.*, 1976, **108**, 175.

[46] R. S. Tewari and S. C. Chaturvedi, *Tetrahedron Lett.*, 1977, 3843; *Indian J. Chem., Sect. B*, 1979, **18**, 359.

[47] W. C. Still and V. J. Novack, *J. Am. Chem. Soc.*, 1981, **103**, 1283.

[48] I. Gosney, D. Lloyd, and W. A. MacDonald, unpublished work.

undergo both substitution and elimination reactions to provide ylides. This method (Scheme 3) was used to prepare the cyclopentadienylide (4).[49]
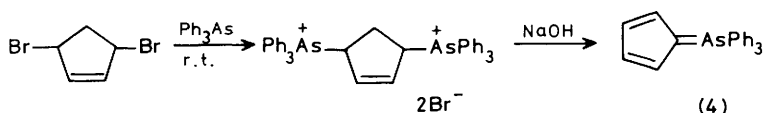
B. Preparation from Arsine Dihalides.—In the presence of triethylamine, triphenylarsine dichloride reacts with a variety of compounds having acidic methylene groups, to give arsonium ylides (Scheme 4).[50] This method is limited to

$$Ph_3AsCl_2 \ + \ CH_2XY \ \xrightarrow{\ Et_3N\ } \ Ph_3As=CXY$$
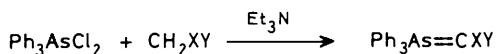
compounds in which X,Y are electron-withdrawing groups, *i.e.* to the preparation of stable ylides.

C. Preparation from Arsine Oxides.—Compounds having reactive methylene groups also react with triphenylarsine oxide, either in acetic anhydride, or in triethylamine with phosphorus pentoxide also present, to give arsonium ylides. First applied to cyclopentadienes bearing either phenyl or acyl substituents,[40,51–53] its use was extended to prepare a variety of stable arsonium ylides.[5,54] When the reaction is carried out in acetic anhydride acetylation may accompany the condensation reaction, *e.g.* Scheme 5.[5,40,51]

The mechanism[5] involves initial formation of an acetylated or phosphorylated cation, which reacts with a carbanion to form a salt which is strongly acidic because of its substituent electron-withdrawing groups. This salt is hence readily converted into an ylide by loss of a proton, whose removal is assisted by the acetic anhydride or triethylamine, *e.g.* Scheme 6. As with method B the arsine oxide method is limited to the preparation of stable ylides, since its success depends on the acidity of the methylene compound. Almost all examples of this method have utilized triphenylarsine oxide; tri-n-butylarsine oxide has been used in triethylamine but gave only intractable products in acetic anhydride.[5]

In a modification of this method, an ylide has been prepared by reaction of acetoacetanilide with diacetoxytriphenylarsorane, the latter compound having

[49] B. H. Freeman and D. Lloyd, *J. Chem. Soc. C*, 1971, 3164.
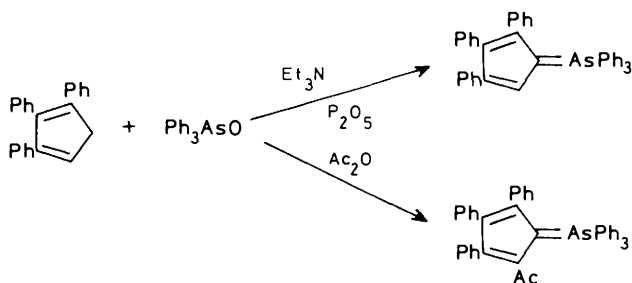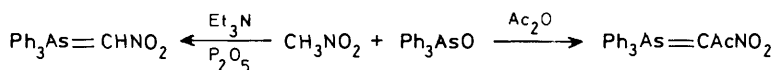[50] L. Horner and H. Oediger, *Chem. Ber.*, 1958, **91**, 437; *Liebigs Ann. Chem.*, 1959, **627**, 142.
[51] G. S. Harris, D. Lloyd, N. W. Preston, and M. I. C. Singer, *Chem. Ind. (London)*, 1968, 1483.
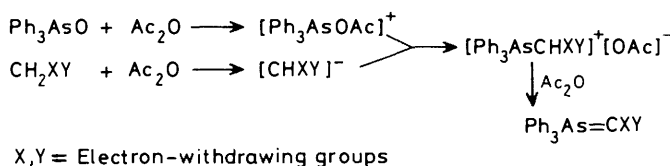[52] D. Lloyd and N. W. Preston, *J. Chem. Soc. C*, 1969, 2464.
[53] B. H. Freeman and D. Lloyd, *Tetrahedron*, 1974, **30**, 2257.
[54] G. S. Harris, D. Lloyd, W. A. MacDonald, and I. Gosney, *Tetrahedron*, 1983, **39**, 297.

$$Ph_3As = CHNO_2 \xleftarrow[P_2O_5]{Et_3N} CH_3NO_2 + Ph_3AsO \xrightarrow{Ac_2O} Ph_3As = CAcNO_2$$

Scheme 5

$$Ph_3AsO + Ac_2O \longrightarrow [Ph_3AsOAc]^+$$

$$CH_2XY + Ac_2O \longrightarrow [CHXY]^-$$

$$\longrightarrow [Ph_3AsCHXY]^+[OAc]^-$$

$$\downarrow Ac_2O$$

$$Ph_3As = CXY$$

X,Y = Electron-withdrawing groups

Scheme 6

been prepared from triphenylarsine and lead tetraacetate.[55]

D. Preparation from Diazo Compounds.—Another method for the preparation of stable arsonium ylides consists of heating a diazo compound in the presence of an arsine. Evidence has been provided that the diazo compound first decomposes to give a carbene which adds to the arsine (Scheme 7).[56] As first introduced for the
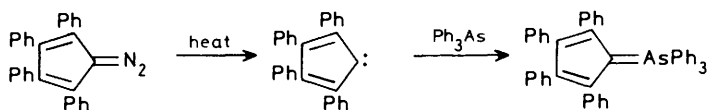
Scheme 7

preparation of arsonium cyclopentadienylides the two reagents were simply heated together.[57] Subsequent improvements include plunging a mixture of the reactants into a preheated bath[53] and, above all, the use of copper or copper salts as

[55] J. I. G. Cadogan and I. Gosney, *J. Chem. Soc., Perkin Trans. 1*, 1974, 466.

[56] B. H. Freeman, G. S. Harris, B. W. Kennedy, and D. Lloyd, *Chem. Commun.*, 1972, 912.

[57] D. Lloyd and M. I. C. Singer, *Chem. Ind. (London)*, 1967, 510.

catalysts.[5,53] Not only may copper derivatives catalyse the reaction, they may also promote ylide formation which does not take place in the absence of catalyst.[5,53] In particular the use[58] of catalysts such as copper acetylacetonate enables reactions to be carried out in solution, for example in boiling benzene, cyclohexane, or ethanol, at temperatures well below the normal decomposition temperature of the diazo compound involved.[53,58] A particularly effective catalyst is copper hexafluoroacetylacetonate;[59,60] arsonium ylides have been prepared even at room temperature in its presence.[60,61] The function of the catalyst appears to be to bring the reactants into close proximity to each other by their co-ordination at the copper; a variety of other metals have proved to be ineffective as catalysts.[58,60] This catalytic method not only simplifies the manipulation but also increases the scope of the reactants which may be employed. A variety of stable arsonium ylides has been prepared in this way, although attempts to obtain ylides from monoacyldiazo compounds such as ethyl diazoacetate were unsuccessful.[5]

Occasionally unexpected products arise. Thus diazo-2,5-diphenylcyclopentadiene gave a 2,4-diphenylcyclopentadienylide, possibly due to rearrangement of the intermediate carbene,[53] and 9-diazofluorene gives fluorenone ketazine, resulting from rapid reaction of the first-formed ylide with unchanged diazo compound.[5,53]

E. Preparation from other Ylides.—Related to the conversion of diazo compounds into arsonium ylides is the formation of arsonium ylides by thermal decomposition of iodonium ylides, either when melted[62] or heated in solution[58] with triphenylarsine in the presence of a copper salt, *e.g.* Scheme 8.

$$\underset{R'CO}{\overset{RCO}{>}}C=IPh \xrightarrow[\text{Cu salt}]{Ph_3As} \underset{R'CO}{\overset{RCO}{>}}C=AsPh_3$$
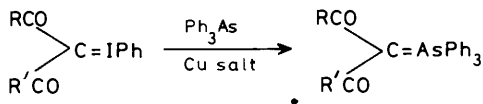
Scheme 8

Preparations of arsonium ylides by reactions of other arsonium ylides with suitable substrates such as acid chlorides,[63] acid anhydrides,[5,63] chlorosilanes,[64] acetylenes,[28] sulphines,[28] or *N*-acylaziridines[65] will be discussed in a later section (6C) dealing with reactions of arsonium ylides.

F. Preparations involving a Reverse-Wittig Reaction.—Triphenylarsine oxide reacts with a number of electrophilic acetylenes with electron-withdrawing substituents in what are, in effect, reverse-Wittig reactions, providing thereby stable arsonium

[58] J. N. C. Hood, D. Lloyd, W. A. MacDonald, and T. M. Shepherd, *Tetrahedron*, 1982, **38**, 3355.
[59] D. Lloyd and S. Metcalfe, *J. Chem. Res. (S)*, 1983, 292.
[60] C. Glidewell, D. Lloyd, and S. Metcalfe, *Tetrahedron*, 1986, **42**, 3887.
[61] C. Glidewell, D. Lloyd, and S. Metcalfe, unpublished work.
[62] K. Friedrich, W. Amann, and H. Fritz, *Chem. Ber.*, 1979, **112**, 1267.
[63] R. S. Tewari and D. K. Nagpal, *Z. Naturforsch., B*, 1980, **35**, 99.
[64] Yanchang Shen, Zhengxiang Cu, Weiyn Ding, and Yaozeng Huang, *Tetrahedron Lett.*, 1984, 4425.
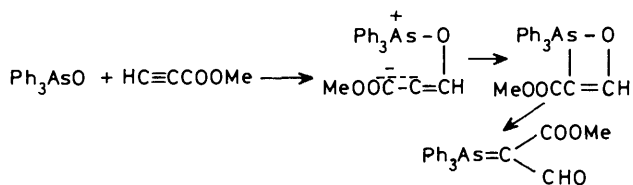[65] H. W. Heine and G. D. Wachob, *J. Org. Chem.*, 1972, **37**, 1049.

ylides (Scheme 9).[66] Reaction is presumably initiated by nucleophilic Michael-type

$$Ph_3AsO + R^1C\equiv CR^2 \longrightarrow Ph_3As=CR^1COR^2$$
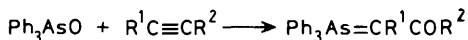
Scheme 9

reaction of the oxide on the acetylene, *e.g.* Scheme 10. As would be expected from such a mechanism, use of an unsymmetric acetylene, as in the foregoing example, results in virtually regiospecific attack by the oxide to give the product shown.

$$Ph_3AsO + HC\equiv CCOOMe \longrightarrow$$

$$\overset{+}{Ph_3As}-\overset{-}{O} \longrightarrow \overset{}{Ph_3As}-O$$

MeOOC−C̄=CH   MeOOCC=CH

$$Ph_3As=C\overset{COOMe}{\underset{CHO}{<}}$$

Scheme 10

G. Some Unusual Arsonium Ylides.—A squaric acid derivative which is also an arsonium ylide has been made (Scheme 11).[67]
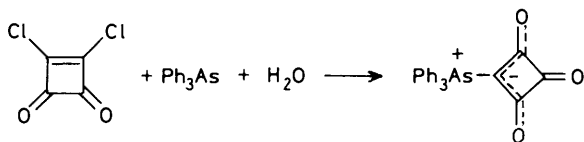
Scheme 11

A cumulated arsonium ylide has been prepared by reaction of a methoxycarbonyl arsonium ylide with sodium bis(trimethylsilyl)amide (Scheme 12).[13]

$$Ph_3As=CHCOOMe + NaN[SiMe_3]_2 \longrightarrow Ph_3As=C=C=O$$

Scheme 12

The bisylide (17) was made by the salt method; it is unstable as a solid and especially in solution (Scheme 13).[68]
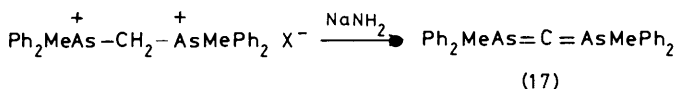
4 Stability of Arsonium Ylides
Many of the stable arsonium ylides are crystalline solids which may be kept in air

[66] E. Ciganek, *J. Org. Chem.*. 1970, **35**, 1725.
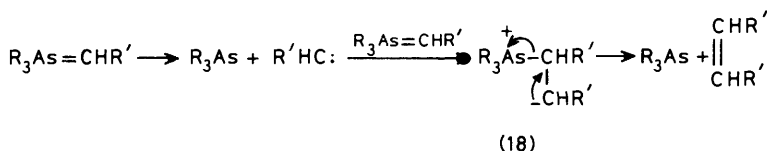[67] A. H. Schmidt, R. Aiméne, and M. Hoch, *Synthesis*, 1984, 754.
[68] H. Schmidbauer and P. Nusstein, *Organometallics*, 1985, **4**, 344.

$$Ph_2MeAs-CH_2-AsMePh_2 \quad X^- \xrightarrow{\;NaNH_2\;} Ph_2MeAs=C=AsMePh_2$$

$$(17)$$

Scheme 13

without significant decomposition. More reactive arsonium ylides need to be made as required and used *in situ.* Their decomposition usually arises from hydrolytic attack; most arsonium ylides appear to be thermodynamically stable at room temperature.

A. Thermal Decomposition.—Some arsonium ylides have been reported to decompose when heated in solution. For example, when triphenylarsonium benzylide was heated in a boiling benzene–ether mixture it decomposed to give triphenylarsine and a mixture of stilbenes.[69] Trimethylarsonium methylide likewise undergoes thermal decomposition to give trimethylarsine and ethylene.[15] A likely mechanism for these reactions involves carbenic decomposition of the ylide followed by attack of the carbene on unchanged ylide with expulsion of an arsine fragment (Scheme 14). An alternative mechanism has, however, been proposed,[69]

$$R_3As=CHR' \longrightarrow R_3As + R'HC: \xrightarrow{\;R_3As=CHR'\;} R_3\overset{+}{A}s\overset{-}{C}HR' \longrightarrow R_3As + \begin{matrix} CHR' \\ \| \\ CHR' \end{matrix},$$

$$(18)$$

Scheme 14

which implicates the presence of some protonated ylide, either residual salt from the mode of preparation, or arising from protonation of the ylide by traces of moisture. This undergoes nucleophilic displacement of its arsine group by a molecule of ylide to give a salt of (18) which then provides the isolated alkene by means of an elimination reaction. Protonated ylide is regenerated so that only catalytic amounts of it need be present. Some support for this latter mechanism as at least a contributing mechanism derives from the observation that thermal decomposition is greatly retarded in the presence of a large amount of base.[69]

The more stable triphenylarsonium benzoylylide could be recovered unchanged from prolonged heating in boiling benzene but decomposed in boiling toluene to give triphenylarsine and *trans*-1,2,3-tribenzoylcyclopropane.[14] The latter product could arise from conjugate addition of unchanged ylide to alkene formed by thermal decomposition of part of the ylide (Scheme 15). In support of this mechanism it is known that arsonium ylides can react with conjugated unsaturated ketones[28,70] or esters[38,71] to give cyclopropane derivatives. The formation of

[69] N. A. Nesmeyanov, V. V. Pravdina, and O. A. Reutov, *Zh. Org. Khim.*, 1967, **3**, 598; *J. Org. Chem. USSR* (*Engl. Trans.*), 1967, **3**, 574.

[70] Huang Yao-tseng, Shen Yan-Chang, MaJing-ji, and Xin Yuan-kong, *Acta Chim. Sinica*, 1980, **38**, 185.

[71] Y. T. Huang, Y. C. Shen, Y. K. Xin, and J. J. Ma, *Sci. Sinica*, 1980, **23**, 1396; *Chem. Abstr.*, 1981, **95**, 7407h.
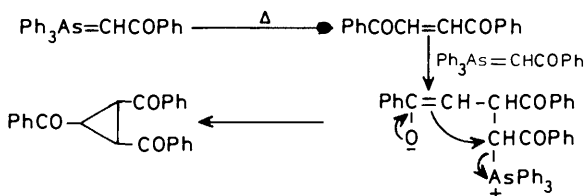
Scheme 15

cyclopropane derivatives from acyl ylides but not from a benzylide or methylide presumably reflects the fact that in the latter cases the alkenes which are formed first are not susceptible to nucleophilic attack.

Keto-stabilized phosphonium ylides undergo thermal decomposition with extrusion of phosphine oxides,[72] but no such reaction takes place with keto-stabilized arsonium ylides, presumably since the driving force to form an arsenic–oxygen bond is much less than that to form a phosphorus–oxygen bond. However an interesting rearrangement seems to be involved in the mass-spectrometric decomposition of triphenylarsonium nitromethylide (19), arising from arsenic–oxygen bond formation, most plausibly explained by a four-centre oxygen transfer reaction (Scheme 16).[5] The phosphonium ylide corresponding to (19) decomposes
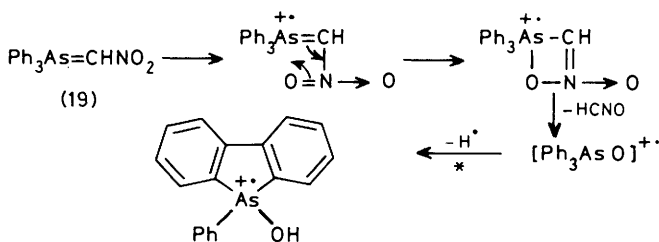
Scheme 16

spontaneously at room temperature to triphenylphosphine oxide and fulminic acid.[73] This is a rare case of an arsonium ylide being more stable than its phosphonium analogue and is also attributed to the much greater energetic drive to produce a P–O bond compared to an As–O bond.

B. Hydrolysis.—Many arsonium ylides are hydrolysed in the presence of moisture to give an arsine oxide and an organic residue. The first reported example described the rapid conversion of the semi-stabilized trimethylarsonium fluorenylide into trimethylarsine oxide and fluorene.[41] More stable arsonium ylides may require heating under reflux with solutions of sodium hydroxide to bring about hydrolysis;

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[72] A. W. Johnson, 'Ylid Chemistry', Academic Press, New York, 1966, p. 105.
[73] S. Trippett and D. M. Walker, *J. Chem. Soc.*, 1959. 3874.

some diketo ylides can be recovered unchanged even under these drastic conditions.[5] Ease of hydrolysis may depend strongly on the solubility of the ylide in the reaction solvent. Thus, whereas triphenylarsonium 2,3,4,5-tetraphenylcyclopentadienylide was recovered essentially unchanged from ethanolic potassium hydroxide solution in which it is barely soluble,[74] it and other triarylarsonium analogues decomposed to provide tetraphenylcyclopentadiene when heated in methanol, in which they are soluble.[48]

It has been speculated[75] that, by analogy with the mechanism proposed for the extensively studied hydrolysis of phosphonium ylides, the steps involved in hydrolysis are protonation, followed by formation of a pentacovalent arsenic species and finally loss of a carbanion (Scheme 17). Presumably for arsonium

$$Ph_3As=CXY \xrightarrow{H_2O} Ph_3\overset{+}{As}CHXY \xrightarrow{HO^-} Ph_3As\underset{CHXY}{\overset{OH}{<}} \xrightarrow{HO^-} Ph_3AsO + {}^-CHXY$$

$$\searrow H_2O$$

$$CH_2XY$$
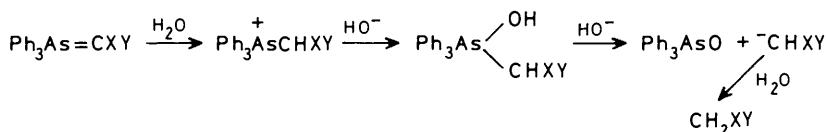
Scheme 17

ylides, as for phosphonium ylides, the group which leaves the arsenic atom in the last step will be the group which provides the most stable carbanion. Thus ethanolysis of triphenylarsonium benzylide provides toluene *via* the intermediacy of the benzyl anion.[28] If there is no group present able to provide a stable anion, reaction may not proceed to give an arsine oxide. For example, triphenylarsonium methylide reacts with water to give the arsonium hydroxide (20)[27] and trimethylarsonium methylide reacts with methanol to provide a pentacoordinate arsorane (21).[76]

$$Ph_3\overset{+}{As}Me \quad HO^-$$

(20)

$$MeOAsMe_4$$

(21)

5 Basicity of Ylides and Acidity of their Conjugated Acids

Many arsonium ylides dissolve in acids to form salts, from which they can be reobtained by treatment with a base, as in the salt method for their preparation. The basicity of the ylides indicates the relative stabilities of the ylides and their salts and in so doing gives some guide to the stability of the ylides. Thus stable ylides are less readily protonated than are reactive ylides and require weaker bases for their preparation from salts.

Stabilizing substituent groups are commonly those which can delocalize the negative charge on the ylidic carbon atom. Measurements on a series of

[74] B. H. Freeman, D. Lloyd, and M. I. C. Singer, *Tetrahedron*, 1972, **28**, 343.

[75] Ref. 72, p. 292.

[76] H. Schmidbaur and W. Richter. *Angew. Chem.*, 1975, **87**, 204; *Angew. Chem.. Int. Ed. Engl.*. 1975, **14**, 183.

triphenylarsonium *p*-substituted benzoylylides (22) showed that their basicity is lower the more electron-withdrawing the *p*-substituent.[3,30,36] Similarly for the ylides (23, X = H), the basicity decreases as the group COZ becomes more capable

$$Ph_3As=CHCOC_6H_4X(p) \qquad (p-XC_6H_4)_3As=CHCOZ$$

$$(22) \qquad\qquad (23)$$
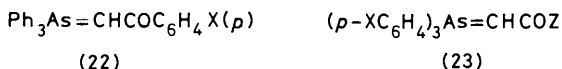
of delocalizing a negative charge; the basicity when Z = alkyl or aryl is much less than when Z = OR or NR_2.[36] Increase in the electron-donating character of X in (23), *e.g.* from H to Me to OMe causes an increase in basicity,[36] as does replacement of a triphenylarsonium group by a trimethylarsonium group.[30] But, while tri-*p*-tolylarsonium tri- and tetra-phenylcyclopentadienylides are more basic than their triphenylarsonium analogues the corresponding *o*-tolylarsonium ylides are less basic;[54] presumably steric factors are relevant in the latter case.

In studies of ylides having different heteronium atoms, *e.g.* on methoxycarbonyl-ylides,[34] benzoyl ylides,[3,30,35] fluorenylides,[77] tetraphenylcyclopentadien-ylides,[14,78] and triphenylcyclopentadienylides,[79] the arsonium ylides were uniformly more basic than their phosphonium or sulphonium analogues.

These results imply that arsenic plays a smaller part than do phosphorus and sulphur in the distribution of negative charge from the adjacent carbanion. This difference has commonly been attributed (*inter alia*[3,12,30,34,35,79–81]) to the lower electronegativity of the arsenic atom, which leads to a lower electrostatic interaction between the arsenic and ylidic carbon atoms, and to a lower effectiveness of $p\pi$–$d\pi$ orbital overlap between these atoms because of the greater size and diffuseness of the arsenic 4*d*-orbitals compared with the 3*d*-orbitals of phosphorus or sulphur. But it has been pointed out that other factors in addition to electronegativity and $p\pi$–$d\pi$ orbital overlap must play a part in determining the relative acidity of the heteronium salts and the stability of the related ylides.[34] The involvement of steric factors has been noted.[54,79]

6 Reactions of Arsonium Ylides

By far the most important reactions are those of the Wittig type, with carbonyl and nitroso compounds. Other carbanionic reactions are considered and a final section deals with the formation of cyclic compounds from arsonium ylides. Hydrolysis has been discussed in Section 4B.

A. Reactions with Carbonyl Compounds.—The first example of a reaction between an arsonium ylide and a carbonyl compound was recorded in a thesis in 1937.[82] It

[77] A. W. Johnson and R. B. LaCount, *Tetrahedron*, 1960, **9**, 130.

[78] D. Lloyd and M. I. C. Singer, *Chem. Ind. (London)*, 1968. 1277.

[79] D. Lloyd and M. I. C. Singer. *Tetrahedron*, 1972. **28**, 353.
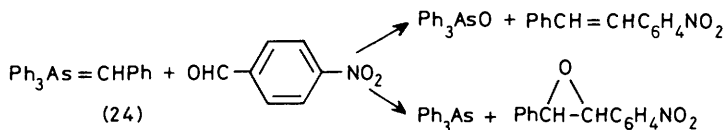
[80] Ref. 72, pp. 284 299.

[81] H. Starzewski, W. Richter, and H. Schmidbauer, *Chem. Ber.*, 1976, **109**, 473.

[82] W. Heffe, Dissertation, University of Berlin, 1937; quoted by G. Wittig, *Pure Appl. Chem.*, 1964, **9**, 249 (W. Heffe was a student with F. Krohnke).

was reported that triphenylarsonium benzoylylide reacted with benzaldehyde to give benzylideneacetophenone.[82] Two publications dealing with the reactions of arsonium ylides with carbonyl compounds appeared in 1960. One described the formation of alkenes in high yield, starting from a fluorenylide,[42] and the other reported that from triphenylarsonium methylide and benzophenone both 1,1-diphenylethylene and phenylacetaldehyde were obtained, with the latter predominating (1:3.5); it was suggested that the aldehyde arose from an initially formed epoxide during an acid work-up of the reaction.[26] Similarly a reaction between triphenylarsonium ethylide and *p*-tolualdehyde gave a mixture of a small amount of alkene and, as principal product, *p*-tolylacetone, again formed by acid induced rearrangement of an initially formed epoxide.[83]

Thus at an early stage in the study of arsonium ylides it was shown that either alkenes or epoxides might be formed, in contrast to the behaviour of phosphonium ylides, which gave only alkenes, and sulphonium ylides, which gave only epoxides.[80] It was also apparent that arsonium ylides were more reactive than their phosphonium analogues, for while triphenylarsonium fluorenylide reacted with *p*-dimethylaminobenzaldehyde to give an alkene in high yield, triphenylphosphonium fluorenylide did not react with this aldehyde.[42] This arsonium ylide reacted in high yield with a number of substituted benzaldehydes and with acetaldehyde; it did not react with acetone or acetophenone but did with the more reactive ketone *p*-nitroacetophenone.[42]

The reaction of triphenylarsonium benzylide (24) with *p*-nitrobenzaldehyde (Scheme 18) provided an alkene and an epoxide in about equal amount, together with equimolar amounts of triphenylarsine and triphenylarsine oxide.[2]

$$Ph_3As=CHPh + OHC-\!\!\left\langle\!\!\!\bigcirc\!\!\!\right\rangle\!\!-NO_2$$

$$\nearrow Ph_3AsO + PhCH=CHC_6H_4NO_2$$

$$\searrow Ph_3As + PhCH\!\!\overset{O}{\underset{\diagdown}{\overbrace{}}}\!\!CHC_6H_4NO_2$$

(24)

Scheme 18

By contrast, in another investigation of the reactions between arsonium ylides and aldehydes, it was found that *either* an alkene *or* an epoxide was formed, depending upon the identity of the ylide, but not both together.[28] Both alkenes and epoxides were always *trans*.[28] This appears usually to be the case.
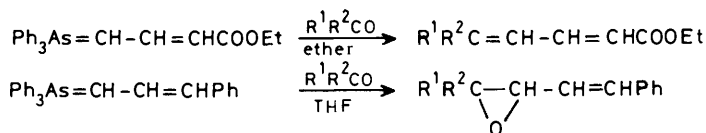
(i) *Comparison of Stable, Reactive, and Semi-stabilized Ylides.* The general pattern which emerged was that stable arsonium ylides provided alkenes whilst reactive arsonium ylides gave epoxides.[2,14,28,32] This was attributed to stabilization of the transition state leading to alkene formation being provided by those same electron-withdrawing groups which stabilized the ylides.[2,28]

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[83] A. Maccioni and M. Secci, *Rend. Seminario Fac. Sci. Univ. Cagliari*, 1964, **34**, 328.

Thus arsonium ylides stabilized by acyl groups,[5,14.31,32,43,84-86] alkoxycarbonyl groups,[5,33,85] cyano groups,[86-87] and cyclopentadiene rings[53.74,78,79] all provided alkenes, predominantly *trans*, as products from reactions with carbonyl compounds. Most ylides with two electronwithdrawing substituents did not, however, take part in Wittig reactions;[5] steric factors may also sometimes inhibit reaction.[54]

Reactive ylides give good yields of *trans*-epoxides.[47] Stereospecificity may vary with conditions. For example use of an arsonium tetrafluoroborate as precursor of the ylide, and potassium bis(trimethylsilyl)amide as base gave 100% *trans*-epoxide, whereas with iodide as counterion and butyl lithium as base, there was less stereospecificity.[47] Reactive ylides generated from optically active arsonium salts reacted with arylaldehydes to give *trans*-epoxides which were optically active.[88]

Allylic arsonium ylides show a similar pattern of reactions. An ethoxycarbonyl-allyl ylide, having the ester group conjugated with the ylidic carbon atom, gave dienes in reactions with aldehydes or ketones,[89] whereas other allylic ylides lacking such an electron-withdrawing substituent gave vinylic epoxides in high yield,[90,91] *e.g.* Scheme 19. In the latter case it was found that the presence of

$$Ph_3As=CH-CH=CHCOOEt \xrightarrow[ether]{R^1R^2CO} R^1R^2C=CH-CH=CHCOOEt$$

$$Ph_3As=CH-CH=CHPh \xrightarrow[THF]{R^1R^2CO} R^1R^2C-CH-CH=CHPh$$
$$\underset{O}{\diagdown\diagup}$$

Scheme 19

hexamethylphosphoramide resulted in the formation of a diene instead of the epoxide.[91]

Semi-stabilized ylides are intermediate in behaviour between stable and reactive ylides, and may provide alkenes and/or epoxides.[3,28,44,45,92] In these cases other factors such as the substituent groups on arsenic, and the nature of the solvent and base, may become important in determining the nature of the product; this will be considered in more detail later. Small changes in the structure of the ylidic moiety may also have a marked effect; for example, whereas triphenylarsonium β-naphthylmethylide reacts to give epoxide, the presence of a bromine atom at the adjacent α-position of the naphthalene ring results in the formation instead of alkenes.[45]

[84] Yaozeng Huang, Yuanyao Xu, and Shong Li, *Org. Prep. Proced. Int.*, 1982, **14**, 373.

[85] P. Bravo, C. Ticozzi, and A. Cezza, *Gass. Chim. Ital.*, 1975, **105**, 109; R. S. Tewari and K. C. Gupta, *Indian J. Chem., Sect. B*, 1976, **14**, 419; 1979, **17**, 637; R. S. Tewari and S. C. Chaturvedi, *Synthesis*, 1978, 616; Yaozeng Huang, Lilan Shi, and Jianhua Yang, *Tetrahedron Lett.*, 1985, **26**, 6447.

[86] Y. Z. Huang, Y. D. Xing, L. L. Shih, F. L. Ling, and Y. Y. Xu, *Acta Chim. Sinica*, 1981, **39**, 348.

[87] Huang Yao-zeng. Shi Li-lan, Li Bin-quan, and Ling Fang-le, *Acta Chim. Sinica*, 1983, **41**, 269.

[88] D. G. Allen, N. K. Roberts, and S. B. Wild, *J. Chem. Soc., Chem. Commun.*, 1978, 346.

[89] Yaozeng Huang, Yanchang Shen, Jianhua Zheng, and Shixiang Zhang, *Synthesis*, 1985, 57.

[90] J. B. Ousset, C. Mioskowski, and G. Solladié, *Tetrahedron Lett.*, 1983, 4419.

[91] J. B. Ousset, C. Mioskowski, and G. Solladié, *Synth. Commun.*, 1983, **13**, 1193.

[92] R. S. Tewari and S. Gupta, *J. Organomet. Chem.*, 1976, **112**, 279.

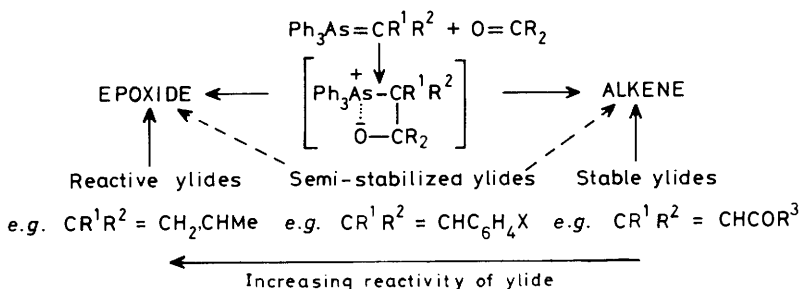These results may be summarized as in Figure 1.

$$Ph_3As=CR^1R^2 + O=CR_2$$

EPOXIDE ⟵ $$\left[Ph_3\overset{+}{As}-\overset{\downarrow}{\underset{|}{C}}R^1R^2 \atop \underset{}{\overset{..}{O}-CR_2} \right]$$ ⟶ ALKENE

Reactive ylides   Semi-stabilized ylides   Stable ylides

e.g. $CR^1R^2 = CH_2,CHMe$ *e.g.* $CR^1R^2 = CHC_6H_4X$ *e.g.* $CR^1R^2 = CHCOR^3$

⟵

Increasing reactivity of ylide

Figure 1

(ii) *Reactivities of Arsonium Ylides compared to those of Phosphonium and Sulphonium Ylides.* Comparative studies involving acyl ylides,[5,84] fluorenylides,[42] and cyclopentadienylides,[52,74,78,79] show that arsonium ylides are markedly more reactive than their phosphonium and sulphonium analogues. In many cases reactions proceed only in the case of the arsonium ylides; this is especially true the more electron-withdrawing are the substituents on the ylide carbon atom, although some arsonium ylides with two electron-withdrawing substituents will not react even with aldehydes as reactive as 2,4-dinitrobenzaldehyde.[5]

The reactions of a series of arsonium ylides with *p*-nitrobenzaldehyde have been shown to be first order for each reagent and there is a general tendency for the more basic ylides to be the more reactive.[36] The correlation is not, however, complete, since factors other than basicity, *e.g.* steric, must also affect the reactivity,[5,54,79] but as a generalization it is largely valid and also must be a significant factor in the greater reactivity of arsonium compared to phosphonium and sulphonium ylides. A fair correlation has also been noted between the chemical shift of the signal from the methine proton in a series of stabilized ylides and their rates of reaction with *p*-nitrobenzaldehyde.[36]

(iii) *Effects of Different Substituents on the Arsenic Atom.* The first report of such effects was in a study of the reactions of a series of tris-(*p*-substituted phenyl) arsonium ylides with benzaldehyde, when all these ylides gave epoxides in high yields save for the tris(*p*-dimethylamino) compound which gave instead the *trans*-alkene.[93] In further experiments replacement of a triphenylarsonium group by a tris-(*p*-methoxyphenyl)arsonium group was found to have little effect on the ratio of products,[28] and inclusion of the arsenic atom in a strained ring also had no effect.[94]

A comprehensive investigation of a series of ylides (25) with benzaldehyde showed that as X,Y became more electron-donating, so the proportion of alkene to epoxide increased.[95] For example, the ratios epoxide:alkene changed from ~11:1

[93] S. G. Dwyer, Ph.D. Thesis, University of North Dakota, 1970.
[94] D. W. Allen and G. Jackson, *J. Organomet. Chem.*, 1976, **110**, 315.
[95] I. Gosney, T. J. Lillie, and D. Lloyd, *Angew. Chem.*, 1977, **89**, 502; *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 487.

(X = Y = H) to ~6.5:1 (X = Y = MeO), ~6:1 (X = H, Y = NMe$_2$), ~4:1 (X = NMe$_2$, Y = H), ~1:1 (X = Y = Me$_2$N). Even more striking is the effect of replacing these aryl groups by alkyl groups, *viz.* ratios epoxide:alkene were Ph$_3$As,

$$(p\text{-}XC_6H_4)_2(p\text{-}YC_6H_4)As=CHPh$$

$$(25)$$
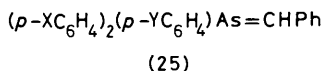
~11:1; Et$_2$PhAs ~1:5; Et$_3$As, ~1:87.[95] These results strongly suggest that remote control of the major pathway followed in reactions of semi-stabilized arsonium ylides with carbonyl compounds might be achieved by choice of the appropriate arsonium group. The reactivity of arsonium ylides is also affected by both electronic and steric effects on the arsenic atom.[48]

(iv) *Solvent Effects.* Initial studies of solvent effects, on the reactions of triarylarsonium benzoylylides with *p*-nitrobenzaldehyde in *N,N*-dimethyl-formamide, dimethyl sulphoxide, or methanol indicated little solvent effect in these cases,[36] but later studies of the more finely balanced reactions of semi-stabilized ylides have provided examples of strong influence due to the effect of different base and solvent when the ylide is generated in the presence of a carbonyl compound.[15,46,91] Thus, when benzyltriphenylarsonium bromide or *p*-chloro-benzyltriphenylarsonium bromide were treated with sodium hydride in benzene in the presence of a variety of *p*-substituted benzaldehydes, the isolated products were alkenes, but if the base was sodium ethoxide in ethanol the isolated products were epoxides.[46] Again scope for the control of the reaction paths at least of semi-stabilized ylides is indicated.

Reactions providing alkenes have been found to be faster in methanol than in benzene; this has been ascribed to hydrogen-bonding rather than to polarity.[36]

(v) *Reactions with Conjugated Enones.* Arsonium ylides may react with conjugated enones or esters to give dienes, or by conjugate addition to provide cyclopropane derivatives,[64,70,71,84,91] *e.g.* Scheme 20.[71] Formation of cyclopropane derivatives is discussed further in Section 6D.
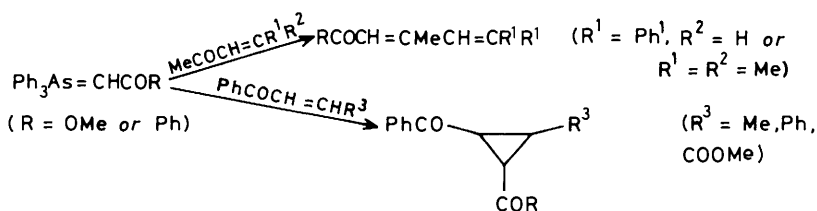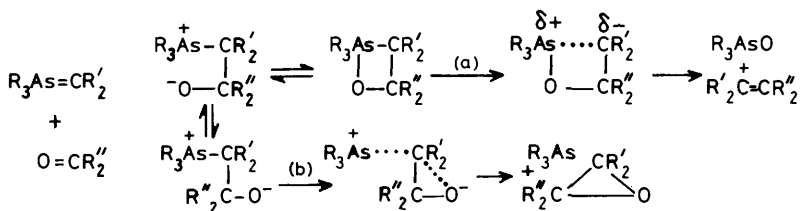

Scheme 20

(vi) *Reactions with other C=X Functions.* Semi-stabilized arsonium ylides react with thioketones; for example with cyclic thioketones triphenylarsonium benzylides

gave only exocyclic alkenes and no thiirans.[96] Benzothiopyrones (and, better, benzopyrones) also react to give exocyclic alkenes, in these cases arylidene-benzopyrans.[97]

Reaction of triphenylarsonium benzylide with benzylideneaniline gave 1,2,3-triphenylaziridine.[28] This reaction is thus analogous to that of reactive arsonium ylides with carbonyl compounds.

(vii) *Mechanism.* Since the behaviour of arsonium ylides in Wittig reactions appeared to be intermediate between that of sulphonium and phosphonium ylides, it was inferred that mechanisms similar to those accepted for the respective reactions of the latter ylides were involved,[2,80] *viz.* Scheme 21. The energetic driving

Scheme 21

force to generate an arsenic–oxygen bond is not as strong as that to form a phosphorus–oxygen bond, so that there is not the same compulsion to alkene formation in the case of arsonium ylides, allowing the alternative pathway (b) to compete.

It was suggested that in the case of stable ylides, wherein R′ is an electron-withdrawing group, the presence of the latter group, which becomes conjugated with the carbon–carbon double bond in the final alkene, also stabilizes the transition state leading to the formation of this alkene, thus promoting pathway (a) with respect to pathway (b).[2,28]

The rates of reaction of acylylides, $Ph_3As{=}CHCOX$ with ketones decreases as X is more electron-withdrawing, making the ylide less nucleophilic.[98] This observation, together with the relation between the reactivity and basicity of the ylide[36] and the second-order character of the reaction,[36,98] all suggest that the first step, which is slow and reversible, is the rate-determining step. The lack of solvent effect in the reactions between benzoylylides and *p*-nitrobenzaldehyde led to the suggestion[36] that in alkene formation reaction goes directly to a four-membered ring transition state without intermediate formation of a betaine. This was seen to be consistent with the large negative entropy of reaction and the very low activation energies observed.[36]

[96] R. S. Tewari, S. K. Suri, and K. C. Gupta, *Z. Naturforsch.. B.* 1980, **35**, 95.

[97] R. S. Tewari, S. K. Suri, and K. C. Gupta. *Synth. Commun..* 1980, **10**, 457.

[98] N. A. Nesmeyanov, E. V. Binshtok, O. A. Rebrova, and O. A. Reutov, *Izv. Akad. Nauk SSSR. Ser. Khim.,* 1972, 2113; *Bull. Acad. Sci. USSR, Div. Chem. Sci.,* 1972, 2056.

Formation of an epoxide must, however, involve an intermediate betaine which reacts further by intramolecular displacement of an arsine.

When pathways (a) or (b) are followed the electrons in the arsenic–carbon bond are displaced in an opposite direction in the two mechanisms. In alkene formation displacement is away from the arsenic atom and in epoxide formation displacement of electrons is towards the arsenic atom. The change in pathway, depending on the nature of the substituents at arsenic, could be associated with this, for electron-donating substituents on arsenic should assist displacement of the electrons away from arsenic and favour alkene formation as observed.[95] For similar reasons electron-withdrawing substituents on the ylidic carbon atom should favour alkene formation.

The observed solvent effects on the type of product formed[46,48] could also be associated with the structure of the intermediate. Formation of alkenes or epoxides necessitates, respectively, *cisoid* and *transoid* arrangements of the arsenic and oxygen atoms, and a *transoid* structure is likely to be much more favoured in a polar protic solvent such as ethanol than in benzene.

(viii) *Coda*. Reactions of arsonium ylides with carbonyl compounds take place much more readily than with phosphonium or sulphonium ylides. The nature of the products depends on the character of substituents on the ylide carbon atom, where electron-withdrawing substituents favour alkene formation, and of substituents on the arsenic atom, where electron-donating substituents favour alkene formation. This may be summarized by Figure 2.
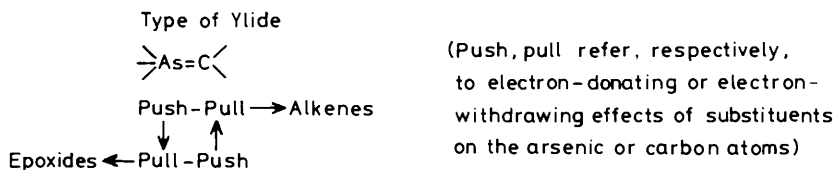
Type of Ylide

$\geq$As=C$\leq$

Push–Pull ⟶ Alkenes

Epoxides ⟵ Pull–Push

(Push, pull refer, respectively, to electron-donating or electron-withdrawing effects of substituents on the arsenic or carbon atoms)
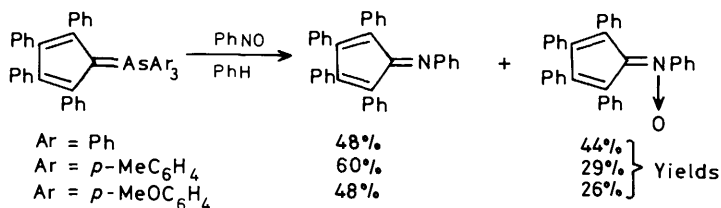
Figure 2

However choice of base and solvent can, in the case of less stabilized ylides, have an effect both on the product distribution and on the stereospecificity of the product. More detailed analysis is still required but it seems likely that, at least in the case of semi-stabilized ylides and possibly for others also, control over the product can be achieved by suitable choice of the substituents on arsenic and of the solvent, thus making a valuable addition to the organic chemist's synthetic armoury.

B. Reactions with Nitrosobenzene.—Ylides may react with nitrosobenzene in a similar manner to their reactions with carbonyl compounds (Scheme 22). Sulphonium ylides give nitrones,[80] phosphonium ylides give anils,[80] and, true to their intermediate character, arsonium ylides may give either anils or nitrones or both.[2,54,74,78,79] Similar considerations should apply to these reactions as to those with carbonyl compounds, and again the reactivity of arsonium ylides is much

$$Ph_3As = CR_2 \rightleftharpoons Ph_3\overset{+}{A}s-CR_2 \rightleftharpoons Ph_3As-CR_2 \rightarrow Ph_3AsO$$
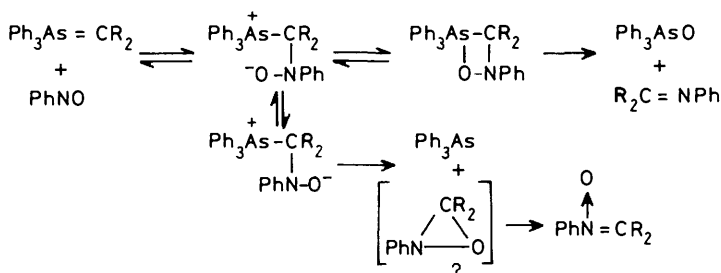
Scheme 22

greater than that of corresponding phosphonium (or sulphonium) ylides.[74,78,79] *p*-Electron-donating substituents in aryl groups attached to arsenic increase the proportion of anil to nitrone, in keeping with their effect on reactions with carbonyl compounds, see for example Scheme 23.[54]

Ar = Ph   48%   44% ⎤
Ar = *p*-MeC₆H₄   60%   29% ⎬ Yields
Ar = *p*-MeOC₆H₄   48%   26% ⎦

Ar = Ph 48% 44% ⎫
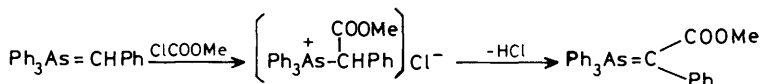Ar = *p*-MeC₆H₄ 60% 29% ⎬ Yields
Ar = *p*-MeOC₆H₄ 48% 26% ⎭

Scheme 23

C. Reactions with other Electrophiles.—Because of the partial negative charge on the ylidic carbon atom, arsonium ylides are also attacked by other electrophiles. The first reported examples of such reactions are shown in Scheme 24.[27,31] Chlorination has been achieved using iodobenzene trichloride.[99]
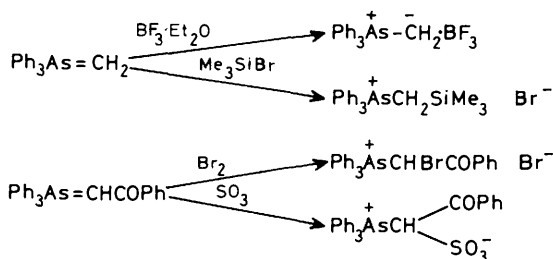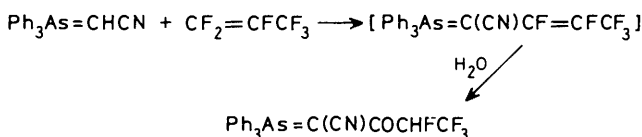
Scheme 24

[99] R. M. Moriarty, I. Prakash, and W. A. Freedman, *J. Am. Chem. Soc.*, 1984, **106**, 6082.

Alkylation of trimethylarsonium methylide with methyl iodide gave ethyltrimethylarsonium iodide,[26] but reaction of triphenylarsonium benzoylylide with ethyl iodide gave an *O*-ethylated product rather than a *C*-ethylated product.[14] Phosphonium ylides undergo *O*-alkylation[100] while sulphonium ylides undergo *C*-alkylation.[101] It is suggested that *O*-alkylation and *C*-alkylation of arsonium ylides result, respectively, from kinetic and thermodynamic control.[14] Alkylation of triphenylarsonium benzylide with methyl chloroformate gave a substituted ylide, by *C*-alkylation (Scheme 25).[12]
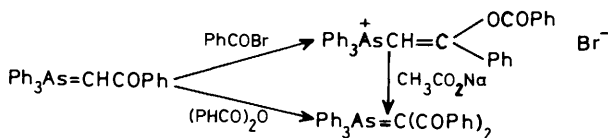
$$Ph_3As=CHPh \xrightarrow{ClCOOMe} \left[Ph_3\overset{+}{As}-\overset{\overset{\displaystyle COOMe}{|}}{C}HPh \right]Cl^- \xrightarrow{-HCl} Ph_3As=C\overset{\displaystyle COOMe}{\underset{\displaystyle Ph}{\diagdown}}$$

Scheme 25

Arsonium ylides react with fluoroalkenes; the isolated products, after hydrolysis, are disubstituted arsonium ylides,[102,103] *e.g.* Scheme 26. In some, but not all cases, the prehydrolysis product has been isolated.

$$Ph_3As=CHCN + CF_2=CFCF_3 \longrightarrow [Ph_3As=C(CN)CF=CFCF_3]$$

$$\downarrow H_2O$$

$$Ph_3As=C(CN)COCHFCF_3$$

Scheme 26

Acylation has been used frequently to convert arsonium ylides into other more stabilized ylides, reagents being acid chlorides,[14,60,66,104,105] acid anhydrides,[5,14,39,63] or esters.[14] These examples all involve *C*-acylation but complications can arise, as Scheme 27 shows.[14] Presumably the reaction with benzoyl

$$Ph_3As=CHCOPh \xrightarrow{PhCOBr} Ph_3\overset{+}{As}CH=C\overset{\displaystyle OCOPh}{\underset{\displaystyle Ph}{\diagdown}} Br^-$$

$$\downarrow CH_3CO_2Na$$

$$(PHCO)_2O \longrightarrow Ph_3As=C(COPh)_2$$

Scheme 27

[100] F. Ramirez and S. Dershowitz, *J. Org. Chem.*, 1957, **22**, 41.
[101] A. W. Johnson and R. T. Amel, *J. Org. Chem.*, 1969, **34**, 1240.
[102] Y. T. Huang, W. Y. Ding, W. Cai, J. J. Ma. and Q. W. Wang, *Sci. Sinica*, 1981, **24**, 189; *Chem. Abstr.*, 1981. **95**, 97923a.
[103] Ding Wei-yu, Cai Wen. Dai Jin-Shan. Huang Yao-zeng, and Zhen Jian-hua, *Acta Chim. Sinica*, 1983, **41**, 67.
[104] K. C. Gupta and R. S. Tewari, *Indian J. Chem.*, 1975, **13**, 834.
[105] P. S. Kendurkar and R. S. Tewari, *J. Organomet. Chem.*, 1975, **102**, 141.

bromide gives a kinetically controlled product which is converted into the thermodynamically controlled product in the presence of acetate.[14]

In this case delocalization of the negative charge leads to acylation at a site other than the ylidic carbon atom. Similarly with cyclopentadienylides, wherein the charge may be delocalized around the ring, acylation takes place at other positions in the ring than the ylidic carbon atom, but, since a carbon–carbon bond is formed, there is no tendency for the acyl group to migrate (Scheme 28).[52,79]
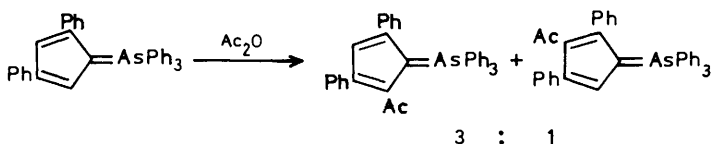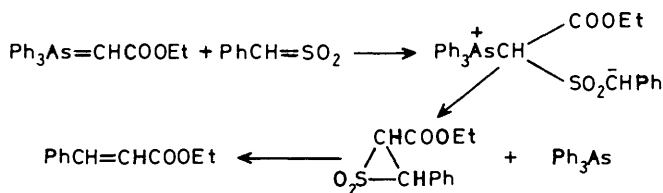
Scheme 28

Aryldiazonium salts also react with cyclopentadienylides to give 2- or 3-phenylazo derivatives.[49,52]

Other reagents which react with arsonium ylides are phenyl sulphine and phenyl sulphene (Scheme 29).[28] Ethyl cinnamate is also a product of the latter reaction, presumably formed by the route shown in Scheme 30. The ylidic carbon atom of a number of acylylides reacted with tropylium bromide to give tropylarsonium salts (26), which decomposed by elimination of triphenylarsine to give β-acylstyrenes
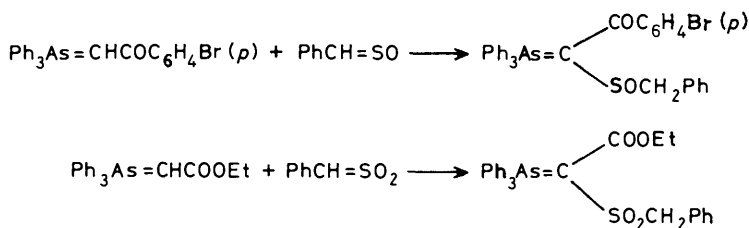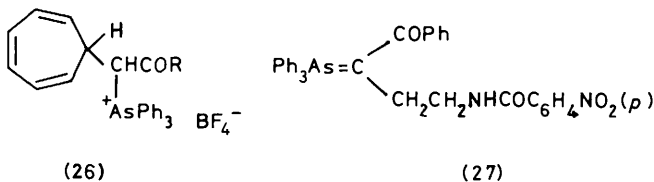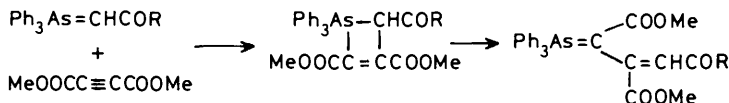
Scheme 29

Scheme 30

and β-acyl-β-tropylstyrenes.[106] Triphenylarsonium benzoylylide was also alkylated with 1-*p*-nitrobenzoylaziridine in boiling toluene to give (27).[65]


(26)   (27)

A more complex reaction ensues between acylylides and dimethyl acetylene-dicarboxylate, the product presumably arising *via* a four-membered ring intermediate (Scheme 31).[28]

Scheme 31

D. Formation of Cyclic Compounds from Arsonium Ylides.—Cyclopropane derivatives have been prepared from reactions of arsonium ylides with α,β-enones[14,28,64,84,107] and α,β-unsaturated esters.[38,70,84] Initial Michael type reaction is followed by intramolecular elimination of triphenylarsine, *e.g.* Scheme 32.[28]
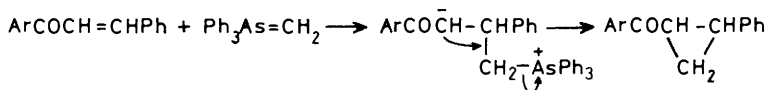
Scheme 32

A variety of heterocycles has been made from arsonium ylides. For example, as mentioned in Section 6A(vi), 1,2,3-triphenylaziridine was obtained by reaction with benzalaniline.[28]

α-Pyrones result from reactions of acylylides with diphenylcyclopropenone, presumably *via* attack by the acyl oxygen atom of the ylide on the cyclopropene ring.[5]

Indoles have been prepared from reactions of *o*-aminophenylketones with reactive[108] or stable[109–111] arsonium ylides. Keto-stabilized ylides reacted with α-chloro-oximes to give *trans*-5-acyl-Δ²-isoxazolines,[112] and isoxazoles have been

[106] G. Covicchio, M. D'Antiono, G. Gaudiano, V. Marchetti, and P. P. Ponti, *Tetrahedron Lett.*, 1977, 3493.
[107] N. A. Nesmeyanov and V. V. Mikul'shina, *Zh. Org. Khim.*, 1971, **7**, 696.
[108] P. Bravo, G. Gaudiano, P. P. Ponti, and M. G. Zubiani, *Tetrahedron Lett.*, 1970, 4535.
[109] R. K. Bansal and S. K. Sharma, *Tetrahedron Lett.*, 1977, 1923.
[110] R. K. Bansal and S. K. Sharma, *J. Organomet. Chem.*, 1978, **149**, 309.
[111] R. K. Bansal and G. Bhagchandari, *Bull. Chem. Soc. Japan*, 1980, **53**, 2423.
[112] P. Bravo, G. Gaudiano, P. P. Ponti, and C. Ticozzi, *Tetrahedron*, 1972, **28**, 3845.

obtained from reactive arsonium ylides and α-isonitrosoketones[113] and from triphenylarsonium methylide and nitrile oxides.[114] The latter ylide reacts similarly with nitrile imines to give pyrazoles.[114] With triphenylarsonium benzylides and benzoylylides benzene diazonium salts give 1,3,4,6-substituted 1,4-dihydro-1,2,4,5-tetrazines in a reaction in which initial coupling of the reagents is followed by a dimerization.[115]

E. Reactions of a Cumulated Arsonium Ylide.—A cumulated arsonium ylide has been found to undergo similar reactions to its phosphonium analogue. The examples shown in Scheme 33 were cited.[13]
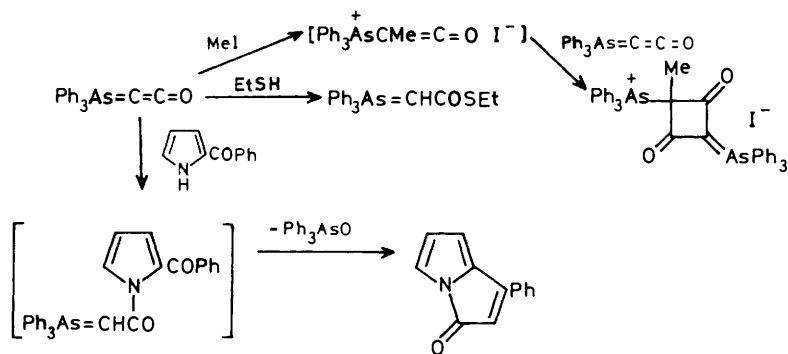
Scheme 33

7 Arsinimines

Arsinimines (28) are the nitrogen analogues of arsonium ylides. They appear to be more resistant to hydrolysis than the ylides for even the simple non-stabilized example (28, R = H) can be handled in air, although it is less stable than its phosphonium analogue.

$$Ph_3As = NR \longleftrightarrow Ph_3\overset{+}{A}s - N\overset{-}{R}$$
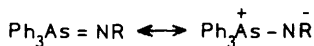
(28)

A. Preparation of Arsinimines.—The methods used for the preparation of arsonium ylides, namely salt method, use of arsine dihalides, condensation reactions with arsine oxides, and trapping of carbenes by arsines, have all been applied to the preparation of arsinimines.

In contrast to the common use of the salt method for making ylides, there is only one example of its use for preparing an arsinimine, to provide what is as yet

[113] P. Bravo, G. Gaudiano, and C. Ticozzi, *Gazz. Chim. Ital.*, 1972, **102**, 395.
[114] G. Gaudiano, C. Ticozzi, A. Umani-Ronchi, and A. Selva, *Chem. Ind. (Milan)*, 1967, **49**, 1343.
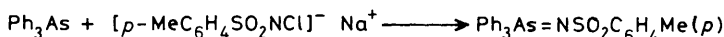[115] R. K. Bansal and S. K. Sharma, *J. Organomet. Chem.*, 1978, **155**, 293.

the simplest reported example (Scheme 34).[116] Arsinimines have been prepared from arsine dihalides, using the reactions between dibromotriphenylarsine and amides.[117,118]

$$Ph_3As + ClNH_2 \longrightarrow Ph_3\overset{+}{A}sNH_2 \ Cl^- \xrightarrow[NH_3]{NaNH_2} Ph_3As=NH$$
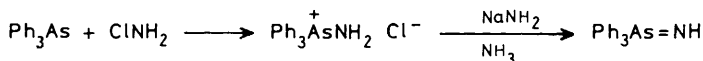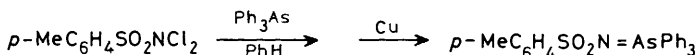
Scheme 34

The first reported example of the preparation of an arsinimine, in 1937, utilized the reaction of the sodium salt of chloramine T with triphenylarsine (Scheme 35).[119] This reaction, which has been repeated by later workers,[120] is not, however, straightforward, and earlier work had shown that chloramine T reacts with the arsine to convert it into an arsine oxide,[121] which then condenses with the tosylamide to provide the final product. Other arsinimines have been made by the same method but in the majority of cases were isolated as their water adducts.[122] In a modification of this reaction, chloramine T itself, rather than a salt, underwent an exothermic reaction with triphenylarsine in dry benzene, and the resultant intermediate, which was not isolated, gave, on treatment with copper powder, an arsinimine (Scheme 36).[123]

$$Ph_3As + [p\text{-}MeC_6H_4SO_2NCl]^- \ Na^+ \longrightarrow Ph_3As=NSO_2C_6H_4Me(p)$$

Scheme 35

$$p\text{-}MeC_6H_4SO_2NCl_2 \xrightarrow[PhH]{Ph_3As} \xrightarrow{Cu} p\text{-}MeC_6H_4SO_2N=AsPh_3$$

Scheme 36

Triphenylarsine oxide reacts with a variety of nitrogen compounds, namely aryl isocyanates,[124,125] acyl isocyanates,[118] *N*-sulphinylamines,[124] and *N*-sulphinyl-amides,[124,126] to provide arsinimines. Nitriles fully substituted on the α-carbon atom add triphenylarsine oxide to give *N*-acylarsinimines;[127] other nitriles did not react or instead condensed with the arsine oxide at the α-carbon atom to give ylides.

Closely related to the arsine oxide method is a ready way for preparing

[116] R. Appel and D. Wagner, *Angew. Chem.*, 1960, **72**, 209.
[117] B. D. Cbernokal'skii, S. S. Nasybullina, R. R. Shagidullin, I. A. Lamanova, and G. Kamai, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, 1966, **9**, 768; *Chem. Abstr.*, 1967, **66**, 76112.
[118] P. Frøyen, *Acta Chem. Scand.*, 1969, **23**, 2935.
[119] F. G. Mann and E. J. Chaplin, *J. Chem. Soc.*, 1937, 527.
[120] G. Wittig and D. Hellwinkel, *Chem. Ber.*, 1964, **97**, 769.
[121] F. G. Mann, *J. Chem. Soc.*, 1932, 958.
[122] D. S. Tarbell and J. R. Vaughan, *J. Am. Chem. Soc.*, 1945, **67**, 41.
[123] A. Schönberg and E. Singer, *Chem. Ber.*, 1969, **102**, 2557.
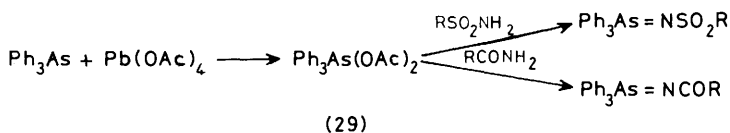[124] P. Frøyen, *Acta Chem. Scand.*, 1971, **25**, 983.
[125] P. Frøyen, *Acta Chem. Scand.*, 1973, **27**, 141.
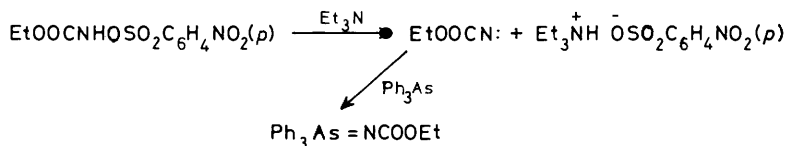[126] A. Senning, *Acta Chem. Scand.*, 1965, **19**, 1755.
[127] G. Gadeau. A. Fouchaud, and P. Merot, *Synthesis*, 1981, 73.

arsinimines by heating together triphenylarsine, an amide, and lead tetraacetate in a one-pot reaction.[55,128] The reaction sequence, which is as shown in Scheme 37, is analogous to that postulated for the formation of arsonium ylides from triphenylarsine oxide in acetic anhydride.[5] Crystalline bisacetoxytriphenylarsine (29) has been isolated and shown to react with amides to give arsinimines.[55,128] Tosyl and mesyl amides and benzamide react with (29) at room temperature, but less nucleophilic amides required heating in boiling 1,2-dichloroethane for reaction to take place.[55]

$$Ph_3As + Pb(OAc)_4 \longrightarrow Ph_3As(OAc)_2 \xrightarrow[\text{RCONH}_2]{\text{RSO}_2\text{NH}_2} \begin{array}{l} Ph_3As = NSO_2R \\ \\ Ph_3As = NCOR \end{array}$$

(29)

Scheme 37

As carbenes react with arsines to give ylides, so nitrenes give arsinimines.[128,129] The nitrenes were generated *in situ* by copper-catalysed decomposition of either azides[128,129] or 3-aryl-1,4,2-dioxazolidin-5-ones.[129] *N*-Ethoxycarbonyl- and *N-p*-tolylsulphonyl-triphenylarsinimines have been prepared by nitrene capture reactions in which the nitrenes were generated by the action of base on, respectively, a sulphonyloxyurethane and a sulphonamide,[129] *e.g.* Scheme 38.

$$EtOOCNHOSO_2C_6H_4NO_2(p) \xrightarrow{Et_3N} EtOOCN: + Et_3\overset{+}{N}H \ \overset{-}{O}SO_2C_6H_4NO_2(p)$$

$$\downarrow Ph_3As$$

$$Ph_3As = NCOOEt$$

Scheme 38

B. Properties of Arsinimines.—Many arsinimines are stable solids, handleable in air; as with arsonium ylides, the presence of electron-withdrawing substituents on the nitrogen atom increases their stability. Infra-red spectra show that in *N*-acylarsinimines the negative charge is delocalized onto the oxygen atom.[118] *N*-Benzyltriphenylarsinimine decomposes when heated to give triphenylarsine oxide and benzonitrile.[118]

Arsinimines are hydrolysed by aqueous base[118,121] or acid,[118] providing triphenylarsine oxide and an amide. With hydrogen chloride they form arsonium halides.[116]

Arsinimines have been alkylated using methyl iodide[118,125] and acylated by acyl halides.[116] In the case of an *N*-acylarsinimine, methylation took place at either the oxygen or the nitrogen atoms (Scheme 39).[118]

[128] J. I. G. Cadogan and I. Gosney, *J. Chem. Soc.. Chem. Commun.*, 1973, 586.
[129] J. I. G. Cadogan and I. Gosney, *J. Chem. Soc., Perkin Trans. 1*, 1974, 460.

$$Ph_3As = NCOPh \xrightarrow{\text{MeI}} Ph_3\overset{+}{As}N = C(OMe)Ph \ I^- + Ph_3\overset{+}{As}NMeCOPh \ I^-$$
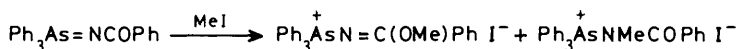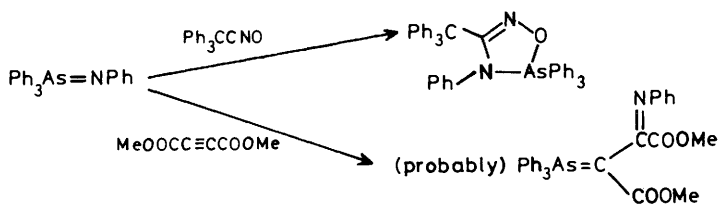
<p align="center">**Scheme 39**</p>

N-Phenyltriphenylarsinimine reacted rapidly with benzophenone and with *p*-nitrobenzaldehyde or quinones, in a reaction analogous to the Wittig reaction, to form imines (Scheme 40).[118] A similar reaction with nitrosobenzene provided azobenzenes.[130]

$$Ph_3As = NPh + RR'CO \longrightarrow RR'C = NPh + Ph_3AsO$$
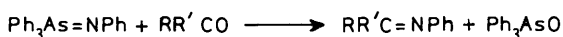
<p align="center">**Scheme 40**</p>

Other reactions with electrophiles include those with phenyl isothiocyanate or carbon disulphide to give a carbodiimide, and with sulphur dioxide to give an *N*-sulphinylaniline.[125] Reactions of *N*-phenyltriphenylarsinimine with triphenyl-acetonitrile-*N*-oxide provided an arsaheterocycle, and with dimethyl acetylene-dicarboxylate gave a product which was probably an arsonium ylide (Scheme 41).[125] A final reaction of some interest was that of *N*-tosyltriphenylarsinimine with phenyllithium to give pentaphenylarsenane, Ph_5As.[120]

<p align="center">**Scheme 41**</p>

8 Stibonium Ylides and Imines

The first stibonium ylide to be isolated was triphenylstibonium tetraphenyl-cyclopentadienylide, obtained by thermal decomposition of diazotetraphenylcyclo-pentadiene in the presence of triphenylstibine.[131] It was less stable than its arsonium or phosphonium analogues, decomposing when heated in ethanol or nitromethane or with alkali. It formed a crystalline perchlorate. Spectroscopic data indicated that the ylide C–Sb bond was more polar and had less double-bond character than in the corresponding arsonium or phosphonium ylides. This was attributed to the less efficient overlap between the $2p$ orbitals of the ylide C-atom and the d-orbitals of Sb, because of the greater size and diffuseness of the d-orbitals in this case.[74-78] The greater dipolarity of the stibonium ylide compared to its arsonium, phosphonium, and sulphonium analogues is also in accord with its

[130] P. Frøyen, *Acta Chem. Scand.*, 1971, **25**, 2781.
[131] D. Lloyd and M. I. C. Singer, *Chem. Ind. (London)*, 1967, 787.

greater basicity and its higher reactivity towards benzaldehydes or nitroso-benzene.[74,78] As a stable ylide it gave alkenes on reaction with aldehydes but, in contrast, the product from nitrosobenzene was a nitrone.

Use of copper hexafluoroacetylacetonate as a catalyst[59,60] has enabled the preparation and isolation of other stibonium ylides, $Ph_3Sb=CX_2$, X = RCO or RSO_2, from diazo-compounds in solution in benzene.[60] They too appear, from their spectra, to be more dipolar than their arsonium analogues but, like the latter, they do not take part in Wittig reactions, even with very reactive aldehydes. They are stable in a dry atmosphere and are basic. In protic solvents they are slowly cleaved to give triphenylantimony oxide and the corresponding methylene compounds CH_2X_2.

The preparation in solution of triphenylstibonium methylide has been reported, by the action of phenyl lithium on methyltriphenylstibonium tetrafluoroborate.[26] Treatment of this solution with benzophenone, followed by acid work-up gave high yields of triphenylstibine and diphenylacetaldehyde,[26] and it has been suggested[86] that the latter product arose by acid-induced rearrangement of initially formed 1,1-diphenylethylene oxide, the likely product from reaction of this reactive ylide with a carbonyl compound.

A stibinimine has been prepared[132] by reaction of triphenylstibine with chloramine T under conditions analogous to those used to prepare its arsenic counterpart. This stibinimine was stable in air, but was hydrolysed by water. Like its arsenic analogue it reacted with phenyl lithium to give pentaphenylantimony.

9 Bismuthonium Ylides and Imines

If $p\pi-d\pi$ orbital overlap between an ylide carbon atom and the heteroatom contributes to the stability of an ylide, then bismuthonium ylides should be much less stable than the other ylides of Group V elements, since the 6d-orbitals of bismuth are likely to be much too large and diffuse to provide any effective overlap.

This is borne out by the properties of the one example of a bismuthonium ylide which has been reported.[133] Triphenylbismuthonium tetraphenylcyclopenta-dienylide was obtained by thermal decomposition of diazotetraphenylcyclo-pentadiene in the presence of triphenylbismuth. Although as a solid it was stable for some time, it decomposed rapidly in solution; it was also decomposed rapidly by acid or base. This bismuthonium ylide is intensely blue, unlike its phosphonium, arsonium, or stibonium analogues which are yellow. Its electronic spectrum closely resembled that of pyridinium tetraphenylcyclopentadienylide,[74] and, like the latter compound but unlike its P, As, and Sb analogues, it was solvatochromic, giving, for example, blue solutions in ether or benzene but red-purple solutions in alcohols.[74,133] In nitrogen ylides $p\pi-d\pi$ orbital overlap is not possible; the spectroscopic similarity between the triphenylbismuthonium and pyridinium tetraphenylcyclopentadienylides and the huge difference between their spectra and those of the related stibonium, arsonium, phosphonium, and sulphonium

[132] G. Wittig and D. Hellwinkel, *Chem. Ber.*, 1964, **97**, 789.
[133] D. Lloyd and M. I. C. Singer, *Chem. Commun.*, 1967, 1042.

analogues, lends substance to the concept of the influence of $p\pi$–$d\pi$ orbital overlap on the properties of ylides.

Again using copper hexafluoroacetylacetonate as catalyst, some other bismuthonium ylides, $Ph_3Bi{=}CX_2$, $X = RCO$ or RSO_2, have recently been prepared by the diazo method and isolated.[61] They appeared to be less stable than stibonium or arsonium analogues and decompose slowly when kept as solids.

There is one report of the preparation of a bismuthimine, by the reaction of chloramine T with triphenylbismuth.[128] This product was not isolated or characterized and quickly decomposed, but it is probable that the bismuthimine was obtained as an unstable product, since it reacted with phenyl lithium to give pentaphenylbismuth.