Organoarsenic Azides: Preparation and Thermal Decomposition

By **D. M. Revitt** and **D. B. Sowerby,*** Department of Chemistry, University of Nottingham, Nottingham NG7 2RD

Eight organoarsenic azides have been prepared by reacting the corresponding halide with lithium azide, and Raman and i.r. spectra of the compounds are reported. On heating alkyl substituted azides, complete loss of nitrogen occurs and substituted diarsines are the products. Bromo- and chloro-azidophenylarsines on the other hand undergo reorganization and halogenodiphenylarsines can be isolated.

ALTHOUGH a number of azides of organic derivatives of various *p*-electron-elements are known[1,2] only one arsenic compound has been prepared. This compound, Ph_2AsN_3, was obtained as an unpurified liquid from diphenylchloroarsine and lithium azide and gave on thermal decomposition a cyclic arsenic–nitrogen compound analogous to the tetraphosphonitriles.[3] This paper reports the preparation of eight further azidoarsines and discusses their spectroscopic properties and behaviour on thermal decomposition. The spectroscopic properties of azidodiphenylarsine are also discussed. Since completion of this work,[4] the preparation of azidodimethylarsine by an alternative method has been reported.[5]

EXPERIMENTAL

Preparation of Organochloroarsines.—Dichlorophenylarsine was obtained by reducing phenylarsonic acid,[6] while chlorodiphenylarsine resulted from redistribution of an arsenic trichloride–triphenylarsine mixture.[7] Hypophosphite reduction of dimethylarsinic acid gave chlorodimethylarsine[8] and the diethyl analogue[9] was obtained from arsenic trichloride and tetraethyl-lead. Alkylation of dichlorophenylarsine with either tetramethyl- or tetraethyl-lead gave the two alkylchlorophenylarsines while reaction with either anhydrous dimethyl- or diethyl-amine in light petroleum led to the aminochlorophenylarsines. All compounds were purified by distillation and had satisfactory analyses.

Preparation of Organoazidoarsines.—In a typical reaction, chlorodimethylarsine (14·9 g, 0·106 mol) was stirred under reflux in acetonitrile solution (100 ml) with an excess of anhydrous lithium azide[10] (10·0 g, 0·2 mol). The solvent had previously been dried over phosphorus pentoxide, redistilled and saturated with nitrogen, and a nitrogen atmosphere was preserved throughout the reaction. After 24 h, the mixture was filtered in an inert atmosphere and the solvent was distilled off at atmospheric pressure. The pressure was then reduced to 100 mmHg and the remaining liquid was distilled in apparatus surrounded by safety screens. Pure azidodimethylarsine (10·5 g, 67% yield) was obtained as a colourless liquid (b.p. 77—78°, 100 mmHg) (Found: C, 16·4; H, 4·4; N, 28·5; Calc. for Me_2AsN_3: C, 16·3; H, 4·1; N, 28·6%).

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[1] J. S. Thayer and R. West, *Adv. Organometallic Chem.*, 1967, **5**, 169; M. F. Lappert and H. Pyszora, *Adv. Inorg. Chem. Radiochem.*, 1966, **9**, 133.

[2] J. S. Thayer, *Organometallic Chem. Rev.*, 1966, **1**, 157.

[3] W. T. Reichle, *Tetrahedron Letters*, 1962, 61.

[4] D. M. Revitt and D. B. Sowerby, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 459.

[5] J. Müller, *Z. anorg. Chem.*, 1971, **381**, 103.

[6] R. L. Barker, E. Booth, A. F. Millidge, and F. N. Woodward, *J. Soc. Chem. Ind.*, 1949, **68**, 289.

[7] A. G. Evans and E. Warhurst, *Trans. Faraday Soc.*, 1948, **44**, 189.

[8] G. P. Van der Kelen, *Bull. Soc. chim. belges*, 1956, **65**, 343.

[9] M. S. Kharasch, E. V. Jensen, and S. Weinhouse, *J. Org. Chem.*, 1949, **14**, 429.

[10] N. Hofman-Bang, *Acta Chem. Scand.*, 1957, **11**, 581.

Other experimental results are summarized in Table 1. The exclusion of oxygen was essential in all preparations but particularly with the dimethyl and amine substituted azides which were readily oxidized to white solids.

Preparation of Azidochlorophenylarsine.—The low yield obtained by heating dichlorophenylarsine in toluene under reflux with lithium azide (1 mol) was increased to 50% by using 1·5 mol of lithium azide and to 75% by changing the solvent to acetonitrile. The amount of lithium azide was not increased further to avoid formation of the diazide. The azidochloride could not be separated from unreacted dichlorophenylarsine by fractional distillation but a small amount of pure compound was obtained by g.l.c. (5′ × ¼″ column packed with 20% SE 30 at 150°) (Found: C, 31·6; H, 2·3; N, 17·9. Calc. for $PhClAsN_3$: C, 31·4; H, 2·2; N, 18·3%).

TABLE 1

Preparative and analytical data

Compound	Solvent	Yield (%)	B.p.		C	H	N
Et_2AsN_3	Acetonitrile	72	65—66°, 15 mmHg	Found	27·5	5·6	23·9
	Pyridine	40		Calc.	27·4	5·7	24·0
$MePhAsN_3$	Acetonitrile	65	57—58°, 10^{-2} mmHg	Found	40·7	3·9	20·5
				Calc.	40·2	3·8	20·1
$EtPhAsN_3$	Acetonitrile	71	61—62°, 10^{-2} mmHg	Found	43·3	4·8	18·6
	Toluene	36		Calc.	43·1	4·5	18·8
$(Me_2N)PhAsN_3$	Acetonitrile	70	72—73°, 10^{-2} mmHg	Found	39·9	4·4	23·6
				Calc.	40·3	4·6	23·5
$(Et_2N)PhAsN_3$	Acetonitrile	72	84—85°, 10^{-2} mmHg	Found	44·9	5·3	21·6
	Pyridine	32		Calc.	45·1	5·6	21·1
Ph_2AsN_3	Toluene	69	104—105°, 10^{-2} mmHg	Found	53·4	3·8	15·4
				Calc.	53·1	3·7	15·5

Preparation of Azidobromophenylarsine.—The corresponding reaction with dibromophenylarsine was much slower and the best yield (72%) was obtained by refluxing for 24 h with lithium azide (2 mol) in toluene. An analytical sample was separated by fractional distillation, b.p. 93—94°, 10^{-2} mmHg (Found: C, 26·4; H, 1·9; N, 15·6. Calc. for $PhBrAsN_3$: C, 26·3; H, 1·8; N, 15·3%).

Thermal Decomposition of Azides.—The compound (*ca.* 5 g) was transferred in a nitrogen atmosphere to a small flask connected *via* a reflux condenser to a mercury non-return valve and the temperature was raised slowly with an oil bath. When nitrogen evolution began the temperature was held until no more gas was evolved and i.r. spectroscopy showed the absence of azide. The remaining material, kept under a nitrogen atmosphere, was purified by an appropriate method. On two occasions explosive decomposition occurred and in all experiments the apparatus was surrounded by safety screens.

TABLE 2

Decomposition of alkylazidoarsines

Compound	Product	B.p.		C	H	As
Me_2AsN_3	Me_4As_2	48°, 15 mmHg		*a*		
Et_2AsN_3	Et_4As_2	110°, 15 mmHg	Found	35·8	7·4	56·1
			Calc.	36·1	7·5	56·4
$MePhAsN_3$	$Me_2Ph_2As_2$	124°, 10^{-2} mmHg	Found	50·3	4·7	44·5
			Calc.	50·3	4·8	44·9
$EtPhAsN_3$	$Et_2Ph_2As_2$	135°, 10^{-2} mmHg	Found	52·6	5·3	42·3
			Calc.	53·0	5·5	42·5

[a] Compound reacts too readily with oxygen for conventional analysis; the i.r. and Raman spectra were identical with those from an authentic sample of tetramethyldiarsine prepared by reducing chlorodimethylarsine with zinc, W. R. Cullen and H. J. Emeleus, *Canad. J. Chem.*, 1960, **38**, 439.

Alkylarsines.—Experiments with alkylazidoarsines are summarized in Table 2. In all cases decomposition was complete after 24 h at *ca.* 220° and the nitrogen-free product was purified by vacuum distillation.

Halogenoarsines.—Because of preparative difficulties, decomposition of both $ClPhAsN_3$ and $BrPhAsN_3$ was carried out in the presence of the corresponding dihalide. Nitrogen evolution was rapid at *ca.* 175° and the product consisted of a viscous, nitrogen-free liquid and a black insoluble solid. In each case the liquid was shown by distillation, analysis, g.l.c., and i.r. spectroscopy [11] to be a mixture of the dihalogenophenyl- and halogenodiphenyl-arsines. No useful information was obtained on the black solid.

Aminoarsines.—The two azides showed no specific decomposition temperature but no azide remained after 12 h at 220°. A suitable method could not be found for purifying the brittle, black product but i.r. spectra showed that phenyl and dialkylamino-groups were still present.

Spectra.—I.r. spectra of the azides were obtained on liquid films using a Perkin-Elmer 521 spectrometer and Raman spectra on samples sealed in 2 mm tubes using a Cary 81 spectrometer with He–Ne laser excitation.

DISCUSSION

Preparative Method.—Reaction of a chloroarsine with lithium azide in acetonitrile is a general method for preparing the corresponding azidoarsine, but with bromoarsine starting materials, toluene is a better solvent probably because of the lower solubility of lithium bromide. The azides are volatile liquids with boiling points generally slightly higher than those of the corresponding chlorides. The dimethyl compound is a little anomalous as it boils at 82—84°, 125 mmHg compared with 57—59°, 125 mmHg for the chloride. This implies association in the liquid phase and ^{14}N n.m.r. measurements [12] appear to support this; no association

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[11] D. M. Revitt and D. B. Sowerby, *Spectrochim. Acta*, 1970, **26***A*, 1581.

[12] W. Beck, W. Becker, K. F. Chew, W. Derbyshire, N. Logan, D. M. Revitt, and D. B. Sowerby, *J.C.S. Dalton*, 1972, **245**.

in the vapour phase could be detected by mass spectrometry. All the compounds could be purified by distillation at reduced pressure but safety screens were always used. The azides are miscible with a variety of organic solvents and are to be included among the type A azides. In the mode of thermal decomposition, however, they deviate from the generalized type A behaviour.[2]

Vibrational Spectra.—There is no structural information for the azidoarsines. In methylazide, the C–N–N angle[13] is 120° but with the arsines the As–N–N angle could be larger due to π-bonding giving a situation similar to that for silylazide[14] or azidomethylsilane.[15]

The compounds will all belong to the C_s point-group and vibrations associated with MN_3, where $M = RR'As$, will be: the asymmetric and symmetric azide stretches, the arsenic–nitrogen stretch, two in-plane deformations (δ_{NNN} and δ_{AsNN}) and one out-of-plane deformation (π_{NNN}).[2] The five in-plane vibrations belong to the species A' and should give polarized Raman bands.

TABLE 3

Raman and i.r. spectra of azides

		$\nu_{as} + \nu_s$	$2\nu_s$	ν_{as}	$2\delta_{NNN}$	ν_s	δ_{NNN}	π_{NNN}	ν_{As-C}	ν_{As-N_3}
Me_2AsN_3	R			2082mw,p		1261w,p	680w,p		581s,p	439ms,p
	I.r.	3315m	2492m	2081vs	1362mw	1257s	676mw	*a*	602sh; 585s	442s
Et_2AsN_3	R			2084m,p		1260m,p	677mw,p		576s,p; 565s,p; 547ms,p	447vs,p
	I.r.	3315m	2500w	2082vs	1350w	1256s	673mw	*a*	574m; 559sh; 541sh	443ms
Ph_2AsN_3	R			2085w,p		1252w,p				441vs,p
	I.r.	3310mw	2487w	2084vs	1348mw	1250s,br		571w		441s
$MePhAsN_3$	R			2080mw,p		1255mw,p			584ms,p	440s,p
	I.r.	3305mw	2489mw	2080vs	1350mw	1252s	667m	*a*	579m	440ms
$EtPhAsN_3$	R			2086w,p		1257w,p			568ms,p; 544sh	443s,p
	I.r.	3312w	2495w	2082s	1352w	1253m	669sh	*a*	563m; 539sh	445s
$(Me_2N)PhAsN_3$	R			2080mw,p		1253mw,p				410s,p
	I.r.	3300mw	2490w	2078vs		1249s	666sh	*a*		408s
$(Et_2N)PhAsN_3$	R			2080mw,p		1256mw,p				405s,p
	I.r.	3300mw		2073vs		1252s	665sh	580w		404ms
$Ph(Cl)AsN_3$	R			2098mw,p		1237w,p				431sh
	I.r.	3300w	2450w	2090s	1348w	1232ms	668sh	570w		435sh
$Ph(Br)AsN_3$	R			2095w,p		1235w				449m,p
	I.r.	3290w	2446w	2090s	1344w	1232m		570w		446sh

[a] Obscured by absorptions of alkyl groups.

There is general agreement on the positions of the stretching vibrations but those of the bending modes are not known with certainty. Selected bands from the i.r. and Raman spectra are summarized in Table **3** but with the exception of the arsenic–carbon stretch, vibrations of the organoarsenic groups are not tabulated as they occur in the usual positions.[11,16]

Stretching Modes.—In all cases, the two azide stretches occur in the i.r. as intense absorptions and as lower intensity polarized Raman bands. The asymmetric mode is apparently not a single band in some cases but this is more likely due to the presence of a combination band, *e.g.* 1481 + 671 in Ph_2AsN_3, rather than to a real splitting of the mode. Of the compounds examined, the two azidohalides show the largest shifts in both azide stretching modes probably resulting from the change in π-bonding within the N_3 grouping due to the electronegative halogen atom.

An intense band at *ca.* 440 cm^{-1} which is polarized in the Raman can be assigned to the arsenic–nitrogen stretch but the assignment is complicated in the phenyl derivatives by a vibrational mode of the phenyl group at a similar position. When dialkylamino groups are present, the arsenic–nitrogen (azide) stretch occurs some 30 cm^{-1} lower than that for other azides (see Table **3**); a similar effect occurs in chloroarsines where the arsenic–chlorine stretch is lowered by *ca.* 50 cm^{-1} from the value (*ca.* 370 cm^{-1}) in compounds not containing amine groups[11,16] (see Table 4). This seems to imply that both arsenic–azide and arsenic–chloride bonds are weakened in the presence of amine substituents, perhaps because stronger π-bonding between the amine and arsenic reduces the possibility for π-bonding from the azide or chloride. Direct confirmatory evidence from the position of the As–N (amine) stretch (see Table 4) is lacking

TABLE 4

Raman and i.r. bands in amino-derivatives

		ν(As–X)	ν[As–N(amine)]
$(Me_2N)PhAsCl$	R	324s,p	580ms,p
	I.r.	323vs	577s
$(Et_2N)PhAsCl$	R	320s,p	603m,p
	I.r.	319s	601ms
$(Me_2N)PhAsN_3$	R	410s,p	577ms,p
	I.r.	408s	573ms
$(Et_2N)PhAsN_3$	R	405s,p	602m,p
	I.r.	404ms	598m

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[13] L. Pauling and L. O. Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 13.

[14] E. A. V. Ebsworth, D. R. Jenkins, M. S. Mays, and T. M. Sugden, *Proc. Chem. Soc.*, 1963, 21.

[15] J. S. Thayer and R. West, *Inorg. Chem.*, 1964, **3**, 889.

[16] D. M. Revitt and D. B. Sowerby, *J. Chem. Soc.* (*A*), 1970, 1218.

but the increase in energy from the dimethylamine to the diethylamine compound may be associated with the expected increased amount of π-bonding to arsenic.

Bending Modes.—A band at *ca.* 680 cm^{-1} occurs in the majority of the spectra, but in phenyl substituted compounds, it is found as a shoulder on a stronger phenyl mode. However, the first overtone at *ca.* 1350 cm^{-1} for most compounds provides confirmatory evidence. The band has usually been assigned to the out-of-plane deformation (π_{NNN}) [2,17] but, as found by Müller [5] for azidodimethylarsine, it is polarized for both the dimethyl and diethyl compounds. This could arise if the molecules had structures without a mirror plane but a more likely alternative is that bands at *ca.* 680 cm^{-1} are associated with the in-plane deformation (δ_{NNN}). Polarized lines would be expected here and this alternative has been preferred. The out-of-plane mode is now assigned to the band at *ca.* 570 cm^{-1}, which is observed only in the diphenyl and halogenophenyl compounds due to masking by strong arsenic–carbon stretches in the alkyl derivatives. For azidodimethylarsine, a value of 569 cm^{-1} can be suggested for this mode from a combination band at 1826 cm^{-1} ($\nu_8 + \pi_{NNN}$).

Rotational Isomerism.—The presence of rotational isomers for both diethyl- and ethylphenyl-azidoarsines is indicated by the increased number of arsenic–carbon stretching modes and the complexity of the spectra in regions associated with carbon–carbon stretching (1000—1050 cm^{-1}) and methylene rocking (690—740 cm^{-1}). The relative intensities of the bands for the diethyl compound are similar to those for the chloride [16] and the conclusions for the latter system are probably also valid here.

Thermal Decomposition.—Volatile (type A) organometallic azides, lose two-thirds of the azide nitrogen on pyrolysis and products containing bonds to nitrogen are obtained. The initial pyrolysis product is expected to be a nitrene-like species which in general will not be isolable. Either a rearrangement or polymerization product will be found and, in this respect, the behaviour is similar to that of organic azides. Higher melting (type B) azides give nitrogen-free products on heating. Breaking of the metal–nitrogen bond is probably the first step and the electron deficient organometallic residue may then stabilize, again either by rearrangement or polymerization.

Although thermal decomposition of azidodiphenylarsine gives the cyclic arsenic–nitrogen compound, $Ph_8As_4N_4$,[3] similar products are not obtained with the dialkyl analogues. In these cases, arsenic–nitrogen bond cleavage takes place probably giving $R_2As\cdot$ radicals which dimerize to diarsines which can be isolated in good yield. It is clear that for arsenic azides the mode of decomposition is strongly dependent on the nature of the attached organic groups. This is perhaps not unexpected as the position of arsenic in the Periodic Table puts it near the changeover point from type A to type B azides.

With the azidohalogenoarsines a different decomposition mechanism applies as the appropriate halogenodiphenylarsine can be isolated. This is obtained in admixture with the dihalogenophenylarsine originally present in the starting material. An involatile, nitrogen-containing residue is also produced but due to insolubility, no information is available on its nature. One possible mechanism would involve initial cleavage of the arsenic–nitrogen bond then migration of a phenyl group; a similar mechanism has been proposed for the decomposition of triphenyl-tin and -lead azides.[18] An attractive alternative, however, involves a redistribution of the azidohalide, *i.e.*

$$2PhAs(N_3)X \longrightarrow Ph_2AsX + As(N_3)_2X$$
$$X = Cl \text{ or } Br$$

Although rapid redistribution does not occur until 250—300° with dichlorophenylarsine, the mixed azidohalide will require a lower temperature, the driving force being partly the stability of chlorodiphenylarsine. The nitrogen containing residues, which behave as polymeric materials, would then result from decomposition of the diazide $As(N_3)_2Cl$.

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[17] P. I. Paetzold and H.-J. Hansen, *Z. anorg. Chem.*, 1966, **345**, 79.

[18] W. T. Reichle, *Inorg. Chem.*, 1964, **3**, 402.