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CLEAVAGE REACTIONS OF ARSENIC TRIFLUORIDE WITH ELEMENT–TRIMETHYLSILYL COMPOUNDS

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SUMMARY

In the reactions of compounds of the types Me_3SiNR_2, Me_3SiOR, Me_3SiSPh, $(Me_3Si)_2NH$, $(Me_3Si)_2NR$, $(Me_3SiNMe)_2CO$, $(Me_3SiO)_2$-*o*-C_6H_4, and $(Me_3Si)_3N$ with arsenic trifluoride, cleavage of the element–silicon bond was observed. Formation of an arsenic–element bond took place in all cases, and the trimethylsilyl group was released in the form of trimethylfluorosilane. Arsenic pentafluoride reacted in a similar manner but, owing to further reactions (especially reduction of $As^{V} \rightarrow As^{III}$) defined products were not normally obtained.

Mono-trimethylsilyl-substituted compounds gave rise to the corresponding $-AsF_2$ derivatives, while some unusual products were obtained from bis- or tris-trimethylsilyl precursors.

^1H and ^{19}F NMR spectroscopy have been used in the characterization of the products obtained.

INTRODUCTION

The cleavage of element–silicon bonds by compounds exhibiting Lewis acid properties such as fluorophosphoranes, R_nPF_{5-n}(n=0, 1, 2, 3), phosphoryl fluoride POF_3, or thiophosphoryl fluoride, PSF_3, has provided a facile means of attaching heteroatoms to phosphorus[1,2]. This versatile preparative method has also been applied to the synthesis of substituted derivatives of sulfur tetrafluoride, SF_4[3], and sulfur oxytetrafluoride, SOF_4[4].

The Lewis acid character of arsenic trifluoride has been established for some time, *e.g.* by the observation of the addition of fluoride ion to AsF_3 with formation[5,6] of tetrafluoroarsenite, $[AsF_4]^-$. It thus seemed worthwhile to explore the

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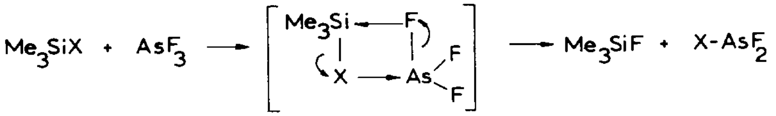
derivative chemistry of arsenic trifluoride by studying its reactions with various element–silicon compounds. Furthermore, this study was extended to arsenic pentafluoride, whose strong acceptor properties are well known.

RESULTS AND DISCUSSION

Arsenic trifluoride was allowed to react with a series of element–trimethylsilyl compounds of types $Me_3Si–X$ (where $X = NMe_2$, NEt_2, OMe, OEt, OPh, SPh), $(Me_3Si)_2Y$ ($Y = NH$, NMe, NPh, $C_6H_4O_2$ = catechol, $OC(NMe)_2$ = *N*, *N'*-dimethylurea), and $(Me_3Si)_3N$.

Invariably, cleavage of the Si–X bond was observed, while the Me_3Si group was released in the form of trimethylfluorosilane. It appears reasonable to formulate the reaction as proceeding via the breakdown of a Lewis acid–base intermediate *via* a four-centered mechanism,



There is precedent for AsF_3 (and AsF_5) functioning as Lewis acids towards organic bases, and defined 1 : 1 adducts are known[7]. Since the Lewis acid character of AsF_3 is more pronounced than that of PF_3, it was to be expected and confirmed that the reactions would proceed readily and in a defined fashion with high yields. By contrast, it was not possible, under the reaction conditions employed by us, to effect substitution of fluorine atoms in arsenic pentafluoride. We found that the expected cleavage of the element–silicon bond was accompanied by reduction of AsF_5, *viz.*

$$Me_3SiF + AsF_5 \rightarrow Me_2SiF_2 + AsF_3 + MeF$$

The arsenic trifluoride thus formed may then also react with the Me_3SiX employed, with the formation of the products described below.

Mono-substituted derivatives of AsF_3 of the types R_2NAsF_2 and $ROAsF_2$ ($R = Me$, Et) were readily obtained from the respective dialkylamino- or alkoxysilanes,

$$R_2NSiMe_3 + AsF_3 \rightarrow R_2NAsF_2 + Me_3SiF$$
$$ROSiMe_3 + AsF_3 \rightarrow ROAsF_2 + Me_3SiF$$

Representatives of both types of compound had already been obtained in the dialkylaminolysis of AsF_3[8], and in the reaction of arsenic acid esters with AsF_3[9],

$$(RO)_3AsO + AsF_3 \rightarrow \text{“}(RO)_2As(O)F\text{”} + ROAsF_2$$

Dialkylamino- and alkoxy-difluoroarsines were obtained as colorless, readily-distillable liquids which are very susceptible to hydrolysis. In the reaction of $EtOSiMe_3$ with AsF_3 the monofluoro-derivative, $(EtO)_2AsF$, was also detected.

A different course of reaction was observed when phenoxy- and phenylthiotrimethylsilyl ether were allowed to react with AsF_3. Regardless of the ratio of the reactants, the fully-substituted derivatives of arsenous acid were obtained,

$$3PhYSiMe_3 + AsF_3 \rightarrow (PhY)_3As + 3Me_3SiF$$
$$(Y = O, S)$$

If the molar ratio $PhYSiMe_3 : AsF_3$ was decreased, unreacted AsF_3 was detected after completion of the reaction. Both $(PhO)_3As$ and $(PhS)_3As$ were identified by comparison with authentic samples prepared by different routes[10,11]. All the compounds were also characterized by ^1H and ^{19}F NMR spectroscopy; the data are listed in Table 3.

While the reactions of AsF_3 with trimethylsilyl derivatives of the type Me_3SiX are straightforward, the situation is more complex when trimethylsilyl compounds of the types $(Me_3Si)_2Y$ and $(Me_3Si)_3N$ are employed. In these cases more complicated products were obtained. Thus, the products formed in the reaction of AsF_3 with both hexamethyldisilazane and tris-(trimethylsilyl)amine were found to be identical by their IR spectra. No conclusive identification was possible. Analyses were not very well reproducible, but seem to point to an approximate composition $[FAsNH]_n$. The products were highly intractable, insoluble in all common solvents without decomposition, did not melt and were decomposed only at very high temperatures. The apparently polymeric, purely inorganic products both form ammonia upon treatment with aqueous alkali hydroxide.

The reactions of *N*-substituted hexamethyldisilazanes, $RN(SiMe_3)_2$ ($R = Me$, Ph) proceeded in a more defined fashion.

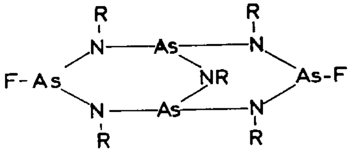
$$5RN(SiMe_3)_2 + 4AsF_3 \rightarrow As_4(NR)_5F_2 + 10Me_3SiF$$

While the *N*-methyl derivative was recovered by distillation from the reaction mixture, the *N*-phenyl compound was precipitated in the course of the reaction.

Nöth and Vetter have observed that arsenic trichloride reacts with methylamine with formation of an adamantane-type compound, $As_4(NMe)_6$ [12],

$$4AsCl_3 + 18MeNH_2 \rightarrow As_4(NMe)_6 + 12(MeNH_3)Cl$$

It thus appeared possible that in our reactions the same type of compound, $As_4(NR)_6$ ($R = Me$, Ph) might be formed. Actually, we have obtained the bicyclic ring system of *N*-pentamethyl(or pentaphenyl)-penta-aza-(2,2′-difluoro)-tetra-arsa-(3,3,1)bicyclononane which may be represented by



(R = Me, Ph)

TABLE 1

REACTIONS OF ARSENIC TRIFLUORIDE WITH Si–N COMPOUNDS

Compound	Reactants (moles)		Reaction conditions (h/°C)	Yield (%)	B.p. or M.p. (°C/mm)	Analyses
Me_2NAsF_2	Me_2NSiMe_3 AsF_3	(0.11) (0.1)	1/30[a]	88	45–47/42	Calc. F, 24.2. Found F, 24.1.
Et_2NAsF_2	Et_2NSiMe_3 AsF_3	(0.11) (0.1)	1/30[a]	83	41–42/20	Calc. F, 20.5. Found F, 22.2.
$As_4(NMe)_5F_2$ (nc)	$MeN(SiMe_3)_2$ AsF_3 in benzene	(0.2) (0.4) (20 ml)	1/30[a]	82.5	142–145/0.3, m.p. 60–63	Calc. C, 12.4; H, 3.3; As, 62.0; F, 7.9. Found C, 12.5; H, 3.3; As, 61.6; F, 7.5. Calc. N, 14.5[b]. Found N, 14.5.
$As_4(NPh)_5F_2$ (nc)	$PhN(SiMe_3)_2$ AsF_3 in benzene	(0.1) (0.2) (20 ml)	1/reflux	97	m.p. 245–247	Calc. C, 45.4; H, 3.2; As, 37.8; F, 4.8. Found C, 44.2; H, 2.7; As, 38.5; F, 4.1. Calc. N, 8.9[c]. Found N, 8.2.
$As_2(NMe \cdot CO \cdot NMe)_3$ (nc)	$OC(NMe \cdot SiMe_3)_2$ AsF_3 in benzene	(0.1) (0.1) (40 ml)	1/reflux	90	m.p. 185–190	Calc. C, 26.4; H, 4.4; As, 20.6. Found C, 24.2; H, 4.4; As, 19.8.

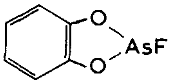
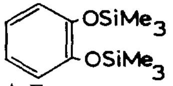
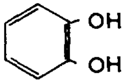
[a] Exothermic reaction.

[b] Mol. wt. (cryoscopically in benzene): calc. 483.8, found 458.

[c] Mol. wt. (cryoscopically in nitrobenzene): calc. 793, found 786.

TABLE 2

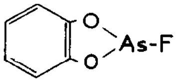
REACTION OF ARSENIC TRIFLUORIDE WITH Si–O AND Si–S COMPOUNDS

Compound	Reactants (moles)		Reaction conditions (h/°C)	Yield (%)	B.p. (°C/mm)	M.p. (°C)	Analyses
MeOAsF$_2$	MeOSiMe$_3$ AsF$_3$	(0.11) (0.1)	1/30^a	81	60–62/760	—	Calc. F, 26.4. Found F, 27.0.
EtOAsF$_2$	EtOSiMe$_3$ AsF$_3$	(0.11) (0.1)	1/30^a	62	70–72/760	—	Calc. F, 24.0. Found F, 23.7.
(EtO)$_2$AsF (nc)	By-product in the preceding reaction			26	30–31/12	—	Calc. F, 10.3. Found F, 11.2.
(PhO)$_3$As	PhOOSiMe$_3$ AsF$_3$	(0.11) (0.1)	2 (reflux)^{b,c}	78	156/0.2	31	—
 (nc)	 AsF$_3$	(0.15) (0.15)	1 (reflux)	98	—	145–147	Calc. C, 35.7; H, 2.0; F, 9.4^d. Found C, 36.0; H, 1.7; F, 8.3.
	 AsF$_3$ in benzene	(0.2) (0.3) (60 ml)	6 (reflux)	^{e}	—	143–151	Calc. C, 35.7; H, 2.0; F, 9.4^f. Found C, 35.9; H, 2.1; F, 9.2. Calc. As, 37.0. Found As, 37.4.
(PhS)$_3$As	PhSSiMe$_3$ AsF$_3$	(0.11)^{a,c} (0.1)	1/30^a	^{c}	—	92	^{g}

[a] Exothermic reaction.
[b] Reaction commenced upon heating to reflux temperature.
[c] Unreacted AsF$_3$ was recovered upon work-up.
[d] Mol. wt. (determined cryoscopically in benzene): calc. 202, found 206.
[e] The yield was not determined in this experiment.
[f] Mol. wt. (determined cryoscopically in benzene): calc. 202, found 198.
[g] The compound was identified by determining a mixed melting point (without depression) with an authentic sample.

TABLE 3

^{1}H AND ^{19}F NMR DATA FOR As–F DERIVATIVES

Compound	δ_H (ppm)	δ_F (ppm)
Me_2NAsF_2	−2.8	+75.0
Et_2NAsF_2	−1.10 −3.25	+82.0
$MeOAsF_2$	−3.85	+68.0
$EtOAsF_2$	−1.30 −4.20	+65.5
$(EtO)_2AsF$	−1.25 −4.20	+67.0
	—	+50.1 [a]

[a] Spectrum recorded in benzene solution.

A compound of identical composition, $As_4(NR)_5F_2$ ($R = i\text{-}C_3H_7$) has been reported by Hass and Cech to be formed in the following reaction[13],

$$4AsF_3 + 8Pr^iNH_2 \rightarrow [FAsNPr^i]_4 + 4[RNH_3][HF_2]$$
$$5[FAsNPr^i]_4 \rightarrow 4As_4(NPr^i)_5F_2 + 4AsF_3$$

The same compound was obtained upon equilibration of a mixture of $As_4(NPr^i)_6$ and AsF_3 or upon fluorination of $As_4(NPr^i)_5I_2$ with silver fluoride[13].

Our compounds, $As_4(NR)_5F_2$, are colorless, crystalline solids which are very sensitive to hydrolysis. The methyl derivative is very soluble, for example, in benzene but less soluble in ether, while the *N*-phenyl compound is poorly soluble in all common organic solvents.

Besides the characterization by elemental analysis and molecular weight determination, ^{1}H and ^{19}F NMR spectrometry were employed in order to determine structure and conformation of the compounds. The spectra were found to be more complex than anticipated, and did not allow structure and conformation to be determined conclusively. Theoretically ten conformers may be postulated for three possible isomers. For steric reasons some of these conformations may be excluded but the spectra were still too complex to allow assignment to be made. In the case of $As_4(NMe)_5F_2$, dissolved in dichloromethane, benzene, or cyclohexane, no change was observed in the ^{1}H NMR spectra between −80 and +70°. Different solvents, however, caused variations in the ^{1}H NMR spectra. Thus, a complex pattern of lines was observed in the ^{1}H spectrum in the region −2.6 to −3.06 ppm, ^{19}F resonances in the region +90 to +98 ppm (benzene was the solvent in both cases).

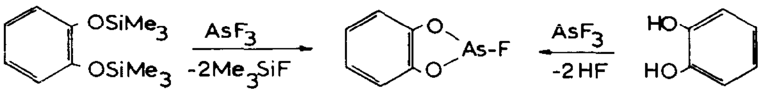
In order to permit a spectral comparison, the compound $As_4(NMe)_5I_2$ was synthesized from $As_4(NMe)_6$ and AsI_3; the same compound had also been obtained through the methylation of $As_4(NMe)_6$ with methyl iodide[12],

$$As_4(NMe)_6 + 3MeI \rightarrow As_4(NMe)_5I_2 + [Me_4N]I$$

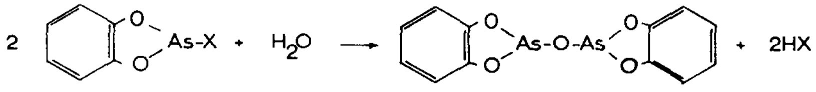
Because there is no H–F coupling in the iodide, the ^1H spectrum should be simplified, compared to $As_4(NMe)_5F_2$. The expected simplification was indeed achieved, and two broad single peaks (δ_H −2.59 and −3.26 ppm from TMS) were observed for a solution of $As_4(NMe)_5I_2$ in benzene. At −80° (dichloromethane solution) only a shift of the peak at −2.59 ppm to −2.83 ppm was observed (relative intensity ratio (δ_H −2.83:δ_H −3.26) *ca.* 4:1). There was no splitting, as in the case of $As_4(NMe)_5F_2$.

The investigation of the reaction of fluorophosphoranes, R_nPF_{5-n} ($n = 0$, 1, 2, 3) with catechol bis-trimethylsilylether gave rise to a series of heterocyclic derivatives, containing 5-coordinate phosphorus as part of a five-membered ring system[14].

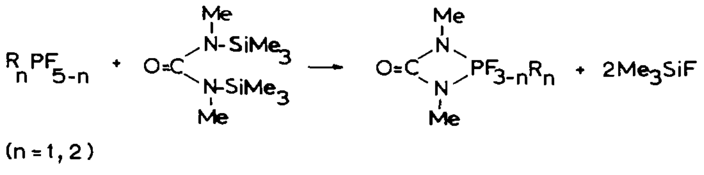
When AsF_3 was allowed to react with the silyl ether, a heterocyclic derivative of trivalent arsenic was obtained which was also accessible *via* the direct reaction of catechol with AsF_3. Because of the formation of HF in the latter reaction it had to be conducted in a metal reactor, while the reaction based on the silyl ether was carried out in ordinary glass apparatus,



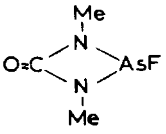
$C_6H_4O_2AsF$, like its known chloro analogue, $C_6H_4O_2AsCl$, could be converted to the known compound $(C_6H_4O_2As)_2O$[15] when exposed to the moist atmosphere or upon controlled hydrolysis,



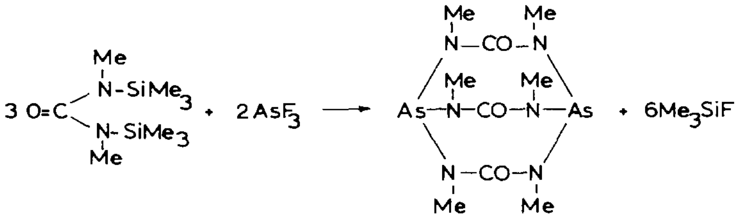
In the reaction of fluorophosphoranes with *N*,*N*′-bis-trimethylsilylurea, derivatives of the phosphadiazetidinone ring system could be obtained[16], *viz.*



It was thought that an analogous ring system involving arsenic, *i.e.*



could be obtained when AsF_3 instead of the fluorophosphoranes was employed. Upon reaction of AsF_3 with *N,N'*-bis-trimethylsilylurea in a 1:1 molar ratio, one third of the AsF_3 was recovered. Thus, the stoichiometry could not be as anticipated. The product was characterized by elemental analysis, molecular weight determination, and ^1H NMR spectroscopy, a single peak at -2.9 ppm from TMS being observed. The product was found to be free of fluorine, and the following course of reaction is suggested,



There is apparently less strain in the symmetric, bicyclic system than in the four-membered ring compound. While the compound is readily formed and thermally stable, it reacts rapidly with moisture to give As_4O_6 and *N,N'*-dimethylurea.

A mass spectrum of the product did not show a molecular ion peak. The fragment of highest mass observed (at *m/e* 391 ±2) may correspond to loss of a CH_3 group from the parent molecule.

EXPERIMENTAL

Reactions with arsenic trifluoride

All reactions of arsenic trifluoride with element–trimethylsilyl compounds were conducted in a similar fashion as follows:

Arsenic trifluoride was placed in a three-necked flask, fitted with thermometer, pressure-equalizing dropping funnel, reflux condenser and magnetic stirrer. This apparatus was carefully flushed with dry nitrogen. The silyl compound (neat in the case of Me_3SiX, dissolved in benzene in the case of $(Me_3Si)_2Y$ and $(Me_3Si)_3N$) was then added drop-wise at such a rate that an inner temperature of 30° was not normally exceeded, external cooling being invariably required.

A trap cooled to −78° was connected to the reflux condenser and protected from atmospheric moisture by means of a drying tube. Trimethylfluorosilane Me_3SiF, formed during the reaction, was collected in the trap and determined quantitatively. The reactions were brought to completion by heating at reflux for a 1–2 h period.

Purification of the reaction products was by either distillation, recrystallization, or sublimation. Further details are contained in Tables 1 and 2.

Reactions with arsenic pentafluoride

These reactions were conducted in Monel cylinders containing the trimethylsilyl compound on to which AsF_5 was condensed *via* a vacuum line. The reaction vessel was cooled to liquid nitrogen temperature during this operation, the temperature being subsequently allowed to reach first −78° and then room temperature.

Volatile products formed in the reactions were collected in a trap cooled with liquid nitrogen and their weight determined. In all cases it was found that volatile products consisted largely of dimethyldifluorosilane, Me_2SiF_2 (δ_F + 130 ppm), with only a few percent of trimethylfluorosilane, Me_3SiF (δ_F + 156 ppm) being present.

In order to study the apparent reaction of AsF_5 with Me_3SiF, approximately equimolar quantities of both compounds were sealed into a quartz NMR tube. Observation of the ^{19}F NMR spectra after a 24 h reaction period showed the following compounds: δ_F + 135.5 ppm, $MeSiF_3$ (Ref. 17); δ_F + 43.5 ppm (singlet), AsF_3[18]; δ_F + 268.0 ppm, J(F–H) 46 Hz (quartet), MeF (Ref. 19). Neither Me_2SiF_2 nor SiF_4 were observed. The presence of $MeSiF_3$ and MeF was further confirmed by their ^1H NMR spectra, δ_H −4.3 ppm, J(H–F) 46.1 Hz (doublet), MeF; δ_H −0.3 ppm, J(H–F) 5.1 Hz (quartet), $MeSiF_3$.

Because of the ease of reduction of AsF_5 thus demonstrated, its reactions with element–trimethylsilyl compounds were not followed up in more detail.

Conversion of $C_6H_4O_2AsF$ to the arsenoxane, $(C_6H_4O_2As)_2O$

A sample of $C_6H_4O_2AsF$ was stored in the atmosphere for 5 weeks. The crude product thus obtained was purified by recrystallization from benzene–petroleum ether. It had a melting point of 150–150.5°. Its IR spectrum was identical to that of the compound $(C_6H_4O_2As)_2O$, prepared by Kamai and Khisamova[15] from $C_6H_4O_2AsCl$ and dimethylamine in the presence of moist air (reported[15] m.p. 147°; found 152–153°).

The arsenoxane was prepared by adding *ca.* 10 g (*ca.* 0.22 mole) of dimethylamine, dissolved in 150 ml of benzene, to a solution of 10.9 g (0.05 mole) of $C_6H_4O_2AsCl$ in 60 ml of benzene during 30 min. The mixture was stirred for another 30 min, filtered, and partially evaporated on a steam bath after the addition of activated carbon, and filtered again. Upon addition of petroleum ether, faintly yellow crystals of melting point 145–147° were obtained which became colorless after a second crystallization from benzene–petroleum ether; m.p. 152–153°. (Found: C, 37.7; H, 2.0; mol. wt. (cryoscopically in benzene) 370. $(C_6H_4O_2As)_2O$ requires C, 37.7; H, 2.1; mol. wt. 382.)

NMR spectra

A Varian HA-60 and a Perkin–Elmer R10 spectrometer were used to obtain ^1H and ^{19}F NMR spectra at 60 and 56.4 MHz, respectively (spinning tubes were used throughout; diameter 5 mm on the HA-60, 4.6 mm on the R10). Tetramethylsilane and trichlorofluoromethane served as internal standards for ^1H and ^{19}F measurements, respectively.

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