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REACTIONS OF XENON DIFLUORIDE. PART 6. SOME REACTIONS OF PHOSPHORUS, ARSENIC AND IODINE COMPOUNDS

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SUMMARY

The reaction of XeF_2 with some organo-phosphorus, -arsenic and -iodine compounds is described. The products were identified by fluorine nmr spectroscopy and the conditions under which fluorine exchange occurs were briefly investigated. Organoiodine(III) difluorides are suitable for the conversion of Ph_2Te to Ph_2TeF_2; the decomposition of RIF_2 liberates IF and fluoroalkane.

RESULTS AND DISCUSSION

As a continuation of our studies of the reaction of XeF_2 with main group compounds [1], we have carried out reactions with some organo-phosphorus, -arsenic and -iodine compounds, and briefly studied the conditions under which fluorine exchange occurs.

The reaction of XeF_2 with $MePh_2P$ and $MePh_2As$ in acetonitrile produced $MePh_2PF_2$ and $MePh_2AsF_2$, respectively, while reaction with 2-$MeC_6H_4P(NEt_2)_2$ gave 2-$MeC_6H_4PF_2(NEt_2)_2$.

$$MePh_2M + XeF_2 \longrightarrow MePh_2MF_2 + Xe \quad (M = P,As)$$

$$2\text{-}MeC_6H_4P(NEt_2)_2 + XeF_2 \longrightarrow 2\text{-}MeC_6H_4PF_2(NEt_2)_2 + Xe$$

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The reaction of XeF_2 with alkyl and aryl iodides [5,6] was extended to CF_3CH_2I, $3,5\text{-}Cl_2C_6H_3I$ and $2\text{-}CF_3C_6H_4I$ and, in each case, the corresponding alkyl(aryl)iodine(III) difluoride was formed and identified by ^{19}F nmr. Excess XeF_2 converted

$$RI + XeF_2 \longrightarrow RIF_2 + Xe$$

$$(R = CF_3CH_2\text{-},\ 3,5\text{-}Cl_2C_6H_3\text{-},\ 2\text{-}CF_3C_6H_4\text{-})$$

$3,5\text{-}Cl_2C_6H_3IF_2$ to $3,5\text{-}Cl_2C_6H_3IF_4$.

Oxidative-fluorination of Ph_2Te with $CF_3CH_2IF_2$ or $MeIF_2$ gave Ph_2TeF_2. The latter compound may also be prepared from XeF_2 and Ph_2Te [1].

The finding that $MeIF_2$ is a source of IF [7] was confirmed by carrying out the decomposition of $MeIF_2$ in the presence of

$$MeIF_2 \longrightarrow MeF + IF \xrightarrow{Ph_2C=CH_2} Ph_2CFCH_2I$$

a trapping agent $Ph_2C=CH_2$ and identifying the product Ph_2CFCH_2I [8].

There is no nmr evidence of intermolecular fluorine exchange in freshly prepared samples of $MeIF_2$, nor is there fluorine exchange between $MeIF_2$ and excess XeF_2, however, the ^1H nmr triplet of $MeIF_2$ does collapse to a single peak after a variable induction period of 30-60 min at 20°C, or in the presence of small amounts of HF or H_2O, or if $MeIF_2$ is stored in glass apparatus.

The reaction of XeF_2 with sulfides [9,10] was extended to 4-methylphenyl sulfide which resulted in α-fluorination, rather than oxidative-fluorination.

$$4\text{-}MeC_6H_4SCH_3 + XeF_2 \longrightarrow 4\text{-}MeC_6H_4SCH_2F + HF + Xe$$

Occasionally, an impurity-catalyzed exchange process could be detected in samples of $MePh_2PF_2$, which resulted in loss of P-F coupling, but this reversible process could be stopped by lowering the temperature to -63°C.

In most instances, samples of $MePh_2AsF_2$ showed no evidence, based on ^1H and ^{19}F nmr, of intermolecular fluorine exchange, however, treating $MePh_2AsF_2$ with a solution of HF in CD_3CN changed the ^1H nmr methyl triplet into a broad single peak. This exchange process, which may be attributed to rapid As-F bond cleavage, is reversible and can be slowed down by lowering the temperature to -33°C, whereupon the triplet is again observed. Addition of a small amount of water to $MePh_2AsF_2$ also changed the ^1H nmr methyl triplet into a single peak.

On the basis of previous studies of impurity-catalyzed fluorine exchange [2-4], it seemed possible that HF or H_2O could generate either 6-coordinate $MePh_2AsF_3^-$ or 4-coordinate $MePh_2AsF^+$, and these species might then be responsible for exchange in samples of $MePh_2AsF_2$.

As an indirect test for the presence of $MePh_2AsF_3^-$, tetrabutylammonium fluoride was added to $MePh_2AsF_2$, but no exchange was initiated. Similarly, adding KF in 18-crown ether to $MePh_2AsF_2$ did not lead to fluorine exchange, thus suggesting that $MePh_2AsF_3^-$ is not involved in the exchange process.

Treating $MePh_2AsF_2$ with PF_5 or BF_3 resulted in the immediate appearance of PF_6^- or BF_4^- in the ^{19}F nmr and the disappearance of the $MePh_2AsF_2$ signal. The $MePh_2AsF^+$ cation, presumably formed in this reaction, could not be directly observed by nmr, but its presence was confirmed by chemical means, namely by adding NaF or CsF, which stopped exchange and resulted in the re-appearance of the $MePh_2AsF_2$ signal. Therefore the exchange process observed by nmr in samples of $MePh_2AsF_2$ when HF, H_2O, PF_5 or BF_3 is added, is assigned to the following rapid equilibrium:

$$MePh_2AsF_2 + MePh_2AsF^+ \rightleftharpoons MePh_2FAs\text{-}F\text{-}AsFPh_2Me^+$$

EXPERIMENTAL

^{1}H and ^{19}F nmr spectra were recorded on a Bruker WH90 spectrometer at 90 and 84.66 MHz. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Reaction of XeF_2 with $MePh_2As$

A solution of XeF_2 (0.64 mmol) in acetonitrile (1 mL) in a syringe was added slowly (about 20 min) to a stirred solution of $MePh_2As$ (0.69 mmol) in acetonitrile (2 mL) held at -20°C in a polytetrafluoroethylene bottle. The reaction mixture was allowed to warm to 20°C and stirred for an additional 20 min. Removal of solvent under vacuum left a white solid which was purified by recrystallization from benzene/n-hexane and identified as $MePh_2AsF_2$ on the basis of its ^{19}F nmr [11]. (Found: C, 55.18; H, 4.73; F, 13.25. $C_{13}H_{13}AsF_2$ requires: C, 55.34; H, 4.64; F, 13.47%).

Reaction of XeF_2 with Phosphorus and Iodine Compounds

The general reaction procedure described for $MePh_2As$ was used for the reactions described below.

The reaction of XeF_2 with $MePh_2P$ gave $MePh_2PF_2$, identified by ^{19}F nmr [12] and by its hydrolysis to $MePh_2P{=}O$.

Reaction of XeF_2 with 2-$MeC_6H_4P(NEt_2)_2$ gave 2-$MeC_6H_4PF_2$-$(NEt_2)_2$: ^{19}F nmr (CD_2Cl_2) -43.2 ppm, J(FP) = 716 Hz.

Reaction of XeF_2 (89 mg, 0.52 mmol) with CF_3CH_2I (115 mg, 0.54 mmol) in acetonitrile/chloroform (2 mL), with stirring at 20°C for 2 days gave $CF_3CH_2IF_2$: ^{19}F nmr -175(IF_2) ppm, -62.9 (CF_3) ppm.

Reaction of XeF_2 (0.12 g, 0.71 mmol) with 3,5-$Cl_2C_6H_3I$ (0.20g, 0.72 mmol) in chloroform (3 mL) with stirring at 20°C for 2 days gave 3,5-$Cl_2C_6H_3IF_2$: ^{19}F nmr ($CDCl_3$) -175 ppm. Further oxidative-fluorination occurred when a 1:1 mixture of XeF_2 and 3,5-$Cl_2C_6H_3IF_2$ was kept in $CHCl_3$ at 20°C for 10 days with stirring, to give 3,5-$Cl_2C_6H_3IF_4$: ^{19}F nmr -16 ppm.

Reaction of XeF_2 with $2\text{-}CF_3C_6H_4I$ gave $2\text{-}CF_3C_6H_4IF_2$: ^{19}F nmr -173 ppm.

The decomposition of $MeIF_2$ in acetonitrile at 20°C was carried out in the presence of 1,1-diphenylethene and the products were Ph_2CFCH_2I, identified by ^{19}F and ^{1}H nmr [8], and CH_3F, identified by ^{19}F nmr and ms. Ph_2CFCH_2I was found to be stable after purification.

Reaction of $MePh_2AsF_2$ with PF_5 and BF_3

PF_5 (0.5 mmol) was condensed onto a solution of $MePh_2AsF_2$ in acetonitrile (0.5 mL) in an nmr tube at -196°C. The reaction mixture was then kept at 20°C for 2 h, after which excess PF_5 was removed and the nmr tube sealed. The ^{19}F nmr showed the presence of PF_6^-, but the peak due to $MePh_2AsF_2$ was not observed. On adding excess NaF, and after several days at 20°C, $MePh_2AsF_2$ was recovered in about 50% yield.

In a similar experiment, the BF_4^- anion was observed after adding BF_3 to $MePh_2AsF_2$.

Reaction of $CF_3CH_2IF_2$ and $MeIF_2$ with Ph_2Te

Ph_2Te (0.31 mmol) was added to $CF_3CH_2IF_2$ (0.42 mmol) in acetonitrile and the reaction mixture stirred at 20°C for 1 h until the yellow colour of Ph_2Te disappeared. The product Ph_2TeF_2 was identified by ^{19}F nmr [13]. A similar reaction occurred immediately with freshly prepared $MeIF_2$ to give Ph_2TeF_2.

Reaction of XeF_2 with $4\text{-}MeC_6H_4SCH_3$

XeF_2 (0.12 g, 0.71 mmol) was added to $4\text{-}MeC_6H_4SCH_3$ (0.10 g, 0.72 mmol) in $CDCl_3$ (1 mL) at -20°C, warmed to 20°C and stirred for 1 h. After addition of $(Me_3Si)_2NH$ to remove HF [2], the product $4\text{-}MeC_6H_4SCH_2F$ was identified by nmr: ^{19}F nmr -183 ppm, J(FH) = 52.9 Hz, ^{1}H nmr 5.6 ppm.

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