REACTION OF HEXAFLUOROACETONE WITH SOME ARSENIC COMPOUNDS

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INTRODUCTION

Previous work on the reactions of fluorinated ketones with Group V compounds has been largely confined to the addition of the ketones to the N–H bonds of ammonia[1], amines[2], amides and ureas[3].

$$RCONH_2 + (CF_3)_2CO \longrightarrow RCONHC(CF_3)_2OH$$

Some work has been done on the reactions of fluorinated ketones with trialkyl phosphites[4] and the products vary with the ketone as is shown in the following examples:

$$(C_2F_5)_2CO + P(OCH_3)_3 \longrightarrow C_2F_5C(OCH_3){=}CFCF_3 + FP(O)(OCH_3)_2$$

$$(ClF_2C)_2CO + P(OC_2H_5)_2 \longrightarrow C_2H_5Cl + (C_2H_5O)_2P(O)OC(CF_2Cl) = CF_2$$

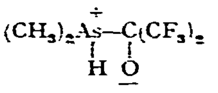
In the present paper some reactions of hexafluoroacetone with arsenic compounds are described.

RESULTS AND DISCUSSION

Hexafluoroacetone reacts readily with dimethylarsine to give the expected arsinopropanol, b.p. 124 ± 0.5°, in good yield.

$$(CH_3)_2AsH + (CF_3)_2CO \longrightarrow (CH_3)_2AsC(CF_3)_2OH$$

The structure of the product is best shown by its ^1H NMR spectrum of only two sharp peaks. This is in contrast with the adducts of the Group IV hydrides in which the oxygen is bonded to the central atom[5]. The difference in reaction products can be explained on a mechanistic basis by assuming that the arsenic hydride reactions proceed by nucleophilic attack by the arsenic lone pair on the highly electrophilic carbon atom of the carbonyl group to form a four-coordinated intermediate:



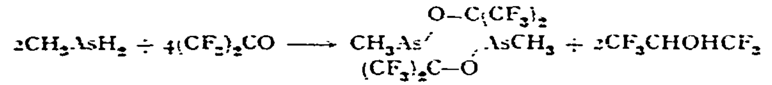
$$(CH_3)_2\overset{+}{\underset{\displaystyle H}{\overset{}{As}}}\!-\!\underset{\displaystyle \underline{O}}{C}(CF_3)_2$$

The Group IV hydride reactions probably involve nucleophilic attack by the carbonyl oxygen.

Methylarsine also reacts very readily with hexafluoroacetone and when excess arsine is used the main product, in high yield, is 2-(methylarsino)hexafluoro-2-propanol, b.p. 117 ± 2°.

$$CH_3AsH_2 + (CF_3)_2CO \longrightarrow (CH_3)HAsC(CF_3)_2OH$$

Further reaction of the remaining As–H bond is much slower, since even in the presence of excess hexafluoroacetone the 1:1 product can be isolated in 47% yield after one day at 20°. This slower reaction is presumably because the electronegative $-C(CF_3)_2OH$ group decreases the availability of the arsenic lone pair. Nevertheless, the 1:1 product reacts completely with hexafluoroacetone eventually to give an unidentified unstable colorless solid which is insoluble in the ketone. A considerable amount of 1,1,1,3,3,3-hexafluoropropanol is also obtained indicating that the main reaction may be represented as follows:



Adams and Palmer[6] have found that phenylarsine reacts with aldehydes in this way.

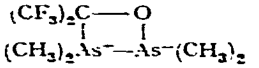
Hexafluoropropanol, a compound recently prepared by reducing the ketone with either lithium aluminum hydride or hydrogen in the presence of a platinum catalyst[7], is also obtained in lower yields from the reactions of dimethylarsine and methylarsine with hexafluoroacetone.

Hexafluoroacetone and tetramethyldiarsine react to give a compound in which there are two sets of inequivalent methyl groups and in which the trifluoromethyl groups are equivalent, as shown by NMR spectroscopy. The chemical shifts in hexafluoroacetone as solvent are markedly dependent on the concentration. Continual pumping on a hexafluoroacetone–diarsine solution which initially contained excess hexafluoroacetone results in the gradual loss of the ketone and the appearance of uncomplexed diarsine. Thus the ^{1}H NMR spectrum of such a solution shows the single diarsine peak as well as those assigned to the complex. This ^{1}H spectrum can be duplicated with a ketone–diarsine solution containing excess diarsine. These results indicate that the complex is moderately easily dissociated at 20°.

$$(CH_3)_2As{-}As(CH_3)_2 + (CF_3)_2CO \rightleftharpoons (CH_3)_2As{-}As(CH_3)_2\cdot(CF_3)_2CO$$

Addition of water to the complex results in the liberation of the diarsine and thus it is likely that the adduct still retains an As–As bond. Hexafluoro-2-butyne reacts with tetramethyldiarsine to give an approximately 1:1 mixture of *cis*- and *trans*-$(CH_3)_2AsC(CF_3){=}C(CF_3)As(CH_3)_2$[8]. Formation of a complex between hexafluoroacetone and tetramethyldiarsine probably results in steric restriction about the As–As bond and consequently a different isomer distribution might be expected in the product of the interaction of the butyne with the complex, and indeed this is found. The infrared spectrum of the reaction product is almost identical with that previously described[8] except that the double bond absorption at 6.36 μ is much stronger indicating a predominance of the *cis*-isomer. The ^{19}F NMR spectrum shows that the 24.3 ppm peak is very much enhanced and therefore this peak is assigned to the *cis*-isomer. The isomer distribution in the product as determined by the relative areas of the peaks in the ^{19}F spectrum is 90 % *cis* and 10 % *trans*. When the butyne is reacted with tetramethyldiarsine in the presence of excess hexafluoroacetone the reaction is even more stereospecific resulting in a product which is 94 % *cis*-isomer.

To account for the stereospecific reaction with the butyne, the liberation of diarsine when treated with water, the absence of any carbonyl frequency in the infrared spectrum, and the NMR spectra, the following structure is suggested for the complex:



$$\begin{array}{ll}(CF_3)_2C & \!\!\!\!\text{———}\,O \\ \quad\;\;| & \quad\;\;| \\ (CH_3)_2As^{+} & \!\!\!\!\text{—}As^{-}(CH_3)_2\end{array}$$

Here one arsenic atom is acting as a donor, being four-coordinated, and the other as an acceptor, being five-coordinated if the lone pair occupies one site.

Trimethylarsine forms an adduct with hexafluoroacetone but this seems to be completely dissociated at 20°, it probably has the structure $(CH_3)_3As^+\text{–}C(CF_3)_2O^-$. Chlorodimethylarsine does not form such an adduct possibly because the lone pair is much less available for donation[9]. However, since trivalent arsenic can act as an electron acceptor as in the species $AsCl_4^-$ and AsF_4^- and presumably the diarsine adduct described above, it is possible that in the trimethylarsine adduct the arsenic acts as the acceptor and the carbonyl oxygen as the donor. A similar situation is found in the stable five-coordinated species $(CH_3)_3SnOCH(CF_3)_2\cdot(CF_3)_2CO$ and in the less stable silicon analogue[5].

EXPERIMENTAL

Reactants and products were manipulated using standard vacuum techniques. Reactions were carried out in thick walled Pyrex tubes. All starting materials were prepared by literature methods with the exception of the hexafluoroacetone which was kindly supplied by the Allied Chemical Corporation. ^1H and ^{19}F NMR spectra were run on varian A-60 and H.R.-60 spectrometers. The spectra are reported in parts per million (ppm) downfield from external tetramethylsilane (^1H) and trifluoroacetic acid (^{19}F). Infrared spectra were run on Perkin-Elmer Infracord (reported in μ) and Model 21 (reported in cm^{-1}) instruments. Microanalyses were performed by Dr. ALFRED BERNHARDT, Mülheim, Germany.

Reaction of dimethylarsine with hexafluoroacetone

Dimethylarsine (2.9 g) and the ketone (3.9 g) were left at 20° for one day although a vigorous exothermic reaction took place immediately on mixing. Dimethylarsine (0.2 g) was recovered and some 1,1,1,3,3,3-hexafluoro-2-propanol (0.1 g) (Found: C, 21.4; H, 1.3; F, 67.2; mol. wt. vapor phase, 172. $C_3H_2F_6O$ calcd.: C, 21.4; H, 1.2; F, 67.9 %; mol. wt., 168.) was produced. The infrared spectrum of the propanol showed the following adsorption bands (vapor): 3664 (w), 2990 (vw), 1426 (w), 1380 (s), 1308 (s), 1273 (vs), 1207 (vs), 1112 (vs), 892 (m), 735 (w), 685 (m) cm^{-1}.

The main product was identified as 2-(dimethylarsino)hexafluoro-2-propanol (6.5 g). (Found: C, 22.1; H, 2.7; As, 27.8; F, 42.1. $C_5H_7AsF_6O$ calcd.: C, 22.1; H, 2.6; As, 27.6; F, 41.9 %.) The boiling point was found to be 124 ± 0.5° by extrapolation of the linear log p against $1/T$ plot. The infrared spectrum showed the following bands (vapor): 3635 (m), 3020 (w), 2950 (w), 1428 (m), 1379 (m), 1269 (vs), 1228 (s), 1205 (vs), 1138 (m), 1107 (s), 943 (m), 873 (m), 851 (m), 750 (m), 726 (w), 708 (m) cm^{-1}. The ^1H NMR spectrum showed peaks at 1.16 ppm (CH_3) and 3.52 ppm (OH). The addition of a large excess of hexafluoroacetone shifted the peaks to 1.20 and 3.45 ppm. The ^{19}F spectrum showed one peak at 6.63 ppm. Addition of excess hexafluoroacetone did not produce any further product peaks.

Reaction of methylarsine with hexafluoroacetone

Methylarsine (4.8 g) and hexafluoroacetone (3.3 g) were left at 20° for three hours. Methylarsine (3.3 g) was recovered and the reaction product 2-(methylarsino)-hexafluoro-2-propanol (4.4 g) identified by analysis (Found: C, 18.4; H, 1.8; As, 28.9; F, 44.4. $C_4H_5AsF_6O$ calcd.: C, 18.6; H, 1.9; As, 29.1; F, 44.1 %.) and by its ^1H NMR spectrum of three peaks at 1.22 (CH_3), 3.62 (OH), and 3.6 ppm (As–H), with $J(As–CH_3)–(As–H) = 7.5$ cps. The infrared spectrum of the arsinopropanol showed the following bands (vapor): 3620 (w), 2955 (w), 2925 (vw), 2145 (m), 1424 (w), 1333 (m), 1277 (vs), 1230 (m, sh), 1206 (vs), 1143 (m), 1106 (s), 953 (m), 882 (m), 843 (w), 741 (m), 700 (m) cm^{-1}. Slight decomposition of the compound occurred on measuring its vapour pressure as a function of temperature, consequently the extrapolated boiling point of 117 ± 2° is not very accurate.

In a second experiment methylarsine (3.5 g) and excess ketone (16.9 g) were left at 20° for one day. Hexafluoroacetone (6.2 g) was recovered and 2-(methylarsino)-hexafluoro-2-propanol (4.7 g) of known infrared spectrum had been produced.

Reaction of 2-(methylarsino)hexafluoro-2-propanol with hexafluoroacetone

The arsinopropanol (4.4 g) and the ketone (6.5 g) were left at 20° for 20 days. Hexafluoroacetone (3.6 g) was recovered. The reaction produced 1,1,1,3,3,3-hexafluoropropanol (0.5 g) of known infrared spectrum, and an involatile colorless solid (6.8 g) which was extremely air sensitive and which was not identified.

Reaction of trimethylarsine with hexafluoroacetone

It was found that mixtures of the ketone and trimethylarsine could not be separated by trap-to-trap distillation. The mixture repeatedly stopped in a trap cooled to −78° thus showing much lower volatility than either component separately. The ^1H NMR spectrum of trimethylarsine showed one peak at 0.74 ppm*. A solution of trimethylarsine in excess hexafluoroacetone gave a ^1H spectrum of one peak at 0.44 ppm; the ^{19}F spectrum also showed only one peak.

Reaction of chlorodimethylarsine with hexafluoroacetone

The chloroarsine (3.2 g) and hexafluoroacetone (6.1 g) were immiscible at 20°, and no reaction had occurred after 12 hours at this temperature. The reactants were then heated to 120° for 3 hours, 200° for 15 hours, and 250° for 5 hours without result. Recovery of both reactants was nearly quantitative.

Reaction of tetramethyldiarsine with hexafluoroacetone

Preliminary studies on a mixture of the diarsine and hexafluoroacetone indicated

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* Chemical shifts relative to benzene and water are given in ref. 10.

that they react to produce a non-volatile liquid which is unstable to air. The ^{1}H NMR spectrum of the diarsine consists of one peak at 1.13 ppm*. A mixture of the diarsine and excess hexafluoroacetone (2:7 by volume) results in two peaks of equal area at 0.71 and 0.93 ppm. In a 1:1 molar mixture the two peaks are shifted downfield to 1.07 and 1.30 ppm, the high field peak being a multiplet ($J \approx 0.8$ cps). The ^{19}F NMR spectrum of the diarsine in excess hexafluoroacetone shows two peaks at 1.36 and 7.94 ppm, the high field peak being due to the excess ketone. An infrared spectrum of a mixture of the diarsine (0.65 g) and hexafluoroacetone (0.2 g) showed the following absorption bands (liquid film): 3.35 (w), 3.45 (w), 3.57 (vw), 5.5 (vw), 5.87 (vw), 7.1 (m), 8.05 (vs), 8.5 (vs), 9.05 (vs), 10.25 (m), 10.65 (m), 11.15 (m), 11.78 (m), 12.13 (m), 12.63 (vw), 13.36 (w), 13.57 (w), 13.8 (w), 14.12 (w) μ.

Reactions of the 1:1 diarsine–hexafluoroacetone adduct

(*a*) *With water.* The diarsine (3.1 g) and hexafluoroacetone (9.7 g) were left at 20° for a few hours. The excess ketone was removed by pumping and water was added to the remaining liquid. Tetramethyldiarsine (3.0 g), of known NMR spectrum, was recovered.

(*b*) *With hexafluoro-2-butyne.* Tetramethyldiarsine (2.8 g) and hexafluoroacetone (5.2 g) were left at 20° for a few hours. The excess ketone (2.8 g) was recovered and hexafluoro-2-butyne (13.7 g) was added to the remaining 1:1 adduct. The reactants were left for a few hours at 20° after which hexafluoro-2-butyne (11.5 g) was recovered. The involatile reaction product was identified as mixture of *cis-* and *trans*-2,3-bis(dimethylarsino)hexafluoro-2-butene by means of its known infrared and ^{19}F NMR spectra[8]. The ^{19}F spectrum consisted of two peaks at 24.3 and 26.3 ppm of relative area 10:1.

Reaction of hexafluoro-2-butyne with tetramethyldiarsine in the presence of hexafluoroacetone

Tetramethyldiarsine (3.5 g) and hexafluoroacetone (10 g) were left at 20° for two hours and then 7.5 g of hexafluoro-2-butyne were added. The product of the reaction isolated two days later proved to be a mixture of *cis-* and *trans*-2,3-bis(dimethylarsino)hexafluoro-2-butene, b.p. 98° (15 mm), [lit. 99° (17 mm)[8]] which the ^{19}F NMR spectrum showed to be 94% *cis*-isomer.

ACKNOWLEDGEMENTS

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SUMMARY

Hexafluoroacetone reacts with the arsines $(CH_3)_2AsH$ and CH_3AsH_2 to give the compounds $(CH_3)_2AsC(CF_3)_2OH$ and $CH_3(H)AsC(CF_3)_2OH$ respectively. The ketone also forms a fairly easily dissociated 1:1 complex with tetramethyldiarsine

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* Harris and Hayter[11] gave 1.11 ppm, relative to internal tetramethylsilane, for a chloroform solution.

which reacts with hexafluoro-2-butyne to give a high yield of *cis*-$(CH_3)_2AsC(CF_3)=C(CF_3)As(CH_3)_2$. A cyclic structure is suggested for the complex.

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Note added in proof. Since this article was written, a paper by PARSHAL[12] has appeared describing the reactions of hexafluorocyclobutanone with phosphine to give $(CF_3)_2C(OH)PH_2$ and $[(CF_3)_3P(OH)]_2PH$.

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SHORT COMMUNICATIONS

Zirconium and titanium derivatives of indene and fluorene

Among the π-complexes of the transition metals, the compounds of the type R_2MCl_2, where R = indenyl or fluorenyl and M = Ti or Zr, have to our knowledge, received only a brief mention in patents concerning their use as catalysts in olefine polymerisation[1]. The preparation, properties and IR spectra of these complexes are described in this paper.

Indenyl derivatives of titanium and zirconium

The first step in the preparation of these compounds is similar to that used for the preparation of the dicyclopentadienyl derivatives. Indenylsodium and the anhydrous metal tetrahalide in molecular proportions 2:1 are reacted together in THF. The main difference is the method for isolating the pure product from the reaction mixture; solvent extraction cannot be used in this case owing to the rapidity with which the product decomposes in solution, at least under normal conditions. This separation can readily be effected with good yields by rapid washing of the solid reaction products with water, thus dissolving all mineral compounds present and leaving a pure insoluble residue. Sublimation can also be used, but this gives lower yields owing to partial decomposition.

Fluorenyl derivatives of titanium and zirconium

Metalation of fluorene with sodium in THF leads to very poor yields of the metal derivative. Although lithium[2] and potassium[3] are reported to give 9-fluorenyl metal derivatives in this solvent, their use in the present preparation did not seem to lead to successful results. Metalation via ethyllithium or phenyllithium was also unsuccessful. It was found, however, that the reaction products of potassium with fluorene in diethyl ether, and sodium or potassium in dimethoxyethane[5] can quite satisfactorily be used as intermediates, at least in preparing the zirconium derivative.