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PERFLUOROALKYL ARSENICALS

X. SOME REACTIONS OF SECONDARY ARSINES AND DIARSINES WITH FLUOROOLEFINS[*]

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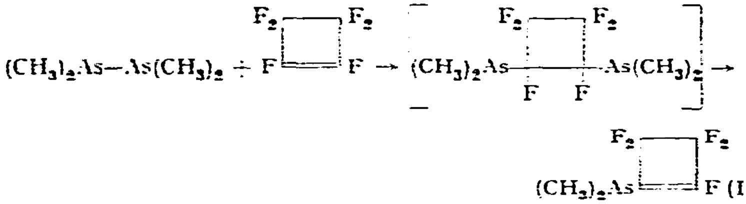
In the work described in Part IX of this series[1] it was found that tetramethyldiarsine and hexafluoropropene afford the 1:1 adduct $(CH_3)_2AsCF_2CF(CF_3)As(CH_3)_2$, but that the same diarsine and hexafluorocyclobutene give 1-(dimethylarsino)pentafluorocyclobutene (I) and fluorodimethylarsine. It was suggested that these products are obtained by elimination of fluorodimethylarsine from an initially formed 1:1 adduct.

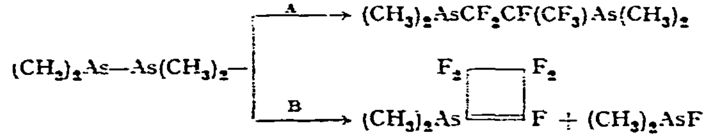


(1)

If the intermediate were formed by *cis* addition, *trans* elimination of the fluoroarsine could account for the products.

RESULTS

Dimethylarsine has now been found to react in an analogous manner with these two fluoroolefins, giving a 1:1 adduct with the propene and (I) with the cyclobutene. However, dimethylarsinomagnesium bromide reacts with both fluoroolefins yielding olefinic products. Methylphenylarsine and perfluorocyclobutene afford 1-(methylphenylarsino)pentafluorocyclobutene (III). These new results and those of Part IX are represented as follows:



(2)

(3)

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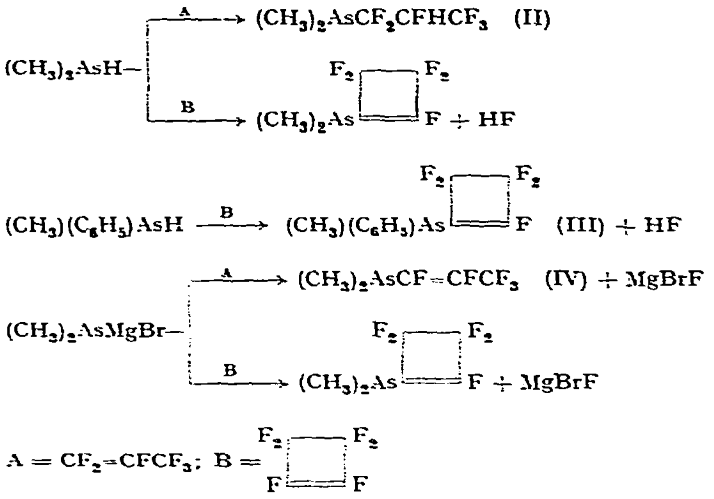
[*] For a preliminary communication see ref. 19. Presented in part at the 3rd Intern. Symp. on Fluorine Chem., Munich, Germany, Sept., 1965.



(4)

(5)

(6)

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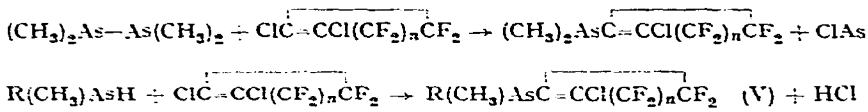
(8)

It has also been found that hydrogen chloride and chlorodimethylarsine can be eliminated from cyclic fluoroolefins in reactions analogous to those of eqns. (3) and (5).



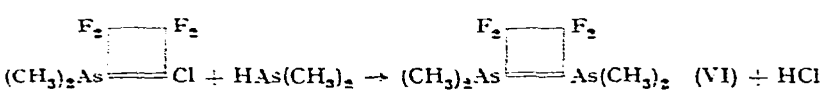
$$(CH_3)_2As{-}As(CH_3)_2 + ClC{=}CCl(CF_2)_nCF_2 \rightarrow (CH_3)_2AsC{=}CCl(CF_2)_nCF_2 + ClAs(CH_3)_2 \quad (9)$$

$$R(CH_3)AsH + ClC{=}CCl(CF_2)_nCF_2 \rightarrow R(CH_3)AsC{=}CCl(CF_2)_nCF_2 \ (V) + HCl \quad (10)$$

$n = 1$ or 2. $n = 1$, $R = CH_3$ or C_6H_5; $n = 2$, $R = CH_3$

The reactions represented by eqns. (5) and (10) ($n = 1$; $R = CH_3$) can be followed by means of the ^1H NMR spectrum of the reaction mixture. It was found that at 20° dimethylarsine reacts with the perfluoroolefin much faster than with the dichloro compound. The former reaction is 35% complete after one day and 85% complete after four. The latter is only 35% complete after twelve days. At 100°, however, the latter is quantitative after 5 days. The reaction of eqn. (6) does not seem to take place at 20° but after 17 hours at 100° it is 30–50% complete. The corresponding reaction of eqn. (10) ($n = 1$; $R = C_6H_5$) is 86% complete after 3 days at 130°.

Under more forcing conditions (140°) further reaction of (V) ($n = 1$; $R = CH_3$) with dimethylarsine results in the formation of 1,2-bis(dimethylarsino)tetrafluorocyclobutene (VI).



(11)

One feature of this reaction is the low yield of (VI) (50% based on dimethylarsine used) and the overall 2:1.2, dimethylarsine/(dimethylarsino)cyclobutene, stoichiometry of the reaction. After taking into account the yield of (VI), the remaining material is approximately 4 parts dimethylarsine to one part (dimethylarsino)cyclobutene. Thus it appears that the allylic fluorines are attacked as well. This type of reaction has been reported by Park and coworkers[2].

STRUCTURES AND SPECTROSCOPIC PROPERTIES OF NEW COMPOUNDS

The structures of the compounds (I), (III) and (V) are established best by analysis (Table 1) and by their ^{19}F NMR spectra. The ^{19}F spectrum of a previously known[3] related molecule 1-(diethylamino)pentafluorocyclobutene is shown in Fig. 1. It is seen that whilst the nature of the spin–spin coupling is complex, absorption occurs in three well defined regions, the high field region (*C*) (area = 1 unit) being associated with the vinylic fluorine and the other two regions (*A*) and (*B*) (each of area 2 units) with the allylic fluorines. In Table 2 are listed data for the cyclobutenes.

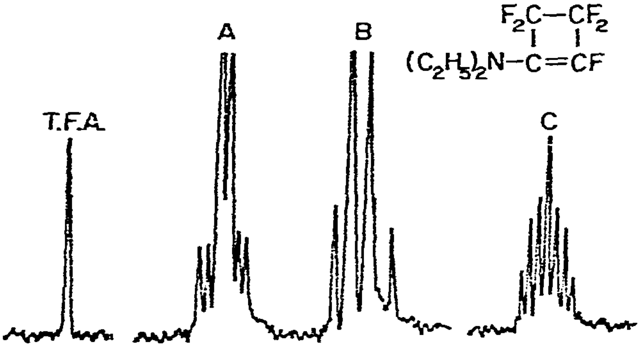


Fig. 1. ^{19}F NMR spectrum of $(C_2H_5)_2N\overline{C{=}CFCF_2CF_2}$.

It is to be noted that the areas of *A* and *B* are equal, and that of *C*, when present, is equal to one half of this. Thus four allylic fluorine atoms are present in each compound, and the chemical shift of these atoms does not change very much with a change in the

TABLE 1

ANALYTICAL DATA FOR NEW COMPOUNDS

Compound	*B.p.* (°*C*)	*Calcd. (found)*					
		C	*H*	*As*	*Cl*	*F*	*Mol. wt.*[a]
$(CH_3)_2As\overline{C{=}CClCF_2CF_2}$	154	27.2 (27.4)	2.3 (2.3)	28.2 (28.4)	13.4 (13.3)	28.7 (28.7)	265 (251)
$(CH_3)_2As\overline{C{=}CClCF_2CF_2CF_2}$	108 (103 mm)	26.8 (26.9)	1.9 (2.0)	23.8 (23.8)	11.3 (11.5)	36.2 (36.2)	315 (300)
$(C_6H_5)(CH_3)As\overline{C{=}CFCF_2CF_2}$	104 (15 mm)	42.0 (42.8)	2.6 (2.1)	24.2 (24.4)		30.6 (30.8)	
$(C_6H_5)(CH_3)As\overline{C{=}CClCF_2CF_2}$	133 (21 mm)	40.4 (40.5)	2.2 (2.5)	22.9 (23.1)	10.9 (11.0)	23.2 (23.3)	
$(CH_3)_2As\overline{C{=}C(As(CH_3)_2)CF_2CF_2}$	120 (47 mm)	28.6 (28.7)	3.6 (3.4)	44.6 (44.8)		23.2 (23.0)	336 (320)
$(CH_3)_2AsCF_2CFHCF_3$	110–110	23.2 (23.4)	2.7 (2.8)	29.3 (29.4)		44.5 (44.3)	
$(CH_3)_2AsCF{=}CFCF_3$	108–110	25.4 (25.4)	2.5 (2.5)	31.8 (31.7)		40.2 (40.5)	

[a] Determined by Rast method.

TABLE 2

^{19}F NMR CHEMICAL SHIFTS[a] FOR 

R	X	A	B	C
$(C_2H_5)_2N$	F	32.9	37.4	79.5
$(CH_3)_2N$	F	33.0	38.1	79.8
$(CH_3)_2As$	F	33.7	39.7	28.9
$(C_6H_5)(CH_3)As$	F	33.7	39.7	27.5
CH_3S	F	37.4	39.0	45.2
$(CH_3)_2As$	Cl	31.7	37.4	
$(C_6H_5)(CH_3)As$	Cl	31.1	37.5	

[a] In ppm upfield from external trifluoroacetic acid.

atom attached to the carbon atom of the double bond. In contrast, the chemical shift of the vinylic fluorine atom changes markedly with change in the atom at the other end of the double bond. The nature of the substituents on that atom do not have a great effect as is seen for (I) and (III). The ^{19}F spectra of perfluorovinyl derivatives of metals and metalloids show a much smaller variation of chemical shift on changing the central atom[4]. The chemical shift of band C for the sulfur compound (Table 2) suggests that band C of a phosphorus compound would have a chemical shift intermediate between that of the arsenic and nitrogen compounds. However, so far attempts to make such a stable compound have been unsuccessful[5].

Compounds (I) and (III) have similar infrared spectra as do the 1-chlorocyclobutenes (V) ($n = 1$). The main bands are compared in Table 3. Although little is known of the spectra of fluorinated cyclobutenes[6] it is interesting to note that the C=C stretching frequency increases from 1659 to 1695 cm^{-1} on going from (I) to (III), and yet is unaltered in the corresponding chlorocyclobutenes (V). The C=C stretching frequency of hexafluorocyclobutene[6] is 1799 cm^{-1} so that there is a large decrease on substituting one fluorine by a dimethylarsino group. Other substituents, lower the frequency less to 1765 (CH_3O), 1720–1730 (alkyl)[6], 1750 [$(C_2H_5)_2N$] and 1670 cm^{-1} (CH_3S)[7]. The frequency for 1,2-dichlorotetrafluorocyclobutene[6] is ~ 1620 cm^{-1} and

TABLE 3

INFRARED DATA FOR ARSINOCYCLOBUTENES[a]

(I)	(III)	(V) $n = 1$ $R = CH_3$	(V) $n = 1$ $R = C_6H_5$
1659	1695	1576	1576
1389	1397	1426	1422
1373	1374	1328	1326
1274	1274	1245	1246
1205	1206	1115	1121
1115	1117	855	855
947	950	810	810
853	865		
810	812		

[a] Main bands only.

the change in frequency on monosubstitution is apparently not so great[6]. Unfortunately there is no obvious correlation between the shift of band C in the NMR spectra and the C=C stretching frequency. The new di(tertiary arsine) (VI) shows only a very weak absorption at 1613 cm^{-1} in the C=C stretching region of the infrared spectrum and therefore the symmetrical structure (VI) is favored over the alternative 1,3- or 1,4-bis(dimethylarsino) formulation both of which would be expected to show stronger infrared absorption in this region[6]. The structure (VI) is also indicated by the result that it forms a complex of the formula (VI)·Fe(CO)$_3$ when reacted with iron pentacarbonyl[7].

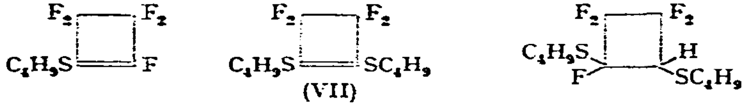
The ^{19}F NMR spectrum of (V) (n = 2) has bands of equal intensity at 29.9, 40.8, and 67.6 ppm thus confirming the structure. In view of the data of Table 2 it seems reasonable to assign the two low-field bands to the fluorine atoms adjacent to the double bond and the high field band to the remaining pair of fluorine atoms. Support for this comes from the spectra of the compounds $\overline{XC{=}CXCF_2'CF_2''CF_2'}$[3] where the approximate chemical shifts for F′ and F″ respectively are 35 and 51 ppm (X = Cl) and 41 and 53 ppm (X = F).

The direction of addition of dimethylarsine to give (II) (eqn. 4), is established by bromine cleavage to afford $BrCF_2CFCHCF_3$. The structure of (IV) (eqn. 7) is established by the C=C stretching band at 1668 cm^{-1}* and by cleavage by aqueous sodium hydroxide to give $HCF{=}CFCF_3$. The isomer distribution (*cis*:*trans*) of (IV) is not yet known. An estimate has been given[6] that the C=C stretching frequency of compounds of the type R′CF=CFR″ lies in the range 1740–1700, however, two exceptions were noted[6]. The arsino derivative (IV) is also outside this range, as are the compounds $(C_2H_5)_3SiCF{=}CFR$, *e.g.* 1670 (R = C_4H_9), 1688 (R = OC_2H_5), and 1637 cm^{-1} (R = C_6H_5)[7].

Reaction mechanisms

A large number of compounds including amines, alkoxides, mercaptans and Grignard reagents are known to react with certain fluoroolefins in such a way as to substitute a halogen and produce a new fluoroolefin[9]. However, the previous use of organometallic or organometalloidal compounds for similar purposes, that is to prepare fluoroolefins which are σ-bonded to a metal or metalloid, is almost unknown[9–11]. Addition–elimination or nucleophilic substitution mechanisms have been suggested for these reactions[9] but no conclusive evidence is available.

In the case of the reaction of n-butylmercaptan with perfluorocyclobutene compounds (VII) were obtained, indicating that an addition–elimination mechanism is operating.



(VII)

The usual reaction of a compound with an As–H bond with an unsaturated compound is addition as in eqn. (4) and the following examples[12,13]:

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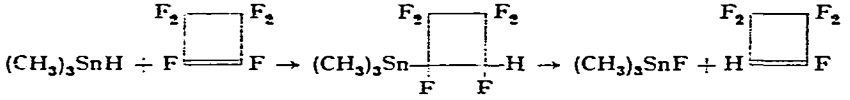
* A value of 1620 cm^{-1} was given erroneously in the preliminary communications of this work.

$$(CH_3)_2AsH + CF_3C{\equiv}CCF_3 \rightarrow (CH_3)_2AsC(CF_3){=}C(CF_3)H \qquad (12)$$

$$C_6H_5AsH_2 + 2\,CH_2{=}CHCN \rightarrow C_6H_5As(CH_2CH_2CN)_2 \qquad (13)$$

Therefore it seems reasonable to postulate an addition–elimination path for the reactions described by eqns. (5), (6), and (10). However, in the present study no evidence for intermediate formation was found in an NMR study of these reactions. In contrast, it has been established that intermediate formation can be observed in the reactions of Group IV hydrides with fluoroolefins as in the example[14]:



(14)

A feature of the secondary arsine reactions with the cyclic fluoroolefins is the ready elimination of hydrogen halide even in the absence of a strong base. Nevertheless the adduct of the acyclic olefin (III) shows no tendency to eliminate hydrogen fluoride at temperatures up to 180°.

The diarsine and arsinomagnesium bromide reactions (eqns. 3, 7, 8, 9) probably also involve an addition–elimination mechanism. This again seems to be the preferred one for describing the interaction of Grignard reagents and organo lithium compounds with fluoroolefins[9]. Diarsines are known to add to unsaturated compounds as in eqn. (2) and the following further examples[1,15]:

$$(CF_3)_2As{-}As(CF_3)_2 + CF_3C{\equiv}CCF_3 \rightarrow (CF_3)_2AsC(CF_3){=}C(CF_3)As(CF_3)_2 \qquad (15)$$

$$(CH_3)_2As{-}As(CH_3)_2 + CF_2{=}CFBr \rightarrow (CH_3)_2AsCF_2CFBrAs(CH_3)_2 \rightarrow (CH_3)_2AsCF{=}CF_2 + BrAs(CH_3)_2 \qquad (16)$$

The initial adduct of eqn. (16) is unstable eliminating the perfluorovinylarsine and presumably bromodimethylarsine. Chloro- and fluorodimethylarsine are eliminated in the reactions of eqns. (3) and (9).

EXPERIMENTAL

Volatile reagents and products were manipulated in a vacuum system. Reactions were done in sealed Pyrex tubes. ^{19}F NMR spectra were obtained using a Varian H.R.-60 instrument (chemical shifts are given in ppm upfield from external trifluoroacetic acid) and infrared spectra using a Perkin–Elmer Model 21 spectrometer (NaCl optics). All fluorocarbons were obtained from Peninsular ChemResearch Inc. and arsenic compounds were prepared by published methods.

Analyses were done by ALFRED BERNHARDT Mikroanalytisches Laboratorium, Mulheim (Ruhr), Germany, and data for new compounds are presented in Table 1.

Reactions of tetramethyldiarsine

(*a*) *With 1,2-dichlorotetrafluorocyclobutene.* Excess cyclobutene (10.1 g) and the diarsine (4.0 g) were left at 20° (21 days) to yield chlorodimethylarsine (2.8 g) and unreacted cyclobutene (4.4 g) in a more volatile fraction (separated by distillation in a nitrogen atmosphere), and a less volatile fraction (4.5 g, 85 % yield) which distilled at 154° and was identified as 1-chloro-2-(dimethylarsino)tetrafluorocyclobutene. ^{19}F NMR spectrum: Table 2. Infrared spectrum (liquid film): 3025 w, 2940 w, 1576 vs, 1426 s, 1328 vs, 1270 s, 1245 vs, 1176 w (sh), 1150 m (sh), 1115 vs, 902 s, 850 vs, 810 s, 725 w cm^{-1}.

(*b*) *With 1,2-dichlorohexafluorocyclopentene.* The diarsine (5.0 g) and cyclopentene (8.6 g) were left at 20° for 21 days. Distillation of the contents of the tube gave unreacted cyclopentene (4.0 g), chlorodimethylarsine (2.9 g), and 1-chloro-2-(dimethylarsino)hexafluorocyclopentene (4.7 g, 64 % yield). ^{19}F NMR spectrum consisted of three resonances of equal intensity at 29.9, 40.8, and 67.6 ppm. Infrared spectrum (liquid film): 3020 w, 2930 w, 1590 s, 1426 s, 1332 vs, 1282 vs, 1262 s, 1233 vs, 1200 vs, 1150 vs, 1145 s, 1097 vs, 997 s, 902 s, 850 vs, 803 s cm^{-1}.

Reactions of dimethylarsine

(*a*) *With hexafluoropropene.* The arsine (2.8 g) and hexafluoropropene (11.0 g) were heated at 100° for 5 days to give 2-H-1-(dimethylarsino)hexafluoropropene, (3.6 g, 90 % yield), b.p. 110–111° (739 mm). An analytical sample was obtained by VPC (5 ft. Ucon Polar column at 110°). Infrared spectrum (vapor): 3090 w, 3030 w, 1424 w, 1381 s, 1290 s, 1212 vs, 1178 vs, 1105 s, 1077 s, 1005 w, 980 vw, 937 w, 904 w, 878 w, 854 m, 791 w, 717 m, 678 m cm^{-1}. The arsinopropane was stable at 180° (21 h). It reacted with excess bromine (20°, 3 weeks) in carbon tetrachloride to yield methyl bromide and 2-H-1-bromohexafluoropropane identified by means of its molecular weight of 227 (calcd. 231) and known infrared spectrum[16].

(*b*) *With hexafluorocyclobutene.* Dimethylarsine (5.9 g) and the cyclobutene (11.9 g) were left at 20° (1 week). After two days etching of the glass tube was apparent. The least volatile fraction (4.6 g, 94 % yield) was identified as 1-(dimethylarsino)pentafluorocyclobutene b.p. 124° (lit.[1] 125°) of known infrared and ^{19}F NMR spectrum.

(*c*) *With 1,2-dichlorotetrafluorocyclobutene.* When the arsine (2.4 g) and 1,2-dichlorotetrafluorocyclobutene (6.9 g) were heated at 100° (5 days) hydrogen chloride (0.85 g, 100 % yield) of molecular weight 36.5 (calcd. 36.5) was isolated. Unreacted butene (2.6 g) was recovered and the reaction product, 1-chloro-2-(dimethylarsino)-tetrafluorocyclobutene (5.8 g, 97 % yield), of known infrared spectrum, condensed in a trap at −23°.

(*d*) *With 1,2-dichlorohexafluorocyclopentene.* The arsine (2.3 g) and cyclopentene (7.9 g) after 2 days at 100° gave a mixture of hydrogen chloride and dimethylarsine (1.3 g) which could not be separated by trap-to-trap distillation[17], unreacted pentene (5.0 g), and 1-chloro-2-(dimethylarsino)hexafluorocyclopentene (3.9 g, 55 % yield) of known infrared spectrum.

(*e*) *With 1-chloro-2-(dimethylarsino)tetrafluorocyclobutene.* Dimethylarsine (2.1 g) and the arsinocyclobutene (8.0 g) were heated at 140° (3 days) affording hydrogen chloride, unreacted arsinocyclobutene (4.9 g), and a least volatile fraction which distilled in a nitrogen atmosphere to give 1,2-bis(dimethylarsino)tetrafluorocyclobutene (3.5 g, 52 % yield), b.p. 120° (47 mm). Infrared spectrum (liquid film): 3000 m, 2920 m, 2810 w, 2105 w, 1913 w, 1420 s, 1329 m, 1300 vs, 1263 s, 1246 m, 1225 vs, 1154 vs, 1130 s, 1084 vs, 897 s, 859 s, 845 s, 803 s, cm^{-1}. The product was slightly air-sensitive.

Reactions of methylphenylarsine

(*a*) *With hexafluorocyclobutene.* When the arsine (3.7 g) and cyclobutene were heated at 100° (17 h) 2.0 g (30%) of an involatile product was obtained which was purified by distillation, b.p. 104° (15 mm), and identified as 1-(methylphenylarsino)-pentafluorocyclobutene. Infrared spectrum (liquid film): 3090 m, 3055 m, 2940 w, 1659 s, 1584 w, 1488 m, 1441 m, 1420 w, 1389 s, 1373 m, 1333 w, 1303 w (sh), 1293 w (sh), 1274 vs, 1205 s, 1115 vs, 1079 m, 1069 w (sh), 1024 m, 1001 m, 947 s, 853 m, 810 s, 735 s, 692 s, 646 m, cm^{-1}. ^{19}F NMR spectrum: Table 2.

(*b*) *With 1,2-dichlorotetrafluorocyclobutene.* The arsine (2.2 g) and the cyclobutene (5.9 g) were miscible at 20°. After the reaction mixture had been heated to 130° (3 days), 3.4 g of unreacted cyclobutene was recovered. The involatile residue distilled at 133° (21 mm) and was identified as 1-chloro-2-(methylphenylarsino)-tetrafluorocyclobutene (86% yield). Infrared spectrum (liquid film): 3100 w, 3050 w, 2935 w, 1575 m, 1489 m, 1442 m, 1422 w, 1358 m (sh), 1326 vs (br), 1246 vs, 1187 w (sh), 1150 m (sh), 1121 vs (br), 1080 m, 1025 w, 1001 w, 855 s, 810 m, 739 m, 725 w (sh), 694 m cm^{-1}.

Reactions of dimethylarsinomagnesium bromide

(*a*) *With hexafluoropropene.* Dimethylarsine (6.2 g) was condensed onto a slight excess of methylmagnesium bromide in diethyl ether (38 ml). The tube was warmed cautiously whilst the methane was evolved and then left for 36 h at 20°; two liquid layers were then present. The methane was pumped away and hexafluoropropene (15.9 g) was added. The reaction mixture, a clear solution containing a small amount of white solid, was left at 20° (25 days). Trap-to-trap distillation gave a fraction less volatile then the solvent. This fraction was distilled in a nitrogen atmosphere to give 2.0 g of a mixture of compounds which was separated by VPC (dinonyl phthalate column at 100°) into two components. The first fraction (75% of the mixture) was identified as 1-(dimethylarsino)pentafluoropropene by means of analysis and its vapor phase molecular weight of 232 (calcd. 236). The second component was identified as 1-(dimethylarsino)-2-H-hexafluoropropane of known infrared spectrum. The arsinopropene gave a 75% yield of 1-H-pentafluoropropene (identified by means of its known infrared spectrum[18]), on heating (100°, 1 day) with 10% aqueous sodium hydroxide. The infrared spectrum of the arsinopropene was as follows (vapor): 2915 w, 1668 m, 1428 m, 1354 vs, 1267 m, 1211 vs, 1163 vs, 1130 s, 1088 vs, 916 s, 852 m, 732 m, 658 w cm^{-1}.

(*b*) *With hexafluorocyclobutene.* The arsinomagnesium bromide from 4.3 g of dimethylarsine was prepared as described in (*a*), and was reacted with perfluorocyclobutene (17.7 g) (20°, 18 h with shaking) to give 1-(dimethylarsino)perfluorocyclobutene, b.p. 127–129° (lit.[1] 125°), of known infrared spectrum, in 50% yield.

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SUMMARY

The secondary arsines $(CH_3)RAsH$ ($R = CH_3$, C_6H_5) react with the fluoro-olefins $X\overline{C{=}CX(CF_2)_nC}F_2$ ($X = Cl, F$; $n = 1, 2$) to yield $(CH_3)RAs\overline{C{=}CX(CF_2)_nC}F_2$ with elimination of HX. $(CH_3)_2As{-}As(CH_3)_2$ and $Cl\overline{C{=}CCl(CF_2)_nC}F_2$ afford $(CH_3)_2As\overline{C{=}CCl(CF_2)_nC}F_2$ with elimination of $ClAs(CH_3)_2$. $(CH_3)_2AsMgBr$ reacts with $CF_2{=}CFCF_3$ and $\overline{CF{=}CFCF_2C}F_2$ to give $(CH_3)_2AsCF{=}CFCF_3$ and $(CH_3)_2As\overline{C{=}CFCF_2C}F_2$ respectively. $(CH_3)_2AsCF_2CFHCF_3$ is obtained from $(CH_3)_2AsH$ and $CF_3CF{=}CF_2$.

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