# PERFLUOROALKYL ARSENICALS

## PART III. THE PREPARATION AND PROPERTIES OF SOME NEW TRIFLUOROMETHYL AND HEPTAFLUOROPROPYL ARSINES[1]

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## ABSTRACT

The reaction of heptafluoroiodopropane with the appropriate phenyl-iodo-arsine in the presence of mercury yields the compounds $C_3F_7As(C_6H_5)_2$, $(C_3F_7)_2AsC_6H_5$, and $C_3F_7(CH_3)AsC_6H_5$. However, the compounds $(CF_3)_2AsR$ ($R = C_2H_5, C_4H_9$) are obtained from the reaction of the compounds $R_2AsI$ with mercury and trifluoroiodomethane. The ultraviolet spectra of the heptafluoropropyl-arsines are discussed.

## DISCUSSION AND RESULTS

In previous papers (1, 2) the preparation of methyl- and phenyl-trifluoromethyl-arsines was described, the method of preparation being to react the appropriate iodo-arsine with trifluoroiodomethane in the presence of excess mercury: for example

$$(C_6H_5)_2AsI + Hg + CF_3I \rightarrow (C_6H_5)_2AsCF_3 + HgI_2.$$

Alkyl iodides react similarly, though in this case the reaction goes further and arsonium derivatives of triiodomercury(II) are obtained (3): for example

$$(C_6H_5)_2AsI + Hg + 2CH_3I \rightarrow (C_6H_5)_2As(CH_3)_2.HgI_3.$$

In order to investigate the generality of these reactions, the preparation of ethyl- and butyl-trifluoromethyl-arsines and phenyl-heptafluoropropyl-arsines was undertaken.

Diethyltrifluoromethylarsine, b.p. 111°, is obtained by the reaction of diethyliodoarsine with trifluoroiodomethane in the presence of mercury; however, the bulk of the product from this reaction is ethylbistrifluoromethylarsine, b.p. 77°. Ethyldiiodoarsine does not react with trifluoroiodomethane under the same conditions, so this substance as an impurity could not have been the source of the ethylbistrifluoromethylarsine. Similarly, when di-*n*-butyliodoarsine is reacted with trifluoroiodomethane and mercury, the only product isolated is *n*-butylbistrifluoromethylarsine, b.p. 118°, though in this case the same compound is produced by the corresponding reaction using *n*-butyldiiodoarsine. A reasonable explanation of these anomalous results is that an exchange reaction takes place between the initially formed dialkyltrifluoromethylarsine and trifluoroiodomethane, producing the alkylbistrifluoromethylarsine; reactions of this sort are now being studied. The reactions of heptafluoroiodopropane with phenyl-iodo-arsines in the presence of mercury are not complicated by side reactions, and heptafluoropropyldiphenylarsine (b.p. 99–102° ($10^{-3}$ mm)), bisheptafluoropropylphenylarsine (b.p. 128° (68 mm)), and heptafluoropropylmethylphenylarsine (b.p. 123° (69 mm)) can be easily isolated.

All the new arsines are colorless mobile liquids of faint odor; they are stable to oxygen and moisture at ordinary temperatures. Solvolysis studies have been made on these compounds and the results will be reported later. The ultraviolet spectra of the heptafluoropropyl-phenyl-arsines are very similar to those of the trifluoromethyl-phenyl-arsines (4). The wavelengths and extinction coefficients of maximum absorption of these compounds are given in Table I.

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[1] *Manuscript received July 10, 1961.*
*Contribution from the Chemistry Department, University of British Columbia, Vancouver, B.C.*

Can. J. Chem. Vol. 39 (1961)

TABLE I

Wavelengths and molar extinction coefficients of the band maxima

| Compound | Methanol | | Cyclohexane, $\lambda_{max}$ | Compound | Methanol, $\lambda_{max}$ (Å) |
|---|---|---|---|---|---|
| | $\lambda_{max}$ (Å) | $\epsilon_{max} \times 10^{-3}$ | | | |
| $(C_6H_5)_2AsC_3F_7$ | 2708 | 1.18 | 2710 | $(C_6H_5)_2AsCF_3$ | 2720 |
| | 2637 | 1.72 | 2640 | | 2690 |
| | 2568 | 1.98 | 2570 | | 2575 |
| | $2355^i$ | 8.35 | $2360^i$ | | 2368 |
| | $2225^{i*}$ | 12.98 | $2355^{i*}$ | | 2240 |
| $C_6H_5As(C_3F_7)_2$ | 2725 | 0.84 | 2725 | $C_6H_5As(CF_3)_2$ | 2718 |
| | 2650 | 1.52 | 2650 | | 2650 |
| | 2590 | 0.79 | 2589 | | 2587 |
| | 2528 | 0.55 | 2528 | | 2530 |
| | 2238 | 9.88 | 2238 | | 2238 |
| $C_6H_5As(CH_3)(C_3F_7)$ | 2702 | 0.44 | 2705 | $C_6H_5As(CH_3)CF_3$ | 2700 |
| | 2634 | 0.58 | 2635 | | 2630 |
| | 2568 | 0.52 | 2571 | | $2565^i$ |
| | $2275^{i*}$ | 5.69 | 2275 | | 2210 |
| | $2175^i$ | 7.36 | 2175 | | |

NOTE: $i$ = estimated from point of inflection.

*Band is actually very weak: the recorded intensity is mainly due to contributions from the very strong short-wavelength absorption and from the other bands recorded above.

All the compounds show a weak series of bands in the region 2520–2730 Å, and by analogy with the interpretation of the spectra of the phenyl-trifluoromethyl-arsines (4) these transitions can be characterized as $\pi$–$\pi^*$ absorptions involving electrons localized in the phenyl groups. The remaining bands in the spectra in the region 2100–2500 Å are much stronger. The bands in the heptafluoropropyl compounds correspond in position number and intensity with those of the trifluoromethyl compounds except for the weak band at ca. 2275 Å in the spectrum of heptafluoropropylmethylphenylarsine. The transitions in this region of the trifluoromethyl compounds have been described as involving electron transfer from the non-bonding electrons on the arsenic to the $\pi$ orbitals of the phenyl groups (4), and again this description of the transitions can probably be carried over to the corresponding bands of the heptafluoropropyl compounds, even though these bands do not shift toward the blue or only shift a little when the solvent is changed from cyclohexane to the more-polar methanol.

The occurrence of two higher-intensity bands in the spectrum of diphenyltrifluoromethylarsine has been interpreted in terms of the steric effect of the $CF_3$ group being such as to destroy the equivalence of the two phenyl groups with respect to the arsenic lone pair. The intensity of the transition to the interacting phenyl group (the lower-energy transition since interaction would stabilize the phenyl group with a resulting lowering of orbital energies) was much higher than the intensity of the transition to the non-interacting ring. Models such as were used previously (4) show that the more bulky $C_3F_7$ group has the same effect in the compound heptafluoropropyldiphenylarsine, so the appearance of two bands in the spectrum of this compound, the one of lower energy being the more intense, is not unexpected. Models also indicate that the phenyl group could interact with the $C_3F_7$ group in the compound heptafluoropropylmethylphenylarsine and almost certainly interacts in the compound bisheptafluoropropylphenylarsine. However, such interaction alone can not account for the presence of two bands in the spectrum of the former compound. The charge transfer band in triphenylarsine occurs at ca. 40,300 cm$^{-1}$ (4) so the effect of substituting a $C_3F_7$ group for a phenyl group is to increase the transition energy by ca. 4500 cm$^{-1}$ (using the energy of low-intensity transition to the non-interacting phenyl group of the compound heptafluoropropyldiphenylarsine). The charge transfer band in methyldiphenylarsine occurs at ca. 41,600 cm$^{-1}$ and the effect of substituting a $C_3F_7$ group for a phenyl group is to increase the energy of the transition by ca. 4300 cm$^{-1}$ if the 2175 Å band in heptafluoropropylmethylphenylarsine is chosen as the charge transfer band, or by ca. 2400 cm$^{-1}$ if the 2275 Å band is the charge transfer band. Thus it is likely that it is the 2175 Å band which is the charge transfer band. The second transition at ca. 2275 Å is very weak. This could arise from a shift or split of the benzene transition which normally occurs at ca. 2000 Å, but its intensity seems to be too low. A more likely explanation is that it is due to an impurity.

The charge transfer bands in the $C_3F_7$ compounds occur at higher or equal energies when compared with the corresponding bands in the $CF_3$ compounds; a result which could indicate that in the first order the $C_3F_7$ group has a greater electron-withdrawing effect on the arsenic lone pair than does the $CF_3$ group.

The infrared spectra of these new arsines are recorded in the experimental section. It is hoped to discuss these in detail at a later date when more correlations can be made.

## EXPERIMENTAL

### *Apparatus and Technique*

Conventional vacuum techniques were used for the manipulation of volatile reactants and products out of contact with moisture and oxygen. Reactions were carried out in sealed Pyrex tubes in the absence of air and light. Infrared spectra were measured on a Perkin–Elmer Model 21 double-beam instrument with rock-salt optics. Ultraviolet spectra were recorded on the Cary Model 14 spectrophotometer. The solvents were spectroscopic grade methyl alcohol or cyclohexane, and the lower wavelength limit of the instrument was ca. 2100 Å as determined by solvent absorption. Gas-phase molecular weights were determined by Regnault's method. Phenyl-iodo-arsines were prepared by the methods previously described (2).

### *Reaction of Ethyldiiodoarsine with Trifluoroiodomethane in the Presence of Mercury*

Ethyldiiodoarsine was prepared from dichloroethylarsine (5) by reacting the chloroarsine with sodium iodide in acetone (6). The product had a boiling point of 126° (11 mm) (lit. value, 126° (11 mm) (6)). The iodo-arsine (18.2 g), trifluoroiodomethane (57.9 g), and mercury (225 g) were shaken at 20° for 11 days. Trap-to-trap distillation of the volatile contents of the tube showed that only one fraction, trifluoroiodomethane (57.6 g), was present.

### *Reaction of Diethyliodoarsine with Trifluoroiodomethane in the Presence of Mercury*

Diethyliodoarsine was prepared from ethyldiiodoarsine as described by Wigren (7). The diiodoarsine in this case was prepared by the procedure used by Burrows and Turner for the preparation of diiodomethylarsine (8). Crude diethyliodoarsine (35 g), trifluoroiodomethane (76 g), and mercury (250 g) were shaken at 20° for 6 days. The unreacted trifluoroiodomethane was separated from the other volatile contents of the tube by trap-to-trap distillation. The less-volatile fraction (14.5 g) was distilled in a nitrogen atmosphere at 760 mm. The bulk of the material boiled at 77°, but a further small fraction boiling at 111° was obtained. Vapor-phase chromatography was used to obtain samples of these two fractions for analysis. The fraction boiling at 77° was identified as *ethylbistrifluoromethylarsine*. Anal. Hydrolysis with 10% aqueous sodium hydroxide at 100° for 2 days gave fluoroform corresponding to a $CF_3$ content of 56.2%. The vapor phase molecular weight was 241. Calc. for $C_4H_5AsF_6$: $CF_3$, 57%; mol. wt., 242. The fraction boiling at 111° was identified as *diethyltrifluoromethylarsine*. Anal. Calc. for $C_5H_{10}AsF_3$: C, 29.7; H, 5.0; As, 37.1; F, 28.2%; mol. wt., 202. Found: C, 29.9; H, 5.1; As, 37.3; F, 27.9%; mol. wt., 230. The infrared spectra of these compounds showed the following absorption bands: $(C_2H_5)_2AsCF_3$ (liquid film): 2980 (s), 2940 (s), 2885 (m), 2350 (w), 2200 (w), 1466 (s), 1425 (w), 1382 (m), 1243 (m)(sh), 1223 (m), 1138 (vs), 1093 (vs), 1038 (m), 1025 (m), 978 (m), 730 (m), 721 (s); $C_2H_5As(CF_3)_2$ (vapor phase): 2980 (s), 2940 (m), 2888 (m), 2250 (w), 2220 (w), 1854 (w), 1469 (m), 1427 (w), 1394 (w), 1245 (s), 1176 (vs), 1157 (vs), 1124 (vs), 1105 (vs), 1056 (m), 1032 (m), 994 (m), 729 (s).

### *Reaction of n-Butyldiiodoarsine with Trifluoroiodomethane in the Presence of Mercury*

The diiodo-arsine was prepared by reduction of *n*-butylarsonic acid using the procedure described by Burrows and Turner for the preparation of diiodomethylarsine (9). The crude arsine (21 g), trifluoroiodomethane (55.1 g), and mercury (210 g) were shaken at 20° for 26 days. Trap-to-trap distillation of the volatile contents of the tube gave unreacted trifluoroiodomethane (40.3 g) and a colorless less-volatile fraction (10.4 g). The latter fraction was distilled in a nitrogen atmosphere at 760 mm: all distilled in the range 110–118°. A middle cut was taken, and this sample was again distilled. The boiling point was 118°, and the sample was identified as *n-butylbistrifluoromethylarsine*. Anal. Calc. for $C_6H_9AsF_6$: C, 26.7; H, 3.34; As, 27.8; F. 42.2%; mol. wt., 270. Found: C, 27.0; H, 3.48; As, 27.6; F, 42.5%; mol. wt., 290. The infrared spectrum showed the following absorption bands (liquid film): 2958 (s), 2925 (s), 2868 (m), 2210 (w), 1470 (m), 1422 (m), 1386 (m), 1347 (w), 1298 (w), 1265 (m), 1204 (s), 1168 (vs), 1132 (vs), 1115 (vs), 1093 (vs), 996 (vw), 967 (vw), 892 (m), 774 (w), 730 (s), 715 (m)(sh); vapor phase (omitting medium and weak bands): 2970 (s), 2935 (s), 1206 (s)(sh), 1179 (vs), 1156 (vs), 1126 (vs), 1107 (vs), (1081, 1076, 1069) (vs), (750, 744, 731) (s).

### *Reaction of Di-n-butyliodoarsine with Trifluoroiodomethane in the Presence of Mercury*

Crude *n*-butyldiiodoarsine, prepared as described above, was used to prepare di-*n*-butyliodoarsine using the method described by Wigren for the preparation of diethyliodoarsine from ethyldiiodoarsine (7). The crude product was dried over calcium chloride and then distilled at $10^{-3}$ mm. The main fraction boiled at 78–82°, and analysis showed it to be mainly di-*n*-butyliodoarsine. Anal. Calc. for $C_8H_{18}AsI$: C, 30.4; H, 5.7; I, 40.2%; mol. wt., 316. Found: C, 27.9; H, 5.3; I. 42.3%; mol. wt., 285. The impure iodo-arsine (10.6 g), trifluoroiodomethane (65.2 g), and mercury (210 g) were shaken at 20° for 20 days. The unreacted trifluoroiodomethane was separated from a less-volatile fraction by trap-to-trap distillation. The less-volatile fraction (13 g) was distilled at 92 mm in a nitrogen atmosphere, and all boiled at 59°. Its infrared spectrum was identical with that of *n*-butylbistrifluoromethylarsine. The fraction, when distilled at 760 mm (in nitrogen), boiled at 116–120°.

### *Reaction of Iododiphenylarsine with Heptafluoroiodopropane in the Presence of Mercury*

The arsine (12.6 g), heptafluoroiodopropane (82.5 g), and mercury (210 g) were shaken at 20° for 3 months. Trap-to-trap distillation isolated only heptafluoroiodopropane (71.8 g). The contents of the reaction tube were extracted with benzene, which was then removed by distillation at 760 mm in a nitrogen atmosphere, leaving a slightly colored involatile liquid (10.6 g). This fraction was distilled at $10^{-3}$ mm, and all the material boiled in the range 99–102°. The liquid was redistilled under the same conditions, and a colorless middle fraction of b.p. 102° was collected, which was identified as *heptafluoropropyldiphenylarsine* (73% yield). Anal. Calc. for $C_{15}H_{10}AsF_7$: C, 45.2; H, 2.51; As, 18.8; F, 33.4%; mol. wt., 398. Found: C, 45.2; H, 2.48; As, 19.0; F, 33.2%; mol. wt., 387. The infrared spectrum showed the following absorption bands (liquid film): 3060 (m), 1976 (vw), 1955 (vw), 1895 (vw), 1877 (vw), 1806 (vw), 1755 (vw), 1650 (vw), 1580 (w), 1485 (m), 1440 (s), 1383 (vw), 1338 (s), 1265 (s), 1227 (vs), 1208 (vs), 1184 (vs), 1174 (vs), 1110 (vs), 1081 (s), 1074 (s), 1034 (s), 1024 (m), 1000 (m), 988 (vw), 968 (vw), 912 (vw), 895 (m), 824 (s), 750 (s), 738 (vs), 732 (vs), 694 (s), 668 (s).

### *Reaction of Diiodophenylarsine with Heptafluoroiodopropane in the Presence of Mercury*

The arsine (22 g), heptafluoroiodopropane (71.8 g), and mercury were shaken at 20° for 2 months. The contents of the tube were worked up as described in the preceding experiment to give heptafluoroiodopropane (59.8 g) and a slightly colored involatile liquid (5.1 g) which boiled in the range 120–124° (63 mm, nitrogen atmosphere). This fraction was redistilled to give a colorless sample of *bisheptafluoropropylphenylarsine*, b.p. 128° (68 mm) (19% yield). Anal. Calc. for $C_{12}H_5AsF_{14}$: C, 29.4; H, 1.02; As, 15.2; F, 54.2%, mol. wt., 490. Found: C, 29.7; H, 1.09; As, 15.6; F, 53.6%; mol. wt., 460. The infrared spectrum showed the following absorption bands (liquid film): 3060 (w), 1890 (vw), 1830 (vw), 1809 (vw), 1756 (vw), 1655 (vw), 1580 (vw), 1485 (m), 1441 (m), 1336 (s), 1274 (s), 1230 (vs), 1210 (vs), 1185 (vs), 1129 (vs), 1117 (vs), 1078 (s), 9040 (s), 1025 (m), 1000 (m), 970 (vw), 935 (vw), 917 (vw), 893 (m), 820 (s), 750 (s), 740 (vs), 733 (vs), 694 (s), 669 (s).

### *Reaction of Iodomethylphenylarsine with Heptafluoroiodopropane in the Presence of Mercury*

The arsine (12 g), heptafluoroiodopropane (70 g), and mercury (215 g) were shaken at 20° for 1 month. Trap-to-trap distillation gave heptafluoroiodopropane (52 g) and a colorless involatile liquid (6.8 g). The latter fraction, when distilled in a nitrogen atmosphere, boiled at 123° (69 mm); it was identified as *heptafluoropropylmethylphenylarsine* (49% yield). Anal. Calc. for $C_{10}H_8AsF_7$: C, 35.7; H, 2.38; As, 22.3; F, 39.6%; mol. wt., 336. Found: C, 35.6; H, 2.47; As, 22.1; F, 39.5%; mol. wt., 322. The infrared spectrum showed the following absorption bands (liquid film): 3060 (w), 2995 (w), 2900 (w), 2400 (vw), 2300 (vw), 2130 (vw), 1980 (vw), 1952 (vw), 1895 (vw), 1875 (vw), 1802 (vw), 1755 (vw), 1645 (vw), 1580 (w), 1485 (m), 1438 (m), 1418 (m), 1338 (s), 1306 (m), 1268 (s), 1224 (vs), 1206 (vs), 1171 (s), 1110 (s), 1080 (s), 1035 (s), 1000 (m), 900 (m), 854 (s), 822 (s), 749 (s), 740 (s), 733 (s), 694 (s), 668 (s).

## ACKNOWLEDGMENTS

The author wishes to acknowledge financial assistance from the National Research Council of Canada. Microanalyses were carried out by Dr. Alfred Bernhardt.

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