771. *Radical Exchange in Organometallic Compounds. Part II.*[1] *Replacement of Trifluoromethyl by Methyl.*

By R. N. HASZELDINE and B. O. WEST.

Tristrifluoromethyl-phosphine or -arsine reacts with methyl iodide to give $(CF_3)_2M{\cdot}CH_3$ (M = P or As); further reaction with methyl iodide yields $CF_3{\cdot}M(CH_3)_2$. The possibility of reversing such exchange reactions has been studied, and reaction schemes are suggested.

THE replacement of methyl by trifluoromethyl in compounds $M(CH_3)_3$ to give $CF_3{\cdot}M(CH_3)_2$ (M = P, As, or Sb) was shown to occur readily by reaction with trifluoroiodomethane at room temperature or below.[1] The possibility of replacement of trifluoromethyl by methyl has now been investigated.

Tristrifluoromethyl-phosphine or -arsine reacts with methyl iodide only at elevated temperatures (240°), to give methylbistrifluoromethyl-phosphine or -arsine $(CF_3)_2M{\cdot}CH_3$ and trifluoroiodomethane. Methylbistrifluoromethyl-phosphine or -arsine will react further with an excess of methyl iodide at this temperature to give the compounds $CF_3{\cdot}M(CH_3)_2$; the phosphorus compound is obtained in low yield as the quaternary salt with methyl iodide, whereas the arsenic compound is obtained in the free state.

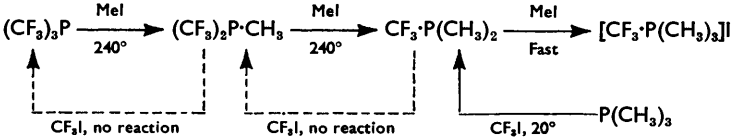
Attempts to prepare tristrifluoromethyl-phosphine or -arsine by reaction of the compounds $(CF_3)_2M{\cdot}CH_3$ with trifluoroiodomethane were unsuccessful, *i.e.*, the reaction of the tristrifluoromethyl compounds with methyl iodide described above was not reversible. Methylbistrifluoromethylphosphine similarly could not be obtained by treatment of dimethyltrifluoromethylphosphine with trifluoroiodomethane, but, by contrast, dimethyltrifluoromethylarsine yielded methylbistrifluoromethylarsine when heated with trifluoroiodomethane.

---

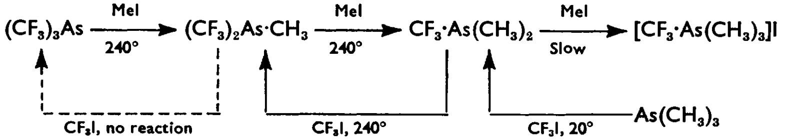
[1] Part I, Haszeldine and West, *J.*, 1956, 3631.

These reactions, and those reported in Part I, can thus be summarised as follows:

Phosphorus:



Arsenic:



These exchange reactions are considered[1] to involve the formation of the quaternary iodide either (*a*) by nucleophilic attack of $M(CH_3)_3$ or $CF_3{\cdot}M(CH_3)_2$ on the iodine atom of trifluoroiodomethane, followed by rapid rearrangement of the intermediate to give iodine as the anion, *e.g.*, $[(CH_3)_3PI]^+CF_3^- \longrightarrow [(CH_3)_3P{\cdot}CF_3]^+I^-$, or (*b*) by nucleophilic attack of $(CF_3)_nM(CH_3)_{3-n}$ on the carbon atom of methyl iodide to give a quaternary compound directly.

The basicity of the substituted phosphine or arsine acting as the nucleophilic reagent is probably of prime importance for (*a*), since trifluoroiodomethane is not readily attacked by weakly nucleophilic reagents, and this accounts for the occurrence of reactions of the type $M(CH_3)_3 + CF_3I$ at room temperature or below. As the number of trifluoromethyl groups in the phosphine or arsine increases, the reaction with trifluoroiodomethane becomes increasingly difficult or impossible.

For reaction (*b*), the ease of nucleophilic attack on the carbon atom of methyl iodide will again decrease as the basicity of the phosphine or arsine decreases, *i.e.*, as the number of trifluoromethyl groups it contains increases. This can be appreciably offset by the relative ease of heterolytic fission of the carbon–iodine bond of methyl iodide, combined with use of much higher reaction temperatures.

Formation of the quaternary compound by mechanism (*a*) or (*b*) would then be followed by its decomposition (i) by nucleophilic attack by the relatively basic phosphine or arsine, *e.g.*:

$$(CH_3)_3P + CH_3\text{–}\overset{+}{P}(CH_3)_2CF_3 \longrightarrow (CH_3)_4\overset{+}{P} + CF_3{\cdot}P(CH_3)_2$$

or (ii) by the splitting out, by pyrolysis, of the most electro-negative group as its iodide, *e.g.*:

$$[(CF_3)_3P{\cdot}CH_3]^+I^- \longrightarrow (CF_3)_2P{\cdot}CH_3 + CF_3I$$

Decomposition (i) will clearly be favoured under conditions where (*a*) operates, and (ii) under conditions where (*b*) operates. A detailed study of the decomposition of the key quaternary compounds postulated above as intermediates was prevented by our failure to synthesise them by alternative routes; despite this most of the results can be understood on the basis of the above reaction schemes.

The failure of tristrifluoromethylphosphine to react with methyl bromide or chloride can be attributed to the negligible Lewis basicity of the phosphine and the greater carbon–halogen bond strength relatively to that in methyl iodide, thus preventing reaction (*a*) or (*b*) respectively.

Methylbistrifluoromethyl-phosphine and -arsine are also substantially non-basic and fail to attack the iodine atom of trifluoroiodomethane even at high temperatures; tristrifluoromethyl-phosphine and -arsine are thus not formed. The increased ease of heterolytic cleavage of the carbon–iodine bond in methyl iodide explains why methylbistrifluoromethyl-phosphine and -arsine react with methyl iodide to give dimethyltrifluoromethylphosphine and -arsine. Dimethyltrifluoromethylphosphine is more basic than the corresponding arsine, and the exchange reaction therefore produces dimethyltrifluoromethylphosphine as its quaternary salt with methyl iodide, but dimethyltrifluoromethylarsine in the free state. Trialkylphosphines are, in general, stronger bases than the corresponding arsines.[2]

Rather surprisingly, dimethyltrifluoromethylphosphine fails to react with trifluoroiodomethane whereas dimethyltrifluoromethylarsine does. Thus only for the arsenic compound is the equilibrium:

$$(CF_3)_2M{\cdot}CH_3 + CH_3I \rightleftharpoons CF_3{\cdot}M(CH_3)_2 + CF_3I$$

possible. Since dimethyltrifluoromethylphosphine is more basic than dimethyltrifluoromethylarsine, some further factor must be involved, probably the weakness of the C–As bond (*ca.* 55 kcal./mole) compared with the C–P bond (*ca.* 65 kcal./mole) which favours the decomposition of the intermediate quaternary salt by scheme (ii).

Fluoroform, often a by-product in the high-temperature exchange reactions, arises by homolytic cleavage of the carbon–iodine bond in trifluoroiodomethane or of the M–CF_3 bond in the arsine or phosphine, followed by attack of the trifluoromethyl free radical on a C–H bond.

The annexed Table of boiling points shows that the dimethyltrifluoromethyl compound has the highest boiling point and that the tristrifluoromethyl compound boils at a lower temperature than the trimethyl compound.

B. p.s of methyl trifluoromethyl derivatives of phosphorus, arsenic, and antimony.

M	$M(CH_3)_3$	$CF_3{\cdot}M(CH_3)_2$	$(CF_3)_2M{\cdot}CH_3$	$(CF_3)_3M$
P	37·8°	46·9°	35·2°	17·0°
As	49·5	58·0	52·0	33·3
Sb	78·5	85·8	(81 *)	73·0

* Predicted.

Investigation of the aqueous alkaline hydrolysis of the compounds $M(CH_3)_3$, $CF_3{\cdot}M(CH_3)_2$, $(CF_3)_2M{\cdot}CH_3$, and $(CF_3)_3M$ ($M = P$, As, or Sb) shows that: (*a*) The trimethyl compounds are stable under the conditions used. (*b*) All the trifluoromethyl compounds yield fluoroform quantitatively with 15—20% aqueous sodium hydroxide at 20°. (*c*) For a given M the rate of hydrolysis increases markedly with the number of trifluoromethyl groups attached to M. (*d*) For a given number of trifluoromethyl groups in the compound the rate of hydrolysis increases $P < As < Sb$. For compounds of the type $CF_3{\cdot}M(CH_3)_2$ the difference in rate is much greater between As and Sb than between P and As.

The hydrolysis results are consistent with initiation by nucleophilic attack by hydroxide ion on the central atom; increase in the number of trifluoromethyl groups attached to M and/or increase in the electropositive character of M with increase in its atomic weight facilitate hydrolysis. Conversely, basicity is reduced: (*a*) Trimethylphosphine gives a stable silver iodide complex, dimethyltrifluoromethylphosphine gives a readily dissociated complex, and methylbistrifluoromethylphosphine and tristrifluoromethylphosphine are virtually non-basic in this sense. (*b*) Basicity decreases in the order $P > As > Sb$, as shown by the ease of formation of quaternary compounds with methyl iodide at room temperature [*e.g.*, $CF_3{\cdot}P(CH_3)_2$ reacts much faster than $CF_3{\cdot}As(CH_3)_2$], by the formation of compounds with carbon disulphide, and by complex formation with silver iodide [*e.g.*, $CF_3{\cdot}P(CH_3)_2$ gives a silver iodide complex, $CF_3{\cdot}As(CH_3)_2$ does not]. Trifluoromethyl derivatives of arsenic and antimony are very weak bases.

---

[2] Addis and Davies, *J.*, 1937, 1622.

EXPERIMENTAL

Conventional vacuum-technique was used for the manipulation of reactants and products as far as possible. Reactions were carried out in 40 ml. Pyrex tubes sealed *in vacuo* and heated when necessary in a tube furnace. Distillation of the products *in vacuo* was combined with infrared spectroscopy of the various fractions. Reference spectra and spectra of known mixtures were recorded to enable quantitative spectroscopic analysis to be carried out in certain cases.

Trifluoroiodomethane was prepared in mole quantities by the reaction of silver trifluoroacetate and iodine.

Preparation of Tristrifluoromethylphosphine.[3, 4]—An improved procedure was to heat white phosphorus (50 g.) and trifluoroiodomethane (20 g.) in a 300 ml. stainless steel autoclave in an oil-bath at 215—217° for 48 hr. The tristrifluoromethylphosphine was removed by fractionation and the unchanged trifluoroiodomethane, together with the iodophosphines $CF_3{\cdot}PI_2$ and $(CF_3)_2PI$, and an additional quantity (50 g.) of trifluoroiodomethane, were returned to the autoclave. The mixture was heated to 220—225° for 48 hr. and the cycle repeated. Fresh trifluoroiodomethane (50 g.) was added at each stage and the temperature was raised to a maximum of 230°. The temperature must be controlled carefully, particularly during the first cycle, to avoid formation of phosphorus trifluoride. The yield of tristrifluoromethylphosphine is *ca.* 20%, and iodotrifluoromethylphosphines are the main products particularly towards the end of the recycling procedure.

Reaction of Tristrifluoromethylphosphine and Methyl Iodide.—Into each of twelve tubes were condensed tristrifluoromethylphosphine (1·19 g., 5 mmoles) and methyl iodide (0·71 g., 5 mmoles); two layers were present at 20°. The tubes were heated to 240° (24 hr.), to give *methylbistrifluoromethylphosphine* (3·5 g., 32%) (Found: F, 61·7%; *M*, 185. $C_3H_3F_6P$ requires F, 61·8%; *M*, 184), trifluoroiodomethane (81%), fluoroform (4%), unchanged tristrifluoromethylphosphine (45%), and a mixture consisting of methylbistrifluoromethylphosphine, tristrifluoromethylphosphine, trifluoroiodomethane, and methyl iodide (analysed spectroscopically). The yield of the compound $(CF_3)_2P{\cdot}CH_3$ based on the tristrifluoromethylphosphine used up was 54%.

The reaction tubes were covered with a thin black deposit and a small quantity of needle-shaped crystals. A second experiment at 240° for 12 hr. gave less carbonaceous material and a better sample of the needles; spectroscopic examination showed these to be a mixture of trimethyltrifluoromethylphosphonium iodide[1] containing approx. 10% of an unknown compound, possibly dimethylbistrifluoromethylphosphonium iodide. Attempts to prepare the compound $[(CF_3)_2P(CH_3)_2]^+I^-$ by reaction of methylbistrifluoromethylphosphine and methyl iodide, and by other routes, to facilitate identification failed.

Methylbistrifluoromethylphosphine.—This is a colourless liquid, denser than, and unaffected by, air-free water. Its vapour pressure is represented by the equation $\log_{10} p$ (mm.) = $7{\cdot}356 - 1379/T$, whence the b. p. is 35·2°, the latent heat of vaporisation is 6310 cal./mole, and Trouton's constant is 20·5. The compound gives no indication of complex formation with carbon disulphide or silver iodide.

Reaction of Tristrifluoromethylphosphine with Methyl Bromide or Methyl Chloride.—Tristrifluoromethylphosphine (1·19 g., 5 mmoles) and methyl bromide (0·47 g., 5 mmoles), heated in a sealed tube at 240° (37 hr.), gave unchanged tristrifluoromethylphosphine (80%), methyl bromide, fluoroform (6%), and bromotrifluoromethane (4%); a carbonaceous deposit covered the walls. Neither methylbistrifluoromethylphosphine nor trimethyltrifluoromethylphosphonium iodide was detected in the products. An experiment at 300° caused complete decomposition of the tristrifluoromethylphosphine without change in the main course of the reaction.

Reaction of tristrifluoromethylphosphine (1·19 g., 5 mmoles) and methyl chloride (0·25 g., 5 mmoles), at 240° for 8 hr. or at 300° for 4 hr., gave only traces of chlorotrifluoromethane. At the lower temperature only unchanged reactants and fluoroform (5%) were produced, and at the higher temperature carbonisation set in. In particular the compounds $(CF_3)_2P{\cdot}CH_3$, $CF_3{\cdot}P(CH_3)_2$, or their quaternary salts were not detected.

Reaction of Methylbistrifluoromethylphosphine with Methyl Iodide.—Methylbistrifluoromethylphosphine (0·463 g., 2·5 mmoles) and methyl iodide (0·364 g., 2·55 mmoles) formed two layers in a sealed tube at *ca.* −40°, but were miscible at 20°. The tube was heated at 58° for

---

[3] Bennett, Emeléus, and Haszeldine, *J.*, 1953, 1565.

[4] Emeléus, Haszeldine, and Walaschewski, *J.*, 1953, 1552.

24 hr., then at 228° for 10 hr. Fractionation gave unchanged methylbistrifluoromethylphosphine and methyl iodide, trifluoroiodomethane (5% based on the loss of one CF_3 group from methylbistrifluoromethylphosphine), and fluoroform (5%). The residual white solid from the reaction tube was identified spectroscopically as trimethyltrifluoromethylphosphonium iodide [1] (4%). Spectroscopic examination showed that dimethyltrifluoromethylphosphine was not present in the gaseous products.

Reaction of Methylbistrifluoromethylphosphine with Trifluoroiodomethane.—The phosphine (0·149 g., 0·81 mmole) and trifluoroiodomethane (0·161 g., 0·82 mmole), heated at 240° for 12 hr., gave unchanged methylbistrifluoromethylphosphine (0·130 g., 84%), trifluoroiodomethane (0·11 g., 69%), and fluoroform (0·014 g.). In a second experiment a similar reaction mixture, sealed in a silica tube, was exposed to ultraviolet light for 12 hr.; only unchanged reactants and a small amount of phosphorus tri-iodide were recovered. In neither of these experiments was tristrifluoromethylphosphine detected spectroscopically.

Reaction of Dimethyltrifluoromethylphosphine with Trifluoroiodomethane.—Dimethyltrifluoromethylphosphine (0·577 g., 4·4 mmoles) and trifluoroiodomethane (0·889 g., 4·5 mmoles), heated at 240° for 24 hr., failed to give methylbistrifluoromethylphosphine and only unchanged reactants were detected.

Methylbistrifluoromethylarsine.[4]—This was prepared in 36% yield by reaction of tristrifluoromethylarsine with methyl iodide at 240°.

Reaction of Methylbistrifluoromethylarsine with Methyl Iodide.—Methylbistrifluoromethylarsine (1·18 g., 5·2 mmoles) and methyl iodide (0·71 g., 5 mmoles), heated at 240° for 24 hr., gave unchanged methylbistrifluoromethylarsine (0·37 g., 32%) and methyl iodide (0·23 g., 32%), dimethyltrifluoromethylarsine [1] (0·46 g., 52%), trifluoroiodomethane (0·28 g., 28%), and fluoroform (0·16 g., 44%). The yield of dimethyltrifluoromethylarsine based on the methylbistrifluoromethylarsine used up is 75%. Arsenic tri-iodide was also formed.

Reaction of Methylbistrifluoromethylarsine with Trifluoroiodomethane.—Methylbistrifluoromethylarsine (1·10 g., 4·8 mmoles) and trifluoroiodomethane (1·96 g., 10 mmoles), heated at 240° for 24 hr., gave only unchanged reactants. A similar result was obtained by exposure of the reactants in a silica tube to ultraviolet light for 12 hr. Spectroscopic examination showed tristrifluoromethylarsine to be absent.

Reaction of Dimethyltrifluoromethylarsine with Trifluoroiodomethane.—The arsine (0·409 g., 2·35 mmoles) and trifluoroiodomethane (0·483 g., 2·45 mmoles), heated at 240° for 24 hr., gave unchanged dimethyltrifluoromethylarsine (0·253 g., 62%), trifluoroiodomethane (0·327 g., 68%), methylbistrifluoromethylarsine (0·17 g., 32%), methyl iodide (*ca.* 0·1 g.), and fluoroform (0·05 g., 29%). The yield of methylbistrifluoromethylarsine based on the dimethyltrifluoromethylarsine used up was 82%.

Hydrolysis of Methyl Trifluoromethyl Derivatives of Phosphorus, Arsenic, and Antimony.—The compounds shown in the annexed Table were shaken with an excess of 20% aqueous sodium hydroxide at 20°. The volatile products were fractionated *in vacuo* to separate fluoroform from the unchanged phosphine, arsine, or stibine. Fluoride was not liberated.

	mmoles	Time (days)	Unchanged (%)	CHF_3 (%)
$CF_3{\cdot}P(CH_3)_2$	2·24	3	93·5	6·5
$(CF_3)_2P{\cdot}CH_3$	1·49	4	8	92
$(CF_3)_3P$	1·65	2	2	98
$CF_3{\cdot}As(CH_3)_2$	1·26	3	91	9
$(CF_3)_2As{\cdot}CH_3$	0·91	3	31	69
$(CF_3)_3As$	0·96	1	0	100
$CF_3{\cdot}Sb(CH_3)_2$	0·723	3	0	100
$(CF_3)_3Sb$	1·00	30 min.	0	100

One of us (B. O. W.) is grateful to the Master and Fellows of Gonville and Caius College for the award of a Rhondda Research Studentship, and to the University of Adelaide for leave of absence (1953—1954).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[*Received, April 5th,* 1957.]