

A Convenient and Efficient Preparation of Trifluoromethyl-phosphorus and -arsenic Hydrides

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The compounds CF_3MH_2 and $(\text{CF}_3)_2\text{MH}$ ($\text{M} = \text{P}$ or As) can be prepared in high yield by the reduction of the corresponding iodides with hydrogen iodide and mercury. Under the same conditions the diphosphine and diarsine, $(\text{CF}_3)_2\text{M}\cdot\text{M}(\text{CF}_3)_2$, can be reduced to $(\text{CF}_3)_2\text{MH}$, and the cyclic tetramer and pentamer, $(\text{CF}_3\text{M})_{4,5}$ to CF_3MH_2 .

ALTHOUGH trifluoromethyl-phosphorus and -arsenic hydrides have long been known the preparations¹⁻⁹ reported (summarised in Table I) are complex and most give only a fair to poor yield. The most useful of these is the reduction of the iodophosphines to the corresponding hydrides with phosphine.^{2,6} This method suffers from the disadvantage that pure phosphine must be prepared. Further, slightly volatile solids produced in the reaction decompose in the vacuum system, necessitating frequent cleaning of the apparatus. Good yields are also obtained in the reduction of the chloroarsines or the diarsine with anhydrous hydrogen chloride and mercury,^{8,9} but the arsenic compound must be first prepared from the iodoarsines which are the natural starting materials for most studies of perfluoroalkyl compounds, thus the preparation of the hydrides by the above method is necessarily a two-step synthesis.

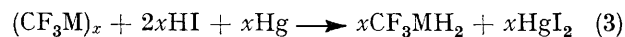
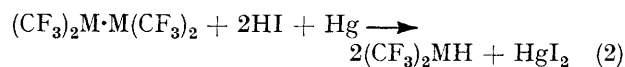
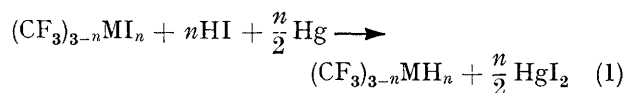
¹ F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1954, 3896.

² A. B. Burg and J. F. Nixon, *J. Amer. Chem. Soc.*, 1964, **86**, 356.

³ W. Mahler and A. B. Burg, *J. Amer. Chem. Soc.*, 1958, **80**, 6161.

⁴ A. B. Burg and W. Mahler, *J. Amer. Chem. Soc.*, 1957, **79**, 4242.

We have found that excess of anhydrous hydrogen iodide and mercury is a very efficient agent for the preparation of the hydrides, either from the corresponding iodides or from the compounds containing P-P or As-As bonds, according to the general equations (1) to (3), where $n = 1$ or 2 , $x = 4$ or 5 , and $\text{M} = \text{P}$ or As .



An excess of hydrogen iodide over that required according to the above equations was used, since some of the hydrogen iodide was consumed by reaction with the

⁵ J. E. Griffiths and A. B. Burg, *J. Amer. Chem. Soc.*, 1962, **84**, 3442.

⁶ G. S. Harris, *J. Chem. Soc.*, 1958, 512.

⁷ H. J. Emeléus, R. N. Haszeldine, and E. G. Walaschewski, *J. Chem. Soc.*, 1953, 1552.

⁸ W. R. Cullen, *Canad. J. Chem.*, 1961, **39**, 1855.

⁹ W. R. Cullen, *Canad. J. Chem.*, 1963, **41**, 317.

mercury. Our results are shown in Table 2. An attractive feature of this procedure is that the products are very easily purified, as there is no other volatile product.

TABLE 1
Preparation of trifluoromethyl-phosphorus and
-arsenic hydrides

Com- pound	Reactant	Reducing agent	Yield (%)	Ref.
CF ₃ PH ₂	CF ₃ PI ₂	H ₂ O	24	1
CF ₃ PH ₂	CF ₃ PI ₂	H ₂ -Raney Ni *	0	1
CF ₃ PH ₂	CF ₃ PI ₂	LiAlH ₄	8	1
CF ₃ PH ₂	CF ₃ PI ₂	PH ₃	88	2
CF ₃ PH ₂	(CF ₃) ₂ P	H ₂ O	21	3
(CF ₃) ₂ PH	(CF ₃) ₂ PI	H ₂ -Raney Ni *	65	1
(CF ₃) ₂ PH	(CF ₃) ₂ PI	LiAlH ₄	0	1
(CF ₃) ₂ PH	(CF ₃) ₂ PI	Hg-protic acid †	35	4
(CF ₃) ₂ PH	(CF ₃) ₂ P·P(CF ₃) ₂	CH ₃ OH	52	5
(CF ₃) ₂ PH	(CF ₃) ₂ PI	PH ₃	73	6
CF ₃ AsH ₂	CF ₃ AsI ₂	LiAlH ₄	49	7
CF ₃ AsH ₂	CF ₃ AsI ₂	Zn-Cu, HCl †	98	7
(CF ₃) ₂ AsH	(CF ₃) ₂ AsI	LiAlH ₄	16	7
(CF ₃) ₂ AsH	(CF ₃) ₂ AsI	Zn-Cu, HCl †	43	7
(CF ₃) ₂ AsH	(CF ₃) ₂ AsCl	Hg-HCl	86	8
(CF ₃) ₂ AsH	(CF ₃) ₂ As·As(CF ₃) ₂	Hg-HCl	84	8
CF ₃ AsH ₂	CF ₃ AsCl ₂	Hg-HCl	79	9

* High-pressure conditions. † Aqueous solution.

TABLE 2
Preparation of the hydrides by use of hydrogen iodide

Compound	Reactant	Reducing agent	Yield (%)
CF ₃ PH ₂	CF ₃ PI ₂	HI-Hg	89
CF ₃ PH ₂	(CF ₃) ₂ P + (CF ₃) ₂ P	HI-Hg	92
(CF ₃) ₂ PH	(CF ₃) ₂ PI	HI-Hg	93
(CF ₃) ₂ PH	(CF ₃) ₂ P·P(CF ₃) ₂	HI-Hg	94
CF ₃ AsH ₂	CF ₃ AsI ₂	HI-Hg	92
CF ₃ AsH ₂	(CF ₃) ₂ As + (CF ₃) ₂ As	HI-Hg	90
(CF ₃) ₂ AsH	(CF ₃) ₂ AsI	HI-Hg	88
(CF ₃) ₂ AsH	(CF ₃) ₂ As·As(CF ₃) ₂	HI-Hg	97
(CF ₃) ₂ PH	(CF ₃) ₂ PI	HI	11
(CF ₃) ₂ PH	(CF ₃) ₂ P·P(CF ₃) ₂	HI	53

Additional experiments in the absence of mercury showed that iodobistrifluoromethylphosphine was slowly reduced (11% in three days) by hydrogen iodide to the hydride, bistrifluoromethylphosphine, and iodine. In contrast the diphosphine quickly consumed one mol. of hydrogen iodide (reaction 4) although the reaction was noticeably slower than in the presence of mercury.



We therefore suggest that mercury, while not essential, accelerates the reactions (1)–(3) by converting any iodo-compound into a derivative with an M–M bond, which then reacts much more rapidly with the hydrogen iodide. We cannot, however, exclude the participation of an intermediate containing a mercury–phosphorus bond as suggested by Burg and Mahler.⁴

In view of these results it is noteworthy that difluorophosphine has been prepared by the reduction of

difluoroiodophosphine with the hydrogen iodide and mercury¹⁰ under similar conditions to those employed here, suggesting that the reaction is quite general. If the action of hydrogen iodide alone on difluoroiodophosphine is as slow as the analogous reduction of iodobistrifluoromethylphosphine described above, the instability¹⁰ of difluorophosphine would preclude its isolation in the absence of mercury.

EXPERIMENTAL

All manipulations were carried out in a vacuum system. Infrared spectra were recorded on a Perkin-Elmer 337, and mass spectra on a A.E.I. MS9 instrument, operating at an ionising voltage of 70 ev. The trifluoromethyl-phosphorus¹¹ and -arsenic^{7,12} starting materials were prepared by literature methods. Commercial hydrogen iodide (Matheson Co.) was fractionally distilled in the vacuum system before use.

Preparation of CF₃PH₂ and (CF₃)₂PH.—Di-iodotrifluoromethylphosphine (1.93 g., 5.46 mmoles), hydrogen iodide (2.09 g., 16.3 mmoles), and mercury (2 ml.) were allowed to warm to room temperature in an evacuated tube. There was an immediate reaction, which was assisted by shaking. After 5 hr. at room temperature, hydrogen was pumped off and a pure sample of CF₃PH₂ (0.493 g., 4.83 mmoles), identified by its infrared spectrum and molecular weight (Found: *M*, 102.5. Calc. for CH₂F₃P: *M*, 102), was separated by fractionation in the vacuum system. In the same way, iodobistrifluoromethylphosphine (0.468 g., 1.58 mmoles), hydrogen iodide (0.368 g., 2.88 mmoles), and mercury (2 ml.) gave (CF₃)₂PH (0.250 g., 1.47 mmoles), identified by its infrared spectrum and molecular weight (Found: *M*, 171. Calc. for C₂H₂F₆P: *M*, 170). Under the same conditions, tetrakisbistrifluoromethyldiphosphine was reduced to (CF₃)₂PH, and a mixture of trifluoromethylphosphorus tetramer and pentamer to CF₃PH₂, in almost quantitative yield. The reactions appeared to be complete within 1 hr. The residual solids had the appearance of a mixture of mercurous and mercuric iodides.

Preparation of CF₃AsH₂ and (CF₃)₂AsH.—A mixture of trifluoromethylarsenic tetramer¹³ and pentamer¹⁴ was prepared by shaking di-iodotrifluoromethylarsine with mercury. The mixture of "CF₃As" (0.080 g., 0.56 mmole), hydrogen iodide (0.439 g., 3.43 mmoles), and mercury (2 ml.) reacted on warming to room temperature to give CF₃AsH₂ (0.075 g., 0.51 mmole), was identified by its infrared spectrum and molecular weight (Found: *M*, 145. Calc. for CH₂AsF₃: *M*, 146). Reaction of tetrakisbistrifluoromethyldiarsine (0.302 g., 0.71 mmole) with hydrogen iodide (0.668 g., 5.21 mmoles), and mercury (2 ml.) gave (CF₃)₂AsH (0.293 g., 1.37 mmoles) (Found: *M*, 214. Calc. for C₂HAsF₆: *M*, 214), also identified spectroscopically. CF₃AsH₂ and (CF₃)₂AsH were prepared in good yield from CF₃AsI₂ and (CF₃)₂AsI, respectively, by the conditions described above.

Reaction of (CF₃)₂PI with HI.—The iodo-compound (0.213 g., 0.72 mmole) and hydrogen iodide (0.091 g., 0.71 mmole), sealed in a tube at room temperature for 3 days, gave iodine, (CF₃)₂PH (0.014 g., 0.08 mmole), and unchanged starting materials. The yield of the hydride was only 11% in the absence of mercury.

¹² E. G. Walaschewski, *Chem. Ber.*, 1953, **86**, 273.

¹³ A. H. Cowley, A. B. Burg, and W. R. Cullen, *J. Amer. Chem. Soc.*, 1966, **88**, 3178.

¹⁴ R. G. Cavell and R. C. Dobbie, unpublished work.

¹⁰ R. W. Rudolph and R. W. Parry, *Inorg. Chem.*, 1965, **4**, 1339.

¹¹ F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1953, 1565.

Reaction of $(\text{CF}_3)_2\text{P}\cdot\text{P}(\text{CF}_3)_2$ with HI.—The diphosphine (0.138 g., 0.41 mmole) and hydrogen iodide (0.095 g., 0.74 mmole) reacted in an evacuated tube (7 hr.) to give $(\text{CF}_3)_2\text{PH}$ (0.075 g., 0.44 mmole), $(\text{CF}_3)_2\text{PI}$ (0.152 g., 0.39 mmole), and unchanged hydrogen iodide. The yield was 107% based on reaction (4), probably because of additional reduction of the iodophosphine by hydrogen iodide.

The purity of the hydrides formed in the above reactions

was also checked by mass spectroscopy. All four compounds showed the molecular ion; there was no significant impurity. Further details of the mass spectra will be given in forthcoming publications.¹⁴

We thank the National Research Council of Canada for financial support and Mr. A. I. Budd for the mass spectra.

[7/123 Received, January 31st, 1967]