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Use of Perfluorodecalin as a Reaction Medium for the Preparation of Anhydrous Metal Bromides

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Metal halides have long served as the starting point for many inorganic and organometallic syntheses, but in general only the anhydrous materials are suitable. Direct combination of metal and halogen is a route to the halides, but in many cases high-temperature reactions are required, while in others the initially sluggish process may become difficult to control as the mixture warms up. The dehydration of hydrated salts with solvents such as thionyl chloride is sometimes an option, but the products of this approach are not always easy to free of the last traces of this reagent.

The synthesis of the metal iodides of main group elements can be readily achieved by reacting the elements together in a suitable solvent. A classic[1] example is the preparation of SnI_4 by refluxing the components in ethanoic anhydride, although the vigor of the reaction invites caution. Indium(III) iodide can be conveniently obtained by the use of either diethyl ether[2] or toluene[3] as the reaction medium. This approach is not feasible with chlorine, and while it might seem viable for bromine, in practice the first quantities of metal bromide formed act as a catalyst for the attack of Br_2 on the solvent; this is especially true for aromatic solvents, since Friedel−Crafts bromination occurs readily in these circumstances.

We have recently shown that these difficulties can be avoided by the use of the solvent perfluorodecalin as the reaction medium. The physical properties of this fluorocarbon are very convenient for this purpose (*e.g.*, bp = 142 °C, $d = 1.92$ g cm^{-3}, kinematic viscosity = 2.66 $mm^2\ s^{-1}$, vp at room temperature = 6.7 mm). For three typical elements (gallium, indium, tin), the reaction with the calculated quantity of bromine in refluxing perfluorodecalin gave the appropriate $MBr_{3,4}$ product in yields of about 90%. The procedure is quite straightforward, and requires no special equipment. An additional advantage is that the solvent can be recovered, after removal of any traces of unreacted bromine *in vacuo*; recoveries were typically >90%. The solvent itself is unaffected by the presence of either bromine or the final product, since the mass spectrum of a sample after a preparation was identical with that of the pure solvent.

The convenience of this preparative method is shown by comparison with those described in the literature for these compounds. Both $GaBr_3$ and $InBr_3$ can be prepared by reacting the heated metal with bromine vapor entrained in a stream of nitrogen or carbon dioxide; the gallium reaction may be dangerously vigorous.[4] The direct reaction of tin and bromine has been described, but again the reaction proceeds with considerable evolution of heat and possible ignition.[5] No such safety hazards were observed in the present work. The reactions reported herein suggest that many other metal bromides may be simply prepared in high yield by this method. Perfluorodecalin also has the possibility of being an excellent medium for the direct chlorination of metals, based on the very high solubility of chlorine in perfluorodecalin (960 cm^{-3} Cl_2/100 cm^{-3}).[6]

Experimental Section

General Procedures. Metallic elements were used as supplied; tin was the powder (Goodfellows Metal), and gallium and indium were in the form of shot (Aldrich). Bromine was 99.5% (Aldrich). Perfluorodecalin (BNFL Fluorochemicals Ltd.) was a mixture of *cis*- and *trans*-isomers, and was used as supplied.

All reactions were carried out under a stream of dry nitrogen, in a round-bottomed flask fitted with a condenser. The product was collected by filtration, dried *in vacuo,* and analyzed. Residual bromine was removed from the solvent before further use.

Bromine microanalyses were carried out by potentiometric titration against a standard $AgNO_3$ solution. Mass spectra of the metal bromides were obtained on a VG Analytical 7070E mass spectrometer. Mass spectra of the solvent before and after use were obtained on a Hewlett-Packard 5890 Series II GC-MS coupled to a VG Trio 1000 bench top quadrupole machine.

Gallium Tribromide. Gallium shot (1.89 g, 27.1 mmol) was heated until molten, for ease of transfer, added to perfluorodecalin (40 mL), and allowed to cool to room temperature. Bromine (5.5 mL, 17.1 g, 107 mmol) was slowly added, and the reaction mixture was stirred without heating for 1 h. The white product was $GaBr_3$ (7.07 g, 22.8 mmol, 84% yield). Anal. Calcd: Br, 77.5. Found: Br, 76.5. Mp 121.5−122 °C (lit.[7] 122 ± 0.6 °C). Ms: M^+ 306−314, M^+(max) 310.

Indium Tribromide. Indium shot (1.98 g, 17.2 mmol) was hammered into a lustrous foil and added to perfluorodecalin (40 mL). Bromine (3.5 mL, 10.9 g, 68 mmol) was slowly added, and the reaction mixture was heated at 100 °C for 3 h. The white product was $InBr_3$ (5.31 g, 15.0 mmol, 87%). The presence of excess bromine was designed to prevent any formation of In_2Br_4 from $InBr_3$ + In. Anal. Calcd: Br, 67.6. Found: Br, 66.95. Mp 434−434.6 °C (lit.[7] 436 °C). Ms: M^+ 352−358, M^+(max) 354.

Tin Tetrabromide. Tin powder (4.62 g, 38.9 mmol) was added to perfluorodecalin (40 mL), and bromine (5.0 mL, 15.5 g, 97 mmol) was slowly added. The reaction mixture was heated to 100 °C for 3 h, giving white, crystalline $SnBr_4$ (15.8 g, 36 mmol, 93% yield). Anal. Calcd: Br, 72.9. Found: Br, 73.1. Mp 29.5−30.0 °C (lit.[7] 31 °C). Ms: M^+ 436−442, M^+(max) 438.

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(1) Palmer, W. G. *Experimental Inorganic Chemistry*; Cambridge University Press: Cambridge, U.K., 1954; p 246.

(2) Gyane, M. J. S.; Wilkinson, W.; Worrall, I. J. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 765.

(3) Freeland, B. H.; Tuck, D. G. *Inorg. Chem.* **1976**, *15*, 475.

(4) Wade, K.; Banister, A. J. *Comprehensive Inorganic Chemistry*; Bailar, J., Trotman-Dickenson, A. F., Eds.; Pergamon: Oxford, U.K., 1973; Vol. I, p 1084.

(5) Brauner, G., ed. *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Academic Press: New York, 1963; Vol. 1, p 733.

(6) Banks, R. E. ed. *Preparation, Properties and Industrial Applications of Organofluorine Compounds*; Ellis Harwood: Chichester, U.K., 1982; p 53.

(7) Weast, R. C., Ed. Handbook of Chemistry and Physics, 63rd ed.; CRC Press: Boca Raton, FL, 1982.

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