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PRELIMINARY COMMUNICATION

A NEW AND CONVENIENT SYNTHESIS OF MONOHALOMETHYL DERIVATIVES OF MERCURY, TIN AND LEAD

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Halomethyl—metal compounds, $R_nM{-}CH_2X$, are very useful reagents. Via their magnesium and lithium derivatives they make possible the preparation and broad study of α-functional organometallic compounds, and some, such as those of mercury[1-3], find useful application as CH_2 transfer agents. A simple and generally applicable preparation of halomethyl—metal compounds would be very desirable.

Halomethyl derivatives of silicon and germanium are readily accessible via direct halogenation of methyl compounds of these elements[4,5]. However, methyl group halogenation of methyl derivatives of the heavier metals such as tin, lead and mercury is not possible due to the ease with which the halogens cleave heavy metal-to-carbon bonds. The currently available routes to halomethyl derivatives of heavy metals are very limited and not very satisfactory. Thus the reaction of diazomethane with metal and organometallic halides serves in a general preparation of halomethyl compounds, including those of tin, lead and mercury[6], but the potential hazards associated with handling diazomethane in large quantities impose a severe limitation on the scale on which such preparations can be carried out. For the preparation of iodomethylmercuric iodide a direct process - irradiation of a mixture of methylene iodide and metallic mercury - can be used[7], but bis(iodomethyl)-mercury, accessible only through the diazomethane route[8], would be a more useful and more easily handled and purified methylenation agent. In view of our interest in halomethyl derivatives of mercury[1-3] and tin[9], we have searched for alternate methods for their preparation. We report here concerning a new and convenient route to halomethyl compounds of these metals, as well as of lead.

The discovery in 1958 by Simmons and Smith[10] that the reaction product of methylene iodide and zinc—copper couple added CH_2 to olefinic double bonds to give cyclopropanes revived interest in this class of zinc reagents which were first reported by Emschwiller in 1929[11]. The work by Simmons and his coworkers established that the cyclopropane-forming process was a direct reaction between the organometallic reagent and the olefin, in which the former had the characteristics of an *electrophilic species*[12,13]. Most current users of this organozinc reagent seem to agree with Emschwiller's original suggestion that the active species in solution is solvated ICH_2ZnI, and recently such a compound was isolated in substance in the form of its 1,4-dioxane solvate[14]. The presence of an $ICH_2{-}Zn$ linkage is, in any case, supported by convincing evidence: hydrolysis gives methyl iodide, while treatment with iodine gives methylene iodide[11]. If a ICH_2–Zn linkage is indeed present in the reagent under discussion, it might be expected that it could serve as a transfer agent for the ICH_2 group via *nucleophilic attack* at a suitable electrophilic center. It may be noted that in the classical work of Frankland over 100 years ago simple alkylzinc compounds were the only reactive alkylating agents available and served in the preparation of tetraethyltin from $SnCl_4$[15], tetraethyllead from lead(II) chloride[16] and diethylmercury from mercuric chloride[17]

In view of the ease of preparation of halomethylzinc halides[18] and, once formed, their stability in solution, the use of ICH_2ZnI, $BrCH_2ZnBr$[18] and $ClCH_2ZnI$[12] as reagents for halomethylation of other metals was worth investigating.

We have found that iodomethylzinc iodide and bromomethylzinc bromide are indeed very effective halomethylation agents. In reactions with trimethyltin chloride, the expected (iodomethyl)trimethyltin, n_{D}^{25} 1.5511 (lit.[9] n_{D}^{25} 1.5510), and (bromomethyl)-trimethyltin, n_{D}^{25} 1.5078 (lit.[9] n_{D}^{25} 1.5070), were produced in yields of 86% and 84%, respectively. The action of iodomethylzinc iodide on mercuric iodide in THF gave $Hg(CH_2I)_2$, m.p. 79–81° (lit.[8] m.p. 80–82°), in 78% yield.

$$\mathrm{XCH_2ZnX + (CH_3)_3SnCl \xrightarrow{THF} (CH_3)_3SnCH_2X + ZnXCl}$$

$$\mathrm{2\,ICH_2ZnI + HgI_2 \xrightarrow{THF} Hg(CH_2I)_2 + ZnI_2}$$

Prepared in similar fashion was bis(bromomethyl)mercury in 43% yield. Iodomethylzinc iodide also was used to prepare bis(iodomethyl)dimethyltin, $Me_2Sn(CH_2I)_2$, a new compound, b.p. 68–70°/0.05 mm, n_{D}^{25} 1.6448, in 56% yield, and (iodomethyl)triphenyllead, Ph_3PbCH_2I, also new, m.p. 72–73.5°, in 31% yield.

The preparation of (iodomethyl)trimethyltin is described in detail as an example of the general procedure used.

A zinc–copper couple was prepared in a flame-dried, nitrogen-swept, 100 ml, three-necked flask equipped with reflux condenser, dropping funnel, nitrogen inlet tube and magnetic stirring unit from 2.60 g (40 mg-atom) of granular zinc by the method of Le Goff[18]. To the dried couple was added 20 ml of dry tetrahydrofuran (THF) and a few drops of CH_2I_2 to initiate the reaction. Subsequently 10.75 g (40.2 mmoles) of methylene iodide diluted with 7 ml of THF was added slowly at such a rate that the temperature could be maintained at *ca.* 40°. After a reaction period of 2.5 h, the reaction mixture was cooled to 0° and filtered with nitrogen pressure through a sintered glass filter–Schlenk tube into another dry, nitrogen-swept, 100 ml, three-necked flask equipped as had been the original reaction vessel. To the filtered zinc reagent solution was added slowly over 30 min 4.25 g (21.3 mmoles) of trimethyltin chloride in 10 ml of THF. The reaction mixture was stirred at 40° for 3 h, cooled and diluted with 25 ml of benzene. Hydrolysis and extraction of the reaction mixture (to remove zinc salts and THF) with four 50 ml portions of distilled water followed. Sodium chloride was added to break any emulsions which formed at times. The aqueous extracts were shaken with benzene and the combined organic layers were dried and distilled to give 5.6 g (86%) of Me_3SnCH_2I, b.p. 54–55°/5.5 mm. NMR (in CCl_4): δ 0.22 (s, 9H, $J(^{117}Sn–H)$ 52 Hz; $J(^{119}Sn–H)$ 55 Hz, Me_3Sn–) and 1.90 ppm (s, 2H, J(Sn–H) 20 Hz, –CH_2I).

We are continuing our investigation of this useful new reaction and are in particular interested in the synthesis of halomethyl derivatives of metals and metalloids other than those reported in the present communication.

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REFERENCES

1 D. Seyferth, M.A. Eisert and L.J. Todd, *J. Amer. Chem. Soc.*, 86 (1964) 121.
2 D. Seyferth, R.M. Turkel, M.A. Eisert and L.J. Todd, *J. Amer. Chem. Soc.*, 91 (1969) in press.
3 D. Seyferth, R. Damrauer, R.M. Turkel and L.J. Todd, *J. Organometal. Chem.*, 17 (1969) 367.
4 C. Eaborn, *Organosilicon Compounds*, Butterworths, London, 1960, p. 379–382.
5 M. Wieber, C.D. Frohning and G. Schwarzmann, *Z. Anorgan. Allg. Chem.*, 355 (1967) 79.
6 D. Seyferth, *Chem. Rev.*, 55 (1955) 1155.
7 E.P. Blanchard, Jr., D.C. Blomstrom and H.E. Simmons, *J. Organometal. Chem.*, 3 (1965) 97.
8 G. Wittig and K. Schwarzenbach, *Ann. Chem.*, 650 (1961) 1.
9 D. Seyferth and E.G. Rochow, *J. Amer. Chem. Soc.*, 77 (1955) 1302; *J. Org. Chem.*, 20 (1955) 250.
10 H.E. Simmons and R.D. Smith, *J. Amer. Chem. Soc.*, 80 (1958) 5323; 81 (1959) 4256.
11 G. Emschwiller, *C.R. Acad. Sci. Paris*, 188 (1929) 1555.
12 E.P. Blanchard and H.E. Simmons, *J. Amer. Chem. Soc.*, 86 (1964) 1337.
13 H.E. Simmons, E.P. Blanchard and R.D. Smith, *J. Amer. Chem. Soc.*, 86 (1964) 1347.
14 K.-H. Thiele and I. Benthin, *Z. Chem.*, 8 (1968) 344.
15 E. Frankland, *Ann. Chem.*, 85 (1853) 340.
16 E. Frankland and W.T. Lawrence, *J. Chem. Soc.*, 35 (1879) 245.
17 E. Frankland, *Ann. Chem.*, 111 (1859) 59.
18 E. Le Goff, *J. Org. Chem.*, 29 (1964) 2048.