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HALOMETHYL–METAL COMPOUNDS

LXII*. PREPARATION OF DIIODOMETHYL–METAL COMPOUNDS

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SUMMARY

The reagents CHI_2MgCl, CHI_2Li, Me_3SiCI_2Li, CH_3CI_2Li and Me_3SnCI_2MgCl have been used to prepare Me_3SnCHI_2, $CH_2{=}CHCH_2CHI_2$, $Me_3SiCI_2CH_3$, $(Me_3Si)_2CI_2$ and $(Me_3Sn)_2CI_2$.

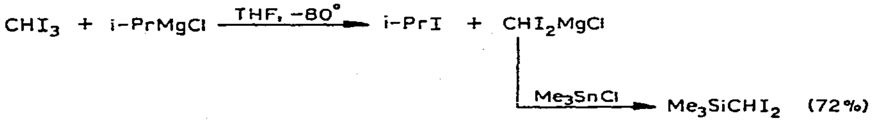
INTRODUCTION

In previous papers we have described the preparation and utilization in further synthesis of silicon and tin compounds of type Me_3MCHCl_2, Me_3MCCl_3, Me_3MCHBr_2, Me_3MCBr_3, $(Me_3M)_2CCl_2$ and $(Me_3M)_2CBr_2$ (M = Si and Sn)[2-5]. As this work progressed, we became interested in analogous silicon- and tin-substituted di- and triiodo compounds for use as precursors in the synthesis of Me_3MCHI- and Me_3MCI_2-substituted zinc and mercury compounds. These, it was hoped, might serve as divalent carbon transfer agents for the Me_3MCH and Me_3MCI species.

When this investigation commenced, no active metal derivatives of type $MCHI_2$ or MCI_2R had been described. Accordingly, we began this study with an investigation of the synthesis and stability of such reagents.

RESULTS AND DISCUSSION

In a previous paper[4], we have reported our earliest results of this study, the preparation of CHI_2MgCl in THF by the Normant/Villieras procedure[6] [eqn. (1)] and the application of this reagent in the synthesis of Me_3SiCHI_2 and $Me_2HSiCHI_2$. This reagent also has been used to prepare Me_3SnCHI_2 in 72% yield.



$$CHI_3 + i\text{-}PrMgCl \xrightarrow{THF,\ -80^\circ} i\text{-}PrI + CHI_2MgCl \xrightarrow{Me_3SnCl} Me_3SiCHI_2 \quad (72\%) \qquad (1)$$

Although this Grignard reagent served satisfactorily in the transfer of the CHI_2

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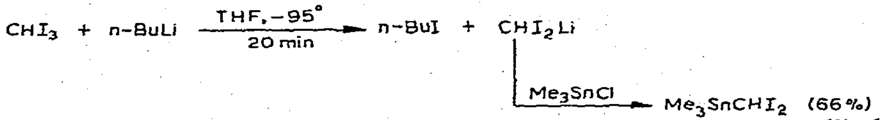
* For Part LXI see ref. 1.

group to other metals, we were interested in examining the stability and synthetic utility of the analogous lithium reagent, CHI_2Li. A reaction of n-butyllithium with iodoform in THF at −95° generated a deep red solution of this reagent in good yield [eqn. (2)]. Similar reaction of CHI_2Li with allyl bromide gave $CH_2{=}CHCH_2\text{-}CHI_2$ in 42% yield*.



(2)

Lithium–hydrogen exchange may also be used to generate *gem*-diiodoalkyllithium reagents. Although dichloromethyllithium has been used in such applications[7,8] [eqn. (3)], the reagent of choice, according to recent studies of Martel and

$$CHCl_2Li+CH_2X_2 \underset{}{\overset{\text{THF, low temp.}}{\rightleftharpoons}} CHX_2Li+CH_2Cl_2 \qquad (3)$$

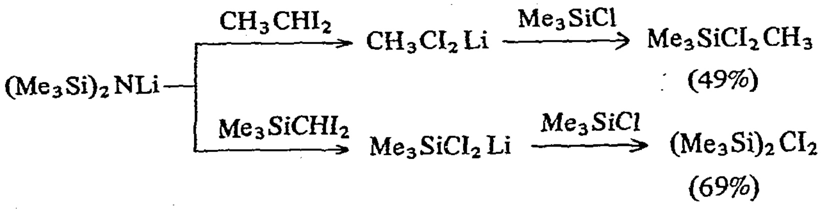
$$(X=Br \text{ or } I)$$

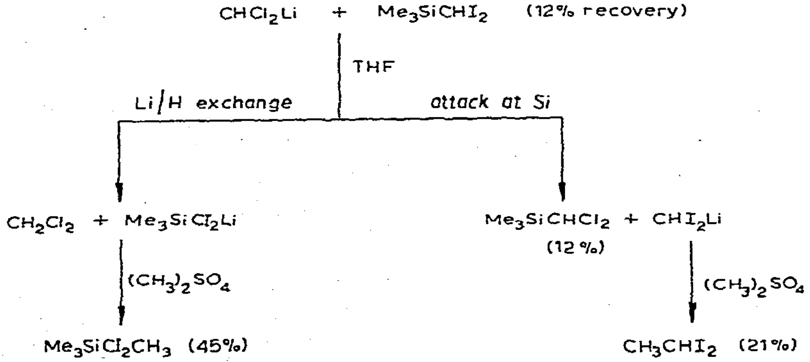
Hiriart[9], is an alkali metal bis(trimethylsilyl)amide. Among the reactions studied by these French workers was that shown in eqn. (4)[9b].

$$(Me_3Si)_2NK+CH_2I_2 \xrightarrow{Et_2O,\ -76°} \xrightarrow{Me_3SiCl} Me_3SiCHI_2 \quad (35\%) \qquad (4)$$

We have used $(Me_3Si)_2NLi$ to generate CH_3CI_2Li and Me_3SiCI_2Li. Reaction of these reagent solutions with trimethylchlorosilane gave trimethylsilyl derivatives in quite good yield as shown in the scheme below. On the other hand, the attack of

$$n\text{-}BuLi+(Me_3Si_2)NH \xrightarrow{THF} (Me_3Si)_2NLi$$





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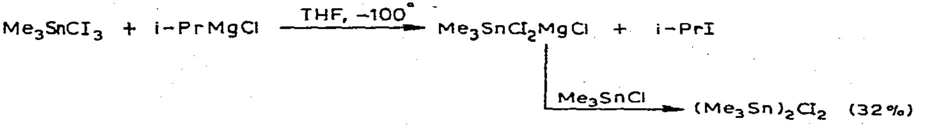
* During the course of this study, the preparation of CHI_2Li by reaction of phenyllithium and iodoform in THF at −100° was reported by Köbrich and Nagel[7]. Reaction with trimethylchlorosilane was reported to give Me_3SiCHI_2 in 22% yield.

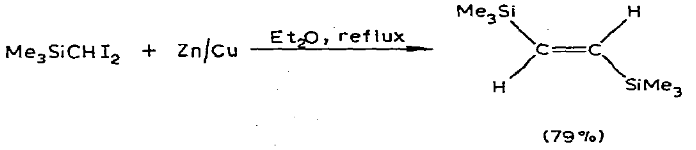
dichloromethyllithium on trimethyl(diiodomethyl)silane appeared to occur both at hydrogen although metalation was the preferred process as shown below.

An analogous tin reagent, Me_3SnCI_2Li, could not be prepared by this procedure because of the facility with which nucleophilic attack at tin can occur. However, the Grignard reagent, Me_3SnCI_2MgCl, was found to be sufficiently stable to use as a preparative reagent [eqn. (5)]. The trimethyl(triiodomethyl)tin used as starting material was prepared by the action of Me_3SnNEt_2 on iodoform. In view of its sensitivity to air and light, it was not isolated and characterized. Instead, the crude solid was treated immediately with the Grignard solution.



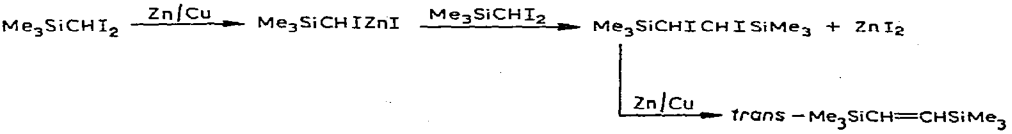
$$Me_3SnCI_3 + i\text{-}PrMgCl \xrightarrow{THF,\ -100^\circ} Me_3SnCI_2MgCl + i\text{-}PrI \qquad Me_3SnCI_2MgCl \xrightarrow{Me_3SnCl} (Me_3Sn)_2CI_2\ (32\%) \qquad (5)$$

The iodine-substituted silicon and tin compounds prepared during the course of this study are light and air-sensitive materials which readily turn from colorless to light yellow and finally to dark red or red-purple even when kept in brown bottles. In view of these unattractive properties, their chemistry has not been examined as extensively as we had intended. We have described the conversion of Me_3SiCHI_2 and Me_3SnCHI_2 to the respective zinc reagents, $Me_3SiCHIZnI$ and $Me_3SnCHIZnI$, in a previous paper of this series[10]. Furthermore, we note that Me_3SiCHI_2 is a good source of *trans*-$Me_3SiCH{=}CHSiMe_3$ [eqn. (6)]. However, 7-(trimethylsilyl)norcarane was not obtained when the reaction of Me_3SiCHI_2 with zinc/copper couple



(6)

was carried out in the presence of cyclohexene. Thus the formation of *trans*-1,2-bis(trimethylsilyl)ethylene very likely occurs via an organometallic route:



$$Me_3SiCHI_2 \xrightarrow{Zn/Cu} Me_3SiCHIZnI \xrightarrow{Me_3SiCHI_2} Me_3SiCHICHISiMe_3 + ZnI_2 \qquad Me_3SiCHICHISiMe_3 \xrightarrow{Zn/Cu} trans\text{-}Me_3SiCH{=}CHSiMe_3$$

In this connection we note the related reaction of $Me_3SiCHBr_2$ with magnesium in diethyl ether. A reaction course similar to that indicated in eqn. (7) very likely was involved, since a low yield of a coupled product, $Me_3SiCHBrCHBrSiMe_3$, was isolated in addition to a 4/1 mixture of *trans*- and *cis*-$Me_3SiCH{=}CHSiMe_3$ in 60% yield.

EXPERIMENTAL

General comments

The low-temperature organolithium and Grignard techniques used in this work have been described in previous papers of this series[2-5] and will not be repeated here. It should be stressed that all reactions were carried out under an atmosphere of prepurified nitrogen. All operations involving organic and organometallic polyiodides were effected with minimal exposure to light. Transfers involving air-sensitive solutions were carried out with syringes and/or cannulae.

The diiodides prepared or utilized in this study all are readily decomposed by daylight and should be stored in brown bottles under an inert atmosphere. Even then, they usually change from colorless to light pink. In daylight, in the presence of air, they rapidly become red to red-purple in color due to liberated iodine.

Infrared spectra were recorded using Perkin–Elmer model 237B, 337, 257 or 457A infrared spectrophotometers, NMR spectra using a Varian Associates T60 spectrometer. Chemical shifts are reported in δ units, ppm downfield from tetramethylsilane. In the case of trimethylsilyl and trimethyltin derivatives, chloroform or cyclohexane was used as internal standard. Gas-liquid chromatography was used extensively to analyze reaction mixtures, determine yields and isolate samples of pure products. F&M Model 700, 720 and 5754 gas chromatographs and M.I.T. isothermal units were used. Yields were determined using the internal standard procedure.

Preparation of trimethyl(diiodomethyl)tin

A flamed-out 500 ml standard low temperature reaction apparatus was charged with 39.0 g (0.1 mol) of iodoform and 200 ml of freshly distilled THF. The mixture was cooled to −95° ± 3° and then a solution of isopropylmagnesium chloride (from 0.11 g-atom of Mg, 15 ml of isopropyl chloride and 40 ml of THF) was added by syringe. The deep red solution of CHI_2MgCl which resulted was stirred for 15 min and then 20 g (0.1 mol) of trimethyltin chloride (M&T Chemicals, Inc.) in 20 ml of THF was added The red color rapidly faded to orange and then light yellow. The reaction mixture was stirred for 1 h at −95° and then allowed to warm to room temperature. Hydrolysis with saturated NH_4Cl solution was followed by concentration of the organic layer at reduced pressure. The residue was extracted with dichloromethane and the extracts were treated with 10% KF in aq. methanol. Concentration of the organic phase was followed by trap-to-trap distillation at 0.03 mmHg (pot temperature to 40°). The transfered volatiles were redistilled to give 31.2 g (72%) of the title compound.

This compound also was prepared by the organolithium procedure. A flamed-out one liter standard low temperature reaction apparatus was charged with 100 g (0.25 mol) of iodoform and 500 ml of THF. The mixture was cooled to −95° and the yellow suspension was treated with 170 ml (0.27 mol) of 1.6 *M* n-butyllithium in hexane during 10 min. The deep red solution of CHI_2Li was stirred at −95° for 20 min and then 50 g (0.25 mol) of Me_3SnCl in 100 ml of THF was added. The intensity of the color gradually decreased during 1 h and then the mixture was warmed to room temperature and concentrated at reduced pressure. The residue was treated with 300 ml of water and 20 ml of 10% aq. methanolic KF. Extraction with chloroform was followed by concentration of the organic phase and vacuum distillation of the residue (20 cm Vigreux column) to give the title compound in 66% yield (71.8 g).

Me_3SnCHI_2. B.p. 65–66°/0.4 mmHg; n_D^{25} 1.6413. (Found: C, 11.34; H, 2.40; I, 58.94. $C_4H_{10}I_2Sn$ calcd.: C, 11.16; H, 2.34; I, 58.94%.) NMR (CCl_4): δ 0.33 [s, 9H, J(Sn–H) 48, 50 Hz, Me_3Sn] and 4.20 ppm (s, 1H, CHI_2).

Preparation of 4,4-diiodo-1-butene

A solution of CHI_2Li in THF was prepared at −95° using the procedure described above and then was treated with 36 g (0.30 mol) of allyl bromide. The reaction mixture was stirred at −95° for 3 h, warmed to room temperature and concentrated at reduced pressure. Addition of 100 ml of chloroform and 200 ml of water to the residue was followed by concentration of the dried organic layer and vacuum distillation of the residue to give 32.4 g (42%) of the title compound, obtained as a faintly pink liquid.

$CH_2{=}CHCH_2CHI_2$. B.p. 67–68°/3.5 mmHg; n_D^{25} 1.6460. (Found: C, 15.61; H, 1.99; I, 82.68. $C_4H_6I_2$ calcd.: C, 15.60; H, 1.97; I, 82.43%.) NMR (CCl_4): δ 3.18 (t, 2H, J 6.5 Hz, CH_2), 5.00 (t, 1H, J 6.5 Hz, CHI_2) and 5.2–6.1 ppm (m, 3H, $CH{=}CH_2$).

Preparation of trimethyl(1,1-diiodoethyl)silane

A 500 ml standard low temperature apparatus was charged with 8.5 g (0.053 mol) of hexamethyldisilazane (Dow Corning Corp.) and 100 ml of dry THF. The solution was cooled to −90° and a solution of 2.3 *M* n-BuLi in hexane (23 ml, 53 mmol) was added by syringe. The temperature of the reaction mixture was allowed to rise slowly to 0°. It then was cooled to −95° again and 14.1 g (50 mmol) of 1,1-diiodoethane[11] was added by syringe during 1 min. The temperature of the mixture was maintained at about −100° while it was stirred for 1 h. Addition of 7 ml (ca. 55 mmol) of trimethylchlorosilane (Union Carbide Corp.) followed. The reaction mixture was stirred at −100° for another 90 min, warmed to room temperature and treated with 50 ml of water. The organic layer, after it had been dried, was evaporated. Crystallization of the residue from methanol gave 8.7 g (49%) of the title compound.

$Me_3SiCI_2CH_3$. M.p. 193–196° (dec). (Found: C, 17.17; H, 3.45; I, 71.79. $C_5H_{12}I_2Si$ calcd.: C, 16.97; H, 3.42; I, 71.68%.) NMR (CCl_4): δ 0.28 (s, 9H, Me_3Si) and 2.90 ppm (s, 3H, CH_3CI_2).

Preparation of bis(trimethylsilyl)diiodomethane

A 500 ml standard low temperature reaction apparatus was charged with 8.5 g (53 mmol) of hexamethyldisilazane, 25 ml of diethyl ether and 75 ml of THF. The reaction mixture was cooled to −90° and 25 ml of 1.6 *M* n-BuLi (56 mmol) was added. The mixture was allowed to warm slowly to room temperature and then was cooled to about −100°. Trimethyl(diiodomethyl)silane (17.0 g, 50 mmol) in 20 ml of THF was added during a 1 min period. The resulting deep purple solution was stirred at −100° for 1 h. Subsequently 8.0 ml (63 mmol) of Me_3SiCl was added; the color was discharged immediately. After the reaction mixture had been stirred at −100° for 1 h, it was allowed to warm to room temperature and treated with 100 ml of water and 70 ml of hexane. The combined organic layers were dried and evaporated at reduced pressure. The residue was crystallized from methanol at low temperature to give 14.2 g (69%) of the title compound.

$(Me_3Si)_2CI_2$. M.p. 161–162.5° (dec). (Found: C, 20.31; H, 4.45; I, 61.56. $C_7H_{18}I_2Si_2$ calcd.: C, 20.40; H, 4.40; I, 61.57%.) NMR (CCl_4): δ 0.37 (s, Me_3Si).

Reaction of trimethylsilyl(diiodomethyl)silane with dichloromethyllithium

A 500 ml standard reaction apparatus was charged with 5.3 g (55 mmol) of dichloromethane and 150 ml of dry THF. The solution was cooled to −95° and 32 ml of 1.6 *M* n-BuLi in hexane (51 mmol) was added during 5 min. The mixture was stirred at −95° for 1 h; subsequently 17.0 g (50 mmol) of Me_3SiCHI_2 in 10 ml of THF was added rapidly. The reagent solution was stirred at −100° for 2 h and then was treated with 5.6 ml (ca. 58 mmol) of dimethyl sulfate. After 1 h, the reaction mixture was allowed to warm slowly to room temperature. Trap-to-trap distillation at 0.02 mmHg and room temperature was followed by treatment of the residue with 50 ml of hexane and 50 ml of water. The hexane solution and the trap-to-trap distillate were combined and analyzed by GLC (10% UC-W98 silicone oil column at 140°) after the solvents had been removed using a 20 cm Vigreux column. The following yields were determined: $Me_3SiCI_2CH_3$ (45%), Me_3SiCHI_2 (12%), CH_3CHI_2, 21% and $Me_3SiCHCl_2$ (12%).

Preparation of bis(trimethyltin)diiodomethane

This entire procedure must be carried out with rigorous exclusion of air and moisture and in the absolute minimum of light.

A 500 ml, three-necked flask equipped with a mechanical stirrer and a nitrogen inlet tube was charged with 10.6 g (45.0 mmol) of Me_3SnNEt_2[12] and 40 ml of freshly distilled THF. The mixture was cooled with a Dry-Ice/acetone bath and then 18.0 (45 mmol) of iodoform in 30 ml of THF was added down the inside wall of the flask by syringe. The mixture was stirred for 5 min and then was allowed to warm slowly to room temperature. During this time, some orange-yellow solid precipitated. After 15 min, the flask was attached to a vacuum manifold and all volatiles were removed at 1.0 mmHg and room temperature. The dry solid residue was dissolved in 150 ml of THF and a pentane thermometer and adapter were added to the apparatus. The mixture was cooled to −100° and then was treated with a solution of isopropylmagnesium chloride (from 50 mg-atom of Mg) in 30 ml of THF during a 5 min period. The very deep red solution which resulted was stirred for 25 min and then 10.0 g (50 mmol) of trimethyltin chloride in 40 ml of THF was added. The reaction mixture was stirred for 3 h at −100° and then allowed to warm slowly to room temperature. Concentration of the pale yellow solution which was present at reduced pressure left a solid which smelled strongly of trimethyltin halide. Treatment with 100 ml of 10% aq. methanolic KF and 200 ml of 1/1 dichloromethane/hexane was followed by evaporation of the organic layer to leave a yellow solid. The latter was recrystallized from 100 ml of warm methanol (filtered with activated charcoal). A yield of 8.6 g (32%) of the title compound was obtained.

$(Me_3Sn)_2CI_2$. M.p. 90–92°, pale yellow plates. (Found: C, 14.26; H, 3.10; I, 42.81. $C_5H_{18}I_2Sn_2$ calcd.: C, 14.17; H, 3.06; I, 42.77%.) NMR (CCl_4): δ 0.35 ppm [Me_3Sn, J(Sn–H) 53, 56 Hz].

Reaction of trimethyl(diiodomethyl)silane with zinc/copper couple.

The couple was prepared by the Le Goff procedure[13] from 2.67 g (40.8 mg-atom) of 20–30 mesh granular zinc in a 100 ml, threenecked flask equipped with a mechanical stirrer. After the couple had been washed with ether and dried, the apparatus was fitted with a reflux condenser and a 60 ml addition funnel. The latter was charged with a solution of 8.33 g (24.2 mmol) of Me_3SiCHI_2 in 20 ml of ether and a few drops of this solution was added to the couple. A vigorous reaction commenced after 20 sec and the rest of the silane solution was added slowly over a period of 25 min.

The ether solution was decanted and washed with two 25 ml portions of 1 *M* HCl, dried and concentrated by distillation. Trap-to-trap distillation of the residue at 0.1 mmHg gave 2.30 g of liquid which GLC (10% DC-200 silicone fluid at 120°) showed to contain only *trans*-bis(trimethylsilyl)ethylene in 79% yield. The *cis* isomer was absent and the GLC conditions used were shown not to cause isomerization of the *cis* isomer to the *trans*. Samples of both isomers were available[14].

A similar reaction carried out in the presence of a large excess of cyclohexene gave no 7-(trimethylsilyl)norcarane. Samples of both *syn* and *anti* isomers were available from a previous study[14].

Reaction of trimethyl(dibromomethyl)silane with magnesium in diethyl ether.

A 500 ml, three-necked flask equipped with a mechanical stirrer, a 250 ml addition funnel and a reflux condenser topped with a nitrogen inlet tube was charged with 5.22 g (21.5 mg-atom) of magnesium turnings and 50 ml of dry ether, and a solution of 49.2 g of $Me_3SiCHBr_2$[4] (0.20 mol) in 200 ml of ether was added to the dropping funnel. The addition of a few ml of this solution to the magnesium was followed by initiation of the reaction with 0.5 ml of 1,2-dibromoethane. The remainder of the $Me_3SiCHBr_2$ was added during 2.5 h at such a rate as to maintain a gentle reflux. The mixture was heated at reflux for 30 min, cooled and hydrolyzed with saturated ammonium chloride solution. The residual salts were extracted with a mixture of ether and 1*N* HCl. The combined ether layers were dried and concentrated. Trap-to-trap distillation at 0.05 mmHg (room temperature) gave a clear distillate which was redistilled to give a fraction boiling between 128–146° at atmospheric pressure. The latter was found by GLC to contain a 4/1 mixture of *trans*- and *cis*-$Me_3SiCH{=}CHSiMe_3$ in 60% yield. Both compounds were identified spectroscopically.

The residue in the trap-to-trap distillation pot was heated to 80° at 0.05 mmHg to give a volatile solid and a small amount of liquid. Recrystallization from ethanol gave fine white needles, m.p. 67–68° with sublimation. (Found: C, 29.09; H, 6.15; Br, 48.37. $C_8H_{20}Br_2Si_2$ calcd.: C, 28.92; H, 6.07; Br, 48.10%.) NMR (CCl_4, $CHCl_3$): δ 0.07 (s, 18H, Me_3Si) and 3.78 ppm (s, 2H, CHBr). Mass spectrum (Hitachi Perkin–Elmer RMU-60 at 80 ev): no molecular ion; the highest observed fragment was found to be $(M-15)^+$ at 315, 317 and 319 in 1/2/1 ratio. Identification as *meso*-$Me_3SiCHBrCHBrSiMe_3$ seems reasonable.

ACKNOWLEDGEMENTS

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