The Alkylation of Tin(IV) Chlorides with Alkylaluminums[1]

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Received March 28, 1960

In the course of an investigation of reactions of aluminum alkyls with metallic halides, we have investigated their reactions with tin(IV) chlorides. Aluminum alkyls have been known for a number of years[2] but had received only limited investigation as intermediates until a convenient synthesis was developed by Ziegler and associates.[3] Recently the reaction of triisobutylaluminum and stannic chloride has been reported[4] and a patent describing the reactions of tin halides, alkali metal halides, and aluminum alkyls has appeared.[5] Apparently, the first reaction of an aluminum-carbon compound with a tin(IV) halide consists of the methylation of stannic chloride with aluminum carbide.[6] This reaction reportedly is productive of methyltin trichloride and dimethyltin dichloride, but does not appear to have been popularized for the synthesis of methyltin compounds. Our investigations revealed that trialkylaluminums and alkylaluminum chlorides will alkylate tin(IV) chlorides in high yields. The reactions were generally highly exothermic, rapid, and were conducted at temperatures between room temperature and 100°. Solvents are sometimes useful as heat transfer media but are not required. The utilization of alkyl groups attached to aluminum is complete when one alkylates stannic chloride, $RSnCl_3$, or R_2SnCl_2 to the R_3SnCl level. The reaction of a tin(IV) chloride with an alkylaluminum chloride[7] represents an excellent one-step method for the preparation of trialkyltin chlorides. Dimethyltin dichloride reacted with methylaluminum sesquichloride to furnish trimethyltin chloride (69% yield) and stannic chloride with ethylaluminum sesquichloride resulted in a 74% yield of triethyltin chloride. When sufficient trialkylaluminum or alkylaluminum chloride was treated with stannic chloride or an organotin chloride with two or more halogens to produce a tetraalkyltin, a product was obtained which was a mixture of trialkyltin halide and tetraalkyltin, the trialkyltin halide usually being present in the larger amount. Thus, *n*-butyltin trichloride and tri-*n*-butylaluminum (mole ratio 1:1) resulted in a mixture of tri-*n*-butyltin chloride and tetra-*n*-butyltin. A mixture of tri-*n*-octyltin chloride and tetra-*n*-octyltin resulted even when di-*n*-octyltin dichloride and tri-*n*-octylaluminum (mole ratio 3:2) were allowed to react at 150°. Prolonged heating at elevated temperatures (140–150°) failed to cause complete utilization of the alkyl groups attached to aluminum in the above instances. Subsequent to the initiation of this investigation, a publication by Russian authors[4] reported that when they treated stannic chloride with triisobutylaluminum (mole ratio 3:4), the product was a mixture composed of tetraisobutyltin and triisobutyltin chloride. The incomplete utilization of alkyl groups attached to aluminum in alkylating tin chlorides to the tetraalkyltin level is possibly due to the reduced activity of the alkylaluminum chlorides formed during the reaction. When aluminum chloride and tetra-*n*-butyltin were heated together at 130°, tetra-*n*-butyltin was recovered unchanged, indicating that an equilibrium does not seem to exist. Tetraalkyltin compounds can be prepared in high yield when trialkyltin chlorides are treated with trialkylaluminums. Triethyltin chloride and triethylaluminum (1:1) resulted in an 89% yield of tetraethyltin and tri-*n*-butyltin chloride and tri-*n*-butylaluminum (1:1) furnished tetra-*n*-butyltin (87%).

The preparation of tin alkyls with mixed groups by treating an alkylated tin halide with an aluminum alkyl compound containing a different alkyl group furnished a spectra of products. The preparation of mixed tin alkyls with predictable structure by this method is therefore not recommended.

EXPERIMENTAL[8]

Trimethyltin chloride. Dimethyltin dichloride[9] (62.8 g.; 0.285 mole) was suspended in 200 ml. of anhydrous ether and methylaluminum sesquichloride (20.9 g.; 0.095 mole) added dropwise to the stirred mixture during 55 min. The dimethyltin dichloride gradually went into solution during the addition and a clear one-phase reaction mixture resulted. The mixture was stirred at room temperature for 30 min. and then hydrolyzed by the dropwise addition of 75 ml. of water. The ether layer was separated and combined with ether extracts from the aqueous layer and dried. After removal of solvents, distillation furnished 39 g. (69% yield) of trimethyltin chloride, b.p. 154–156° (739 mm.). No material boiling in the range of tetramethyltin was observed, but a still pot residue (6 g.) of impure unchanged dimethyltin dichloride was obtained. The trimethyltin chloride solidified upon standing and was further identified by conversion in the conventional manner[10] to trimethyltin fluoride in quan-

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(1) Presented before the Division of Organic Chemistry at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September 1959.

(2) G. B. Buckton and W. Odling, *Ann. Spl.*, **4**, 109 (1865).

(3) K. Ziegler, H. G. Gellert, K. Zoesel, W. Lehmkuhl, and W. Pfohl, *Angew. Chem.*, **67**, 424 (1955).

(4) L. E. Zakharkin and O. Yu. Okhlobystin, *Doklady Akad. Nauk S.S.S.R.*, **116**, 236 (1957).

(5) British Patent 802,796 (Oct. 8, 1958); *Chem. Abstr.*, **53**, 9061 (1959).

(6) S. Hilpert and M. Ditmar, *Ber.*, **46**, 3738 (1913).

(7) For a discussion concerning this class of compounds, see A. v. Grosse and J. M. Marvity, *J. Org. Chem.*, **5**, 106 (1940).

(8) All reactions involving aluminum alkyls were conducted in an anhydrous, nitrogen-blanketed system. All melting points and boiling points are uncorrected values.

(9) Purchased from Metal and Thermit Corporation, Rahway, N. J.

(10) E. Krause, *Ber.*, **51**, 1447 (1918).

titative yield, m.p. ~375° (sealed tube) (reported[10] m.p. ~375°).

Anal. Calcd. for C_3H_9FSn: C, 19.71; H, 4.96; F, 10.40. Found: C, 19.46; H, 4.91; F, 10.21.

Triethyltin chloride. Ethylaluminum sesquichloride (77 g.; 0.31 mole) was added dropwise with stirring to stannic chloride (75 g.; 0.29 mole) during 90 min. The addition was accompanied by a strong exothermic reaction and the pot temperature rose from 25° to 70°. The product was worked up by dilute hydrochloric acid hydrolysis essentially as described above. There was obtained 52 g. of triethyltin chloride (74%), b.p. 96–97° (15 mm.); n_{D}^{25} 1.5042 [reported[11] b.p. 94° (13 mm.); n_{D} 1.50553].

Anal. Calcd. for $C_6H_{15}ClSn$: C, 29.86; H, 6.27; Cl, 14.70. Found: C, 30.07; H, 6.50; Cl, 14.89.

When an excess of ethylaluminum sesquichloride (0.39 mole) was treated with stannic chloride (0.29 mole) and the resulting reaction mixture heated for 2 hr. at 100°, triethyltin chloride was the exclusive product. The fluoride was prepared and its melting point (take in a sealed tube) was found to be in agreement with the previous literature value,[10] m.p. 297–298°.

Tetraethyltin. Triethylaluminum (11.4 g.; 0.1 mole) was added dropwise during 20 min. to triethyltin chloride (24.1 g.; 0.1 mole). The pot temperature increased from 20° to 54° during the addition and was heated thereafter for 1 hr. at 100°. There was obtained upon workup and distillation 21 g. (89%) of tetraethyltin, b.p. 67–67.5° (14 mm.); n_{D}^{25} 1.4692 [reported[11] b.p. 78° (13 mm.); n_{D} 1.47243].

Anal. Calcd. for $C_8H_{20}Sn$: C, 40.90; H, 8.58. Found: C, 41.04; H, 8.81.

n-Butyltin trichloride and tri-n-butylaluminum. Tri-*n*-butylaluminum (64 g.; 0.32 mole) was added dropwise during 35 min. to *n*-butyltin trichloride[9] (84.6 g.; 0.3 mole). The exothermic reaction caused the pot temperature to increase from 30° to 52° during the addition. The mixture was stirred and heated at 140–145° for 4 hr. There was obtained 86 g. of a mixture of tributyltin chloride and tetrabutyltin, b.p. 155–160° (15 mm.), n_{D}^{25} 1.4880.

Anal. Calcd. for $C_{16}H_{36}Sn$: C, 55.36; H, 10.45; Cl, 0.00. Calcd. for $C_{12}H_{27}ClSn$: C, 44.27; H, 8.36; Cl, 10.89. Found: C, 45.03; H, 8.48; Cl, 10.60.

Tetra-n-butyltin. Tri-*n*-butylaluminum (53 g.; 0.27 mole) was added slowly dropwise to tri-*n*-butyltin chloride (81.4 g.; 0.25 mole). The addition required 30 min. and was accompanied by an increase in the pot temperature from 25–46°. The mixture was then heated for 2 hr. at 100°. Workup, as described above, furnished 76 g. (87%) of tetrabutyltin, b.p. 160–165° (20 mm.); n_{D}^{25} 1.4711 [reported[12] b.p. 145° (10 mm.)].

Anal. Calcd. for $C_{16}H_{36}Sn$: C, 55.36; H, 10.45; Sn, 34.20. Found: C, 55.40; H, 10.29; Sn, 34.09.

Tetra-n-butyltin and aluminum trichloride. Equimolar amounts of tetra-*n*-butyltin and aluminum trichloride (0.096 mole) were heated at 130° for 3 hr. The aluminum chloride went into solution and a homogeneous reaction mixture resulted. The reaction mixture was hydrolyzed by the addition of 5% hydrochloric acid, dried, and distilled. There was obtained a 91% recovery of the tetrabutyltin, b.p. 155–157° (15 mm.); n_{D}^{25} 1.4735. A test for chloride ion in the distillate was negative.

Di-n-octyltin dichloride and tri-n-octylaluminum. Tri-*n*-octylaluminum[13] (74 g.; 0.20 mole) was added dropwise to di-*n*-octyltin dichloride[9] (120 g.; 0.29 mole) during 15 min. The reaction mixture became fluid at the early stages of the addition. During the addition, the pot temperature increased from 24° to 55°. The mixture was heated at 100° for 3 hr. and then 6 hr. at 150°. A fluid, grayish black reaction mixture resulted, which when cooled to room temperature and hydrolyzed with 100 ml. of water furnished two nearly colorless layers. The oily layer was separated, the water layer extracted with ether, and the combined organic material dried. Removal of the solvent and a short heating period at a pot temperature of 240° at 0.4 mm. resulted in 149 g. of a yellowish oily residue, n_{D}^{25} 1.4758 believed to be a mixture of trioctyltin chloride and tetraoctyltin.

Anal. Calcd. for $C_{24}H_{51}ClSn$: C, 58.38; H, 10.41; Cl, 7.18. Found: C, 61.17; H, 10.82; Cl, 4.72.

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[11] G. Grüttner and E. Krause, *Ber.*, **50**, 1802 (1917).

[12] W. J. Jones, D. P. Evans, T. Gulwell, and D. C. Griffiths, *J. Chem. Soc.*, 39 (1935).

[13] Prepared by treating octene-1 with triisobutylaluminum as described by K. Ziegler and associates [see ref. 3].

Fluoroolefins. VIII. The Preparation of 2-Perfluoroalkyl-1,3-butadienes[1]

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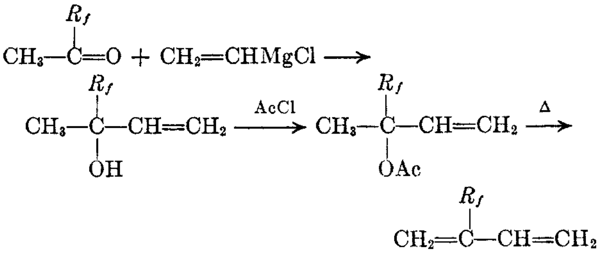
Received March 17, 1960

Previous investigators[1,2] have obtained 2-trifluoromethyl-1,3-butadiene by multistep methods starting with trifluoroacetone. The over-all yields were low and at least one step in each synthetic method was inconvenient to carry out. The synthesis of other 2-perfluoroalkyl-1,3-butadienes has not been reported.

We have developed a more direct route to these compounds by use of the following reactions:



The reaction between trifluoromethyl-, pentafluoroethyl- and heptafluoropropyl methyl ketone and vinylmagnesium chloride in tetrahydrofuran[3] proceeded smoothly to give the corresponding carbinols in yields of 60–80%. It was not possible to isolate pure samples by distillation and the crude material contained about 20% tetrahydrofuran. Analytic samples were obtained by the use of a large-scale vapor phase chromatographic column packed with dinonyl phthalate on celite.

The patent literature claims[4] that 2-trifluoromethyl-1,3-butadiene can be obtained by the dehydration of 2-trifluoromethyl-3-buten-1-ol (I) with sulfuric acid, oxalic acid, or succinic anhy-

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[1] Paper VII. *J. Org. Chem.*, **24**, 1888 (1959).

[2] A. L. Henne and P. E. Hinkamp, *J. Am. Chem. Soc.*, **76**, 5147 (1954).

[3] H. E. Ramsden, *et. al.*, *J. Org. Chem.*, **22**, 1604 (1957).

[4] H. M. Hill and E. B. Towne, U. S. Patent **2,490,753** (1949).