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The Preparation of Organolithium Compounds by the Transmetalation Reaction. VI. Cyclopropyllithium[1]

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The transmetalation reaction between *n*-butyllithium and tetracyclopropyltin in 2:1 molar ratio has been used to prepare solid cyclopropyllithium in good yield. Some qualitative evidence was obtained for the existence of solid, mixed organolithium complexes involving *n*-butyl- and cyclopropyllithium. Such transmetalation reactions also can be carried out in diethyl ether solution. In ether *ca*. three, but not all four, of the cyclopropyl groups of tetracyclopropyltin can be utilized. Exchange reactions between cyclopropyllithium and cyclopropyl-containing tetraorganotin compounds in ether are described, and their preparative implications are pointed out.

For a study[3] of the stability of cyclopropyllithium in ether solvents and for a determination of the n.m.r. spectrum of this reagent, it was desirable to have solutions of cyclopropyllithium free of lithium halide. Since we had prepared vinyllithium[4] and allyllithium[5] free of lithium halides by the transmetalation reaction between the corresponding tetraorganotin compound and *n*-butyllithium in pentane, this procedure was investigated as a possible synthesis of cyclopropyllithium.

When tetracyclopropyltin[3,6] was treated with two equivalents of *n*-butyllithium (0.32 *M* in pentane), cyclopropyllithium precipitated within 3–4 hr. as an amorphous, white solid. Addition of a pentane solution of trimethyltin bromide to the reaction mixture resulted in formation of cyclopropyltrimethyltin in 79% yield and *n*-butyltrimethyltin in 4% yield. When three equivalents of *n*-butyllithium were used, precipitation occurred on mixing the reagents, but this precipitate dissolved again after all of the *n*-butyllithium solution had been added. However, within 4 hr. a white solid precipitated again. Addition of trimethyltin bromide to this mixture gave cyclopropyltrimethyltin (50%) and *n*-butyltrimethyltin (34%). Similar behavior was observed when four equivalents of *n*-butyllithium was added per mole of tetracyclopropyltin. Addition of ethereal trimethylchlorosilane in this case produced cyclopropyl- and *n*-butyltrimethylsilane in yields of 42 and 34%, respectively. That some *n*-butyllithium is held rather tenaciously by the cyclopropyllithium was shown in another reaction of tetracyclopropyltin with two equivalents of *n*-butyllithium. In this experiment the solid cyclopropyllithium was filtered off, washed with pentane, and redispersed in pentane. To both the filtrate and the lithium compound suspension was added trimethyltin

bromide. The products from the filtrate were cyclopropyltrimethyltin (8.1%) and *n*-butyltrimethyltin (0.14%); from the suspension, cyclopropyltrimethyltin (66%) and *n*-butyltrimethyltin (2.3%). Very similar results were obtained in a second experiment. In each case the yield of *n*-butyltrimethyltin formed from the reaction of trimethyltin bromide with the filtrate was found to be less than one tenth that formed in the reaction with the solid dispersion. These results are rather surprising in view of the good solubility of *n*-butyllithium in pentane in the absence of an insoluble lithium reagent, and they suggest strongly that *n*-butyllithium units have been incorporated into the basic solid cyclopropyllithium structure. That is, one has to some extent a *mixed organolithium polymer* of type

$$[(\triangleright\text{-Li})_n(n\text{-C}_4\text{H}_9\text{Li})_m]$$
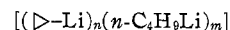
where, in view of the results of others on the structures of ethyllithium[7] and *t*-butyllithium,[8] $(n + m)$ would be 6, or, more likely, 4. This then would be the first experimental evidence for such mixed organolithium complexes.[8a] The formation of such species when cyclopropyllithium precipitates from solutions containing *n*-butyllithium is not unreasonable.

The reaction of tetracyclopropyltin with *n*-butyllithium in pentane also can be complicated by formation of soluble complexes between *n*-butyllithium and cyclopropyllithium when more than minimal amounts of unreacted *n*-butyllithium are present. This is indicated by the experiments above in which a solid precipitated during the initial addition of the first portions of *n*-butyllithium when three or four equivalents were added; this solid, however, dissolving after all of the *n*-butyllithium had been added. This is further suggested by an experiment with 2.4 equivalents of *n*-butyllithium per mole of tetracyclopropyltin, in which it was found that cyclopropyllithium is much more soluble in the presence of *n*-butyllithium.

When all factors are taken into consideration, the

(1) (a) Presented in part at the Colloque International de Chimie Organique du Centre de la Recherche Scientifique, Paris, Sept. 24–28, 1962; (b) part V of this series: D. Seyferth, D. E. Welch, and G. Raab, *J. Am. Chem. Soc.*, **84**, 4266 (1962).

(2) (a) Alfred P. Sloan Research Fellow; (b) Allied Chemical Corporation Fellow, 1960–1961.

(3) D. Seyferth and H. M. Cohen, *J. Organometallic Chem.*, in press.

(4) D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **83**, 3583 (1961).

(5) D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **26**, 4797 (1961).
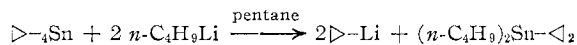
(6) D. Seyferth and H. M. Cohen, *Inorg. Chem.*, **1**, 913 (1962).

(7) T. L. Brown, D. W. Dickerhoof, and D. A. Bafus, *J. Am. Chem. Soc.*, **84**, 1371 (1962).

(8) M. A. Weiner, G. Vogel, and R. West, *Inorg. Chem.*, **1**, 654 (1962).
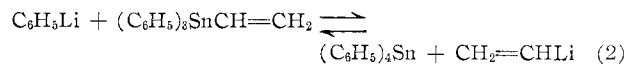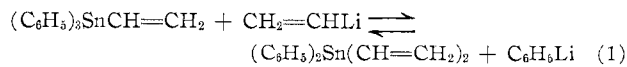
(8a) NOTE ADDED IN PROOF.—Independent discovery of mixed organolithium complexes and their physical characterization was reported after this manuscript was submitted for publication: M. A. Weiner and R. West, *J. Am. Chem. Soc.*, **85**, 485 (1963).

reaction of tetracyclopropyltin with two equivalents of *n*-butyllithium (or slightly less, but in any case added slowly) is the optimum for the preparation of relatively pure, solid cyclopropyllithium, and this procedure was used in our further studies.[3]
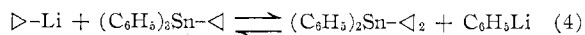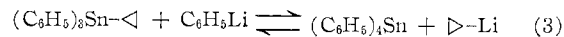
$$\triangleright\text{--}_4\text{Sn} + 2\,n\text{-C}_4\text{H}_9\text{Li} \xrightarrow{\text{pentane}} 2\triangleright\text{--Li} + (n\text{-C}_4\text{H}_9)_2\text{Sn}\text{--}\triangleleft_2$$

It might be predicted that the reaction of tetracyclopropyltin with *n*-butyllithium in diethyl ether would be free from such complications of complex formation. This is the case. It was found that the addition of triethylchlorosilane to the reaction mixture of tetracyclopropyltin with one equivalent of *n*-butyllithium in diethyl ether resulted in formation of cyclopropyltriethylsilane in 77% yield. No *n*-butyltriethylsilane was detected. When four equivalents of *n*-butyllithium was used, the cyclopropyltriethylsilane (74%) was accompanied by *n*-butyltriethylsilane in 12% yield. It is evident that this metal–metal exchange reaction proceeds more smoothly in diethyl ether than in pentane. However, the incomplete utilization of all four cyclopropyl groups of tetracyclopropyltin eliminated this method from further study. Unless there are compelling reasons for avoiding the presence of lithium halide, the direct reaction of cyclopropyl bromide with metallic lithium serves best for the preparation of cyclopropyllithium in ether solution.[3] It should be noted that it is still uncertain whether the incomplete cleavage of cyclopropyl groups from tin by *n*-butyllithium is due to kinetic or thermodynamic factors. The same is true for the cleavage of cyclopropyl groups by phenyllithium discussed below.

The reaction of tetracyclopropyltin with four equivalents of phenyllithium during 3 days at 2–3° did not lead to the precipitation of tetraphenyltin. However, on addition of trimethylchlorosilane to the reaction mixture, a 13% yield of cyclopropyltrimethylsilane and a 70% yield of trimethylphenylsilane were realized. Treating cyclopropyltriphenyltin with one equivalent of phenyllithium in ether resulted in an immediate precipitate of tetraphenyltin. After 30 min., the addition of trimethyltin bromide produced trimethylphenyltin (28%) and cyclopropyltrimethyltin in only 8% yield. The latter yield is unexpectedly low in view of a 66% yield of tetraphenyltin obtained in this reaction. In a second experiment where high-speed stirring was employed, the results were similar: a 54% yield of tetraphenyltin, a 44% yield of trimethylphenyltin, and a 10% yield of cyclopropyltrimethyltin. The low yield of the latter cannot be attributed to loss of cyclopropyllithium by reaction with solvent, since we have shown that this lithium reagent has a half-life of about 138 hr. at room temperature in diethyl ether.[3] The most probable explanation was suggested by our previous finding that the reaction of vinyllithium with triphenylvinyltin in ether leads to tetraphenyltin in good yield.[9] These results were explained by postulating the equilibria

(9) D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **84**, 361 (1962).

$$(\text{C}_6\text{H}_5)_3\text{SnCH}\!=\!\text{CH}_2 + \text{CH}_2\!=\!\text{CHLi} \rightleftharpoons$$
$$(\text{C}_6\text{H}_5)_2\text{Sn}(\text{CH}\!=\!\text{CH}_2)_2 + \text{C}_6\text{H}_5\text{Li} \quad (1)$$

$$\text{C}_6\text{H}_5\text{Li} + (\text{C}_6\text{H}_5)_3\text{SnCH}\!=\!\text{CH}_2 \rightleftharpoons$$
$$(\text{C}_6\text{H}_5)_4\text{Sn} + \text{CH}_2\!=\!\text{CHLi} \quad (2)$$

It is known that reaction 2 proceeds far to the right. It is not unreasonable to postulate a similar set of equilibria in the case in question, *viz.*
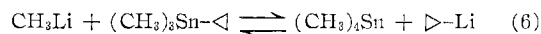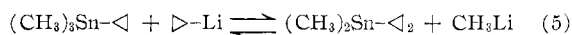
$$(\text{C}_6\text{H}_5)_3\text{Sn}\text{--}\triangleleft + \text{C}_6\text{H}_5\text{Li} \rightleftharpoons (\text{C}_6\text{H}_5)_4\text{Sn} + \triangleright\text{--Li} \quad (3)$$

$$\triangleright\text{--Li} + (\text{C}_6\text{H}_5)_3\text{Sn}\text{--}\triangleleft \rightleftharpoons (\text{C}_6\text{H}_5)_2\text{Sn}\text{--}\triangleleft_2 + \text{C}_6\text{H}_5\text{Li} \quad (4)$$

The net result would be the production of compounds of the type $(\text{C}_6\text{H}_5)_n\text{Sn}\text{--}\triangleleft_{4-n}$, of which only the tetraphenyltin would have been detected, and the loss of cyclopropyllithium.

This type of reversible equilibrium was investigated more fully for another system. It was found that when cyclopropyllithium in diethyl ether was characterized by adding an excess of trimethyltin bromide to the lithium reagent, both tetramethyltin and dicyclopropyldimethyltin were obtained, each in *ca.* 10% yield. This apparent disproportionation might have been caused by the presence of lithium bromide, a very weak Lewis acid (note similar disproportionations caused by zinc iodide[6]). This, however, was shown not to be the case by refluxing an ether solution of cyclopropyltrimethyltin containing an equimolar amount of soluble lithium bromide and recovering only unreacted starting material. However, when cyclopropyltrimethyltin was treated with cyclopropyllithium (from tetracyclopropyltin and *n*-butyllithium in pentane) in diethyl ether, a disproportionation to tetramethyltin and dicyclopropyldimethyltin was observed. The relative amount of each compound was related to the amount of cyclopropyltrimethyltin in the final reaction mixture in the following way

$$\frac{(\text{CH}_3)_4\text{Sn}}{(\text{CH}_3)_3\text{Sn}\text{--}\triangleleft} = 0.36 \quad \text{and} \quad \frac{(\text{CH}_3)_2\text{Sn}\text{--}\triangleleft_2}{(\text{CH}_3)_3\text{Sn}\text{--}\triangleleft} = 0.67$$

These data may be explained by the same type of equilibria cited above, *viz.*

$$(\text{CH}_3)_3\text{Sn}\text{--}\triangleleft + \triangleright\text{--Li} \rightleftharpoons (\text{CH}_3)_2\text{Sn}\text{--}\triangleleft_2 + \text{CH}_3\text{Li} \quad (5)$$

$$\text{CH}_3\text{Li} + (\text{CH}_3)_3\text{Sn}\text{--}\triangleleft \rightleftharpoons (\text{CH}_3)_4\text{Sn} + \triangleright\text{--Li} \quad (6)$$

In agreement with this formulation, it is noted above that when an excess of trimethyltin bromide was used to characterize cyclopropyllithium, equal amounts of tetramethyltin and dicyclopropyldimethyltin were formed. This is what we would expect from the above equations. However, one also should expect that in the absence of trimethyltin bromide, *i.e.*, in a simple hydrolytic work-up, the yield of tetramethyltin would be lower than that of dicyclopropyldimethyltin. This is observed.

If the above considerations are valid, we should expect that if we reversed the mode of addition, *i.e.*, added the cyclopropyllithium solution to the trimethyltin bromide (in 1:1 molar ratio), we would expect very little tetramethyltin and dicyclopropyldimethyltin, or none at all, since the product cyclopropyltrimethyltin would never see an excess of cyclopropyllithium. In

such an experiment cyclopropyltrimethyltin was obtained in 66% yield; more important, neither tetramethyltin nor dicyclopropyldimethyltin was detected. The implications for preparative purposes are clear: (1) When preparing unsymmetrical tin compounds with cyclopropyllithium, the lithium reagent should be added to the organotin halide with rapid stirring. An excess of the lithium reagent should be avoided (unreacted organotin halide may be removed by conversion to the insoluble fluoride or to the insoluble ammonia adduct). (2) The mode of addition is irrelevant for the preparation of tetracyclopropyltin. Indeed, as mentioned,[3] an 88% yield of tetracyclopropyltin could be obtained by adding tin tetrachloride to an excess of the lithium reagent. (3) The mode of addition is irrelevant for the preparation of unsymmetrical, cyclopropyl-containing silanes, since such disproportionations do not occur.

While these generalizations are given specifically with regard to the preparation of cyclopropyltin compounds by the organolithium route, it is probable that they will be valid for many other organotin syntheses using organolithium reagents.

Experimental[10]

Preparation of Starting Materials.—*n*-Butyllithium was prepared in pentane by the method of Gilman, *et al.*,[11] and phenyllithium in ether by the procedure of Jones and Gilman.[12] The cyclopropyltin compounds used in this study were prepared by the Grignard route[6] or using cyclopropyllithium prepared from cyclopropyl bromide.[3]

Reactions of Tetracyclopropyltin with *n*-Butyllithium in Pentane. (a) **2 *n*-C₄H₉Li per (cyclo-C₃H₅)₄Sn.**—To 16.2 mmoles of tetracyclopropyltin (henceforth R₄Sn) was added rapidly 98 ml. of *n*-C₄H₉Li solution in pentane (32.4 mmoles). The solution became turbid, and a white solid settled out after 3 hr. The reaction mixture was stirred for an additional 1 hr., and a solution of 32.4 mmoles of trimethyltin bromide in a few ml. of pentane was added. The resulting mixture was stirred for 16.5 hr., cooled to 0°, and hydrolyzed with 55 ml. of 5% HCl. The pentane layer was washed with water and with 25 ml. of 10% aqueous–methanolic KF solution; no organotin fluorides precipitated. The dried organic phase was distilled carefully to remove most of the solvent, and the residual liquid (13.1 ml.) was analyzed by gas chromatography (30% Dow Corning 710 silicone fluid on 60–80 mesh Chromosorb P, jacket at 114°, preheater at 130°, 12.5 p.s.i. helium).[13] Cyclopropyltrimethyltin (henceforth RSn(CH₃)₃) was identified by its infrared spectrum and retention time, *n*-butyltrimethyltin by its retention time, and di-*n*-butyldicyclopropyltin by its infrared spectrum and refractive index, n^{25}D 1.4920 (lit.[6] n^{25}D 1.4912). The yields obtained were: RSn(CH₃)₃: 79%; *n*-C₄H₉Sn(CH₃)₃: 3.7%; (*n*-C₄H₉)₂SnR₂, 95%.

(b) **3 *n*-C₄H₉Li per R₄Sn.**—This reaction was carried out as above with 18.7 mmoles of R₄Sn and 69 ml. (56 mmoles) of *n*-C₄H₉Li solution. Upon addition of about 2/3 of the lithium reagent solution, a copious white precipitate appeared, which dissolved on the addition of the remaining *n*-C₄H₉Li to give a clear, light yellow solution. After the solution had been stirred for an additional 30 min., it became cloudy; after 4 hr. white solid had precipitated. Two hr. later 60 mmoles of (CH₃)₃SnBr was added and the mixture stirred overnight. It then was hydrolyzed, washed, and the pentane removed as before. The residual solution (17.0 ml.) was analyzed by gas chromatography for the trimethyltin compounds present. RSn(CH₃)₃ was obtained in 49.5% yield, *n*-C₄H₉Sn(CH₃)₃ in a yield of 34.3%.

(c) **4 *n*-C₄H₉Li per R₄Sn.**—The reaction was carried out as above with 13.7 mmoles of R₄Sn and 63.7 ml. (54.8 mmoles) of *n*-C₄H₉Li in pentane. As in the above reaction, the initial precipitate dissolved on addition of all of the lithium reagent solution. Again, white solid reprecipitated within 4 hr. After an additional 1 hr., a solution of 7.00 ml. (55 mmoles) of freshly distilled trimethylchlorosilane in 50 ml. of diethyl ether was added and the solution stirred overnight. After hydrolysis, washing, drying, and removal of solvent, volatile liquids were distilled *in vacuo* into a liquid nitrogen-cooled flask. The distillate (17.5 ml.) was analyzed by gas chromatography on a Dow Corning 710 silicone fluid column (30% on Chromosorb P, jacket at 98°, preheater at 136°, 12.5 p.s.i. He). The yield of RSi(CH₃)₃ was 42%, of *n*-C₄H₉Si(CH₃)₃, 30%. Cyclopropyltrimethylsilane was identified by its retention time and infrared spectrum.[6] *n*-Butyltrimethylsilane was identified by its refractive index, n^{20}D 1.4025 (lit.[14] 1.4030), and by comparing its infrared spectrum with that reported by Westermark.[15]

(d) **2 *n*-C₄H₉Li per R₄Sn; Isolation of Solid Cyclopropyllithium.**—For this and subsequent experiments in which cyclopropyllithium was isolated, a special flask (flask A) was used consisting of a three-necked flask to whose bottom had been joined a sintered disk, stopcock, and 24/40 inner joint, in that order, and which was fitted with a mechanical stirrer, a water condenser topped with a nitrogen inlet tube, and an addition funnel. In general, the bottom joint was inserted into a second three-necked flask (flask B) fitted with a mechanical stirrer or a bar magnet for use with a magnetic stirrer and a nitrogen inlet tube.

To flask A was added 18.3 mmoles of R₄Sn in 75 ml. of pentane. On addition of 36.2 ml. (36.6 mmoles) of *n*-C₄H₉Li solution, the mixture became light yellow and slightly turbid. Within 3.5 hr. a copious white precipitate had formed. After another 1.5 hr., the mixture was filtered by nitrogen pressure into flask B. To the solid in flask A, after it had been washed with a small amount of pentane and redispersed in 50 ml. of that solvent, was added 41 mmoles of (CH₃)₃SnBr (reaction mixture I). To the filtrate, cooled to 0°, also was added 41 mmoles of (CH₃)₃SnBr (reaction mixture II). Both reaction mixtures I and II were stirred for 17 hr., then were hydrolyzed with 30 ml. of 5% HCl. The pentane layers were washed, dried, and freed from most of the pentane. Residual liquids were analyzed by gas chromatography for trimethyltin derivatives using *p*-xylene as an internal standard. The yields obtained were: reaction mixture I: RSn(CH₃)₃, 66%; *n*-C₄H₉Sn(CH₃)₃, 2.3%; reaction mixture II: RSn(CH₃)₃, 8.1%; *n*-C₄H₉Sn(CH₃)₃, 0.14%.

The solubility of cyclopropyllithium in pentane was estimated as 2.95 mmoles per 110 ml. or 0.027 mole per l. from these data. That *n*-butyllithium is retained selectively by the cyclopropyllithium solid is evident on examining the yields of *n*-C₄H₉Sn-(CH₃)₃ in reaction mixtures I and II. It should be noted that *n*-octane, which is present in the *n*-butyllithium solutions to start with, was washed quantitatively into the filtrate.

(e) **2.4 *n*-C₄H₉Li per R₄Sn. Isolation of Solid Cyclopropyllithium.**—To flask A was added 22.8 mmoles of R₄Sn in 15 ml. of pentane. On addition of 66.2 ml. (55.6 mmoles) of *n*-C₄H₉Li solution in pentane the mixture became slightly turbid and yellow, but no solid settled out even after 6 hr. The mixture was stirred overnight, after which time the solution had become red-brown

(10) All reactions were carried out under an atmosphere of argon or of prepurified nitrogen.

(11) H. Gilman, F. W. Moore, and O. Baine, *J. Am. Chem. Soc.*, **63**, 2479 (1941).

(12) R. G. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 339–366.

(13) Details of gas chromatographic analyses and calculations of yields are available in the Ph.D. thesis of H. M. C., Massachusetts Institute of Technology, 1962.

(14) F. C. Whitmore, L. H. Sommer, P. D. DiGiorgio, W. A. Strong, R. E. Van Strien, D. L. Bailey, H. K. Hall, E. W. Pietrusza, and G. T. Kerr, *J. Am. Chem. Soc.*, **68**, 475 (1946).

(15) H. Westermark, *Acta Chem. Scand.*, **9**, 950 (1955).

in color and a copious white precipitate had formed. The mixture was filtered, and the solid was washed with pentane and redispersed in 60 ml. of that solvent. Trimethyltin bromide was added to flasks A and B (55.6 mmoles each) to give reaction mixtures I and II, respectively. The usual work-up procedure established the following yields based on *n*-butyllithium; reaction mixture I: $RSn(CH_3)_3$, 21.2%; *n*-$C_4H_9Sn(CH_3)_3$, 1.3%; reaction mixture II: $RSn(CH_3)_3$, 22.0%; *n*-$C_4H_9Sn(CH_3)_3$, 19.3%.

The much higher solubility of cyclopropyllithium in the presence of *n*-butyllithium is attributed to complex formation. Since the previous experiment demonstrated that we might expect a 4% yield of $RSn(CH_3)_3$ from solubility considerations, it is not unreasonable to attribute the abnormally high solubility to a 1:1 complex between the two organolithium reagents.

Reactions of Tetracyclopropyltin wih *n*-Butyllithium in Diethyl Ether. (a) 1 *n*-C_4H_9Li per R_4Sn.—To a solution of 9 mmoles of R_4Sn in 110 ml. of diethyl ether was added 8.9 ml. (9 mmoles) of *n*-butyllithium in pentane. The solution was stirred for 5 hr., then cooled to 0°, and 11 mmoles of triethylchlorosilane was added. The mixture was stirred at room temperature for 15 hr. and then hydrolyzed. The dried ether layer was analyzed directly by gas chromatography using benzonitrile as internal standard. The complete absence of *n*-$C_4H_9Si(C_2H_5)_3$ was noted under conditions where 1% would have been detected readily. The yield of cyclopropyltriethylsilane was 77%. Since this is a new compound, an analytical sample, $n^{25}D$ 1.4423, was isolated.

Anal. Calcd. for $C_9H_{20}Si$: C, 69.14; H, 12.89. Found: C, 69.13; H, 12.69. Its infrared spectrum was similar to that of $RSi(CH_3)_3$: strong bands at 900 and 1030 cm.$^{-1}$, indicative of the cyclopropyl–silicon system.

(b) 4 *n*-C_4H_9Li per R_4Sn.—This reaction was carried out in the same manner as the previous one with 9 mmoles of R_4Sn in 450 ml. of ether and 40 ml. (36 mmoles) of *n*-butyllithium in pentane. Five hr. after the reagents were mixed, 49 mmoles of $(C_2H_5)_3SiCl$ was added. The mixture was stirred for 12 hr. and worked up as above. Gas chromatography established that $RSi(C_2H_5)_3$ and *n*-$C_4H_9Si(C_2H_5)_3$ had been formed in yields of 74 and 14%, respectively, based on *n*-butyllithium.

Reaction of Tetracyclopropyltin with Phenyllithium in Diethyl Ether.—To 18 mmoles of R_4Sn in 50 ml. of ether was added 65.5 ml. (72 mmoles) of ethereal phenyllithium while the temperature was maintained at −15°. Ten min. after the addition was complete, the flask was allowed to warm to 0° and 2 hr. later to room temperature. After 1 hr. at room temperature the solution was clear and colorless. The flask was kept at 2–3° and the contents stirred for 3 days. No solid precipitated. To the solution then was added 72 mmoles of $(CH_3)_3SiCl$ in 5 ml. of ether. The solution was stirred at 2–3° overnight, then was hydrolyzed. The ether layer was carefully fractionally distilled to remove ether. The residual liquid (16.97 g.) was analyzed by gas chromatography using *p*-xylene as internal standard. Trimethylphenylsilane (obtained in 69.8% yield) and $RSi(CH_3)_3$ (obtained in 12.5% yield) were identified by their retention times and infrared spectra.

Reaction of Cyclopropyltriphenyltin with Phenyllithium in Diethyl Ether.—To 10 mmoles of $RSn(C_6H_5)_3$ in 30 ml. of ether was added 8.4 ml. (10 mmoles) of ethereal C_6H_5Li. A white solid precipitated. The mixture was stirred for 30 min., then 12 mmoles of $(CH_3)_3SnBr$ was added. The reaction mixture was stirred for 3 hr. and then hydrolyzed with 20 ml. of 5% HCl. The solid was filtered off, washed with ether and water, and dried *in vacuo* to give 2.82 g. (66%) of tetraphenyltin, m.p. 220–222°. Recrystallization from tetrahydrofuran gave pure material, m.p. 223–224°. A mixture m.p. with authentic material showed no depression.

The ether layer from the filtrate was separated and washed with water. The ether was distilled from the dried ether phase and the residue analyzed by gas chromatography, using *p*-xylene as internal standard. This established that $RSn(CH_3)_3$ had been formed in 8% yield and $(CH_3)_3SnC_6H_5$ in 28% yield. The latter figure was obtained using mesitylene as internal standard.

In an effort to increase the yield of $RSn(CH_3)_3$ a longer time

for the transmetalation was employed (1 hr.) and high speed stirring was used. This reaction was carried out on a 20-mmole scale. Tetraphenyltin was isolated in 56% yield, and the yields of $RSn(CH_3)_3$ and $(CH_3)_3SnC_6H_5$ were 10.7 and 46%, respectively.

Redistribution During the Preparation of Cyclopropyltrimethyltin *via* Cyclopropyllithium.—To a three-necked flask equipped in the usual manner was added 1.5 g. (0.22 mole) of small lithium wire pieces and 100 ml. of diethyl ether. A solution of cyclopropyl bromide (12.1 g., 0.1 mole) was added dropwise with rapid stirring at such a rate as to maintain a gentle reflux; 45 min. after the addition had begun, the reaction had subsided, and the resulting solution was orange-brown and quite turbid. After an additional 90 min., only a very small amount of lithium remained. To this solution was added 36.5 g. (0.15 mole) of $(CH_3)_3SnBr$.[16] After 3 hr. the solution was cooled and hydrolyzed with dilute HCl. The mixture was filtered through glass wool and the ether phase dried and distilled carefully to remove most of the ether. The residual liquid was analyzed by gas chromatography as usual. The following products were obtained: $(CH_3)_4Sn$, 9.6%; $RSn(CH_3)_3$, 45%; and $R_2Sn(CH_3)_2$, 9.6%. The first two compounds were identified by their retention times and infrared spectra. Dicyclopropyldimethyltin initially was identified on the basis of its infrared spectrum, *i.e.*, the spectrum was identical with that of $RSn(CH_3)_3$ in all respects except in the 3000 cm.$^{-1}$ region. This region had been used previously for the determination of the presence of methyl groups in cyclopropyltin compounds.[6] In $RSn(CH_3)_3$ the absorbance at 2950 cm.$^{-1}$ is more intense than that at 3100 cm.$^{-1}$. In the infrared spectrum of $R_2Sn(CH_3)_2$ the reverse is true, indicating that the compound is not $RSn(CH_3)_3$. The possibility of its being R_3SnCH_3 was ruled out by combustion analysis. The analytical sample, $n^{25}D$ 1.4934, was isolated by gas chromatography.

Anal. Calcd. for $C_8H_{16}Sn$: C, 41.61; H, 6.99. Found: C, 41.81; H, 7.12.

Reaction of Cyclopropyltrimethyltin with Cyclopropyllithium in Diethyl Ether.—Solid cyclopropyllithium was prepared as previously described from 9.1 mmoles of R_4Sn in 40 ml. of pentane and 17.7 ml. (18 mmoles) of *n*-butyllithium in pentane. The solid was dispersed in 20 ml. of ether, and 9 mmoles of $RSn(CH_3)_3$ was added. Most of the cyclopropyllithium appeared to dissolve. The mixture was stirred at room temperature for 7 hr. An aliquot then was withdrawn and hydrolyzed. The ether layer was separated, dried, and analyzed by gas chromatography using a Dow Corning 710 silicone fluid column (35% on Chromosorb P). Analysis at a jacket temperature of 105° gave the ratio of $(CH_3)_4Sn$ to $RSn(CH_3)_3$ as 0.32, and analysis at a jacket temperature of 178° gave the ratio of $R_2Sn(CH_3)_2$ to $RSn(CH_3)_3$ as 0.81. These products were identified by their retention times and infrared spectra. Another aliquot was hydrolyzed and analyzed after a reaction time of 43 hr. The $(CH_3)_4Sn/RSn(CH_3)_3$ ratio was found to be 0.36 and the ratio $R_2Sn(CH_3)_2/RSn(CH_3)_3$ was 0.67.

Preparation of Cyclopropyltrimethyltin *via* Cyclopropyllithium in Diethyl Ether. (Conditions which Avoid Redistribution).—Cyclopropyllithium was prepared at 0° from 50 mmoles of cyclopropyl bromide and 0.12 g.-atom of lithium in 100 ml. of ether.[3] This solution was filtered under nitrogen through glass wool into an addition funnel fitted on a three-necked flask equipped with a mechanical stirrer and water condenser, which contained 50 mmoles of $(CH_3)_3SnBr$. The lithium reagent solution was added to the tin bromide. After the addition was complete, the reaction mixture was washed with aqueous–methanolic KF solution (no precipitate) and water. The dried ether layer was analyzed by gas chromatography. Cyclopropyltrimethyltin had been formed in 66% yield. No $(CH_3)_4Sn$ or $R_2Sn(CH_3)_2$ was detected.

Preparation of Cyclopropyltrimethyltin *via* Cyclopropyllithium

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(16) It should be noted that these conditions were used in the preparation of cyclopropyltrimethylsilane in 75% yield.[3]

in Pentane: Additional Comments.—It is to be noted that no evidence for such redistribution of $RSn(CH_3)_3$ to $(CH_3)_4Sn$ and $R_2Sn(CH_3)_2$ was found in those reactions where $(CH_3)_3SnBr$ was added to cyclopropyllithium in pentane, where the lithium reagent had been obtained by the transmetalation procedure (see experiments above). Apparently such redistribution occurs with facility in the case in question only in diethyl ether solution.

Magnetic Properties and Thermochromism of Copper(II) Complexes with N-Alkylethylenediamines

By WILLIAM E. HATFIELD, T. S. PIPER,[1a] AND ULRICH KLABUNDE[1b]

The magnetic and spectral properties of both the red and blue forms of bis-(N,N-diethylethylenediamine)-copper(II) perchlorate have been investigated, and possible mechanisms for the thermochromism have been considered. The antiferromagnetic character of some binuclear copper complexes of the general formula $[Cu_2(OH)_2(amine)_2](ClO_4)_2$ has been established, and the energy differences between the singlet and triplet states have been measured.

In 1938, Pfeiffer and Glaser[2] published the results of their investigations of the donor properties of some N-alkylethylenediamines toward copper(II) perchlorate. With N-methyl-, N,N'-diethyl-, and N,N-diethylethylenediamine, complexes of the general formula $[Cu(ligand)_2](ClO_4)_2$ were formed. However, with more alkyl substitution, *i.e.*, with N,N-diethyl-N'-methyl- and N,N,N'-triethylethylenediamine, complexes with the unusual composition $Cu(amine)(OH)(ClO_4)$ were isolated. Pfeiffer and Glaser[2] formulated these compounds as binuclear copper complexes with hydroxy bridges. The steric requirements of the N-alkyl groups which govern the formation of the binuclear complexes have been demonstrated.[3,4]

The bis-(N,N-diethylethylenediamine)-copper(II) perchlorate was found to exhibit an especially interesting property in that it is brick red at room temperature and blue above 44°. Pfluger and Eihausen[5] have shown that a change in the crystal form from triclinic to monoclinic accompanies the color change. Pfeiffer and Glaser[2] also reported that μ-dihydroxy-bis-(N,N-diethyl-N'-methylethylenediamine)-dicopper(II) perchlorate which is blue at room temperature has a blue to red transition between −100 and −120°.

We now wish to report the results of our magnetic and spectral investigations of some of these compounds.

Experimental

Preparation of the Compounds.—The compounds were prepared by Pfeiffer and Glaser's method,[2] purified by recrystallization, and analyzed to establish their purity.

In addition to the perchlorate salt of bis-(N,N-diethylethylenediamine)-copper(II) the NO_3^-, ClO_3^-, IO_4^-, IO_3^-, BrO_3^-, I^-, Cl^-, Br^-, PF_6^-, BF_4^-, CN^-, SCN^-, $CO_3{}^{2-}$, $SO_4{}^{2-}$, $SiF_6{}^{2-}$, OH^-, and *o,p*-dinitrobenzenesulfonate salts were prepared and checked for thermochromism. All of these compounds except the NO_3^- and SCN^- salts were blue at room temperature and did not change color when cooled in a liquid nitrogen bath. The red NO_3^- salt and the green SCN^- salt also did not exhibit thermochromism.

Magnetic Susceptibility Determinations.—The magnetic susceptibilities were determined by the method that has been described previously[6] using $Hg[Co(CNS)_4]$ as a standard.[7]

Spectral Studies.—The reflectance spectra were obtained with a Bausch and Lomb spectrophotometer equipped with the standard reflectance attachment. For the high temperature spectrum the sample was mounted on a block in which a heating element was embedded. Reagent grade magnesium carbonate was used as a standard.

The infrared spectra of salts intimately ground with mineral oil were obtained with a Beckman IR7 spectrophotometer equipped with a thermostated sample compartment.

Results

The reflectance spectra of bis-(N,N-diethylethylenediamine)-copper(II) perchlorate were recorded for both the high temperature and low temperature forms and are shown in Fig. 1. The maximum of the band in the spectrum of the high temperature form is shifted 30 $m\mu$ to the red, *i.e.*, from 490 to 520 $m\mu$, with respect to the band in the spectrum of the low temperature form.

The temperature dependence of the magnetic susceptibility of bis-(N,N-diethylethylenediamine)-copper(II) perchlorate was determined. The diamagnetic correction was calculated from Pascal's constants.[8] There was no discontinuity or change in slope of the plot of the reciprocal of the corrected magnetic sus-

(1) (a) Alfred P. Sloan Foundation Fellow; (b) Undergraduate Research Participant, N. S. F. Summer Program, 1961.

(2) P. Pfeiffer and H. Glaser, *J. prakt. Chem.*, [2] **151**, 134 (1938).

(3) F. G. Mann and H. R. Watson, *J. Chem. Soc.*, 2772 (1958).

(4) F. Basolo and R. K. Murmann, *J. Am. Chem. Soc.*, **74**, 5343 (1952); *ibid.*, **76**, 211 (1954).

(5) C. E. Pfluger and J. W. Eihausen, private communication; the space group in the high temperature form is C2/c with Z = 4. A complete crystal structure determination is in progress.

(6) W. E. Hatfield, R. C. Fay, C. E. Pfluger, and T. S. Piper, *J. Am. Chem. Soc.*, **85**, 265 (1963).

(7) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(8) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 403.