mixture was heated with agitation for 5.5 hr. at 180–190° and 500–700 p.s.i.g. There was little or no hydrogen absorption in the last 0.5 hr. The autoclave was cooled and depressurized and its contents were filtered to remove the catalyst. The filtrate was concentrated under reduced pressure until the pot temperature reached 185° at 22 mm. The residue product consisted of 182 g. (quantitative yield) of N-isopropyl-N′-phenyl-*p*-phenylenediamine, m.p. 67–77.5° (mostly 70.5–77.5°), identified by its infrared spectrum. The distillate was shown by titration to contain little or no aliphatic amines, indicating the absence of carbon–nitrogen cleavage, and was shown by gas–liquid chromatographic analysis to contain little or no isopropyl alcohol, indicating the lack of ketone reduction.

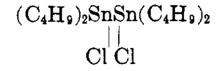
Organotin Chemistry. IV.[1] Reduction of Hexaorganoditins with Lithium Aluminum Hydride

Gerald A. Baum and W. J. Considine

Research Laboratory, M and T Chemicals, Inc.,
Rahway, New Jersey

Received January 5, 1963

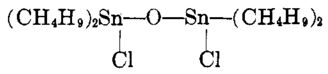
Noltes and van der Kerk[2] have reported the reductive cleavage of the tetrabutyldichloroditin (I), re-



$$(C_4H_9)_2\underset{\substack{|\\ Cl}}{Sn}\underset{\substack{|\\ Cl}}{Sn}(C_4H_9)_2$$

I

ported by Johnson and Fritz,[3] to yield dibutyltin dihydride. Subsequently, I has been reformulated as bistetrabutyldichlorotin oxide (II).[4]



$$(CH_4H_9)_2\underset{\substack{|\\ Cl}}{Sn}—O—\underset{\substack{|\\ Cl}}{Sn}—(CH_4H_9)_2$$

II

Therefore, the work of Noltes and van der Kerk must be taken as evidence for reduction of the tin–oxygen bond. This hypothesis was further strengthened by the work of Considine and Ventura[5] who reduced bistributyltin oxide with lithium aluminum hydride and obtained good yields of tributylin hydride.

It, therefore, seemed appropriate to determine whether the Sn–Sn bond was, in fact, cleaved by lithium aluminum hydride.

The cleavage of ditins with reagents such as lithium in tetrahydrofuran is well-known. Both hexabutylditin and hexaphenylditin have been reduced with the above reagent to yield the corresponding triorganotin hydride.[6]

Table I

Reaction of Hexabutylditin with Lithium Aluminum Hydride

Solvent	Temp., °C.	Time, hr.	Products after work-up (%)
Ether	35	18	Recovered ditin (90), Bu_3SnH (4)
Tetrahydrofuran	64	18	Recovered ditin (73), Bu_3SnH (18)
Tetrahydrofuran	64	168	Recovered ditin (71), Bu_3SnH (19)
Dioxane	100	3	Recovered ditin (85), Bu_3SnH (10)
Dioxane	100	6.5	Recovered ditin (80), Bu_3SnH (10) (remainder tar)
Dioxane	100	21	Recovered ditin (26), Bu_3SnH (5), Bu_2SnO (33), Sn metal (5) (remainder tarry products)
Diglyme	135	2.5	Recovered ditin (20), Bu_3SnH (19), Bu_2SnO (22), Sn metal (17) (remainder tar)

Hexabutylditin was treated with a large excess of lithium aluminum hydride in various solvents at different temperatures for different time periods. The results are shown in Table I. The reaction is complex. It appears to be an equilibrium reaction at lower temperatures giving, as the major cleavage product, tributyltin hydride. Presumably, the first step in the reaction is cleavage of the ditin by hydride ion (or its equivalent) as indicated below.

$$(C_4H_9)_3SnSn(C_4H_9)_3 \overset{H^-}{\rightleftharpoons} (C_4H_9)_3SnH + (C_4H_9)_3Sn^-$$

The anion is neutralized by a cation such as Li^+ or its equivalent to form tributyltin lithium or its equivalent. Hydrolysis of this compound would give additional amounts of tributyltin hydride as well as regenerating starting material. The reverse reaction involved in the equilibrium, the regeneration of starting hexabutylditin, could be the attack of the tributyltin anion on tributyltin hydride. Gilman[7] has demonstrated in the phenyltin series the reaction of phenyllithium with triphenyltin hydride to give tetraphenyltin and lithium hydride.

Tributyltin lithium was prepared by the procedure of Gilman and Rosenberg[8] from stannous chloride and butyllithium. The reagent was hydrolyzed with ammonium chloride solution to yield 38% tributyltin hydride and 55% dibutyltin oxide. Coates[9] was unable to detect any tributyltin hydride among the hydrolysis products of tributyltin lithium prepared by the above method, while Tamborski[10] reported a 54% yield of tributyltin hydride and a 29% yield of hexabutylditin from hydrolysis of tributyltin lithium prepared from tributyltin chloride and lithium in tetrahydrofuran. It, therefore, appears that the hydrolysis products of tributyltin lithium vary, depending on the method of preparation as well as on the reaction solvent.

An equilibrium reaction is also indicated by the data in Table I which show that both 18- and 168-hr. reflux in tetrahydrofuran gave identical yields (20%) of tributyltin hydride. In a subsequent experiment, 20 mole % of tributyltin hydride was added to hexabutylditin, and the mixture reacted with lithium aluminum hydride. Instead of the expected 40% yield of tributyltin hydride, there was only obtained a 27% total yield showing that the equilibrium had been displaced to the left by the inclusion in the reaction of one of the products.

---

[1] Paper III: W. J. Considine and J. J. Ventura, *J. Org. Chem.*, **28**, 221 (1963).

[2] J. Noltes and G. van der Kerk, "Functionally Substituted Organotin Compounds," Tin Research Institute, Greenford, England, 1958, p. 43.

[3] O. Johnson and H. Fritz, *J. Org. Chem.*, **19**, 74 (1954).

[4] A. Gibbons, A. Sawyer, and A. Ross, *ibid.*, **26**, 2304 (1961).

[5] W. J. Considine and J. J. Ventura, *Chem. Ind.* (London), 1683 (1962)

[6] C. Tamborski, F. E. Ford, W. L. Lehn, G. J. Moore, and E. J. Soloski, *J. Org. Chem.*, **27**, 619 (1962).

[7] H. Gilman and H. Melvin, *J. Am. Chem. Soc.*, **71**, 4050 (1949).

[8] H. Gilman and S. Rosenberg, *ibid.*, **75**, 2507 (1953).

[9] G. Coates, "Organometallic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 193.

[10] C. Tamborski, F. Ford, and E. Soloski, *J. Org. Chem.*, **28**, 237 (1963).

As the temperature was raised, the reaction became even more complex and more profound cleavage products were formed so that, at 135° (in refluxing diglyme), the ultimate cleavage product, tin metal, was formed. The higher temperatures may promote the disproportionation of the intermediate tributyltin lithium.[11]

$$Bu_3SnLi \longrightarrow Bu_2Sn + BuLi$$

Air oxidation of the dibutyltin during work-up would lead to the product actually found, dibutyltin oxide, but the origin of the tin metal is obscure.

The reaction of hexaphenylditin with excess lithium aluminum hydride is also complex. As shown in Table II, at lower temperatures, the product isolated is diphenyltin oxide while, at elevated temperatures, tin metal is the product. No triphenyltin hydride could be detected in either reaction. It is difficult to explain the cleavage products as arising from the disproportionation of the intermediate triphenyltin lithium, since Tamborski[12] has indicated that the above intermediate is stable in refluxing tetrahydrofuran for 24 hr. No degradation of hexaphenylditin was noted in an experiment when the ditin was refluxed in tetrahydrofuran for 21 hr.; 98% of the ditin was recovered unchanged.

TABLE II
REACTION OF HEXAPHENYLDITIN WITH LITHIUM ALUMINUM HYDRIDE

Solvent	Temp., °C.	Time, hr.	Products (%)
Ether	35	18	Diphenyltin oxide (85), hexaphenylditin (5) (remainder tar)
Tetrahydrofuran	64	21	Tin metal (75) (residue unidentified tar containing 10% tin by analysis)

A preliminary experiment showed that tetraphenyltin is also cleaved by lithium aluminum hydride. The reaction was run at 0° for 6.5 hr. in tetrahydrofuran. Approximately 87% of starting material was recovered, but a trace of diphenyltin oxide was also found, and the presence of benzene was detected in the solvent distillate by vapor phase chromatography.

Experimental

Reaction of Hexabutylditin with Lithium Aluminum Hydride.—All of the reactions reported in Table I were run by the typical procedure shown below. In a typical run, 91 g. (0.157 mole) of hexabutylditin which had been freshly distilled (b.p. 180–200° at 1 mm.) was dissolved in 100 ml. of dry tetrahydrofuran and added dropwise under nitrogen to a slurry of 8.0 g. (0.84 equiv.) of lithium aluminum hydride in 400 ml. of tetrahydrofuran. The mixture warmed slightly and turned dark green after 1 hr. It was then refluxed and stirred for 18 hr. The mixture was then hydrolyzed with sodium potassium tartrate according to the procedure of van der Kerk,[13] but an incomplete separation occurred. The aqueous layer was, therefore, extracted with three 200-ml. portions of ether; the ethereal layer was combined with tetrahydrofuran layer formed on hydrolysis. The extracts were dried over exsiccated magnesium sulfate, and the mixed solvents were distilled through a 25-cm. Vigreux column. The still residue was then distilled through a small 10-cm. Vigreux column and there was obtained 17.0 g. (0.0585 mole, 18.5% yield) of tributyltin hydride, b.p. 75–85° (0.025 mm.), $n^{30}\text{D}$ 1.4682, lit.[14] $n^{22}\text{D}$ 1.4720; and 70.0 g. (0.121 mole, 77% recovery) of hexabutylditin, b.p. 156–160° (0.025 mm.), $n^{25}\text{D}$ 1.5100, lit.[14] $n^{25}\text{D}$ 1.5090.

The infrared spectrum of the tributyltin hydride was superimposible upon the spectrum of an authentic sample of tributyltin hydride prepared by reduction of bis(tributyltin oxide) with lithium aluminum hydride.

Preparation and Hydrolysis of Tributyltin Lithium.—Tributyltin lithium was prepared by the method of Gilman and Rosenberg[8] using 25.6 g. (0.135 mole) of stannous chloride and 173 g. of a 15% solution of *n*-butyllithium in hexane (0.405 mole of *n*-butyllithium). The mixture was hydrolyzed for 15 min. after preparation with saturated ammonium chloride solution, and then was worked up in the usual manner to yield 15 g. (0.052 mole) of tributyltin hydride, b.p. 123° (1.5 mm.), infrared spectrum and vapor phase chromatogram identical with an authentic sample; and 18.5 g. (0.075 mole) of di-*n*-butyltin oxide.

Anal. Calcd. for $(C_4H_9)_2SnO$: Sn, 47.8. Found: Sn, 47.65.

Reaction of Hexaphenylditin with Lithium Aluminum Hydride.—This reaction was carried out in a fashion similar to that described above. In a typical run, 90 g. (0.128 mole) of recrystallized hexaphenylditin [m.p. 230–231° (uncor.)] was mixed under nitrogen with a slurry of 15.0 g. (1.6 equiv.) of lithium aluminum hydride in 400 ml. of dry tetrahydrofuran. The initial dark green color turned dark brown on refluxing for 21 hr. The mixture was worked up as with hexabutylditin to yield 22.7 g. (0.191 mole, 74.3% yield) of metallic tin in the form of small spheres.

Anal. Calcd.: Sn, 100.0. Found: Sn, 99.0 (emission spectrograph shows all Sn lines).

There was also isolated 20 g. of an unidentified dark red-brown material from evaporation of the mixed solvents, probably polymeric diphenyltin. This material, on standing in air, slowly decolorized and formed a white powder which was probably impure diphenyltin oxide.

Anal. Calcd. for $(C_6H_5)_2SnO$: Sn, 41.2. Found: Sn, 41.0.

Considerable quantities of benzene were identified in the mixed solvent distillate by vapor phase chromatography, thus indicating phenyl–tin cleavage.

Reaction of Hexaphenylditin with Tetrahydrofuran.—Fifty grams (0.714 mole) of hexaphenylditin (m.p. 233–234°) was refluxed under nitrogen with 200 ml. of tetrahydrofuran for 21 hr. The ditin dissolved in the hot solution and reprecipitated when the solution was cooled. The filtrate was evaporated to 30 ml. and cooled; additional material precipitated. Both crops of crystals had m.p. 232–234°, and a mixture melting point with the starting material of 232–234°, thus confirming the identity of the recovered material as substantially pure starting material. The yield of recovered material was 49.1 g. (98%, substantially quantitative).

Reaction of Tetraphenyltin with Lithium Aluminum Hydride.—Seventy-five grams (0.15 mole) of tetraphenyltin was treated with 15 g. (0.394 mole) of lithium aluminum hydride in 400 ml. of tetrahydrofuran at 0° for 6.5 hr. under nitrogen. After work-up in the usual manner there was recovered 65.5 g. (87.4% recovery) of tetraphenyltin, m.p. and m.m.p. (with starting material) 222–224°.

A trace of diphenyltin oxide was also found as a precipitate in the mixed solvent–water layers after hydrolysis, and the presence of benzene was detected in the tetrahydrofuran layer by vapor phase chromatography.

---

[11] See ref. 9.

[12] C. Tamborski, F. Ford, and E. Soloski, *J. Org. Chem.*, **28**, 181 (1963).

[13] See ref. 2, p. 93.

[14] C. Tamborski, F. Ford, and E. Soloski, *J. Org. Chem.*, **28**, 237 (1963).

Dicarbenes. Some Isolable Bisdiazoalkanes

ROBERT W. MURRAY AND ANTHONY M. TROZZOLO

Bell Telephone Laboratories, Inc.,
Murry Hill, New Jersey

Received September 19, 1963

In connection with a study of species containing two divalent carbon atoms we have reported[1] the prepara-

---

[1] R. W. Murray and A. M. Trozzolo, *J. Org. Chem.*, **26**, 3109 (1961).