71–72°/20 mm., n_D^{25} 1.4287 (reported,[21] b.p. 172°; n_D^{25} 1.4330).

After washing with cupric sulfate to remove traces of 3-methyl-2,4-pentanedione,[21] the material was redistilled. It showed exactly the same boiling point and refractive index.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.6; H, 9.4. Found: C, 65.6; H, 9.4.

Oxidation of 3,3-dimethyl-2,4-pentanedione. The reaction was carried out using 100 ml. of *tert*-butyl alcohol, 25.6 g. (0.20 mole) of diketone, 28.5 g. (0.25 mole) of 29.9% hydrogen peroxide, and 0.10 g. of sulfuric acid. At the end of 1 hr. on the steam bath, 0.04 mole of peroxide remained and 475 ml. of oxygen had been evolved (corresponding to about 0.04 mole of peroxide).

After the addition of 0.2 g. of sodium acetate and a pinch of palladium on charcoal, distillation was carried out using a 0.7 × 50-cm. glass spiral-packed column to give 15.5 g. (76% yield) of pivalic acid, b.p. 67–70°/15 mm., m.p. 26–30° (reported,[22] b.p. 75–78°/20 mm., m.p. 35°).

A *p-phenylphenacyl ester* derivative showed m.p. and mixed m.p. 113–114°.

3-Methyl-2,4-pentanedione. A solution of 54 g. (1.0 mole) of sodium methylate in 500 ml. of absolute ethanol was stirred at 25–30° as 100 g. (1.0 mole) of 2,4-pentanedione was added portionwise with cooling. The addition of 154 g. (1.1 moles) of methyl iodide initiated a mildly exothermic reaction. Slight cooling was used to hold the temperature at 50–55°. When no longer exothermic, the mixture was held at the same temperature for 0.5 hr. and finally at reflux for 0.5 hr.

After concentration of the water pump using a bath temperature of 40°, the residue was dissolved in 300 ml. of water and extracted with four 150-ml. portions of chloroform. The combined chloroform was washed, dried, and concentrated on the steam bath. Distillation through a 10-tray Oldershaw column afforded 70 g. (62% yield) of 3-methyl-2,4-pentanedione, b.p. 68–70°/20 mm., n_D^{25} 1.4428 (lit., b.p. 86°/60 mm., n_D^{20} 1.4455[23]; b.p. 170°, n_D^{24} 1.4515[24]).

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.1; H, 8.8. Found: C, 63.3; H, 8.8.

Oxidation of 3-methyl-2,4-pentanedione. A solution of 45.6 g. (0.40 mole) of diketone, 0.60 mole of 30% hydrogen peroxide, and 1 ml. of sulfuric acid in 200 ml. of *tert*-butyl alcohol was allowed to reflux for about 3 hr. Gas evolution amounted to 2.2 l., and 0.02 mole of hydrogen peroxide remained.

Distillation through a 10-tray Oldershaw column was carried out at 50 mm. until a head temperature of 37° was reached. Bottoms from this operation were poured into 200 ml. of chloroform and extracted with a solution of 20 g. of potassium carbonate in 100 ml. of water. This solution, after springing with sulfuric acid and extraction with chloroform, gave on distillation 2.4 g. of material, b.p. 55–59°/10 mm., n_D^{25} 1.3954.

Anal. Calcd. for $C_5H_{10}O_2$: Neut. equiv., 102. Found: Neut. equiv., 98.

The *p-phenylphenacyl ester* derivative, after three crystallizations from ethanol, had a constant m.p. of 108–109°. A mixture with the derivative from pivalic acid melted at 111–112°.[25]

Neutral material remaining in the chloroform after extraction with carbonate was isolated by distillation, b.p. 67–70°/20 mm., n_D^{25} 1.4361. It weighed 11.7 g. (26% recovery) and had an infrared absorption spectrum essentially identical with that of the starting diketone.

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[21] R. G. Pearson and E. A. Mayerle, *J. Am. Chem. Soc.*, **73**, 926 (1951).

[22] Ref. 11, Vol. IV, p. 224.

[23] R. G. Kelso, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **77**, 1751 (1955).

[24] R. G. Pearson and J. M. Mills, *J. Am. Chem. Soc.*, **72**, 1692 (1950).

[25] Pivalic acid was undoubtedly produced from 3,3-dimethyl-2,4-pentanedione impurity in the starting material.

[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

Preparation of Organolithium Compounds by the Transmetalation Reaction. III. Allyllithium and Methallyllithium[1,2a]

DIETMAR SEYFERTH AND MICHAEL A. WEINER

Received June 15, 1961

The transmetalation reaction occurring between phenyllithium and allyltriphenyltin (1:1 molar ratio) or phenyllithium and tetraallyltin (4:1 molar ratio) in ether produces allyllithium in good yield. A similar reaction between *n*-butyllithium and tetraallyltin (2:1 molar ratio) in pentane gives solid allyllithium, which is only sparingly soluble in pentane. The use of allyllithium in the preparation of a number of previously known allyl compounds, as well as of the new $[B(CH_2CH{=}CH_2)(C_6H_5)_3]^-$ ion, is described.

In Part I of this series[2b] we reported the preparation of vinyllithium by the exchange reaction between vinyltin compounds and phenyl- or *n*-butyllithium. We have extended this general method to the synthesis of allyllithium and methallyllithium by reaction of allyl- or methallyltin compounds with organolithium reagents.

The preparation of allyl derivatives of active metals presents special problems. If the synthesis of the allylic metallic reagent is based on the reaction of an allyl halide with an active metal, a coupling reaction between the allylmetal compound and the allylic halide is a serious complicating factor. Conditions have been defined which allow the preparation of allylmagnesium halides in good

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[1] Preliminary communication: D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **24**, 1395 (1959).

[2a] Part II: D. Seyferth and J. F. Helling, *Chem. & Ind.* (*London*), 1568 (1961).

[2b] D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **83**, 3583 (1961).

yield by the reaction of allyl chloride[3] or bromide[4] with magnesium. However, no satisfactory preparation of allyllithium by a reaction of allyl halides with metallic lithium is available. A brief investigation of the action of allyl chloride and bromide on lithium formed a part of the present study, but only negative results were obtained. However, Kawai and Tsutumi[5] have reported recently conditions for carrying out such reactions, which do appear to lead to low yields of allyllithium. Thus, the reaction of allyl bromide with a large excess of lithium in ether medium produced chiefly biallyl, but on addition of acetophenone to the reaction mixture a small amount of product reported to be 1,5 - dimethyl - 1,5 - diphenylpent - 2 - ene - 1,5-diol was formed. It was believed that this product resulted from the initial reaction of allyllithium with acetophenone, followed by the metalation of the terminal carbon atom of the allyl group of the product and reaction of this new lithium derivative with acetophenone.

A synthesis of allyllithium from the allyl Grignard reagent and metallic lithium has been described in the patent literature.[6] However, the data presented indicated that this reaction did not proceed in complete conversion, and a mixture of allyllithium and allylmagnesium chloride was present. Since no satisfactory method for the preparation of pure allyllithium in high yield appeared to be available, the possible preparation of this reagent by the transmetalation route was of special interest.

The present work has shown that the lithium-tin transmetalation reaction provides a practical synthesis for allyllithium in good yield. Since this procedure does not require allyl halides, coupling reactions are avoided, and all the allyllithium formed is available for further reactions. This procedure also makes possible for the first time the isolation of solid allyllithium. As in the case of vinyllithium, this exchange reaction may be carried out in a hydrocarbon solvent as well as in diethyl ether.

Although tetraallyltin would be the most practical starting material, allyltriphenyltin was used during most of this work because it was very easily prepared by the Barbier procedure in 75–80% yield. Tetraallyltin became available in developmental quantities (Metal & Thermit Corp.) during the later stages of this research and gave as satisfactory a yield of allyllithium as had been obtained using allyltriphenyltin. The reaction between phenyllithium and allyltriphenyltin in ether solution produced an almost quantitative yield of ether-insoluble tetraphenyltin and a solution of allyllithium:

$$(C_6H_5)_3SnCH_2CH{=}CH_2 + C_6H_5Li \longrightarrow (C_6H_5)_4Sn + CH_2{=}CHCH_2Li$$

Allyllithium in ether reacted readily with a variety of organic and organometallic substrates. Its reactions are summarized in Table I.

TABLE I

Reactions of Allyllithium in Ether Solution

Substrate	Product	Yield[a]
$(n\text{-}C_4H_9)_3SnCl$	$(n\text{-}C_4H_9)_3SnCH_2CH{=}CH_2$	69%
$(n\text{-}C_4H_9)_3SnCl$[b]	$(n\text{-}C_4H_9)_3SnCH_2CH{=}CH_2$	69
$(n\text{-}C_4H_9)_3SnCl$[c]	$(n\text{-}C_4H_9)_3SnCH_2CH{=}CH_2$	74
$(C_6H_5)_3SiCl$	$(C_6H_5)_3SiCH_2CH{=}CH_2$	74
$(C_6H_5)_3GeBr$	$(C_6H_5)_3GeCH_2CH{=}CH_2$	54
$(C_6H_5)_3SiH$	$(C_6H_5)_3SiCH_2CH{=}CH_2$	60
$n\text{-}C_5H_{11}I$	$CH_3(CH_2)_5CH{=}CH_2$	52
$(C_6H_5)_3B$	$Li[B(C_6H_5)_3(CH_2CH{=}CH_2)]$[d]	
$(i\text{-}C_4H_9)CH_3C{=}O$	$CH_2{=}CHCH_2(i\text{-}C_4H_9)CH_3COH$	65
$(i\text{-}C_4H_9)CH_3C{=}O$[c]	$CH_2{=}CHCH_2(i\text{-}C_4H_9)CH_3COH$	73
CO_2	$CH_2{=}CHCH_2COOH$	36

[a] Based on the amount of substrate used. [b] $(n\text{-}C_4H_9)_3SnCl$ added after the reagent mixture had been left standing under nitrogen for 20 hr. [c] $(CH_2{=}CHCH_2)_4Sn$ used instead of $(C_6H_5)_3SnCH_2CH{=}CH_2$. [d] Isolated as the $[(CH_3)_4N]$ and $[(C_6H_5)_3CH_3P]$ salts.

Solid allyllithium was prepared in pentane, in which it is only sparingly soluble, by the reaction of *n*-butyllithium with tetraallyltin. Because the reaction of four moles of *n*-butyllithium in pentane with one mole of tetraallyltin did not proceed to completion, the reaction of two moles of the lithium compound to one mole of the tin compound was utilized in order to obtain maximum synthetic efficiency. Yields of 80–87% of allyllithium were obtained from the latter reaction. The precipitated allyllithium was filtered, washed with pentane, dissolved in ether, and then used in subsequent reactions. Solid allyllithium, obtained as a white powder, was violently pyrophoric in air.

The infrared spectrum of allyllithium was determined. In ether the C=C stretching frequency appeared at 1540 cm.$^{-1}$, in a Nujol mull of the solid reagent at 1542 cm.$^{-1}$ These values are much closer to the observed C=C stretching frequency of allylsodium (1535 cm.$^{-1}$ in a Nujol mull), which has been assumed to be ionic,[7] than that of allylmagnesium chloride[8] (1580 cm.$^{-1}$ in ether solution, 1565 cm.$^{-1}$ in tetrahydrofuran) or bromide[8] (1588 cm.$^{-1}$ in ether, 1570 cm.$^{-1}$ in tetrahydrofuran), which are believed[8,9] to exist in the covalent form. However, the NMR spectrum of allyllithium, like that of allylmagnesium bromide, was of the

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[3] M. S. Kharasch and C. F. Fuchs, *J. Org. Chem.*, **9**, 359 (1944).

[4] H. Gilman and J. H. McGlumphy, *Bull. soc. chim. France*, [4], **43**, 1322 (1928).

[5] W. Kawai and S. Tsutumi, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **81**, 109 (1960).

[6] E. Londergan, U. S. Patent **2,734,091** (1956); *Chem. Abstr.*, **50**, 15588 (1956).

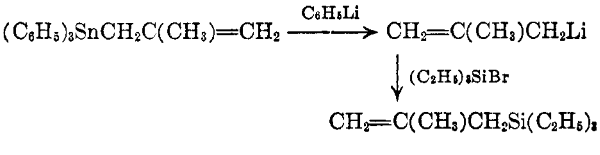
[7] E. J. Lanpher, *J. Am. Chem. Soc.*, **79**, 5578 (1957).

[8] C. Prévost and B. Gross, *Compt. rend.*, **252**, 1023 (1961).

[9] J. E. Nordlander and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 1769 (1959).

AX_4 type,[10] and this observation has been interpreted in terms of rapid intra- or intermolecular lithium or magnesium exchange involving the covalent allyllithium molecule or Grignard reagent.[9] The lack of change in the C=C stretching frequency when the spectra of allyllithium in the solid state and in ether solution were compared is somewhat surprising, in view of the changes observed in the spectrum of the allyl Grignard reagents when the ether solvent is replaced by tetrahydrofuran. Further studies clearly are required before the exact nature of the species present in a solution of allyllithium is understood; in particular, the extent of association would be a subject of interest.

Methallyllithium was prepared by the exchange reaction between phenyllithium and methallyltriphenyltin in ether. This new reagent was used to obtain 2-methylpent-1-en-4-ol (59%) from acetaldehyde and triethylmethallylsilane (68%) from triethylbromosilane:



$$(C_6H_5)_3SnCH_2C(CH_3){=}CH_2 \xrightarrow{C_6H_5Li} CH_2{=}C(CH_3)CH_2Li \xrightarrow{(C_2H_5)_3SiBr} CH_2{=}C(CH_3)CH_2Si(C_2H_5)_3$$

EXPERIMENTAL[11]

Preparation of allyltriphenyltin and methallyltriphenyltin. Magnesium turnings (24.3 g., 1.0 g.-atom) were placed in a 2-l., three necked flask equipped with a water condenser, mechanical stirrer, and addition funnel. Tetrahydrofuran (320 ml.) was added, and the reaction was initiated by adding a small amount of allyl bromide. The rapidly stirred mixture then was heated to reflux, and a solution of 96 g. (0.25 mole) of triphenyltin chloride (Metal and Thermit Corp.) and 47 g. (0.39 mole) of allyl bromide in 240 ml. of tetrahydrofuran was added slowly over the course of 3 hr. After the addition had been completed, the reaction mixture was heated at reflux overnight, cooled, and hydrolyzed with saturated ammonium chloride solution. After decanting the supernatant organic phase and washing the inorganic salts with ether, the combined organic layers were distilled to remove solvent. The residue was dissolved in ether and shaken with a solution of potassium fluoride in a methanol-water mixture. No triphenyltin fluoride precipitated, indicating complete conversion of triphenyltin chloride. The ether layer was separated and the ether removed at reduced pressure. The solid residue was recrystallized from ligroin to give 67 g. of allyltriphenyltin, m.p. 72.5–74°. On concentrating the filtrate, an additional 9 g. of product, m.p. 70–72°, was obtained; reported m.p.: 73.5–74.5°.[12] The total yield was 78%.

The preparation of methallyltriphenyltin, a new compound, was accomplished using the same general procedure. In this case methallyl chloride was used. Recrystallization of the crude product from a methanol-ethanol mixture and subsequently from ligroin gave pure material, m.p. 72–73°.

Anal. Calcd. for $C_{22}H_{22}Sn$: C, 65.22; H, 5.48. Found: C, 65.13; H, 5.46.

Preparation of allyllithium in diethyl ether and its reaction with tri-n-butyltin chloride. Allyltriphenyltin (30 g., 0.077 mole) in 150 ml. of ether was placed in a 500-ml., three necked flask equipped with an addition funnel, stirrer, and water condenser topped with a nitrogen inlet tube. A solution of 65 ml. of 1.29*M* phenyllithium (0.084 mole) in ether was added. A white precipitate formed immediately. The mixture was stirred under nitrogen for 30 min., and 25 g. (0.077 mole) of tri-*n*-butyltin chloride in 50 ml. of ether was added. The resulting mixture was stirred overnight and hydrolyzed with 150 ml. of distilled water. The solid material then was filtered and washed twice with ether. The organic layer was separated and shaken twice with an aqueous potassium hydroxide solution. Distillation of the organic layer from this treatment gave 17.5 g. of liquid distilling at 152–156° (17 mm.). A second distillation gave pure allyltri-*n*-butyltin, b.p. 94–95° (0.55 mm.), n_D^{25} 1.4833, d_4^{25} 1.073, $\nu_{C=C}$ 1624 cm^{-1}.

Anal. Calcd. for $C_{15}H_{32}Sn$: C, 54.41; H, 9.74. Found: C, 54.61; H, 9.86.

A nearly quantitative yield of crude tetraphenyltin was obtained (m.p. 215–220°). Recrystallization from tetrahydrofuran gave pure material, m.p. 224–227°, which was shown to be tetraphenyltin by mixed melting point and infrared spectrum.

A similar procedure was used when tetraallyltin (4.6 g., 0.0163 mole) was used to prepare allyllithium by reaction with 61 ml. of 1.07*M* phenyllithium in ether. Addition of 0.065 mole of tri-*n*-butyltin chloride, followed by the procedure described above, resulted in 15.8 g. (74%) of allyltri-*n*-butyltin and a 95% yield of tetraphenyltin.

Reaction of allyllithium with triphenylchlorosilane. A solution of allyllithium was prepared as described above from 0.04 mole of allyltriphenyltin. To this solution was added 10.3 g. (0.035 mole) of triphenylchlorosilane (Dow Corning Corp.) dissolved in 75 ml. of ether. After a 2.5-hr. reflux period, the mixture was hydrolyzed with 100 ml. of distilled water. The tetraphenyltin (92%) was filtered and washed with ether. The ether layer was separated and the solvent removed at reduced pressure, leaving a white solid residue which was crystallized from ethanol to give 6.4 g. of allyltriphenylsilane, m.p. 92–94° (lit.[13] m.p. 91–92°). On concentrating the mother liquor, another 1.4 g. (m.p. 90.5–93.5°) was obtained; total yield, 74%.

Essentially the same procedure was used in the preparation of allyltriphenylsilane from triphenylsilane and of allyltriphenylgermane from triphenylgermanium bromide.

Reaction of allyllithium with n-amyl iodide. To a solution of allyllithium prepared from 0.127 mole each of allyltriphenyltin and phenyllithium was added 23.8 g. (0.12 mole) of *n*-amyl iodide. The mixture was refluxed for 4 hr. Unchanged *n*-amyl iodide was removed by its conversion to the Grignard reagent, the hydrolysis of which would give pentane. Magnesium and a small amount of 1,2-dibromoethane were added to the reaction mixture. After the mixture had been refluxed for 2 hr., it was hydrolyzed. The organic layer was separated and distilled to give 7.0 g. (52%) of 1-octene, b.p. 38.5–41.5° (41 mm.), n_D^{25} 1.4080 (lit.[14] b.p. 121° (758 mm.), n_D^{25} 1.4062). Its infrared spectrum was identical with the published[15] infrared spectrum of 1-octene.

Reaction of allyllithium with 4-methyl-2-pentanone. Twelve grams (0.12 mole) of 4-methyl-2-pentanone was added to an

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(10) C. S. Johnson, M. A. Weiner, J. S. Waugh, and D. Seyferth, *J. Am. Chem. Soc.*, **83**, 1306 (1961).

(11) Analyses were performed by Dr. S. M. Nagy (M.I.T.), by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Dr. Carol Fitz, Needham Heights, Mass. Melting points were taken using a calibrated Fisher-Johns or Mel-Temp apparatus and are uncorrected. For most experiments anhydrous reagent grade ether was distilled from lithium aluminum hydride before use. Tetrahydrofuran was stored over sodium and distilled from lithium aluminum hydride.

(12) H. Gilman and J. Eisch, *J. Org. Chem.*, **20**, 763 (1955).

(13) A. D. Petrov and L. L. Shchukovskaya, *Zhur Obshcheĭ Khim.*, **25**, 1083 (1955).

(14) H. Gedoff and J. P. Wibaut, *Rec. Trav. Chim.*, **67**, 105 (1948).

(15) U. S. Naval Research Laboratory, American Petroleum Institute Research Project 44, Ser. No. 474 (1946).

allyllithium solution prepared by reaction of 0.127 mole of allyltriphenyltin with an equivalent of phenyllithium in ether. The mixture was refluxed for 1.5 hr. and hydrolyzed with 200 ml. of water. The tetraphenyltin (98%) was filtered off. Distillation of the organic layer gave 11.1 g. (65%) of 4,6-dimethylhept-1-en-4-ol at 70–71° (20 mm.), n_D^{20} 1.4400 (lit.[16] b.p. 68–69° (20 mm.), n_D^{20} 1.4402). The infrared spectrum of the product showed a band at 1645 cm.$^{-1}$ ($\nu_{C=C}$), a band at 916 cm.$^{-1}$ (and its overtone at 1832 cm.$^{-1}$) due to the $=CH_2$ out-of-plane deformation mode, a band at 1000 cm.$^{-1}$ ($=CH-$ out-of-plane deformation) and a broad band centered at about 3450 cm.$^{-1}$

Preparation of solid allyllithium and its carbonation. n-Butyllithium in pentane (375 ml. of a 0.45*M* solution, 0.17 mole) was added to 24 g. (0.085 mole) of tetraallyltin. The mixture was stirred in a stream of nitrogen. The allyllithium which precipitated was filtered under nitrogen, washed with pentane, and dissolved in ether. The concentration of the resulting solution, determined by titration, was 0.43*M*. A total of 0.133 mole of allyllithium (310 ml. of solution) was obtained in this manner (79% yield). Two similar experiments produced allyllithium in 82 and 87% yield.

Dry Ice (*ca.* 300 g.) was crushed and suspended in 100 ml. of ether to which a little hydroquinone had been added. To this slurry was added 290 ml. (0.125 mole) of the 0.43*M* allyllithium solution. The resulting mixture was stirred until the excess Dry Ice had evaporated. After slow addition of 80 ml. of 3*N* sulfuric acid at room temperature, the organic layer was separated and the aqueous layer shaken twice with ether. The combined organic layers were dried and distilled to give 3.9 g. (36%) of vinylacetic acid, b.p. 69–75° (11 mm.), n_D^{20} 1.4223. The material was redistilled, and 3.2 g. (30%) of product was obtained at 68–70° (10 mm.), n_D^{20} 1.4223; lit.[17] b.p. 71° (12 mm.), n_D^{20} 1.4221.

Reaction of allyllithium with triphenylborane. A solution of allyllithium in ether was prepared from solid allyllithium as described in the preceding experiment. Freshly distilled triphenylborane (3.8 g., 0.0157 mole) was dissolved in 150 ml. of ether, and 100 ml. of the 0.17*M* allyllithium solution was added. A heavy oil settled out. After the mixture had been stirred at room temperature in an atmosphere of nitrogen overnight, the oil was drawn off. It appeared to be stable in air and in methanol solution. To a portion of the oil in methanol was added a methanolic solution of tetramethylammonium bromide. A precipitate appeared within 1 min.; this was filtered and recrystallized from methanol to give white, solid tetramethylammonium allyltriphenylboron, which decomposed at 255–260°.

Anal. Calcd. for $C_{25}H_{32}NB$: C, 84.02; H, 9.03. Found: C, 84.04; H, 9.07.

To a second portion of the oil in methanol was added a solution of methyltriphenylphosphonium bromide in methanol. The crude methyltriphenylphosphonium allyltriphenylboron, m.p. 155–160°, which precipitated was recrystallized twice from methanol to give pure material, m.p. 168–170°.

Anal. Calcd. for $C_{40}H_{38}PB$: C, 85.71; H, 6.83. Found: C, 85.92; H, 7.06.

Preparation of methallyllithium and its reaction with acetaldehyde. To 40.5 g. (0.1 mole) of methallyltriphenyltin in 200 ml. of ether was added 73 ml. of 1.37*M* phenyllithium in ether. After the mixture had been stirred for 30 min. under nitrogen, 4.4 g. (0.1 mole) of acetaldehyde was added. The resulting mixture was refluxed for 1 hr. Hydrolysis with 150 ml. of water, filtration of the tetraphenyltin (41 g., 96%), and separation of the organic layer followed. The aqueous layer was extracted with ether, and the combined ether layers were dried and distilled to give 5.3 g. (53%) of 2-methylpent-1-en-4-ol at 43° (17 mm.), n_D^{18} 1.4339. A second fractional distillation caused no change in refractive index. Reported for the + isomer: b.p. 42° (15 mm.), n_D^{18} 1.4339.[18]

Reaction of methallyllithium with triethylbromosilane. A 1.28*M* solution of phenyllithium (78 ml., 0.1 mole) in ether was added to 40.5 g. (0.1 mole) of methallyltriphenyltin in 200 ml. of ether. After 45 min. 17.6 g. (0.09 mole) of triethylbromosilane was added, the mixture refluxed under nitrogen for 3 hr. and then hydrolyzed with 200 ml. of water. The tetraphenyltin (96%) was filtered off and washed with ether. The organic layer was separated, dried, and distilled to give 10.5 g. (68%) of triethylmethallylsilane, b.p. 48–52° (3.5–4.5 mm.), n_D^{20} 1.4495 (lit.[19] b.p. 189° (750 mm.), n_D^{20} 1.4505).

Acknowledgment. The authors are grateful for support of this work by the National Science Foundation under Grant G-7325 and to the National Institutes of Health for a Predoctoral Fellowship to M.A.W.

CAMBRIDGE 39, MASS.

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(18) J. Kenyon and D. P. Young, *J. Chem. Soc.*, 1452 (1938).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RICE UNIVERSITY]

trans-Decalin-2,9-dicarboxylic Acid and Related Derivatives

RICHARD B. TURNER, R. E. LEE, JR., AND ERNEST G. HILDENBRAND

Received June 22, 1961

The preparation of *trans*-decalin-*trans*-2,9-dicarboxylic acid, *trans*-decalin-*cis*-2,9-dicarboxylic acid, the corresponding diesters, and the four isomeric half-esters is described. The acyloin condensation of *cis*-2,9-dicarbomethoxy-*trans*-decalin has been investigated, and the structure of the derived acyloin established.

In connection with an interest in the total synthesis of diterpenes containing bridged rings—*e.g.*, phyllocladene, garryine, etc.—we have examined the behavior of *cis*-2,9-dicarbomethoxy-*trans*-decalin (VIb) in the acyloin reaction. The preparation of this substance was carried out as indicated in the accompanying chart.

Although the β-keto ester I[1] fails to react with 4-diethylamino-2-butanone methiodide and sodium

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(1) H. T. Openshaw and R. Robinson, *J. Chem. Soc.*, 912 (1946).