was treated with an excess of *n*-butyllithium by the method used for triphenylsilanol.[1] Upon carbonation of the reaction mixture, phenylpropiolic acid and *n*-butyltriphenylsilane were isolated, indicating that there had been cleavage of a carbon-to-silicon bond in this R_4Si compound in accordance with the equation

$$(C_6H_5)_3SiC{\equiv}CC_6H_5 + n\text{-}C_4H_9Li \longrightarrow n\text{-}C_4H_9Si(C_6H_5)_3 + C_6H_5C{\equiv}CLi$$

When, in a similar manner, triphenylbenzylsilane was treated with an excess of *n*-butyllithium, and the reaction mixture was again carbonated, triphenylsilanol and phenylacetic acid were isolated. In view of the results[1] obtained in the reaction of *n*-butyllithium with trimethyl-9-fluorenylsilane, it seemed reasonable to suppose that the initial reaction was metalation rather than cleavage of a carbon-to-silicon bond. Therefore, a second trial was made in the same manner, except that this time a portion of the reaction mixture of *n*-butyllithium with triphenylbenzylsilane was hydrolyzed instead of carbonated. The starting material was recovered in good yield from this hydrolyzed portion of the reaction mixture, indicating that the initial reaction is a metalation, and that the acid formed on carbonation is quite unstable, resulting in cleavage of a carbon-to-silicon bond, as had been postulated for the case of trimethyl-9-fluorenylsilane.

$$(C_6H_5)_3SiCH_2C_6H_5 \underset{H_2O}{\overset{n\text{-}C_4H_9Li}{\rightleftharpoons}} (C_6H_5)_3SiCHC_6H_5 \xrightarrow{CO_2} (C_6H_5)_3SiCHC_6H_5 \xrightarrow{H_2O} (C_6H_5)_3SiOH + C_6H_5CH_2COOLi$$

(Li; COOLi)

The other portion of the reaction mixture of triphenylbenzylsilane with *n*-butyllithium was carbonated, and from this carbonated mixture triphenylsilanol and phenylacetic acid were isolated as in the first trial.

Experimental

Triphenyl-(phenylethynyl)-silane and *n*-Butyllithium.—To 10.0 g. (0.0278 mole) of triphenyl-(phenylethynyl)-silane (m.p. 100–101°)[3] dissolved in 50 ml. of dry ether was added 144 ml. of an ethereal solution of 0.0875 mole of *n*-butyllithium.[4] The resulting yellow-orange solution was refluxed, with stirring, in an atmosphere of dry nitrogen for 24 hours. The reaction mixture was poured jetwise on a slurry of crushed Dry Ice in ether, and the carbonated mixture was acidified with dilute hydrochloric acid. The aqueous layer was separated and washed with ether. The combined ether extracts were extracted with aqueous sodium bicarbonate. The aqueous bicarbonate solution was acidified with hydrochloric acid, and the acidic solution was extracted with ether. The ether extract was dried, and the solvent was distilled. The partially crystalline residue was recrystallized from hot water with the aid of Norit to give 0.77 g. (19%) of phenylpropiolic acid melting at 135–136°. The identity of the acid was confirmed by a mixed melting point.

The ethereal solution remaining after the bicarbonate extraction was dried, and the solvent was distilled. The crystalline residue was recrystallized first from petroleum ether (b.p. 28–38°), then from a methanol–ethyl acetate solution, to give 5.97 g. of material melting at 83–84°. Another recrystallization from a methanol–ethyl acetate solution gave 5.12 g. (58%) of *n*-butyltriphenylsilane melting at 85–86°. The identity of the material was confirmed by a mixed melting point.

Triphenylbenzylsilane and *n*-Butyllithium.—To 15.0 g. (0.0429 mole) of triphenylbenzylsilane (m.p. 97–98°)[3] dissolved in 100 ml. of dry ether was added 194 ml. of an ethereal solution of 0.151 mole of *n*-butyllithium.[4] The solution was refluxed, with stirring, in an atmosphere of dry nitrogen for 24 hours. The reaction mixture was then divided into two equal portions of 130 ml. each.

One portion of the reaction mixture was poured jetwise on a slurry of crushed Dry Ice in ether; water was then added to the carbonated mixture. More ether was added, and the aqueous layer was separated. The aqueous solution was heated to boiling to remove dissolved ether. The alkaline solution was then extracted[5] with petroleum ether (b.p. 60–70°) in a continuous extractor for 18 hours to remove non-acidic organic impurities. The aqueous solution was acidified, and the acidic solution was extracted with petroleum ether (b.p. 60–70°) in a continuous extractor for 24 hours. Upon evaporation of the petroleum ether, together with the valeric acid which it contained, there remained 1.25 g. (43%) of phenylacetic acid melting at 71–74°. The identity of the acid was confirmed by a mixed melting point.

The ether layer of the aqueous carbonated reaction mixture was dried, and the solvent was distilled. The partially crystalline residue was recrystallized from petroleum ether (b.p. 77–115°) to give 3.8 g. of material melting at 144–152°. A second recrystallization from petroleum ether (b.p. 77–115°) gave 3.1 g. (52%) of triphenylsilanol melting at 151–153°. The identity of the material was confirmed by a mixed melting point.

The other 130-ml. portion of the reaction mixture was hydrolyzed without carbonating. The ether layer was separated and dried, and the solvent was distilled. The crystalline residue was recrystallized from a methanol–ethyl acetate solution to give 6.0 g. of triphenylbenzylsilane melting at 96–98°, representing a recovery of 80% of the silane used in the reaction. The identity of the material was confirmed by a mixed melting point.

Acknowledgment.—The authors are grateful to G. E. Dunn for assistance.

(3) Kindly provided by Dr. L. S. Miller.

(4) The *n*-butyllithium was prepared by the method of H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, **71**, 1499 (1949). The normality of the *n*-butyllithium was determined by the analytical procedure of H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

(5) H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

CHEMICAL LABORATORY
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED MARCH 19, 1951

Cyclization of Aryl-Aliphatic Esters with Phosphorus Pentoxide in Phosphoric Acid

BY RICHARD C. GILMORE, JR.

The general usefulness of phosphorus pentoxide in 85% orthophosphoric acid for the cyclization of aryl-aliphatic acids in high yield without a great expenditure of time and labor has been reported.[1,2] On further investigating the usefulness of this polyphosphoric acid mixture for cyclizations, it was most surprising to find that esters could be used to give products identical to those obtained from the corresponding acids.

Methyl β-phenylpropionate was cyclized to α-hydrindone in 93% yield. β-Phenylpropionic acid produced the desired ketone in an amount comparable to that obtained when the ester was used. This is in direct opposition to the result achieved when the acid was treated with phosphorus pentoxide in which reaction 40% truxene and no α-hydrindone was isolated.[3] The amount of com-

(1) W. E. Bachmann and W. J. Horton, THIS JOURNAL, **69**, 58 (1947).

(2) R. C. Gilmore, Jr., and W. J. Horton, *ibid.*, **73**, 1411 (1951).

(3) F. S. Kipping, *J. Chem. Soc.*, **65**, 269 (1894).

pound obtained was practically the same when either γ-phenylbutyric acid or its methyl ester was cyclized, the yields being 70 and 72%, respectively. Methyl δ-phenylvalerate has been used to give benzosuberone in 90% yield as compared to that of 85% from the corresponding acid.[2]

Experimental[4]

Esterifications.—In all cases the esters were produced by refluxing the acid in 4% methanolic hydrochloric acid and isolating the neutral fraction in the usual manner. Although only methyl esters have been used in the present reported investigation, ethyl esters have been employed with equal success.

Ring Closures.—The preparation of the phosphorus pentoxide–85% orthophosphoric acid slurry and the isolation of the neutral ketonic material were carried out in a manner already described in detail.[2] To ensure homogeneity of the neutral compound from each cyclization, the compound was refluxed for 1 hour in 50 ml. of aqueous ethanol containing 2 g. of sodium hydroxide. The neutral material isolated from this procedure was used for determining the yield of compound and for preparing the reported derivatives. Fifty-four grams of slurry per gram of ester or acid was employed in all instances. The mixture of compound and slurry was heated in a flask protected from moisture by a calcium chloride tube for two hours on a steam-cone, although a shortened working time resulted in no decrease in yield of ketone in one instance.[5]

Derivatives.—The oxime and semicarbazone were prepared by refluxing the neutral compound from each cyclization in absolute ethanol and anhydrous pyridine containing either hydroxylamine hydrochloride or semicarbazide hydrochloride. Mixed melting points of these derivatives were not depressed when prepared from material obtained by cyclizing either the ester or its corresponding acid.

α-Hydrindone.—To 2 g. of methyl β-phenylpropionate was added the commensurate quantity of polyphosphoric acid slurry and the mixture heated. There was obtained 1.5 g. (93%) of neutral compound; oxime, m.p. 143–144°, reported,[6] 143–144°; semicarbazone, m.p. 237° (dec.), reported,[7] 239° (dec.).

α-Tetralone.—One gram of methyl γ-phenylbutyrate and 54 g. of slurry yielded, after the usual procedure, 0.59 g. (72%) of neutral compound; oxime, m.p. 101–102°, reported,[8] 102.5–103.5°; semicarbazone, m.p. 213–215°, reported,[8] 217°.

Benzosuberone.—A sufficient amount of polyphosphoric acid slurry was poured into a flask containing 1.8 g. of methyl δ-phenylvalerate and the usual procedure carried out to give 1.3 g. (90%) of neutral product; oxime, m.p. 107–108°, reported,[9] 108–109°; semicarbazone, m.p. 206–207°, reported,[9] 206–207°.

(4) Melting points are uncorrected.

(5) Methyl γ-phenylbutyrate was cyclized to α-tetralone by heating for only 15 minutes.

(6) F. S. Kipping, *J. Chem. Soc.*, **65**, 490 (1894).

(7) C. Revis and F. S. Kipping, *ibid.*, **71**, 241 (1897).

(8) F. S. Kipping and A. Hill, *ibid.*, **75**, 151 (1899).

(9) F. S. Kipping and A. E. Hunter, *ibid.*, **79**, 607 (1901).

DEPARTMENT OF BIOCHEMISTRY
SOUTHWESTERN MEDICAL SCHOOL OF THE
UNIVERSITY OF TEXAS
DALLAS 4, TEXAS

RECEIVED AUGUST 1, 1951

Occurrence of *d*-Pinitol in Red Spruce (*Picea rubra*)

BY SIDNEY GOTTLIEB AND F. E. BRAUNS

d-Pinitol, the monomethyl ether of *d*-inositol, occurs in many species of plants, having been reported in *Pinus lambertiana*,[1] senna leaves,[2] *Mateza roritina*,[3] *Sequoia sempervirens*,[4] *Pinus strobus*,[5] *Astragulus wootoni*,[6] *Astragulus earliei*,[7] *Oxytropis lambertii*,[7] *Lotononis laxi*[8] and *Lupinus caudatus*.[9]

In the course of the preparation of "native lignin" from red spruce (*Picea rubra*), a crystalline compound was isolated in small yield from the dioxane–ether filtrate obtained in the precipitation of dioxane solutions of crude native lignin into ether. This compound was identified as *d*-pinitol. The yield was 2.5 g. of *d*-pinitol from 100 pounds of sawdust.

Freshly cut logs of 12 year-old red spruce were stripped of bark and reduced to sawdust. The sawdust was thrice extracted in copper percolators with 95% alcohol and worked up according to the method of Brauns.[10] Instead of separating the water-soluble fraction of the initial alcohol extract by decantation from the insoluble solids, dioxane was added and the water and alcohol were removed by azeotropic distillation resulting in a dioxane solution containing the total alcohol extract (except volatile materials). The precipitation of this dioxane solution (adjusted to a concentration of 10% solids) into 20 volumes of diethyl ether and subsequent centrifugation resulted in a clear yellow solution which, when concentrated to a small volume of dioxane, deposited small white prismatic crystals of *d*-pinitol which, after several recrystallizations from hot butanol, melted at 185–186° (cor.). $[\alpha]^{20}D$ −65.8° (previous values reported −67.7,[5] −62.5,[6] −65.3,[11] −65[7]).

Anal. Calcd. for $C_7H_{14}O_6$: C, 43.27; H, 7.27; OCH_3, 15.9; mol. wt., 194. Found: C, 43.55; H, 7.50; OCH_3, 16.0; mol. wt. (Rast), 189 and 197.

A mixture of the compound with an authentic sample of *d*-pinitol melted at 185–185.5°.

The pentacetyl and pentabenzoyl derivatives were prepared according to the procedure of Griffin and Nelson[11]; the crystalline pentacetate, m.p. 97.5–98°, $[\alpha]^{20}D$ −9.3°; the amorphous pentabenzoate, m.p. 96–97° $[\alpha]^{20}D$ −31.5°, in good agreement with the values reported in the literature.

A small amount of *d*-pinitol (0.5 g. per 100 g. sawdust) could be isolated by the direct extraction of ground red sprucewood (60 mesh) with cold water.

Acknowledgment.—The work reported was done under a contract between the Office of Naval Research and the University of Maryland with facilities kindly provided by the Institute of Paper Chemistry during the summer of 1950.

(1) Berthelot, *Ann. chim. phys.*, **46**, 76 (1856).

(2) Dragendorff and Kubly, *Z. Chem.*, 411 (1866).

(3) Girard, *Compt. rend.*, **77**, 995 (1873); *ibid.*, **110**, 84 (1890).

(4) Sherrard and Kurth, *Ind. Eng. Chem.*, **20**, 722 (1928).

(5) Erdtman, *Svensk Kem. Tid.*, **56**, 2 (1944).

(6) Knowles and Elderfield, *J. Org. Chem.*, **7**, 389 (1942).

(7) Pease, Reider and Elderfield, *ibid.*, **5**, 1989 (1940).

(8) de Waal, *Onderstepoort J. Vet. Sci. Animal Ind.*, **13**, 22 (1939).

(9) Soine and Jenkins, *Pharm. Arch.*, **12**, 65 (1941).

(10) Brauns, THIS JOURNAL, **61**, 2120 (1939).

(11) Griffin and Nelson, *ibid.*, **37**, 1568 (1915).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MARYLAND
COLLEGE PARK, MARYLAND, AND
INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN

RECEIVED APRIL 12, 1951

The Diffusion Coefficient of Magnesium Sulfate in Dilute Aqueous Solution at 25°

BY HERBERT S. HARNED AND ROBERT M. HUDSON

Recently, the diffusion coefficient of zinc sulfate[1] at high dilutions in water was determined by the conductance method. The present measurements of the diffusion coefficient of magnesium sulfate, extended to somewhat lower concentrations, were carried out to supplement our knowledge of the diffusion behaviors of 2-2 electrolytes.

(1) H. S. Harned and R. M. Hudson, THIS JOURNAL, **73**, 3781 (1951).