Acetylation of β-D-Glucopyranosylbenzene (V).—The sirupy V, treated with acetic anhydride and pyridine at room temperature for eighteen hours, yielded quantitatively tetraacetyl-β-D-glucopyranosylbenzene (II), m. p. 155–156°.

Tetraacetyl-α-D-mannopyranosylbenzene.—Phenyllithium (0.25 mole) and sirupy tetraacetyl-α-D-mannopyranosyl bromide (8.2 g. or 0.02 mole) reacted to produce methyldiphenylcarbinol (86% yield) and a carbohydrate derivative isolated, after acetylation, as a dark sirup (6 g., 74%). The crude acetate was separated by use of an alumina column into three fractions: (1) 2.24 g. (27.4%) of tetraacetyl-α-D-mannopyranosylbenzene,[4] m. p. 137–138°; (2) 1.20 g. (14.7%) of sirup, $[\alpha]^{28}$D 4.7° (*c* 3.186 in chloroform); (3) black, tarry material.

1-(Tetraacetyl-α-D-glucosyl)-butane.—Butyllithium (0.25 mole) and tetraacetyl-α-D-glucosyl bromide (0.02 mole) yielded 10.4 g. (82%) of methyldibutylcarbinol,[8] b. p. 82–83° (8 mm.), and a carbohydrate fraction. Acetylation of the latter with acetic anhydride and sodium acetate at 100° yielded 5.40 g. (70%) of dark brown sirup, which was subsequently separated by chromatographing through alumina into two sirupy fractions. The first fraction yielded 0.60 g. (7.7%) of 1-(tetraacetyl-α-D-glucosyl)-butane, m. p. 109–110°. Mixed m. p. with a sample prepared by means of the Grignard glycosylation was not depressed. The mother liquor yielded a sirup $[\alpha]^{24}$D 10.2° (*c* 1.976 in chloroform).

Tetraacetyl-α-D-glucosyl Bromide and 2-Pyridylmethyllithium.—The aqueous layer from the hydrolyzed reaction mixture yielded 4.94 g. (58%) of a dark red-brown sirup on acetylation after evaporation of the water. Crystalline products were not isolated.

The ether phase from the hydrolysis mixture yielded 15.54 g. of a red oil. On distillation at 8–9 mm., the oil was separated into four fractions; b. p. (1) 115–125°, (2) 125–130°, (3) 130–160° and (4) 160–180°. Each fraction yielded a picrate; m. p. (1) 137–139°, (2) 125–140°, (3) 160–180° and (4) 170–180°. On the basis of these data the liquid products were probably mixtures containing α-picoline, 2-acetonylpyridine, 1,3-dipyridyl-2-methyl-2-propanol and perhaps its dehydration product.

Attempted Coupling of Tetraacetyl-α-D-glucosyl Bromide with Sodium and Lithium Acetylides.—The acetylides were prepared by addition of sodium or lithium to liquid ammonia which was kept saturated with acetylene. The ammonia was removed and toluene was added from time to time during this process. The suspension of the acetylide in toluene was refluxed for twenty-four hours with tetraacetyl-α-D-glucosyl bromide. The mixture was worked up as usual but only small amounts of black tars could be isolated.

Phenylsodium and Tetraacetyl-α-D-glucosyl Bromide.—Phenylsodium[9] (0.25 mole) and tetraacetyl-α-D-glucosyl bromide (0.02 mole), heated twelve hours under reflux in benzene, yielded a small amount of biphenyl and considerable tarry products. The aqueous phase from the hydrolyzed reaction mixture was optically active. Acetylation of the product isolated from the aqueous phase yielded 2.40 g. of colored sirup, $[\alpha]^{28}$D 11.3° (*c* 1.770 in chloroform). No crystalline products could be isolated even after chromatographing.

Microanalyses.—Analyses for carbon and hydrogen were performed by J. Gibbs and M. Hines.

Summary

Phenyllithium acted on tetraacetyl-α-D-glucopyranosyl halides in a manner similar to the action of a Grignard reagent on a polyacylglycosyl halide. Methyldiphenylcarbinol was formed in substantially quantitative yield along with a mixture of glucosylbenzenes. Acetylation of the products yielded an unidentified tetraacetylhexopyranosylbenzene along with the known tetraacetyl-β-D-glucosylbenzene and sirupy products. The anticipated coupling of phenyllithium with tetraacetyl-α-D-mannosyl bromide proceeded smoothly to yield mannosylbenzene, isolated as crystalline tetraacetyl-α-D-mannopyranosylbenzene.

Butyllithium and tetraacetyl-α-D-glucopyranosyl bromide reacted to give products which appeared to be the same as those obtained in the Grignard glucosylation of butane.

2-Pyridylmethyllithium, lithium and sodium acetylides, and phenylsodium all failed to yield any identifiable products when they were allowed to react with tetraacetyl-α-D-glucosyl bromide.

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[8] Stadknikoff, *Ber.*, **47**, 2139 (1914); Whitmore and Woodburn, THIS JOURNAL, **55**, 363 (1933).

[9] Morton and Massengale, *ibid.*, **62**, 120 (1940).

EVANSTON, ILLINOIS RECEIVED JULY 29, 1949

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF TEXAS]

Alkenylbiphenyls. I. *o*-Substituted

BY J. R. DICE, T. E. WATKINS[1] AND H. L. SCHUMAN[1]

Because of a number of interesting features, the study of the ultraviolet light absorption of biphenyl derivatives has received considerable attention.[2] The literature reports are, in general, restricted to biphenyl derivatives with small substituents such as amino, cyano and nitro groups. A series of biphenyl derivatives containing various alkenyl groups is being prepared and studied in these laboratories. The spectra and other data will be reported in a later communication.

Interactions of 2-biphenylylmagnesium halides with propionaldehyde and phenylacetaldehyde gave the appropriate carbinols which were dehydrated by heating with potassium hydrogen sulfate to 1-(2-biphenylyl)-propene and 1-(2-biphenylyl)-2-phenylethylene, respectively. Analogous olefins have been similarly prepared previously from acetone,[3] acetophenone[4] and acetaldehyde.[5] In an attempt to improve one of the dehydration reactions, it was found that when

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[1] From the M.A. theses of T. E. Watkins, 1948, and H. L. Schuman, 1949, The University of Texas.

[2] Pickett, Walter and France, THIS JOURNAL, **58**, 2296 (1936); Pestemer and Meyer-Pitsch, *Monatsh.*, **70**, 104 (1937).

[3] (a) Bradsher and Amore, THIS JOURNAL, **65**, 2016 (1943); (b) Mowry, Dazzi, Renoll and Shortridge, *ibid.*, **70**, 1916 (1948).

[4] Bradsher, *ibid.*, **66**, 45 (1944).

[5] Bradsher and Wert, *ibid.*, **62**, 2806 (1940); Haber, Renoll, Rossow and Mowry, *ibid.*, **68**, 1109 (1946).

1-(2-biphenylyl)-1-phenylethanol was treated successively with thionyl chloride and methanolic potassium hydroxide, 9-methyl-9-phenylfluorene was formed.

3-(2-Biphenylyl)-propene was prepared from 2-biphenylylmagnesium bromide and allyl bromide. The reaction of ethylene oxide and the biphenylyl Grignard reagent yielded 2-(2-biphenylyl)-ethanol which was converted to 2-(2-biphenylyl)-1-bromoethane by treatment with hydrobromic acid. The structure of the bromide was proved by using it in the preparation of the known 3-(2-biphenylyl)-propionic acid.[6] 4-(2-Biphenylyl)-1-butanol was prepared by treating the Grignard reagent obtained from 2-(2-biphenyl)-1-bromoethane with ethylene oxide. An attempted conversion to 4-(2-biphenylyl)-1-butene gave a substance which could not be obtained analytically pure.

Experimental[7]

2-(2-Biphenylyl)-propene.—2-(2-Biphenylyl)-propene was prepared following the directions of Bradsher and Amore[3a]; b. p. 109–112° (3 mm.), $n^{25}{}_D$ 1.5973, $d^{25}{}_4$ 1.1470; (reported b. p. 125–128° (7 mm.)).

1-(2-Biphenylyl)-1-propanol.—To the stirred, ice-cold Grignard reagent prepared from 5.38 g. of magnesium, 200 ml. of dry ether (in some experiments an equal volume of dry benzene was added after the reaction had started) and 51.5 g. of 2-bromobiphenyl[8] was added a solution of 25.7 g. of propionaldehyde and 75 ml. of anhydrous ether over a period of two hours. After being refluxed for two and one-half hours, the mixture was hydrolyzed with ice and hydrochloric acid. The ether layer was washed with water, dried over magnesium sulfate and distilled at 160–168° (8–9 mm.). The yellow liquid crystallized on standing; yield 25 g. (60%). Crystallization from 85–100° Skellysolve gave colorless plates; m. p. 64.5–65.5°.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.9; H, 7.6. Found: C, 84.8; H, 7.5.

1-(2-Biphenylyl)-propene.—Ten grams of 1-(2-biphenylyl)-1-propanol was mixed intimately with 30.6 g. of finely powdered potassium hydrogen sulfate and heated to 160–165° for seventy-five minutes. The cooled mixture was treated several times with benzene and water. The combined benzene layer was dried over magnesium sulfate and distilled at 139–140° (5 mm.) yielding 8.4 g. (92%) of a colorless oil. A center cut from a redistillation had the following physical constants: $n^{25}{}_D$ 1.6081, $d^{25}{}_4$ 1.0241.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.7; H, 7.3. Found: C, 92.4; H, 6.9.

3-(2-Biphenylyl)-propene.—To the Grignard reagent prepared from 32.0 g. of 2-bromobiphenyl was added 19.7 g. of allyl bromide[9] over a two-hour period. After a one-hour reflux time, the mixture was hydrolyzed with ice and hydrochloric acid and was separated, washed and dried as previously described; yield 16.0 g. (60%) of a slightly yellow oil, b. p. 130–140° (7 mm.). Redistillation gave a colorless oil; b. p. 132–135° (7 mm.), $n^{25}{}_D$ 1.5888, $d^{25}{}_4$ 1.0039.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.7; H, 7.3. Found: C, 92.4; H, 7.0.

2-(2-Biphenylyl)-ethanol.—To the Grignard reagent prepared from 20 g. of 2-iodobiphenyl[3b] was added 8 g. of gaseous ethylene oxide which had been dried by passage through a tower filled with potassium hydroxide pellets. After being refluxed for twelve hours, the mixture was hydrolyzed with cold saturated ammonium chloride solution and treated as in previous cases. Vacuum distillation gave 10.5 g. (76%) of a yellow oil boiling at 175–185° 15–16 mm.). Distillation at 173–178° (12 mm.) gave a colorless oil which would not crystallize. **The carbanilate** of 2-(2-biphenylyl)-ethanol crystallized from ethanol as fluffy, colorless needles, m. p. 94–96°.

Anal. Calcd. for $C_{21}H_{19}O_2N$: C, 79.5; H, 6.0; N, 4.4. Found: C, 79.5; H, 5.9; N, 4.5.

2-(2-Biphenylyl)-1-bromoethane.—A mixture of 20 g. of 2-(2-biphenylyl)-ethanol, 52.5 g. of 40% hydrobromic acid and 6.5 ml. of sulfuric acid (sp. gr. 1.84) was refluxed for five and one-half hours. The cooled reaction mixture was diluted with water, the organic layer was separated and the aqueous phase was extracted with benzene. The combined organic layer was washed with 3 ml. of concentrated sulfuric acid, water and 5% sodium carbonate solution. Distillation at 165–175° (5 mm.) gave 15 g. (60%) of a yellow oil which gave a positive qualitative test for halogen.

3-(2-Biphenylyl)-propionic Acid.—Dry carbon dioxide was passed for two and one-half hours over the surface of the rapidly stirred, ice-cold Grignard reagent prepared from 13.5 g. of 2-(2-biphenylyl)-1-bromoethane. The mixture was hydrolyzed and the combined organic layer was extracted with several portions of 25% sodium hydroxide. Acidification precipitated a tan oil which was washed with water by decantation. The acetone solution of the residue was filtered and evaporated *in vacuo*. Crystallization from ethanol gave colorless conglomerate crystals; m. p. 122–124.5° (reported[6] 125°); yield 5.0 g. (45%).

4-(2-Biphenylyl)-1-butanol.—To the stirred, cooled Grignard reagent prepared from 33 g. of 2-(2-biphenylyl)-1-bromoethane was added 30 g. of dried ethylene oxide as previously described over a period of three hours and the mixture was refluxed for twelve hours. Hydrolysis was effected by means of cold saturated ammonium chloride solution; the combined organic layer was dried over sodium sulfate and the solvent was evaporated. Distillation of the residue yielded 11 g. of slightly yellow oil at 190–205° (6 mm.). Redistillation gave a colorless oil.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.9; H, 8.0. Found: C, 84.6; H, 8.0.

9-Methyl-9-phenylfluorene.—1-(2-Biphenylyl)-ethanol[4] (15 g.) in 25 ml. of dry benzene was treated with a solution of 20 g. of thionyl chloride in 50 ml. of dry benzene and 15 ml. of dry pyridine. After being refluxed for three hours, the solvents were evaporated; the residue was triturated several times with benzene, as previously described. The combined benzene extract was mixed with 25 g. of potassium hydroxide in 300 ml. of methanol and the mixture was refluxed for three hours. Most of the solvent was evaporated, benzene was added and the mixture was washed twice with water. The organic layer was dried over calcium chloride and the solvent was evaporated. Distillation of the residue at 200–210° (4 mm.) gave 4 g. of a nearly colorless oil which crystallized on cooling. Crystallization from methanol yielded colorless needles; m. p. 86–87° both alone and when mixed with 9-methyl-9-phenylfluorene which had been prepared by an entirely different method.[10]

1-(2-Biphenylyl)-2-phenylethanol.—To the Grignard reagent from 50 g. of 2-iodobiphenyl was added 21.4 g. of freshly purified phenylacetaldehyde in 50 ml. of dry ether over a period of one hour and the mixture was refluxed for twelve more hours. After hydrolysis with cold saturated ammonium chloride solution, the organic layer was washed with 5% sodium hydroxide solution and water and dried over sodium sulfate. After evaporation of the solvent, the residue was distilled at 210–215° (3 mm.) as a viscous yellow liquid; yield 9.5 g. (19%). **The carbanilate** crystallized from ethanol as white fluffy crystals; m. p. 162–163°.

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[6] v. Braun and Manz, *Ann.*, **468**, 258 (1929).

[7] All melting points and boiling points are uncorrected. Some of the analyses were by Clark Microanalytical Laboratories, Urbana, Ill.

[8] Zaheer and Faseeh, *J. Indian Chem. Soc.*, **21**, 27 (1944).

[9] Another run using allyl chloride gave the same results.

[10] Bergmann and Bondi, *Ber.*, **64**, 1455 (1931).

Anal. Calcd. for $C_{17}H_{23}NO_2$: C, 82.4; H, 5.9. Found: C, 82.2; H, 6.2.

1-(2-Biphenylyl)-2-phenylethylene.—An intimate mixture of 7.5 g. of 1-(2-biphenylyl)-2-phenylethanol and 20 g. of potassium hydrogen sulfate was heated and the product isolated as described in previous dehydration experiments. Distillation at 190–210° (4–5 mm.) gave 5.6 g. (80%) of a yellow oil. Evaporative distillation at 140–150° (0.01 mm.) gave a colorless oil which could not be crystallized and which would not form a picric acid or trinitrobenzene derivative.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.7; H, 6.3. Found: C, 93.4; H, 6.1.

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Summary

The synthesis of some *o*-alkenylbiphenyls is described.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

sym-Tetraphenylacetone. A Study of its Synthesis[1]

BY DOUGLAS O. DEAN, WILLIAM B. DICKINSON, OSBORNE R. QUAYLE AND CHARLES T. LESTER[2]

For some time we have been interested in the synthesis of tetraphenylacetone. We have tried a variety of methods for its synthesis. Among these are: (1) sodium and ethyl diphenylacetate,[3] (2) sodium and diphenylacetyl chloride, (3) diphenylmethylpotassium and diphenylacetyl chloride and (4) diphenylmethylpotassium and diphenylketene. Method (1) we consider the best, since it gives good yields and requires the least attention.

The Synthesis of Tetraphenylacetone. (1) Sodium and Ethyl Diphenylacetate.[4]—A mixture of 60 g. (0.25*M*) of ethyl diphenylacetate, 600 ml. of dry ether and 10 g. of sodium wire was allowed to sit at room temperature for four days. The mixture was cooled to 0° and the residual sodium destroyed with ethanol. The mixture was diluted with 500 ml. of water, the ether layer removed and washed with 200 ml. of 5% sodium bicarbonate solution. The ether was removed by distillation, the oily residue treated with 50 ml. of 5% sodium hydroxide solution[5] and this mixture steam distilled until organic material was no longer present in the distillate. The crystalline residue was filtered and recrystallized from hot ethanol, yielding tetraphenylacetone, m. p. 133–134°.[3,6] The steam distillate was extracted with ether, the ether dried over sodium sulfate, decanted and removed by distillation. The residue was identified as diphenylmethane by m. p., 27°, and by oxidation to benzophenone. When all the aqueous layers accumulated in this process were acidified, diphenylacetic acid was recovered. Average yields based on five such preparations: tetraphenylacetone, 17.5 g., 38.8%; diphenylmethane, 13 g., 31%; diphenylacetic acid, 16 g., 30%.[7]

(2) Sodium and Diphenylacetyl Chloride.—A mixture of 11.5 g. (0.05*M*) of diphenylacetyl chloride and 2.8 g. (0.12*M*) of powdered sodium in 200 ml. of dry toluene was heated with stirring for six hours. It was then processed as in (1), yielding 3.6 g., 40%, tetraphenylacetone, 2.0 g., 23.7%, diphenylmethane and 3.6 g., 35.6%, diphenylacetic acid.

(3) Diphenylmethylpotassium and Diphenylacetyl Chloride.—An approximately 0.2*M* suspension of diphenylmethylpotassium in 200 ml. of dry toluene was prepared as previously described.[8] After cooling to −30°, 0.2*M* of diphenylacetyl chloride was added as rapidly as possible with vigorous stirring. The mixture was allowed to warm spontaneously to room temperature, refluxed for thirty minutes and processed as in (1), yielding 5.6 g., 31%, tetraphenylacetone.

(4) Diphenylmethylpotassium and Diphenylketene.—An ether solution of diphenylketene was prepared from 5.85 g. (0.025*M*) of diphenylacetyl chloride and 3.3 g. (0.025*M*) of triethylamine.[9] After standing overnight and filtering, the solution was added dropwise to a suspension of approximately 0.05*M* diphenylmethylpotassium in 125 ml. of toluene. The mixture was heated at reflux for two and one-half hours, allowed to sit overnight and processed as in (1), yielding 1.3 g., 15% (based on diphenylacetyl chloride), tetraphenylacetone.

Although the reaction of ethyl diphenylacetate with sodium to produce tetraphenylacetone superficially resembles a Claisen condensation, followed by a ketonic cleavage, such a path is at variance with present ideas concerning the reaction of an ester and sodium.[10] In order to determine the course of this reaction we have investigated several possible paths by (a) attempting self-condensation of the ester with sodium hydride and potassium amide, (b) preparing the β-keto-ester that would result from self-condensation and attempting ketonic cleavage, (c) attempting cleavage of the ester with excess sodium hydride and lithium aluminum hydride and (d) making a quantitative study of the products of the reaction of ester and sodium.

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(1) Parts of this work were taken from the Master's Theses of Douglas O. Dean, Emory University, 1948, and William B. Dickinson, Emory University, 1947.

(2) Address communications concerning paper to this author.

(3) Vorlander, *Ber.*, **56**, 1125 (1923).

(4) Rehberg, Master's Thesis, Emory University, 1937.

(5) Unless the base is added at this point, unreacted ester remains with the ketone. This necessitates a tedious purification by crystallization, ref. 4.

(6) All melting points reported are uncorrected.

(7) Almost identical quantities of ketone, hydrocarbon and acid were obtained when the reaction was run in toluene at 80° for five hours or Eastman Kodak Co. "Heptane" at reflux for eight hours. When Vorlander's original procedure was followed (*cf.* ref. 3) the yield of ketone was 14% and the yield of hydrocarbon 51%.

(8) Hauser and Yost, THIS JOURNAL, **69**, 2325 (1947).

(9) Staudinger, *Ber.*, **40**, 1148 (1907).

(10) Hauser and Hudson, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 273; McElvain, *ibid.*, Vol. IV, 1948, p. 261.