Bromination of 2-(Tetraacetyl-β-D-glucopyranosyl)-thiophene.—Sixteen grams of a 0.5% solution of bromine in carbon tetrachloride was added in about one hour to an ice-cold stirred solution of 0.20 g. of 2-(tetraacetyl-β-D-glucopyranosyl)-thiophene in 50 ml. of carbon tetrachloride. The cooling bath was removed. After attaining room temperature, the mixture was washed twice with sodium bicarbonate solution, then with water, and dried with calcium chloride. Removal of the solvent left a solid residue which was recrystallized from 2-propanol. There was obtained 0.15 g. (61% yield) of white crystals, m. p. 134–135°, $[\alpha]^{30}D$ −18.6°, *c* 3.470 in chloroform. A mixed melting point with 5-bromo-2-(tetraacetyl-β-D-glucopyranosyl)-thiophene was not depressed.

Deacetylations.—The polyacetylglycosyl derivative (1–2 g.) was dissolved in methanol (25 ml.) and about 10 cu. mm. of freshly cut sodium was added. After standing overnight at room temperature, the solution was processed. The resulting glycosylbenzenes or thiophenes were soluble in water and alcohols.

Acetylation.—All of the sirupy glycosyl-substituted benzenes and thiophenes could be reacetylated quantitatively with acetic anhydride and pyridine at room temperature for eighteen to twenty-four hours. All the crystalline products reported herein were recrystallized from 2-propanol or ethanol.

Periodate Oxidation of Mannopyranosylbenzenes.—Weighed samples of the α- and β-tetraacetyl derivatives were deacetylated as above, dissolved in 25 ml. of water, and oxidized quantitatively by means of 0.0488 *N* potassium periodate solution using standard methods.[10] There was formed in solution from the α-derivative 99.3 and from the β-derivative 98.1% of the calculated amounts of formic acid.

Oxidation of Glycosylation Products.—The glucosylated thiophenes and the mannosylated benzenes were oxidized to the corresponding 2-thenoic or benzoic acids. A mixture of 1.0 g. of substance, 3.0 g. of potassium permanganate, 0.3 g. of potassium hydroxide and 50 ml. of water was refluxed for half an hour. It was then cooled, acidified, and treated with solid sodium bisulfite until a clear solution resulted. The solution was extracted thrice with ether to obtain the crude carboxylic acid which was recrystallized from water. 2-(Tetraacetyl-β-D-glucopyranosyl)-thiophene and the sirupy α-isomer both yielded 2-thenoic acid, needles, m. p. 125–126°. The reported[11] m. p. for this acid is 126–127°. 5-Bromo-2-β-D-glucosylthiophene yielded 5-bromo-2-thenoic acid, m. p. 140–141°, one degree lower than the reported[4] m. p. α-D-Mannopyranosylbenzene and its β-anomer both yielded benzoic acid in excellent yields.

Carbinols.—The carbinols, CH_3CR_2OH, were isolated from the ether phase after hydrolysis of the Grignard reaction mixture. Methyldiphenylcarbinol crystallized readily; however, methyldi-2-thienylcarbinol apparently dehydrated and the resulting product resinified during the attempted purification. Likewise, methylbis-(5-bromo-2-thienyl)-carbinol decomposed and yielded a tarry mass during isolation.

(10) Jackson, "Organic Reactions," Vol. II, p. 361, John Wiley and Sons, Inc., New York, N. Y., 1946.

(11) Steinkopf and Ohse, *Ann.*, **437**, 14 (1924).

EVANSTON, ILLINOIS RECEIVED JUNE 6, 1949

Summary

The reactions of polyacetylglycosyl halides with Grignard reagents have been extended further with Grignard reagents from the thiophene series and to these carbohydrates: maltose, gentiobiose, D-mannose.

β-Maltosylbenzene and β-gentiobiosylbenzene, isolated as acetates, have been obtained from the reaction of the corresponding heptaacetylglycosyl halides with phenylmagnesium bromide.

In the mannose series tetraacetyl-α-D-mannosyl bromide reacted with phenylmagnesium bromide to yield both of the anomeric D-mannosylbenzenes. In this case both isomers and their acetates were crystalline.

2-(Tetraacetyl-β-D-glucopyranosyl)-thiophene and 5-bromo-2-(tetraacetyl-β-D-glucopyranosyl)-thiophene were prepared from the corresponding Grignard reagents. Attempts to prepare 2,5-diglucosylthiophene were unsuccessful.

The yields and relative proportions of D-glucosylbenzenes were the same whether tetraacetyl-α-D-glucopyranosyl chloride or its β-anomer was allowed to react with phenylmagnesium bromide.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Reactions of Polyacetylglycosyl Halides with Organoalkali Metal Reagents

BY CHARLES D. HURD AND ROMAN P. HOLYSZ[1]

Reactions of polyacetylglycosyl halides with Grignard reagents[2,3,4] have been investigated. In many respects organolithium compounds resemble Grignard reagents. Both types are generally covalent and are soluble in organic solvents. Although organolithium compounds are considerably more reactive than Grignard reagents, they are less reactive than the corresponding organosodium compounds which are polar and usually insoluble in organic solvents such as ether, ligroin or benzene. For these reasons the organolithium compounds might be expected to react with polyacetylglycosyl halides in a manner similar to the action of a Grignard reagent on the acetylated glycosyl halide.

The organolithium compounds were prepared and handled in the same manner as Grignard reagents.[5] At least nine-mole proportions (actually twelve were used) were allowed to react with one of tetraacetyl-α-D-glucopyranosyl chloride in ether solution. The reaction mixture was hydrolyzed and the theoretical quantity of methyldiphenylcarbinol was isolated. The carbohydrate product was acetylated and the resulting acetate was separated into two crystalline fractions and a sirup.

One of the crystalline compounds, namely,

(1) du Pont Fellow, 1947–1948.

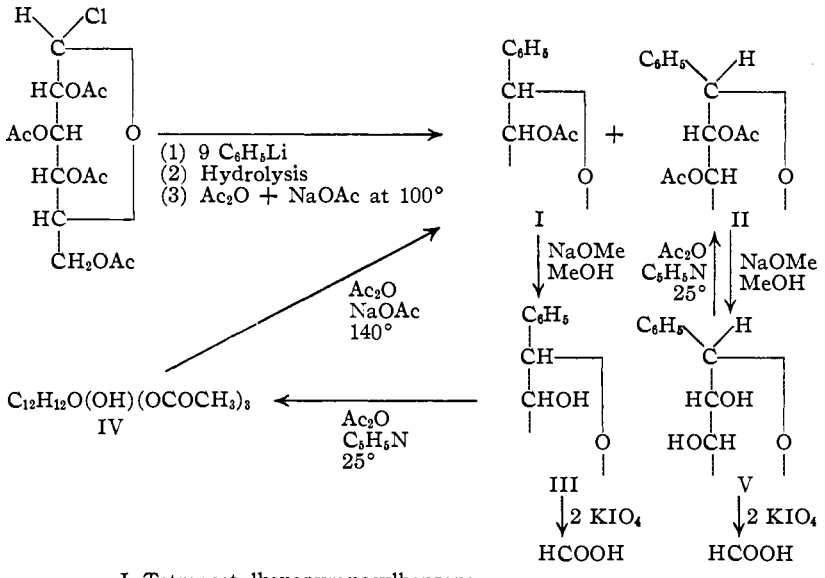
(2) Hurd and Bonner, THIS JOURNAL, **67**, 1972 (1945).

(3) Bonner, *ibid.*, **68**, 1711 (1946).

(4) Hurd and Holysz, *ibid.*, **72**, 1732 (1950).

(5) Gilman, *et al.*, *ibid.*, **54**, 1957 (1932); **55**, 1252 (1933); **62**, 2327 (1940).

tetraacetyl-β-D-glucopyranosylbenzene, was obtained in approximately 10% yield. The other crystalline compound, obtained in about 30% yield, also seemed to be a tetraacetylhexopyranosylbenzene. In this respect this reaction differed from the comparable reaction with phenylmagnesium bromide, where the only crystalline product obtained in fair yield was tetraacetyl-β-D-glucosylbenzene. Both of the crystalline compounds, on deacetylation, yielded glucosylbenzenes which were oxidizable to benzoic acid with alkaline potassium permanganate. Both also reacted with two equivalents of periodate ion, liberating one equivalent of formic acid, thereby fixing the ring size. There was no difficulty in reacetylating the glucosylbenzene derived from tetraacetyl-β-D-glucosylbenzene to the tetraacetate, but under the same conditions the other isomer was converted in good yield into a crystalline triacetate. Considerably more drastic conditions were necessary to convert the triacetate to the completely acetylated product, tetraacetyl-α-D-glucopyranosylbenzene. This series of reactions is summarized diagrammatically.



I, Tetraacetylhexopyranosylbenzene
II, Tetraacetyl-β-D-glucopyranosylbenzene
III, Hexopyranosylbenzene
IV, Triacetylhexopyranosylbenzene
V, β-D-Glucopyranosylbenzene

The stereochemical configuration of the tetraacetate (I) is not known. The *alpha* anomer of tetraacetyl-β-D-glucopyranosylbenzene was ruled out on the basis of some work of W. A. Bonner and James Craig,[5a] who isolated tetraacetyl-α-D-glucopyranosylbenzene, m. p. 70–71°, $[\alpha]^{28}D$ 95.1 (*c*, 4.43 in chloroform). Analytical data, periodate oxidation data, and oxidation of both to benzoic acid supported the belief that our two crystalline tetraacetates were isomers possessing the same carbon skeleton. Seemingly, inversion must have occurred at one or more of the optically active centers under the conditions of the reactions.

Similarly, tetraacetyl-α-D-glucopyranosyl bromide reacted with phenyllithium to give a 25% yield of glucopyranosylbenzene, isolated as the crystalline tetraacetylhexopyranosylbenzene. In this particular experiment none of the tetraacetyl-β-D-glucopyranosylbenzene was isolated; the experiment was conducted on a smaller scale, however, making isolation of a minor reaction product more difficult.

Phenyllithium acted on tetraacetyl-α-D-mannosyl bromide in the usual manner to produce methyldiphenylcarbinol and a 74% yield of carbohydrate derivative. Tetraacetyl-α-D-mannopyranosylbenzene was isolated in 27% yield from the acetylated carbohydrate product.

Butyllithium acted on tetraacetyl-α-D-glucopyranosyl bromide in ethyl ether solution to give methyldibutylcarbinol and a 70% yield of carbohydrate derivative. On acetylation of the latter, an 8% yield of crystalline 1-(tetraacetyl-α-D-glucopyranosyl)-butane was isolated, the remaining product being an optically active sirup. The crystalline product was identical to that obtained from the reaction products of tetraacetyl-α-D-glucosyl halide and butylmagnesium chloride.[2]

2-Pyridylmethyllithium, prepared by metalation of α-picoline with phenyllithium, reacted with tetraacetyl-α-D-glucosyl bromide to yield a dark-colored oily product and a water-soluble carbohydrate product. The dark oil was not identified, but some evidence indicated it was a mixture consisting of α-picoline, 2-acetonylpyridine and 1,3-dipyridyl-2-methyl-2-propanol. Acetylation of the carbohydrate fraction of the reaction products gave rise to a very dark sirup in about 60% yield; however, no crystalline products could be isolated from it.

The reaction of lithium and sodium acetylides with tetraacetyl-α-D-glucosyl bromide resulted in low yields of tar-like products. When a benzene solution of tetraacetyl-α-D-glucopyranosyl bromide was refluxed with phenylsodium, resinous products, a small amount of biphenyl and a poor yield of an optically active sirup were obtained. In these unsuccessful attempts to glucosylate acetylene by means of the alkali metal acetylides, or to glucosylate benzene with phenylsodium, the

(5a) Bonner and Craig, private communication.

organometallic reagents were insoluble in the reaction media. Bonner[3] had indicated previously that Grignard reagents generally attack the ester functions of a polyacylglycosyl halide in preference to the halide function. Therefore, as the ester groups are attacked, the carbohydrate derivative becomes insoluble in the reaction medium before the halide function reacts to any appreciable extent. Ordinary Grignard reagents and the non-polar organolithium reagents are soluble in the reaction medium, and although the carbohydrate derivative becomes insoluble as the reaction proceeds, at least one reactant remains in solution, thereby facilitating completion of the reaction.

Experimental

Organic Lithium Compounds.—Phenyllithium and butyllithium were prepared from the corresponding phenyl and butyl halides and metallic lithium according to the procedures of Gilman.[5] 2-Pyridylmethyllithium was obtained from phenyllithium and α-picoline.[6]

Tetraacetyl-α-D-mannosyl Bromide.—Although described as a low-melting (53°) solid by Levene and Tipson,[7] this substance was obtained as a thick sirup, $[\alpha]^{26}D$ 116° (*c*, 5.333 in chloroform). The reported rotation was 123° in chloroform.

Tetraacetyl-α-D-glucosyl Halides and Organolithium Reagents.—The general method for carrying out these reactions is illustrated in a specific example. Other reactions were conducted analogously.

Tetraacetyl-α-D-glucopyranosyl chloride (14.7 g., 0.04 mole) in 150 ml. of absolute ethyl ether was added over a period of approximately three hours to phenyllithium (0.50 mole) in 150 ml. of absolute ether. The mixture was kept stirring overnight at room temperature under an atmosphere of nitrogen. The mixture was then refluxed four hours, cooled to ice temperature and hydrolyzed by the slow addition of 150 ml. of water. The resulting mixture was neutralized with acetic acid. The layers were separated and the aqueous layer was extracted with 100 ml. of ether.

The ether phase was dried over sodium sulfate at 0°. Removal of the solvent by distillation left 31.2 g. (98.5% yield) of crude methyldiphenylcarbinol. A sample recrystallized several times from aqueous alcohol melted at 79–80°.

The aqueous layer from the hydrolyzed reaction mixture was evaporated to dryness at reduced pressures. The solid residue was heated on a steam-bath for two hours with 100 ml. of acetic anhydride and 5 g. of sodium acetate. At the start of the acetylation the vigor of the reaction undoubtedly raised the temperature above 100°; however, the initial vigor subsided quickly and it was not necessary to apply external cooling. After cooling, the acetylation mixture was poured into one liter of cold water and stirred for a few hours to hydrolyze excess anhydride. The gummy solid which formed was extracted into ether, and the extract was washed with water, saturated sodium bicarbonate solution and again with water. Removal of the solvent from the dried ether solution left 11.4 g. (69.5%) of crude acetates.

The crude product (a dark sirup) was dissolved in 50 ml. of ether and the solution was concentrated by boiling to a volume of 35–40 ml. After standing overnight at room temperature, large crystals had separated which were filtered off (3.94 g.) and recrystallized from 2-propanol; m. p. 142–143°. The filtrate was concentrated to 20–25 ml. Petroleum pentane (*ca.* 3–4 ml.) was added, and after standing overnight at 0°, fine crystals (1.02 g.) separated. These crystals were tetraacetyl-β-D-glucosylbenzene as shown by melting point and mixed melting point data. The mother liquor was evaporated to a sirup (6.90 g.) which was dissolved in 10 ml. of benzene. The solution was chromatographed on alumina. Elution of the column with benzene yielded a pale yellow sirup, from which 0.64 g. of crystals, m. p. 150–153°, was isolated on crystallization of the sirup from 2-propanol. These crystals were also tetraacetyl-β-D-glucosylbenzene (m. p. and mixed m. p. after recrystallization). The remaining sirup (5.26 g.) could not be crystallized from a variety of solvents. The products from this reaction were (1) 4.0 g. of crystalline material, m. p. 142–143°; (2) 1.7 g. tetraacetyl-β-D-glucosylbenzene, m. p. 155°; and (3) 5.3 g. of sirup, $[\alpha]^{24}D$ 16.7°, *c* 4.506 in chloroform.

Tetraacetylhexopyranosylbenzene (I).—M. p. 142–143°; $[\alpha]^{24}D$ −2.3° (*c* 3.103 in chloroform); mixed m. p. with tetraacetyl-β-D-glucopyranosylbenzene of $[\alpha]D$ −16° was 120–126°.

Anal. Calcd. for $C_{20}H_{24}O_9$: C, 58.81; H, 5.92; CH_3CO–, 42.15. Found: C, 58.31; H, 6.00; CH_3CO–, 42.08.

Oxidation of Tetraacetylhexopyranosylbenzene.—One-half gram of the tetraacetate was heated under reflux for three hours in 75 ml. of aqueous solution containing 2 g. of potassium permanganate and a pellet of potassium hydroxide. Benzoic acid (0.07 g., 48% yield), m. p. 121–121.5°, was isolated.

Hexopyranosylbenzene (III).—Tetraacetylhexopyranosylbenzene was deacetylated catalytically with sodium methoxide in methanol solution. Evaporation of the solvent left a colorless, water-soluble sirup, $[\alpha]^{24}D$ 11° (*c* 2.340 in methanol).

Triacetylhexosylbenzene (IV).—The sirupy glycosylbenzene 0.62 g. was acetylated with acetic anhydride and pyridine overnight at room temperature. A crystalline acetate was isolated in 0.74-g. yield, and after repeated recrystallization from 95% ethanol, it melted at 161.5–162°; $[\alpha]^{24}D$ 49.3° (*c* 2.800 in chloroform).

Anal. Calcd. for $C_{18}H_{22}O_8$: C, 59.01; H, 6.05; CH_3CO–, 35.24. Found: C, 59.23; H, 6.12; CH_3CO–, 35.14.

Deacetylation of 77 mg. of the triacetate of m. p. 161.5–162° in methanol with 2 mg. of sodium gave rise to 53 mg. of water-soluble sirup, $[\alpha]^{24}D$ 5.9°, *c* 1.786 in water. Reacetylation of this anhydrous sirup with 5 ml. of acetic anhydride and 0.5 g. of sodium acetate at 100° for three hours produced 70 mg. of crystalline product. After one recrystallization from alcohol, it melted at 160.5–161.5°.

If this crystalline product of m. p. 161° was redissolved in 5 ml. of acetic anhydride containing 0.5 g. of sodium acetate and the mixture refluxed (140°) for one hour, there was obtained the tetraacetate. It melted sharply at 142.5–143° after crystallization from 2-propanol. The mixed m. p. with (I) also was 142–143°.

Periodate Oxidation of Hexosylbenzene (III).—The method has been described elsewhere.[4] The sample was weighed as the tetraacetate (I). Wt. of sample, 0.1902 g.; vol. of 0.0442 *N* potassium periodate soln., 60.00 ml.; vol. of 0.1000 *N* sodium arsenite soln., 50.00 ml.; vol. of 0.0988 *N* iodine soln., 44.50 ml.; potassium periodate consumed, 0.995 millimole; subst. oxidized, 0.466 millimole; subst.:potassium periodate, 1.000:2.136; vol. of 0.0323 *N* sodium hydroxide, 12.03 ml.; acidity as formic acid, 0.389 millimole; subst.:formic acid, 1.000:0.835.

Periodate Oxidation of β-D-Glucopyranosylbenzene (V).—Sample weighed as the tetraacetate (II). Wt. of sample, 0.1993 g.; vol. of 0.0442 *N* potassium per iodate soln., 60.00 ml.; vol. of 0.1000 *N* sodium arsenite soln., 50.00 ml.; vol. of 0.0988 *N* iodine soln., 43.85 ml.; potassium per iodate consumed, 0.988 millimole; subst. oxidized, 0.488 millimole; subst.:potassium per iodate, 1.000:2.025; vol. of 0.0323 *N* sodium hydroxide, 13.00 ml.; acidity as formic acid, 0.420 millimole; subst.:formic acid, 1.000:0.860.

β-D-Glucopyranosylbenzene (V).—Deacetylation of tetraacetyl-β-D-glucopyranosylbenzene (II) yielded V, a colorless sirup, $[\alpha]^{26}D$ 23.2° (*c* 4.993 in methanol).

(6) Beets, *Rec. trav. chim.*, **63**, 120 (1944).

(7) Levene and Tipson, *J. Biol. Chem.*, **90**, 89 (1931).

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.

(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

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.

[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

(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).