TABLE I

ALKYLPHENOLS AND ALKYLCYCLOHEXANOLS

Compound	Yield, %	B. p., °C.	Mm.	n^{25}_D	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Phenylurethan	Phenylurethan M. p., °C.	Phenylurethan Nitrogen, % Calcd.	Phenylurethan Nitrogen, % Found
2-Ethyl-4-*n*-propylphenol	75	123–125	10	1.5178	$C_{11}H_{16}O$	80.4	80.0	9.8	9.8	$C_{18}H_{21}O_2N$	132–134	4.95	4.89
2-Ethyl-4-*n*-butylphenol	80	137–139	10	1.5103	$C_{12}H_{18}O$	81.2	81.2	9.1	8.9	$C_{19}H_{23}O_2N$	121–123	4.71	4.75
2-Methyl-4-ethylcyclohexanol	86	80–83 199–200	7 750	1.4612	$C_9H_{18}O$	76.0	76.1	12.8	12.8	$C_{16}H_{22}O_2N$	122–123	5.36	5.27
2-Methyl-4-*n*-propylcyclohexanol	80	113–114 215.5	215 740	1.4610	$C_{10}H_{20}O$	76.8	76.8	12.9	12.9	$C_{17}H_{24}O_2N$	121–122.5	5.09	5.14
2-Methyl-4-*n*-butylcyclohexanol	84	119–120 234	15 740	1.4620	$C_{11}H_{22}O$	77.6	77.6	13.0	13.1	$C_{18}H_{26}O_2N$	112–113	4.84	4.86
2-Methyl-6-*n*-butylcyclohexanol	81	113 228	155 740	1.4631	$C_{11}H_{22}O$	77.6	77.4	13.0	13.0	....	....	..	..
3-Methyl-4-ethylcyclohexanol	84	109.5–110.5 209	21 740	1.4650	$C_9H_{18}O$	76.0	75.9	12.8	12.8	....	....	..	..
3-Methyl-6-*n*-butylcyclohexanol	78	70 233.5	1 740	1.4603	$C_{11}H_{22}O$	77.6	77.5	13.0	13.0	....	....	..	..
4-Methyl-2-ethylcyclohexanol	75	101–102.5 197.5	23 740	1.4599	$C_9H_{18}O$	76.0	75.9	12.8	12.8	$C_{16}H_{19}O_6N_2$[a]	82–83	8.36	8.42
4-Methyl-2-*n*-butylcyclohexanol	85	90–91 231	3 740	1.4601	$C_{11}H_{22}O$	77.6	77.5	13.0	13.0	....	....	..	..
2,4-Diethylcyclohexanol	92	97.5–99.5	9	1.4622	$C_{10}H_{20}O$	76.8	76.5	12.9	12.9	$C_{17}H_{25}O_2N$.	110–114	5.14	5.34
2-Ethyl-4-*n*-butylcyclohexanol	96[b]	158–162 (semi-solid)	10	1.4667	$C_{12}H_{24}O$	78.2	78.3	13.1	13.3	....	....	..	..

[a] 3,5-Dinitrobenzoate. [b] This is a total yield, including a lower boiling (126–127° (11 mm.)) liquid fraction which is probably a different isomer, but was not completely characterized.

derivatives of those alkylphenols and alkylcyclohexanols not previously reported in the literature are listed in Table I. The yields of the alkylphenols and alkylcyclohexanols which were prepared in the course of this work and have been described previously in the literature, were comparable to those listed in Table I.

Summary

A number of aryl esters have been converted to acylphenols, alkylphenols and alkylcyclohexanols in good yields, through the application of the Fries rearrangement and catalytic hydrogenations.

MADISON, WISCONSIN RECEIVED JUNE 9, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Reactions of Polyacylglycosyl Halides with Grignard Reagents

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

The present work is an extension using other carbohydrates and other organomagnesium compounds, of the findings of Hurd and Bonner[2] dealing with the formation of glycosylated hydrocarbons by interaction of polyacylglycosyl halides and Grignard reagents.

Maltose.—Heptaacetyl-α-maltosyl chloride reacted readily with phenylmagnesium bromide to give methyldiphenylcarbinol and a mixture of maltosylbenzenes. About four-fifths of the latter was acetylated and characterized as crystalline heptaacetyl-β-maltosylbenzene. On the basis of analytical and optical rotation data, the remaining glassy product was probably the anomeric heptaacetyl-α-maltosylbenzene.

Gentiobiose.—Heptaacetyl-β-gentiobiosylbenzene and its α-anomer have been obtained (40 and 25% yields, respectively) from the acetylated reaction products of heptaacetyl-α-gentiobiosyl bromide with phenylmagnesium bromide. Deacetylation of these acetates gave the α- and β-gentiobiosylbenzenes as sirups.

Mannose.—The product of reaction of phenylmagnesium bromide and tetraacetyl-α-D-mannopyranosyl bromide gave on acetylation a sirup (which was not investigated) and two crystalline products, one of which was designated as tetraacetyl-α-D-mannopyranosylbenzene because of its high rotation, $[\alpha]_D$ 53.6°. The yield was 41%. Deacetylation gave α-D-mannopyranosylbenzene, $[\alpha]_D$ 65.2°, whose consumption of two equivalents of periodate and liberation of one equivalent of formic acid indicate a six-membered ring, and which gives benzoic acid on oxidation with alkaline permanganate. The second crystalline acetate, $[\alpha]_D$ −25.6°, obtained in 24% yield, was deacetylated to β-D-mannopyranosylbenzene, $[\alpha]_D$ 60.0°, which gave benzoic acid on permanganate oxidation, leading to designation of the second acetate as tetraacetyl-β-D-mannopyranosylbenzene. Oxidation with periodate also supported the pyranose structure.

This is the first instance wherein two crystalline

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[1] Corn Products Refining Company Fellow, 1945–1947; present address: Commercial Solvents Corporation, Terre Haute, Ind.

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

anomeric polyacetylglycosyl-substituted hydrocarbons were isolated. In all previous reactions of this type only one of the anomeric glycosylated hydrocarbons, generally the β-form, could be obtained crystalline.

Glycosylation with Tetraacetyl-β-D-glucosyl Chloride.—Since all of the polyacylglycosyl halides which have been subjected to the action of Grignard reagents have been the more common α-forms, it seemed desirable to investigate the reaction between phenylmagnesium bromide and tetraacetyl-β-D-glucopyranosyl chloride. The latter was allowed to react with phenylmagnesium bromide under conditions comparable to those employed for the reaction of the corresponding α-anomer. An 85% yield of glycosylbenzenes was realized, and the acetylated product was separated into tetraacetyl-β-D-glucopyranosylbenzene and a sirup in the ratio 68:32, about the same total yield and β:α ratio as were observed[2] starting with the α-anomer of the chloride. Whether the two forms of tetraacetyl-D-glucosyl chloride reacted with phenylmagnesium bromide through different mechanisms or whether the β-anomer rearranged (as polyacetyl-β-D-glycosyl halides are known to do in the presence of certain inorganic halides) under the influence of the Grignard reagent or magnesium salts present in the reaction mixture could not be ascertained from the available data.

On the basis of the arguments expounded by Hurd and Bonner,[2] it is reasonable to assume that no inversion or racemization of any of the asymmetric alcoholic carbon atoms accompanied the Grignard glycosylation. The α- and β-designations of isomers are in accordance with Hudson's definition of alpha as being the more dextrorotatory isomer in the D-series.

Glucosylthiophenes.—This type of work was extended to the thiophene series for two reasons: (1) this would be the first heterocyclic application; (2) thiophene offered possibilities of attracting two glucosyl groups to its nucleus in view of the difunctional Grignard reagents in this series.

2-Thienylmagnesium bromide reacted readily with tetraacetyl-α-D-glucopyranosyl bromide to form about a 75% yield of 2-D-glucosylthiophenes. Acetylation of the product facilitated its separation into crystalline 2-(tetraacetyl-β-D-glucopyranosyl)-thiophene and its sirupy α-anomer. Identity of the products was established by means of analytical data, optical rotation data, and oxidation to 2-thenoic acid. As in most reactions of this type, the crystalline β-anomer made up the bulk of the product, about three-fourths in this instance. Deacetylation of both the crystalline and sirupy tetraacetylglucosylthiophenes gave rise to sirupy glucosylthiophenes.

In the work of Steinkopf and his associates there are many references which have been made to reactions apparently involving a thiophenebis-(magnesium halide) as an intermediate.[3] For example, 2,3,5-tribromothiophene when treated with an equal weight of methyl bromide and the appropriate amount of magnesium gave rise to a small amount of 3-bromothiophene, apparently resulting from the hydrolysis of 3-bromo-2,5-thiophenebis-(magnesium bromide).[4] Thomas[5] reported that when 2,5-diiodothiophene was treated with two mole proportions of magnesium in an ether–benzene mixture, 80 to 85% of the magnesium dissolved, and hydrolysis of the mixture resulted in the generation of thiophene and unidentified resins in unspecified yields. Numerous other examples of these types of reactions may be found in these references and others by Steinkopf and his associates; but the yields of the products obtained as a result of two apparent Grignard functions per mole have seldom exceeded 10%.

In attempting to prepare a difunctional thiophene Grignard reagent, to be used in making a diglucosylthiophene, 2,5-dibromothiophene and magnesium were allowed to react under the usual Grignard conditions, as well as under specially controlled conditions using ethyl bromide as an activator (see Experimental part). Carbonation of the Grignard solution always yielded 5-bromo-2-thienoic acid, but no thiophenedicarboxylic acid. When such a Grignard reagent was treated with tetraacetyl-α-D-glucopyranosyl bromide, the major product, a sirup, was acetylated to yield crystalline 5-bromo-2-(tetraacetyl-β-D-glucopyranosyl)-thiophene. Deacetylation and subsequent oxidation with alkaline potassium permanganate yielded the known 5-bromo-2-thenoic acid.

Careful bromination of the crystalline 2-(tetraacetyl-β-D-glucopyranosyl)-thiophene yielded 5-bromo-2-(tetraacetyl-β-D-glucopyranosyl)-thiophene. This transformation indicated that the configurational relationships within both of these compounds were the same.

Acetylene.—Acetylene is another compound for which there is evidence of a bis Grignard reagent. The coupling of ethynebis-(magnesium bromide) with tetraacetyl-α-D-glucopyranosyl bromide was attempted under a wide variety of forcing conditions (see Experimental part) but only intractable tars resulted.

The properties of the new compounds obtained in this study are presented in Table I.

Experimental

Grignard Glycosylation Reactions.—The general method for carrying out the reactions between Grignard reagents and polyacetylglycosyl halides has been described in complete detail by Hurd and Bonner.[2] The products and yields from the glycosylation reactions are found in Table II.

Polyacetylglycosyl Halides.—The polyacetylglycosyl halides were all known compounds. The bromides were

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[3] Steinkopf, "Die Chemie des Thiophens," Theodor Steinkopff, Dresden, 1941, pp. 106–107.

[4] Steinkopf, Jacob and Penz, *Ann.*, **512**, 136 (1934).

[5] Thomas, *Compt. rend.*, **181**, 218 (1925).

TABLE I

PROPERTIES OF GLYCOSYLATION PRODUCTS

		Sp. rotation[a]				Analyses,[b] % Carbon		Hydrogen		Acetyl	
	M. p., °C.	$[\alpha]_D$	°C.	Concn.	Solvent	Calcd.	Found	Calcd.	Found	Calcd.	Found
Heptaacetyl-α-maltosylbenzene	Glass	79.2	25	1.680	$CHCl_3$	...	...	..	..	43.25	42.37
Heptaacetyl-β-maltosylbenzene	197.5–198	61.5	25	3.450	$CHCl_3$	55.17	55.20	5.79	6.10	43.25	43.58
β-Maltosylbenzene	125 dec.	126.4	24	3.363	CH_3OH	53.73	51.93	6.51	6.74	...	...
Heptaacetyl-α-gentiobiosylbenzene	Sirup	17.3	27	3.353	$CHCl_3$	...	...	..	..	...	...
Heptaacetyl-β-gentiobiosylbenzene	180–180.5	−18.8	26	3.433	$CHCl_3$	55.17	54.78	5.79	6.15	...	...
β-Gentiobiosylbenzene	Sirup	2.2	28	4.493	CH_3OH	...	...	..	..	...	...
2-(Tetraacetyl-α-D-glucopyranosyl)-thiophene	Sirup	61.5	24	5.699	$CHCl_3$	...	...	..	..	...	...
2-(Tetraacetyl-β-D-glucopyranosyl)-thiophene	123–124	−13.8	24	5.376	$CHCl_3$	52.17	52.11	5.35	5.50	...	...
2-α-D-Glucopyranosylthiophene	Sirup	68.5	24	2.660	CH_3OH	...	...	..	..	...	...
2-β-D-Glucopyranosylthiophene	Glass	21.8	26	2.530	CH_3OH	...	...	..	..	...	...
5-Bromo-2-(tetraacetyl-β-glucopyranosyl)-thiophene[c]	135–136	−19.1	28	4.383	$CHCl_3$	43.82	44.43	4.29	4.38	...	...
5-Bromo-2-β-D-glucopyranosylthiophene	Sirup	8.4	28	2.990	CH_3OH	...	...	..	..	...	...
Tetraacetyl-α-D-mannopyranosylbenzene	139.5–140	53.6	26	3.480	$CHCl_3$	58.81	59.16	5.92	5.85	42.15	42.00
Tetraacetyl-β-D-mannopyranosylbenzene	107–108	−25.6	27	3.193	$CHCl_3$	58.81	59.06	5.92	6.02	42.15	41.97
α-D-Mannopyranosylbenzene	184–185	65.2	26	2.493	H_2O	59.99	59.79	6.71	6.55	...	...
β-D-Mannopyranosylbenzene	206–207	60.0	26	2.710	H_2O	59.99	60.00	6.71	6.79	...	...

[a] All rotations were taken in a 2-dm. tube of *ca.* 2-ml. volume. [b] Carbon and hydrogen analyses were made by M. Ledyard, P. Craig and J. Gibbs. [c] Calcd.: Br, 16.20; S, 6.50. Found: Br, 16.02; S, 6.41 (by peroxide fusion, Br as AgBr and S as $BaSO_4$).

TABLE II

PRODUCTS FROM THE GRIGNARD GLYCOSYLATIONS

Polyacetyl-glycosyl bromide	R- in RMgBr	Carbohydrate product after acetylation	Yield, % α	β	Crude yield of carbinol, CH_3CR_2OH, %
Maltose[a]	Phenyl	Heptaacetylmaltosylbenzene	10	55	96
Gentiobiose	Phenyl	Heptaacetylgentiobiosylbenzene	25	40	95
D-Glucose	2-Thienyl	2-Tetraacetylglucopyranosylthiophene	18	55	90[c]
D-Glucose	5-Bromo-2-thienyl	5-Bromo-2-tetraacetylglucopyranosylthiophene	9	47	68[c]
D-Mannose	Phenyl	Tetraacetylmannopyranosylbenzene	41	24	94
D-Glucose[b]	Phenyl	Tetraacetylglucopyranosylbenzene	27	58	98

[a] Heptaacetyl-α-maltosyl chloride. [b] Tetraacetyl-β-D-glucopyranosyl chloride. [c] These carbinols were not characterized.

prepared from the acetylated sugar and anhydrous hydrogen bromide in glacial acetic acid solution. Heptaacetyl-α-maltosyl chloride was prepared from maltose octaacetate and titanium tetrachloride in chloroform solution. Although tetraacetyl-α-D-mannopyranosyl bromide was described as a relatively low-melting solid (m. p. 53–54°) by Levene and Tipson,[6] it was obtained in the present study as a thick sirup. Nevertheless, the specific rotation, $[\alpha]^{26}\text{D}$ 116°, 5.333 in chloroform, indicated that the sirup was substantially the desired product. Levene and Tipson reported $[\alpha]^{26}\text{D}$ 123° in chloroform.

Tetraacetyl-β-glucopyranosyl Chloride.—When Schlubach and Gilbert's directions[7] for making silver chloride were followed, with which to convert tetraacetyl-α-D-glucopyranosyl bromide into the β-chloride, unsatisfactory results always ensued, since a pure, crystalline product was unobtainable. If, however, the silver chloride was precipitated in the dark at 0° in the presence of a suspension of Celite, a crystalline β-chloride was obtained with no difficulty.

A solution of 8.22 g. (0.02 mole) of tetraacetyl-α-D-glucopyranosyl bromide in 50 ml. of absolute ether was added rapidly to a suspension of 53.6 g. of the dried (over phosphorus pentoxide in darkness) silver chloride on Celite (25.0 g. of Celite) in dry ether at room temperature in the dark. After ten minutes, the solution was filtered and processed to yield once-crystallized tetraacetyl-β-D-glucosyl chloride; 4.02 g. (55%); m. p. 95–97°; $[\alpha]^{26}\text{D}$ −12.5°, *c* 1.600 in carbon tetrachloride. Schlubach reported the following constants for tetraacetyl-β-D-glucosyl chloride; m. p. 99–100°, $[\alpha]^{23}\text{D}$ −18.6° in carbon tetrachloride.

5-Bromo-2-thienylmagnesium Bromide.—An attempt was made to prepare 2,5-thiophenebis-(magnesium bromide) under the following conditions. In the usual Grignard apparatus there was placed 12.16 g. (0.50 mole) of magnesium turnings and 50 ml. of absolute ether. A solution of 1.10 g. (0.01 mole) of ethyl bromide in 25 ml. of ether was added gradually. Reaction started immediately. After addition of the solution of the ethyl bromide but before the vigor of the reaction had subsided, the addition of the solution of 2,5-dibromothiophene[8] was begun. The solution of 10.0 g. (0.04 mole) of the 2,5-dibromothiophene in 200 ml. of ether was added over a period of fifteen hours. The mixture was kept refluxing gently throughout the addition, and after the third hour about 1 g. of magnesium was added every hour until another 12.16 g. (0.50 mole) had been added. Carbonation with powdered Dry Ice of such a mixture yielded 5.06 g. (59%) of 5-bromo-2-thenoic acid, m. p. 140–141°.[4] The recovered magnesium amounted to 23.12 g., corresponding to a consumption of 1.20 g. (0.0495 mole), indicating only one bromine had reacted under these conditions.

Ethynebis-(magnesium Bromide) and Attempted Reaction with Tetraacetyl-α-D-glucopyranosyl Bromide.—Ethynebis-(magnesium bromide) was prepared from ethylmagnesium bromide and acetylene.[9] The reaction with tetraacetyl-α-D-glucopyranosyl bromide was attempted under a wide variety of conditions such as refluxing in ethyl ether for six hours, or at 100° in *n*-butyl ether for fourteen hours in the presence of a large excess of the Grignard reagent, or in the presence of a catalytic quantity of cuprous chloride. In all experiments very dark colored tar-like products were obtained in small quantities. Solutions of these products were kept cold for long periods of time, without inducing crystallization.

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[6] Levene and Tipson, *J. Biol. Chem.*, **90**, 89 (1931).

[7] Schlubach and Gilbert, *Ber.*, **63**, 2292 (1903).

[8] Blicke and Burckhalter, THIS JOURNAL, **64**, 477 (1942).

[9] Jozitsch, *Bull. soc. chim.*, **30**, 210 (1903); Wieland and Wesche, *Ann.*, **431**, 39 (1923).

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°, $[\alpha]^{30}\mathrm{D}$ −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.

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.

EVANSTON, ILLINOIS RECEIVED JUNE 6, 1949

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[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).

[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,

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[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).