

A detailed report of this will be published later.

Experimental

Preparation of Phenylcyclohexene.—This compound was prepared according to Haworth.⁵

Oxidation of Phenylcyclohexene.—Fourteen cubic centimeters of xylene containing 4.57 g. of chloranil and 1.463 g. of phenylcyclohexene was refluxed for four hours. The reaction mixture was cooled and 2.9 g. of chloranil hydroquinone was separated by filtration. The mixture was diluted with an equal volume of ether, washed

(5) Haworth, *J. Chem. Soc.*, **103**, 1246 (1913).

with 4% potassium hydroxide, dried and fractionated; yield of biphenyl, 0.755 g. The structure of this sample was determined by mixed melting with an authentic sample and the preparation of 4-nitrobiphenyl as a derivative.

Other Oxidations.—The other examples listed in Table I were run in a similar fashion to that described above. The last step of course depends on the nature of the product. In each of these cases the materials were identified in the usual manner.

Summary

A low temperature procedure for the dehydrogenation of hydroaromatic rings by chloranil has been discussed.

The advantage of this method over that of selenium dehydrogenation has been pointed out.

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RECEIVED MARCH 13, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Behavior of the Dimethyl Acetals of Glucose and Galactose Under Hydrolytic and Glycoside-forming Conditions

BY M. L. WOLFROM AND S. W. WAISBROT

Hudson and co-workers¹ have prepared the dimethyl acetal of *d*-arabinose by a series of reactions discovered by them for the arabinose structure. The synthesis of the crystalline dimethyl acetals of *d*-glucose² and of *d*-galactose³ has been reported from this Laboratory. Practically simultaneously, Campbell and Link⁴ reported the synthesis of galactose dimethyl acetal. As these compounds are postulated intermediates in the Fischer glycoside synthesis,⁵ with methanol-hydrogen chloride, their behavior under such conditions is of interest. When these acetals are placed in methanol containing hydrogen chloride, a very rapid initial reaction takes place. This initial reaction is so rapid that it is necessary to use a very small amount of hydrogen chloride (0.05%) in order to follow it polarimetrically at 25°. Campbell and Link employed a methanol solution containing 0.5% hydrogen chloride at

25° with galactose dimethyl acetal and their data do not show this initial change, although their first observed specific rotation was +40°, while that of the acetal in pure methanol was recorded by them as +20°. The polarimetric data that we have obtained under glycoside-forming conditions are tabulated in Tables I and II and are diagrammed on a logarithmic time scale in Figs. 1 and 2. Following the rapid attainment of this initial maximum, the polarimetric curve for the glucose compound moves very slowly downward to a minimum and then rises very slowly. In the case of the galactose compound, the minimum in the curve is not shown with our very low concentration of hydrogen chloride but it is observable distinctly in the data of Campbell and Link at the higher concentration of hydrogen chloride.

We have investigated the reaction mixtures at the maximum and final points in the curves for their content of easily acid-hydrolyzable material (Table V) according to the procedure of Levene, Raymond and Dillon.⁶ The procedure employed by these authors was to determine the amount of

(1) Edna M. Montgomery, R. M. Hann and C. S. Hudson, *THIS JOURNAL*, **59**, 1124 (1937).

(2) M. L. Wolfrom and S. W. Waisbrot, *ibid.*, **60**, 854 (1938).

(3) M. L. Wolfrom, L. J. Tanghe, R. W. George and S. W. Waisbrot, *ibid.*, **60**, 132 (1938).

(4) H. A. Campbell and K. P. Link, *J. Biol. Chem.*, **122**, 635 (1938).

(5) E. Fischer, *Ber.*, **26**, 2400 (1893).

(6) P. A. Levene, A. L. Raymond and R. T. Dillon, *J. Biol. Chem.*, **95**, 699 (1932).

TABLE I
MUTAROTATION OF *d*-GLUCOSE DIMETHYL ACETAL IN METHANOL CONTAINING 0.05% (BY WEIGHT) OF HYDROGEN CHLORIDE

<i>c</i> , ^a 3.702; temp., 25°; <i>l</i> , 2-dm.			
Time, min.	[α] _D	Time, min.	[α] _D
0 ^b	+21.5°	30	+38.9°
2	36.1	45	36.5
4	39.8	60	33.4
6	42.5	90	27.6
8	43.9	155	17.0
10	44.6	335	2.2
14	42.5	1115	-12.2
20	41.7	1295	-12.2
26	40.0	Final ^c	-7.2 ^d

^a *c* = g. dimethyl acetal per 100 cc. soln. ^b Observed in pure methanol; also observed directly in 0.01% HCl-MeOH soln. ^c Attained in approximately sixty-five hours. ^d Equivalent to -8.3° on the basis of methyl glucoside.

TABLE II
MUTAROTATION OF *d*-GALACTOSE DIMETHYL ACETAL IN METHANOL CONTAINING 0.05% (BY WEIGHT) OF HYDROGEN CHLORIDE

<i>c</i> , ^a 3.658; temp., 25°; <i>l</i> , 2-dm.			
Time, hr.	[α] _D	Time, hr.	[α] _D
0 ^b	+18.5°	23	-3.1°
.033	18.3		
.167	20.9	30	-8.7
.333	22.9	43	-19.7
.500	24.6	53.5	-25.8
.666	26.2	77	-29.8
.834	26.7	89	-33.5
1.1	27.8	102.5	-39.1
1.60	26.2	126	-44.8
2.10	24.7	149	-54.3
4	23.9	174	-56.2
6.5	13.1	198.5	-57.7
18	-0.3	Final ^c	-57.9 ^d

^a *c* = g. dimethyl acetal per 100 cc. solution. ^b Observed in pure methanol. ^c Attained in approximately two hundred and twenty hours. ^d Equivalent to -67.5° on the basis of methyl galactoside.

material hydrolyzable by the action of 0.05 *N* aqueous hydrochloric acid for ten minutes at steam-bath temperature (95-100°). They used this as a rough measure of furanoside content. This procedure is based upon the well-established fact that furanosides of aldoses (although not of ketoses⁷) are hydrolyzed with a much greater ease than pyranosides. Micheel and Suckfüll⁸ have

(7) C. B. Purves and C. S. Hudson, *THIS JOURNAL*, **59**, 1170 (1937).

(8) F. Micheel and F. Suckfüll, *Ann.*, **502**, 85 (1933), suggested the term "septanose" for this seven-membered carbohydrate ring, preferring this term to "heptanose" because of the possibility of confusion with "galactoheptoside," a term used in the Fischer higher sugar nomenclature. The present authors do not believe that the facts warrant such a radical alteration in organic nomenclature as changing the well-established and fundamental prefix "hept-" to "sept-."

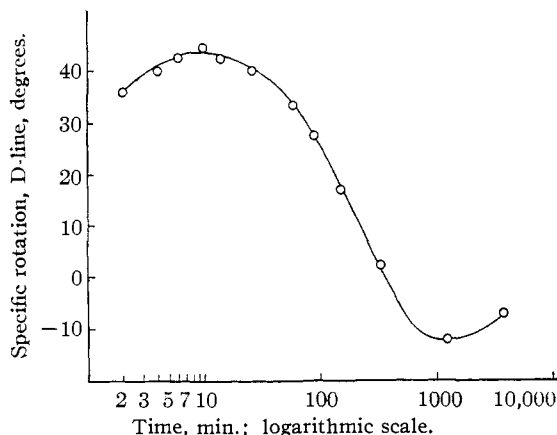


Fig. 1.—Rotation changes of *d*-glucose dimethyl acetal at 25° in methanol containing 0.05% hydrogen chloride, *c* 3.7.

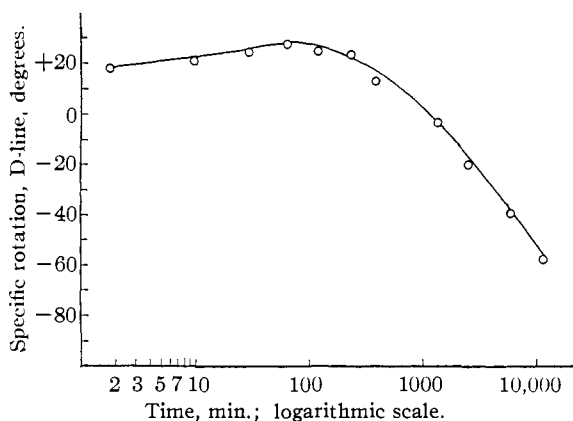


Fig. 2.—Rotation changes of *d*-galactose dimethyl acetal at 25° in methanol containing 0.05% hydrogen chloride, *c* 3.7.

shown later that α -methyl-*d*-galactoheptanoside is hydrolyzed by dilute hydrochloric acid with the same ease as a furanoside. In our case, the added complication enters that the dimethyl acetals are hydrolyzed under these same conditions.

The figures which we have obtained for easily acid-hydrolyzable material present at the maximum and final points of the curves are only very roughly quantitative in nature. In the case of the glucose acetal, a large percentage (79% of the calculated glucose content) of easily acid-hydrolyzable material is present at both points. With galactose acetal a higher content of easily acid-hydrolyzable material is present at the maximum (35.5%) than at the final point (6.5%) of our data, where this final point is still short of the true minimum.

We believe that the above data may be best interpreted with the information at present

available in the following manner. The presence of a maximum followed by a minimum in the polarimetric curve indicates at least two consecutive reactions. The first very rapid reaction represents the hydrolysis of at least one of the methoxyl groups of the dimethyl acetals. The acyclic structure thus formed, which is probably the methyl hemiacetal, then undergoes ring closure to form largely ring structures that are not of the pyranoid type and are unstable. These unstable ring types then rearrange, with probable intermediate hydrolysis, to form the stable pyranosides. That the pyranosides are the ultimate product of the vigorous action of methanol containing hydrogen chloride upon the dimethyl acetals was demonstrated by Campbell and Link⁴ in the case of the galactose acetal and is shown by us to be the case likewise for the glucose acetal.

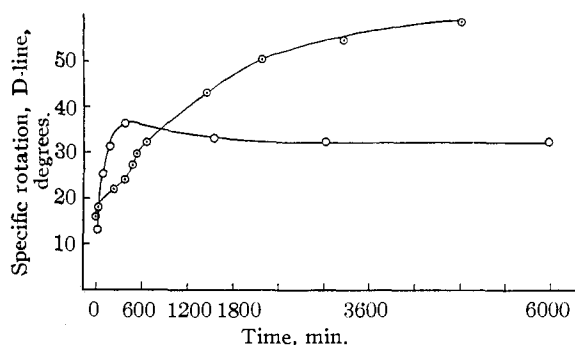


Fig. 3—Rotation changes of *d*-glucose dimethyl acetal, ○; and of *d*-galactose dimethyl acetal, ◻; at 25° in 0.05% aqueous hydrochloric acid, *c* 3.7.

The data of Tables III and IV and the curves of Fig. 3 show the behavior of the dimethyl acetals of glucose and galactose under the same conditions as described above but in an aqueous me-

TABLE III

MUTAROTATION OF *d*-GLUCOSE DIMETHYL ACETAL IN 0.05% (BY WEIGHT) HYDROCHLORIC ACID
c,^a 3.720; temp., 25°; *l*, 2-dm.

Time, min.	[α] _D	Time, min.	[α] _D
0 ^b	+15°	117	+27.6°
2	13.3	147	30.2
7	14.4	177	31.3
17	16.1	207	32.9
27	18.0	267	35.8
37	19.4	370	36.5
57	20.3	1540	33.3
87	25.4	3010	32.6
		5980	32.6 ^c

^a *c* = g. dimethyl acetal per 100 cc. solution. ^b Observed in water. ^c Equivalent to +40.9° on the basis of *d*-glucose.

TABLE IV
MUTAROTATION OF *d*-GALACTOSE DIMETHYL ACETAL IN 0.05% (BY WEIGHT) HYDROCHLORIC ACID
c,^a 3.720; temp., 24°; *l*, 2-dm.

Time, hr.	[α] _D	Time, hr.	[α] _D
0 ^b	+16°	12.23	+34.9°
.08	17.3	24.23	43.5
.30	17.7	29.23	45.6
4.00	22.0	36.23	50.7
5.23	23.2	50.23	53.2
6.23	24.3	54.23	55.0
7.73	27.4	71.73	57.2
9.23	29.8	73.43	58.8
11.23	32.3	80.57	59.0 ^c

^a *c* = g. dimethyl acetal per 100 cc. solution. ^b Observed in water. ^c Equivalent to +74.1° on the basis of *d*-galactose.

dium instead of a methanol solution. In this case, a distinct maximum in the early part of the curve is observable for the glucose compound and for the galactose compound an inflection point appears at the same place on the time axis. The data of Table V indicate that the final points do not represent complete hydrolysis to the free sugar, but a 67% hydrolysis in the case of glucose dimethyl acetal and only 24% in the case of the galactose dimethyl acetal. From these data and the known equilibrium rotations of the free sugars,

TABLE V
REDUCTION VALUES^a

Substance	Sample, mg.	KMnO ₄ , cc. ^b	C ^c Av.
Methyl- <i>d</i> -glucopyranoside (α,β-mixture)	120	0.0	0
<i>d</i> -Glucose dimethyl acetal	120	21.5	86
<i>d</i> -Glucose dimethyl acetal	120	22.65	91
Table I, 10 min. point	120 ^d	20.5	82
Table I, 10 min. point	120	19.0	76
Table I, 1115 min. point	150	23.5	76
Table I, 1115 min. point	150	25.0	82
Table III, final point ^e	74.5	7.7	67
Methyl- <i>d</i> -galactopyranoside (α,β-mixture)	120	0.0	0
<i>d</i> -Galactose dimethyl acetal	84.2	10.9	60
<i>d</i> -Galactose dimethyl acetal	71.6	9.1	60
Table II, 1.10 hr. point	105 ^d	7.9	35
Table II, 1.10 hr. point	105	8.0	36
Table II, final point	110	9.8	6
Table II, final point	110	11.8	7
Table IV, final point ^e	149	5.4	24

^a After neutralization with silver carbonate, removal of solvent and hydrolysis with 5 cc. 0.05 *N* HCl for ten minutes at 98°. ^b 1 cc. KMnO₄ ≡ 6.968 mg. Cu. ^c Bertrand reduction as % glucose (galactose) equivalent of sample. ^d All samples from points on curves expressed as dimethyl acetal equivalent. ^e Hydrolysis omitted. With exception of these two samples, all samples were non-reducing before hydrolysis.

we may calculate the rotation of the non-hydrolyzed moiety.

$$\text{For glucose, } (0.671)52.2 + (0.329)x = +40.9^\circ \\ x = +18^\circ$$

$$\text{For galactose, } (0.244)80.5 + (0.756)x = +74.1^\circ \\ x = +72^\circ$$

The above figures are within the range of a pyranoside mixture which is probably present.

Experimental

Conversion of *d*-Glucose Dimethyl Acetal into α -Methyl *d*-Glucopyranoside.⁹—*d*-Glucose dimethyl acetal (1.8 g.) was dissolved in 10 cc. of methanol containing 1.0% of dry hydrogen chloride and the solution was heated in a sealed tube at 80° for three days. α -Methyl-*d*-glucopyranoside crystallized on concentration of the solution; yield 0.9 g., m. p. 162–163°. Pure material was obtained on one recrystallization from methanol; m. p. 165–166°

(9) Experiment performed by Mr. Robert L. Brown.

(mixed m. p. unchanged), $[\alpha]_D^{25} +159^\circ$ (c, 2.1 g. per 100 cc. of water solution).

Summary

1. The mutarotation of the dimethyl acetals of *d*-glucose and *d*-galactose at 25° and in the presence of 0.05% hydrogen chloride has been observed in aqueous and in methanol solutions.

2. The amount of material readily hydrolyzable by mild aqueous acidity has been determined at various significant points during the above mutarotations.

3. It is shown that the data obtained in (1) and (2) are interpretable on the basis of a very rapid initial reaction due to hydrolysis of the acetal followed by the formation of unstable, non-pyranoid glycosides which in turn are slowly converted into the stable pyranosides.

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RECEIVED DECEMBER 22, 1938

* [CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Rearrangement of 1,3-Dimethyl-4-*t*-butylbenzene with Aluminum Chloride

BY LEE IRVIN SMITH AND HAROLD O. PERRY

The reaction between *t*-butyl chloride and *m*-xylene in the presence of anhydrous aluminum chloride was carried out first by Bauer.¹ The product obtained by him was 1,3-dimethyl-5-*t*-butylbenzene, for on oxidation it gave 3,5-dimethylbenzoic acid. This hydrocarbon also has been prepared by the action of isobutyl alcohol and sulfuric acid upon *m*-xylene,² and commercially by the action of isobutylene on *m*-xylene in the presence of aluminum chloride,³ while recently a synthesis from *m*-xylene, triisobutyl borate and aluminum chloride has been reported.⁴

The yields in these syntheses are reported to be very high, and the product appears to be a single substance. The two methyl groups would be expected to direct a new substituent mainly into the 4-position; thus *m*-xylene and acetyl chloride, in the Friedel-Crafts reaction, give exclusively 2,4-dimethylacetophenone.⁵ The fact that the 1,3,5-compound is practically the only product when *t*-butyl chloride is used must mean that

either the methyl groups do not exert their usual directing effects in this synthesis, or the 1,3,4-compound is the primary product and this is rearranged to the 1,3,5-compound by the aluminum chloride. If the second of these alternatives should be true, it would be of interest, for although aluminum chloride is known to bring about rearrangements of alkyl groups in alkyl benzenes, it is rare that the final product is a single substance.

We therefore undertook an investigation of this reaction, and of the effect of aluminum chloride on 1,3-dimethyl-4-*t*-butylbenzene. We prepared the symmetrical compound from *m*-xylene,⁶ *t*-butyl chloride and aluminum chloride. Although we did not obtain particularly good yields, the product contained no other dimethylbutylbenzene and it had the 1,3,5-orientation for it gave trimelic acid on oxidation.

The 1,3,4-isomer was prepared from 2,4-dimethylphenylmagnesium iodide and *t*-butyl chloride. The yield of pure product was poor, but it showed a constant boiling point and on oxidation gave trimellitic acid. When this hydrocarbon was heated on the steam-bath for two hours with

(1) Bauer, *Ber.*, **24**, 2840 (1891).
 (2) Noelting, *ibid.*, **25**, 791 (1892).
 (3) German Patent 184,230, *Chem. Centr.*, **78**, II, 366 (1907).
 (4) French Patent 720,034 (1932).
 (5) Claus, *Ber.*, **19**, 230 (1886); Frey and Horowitz, *J. prakt. Chem.*, [2] **43**, 120 (1891); Verley, *Bull. soc. chim.*, [3] **17**, 910 (1897); Bouveault, *ibid.*, [3] **17**, 1021 (1897); Meissel, *Ber.*, **32**, 2420 (1899).

(6) The *m*-xylene used in this work was supplied to us by E. I. du Pont de Nemours and Co., whom we wish to thank for this courtesy.