

of any solid phase other than the monohydrate; cooling curves also gave no indication of a change of phase down to the eutectic temperature, -0.75° .

By the method of least squares, the parabolic curve for the solubility was calculated with the following constants: wt. per cent. solubility = $2.314 + 0.06272t + 0.001714t^2$. The solubilities at round temperatures calculated by this equation are given in Table II. When compared with the figures of Table I, the solubilities calculated from the equation show an average deviation of $\pm 0.073\%$ with respect to the total solution, or $\pm 0.84\%$ with respect to the ammonium oxalate concentration; when comparison is made with the average curve given in "International Critical Tables,"² it is indicated that that curve is approximately 5% too low at 0° and 3.9% too low at 50° .

TABLE II
SOLUBILITY OF AMMONIUM OXALATE IN WATER
Calculated by equation:
Soly. = $2.314 + 0.06272t + 0.001714t^2$

T, °C.	Wt. per cent. (NH ₄) ₂ C ₂ O ₄	T, °C.	Wt. per cent. (NH ₄) ₂ C ₂ O ₄
0	2.314	50	9.735
10	3.112	60	12.25
20	4.254	70	15.10
25	4.953	80	18.30
30	5.738	90	21.84
40	7.565	100	25.73

Summary

The solubility of ammonium oxalate in water has been determined from 0 to 100° ; the solid phase is the monohydrate throughout the entire range; the average figures in "International Critical Tables" are distinctly too low at 0 and at 50° .

NEW YORK CITY

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[CONTRIBUTION FROM THE KENT AND GEORGE HERBERT JONES CHEMICAL LABORATORIES, UNIVERSITY OF CHICAGO]

The Catalytic Hydrogenation of Aldonic Acid Delta and Gamma Lactones and of the Aldoses

BY J. W. E. GLATTFELD AND G. WEBER SCHIMPF¹

These laboratories have been occupied for some time in the development of a practical method for the reduction of the C₄-saccharinic (dihydroxybutyric and dihydroxyisobutyric) acids to the corresponding aldehydes and also in the reduction of *dl*-erythronic lactone to *dl*-erythrose. The work reported in this paper was carried out chiefly in connection with the second of these problems. Since difficulties were encountered when the reduction of *dl*-erythronic lactone was attempted, a study was made of the reduction of similar but less expensive lactones. As a result of this work the conditions for the reduction of *dl*-erythronic butyl ester to crystalline erythritol in good yield have been established,² but, as yet, *dl*-erythrose has not been obtained. Efforts in this direction are being continued.

A preliminary study of the method of catalytic hydrogenation in the presence of platonic oxide as applied to the aldonic acids was made by Glattfeld and Shaver.³ They found it possible to re-

duce *d*-gluconic acid, freshly liberated from its calcium salt by means of sulfuric acid, to *d*-glucose in 14–28% yield (measured as osazone).

In the present study the procedure used by Glattfeld and Shaver was modified and applied to the reduction of the delta and gamma lactones of certain of the aldonic acids, and it was further extended to the reduction of several of the aldoses. Efforts were made to determine the conditions for the production, in the first case, of a maximum yield of the corresponding sugar with a minimum of the corresponding alcohol (hereinafter called alcohol), and in the second, of a high yield of alcohol.

The work was begun with a study of the hydrogenation of the pure delta lactone of *d*-gluconic acid. This substance should upon reduction give the sugar with the 1,5-ring, which should be less easily reduced to the alcohol than the sugar with the 1,4-ring that would be expected to result from the reduction of the gamma lactone of the acid. Glacial acetic acid was the solvent first used, because it was thought that in this solvent the conversion of the delta lactone to gamma lac-

(1) This article is from the dissertation presented by G. Weber Schimpf in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

(2) Results to be communicated in a forthcoming article.

(3) Glattfeld and Shaver, *THIS JOURNAL*, **49**, 2305 (1927).

TABLE I
REDUCTION OF ALDONIC ACID LACTONES IN AQUEOUS SOLUTION

Expt. no.	Lactone	Agitation cycles/min.	Vol. of soln., ml.	Molarity	Catalyst, g.	Time of hydrogenation, min.	Unreduced soln. ^a	[α] _D ^b Reduced soln.	Sugar, %	Acid, %	Alcohol, %
1	<i>d</i> -Gluconic delta	120	100	0.281	0.9 ^b	1200		+31.1	50.6	36.7	13
2	<i>d</i> -Gluconic delta	120	50	.200	.2	780		+21.0	27.0	73.0	0
					.2	1200		+31.6	48.0	38.0	14
					.2	1500		+40.4			
					.2	1980		+35.4	48.8	20.0	31
3	<i>d</i> -Gluconic delta	120	100	.200	.2	1980		+31.6	55.1	17.8	27
4	<i>d</i> -Gluconic delta	120	100	.281	1.2	840		+30.2	42.1		
5	<i>d</i> -Gluconic delta	120	100	.281	0.4	180		+19.5	24.5		
6	<i>d</i> -Gluconic delta	120	100	1.123	2.1 ^c	3000		+30.2	40.3		
7	<i>d</i> -Gluconic delta	120	175	1.123	0.6	4440		+24.0	25.8		
8	<i>d</i> -Gluconic delta	120	200	1.123	1.0	1200		+30.0	44.6		
9	<i>d</i> -Gluconic delta	120	200	0.168 ^d	0.5	1080		+33.3	51.6		
10	<i>d</i> -Gluconic delta	350	100	.200	1.0	30			47	49.8	3
11	<i>d</i> -Gluconic delta	350	100	.200	1.0	60			51	43.1	6
12	<i>d</i> -Gluconic delta	350	100	.200	2.0	20			72	27.2	0
13	<i>d</i> -Gluconic delta	350	100	.200	2.0	30			78	23.0	0
14	<i>d</i> -Gluconic delta	350	100	.200	2.0	35			80	19.0	0
15	<i>d</i> -Gluconic delta	350	100	.200	2.0	35			80	19.0	0
16	<i>d</i> -Gluconic delta	350	100	.200	2.0	40			78	23.2	0
17	<i>d</i> -Gluconic delta	350	100	.200	3.0	10			68	19.6	12
18	<i>d</i> -Gluconic delta	350	100	.200	3.0	20			61	12.0	27
19 ^e	<i>d</i> -Gluconic delta	120	200	.042	0.6	30			28	58.0	14
					.3	80			38.9	38.4	23
					.2	110			44.8	33.5	22
					.2	140			43.0	23.0	34
					.2	170			39.1	15.1	46
20	<i>d</i> -Gluconic gamma	350	100	.200	2.0	20			23.4	53	24
21	<i>d</i> -Gluconic gamma	350	100	.200	2.0	60			46.8	12.4	41
22	<i>d</i> -Mannonic delta	350	100	.200	1.0	30		+31.5	51	44	5
23	<i>d</i> -Mannonic delta	350	100	.200	1.0	60		+10.9	76	20	4
24	<i>d</i> -Mannonic delta	350	100	.200	1.0	90		+ 5.1	37	15	48
25	<i>d</i> -Mannonic delta	350	100	.200	2.0	20		+11.2	70	28	2
26	<i>d</i> -Mannonic delta	350	100	.200	2.0	40			77	20	3
27	<i>d</i> -Mannonic gamma	350	25	.100	0.5	5		+38.2	69.4		
28	<i>d</i> -Mannonic gamma	350	25	.100	0.5	20		+35.9	76.4		
29	<i>l</i> -Rhammonic delta	350	24	.100	0.5	5	-73.6	-48.2	13.9	76.3	10
30	<i>l</i> -Rhammonic delta	350	24	.100	0.5	20	-73.6	-33.9	19	61.1	20
31	<i>l</i> -Rhammonic gamma	350	24	.100	0.5	5	-36.8	-29.6	3.5	80.5	16
32	<i>l</i> -Rhammonic gamma	350	24	.100	0.5	20	-36.8	-21.0	6.2	74.2	20
33	Lactobionic delta	350	24	.100	2.0	5	+38.2	+34.1	38	25.3	36.7
34	Lactobionic delta	350	24	.100	2.0	20	+38.2	+33.0	32	17	51
35	Lactobionic delta	350	24	.100	0.5	5	+42.3	+38.5	72	26.8	1.2
36	Lactobionic delta	350	24	.100	0.5	20	+42.3	+38.5	79	24	0

^a A portion of the original solution was set aside; the rotations of this sample and of the reduced solution were observed in rapid succession at the close of the period of hydrogenation. ^b Catalyst was added in 0.3-g. portions, $t = 0, 9, 15$ hrs. ^c Addition of catalyst: 0.6 g. at 0 hrs.; 0.3 g. portions at 4, 9, 29, 31, 38 hrs. ^d This solution consisted of 30 ml. of the final solution from Experiment 7, diluted to a volume of 200 ml. ^e Glacial acetic acid was used as the solvent. The acid was removed by reduced pressure distillation before analyses were made.

tone and free acid⁴ would be less rapid than in water. Although a reduction of 44.8% was obtained, this solvent was abandoned, because it was found that the use of aqueous solutions resulted in a greater reduction and permitted a simpler experimental procedure.

(4) (a) Nef, *Ann.*, **403**, 306 (1914); (b) Hedenburg, *THIS JOURNAL*, **37**, 345 (1915).

The effects of other variables—(1) concentration of solution, (2) amount of catalyst, (3) time of hydrogenation and (4) rate of agitation—on the reduction of *d*-gluconic delta lactone were also studied. It was found that an increase in the concentration of the lactone was attended by a marked decrease in the rate of reduction. A con-

centration of 0.2 molar was finally chosen as satisfactory, for it favored rapid reduction and at the same time permitted the treatment of rather large quantities of lactone. In regard to the amount of catalyst, it was observed that large quantities favored the production of alcohol, and small quantities necessitated an increase in the time of hydrogenation, a factor which in itself tended to increase the amount of alcohol formed. The rate of shaking of the solution was found to be a factor of the utmost importance. In solutions of approximately the same concentration, with equal quantities of catalyst, it was found that the time necessary to secure a 50% reduction was decreased from twenty hours to thirty minutes when the rate of shaking was increased from 120 to 350 cycles per minute (see experiments 1 and 10, Table I).

Various other lactones were then used in place of the delta lactone of *d*-gluconic acid. When the gamma lactone of *d*-gluconic acid was used, it was found that it was reduced more slowly than was the delta lactone and that it gave a higher yield of alcohol. Under conditions that resulted in an 80% yield of *d*-glucose with no alcohol from the delta lactone, there was obtained from the gamma lactone 23.4% sugar and 24% alcohol. In marked contrast was the behavior of the two lactones of *d*-mannonic acid. Both were reduced very readily. On the other hand, both lactones of *l*-rhammonic acid were reduced slowly and both gave relatively high yields of alcohol; the gamma lactone gave three to four times as much alcohol

as sugar, whereas the delta lactone gave approximately equal amounts of the two products. These results led to the same conclusion as did the work with the lactones of *d*-gluconic acid, *viz.*, the gamma lactone yields a sugar which is more readily reduced to the alcohol than the sugar from the delta lactone. In the case of lactobionic acid only the delta lactone is known. This substance was reduced to the extent of 79% in twenty minutes, with the production of practically no alcohol. The variations in experimental conditions with the results obtained are recorded in detail in Table I.

The method of catalytic hydrogenation developed for the aldonic acids was then applied to the reduction of aldoses in aqueous solution. It was found possible to reduce almost completely *d*-glucose, *d*-mannose, *l*-arabinose, *d*-xylose, *l*-rhamnose hydrate and lactose monohydrate. In several of the experiments the alcohols were isolated in yields varying from 63 to 80%. The results of these experiments are recorded in Table II.

Further work is in progress in these Laboratories both on the method herein described and on modifications which may render it applicable to reactions at high pressure and high temperature.

Experimental Part

Apparatus.—The apparatus possessed the essential features of the equipment used by Glattfeld and Shaver,³ but the details of design were similar to those of the hydrogenation apparatus now manufactured by the Burgess-Parr Company of Moline, Illinois.

TABLE II

Expt. no.	Sugar	REDUCTION OF ALDOSES IN AQUEOUS SOLUTION											
		Agitation, cycles/min.	Vol. of soln., m	Molarity	Catalyst, g.	Time of hydrogenation, hrs.	Initial soln., $t = 0$	[α] _D Reduced soln.	Sugar, %	Alcohol, %	Amount isolated, g.	Yield, ^a %	M. p., °C.
37	<i>d</i> -Mannose	120	195	1.00	15	122	+14.3	+ 0.1	9.3 ^b	90.7	25.2	75	164–165
38	<i>d</i> -Galactose	120	190	1.11	4.5	287	+74.1	+ 0.1			29.5	77.6	186–187
39	<i>d</i> -Glucose	120	100	0.20	5.1	99	+51.6	+ 0.9	nil	99.9			Sirup ^c
40	<i>l</i> -Arabinose	120	190	1.00	6	64	+92.2	– 0.8	0.4 ^d	99.6	21.6	80	97–99
41	<i>d</i> -Xylose	120	190	1.00	6	594	+19.7	+ 1					Sirup
42	<i>l</i> -Rhamnose monohydrate	120	100	1.00	5	69			8 ^e	92	8.2	54 ^f	120–122
43	Lactose monohydrate	350	95	0.20	12	12	+52.8	+17.8	1 ^g	99	8 ^h	63	79–80
44	Lactose monohydrate	350	95	0.20	12	12	+52.8	+16.4	1	99			

^a The yield was calculated on the basis of the amount of alcohol theoretically present in the solution which remained at the end of the experiment, after various samples had been removed for analysis. ^b The reducing value of *d*-mannose was considered equivalent to that of *d*-glucose. ^c The dibenzaldehyde derivatives of the sirup and of *d*-sorbitol (Pfanstiehl) were prepared. Both derivatives, which were amorphous, melted at 195–200°. A mixture of the two products melted at the same temperature. ^d The conversion factor 0.92 was used [Vogel and Georg, "Tabellen der Zucker und ihrer Derivate," Verlag Julius Springer, Berlin, 1931, p. 9]. ^e The conversion factor of *l*-rhamnose was found to be 0.97. A second crop could have been obtained, but time did not permit. ^f The conversion factor 0.655 was used [Vogel and Georg, *ibid.*, p. 49]. ^g The solutions of experiments 43 and 44 were combined for the isolation of the lactitol.

Materials.—(1) Commercial electrolytic hydrogen was used without purification. (2) Platonic oxide monohydrate was prepared according to the method described by Adams, Voorhees and Shriner.⁵ However, it was found possible to prepare at a single fusion ten times the quantity specified. (3) *d*-Mannose was prepared according to the method of Clark;⁶ $[\alpha]_D +14.1^\circ$. (4) *d*-Mannonic delta lactone was prepared from calcium *d*-mannonate dihydrate.⁷ This salt was converted into the sodium salt by means of sodium oxalate. After the removal of the calcium oxalate, the filtrate was taken to dryness under diminished pressure at 50–60°. The solid residue was dried in a vacuum desiccator over concentrated sulfuric acid; yield, 96%. The sodium salt was then converted into the delta lactone according to the method of Brackenbury and Upson;⁸ yield, 77.8%; m. p. 156–157°; $[\alpha]_D +113.4^\circ$ (four min.). (5) *d*-Mannonic gamma lactone was prepared by an adaptation of the methods reported by Nef,^{4a} by Hedenburg,^{4b} and by Isbell and Frush.⁹ A dry mixture of 23.32 g. (0.05 mole) of calcium *d*-mannonate dihydrate and 6.30 g. (0.05 mole) of powdered oxalic acid dihydrate was added to 24 ml. of boiling water. The hot thick paste was kept on a steam-bath with constant stirring for twenty minutes. The calcium oxalate was separated and washed with a total of 50 ml. of hot water. The washings and 4 drops of concentrated hydrochloric acid were added to the filtrate, and the entire solution was concentrated to a thick sirup at 50° under reduced pressure. This sirup was diluted with 20 ml. of water, transferred to a crystallizing dish, and placed in a vacuum desiccator over concentrated sulfuric acid. Crystals soon appeared; when the mass became solid, it was transferred to a Büchner funnel and the solid washed with about 200 ml. of absolute ethanol. The crystals were dried in a vacuum desiccator; m. p. 151–152°; $[\alpha]_D +51.7^\circ$ (50 min.); yield, 12.1 g. (68%). (6) The delta and gamma lactones of *d*-gluconic acid were purchased from the Pfanstiehl Chemical Company, Waukegan, Illinois. (7) *l*-Rhammonic delta lactone was kindly supplied by Professor Fred W. Upson, Department of Chemistry, University of Nebraska; m. p. 172–177°, $[\alpha]_D -97.9^\circ$ (5 min.). (8) *l*-Rhammonic gamma lactone was prepared by Mr. B. D. Kribben of this Laboratory from *l*-rhamnose monohydrate isolated from quercitrin; m. p. 147–149°; $[\alpha]_D -37.6^\circ$ (20 min.). (9) Lactobionic delta lactone was kindly supplied by Dr. Horace S. Isbell of the Bureau of Standards, Washington, D. C.; m. p. (dec.) 195–196°; $[\alpha]_D +53.4^\circ$ (2 min.). (10) *d*-Galactose, *l*-arabinose, *d*-xylose and lactose monohydrate were purchased from the Kahlbaum Chemical Company. (11) *l*-Rhamnose monohydrate was kindly supplied by Dr. M. E. Hanke, Department of Physiological Chemistry, University of Chicago; m. p. 101–103°; $[\alpha]_D +8.64^\circ$ (final).

Reduction of Lactones.—An experiment with *d*-gluconic delta lactone (see experiment 3, Table I) will be described,

(5) Adams, Voorhees and Shriner, "Organic Syntheses," 1928, John Wiley and Sons, Inc., New York City, Vol. VIII, p. 98.

(6) Clark, *Sci. Papers Bur. Standards*, **17**, 587 (1922).

(7) The method used for the preparation of the calcium salt was similar to that used by Hudson and Isbell [THIS JOURNAL, **51**, 2225 (1929)] for calcium *d*-gluconate.

(8) Brackenbury and Upson, *ibid.*, **55**, 2512 (1933).

(9) Isbell and Frush, *Bur. Standards J. Research*, **11**, 649 (1933).

since the operations are typical of those used in all the experiments conducted in aqueous solution. A 3.562-g. sample (0.02 mole) was dissolved in water and the volume made up to 100 ml. The solution was transferred to the reaction bottle and 0.2 g. of catalyst added; the bottle was thoroughly evacuated, filled with hydrogen until the gage registered a pressure of 35 pounds,¹⁰ and shaken at the rate of 120 cycles per minute for thirty-three hours. At the end of that time the platinum black was allowed to settle; the rotation of the solution was observed; a sample was analyzed for reducing material by means of a micro-modification of the Benedict method,^{11,12} and a sample was titrated for total acidity. The percentage alcohol was calculated by subtracting from 100 the sum of the percentages of sugar and acid. In some experiments (see experiment 2, Table I) the shaking was interrupted, samples were removed for analysis, more catalyst was added and then the hydrogenation continued.

Isolation of *d*-Glucose.—In experiment 6 (Table I), the platinum black was removed by filtration after the final analysis, and the volume of the solution measured (84 ml. which contained 6.72 g. of *d*-glucose by analysis). The solution was diluted to 200 ml., warmed in a water-bath at 50°, and neutralized with calcium carbonate. The filtrate from the excess carbonate was concentrated to a thick sirup at reduced pressure (water-bath 50°). This sirup was diluted to 30 ml. with hot water and triturated with about 1200 ml. of absolute ethanol. The solid calcium *d*-gluconate which separated was powdered and washed with 200 ml. of absolute ethanol (weight 11.6 g., air dry). The ethanol solutions were combined and concentrated at reduced pressure to a volume of about 250 ml. (bath 40°). The volume was further reduced to about 30 ml. in a vacuum desiccator. The crystalline *d*-glucose was separated by filtration, washed with absolute ethanol and absolute ether, and dried in a vacuum desiccator; weight 5.2 g.; recovery 77.4%. After two recrystallizations from absolute ethanol, the m. p. was 145.5–146.6°; $[\alpha]_D +51.9^\circ$ (17 min.).

Reduction of Aldoses.—The procedure used for the reduction of the sugars was practically identical with that outlined above, except that the process was usually interrupted at convenient intervals for the analysis of the solution and the introduction of catalyst. The process was discontinued when analysis showed 10% or less of sugar. The alcohol was usually isolated from the solution left after the removal of the platinum black, by the addition of an appropriate mixture of 95% ethanol and ordinary ether followed by storage of the solution in the refrigerator until crystallization had taken place. After the removal of the crystals, the mother liquor was concentrated under diminished pressure at 50° to a small volume, and the above treatment repeated for the obtaining of a second crop. It was not possible to obtain the *d*-sorbitol or the xylitol in crystalline form.

Isolation of Lactitol.—After the removal of the platinum black, the solution was evaporated to dryness at reduced

(10) A pressure of two to three atmospheres was used throughout the work.

(11) Mathews, "Physiological Chemistry," William Wood and Company, Baltimore, Md., 5th ed., p. 1188.

(12) In the calculation of the percentage of reducing material, the molecular weights of the sugar and acid lactone were considered identical, even though their formulas differ by two hydrogen atoms.

pressure (bath 50°). The residue was triturated for several hours with absolute acetone. The resulting white solid, which was very hygroscopic, was carefully dried in a vacuum desiccator over phosphorus pentoxide (weight 8.0 g., 63%). A 0.900-g. sample was weighed rapidly, dissolved in water, and the solution diluted to 10 ml. The rotation of the solution in a 1-dcm. tube was found to be +1.48°; $[\alpha]_D +16.4^\circ$. The only value given in the literature is the one reported by Senderens,¹³ who found $[\alpha]_D +12.2^\circ$ for the monohydrate of lactitol. He reported the m. p. to be 78°. Our product melted to a milky liquid at 79–80° and increased in volume about five-fold; at 130–140° the mass turned to a yellow glass-like solid which decomposed at 190–200°. Neuberg and Marx¹⁴ reported that anhydrous lactitol decomposed at 200°.

(13) Senderens, *Compt. rend.*, **170**, 47 (1920).

(14) Neuberg and Marx, *Biochem. Z.*, **3**, 539 (1907).

Summary

1. A method of catalytic hydrogenation has been developed whereby the delta lactones of aldonic acids are reduced in good yield to the corresponding sugars. The gamma lactones are also reduced, but they usually give lower yields of the sugars owing to the further reduction of the sugars to the corresponding sugar alcohols.

2. The method has been adapted to the reduction of the sugars to the corresponding sugar alcohols. It is possible to obtain practically complete reduction and to isolate the sugar alcohols in 63–80% yields.

CHICAGO, ILLINOIS

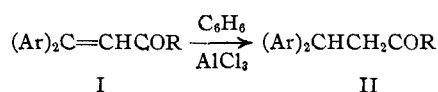
RECEIVED AUGUST 29, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

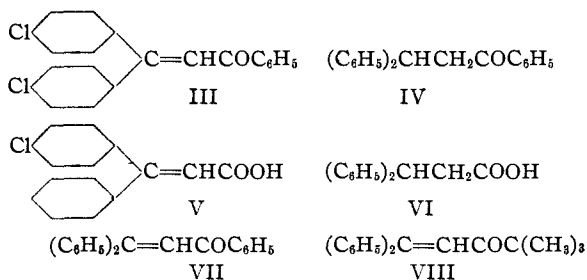
The Reversibility of the Friedel–Crafts Condensation. Hydrogenation Phenomena

BY L. L. ALEXANDER, A. L. JACOBY AND REYNOLD C. FUSON

It was to be predicted that the reversible addition of aromatic hydrocarbons to α,β -unsaturated carbonyl compounds¹ would be prevented by the presence of suitable substituents on the *beta* carbon atom. Several examples of conjugated systems have now been found which do not yield addition products but instead undergo hydrogenation. Thus, 1,1-diaryl-2-acylethylenes do not condense with benzene in the presence of aluminum chloride, but, instead, *are hydrogenated to the corresponding saturated diaryl ketones*.



For example, 1,1-di-(*p*-chlorophenyl)-2-benzoyl-ethylene (III) is converted to α -benzohydrylaceto-phenone (IV).



Similarly, β -(*p*-chlorophenyl)-cinnamic acid (V)

gives β,β -diphenylpropionic acid (VI). In both of these examples replacement as well as hydrogenation is involved. However, the chlorine-free analog of III—1,1-diphenyl-2-benzoyl-ethylene (VII)—appears to undergo only the latter change; it gives IV. In a similar fashion, 1,1-diphenyl-2-trimethylacetyl-ethylene (VIII) is transformed into its hydrogenation product, α -benzohydrylpinacolone.

However, it seemed possible that this type of transformation might not be dependent on the presence of a hetero conjugated system, but might be simply a property of stilbenes. In order to clear up this point stilbene, *p*-bromostilbene and *p,p'*-dichlorostilbene were each subjected to treatment with benzene in the presence of anhydrous aluminum chloride. *In each case the product was dibenzyl*. The generalized form of the equation is $\text{XC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{X} + 2\text{C}_6\text{H}_6 + 2\text{H} = \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5 + 2\text{C}_6\text{H}_5\text{X}$. It is seen that this process involves replacement of aryl groups as well as hydrogenation at the double bond.

The various mechanisms which suggest themselves for these processes raise the question as to whether the addition of benzene, the elimination of the substituted phenyl group and the hydrogenation are related processes and, if so, in what sequence they occur. The work is being continued from this point of view.

(1) For references to earlier papers of this series, see Woodward, Borchardt and Fuson, *This Journal*, **56**, 2103 (1934).