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1,2,3,4-Dibenzylidene-D-sorbitol

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In 1890 Meunier¹ reported that two dibenzylidene-D-sorbitols could be obtained by the condensing action of strong mineral acids on a mixture of benzaldehyde and sirupy D-sorbitol. One of these diacetals was a colorless powder (m. p. 162°) which was insoluble even in boiling water; the second one was soluble in boiling water and deposited from the cooled aqueous solution in the form of a gel, which could be dried to a powder melting at 200°. The present communication outlines the experimental procedures necessary to obtain the latter compound in pure condition and describes the reactions which lead to the definitive conclusion that its structure is that of 1,2,3,4-dibenzylidene-D-sorbitol. Under the experimental conditions which were employed, we did not encounter the compound reported as melting at 162°.

Initial efforts to obtain a dibenzylidene-D-sorbitol by condensation of *two* molecular equivalents of benzaldehyde with one equivalent of D-sorbitol through the influence of various concentrations of hydrochloric acid yielded a mixture of tribenzylidene-D-sorbitol and a gel which could not be readily separated into its components. However, when only *one* equivalent of benzaldehyde was employed and the condensing agent was 4 *N* hydrochloric acid, no formation of tribenzylidene-sorbitol was observed and the resulting condensate contained a small amount of the 2,4-monobenzylidene-D-sorbitol described by

Vargha,² together with a second product which could be converted in high yield (88%) to a crystalline dibenzoyl-dibenzylidene-D-sorbitol. This pure recrystallized dibenzoate, upon debenzoylation in chloroform solution with sodium methylate, yielded a gel which could be dried to a cryptocrystalline powder analyzing correctly for a dibenzylidene-hexitol and showing a melting point of 219–221° (cor.) and a specific rotation $[\alpha]^{20}_D$ of +21.6° in pyridine. A second portion of the crude dibenzylidene-D-sorbitol was converted to a crystalline diacetyl-dibenzylidene-D-sorbitol, and the latter compound, upon deacetylation, regenerated dibenzylidene-D-sorbitol agreeing in melting point and rotation with that obtained from the dibenzoate. The diacetal that was obtained from the crystalline diacetate was in turn converted in high yield (95%) to dibenzoyl-dibenzylidene-D-sorbitol which was identical with the dibenzoate previously mentioned. These interconversions leave no doubt that the dibenzylidene-D-sorbitol of m. p. 219–221° is a single chemical entity and not a mixture of isomers. The problem of establishing its structure was first studied through its reaction with lead tetraacetate in glacial acetic acid solution. It was observed that one molecular equivalent of lead tetraacetate was reduced in three hours and that an additional four molecular equivalents were slowly consumed over a period of twelve days; these results suggested that a glycol group was oxidized in the

(1) Meunier, *Ann. chim. phys.*, [6] **22**, 412 (1891).

(2) Vargha, *Ber.*, **68**, 23, 1337 (1935).

initial stage of the reaction and that the primary oxidation products were then slowly attacked by the reagents and further oxidized. A second oxidation was therefore interrupted at the end of four hours, and the oxidation products isolated at once; they proved to be formaldehyde and an aldehydo-dibenzylidene-pentose (isolated as a crystalline methyl hemiacetal). These results limited the structure of the dibenzylidene-D-sorbitol to 1,2,3,4-dibenzylidene-D-sorbitol or 3,4,5,6-dibenzylidene-D-sorbitol. Decision between these two structures depended upon whether the aldehydo-dibenzylidene-pentose was aldehydo-2,3,4,5-dibenzylidene-L-xylose or aldehydo-2,3,4,5-dibenzylidene-D-arabinose. The methyl hemiacetal was therefore subjected to acid hydrolysis; the resulting pentose sugar proved to be L-xylose as shown by its melting point, final rotation and mutarotation rate; the L-xylose was further characterized by conversion to its phenylosazone and phenylosazone triacetate, which were found to be enantiomorphs of the corresponding derivatives of D-xylose. The identity of the pentose with L-xylose is a definite proof that the aldehydo-dibenzylidene-pentose, obtained by oxidation of dibenzylidene-D-sorbitol, is aldehydo-2,3,4,5-dibenzylidene-L-xylose and this fact limits the structure of the dibenzylidene-hexitol to that of 1,2,3,4-dibenzylidene-D-sorbitol. Supporting evidence for this structure was obtained by the observation that dibenzylidene-D-sorbitol, upon reaction with two equivalents of triphenylmethyl chloride under mild conditions, yielded a mono-trityl derivative, a result which indicated that a single primary hydroxyl group was present in the diacetal. Attention has previously³ been directed to the difficulty of assigning a definitive structural and stereochemical formula to a dibenzylidene-hexitol. Although Vargha² has demonstrated that monobenzylidene-D-sorbitol is 2,4-monobenzylidene-D-sorbitol, we have not succeeded in condensing it with further amounts of benzaldehyde to yield the dibenzylidene-D-sorbitol melting at 219–221° (cor.), and it is possible at the present time, therefore, to designate the latter compound only as 1,2,3,4-dibenzylidene-D-sorbitol.

We express our appreciation to Dr. A. T. Ness for performing the microchemical analyses and to Dr. C. P. Saylor, of the National Bureau of Standards, for assistance in the microscopic examination of 1,2,3,4-dibenzylidene-D-sorbitol,

(3) Haskins, Hann and Hudson, *THIS JOURNAL*, **64**, 138 (1942).

which showed the substance to be cryptocrystalline.

Experimental

5,6-Dibenzoyl-1,2,3,4-dibenzylidene-D-sorbitol.—To a solution of 10.0 g. of crystalline D-sorbitol in a mixture of 10 cc. of water and 5 cc. of concentrated hydrochloric acid, 5 cc. of benzaldehyde (1.1 molecular equivalents) was added; the reaction mixture, upon agitation at room temperature, formed a homogeneous solution which set to a gel after one hour. The next day the mass was broken into small pieces, transferred to a Büchner funnel, washed successively with water and ether, and dried; the dry powder was pulverized and leached with 100 cc. of boiling water and the undissolved solid was separated by filtration and dried to constant weight. The yield was 7.1 g. (70% based on the benzaldehyde used). The substance was dissolved in 35 cc. of pyridine and after addition of 15 cc. of benzoyl chloride the mixture was allowed to stand overnight at room temperature; the next day 200 g. of ice was added and the gummy precipitate of dibenzoate which formed, crystallized slowly. The compound deposited from its solution in 10 parts of alcohol in the form of long silky needles, which melted at 195–196° (cor.) and exhibited a specific rotation⁴ of -41.5° (c , 0.69) in chloroform.

Anal. Calcd. for $C_{34}H_{30}O_8$: C, 72.06; H, 5.34; C_6H_5CO , 37.1. Found: C, 72.14; H, 5.28; C_6H_5CO , 36.4.

1,2,3,4-Dibenzylidene-D-sorbitol.—A solution of 91.0 g. of 5,6-dibenzoyl-1,2,3,4-dibenzylidene-D-sorbitol in 700 cc. of chloroform was cooled in ice and 50 cc. of 0.1 *N* sodium methylate in methanol solution was added. After eighteen hours the gel which had formed was dried *in vacuo* at 65° to remove the chloroform and methyl benzoate, and the residual powder was washed with water and dried. The yield was 57.0 g. (99%). The compound melted at 219–221° (cor.) and showed a specific rotation of $+21.6^\circ$ (c , 1.04) in pyridine. The substance was soluble in warm ethyl alcohol, methyl alcohol, acetone, and acetic acid, but the solutions on cooling deposited gels. The homogeneity of the material was demonstrated, however, by repeated solution and recovery from 65 parts of alcohol; the material recovered after three such treatments, agreed in melting point and rotation with the original sample and also with 1,2,3,4-dibenzylidene-D-sorbitol obtained by the deacetylation of the crystalline 5,6-diacetyl-1,2,3,4-dibenzylidene-D-sorbitol that is described in the following paragraph.

Examination of the substance under the petrographic microscope by Dr. C. P. Saylor of the National Bureau of Standards revealed that little or no birefringence was detectable in mounts prepared with aqueous media, presumably because of extensive scattering of light by dust of the compound covering the surface of the crystals. However, mounts in liquids of higher refractive index (methyl phthalate, aniline) allowed observation of the high birefringence characteristic of the compound. Since there were complex changes of optical crystallographic direction within the crystal units, the compound may be designated as cryptocrystalline.

(4) All of the crystalline compounds described in the experimental part were recrystallized to constant melting point and specific rotation. $[\alpha]_D^{20}$; c is the concentration in grams in 100 cc. of solution; the tube length was 4 dm.

Anal. Calcd. for $C_{20}H_{22}O_6$: C, 67.04; H, 6.19. Found: C, 67.08; H, 6.23.

5,6-Diacetyl-1,2,3,4-dibenzylidene-D-sorbitol.—A solution of 2.0 g. of 1,2,3,4-dibenzylidene-D-sorbitol (obtained by debenzoylation of 5,6-dibenzoyl-1,2,3,4-D-sorbitol) in a mixture of 5 cc. of pyridine and 5 cc. of acetic anhydride was heated on the steam-bath for one hour and then cooled and poured upon crushed ice. The yield of 2.35 g. (95%) of diacetate was recrystallized from 15 parts of acetone and it deposited in prisms which melted at 202–205° (cor.) and rotated +4.1° (*c*, 0.95) in chloroform. Upon deacetylation with sodium methylate, 1,2,3,4-dibenzylidene-D-sorbitol, agreeing in rotation and melting point with the compound prepared from the dibenzoate, was obtained in a 93% yield.

Anal. Calcd. for $C_{24}H_{26}O_8$: C, 65.15; H, 5.92; CH_3CO , 19.4. Found: C, 65.25; H, 5.94; CH_3CO , 19.2.

5,6-Dibenzoyl-1,2,3,4-tetraacetyl-D-sorbitol.—A solution of 1.25 g. of 5,6-dibenzoyl-1,2,3,4-dibenzylidene-D-sorbitol in 50 cc. of an acid acetylating solution (prepared by adding 1 cc. of concentrated sulfuric acid dropwise to an ice-cold mixture of 35 cc. of acetic anhydride and 15 cc. of acetic acid) was allowed to stand at 20° for twenty-four hours. The reaction mixture was poured upon crushed ice and the thick sirup which precipitated was washed several times with water and dissolved in warm alcohol. As the solution cooled it deposited 5,6-dibenzoyl-1,2,3,4-tetraacetyl-D-sorbitol (0.95 g., 73%) in the form of prisms. After two recrystallizations from 6 parts of alcohol, the substance melted at 96–97° (cor.) and showed a specific rotation of +14.4° (*c*, 0.48) in chloroform.

Anal. Calcd. for $C_{24}H_{26}O_8$: C, 60.21; H, 5.42; sapon. titer, 10.7 cc. of 0.1 *N* alkali for 100 mg. Found: C, 60.34; H, 5.43; sapon. titer, 10.5 cc. of 0.1 *N* alkali for 100 mg.

5,6-Ditosyl-1,2,3,4-dibenzylidene-D-sorbitol.—Five grams of 1,2,3,4-dibenzylidene-D-sorbitol was dissolved in 15 cc. of absolute pyridine on the steam-bath and the solution was then cooled to 0° to form a gel; to this gel an ice-cold solution of 6.0 g. of *p*-toluenesulfonyl chloride in 10 cc. of pyridine was added and the reaction mixture was agitated vigorously at 0° for three hours and then allowed to stand at 15° for a further eighteen hours. The solution was then poured over crushed ice and the precipitated ditosylate (7.9 g., 84%) was recrystallized from a mixture of 10 parts of alcohol and 4.5 parts of acetone. The compound crystallized in cotton-like needles, which showed a specific rotation of +1.2° (*c*, 0.6) in acetone. The melting point of the compound varied with the rate of heating; when the bath was heated at a rate of 1° in three minutes, it melted at 155–156°, at a rate of 2° in one minute the melting point was 159–160° (cor.). When the tosylation was conducted at a temperature higher than 15°, the mixture of products which was obtained gave a strong Beilstein test for halogen, indicating that some substitution of chlorine had occurred.

Anal. Calcd. for $C_{24}H_{34}O_{10}S_2$: C, 61.24; H, 5.14. Found: C, 61.12; H, 5.29.

6-Trityl-1,2,3,4-dibenzylidene-D-sorbitol.—A solution of 2.0 g. of 1,2,3,4-dibenzylidene-D-sorbitol and 3.4 g. (2.2 molecular equivalents) of triphenylmethyl chloride in 15

cc. of pyridine was allowed to stand at room temperature for seventy-two hours. The mixture was poured into 100 cc. of ice water and the supernatant liquor, which contained crystalline triphenylcarbinol, was decanted from the insoluble gummy trityl derivative. The latter material was suspended in 50 cc. of cold alcohol and in the course of one week it crystallized in a yield of 3.3 g. (96%). This product was recrystallized twice from 10 parts of ethyl acetate and formed elongated prisms which melted slowly over a range of 110–115° (cor.) to a clear oil, then solidified in the form of needles and remelted at 182–183° (cor.). This behavior is exhibited only by material freshly crystallized from ethyl acetate; after drying at 50° overnight, the transition to the needle form is complete and only the higher melting point is observed; apparently the substance is dimorphic. The needles gave a specific rotation of +16.8° (*c*, 0.6) in ethyl acetate.

Anal. Calcd. for $C_{42}H_{48}O_7$: C, 76.61; H, 5.96. Found: C, 76.54; H, 6.01.

5-Acetyl-6-trityl-1,2,3,4-dibenzylidene-D-sorbitol.—This compound was obtained in quantitative yield by the action of acetic anhydride and pyridine on 6-trityl-1,2,3,4-dibenzylidene-D-sorbitol. It deposited from its solution in 80 parts of alcohol in long needles which melted at 117–119° (cor.) to a clear oil, then resolidified in the form of plates and remelted at 186–187° (cor.). The lower melting form showed no change on preservation at room temperature for several months. It exhibited specific rotations of –41.8° (*c*, 0.6) in ethyl acetate and –46.5° (*c*, 0.4) in chloroform.

Anal. Calcd. for $C_{42}H_{48}O_7$: C, 76.61; H, 5.96; CH_3CO , 6.58. Found: C, 76.54; H, 6.01; CH_3CO , 6.25.

Lead Tetraacetate Oxidation of 1,2,3,4-Dibenzylidene-D-sorbitol.—A sample of 0.1198 g. of 1,2,3,4-dibenzylidene-D-sorbitol was dissolved in 20 cc. of glacial acetic acid, and after the addition of 16.22 cc. of 0.0904 *M* lead tetraacetate (2.2 molecular equivalents) in glacial acetic acid, the volume was adjusted to 50 cc. with glacial acetic acid. Analysis of 5-cc. aliquots at the expiration of fifteen and thirty minutes, one, three and nineteen hours showed that 0.43, 0.63, 0.79, 0.97 and 1.15 molecular equivalents of oxidant had been consumed. In a second experiment, 5.5 molecular equivalents of lead tetraacetate were added and it was observed that 1.0 equivalent was reduced in a period of three hours and a further 4.0 equivalents was reduced very slowly over a period of twelve days. The rapid reaction was due to the oxidation of the glycol grouping at carbons five and six (see the following section) and the slower one occurred presumably as a result of a slow hydrolysis of the benzylidene groups and subsequent oxidation of the hydrolysis products. The final consumption of lead tetraacetate (5.0 molecular equivalents) agreed with that expected for such a series of reactions.

Isolation of Aldehyde-2,3,4,5-dibenzylidene-L-xylose Methyl Hemiacetal.—A suspension of 21.5 g. of 1,2,3,4-dibenzylidene-D-sorbitol and 40 g. of pulverized lead tetraacetate (1.1 molecular equivalents) in 400 cc. of glacial acetic acid was agitated vigorously for four hours with occasional cooling to maintain the temperature below 25°; the amorphous reaction product was separated by filtration, pulverized and dried over potassium hydroxide until free of acetic acid. The product (21.2 g.), which was

sufficiently pure for synthetic operations, was dissolved in a warm mixture of 100 cc. of methyl alcohol and 100 cc. of chloroform and as the solution cooled it deposited the methyl hemiacetal of aldehydo-2,3,4,5-dibenzylidene-L-xylose in the form of needles. The compound, after recrystallization to constant rotation from 80 parts of a 1:1 mixture of methyl alcohol and chloroform, melted at 187–188° (cor.) and exhibited a rotation of +40.4° (*c*, 0.46) in pyridine. The yield of hemiacetal was 15.0 g. (70%).

Anal. Calcd. for C₂₀H₂₂O₆: C, 67.03; H, 6.19; OCH₃, 8.65. Found: C, 67.05; H, 6.38; OCH₃, 8.38.

Identification of Formaldehyde as an Oxidation Product.

—The acetic acid filtrate from the oxidation mixture was refluxed while a gentle current of carbon dioxide was passed through it; the gas was led through an efficient condenser and into 100 cc. of ice-cold water. At the end of six hours, an aliquot of the aqueous solution was tested with dimethyl-dihydroresorcinol; the characteristic formaldimethone which formed, melted at 189–190° (cor.) and no depression of the melting point was observed upon admixture with authentic formaldimethone.

Aldehydo-2,3,4,5-dibenzylidene-L-xylose.—A sample of the methyl hemiacetal of aldehydo-2,3,4,5-dibenzylidene-L-xylose was sublimed in a vacuum at 140–145° and the sublimate, which was partially crystalline, was recrystallized from 5 parts of dioxane. The compound was obtained in the form of small needles which melted at 186–187° (cor.) and showed a rotation of –33.4° (*c*, 0.52) in pyridine.

Anal. Calcd. for C₁₉H₁₈O₆: C, 69.93; H, 5.56. Found: C, 69.84; H, 5.66.

Aldehydo-2,3,4,5-dibenzylidene-L-xylose Oxime.—A suspension of 1.0 g. of aldehydo-2,3,4,5-dibenzylidene-L-xylose in a solution containing 25 cc. of methanol, 5 cc. of water, 1.0 g. of hydroxylamine hydrochloride and 1.0 g. of fused sodium acetate was refluxed for twenty minutes, during which period complete solution occurred; the crystalline product, which deposited as the solution cooled, was recrystallized from 240 parts of alcohol and yielded 0.9 g. (86%) of oxime in the form of colorless needles which melted with decomposition at 239–240° (cor.) and gave a rotation of –108.9° (*c*, 0.41) in pyridine.

Anal. Calcd. for C₁₉H₁₉NO₆: C, 66.85; H, 5.61; N, 4.10. Found: C, 66.86; H, 5.57; N, 4.28.

L-Xylose from Aldehydo-2,3,4,5-dibenzylidene-L-xylose Methyl Hemiacetal.—A suspension of 10.6 g. of 1,2,3,4-dibenzylidene-L-xylose methyl hemiacetal in a mixture of 280 cc. of methyl alcohol, 15 cc. of water and 3 cc. of concentrated hydrochloric acid was refluxed for one hour, during which time complete solution occurred and a strong odor of benzaldehyde developed. The solution, following the removal of the hydrochloric acid by silver carbonate in the usual manner, was concentrated *in vacuo* to a sirup, presumably a mixture of α - and β -methyl-L-xylosides. The sirup, which resisted crystallization, was dissolved in 100 cc. of 1% sulfuric acid and hydrolyzed for two hours on the steam-bath. The acid was neutralized with barium hydroxide and the neutral solution concentrated *in vacuo* to a sirup, which deposited crystalline L-xylose upon treatment with 3 cc. of glacial acetic acid. The yield was 1.7 g. (40%). The pentose melted at 143–145° (cor.) and gave

an extrapolated initial rotation of –92° and an equilibrium value of –19.4° (*c*, 0.88) in aqueous solution. Its mutarotation rate at 20° was 20.2×10^{-3} , which agrees with the known rate for D-xylose. Vargha² records a melting point of 144° and initial and equilibrium rotations of –79.3° and –18.6°, respectively, for the L-xylose which he prepared by the lead tetraacetate oxidation of 2,4-benzylidene-D-sorbitol. Isbell⁵ reports an initial rotation of +94.8° and an equilibrium rotation of +18.3° for a 4.4% aqueous solution of D-xylose.

Anal. Calcd. for C₅H₁₀O₅: C, 40.00; H, 6.71. Found: C, 39.86; H, 6.57.

D,L-Xylose.—A mixture of 100 mg. each of D-xylose and L-xylose was dissolved in 2 cc. of warm methanol and diluted with 5 cc. of glacial acetic acid. The D,L-xylose (110 mg., 55%) obtained was optically inactive in aqueous solution and melted at 128–130° (cor.) in good agreement with the value of 129–131° recorded by Fischer⁶ for D,L-xylose.

Racemic Xylose Phenylsazone.—A mixture of 0.5 g. of L-xylose, 1.5 cc. of phenylhydrazine, 1.0 cc. of acetic acid and 5 cc. of water was heated on the steam-bath for one hour. The L-xylose phenylsazone (yield, 0.8 g.; 74%) was recrystallized from aqueous acetone and obtained as fine yellow needles melting at 161–163° (cor.). Reichstein, Grüssner and Oppenauer⁷ reported a melting point of 160–162° (cor.) for D-xylose phenylsazone. A mixture of 100 mg. each of D- and L-xylose phenylsazones was dissolved in 10 cc. of warm acetone; the precipitate (171 mg.; 85%), which formed on cooling the solution, was recrystallized from 10 cc. of acetone and obtained as fine needles which decomposed at 207° (cor.) and were devoid of optical activity in pyridine solution. These properties are in substantial agreement with those reported by Fischer⁶ for the racemic xylose phenylsazone which he obtained from D,L-xylose and also from the oxidation of xylitol.

Anal. Calcd. for C₁₇H₂₀O₅N₂: C, 62.18; H, 6.14. Found: C, 62.30; H, 6.13.

L-Xylose Phenylsazone Triacetate.—This compound was obtained in a yield of 0.672 g. (97%) by acetylation of L-xylose phenylsazone (0.5 g.) in a mixture of 3 cc. of pyridine and 2 cc. of acetic anhydride. The substance was recrystallized by solution in 12 parts of alcohol and the gradual addition of 8 parts of water. It was obtained in fine yellow needles which melted at 116–117° (cor.) and rotated +44.3° (*c*, 0.34) in chloroform. Percival and Percival⁸ reported a melting point of 116–117° and a specific rotation $[\alpha]^{16}_D$ of –46° for the D-form. We find a melting point of 116–117° (cor.) and a specific rotation $[\alpha]^{20}_D$ of –44.2° (*c*, 0.47) for D-xylose phenylsazone triacetate.

Racemic Xylose Phenylsazone Triacetate.—A mixture of 100 mg. each of the D- and L-forms of xylose phenylsazone triacetate was dissolved in 2 cc. of warm alcohol; upon addition of 1 cc. of water the racemate deposited from the solution in the form of fine yellow needles. The yield was 165 mg. (82%). The recrystallized compound was

(5) Isbell, *J. Research Natl. Bur. Standards*, **13**, 515 (1934).

(6) Fischer, *Ber.*, **27**, 2488 (1894).

(7) Reichstein, Grüssner and Oppenauer, *Helv. Chim. Acta*, **16**, 1024 (1933).

(8) Percival and Percival, *J. Chem. Soc.*, 1320 (1937).

devoid of optical activity in chloroform solution; it melted at 131–132° (cor.), which is much higher than the melting point of its components, from which fact it is evident that the crystalline substance is a true racemate.

Summary

D-Sorbitol, in solution with 4 *N* hydrochloric acid and *one* molecular equivalent of benzaldehyde, condenses to yield principally a cryptocrystalline dibenzylidene-D-sorbitol melting at 219–221°. The latter substance, upon oxidation with lead tetraacetate in glacial acetic acid, produces formaldehyde and aldehydo-2,3,4,5-dibenzylidene-L-xylose, which is conveniently isolated as a crys-

talline methyl hemiacetal. This hemiacetal is converted by acid hydrolysis to L-xylose, which was isolated as the crystalline sugar and further characterized by preparation of L-xylose phenylosazone; the latter compound combines with D-xylose phenylosazone to yield the long known racemic xylose phenylosazone. Also, L-xylose phenylosazone triacetate forms a true racemate with D-xylose phenylosazone triacetate.

The work constitutes a definitive proof that the structure of dibenzylidene-D-sorbitol is that of 1,2,3,4-dibenzylidene-D-sorbitol.

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The Action of Alkali on Cyclohexenecarbonals¹

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Although the cyclohexenecarbonals possess alpha hydrogens, one might reasonably expect reactions like those of the aromatic series toward alkaline reagents, because of the steric effect of the large radical attached to the alpha carbon. In order to test this supposition, we have investigated the reactions with several 3-cyclohexenecarbonals, particularly the 3,4,6-trimethyl derivative. Concentrated aqueous solutions of sodium or potassium hydroxide acted on this aldehyde forming a tripolymer. Similar tripolymers of cyclohexanecarbal and of 3-cyclohexenecarbal had previously been prepared by the action of mineral acids.² Saturated aqueous solutions of barium hydroxide gave very small yields of the polymer, most of the aldehyde being recovered. A cold 10% solution of potassium hydroxide in methyl alcohol was also without action on the aldehyde. At 70°, using a methyl alcohol-water solution, reaction took place with the formation of the corresponding acid and the alcohol. The acid had previously been prepared from ethyl crotonate and 2,3-dimethylbutadiene.³ The structure of the alcohol was shown by its synthesis from the aldehyde using aluminum *isopropoxide*, and by carbon and hydrogen analyses of the naphthyl urethan.

(1) This work is part of the thesis material to be submitted by Mr. Gallagher to the graduate faculty of the University of Missouri.

(2) Wallach, *Ann.*, **347**, 336 (1906); Zelinsky and Gutt, *Ber.*, **40**, 3051 (1907); Chayanov, *J. Gen. Chem.* (U. S. S. R.), **8**, 460 (1938).

(3) Farmer and Pitkethly, *J. Chem. Soc.*, 11 (1938).

Under similar conditions, 3,4-dimethyl-6-phenyl-3-cyclohexenecarbal, 6-methyl-3-cyclohexenecarbal, and 3-cyclohexenecarbal were found to give the Cannizzaro reaction. In all cases the acids formed were known compounds⁴ but the alcohols had not previously been reported. These were identified by their syntheses from the aldehydes using aluminum *isopropoxide*, and analyses of their phenyl or naphthyl urethans. Yields of the pure acids were of the order of 80%. Varying amounts of polymerization products were obtained if the temperature of reaction was much in excess of 70°.

Freshly distilled 6-methyl-3-cyclohexenecarbal gave but a trace of reaction in the usual reaction time, while aldehyde used after long standing, or through which air had been bubbled, readily entered into the reaction. This is in accord with the observation that peroxide is a catalyst for the Cannizzaro reaction.⁵

Each of the aldehydes was dissolved in aqueous methyl alcohol and heated to approximately 70° with potassium hydroxide and formalin solution. Diols, in yields of from 50 to 60% of the pure redistilled or recrystallized compounds, were obtained in all cases. The formation of these compounds presumably follows the course indicated by the equation

(4) Fujisi, Horiuchi, and Takahashi, *Ber.*, **69**, 2102 (1936); Chayanov and Grishiu, *Colloid J.* (U. S. S. R.), **3**, 461 (1937); Perkin, *J. Chem. Soc.*, **85**, 416 (1904).

(5) Kharasch and Foy, *THIS JOURNAL*, **57**, 1510 (1935).