cis-9-Keto-*as*-octahydrophenanthrene yields two secondary alcohols, m. ps. 116° and 133°. The isomeric *trans*-ketone also yields two epimeric alcohols, m. ps. 91° and 101°.

Hydrogenation of *cis*-9-keto-*as*-octahydrophenanthrene over platinum in alcohol gives *cis-syn-cis*-perhydro-9-phenanthrol and the two octahydro alcohols. Hydrogenation of *cis-as*-octahydro-9-phenanthrol gave the same *cis-syn-cis*-perhydro alcohol. When the *cis-syn-cis*-perhydro alcohol was oxidized by chromic acid at 0–25° it yielded *cis-syn-cis*-9-keto-perhydrophenanthrene. However, when the same oxidation was completed at 100° the product was the isomeric ketone with the *trans-syn-cis* configuration, presumably identical with a ketone isolated by Marvel and coworkers. The inversion of the *cis-syn-cis* ketone has been studied and is correlated with that of *cis-α*-decalone.

The *cis-syn-cis*-perhydro alcohol and ketone were oxidized by nitric acid to *cis-syn-cis*-perhydrodiphenic acid. The *trans-syn-cis* ketone yielded *cis-syn-trans*-perhydrodiphenic acid on nitric acid oxidation and a new perhydro alcohol on catalytic hydrogenation.

Three forms of the perhydrophenanthrene ring have therefore been made and oriented.

Pure *trans*-2-phenylcyclohexaneacetic acid has been obtained, m. p. 114°. When heated to 200°, 2-phenylcyclohexylidenecyanoacetic ester spontaneously cyclizes to tetrahydro-10-cyano-9-phenanthrol.

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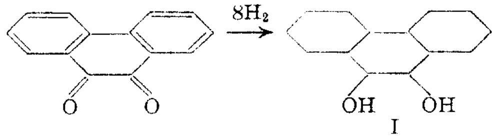
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Stereochemistry of Catalytic Hydrogenation. VII. The Complete Hydrogenation of Phenanthraquinone

BY R. P. LINSTEAD AND PHILIP LEVINE

The catalytic hydrogenation of 9,10-phenanthraquinone has already been investigated by von Braun and Bayer[1] and by Skita,[2] but they did not succeed in bringing about the complete hydrogenation of the molecule. Skita observed a reduction over colloidal platinum to *sym*-decahydro-9,10-dihydroxyphenanthrene (II). von Braun and Bayer, working with a nickel catalyst at high temperatures, also observed a preferential hydrogenation of the lateral rings, but their products suffered a partial or complete removal of the oxygen atoms.



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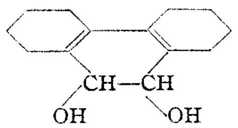

II

We find that phenanthraquinone can be completely hydrogenated both over platinum at room temperature and over Raney nickel at 160° without loss of oxygen. Eight molecular proportions of hydrogen are taken up and the products are perhydro-9,10-dihydroxyphenanthrenes (I). Four beautifully crystalline stereoisomers of this structure have been obtained.

When the hydrogenation was carried out under about 4 atmospheres pressure over Adams platinum oxide in acetic acid solution, a homogeneous glycol, m. p. 174°, was obtained. Over Raney nickel in ethanol at 160° and about 170 atmospheres the reaction yielded principally two isomeric glycols, melting at 174 and 155°, respectively, together with a very small amount of a fourth isomer of m. p. 184°. The glycol of m. p. 174° obtained over nickel differed in crystalline form from that of the same m. p. obtained by the use of platinum, depressed its melting point, and gave a different dibenzoate. All the four products gave analyses corresponding to the perhydroglycol structure, $C_{14}H_{24}O_2$, and yielded distinct dibenzoates. They gave positive Criegee tests for 1,2-glycols.[3]

Corresponding to the six inactive stereoisomeric forms of the fundamental perhydrophenanthrene skeleton[4] there are twenty inactive 9,10-glycols. Each of the *cis-cis* and *trans-trans*

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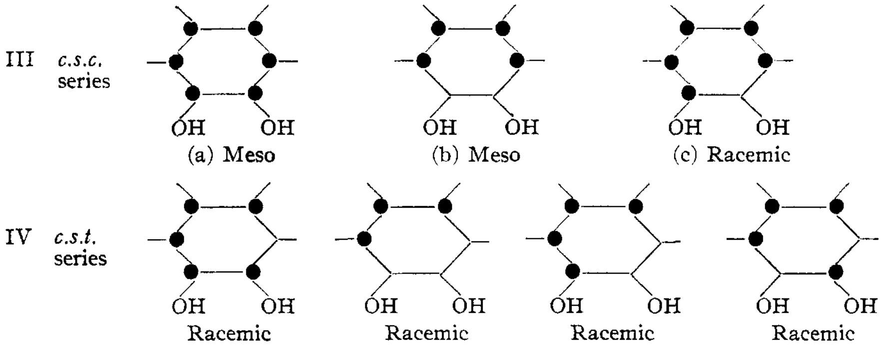
[1] von Braun and Bayer, *Ber.*, **58**, 2667 (1925).

[2] Skita, *ibid.*, **58**, 2685 (1925).

[3] Criegee, *ibid.*, **64**, 260 (1931).

[4] Linstead and Walpole, *J. Chem. Soc.*, 842 (1939); Linstead, Whetstone and Levine, THIS JOURNAL, **64**, 2014 (1942).

forms (*i. e.*, the *cis-syn-cis*, *cis-anti-cis*, *trans-syn-trans* and *trans-anti-trans* configurations) can give rise to *three* glycols (see III below). The remaining two perhydrophenanthrene structures (*cis-syn-trans* and *cis-anti-trans*) can give rise to four glycols each. The extra isomer comes from the fact that both when the two hydroxyl groups are *cis* and when they are *trans*, two forms are possible (see IV below). These possibilities are outlined below for the cases of the *cis-syn-cis* and *cis-syn-trans* series. Only the central ring is shown, for brevity.



[The dots represent hydrogen atoms *above* the plane of the ring.[4]]

To determine the configuration of the perhydrophenanthrene skeleton, the oxidation of the four glycols to the corresponding perhydrodiphenic acids was studied. The configurations of the latter are known.[5] The following reagents were successful for this purpose: lead tetraacetate, potassium periodate, Beckmann's mixture, chromic and acetic acids, and peracetic acid. The following reagents failed: potassium permanganate, nitric acid and potassium hypobromite. In no case was the yield particularly good. The same product was obtained from the three easily obtained glycols (Pt 174°, Ni 174°, Ni 155°). This was the *cis-syn-cis*-perhydrodiphenic acid, m. p. 289°,[6] and in each case was identified by direct comparison and by conversion into the dimethyl ester, m. p. 73°.

It is thus established that these three glycols have the same skeletal configuration and differ only in the orientation of the hydroxyl groups. They therefore correspond with the three formulas III (a), (b), and (c) given above, and all the possible members of this series (*c.s.c.*) have been prepared.

The rare glycol, m. p. 184°, obtained in small amount from the hydrogenation over nickel, was oxidized by chromic and acetic acids to *cis-syn-trans*-perhydrodiphenic acid,[5,6] m. p. 198–200° This was further identified by conversion into the anhydride,[6] m. p. 104°.

As far as the evidence from the isolated products is concerned, therefore, it may be deduced that phenanthraquinone is hydrogenated *cis-syn-cis* over platinum, and almost completely *cis-syn-cis* over nickel. A small amount of *cis-syn-trans* hydrogenation occurs under the conditions of our experiments over the latter catalyst.

In view of the work of Tiffeneau[7] (compare Bartlett[8]) on cyclohexane-1,2-diols, it appeared that it might be possible to dehydrate the glycols obtained from phenanthraquinone into 9-ketoperhydrophenanthrenes. For example, Tiffeneau has shown that *cis*-cyclohexane-1,2-diol yields cyclohexanone when its vapor is passed over alumina at 250–300°. Attempts were therefore made to carry out a parallel dehydration of the reduction products of phenanthraquinone, using both activated alumina and a precipitated alumina catalyst prepared according to Adkins and Krause.[9] In all cases the yield of carbonyl compound was very low. A positive test was obtained by means of Brady's reagent but no oxime or semicarbazone could be isolated. Neither could a ketone be obtained by dehydration with potassium bisulfate, and further experiments in this direction were abandoned.

When the hydrogenation of phenanthraquinone over Raney nickel was carried out at a temperature of 120°, the main product was an incompletely hydrogenated glycol, apparently identical with that of Skita,[2] to which he assigns the decahydro-9,10-dihydroxyphenanthrene structure (II).

Experimental[10]

Phenanthraquinone.—For the purpose of hydrogenation, the quinone was prepared and purified as follows.[11] To a

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(5) Linstead and Doering, THIS JOURNAL, **64**, 2003 (1942).

(6) Linstead and Doering, *ibid.*, **64**, 1991 (1942); Linstead and Walpole, *J. Chem. Soc.*, 850 (1939).

(7) Tiffeneau and Tchoubar, *Compt. rend.*, **199**, 1624 (1934); **202**, 1931 (1936).

(8) Bartlett and Rosenwald, THIS JOURNAL, **56**, 1990 (1934).

(9) Adkins and Krause, *ibid.*, **44**, 385 (1922).

(10) All melting points are corrected, unless otherwise stated.

(11) Compare Oyster and Adkins, THIS JOURNAL, **43**, 208 (1921).

hot mixture of 500 cc. of concentrated sulfuric acid and 1500 cc. of water in a 4-l. beaker, 100 g. of crude phenanthrene was added. Potassium dichromate (300 g.) was then added slowly with mechanical stirring and the mixture subsequently stirred for one hour. The product was diluted to *ca.* 4 l. and the crude quinone collected and washed. The products from two such reactions were united and re-oxidized using 1300 cc. of water, 500 cc. of sulfuric acid and 350 g. of potassium dichromate. The final product was worked up as before and dried, yield 185 g. from 200 g. of crude phenanthrene.

This crude quinone was purified through the bisulfite addition product, by heating 75 g. with 1500 cc. of saturated sodium bisulfite solution. The product was filtered and decomposed with an excess of a concentrated aqueous solution of sodium hydroxide. This regenerated phenanthraquinone (58 g.) which was filtered, washed and crystallized from acetic acid (charcoal), yield 47 g., m. p. 205–207°. As a further precaution, in the case of the hydrogenation over platinum, the quinone was again recrystallized from xylene–acetic acid, and from acetic acid before hydrogenation.

Hydrogenation over Platinum.—The quinone (7.5 g.) in 190 cc. of acetic acid was shaken with 1 g. of Adams platinum oxide under about 4 atmospheres of hydrogen. At first the pressure fell very rapidly, and the orange color changed to a blue fluorescence. The reaction later became slower and an additional gram of catalyst was added on the second day. The theoretical amount of hydrogen was taken up on the fifth day. On exposure to air the resulting solution turned yellow and then a deep red. Removal of the solvent left an intensely red residue, which on crystallization from either benzene or toluene gave colorless crystals (2.3 g.). After several crystallizations from toluene α-*cis-syn-cis*-**perhydro-9,10-dihydroxyphenanthrene** was obtained as bold colorless needles, m. p. 173.9–174.4°.

Anal. Calcd. for $C_{14}H_{26}O_2$: C, 74.93; H, 10.80. Found: C, 74.92; H, 10.79.

A mixture of 0.3 g. of the α-glycol, 4 cc. of dry pyridine and 0.6 cc. of benzoyl chloride was heated at 50° for one week. The mixture was poured into dilute acid and extracted with chloroform. The extract was washed with aqueous sodium carbonate and with water, warmed with charcoal, and dried with sodium sulfate. The solvent was removed and the residue crystallized from hexane. The yield of the α-**dibenzoate** was 0.5 g., m. p. 153.5–154°.

Anal. Calcd. for $C_{28}H_{32}O_4$: C, 77.71; H, 7.46. Found: C, 77.40; H, 7.53.

Hydrogenation over Nickel.—A preliminary experiment indicated that at 110° and 80 atmospheres, the hydrogenation of phenanthraquinone over Raney nickel came to a stop after about two hours when about 60% of the theoretical amount of hydrogen had reacted. This would correspond approximately to the formation of Skita's compound (II) which involves the reaction of 6 of the total 8 mols of hydrogen (75%). On raising the temperature to 160° the reaction was resumed and the full amount of hydrogen was taken up in just under two days.

The preparation was accordingly carried out as follows. A steel bomb of 1-l. capacity was charged with a mixture of 26 g. of pure phenanthraquinone, 150 cc. of absolute alcohol and 6 cc. of Raney nickel. The hydrogenation was allowed to proceed at 160° and 170 atmospheres and took nearly thirty-six hours. The resulting solution turned dark brown on exposure to air. It was diluted to about 200 cc. with alcohol and filtered hot through a column of charcoal and alumina. This removed almost all the color. The filtrate deposited 3.75 g. of crystals, m. p. 170–172°. Two crystallizations of this material from benzene yielded pure β-*cis-syn-cis*-**perhydro-9,10-dihydroxyphenanthrene,** m. p. 173.9–174.4°. The crystals are denser and more massive than those of the α-isomer. A mixture of the two compounds melts at 142–150°.

The filtrate from the above material was evaporated to 100 cc. and seeded with the β-glycol. This yielded a further 2.5 g. of nearly pure β-glycol. On further evaporation a little more β-glycol separated together with a second product which crystallized in large, clear prisms. These were separated partly mechanically and partly by taking advantage of the fact that the β-glycol dissolved faster in warm alcohol. The prisms melted at 148–152° and after three recrystallizations from benzene yielded the pure γ-*cis-syn-cis*-**perhydro-9,10-dihydroxyphenanthrene,** m. p. 154.5–155°.

The final residue from the fractional crystallizations was submitted to vacuum distillation. After removal of a viscous liquid boiling up to 180° (8 mm.) (which is probably partially de-oxygenated), the main portion distilled at 198–200° and set to a glassy solid. Crystallization of this from benzene with suitable seeding yielded more of the β- and γ-glycols.

The fraction boiling between 180 and 198° was mixed with hexane and allowed to stand. A crystalline solid was slowly deposited. The first crop was recrystallized from benzene. The crystals so obtained (60 mg.) melted at 179–183° and after two further crystallizations from benzene gave pure α-*cis-syn-trans*-**perhydro-9,10-dihydroxyphenanthrene,** long clear prisms, m. p. 184–184.5°. Further fractional crystallization of the remainder of the material led to the separation of more of all three forms (β- and γ-*cis-syn-cis*, m. p.'s 174 and 155°, and α-*cis-syn-trans*, m. p. 184°).

The total yield of crystalline glycols was 7.54 g. of the β-form, m. p. 174°, 3.96 g. of the γ-form, m. p. 155°, and 138 mg. of the *cis-syn-trans* form, m. p. 184°.

Anal. Calcd. for $C_{14}H_{24}O_2$: C, 74.93; H, 10.80. Found—for the β-glycol: C, 74.86; H, 10.94; for the γ-glycol: C, 75.05; H, 10.91; for the *cis-syn-trans*-glycol[12]: C, 74.81; H, 10.56.

By the method described above for the α-glycol, the β- and γ-glycols were converted into their dibenzoates. These melted at 115.5–116° (β), and 114.2–115° (γ), respectively. A mixture melted at 102–106°.

Anal. Calcd. for $C_{28}H_{32}O_4$: C, 77.71; H, 7.46. Found— for the β-dibenzoate: C, 77.46; H, 7.55; for the γ-dibenzoate: C, 77.50; H, 7.53.

Oxidation of the Glycols. (a) α-*cis-syn-cis*-**Glycol (m. p. 174°).**—This glycol (500 mg.) and 1.20 g. of lead tetraacetate were added to 50 cc. of benzene. The solid gathered in a lump which was crushed. After a few minutes the product was filtered and the insoluble solid washed with benzene. The filtrate and washings were freed from

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(12) Analysis by Miss Eleanor Werble.

solvent and the oily residue was allowed to stand for two days at 4° with 3 cc. of 33% hydrogen peroxide and 5 cc. of 10% aqueous sodium hydroxide. The product was extracted with ether and the aqueous layer acidified. This precipitated a gummy mass, which was boiled with benzene and the insoluble portion crystallized from alcohol. This yielded *cis-syn-cis*-perhydrodiphenic acid (10 mg.), m. p. 273–280°, mixed m. p. 280–285°. The acid was further identified by conversion into the dimethyl ester, m. p. 69–71°, mixed m. p. 71–73°.

An attempt at the oxidation of the same glycol with potassium permanganate in acetone and with nitric acid at 50° failed to yield a solid acid.

(b) ***β-cis-syn-cis*-Glycol (m. p. 174°).**—The glycol (500 mg.) was dissolved in 50 cc. of hot benzene and the solution treated at 34° with 1.25 g. of lead tetraacetate. A very small temperature rise occurred. The mixture was allowed to stand overnight, filtered and the filtrate treated with alkaline hydrogen peroxide as described above. *cis-syn-cis*-Perhydrodiphenic acid was isolated in the manner already described, yield 30 mg., m. p. 275°, mixed m. p. 280°. The dimethyl ester had m. p. 72–73°, mixed m. p. 73–74°.

The same glycol (250 mg.) was shaken with potassium periodate (230 mg.) and dilute methanol, and then left at 55° overnight. Most of the methanol was removed, a solution of bromine in potassium hydroxide was added, and the product was extracted with ether. Acidification of the alkaline solution gave 40 mg. of acid melting at about 250°, and after one crystallization at 260–267°.

The *β*-glycol (300 mg.) was dissolved in acetic acid (10 cc.) and a solution of 900 mg. of chromic acid in a little water was added slowly. The solution was divided in half. The first half was allowed to stand at 0° for two hours, and the second half was kept at 75° for the same time. On dilution with water both portions gave *cis-syn-cis*-perhydrodiphenic acid [m. p. (crude) 275–277°] but the yield from the cold oxidation (30 mg.) was twice that from the reaction at 75°.

A very small yield of the same acid was obtained by oxidizing the *β*-glycol with Beckmann's mixture. No solid acid could be isolated by oxidations from potassium hypobromite.

(c) ***γ-cis-syn-cis*-Glycol (m. p. 155°).**—The glycol (100 mg.) was suspended in 1 cc. of acetic acid and a solution of chromic acid (120 mg.) in 2 cc. of dilute acetic acid was added during one hour at room temperature. The product was warmed on the steam-bath for five minutes. Addition of 10 cc. of water precipitated 18 mg. of *cis-syn-cis*-perhydrodiphenic acid, m. p. 270–274°. The identity was confirmed by the preparation of the dimethyl ester, m. p. 67–70°, mixed m. p. 70–72°.

The same acid was obtained by the oxidation of the 152° glycol (109 mg.) with peracetic acid (1.5 g. of 11.2%) for two months at room temperature. Evaporation of the solvent left a gum and a small amount of crystalline solid. The gum was removed by washing with cold benzene. There remained 5 mg. of *cis-syn-cis*-perhydrodiphenic acid, which was identified by m. p. and mixed m. p. Oxidation of the *γ*-glycol with lead tetraacetate or with potassium periodate did not yield a crystalline acid.

(d) ***α-cis-syn-trans*-Glycol (m. p. 184°).**—The glycol (100 mg.) was dissolved in glacial acetic acid (4 cc.) and a solution of 130 mg. of chromic acid in 1 cc. of acetic acid and 1 cc. of water was added slowly. The solution was allowed to stand at 4° overnight, diluted to 20 cc. with water and extracted four times with 5-cc. portions of ether. The ether was extracted with aqueous sodium hydroxide and the alkaline extract acidified and again extracted with ether. The ether was removed and the residual acetic acid solution was diluted with water. This yielded 41 mg. of *cis-syn-trans*-perhydrodiphenic acid, m. p. 197.5–199.5°, either alone or in admixture with authentic material. The second crop of acid was identical and equally pure. The identity was confirmed by the preparation of the anhydride, m. p. and mixed m. p. 103–104°.

Dehydration of the Glycols.—The method used was essentially that of Tiffeneau.[7] None of the three *cis-syn-cis* glycols yielded a ketone in sufficient amount to permit of the isolation of an oxime or semicarbazone, although indications of a positive reaction with 2,4-dinitrophenylhydrazine were obtained.

The *γ*-glycol, m. p. 155°, (150 mg.) was heated with 600 mg. of fused potassium bisulfate for four hours at 150–160°. The product was partitioned between chloroform and water. Evaporation of the chloroform layer left a mixture of an oil and a crystalline solid, which was washed with cold methanol. The methanol solution gave a very small amount of an oxime in the cold; this melted at 190–200° without crystallization. The residual crystals were almost insoluble in boiling alcohol, but easily soluble in hexane and benzene. After three crystallizations from ethyl acetate a pure *compound* was isolated which analyzes to $C_{14}H_{22}O$, or a polymer of this. It melts at 202–203° and is not affected by bromine in chloroform. This last property and the high m. p. do not agree with the decahydro-9-phenanthrol structure suggested by the analysis. A bimolecular structure with two ethereal oxygen atoms is possible, but the solubility in hydrocarbons seems high for so large a molecule.

Anal.[12] Calcd. for $C_{14}H_{22}O$: C, 81.49; H, 10.75. Found: C, 81.53; H, 10.55.

***sym*-Decahydro-9,10-dihydroxyphenanthrene.**—Phenanthraquinone (3 g.) and 0.8 cc. of Raney nickel were treated with 20 cc. of alcohol and hydrogenated at 120°. Nearly exactly 5 mols of hydrogen was taken up. The resulting solution turned brown and later red in air. The solvent was removed under reduced pressure and the product crystallized from hexane. Fine white needles of the decahydro-glycol separated, m. p. 135–136° (Skita[2] gives m. p. 136°), yield 1.5 g. A mixture with *sym*-octahydro-9-phenanthrol (m. p. 135°) melted at 110–125°. Acetylation with sodium acetate and acetic anhydride gave a product of m. p. 160–161°. Skita[2] describes the diacetate as melting at 160°. Attempts to convert the decahydro-glycol to *sym*-octahydro-9-phenanthrol by means of potassium bisulfate and *p*-toluenesulfonic acid were unsuccessful. Oxidation of the decahydro-glycol with peracetic acid by Böeseken's method failed to yield an octahydrodiphenic acid.

Summary

The possibilities of stereoisomerism among the perhydro-9,10-dihydroxyphenanthrenes are indicated.

Phenanthraquinone is per-hydrogenated over platinum at 25° to a perhydro-9,10-dihydroxyphenanthrene, m. p. 174°, and over nickel at 160° to a mixture of three stereoisomers of the above, with m. p.'s 174° (not identical with the platinum product), 155 and 184°, respectively. The first three products have the *cis-syn-cis* configuration and may be oxidized to *cis-syn-cis*-perhydrodiphenic acid. The glycol of m. p. 184°, which is obtained in very small yield, has a *cis-syn-trans* configuration as it gives the *cis-syn-trans*-perhydrodiphenic acid on oxidation. The three *cis-syn-cis* glycols differ in the orientation of their hydroxyl groups and represent all the forms with this skeletal configuration which are theoretically possible. Over nickel at 120°, phenanthraquinone yields mainly Skita's decahydro-9,10-dihydroxyphenanthrene.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS RECEIVED APRIL 30, 1942

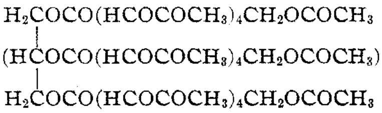
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

O-Pentaacetyl-*d*-gluconates of Polyhydric Alcohols and Cellulose[1]

BY M. L. WOLFROM AND P. W. MORGAN[2]

To our knowledge, only the methyl[3] and ethyl[4] esters of *d*-gluconic acid pentaacetate have been reported. The object of the present investigation was to prepare and characterize the O-pentaacetyl-*d*-gluconates of polyhydric alcohols and cellulose. Such esters were prepared from ethylene glycol, propanediol-1,3 (trimethylene glycol), bis-(2-hydroxyethyl) ether (diethylene glycol), glycerol, (*dextro*)-sorbitol, *d*-mannitol, α-methyl-*d*-glucoside, mercerized cotton linters and a modified cellulose acetate by reaction of these substances with an excess of *d*-gluconyl chloride pentaacetate in pyridine solution.

Ethylene glycol, propanediol-1,3 and bis-(2-hydroxyethyl) ether formed crystalline di-esters. Glycerol, (*dextro*)-sorbitol, *d*-mannitol and α-methyl-*d*-glucoside yielded fully esterified products in the form of colorless, amorphous powders. This lack of crystallizing power is not surprising, as the molecular weights of these esters are very high. Thus the ethylene glycol derivative has a molecular weight of 839 and the hexitol derivative ($C_{102}H_{134}O_{72}$, shown below) has a molecular weight of 2512.



$$\begin{array}{l} H_2COCO(HCOCOCH_3)_4CH_2OCOCH_3 \\ \;\;\;| \\ (HCOCO(HCOCOCH_3)_4CH_2OCOCH_3)_4 \\ \;\;\;| \\ H_2COCO(HCOCOCH_3)_4CH_2OCOCH_3 \end{array}$$

In the case of mercerized cotton linters, pyridine was found unsatisfactory as a reaction medium because the intense coloration developed by the acid chloride and pyridine, even at room temperature, was very strongly adsorbed on the fibers. Of several other tertiary bases tried as a substitute for pyridine in the reaction with cellulose, triethylamine in an inert solvent was found most satisfactory for the elimination of color. Using triethylamine as the base, a cream-colored, fibrous cellulose O-pentaacetyl-*d*-gluconate was obtained containing 0.45 O-pentaacetyl-*d*-gluconyl group per anhydroglucose unit. In pyridine, a modified cellulose acetate (1.72 acetyl group per anhydroglucose unit) yielded a mixed ester containing 0.75 O-pentaacetyl-*d*-gluconyl group per anhydroglucose unit, while with triethylamine in chloroform a product with 0.33 O-pentaacetyl-*d*-gluconyl groups was produced. The former was obtained as a cream-colored powder that was acetone and chloroform soluble and formed brittle films. The latter product was colorless, was acetone and chloroform soluble, and formed strong, flexible, transparent films.

Experimental

Preparation of the O-Pentaacetyl-*d*-gluconates of Several Polyhydric Alcohols.—The anhydrous polyhydric alcohol (0.5 g.) was dissolved in dry pyridine (50 cc.). Gluconyl chloride pentaacetate[4b] (9 g.) was quickly ground and added in approximately 1-g. portions to the solution with shaking. The mixture became warm and slowly turned deep orange in color. A crystalline water-soluble pyridine-complex separated after a few minutes. After standing overnight, the reaction mixture was diluted to incipient turbidity with water and the material crystallized. More water was added gradually until the volume was about 1 liter. This procedure was followed for the

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[1] Presented in essentially the present form before the Division of Cellulose Chemistry at the 101st Meeting of the American Chemical Society, St. Louis, Missouri, April 9, 1941.

[2] Du Pont Cellulose Research Fellow.

[3] G. B. Robbins and F. W. Upson, THIS JOURNAL, **62**, 1076 (1940).

[4] (a) F. Volpert, *Ber.*, **19**, 2622 (1886); (b) R. T. Major and E. W. Cook, THIS JOURNAL, **58**, 2474, 2477 (1936).