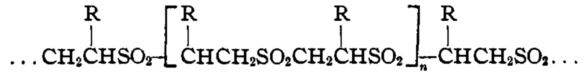
Summary

1. Those polysulfones prepared from sulfur dioxide and olefins, which dissolve in liquid ammonia, are converted by this treatment into cyclic disulfones.
2. Styrene (phenylethylene) adds sulfur dioxide to give a polysulfone.
3. Evidence is presented to show that polysulfones prepared from olefins of the type $RCH=CH_2$ have the general formula



$$\ldots CH_2\overset{R}{C}HSO_2-\left[\overset{R}{C}HCH_2SO_2CH_2\overset{R}{C}HSO_2\right]_n-\overset{R}{C}HCH_2SO_2\ldots$$

in which like parts of the hydrocarbon residues are joined to each other by sulfone linkages.

URBANA, ILLINOIS RECEIVED JANUARY 29, 1937

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Studies in the Ketone Sugar Series. VI. The Effect of Zinc Chloride on Ketose Acetates

BY FRANCIS B. CRAMER[1] AND EUGENE PACSU

In preparing new sugar derivatives for testing the isorotation rules in the aldose group, Hudson and co-workers have made extensive use of zinc chloride dissolved in acetic anhydride as a reagent in converting the β-acetates into the α-forms. An earlier physico-chemical investigation of the process by Jungius[2] showed that in the case of glucose pentaacetates equilibrium was reached when the proportion was nine moles of the α- to one mole of the β-form. In the case of most aldose acetates the equilibrium contains the two forms in similar proportion. Exceptions are found in the pentaacetates of galactofuranose[3] and galactoseptanose[4] where the equilibrium is in favor of the β-isomers. In 1915, Hudson and Brauns[5] attempted to apply this method to β-pentaacetylfructose. When zinc chloride was added to a solution of this substance in acetic anhydride, only a very small change in rotation was observed whereas a large one was anticipated. Since some coloration occurred, the authors evidently ascribed the change in rotation to slight decomposition and after recovering about one-third of the starting material and conducting confirmatory experiments, concluded that the method was not applicable in the ketose series. It has now been discovered that the small change in rotation observed by Hudson and Brauns was due to the formation of the new isomer described in Part V[6] as the true α-pentaacetylfructopyranose.

The structure of β-pentaacetylfructose is generally accepted as that of a normal acetate possessing a $<2,6>$ ring. The evidence leading to this conclusion is extensive and will not be reviewed here. To establish the structure of the new fructose acetate as the normal α-pentaacetate, it would be sufficient to show that it differs from the known β-compound only in the configuration of carbon atom 2. If this glycosidic carbon atom were selectively inverted, the β-pentaacetate should result.

When a trace of zinc chloride was added to the acetic anhydride solution of the new fructose acetate, the rotation dropped rapidly, changing sign, and within a few minutes became constant at $-107°$. From the rotations of α- and β-pentaacetylfructose in acetic anhydride (42.3 and $-122°$, respectively) it may be calculated that the equilibrium mixture contained 91% of the β-form. When the solution was worked up a large amount of β-pentaacetylfructose was obtained.

Similarly, when pure β-pentaacetylfructose was treated with zinc chloride in acetic anhydride after the manner of Hudson and Brauns,[5] the rotation again became $-107°$. On carefully working up this mixture, a small amount of the α-compound was isolated in pure form.

This interconversion of the two acetates gives definite proof that the new compound is the true α-pentaacetylfructose $<2,6>$. Supporting evidence is afforded by the method of preparation, both α- and β-pentaacetates being formed simultaneously by replacing the chlorine atom in β-acetochlorofructose with the acetoxyl radical. In

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[1] This paper is based upon a thesis submitted by Francis B. Cramer to the Faculty of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Jungius, *Z. physik. Chem.*, **52**, 101 (1905).

[3] Hudson and Johnson, THIS JOURNAL, **37**, 1519 (1915).

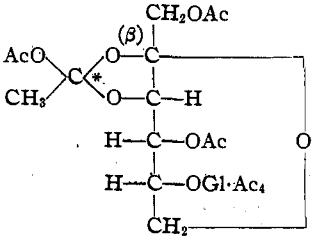
[4] Micheel and Suckfüll, *Ann.*, **502**, 85 (1933).

[5] Hudson and Brauns, THIS JOURNAL, **37**, 2736 (1915).

[6] Pacsu and Cramer, *ibid.*, **57**, 1944 (1935).

addition, both isomers are reconverted into the starting material by treatment with titanium tetrachloride in chloroform solution. The structure of the new pentaacetate is thus established.

The discovery of the effect of zinc chloride in acetic anhydride solution upon the acetates of fructose suggested the application of this isomerization to the acetates of other ketoses. In Part I,[7] there have been described four isomeric octaacetates of turanose which are referred to by giving the ordinal number of their sequence in discovery. The third octaacetate has been shown in Part III[8] to have an open-chain structure. Since this compound can possess no α- or β-isomer, it holds no interest in connection with the action of zinc chloride. The first and fourth octaacetates have been described as representing a pair of isomeric orthoester acetates which differ only in the configuration of the newly formed asymmetric carbon atom C* (I). This carbon atom is not part of the turanose skeleton and both compounds have been regarded as derivatives of β-turanose. The second octaacetate (II) has been *assumed* to be an α-derivative of turanose with a normal <2, 6> ring in the fructose residue.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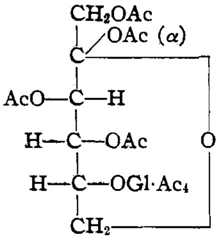
II

When the solution of the second octaacetate in acetic anhydride was treated with zinc chloride at room temperature, a rapid though small change in rotation from the original value of 106.5° to the equilibrium value of 98° was observed. Although this equilibrium can scarcely be regarded as favorable, an attempt was made to prepare the expected new acetate by this method. Out of 10 g. of the second octaacetate 7 g. of pure starting material was recovered. The residual sirup could not be brought to crystallization. The rotation of this material was 63.1° in acetic anhydride, indicating a considerable concentration of the expected β-compound. Treatment of the sirup on the steam-bath with acetic anhydride and sodium acetate produced no change in the rotation of the material. However, when the sirup dissolved in acetic anhydride was treated with zinc chloride at room temperature, the rotation rose almost immediately to the equilibrium value of 98°. Upon working up the solution and recrystallizing the product, the pure second octaacetate was obtained in good yield.

The above evidence indicates definitely that a fifth octaacetate of turanose of β-configuration exists. The position of the equilibrium with zinc chloride as well as several other facts[7] sharply differentiate the behavior of the turanose acetate under consideration from that of the normal α-pentaacetylfructose. The structure of the second octaacetate of turanose may, therefore, be regarded as still open to investigation.

Attention may now be turned to the first and fourth octaacetates of turanose (I) which have been characterized in Part I[7] as a diastereomeric pair having orthoester structure. The first has the low positive rotation of 20.5°. The other has a positive rotation of 103.2°. When this higher-rotating isomer was treated with zinc chloride in acetic anhydride solution, the rotation dropped rapidly to 40° indicating the formation of an equilibrium mixture containing 87% of the first octaacetate which was isolated easily from the reaction mixture. This bears a striking resemblance to the behavior of the normal pentaacetates of fructose under like conditions, where the positive-rotating α-compound is converted 90% into the negative-rotating β-compound. Indeed, comparison of these two pairs of ketose acetates reveals much similarity and little difference.

The lower-rotating acetates may be converted[7,9] into the corresponding β-acetohalogeno compounds, and the latter react with a metal acetate to give the higher-rotating acetates.[6,7] These higher-rotating acetates when treated according to standard methods give the original β-acetohalogeno compounds as sole products.

Further facts for comparison now appeared highly desirable. The problem is more difficult because no test for orthoester structure in the case of sugar acetates is available. The conversion of these acetates to glycosides where orthoester structure can be proved may involve unpredictable changes in structure.[10]

Attention was directed to the acetohalogeno compounds as the only derivatives which are

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[7] Pacsu, This Journal, **54**, 3649 (1932).

[8] Pacsu and Rich, *ibid.*, **55**, 3018 (1933).

[9] Brauns, *ibid.*, **42**, 1846 (1920).

[10] Pacsu, *ibid.*, **55**, 2451 (1933).

prepared directly from the acetates. It is known that acetobromoturanose reacts with methyl alcohol and silver carbonate to give an orthoester glycoside acetate.[10] When similarly treated, acetobromofructose also yielded an orthoester glycoside acetate. Some of Schlubach's normal α-tetraacetylmethylfructoside was simultaneously formed, exactly as when acetochlorofructose was used.[11]

It has been reported in Part I[7] that acetobromoturanose undergoes a marked change when dissolved in pyridine. The observed rotation, at first negative (−3.1°), becomes strongly positive (6.3°) where it remains constant. When a stronger solution is prepared, it soon turns to a jelly, the latter shortly becoming a clear solution again. The aged solution acquires the ability to reduce an acetone solution of potassium permanganate very rapidly. This reaction was assumed to be due to the formation of a ketene-acetal which would have definitely indicated orthoester structure for the acetobromoturanose. It has now been found that this behavior is closely paralleled by a solution of acetobromofructose in pyridine. A large drop of the highly negative rotation almost to zero was observed and the solution acquired the ability to reduce an acetone solution of potassium permanganate with great rapidity.

Acetochlorofructose has been shown to undergo no change when dissolved in pyridine.[11] The same behavior was displayed by acetochloroturanose. Attempts to prepare the pyridinium salts of the acetochloro compounds by the method of Fischer[12] resulted in the recovery of unchanged starting material.

A correct interpretation of the experimental results enumerated above is not an easy matter. The use of Hudson's rules provide two apparent facts to start with. These facts are, first, α- and β-pentaacetylfructose do not possess orthoester structure and, second, the first and fourth octaacetates of turanose do not possess the same structures as the fructose acetates.

The first conclusion follows from the fact that the value for $b_{\text{fruct. Ac.}}$ can be used to calculate the rotations of the methyl- and ethylfructoside acetates. These latter compounds are of normal structure and have properties sharply differentiating them from the known methyl- and ethylfructoside acetates of orthoester structure.[11]

The second conclusion follows from the fact that it is impossible by means of the customary mathematical manipulation of the rotations of turanose octaacetates to obtain a value for a_{OAc} which would agree satisfactorily with the value of a_{OAc} calculated from the α,β pair of fructose pentaacetates <2, 6>. It may, therefore, be concluded that the glycosidic portion of the turanose acetate molecule possesses a fundamentally different structure from that of the glycosidic portion of the fructose acetates.

At present, only two types of structure about the glycosidic carbon atom of the acetylated sugars are recognized, these being the normal and the orthoester structures. Unfortunately, as stated above, it is not possible to determine by any chemical or physical means whether a sugar acetate possesses an orthoester structure or a normal structure. The only conclusion, therefore, is that the acetates of fructose possess normal structures and the first and fourth acetates of turanose have orthoester structures. Careful consideration of the behavior of the acetohalogeno compounds derived from these acetates reveals little or nothing concerning the structures of the parent acetates. On the basis of Hudson's rules, the similarity between the pairs of turanose octaacetates and fructose pentaacetates which has been mentioned earlier must be regarded as coincidental until new contradictory evidence is discovered.

Experimental Part

Action of Zinc Chloride on the Pentaacetates of Fructose.—The specific rotation[13] of α-pentaacetylfructose in pure acetic anhydride was found to be 42.3°. In 20 cc. of distilled acetic anhydride was dissolved 0.3132 g. of this substance and the solution was made up to 25 cc. with a solution of 0.1 g. of fused zinc chloride in 20 cc. of the same solvent. The following specific rotations were observed after 54, 85, and 270 seconds, respectively: 12, −10.4, and −71.5°. After twenty minutes the rotation remained constant at −107°. Two and eight-tenths grams of pure α-pentaacetylfructose was treated similarly and the equilibrated solution was evaporated to a sirup *in vacuo*, the residue taken up in chloroform, and washed with sodium bicarbonate solution until neutral. The chloroform solution was then dried with calcium chloride, filtered, and evaporated to a thin sirup *in vacuo*. This was taken up in absolute ether and placed in the ice box. After separation as described in Part V[8] and recrystallization, 1.9 g. of β-pentaacetylfructose and 0.028 g. of the original α-pentaacetate were isolated in pure form.

Ten grams of pure β-pentaacetylfructose was dissolved by heating in 10 cc. of distilled acetic anhydride. To the

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(11) Pacsu, THIS JOURNAL, 57, 745 (1935).

(12) Fischer, *Ber.*, 43, 1750 (1910).

(13) Unless otherwise indicated, the rotations here recorded were measured at 20°, using light of the wave length of the sodium D lines, and chloroform as solvent.

cooled solution was added 0.1 g. of fused zinc chloride dissolved in 5 cc. of the same solvent. After standing for half an hour at room temperature, the solution was poured into cracked ice and triturated with ice water until the gummy residue solidified. This was filtered off, washed and dried. Seven grams of material having the specific rotation −113° was obtained. The acidic aqueous mother liquor and washings were combined, neutralized with sodium bicarbonate, and placed in the ice box, when 1.9 g. of material having the specific rotation −97.3° separated. The aqueous mother liquor of this was extracted three times with chloroform, the extracts combined, dried with calcium chloride and evaporated *in vacuo*. The residual sirup was taken up in absolute ether and placed in the ice box. The solution deposited 0.7 g. of sticky crystals which had the rotation −96.6°. Upon working up the three crystalline fractions as before, 7.2 g. of pure starting material was recovered, and 0.2 g. of α-pentaacetylfructose was isolated in pure form.

Action of Zinc Chloride on the Second Octaacetate of Turanose.—The specific rotation of the second octaacetate of turanose in acetic anhydride was found to be 106.5°. A 0.2656-g. sample of this material was dissolved in 20 cc. of distilled acetic anhydride. The solution was made up to 25 cc. using a solution of 0.1 g. of fused zinc chloride in 20 cc. of the same solvent. Four minutes after mixing the specific rotation had fallen to 101°. In thirty minutes the rotation became 98° and remained constant at that value. Ten grams of the pure second octaacetate was now dissolved in 50 cc. of distilled acetic anhydride by warming on the steam-bath. To the cooled solution was added 0.1 g. of fused zinc chloride dissolved in 10 cc. of the same solvent. In thirty minutes the rotation of the solution became constant. After an additional half hour, the mixture was poured into 400 g. of crushed ice. After three hours of intermittent stirring, the material was left overnight in the ice box, the suspension of white powder was filtered and washed with water. The dried solid was taken up in 25 cc. of absolute ether and placed in the ice box where it crystallized; yield 7.4 g., and specific rotation, 101.8°. After two recrystallizations from hot alcohol, 7 g. of pure starting material was recovered. On systematically working up the mother liquors including the acidic aqueous mother liquor, 2.9 g. of a sirup was obtained having a specific rotation of 67.4°. In an acetyl estimation by the method of Kunz[14] 0.280 g. of material used 31.9 cc. of 0.1 normal sodium hydroxide solution. The value calculated for 8 acetyl groups is 33.0 cc. A sample of this material weighing 0.5776 g. was dissolved in 10 cc. of distilled acetic anhydride. The specific rotation in this solvent was 63.1°. To this solution was added 0.05 g. of fused zinc chloride and the rotation rose within ten minutes to 94.2° where it remained constant. The solution was poured into 100 g. of crushed ice. After two hours the solid material was filtered out, washed with ice water, and dried; yield 0.4 g. After two recrystallizations from hot alcohol, 0.3 g. of beautiful crystals of the α-octaacetate having the specific rotation 105.5° was obtained. Another portion of the sirup was acetylated with fused sodium acetate and acetic anhydride by heating the mixture on the steam-bath for half an hour. Upon working up the mixture a sirupy product was obtained showing the unchanged rotation of 67.6°.

Action of Zinc Chloride on the Fourth Octaacetate of Turanose.—In 8 cc. of distilled acetic anhydride was dissolved 0.1012 g. of the fourth octaacetate of turanose and the solution made up to 10 cc. with a solution of 0.1 g. of fused zinc chloride in 20 cc. of the same solvent. The following specific rotations were observed after 1.5, 5, 10, and 30 minutes, respectively: 84.5, 60.8, 47.3 and 41.5°. After two hours, the rotation remained constant at 40.6°. The mixture was then worked up in the usual way using sodium bicarbonate solution and the product recrystallized from absolute ether; yield, 0.06 g. having the specific rotation 28.1°. After recrystallizing from alcohol, 0.048 g. of the first octaacetate of turanose having the correct specific rotation 19.6° was obtained.

Action of Pyridine on β-Acetochloro-fructose and -turanose.—Following the procedure of Fischer in preparing the pyridinium salt of acetobromoglucose,[12] 5 g. of crystalline acetochlorofructose was dissolved in 10 cc. of pyridine freshly distilled from barium oxide. The solution was kept for two days in a glass-stoppered flask. The only observable change was a slight darkening. Neither the aged nor the fresh solution reduced an acetone solution of potassium permanganate. The solution was poured into a beaker and kept in a vacuum desiccator over concentrated sulfuric acid until the odor of pyridine had almost disappeared. The sticky brown residue was extracted with *ca.* 50 cc. of absolute ether at room temperature. A small gummy residue remained. The ether solution at 0° deposited 3.2 g. of the pure starting material. The same experiment was repeated with 0.38 g. of acetochloroturanose dissolved in 25 cc. of absolute pyridine. The yield of recovered unchanged starting material was 0.25 g. of crystals showing the correct m. p. of 166°.

Action of Pyridine on β-Acetobromofructose.—In 25 cc. of absolute pyridine was dissolved 1.0822 g. of crystalline acetobromofructose. Three and one-half minutes after adding the solvent the specific rotation was −188°. In ten minutes the rotation had dropped to −166° and in one hour to −50°. After three hours the rotation reached the value of −5.53°. The direction of the change then reversed and the rotation slowly became more negative. After slowly changing for three weeks, the rotation became constant at −45°. In 10 cc. of absolute pyridine was dissolved 2.0 g. of acetobromofructose. In a few minutes a gelatinous precipitate formed in the clear solution and on shaking soon redissolved. The material slowly acquired the ability to reduce an acetone solution of potassium permanganate. After several days, the reduction took place within a few seconds. No pyridinium hydrobromide separated on careful addition of absolute ether in contrast to the behavior of acetobromoturanose as reported in Part I.[7]

Reaction of β-Acetobromofructose with Methyl Alcohol.—The general procedure given in Part IV[11] for the acetochloro compound was followed. To a suspension of 10 g. of silver carbonate in 25 cc. of absolute methyl alcohol in a glass-stoppered flask was added 2.3 g. of acetobromofructose, and the mixture vigorously shaken. A very rapid reaction ensued, the evolution of carbon dioxide ceasing in less than one minute. After shaking for fifteen

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(14) Kunz and Hudson, This Journal, **48**, 1892 (1926).

minutes, the solution no longer gave a test for labile bromine when boiled with alcoholic silver nitrate and nitric acid. The solution, which showed no action toward Fehling's solution, consisted of a mixture of α-methylfructoside tetraacetate and a large amount of β-methylfructoside tetraacetate with orthoester structure. In order to prove the presence of the latter compound, a few drops of the solution was diluted with 2 cc. of cold water and 1 drop of dilute hydrochloric acid was added. After *ca.* ten seconds at room temperature, considerable reduction took place on boiling with Fehling's solution. To isolate the normal α-methylfructoside tetraacetate, the reaction mixture was now filtered free of silver salts, and evaporated *in vacuo* to a thick sirup. To this was added 50 cc. of boiling water, and the mixture kept at 100° with vigorous shaking to hydrolyze the orthoester. In ten minutes a clear yellow solution was obtained. After filtering with charcoal, the colorless solution was placed in the ice box. Upon seeding with α-methylfructoside tetraacetate, the solution deposited 0.28 g. of crystals having the specific rotation 42.3°, and m. p. 110–111°. The aqueous mother liquor reduced Fehling's solution strongly due to the tetraacetylfructose formed by the hydrolysis of the orthoester. The crystalline material obtained above reduced Fehling's solution only after long boiling with acid.

Summary

The recent discovery of the true α-pentaacetylfructose <2, 6> has made possible for the first time the study of the behavior of the α,β pair of ketose acetates toward different agents.

It has been shown that the use of zinc chloride as a catalyst in the isomerization of the sugar acetates is applicable in the ketose series.

The application of this method to the first and fourth octaacetates of turanose of supposed orthoester structure has revealed a strong similarity in properties to those of the normal fructose acetates. This similarity has been shown to exist also between the corresponding acetohalogeno derivatives of fructose and turanose although the former are generally assigned normal structure whereas an orthoester structure had been advanced for the latter. Application of Hudson's rules confirms the normal structure of the fructose acetates but excludes such for the turanose acetates.

The formation of a fifth octaacetate of turanose from the so-called second or α-octaacetylturanose <2, 6> has been observed. Marked difference in the behavior of this pair from that of the normal fructose pentaacetates makes the structure assumed for the second octaacetate of turanose uncertain.

The behavior of the crystalline acetochloro compounds of fructose and turanose toward pyridine has been found to be radically different from that of the corresponding acetobromo compounds.

PRINCETON, N. J. RECEIVED FEBRUARY 13, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

The Synthesis of Long Chain Substituted Isocyclics and Similarly Substituted Adipic Acids.[1] The Preparation of γ-*t*-Octylcyclohexanol, Hexene, Hexanone, Hydroxylamine, Amine, Phenol and β-*t*-Octyl Adipic Acid

BY JOSEPH B. NIEDERL AND RICHARD A. SMITH

Introduction

On account of the renewed interest and present-day commercial importance of the alkyladipic acids[2] it was considered appropriate to give in this communication an account of the synthesis of a long chain adipic acid, namely, the β-diisobutyladipic acid. For the preparation of this acid (VI) the γ-diisobutylcyclohexanol (I), obtained by the catalytic hydrogenation of *p*-diisobutylphenol (*p*-($\alpha,\alpha,\gamma,\gamma$-tetramethyl)-butylphenol),[3] served as the starting material in the subsequent oxidation processes. The cyclic ketone (γ-diisobutylcyclohexanone) (III) as well as the above β-diisobutyladipic acid (VI) were obtained in excellent yields employing the conventional oxidation processes.[4] The oxime (IIIa) of the above ketone was prepared in the usual manner and from this oxime the γ-diisobutylcyclohexylhydroxylamine (IV) was prepared by catalytic hydrogenation. More strenuous reduction with sodium and alcohol yielded the γ-diisobutylcyclohexylamine (V). Dehydration of the γ-diisobutylcyclohexanol (I) yielded the corresponding γ-

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(1) Presented at the St. Petersburg meeting of the American Chemical Society, March 27, 1934. Original manuscript received July 25, 1934.

(2) R. Kuhn, *Ber.*, **67**, 1130 (1934); K. Ruzicka, *Helv. Chim. Acta*, **9**, 249 (1926); **16**, 1323, 1339 (1933); Ziegler and co-workers, *Ann.*, **504**, 94 (1933); R. P. Perkins, U. S. Patent 1,960,211 (1934).

(3) J. B. Niederl, U. S. Patent 2,008,032 (1935); Niederl and co-workers, THIS JOURNAL, **55**, 257 (1933).

(4) A. Baeyer, *Ann.*, **278**, 100 (1894); Bouveault and Locquin, *Bull. soc. chim.*, [4] **3**, 438 (1908); Mannich, *Ber.*, **39**, 1595 (1906); Wislicenus and Mager, *Ann.*, **275**, 363 (1893); Ciamician and Silber, *Ber.*, **46**, 3077 (1913).