chloro-1-hexyne.[4,5] 6-Heptenoic acid has also been prepared by the malonic ester synthesis,[6,7] by action of nitrous acid on 7-aminoheptanoic acid,[8] and by the dehydrohalogenation of 7-chloroheptanoic acid.[9]

EXPERIMENTAL

1,2,6-Tribromohexane. Practical grade 1,2,6-hexanetriol (230 g., 1.7 moles) was treated with phosphorus tribromide (500 g., 1.85 moles) according to the procedure which has been given by Schurink for the synthesis of pentaerythrityl bromide.[10] Two slight modifications were (a) the flask was not heated until all the phosphorus tribromide had been added, and (b) heating was discontinued shortly after the orange color appeared.

After adding the flask contents to 500 ml. of water, the bottom layer was separated, washed twice with cold 2% sodium hydroxide solution, once with water, and dried over anhydrous calcium chloride. The crude tribromide was distilled twice by simple vacuum distillation, b.p. 104° at 1.2 mm. (uncorr.). The yield of pure product, d^{20}_4: 1.959; $n^{25}D$: 1.5507 was 318 g. (58 %).

Anal.[11] Calcd. for $C_6H_{11}Br_3$: C, 22.32; Br, 74.25. Found: C, 22.43; H, 3.32; Br, 74.19.

This previously unreported tribromide was found to lose hydrogen bromide slowly upon standing; hence it was used immediately after distillation.

5-Hexenylmagnesium bromide and 6-heptenoic acid. The Grignard reagent was prepared from 240 g. (0.74 mole) of 1,2,6-tribromohexane and 50 g. (2.06 g.-atoms) of magnesium turnings, and subsequently carbonated with Dry Ice by the usual procedure.[12] The crude 6-heptenoic acid was distilled under reduced pressure, b.p. 78° at 1.0 mm. The yield of pure acid, neut. equiv. 128.2, 128.7 (calcd. 128.2), was 63 g., or 66 % based on the tribromide.

The acid thus obtained gives an infrared spectrum which is identical to that of an authentic sample of 6-heptenoic acid which had been prepared by the method of Gaubert, Linstead, and Rydon.[6] Oxidation of a sample of the acid, prepared by the method described here, with an excess of hot concentrated nitric acid gave a white, crystalline substance in good yield, which by its m.p. 150–151° (rep. 151–153°),[13] and by its neut. equiv. 73.7 (calcd. 73.1), has been identified as adipic acid.

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Catalysis of Acetylation Reactions of Sugars with an Ion Exchange Resin

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Received October 9, 1961

Ion exchange resins have been widely used in many types of physical and chemical studies for many purposes. Resins have been used in many chemical reactions as catalysts and their application and properties as catalysts have been reviewed.[1] The resin used in the acetylation reactions reported herein, Amberlite IR-120,[2] bearing the sulfonic acid group, has been used to promote the hydrolysis of disaccharides, starch, and methylated polysaccharides,[3] the preparation of certain glycosides,[3,4] and to catalyze the inversion of sucrose,[5] and catalyze or promote many other chemical reactions.[6]

Acetylated sugars are usually prepared at precise temperatures using an excess of acetic anhydride plus catalytic amounts of pyridine,[7,8] sulfuric acid,[9] zinc chloride,[10,11] or sodium acetate.[12] The particular ring modification of the sugar derivative which is formed depends upon the type of catalyst and the reaction temperature,[11] but often a crystalline product is difficult to obtain because of unfavorable equilibria between these modifications even under carefully controlled conditions. In addition, crystallization is impeded in some cases by trace amounts of those catalysts which are difficult to separate from the product.

Crystalline acetyl derivatives of three sugars were prepared at specified temperatures using Amberlite IR-120 as a catalyst. The insoluble character of the cation exchange resin simplified the isolation and purification of the products and probably is a significant reason why crystalline products in relatively high yield were obtained.

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These derivatives were prepared as authentic reference samples in order to identify sugars being investigated in another research project.

EXPERIMENTAL

Acetylation of D-*glucose.* Finely powdered D-glucose (5.145 g.) was mixed with acetic anhydride (60.0 ml.) and Amberlite IR-120 cation exchange resin (0.100 g.). The mixture was heated to 98–99° with stirring and within 1.5 hr. dissolution of the sugar was complete. After stirring for 7 hr. at this temperature, the refractive index of the solution became constant. The solution was then decanted from the resin, and the resin was washed several times with small portions of acetic anhydride; the washings being then added to the main portion of the solution. This solution was then concentrated (*in vacuo*) at 85–90° to a thin sirup, cooled to room temperature and poured with stirring into 300 ml. of ice and water. While standing at 5° for 12 hr. a sirup separated from the aqueous phase. This liquid was removed from the sirup by decantation and extracted three times with ethyl ether. The extracts were combined, concentrated (*in vacuo*) at 50° and added to the sirup. Aqueous methanol (80 ml. of 75% w./w.) was used to dissolve the viscous product which crystallized at −10° within 24 hr. The pentaacetate, three times recrystallized from aqueous methanol, showed a melting point of 97° and a specific rotation of $[\alpha]^{25}D$ +148°, in chloroform (*c*, 1). Further recrystallization from aqueous methanol did not alter the melting point nor the specific rotation. The yield was 58.0%. The product is believed to be 2,3,4,6-tetraacetyl-α-acetyl-D-glucopyranoside.

Anal. Calcd. for $C_{16}H_{22}O_{11}$: acetyl, 55.10. Found: acetyl, 54.84.

Acetylation of sucrose. Powdered sucrose (5.000 g.), acetic anhydride (100 ml.) and Amberlite IR-120 (0.200 g.), were stirred for 6 hr. at 55–60°. After cooling to room temperature, the solution was separated from the resin by decantation and poured slowly into 600 ml. of ice and water. The resin was washed several times with 10-ml. portions of acetic anhydride, and the washings were also added to the ice and water. The sirup which separated from the aqueous phase after severals hours was isolated by decantation of the aqueous solution. The aqueous phase was extracted three times with 30-ml. portions of chloroform, and the extracts were combined, concentrated (*in vacuo*) at 50° and added to the sirup. The sirup was dissolved in ethanol (30 ml.), and water was added (approx. 5 ml.) until the solution became slightly turbid. Crystallization at 5° began very slowly but was complete after approximately 7 days. The product was recrystallized twice from aqueous ethanol. Further recrystallization did not alter the melting point nor the specific rotation; m.p., 73.5°; $[\alpha]^{25}D$ +60.65°, in chloroform (*c*, 1). The yield of octaacetyl sucrose 44.2%.

Anal. Calcd. for $C_{28}H_{37}O_{19}$: acetyl, 50.74. Found: acetyl, 49.59.

Acetylation of D-*fructose.* Powdered D-fructose (5.000 g.). was added at room temperature to acetic anhydride (100 ml.) containing a suspension of Amberlite IR-120 (0.300 g.). The reactants were stirred and the temperature was raised to 50° and kept at that temperature for 2 hr. After cooling to room temperature (0.5 hr.), the solution was decanted from the resin and slowly stirred into a mixture of ice and water (500 ml.). The resin was washed several times with 20-ml. portions of acetic anhydride; the washings being also added slowly to the ice and water. While stirring was continuing for 12 hr. a sirup separated from the aqueous phase. This phase was removed and extracted three times with 20-ml. portions of ethyl ether. The extracts and sirup were combined in a separatory funnel and washed with saturated sodium bicarbonate solution until effervescence ceased. After washing twice with water, the product was concentrated (*in vacuo*) at 50° to a thin sirup. Seed crystals were obtained by dissolving a small amount of sirup in a small volume of ethyl ether and permitting the solvent to evaporate very slowly at 5°. The main portion of the product was then crystallized at 5° from chloroform. After recrystallizing three times from chloroform, the melting point, 128–129°, and the specific rotation, $[\alpha]^{25}D$ −80.1° in chloroform (*c*, 1.5), remained constant. The yield was 40.1%.

Anal. Calcd. for $C_{16}H_{22}O_{11}$: acetyl, 55.10 Found: acetyl, 54.90.

The product is believed to be the 2,3,4,5-tetraacetyl-β-acetyl derivative of D-fructose.

Acknowledgment. The author wishes to acknowledge the assistance of Miss Kathleen Simo and Mr. Ronald Swor for their participation in part of this work. This research was supported in part by Grant R 67233 from the National Institutes of Health, U. S. Public Health Service.

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A Chart of Ultraviolet Absorption Maxima of 2,4-Dinitrophenylhydrazones

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Received November 21, 1961

Probably the largest single group of very similar compounds for which ultraviolet spectra in a single solvent have been determined is the 2,4-dinitrophenylhydrazones of aldehydes and ketones in chloroform. A survey of three volumes of "Organic Electronic Spectral Data" [1] supplemented by a few collections of data from earlier and later literature[2,3] readily yielded about 740 distinct compounds of this class plus a number of duplicates. Fortunately the reproducibility of duplicates was rarely worse than 2–3 mμ.

The size of this group suggested the possibility of making a useful Colthup-type chart of the range of wave lengths for the principal absorption maximum as a function of the carbonyl compound structure. Although the rather unspecific relations of structure and spectrum in the ultraviolet as compared to the infrared might make such a chart disappointingly vague, its utility as a speedy reference made the effort worth a trial. Because of classification problems and the desire to avoid too many separate categories only 459 compounds found their way into the final chart (Fig. 1). Since many steroids, most natural products, and most naphthalenones and

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