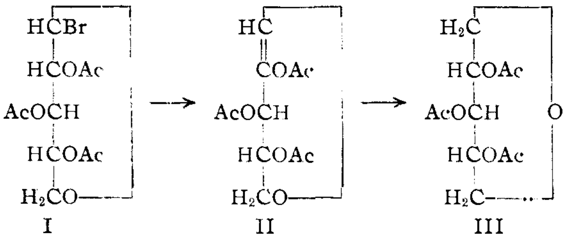
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

1,5-Anhydro-xylitol

BY HEWITT G. FLETCHER, JR., AND C. S. HUDSON

In 1930 Zervas[1] reported the catalytic reduction of 2,3,4,6-tetraacetyl-2-hydroxy-D-glucal to a sirup which on hydrolysis gave the naturally occurring anhydro-hexitol, styracitol. Later work in several laboratories[2] established styracitol as 1,5-anhydro-D-mannitol. A few other 2-hydroxyglycal derivatives have also been reduced catalytically. Maurer and Plötner,[3] for instance, reduced heptaacetyl-hydroxygentiobial and heptaacetyl-hydroxycellobial to what they consider by analogy to be heptaacetyl-6-β-D-glucopyranosyl-styracitol and heptaacetyl-4-β-D-glucopyranosyl-styracitol, respectively. However, no definite proof was offered for these structures and they may, conceivably, be derivatives of polygalitol, 1,5-anhydro-D-sorbitol. In other than the glucose series there appears to be but one example of anhydro-hexitol synthesis by this process. Freudenberg and Rogers[4] obtained a tetraacetyl-1,5-anhydro-hexitol by the reduction of 2,3,4,6-tetraacetyl-2-hydroxy-D-galactal. Whether this reduction product is an anhydro-galactitol or an anhydro-talitol was not ascertained.

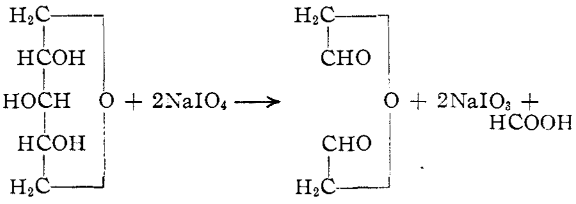
The purpose of the present investigation is to extend this apparently general synthetic method to the pentitol series. For this purpose 2,3,4-triacetyl-α-D-xylopyranosyl bromide (I), prepared by conventional methods, was used as a starting material. In accordance with the procedure of Maurer and Mahn[5] it was dehydrohalogenated in dry benzene solution with diethylamine to give 2,3,4-triacetyl-2-hydroxy-D-xylal (II). Catalytic reduction of this xyloseene triacetate might be expected to give the triacetate of either 1,5-anhydro-D-arabitol or 1,5-anhydro-xylitol (III). The former would be optically active while the latter represents a *meso* structure and should, therefore, show no rotation. Experimentally, it was found that the reduction of 2,3,4-triacetyl-2-hydroxy-D-xylal in the presence of palladium led to the isolation of an optically inactive anhydro-pentitol triacetate in a yield of 83%. It showed no activity in pyridine, glacial acetic acid or chloroform and therefore the *meso* configuration, III, seems certain. Deacetylation of this triacetate gave a crystalline anhydro-pentitol, IV, which is also optically inactive. That the pyranoid ring structure of the original 2,3,4-triacetyl-α-D-xylopyranosyl bromide had been retained was confirmed by sodium metaperiodate oxidation. Two molar equivalents of this oxidant were consumed and one molar equivalent of formic acid was produced. The anhydro-pentitol is therefore 1,5-anhydro-xylitol, IV.



I 2,3,4-Triaceytl-α-D-xylopyranosyl bromide

II 2,3,4-Triacetyl-2-hydroxy-D-xylal

III 2,3,4-Triacetyl-1,5-anhydro-xylitol



IV

1,5-Anhydro-xylitol

Subsequent to the above work it was found possible to synthesize 2,3,4-triacetyl-1,5-anhydroxylitol from D-xylose by a wholly different and simple process which constitutes an independent proof of its configuration. The recent observation by one of us[6] of the reductive desulfurization of ethyl tetraacetyl-D-glucopyranosyl xanthate by Raney nickel to tetraacetyl-1,5-anhydro-D-sorbitol suggested the possibility of similarly reducing the readily prepared and often beautifully crystalline acetylated aryl 1-thioglycosides. It was then found that phenyl 1-thio-β-D-xylopyranoside triacetate, originally prepared by Purves,[7] reacted in alcoholic solution with Raney nickel to give a 71% yield of 2,3,4-triacetyl-1,5-anhydro-xylitol, identical with the reduction product of 2,3,4-triacetyl-2-hydroxy-D-xylal.

An attempt was made to synthesize 2,3,4-tribenzoyl-1,5-anhydroxylitol by the reduction of 2,3,4-tribenzoyl-2-hydroxy-D-xylal. Contrary to our expectations, 2,3,4-tribenzoyl-2-hydroxy-D-xylal was found resistant to reduction under the conditions employed with 2,3,4-triacetyl-2-hydroxy-D-xylal; however, the intermediates in the attempted synthesis are reported here because their physical constants were found to vary some-

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(1) L. Zervas, *Ber.*, **63**, 1689 (1930).

(2) L. Zervas and I. Papadimitriou, *ibid.*, **73**, 174 (1940); N. K. Richtmyer and C. S. Hudson, THIS JOURNAL, **65**, 64 (1943); N. K. Richtmyer, C. J. Carr and C. S. Hudson, *ibid.*, **65**, 1477 (1943); R. C. Hockett and Maryalice Conley, *ibid.*, **66**, 464 (1944).

(3) K. Mauer and K. Plötner, *Ber.*, **64**, 281 (1931).

(4) W. Freudenberg and E. F. Rogers, THIS JOURNAL, **59**, 1602 (1937).

(5) K. Maurer and K. Mahn, *Ber.*, **60**, 1316 (1927); *cf. ibid.*, **62**, 332 (1929).

(6) H. G. Fletcher, THIS JOURNAL, **69**, 706 (1947).

(7) C. B. Purves, *ibid.*, **51**, 3619 (1929).

what from those reported by Major and Cook.[8] The benzoylation of 1,5-anhydro-xylitol readily yields the crystalline tribenzoate, which is devoid of optical activity because of *meso* configuration.

One of us (H. G. F.) held the Chemical Foundation Research Associateship while carrying out this research.

We are indebted to Mr. Charles A. Kinser for combustion analyses.

Experimental

2,3,4-Triacetyl-2-hydroxy-D-xylal.[9]—2,3,4-Triacetyl-α-D-xylopyranosyl bromide was readily prepared from β-D-xylopyranose tetraacetate by a procedure adapted from those of Hudson and Johnson[2] and Levene and Raymond.[10] A suspension of 50 g. of this halide in a mixture of 110 ml. of dry, thiophene-free benzene and 21.6 g. (2 molecular equivalents) of dry diethylamine in a ground-glass stoppered flask was shaken gently at room temperature (27°) for one and one-half hours; at the end of that time the starting material had dissolved and flakes of crystalline diethylamine hydrobromide had begun to appear. The mixture was kept for seven days with occasional shaking, the solution slowly darkening to a brownish-yellow color and becoming a thin slurry through the crystallization of diethylamine hydrobromide. This salt was then removed by filtration and washed with anhydrous ether (65 ml.); the wt. of the pure white salt was 22.05 g. (yield, 97%); it melted at 218–220° (211–213° uncor.) Wagner[11] reported a value of 213.5° for diethylamine hydrobromide. The combined filtrate and ether washings were concentrated *in vacuo* (45° bath) to a light brownish yellow sirup which was taken up in 33 ml. of glacial acetic acid. Water (150 ml.) was then added and the turbid mixture aerated to remove residual traces of benzene and ether. Seed crystals, first obtained by scratching a drop of the precipitated sirup on a watch glass, were then added. As crystallization of the boat-shaped prisms proceeded, fifty more ml. of water could be added in portions without precipitating more sirup; the crystallization was completed by keeping the mixture in an ice-box for three days. The nearly white crystals were then removed by filtration and washed with 25 ml. of cold 10% alcohol; wt. 10.76 g. (yield, 28%), m. p. 79–82°. Three recrystallizations yielded, with little loss, large prisms of pure 2,3,4-triacetyl-2-hydroxy-D-xylal of m. p. 81–82° and $[\alpha]^{20}\mathrm{D}$ −276° in chloroform (*c*, 3.27) and −259° in glacial acetic acid (*c*, 3.33). The dispersion of the substance is so different from quartz that it is necessary to measure its rotation in a polarimeter rather than in a quartz wedge saccharimeter. The substance is soluble in acetone, sparingly soluble in ether and water and insoluble in petroleum ether.

Anal. Calcd. for $C_{11}H_{14}O_7$: C, 51.16; H, 5.46. Found: C, 51.19; H, 5.40.

2,3,4-Triacetyl-1,5-anhydro-xylitol from 2,3,4-Triacetyl-2-hydroxy-D-xylal.—Palladous oxide[12] (0.82 g.) was suspended in 20 ml. of glacial acetic acid and reduced by shaking at room temperature (27°) under a slight positive pressure of hydrogen. To the resulting suspension of palladium there was added a solution of 5 g. of 2,3,4-triacetyl-2-hydroxy-D-xylal in 20 ml. of glacial acetic acid and hydrogenation conducted in the usual manner. After twenty-three hours, absorption of hydrogen could no longer be detected and the catalyst was removed by filtration. Concentration of the solution *in vacuo* (40° bath) resulted in the spontaneous formation of colorless prisms. The crystalline mass was dissolved in 25 ml. of hot absolute alcohol, filtered while still hot through a filter thinly precoated with activated carbon, seeded and allowed to cool slowly to ice-box temperature. When crystallization had practically ceased the crystals were removed by filtration, washed with absolute alcohol and dried *in vacuo*. The yield of 2,3,4-triacetyl-1,5-anhydro-xylitol thus obtained was 4.17 g. (83%). One more recrystallization from alcohol gave 3.98 g. of compound melting at 122–123°. In pyridine, glacial acetic acid and chloroform the pure substance showed no optical activity. It is readily soluble in these solvents and in hot alcohol but sparingly soluble in cold alcohol. In water and petroleum ether it is insoluble. At an elevated temperature the compound readily sublimes undecomposed.

Anal. Calcd. for $C_{11}H_{16}O_7$: C, 50.77; H, 6.19; saponification equivalent, 86.0. Found: C, 50.90; H, 6.17; saponification equivalent, 86.7.

2,3,4-Triacetyl-1,5-anhydro-xylitol from Phenyl 1-Thio-β-D-xylopyranoside Triacetate.—Phenyl 1-thio-β-D-xylopyranoside triacetate, prepared according to the method of Purves,[7] was found to melt at 78–79° and show $[\alpha]^{20}\mathrm{D}$ −60.8° in chloroform (*c*, 1.052), in agreement with his measurements. Five grams of this compound, dissolved in 50 ml. of absolute alcohol, was treated with about 30 g. of Raney nickel suspended in absolute alcohol and warmed under reflux for two hours. The nickel was then removed by filtration through sintered glass and the filtrate evaporated *in vacuo* (45° bath). Crystallization of 1,5-anhydro-xylitol triacetate in the form of quadrilateral plates was spontaneous; 2.423 g. (69% of the theoretical). The substance melted at 122–123°, either alone or in admixture with 1,5-anhydro-xylitol triacetate prepared by the reduction of 2,3,4-triacetyl-2-hydroxy-D-xylal. A small crop of less pure material was subsequently obtained from the mother liquors and it raised the total yield of crystalline material to 71% of the theoretical.

1,5-Anhydro-xylitol.—2,3,4-Triacetyl-1,5-anhydro-xylitol (2.1169 g.) was dissolved in 15 ml. of warm anhydrous methanol, the solution cooled to room temperature and treated with 1.00 ml. of 0.7529 *N* methanolic barium methylate. After seventeen hours the barium methylate was neutralized with 0.1 *N* sulfuric acid, the solution passed through a filter precoated with activated carbon and then evaporated on the steam-bath to a thick, clear and nearly colorless sirup. Dissolved in a mixture of 3 ml. of isopropyl alcohol and 1 ml. of petroleum ether and left at room temperature, the material crystallized spontaneously, 3 ml. more of petroleum ether being added after several hours without producing a cloud. The dried crystalline material (0.547 g.) melted at 116–117°. Concentration of the mother liquors to dryness gave a crystalline mass which was dissolved in 2 ml. of warm absolute alcohol and left in the ice box. After crystallization had practically ceased, 4 ml. of ethyl acetate was added and the mixture cooled in the ice box for one hour. The resulting crop had practically the same melting point as the first and, combined with it, raised the yield to 0.916 g. (84%). One recrystallization from hot absolute alcohol gave practically the same quantity of material as stubby prisms melting at 116–117° and showing no rotation in aqueous solution. 1,5-Anhydro-xylitol is soluble in water, methanol and hot alcohol, sparingly soluble in cold alcohol and insoluble in petroleum ether and ethyl acetate.

Anal. Calcd. for $C_5H_{10}O_4$: C, 44.78; H, 7.51. Found: C, 44.61; H, 7.26.

Sodium Metaperiodate Oxidation of 1,5-Anhydro-xylitol.—The technique of Jackson and Hudson[13] was employed. The 1,5-anhydro-xylitol (0.1008 g.) was dissolved in a little water, treated with 5 ml. of 0.4352 *M* aqueous sodium metaperiodate and the solution diluted to

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[8] R. T. Major and E. W. Cook, This Journal, **58**, 2333 (1936).

[9] The conditions for the preparation are modeled after those by which Maurer and Mahn [*Ber.*, **60**, 1316 (1927); *cf. ibid.*, **62**, 332 (1929)] prepared 2,3,4-tetraacetyl-2-hydroxy-D-glucal.

[10] C. S. Hudson and J. M. Johnson, This Journal, **37**, 2748 (1915); P. A. Levene and A. L. Raymond, *J. Biol. Chem.*, **90**, 247 (1931).

[11] L. Wagner, *Z. Krist.*, **43**, 164 (1907).

[12] D. Starr and R. M. Hixon, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 566.

[13] E. L. Jackson and C. S. Hudson, This Journal, **59**, 994 (1937).

25 ml. with water. After twenty-three hours at room temperature (27°) separate 5 ml. samples were titrated for formic acid and for residual oxidant. On a basis of one mole of anhydro-xylitol, 1.99 moles of oxidant was consumed and 0.995 mole of formic acid produced.

2,3,4-Tribenzoyl-1,5-anhydro-xylitol.—1,5-Anhydro-xylitol (0.3058 g.) was dissolved in 1.5 ml. of pyridine, chilled in an ice-bath and the solution treated with 0.8 ml. of benzoyl chloride. After fifteen minutes in the ice-bath the reaction mixture was left at room temperature overnight and then treated with dilute ice cold sodium bicarbonate solution. Removed by filtration and washed with water the crystalline material weighed 0.9193 g. (90.5%). Recrystallized thrice from 19 parts of warm alcohol the fine needle-like crystals melted at 146–147° and in chloroform solution were devoid of optical activity.

Anal. Calcd. for $C_{19}H_{18}O_6$: C, 66.94; H, 4.97. Found: C, 69.89; H, 5.04.

α-D-Xylopyranose Tetrabenzoate.—Twenty-fives gram of D-xylose was added in small portions over the course of one-half hour to a well-stirred mixture of 95 ml. of benzoyl chloride, 100 ml. of dry pyridine and 190 ml. of freshly purified chloroform[14] kept well chilled in an ice-bath. When the reaction mixture became nearly homogeneous it was left at room temperature overnight and then poured in a thin stream on finely chipped ice. After separation, the non-aqueous layer was washed twice with ice-cold 3 *N* sulfuric acid, once with aqueous sodium bicarbonate, and finally dried with anhydrous sodium sulfate. After removal of the desiccant, the filtrate was concentrated *in vacuo* (55° bath) to a thick sirup from which 150 ml. of absolute alcohol was evaporated. This sirup was then dissolved in 200 ml. of a mixture consisting of one volume of pyridine and nine volumes of alcohol. After seeding,[15] crystallization was allowed to proceed at room temperature.

The crude α-D-xylopyranose tetrabenzoate (73.2 g.; yield, 78%), recrystallized three times from ten parts of hot alcohol, melted at 118–120° and showed $[\alpha]^{20}\mathrm{D}$ +143.7° in chloroform. This yet impure material was treated with one part of benzene which rapidly dissolved the fine needle-like crystals of the desired form and left the prismatic crystals of the β-form, from which the solution was quickly decanted. Addition of isopentane to incipient turbidity gave material melting at 119–120° and rotating $[\alpha]^{20}\mathrm{D}$ +149.5° in chloroform (*c*, 2.09).[16] Further recrystallization, as from aqueous acetic acid, failed to alter these values. The compound shows the usual solubility characteristics of a sugar benzoate.

β-D-Xylopyranose Tetrabenzoate.—Fifty grams of D-xylose was dissolved in 200 ml. of boiling pyridine and the resulting solution cooled in an ice-bath. While kept thoroughly cooled and constantly agitated there was gradually added to this solution over the course of one-half hour a solution of 190 ml. of benzoyl chloride in 380 ml. of ethylene dichloride. After a further forty-five minutes in the ice-bath the heavy slurry was left at room temperature overnight. It was then poured in a thin stream on finely chipped ice and the resulting non-aqueous layer washed twice with cold 3 *N* sulfuric acid. After being washed with aqueous sodium bicarbonate solution and with water, the solution was dried with calcium chloride and concentrated *in vacuo* (55° bath) to a sirup. Dissolved in 57 ml. of alcohol, this material crystallized spontaneously at room temperature. After standing overnight the crystalline mass was washed with 100 ml. of 1:9 pyridine-alcohol mixture; wt. 97.8 g. (yield, 52%).[17] When recrystallized three times from a warm mixture of five parts of acetone and one part of water, the β-D-xylopyranose tetrabenzoate showed a specific rotation $[\alpha]^{20}\mathrm{D}$ −42.1° in chloroform (*c*, 2.27). The prismatic crystals melted at 173° to a liquid which resolidified when held at 172° and remelted at 177°. The compound may advantageously be recrystallized from methyl ethyl ketone, benzene or ethyl lactate.

2,3,4-Tribenzoyl-α-D-xylopyranosyl Bromide.—This compound could be prepared equally well from either of the above isomeric tetrabenzoates. Thirty grams of crude α-D-xylopyranose tetrabenzoate (m. p. 118–120°; $[\alpha]^{20}\mathrm{D}$ +143.7° in chloroform) was dissolved in 30 ml. of ethylene dichloride.[18] The solution was cooled in an ice-bath, treated with 60 ml. of 30% hydrogen bromide in glacial acetic acid and allowed to stand tightly stoppered at room temperature for two hours. Fifty milliliters of glacial acetic acid was then stirred into the crystalline magma and, after thirty minutes in the ice-box, the solid material was filtered off and washed successively with 20 ml. of cold glacial acetic acid and 50 ml. of isopentane. The dry material (23 g., 83%) melted at 135–136°. Recrystallization from four parts of benzene and four parts of hexane gave material melting at 136–137° and showing $[\alpha]^{20}\mathrm{D}$ in chloroform (U. S. P.) +118.7° (*c*, 2.15).

2,3,4-Tribenzoyl-2-hydroxy-D-xylal.—Thirty grams of 2,3,4-tribenzoyl-α-D-xylopyranosyl bromide was dissolved in a mixture of 8.4 g. (2 molecular equivalents) of anhydrous diethylamine and 60 ml. of benzene by warming briefly in a bath at 55°. After eleven days at room temperature the diethylamine hydrobromide (8.55 g., 97%) was removed by filtration and the solution concentrated *in vacuo* (40° bath) to a thick sirup. Evaporation *in vacuo* of two 50-ml. portions of absolute alcohol from this sirup served to remove residual traces of benzene and diethylamine. The sirup was dissolved in 30 ml. of absolute alcohol, left at room temperature until crystallization had practically ceased, and finally kept in the ice-box for twenty-four hours. The crude, tan-colored material was then filtered off and freed of much of its color by washing with 30 ml. of glacial acetic acid. It amounted to 5.9 g. (23%), melted at 120–124° and showed a rotation ($[\alpha]^{20}\mathrm{D}$) in chloroform of −259°. Recrystallized first from 17 and then from 19 parts of hot absolute alcohol the 2,3,4-tribenzoyl-2-hydroxy-D-xylal formed colorless prismatic needles which melted at 129–130° and rotated in U. S. P. chloroform $[\alpha]^{20}\mathrm{D}$ −285° (*c*, 0.845). Further recrystallization failed to change these constants. In glacial acetic acid the compound showed $[\alpha]^{20}\mathrm{D}$ −301° (*c*, 0.440). The substance is sparingly soluble in alcohol, practically insoluble in water and petroleum ether and soluble in other common organic solvents.

Summary

The dehydrohalogenation of 2,3,4-triacetyl-α-D-xylopyranosyl bromide with diethylamine gives 2,3,4-triacetyl-2-hydroxy-D-xylal which may be reduced with hydrogen in glacial acetic acid solution and in the presence of palladium to give 2,3,4-triacetyl-1,5-anhydro-xylitol.

Reductive desulfurization of phenyl 1-thio-β-D-xylopyranoside triacetate with Raney nickel afforded the same 2,3,4-triacetyl-1,5-anhydroxylitol, a *meso* substance.

Deacetylation of this triacetate gave 1,5-anhydro-xylitol, the structure and *meso* con-

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[14] Ethylene dichloride, a more stable solvent, may conveniently be substituted for the chloroform here.

[15] Seeds were obtained by rubbing a small sample of the original sirup with glacial acetic acid.

[16] Major and Cook (ref. 8) measured the rotations of the compounds which they reported in alcohol-free chloroform. Values found for the rotations of both α- and β-xylopyranose tetrabenzoates in alcohol-free chloroform and in U. S. P. chloroform were found in the course of the present research to be identical within the limits of experimental error.

[17] The combined mother liquors and washings, when diluted with a mixture of 16 ml. of pyridine and 90 ml. of alcohol and seeded with crystals of the α-isomer gave 35.5 g. of crude α-D-xylopyranose tetrabenzoate, making the total yield of crystalline material 71%.

[18] Omission of this solvent from the reaction mixture results in the formation of a mass of very fine crystalline material which cannot be separated completely from the mother liquors by filtration.

figuration of which were established by its optical inactivity and its behavior with sodium metaperiodate.

Improved procedures are given for the preparation of α- and β-D-xylopyranose tetrabenzoates, 2,3,4-tribenzoyl-α-D-xylopyranosyl bromide and 2,3,4-tribenzoyl-2-hydroxy-D-xylal. The latter compound was found resistant to hydrogenation under the conditions employed for the reduction of its acetyl analog. Revised physical constants for some of the substances are recorded.

BETHESDA, MARYLAND RECEIVED DECEMBER 12, 1946

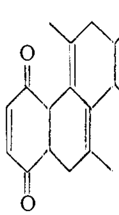
[CONTRIBUTION FROM THE BUREAU OF ANIMAL INDUSTRY, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Synthesis of Condensed Ring Compounds. XVI.[1] The Addition of Quinones to a Dienyne[2]

BY LEWIS W. BUTZ, ADAM M. GADDIS AND ELEANORE W. J. BUTZ

2,5-Dimethyl-1,5-hexadien-3-yne reacts with two moles of *p*-benzoquinone at 130° to give a brilliant yellow crystalline compound. Absorption in the ultraviolet was $\lambda_{max.}$ 2250 Å., ϵ 30000; inflection 2900 Å., ϵ 700; $\lambda_{max.}$ 3500 Å., ϵ 340. Hydrogenation at room pressure and temperature in the presence of platinum oxide–palladium oxide catalyst gave a decahydro derivative which formed a diacetate.

By analogy with other dienyne double additions[3] structure I can be considered for the yellow compound $C_{20}H_{18}O_4$. The properties are in good agreement with this formulation. The diacetate of the decahydro derivative, which showed no absorption in the ultraviolet characteristic of conjugation, is probably one of the diacetoxydimethyl-8-chrysitenediones, II. Open chain structures for the adduct, such as III, would appear to be excluded on the basis of the properties.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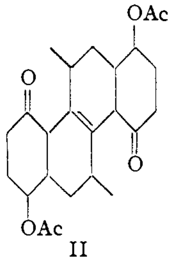
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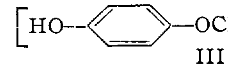
III

2,5-Dimethyl-1,5-hexadien-3-yne combined with one mole of tetrachloro-*p*-benzoquinone at room temperature to give a nearly colorless crystalline compound which dissolved in cold aqueous sodium hydroxide. Acidification of this alkaline solution with hydrochloric acid precipitated a white substance. In the ultraviolet the adduct showed $\lambda_{max.}$ 2720 Å., ϵ 8600 which is characteristic of phenols.[4]

Experimental[5]

Reaction of 2,5-Dimethyl-1,5-hexadien-3-yne with *p*-Benzoquinone.—Two and a half grams of freshly sublimed quinone and 2.45 g. of dienyne[6] were heated together without solvent in a sealed Pyrex tube, filled with carbon dioxide, at 130° for two hours. The resulting mixture was extracted with 200 ml. of ether. Eighty per cent. of the quinone taken was recovered from the ether extract. The brown solid residue (115 mg., 3%) of crude adduct melted at 214–216°. Recrystallization of 655 mg. of such crude adduct, which is quite insoluble in many common solvents, by continuous extraction with acetone and cooling gave 421 mg. of brilliant yellow crystals, m. p. 225–228° (dec. 219°).

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.5; H, 5.6. Found: C, 74.5; H, 5.7.

The compound was dissolved in dioxane for observation of the ultraviolet absorption spectrum.

The Decahydro Derivative of the Adduct.—Seventy milligrams of dimethylhexadienyne-*p*-benzoquinone adduct in 20 ml. of acetic acid (distilled from permanganate) was hydrogenated in the presence of 25.5 mg. of Adams catalyst containing 4% of palladium oxide. Four moles of hydrogen were taken up during the first hour and 0.9 mole during the next two hours. Filtration of the catalyst, removal of the acetic acid at 40–50° and 15 mm., and recrystallization of the residue from benzene gave 39.5 mg. of a colorless substance, m. p. 237–239° (in evacuated tube). No absorption was found in the ultraviolet at 2200–3000 Å. In anticipation of partial acetylation during the hydrogenation, the product was acetylated before analysis by refluxing with 2 ml. of pyridine and 1 ml. of acetic anhydride for twenty-five minutes. After working up as usual, the product was recrystallized first from hexane containing 1% of benzene and then from ether. The colorless product, which melted at 238–240° (evacuated tube), is probably the diacetate II.

Anal. Calcd. for tetraacetate, $C_{28}H_{36}O_8$: C, 67.2. Calcd. for diacetate, $C_{24}H_{32}O_6$: C, 69.2; H, 7.7. Found: C, 68.9; H, 7.6.

Reaction of 2,5-Dimethyl-1,5-hexadien-3-yne with Tetrachloro-*p*-benzoquinone.—Seventeen grams of the quinone was dissolved in 330 ml. of boiling benzene and the solution was cooled rapidly. Two moles (14.5 g.) of the dienyne and 1 ml. of 33% aqueous trimethylamine[7] were added and the mixture was shaken at 40° for ten days. Thereafter it was allowed to stand in the sunlight[7] at room temperature for two days. Five and a half grams of unchanged tetrachloro-*p*-benzoquinone was removed from the mixture of products by filtration, the filtrate was evaporated to dryness, and the residue was taken up in 150 ml. of boiling Skellysolve "C" (heptanes).

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[1] For preceding paper see THIS JOURNAL, **69**, 117 (1947).

[2] This work was supported by an allotment from the Special Research Fund (Bankhead-Jones Act of June 29, 1935). Not subject to copyright.

[3] Butz and Joshel, THIS JOURNAL, **64**, 1311 (1942), and earlier papers.

[4] Schjånberg, *Svensk Kem. Tid.*, **52**, 185 (1940).

[5] Melting points are corrected. Analyses by Arlington Laboratories, Fairfax, Virginia.

[6] Butz, Gaddis, Butz and Davis, *J. Org. Chem.*, **5**, 379 (1940).

[7] Albrecht, *Ann.*, **348**, 45 (1906).