Iodometric Determination of Sulfur.—Calcd. for $C_{20}H_{15}N_2SO_5Na$: S, 7.65. Found: S, 7.31.

Two grams of the monobisulfite compound was treated with 10 cc. of 35% sodium bisulfite compound at 70°. After twenty-four hours the product dissolved completely. Yellow needles in all respects similar to those obtained in (4) settled out of the solution.

When treated with bisulfite in the cold, the monobisulfite compound is not converted to the dibisulfite compound even after forty-eight hours.

(b) **Complete Hydrolysis.**—The same results are obtained from hydrolysis of both the monobisulfite and dibisulfite compounds of 1,5′-dihydroxy-4,4′-azonaphthalene (XI).

One gram of the bisulfite compound was treated with 10 cc. of 25% sodium hydroxide solution. Very fine violet needles settled out in the cold, and on heating with excess sodium hydroxide, a violet solution was obtained. On cooling this solution, large violet needles with a metallic luster settled out. The product was recrystallized from hot alkali solution, washed with water to neutral reaction, and dried at 100°. According to the analysis, the product is the monosodium salt of the dihydroxyazo dye.

Analysis of the products obtained from the dibisulfite (1) and monobisulfite (2) compounds of the dihydroxyazonaphthalene: (1) Calcd. for $C_{20}H_{13}N_2O_2Na$: Na, 6.84; N, 8.5. Found: Na, 6.95; N, 8.3. (2) Calcd. for $C_{20}H_{13}N_2O_2Na$: Na, 6.84. Found: Na, 7.04.

On treating the hot (80°) alkaline solution of the dye with excess hydrochloric acid, all of the dye settles out in the form of reddish-violet powder which is absolutely identical with the product obtained in (3). The precipitate is washed thoroughly with water and dried at 100°.

The monosodium compound of the dye is insoluble in both hot and cold water, readily soluble in alcohol, ether, ethyl acetate and chloroform. It dissolves with difficulty in cold, better in hot benzene, toluene, nitrobenzene and glacial acetic acid. It is insoluble in cold alkalies but dissolves completely in hot alkalies. It is insoluble in both hot and cold soda solution.

The free dihydroxyazo dye behaves like the sodium compound toward solvents.

Summary

1. It has been shown, contrary to the statement of A. King, that it is possible to obtain addition products containing two molecules of bisulfite from monoazo dyes with two auxochromes. This proves the dominant importance of the auxochrome group (and the nucleus containing it) in the reaction of naphthaleneazo dyes with bisulfite and disproves Spiegel's theory.

2. The dibisulfite compound of the dye prepared from diazotized 1,8-aminonaphthol and α-naphthol may be obtained easily from the monobisulfite compound. Due to side reactions, a pure product cannot be obtained from the dye which contains no bisulfite group.

3. The formation of the dibisulfite compound from the monobisulfite compound of the α-naphthylamine dye is accompanied by hydrolysis of the amino group and the transition of the organic nucleus to the dihydroxy dye.

4. On hydrolysis of the dibisulfite compound of the dye in alkaline solution, stepwise decomposition takes place. First one molecule of bisulfite splits off, giving the monobisulfite compound. Then the second molecule splits off, forming the free dye.

5. The formation of bisulfite compounds corresponding to both the azoid and hydrazone forms is possible.

MOSCOW, U. S. S. R. RECEIVED JULY 24, 1936

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Preparation and Properties of Xyloseen-(1,2) Tribenzoate

BY RANDOLPH T. MAJOR AND ELMER W. COOK

In the course of the investigation of various new syntheses of ascorbic acid an attempt was made to prepare xyloseen-(1,2) triacetate. Only a gum was obtained. The preparation of xyloseen-(1,2) tribenzoate was then undertaken in the hope that it might crystallize. This proved to be the case. Xyloseen-(1,2) tribenzoate was prepared by a procedure similar to that described by Maurer and Petsch[1] for the preparation of glucoseen tetrabenzoate.

Experimental

***d*-Xylose Tetrabenzoate.**—*d*-Xylose (50 g.) was added gradually to a mixture consisting of 190 cc. of benzoyl chloride, 200 cc. of anhydrous pyridine and 380 cc. of anhydrous chloroform, cooled in an ice-bath. The xylose soon dissolved and the solution was allowed to stand for twenty-four hours. Chloroform (600 cc.) was then added and the solution was washed successively with cold dilute sulfuric acid, sodium bicarbonate and water. After drying over calcium chloride the chloroform was removed by evaporation *in vacuo*. The crystalline residue of α-*d*-xylose tetrabenzoate was recrystallized from dioxane with the addition of methanol. It was also recrystallized either

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[1] Maurer and Petsch, *Ber.*, **66**, 998 (1933).

from absolute alcohol containing 10% pyridine or from benzene with the addition of petroleum ether; yield, 90%. The product was quite insoluble in water or petroleum ether and only slightly soluble in warm methanol. It was soluble in chloroform, dioxane and benzene; m. p. 115–116°; $[\alpha]^{20}_D$ +115° in dry chloroform, $c = 2$.

Anal. Calcd. for $C_{33}H_{26}O_9$: C, 69.94; H, 4.63. Found: C, 70.15; H, 4.74.

***l*-Xylose Tetrabenzoate.**—*α-l*-Xylose tetrabenzoate was obtained in a similar manner; m. p. 115–116° and with the same rotation, but of opposite sign. However, on one occasion when crystallizing the reaction product from absolute alcohol containing 10% pyridine, the *β*-isomer was obtained; yield 29%; m. p. 173–174°; $[\alpha]^{20}_D$ +44.5°, in dry chloroform, $c = 2$.

Anal. Calcd. for $C_{33}H_{26}O_9$: C, 69.94; H, 4.63. Found: C, 69.91; H, 4.64.

Benzobromo-*d*-xylose.—*α-d*-Xylose tetrabenzoate (25 g.) was dissolved in a mixture of anhydrous dioxane and chloroform. A saturated solution of hydrogen bromide in glacial acetic acid (50 cc.) was added and the whole allowed to stand for twenty-four hours. By this time benzobromo-*d*-xylose had precipitated. The mixture was cooled, filtered and washed with petroleum ether. The product was recrystallized from benzene by the addition of petroleum ether; yield 60%; m. p. 134–135°; $[\alpha]^{20}_D$ +117°, in dry chloroform, $c = 2$.

Anal. Calcd. for $C_{26}H_{21}O_7Br$: C, 59.42; H, 4.03; Br, 15.22. Found: C, 59.62; H, 4.22; Br, 15.08.

The benzobromo-*d*-xylose was soluble in dioxane, chloroform, acetone and fairly soluble in methanol. It was insoluble in water, and only slightly soluble in petroleum ether.

Benzobromo-*l*-xylose.—Both *α-l*-xylose tetrabenzoate of m. p. 115–116° and *β-l*-xylose tetrabenzoate of m. p. 173–174° gave the same benzobromo-*l*-xylose of m. p. 134–135° and $[\alpha]^{20}_D$ −116° in dry chloroform, $c = 2$.

***d*-Xylose Tribenzoate.**—Benzobromo-*d*-xylose (20 g.) was dissolved in 50 cc. of acetone and 0.8 cc. of water was added. The solution was cooled in an ice-bath and 12 g. of silver carbonate was added. After short stirring effervescence stopped. The mixture was then shaken an hour at room temperature. The insoluble silver salts were filtered and the filtrate evaporated *in vacuo* until a crystalline residue was left. The product was recrystallized from anhydrous benzene; yield, 98%; m. p. 188–189° (Pyrex capillary tube); $[\alpha]^{20}_D$ +39.5°, in dry chloroform, $c = 2$.

Anal. Calcd. for $C_{26}H_{22}O_8$: C, 67.51; H, 4.80. Found: C, 67.54, 67.62; H, 4.85, 5.02.

Xyloseen-(1,2) Tribenzoate.—Benzobromo-*d*-xylose (20 g.) and anhydrous diethylamine (8.7 cc.) were dissolved in anhydrous benzene contained in a tightly capped bottle. The solution was heated at 55° for three hours, at the end of which time about 75% of the theoretical amount of diethylamine hydrobromide had precipitated. After cooling 150 cc. benzene was added and the mixture filtered. The filtrate was washed with iced dilute sulfuric acid and twice with ice water. The benzene extract was dried over calcium chloride and evaporated *in vacuo* to a gum. The gum was dissolved in 50 cc. of warm absolute ethanol and petroleum ether added to a faint turbidity. Upon allowing this to stand two to three days in an ice box, xyloseen-(1,2) tribenzoate precipitated. It was recrystallized from absolute ethanol; yield, 11%; m. p. 126–128°; $[\alpha]^{20}_D$ −280°, in dry chloroform, $c = 0.5$.

Anal. Calcd. for $C_{26}H_{20}O_7$: C, 70.24; H, 4.54. Found: C, 70.34, 70.15; H, 4.80, 4.71.

Similarly *l*-xyloseen-(1,2) tribenzoate of the same melting point, and optical rotation, $[\alpha]^{20}_D$ +280°, in dry chloroform; $c = 2$ was prepared.

Xyloseen-(1,2) Tribenzoate Dichloride.—*l*-Xyloseen-(1,2) tribenzoate (2.5 g.) was dissolved in 200 cc. of anhydrous benzene and chlorine was passed in until a permanent greenish-yellow color remained. After evaporating the solution *in vacuo* the gummy residue was crystallized from absolute ethanol. The 1-xyloseen-(1,2) tribenzoate dichloride was recrystallized from anhydrous benzene with the addition of petroleum ether; yield, 17%; m. p. 178–180°; $[\alpha]^{20}_D$ +110°, in dry chloroform, $c = 1.5$.

Anal. Calcd. for $C_{26}H_{20}O_7Cl_2$: C, 60.57; H, 3.91; Cl, 13.77. Found: C, 60.70; H, 4.07; Cl, 13.26.

Summary

1. Dextro and levo xylose tetrabenzoate have been synthesized. The *α* form of the former has been isolated and both the *α* and *β* forms of the latter were made.

2. Benzobromo-*d*- and *l*-xylose have been made.

3. *d*-Xylose tribenzoate has been made from *d*-benzobromo-*d*-xylose.

4. Dextro and levo xyloseen-(1,2) tribenzoate have been synthesized.

5. *l*-Xyloseen-(1,2) tribenzoate dichloride was made by the addition of chlorine to *l*-xyloseen-(1,2) tribenzoate.

RAHWAY, N. J. RECEIVED SEPTEMBER 25, 1936