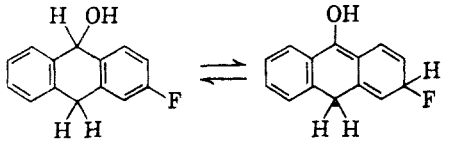
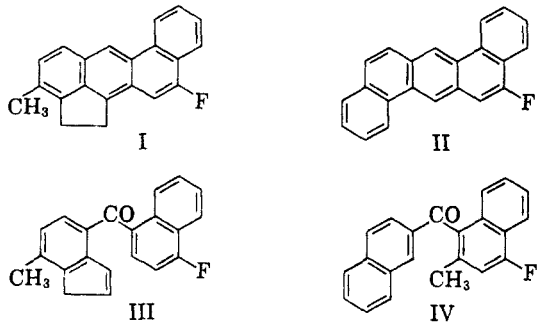


creating a nonaromatic fluorine atom and thus facilitating its elimination.[4] Similar schemes have been suggested in other abnormal reactions.[5]

It is recalled that the synthesis of the chloro- and methoxy-analogs of I also resulted at least very largely in the elimination of the substituents,[6] while 2- and 3-methoxy-[6-8] and 3-chloro-20-methyl-cholanthrene[8] could be obtained without difficulties.



EXPERIMENTAL

4-Methyl-7-(4-fluoro-1-naphthoyl)hydrindene (III). Following Fieser and Seligmann's work[9] for the synthesis of methylcholanthrene, 50 ml. of dry benzene and 17 g. of 4-methyl-7-cyanohydrindene[9] in 80 ml. of benzene were added to a Grignard solution prepared from 4 g. of magnesium and 27 g. of 4-fluoro-1-bromonaphthalene in 100 ml. of ether. The reaction mixture was refluxed and stirred for 12 hr. and decomposed with cold 18% hydrochloric acid. The organic solvents were then removed by steam distillation and the remaining imine hydrochloride of III was filtered and hydrolyzed by refluxing it for 3 hr. with a mixture of 100 ml. of hydrochloric acid, 200 ml. of water, 100 ml. of glacial acetic acid, and 120 ml. of toluene. The aqueous layer was extracted with toluene and the combined toluene solutions were treated with steam in the presence of 10% sodium hydroxide solution. A dark oil was obtained which was dissolved in benzene, dried, and distilled. The fraction boiling at 205° (0.5 mm.) was a viscous oil which crystallized quickly upon trituration with ether. From methanol, beautiful crystals of m.p. 123° were obtained. Yield, 22 g. (95%).

Anal. Calcd. for $C_{21}H_{17}FO$: C, 82.9; H, 5.6; F, 6.2. Found: C, 82.8; H, 5.7; F, 6.0.

Pyrolysis. The foregoing ketone (18 g.) was pyrolyzed for 40 min. at 410°. The product was dissolved in benzene and flash-distilled under 2 mm. pressure after drying. Thus, 1.3 g. of a product was obtained which upon addition of ether to its benzene solution deposited yellow crystals (0.85 g.) of m.p. 180–181° (lit.[9] m.p. 179.5–180°). The analysis and properties showed that 20-methylcholanthrene had been isolated; yield, 5%.

Anal. Calcd. for $C_{21}H_{16}$: C, 94.0; H, 6.0. Found: C, 93.6; H, 6.0.

By working at somewhat lower temperatures (365°) one can raise the yield to about 15%, but even under these conditions no fluorine-containing substance could be isolated.

1-Fluoro-3-methylnaphthalene. The diazotization of 9 g. of 1-amino-3-methylnaphthalene hydrochloride, prepared by the reduction of the nitro-compound,[10] was carried out with 15 ml. of concentrated hydrochloric acid, 20 ml. of water, and 3.5 g. of sodium nitrite at 0°. To the clear solution, 10 ml. of 56% fluoboric acid was added and the precipitate filtered after 30 min. Thermal decomposition of the salt gave a dark oil which was dissolved in benzene, washed with alkali, dried, and distilled. B.p. 123° (20 mm.); yield, 5 g. (62%).

Anal. Calcd. for $C_{11}H_9F$: C, 82.5; H, 5.6; F, 11.8. Found: C, 82.3; H, 5.7; F, 11.7.

4-Fluoro-2-methyl-1-(2-naphthoyl)-naphthalene (IV). To a mixture of 4.5 g. of 1-fluoro-3-methylnaphthalene, 4.5 g. of 2-naphthoyl chloride, and 50 ml. of carbon disulfide, 4.5 g. of aluminum chloride was added. The mixture was stirred at 0° for 5 hr. and decomposed by addition of 20 ml. of cold 18% hydrochloric acid. Upon distillation with steam, a brown oil remained which crystallized after trituration with petroleum ether. The solid was treated with hot 10% sodium carbonate solution, dried, and recrystallized successively from glacial acetic acid and ethanol. Thus 7.2 g. (91%) of almost colorless crystals of m.p. 136° was obtained.

Anal. Calcd. for $C_{22}H_{15}FO$: C, 84.1; H, 4.8; F, 6.0. Found: C, 83.8; H, 5.0; F, 6.5.

Pyrolysis. The pyrolysis of 4 g. of the foregoing ketone was carried out at 420° for 1 hr. and the product flash-distilled at 2 mm. pressure. The distillate was dissolved in hot benzene and separated upon cooling as glistening, yellowish platelets of m.p. 260–262°. They were identified by analysis as 1,2,5,6-dibenzanthracene (lit.[7], m.p. 266°). Yield, 0.35 g. (10%).

Anal. Calcd. for $C_{22}H_{14}$: C, 95.0; H, 5.0. Found: C, 94.7; H, 5.4.

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Preparation of L-Xylose

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L-Xylose has been prepared from D-glucose by Reichstein *et al.*[2] The preparation involved oxi-

(1) Part of a thesis to be submitted to the Senate of the Hebrew University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

dation of D-glucose to D-glucosaccharic acid, with subsequent reduction of D-glucosaccharic acid γ-lactone to L-gulonic acid γ-lactone, and degradation of the calcium salt of the latter acid with hydrogen peroxide to L-xylose.

Vargha[3] very markedly simplified the preparation of L-xylose by oxidizing 2,4-benzal-D-sorbitol with lead tetraacetate to 2,4-benzal L-xylose which was extracted from the oxidizing mixture with ethyl acetate and crystallized. Subsequent hydrolysis of the benzal moiety with 15% acetic acid resulted in the formation of the free sugar.

L-Xylose is a starting material in a chemical synthesis of L-ascorbic acid.[2] New interest in this sugar arose when it was found that the L-aldopentose sugar is an intermediate in the normal metabolic breakdown of L-ascorbic acid in the guinea pig.[4]

This note describes a simplified preparation of L-xylose from 2,4-benzal-D-sorbitol.

EXPERIMENTAL[5]

Benzal sorbitol. Benzal sorbitol was prepared according to the directions of Vargha.[3] One recrystallization from ethanol gave needles of m.p. 172–173°, yield 50–60% of theory.

L-Xylose. A 13.5-g. sample of 2,4-benzal-D-sorbitol (0.05*M*) was suspended in 50 ml. hot dioxane. Water, 50 ml., was added to the hot suspension with stirring, and warming was continued until all the solid had dissolved. After cooling to 35–45°, 100 ml. of 0.5*M* periodic acid solution was added, mixed well, and the solution kept in the refrigerator for 30 min. The excess periodate and iodate formed were reduced to iodide by bubbling a slow stream of hydrogen sulfide through the solution for approximately 45 min. The solution turned brown (iodine) and then colorless again with the appearance of a cake of sulfur and sometimes a drop or emulsion of benzaldehyde. The solution was decanted from the sulfur cake into an Erlenmeyer flask and the sulfur treated with a little hot water and hydrogen sulfide gas to extract the sugar derivative and reduce the iodine which adhered to the sulfur. This extraction was repeated twice.

Hydrolysis of 2,4-benzal-L-xylose was performed by immersing the combined water extracts in a boiling water bath for 1 hr. The cloudy solution obtained was decanted from a drop of oil (benzaldehyde) which settled to the bottom of the flask. Silver carbonate, 20 g., was added to the cooled solution to precipitate iodide ion. The suspension was swirled occasionally and usually left overnight. A filtered aliquot of the supernatant solution usually contained soluble silver ion and the *p*H of the solution rose to 5.0–6.0. The solution was boiled with carbon (Norit A) filtered by suction and the filtrate freed of silver ion with hydrogen sulfide. Vacuum filtration with carbon (Norit A) gave a clear, colorless solution, which was concentrated *in vacuo* to approximately 150 ml. The concentrate was sometimes cloudy and was extracted in liquid-liquid Soxhlet extraction apparatus for 24–48 hr. with freshly distilled ether. A slight white precipitate containing sulfur sometimes deposited during the ether extraction.

The extracted solution was treated with carbon (Norit A) and concentrated *in vacuo* (50°) to a sirup, which was dried in a desiccator over phosphorus pentoxide. After recrystallization from absolute ethanol and standing in the refrigerator, white prisms were obtained within 24 hr. Yield 6.2 g., 80% of the theoretical, m.p. 142°.

L-Xylose-2,4-dinitrophenylhydrazone. A suspension of 0.01*M* 2,4-dinitrophenylhydrazine (1.98 g.) in 200 ml. ethanol was added to 0.01*M* L-xylose (1.5 g.), dissolved in 5 ml. of water and refluxed for 12 hr. The solution was filtered when warm, kept at room temperature overnight and the clear solution was concentrated *in vacuo* to dryness. The residue thus obtained, a mixture of red plates and yellow needles, was extracted with 50 ml. of hot ethyl acetate and filtered. Upon recrystallization of the undissolved fraction from ethanol-water (1:1) red plates and yellow needles were formed. By fractional crystallization from ethanol-water (1:1) pure yellow needles, m.p. 165°, were obtained. The melting point of the D-isomer as recorded by Lloyd *et al.*[6] is 162–163°.

Anal. Calcd. for $C_{11}H_{14}O_8N_4$: C, 40.00; H, 4.24; N, 16.96. Found: C, 39.51; H, 4.01; N, 16.85. C, 39.81; H, 4.08, N, 16.80.

L-Xylose p-nitrophenylhydrazone. A 1.5-g. sample of *p*-nitrophenylhydrazine (0.01*M*) was dissolved in 100 ml. ethanol. To the clear solution 1.5 g. L-xylose (0.01*M*) was added and the solution was heated to boiling. The solution was kept at room temperature for 1 hr. and concentrated under reduced pressure to a crystalline mass. The crystals were washed with cold water, then with cold ethanol and recrystallized from ethyl acetate as prismatic needles, m.p. 152°.

Anal. Calcd. for $C_{11}H_{15}O_6N_3$: C, 46.31; H, 5.26; N, 14.73. Found: C, 46.46; H, 5.48; N, 14.70.

(L-xylo)-1,2,3,4-tetrahydroxybutylbenzimidazole hydrochloride (L-xylose benzimidazole hydrochloride). Barium L-xylonate was prepared according to the directions of Moore and Link.[7] A 1.7-g. sample of L-xylose yielded a white hygroscopic barium salt which was washed by three centrifugations in methanol. The salt was suspended in 20 ml. of water and a slight excess of 1*N* sulfuric acid was added. Precipitated barium sulfate was removed by centrifugation and the supernatant liquid was concentrated under reduced pressure. The sirup obtained was dissolved in ethanol (5 ml.). To the cloudy solution, 55 ml. *n*-butanol, 0.9 g. *o*-phenylenediamine dihydrochloride and 0.6 g. *o*-phenylenediamine were added, and the mixture was then refluxed for 8 hr.

The solution obtained after filtration was concentrated under reduced pressure to about 30 ml. The crystallization of L-xylo-benzimidazole hydrochloride was spontaneous; the crystals were twice crystallized from *n*-butanol as long prisms, m.p. 180°. $[n]^{20}_D$, −15.5° (*c*, 2; H_2O). Huebner *et al.*[8] report m.p. 181–182°, $[n]^{20}_D$, +17.3 (*c*, 2; H_2O), for the D-isomer.

Anal. Calcd. for $C_{11}H_{15}O_4N_2Cl$: C, 48.1; H, 5.5; N, 10.2. Found: C, 48.3; H, 5.5; N, 9.8.

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