carbon. The barium carbonate derived from C-20 of the biosynthesized cortisol-C^{14} contained 48,000 d/m/mM.

On the basis of the scheme postulated by Woodward and Bloch[5] one would expect ten radioactive carbons to be incorporated into the first 21 carbons of cholesterol from acetate-1-C^{14}. If one assumes that corticosteroids are biosynthesized from acetate-1-C^{14} through cholesterol then the arrangement of all carbons and the number of C^{14} atoms in corticosteroids would be expected to be the same as that found in the first 21 carbons of cholesterol. Our findings demonstrate the absence of radioactivity in carbons 21 of both cortisol-C^{14} and corticosterone-C^{14}. By our method of counting we can say that if radioactivity was present in C-21 of cortisol the value must be less than 8.1% of that found in C-20. The count of 48,000 d/m/mM. found in C-20 of cortisol-C^{14} is in reasonable agreement with the calculated value of 52,500 d/m/mM. Our findings demonstrate that the arrangement of methyl and carboxyl carbons in the corticoid side chain is identical to that of carbons 20 and 21 of cholesterol.

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The Preparation of 3,4-Bis(2-furyl)-1,2,5-oxadiazole[1,2]

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INTRODUCTION

A compound, later identified as 3,4-bis(2-furyl)-1,2,5-oxadiazole, precipitated gradually from urea solutions of α-furildioxime prepared in connection with a study of the effect of urea on the solubility of water-soluble *vic*-dioximes. 3,4-Bis(2-furyl)-1,2,5-oxadiazole was characterized by Tsumaki and Yamaguchi[3] who originally obtained it as a product of the pyrolysis of bis(α-furildioximato-N,N′)-nickel(II).

3,4-Bis(2-furyl)-1,2,5-oxadiazole has been prepared in 58% yield by treating α-furildioxime with urea solution. This compound has been prepared also from both the α- and γ-furildioxime by modifying the conditions of a sealed tube reaction described by Auwers and Meyer[4] for the preparation of diphenylfurazan.

The effect of urea on the aqueous solubility of 2,3-butanedionedioxime, 1,2-diaminoethanedionedioxime, 3-methyl-, 4-methyl-, 3-ethyl-, 4-isopropyl-, and 4-*tert*-amyl-1,2-cyclohexanedionedioxime, 1,2-cycloheptanedionedioxime, 1,2-cyclohexanedionedioxime and α-benzildioxime was also studied. This catalytic dehydration by urea does not seem to be a general reaction since none of the above aliphatic, alicyclic or aromatic *vic*-dioximes were converted to the corresponding 1,2,5-oxadiazoles by urea under the conditions found most satisfactory for preparing 3,4-bis(2-furyl)-1,2,5-oxadiazole.

EXPERIMENTAL WORK

From α-furildioxime. α-Furildioxime, 1.2556 g. (0.0057 mole) was treated with 25 ml. of 50% (w/w) urea solution, and the mixture was warmed to 80°. The solution soon became discolored and cloudy, and an oily phase appeared. Heating was continued until the aqueous phase became clear. As the mixture cooled, the 3,4-bis(2-furyl)-1,2,5-oxadiazole solidified and was collected by filtration. This material was dissolved in the minimum amount of methanol and was precipitated by the addition of 150 ml. of distilled water. The yield of 3,4-bis(2-furyl)-1,2,5-oxadiazole, m.p. 61–62°, was 0.6602 g. (58%).

α-Furildioxime, 1.3625 g. (0.006 mole) and water, 2.5 g. (0.14 mole), were sealed in a 200-ml. container constructed from borosilicate tubing ($1^3/_4$-inch O.D., $^3/_{32}$-inch wall thickness). The container then was placed in a 12-inch section of 2-inch iron pipe closed at both ends with pipe caps. The container was heated in an oven at 175° for 8 hours. Upon cooling, the container was opened, and the contents were rinsed out with methanol. The methanolic solution of the product was heated, filtered, and concentrated by evaporation to a volume of 5 ml. Crystallization of the 3,4-bis(2-furyl)-1,2,5-oxadiazole was effected by the addition, with swirling, of 150 ml. of distilled water. The yield was 0.1515 g. (12%).

From γ-furildioxime. 3,4-Bis(2-furyl)-1,2,5-oxadiazole was obtained by heating γ-furildioxime with water in a sealed container for 12 hours in an oven at 165°. The amount of water necessary to produce a pressure of 25 atmospheres was calculated from the simple gas law. The product was purified by the previously described procedure. The yield from this isomer of the dioxime was 20.5%.

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[1] No. XIX in a series on "Chemistry of the *vic*-Dioximes." Previous paper in this series is No. XVIII, *J. Org. Chem.*, **21**, 547 (1956).

[2] Contribution No. 430; work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[3] Tsumaki and Yamaguchi, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **70**, 10 (1949).

[4] Auwers and Meyer, *Ber.*, **21**, 810 (1888).

Phenylboronates of Pentoses and 6-Deoxyhexoses

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Although it is known that boric acid and boric acid derivatives react with polyhydric alcohols and with sugars, stable products have not been isolated from the reducing sugars.[2-4] Kuivila and coworkers[4] have described the phenylboronates, a new

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[1] Fellow of the American-Swiss Foundation for Scientific Exchange.

[2] Böeseken, *Advances in Carbohydrate Chem.*, **4**, 189 (1949).

[3] Rippere and La Mer, *J. Phys. Chem.*, **47**, 204 (1943).

[4] Kuivila, Keough, and Soboczenski, *J. Org. Chem.*, **19**, 780 (1954).

TABLE I

YIELD, PROPERTIES, AND COMPOSITION OF ALDOSE PHENYLBORONATES

bis(Phenylboronate)[a] of:	Yield, %	M.p., °C.[b]	$[\alpha]^{25}_{D}$, C_6H_6, c, <5	Formula	C		H		B		Phenylboronic acid,[d] millimoles/g.	
					Calc'd	Found[c]	Calc'd	Found[c]	Calc'd	Found[c]	Calc'd	Found
L-Arabinose[e]	45	166	+ 8.5°	$C_{17}H_{16}B_2O_5$	63.43	63.55	5.01	5.04	6.72	6.85	6.21	6.23
D-Ribose	24	140–142	+116	$C_{17}H_{16}B_2O_5$	63.43	63.66	5.01	5.00	6.72	6.52	6.21	6.22
D-Xylose	41	137	− 8.5	$C_{17}H_{16}B_2O_5$	63.43	63.58	5.01	4.93	6.72	6.77	6.21	6.21
D-Lyxose	25	109–110	− 60.4	$C_{17}H_{16}B_2O_5$	63.43	63.55	5.01	5.09	6.72	6.73	6.21	6.20
L-Fucose	30	109.5	+ 29.4	$C_{18}H_{18}B_2O_5$	64.35	64.45	5.39	5.42	6.44	6.61	5.95	5.96
L-Rhamnose[e]	35	107.5	+ 87	$C_{18}H_{18}B_2O_5$	64.35	64.43	5.39	5.36	6.44	6.64	5.95	5.99

[a] On qualitative paper chromatograms (Whatman paper No. 1, butanol:ethanol:water/40:11:19, silver nitrate-ammonia spray indicator), every ester showed decomposition into phenylboronic acid and the original sugar (identified by comparison with authentic specimens). [b] Kofler stage melting point. [c] Analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.; dried to constant weight at 45° and 1–2 mm. [d] Method of Kuivila and co-workers, ref. 4. [e] Mol. wt. (cryoscopic in benzene): 309 for L-arabinose *bis*(phenylboronate) (calc'd, 322); 321 for L-rhamnose *bis*(phenylboronate) (calc'd, 336); determined by Mr. J. B. Miller of this Laboratory.

type of derivative in this field. The present communication reports the preparation of crystalline esters of phenylboronic acid with all of the pentose structures and with the two 6-deoxyhexoses L-fucose and L-rhamnose (Table I). The procedure of Kuivila, Keough, and Soboczenski,[4] while suitable for the acyclic alditols, failed to yield isolable crystalline products with the cyclic sugar structures. The present authors obtained phenylboronates of cyclic sugars by fusion techniques followed by product isolation with hydrocarbon solvents. The crude reaction product appeared to be a mixture from which a pure individual substance was obtained, on repeated crystallization, in yields of 24–45%. The products, so isolated and purified, were *bis*(phenylboronates) in which all four of the available hydroxyl groups were presumably esterified.

All of the products characterized were well crystallized and were stable in air. They were soluble in hydrocarbon solvents and were best recrystallized from petroleum ether. On the addition of water to their alcoholic solutions, the compounds were decomposed into their components, detectable by paper chromatography. The *bis*(phenylboronate) of L-arabinose was so hydrolyzed and the products obtained were identified by isolation methods. While not established, it is probable that this process involved a trans-esterification in the alcohol followed by hydrolysis, on the addition of water, of the dialkyl phenylboronate formed.

EXPERIMENTAL

Preparation of aldose bis(*phenylboronates*). An amount of 4.0 millimoles (0.60 g. of pentose, 0.66 g. of 6-deoxyhexose) of aldose and 8.0 millimoles (0.98 g.) of phenylboronic acid[5] were placed in a 50 ml. round-bottomed flask which then was evacuated to 10–15 mm. The mixture was heated slowly to fusion (110–160°) and maintained in the fused condition for 1 to 3 min. After cooling, 30–40 ml. of petroleum ether (b.p. 65–110°) was added and the mixture was refluxed, with stirring, for 10 min. and then was filtered through a fritted glass filter. This extraction was repeated with two further 20-ml. portions of petroleum ether. The combined filtrates were concentrated to 15–30 ml. The derivatives crystallized on allowing the concentrates to stand first at 30° and then, without filtering, at 0°. The crystals were removed and recrystallized six to eight times from hot petroleum ether to constant melting point. Data on the substances synthesized are recorded in Table I. The crystals were soluble in benzene, ether, methanol, ethanol and in warm petroleum ether; they were insoluble in water.

Hydrolysis of L-arabinose bis(*phenylboronate*). An amount of 400 mg. of L-arabinose *bis*(phenylboronate) was dissolved in 50 ml. of boiling methanol, 50 ml. of water was added, and the solution was concentrated under reduced pressure to remove the methanol. The cooled solution was extracted with ether and the residue obtained on solvent removal from the dried ether extract was crystallized from water and identified as phenylboronic acid by melting point, mixture melting point (217°) and paper chromatographic behavior (footnote *a*, Table I). The ether-extracted aqueous solution was concentrated to dryness under reduced pressure and the residue, crystallized from water-methanol, was identified as arabinose by melting point, mixture melting point (160°), and paper chromatographic behavior (footnote *a*, Table I).

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(5) Bean and Johnson, *J. Am. Chem. Soc.*, **54**, 4415 (1932).

Cyclopropanes. XXI.[1]

1-Acetyl-2-nitro-2,3,3-trimethylcyclopropane

LEE IRVIN SMITH AND W. L. KOHLHASE

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As a part of a study of the action of bases upon nitrocyclopropyl ketones,[2] the preparation of the first two examples (Ia and Ib) of a nitrocyclopropyl ketone having only a single ring hydrogen atom was undertaken. Action of bases upon these 1-

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(1) Paper XX, Smith and Scribner, *J. Am. Chem. Soc.*, **78**, 3412 (1956).

(2) Paper XIX, Smith, Brotherton, and Kohlhase, *J. Am. Chem. Soc.*, **78**, 2532 (1956).