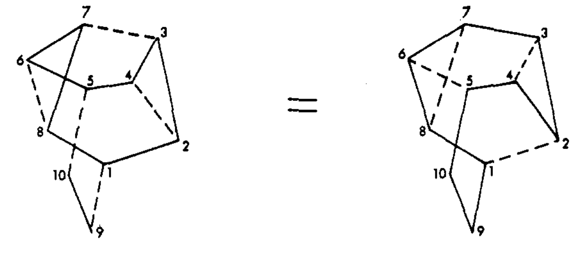
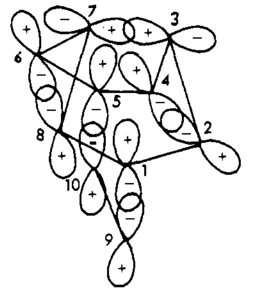


5 5



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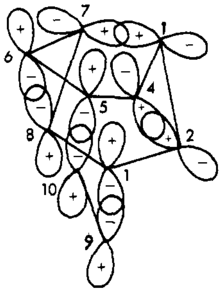

7

The overlap of the 2p atomic orbitals is in phase for formation of the potential σ bonds and the movement about the C_1–C_8, C_5–C_6, and C_1–C_2 and C_4–C_5 bonds is inwardly disrotatory. The cycloaddition may also be described as a ${}_\pi 2_a + {}_\pi 2_a + {}_\pi 2_s + {}_\pi 2_s + {}_\pi 2_s$ formation of the C_6–C_8, C_7–C_3, and C_4–C_2 bonds occurring in the antara manner.[7] Bonding of the azo group to Cu(I) does not change the occupancy of the atomic orbitals but does lower the energy of activation for the alternative retroelectrocyclization to yield cyclooctatetraene and nitrogen.

Now it should be recognized that the forward reaction, namely, the Diels–Alder cycloaddition of a 2π system to cyclooctatetraene, cannot give an analog to **2**. This is because Diels–Alder adducts usually derive from the bicyclo[4.2.0]octa-2,4,7-triene valence tautomer.[8,9] We argue that even though formation of an adduct analogous to **2** is thermally allowed, the reaction between the 2π dienophile takes precedence. However, the present example, $\mathbf{2} \rightarrow \mathbf{4} + N_2$, represents the allowed reverse of this hypothetical reaction. An interesting corollary of this interpretation is that metal complexation of the azodienophile in reaction with cyclooctatetraene should yield an adduct analogous to **2**. This point is under investigation.

Acknowledgment. The authors wish to thank Professor D. G. Gorenstein of this department and Professor H. E. Zimmermann, University of Wisconsin, for helpful discussions.

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(7) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(8) R. Huisgen and F. Mietzsch, *ibid.*, 3, 83 (1964).

(9) For examples in which COT reacts directly in the Diels–Alder reaction see: A. B. Evin, R. D. Miller, and G. R. Evanega, *Tetrahedron Lett.*, 5863 (1968); E. Vedejs and R. A. Shepherd, *ibid.*, 1863 (1970).

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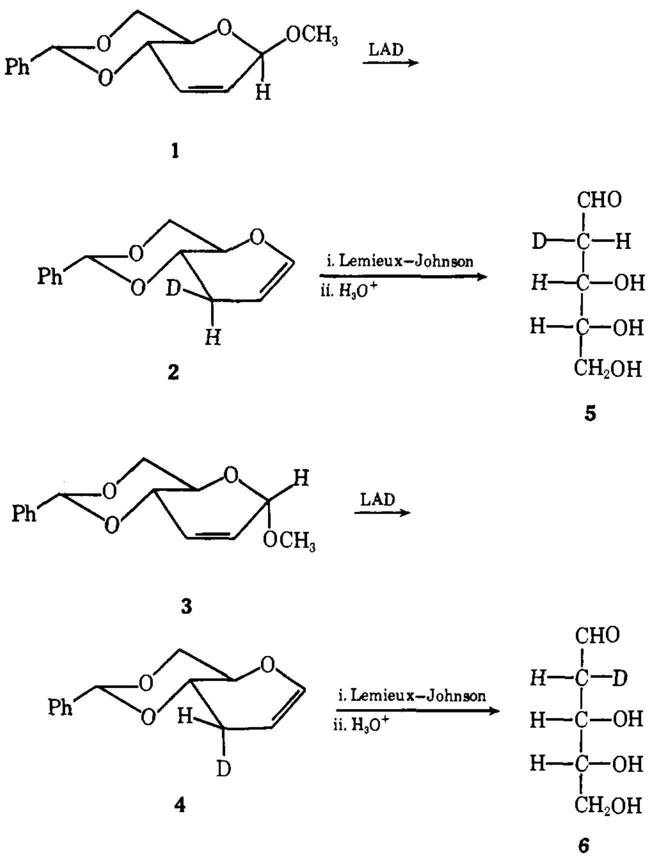
The Specifically 2-Monodeuterated 2-Deoxy-D-riboses (2(*S*)- and 2(*R*)-Deuterio-2-deoxy-D-erythropentoses)

Sir:

A recent report from this laboratory described the completely stereospecific production of the deuterated glycals **2** and **4** from acetals **1** and **3**, respectively.[1] We now report that the 2-monodeuterated 2-deoxy-D-riboses, 2(*S*)- and 2(*R*)-deuterio-2-deoxy-D-erythropentoses, **5** and **6**, respectively, are readily obtainable from **2** and **4** *via* cleavage of the olefin and subsequent debenzylidenation, with complete retention of stereospecificity of the label.



1 2 5 3 4 6

Lemieux–Johnson oxidation[2] of glycal **2** (219 mg; 1.0 mmol) dissolved in 16 ml of dioxane–water (3:1) mixture using osmium tetroxide (2×10^{-2} mmol)[3] and sodium metaperiodate (1.07 g; 5 mmol) was complete (tlc) in 0.5 hr. The excess periodate was destroyed with ethylene glycol and the product recovered by extraction into ether.[4] The semicrystalline residue was treated for 1.5 hr with dilute sulfuric acid and the neutralized aqueous layer freed from benzaldehyde by chloroform extraction. The deuterated sugar, **5**, was present in the syrup obtained upon evaporation of the

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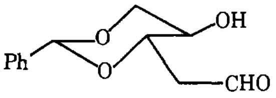
(1) B. Fraser-Reid and B. Radatus, *J. Amer. Chem. Soc.*, **92**, 6661 (1970).

(2) R. Pappo, D. S. Allen, R. U. Lemieux, and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956).

(3) Added as 1 ml of a solution of 0.1 g of OsO_4 in 20 ml of *tert*-BuOH.

(4) The Lemieux–Johnson oxidation product from the ^1H analog of 2^1 was on occasion isolated and shown to be i by spectral data and



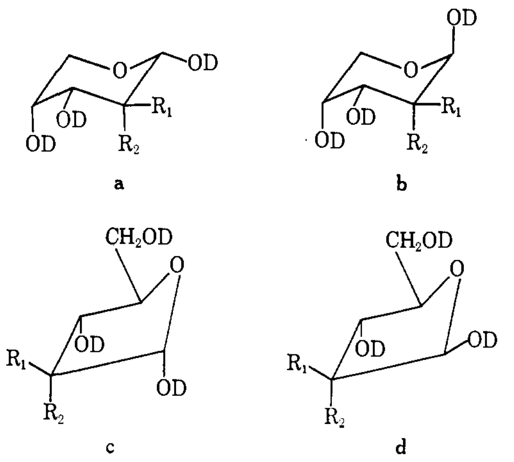
i

microanalysis of the derived semicarbazone.

water. The diastereomer **6** was obtained in an analogous manner from the glycal **4**.[1]

The pure sugars **5** and **6** could be obtained either from preparative paper chromatograms,[5] or alternatively by conversion to, and regeneration from their *N*-phenylglycosylamines ("anilides"),[6] although the latter route gave a somewhat lower overall yield (52 *vs.* 65%). However, since the favored derivative of 2-deoxyribose (**7**) is the *N*-phenylglycosylamine, it is advantageous to note that the corresponding derivatives of **5** and **6**[7] may be (i) mutarotated to equilibrium in pyridine, and/or (ii) hydrolyzed, then reconverted to the "anilide," without any change in the ratio of the M, M − 1, and M + 1 ion peaks in the mass spectra. Furthermore, there was absolutely no change in the nmr pattern (*vide infra*) for H-1 of **5** and **6** before conversion to, and after regeneration from, the *N*-phenylglycosylamines. Hence isolation, purification, and characterization of **5** and **6** as these derivatives and subsequent acid-catalyzed regeneration of the free sugars may be undertaken in confidence that no scrambling of the label will occur.

Table I. Some 220-MHz Nuclear Magnetic Resonance Parameters for Equilibrated Solutions of **5**, **6**, and **7** in D_2O[a]



5, $R_1 = D$; $R_2 = H$
6, $R_1 = H$; $R_2 = D$
7, $R_1 = R_2 = H$

	H-1	H-2	J_{12}, Hz
5a	5.19	8.22	8.5
5b	4.97	8.00	3.3
5c	4.38	8.10	5.7
5d	4.44	7.83	~1.5
6a	5.17	8.00[b]	5.0
6b	4.97	8.20[b]	4.5
6c	4.37	7.59	3.2
6d	4.43	7.85	5.4
7a	5.19		2.5, 8.4
7b	4.97		3.5, 3.5
7c	4.38	7.56	
7d	4.44	7.82, 7.82	

[a] Spectra were recorded at 60° with internal TSP as standard. Chemical shifts are in τ values and the *J* values shown were read directly from the spectra. [b] These signals were broad due, undoubtedly, to large geminal H–D coupling estimated to be ~2.5 Hz.

For the *N*-phenylglycosylamines of **5**, **6**, and **7** the melting points are 179.0–179.5, 178.0–178.5, and 173–174°.[8] The optical rotations, $[\alpha]^{23}\mathrm{D}$, at equilibrium (*c* 0.85, pyridine) are +61.5 (120 hr), +133.8 (24 hr), and 41.7 (72 hr).[8]

Detailed analysis of the nuclear magnetic resonance spectra of **5** and **6** is underway, but some useful information available directly from the 220-MHz spectra of their equilibrated solutions in deuterium oxide is shown in Table I along with data for 2-deoxyribose (**7**). The values for H-1 are compatible with those determined earlier for **7** by Lemieux and Stevens.[9] The chemical shifts reported for H-2 of the pyranose contributors are in excellent agreement with the calculated values using Hall's data,[10] and the spacings J_{12} affirm the disposition of the deuterium in **5** and **6**. The latter affirmation and cognizance of the parameters for the methylene protons in some β-nucleosides[11] permit the assignments for the furanose systems c and d shown in Table I.[12]

Acknowledgment. Financial assistance from the National Research Council of Canada and from Bristol Laboratories is gratefully acknowledged.

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(5) P. A. J. Gorin and J. K. N. Jones, *Nature (London)*, **172**, 1051 (1953).

(6) G. N. Richards, *Methods Carbohyd. Chem.*, **1**, 180 (1962).

(7) Per cent deuteration for both derivatives by mass spectrometry was 98.5. *Anal.* Calcd for $C_{11}H_{14}DO_3N$: C, 62.85; H, 7.67; N, 6.66. Found for the *N*-phenylglycosylamine of **5**: C, 63.29; H, 7.40; N, 6.61. Of **6**: C, 63.21; H, 7.28; N, 6.84.

(8) In agreement with literature values.[5]

(9) R. U. Lemieux and J. D. Stevens, *Can. J. Chem.*, **44**, 249 (1966).

(10) L. D. Hall and J. F. Manville, *Advan. Chem. Ser.*, **No. 74**, 228 (1968). Using the values for 2-deoxy-D-arabinohexopyranose as a guide, the expected difference in chemical shift for the pertinent protons in **6a** and **6b** should be 0.13 ppm. This is in good agreement with the observed value of 0.20 ppm.

(11) (a) M. P. Schweizer, S. I. Chan, and P. O. P. Ts'O, *J. Amer. Chem. Soc.*, **87**, 5241 (1965); (b) R. U. Lemieux, *Can. J. Chem.*, **39**, 116 (1961); (c) "High Resolution NMR Spectra," Vol. II, Varian Associates, Palo Alto, Calif., 1960, no. 566.

(12) In thymidine, for example, the methylene protons appear as a poorly resolved quartet.[11c] Against this precedent, the triplet at τ 7.82 in the spectrum of 2-deoxy-D-ribose 7 is assigned to the carbon-2 protons of the β-D-furanose form, 7**d**. In accordance with this, both **5d** and **6d** show a signal at the same frequency (τ 7.83 and 7.85). There remains unassigned only the methylene protons for the α-D-furanose forms. The signal present in **9c** (τ 7.56) and in **6c** (τ 7.59) obviously arises when $R_1 = H$, since it is absent in **5c** (where $R_1 = D$). Accordingly, in the latter the proton ($R_2 = H$) has been assigned at τ 8.10.

(13) Undergraduate research participant.

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The Isolation and Structure Determination of Dictyopterenes C′ and D′ from *Dictyopteris*. Stereospecificity in the Cope Rearrangement of Dictyopterenes A and B

Sir:

The essential oil of *Dictyopteris*, one of the few genera of seaweed to possess odor, is composed of C_{11} hydrocarbons. Dictyopterene A [(+)-(*R*,*R*)-*trans*-1-(*trans*-hex-1′-enyl)-2-vinylcyclopropane (**1**)][1] and dictyopterene B [(−)-(*R*,*R*)-*trans*-1-(*trans*,*cis*-hexa-1′,3′-dienyl)-2-vinylcyclopropane (**2**)][2] are the major constituents and *trans*,*cis*,*cis*-undeca-1,3,5,8-tetraene (**3**),[2] *trans*,*trans*,*cis*-undeca-1,3,5,8-tetraene (**4**),[3] *trans*,*cis*-undeca-1,3,5-triene (**5**),[3] and *trans*-*trans*-undeca-1,3,5-triene (**6**)[3] are

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(1) R. E. Moore, J. A. Pettus, Jr., and M. S. Doty, *Tetrahedron Lett.*, 4787 (1968).

(2) J. A. Pettus, Jr., and R. E. Moore, *Chem. Commun.*, 1093 (1970).