Table II. Calculated a_H Values for Anion Radicals II and VI ($a_H = Q\rho$)

Species	Calculation	a_H values for hydrogens at positions 1	2	3	4
VI, $Q = 27.44$	Hückel[a] ρ		0.2716	0.0538	0.1746
	Hückel[a]		7.45	1.48	4.79
	McLachlan[a]		9.97	−0.76	4.51
	McLachlan[b]		9.32	−0.48	4.88
	McLachlan[c]		8.64	−0.15	5.22
	Assigned		8.11	$<\|0.10\|$	5.61
VI, $Q = 24.66$	Hückel[a]		6.70	1.33	4.31
	McLachlan[a]		8.96	−0.69	4.05
	McLachlan[b]		8.38	−0.43	4.39
	McLachlan[c]		7.77	−0.13	4.70
	Assigned		8.11	$<\|0.10\|$	4.22
II, $Q = 27.40$	Hückel[d] ρ	0.1677	0.0769	0.1549	0.1008
	Hückel[d]	4.59	2.11	4.24	2.76
	McLachlan[d]	6.10	0.99	4.75	1.88
	Assigned	5.72	0.87	5.12	1.99

[a] $\beta_{23} = \beta_{34} = \beta_{45} = 1.00\beta_0$. [b] $\beta_{23} = \beta_{45} = 1.00\beta_0$; $\beta_{34} = 0.90\beta_0$. [c] $\beta_{23} = \beta_{45} = 1.00\beta_0$; $\beta_{34} = 0.80\beta_0$. [d] $\beta_{18} = 0.600\beta_0$; $\beta_{12} = 0.890\beta_0$; $\beta_{23} = 0.925\beta_0$; $\beta_{34} = 0.808\beta_0$; $\beta_{45} = 1.00\beta_0$.

system, but it is experimentally quite similar to that for a known hexatriene anion radical, namely VII, generated from cycloheptatriene by Levy and Myers[5] (Table I). A strong argument in favor of structure VI may be based on the observed Q value. Thus, the sum of a_H values, 24.66 or 27.44, for C_2 to C_7 is a reasonable value for Q. On the other hand, the sum of a_H values, 35.88, for C_1 to C_8 is well out of the range of known Q values. This strongly supports structure VI with the C_1–C_8 cyclopropane electrons excluded from the delocalized π-electron system. The observed a_H value of 5.61 or 4.22 G for $C_{1,8}$ is also appropriate for protons β to the hexatriene anion radical system in VI.

The inclusion of the C_1–C_8 cyclopropane electrons in the delocalized electronic system in anion radical II and their exclusion in VI is very significant. The difference between the two cases may be understood with the aid of an orbital symmetry argument of the type employed by Woodward and Hoffmann[6,7] for electrocyclic reactions. Examining the highest occupied molecular orbital in an octatetraene anion radical, the conversion of a cyclononatetraene anion radical (*e.g.*, IV) to a bicyclic hexatriene anion radical (*e.g.*, III) and the reverse reaction are predicted to be disrotatory. The opening of the anion radical from *cis*-I leads to the anion radical of the all-*cis* cyclononatetraene, and geometry is favorable for a compromised delocalized electronic system intermediate in character between the bicyclic hexatriene and monocyclic cyclononatraene anion radical extremes. *trans*-V has the C_2–C_7 hexatriene system in a nearly planar arrangement. Thus, the situation is more favorable for conjugation in the triene portion of the hydrocarbon[8] or in a triene anion radical system than it is in the tub-like *cis*-I. The disrotatory opening of anion radical VI is toward a very uncomfortable *trans,cis,cis,cis*-cyclononatetraene anion radical. Models of the *trans,cis,cis,cis*-tetraene show the relative orientation of olefinic groups to be very unfavorable for conjugation in the hydrocarbon and in the corresponding anion radical. It is also very unfavorable for a C_1–C_8 interaction in the latter. It is thus clearly more advantageous for VI to remain a relatively favorable hexatriene type anion radical than to open partially or fully.

The occurrence of nonclassical electron delocalization in any particular system depends on stereoelectronic and quantum mechanical factors. This is illustrated by the pair of anion radicals discussed above, namely, classical VI and nonclassical II. Another illustration is provided by the $C_8H_9^+$ species from protonation of cyclooctatetraene. Thus, the free $C_8H_9^+$ and its six-π-electron metal carbonyl complexes, $C_8H_9^+Mo(CO)_3$ and $C_8H_9^+W(CO)_3$, are nonclassical homotropylium species,[9] while the four-π-electron iron complex, $C_8H_9^+Fe(CO)_3$, is a classical one.[9]

Acknowledgment. We are grateful to Drs. D. Kivelson and R. Holtzer for the use of their esr and programmed plotting facilities.

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(5) D. H. Levy and R. J. Myers, *J. Chem. Phys.*, **41**, 1062 (1964).

(6) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

(7) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(8) For example, the λ_{max} for ultraviolet absorption is at 311 mμ for V[3] and at 247 mμ for I.

(9) (a) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Am. Chem. Soc.*, 87, 3267 (1965); (b) S. Winstein, Special Publication No. 21, The Chemical Society, London, 1967, p 5.

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Synthesis of a Branched-Chain Sugar

Sir:

In this communication we wish to report a facile synthesis of a branched-chain sugar by application of the oxo reaction[1] to 1,2,4,6-tetra-*O*-acetyl-3-deoxy-α-D-*erythro*-hex-2-enopyranose. In earlier work[2,3] it was shown that glycals react with carbon monoxide and hydrogen to give epimeric anhydrodeoxyalditols and anhydrodeoxyaldoses having one more carbon than the starting compound. When 1,2,4,6-tetra-*O*-acetyl-3-deoxy-α-*erythro*-hex-2-enopyranose (I)[4] was allowed to react with synthesis gas in the presence of preformed dicobalt octacarbonyl at 150–160° for 2 hr, a mixture of oxo products was obtained. After the product was freed from catalyst, it was fully acetylated using acetic anhydride and pyridine. Preparative vpc of the latter acetate on an Aerograph Model 1525 using a 12-ft column of Chromosorb W carrying 10% (by weight) silicone gum rubber SE-52 operated at 280° gave compound II (having the longest retention time), isolated in about 30% yield. Alternatively, the mixture was partially separated by column chromatography using alumina as adsorbent and ether as developer. Substance II was recrystallized from ether–petroleum ether (bp 30–60°), mp 100°, $[\alpha]^{22}$ +58° (c 4, benzene). *Anal.* Calcd for $C_{17}H_{24}O_{11}$: C, 50.47; H, 5.98; mol wt, 404. Found: C, 50.41; H, 5.98; mol wt, 404 (added 43 to parent peak) (m/e 361, loss of CH_3CO).[5]

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(1) I. Wender, H. W. Sternberg, and M. Orchin, *Catalysis*, **5**, 73 (1957).

(2) A. Rosenthal and D. Abson, *Can. J. Chem.*, **42**, 1811 (1964).

(3) A. Rosenthal and D. Abson, *J. Am. Chem. Soc.*, **86**, 5356 (1964).

(4) (a) R. U. Lemieux, D. R. Lineback, M. L. Wolfrom, F. B. Moody, E. G. Wallace, and F. Komitsky, Jr., *J. Org. Chem.*, 30, 1092 (1965); (b) R. J. Ferrier, W. G. Overend, and G. H. Sankey, *J. Chem. Soc.*, 2830 (1965).

(5) Molecular weight by mass spectroscopy using an A.E.I.-M.S.9 spectrometer.

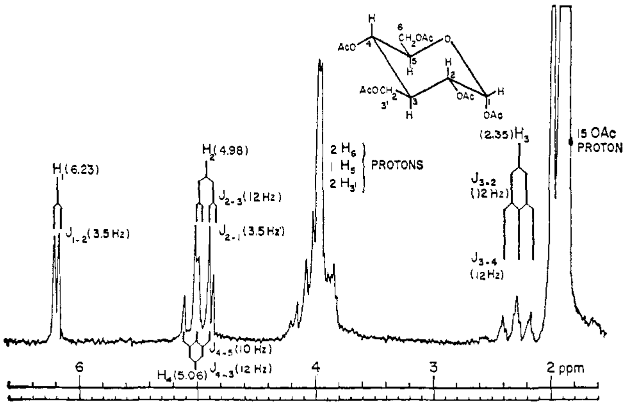


Figure 1. Nmr spectrum of 1,2,3′,4,6-penta-*O*-acetyl-3-deoxy-3-*C*-(hydroxymethyl)-α-D-glucose in $CDCl_3$ at 100 MHz.

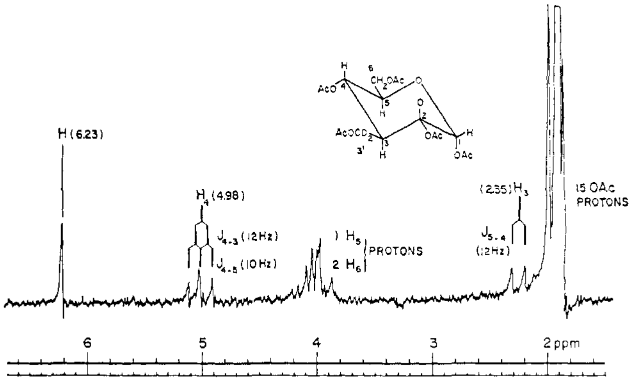
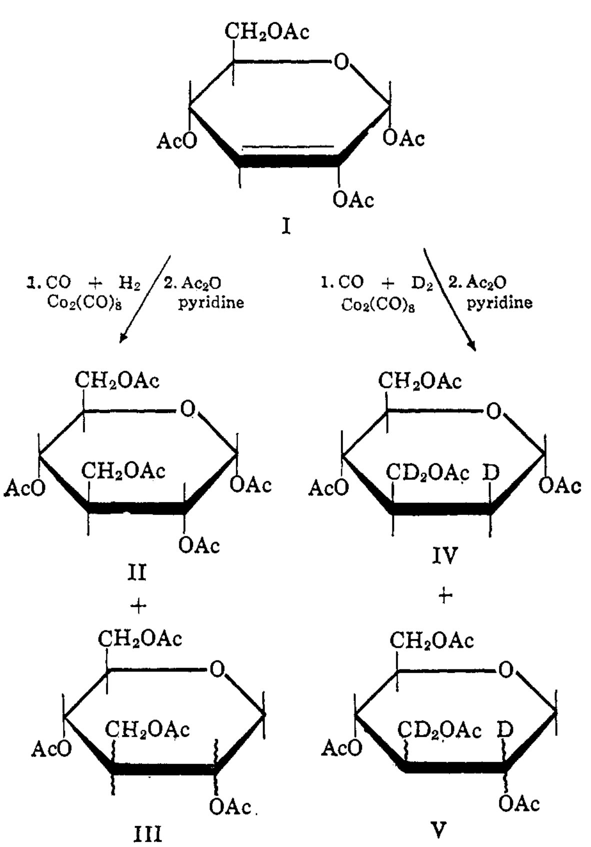


Figure 2. Nmr spectrum of 1,2,3′,4,6-penta-*O*-acetyl-3-deoxy-3-*C*-(hydroxymethyl)-α-D-glucose-2,3′,3′,-$^2H_3$ (*cis*) in $CDCl_3$ at 100 MHz.

Similar application of the oxo reaction (using carbon monoxide and deuterium) to I gave the partially deuterated analog IV; *m*/*e* 364, loss of CH_3CO.



Figures 1 and 2 show the nmr spectra[6] of compounds II and IV, respectively. Based on the assumption that compounds II and IV are in the normal chair conformation, then the chemical shifts of the C-1 anomeric hydrogen (6.23 ppm) of both suggest that they are α anomers (no anomerization has occurred during the oxo reaction), which agrees with the corresponding chemical shift of the C-1 hydrogen of α-D-glucopyranose pentaacetate (6.31 ppm).[7] The coupling constant of H-1 and H-2 is 3.5 Hz (shown in Figure 1), which is similar to that of H-1 and H-2 of α-D-glucopyranose pentaacetate (J_{1-2} = 3.5 Hz) and not to that of α-D-mannopyranose pentaacetate (J_{1-2} = 1.0 Hz). Therefore, the C-2 proton must be in an axial orientation, and II has the D-*gluco* configuration. In the deuterated compound IV the C-2 proton has been replaced by a deuteron and the anomeric signal becomes a singlet (see Figure 2), thus confirming that deuterium has added to C-2 and, therefore, the hydroxymethyl group must have added to C-3. Figure 2 clearly shows the single H-3 methine hydrogen at 2.35 ppm, with J_{3-4} = 12 Hz. In the deuterated analog IV, H-3 is coupled only with H-4 which is in an axial orientation. The large coupling constant of J_{3-4} strongly indicates that H-3 must be in an axial orientation, and therefore the branched-chain must be equatorial. This hypothesis is strongly supported by previous findings[8,9] that the oxo reaction proceeds *via* a *cis* addition of hydrogen and a hydroxymethyl group to the carbon–carbon double bond. Hence, H-2, H-3, and H-4 must be all *trans* diaxial and, therefore, compounds II and IV are penta-*O*-acetyl-3-deoxy-3-*C*-(hydroxymethyl)-α-D-glucopyranose and penta-*O*-acetyl-3-deoxy-3-*C*-(hydroxymethyl)-α-D-glucopyranose-2,3′,3′-$^2H_3$.

The vpc rerun of the major component (about 50%) at 180° showed the presence of two zones (never separated in 100% purity). The nmr of these zones showed the absence of anomeric protons but the presence of branched chains. These anhydro branched-chain sugars were presumed to be tetra-*O*-acetyl-1,5-anhydro-3-deoxy-3-*C*-(hydroxymethyl)-D-glucitol and -D-altritol (III).

The more mobile zones of the vpc chromatogram isolated in very low yield (about 5%) were presumed to be hydrogenation products of the 2,3-ene I. Support for this contention was provided by carrying out a platinum-catalyzed hydrogenation in ethanol of I whereby two main components (exhibiting no anomeric hydrogen in their nmr) were obtained with retention times identical with those of the two fast moving minor components in the fully acetylated oxo product of I.

The preferential formation of the D-*gluco* isomer II can be explained by the assumption that the 2,3-ene I probably exists mainly in a conformation in which the C-4 acetoxy and C-5 acetoxymethyl groups are in pseudo-equatorial orientations. The bulky C-1 and C-6 acetoxy groups might be expected to impede ap-

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[6] Nuclear magnetic resonance spectra were determined on a Varian HA-100 spectrometer using TMS as an internal reference.

[7] R. U. Lemieux and J. D. Stevens, *Can. J. Chem.*, **43**, 2059 (1965).

[8] A. Rosenthal and D. Abson, *Carbohydrate Res.*, **3**, 112 (1966).

[9] A. Camerman, H. J. Koch, A. Rosenthal, and J. Trotter, *Can. J. Chem.*, **42**, 2630 (1964).

proach of the catalyst, $HCo(CO)_4$, from the α side of the 2,3-ene, and as a consequence it would react preferentially on the β side, leading to one product. Once hydrogenolysis of the allylic anomeric acetate occurs, the steric hindrance of the C-1 acetate is lost, and approach of the catalyst can occur from both sides, thus leading to both the D-*gluco* and the D-*altro* branched-chained anhydroalditols III.

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The Nuclear Magnetic Resonance Spectra of Enantiomers in Optically Active Liquid Crystals

Sir:

Pirkle and Beare[1] have reported the observation of distinct nmr spectra for the *d* and *l* enantiomers of a suitable compound when dissolved in an optically active solvent. The difference of the spectra can be interpreted as resulting from a difference in the chemical shifts of the two enantiomers: the disparity of their geometry in relation to the solvent environment results in unequal solvent effects.

In a recent communication,[2] we have noted that a similar differentiation will be expected for enantiomers dissolved in an optically active liquid crystal. Here the major differentiating factor would be the degree of orientation of the solute molecules. We believe the situation can be described as follows. It is well known that nematic liquid crystals become macroscopically oriented in a magnetic field, and this orientation is transferred to dissolved molecules. As a result of this orientation, the direct nuclear dipole–dipole interactions are no longer zero and, in fact, become the dominant interaction in the interpretation of the nmr spectrum.[3] The basic idea of the experiment is to use a liquid-crystal solvent that exhibits not only orientation anisotropy but a screw sense as well. This can be achieved by using an optically active liquid crystal. In such a solvent the degree of orientation of optically active solute molecules will differ for the *d* and the *l* geometry. Thus the nuclear dipole–dipole interactions will be different, and distinct spectra for the two enantiomers will result.

In this note we report observations confirming this expectation. The actual situation, however, is not quite so straightforward. It was shown in ref 2 that, when an asymmetric center is introduced in a molecular species which gives a nematic phase, the screw sense of the molecules prevents parallel stacking, and a helical (that is cholesteric) structure, rather than a nematic one, results. No high-resolution nmr spectra can be obtained in such a phase. The way out is the use of a "compensated" mixture of cholesteryl chloride and a cholesteryl ester, described in ref 2. The crucial point is that, although such a mixture can be so adjusted that the solvent molecules will stack parallel to each other on the average, compensation relative to the solute molecules will not in general be complete. In other words, the solute molecules will be in a helical local environment, even if no macroscopic helicity is present.

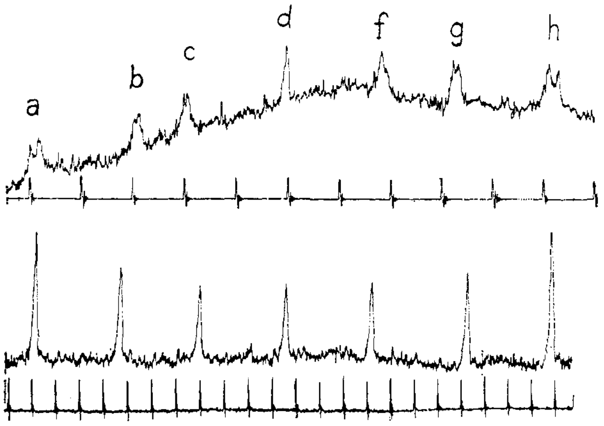

Figure 1. The upper trace gives the 60-MHz nmr spectrum at 40° of a mixture of 0.01 g of racemic 3,3,3-trichloropropylene oxide, 0.53 g of cholesteryl chloride, and 0.28 g of cholesteryl myristate. The very broad background is due to the solvent. The lower trace gives the spectrum of 0.01 g of racemic 3,3,3-trichloropropylene oxide in 0.1 g of *p,p'*-di-*n*-hexyloxyazoxybenzene at 90°. The trace below each spectrum gives frequency markers, spaced 106 Hz apart.

The observed nmr spectra of racemic 3,3,3-trichloropropylene oxide (I) are displayed in Figure 1. The upper spectrum was obtained in a 1.9:1 by weight mixture of cholesteryl chloride and cholesteryl myristate. The lower spectrum was obtained in nematic *p,p'*-di-*n*-hexyloxyazoxybenzene. We interpret the doubling of lines in the upper spectrum to be due to slightly different spectra of *d* and *l* molecules of the racemic solute. When the solvent is optically inactive as in the lower spectrum, no doubling occurs. The observed line positions are given in Table I.

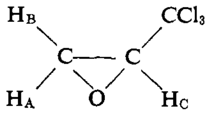

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Table I. Experimental Line Positions in Hertz for the Spectra in Figure 1

Solvent	a	b	c	d	f	g	h
Cholesteryl mixtures	−529	−325	−225	−20	176	325	524
	−548	−335	−233	−20	185	335	543
Hexyloxy-azoxybenzene	−1207	−815	−447	−54	344	791	1189

An analysis[4] and computer simulations[5] of the observed spectra have been made. We are able to obtain a close fit of the spectrum observed in the optically active solvent only if we attribute the lines in row 1 of

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[1] W. H. Pirkle and S. D. Beare, *J. Am. Chem. Soc.*, **89**, 5485 (1967).

[2] E. Sackmann, S. Meiboom, and L. C. Snyder, *ibid.*, **89**, 5981 (1967).

[3] G. Englert and A. Saupe, *Mol. Cryst.*, **1**, 503 (1966).

[4] L. C. Snyder, *J. Chem. Phys.*, **43**, 4041 (1965).

[5] The spectrum simulation programs were written by R. L. Kornegay.