to the preparation of enantiomerically pure acyclic diol ketones has been less successful.[16,17]

Acknowledgment is made to the National Science Foundation (Grant CHE83-06594) and to the Monsanto Company for support ot this research.

(16) Satisfactory microanalysis and/or high-resolution mass spectra were obtained on all new compounds involved in this study.

(17) A remote sulfoxide group has been found to control the stereospecific hydroxylation at an olefinic center by osmium tetroxide. Hauser, F. M.; Ellenberger, S. R.; Clardy, J. D.; Bass, L. S. *J. Am. Chem. Soc.*, Preceding paper in this issue.

Isotopic Multiplets in the ^{13}C NMR Spectra of Polyols with Partially Deuterated Hydroxyls. 2.[1] Effects of Cis–Trans Isomerism in Cyclic Vicinal Diol Systems

Jacques Reuben

Hercules Incorporated, Research Center
Wilmington, Delaware 19894
Received January 16, 1984

The assignment of carbon-13 NMR spectra of polyols in general and carbohydrates in particular is greatly facilitated by the characteristic multiplets in the proton-decoupled spectra of Me_2SO solutions of materials with partially deuterated hydroxyls.[1-4] These multiplets are due to upfield deuterium isotope effects on the carbon-13 chemical shifts: 0.09–0.12 ppm for directly bonded hydroxyls (β-effect, Δ_β) and 0.07 ppm or less for hydroxyls on vicinal carbons (γ-effect, Δ_γ).[1-6] Thus, if only part of the molecules are deuterated, the resonance of a hydroxylated carbon will be split into a doublet with a spacing of Δ_β. In partially deuterated vicinal diols, the ^{13}C NMR spectral line of each hydroxylated carbon appears as a quartet (with components corresponding to the HH, HD, DH, and DD species) with spacings of Δ_β and Δ_γ. Up to eight components (octet) can be observed for a hydroxylated carbon flanked by two hydroxylated carbons.[1,4]

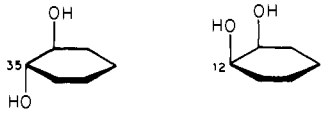
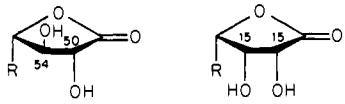
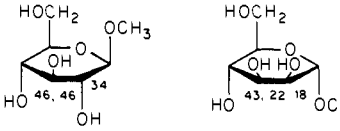
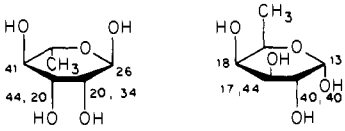
This communication presents results on the dependence of the γ-effect in cyclic vicinal diol systems on the relative orientation, cis or trans, of the hydroxyls. On the basis of this finding, one can use the approach of isotopic multiplets for more detailed structural interpretations as well as for spectral assignments. Examples showing the effects of cis–trans isomerism on the magnitude of the γ-effect, Δ_γ, are given in Table I. The data show that in general

$$\Delta_\gamma(\text{trans}) > \Delta_\gamma(\text{cis}) \qquad (1)$$

Since the isotopic state ("light" or "heavy") of a hydroxyl is analogous to the spin state ($+^1/_2$ or $-^1/_2$) of a spin $^1/_2$ nucleus in a magnetic field, there is a remarkable similarity between isotopic multiplets and those due to spin–spin couplings.[1] Owing to the cis–trans relationship of eq 1, this analogy can been carried one step further: *isotopic multiplets of vicinal hydroxylated carbons have similar spacings*. Thus, from the multiplicity and spacings in the isotopic multiplets, one can trace the pairwise connectivity of such atoms. Note, however, that, unlike spin–spin interactions, the Δ_β and the Δ_γ values are not necessarily the same for both carbons.

The isotopic multiplets in the ^{13}C NMR spectra of α-L-rhamnopyranose (**1**) and α-D-fucopyranose (**2**) with partially deuterated hydroxyls are shown in Figure 1.[7] These molecules

Table I. Effects of Cis–Trans Isomerism on the Three-Bond Isotope Shift (Δ_γ in ppb) due to Hydroxyl Deuteration

	Δ_γ(trans) – Δ_γ(cis)
	C-1: 23
	C-2: 35 C-3: 39
R = CHOHCH$_2$OH	
	C-2: 16 C-3: 24
	C-1: 13 C-2: 20, –6 C-3: 24, 27 C-4: 23
1	2

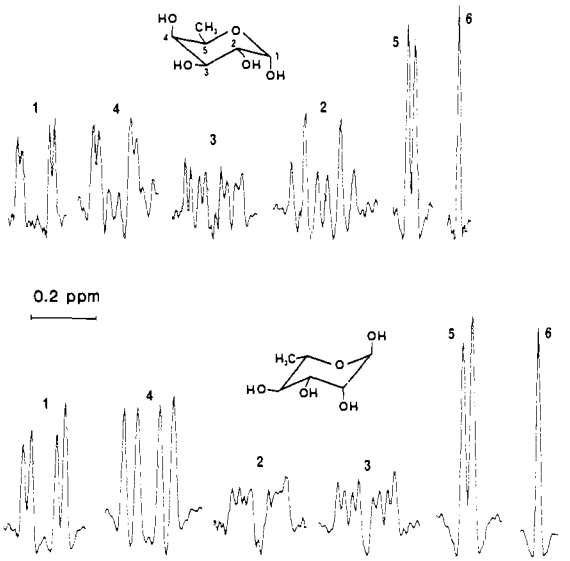


Figure 1. Isotopic multiplets in the 90.55-MHz ^{13}C NMR spectra (resolution enhanced) of Me_2SO solutions of α-L-rhamnopyranose (**1**) (bottom) and α-D-fucopyranose (**2**) (top) with partially deuterated hydroxyls. The chemical shifts (in ppm from TSP) of the protio forms (leftmost component of each multiplet): (**1**) 95.77, 74.15, 73.27, 72.16, 69.46, 19.79; (**2**) 94.26, 73.54, 71.23, 70.16, 66.84, 18.35.

form an interesting pair: the configuration of each vicinal diol fragment, as well as the configuration at carbon 5, changes from cis to trans in going from one molecule to the other. As a result, the resonances of the carbon atoms involved show conspicuous differences in the Δ_γ spacings in comparing the spectrum of one with that of the other. For C-2 of α-rhamnose (**1**), the isotope effect due to the trans hydroxyl on C-1 (34 ppb) is smaller than that (40 ppb) in a α-fucose (**2**), where the configuration is cis. This anomaly, which has also been observed by Pfeffer et al.,[5] seems to occur only when the anomeric carbon is part of a diaxial array. For diequatorial trans hydroxyls in similar positions, much larger γ-effects have been observed, e.g., 67 ppb for C-2 in β-D-glucopyranose.[1]

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(7) The assignment of such spectra is a fairly simple matter.[1,4] The acronym SIMPLE, which stands for secondary isotope multiplets of partially labeled entities, emphasizes this point.[4]

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Owing to the effects of cis–trans isomerism on the value of Δ_γ, carbon atoms in hydroxylic environments of a given configuration give rise to characteristic multiplet features. Thus, molecular fragments along with their stereochemistry can be readily identified. In favorable cases, there may be only one possible way to join these fragments into a complete molecular structure. In more complex molecules, e.g., oligosaccharides, the presence of a molecular fragment may reveal the identity of a whole monosaccharide residue. Furthermore, *the absence* of certain multiplet features can serve to identify the substitution pattern of a monosaccharide residue within an oligosaccharide. Thus, isotopic multiplets should be useful in the sequencing of oligosaccharides.

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Production of Arene Oxides by the Caroate–Acetone System (Dimethyldioxirane)

Ramasubbu Jeyaraman and Robert W. Murray*

Department of Chemistry
University of Missouri—St. Louis
St. Louis, Missouri 63121

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Dioxiranes (**1**) are isomeric with the better known carbonyl oxides (**2**) one of the peroxidic intermediates involved in the

1a, R = R′ = H
b, R = R′ = Cl_3
c, R = Cl_3; R′ = Cl_2Cl
d, R = R′ = CH_3

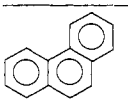
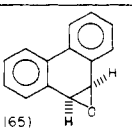
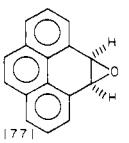
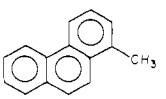
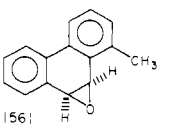
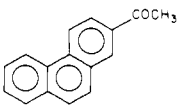
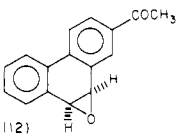
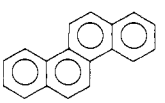
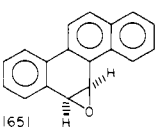
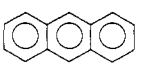
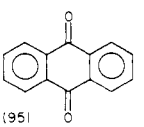
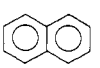
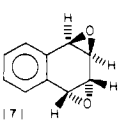
2

ozonolysis process. Dioxirane (**1a**), produced via ozonolysis of ethylene, has been characterized by both mass spectral and microwave methods.[1-3] In two cases, **1b** and **1c**, it has been reported[4] that dioxiranes have been isolated and characterized by physical and chemical methods. In these cases the dioxiranes were synthesized by oxidation of the corresponding dilithio alkoxides.

Dioxiranes have been postulated as intermediates in two cases involving peracids. In one of these Edwards, Curci, and coworkers[5-9] have provided kinetic, stereochemical, and ^{18}O-labeling evidence that the peroxymonosulfate (caroate)–acetone system generates dimethyldioxirane (**1d**) as a reactive intermediate. This intermediate undergoes facile one oxygen atom transfer reactions including one[5] that produces epoxides in a high yield, stereospecific manner. A second possible source of **1d** has been described[10] by us and uses peracetic acid and acetone to produce an epoxidizing intermediate.

We now report that the caroate–acetone system can be used to convert arenes to arene oxides. In many cases the yields obtained suggest that this procedure may be synthetically useful (Table I). Observation of arene oxide formation under these conditions is highly significant in view of the suggestion[1] that gas-phase ozonolyses are likely dioxirane sources and the relationship of arene oxides to mutagenesis/carcinogenesis in polycyclic aromatic hydrocarbons (PAH).[11-14]

Table I. Reaction of Arenes with Caroate–Acetone (Dimethyldioxirane)[a]

arene	T, °C	reaction time, min	product (% conversion)[b]	isolated yield, %[c]
 1	0–10	5.5	 (65)	60
 2	0–5	1.5	 (77)	45
 3	25	6.5	 (56)	29.5[d]
 4	25	8	 (12)	8
 5	25	6	 (65)	*e*
 6	25	1.5	 (95)	85
 7	0–5	2	 (7)	5
 8	25	6	NR[f]	

[a] Reactions used excess acetone and potassium peroxymonosulfate (Du Pont oxone: $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) in H_2O and CH_2Cl_2 with phosphate buffer and PTC (tetra-*n*-butylammonium hydrogen sulfate). [b] Percent conversions are based on NMR integration data for the crude reaction mixtures. [c] Products isolated using preparative TLC. [d] Product was 96% pure after three recrystallizations. [e] The arene oxide consistently rearranged during workup. [f] NR = no reaction.

In a typical reaction a mixture of acetone (250 mL), phosphate buffer (50 mL), methylene chloride (100 mL), tetra-*n*-butylammonium hydrogen sulfate (200 mg), and phenanthrene (900 mg) was stirred vigorously at 0–10 °C while a solution of potassium peroxymonosulfate (Oxone (Du Pont): $2KHSO_5 \cdot$

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