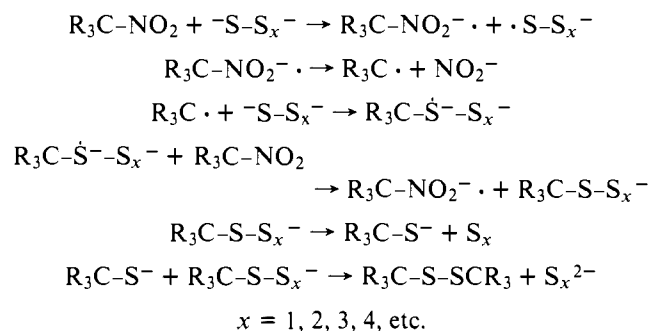


The residual oil is heated in a kugelrohr to 60 °C and 1 mm to remove butanedithiol and 1,2-dithiacyclohexane. The temperature is then raised to 120 °C to distill the pure mercaptan,¹⁰ yield 0.570 g (74%), mp 57–58 °C.

The usefulness of this reaction will be further enhanced if primary and secondary nitro compounds also can be transformed into thiols. However, preliminary studies with several secondary nitro compounds do not inspire optimism.

Although the uncertainties and complexities associated with polysulfide solutions¹¹ preclude a detailed mechanistic discussion, enough is known about electron-transfer substitution reactions of aliphatic nitro compounds² to enable one to put forth the broad outlines of a mechanism; a number of closely related variants can readily be envisioned.



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References and Notes

- (1) Paper 19 in the series "Substitution Reactions which Proceed via Radical Anion Intermediates". For the preceding paper, see ref 3.
- (2) N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, **14**, 734 (1975).
- (3) N. Kornblum, S. C. Carlson, and R. G. Smith, *J. Am. Chem. Soc.*, **100**, 289 (1978).
- (4) $Na_2S \cdot 5H_2O$ is obtained as follows. Finely powdered $Na_2S \cdot 9H_2O$ is held at $\sim 50^\circ C$ and subjected to the vacuum of a water aspirator. After 1 to 2 h, during which time the flask is shaken occasionally, the aspirator is replaced by an oil pump, the flask is attached to a rotary evaporator, and the temperature is dropped to $\sim 30^\circ C$. Pumping is discontinued when the white powder just begins to turn yellow (~ 1 h). This material can be stored under N_2 for extended periods. It has a neut equiv of 170, calculated 168.
- (5) We thank the Crown-Zellerbach Corp. for a generous supply of Me_2SO .
- (6) Prepared as described for the ethyl ester: N. Kornblum, S. D. Boyd, and F. W. Stuchal, *J. Am. Chem. Soc.*, **92**, 5783 (1970).
- (7) See N. Kornblum, S. C. Carlson, J. Widmer, M. J. Fifolt, B. N. Newton, and R. G. Smith, *J. Org. Chem.*, **43**, 1394 (1978).
- (8) Occasionally a small amount of sulfur remains suspended.
- (9) Strips of Al foil are dipped into 2% aqueous $HgCl_2$ for 15 s and then immersed for a few seconds in absolute ethanol and then in anhydrous ether. The strips are immediately cut into small pieces ($\sim 1 \times 0.5$ cm) and used at once. The use of Al amalgam to cleave disulfides was first reported by F. Kipnis, I. Levy, and J. Ornfelt, *J. Am. Chem. Soc.*, **71**, 2270 (1949).
- (10) Satisfactory elemental analyses and NMR spectra were obtained for all new compounds.
- (11) See, for example, F. Seel and H.-J. Güttler, *Z. Naturforsch., B*, **30**, 88 (1975), and references there cited.
- (12) Anhydrous Na_2S was obtained from Research Organic/Inorganic Chemical Corp., Bellville, N.J. 07109.

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Vibrational Circular Dichroism and Individual Chiral Centers. An Example from the Sugars

Sir:

Of late, there has been considerable activity, both experimental¹ and theoretical,² in the area of vibrational circular

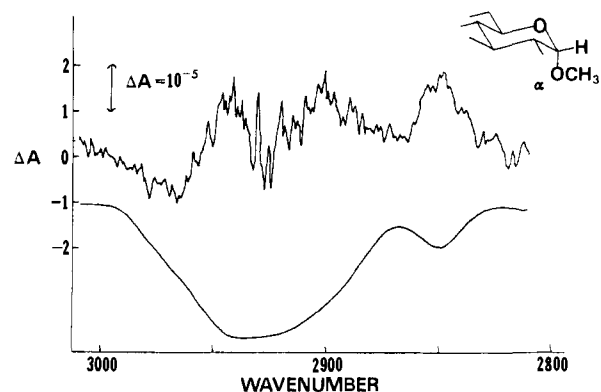


Figure 1. VCD spectrum (top) and IR transmission spectrum (bottom) of α -methyl D-glucoside in D_2O solution. The structure shown in the upper right assumes that an OH is attached to the end of each unconnected line. The concentration is 1.0 M and the path length is 0.056 mm. Because of proton exchange in D_2O solution, most of the OH groups will actually be deuterated.

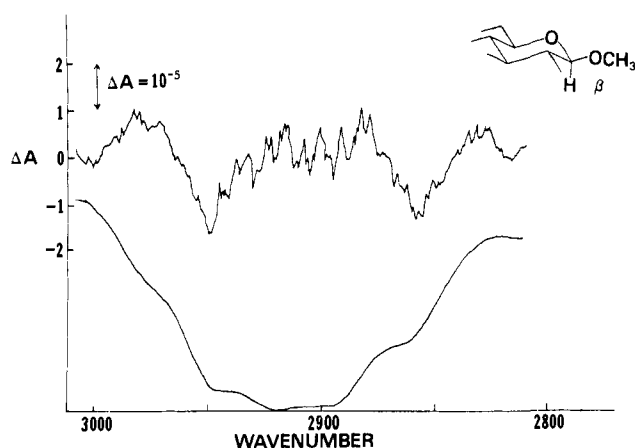


Figure 2. VCD spectrum (top) and IR transmission spectrum (bottom) of β -methyl D-glucoside in D_2O solution. The structure shown in the upper right assumes an OH is attached to the end of each unconnected line. The concentration is 1.0 M and the path length is 0.056 mm. Because of proton exchange in D_2O solution, most of the OH groups will actually be deuterated.

dichroism (VCD). One motivation is the potential ability of VCD to focus on single chiral centers, even when a multiplicity of such centers is present in a molecule. We report here the first experimental evidence that selective stereochemical information of this sort may indeed be forthcoming from VCD measurements in favorable circumstances.

We are currently studying the VCD in sugars for a number of reasons. For one, the sugars constitute a group of closely related compounds that provide a variety of diastereomeric relationships among their similarly substituted chiral centers. In the course of monitoring the CH-stretching region of a number of pyranose sugars, we noticed that a change in absolute configuration at a selected chiral center can have a dramatic effect on the VCD spectrum.

In Figures 1 and 2 we show the structures and CD spectra for 1-*o*-methyl α -D-glucopyranoside (α -methyl D-glucoside) and 1-*o*-methyl β -D-glucopyranoside (β -methyl D-glucoside) between 3010 and 2810 cm^{-1} .³ The single-beam infrared transmission spectrum run under the same conditions as the CD spectrum is also shown for each sugar. The measurements were made using the Holzwarth-Chabay spectrometer⁴ which is now in our laboratory. "Absorption base lines"^{4,5} have been subtracted from each CD spectrum using a Fabri-Tek Model FT-1074 signal averager and each CD spectrum represents the average of eight scans. We used a time constant of 3 s and

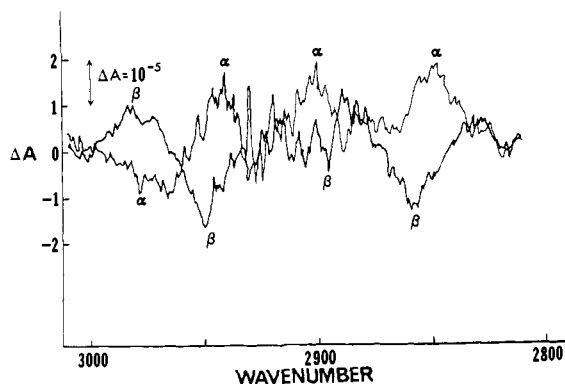


Figure 3. A superposition of the VCD spectra for α - and β -methyl D-glucoside which were shown in Figures 1 and 2, respectively.

resolution of $\sim 10 \text{ cm}^{-1}$, and the sugars were run at 1.0 M concentrations using D_2O as the solvent. $|\Delta A/A| \approx 4 \times 10^{-5}$ at the maxima of the major VCD bands shown in Figures 1 and 2.

In Figure 3 we show an overlay of Figures 1 and 2. At least three of the CD bands appear to have changed sign and there has been a 7-cm^{-1} shift in the frequency of all of the band maxima of one spectrum relative to the other. Note, however, that α - and β -methyl glucoside are not enantiomers, but differ in absolute configuration only at the anomeric carbon atom. The other four asymmetric centers have the same absolute configuration in both the α and β forms.

At present the individual CH-stretching bands in pyranose sugars have not been positively assigned. The low frequency stretch, which occurs at 2850 cm^{-1} in the α -methyl D-glucoside, is usually assigned as the symmetric methyl stretch.⁶ The asymmetric methyl stretches probably occur at $\sim 2950 \text{ cm}^{-1}$ with the single CH stretches and the methylene stretches providing the broad background of bands between 2980 and 2880 cm^{-1} .⁷ The CD bands that change sign are most likely due to the methyl stretching modes and the anomeric CH stretch. This is supported by VCD measurements on D-glucose, which exists as a thermodynamic mixture of α and β forms in D_2O , and β -methyl- d_3 glucoside- d , where only the methyl group is deuterated. Both of these sugars show substantially smaller VCD signals in the CH-stretching region, indicating that the O-CH₃ group is making the dominant contribution to the CH-stretch VCD.

Further studies on the sugars, including normal coordinate analyses and VCD intensity calculations, are in progress.

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- (3) The samples of α - and β -methyl D-glucoside were obtained from the Sigma Chemical Co. and used without further purification.
- (4) I. Chabay and G. Holzwarth, *Appl. Opt.*, **14**, 454 (1975).
- (5) I. Chabay, E. C. Hsu, and G. Holzwarth, *Chem. Phys. Lett.*, **15**, 211 (1972).

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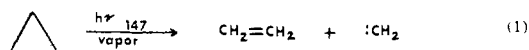
Organic Photochemistry with 6.7-eV Photons: Bicyclo[*n*.1.0]alkanes and Tricyclo[3.2.1.0^{2,4}]octane[†]

Sir:

The ultraviolet absorption spectrum of cyclopropane extends to longer wavelengths than those of other cyclic alkanes^{1,2} in keeping with the special nature of the bonding in this strained molecule. Cyclopropane absorbs weakly at 185 nm and alkyl cyclopropanes such as bicyclo[3.1.0]hexane (**1**) and bicyclo[4.1.0]heptane (**2**) absorb moderately at this wavelength (ϵ 510 and 610 L/mol-cm, respectively). The identity of the



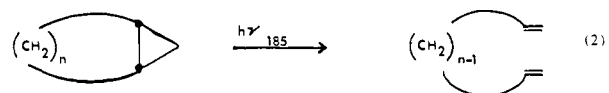
excited state that is reached with 185-nm radiation seems to be controversial.³ At least in solution, the absorption is probably a valence shell excitation.³ Photochemical studies of cyclopropane derivatives in solution have been limited to molecules in which a chromophore that is capable of absorbing at wavelengths $>200 \text{ nm}$ is attached to the ring.⁴ The principal reaction is the cleavage of one bond to give a diradical. Cyclopropane and alkyl cyclopropanes have been studied⁵ in the gas phase at wavelengths of 147 nm or less. The principal reactions under these conditions are fragmentations of various kinds the most important of which is a split to give a carbene and an olefin (eq 1). This represents the inverse of the usual



method of synthesis of a cyclopropane and requires the simultaneous or successive break of two of the C-C bonds in the cyclopropane ring. We show here that four hydrocarbons which incorporate a cyclopropane ring, on irradiation with 185-nm light in solution, undergo a parallel reaction with fewer side products.

Results on the photolysis of compounds 1-4 are listed in Table I. These experiments were carried out in pentane solution ($\sim 10^{-2} \text{ M}$) in a Suprasil tube with the unfiltered light from a mercury resonance lamp, the useful radiation being the line at 185 nm. Since the olefinic products absorb at this wavelength much more intensely than the reactants, the rates and yields are based on data obtained at low conversions ($<10\%$) from gas chromatograms and extrapolated to zero time.

The reaction which corresponds to the scission of two of the three bonds in the cyclopropane ring (eq 2) is the most general



one and yields 33-95% of the products. Cyclic olefin formation which is the usual reaction that is associated with the cleavage of the strained internal bond of the cyclopropane assumes

[†] Dedicated to Professor E. Havinga on his 70th birthday.