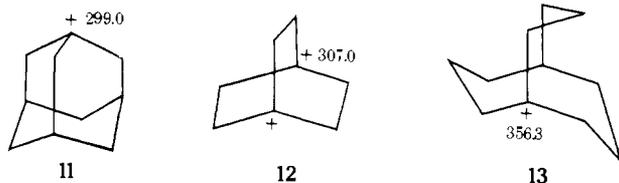


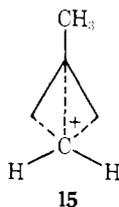
at $-34\text{ }^{\circ}\text{C}$ and 39.6 for **10** at $-60\text{ }^{\circ}\text{C}$. Ions **9** and **10** could be frozen out to the static substituted phenylcyclobutyl cations at -114 and $-123\text{ }^{\circ}\text{C}$, respectively. Under these conditions ions **9** and **10** compare well with the classical phenylcyclobutyl cation (**8**), which does not show temperature dependence. The ^{13}C NMR data are tabulated in Table I.

The observed NMR data for the ion **1** are in our view not in accordance with a classical 1-methylcyclobutyl cation (**6**) containing an sp^3 -hybridized carbenium center. Rather, they indicate a σ -delocalized 1-methylcyclopropylcarbiny cation containing two different methylene groups ($\delta(^{13}\text{C})$ 72.7 and -2.83), one of which is highly shielded suggesting a five-coordinated carbon. All available structural and theoretical studies on carbocations mitigate against the existence of a relatively unstrained sp^3 -hybridized classical carbocation. Unstrained trivalent carbocations contain a close to planar carbocation center which displays an extremely deshielded ^{13}C NMR chemical shift. In strained and thus nonplanar carbocations such as **11**, **12**, and **13**,⁵⁻⁷ the ^{13}C NMR shifts of the



carbocation center are still highly deshielded ($\geq \delta(^{13}\text{C})$ 300). Thus, if an sp^3 -like trivalent carbocation center would indeed exist in ion **1** (as suggested in structure **6**), the ^{13}C NMR shift would be expected to be more highly deshielded than the observed shift of $\delta(^{13}\text{C})$ 163.

The observed spectrum of **1** at $-156\text{ }^{\circ}\text{C}$ is thus not that of a frozen out static ion, but of either a degenerate set of σ -delocalized nonplanar bicyclobutonium like ions^{3b} such as **4**, rapidly interconverting through a symmetrical σ -delocalized puckered species **15** which renders the β -methylene carbon pentacoordinated, or the symmetrical ion **15** itself. The clas-



sical 1-methylcyclobutyl cation (**2**) or the bisected σ -delocalized 1-methylcyclopropylcarbiny cations (**3**) which scramble the methylene carbons at higher temperatures ($\geq -140\text{ }^{\circ}\text{C}$) do not contribute to the NMR chemical shifts and, thus, must be at least 2 kcal/mol higher in energy than ions **4**. The energy barrier of 5.6 kcal/mol frozen out by Sorensen² must be thus between **4** and **3**, or **4** and **2**, with **3** or **2** being unstable reaction intermediates whose formation from the stable state **4** permits equilibration of the methylene groups.

The five coordinated β -methylene carbon in **4** resonates at $\delta(^{13}\text{C}) -2.83$. This kind of highly deshielded carbon has been observed in nonclassical pyramidal cations.⁸

The significant point to be made is that, if equilibration occurs between degenerate highly σ -delocalized unsymmetrical nonclassical ions (i.e., **4**) through a symmetrical nonclassical ion (**15**) via low energy barriers, for all practical purposes such systems would show symmetrical nature in the NMR spectra. Thus, the double energy minima would be indistinguishable from a single minimum, as the interconversions would take place through a very low energy barrier, i.e. ≤ 2 kcal/mol. This is also the case with the 2-norbornyl cation,⁹ but again the question is not possible equilibration between classical ions vs.

the symmetrical, bridged nonclassical ion, ruled out by direct, spectroscopic studies of the long-lived ion, but of possibly still-equilibrating nonclassical σ -delocalized, but somewhat unsymmetrical, ions (double minima) vs. the symmetrical nonclassical ion (single minimum).⁹ These are becoming by necessity indistinguishable by usual studies. It is important to recognize that σ -delocalized nonclassical ions are not necessarily static symmetrically bridged species, contrary to claims made to this effect.¹⁰

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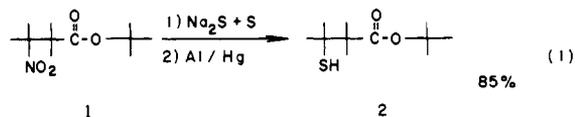
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Direct Conversion of Nitro Compounds to Thiols¹

Sir:

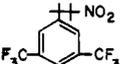
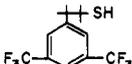
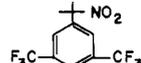
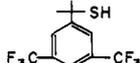
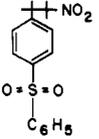
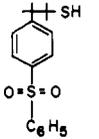
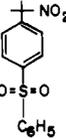
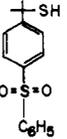
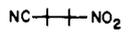
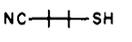
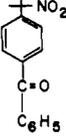
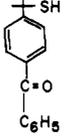
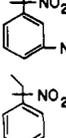
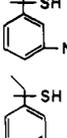
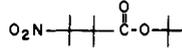
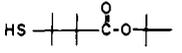
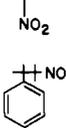
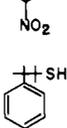
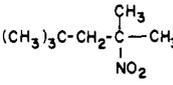
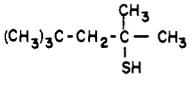
In recent years methods for the synthesis of a wide range of highly branched aliphatic and alicyclic tertiary nitro compounds have been devised.^{2,3} As a consequence any reaction which results in the replacement of a nitro group by another group is of considerable interest. One such process—replacement by hydrogen—has been reported.³

The present communication describes another new reaction—the replacing of a nitro group by the mercapto group. When a tertiary nitro compound is treated with a solution of sodium sulfide and sulfur in Me_2SO at $25\text{ }^{\circ}\text{C}$ smooth conversion to a mixture of the corresponding thiol and dialkyl polysulfides occurs; on subjecting this mixture to the action of amalgamated aluminum at $0\text{ }^{\circ}\text{C}$ the polysulfides are converted to the thiol. Equation 1 is illustrative and Table I summarizes our results; yields refer to pure, isolated products.



Precisely what reagent is responsible for the initial transformation of eq 1 is not known. Sodium sulfide is ineffective; it reacts very slowly with tertiary nitro compounds and gives little, if any, of the desired product. But, if elemental sulfur is added to the sodium sulfide so that for each sulfide ion there is one sulfur atom, i.e., so that the gross composition is Na_2S_2 ,

Table I. Replacement of the Nitro Group by the Mercapto Group^a

nitro compd	reaction time	thiol	yield, % ^b	nitro compd	reaction time	thiol	yield, % ^b
	1 h		92		4 h		70
	55 min.		86		4.5 h		81
	30 min.		93		5 h		82
	70 min.		78		3 h		80
	35 min.		74		8 h		74
	20 min.		71		15 h		85
	45 sec		73		18 h ^c		77
	18 h		78		16 h ^d		38
					16 h ^e		85

^a Unless otherwise noted all reactions were carried out at 25 °C in Me₂SO using Na₂S · 5H₂O + 1/8 S₈ ("Na₂S₂"). For each millimole of nitro compound 4 mmol of "Na₂S₂" was employed except with α-nitrocumenes where only 2 mmol of "Na₂S₂" /mmol of nitro compound was used. Many of these reactions were carried out with exposure to two 20-W fluorescent lights; subsequently it has been found that such illumination is not necessary and, indeed, with the α-nitrocumenes it is better to carry out the "Na₂S₂" step in the dark. ^b Pure, isolated product. ^c Anhydrous "Na₂S₂"¹² and Me₂SO distilled from CaH₂ were employed. ^d Anhydrous "Na₂S_{1.5}", Me₂SO distilled from CaH₂, and a temperature of 125–130 °C were employed. ^e Anhydrous "Na₂S_{1.5}", Me₂SO distilled from CaH₂, and a temperature of 55 °C were employed.

then the reaction of eq 1 proceeds smoothly. In general, further addition of sulfur is not beneficial; at the Na₂S₃, Na₂S₄, or Na₂S₅ levels, the rate of reaction is sharply reduced.

A typical example follows. Under N₂ a mixture of Na₂S · 5H₂O⁴ (1.34 g, 8 mmol) and sulfur (0.0256 g, 1 mmol) is stirred with 20 mL of Me₂SO.⁵ After 1 to 2 h the initial blue-green mixture turns to a yellow solution at which point *tert*-butyl 3-nitro-2,2,3-trimethylbutanoate (**1**,⁶ 0.462 g, 2 mmol) is added without opening the system.⁷ The resulting solution is stirred for 18 h and then is poured into 200 mL of 2% aqueous ammonium chloride. After two extractions with ethyl acetate, the aqueous phase is brought to a pH of ~1 with 5% hydrochloric acid and again extracted twice with ethyl acetate. The combined ethyl acetate solutions are washed repeatedly with H₂O and dried (anhydrous Na₂SO₄). The ethyl acetate is removed, the residue is dissolved in 10 mL of THF, 1 mL of H₂O is added, and the resulting solution⁸ (blanketed with N₂) is cooled in an ice bath and treated with aluminum amalgam⁹ prepared from 0.200 g (0.0074 g-atom) of Al foil. The mixture is cooled in ice and shaken occasionally, and after about 2 h ethyl ether (20 mL) is added. Then, while stirring vigorously, the system is rendered strongly acidic (pH < 1) by the addition

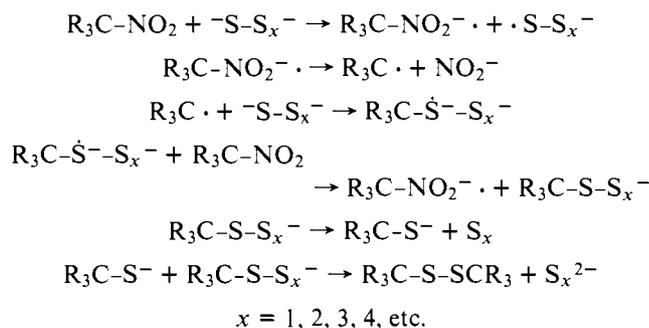
of cold 5% HCl. Cooling and stirring are continued for ~5 min, during which time most of the initial fine gray precipitate dissolves. The mixture is filtered to remove excess Al amalgam, the amalgam is washed with ethyl ether, and the washings are added to the filtrate. The aqueous portion of the filtrate is extracted with ethyl ether, the ether extracts are combined with the organic phase of the filtrate, and the resulting solution is washed with water. After drying (anhydrous Na₂SO₄) the ether is removed. The residual oil on kugelrohr distillation at 60 °C and 1 mm gives 0.370 g (85% yield) of pure **2**.¹⁰

When keto or nitro groups are present a different procedure for cleaving polysulfides is employed. Thus 0.807 g (3 mmol) of *p*-benzoyl-α-nitrocumene is treated with a solution of 1.008 g (6 mmol) of Na₂S · 5H₂O and 0.192 g (0.75 mmol) of sulfur in 15 mL of Me₂SO for 35 min and then worked up in the usual way. To the residue obtained on removing the ethyl acetate is added 6 mL each of absolute ethanol and benzene and, then, under N₂, 1.7 mL (12 mmol) of triethylamine and 0.70 mL (6 mmol) of 1,4-butanedithiol are introduced and solution is stirred in the dark at 25 °C. After 30 min the solution is poured into excess 5% HCl and extracted with benzene. The benzene phase is washed with H₂O and dried, and the solvent removed.

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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- (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).
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- (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

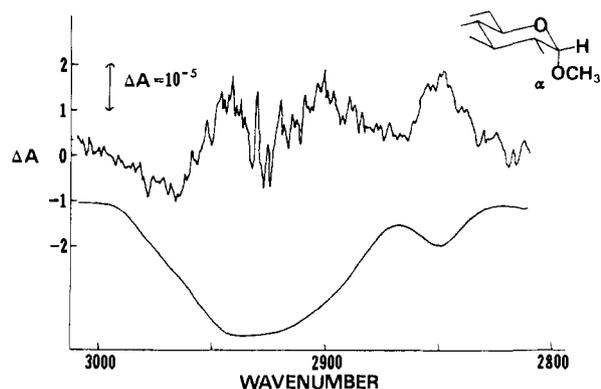


Figure 1. VCD spectrum (top) and IR transmission spectrum (bottom) of α -methyl D-glucoside in D_2O solution. The structure shown in the upper right assumes that an OH is attached to the end of each unconnected line. The concentration is 1.0 M and the path length is 0.056 mm. Because of proton exchange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

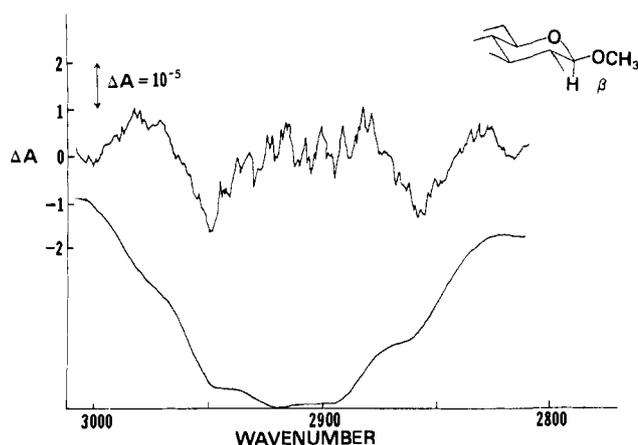


Figure 2. VCD spectrum (top) and IR transmission spectrum (bottom) of β -methyl D-glucoside in D_2O solution. The structure shown in the upper right assumes an OH is attached to the end of each unconnected line. The concentration is 1.0 M and the path length is 0.056 mm. Because of proton exchange in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