filtered, and reduced under pressure (38 psi) with Adams platinum catalyst (1.8 g of platinum oxide) for 4 hr. The catalyst was filtered off, and the basic solution obtained was then evaporated *in vacuo*.

The residue was examined by descending paper chromatography on Whatman No. 1 paper with *n*-butyl alcohol–acetic acid–water (25:6:25, upper phase), revealing two ninhydrin positive spots at $R_{\text{2-Amino-2-deoxy-D-glucose}}$ 1.57 (brown) and 2.38 (pink). When checked by high-voltage paper electrophoresis on Whatman No. 1 paper in 1.2 *M* pyridine adjusted to pH 6.5 with acetic acid at 60 V/cm for 20 min, the first spot had an $M_{\text{2-Amino-2-deoxy-D-glucose}}$ value of 1.24 and the second 1.02.

Dry pyridine (30 ml) was added to the residue and evaporated. The oily material was redissolved in pyridine (2 ml) and after cooling to 0° acetic anhydride (2 ml) was added. The acetylation mixture was left overnight at room temperature. Water (0.3 ml) was then added and the mixture was kept for an additional 2 hr at room temperature. The mixture was evaporated *in vacuo*, extracted with ethyl acetate (5 ml), filtered, and placed on an alumina column (Merck, acid washed, 30 g, 1.5 cm diameter). The column was monitored by tlc on alumina G using acetone as solvent. The column was washed with ethyl acetate (150 ml) and the first compound which emerged (0.12 g) was eluted with the first portion of 1% methanol in ethyl acetate (90 ml). It did not contain nitrogen and had a R_{SR} of 0.87. It was not further investigated. Compound **5**, R_{SR} 0.67 (0.26 g, 10.8%), started to emerge after an additional volume (110 ml) of the same solvent, and its elution was completed with 200 ml of 2% methanol in ethyl acetate. The last fraction, compound **6**, R_{SR} 0.56 (0.156 g, 6.5%), started to emerge after an additional volume (200 ml) of 2% methanol in ethyl acetate and was eluted with the same solvent (300 ml).

On a small scale the mixture of compounds **5** and **6** was obtained also through acetylation in pyridine of the material of $R_{\text{2-Amino-2-deoxy-D-glucose}}$ 1.57 isolated by preparative paper chromatography.

Compound **5** was obtained from ethyl acetate as an amorphous white solid, mp 272°, $[\alpha]^{24}$D −168 ± 1.6° (*c* 0.29, chloroform). It had the expected ir spectrum; nmr (100 MHz, methyl sulfoxide-*d*, hexamethylsiloxane as an external standard) τ 5.09 (1-proton triplet, H-3, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 3.0 Hz), 5.23 (1-proton doublet, H-1, $J_{1,2}$ = 3.0 Hz), 5.5–6.3 (3 protons, un-

resolved multiplets), 6.50 (3-proton singlet, OCH₃), 7.82 (3-proton singlet, OCOCH₃), 8.04 and 8.06 (two 3-proton singlets, NCOCH₃), 8.74 (3-proton doublet, C-5 CH₃, $J_{5,6}$ = 6.0 Hz); nmr (60 MHz, chloroform-*d*) τ 6.55 (3-proton singlet, OCH₃), 7.88 (3-proton singlet, OCOCH₃), 8.04 and 8.07 (two 3-proton singlets, NCOCH₃), 8.75 (3-proton doublet, C-5 CH₃).

Anal. Calcd for $C_{13}H_{22}N_2O_6$: C, 51.64; H, 7.34; N, 9.27. Found: C, 52.08; H, 7.61; N, 8.93.

Compound **6** was crystallized from ethyl acetate as colorless needles, mp 261° dec, $[\alpha]^{22}$D −60 ± 1.3° (*c* 0.38, chloroform). It also had the expected ir spectrum; nmr (100 MHz, methyl sulfoxide-*d*, hexamethyl siloxane as an external standard) τ 5.05 (1-proton triplet, H-3, $J_{2,3}$ = 6.0 Hz, $J_{3,4}$ = 6.0 Hz), 5.19 (1-proton doublet, H-1, $J_{1,2}$ = 4.0 Hz), 5.61 (1-proton octet, H-5, $J_{4,5}$ = 4.0 Hz, $J_{5,6}$ = 6.5 Hz), 5.8–6.1 (2-proton multiplet, H-2, H-4), 6.51 (3-proton singlet, OCH₃), 7.81 (3-proton singlet, OCOCH₃), 7.91 and 7.97 (two 3-proton singlets, NCOCH₃), 8.68 (3-proton doublet, C-5 CH₃); nmr (100 MHz, chloroform-*d*) τ 6.61 (3-proton singlet, OCH₃), 7.92 (3-proton singlet, OCOCH₃), 8.07 and 8.10 (two 3-proton singlets, NCOCH₃), 8.79 (3-proton doublet, C-5 CH₃).

Anal. Calcd for $C_{13}H_{22}N_2O_6$: C, 51.64; H, 7.34; N, 9.27. Found: C, 51.77; H, 7.64; N, 9.14.

The Crystal and Molecular Structure of (2S,3S)-1-Cyano-2-hydroxy-3,4-epithiobutane-α-naphthylurethane

R. B. BATES,* R. A. GRADY, AND T. C. SNEATH

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

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The constitution, relative configuration, and partial conformation proposed for (2S,3S)-1-cyano-2-hydroxy-3,4-epithiobutane and its acetate on the basis of spectral evidence were confirmed by an X-ray study on its α-naphthylurethane. The structure was solved by symbolic addition and refined to an *R* of 0.048. The shortness of the carbon–carbon single bond joining the episulfide ring to the other atoms supports the view that the carbons in an episulfide ring are between sp³ and sp² in hybridization. The naphthalene ring and urethane group form a dihedral angle of 55°; this unexpected lack of coplanarity probably occurs to allow intermolecular hydrogen bonding between N–H and carbonyl oxygen.

Enzymic hydrolysis of the thioglucosides progoitrin and epiprogoitrin produces four compounds formulated as the stereoisomeric 1-cyano-2-hydroxy-3,4-epithiobutanes; this unusual reaction probably involves episulfide formation by intramolecular transfer of thioglucoside sulfur to an isolated olefinic bond.[1] An ir–nmr study of these episulfides and their acetates permitted complete stereochemical assignments to be made, and further suggested that the hydrogens attached to the asymmetric carbons are trans to one an-

other in the most stable conformation of each stereoisomer.[2] To check the constitution, relative configuration, and conformation of one of these substances and to gain further information about bond parameters in episulfide groups, we undertook an X-ray study on the title compound.[3]

(1) M. E. Daxenbichler, C. H. VanEtten, and I. A. Wolff, *Phytochemistry*, **7**, 989 (1968), and references cited therein.

(2) K. D. Carlson, D. Weisleder, and M. E. Daxenbichler, *J. Amer. Chem. Soc.*, **92**, 6232 (1970).

(3) This derivative, mp 134–136°, was kindly provided by M. E. Daxenbichler and I. A. Wolff. It was prepared by reacting episulfide B from epiprogoitrin with α-naphthyl isocyanate in the presence of dicyclohexylethylamine.

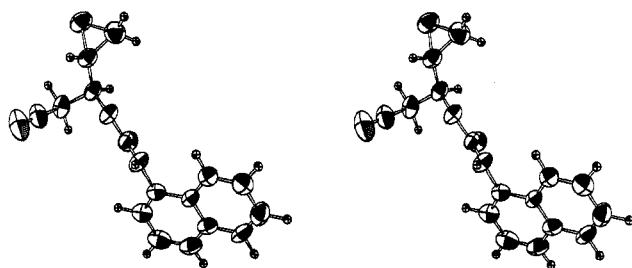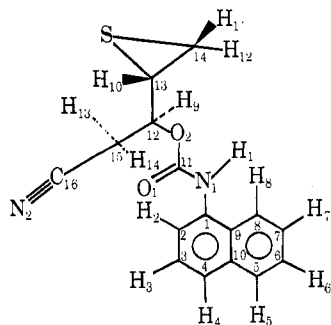Figure 1.—Stereoscopic view of (2S,3S)-1-cyano-2-hydroxy-3,4-epithiobutane-α-naphthylurethane. Thermal ellipsoids enclose 50% probability. Hydrogen atoms are shown as spheres.
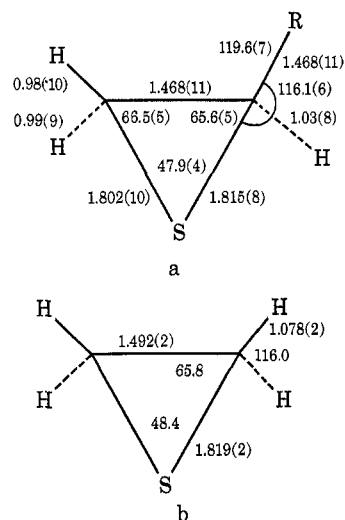

Figure 2.—Bond distances and angles in episulfides, with standard deviations in parentheses: (a) X-ray on the title compound; (b) microwave study on ethylene sulfide.[10]
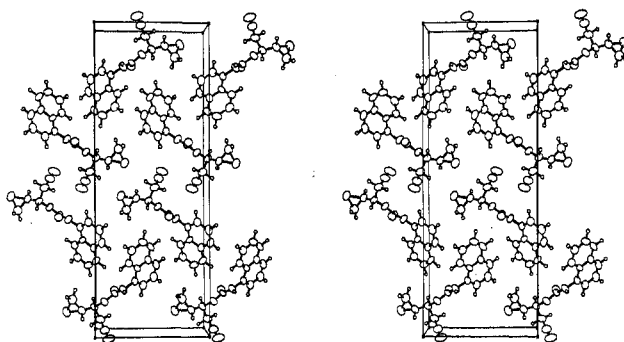

Figure 3.—Stereoscopic view of the unit cell, *a* axis projection. The *b* axis is horizontal and the *c* axis vertical.

dropped R to its final value, 0.0476. No corrections were made for extinction or absorption ($\mu = 19.1$ cm^{-1}).[7]

Results and Discussion

As can be seen from the ORTEP[8] plot in Figure 1, this study confirms the constitution, relative configuration, and trans arrangement of the protons attached to the asymmetric carbons. No attempt was made to verify the absolute configuration.

This is the first X-ray study of a substance containing an episulfide ring. Some bond distances and angles in the vicinity of this grouping are shown in Figure 2a;[9] they show geometry similar to that found for ethylene sulfide itself in a microwave study (Figure 2b).[10] The present study gives for the first time a value for the length of a carbon–carbon single bond between a carbon in an episulfide ring and another carbon: 1.468(11) Å, between C-12 and C-13. The shortness

Experimental Section

Collection and Reduction of the Data.—A slightly amber needle of dimensions $0.2 \times 0.3 \times 0.8$ mm of (2S,3S)-1-cyano-2-hydroxy-3,4-epithiobutane-α-naphthylurethane was mounted for rotation about the needle axis (*a*). Oscillation and Weissenberg photographs indicated space group $P2_12_12_1$ or $P2_12_12$; the former was later definitely established by the full intensity data. The crystal was mounted on a Picker FACS-I four-circle automated diffractometer set for graphite-monochromatized Cu Kα radiation, $\lambda = 1.54051$ Å. The unit cell dimensions, determined by least-squares refinement of the angular settings of nine reflections, were $a = 4.824(2)$, $b = 10.803(7)$, and $c = 28.679(16)$.

For data collection, the 2θ scan technique using a basic 2° scan width modified for radiation dispersion was employed. After scanning at 1°/min, 10 sec background counts were taken at both ends of the scan. Three standard reflections were measured 31 times during the data collection. The crystal decomposed approximately 4%. Of 1474 unique reflections measured up to $2\theta = 125°$, 935 were determined to be statistically significant on the basis $I \geqslant 2\sigma$.

Solution and Refinement.—The structure was solved by symbolic addition[4] using the MULTAN programs.[5] Using all 140 E's $\geqslant 1.50$, the program selected 103, 017, 036, and 108 as the origin- and enantiomorph-fixing reflections. An E map was constructed using the set of phases having the highest figure of merit (0.92). The largest peak on the E map corresponded to the sulfur position as determined by a sharpened Patterson. The positions of all 21 nonhydrogen atoms were found in the top 25 peaks in the E map. After four cycles of isotropic refinement, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.105$.[6] The R was 0.074 after three cycles of anisotropic refinement. A difference map revealed all 14 hydrogens. Two additional cycles of anisotropic refinement including hydrogens (given the same anisotropic temperature factors as the atom to which they were attached)

(4) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

(5) G. Germain, P. Main, and M. M. Woolfson, *ibid.*, **26**, 274 (1970).

(6) Refinements were by full matrix least squares with the ORFLS program of W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-305, Oak Ridge National Laboratory, 1962. Unit weights were used. Form factors were obtained by graphical interpolation of those in the International Tables for X-Ray Crystallography, Vol. III, Table 3.3.1A, except for hydrogen, for which the form factors of R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965), were used.

(7) Listings of coordinates, temperature factors, bond distances and angles, least squares planes, and structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-72-2145. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

(8) C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory, 1966.

(9) These values and their standard deviations were calculated using ORFFE, W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-306, Oak Ridge National Laboratory, 1964.

(10) G. L. Cunningham, Jr., A. W. Boyd, R. J. Myers, W. D. Gwinn, and W. I. Le Van, *J. Chem. Phys.*, **19**, 676 (1951).

of this bond might be considered to provide further evidence that the hybridization of the carbons in an episulfide ring is closer to sp² than sp³.[10,11]

The naphthalene ring and urethane group, normally expected to be planar to attain full p-orbital overlap, form a dihedral angle of 55.1°; C-11 is 1.05 Å out of the plane of the naphthalene ring. The disruption in p-orbital overlap is reflected in the relatively long bond [1.428(9) Å] between C-1 and N-1 as compared to the 1.325(9) Å bond between N-1 and C-11. The non-coplanarity may be partially caused by nonbonded steric interaction between H-2 and O-1; the energy lost by the disruption of p-orbital overlap is at least partially offset by that gained in the formation of an intermolecular hydrogen bond [2.24(9) Å] between

H-1 and O-1 (perpendicular to the viewing axis in Figure 1 and in the packing diagram, Figure 3). This is the shortest intermolecular distance; the N-1–H-1 bond length is 0.74 Å, and the shortest intermolecular distance between nonhydrogen atoms (O-1 and N-1) is 2.89(8) Å.

(11) D. R. Lide, Jr., *Tetrahedron,* **17**, 129 (1961). This sort of shortening has also been observed in substituted cyclopropanes: I. L. Karle, R. D. Gilardi, A. V. Fratini, and J. Karle, *Acta Crystallogr., Sect. B,* **25**, 1469 (1969).

# Studies on a β-Keto Sulfone. Halogenation and Cyclization of γ-Methylsulfonyl-γ-benzoylbutyronitrile

Dov Diller and Felix Bergmann*

Department of Pharmacology, Hebrew University-Hadassah Medical School, Jerusalem, Israel

γ-Methylsulfonyl-γ-benzoylbutyronitrile (2) can be halogenated at the α position to the carbonyl group in weakly alkaline media. The halogen derivatives 3 are, however, unstable under alkaline conditions and split off the benzoyl group; therefore they are unable to undergo the Ramberg–Bäcklund rearrangement. Anhydrous acids cyclize compound 2 to 3,4-dihydro-5-methylsulfonyl-6-phenyl-2-pyridone (7), while with bromine 2 is converted into the 3-bromo derivative of 7. Photolysis of 2 proceeds either by a Norrish type II cleavage to ω-methylsulfonylacetophenone (12) or by rupture of the C–S bond to γ-benzoylbutyronitrile (13).

Addition of acrylonitrile to ω-methylsulfinylacetophenone yields the β-keto sulfoxide 1, which is oxidized by hydrogen peroxide to the corresponding β-keto sulfone, γ-methylsulfonyl-γ-benzoylbutyronitrile (2)[1] (see Scheme I). The reactions and properties of the latter form the subject of the present investigation.

SCHEME I
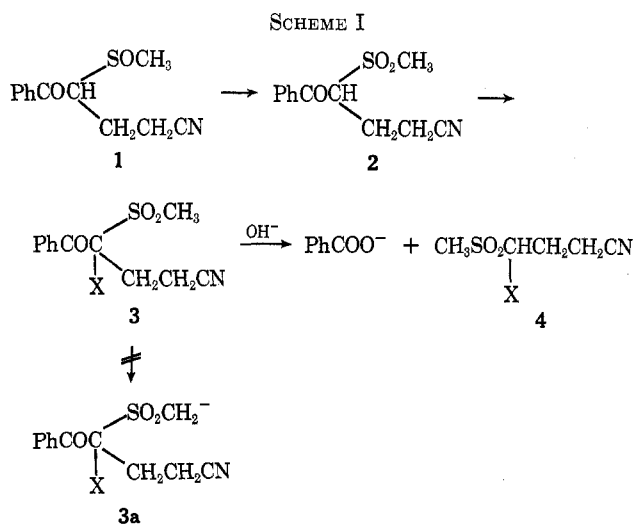
Halogenation of 2 with bromine in aqueous methanolic bicarbonate gave 3 (X = Br). Another successful

(1) F. Bergmann and D. Diller, *Israel J. Chem.,* **7**, 57 (1969).

procedure was treatment of a chloroform solution of 2 with N-bromo- or N-chlorosuccinimide.

The halogen derivatives 3 proved unstable under a variety of conditions. (1) They easily underwent reduction to 2 when heated in THF or when treated with sodium azide or potassium cyanide in acetonitrile.[2] (2) Dilute (0.5 N) NaOH in 50% dioxane or NaHCO₃ in dilute methanol splits compounds 3 into benzoate and γ-halogeno-γ-methylsulfonylbutyronitrile (4) (see Scheme I), the bromo derivative reacting about twice as fast as the chloro compound. Similarly, the chloro derivative 3 (X = Cl) was decomposed by sodium methoxide in absolute methanol to 4 (X = Cl) and methyl benzoate.

Attempts to iodinate 2 at room temperature in methanolic solution, in the presence of NaHCO₃, directly led to the formation of 4 (X = I). Apparently, the sensitivity of 3 to alkaline fission increases in the order X = Cl < Br < I.

Compound 2 itself proved much more stable to alkali. Only contact with 1 N NaOH (2 equiv) at room temperature for 24 hr split this compound into benzoic acid and the known γ-methylsulfonylbutyronitrile.[3]

It should be noted that, in contrast to the behavior of 3-substituted pentane-2,4-diones,[4] enolization of

(2) Similar reductions of α-halogenosulfones have been described by F. G. Bordwell and B. B. Jarvis, *J. Org. Chem.,* **33**, 1182 (1968).

(3) W. E. Truce, W. W. Bannister, and R. H. Knospe, *ibid.,* **27**, 2821 (1962).

(4) J. B. Conant and A. F. Thompson, *J. Amer. Chem. Soc.,* **54**, 4036 (1932).