Presumably this is why the amount of racemization is insensitive to temperature.

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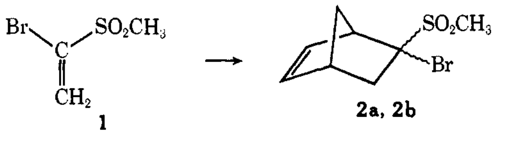
Bromovinyl Sulfone Chemistry. Synthesis and Rearrangement of the 5-Bromo-5-methylsulfonylbicyclo[2.2.1]hept-2-enes

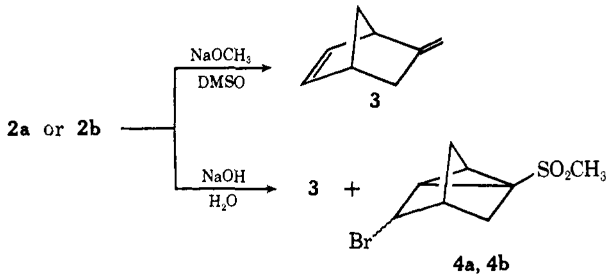
Sir:

The Ramberg–Bäcklund rearrangement of α-halo sulfones is a particularly attractive method for the introduction of double bonds within a molecular framework.[1] The usual synthetic sequence consists of sulfide preparation, α-halogenation, oxidation of sulfur to the sulfone, and subsequent base-induced rearrangement of the α-halo sulfone. We would like to communicate an alternative, short sequence that involves preparation of the requisite α-halo sulfone *via* a cycloaddition reaction of methyl α-bromovinyl sulfone (**1**). In addition, we would like to present evidence of homolytic cleavage of the carbon–bromine bond of α-bromo sulfones under traditional conditions of the Ramberg–Bäcklund rearrangement.

Methyl α-bromovinyl sulfone (**1**), bp 63–64° (0.4 mm),[2] was prepared in 80% overall yield by bromination–dehydrobromination of methyl vinyl sulfone.[3] The Diels–Alder reaction of **1** with cyclopentadiene afforded a mixture of α-bromo sulfones **2a**, **2b**[2] in 85% yield. Bromo sulfone **2a**, mp 101.5–102.5°,[2] could be purified by fractional recrystallization of the crude mixture of isomers from chloroform–hexane: $\nu_{max}^{CCl_4}$ 1144 and 1323 cm^{-1}; $\lambda_{max}^{CCl_4}$ (near ir) 1.655 μ (ε 0.640); $\delta_{TMS}^{CDCl_3}$ 1.45–2.93 (m, 4, methylene), 3.10 (m, 1, bridgehead), 3.22 (s, 3, SO_2CH_3), 3.55 (m, 1, bridgehead), 6.20 (four-line pattern, 1, vinyl), 6.45 (four-line pattern, 1, vinyl). Isomer **2b**, mp 103.5–104.5°,[2] was obtained in pure form by column chromatography of the mixture of isomers on silica gel: $\nu_{max}^{CCl_4}$ 1146 and 1326 cm^{-1}; $\lambda_{max}^{CCl_4}$ (near ir) 1.655 μ (ε 0.550); $\delta_{TMS}^{CDCl_3}$ 1.70–2.55 (m, 4, methylene), 3.11 (m, 1, bridgehead), 3.13 (s, 3, SO_2CH_3), 3.47 (m, 1, bridgehead), 6.11 (four-line pattern, 1, vinyl), 6.31 (four-line pattern, 1, vinyl).

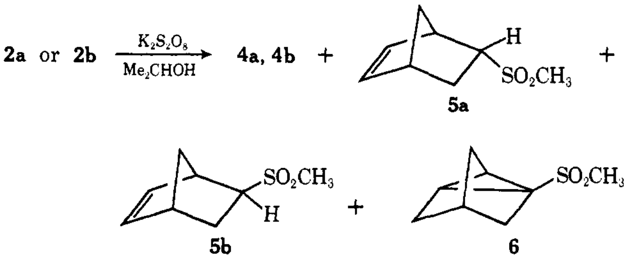


While treatment of **2a** or **2b** with sodium methoxide in dry DMSO resulted in formation of the expected 5-methylene-2-norbornene (**3**) in >90% yields, treatment of either isomer with refluxing 2 *N* sodium hydroxide solution unexpectedly afforded a mixture of rearranged bromo sulfones **4a** and **4b**,[4] in addition to olefin **3**.



Chromatography of the sulfone mixture (**4a**, **4b**) on silica gel with increasing percentages of ether–petroleum ether as eluent gave pure **4a**: mp 96–97°;[2] $\nu_{max}^{CCl_4}$ 1128, 1148, 1181, and 1323 cm^{-1}; $\lambda_{max}^{CCl_4}$ (near ir) 1.655 μ (ε 1.085); $\delta_{TMS}^{CDCl_3}$ 1.60–2.56 (7, methylene and bridgehead), 3.03 (s, 3, SO_2CH_3), 4.01 (m, 1, $CHBr$). Further elution afforded pure **4b**: mp 102.5–103.5°;[2] $\nu_{max}^{CCl_4}$ 1127, 1150, and 1323 cm^{-1}; $\lambda_{max}^{CCl_4}$ (near ir) 1.655 μ (ε 0.849); $\delta_{max}^{CDCl_3}$ 1.52–2.52 (7, methylene and bridgehead), 2.95 (s, 3, SO_2CH_3), 4.02 (m, 1, $CHBr$). The gross structures and diastereomeric relationship of **4a** and **4b** were deduced from the following data: the similar nmr spectra with no vinyl proton absorptions but with characteristic absorptions for SO_2CH_3 and $CHBr$; the incorporation of only three deuteriums upon exchange with sodium deuteroxide–deuterium oxide; the near-infrared absorptions with extinction coefficients of a magnitude expected for the nortricyclane ring structure;[5] and the identical mass spectral fragmentation patterns of the two isomers.

Some insight into the origin of **4a** and **4b** was gained from the following observations. Isomers **4a** and **4b** are obtained from **2a** or **2b** by the action of free-radical initiators such as benzoyl peroxide or potassium persulfate[6] in the absence of base. Specifically, treatment of solutions of **2a** or **2b** in *tert*-butyl alcohol–water (1:1 by volume) with 10 mol % of potassium persulfate at 100° afforded a mixture of **4a** and **4b** in 80–90% yield (**4a**:**4b** = 57:43). No olefin was detected under these conditions. Replacement of the *tert*-butyl alcohol with isopropyl alcohol resulted in the formation of three additional bromine-free sulfones presumably by hydrogen abstraction from isopropyl alcohol. Two of these new products, **5a** and **5b**,[2] were identical with the Diels–Alder adducts of cyclopentadiene and methyl vinyl sulfone.[7] The structure of the sulfone **6**, mp 111.5–113°,[2] was assigned on the basis of elemental analysis, the presence of only three exchangeable hydrogens, spectral data, *e.g.*, the simple nmr spectrum $\delta_{TMS}^{CDCl_3}$ 2.95 (s, 3, SO_2CH_3), 2.28 (br m, 1, bridgehead), 2.11 (br s, 2,



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(2) All new compounds cited herein gave acceptable (±0.3%) combustion analysis values.

(3) G. D. Buckley, J. L. Charlish, and J. D. Rose, *J. Chem. Soc.*, 1514 (1947).

(4) The ratio of **4a**:**4b** is 57:43 from either **2a** or **2b**. The yield of **4a**, **4b** is 37% from **2a** and 59% from **2b**.

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(6) (a) P. D. Bartlett and J. D. Cotman, Jr., *ibid.*, **71**, 1419 (1949); (b) I. M. Kolthoff and I. K. Miller, *ibid.*, **73**, 3055 (1951).

(7) (a) H. R. Snyder, H. V. Anderson, and D. P. Hallada, *ibid.*, **73**, 3258 (1951); (b) J. C. Philips and M. Oku, unpublished results.

cyclopropyl), 1.67 (d, $J = 2$ Hz, 2, C-7 methylene), 1.50 (m, 4, C-3 and C-5 methylene), and its formation by hydrogenolysis of **4a, 4b** over Pd/C. In addition, sulfone **6** has been synthesized independently from a mixture of **5a** and **5b** by a sequence consisting of oxymercuration–demercuration, mesylation of the alcohol mixture, and 1,3 elimination. Treatment of **2a** or **2b** with 2 *N* sodium hydroxide in the presence of isopropyl alcohol afforded not only **3**, **4a**, and **4b** but also **5a**, **5b**, and **6**. Since the rearranged bromo sulfones **4a** and **4b** are inert under these conditions, the three additional sulfones **5a**, **5b**, and **6** must arise directly from **2a** or **2b** *via* a free-radical intermediate and subsequent capture of hydrogen from isopropyl alcohol at C-2 or -5. The presence of 10 mol % iodine under reaction conditions employing 2 *N* sodium hydroxide inhibits the formation of **4a** and **4b**. Under these conditions, olefin **3**, the normal product of the Ramberg–Bäcklund rearrangement, is isolated in 80–90% yield.

Although the stereochemistry of **2a** and **2b** may be deduced from chemical-shift data of the $\mathrm{SO_2C}H_3$ moiety[8] and the change in chemical shifts of the $\mathrm{SO_2C}H_3$ absorptions upon saturation of the double bond[9] we prefer to await the results of X-ray studies presently in progress for definitive stereochemical assignments for **2a**, **2b** and **4a**, **4b**.

We expect to report on further observations of the synthetic utility and mechanistic complexity of bromovinyl sulfone chemistry at a future date.

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Cleavage of Thymine Dimers Sensitized by Quinones. Chemically Induced Dynamic Nuclear Polarization in Radical Ions

Sir:

The photosensitized cleavage of thymine photodimers is being investigated in several laboratories[1] in order to provide guidelines for understanding the light-requiring step in photoreactivation,[2] the photoenzymatic reversal of pyrimidine dimer formation in DNA. Among the variety of sensitizers employed, quinones, *e.g.*, 2-anthraquinone sulfonate (A), first suggested by Ben-Hur and Rosenthal,[1d] were found to be particularly effective. For this group of sensitizers several experimental results[1f,g] suggest a mechanism involving electron transfer as the initial step, *i.e.*, the formation of quinone anions paired with substrate cations.

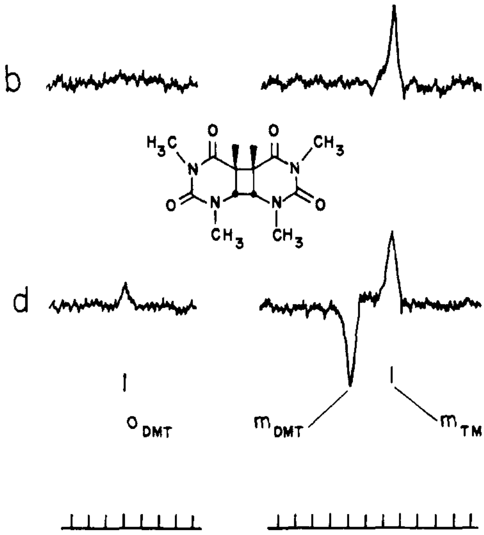

Figure 1. Pmr spectra (60 MHz) of 0.02 *M* solutions of A in D$_2$O containing 5 mg/ml TM$\widehat{\mathrm{TT}}$ before (b) and during (d) ultraviolet irradiation. The regions of the olefinic (o) and the *C*-methyl resonances (m$_{\mathrm{DMT}}$, m$_{\mathrm{TM\widehat{TT}}}$) are shown. The spectra obtained after irradiation were identical with spectrum b. The calibration marks are separated by 10.6 Hz.

Since chemical processes involving radical pairs can give rise to nuclear spin polarization (CIDNP),[3] we sought direct support for the electron-transfer mechanism in pmr experiments, investigating the photoreactions of several quinones with the cis-syn dimer (TM$\widehat{\mathrm{TT}}$) of 1,3-dimethylthymine (DMT). In this communication we present the CIDNP effects we found in these systems, to our knowledge the first report of CIDNP arising from pairs of radical ions.[4]

When deoxygenated solutions of A (0.02 *M*) containing low concentrations of TM$\widehat{\mathrm{TT}}$ were photolyzed in the probe of an nmr spectrometer,[5] two enhanced signals were observed (Figure 1): a broad absorption signal (~5.1 ppm) and a stronger signal in emission (~1.4 ppm). The chemical shifts of the enhanced signals match those of the olefinic proton and the allylic methyl group of the monomer DMT. We were unable to detect any enhancement of TM$\widehat{\mathrm{TT}}$ signals. The CIDNP signals of the monomer disappeared very quickly after the light was extinguished and reappeared upon resumed irradiation. During the brief irradiation periods (<10 sec) required for recording these signals only a small fraction (<10%) of the dimer was monomerized. No enhanced resonances were observed in the

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(2) C. S. Rupert in "Photophysiology," Vol. 2, A. C. Giese, Ed., Academic Press, New York, N. Y., 1964, pp 283–327.

(3) (a) J. Bargon, H. Fischer, and U. Johnson, *Z. Naturforsch.*, *A*, **22**, 1551 (1967); (b) H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5518 (1967).

(4) Nuclear spin polarization induced in pairs of radical ions was independently found during the quenching of excited aromatic hydrocarbon singlets by electron acceptors: G. N. Taylor, private communication.

(5) With a 2500-W high-pressure mercury lamp, Corning filter 052 (cut-off, 340 nm).