

STEREOCHEMICAL CONTROL IN BROMINATION-
DEHYDROBROMINATIONS OF VINYL SULFONES

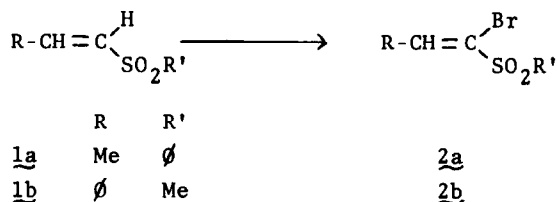
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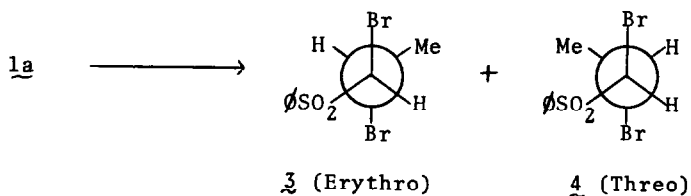
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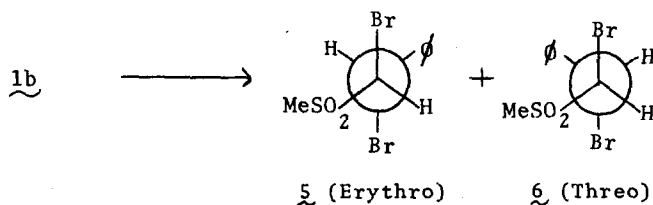
An interest in the synthetic utility of α -bromovinyl sulfones,¹ particularly with derivatives of defined stereochemistry, has led us to examine closely the stereochemical outcome of the bromination-dehydrobromination sequence for the conversion of 1 to 2. In this communication we wish to



report methods for stereochemical control of both steps in this sequence and to comment on the important role of the sulfonyl group's steric requirement in these reactions.

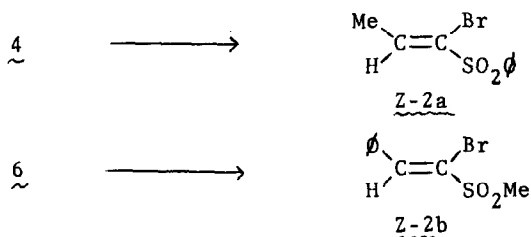
The known E- and Z-isomers of 1a^{2,3} and 1b² were brominated with molecular bromine or with pyridinium hydrobromide perbromide (PHP) to afford the erythro and threo dibromides (3-6).⁴ While the molecular bromination



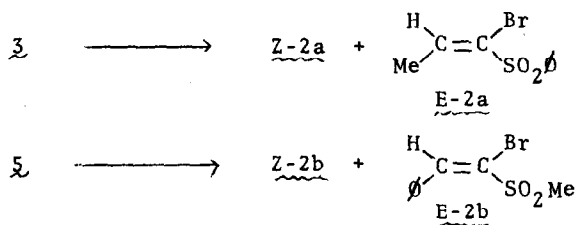


reactions always gave mixtures containing considerable amounts of each dibromide, the PHP reactions were very nearly stereospecific anti brominations and afforded pure erythro or threo dibromides (3-6) by simple recrystallization of the product obtained from the appropriate E- or Z-isomer of 1a or 1b, e.g., E-1a affords pure 3 and Z-1a affords pure 4. Subsequently it was discovered⁵ that molecular bromine catalyzed cis-trans isomerization in the 1a and 1b systems with a faster rate than that of normal addition, i.e., Z-1a or Z-1b or E,Z-mixtures could be completely isomerized to pure E-1a or E-1b, respectively.

The triethylamine-induced dehydrobrominations of 3-6 gave quantitative yields of α -bromovinyl sulfones, with threo dibromides 4 and 6 affording Z-2a⁴ and Z-2b⁴ in exclusive anti eliminations in a wide variety of solvents. Erythro dibromides 3 and 5 afforded mixtures of the E- and Z-bromovinyl



sulfones.⁶ While the vinyl sulfones are stable to the elimination conditions, catalytic amounts of molecular bromine were successful again



in achieving complete isomerization of the olefin mixtures to the more stable isomer (Z) in which the β substituent is trans to the bulky sulfonyl group but cis to bromine. Thus Z-2a⁴ and Z-2b⁴ may be obtained in pure form from either the erythro or the threo dibromides. The E-bromovinyl sulfones⁴ are most readily obtained pure by recrystallization of the mixtures obtained from tetrabutylammonium acetate-induced dehydrobrominations of 3 and 5 in acetone which afford approximately 9:1 ratios of E-2a:Z-2a and E-2b:Z-2b.

It seems clear from this work and previously reported examples that intermolecular non-cyclic eliminations of hydrogen chloride,⁷ hydrogen bromide,⁸ hydrogen iodide,⁹ and p-bromobenzenesulfonic acid¹⁰ from acyclic sulfonyl activated systems will occur exclusively in an anti fashion if the bulky sulfonyl group and the β substituent can attain a trans geometry. For isomers where anti elimination would lead to a cis relationship between the sulfonyl group and the β substituent, the actual stereochemistry of the elimination process may vary anywhere from 100% anti⁸⁻¹⁰ to 100% syn.⁷ The interesting dehydrofluorination studies of Naso¹¹ again demonstrate the steric influence of the sulfonyl group but, surprisingly, *via* a syn elimination pathway with cyclic ion-pair species being invoked in explanation. Thus it would seem that ion-pair phenomena^{11,12} and the steric requirement of the sulfonyl group are two factors that can exert a dominant influence on the syn or anti course of these eliminations. We hope to present further mechanistic details on the dehydrobrominations at a later date.

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- (4) Satisfactory elemental analyses and spectra were obtained for all new compounds reported herein. The structures of dibromides 3-6 were proven by potassium iodide in acetone debrominations. The structures of the E- and Z-isomers of 2a and 2b were proven by zinc in acetic acid reductions.
- (5) Bromine-induced cis-trans isomerization in the 1a system has been observed independently by C. Y. Meyers and I. Sataty, Department of Chemistry, Southern Illinois University; I. Sataty, Ph.D. Dissertation 1970. I. Sataty and C. Y. Meyers, Tetrahedron Lett., accompanying paper.
- (6) For example, 3 affords 68% Z-2a and 32% E-2a in methanol or t-butyl alcohol. In benzene 3 gives 80% Z-2a and 20% E-2a. Similar results were obtained for 5.
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