effects to bring about inversion of the n,π^* and first π,π^* singlet states.

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A 1,3 Elimination Proceeding by Double Inversion

Sir:

There is relatively little evidence available concerning the stereochemistry of 1,3-elimination reactions to form C–C bonds in systems wherein the configuration at both C-1 and C-3 can be examined. The much more rapid reaction of *exo-* than *endo*-norbornene-boronic acid with mercuric chloride to form nortri-cyclylmercuric chloride indicates an appreciable preference for inversion at each carbon center during the ring closure step.[1] On the other hand, in the base-

8; 1275 reflections were obtained by θ–2θ scan techniques on a Picker four-angle diffractometer. The structure has refined to a conventional R factor of 0.08, using 92 parameters; refinement continues. Bond lengths and angles are normal. One of the bromine atoms is *cis* to, and flanked by, the sulfonyl oxygen atoms.

Triphenylphosphine is assumed to initiate attack on bromine to form an ion pair, $[Ph_3PBr]^+[carbanion]^-$. In the presence of methanol protonation of the carbanion competes with intramolecular displacement, but the stereochemistry for the latter remains unchanged (Table I). α-Sulfonyl carbanions of this type are known to be asymmetric and to maintain configuration for appreciable periods of time.[5] In closely analogous systems there is evidence for a nearly planar, pyramidal carbanion which has an appreciable barrier for rotation, but not for inversion.[6] Furthermore, there is evidence that the carbanion is formed from a conformation in which the proton abstracted is *cis* to, and flanked by, the sulfonyl oxygen atoms.[6c] If it is assumed that the carbanion in the present instance is formed from a

Table I. Products from 1,3 Eliminations from *dl-* and *meso*-PhCHBrSO$_2$CHBrPh (**1** and **2**, respectively)

Isomer	Solvent	Nucleophile	PhCH=CHPh % cis[a]	PhCH=CHPh % trans[a]	PhCBr=CHPh % cis[b]	PhCBr=CHPh % trans[b]	Yield, %
1	C$_6$H$_6$	Ph$_3$P	4	96			85–90
2	C$_6$H$_6$	Ph$_3$P	95	5			85–90
1	2% MeOH in C$_6$H$_6$	Ph$_3$P	7	93			90[c]
2	2% MeOH in C$_6$H$_6$	Ph$_3$P	96	4			90[c]
1	DMF	DMF	1[d]	2[d]	79	21	85–90[e]
2	DMF	DMF	2[d]	4[d]	9	91	85–90[e]

[a] Based on 100% PhCH=CHPh. [b] Based on 100% PhCBr=CHPh. [c] About 40% stilbenes and 60% reduction products. [d] Based on total yield [e] Consisting of 73–75% PhCBr=CHPh, 3–6% PhCH=CHPh, and 24–19% PhC≡CPh.

initiated 1,3 elimination of *p*-toluenesulfonic acid from *exo-* and *endo*-norbornyl tosylates to form nortri-cyclene the 6-*endo* proton was lost somewhat more readily in each instance, indicating some preference for retention of configuration at C-6.[2] Base-catalyzed ring openings of cyclopropanols occur with inversion of configuration at the carbon atom being protonated, but acid-catalyzed ring openings occur with retention of configuration.[3] Ring opening of quadricycloheptane-2,3-dicarboxylic acid by bromine occurs with inversion at both carbon atoms of the cyclopropane ring.[4]

We wish to report that 1,3 elimination of bromine from *dl-* and *meso*-PhCHBrSO$_2$CHBrPh (**1** and **2**, respectively) by the action of triphenylphosphine occurs in a highly stereoselective manner with inversion at C-1 and at C-3. Dimethylformamide (DMF) catalyzes stereoselective loss of hydrogen bromide from **1** and **2**; once again inversion of configuration occurs at C-1 and at C-3.

The two diastereoisomers of PhCHBrSO$_2$CHBrPh were distinguished unambiguously by a three-dimensional, single-crystal X-ray analysis of **2**, which was shown to be the *meso* isomer. The space group is Pbca, with $a = 16.53$, $b = 12.81$, $c = 13.46$ Å, $Z =$

conformation in which the bromine atom being removed is *cis* to the two sulfonyl oxygen atoms, one arrives at the representation shown below.[7]

The transformation of carbanion conformation **3a** to **3b** involves rotation around the S–CHBrPh bond to provide the proper orientation of atoms for double inversion. Loss of sulfur dioxide from *cis* episulfone **4** (or from its *trans* isomer) has been shown to occur stereospecifically with retention of configuration in the absence of base.[12]

(1) D. S. Matteson and M. E. Talbot, *J. Am. Chem. Soc.*, **89**, 1119, 1123 (1967).

(2) A. Nickon and N. H. Werstiuk, *ibid.*, **89**, 3915, 3917 (1967).

(3) (a) C. H. DePuy, F. H. Breitbell, and K. R. DeBruin, *ibid.*, **88**, 3347 (1966); (b) A. Nickon, J. L. Lambert, R. G. Williams, and N. H. Werstiuk, *ibid.*, **88**, 3354 (1966).

(4) S. J. Cristol and R. T. LaLonde, *ibid.*, **80**, 4355 (1958).

(5) See D. J. Cram, R. D. Trepka, and P. St. Janiak, *ibid.*, **88**, 2749 (1966), and references cited therein.

(6) (a) E. J. Corey, H. Konig, and T. H. Lowry, *Tetrahedron Letters*, 515 (1962); (b) E. J. Corey and T. H. Lowry, *ibid.*, 793 (1965); (c) E. J. Corey and T. H. Lowry, *ibid.*, 803 (1965); (d) F. G. Bordwell, D. D. Phillips, and J. M. Williams, Jr., *J. Am. Chem. Soc.*, **90**, 426 (1968).

(7) The stereochemical evidence could also be rationalized by a mechanism involving retention of configuration at each asymmetric center. There is abundant evidence to show, however, that 1,3-intramolecular displacements by nucleophiles, *e.g.*, –O–,[8] >S,[9] >N:,[10] and >C–,[11] involve inversion at the carbon atom holding the leaving group. Furthermore, 1,3-intramolecular displacements initiated by carbanions fail when a front-side attack is required.[11b-d] A double-retention mechanism appears, therefore, to be highly unlikely.

(8) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **61**, 1576 (1939).

(9) H. L. Goering, D. I. Relyea, and D. W. Larson, *ibid.*, **78**, 348 (1956).

(10) N. J. Leonard, *Record Chem. Progr.*, **26**, 211 (1965).

(11) (a) H. M. Walborsky and C. G. Pitt, *J. Am. Chem. Soc.*, **84**, 4831 (1962); (b) J. Meinwald and J. K. Crandall, *ibid.*, **88**, 1292 (1966); (c) S. J. Cristol, J. K. Harrington, and M. S. Singer, *ibid.*, **88**, 1529 (1966); (d) S. J. Cristol and B. B. Jarvis, *ibid.*, **88**, 3095 (1966); **89**, 401 (1967).
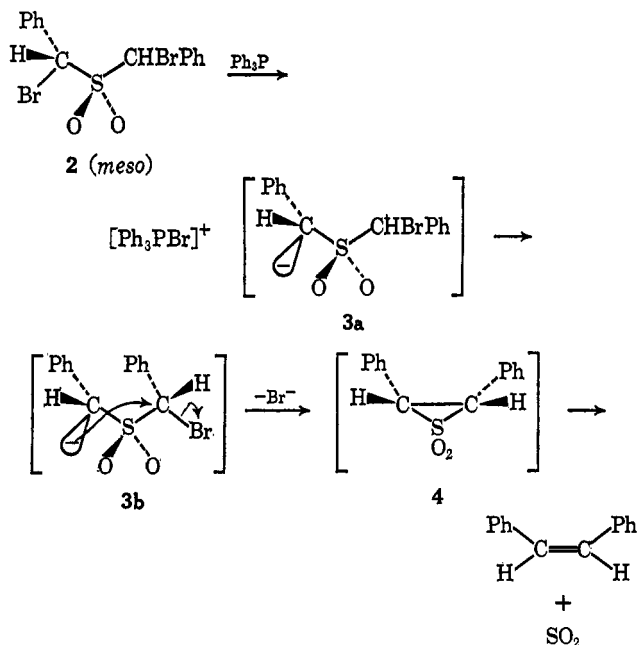
(12) N. Tokura, T. Nagai, and S. Matsumura, *J. Org. Chem.*, **31**, 349

2 (meso)

[Ph₃PBr]⁺

3a

3b   4

+

SO₂

In the 1,3 eliminations initiated by DMF a comparable mechanism (W type in the Nickon–Werstiuk classification[2]) appears reasonable, with proton removal occurring from a conformation in which the proton is *cis* to the sulfone oxygen atoms.

If one further assumption is made, this W-type mechanism can be used to rationalize the observation that base-initiated 1,3 eliminations from RCH₂SO₂CHXR α-halo sulfones give *cis*-alkenes (*via cis*-dialkyl episulfones) in greater amount than *trans*-alkenes.[13] The required assumption is that proton removal occurs from a particular conformation, *e.g.*, 5, in which the halogen atom is oriented *trans* to the sulfonyl oxygen atoms and in which the alkyl groups are *trans* to one another. The W-type mechanism then requires reaction *via* conformation 6 to give the *cis* episulfone.[14,15]

5   6
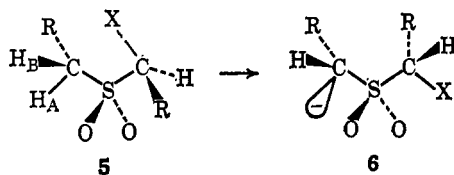
Acknowledgment. We are grateful to the National Science Foundation (GP 7065) for support of this investigation.

(1966); F. G. Bordwell, J. M. Williams, Jr., E. B. Hoyt, Jr., and B. B. Jarvis, *J. Am. Chem. Soc.*, 90, 429 (1968).

(13) See N. P. Neureiter, *ibid.*, 88, 558 (1966), and references cited therein.

(14) J. M. Williams, Jr., Ph.D. Dissertation, Northwestern University, Aug 1966, pp 53–57.

(15) According to this representation the *cis*:*trans* ratio of episulfones formed will depend principally on the extent to which removal of proton H$_A$ of 5 is preferred to removal of proton H$_B$ (from, *e.g.*, the alternative conformation in which the R groups are *cis*). Since, however, proton removal is reversible,[13] the ratio will also depend on the relative rates of episulfone formation from the two isomeric, asymmetric carbanions. The decrease in *cis*:*trans* ratio for R = Me, Et, Pr[13] can be accommodated by assuming appropriate values for the two equilibrium constants and the two rate constants.

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Substituent Effects in Unimolecular Ion Decompositions. XIII.[1] The Quantitative Effect of Product Ion Stability

Sir:

Since our earlier work describing aromatic systems in which the effect of substituents on mass spectra was related to Hammett σ constants with a high degree of correlation,[2] other systems have been reported that show less or no such correlation.[3] Recently one of us proposed[1] that there are five major factors by which a substituent can affect product ion abundance; we report here the first quantitative study in which one of these factors can be observed independently. The factor studied, the effect of product ion stability, has previously been postulated to be a major driving force in mass spectral reactions, but only qualitative correlative evidence has been available to support this postulate.[4]

The abundant C₇H₇⁺ and YC₇H₆⁺ ions in the spectra of substituted bibenzyls, YC₆H₄CH₂CH₂C₆H₅, were chosen for study because of the continuing interest in the possibility of tropylium *vs.* benzyl structures for such ions.[5] In a recent independent study Brown[6] presents persuasive substituent-effect evidence that YC₇H₆⁺ ions from YC₆H₄CH₂OC₆H₅ have the benzyl structure, despite evidence for the tropylium structure in both decomposing[5,7] and minimum-energy[8] YC₇H₆⁺ ions. As Brown recognized,[6] a less probable explanation for his evidence involves the effect of substituents on the molecular ion energies. Evidence from our system, in which this effect is eliminated, supports his conclusions fully.

To eliminate this substituent effect on the distribution of the internal energy values of the precursor ions[9] and the substituent effect on bond strength and competitive reactions ("factors 1, 3, and 4"[1]), the abundances of the substituted product ion YC₇H₆⁺ can be compared directly to that of the reference ion C₇H₇⁺ in each spectrum. Further decomposition of these ions ("factor 5"[1]) is made negligible by utilizing 15.3-eV ionizing electrons. The results, [YC₇H₆⁺]/[C₇H₇⁺], which should represent the ratio of the averaged rates of formation of these ions, are plotted *vs.* σ⁺ constants in Figure 1.

The observed variation of [YC₇H₆⁺]/[C₇H₇⁺] is >10⁶, exceeding the dynamic range of the instrument; ρ = −3.3, a much larger absolute value than any previously observed.[10] This provides dramatic quantitative support of the postulation that product ion stability is a major driving force for mass spectral reactions and that the structure of the transition state of this endothermic

(1) Part XII: F. W. McLafferty, submitted for publication.

(2) M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, 88, 529 (1966).

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(5) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 10, and references cited therein.

(6) P. Brown, *J. Am. Chem. Soc.*, 90, 2694 (1968).

(7) K. L. Rinehart, A. C. Buchholz, G. E. Van Lear, and H. L. Cantrill, *ibid.*, 90, 2983 (1968).

(8) J. M. S. Tait, T. W. Shannon, and A. G. Harrison, *ibid.*, 84, 4 (1962).

(9) To be distinguished from the distribution of the internal energy within a particular ion.

(10) The experimental values correlate with σ approximately as well, yielding ρ = −5.1.