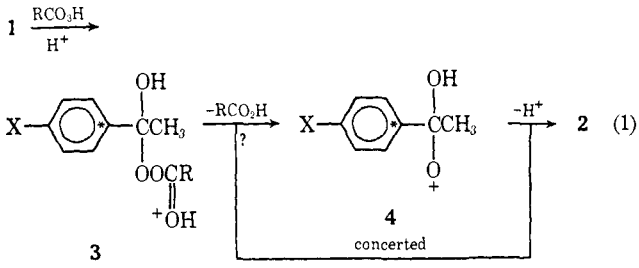
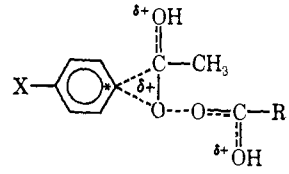
For each compound, isotope effect measurements were made at five fractions of reaction, ranging from 8 to 60%. The reaction mixtures were quenched with sodium hydroxide solution. For ^{14}C assay using a Beckman LS100 liquid scintillation counter,[8] the phenols resulting from basic hydrolysis of the recovered acetates were converted to benzoates and the recovered unreacted ketones were converted to oximes. The internal consistency of the isotope effect data is high, as evidenced by the relatively small errors, by the lack of any trend in k^{12}/k^{14} with fraction of reaction, and by the excellent agreement in the k^{12}/k^{14} values calculated separately from the decrease in radioactivity of product ester and the increase in radioactivity of the recovered ketone.

Most features of the mechanism of the peracid oxidation of ketones to esters are reasonably well understood.[12] For most, if not all, cases the reaction is first order in peracid and first order in ketone[11,13] and is general acid catalyzed.[11,14] The migrating group does so with retention of configuration,[15] and electron-donating substituents in the migrating group speed the reaction.[10,12] The ketone oxygen becomes the carbonyl oxygen of the ester.[16] Our version of the Criegee mechanism[17] may be applied to the present case as shown in eq 1.



The main question of timing is whether electron-deficient species **4** actually exists or whether **3** is converted to **2** (or its conjugate acid) by a concerted process. Although no previous research is definitive, most previous studies, especially that of Hawthorne and Emmons,[11] support a concerted reaction mechanism. The present isotope effect results lead unambiguously to the conclusion that the present reaction is concerted. No isotope effect would be expected for rate-determining formation of **3** or **4** since those steps do not involve significant alteration of the bonding at the labeled position.[18] Since a large isotope effect is found, neither formation of **3** nor its decomposition to **4** can be rate determining. On the other hand, in the rate-determining concerted conversion of **3** to **2**, bonding at the labeled position is extensively altered, and an isotope effect would be expected,[18] as is observed. (Of course the possibility exists that a different step might be rate determining for other compounds or conditions.) The activated complex (**5**) for this concerted reaction may be formulated as being similar to that suggested by Hawthorne and Emmons.[11]



5

The variation of isotope effect with substituent, which is far larger than the variations observed in any previous work, can be rationalized in terms of activated complex **5**. Increased bonding at a labeled position in an activated complex relative to reactants results in a decreased isotope effect; decreased bonding has the opposite effect.[18] In considering the bonding of the labeled ring carbon with the carbon at the migration origin and the oxygen at the migration terminus as the ring moves from one to the other, it is clear that different substituents will be able to satisfy the electron deficiency in the three-membered ring more or less readily. A good electron-donating group like methoxy will result in a high electron density in the three-membered ring, resulting in a "tight" activated complex with increased bonding between the ring carbon and the migration origin and terminus. This is equivalent to saying that the activated complex force constants at the labeled position are increased, and this results in a lowered isotope effect. An electron-withdrawing group will have the opposite effect, leading to a "loose" activated complex and a high isotope effect. This is exactly the trend observed experimentally. Because of the relative positions of the substituent, the labeled atom, and the electron-deficient center, a system such as the present one offers maximum opportunity for substituents to influence the isotope effect.

(12) Previous literature is very well reviewed by M. F. Hawthorne, W. D. Emmons, and K. S. McCallum, *J. Amer. Chem. Soc.*, **80**, 6393 (1958).
(13) Y. Yukawa and T. Yokoyama, *J. Chem. Soc. Jap.*, **73**, 371 (1952).
(14) W. E. Doering and L. Spears, *J. Amer. Chem. Soc.*, **72**, 5515 (1950).
(15) K. Mislow and J. Brenner, *ibid.*, **75**, 2319 (1953).
(16) W. E. Doering and E. Dorfman, *ibid.*, **75**, 5595 (1953).
(17) R. Criegee, *Justus Liebigs Ann. Chem.*, **560**, 127 (1948).
(18) For a qualitative review of the general concepts leading to this conclusion, and for leading references to the basic theory, see A. Fry, *Pure Appl. Chem.*, **8**, 409 (1964).

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Structure and Stereochemical Behavior of Asymmetric α-Sulfonyl Carbanions

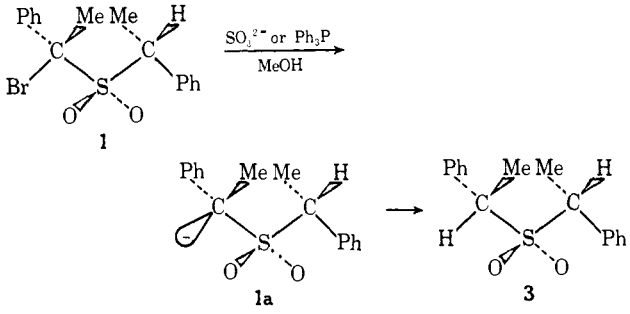
Sir:

Two monobromo diastereomers, mp 76° and 112°, have been obtained by bromination of either *dl*- or *meso*-bis-α-methylbenzyl sulfone with N-bromosuccinimide. Single-crystal X-ray analysis using counter data has shown that the higher melting isomer has the *erythro* configuration **1**, crystallizing in space group $P2_1/c$. All of the atoms were successfully located on a three-dimensional Fourier map phased by the bromine atom, and $R = 0.06$ for 1500 reflections above background.

Reduction of **1** with sodium sulfite or triphenylphosphine in methanol occurred in a highly stereoselective manner (90% or more) to give bis-α-methylbenzyl sulfone, mp 140°, which has been shown to be the *meso* isomer (**3**).[1] Similarly, *threo*-α-bromo-α-methylbenzyl

(1) C. Y. Meyers and A. M. Malte, *J. Amer. Chem. Soc.*, **91**, 2123 (1969).

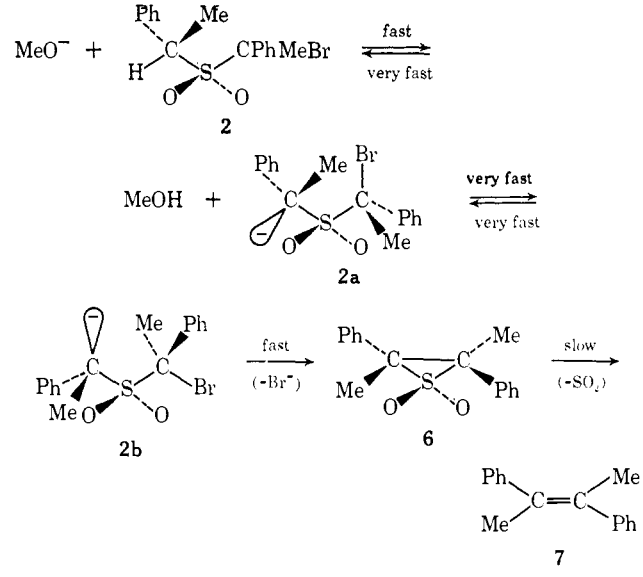
α-methylbenzyl sulfone (**2**), mp 76°, gave principally *dl*-bis-α-methylbenzyl sulfone on reduction. Retention of configuration in these reductions is consistent with a wealth of accumulated data which has shown that α-sulfonyl carbanions, such as **1a**, are asymmetric and are protonated with retention of configuration.[2,3]



A Ramberg–Bäcklund reaction of **1** with sodium methoxide in methanol gave 93% of *cis*-α,α′-dimethylstilbene (**5**) and 7% of the *trans* isomer (**7**). Reaction of **2** with sodium methoxide in methanol was also highly stereoselective, 5% of **5** and 95% of **7** being formed. Recovery of deuterated **1** (or **2**) from incomplete reactions carried out in methanol-O-*d* established the presence of carbanion intermediates. The ratio of exchange to epimerization occurring during these protonations was about 50:1, which agrees well with k_e/k_α ratios observed for optically active sulfones under these conditions.[2]

Spectrophotometric measurement of the rate of appearance of **5** from **1** showed the reaction to be first order in methoxide ion and first order in **1**. This rate was identical, within experimental error, with the titrimetric rate of release of bromide ion from **1** under these conditions ($k = 2.0 \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$ at 25°). Bromide-ion release from **2** occurred at a slightly faster rate ($2.5 \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$ at 25°), but the (spectrophotometric) appearance of **7** from **2** occurred at an appreciably slower rate and was *independent of the methoxide ion concentration*. The result is most simply interpreted as indicating the rapid formation, under base catalysis, of an intermediate which decomposes in a subsequent first-order rate-limiting step. It, therefore, constitutes kinetic evidence for the proposed formation of episulfone (thiirane 1,1-dioxide) intermediates in the Ramberg–Bäcklund reaction.[4] In this particular instance the overall reaction rate will be controlled by the first-order decomposition of *trans*-2,3-diphenyl-2,3-dimethylthiirane 1,1-dioxide (**6**).[5] It is noteworthy in this respect that the observed first-order rate for the conversion of **2** to **7** ($7.3 \times 10^{-4}\ \text{sec}^{-1}$ at 25° in methanol) is intermediate to the rates of decomposition of *cis*- and *trans*-2,3-diphenylthiirane 1,1-dioxides under these conditions (3.6×10^{-4} and $2.4 \times 10^{-2}\ \text{sec}^{-1}$, respectively[6]). This is the first example of a Ramberg–Bäcklund reaction in which decomposition of the episulfone intermediate is rate limiting; in the conversion of **1** to **5**, and in other examples where mechanistic details are known,[7] loss of halide ion is rate limiting.

For reasons stated earlier[8] we have accepted the view of Corey and Lowry[9] that asymmetric α-sulfonyl carbanions are formed by preferential removal of the proton from a conformation wherein this proton is flanked by the two oxygen atoms of the sulfonyl group. Applied to **2** this view leads to the prediction that the carbanion will have its lone pair directed along the bisector of the OSO angle, as in **2a**. It is further postulated, as indicated in the equations, that both inversion of the carbanionic center and rotation around the S–CPhMeBr bond occur rapidly; asymmetry is maintained because rotation is restricted around the bond between the sulfur atom and the carbanionic center.[10] Loss of bromide ion is believed to occur from conformation **2b** which allows an intramolecular displacement with inversion at the C–Br center.



The overall conversion of **2** to **6** involves *inversion at each asymmetric carbon atom*.[12] This double inversion

(2) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter III.

(3) The conformation shown for **1** is that present in the crystal.

(4) F. G. Bordwell and G. D. Cooper, *J. Amer. Chem. Soc.*, 73, 5187 (1951). For recent surveys of the Ramberg–Bäcklund reaction see F. G. Bordwell, "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience Publishers, New York, N. Y., 1967, Chapter 16; L. A. Paquette, *Accounts Chem. Res.*, 1, 209 (1968); L. A. Paquette, "Mechanisms of Molecular Migrations," Vol. 1, B. S. Thyagarajan, Ed., Interscience Publishers, New York, N. Y., 1968, pp 121–156.

(5) The failure of methoxide ion to accelerate the decomposition of **6** is contrary to the report that the rate of decomposition of *trans*-2,3-diphenylthiirane 1,1-dioxide is accelerated by methoxide ion:[6] re-examination of the data indicates that the acceleration observed earlier is probably too small to be significant.

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

(7) F. G. Bordwell and J. M. Williams, Jr., *ibid.*, 90, 435 (1968).

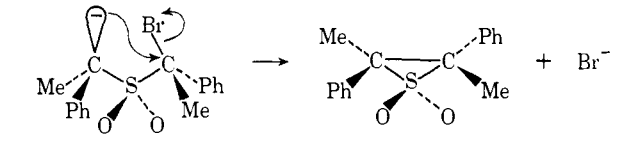
(8) F. G. Bordwell, D. D. Phillips, and J. M. Williams, Jr., *ibid.*, 90, 426 (1968).

(9) E. J. Corey and T. H. Lowry, *Tetrahedron Lett.*, 803 (1965).

(10) Recent calculations by S. Wolfe, A. Rauk, and I. G. Csizmadia (*J. Amer. Chem. Soc.*, 91, 1567 (1969)) indicate that α-sulfonyl carbanions are pyramidal and that the more stable configuration is that with the lone pair directed along the bisector of the OSO angle. Our hypothesis disagrees with these calculations only in that we visualize a low barrier to inversion. The observation that replacement of the Hex group in *n*-HexC*HCH$_3$SO$_2$R by phenyl causes but little change in the k_e/k_α ratio,[8,9] despite an eight-unit lowering of pK_a,[8] supports the postulate of a low barrier to inversion, particularly in view of the demonstration that a phenyl substituent on nitrogen markedly decreases the barrier to inversion in aziridines.[11]

(11) A. T. Bottini and J. D. Roberts, *ibid.*, 80, 5203 (1958).

(12) The conversion of **1** to **5** also involves double inversion. A double retention mechanism, *e.g.*



mechanism is further supported by a similar result in an analogous system,[13] and by the demonstration that the Ramberg–Bäcklund reaction is successful with 1-bromo- or 1-chloro-8-thiabicyclo[3.2.1]octane,[14,15] where a double inversion mechanism is possible but a double retention mechanism is excluded for steric reasons.

Acknowledgment. This work was supported by the National Science Foundation (GP 7065 and GP 8534).

is not excluded by the data but seems highly unlikely for reasons given earlier.[13]

(13) F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, 90, 5298 (1968).

(14) E. J. Corey and E. Block, *J. Org. Chem.*, 34, 1233 (1969).

(15) L. A. Paquette and R. W. Houser, *J. Amer. Chem. Soc.*, 91, 3870 (1969).

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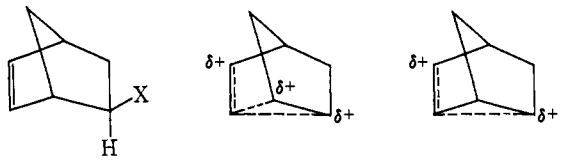
Temperature Effects in the Acetolysis of *exo*-Dehydro-2-norbornyl Brosylate[1]

Sir:

In 1955, Roberts and coworkers[2] reported that from the acetolysis of *exo*-dehydro-2-norbornyl-2,3-$^{14}C_2$ brosylate (I-2,3-^{14}C-OBs), there was a 38% rearrangement of the isotopic label from C-2,3 to C-1,4–7 in the resulting *exo*-dehydro-2-norbornyl acetate (I-x-^{14}C-OAc) (the major product was nortricyclyl acetate). Since the intervention of a symmetrical intermediate such as II would give rise to 50% rearrangement, it was proposed that the unsymmetrical homoallylic cation III was formed first, and that some of this ion was trapped by solvent before it isomerized to its enantiomer IV, or to the symmetrical ion II. However, Cristol and coworkers[3]



I-X II III

IV

have recently found that the acetolysis of *exo*-dehydro-2-norbornyl-3-*exo*-*d* brosylate (I-3-*d*-OBs) gave a product I-x-*d*-OAc, the mass spectral analysis of which indicated an essentially 50% rearrangement of the D label from C-3 to C-7. It was suggested that this isotopic distribution was the result of the involvement of symmetrical ion II or rapidly equilibrating ions III and IV. It has also been stated in a literature survey[4] that the unsymmetrical distribution of the label reported by Roberts and coworkers[2] "appears to be definitely incorrect." In an attempt to clarify the apparent discrepancy between the results obtained from I-2,3-^{14}C-OBs and I-3-*d*-OBs, we have studied the acetolysis of *exo*-dehydro-2-norbornyl-2-*d* brosylate (I-2-*d*-OBs), and analyzed the unsaturated product, I-x-*d*-OAc, by nmr and by mass spectrometry using Cristol's method.[5]

I-2-*d*-OBs was prepared in a manner analogous to the preparation of *exo*-2-norbornyl-2-*d* brosylate.[6] Dehydronorcamphor was reduced with $LiAlD_4$ to give a 9:1 mixture of *endo*:*exo* dehydro-2-norborneol-2-*d* and then converted to the mixed brosylates. Selective solvolysis in aqueous acetone removed the *exo* isomer, and treatment of the pure *endo*-brosylate with $(CH_3)_4N^+OAc^-$ in dry acetone gave I-2-*d*-OAc, which was reduced with $LiAlH_4$ and then converted to the desired I-2-*d*-OBs.

Initially, the acetolysis was carried out with 0.48 *M* I-2-*d*-OBs in the presence of 10% excess KOAc at 45° for 1 hr (Roberts' conditions) or with 0.24 *M* I-2-*d*-OBs in the presence of a tenfold excess of NaOAc at 24° for 11 hr (similar to one set of Cristol's conditions, with the exception that Cristol used a less concentrated solution of the brosylate). The I-x-*d*-OAc produced was separated from the nortricyclyl acetate by preparative vpc (25% Carbowax 20 M on Chromosorb P at 150°). Mass spectral analysis of the I-x-*d*-OAc based on the formation of the cyclopentadiene cation as described by Cristol and coworkers[5] gave the per cent rearrangement of the D label from C-2,3 to C-1,4–7. Similarly, from the nmr spectrum of the I-x-*d*-OAc, the H absorption at C-2 gave another measure of the extent of rearrangement of the D label from C-2 to the rest of the carbon positions. The results, given in Table I, show that the previously reported data of Roberts[2] and Cristol[3] were both substantially correct.

The different extents of isotopic scrambling observed by Roberts and by Cristol, and confirmed by the present work, apparently must be due to some difference in experimental conditions. The experiments reported by Cristol[3] included some variations in brosylate concentration, amount of NaOAc added, and reaction time, and all these experiments gave about 50% rearrangement. However, Cristol's data were obtained from reactions at 24° (except for one experiment at 28°), while Roberts used a reaction temperature of 45°. This temperature difference thus appeared to be a probable factor in determining the difference in the per cent rearrangements observed. In order to confirm that the reaction temperature does influence the extent of isotopic scrambling, the acetolysis of I-2-*d*-OBs was also carried out at 65 and 14° (the lowest practical temperature without freezing the reaction mixture). The results are included in Table I.

From the changes in appearance of the C-2 absorption in the nmr spectra of samples of brosylate recovered after partial acetolysis of I-3-*d*-OBs, Cristol[3] concluded that there was internal return from ion pairs to

(1) Supported by a grant from the National Research Council of Canada.

(2) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, 77, 3034 (1955).

(3) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *ibid.*, 88, 3087 (1966).

(4) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms, 1966," Interscience Publishers, New York, N. Y., 1967, p 25.

(5) S. J. Cristol, R. A. Sanchez, and T. C. Morrill, *J. Org. Chem.*, 31, 2738 (1966).

(6) C. C. Lee and E. W. C. Wong, *J. Amer. Chem. Soc.*, 86, 2752 (1964).