azine ring is bulkier than the β side and, therefore, in a preferred conformation the α side of the diketopiperazine will stay as far as possible from the bulky indole part.

By the usual method, the alcohol **12a** was converted to the acetate **13a**[3a,11] [95% with acetic anhydride and pyridine; mp 176–178°; $\delta_{\text{ppm}}^{\text{CDCl}_3}$ 1.89 (3 H, s), 2.08 (3 H, s), 3.24 (3 H, s), 3.77 (3 H, s), 3.90 (3 H, s), 3.94 (3 H, s), and 4.00 (3 H, s)] which was oxidized with iodosobenzene diacetate in acetonitrile containing dimethyl sulfide, to afford the cyclized diacetate **14a**[3b,11] [amorphous solid; M^+ (found) 677.1288 and 679.1266, (cald) 677.1268 and 679.1239; $\delta_{\text{ppm}}^{\text{CDCl}_3}$ (1.2 mg in 0.3 ml) 1.63 (3 H, s), 1.95 (3 H, s), 2.01 (3 H, s), 3.02 (3 H, s), 3.51 (3 H, s), 3.80 (3 H, s), 3.86 (3 H, s), 3.87 (3 H, s)][12] in 30% yield.[11,13] The two new asymmetric centers introduced in this step are expected to be desired ones for the steric reasons.

The synthetic diacetate **14a** was identified by comparison of spectroscopic data (nmr, ir, uv, and mass spectral)[12] as well as tlc behavior with the authentic diacetate **14a**, which was prepared from natural sporidesmin A (**1**)[14] in three steps: sodium borohydride reduction in methanol, anisaldehyde treatment in methylene chloride containing boron trifluoride etherate, and acetylation with acetic anhydride and pyridine.[15]

The authentic diacetate **14a** was successfully converted back to sporidesmin A (**1**) in 25% overall yield in three steps: sodium hydroxide in aqueous methanol at room temperature, *m*-chloroperbenzoic acid in methylene chloride at room temperature, and boron trifluoride etherate in methylene chloride at room temperature. Therefore, the synthesis of the diacetate **14a** formally constitutes the completion of a total synthesis of sporidesmin A (**1**).

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[12] We thank Drs. Dudek and Balaram, Harvard University, for the measurement of the exact mass spectrum and the FT-nmr spectrum.

[13] The same type of reaction takes place with **12** and **13** by NBS-oxidation in methylene chloride to yield the cyclized compound bearing a bromine in place of the tertiary acetoxy group in **14**.

[14] We are indebted to Dr. Safe, National Research Council of Canada, Halifax, and Dr. E. P. White, Ruakura Animal Research Station, New Zealand, for their generous gifts of natural sporidesmin A.

[15] By preparative tlc (silica gel), the diastereomers **14a** (amorphous solid) and **14b** [amorphous solid: $\delta_{\text{ppm}}^{\text{CDCl}_3}$ (1 mg in 0.3 ml) 1.62 (3 H, s), 1.93 (3 H, s), 2.06 (3 H, s), 3.15 (3 H, s), 3.45 (3 H, s), 3.80 (3 H, s), and 3.85 (6 H, s)] were separated at this stage. The diastereomer **14b** corresponds to the (**11b** → **12b** → **13b** → **14b**) series (see ref 11).

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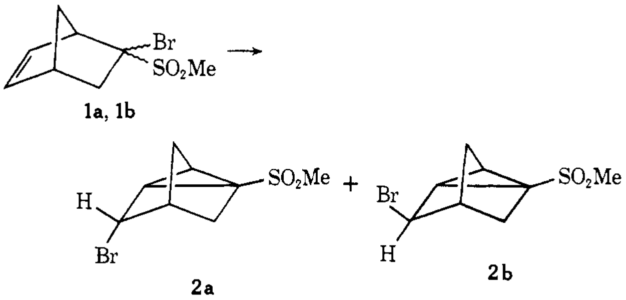
Free Radicals from α-Bromo Sulfones

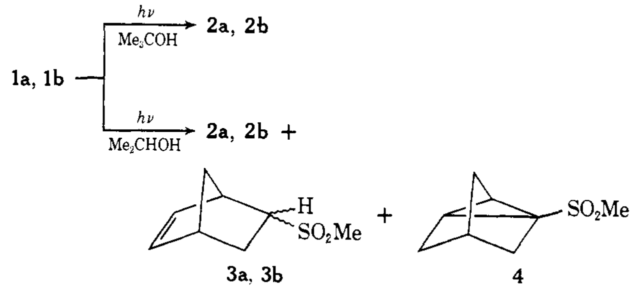
Sir:

Recently we reported evidence for the unprecedented formation of free-radical intermediates in competition with the normal Ramberg–Bäcklund rearrangement of bromo sulfones **1a**, **1b**.[1] The formation of **2a** and **2b**[2]



was observed in an aqueous sodium hydroxide medium, or more conveniently **1a** or **1b** could be rearranged to **2a**, **2b** by the action of free-radical initiators, *e.g.*, benzoyl peroxide or potassium persulfate in the absence of base.[1] In this communication we wish to describe the photochemistry of **1** and **2** and to comment on the mechanistic aspects and the generality of this free-radical chemistry.

Direct irradiation of **1a** or **1b** in *tert*-butyl alcohol with 2537-Å light for 3 hr afforded a **2a**, **2b** mixture of identical composition to that resulting from treatment of **1a**, **1b** with aqueous sodium hydroxide or with potassium persulfate in 50% aqueous *tert*-butyl alcohol or with benzoyl peroxide in benzene. In all of the above reactions the **2a**:**2b** ratio was 57:43. The same photochemical reaction in pure isopropyl alcohol, a hydrogen atom donor solvent, afforded **3a**, **3b**[3] and **4** in addition to **2a** and **2b**. These same three bromine-free sulfones were obtained in addition to **2a**, **2b** in the reactions induced by persulfate[1] and hydroxide ions in aqueous isopropyl alcohol. A careful tlc and nmr analysis of incomplete transformations revealed no interconversion of **1a** and **1b** in any of the above reactions.



The formation of nortricyclane sulfone **4** as a major product of the reaction in aqueous isopropyl alcohol prompted us to investigate the photochemistry of **2a** and **2b** with the intention, among other things, of producing a cleaner, synthetically useful preparation of **4**. Irradiation of either **2a** or **2b** in pure *tert*-butyl alcohol produced the same **2a**, **2b** mixture observed in previous reactions. While this photochemical epimerization demonstrates the lability of the carbon–bromine bond in **2a** and **2b**, the presence of norbornenyl bromo sulfones **1a** or **1b** could not be detected. Irradiation of **2a**, **2b** in 10% aqueous isopropyl alcohol containing 1 equiv of sodium carbonate afforded a 92% yield of

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[1] J. C. Philips and M. Oku, *J. Amer. Chem. Soc.*, **94**, 1012 (1972).

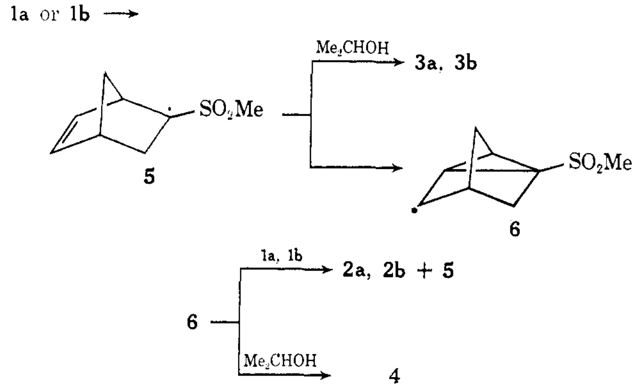
[2] Independent syntheses confirming the gross structures and stereochemistry of **2a** and **2b** will be reported in the full paper.

[3] J. C. Philips and M. Oku, *J. Org. Chem.*, **37**, 4479 (1972).

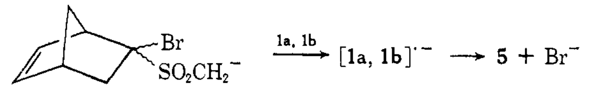
nortricyclane sulfone **4**, again with the absence of detectable amounts of the corresponding norbornenyl sulfones **3a** and **3b**. Both **2a** and **2b** are inert to the persulfate, peroxide, and aqueous hydroxide conditions and are epimerized photochemically at a much slower rate than they are formed from **1a** or **1b**.

The formation of the identical mixture of **2a**, **2b** from either **1a** or **1b** under persulfate, peroxide, photochemical, or aqueous hydroxide ion conditions, or *via* the photochemical epimerization of either pure **2a** or **2b**, argues for a common intermediate. In Scheme I a free-radical mechanism is outlined that satisfies all the data at hand. The intermediacy of **5** and **6** in these reactions is demonstrated by the reduction observed in isopropyl alcohol and the absence of this process in *tert*-butyl alcohol. Further substantiation of this hypothesis is provided by the inhibiting effect of iodine in the hydroxide[1] and the persulfate reactions. The fact that only 10 mol % of peroxide or persulfate is necessary for an essentially complete conversion of **1a**, **1b** to **2a**, **2b** supports the contention of a radical chain process in which the reaction of **6** with **1a**, **1b** serves as a propagation step. The ultimate products of these reactions are derived primarily from radical **6**. No **1a**, **1b** is observed in the photochemical generation of **6** from **2a** or **2b** in *tert*-butyl alcohol, nor is **3a**, **3b** observed in the analogous photochemical reaction in isopropyl alcohol. However, radical generation from **1a**, **1b** in isopropyl alcohol always affords **3a**, **3b** and **4** with **4** as the major product. The heavy preponderance of nortricyclic products derived from **6** is a common observation in similar homoallyl–cyclopropylcarbinyl systems and may reflect the position of the equilibrium between **5** and **6** or the relative rates of chain transfer of **5** and **6** or a combination of these factors.[4]

Scheme I



One puzzling aspect of this chemistry is the ready formation of **2a**, **2b** from **1a**, **1b** by the action of aqueous sodium hydroxide solution. Our early speculation concerning this nonthermal initiation process involved the hydroxide ion only as a source of carbanion **7**,



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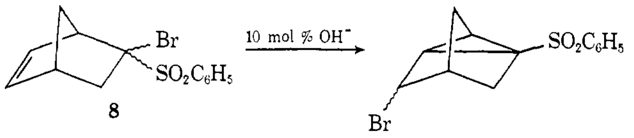
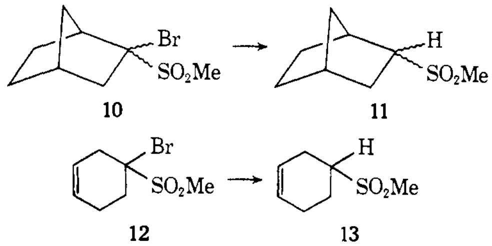
which was thought to serve as an electron transfer agent[5] ultimately leading to radical **5**. That this is not the case is demonstrated by the ready rearrangement of **8**[6] to **9**[6] even though **8** cannot form a carbanion analogous to **7**. Thus, this difficult question remains unanswered. As suggested by a referee, it is possible that a homoallylic anion, generated by nucleophilic attack on bromine,[7] may serve as an electron transfer agent initiating the radical chain reaction.



8 **9**

Finally, it is important to point out that this type of free-radical generation from α-bromo sulfones does not depend on the presence of a homoallylically situated double bond, nor is it restricted to norbornenyl derivatives. When bromo sulfones **10**,[6] the dihydro isomers of **1a**, **1b**, were treated with potassium persulfate in refluxing 50% aqueous isopropyl alcohol, or when they were simply irradiated in isopropyl alcohol, clean reduction to the corresponding bromine-free sulfones **11** was observed with the major isomer resulting from exo hydrogen capture, as expected.[8] Similarly, treatment of 4-bromo-4-methylsulfonylcyclohexene (**12**)[6] with potassium persulfate in aqueous isopropyl alcohol generated the corresponding reduction product **13**[6] but none of the bicyclo[3.1.0] system. The absence of cyclopropylcarbinyl compounds here is analogous to what is observed in the photoinitiated tri-*n*-butyltin hydride reduction of 4-chlorocyclohexene.[9]



We hope to report on the sensitized photochemistry in these and related systems where cation generation is possible[10] at a later date.

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(4) D. I. Davies, J. N. Done, and D. H. Hey, *Chem. Commun.*, 725 (1966), and references cited therein.

(5) For examples of electron transfer processes to halogenated substances see (a) D. G. Korzan, F. Chen, and C. Ainsworth, *Chem. Commun.*, 1053 (1971); (b) J. F. Garst, J. T. Barbas, and F. E. Barton, II, *J. Amer. Chem. Soc.*, **90**, 7159 (1968); (c) G. D. Sargent and G. A. Lux, *ibid.*, **90**, 7160 (1968); (d) N. Kornblum, *Proc. XXIIIrd Int. Congr. Pure Appl. Chem.*, 4, 81 (1971), and references cited therein.

(6) New compounds cited gave acceptable ($\pm 0.3\%$) combustion analyses.

(7) See F. G. Bordwell and B. B. Jarvis, *J. Amer. Chem. Soc.*, **95**, 3585 (1973); F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, *ibid.*, **90**, 5298 (1968) for precedent.

(8) P. D. Bartlett, G. N. Fickes, F. C. Haupt, and R. Helgeson, *Accounts Chem. Res.*, 3, 177 (1970).

(9) E. C. Friedrich and R. L. Holmstead, *J. Org. Chem.*, 37, 2550 (1972). See also L. H. Slaugh, *J. Amer. Chem. Soc.*, **87**, 1522 (1965).

(10) S. J. Cristol and G. C. Schloemer, *J. Amer. Chem. Soc.*, **94**, 5916 (1972), and references cited therein.