The structure of **1**, which included the absolute stereochemistry at 11 chiral centers, was obtained by X-ray crystallographic methods (Figure 1).[8] The rearranged structure and the presence of the 2-ketobicyclo[3.1.0]hexane fragment suggested that **1** may have been photochemically produced from a cyclohexenone precursor. To pursue this notion, the remaining metabolites of *E. caribaeorum* were examined. Erythrolide B (**2**), another major metabolite, was readily recognized[6] to possess a cyclohexenone group and thus to be a potential precursor of **1**. Irradiation of **2** under a variety of conditions[9] yielded **1** as the sole product. Working backward from the secure structure of **1** to assign the structure of **2** showed that the photochemical interconversion did *not* involve a typical cyclohexenone rearrangement but was instead consistent with a di-π-methane rearrangement.[10]

The possibility that erythranes **1** and **2** were artifacts of isolation was explored. Samples of fresh *E. caribaeorum* were extracted immediately following their collection from several habitats and locales. TLC analysis of the extract consistently showed **1** and **2** as the major components. While we cannot completely rule out the possibility that the conversion of **2** to **1** is an enzyme-mediated process, the measured half-life for the sunlight-induced conversion[9] is consistent with a slow photochemical process occurring within the illuminated tissues of *E. caribaeorum*.[12]

Acknowledgment. This report is contribution No. 129 of the IMSWE (Inshore Marine Shallow Water Ecosystem) Reef and Mangrove Investigation in Carrie Bow Cay, Belize. The IMSWE program is sponsored by the Smithsonian Institution and supported, in part, by the Exxon Corp. We thank Dr. Klaus Reutzler, program director, for the kind invitation to participate. Mass spectra were kindly provided by the Mass Spectrometry Resource Center, School of Pharmacy, University of California, San Francisco (A. L. Burlingame, Director) which is supported by NIH Grant RR00719. Support for this research at the Scripps Institution was kindly provided by the National Science Foundation, Chemistry Division, under Grant CHE81-11907. Research at Cornell University was supported by the NIH both through a training grant to D.V.E. and through Grant CA24487 to J.C. and by the New York State Sea Grant Program. We wish to thank Dr. Frederick M. Bayer at the Smithsonian Institution for his identification of *E. caribaeorum*.

Registry No. 1, 89999-14-4; **2**, 89999-15-5; **3**, 89999-16-6.

Supplementary Material Available: Description of the X-ray diffraction determination of **1**, tables of fractional coordinates, thermal parameters, bond distances, bond angles, and observed and calculated structure factors, and spectral data for **1** and **2** (20 pages). Ordering information is given on any current masthead page.

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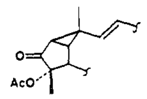
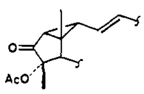
[8] We suggest the name "erythrane" and the numbering shown in **1** for this new rearranged diterpenoid skeleton. Experimental details and results of the X-ray diffraction experiment have been deposited as supplementary material.

[9] Irradiation of **2** in benzene (quartz) using a medium-pressure Hg lamp yielded **1** (87% conversion in 3 h). Irradiation of **2** in 5% methanolic seawater (glass) with sunlight yielded **1** (37% conversion in 8 days).

[10] A typical cyclohexenone photorearrangement of **2**, i.e., C-2 to C-4 and C-3 to C-5 bonding (cyclohexenone numbering), would be expected to yield partial structure i. The conversion of **2** to partial structure ii indicates the



i



ii

participation of the C-2–C-3 olefinic bond in a di-π-methane rearrangement with the C-13, C-14 olefin.[11]

[11] The di-π-methane rearrangement is also classified as a photochemically allowed ${}_{\sigma}2_a + {}_{\pi}2_a$ cycloaddition reaction: see: Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie GmbH, Academic Press: NewYork, 1970.

[12] Most octocorals found in the Caribbean Sea contain symbiotic algae known as "zooxanthellae", which, through photosynthesis and carbon transfer, provide a large portion of the nutrient requirements of the octocoral. Hence, for proper nutrition and growth the octocorals must occupy habitats exposed to sunlight.

Evidence for a Single Transition State in the Intermolecular Transfer of a Sulfonyl Group between Oxyanion Donor and Acceptors[1]

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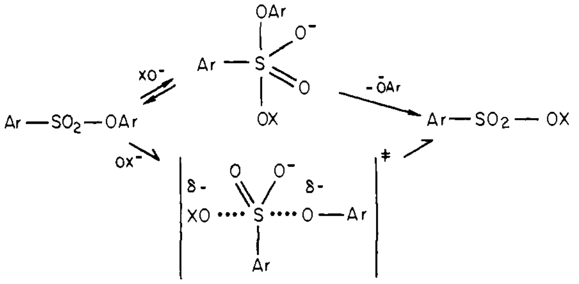
We describe a linear Brønsted-type relationship for the transfer of a sulfonyl group to a series of oxyanions with basicities both smaller and larger than the donor 4-nitrophenolate group. This evidence is consistent with a mechanism with only one transition state which must therefore be concerted.

Displacement reactions of oxyanions with a sulfonate ester yield a symmetrical reaction when the difference between donor and acceptor basicities (ΔpK) is zero. If a stepwise mechanism (eq 1) is followed, a change in rate-limiting step should occur as the acceptor becomes more or less basic than the leaving 4-nitrophenolate ion. A nonlinear Brønsted relationship with a break at $\Delta pK = 0$ is thus expected for the stepwise mechanism which has two electronically distinct transition states. A concerted process, with a single transition state, will give a linear or gently curving Brønsted correlation. Whereas we can predict the breakpoint in the present reaction for the stepwise process, this is not possible for previous studies of sulfonyl group transfer.[2a-d] Recent work where the breakpoint pK can be predicted and is spanned by the pK's of a range of similar nucleophiles is that on the related but completely distinct phosphoryl ($-PO_3^{2-}$)[2e,f] and sulfate ($-SO_3^-$)[2g] group-transfer reactions.



(1)

The reactivity of oxyanions with 4′-nitrophenyl 4-nitrobenzenesulfonate obeys the equation $\log k_{XO^-}/q = (0.64 \pm 0.11)(pK_{XOH} + \log (p/q)) - (7.8 \pm 0.3)$ ($r = 0.986$). Acetate ion, succinate dianion, and hexafluoroisopropoxide ion are very close in reactivity to phenolate ions of similar pK, and it is therefore assumed that trifluoroethoxide ion, which fits the line, should also be included in the correlation. Ortho fluorine substituents are assumed to have similar steric requirements to hydrogen; increase in steric factors could only reduce the reactivity of the two fluorine-substituted phenols. In several diverse reactions, under conditions where only one transition state is involved throughout, carboxylate, phenolate, and alcoholate leaving groups fit a single linear free energy relationship.[3] It is usually unsafe to use a multiplicity of structural types in a linear free energy relationship but oxyanions excluding α-effect nucleophiles and sterically hindered species should be sufficiently well-behaved to reveal changes in transition-state structure caused by a change in rate-limiting step.

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[1] We are grateful to the S.E.R.C. and N.A.T.O. (RG 115.80) for support of this work.

[2] (a) Suttle, N. A.; Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1563. (b) Deacon, T.; Farrar, C. R.; Sikkel, B. J.; Williams, A. *J. Am. Chem. Soc.* **1978**, *100*, 2525. (c) Kice, J. L.; Legan, E. *Ibid.* **1973**, *95*, 3912. (d) Deacon, T.; Steltner, A.; Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1778. (e) Skoog, M. T.; Jencks, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 3356. (f) Bourne, N.; Williams, A.; *Ibid.* **1983**, *105*, 3357. (g) Hopkins, A. Bourne, N.; Williams, A. *Ibid.* **1983**, *105*, 3358.

[3] (a) Gerstein, J.; Jencks, W. P. *J. Am. Chem. Soc.* **1964**, *86*, 4655. (b) Jencks, W. P.; Gilchrist M. *Ibid.* **1964**, *86*, 4651. (c) Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1244. (d) Kirby, A. J.; Varvoglis, A. G. *J. Am. Chem. Soc.* **1967**, *89*, 415.

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J. Am. Chem. Soc. 1984, 106, 5028-5030

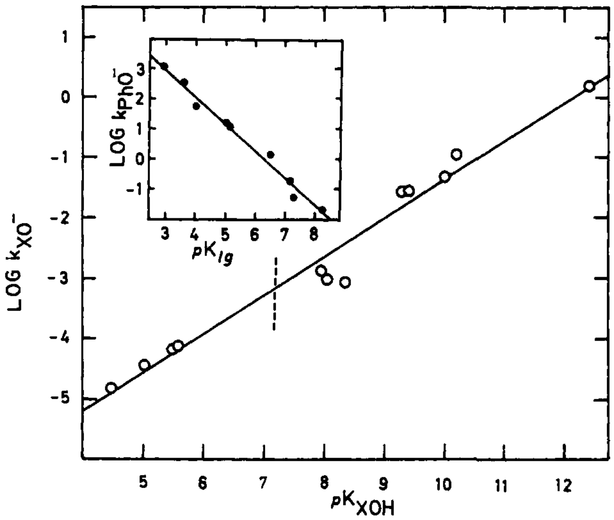

Figure 1. Reaction of oxyanions with 4-nitrophenyl 4-nitrobenzenesulfonate (○). Nucleophiles in increasing order of pK: acetate, succinate, dianion, pentafluorophenolate, 2,3,5,6-tetrafluorophenolate, 4-cyanophenolate, 4-acetylphenolate, 3,4,5-trichlorophenolate, hexafluoroisopropoxide, 4-chlorophenolate, phenolate, 4-methoxyphenolate, and trifluoroethoxide. Inset: Reaction of phenolate ion with substituted phenyl esters of 4-nitrobenzenesulfonic acid (●). Phenol leaving groups in ascending order of pK: 4-chloro-2,6-dinitro, 2,6-dinitro, 2,4-dinitro, 2,4-dichloro-6-nitro, 2,5-dinitro, 4-chloro-2-nitro, 4-nitro, 2-nitro, and 3-nitro. Conditions for the kinetics (units, M^{-1} s^{-1}): 50 °C, 10% dioxan and ionic strength made up to 0.5 M with KCl. The lines are calculated from the equations in the text and the dashed line indicates the expected breakpoint for the putative stepwise process.

The results indicate no substantial change in transition-state structure over the range of basicity represented by 8 pK units even when ΔpK's for phenols alone range well above and below zero. Since the reaction is symmetrical, the effective charge on oxygen in forming and cleaving bonds must be identical in the transition state. Reaction of phenolate ion with a series of aryl esters of 4-nitrobenzenesulfonic acid obeys a linear Brønsted-type relationship: log $k_{\text{PhO}^-} = (-0.91 \pm 0.09)\, \text{p}K_{\text{LG}} + (5.80 \pm 0.60)$ ($r = 0.991$). No evidence is seen of a steric effect of ortho substituents (see Figure 1). The β_{EQ} for the reaction is the sum of the two β values ($\beta_{\text{EQ}} = 1.6 \pm 0.2$) obtained in this work[4] since there is only one transition state. The change in effective charge on entering and leaving oxygen (respectively +0.64 and −0.91 in a total change of 1.6) is consistent with relatively weak S–O bonds.

Martin and co-workers[5] demonstrated that the apical S–O bond lengths in pentacoordinate analogues of the putative intermediate are substantially increased over the lengths in the tetrahedral structures. This does not agree with the observation of a single transition state, although we cannot exclude the possibility that a (very reactive) pentacoordinate intermediate is formed at a very shallow well at the apex of the potential energy maximum so that the two transition states would have closely similar electronic structures. Confirmation of the concerted mechanism is not yet possible by ^{17}O,^{18}O-stereochemical labeling, but it is established that the stereochemistry of sulfur is inverted during transfer of the sulfinate group.[6] The stereochemical probe is not, however, able to distinguish a very reactive intermediate from a concerted mechanism.

These results must not be taken to imply that *all* sulfonyl-transfer reactions are concerted. There is evidence that an intramolecular reaction could be stepwise.[7] It has now been conclusively established that the analogous phosphoryl transfer can be *either* concerted *or* stepwise.[8,9]

The reactions were followed by observing the increase in absorbance at 400 nm. Second-order rate constants were obtained from the slope of plots of values of k_{obsd} against the concentration of the nucleophile in the range 0–0.2 M; the increase in k_{obsd} was always substantially in excess of 100%, and the derived second-order rate constants were independent of added buffer. The reactions were demonstrated to involve nucleophilic attack by the oxyanion rather than general base catalyzed hydrolysis. An essentially theoretical yield of the phenyl ester was obtained when the 4-nitrophenyl ester was reacted in the presence of phenolate buffers. A negligible deuterium oxide solvent isotope effect was seen with acetate reacting with the 4-nitrophenyl ester ($k_{\text{AcO}}{}^{\text{H}_2\text{O}}/k_{\text{AcO}}{}^{\text{D}_2\text{O}} = 0.93$). Reaction of hindered reagents (2,2-diethylmalonate-dianion and 2,4,6-collidine) with the 4-nitrophenyl ester gave reactivities at least an order of magnitude below that calculated from the equation.

Registry No. 4-Nitrophenyl 4-nitrobenzenesulfonate, 30362-87-9; acetate, 71-50-1; succinate dianion, 56-14-1; pentafluorophenolate, 26910-95-2; 2,3,5,6-tetrafluorophenolate, 91178-72-2; 4-cyanophenolate, 14609-76-8; 4-acetylphenolate, 18983-84-1; 3,4,5-trichlorophenolate, 60154-34-9; hexafluoroisopropoxide, 44870-01-1; 4-chlorophenolate, 24573-38-4; phenolate, 3229-70-7; 4-methoxyphenolate, 29368-59-0; trifluoroethoxide, 24265-37-0; 4-chloro-2,6-dinitrophenol, 88-87-9; 2,6-dinitrophenol, 573-56-8; 2,4-dinitrophenol, 51-28-5; 2,4-dichloro-6-nitrophenol, 609-89-2; 2,5-dinitrophenol, 329-71-5; 4-chloro-2-nitrophenol, 89-64-5; 4-nitrophenol, 100-02-7; 2-nitrophenol, 88-75-5; 3-nitrophenol, 554-84-7.

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(4) This is close to a value obtained for a different sulfonyl-group-transfer equilibrium.[2b]

(5) (a) Perozzi, E. F.; Martin, J. C.; Paul, I. C. *J. Am. Chem. Soc.* **1974**, *96*, 6735. (b) Paul, I. C.; Martin, J. C.; Perozzi, E. F. *Ibid.* **1972**, *94*, 5010.

(6) Tillett, J. G. *Chem. Rev.* **1976**, *76*, 747.

(7) Graafland, T.; Wagenaar, A.; Kirby, A. J.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1979**, *101*, 6981.

(8) Buchwald, S. L.; Knowles, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1438.

(9) (a) Buchwald, S. L.; Pliura, D. H.; Knowles, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 845. (b) Westheimer, F. H. *Acc. Chem. Res.* **1968**, *1*, 70.

Carbon–Carbon Bond Formation by Induced Elimination from Unsymmetrically Substituted (Allyl)(allyl′)palladium Complexes

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We recently developed procedures to utilize (η^3-allylic)(η^1-alkenyl)palladium(II) intermediates in stereospecific coupling reactions in which C–C bond formation occurs by reductive elimination from diorganopalladium(II) intermediates;[1] comparable methodology could be envisaged to be applicable to the recurrent problem of allylic cross-coupling.[2] Indeed, we have now found it possible to specifically prepare *unsymmetrically* substituted (allyl)(allyl′)palladium(II) complexes and to induce reductive elimination to give high yields of 1,5-dienes in which "head-to-head" coupling predominates.

The preparation of (η^3-allylic)palladium(II) halide complexes from olefins is well documented,[3] as is the reaction between various metal salts and allylic metallic species.[4] Symmetrical bis(η^3-allyl)palladium(II) species have been prepared thusly.[5] Spon-

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(1) (a) Temple, J. S.; Riedeker, M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1310. (b) Hayasi, Y.; Riediker, M.; Temple, J. S.; Schwartz, J. *Tetrahedron Lett.* **1981**, 2629.

(2) (a) Katzenellenbogen, J. A., Lenox, R. S. *J. Org. Chem.* **1973**, *38*, 326. (b) Stork, G.; Grieco, P. A.; Gregson, M. *Tetrahedron Lett.* **1969**, 1393. (c) Axelrod, E. H.; Milne, G. M.; van Tamelen, E. E. *J. Am. Chem. Soc.* **1970**, *92*, 2139. (d) Biellmann, J. R.; Ducep, J. B. *Tetrahedron Lett.* **1969**, 3707. (e) Godschalx, J. P., Stille, J. K. *Ibid.* **1983**, 1905. (f) Corey, E. J.; Hegedus, L. S.; Semmelhack, M. F. *J. Am. Chem. Soc.* **1968**, *90*, 2416. (g) van Tamelen, E. E.; Åkermark, B.; Sharpless, K. B. *Ibid.* **1969**, *91*, 1552. (h) Yamada, Y.; Momose, D.; Iguchi, K.; Sugiyama, T. *Tetrahedron Lett.* **1983**, 921. (i) Trost, B. M.; Keinan, E. *Ibid.* **1980**, 2595. (j) Godschalx, J.; Stille, J. K. *Ibid.* **1980**, 2599.

(3) Trost, B. M. *Tetrahedron* **1977**, *33*, 2649 and reference cited therein.

(4) Wilke, G.; et al. *Angew Chem., Int. Ed. Engl.* **1966**, *5*, 151.

(5) Wilke, G.; et al. *J. Organomet. Chem.* **1980**, *191*, 425.

0002-7863/84/1506-5028$01.50/0