ethynyldimethylaluminum diethyl ether complex,[14] prepared as a 2 M solution in toluene, afforded a 65% isolated yield of a 1,2-diol, which was efficiently converted into the corresponding terminal epoxide **15** in a single reaction by initial treatment with *p*-toluenesulfonyl chloride followed by quenching with a methanolic solution of Triton B. Deprotonation of **15** at −78 °C resulted in a well-behaved acetylide, and condensations with **2** were extremely stereoselective, affording propargylic alcohol **16a** via an α-chelation-controlled addition (75:1 ratio). Hydrogenation to the Z-allylic alcohol and oxidation provided our key intermediate **17**. Although our epoxidation was nearly quantitative, the β-oxirane **17a** (57% isolated yield) was a result of the Henbest directive effects of a neighboring allylic β-alcohol at C_7 in spite of considerable steric factors, which also promoted formation of undesired α-epoxide.[15]

The three heterocyclic rings of breynolide were established from our acyclic precursor **17** as initiated by nucleophilic attack of sodium hydrogen sulfide. Initial opening of the terminal oxirane directed an intramolecular backside displacement at C_{17} with formation of the tetrahydrothiophene nucleus. Further treatment with *p*-toluenesulfonic acid spontaneously effected a kinetic spiroketalization, affording an 88% yield of 1,6-dioxaspiro[5.4]-ketals **18a** and **18b** in a 1:3 ratio.[16] Each spiro ether was independently converted to the natural product via a five-step sequence. Protection of the diols as their MEM ethers and subsequent desilation gave our penultimate precursor **19**, which upon Swern oxidation at −78 °C provoked an immediate intramolecular aldol upon addition of triethylamine at −78 °C with warming to −60 °C.[17] This led to a 90% isolated yield of a single keto alcohol **20** (R = MEM). Subsequent deprotection of **20** afforded a crystalline tetrol, (*C_6-epi*-breynolide), **20** (R = H), mp 218–221 °C (EtOAc). Our decoupling studies suggested that **20** was the undesired diastereomeric equatorial alcohol at C_6, as later confirmed by X-ray crystallography.[18] Finally, the total synthesis of **1** was completed by Mitsunobu inversion[19] with aqueous sodium formate in tetrahydrofuran at 0 °C (92%). Deprotection using aqueous hydrobromic acid (THF; room temperature; 72 h, 74%) slowly hydrolyzed each of the three MEM ethers, yielding fine white crystalline needles of (+)-breynolide, mp 241–243 °C (EtOAc), as confirmed by X-ray diffraction of our synthetic material.[20]

Acknowledgment. We thank the National Institutes of Health (AI17668), the National Science Foundation (CHE8618955), and the Indiana Affiliates of the American Heart Association for their financial support of this research.

Supplementary Material Available: IR, NMR, and HRMS data for key substances (9 pages). Ordering information is given on any current masthead page.

(14) For use of dialkylalkynylalanes: Fried, J.; Sih, J. C.; Lin, C. H.; Dalven, P. *J. Am. Chem. Soc.* **1972**, *94*, 4343. Murray, T. F.; Samsel, E. G.; Varma, V.; Norton, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 7520 and references therein.

(15) The Henbest oxidation often provides excellent hydrogen-bonded directivity for Z-allylic alcohols. Narula, A. S. *Tetrahedron Lett.* **1983**, *24*, 5421. Kishi, Y.; Hasan, I. *Ibid.* **1980**, *21*, 4229 and references therein. A detailed study of epoxidation reactions within the series of Z-allylic alcohols from **16ab** will be described in the full account.

(16) Prolonged acid treatment at warmer temperatures (0 °C) led to substantial decomposition of **18b**. The series of compounds bearing the unnatural C_9 spiroketal configuration is characteristically recognized by the chemical shift of its axial methyl (**18a**: δ = 1.02), whereas the natural diastereomer configurations display the methyl significantly upfield (**18b**: δ = 0.91).

(17) For previous studies of our intramolecular aldol condensations, see: Williams, D. R.; Klingler, F. D. *J. Org. Chem.* **1988**, *53*, 2134. Williams, D. R.; Klingler, F. D.; Dabral, V. *Tetrahedron Lett.* **1988**, *29*, 3415.

(18) Structure assignment of 6-*epi*-breynolide was unambiguously confirmed by a single-crystal X-ray diffraction study (at −155 °C). All atoms, including hydrogens, were located. Complete crystallographic data are available from the Indiana University Chemistry Library. Request Molecular Structure Center Report 89165. Spiroketal diastereomers at C_9 of **20** are isomerized to the natural configuration in the final deprotection with HBr.

(19) Mitsunobu, O. *Synthesis* **1981**, 1.

(20) We gratefully acknowledge Dr. Yoshio Abe, Bristol-Myers Research Institute, Tokyo, for his help in obtaining an authentic sample of breynin A for ^{1}H NMR comparisons. Structure assignment of our synthetic (+)-breynolide was unambiguously confirmed by a single-crystal X-ray diffraction (at −172 °C). All atoms, including hydrogens, were located, and diffraction data was directly compared with results for natural material. Complete crystallographic data are available from the Indiana University Chemistry Library. Request Molecular Structure Center Report 90070.

Characterization of the in Vitro Cyclization Chemistry of Calicheamicin and Its Relation to DNA Cleavage

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Received February 2, 1990

At dramatically low concentrations in the presence of thiols, calicheamicin γ_1^I (**1**)[1,2] shares with the esperamicins[3,4] and the neocarzinostatin chromophore[5] the ability to cause single- and, notably with the former, double-strand cleavages of DNA. The mechanism of DNA scission has been proposed[1] to involve four steps (Scheme I): (1) bioreductive cleavage (e.g., by reaction with glutathione in vivo) of the allylic methyl trisulfide of **1**, (2) β-addition of the resulting thiol to the enone to form dihydrothiophene **2**, (3) cyclization of **2** to generate a 1,4-diyl[6] **3** that, when bound in the minor groove of DNA,[2] is hypothesized to abstract a hydrogen from the deoxyribose backbone of each opposed strand to give carbon-centered radicals that, in turn, (4) scavenge dissolved oxygen to initiate a cascade of reactions leading ultimately to the observed cleavages. In this paper we present solution NMR studies that demonstrate for the first time the existence of intermediate **2** and provide an estimate of its lifetime at physiological temperature. These findings permit formulation of an overall kinetic scheme for the reaction of calicheamicin with DNA that frames specific questions about the relative importance of kinetic and thermodynamic factors in the sequence selectivity of its cleavages.

Variable-temperature NMR experiments were undertaken to examine the behavior of the proposed intermediates between **1** and **4**. Methyl thioglycolate (8 equiv, 14 mM) and triethylamine (5 equiv) were added to a methanol-d_4[7] solution of calicheamicin γ_1^I (1.6 mM) at −72 °C. Despite the deceptively simple pseudo-first-order disappearance of the methyl trisulfide resonance at δ 2.50 ($k_{obsd} = 2 \times 10^{-4}$ s^{-1}), the sulfur chemistry that occurred was obviously complex. The appearance of multiple signals for H-4, H-5, and H-8 indicated the presence of a variety of calicheamicin-derived species, while in the upfield region of the NMR spectrum, several methylthio-containing compounds were visible, which equilibrated to the methyl disulfide of methyl thioglycolate ($RSSCH_3$, δ 2.44).[8] This reaction manifold was monitored further

(1) Lee, M. D.; Dunne, T. S.; Siegel, M. M.; Chang, C. C.; Morton, G. O.; Borders, D. B. *J. Am. Chem. Soc.* **1987**, *109*, 3464–3466. Lee, M. D.; Dunne, T. S.; Chang, C. C.; Ellestad, G. A.; Siegel, M. M.; Morton, G. O.; McGahren, W. J.; Borders, D. B. *Ibid.* **1987**, *109*, 3466–3468.

(2) Zein, N.; Sinha, A. M.; McGahren, W. J.; Ellestad, G. A. *Science* **1988**, *240*, 1198–1201. Zein, N.; Poncin, M.; Nilakantan, R.; Ellestad, G. A. *Ibid.* **1989**, *244*, 697–699.

(3) Golik, J.; Clardy, J.; Dubay, G.; Groenwold, G.; Kawaguchi, H.; Konishi, M.; Krishnan, B.; Ohkuma, H.; Saitoh, K.-i.; Doyle, T. W. *J. Am. Chem. Soc.* **1987**, *109*, 3461–3462. Golik, J.; Dubay, G.; Groenwold, G.; Kawaguchi, H.; Konishi, M.; Krishnan, B.; Ohkuma, H.; Saitoh, K.-i.; Doyle, T. W. *Ibid.* **1987**, *109*, 3461–3462.

(4) Long, B. H.; Golik, J.; Forenza, S.; Ward, B.; Rehfuss, R.; Dabrowiak, J. C.; Cating, J. J.; Musial, S. T.; Brookshire, K. W.; Doyle, T. W. *Proc. Natl. Acad. Sci. U.S.A.* **1989**, *86*, 2–6. Sugiura, Y.; Uesawa, Y.; Takahashi, Y.; Kuwahara, J.; Golik, H.; Doyle, T. W. *Ibid.* **1989**, *86*, 7672–7676.

(5) Beerman, T. A.; Goldberg, I. H. *Biochem. Biophys. Res. Commun.* **1974**, *59*, 1254–1261. Hensens, O. D.; Dewey, R. S.; Liesch, J. M.; Napier, M. A.; Reamer, R. A.; Smith, J. L.; Albers-Schonberg, G.; Goldberg, I. H. *Ibid.* **1983**, *113*, 538–547. Myers, A. G.; Proteau, P. J.; Handel, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 7212–7214.

(6) Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25–31.

(7) Ellestad, G. A.; Hamann, P. R.; Zein, N.; Morton, G. O.; Siegel, M. M.; Pastel, M.; Borders, D. B.; McGahren, W. J. *Tetrahedron Lett.* **1989**, *30*, 3033–3036.

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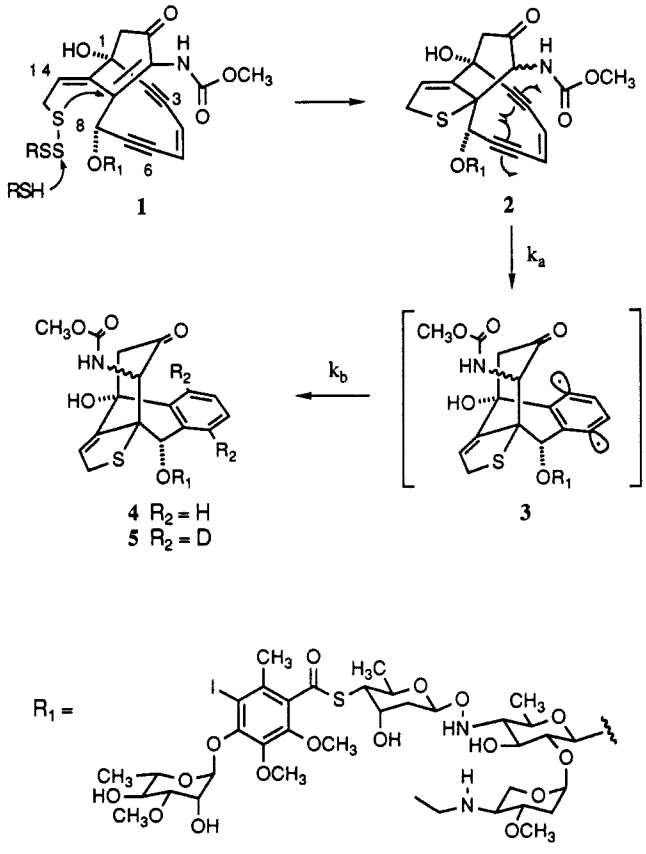
Scheme I

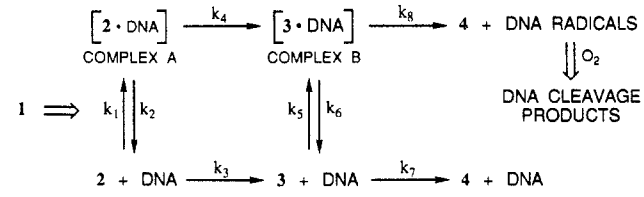


at −57 and −42 °C. Finally, at −10 °C there were indications that a discrete intermediate formed that underwent decomposition to **5** at a convenient rate. On the basis of subsequent experiments (vide infra), these resonances could be assigned to the dihydrothiophene **2**.

To obviate the complicated sulfur chemistry initiated by exposure to thiols, **1** was treated with tri-*n*-butylphosphine with the expectation[7,9] that the trisulfide would undergo preferential attack at the central sulfur atom. It was hoped that intramolecular β-addition of the resultant thiolate to produce **2** would compete successfully with disulfide formation. Indeed, when **1** (2.3 mM in methanol-d_4, −67 °C) was treated with *n*-Bu_3P (6 equiv), **2** was the *only* species identified in less than 10 min of reaction time. The structural assignment of **2** was based on several key changes in the NMR spectrum.[10] In particular, the resonance for H-8 in **1** (δ 6.27) moved to δ 5.35 in **2**, consistent with the loss of the adjacent double bond owing to thiolate addition to the enone system. This assignment was confirmed by homonuclear decoupling of the signal at 5.35 ppm, which removed the characteristic[11] long-range coupling to H-5 (^5J = 2.2 Hz).

The dihydrothiophene **2** was stable at −67 °C for several hours. Upon warming to −11 °C,[12] however, a smooth first-order conversion of **2** to **5** occurred. The resulting ϵ-component **5** was isolated in 70% yield and gave no detectable protium content at C-3 or C-6 by ^{1}H NMR spectroscopy, an outcome consistent with abstraction of solvent deuterium by the proposed 1,4-diyl **3**.[1] Therefore, making the reasonable assumptions that quenching of the diradical species **3** is both irreversible and significantly faster than its rate of formation from **2**, i.e., $k_a \ll k_b$ (Scheme I), then

Scheme II



$k_{obsd} = k_a$. The progress of the reaction could be conveniently followed by monitoring the disappearance of the resonances corresponding to H-14, H-4, and H-5 in **2** and their subsequent appearance in **5**. A first-order rate constant ($(5 \pm 2) \times 10^{-4}$ s^{-1}) could be determined over three half-lives from which a $\Delta G^{\ddagger}$ for the conversion of **2** to **3** could be estimated[13] as 19.3 ± 0.2 kcal/mol, a value quite similar to that calculated for the analogous rearrangement step of the neocarzinostatin chromophore.[14] This free energy of activation is approximately 4.5 kcal/mol lower than that measured by Nicolaou for a simple 10-membered cyclic enediyne,[15] suggesting that the presence of the five- and six-membered fused rings greatly accelerates the rate of this cyclization reaction.[16]

In a seminal observation made by Zein and Ellestad, hydrogen abstraction by **3** in the presence of DNA occurs largely, if not exclusively, from the deoxyribose backbone rather than from the medium.[17] To represent the competing potential fates of **1** more precisely, Scheme II is proposed. While at sufficiently low concentrations the bimolecular reaction of **1** and thiol could become rate-limiting overall in a kinetic description of DNA cleavage,[18] the long solution half-life of the dihydrothiophene **2** (4.5 ± 1.5 s, 37 °C)[19] makes the binding to and reaction with DNA of this intermediate (and **3**), rather than **1** itself,[18] the important events with respect to the critical sequence-selective[2] hydrogen abstraction step (k_8 in Scheme II). The preferential abstraction of hydrogen from DNA by **3** requires the net flux through complex B to compete successfully with the equilibrium defined by k_5/k_6 and the rapid trapping of **3** free in solution, i.e., k_7. The upper pathway depicted in Scheme II, therefore, is the kinetically significant one in the presence of DNA. It is of fundamental importance to consider whether the sequence-selective DNA cleavages caused by this drug are purely a manifestation of the thermodynamic binding of **2** to particular sequences of DNA and k_4 differs little from k_3, or, in the recognition of and binding to DNA, the activated drug **2** may track rapidly along the minor groove to specific sites whose helix conformations confer favorable steric and electronic environments to *accelerate* the rate of cyclization to **3**, i.e., k_4 is greater than k_3.[20] The relative importance of these potential kinetic effects versus the thermodynamic determinants

(8) The multiplicity of sulfur species was not unexpected: Evans, M. B.; Saville, B. *Proc. Chem. Soc.* **1962**, 18–19.

(9) Harpp, D. N.; Smith, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 6045–6051.

(10) Partial assignment for **2**: ^{1}H NMR (400 MHz, methanol-d_4) δ 6.43 (1 H, cm, H-14), 6.05 (1 H, AB quartet, J = 9.7 Hz, H-4), 5.99 (1 H, d × AB quartet, J = 9.7, 2.2 Hz, H-5), 5.35 (1 H, d, J = 2.2 Hz, H-8).

(11) Unpublished work at Lederle Laboratories characterizing **1**; see also: Kende, A. S.; Smith, C. A. *Tetrahedron Lett.* **1988**, *29*, 4217–4220 and footnotes 17 and 19.

(12) Methyl thioglycolate was added to serve as a deuterium source.

(13) The calculation was made by using the Eyring equation: Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987; p 209.

(14) Myers, A. G.; Proteau, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 1146–1147.

(15) Nicolaou, K. C.; Ogawa, Y.; Zuccarello, G.; Kataoka, H. *J. Am. Chem. Soc.* **1988**, *110*, 7247–7248.

(16) Some potential effects on $\Delta G^{\ddagger}$ have been discussed previously: Snyder, J. P. *J. Am. Chem. Soc.* **1989**, *111*, 7630–7632. Magnus, P.; Carter, P. A. *Ibid.* **1988**, *110*, 1626–1628.

(17) Zein, N.; McGahren, W. J.; Morton, G. O.; Ashcroft, J.; Ellestad, G. A. *J. Am. Chem. Soc.* **1989**, *111*, 6888–6890.

(18) It is an interesting possibility, however, that on binding of **1** to DNA, the amino sugar may assume a conformation favorable to thiol deprotonation in close proximity to the allylic methyl trisulfide and greatly enhance the rate of this bimolecular process and hence the formation of complex A (see footnote 10 in ref 7).

(19) The calculated lifetime is based on two assumptions. First, $\Delta G^{\ddagger}$ is taken to be approximately constant over the temperature range under consideration.[13] Second, the half-life of **2** in methanol would reasonably approximate that in water owing to the minimal charge development presumed in the transition state leading to the diyl **3** and the consequent insensitivity to solvent polarity in the rate of this cyclization process.

(20) For an excellent critical review of similar considerations in the binding and covalent interactions of small molecules with DNA, see: Warpehoski, M. A.; Hurley, L. H. *Chem. Res. Toxicol.* **1988**, *1*, 315–333. An analogous role in DNA recognition and cleavage may be played by the cumulene intermediate observed in the thiol activation of neocarzinostatin.[14]

of binding, and the extent to which the latter are associated with the carbohydrate side chain or the enediyne,[21] will emerge in further experiments.

Acknowledgment. We are pleased to acknowledge stimulating discussions over several years on the mechanism of calicheamicin action with Drs. G. A. Ellestad, D. B. Borders, and M. D. Lee (Lederle Laboratories). We are deeply grateful to Lever Brothers (J.J.H.) and The Royal Commission for The Exhibition of 1851 and the Dimitri V. d'Arbeloff Fund (J.J.DeV.) for fellowship support.

Supplementary Material Available: Partial ^1H NMR spectra for **2** and **5** and homonuclear decoupling of H-8 in **2** (1 page). Ordering information is given on any current masthead page.

(21) Experiments conducted with the esperamicin series suggest that while the various carbohydrate segments confer differing affinities to DNA, it is the enediyne portion that appears principally responsible for the sequence specificity of the DNA cleavages exhibited by this class of antibiotics.[4]

1-Cyano- and 2-Cyano-2-bicyclo[2.1.1]hexyl Cations

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Received January 11, 1990

Over the past decade, electron-deficient carbocations have been studied extensively.[1,2] Both α- and β-cyano-substituted cations form at greatly reduced rates relative to their H analogues. A β-cyano group is more rate retarding ($k_H/k_{\beta\text{-CN}} = 10^5$–$10^7$)[3,4] than an α-cyano group ($k_H/k_{\alpha\text{-CN}} = 10^3$–$10^4$).[4,5] Since α-cyano groups appear to be less cation destabilizing than would be expected on the basis of a purely inductive effect, resonance stabilization has been invoked (eq 1).[5-8] Partial nitrenium character is also indicated by the ^{13}C and ^{15}N NMR spectra of α-cyano carbocations (R = Ar).[9]

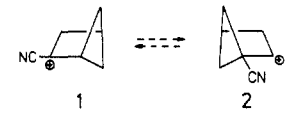
$$R_2C^+—C\equiv N \leftrightarrow R_2C=C=N^+ \qquad (1)$$

Product studies are less definitive. Many α-cyano substrates prefer elimination to substitution.[4,5] Others rearrange with predominant formation of β-cyano products,[3,10] derived from the allegedly less stable cations. In an effort to resolve these inconsistencies, and to adduce stereochemical evidence, we report here on the 2- and 1-cyano-2-bicyclo[2.1.1]hexyl cations (**1** and **2**). Our experience with the parent ion[11] suggested that elimination would not occur, and interconversion of **1** and **2** by Wagner-Meerwein rearrangement would directly attest to the relative stabilities. We find that the α-cyano cation **1** is *less* stable than the β-cyano cation **2**. The solvolysis rates of the triflates **3b** and **4b** do not reflect the relative stabilities of the cations, due to large counteracting ground-state effects.

Table I. Solvolysis Rate Constants of **3** and **4**

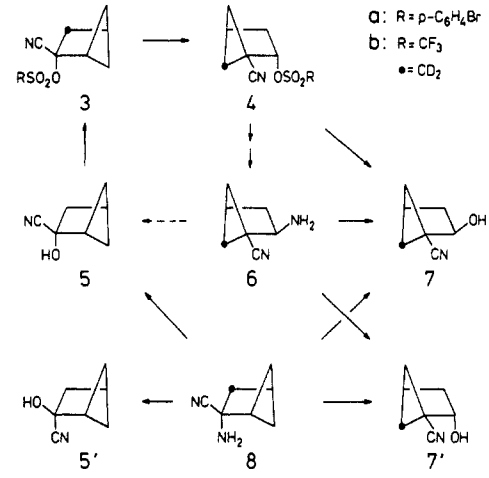
substrate, conditns	$k \times 10^4$ (s^{-1})	rel rates
2-bicyclo[2.1.1]hexyl brosylate, 80% EtOH, 75 °C[a]	73	$1.6 \cdot 10^3$
3a, 80% EtOH, 75 °C	0.048 ± 0.003	1
3b, 80% EtOH, 0 °C	3.2 ± 0.5	
3b, dioxane–H_2O (1:1), 0 °C	4.6 ± 0.7	2.6×10^2
4b, dioxane–H_2O (1:1), 29.9 °C	0.87 ± 0.01	
4b, dioxane–H_2O (1:1), 34.8 °C	1.66 ± 0.02	
4b, dioxane–H_2O (1:1), 41.9 °C	3.63 ± 0.05	
4b, dioxane–H_2O (1:1), 50.2 °C	8.91 ± 0.13	
4b, dioxane–H_2O (1:1), 0 °C[b]	0.018	1

[a] Bentley, T. W.; Goer, B.; Kirmse, W. *J. Org. Chem.* **1988**, *53*, 3066. The titrimetric rate constant is not corrected for internal return (62% in dioxane–H_2O[11]). [b] Extrapolated from other temperatures.



1 2

Bicyclo[2.1.1]hexan-2-one[12] was converted to the cyanohydrin **5** by standard procedures[13] (Me_3SiCN/ZnI_2 followed by 3 N HCl; 86%). Brosylation of the cyanohydrin (BsCl/Py, 0 → 20 °C, 6 days, 84%) afforded **3a**. In 80% EtOH at 75 °C, **3a** rearranged slowly to give 1-cyano-2-bicyclo[2.1.1]hexyl brosylate (**4a**), which proved to be extremely unreactive. Brosylate **3a**, containing 47% alkoxy-^{18}O, was rearranged to give **4a** with 36% alkoxy-^{18}O, i.e., with partial redistribution of ^{18}O to the sulfonyl group.[14] These data indicate that ionization of **3a** leads to tight ion pairs which recombine with exclusive formation of **4a**. The rate of the rearrangement, **3a** → **4a**, was found to be slower than the solvolysis rate of 2-bicyclo[2.1.1]hexyl brosylate by a factor of 2×10^3 (Table I), in good agreement with previous results for α-cyano sulfonates.[4,5]



3 4 5 6 7 5′ 8 7′

For a comparison of α- and β-cyano substrates, we prepared the triflate **3b** from the cyanohydrin (Tf_2O/Py, 0 °C, 2 h, 75%). Dilute solutions of **3b** in nonpolar solvents were stable for several days. In polar solvents, **3b** rearranged rapidly and quantitatively with formation of the 1-cyano isomer **4b**.[15] The enthalpy of the

(1) For reviews, see: (a) Gassman, P. G.; Tidwell, T. T. *Acc. Chem. Res.* **1983**, *16*, 279. (b) Tidwell, T. T. *Angew. Chem.* **1984**, *96*, 16; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 20.
(2) For a comprehensive list of references, see: Creary, X.; Mehrsheikh-Mohammadi, M. E.; Eggers, M. D. *J. Am. Chem. Soc.* **1987**, *109*, 2435.
(3) Gassman, P. G.; Saito, K.; Talley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 7613.
(4) Gassman, P. G.; Saito, K. *Tetrahedron Lett.* **1981**, 1311.
(5) Gassman, P. G.; Talley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 1214.
(6) Dixon, D. A.; Charlier, P. A.; Gassman, P. G. *J. Am. Chem. Soc.* **1980**, *102*, 3957.
(7) Paddon-Row, M. N.; Santiago, C.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6561.
(8) Dixon, D. A.; Eades, R. A.; Frey, R.; Gassman, P. G.; Hendewerk, M. L.; Paddon-Row, M. N.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 3885.
(9) (a) Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M. *J. Am. Chem. Soc.* **1980**, *102*, 6640. (b) Olah, G. A.; Arvanaghi, M.; Prakash, G. K. S. *Ibid.* **1982**, *104*, 1628. (c) Krishnamurthy, V. A.; Prakash, G. K. S.; Iyer, P. S.; Olah, G. A. *Ibid.* **1986**, *108*, 1575.
(10) Gassman, P. G.; Talley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 4138.
(11) Kirmse, W.; Zellmer, V.; Goer, B. *J. Am. Chem. Soc.* **1986**, *108*, 4912.
(12) Bond, F. T.; Jones, H. L.; Scerbo, I. *Tetrahedron Lett.* **1965**, 4685. Bond, F. T.; Jones, H. L.; Scerbo, I. *Photochem. Synth.* **1971**, *1*, 33.
(13) Gassman, P. G.; Talley, J. J. *Tetrahedron Lett.* **1978**, 3773.
(14) Internal return of sulfonates with incomplete scrambling of ^{18}O is common; see: Goering, H. L.; Jones, B. E. *J. Am. Chem. Soc.* **1980**, *102*, 1628 and references cited therein.

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