

tionalized such that they may be connected chemically. For molecular realization of this structure, we felt that Sauvage catenanes⁶ and tetrakis(hydroxymethyl)ethylene (THYME) polyether rungs and uprights⁴ would prove nicely complementary.

Synthesis of the hook and ladder (actually two homologues, **9a** and **9b**) is shown in Scheme I.⁷ One notable aspect of the synthesis is obviation of the need for orthogonal hydroxyl protecting groups by taking advantage of the differing reactivities of the phenolic and THYME hydroxyl groupings. Use of orthogonal protecting groups was a key feature of the Möbius ladder syntheses.⁴ In addition, while the Sauvage catenane formation occurred more rapidly in the reaction forming a 38-membered ring (**4a** → **7a**), the yield of linked product was better in the 32-membered ring system (**4b** → **7b**) due to improved inhibition of unwanted decomplexation of diphenol **3** from the catenate precursor of **7b**.

Intramolecular cyclization of the hook and ladder molecules affords only one possible product from the initial cyclization. The second cyclization step may afford a number of possible topological diastereomers—the simplest being the racemic $1/4$ -twist diastereomers **10a,b**, as illustrated in Scheme II. Examination of CPK models indicates that more highly twisted isomers of **10** are more strained and/or less flexible. This, in combination with our prior experience with the THYME polyethers suggesting that twisting in the THYME ladders is disfavored,^{4b} led to the expectation that the major product of the cyclization would be the minimally twisted cyclized hook and ladder **10** as shown.

Cyclization of compounds **9a** and **9b** proceeded in a similar fashion, affording a single major product along with minor products as evidenced by TLC of the crude reaction mixture. In the latter case, two preparative runs each gave about a 60% yield of the major product after flash chromatographic purification on silica gel, allowing isolation of over 50 mg of the material.

In both cases, the ¹H NMR spectrum of the major product is nicely consistent with the expected $1/4$ -twist structure **10**,⁷ though the data do not rigorously rule out the possibility of knotted structures. Thus, the representation of structures **10** shown in Scheme II is a careful schematic illustration of the proposed preferred conformation (actually a large set of similar conformations) of compound **10b** as indicated by CPK models. This structure is consistent with the clear 2-fold symmetry observed in the room-temperature ¹H spectrum of compound **10b**. Thus, there are two sets of diphenylphenanthroline resonances (separate doublets for H_m and H_{m'}, H_o and H_{o'}, H₃ and H₈, H₄ and H₇, and an AB quartet for protons H₅ and H₆), consistent with the diastereotopic nature of these protons in conformation **10**.⁸ While the spectrum of **10a** is not as well resolved, it is clearly consistent with this argument.

When heated in DMF-*d*₇ solution, the spectrum for each cyclized hook and ladder collapses in the high-temperature limit to one showing a single diphenylphenanthroline system.⁸ The coalescence temperatures for the various pairs of protons all indicate an effective free energy of activation Δ*G*[‡] of about 20 kcal/mol for both compounds **10a** and **10b** for the process leading to ex-

change on the NMR time scale. This observation seems consistent with CPK modeling, where conformational changes can indeed exchange the protons which are diastereotopic in the conformation shown.

In conclusion, synthesis of the simplest cyclized hook and ladder graph has been achieved. The structure represents a new form of topologically chiral molecule possessing none of the classical elements of topological dissymmetry (an oriented link, a chiral link with more than two crossings, a knot, or a nonplanar graph).^{9,10} Additional studies on the structure and properties of compounds **10** and other members of this unique class of topological stereoisomers will be reported in due course.

Acknowledgment. The authors are greatly indebted to the Office of Naval Research for partial financial support of this work. We would also like to acknowledge the related studies of Dr. Wen Liang Tsai in this group, whose efforts were utilized to great benefit in this work, and Dr. Steve Wilson and his group at NYU for performing the electrospray mass spectrometry of compound **10b**.

Supplementary Material Available: Full experimental details for the preparation of all new compounds in the sequence leading to **10b** and analogue ¹H NMR spectra for compound **10b** taken at 25, 100, and 145 °C (15 pages). Ordering information is given on any current masthead page.

(9) Walba, D. M. *Tetrahedron* **1985**, *41*, 3161-3212.

(10) The uncolored $1/4$ -twist hook and ladder is topologically achiral. Structure **10**, however, is topologically chiral due to the coloring introduced by the phenanthroline units and the double bonds. We thank Professor Jonathan Simon of the University of Iowa Department of Mathematics for providing a proof of the topological chirality of this graph prior to publication.

Preparation, Characterization, and Crystal Structures of Octasilacubanes and Octagermacubanes¹

Akira Sekiguchi,* Tetsuo Yatabe, Hirokazu Kamatani, Chizuko Kabuto, and Hideki Sakurai*

Department of Chemistry and Organosilicon Research Laboratory, Faculty of Science Tohoku University, Aoba-ku, Sendai 980, Japan

Received March 10, 1992

The chemistry of group 14 polyhedranes is receiving current intense interest.² In 1989, we reported the preparation and crystal structure of hexagermacubane.³ Sita and Kinoshita reported octastannacubane with its crystal structure.⁴ Matsumoto et al. also reported octasilacubane⁵ in 1988, but no crystal structure has been given so far.⁶ We report here the first successful syntheses

(6) (a) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Kern, J.-M. *J. Am. Chem. Soc.* **1984**, *106*, 3043-3045. (b) Dietrich-Buchecker, C. O.; Sauvage, J. P. *Chem. Rev.* **1987**, *87*, 795-810.

(7) All new compounds in the sequence leading to **10a** were tentatively identified by ¹H NMR spectroscopy. Compounds **4a**, the copper complex of **4a** with **3**, **7a**, the copper complex of **7a**, the dichloride precursor of **8a**, and **9a** were characterized by FAB mass spectrometry. All new compounds in the sequence leading to **10b** gave consistent ¹H and ¹³C NMR, IR, and FAB mass spectra, and compound **10b** was also characterized by electrospray mass spectrometry. Compounds **1**, **2b**, **4b**, and **6** gave satisfactory combustion analyses. The catenanes in the sequence consistently gave combustion analyses low in carbon, presumably due to inclusion of small amounts of solvent in the glassy products. Experiments aimed at producing high-resolution FAB mass spectra for the new compounds are in progress.

(8) The difference in chemical shift for the diastereotopic pairs of protons for **10b** is as follows: Δ*ν* H_{o,o'} = 48.9 Hz, H_{m,m'} = 31.5 Hz, H_{3,8} = 42 Hz, H_{4,7} = 32 Hz, and H_{5,6} = 8 Hz. At 145 °C, H₅ and H₆ give rise to a sharp singlet and H_m and H_{m'} collapse to a single doublet. The pairs of protons with a large Δ*ν* (H_{3,8} and H_{o,o'}) coalesce, but remain very broad at 145 °C. The signal for protons H₄ and H₇, presumably a doublet, is hidden within the broad peak associated with the H_{o,o'} protons.

(1) Chemistry of Organosilicon Compounds. 293.

(2) (a) Sekiguchi, A.; Sakurai, H. *Kagaku (Chemistry)* **1990**, *45*, 874. (b) Sekiguchi, A.; Sakurai, H. *The Chemistry of Inorganic Ring Systems*; Steudel, R., Ed.; Elsevier: New York, 1992; Chapter 7.

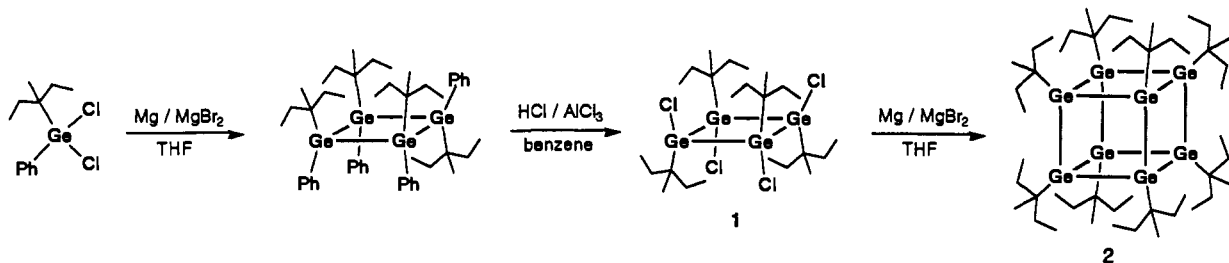
(3) Sekiguchi, A.; Kabuto, C.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 55.

(4) Sita, L. R.; Kinoshita, I. *Organometallics* **1990**, *9*, 2865.

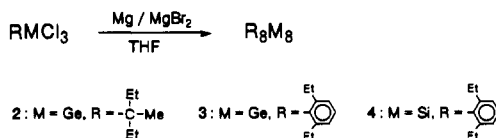
(5) Matsumoto, H.; Higuchi, K.; Hoshino, Y.; Koike, H.; Naoi, Y.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1083.

(6) For related papers of group 14 polyhedranes, see: (a) Nagase, S.; Kudo, T.; Aoki, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1121. (b) Sax, A. F.; Janoschek, R. *Phosphorus Sulfur* **1986**, *28*, 151. (c) Sax, A. F.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 651. (d) Sax, A. F.; Kalcher, J. *J. Chem. Soc., Chem. Commun.* **1987**, 809. (e) Baudler, M.; Scholz, G.; Tebbe, K. F.; Feher, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 339. (f) Nagase, S.; Nakano, M. *Ibid.* **1988**, *27*, 1081. (g) Kabe, Y.; Kuroda, M.; Honda, Y.; Yamashita, O.; Kawase, T.; Masamune, S. *Ibid.* **1988**, *27*, 1725. (h) Kuroda, M.; Kabe, Y.; Hashimoto, M.; Masamune, S. *Ibid.* **1988**, *27*, 1727. (i) Sekiguchi, A.; Naito, H.; Nameki, H.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Organomet. Chem.* **1989**, *368*, C1. (j) Weidenbruch, M.; Grimm, F.-T.; Pohl, S.; Saak, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 198. (k) Gleiter, R.; Pfeifer, K. H.; Baudler, M.; Scholz, G.; Wettling, T.; Regitz, M. *Chem. Ber.* **1990**, *123*, 757. (l) Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.* **1991**, *113*, 1856.

Scheme I



Scheme II



of alkyl- and aryl-substituted octagermacubanes. The first crystal structure of octasilacubane is also established.

We thought that tetrahalocyclotetragermane through possible cyclotetramerene or cyclotetrameradiene intermediates. The choice of the substituent is also crucial. Therefore, we have chosen 1,2,3,4-tetrachloro-1,2,3,4-tetrakis(1-ethyl-1-methylpropyl)-cyclo-tetragermane (**1**) as a candidate precursor of octagermacubane (Scheme I). Condensation of dichloro(1-ethyl-1-methylpropyl)phenylgermane with Mg/MgBr₂ in THF afforded a mixture of tetrakis(1-ethyl-1-methylpropyl)tetraphenylcyclo-tetragermane (the main isomer: cis-cis-trans) in 72% yield. The cyclotetramerene was allowed to react with gaseous hydrogen chloride in the presence of aluminum chloride in benzene to give **1** with a trans-trans-trans configuration in 45% yield.⁷

Octakis(1-ethyl-1-methylpropyl)pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octagermane (octagermacubane **2**) was synthesized by the dehalogenative coupling reaction of **1** with Mg/MgBr₂ in 16% yield as yellow crystals: mp > 215 °C; ¹H NMR (300 MHz, C₆D₆, δ) 1.08 (t, 48 H, J = 7.4 Hz, CH₂CH₃), 1.59 (s, 24 H, CCH₃), 1.95–2.16 (m, 32 H, CCH₂CH₃); ¹³C NMR (75.5 MHz, C₆D₆, δ) 11.4, 25.9, 33.8, 46.4. The mass spectrum of **2** showed the M⁺ cluster ion in the range of 1248–1276 consistent with the calculated formula of C₄₈H₁₀₄Ge₈. An absorption maximum at 240 nm (ε 4.87 × 10⁴, hexane) has a long skirt to the visible region. After isolation and purification, cubane **2** was relatively stable to atmospheric oxygen and moisture.⁸

Cubane **2** was also obtained by a direct coupling of trichloro(1-ethyl-1-methylpropyl)germane in 3% yield. Although the yield is low, a one-pot synthesis is operationally simple and thus useful. Aryl-substituted octagermacubane **3**, octakis(2,6-diethylphenyl)octagermacubane,⁹ was prepared by dehalogenative coupling of (2,6-diethylphenyl)trichlorogermane with Mg/MgBr₂ in THF (1%). The first aryl-substituted octasilacubane, **4**¹⁰ (1%),

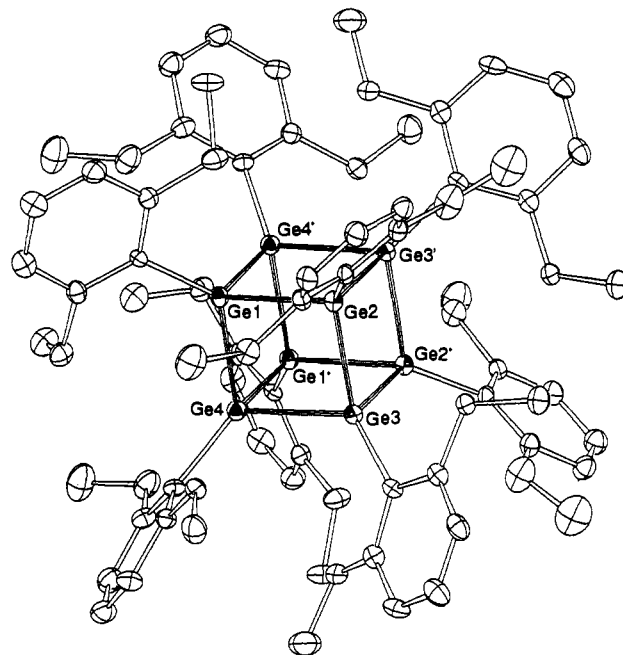


Figure 1. ORTEP drawing of **3**. Selected bond lengths (Å): Ge1–Ge2 2.478, Ge1–Ge4 2.492, Ge2–Ge3 2.486, Ge3–Ge4 2.503, Ge1–Ge4' 2.500, Ge2–Ge3' 2.482 (esd = 0.001 Å). Selected bond angles (deg): Ge2–Ge1–Ge4 90.6, Ge2–Ge1–Ge4' 90.3, Ge4–Ge1–Ge4' 90.3, Ge1–Ge2–Ge3 89.9, Ge1–Ge2–Ge3' 90.3, Ge3–Ge2–Ge3' 88.9, Ge2–Ge3–Ge4 90.2, Ge2–Ge3–Ge2' 91.1, Ge4–Ge3–Ge2' 90.1, Ge1–Ge4–Ge3 89.2, Ge1–Ge4–Ge1' 89.2, Ge3–Ge4–Ge1' 89.3 (esd = 0.0°).

was also prepared in a similar manner (Scheme II).

The structure determined by X-ray analysis established unequivocally the cubane structures for **3**¹¹ and **4**.¹² Crystals of **3** and **4** including toluene are crystallographically isomorphous with crystallographic 2-fold axes of symmetry, the ORTEP drawing of **3** being shown in Figure 1.

The results of X-ray structures indicate almost perfect cubic structures of the frameworks. Ge–Ge bond lengths of 2.478–2.503 Å (average 2.490 Å) and Ge–Ge–Ge bond angles of 88.9–91.1° (average 90.0°) are found for **3** and Si–Si bond lengths of 2.384–2.411 Å (average 2.399 Å) and Si–Si–Si bond angles of 88.9–91.1° (average 90.0°) for **4**. The exocyclic M–C (M = Ge, Si) bonds are slightly elongated: 1.982 Å (average) for **3** and 1.911 Å (average) for **4**. In addition, the M–M–C bond angles are significantly expanded (124.6° for **3** and 124.4° for **4**) due to the endocyclic angular constraint. The M–M bond lengths of **3** and **4** are in close agreement with the Ge–Ge bond lengths of 2.527

(7) Compound **1**: mp 148–150 °C; ¹H NMR (300 MHz, CDCl₃, δ) 0.97 (t, 24 H, J = 7.5 Hz), 1.40 (s, 12 H), 1.73–2.00 (m, 32 H); ¹³C NMR (75.5 MHz, CDCl₃, δ) 9.52, 23.0, 29.8, 53.7; MS (FAB) *m/e* 762–784 (M⁺ cluster). NMR data simply indicate an all-trans or all-cis configuration for **1**. However, 1,2,3,4-tetra-*tert*-butyl-1,2,3,4-tetrachlorocyclo-tetragermane was prepared in 86% yield in the same way, and the all-trans configuration was confirmed by X-ray analysis. The high yield of the trans-trans-trans isomer indicates possible stereochemical isomerization during the reaction. Details will be reported elsewhere.

(8) At this moment, we cannot get sufficient refinement for the crystal structure of **2**; however, the preliminary results show the cubic structure.

(9) Compound **3**: yellow crystals; mp > 200 °C; ¹H NMR (300 MHz, C₆D₆, δ) 0.82 (t, 48 H, J = 7.4 Hz), 2.76 (q, 32 H, J = 7.4 Hz), 6.97 (d, 16 H, J = 7.6 Hz), 7.15 (t, 8 H, J = 7.6 Hz); ¹³C NMR (75.5 MHz, C₆D₆, δ) 14.1, 31.3, 124.8, 129.0, 146.0, 148.7; MS (FAB) *m/e* 1632–1662 (M⁺ cluster).

(10) Compound **4**: yellow-orange crystals; mp > 200 °C; ¹H NMR (300 MHz, C₆D₆, δ) 0.81 (t, 48 H, J = 7.4 Hz), 2.82 (q, 32 H, J = 7.4 Hz), 6.96 (d, 16 H, J = 7.6 Hz), 7.16 (t, 8 H, J = 7.6 Hz); ¹³C NMR (75.5 MHz, C₆D₆, δ) 13.8, 31.9, 124.2, 129.2, 139.5, 150.0; ²⁹Si NMR (59.6 MHz, C₆D₆, δ) 0.36; MS (EI) *m/e* 1288–1294 (M⁺ cluster).

(11) Crystal data of **3** at 150 K: C₈₀H₁₀₄Ge₈·C₇H₈, monoclinic, space group C2/c, *a* = 24.461 (4) Å, *b* = 14.472 (7) Å, *c* = 22.989 (4) Å, β = 102.49 (1)°, *V* = 7945.7 (40) Å³, *Z* = 4, final *R* = 0.0483, *R_w* = 0.0536.

(12) Crystal data of **4** at 200 K: C₈₀H₁₀₄Si₈·C₇H₈, monoclinic, space group C2/c, *a* = 24.036 (10) Å, *b* = 14.393 (3) Å, *c* = 22.896 (6) Å, β = 102.59 (2)°, *V* = 7730.9 (45) Å³, *Z* = 4, final *R* = 0.0736, *R_w* = 0.0784. Selected bond lengths (Å): Si1–Si2 2.384, Si1–Si4 2.400, Si2–Si3 2.399, Si3–Si4 2.411, Si1–Si4' 2.406, Si2–Si3' 2.396 (esd = 0.002 Å). Selected bond angles (deg): Si2–Si1–Si4 90.8, Si2–Si1–Si4' 90.3, Si4–Si1–Si4' 91.1, Si1–Si2–Si3 89.8, Si1–Si2–Si3' 90.3, Si3–Si2–Si3' 89.1, Si2–Si3–Si4 90.2, Si2–Si3–Si2' 90.8, Si4–Si3–Si2' 89.9, Si1–Si4–Si3 89.1, Si1–Si4–Si1' 88.9, Si3–Si4–Si1' 89.4 (esd = 0.0°).

Å and the Si-Si bond lengths of 2.382 Å calculated for Ge₈H₈ and Si₈H₈.¹³

Acknowledgment. We are grateful for the financial support of the Ministry of Education, Science and Culture of Japan (Specially Promoted Research No. 02102004). A.S. is grateful for the Kurata Research Grant. We also thank the ASAI Germanium Research Institute for the gift of tetrachlorogermane.

Supplementary Material Available: Details of X-ray experiments, atomic parameters, anisotropic temperature factors, and lists of distances and angles for 3 and 4 (20 pages); listing of observed and calculated structure factors for 3 and 4 (50 pages). Ordering information is given on any current masthead page.

(13) (a) Nagase, S.; Nakano, M.; Kudo, T. *J. Chem. Soc., Chem. Commun.* 1987, 60. (b) Nagase, S. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 329.

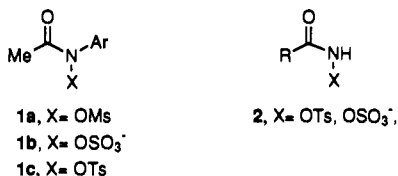
Efficient Conversion of O-Sulfonylated Arylacetoxyhydroxamic Acids to 2-Substituted Secondary Amides

Robert V. Hoffman,* Naresh K. Nayyar, and Bruce W. Klinekole

Department of Chemistry
New Mexico State University
Las Cruces, New Mexico 88003-0001

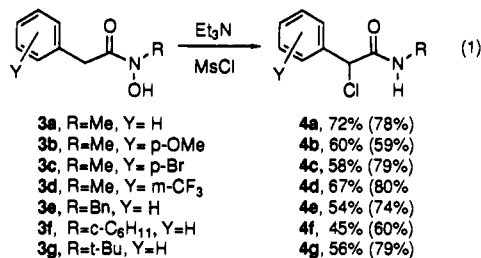
Received April 24, 1992

In connection with a study of new methods for the generation of *N*-acyl iminium ions, we sought to prepare *O*-sulfonylated *N*-alkyl hydroxamic acids. This particular class of hydroxamic acid derivative is little known,¹ but *O*-methylsulfonyl *N*-aryl hydroxamates, 1a, have been used as solvolysis precursors by Gassman,² and *O*-sulfonylated *N*-aryl hydroxamates, 1b, have been used similarly by Novak.³ Intramolecular 3,3-rearrangements of the tosylate group of *O*-tolylsulfonyl *N*-aryl hydroxamates, 1c, have been studied by Lwowski.⁴ Furthermore, *N*-unsubstituted *O*-sulfonylated hydroxamic acids, 2, are well-known substrates for the Lossen rearrangement.⁵ The very recent communication of Miller on reactions of *N*-sulfonyloxy β-lactams⁶ prompts us to disclose the mechanistic details of a related transformation found in acyclic hydroxamic acid derivatives.



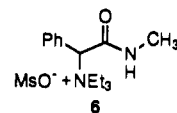
Treatment of *N*-methylphenylacetohydroxamic acid (3a), with triethylamine (2.25 equiv) and methanesulfonyl chloride (1.1 equiv) at 0 °C in dichloromethane² produced 2-chloro-*N*-methylphenylacetamide (4a) in 72% isolated yield (eq 1).⁷ Compounds 3b-g gave comparable yields.

This transformation is unusual from two points of view. Mechanistically, the oxidation states of the nitrogen atom and the α-carbon are exchanged. Preparatively, it offers a potential



method for a general synthesis of 2-substituted secondary amides. It was assumed that 3a is initially sulfonylated on oxygen to give 5a and that excess triethylamine and the triethylammonium chloride byproduct from the formation of 5a caused the conversion of 5a to 4a (Scheme I). This general scenario was verified by reaction of 3a with methanesulfonyl chloride and 1 equiv of triethylamine to give *N*-mesylate 5a (79%). (*O*-Sulfonylated hydroxamic acids 5b-g were also prepared in this manner.) Mesylate 5a is readily converted to 2-chloro amide 4a (78%) by triethylamine and triethylammonium chloride.

Several observations help delineate the gross mechanistic details of how 5a is converted to 4a by triethylamine and triethylammonium chloride. First, both triethylamine and chloride ion are required. Second, a conjugating group (aromatic or vinyl) must be present at C-2 for reaction to occur. Third, triethylamine alone causes decomposition of 5a and formation of 2-triethylammonium amide 6. Fourth, substrates 5a, 5b, and 5d required 35, 125, and 5 min, respectively, for complete reaction, which is qualitatively equivalent to a positive ρ-value for the reaction.⁸ Fifth, partial reaction (10 min) of 5a with triethylamine in the presence of D₂O and reisolation of the starting material revealed that no deuterium was incorporated at the α-position. Finally, when the mesylate leaving group of 5a was replaced with a triflate leaving group, the triflyloxy compound was found to react instantaneously, while mesylate 5a required 35 min for complete reaction.



These observations suggest that triethylamine first converts mesyloxy amide 5a to its enolate 7 (or its enol 7-H). A conjugating group at C-2 is probably needed to acidify the α-proton (or to increase the proportion of enol form). The conversion of 7 (or 7-H) to 4a could take place by one of three processes (Scheme II). Concerted 3,3-sigmatropic rearrangement of mesylate to give 8 and then 4a (path a) is the first process. Such sulfonate 3,3-rearrangements have been reported for several systems.^{4,9,10} A second alternative is S_N2' displacement of the mesylate from enol 7-H (path b). This pathway was suggested by Miller in sulfonylated *N*-hydroxy β-lactams.⁶ A third alternative is formation of ion pair 9 from 7 and chloride capture to give 4a (path c), similar to the ion pair pathway proposed for the Favorski rearrangement.¹¹

Path a was ruled out by observing that authentic 8 undergoes practically no conversion to 4a under the reaction conditions. It was next determined that the time required for complete conversion of 5a to a 2-halo amide product was the same for both chloride and bromide nucleophiles, even though bromide is a significantly

(1) Scott, A. I.; Yoo, S. E.; Chung, S.-K.; Lacadie, J. A. *Tetrahedron Lett.* 1976, 1137.

(2) Gassman, P. G.; Granrud, J. E. *J. Am. Chem. Soc.* 1984, 106, 1498 and 2448.

(3) Novak, M.; Pelecanou, M.; Roy, A. K.; Andronico, A. F.; Plourde, F. M.; Olefirowicz, T. M.; Curtin, T. J. *J. Am. Chem. Soc.* 1984, 106, 5623.

(4) Tisue, G. T.; Grassmann, M.; Lwowski, W. *Tetrahedron* 1968, 24, 999.

(5) (a) Hartmann, W. *Synthesis* 1988, 807 and references therein. (b) Groutas, W. C.; Stanga, M. A.; Brubaker, M. J. *J. Am. Chem. Soc.* 1989, 111, 1931.

(6) Gasparski, C. M.; Teng, M.; Miller, M. J. *J. Am. Chem. Soc.* 1992, 114, 2741.

(7) Slightly lower yields of 4a were obtained from 3a using *p*-nitrobenzenesulfonyl chloride (50%), tosyl chloride (36%), or triflyl chloride (50%).

(8) These were not rigorous kinetic experiments, but they measured the time required for complete reaction under standard reaction conditions and are capable of indicating major changes (2-3-fold) in rate that result from alteration of reaction parameters.

(9) (a) Oae, S.; Sakurai, T. *Tetrahedron* 1976, 32, 2289. (b) Krower, J. S.; Richmond, J. P. *J. Org. Chem.* 1978, 43, 2464.

(10) Hoffman, R. V.; Carr, C. S.; Jankowski, B. C. *J. Org. Chem.* 1985, 50, 5148.

(11) (a) Bordwell, F. G.; Springer, W. R.; Scamehorn, R. G. *J. Am. Chem. Soc.* 1969, 91, 2087. (b) Bordwell, F. G.; Carlson, M. W.; Knipe, A. C. *Ibid.* 1969, 91, 3949. (c) Bordwell, F. G.; Carlson, M. W. *Ibid.* 1971, 93, 3951.