Å and the Si-Si bond lengths of 2.382 Å calculated for Ge_8H_8 and Si_8H_8.[13]

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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.

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

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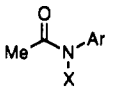
In connection with a study of new methods for the generation of *N*-acyl iminium ions, we sought to prepare O-sulfonylated *N*-alkyl hydroxamic acids. This particular class of hydroxamic acid derivative is little known,[1] but *O*-methylsulfonyl *N*-aryl hydroxamates, **1a**, have been used as solvolysis precursors by Gassman,[2] and O-sulfonated *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-lactams[6] prompts us to disclose the mechanistic details of a related transformation found in acyclic hydroxamic acid derivatives.

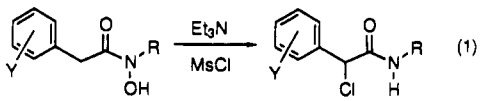


1a, X= OMs
1b, X= OSO_3^-
1c, X= OTs

2, X= OTs, OSO_3^-

Treatment of *N*-methylphenylacetohydroxamic acid (**3a**), with triethylamine (2.25 equiv) and methanesulfonyl chloride (1.1 equiv) at 0 °C in dichloromethane[2] 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



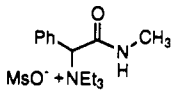
(1)

3a, R=Me, Y= H
3b, R=Me, Y= p-OMe
3c, R=Me, Y= p-Br
3d, R=Me, Y= m-CF_3
3e, R=Bn, Y= H
3f, R=c-C_6H_{11}, Y=H
3g, R=t-Bu, Y=H

4a, 72% (78%)
4b, 60% (59%)
4c, 58% (79%)
4d, 67% (80%
4e, 54% (74%)
4f, 45% (60%)
4g, 56% (79%)

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 D_2O 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.



6

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

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(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.
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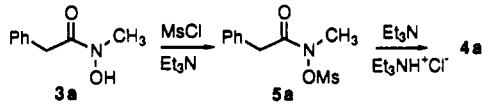
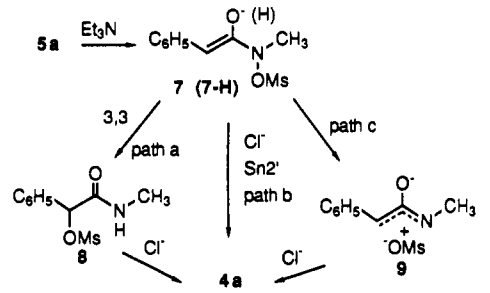
Scheme I

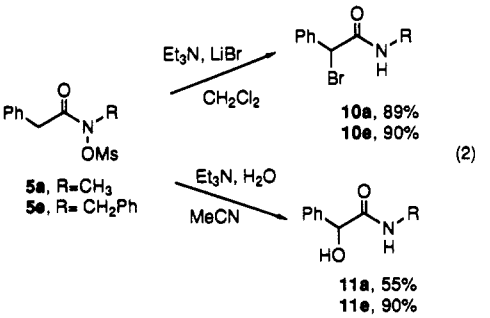


Scheme II



better nucleophile.[12] This result shows that S_N2' attack on enol 7-H is not rate determining (second step of path b). Furthermore, the formation of enol 7-H (first step of path b) is governed by a proton-transfer equilibrium, not by irreversible proton removal as is found (vide infra). Path b is thus discounted since neither step is consonant with the observed behavior.

The results from the substituent effect experiments and the requirement of a conjugating group at C-2 suggest that proton removal by base is occurring in the rate-determining step. The lack of deuterium incorporation means that proton removal is not reversible. The greater reactivity of triflate over mesylate might be attributed to an increase in acidity of the α-proton from the greater electron-withdrawing ability of the triflate group. A mechanism involving conversion of **5a** to enolate **7** followed by formation of ion pair **9** is consistent with the results.[13] Capture of this ion pair by chloride gives the α-chloro amide product. The simple expedient of adding excess chloride ion (5 equiv) to the reaction mixture increases the capture efficiency and gives increased yields (yields in parentheses, eq 1). If no chloride ion is present, the ion pair capture by triethylamine gives salt **6**. The use of other nucleophiles to capture **9** could lead to a general synthesis of 2-substituted secondary amides. We were delighted to find that treatment of both **5a** and **5e** with triethylamine and lithium bromide in dichloromethane gave 2-bromo amides **10a,e** in high yields. Alternatively, treatment of **5a,e** with triethylamine and water in acetonitrile gave 2-hydroxy amides **11a,e** in high yields also (eq 2).



(2)

These results support the idea that nucleophilic capture of ion pairs produced from O-sulfonylated hydroxamic acids offers a very versatile route to 2-substituted amides. In contrast, Miller has recently suggested that an S_N2' pathway is followed in the reactions of sulfonyloxy β-lactams with nucleophiles.[6] Studies are in progress to resolve these mechanistic issues and to fully explore the synthetic potential of these processes.

Acknowledgment. This work was supported by the National Science Foundation (9004980) and the National Institutes of Health (GM44529-01). B.W.K. is a participant in the MARC program sponsored by the National Institutes of Health.

Supplementary Material Available: Experimental deatils for preparations and experiments described in the text (5 pages). Ordering information is given on any current masthead page.

(12) The *n*-values for chloride and bromide are 4.37 and 5.79, respectively. Pearson, R. G.; Sobel, H.; Songstad, J. *J. Am. Chem. Soc.* **1968**, *90*, 319.

(13) It is also possible that an aziridinone (α-lactam) is formed from enolate **7**. The α-lactam is a valence tautomer of ion pair **9**. While an α-lactam cannot be specifically ruled out as the reactive intermediate, the efficient capture of weak nucleophiles like chloride under neutral conditions is more consistent with the ion pair as the reactive species. Lengyel, I.; Sheehan, J. C. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 25.

The Asymmetric Mixed-Valent Complex {[Mn(2-OH-3,5-Cl_2-SALPN)]$_2$(THF)}ClO_4 Shows a Temperature-Dependent Interconversion between $g = 2$ Multiline and Low-Field EPR Signals

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Considerable debate has focused on the origin of the $g = 2$ "multiline" and $g = 4.1$ EPR signals observed in the S_2 state of the photosynthetic oxygen-evolving complex.[4,5] One explanation of these signals is that they arise from the ground and excited states of a single manganese cluster or from different spin states of a conformationally perturbed cluster.[5] Mixed-valent Mn(II/III) dimers have shown temperature-dependent EPR signals.[6] However, there are no examples where the strongly coupled Mn(III/IV)(μ_2-O)$_2$ cores ($J = -120$ cm^{-1}) exhibit additional features beyond the 16-line spectrum of the $S = {}^1/_2$ ground state.[7] This is significant since it is believed that the S_2 multiline arises from a cluster containing Mn(III) and Mn(IV).[8] Herein we report a highly asymmetric Mn(III/IV) dimer, **1**, which has an exceptionally long Mn–Mn separation and weak antiferromagnetic coupling and provides the first observation of a reversible, thermally regulated transition from an $S = {}^1/_2$ ground-state multiline to a low-field transition ($g \approx 5$) from an $S = {}^3/_2$ first excited state.

[Mn^{III}(2-OH-3,5-Cl_2-(SALPN)]$_2$(MeOH)], **2** (where 2-OH-3,5-Cl_2-(SALPN) = *N*,*N*′-bis(3,5-dichlorosalicylidene)-1,3-di-

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