and benzophenone immediately before use. The "extracting solvent" used was a mixture of recovered organic solvents, including methylene chloride, ethyl acetate, and petroleum ether. The solvent mixtures used for chromatography are volume/volume mixtures. R_f values indicated refer to thin-layer chromatography (TLC) on Analtech (2.5 × 10 cm, 250 μm) analytical plates coated with silica gel GF. Column chromatography was carried out with TLC-mesh silica gel, following the procedure we have described.[9]

Preparation of 1b. A flame-dried, one-necked flask equipped with an N_2 inlet and septum was charged with **1a** (523 mg, 2.6 mmol), methanesulfonyl azide [*Caution: Although we have never had any trouble with mesyl azide, it is potentially explosive!*] (351 mg, 2.9 mmol, 1.1 equiv), and CH_3CN (5 mL). To this solution was added triethylamine (0.74 mL, 5.3 mmol, 2 equiv). The reaction was followed by TLC. Typically, it was complete in 3 h. The mixture was diluted with 10% aqueous NaOH and extracted with extraction solvent (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo. The residual oil was chromatographed on 20 g of silica gel with 2.5% EtOAc/petroleum ether. The first 100 mL was discarded. The next 250 mL was concentrated in vacuo to give α-diazo β-ketoester **1b** as a clear yellow oil: 549 mg (94%); R_f (20% EtOAc/hexane) 0.54; ^{1}H NMR δ 0.9–1.9 (m, 11 H), 2.74 (d, J = 6.8 Hz, 2 H), 3.84 (s, 3 H); ^{13}C NMR: 26.1 (t, 2), 26.2 (t), 33.1 (t, 2), 34.6 (d), 47.3 (t), 52.1 (q), 76.05 (s), 161.8 (s), 192.4 (s); IR 2930, 2850, 2140, 1730, 1660, 1560, 1455, 1440, 1315, 1200, 1020, 910 cm^{-1}; MS, m/z (relative intensity) 143 (23), 142 (100), 125 (11), 101 (21); exact mass calcd for $C_{11}H_{16}N_2O_3$ 224.116, obsd 224.116.

Preparation of 2b: A flame-dried, two-necked, 25-mL round-bottomed flask equipped with a septum and nitrogen purge was flushed with N_2 and charged with 144 mg (3.03 mmol) of 50% sodium hydride dispersion in mineral oil, one drop of absolute ethanol, and 2 mL of anhydrous ether. This mixture, while magnetically stirred, was cooled in an ice bath. Then 200 mg (1.01 mmol) of dihexyl ketone and 222 mg (3.01 mmol) of ethyl formate in an additional 2 mL of ether were added dropwise. This reaction was stirred for 3 h in the ice/water bath and then overnight at room temperature. Mesyl azide (363 mg, 3.03 mmol) in 5 mL of ether was then added, and stirring was continued for an additional 2 h. The reaction was quenched with 1 mL of water. The organic layer was washed with 30 mL of 10% aqueous NaOH solution, and the aqueous layer was back extracted with three 30-mL portions of extraction solvent. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on 20 g of silica gel with 1% EtOAc/petroleum ether. The first 120 mL was discarded. The next 120 mL was concentrated in vacuo to give 160 mg (0.714 mmol, 71%) of **2b** as a yellow oil: R_f (10% EtOAc/hexane) 0.51; ^{1}H NMR δ 0.88 (s, 6 H), 1.29 (bs, 10 H), 1.47 (m, 2 H), 1.62 (m, 2 H), 2.34 (t, J = 7 Hz, 2 H), 2.43 (t, J = 7 Hz, 2 H); ^{13}C NMR δ 14.0 (q, 2), 22.4 (t, 2), 22.5 (t), 24.9 (t), 26.7 (t), 28.9 (t), 31.0 (t), 31.6 (t), 38.1 (t), 66.5 (s), 194.6 (s); IR 2959, 2931, 2860, 2064, 1643 cm^{-1}; MS, m/z (relative intensity) 196 (27), 167 (50), 126 (60), 125 (31), 113 (100), 112 (55), 111 (95); methane chemical ionization exact mass calculated for $C_{13}H_{25}N_2O$ 225.1966, obsd 225.196.

Preparation of 3b: R_f (20% EtOAc/hexane) 0.50; ^{1}H NMR δ 1.20–1.85 (m, 16 H) 2.0–2.15 (m, 1 H), 2.15–2.30 (m, 1 H), 2.70–2.90 (m, 2 H); ^{13}C NMR δ 22.6 (t), 23.4 (t), 23.6 (t, 2), 23.9 (t), 24.0 (t), 25.0 (t), 25.3 (t, 2), 38.6 (t), 65.7 (s), 196.3 (s); IR 2934, 2064, 1640, 1341 cm^{-1}; MS m/z (relative intensity) 180 (39), 137 (30, 123 (48), 112 (30), 111 (48), 110 (42), 109 (100). Methane chemical ionization exact mass calculated for $C_{12}H_{21}N_2O$: 209.1653, obsd 209.164.

Preparation of 4b: R_f (20% EtOAc/hexane) 0.25; ^{1}H NMR δ 0.96 (s, 9 H), 1.30–1.55 (m, 2 H), 1.90–2.05 (m, 1 H), 2.25 (dt, J = 5, 7 Hz, 1 H), 2.35–2.75 (m, 3 H); ^{13}C NMR δ 23.4 δ (t), 23.8 (t), 27.2 (q, 2), 32.7 (s), 37.8 (t), 44.5 (d), 65.8 (s), 194.4 (s); IR 2965, 2084, 1635, 1337, 1227 cm^{-1}; MS, m/z (relative intensity) 152(82), 125(73), 115 (83), 109 (100); methane chemical ionization exact mass calculated for $C_{10}H_{17}N_2O$ 181.134, obsd 181.134.

Preparation of 5b: R_f (20% EtOAc/hexane) 0.37; ^{1}H NMR δ 2.10 (s, 3 H), 7.30–7.70 (m, 5 H); ^{13}C NMR δ 9.6 (q), 62.8 (s), 127.3 (d, 2), 128.6 (d, 2), 131.4 (d,), 137.8 (s), 190.1 (s); IR 2070, 1628, 1341 cm^{-1}; MS, m/z (relative intensity) 132 (16), 106 (17), 105 (100), 104 (38), 103 (25); methane chemical ionization exact mass calculated for $C_9H_9N_2O$ 161.0714, obsd 161.075.

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Registry No. **1a**, 51414-42-7; **1b**, 104156-32-3; **2a**, 462-18-0; **2b**, 104156-33-4; **3a**, 830-13-7; **3b**, 14078-83-2; **4a**, 98-53-3; **4b**, 104156-34-5; **5a**, 93-55-0; **5b**, 14088-57-4; $MeSO_2N_3$, 1516-70-7.

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The Iodide Reduction of Sulfilimines. Secondary Deuterium Isotope Effects on Sulfurane Formation

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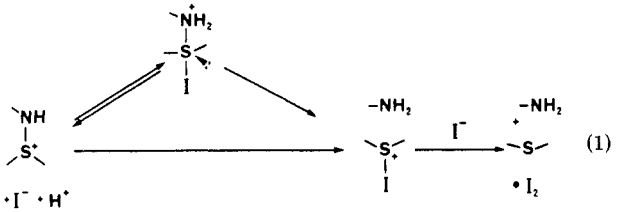
Introduction

Sulfilimmonium cations are readily reduced by iodide anion in dilute acid solution to give iodine, the amine, and the corresponding sulfide.[1-6] The mechanism of the reaction is suggested to involve addition of iodide anion to the tricoordinate sulfur to give a tetracoordinate sulfurane intermediate.[2,4,6] Protonation of this intermediate followed by cleavage of the sulfur–nitrogen bond gives the free amine and an iodosulfonium ion which is rapidly reduced by a second mole of iodide to give the observed products (eq 1).



(1)

Addition–elimination reactions such as these offer a variety of mechanistic possibilities in which different steps may be rate-limiting, depending on intermediate lifetimes, proton transfer rates, etc.[7] In addition–elimination reactions occurring at carbonyl carbons, β-deuterium isotope effects have proven to be useful in both diagnosing the rate-limiting step and in understanding the subtleties of transition state structure.[8] In order to explore the utility of secondary isotope effects in reactions at tricoordinate sulfur we have examined the rates of the proton-catalyzed iodide reduction of *N*-substituted-*S*,*S*-di(methyl-d_3)-

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Table I. Third-Order Rate Constants and β-Deuterium Isotope Effects for the Proton-Catalyzed Iodide Reduction of *N*-Substituted-*S*,*S*-di(methyl-d_3)sulfilimines[a]

substituent	$k^H/M^{-2}\ s^{-1}$[b]	k^D/k^H[c]
N-phenyl	0.467	1.052 ± 0.004
N-(3-chlorophenyl)	0.108	1.056 ± 0.004
N-benzoyl	0.000166	1.09 ± 0.01
N-phenylsulfonyl	0.000228	1.12 ± 0.01
N-(4-chlorophenylsulfonyl)	0.000298	1.15 ± 0.015

[a] Aqueous solution, 25 °C, ionic strength 1.0 with KCl. [b] Third-order rate constant for the proton-catalyzed reduction of the ^1H isotopically substituted compound. [c] Observed isotope effect and standard error.

sulfilimines. We have found that the isotope effects for these reactions are unexpectedly small.

Experimental Section

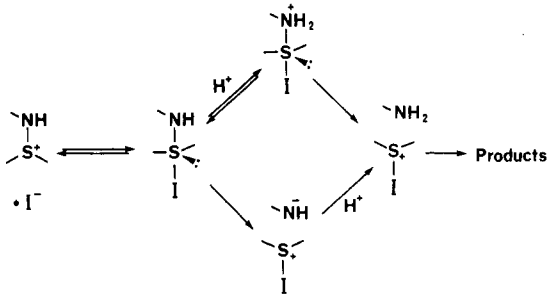
Synthesis. *N*-(Substituted-phenyl)-*S*,*S*-dimethylsulfilimmonium salts were prepared from trifluoroacetic anhydride, dimethyl sulfoxide or dimethyl-d_6 sulfoxide (Aldrich, 99.9% *d*) and the corresponding aniline according to the method described by Swern et al.[9] All sulfilimines were isolated as the picrate salts and subsequently converted to the chloride by passing methanolic solutions over Dowex anionic exchange resins. *N*-(Carboxyphenyl)- and *N*-(phenylsulfonyl)-*S*,*S*-dimethylsulfilimines were also prepared by the TFA/Me_2SO method and were isolated as the neutral ylide.[9] All compounds were recrystalized from dichloromethane/ether mixtures at 4 °C and had melting points and NMR spectra consistent with literature data. Elemental analyses were performed on all new solid compounds, and these analyses were within acceptable error limits on carbon, hydrogen, and nitrogen.[2]

Kinetic Studies. All kinetic runs were performed by following the appearance of I_3^- at 353 nm on a Hitachi 100-60 UV–vis spectrophotometer equipped with an automatic cell changer and a thermostated cell compartment. Temperature was maintained at 25 °C, and the ionic strength was maintained at 1.0 with KCl. The pH of each cell was determined immediately after each run by using a Corning pH meter with a combined glass electrode. For aniline leaving groups, observed first-order rate constants were obtained from semi-logarithmic plots of $A_\infty - A_t$ against time. Such plots were typically linear for over 4 half-lives. Kinetic studies involving sulfilimines with amide and sulfonamide leaving groups were too slow to follow to completion, and observed rate constants for these compounds were calculated from the initial rate of the first 1% of reaction. The value of 26 400 was used for the extinction coefficient of I_3^- at 343 nm.[4] All cells were purged with nitrogen prior to beginning the kinetic studies in order to minimize oxidation of I_2 at low pH values. Third-order rate constants for the proton-catalyzed reduction reaction were obtained from plots of observed rate constants against proton activity, as measured by the glass electrode in the pH region 0.5–2.0. For anilines, the slopes of these plots were 1.00 ± 0.01. For amide leaving groups, both first- and second-order terms in proton activity contribute to the rate law and third-order rate constants for proton catalysis were obtained from "second order" plots, as previously described.[2] Each isotope effect reflects an average of between eight and eighteen separate determinations.

Results and Discussion

The isotope effects for the substituents examined are collected in Table I. In general, the isotope effects are inverse and small, with the largest effects (as k^D/k^H) occurring with the sulfonamide leaving groups. The mechanism of the proton-catalyzed iodide reduction of sulfilimines has been suggested[2] to involve the partitioning of a common sulfurane intermediate (Scheme I). For aniline leaving groups, general catalysis is observed and the rate-limiting step involves proton transfer to the sulfurane

Scheme I



nitrogen in a reaction that is probably coupled with some lengthening of the S–N bond.[2] The isotope effect on the proton transfer reaction would be expected to be small and inverse, based on the effect of deuterium on the pK_a of $(CL_3)_3CCOOH$[10] of about $1.0044/d$. For the d_6 compounds used here, the maximum effect would be about 1.026, and the observed effect for about 70% proton transfer (based on the Bronsted α) would be about 1.02.[8] Since the observed effect is 1.056 for aniline, the isotope effect on the equilibrium formation of the sulfurane intermediate is about $K^D/K^H \simeq 1.035$.

For amide leaving groups, the ground state of the sulfilimine in the pH region examined is the zwitterionic ylide.[11] The mechanism of the reduction by iodide is suggested to involve preequilibrium protonation followed by attack of iodide to give the sulfurane.[1,2] Expulsion of amide anion, with a large amount of anionic character on the nitrogen, is suggested to be rate-limiting.[2,4] The isotope effect on the preequilibrium protonation of the ylide will be larger than the effect on sulfurane protonation and can be estimated to be comparable to the effects observed for the ionization of CL_3COOH ($K_a^D/K_a^H = 1.020/d$).[10] The effect on the d_6 compounds used here is then estimated to be about 1.12. The combined isotope effect on the formation of the sulfurane intermediate and its breakdown in a very late transition state[2] will about cancel with the largest residual effect being observed for the most stable amide anion (the sulfonamides). The ordering is consistent with the data in Table I, although it is unlikely that transition state variability is sufficient to account for the low effect observed for benzamide (1.09). This most likely reflects a smaller isotope effect on the preequilibrium protonation step, possibly because of protonation occurring on the amide oxygen in this compound.[12]

The most important conclusion from these data is that the isotope effect on sulfurane formation seems to be quite small. A reasonable model for the isotope effect expected for addition of an anionic nucleophile to tricoordinate sulfur to give a tetracoordinate addition compound is the addition of sulfite anion to acetone. In the addition direction, the observed value is $K^D/K^H = 1.29$.[13] Using the value of K_a^D/K_a^H of 1.026, as above, for the isotope effect on protonation of the anionic addition product, the isotope effect on the actual addition step is about $k^D/k^H = 1.27$. Although there is some disagreement, the origin of this large effect is generally attributed to hyperconjugation between the methyl groups and the carbonyl carbon.[8,14]

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A similar mechanism of hyperconjugation can also be suggested for the dimethylsulfilimines used in the present study. In the sulfonium ground state, hyperconjugation can occur by overlap between the methyl p orbitals and the low-lying d orbitals on the sulfur. The importance of this hyperconjugation is a simple measure of the energetic feasibility of this p–d overlap. Since it is very unlikely that the overlap intergrals for the tetrahedral sulfonium and bipyramidal sulfurane ground states would be identical, the observation of the small isotope effect for sulfurane formation strongly suggests that such hyperconjugative overlap is of little importance in sulfonium compounds.

Further support for this conclusion can be found in the very nature of the sulfilimine ground state, as measured by X-ray crystallography. For the cyclic sulfilimine, dehydromethionine,[15] the sulfilimine nitrogen is clearly tetrahedral in spite of the possibility of p–d overlap with the adjacent sulfonium center. Results from other sulfilimines are comparable.[1]

Another measure of the ability of sulfur d orbitals to overlap with adjacent π-systems is the magnitude of the "resonance contribution" to equilibrium ionization of thiophenols, relative to phenols. The resonance component of the Hammett ρ for the ionization equilibrium can be obtained from the dual parameter equation $\log (k/k_0) = [\sigma^n + (\rho^r/\rho)(\sigma^- - \sigma^n)]$ as described by Yukawa[16] and others.[17] Using this approach, the ratio ρ^r/ρ is 0.5 for thiophenols ($\rho = -1.87$; $\rho^r = -0.94$)[18] and 1.0 for phenols (by definition of the σ^- scale). This again indicates that overlap, even from a thiolate anion, with an adjacent carbon π-system is not energetically favorable.

If formal p–d overlap does not provide significant stabilization in these systems, the observed stabilization of carbanions adjacent to thioether or sulfonyl linkages most likely originates from d orbital polarization effects.[19,20]

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Registry No. $(D_3C)_2S{=}NC_6H_5$, 104241-56-7; 3-$(D_3C)_2S{=}NC_6H_4Cl$, 104241-57-8; $(D_3C)_2S{=}NCOC_6H_5$, 104241-58-9; $(D_3C)_2S{=}NSO_2C_6H_5$, 104241-59-0; 4-$(D_3C)_2S{=}NC_6H_4Cl$, 104241-60-3; I_2^-, 12190-71-5; D_2, 7782-39-0.

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Communications

A Selective Method for the Synthesis of Stereodefined Exocyclic Alkenes via Allylmetalation of Propargyl Alcohols[1]

Summary: A potentially versatile and highly regio- and stereoselective method for preparing exocyclic alkenes involving the use of 2-allyl-substituted allylic alcohols 1 as key intermediates is described.

Sir: Despite advances over the past several years, highly selective synthesis of stereodefined exocyclic alkenes remains one of the underdeveloped areas in organic synthesis. In particular, procedures that are versatile and permit highly stereoselective (≥98%) synthesis of either *E* or *Z* isomers in high yields are scarce. Since a large number of natural and unnatural exocyclic alkenes of biological and medicinal importance, such as prostacyclin,[3a] carbacyclin,[3b] zoapatanol,[3c] pumiliotoxins,[3d] and fusidic acid,[3e] demand stereoselective methods for their satisfactory synthesis, development of such methods is highly desirable. In the past, exocyclic alkenes containing vinyl ethers and ω-alkylidene lactones have been prepared by cyclization via addition–elimination of stereodefined alkenes,[4a-c] stereoselective addition to alkynes,[4d-f] and epoxysilane opening–elimination.[4g] In cases where the exocyclic alkene moiety contains only H and C substituents, reactions of stereodefined alkenylsilanes[5a-e] and alkenylcoppers[5f] with carbon electrophiles have been successfully employed, although their applicability is still very limited. Also promising is partial hydrogenation of vinylcycloalkenes.[6] Controlling the stereochemistry of cyclic carbometalation has been generally difficult, although a few moderately successful examples[7] are known. Transition-

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