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β-Halo-α,*β*-unsaturated *γ*-Sultones

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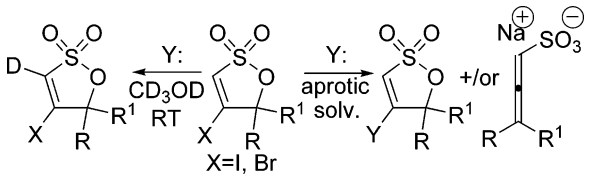

The reaction of *β*-iodo-α,*β*-unsaturated *γ*-sultones (i.e., 4-halo-1,2-oxathiole 2,2-dioxides) in aprotic polar solvents such as DMSO or acetone, with 'soft' nucleophiles such as iodide or thioacetate, yields an allenesulfonate by a very facile halophilic ring-opening E_2-elimination. The 'harder' nucleophile, azide ion, reacts under the same conditions to yield the corresponding *β*-azido-α,*β*-unsaturated *γ*-sultone (i.e., 4-azido-1,2-oxathiole 2,2-dioxide), displacing the *β*-halide by an addition−elimination mechanism. In contrast, in the hydroxylic solvent CD_3OD at ambient temperature, various nucleophiles yield neither of the above-mentioned products, but catalyze a rapid replacement of the C_α-H by deuterium. Factors underlying this intriguing rapid exchange are proposed. Interestingly, the *β*-bromo analogue exhibits similar reactivity except for the halophilic ring-opening. Calculations indicate the relative importance of the *β*-halogen and the S−O(−C) bonds in enhancing the acidity of the H-C_α-$S(O)_2$- grouping.

Introduction

In a recent and in previous communications, we reported on methods for the preparation of α,*β*-unsaturated *γ*-sultines and their *β*-bromo (**1**, X = Br) and *β*-iodo (**2**, X = I) derivatives from allenesulfinate (**3**) and allenethiosulfinate (**4**) esters.[1a,c−g] These esters were accessed via [2,3]-sigmatropic rearrangements of dipropargyl sulfoxylates (**5**)[1a,c−g] and of the novel propargyloxy allyl disulfides (**6**),[1b] respectively (Scheme 1).

The α,*β*-unsaturated *γ*-sultines are of interest, inter alia, because of their possible biological activity, since they are sulfur analogues of *γ*-butenolides.[2] The same may be said of α,*β*-unsaturated *γ*-sultones (**7**), which are available by oxidation of the corresponding sultines (Scheme 2). Though there is recent chemical literature on *γ*-sultones in general,[3] there is a relative dearth of information on the reactivity of α,*β*-unsaturated *γ*-sultones, and particularly of *β*-halo-substituted representatives of this family. We therefore embarked on a systematic study of their chemistry, and herein, we report some intriguing findings.

Our initial expectation was that a variety of *β*-substituents might be introduced into the structure by nucleophilic displacement of the *β*-halogen of the *β*-bromo- or *β*-iodo-α,*β*-unsaturated *γ*-sultone via an addition−elimination mechanism (Scheme 2). Consequently, our investigations commenced in that direction. In the event, it was discovered that the loci and products of the reactions of the title compounds with nucleophiles were highly sensitive to the solvent and to the nature of the nucleophile.[1f,g]

Results and Discussion

The sultones used in this investigation were obtained by oxidation of the corresponding sultines with *m*-chloroperbenzoic acid in CH_2Cl_2 solution. The sultines were prepared by one of the paths reported previously (Scheme 1).[1a, c−g] The substitution pattern of the various compounds and their designations are shown in Table 1. The sultones listed in Table 2 were reacted in d_6-DMSO or in d_6-acetone solution with the specified nucleophiles under the stated conditions. The reactions were

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(1) (a) Braverman, S.; Pechenick, T.; Sprecher, M. *J. Org. Chem.* **2006**, *71*, 2147−2150. (b) Braverman, S.; Pechenick, T.; Gottlieb, H. E.; Sprecher, M. *Tetrahedron Lett.* **2004**, *45*, 8235−8238. (c) Braverman, S.; Reisman, D. *J. Am. Chem. Soc.* **1977**, *99*, 605−607. (d) Braverman, S.; Reisman, D. *Tetrahedron Lett.* **1977**, *20*, 1753−1756. (e) Braverman, S.; Duar, Y. *J. Am. Chem. Soc.* **1983**, *105*, 1061−1063.(f) Braverman, S.; Pechenick-Azizi, T.; Sprecher, M. 1st European Chemistry Congress, Budapest, Hungary, Aug. 27−31, 2006, abstract, p 308. (g) Braverman, S.; Pechenick-Azizi, T.; Sprecher, M. 18th Conference on Physical Organic Chemistry, Warsaw, Poland, Aug. 20−25, 2006, abstract, p 39.

(2) Ma, S.; Shi, Z. *J. Org. Chem.* **1998**, *63*, 6387−6389.

(3) For example, Enders, D.; Harnying, W.; Raabe, G. *Synthesis* **2004**, 590−594.

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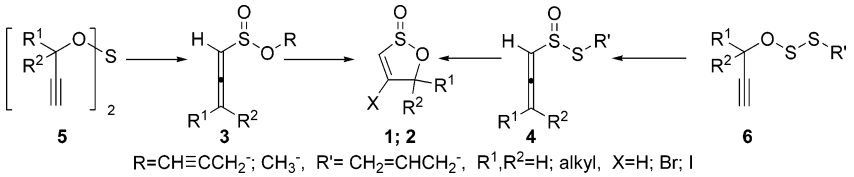
SCHEME 1



SCHEME 2

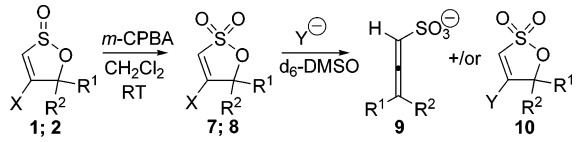


TABLE 1. Designation of *γ*-substituents of 1 (X = Br), 2 (X = I), 3, 7 (X = Br), 8 (X = I), 9, 10 (Y = N_3), and 11 (X = H)

	R^1	R^2
a	H	H
b	H	CH_3
c	CH_3	CH_3
d	$-(CH_2)_5-$	
e	H	Ph

monitored by NMR spectroscopy and, unless otherwise stated, were allowed to proceed until the starting sultone was completely converted to product. In cases in which a defined product was obtained (lines 1−8), the only product formed (and isolated) was the corresponding allenesulfonate salt (**9**), resulting from a ring-opening halophilic 1,2-elimination reaction (Scheme 2). Such reaction was observed only with *β*-iodo sultones and not with a *β*-bromo sultone (line 13).

Such elimination reactions are well-known,[4] and these particular examples are noteworthy only for the mild conditions under which they occur. Presumably, the combination of the preexistence of the anti-periplanar location of the vicinal iodide and sulfonate ester functions, the propensity of the sulfonate anion to act as a leaving group, and the release of ring strain results in a facile E_2-type elimination involving a 'soft−soft' interaction. The formation of I_2 in this reaction is evidenced by the appearance of iodine color which is discharged upon addition of $Na_2S_2O_3$ solution. The elimination is very rapid in the case of sultone **8e** (Table 2, lines 6 and 7), in which the *γ*-carbon is benzylic, and is faster in the cases of **8c** (line 4) and **8d** (line 5) in which the *γ*-carbon is tertiary, than in the case of **8b** (lines 1−3), in which it is secondary. However, such a comparison of rates must take into account that, in the reactions of the three mentioned *γ*-alkyl-substituted sultones with NaI, the presence of 25 equiv of the latter were found necessary to drive (and 'pull', by I_3^- formation) the elimination to completion. This indicated that the halophilic elimination was reversible, a conclusion which was confirmed by the finding that the addition of I_2 (25 equiv) + NaI (25 equiv) to a DMSO solution of the 3,3-dimethylallenesulfonate salt **9c** at ambient temperature converted it quantitatively to the iodo sultone **8c**.

The nucleophilic displacement of the *β*-halogen, a carbophilic reaction, was achieved in d_6-DMSO at ambient temperature only with the 'harder' nucleophile, azide ion.[5] The reaction is illustrated in Scheme 3, and the findings are summarized in Table 3.

Thus, the four *β*-halo-α,*β*-unsaturated *γ*-sultones, **7b**, **7c**, **8a**, and **8b**, were each quantitatively converted to the corresponding *β*-azido-α,*β*-unsaturated *γ*-sultones **10b**, **10c**, **10a**, and **10b**, respectively, under the conditions and in the times stated. The fact that the bromo sultone **7b** reacted about twice as fast as the iodo sultone **8b** ($t_{1/2}$ 15 vs 29 min) suggests that the reaction proceeds via an addition−elimination mechanism in which the first step is rate-determining. In the reaction of the *β*-iodo *γ*-sultone **8c**, dimethyl substituted on C-*γ*, the halophilic *β*-elimination competed with the nucleophilic displacement (Table 3, lines 5). Relating to the rate of displacement only, the bromo compound **7c** reacted approximately 120 times as fast as the corresponding iodo compound **8c**, in agreement with the aforementioned conclusion as to mechanism. Steric hindrance to approach to the *β*-carbon is presumably responsible for the fact that nucleophilic displacement on the *γ*,*γ*-dimethyl sultone is significantly slower than on the *γ*-monoalkyl sultones.

Reaction of *β*-Halo-α,*β*-unsaturated *γ*-Sultones with Nucleophiles in Methanol. Our most surprising finding, at first sight, was when we reacted the iodo and the bromo sultones with nucleophiles in CD_3OD solution at ambient temperature. Under these conditions, neither carbophilic nucleophilic displacement of the halide nor halophilic *β*-elimination occurred (except in one case; Table 4, line 16). Rather, a complete exchange of the α-hydrogen of the sultones for deuterium took place. In some cases, this exchange was extremely rapid, though the nucleophiles involved are very weak bases. The data are summarized in Table 4. Be it noted that the *γ*-phenyl sultone, **8e**, exchanged its α-hydrogen, but not its benzylic hydrogen, though it is also vinylogously α to the sulfonate function (line 17). In control experiments (CD_3OD, NaN_3 2 equiv, room temperature), it was found that neither the sultine **2b** (corresponding to sultone **8b)**, the sodium allenesulfonate salts (**9**), nor divinyl sulfone suffered H−D exchange.

It is well-known, and rationalized in terms of solvation and hydrogen bonding, that nucleophilicity is significantly attenuated in going from an aprotic solvent to a hydroxylic one. However, the same is true for basicity, which, in its kinetic aspect relevant in the current context, may be viewed as nucleophilic attack on H.[6] The drastic change of reaction type observed in the present context was therefore unexpected. Implicit in the foregoing statements is the assumption that the observed H−D exchange with the solvent proceeds in a simple and direct manner by proton/deuteron transfers, starting with deprotonation (carbanion formation) at the α-carbon of the sultone by the nucleophile (= base) in question (Scheme 4). However, a priori, two other pathways may be considered for the exchange. One possibility is a Michael type addition of the nucleophile to the *β*-carbon, producing an α-carbanion which takes up a deuteron from the solvent and then yields its proton to a base, thereby reverting

(4) Zefirov, N. S.; Makhon'kov, D. I. *Chem. Rev.* **1982**, *82*, 615−624.
(5) (a) Tse-Lok Ho *Chem. Rev.* **1975**, *75*, 1−20. (b) *Advanced Organic Chemistry, Part A. Structure and Mechanisms*, 4th ed.; Carey, F. A., Sundberg, R. J., Eds.; Kluwer Academic, New York, 2000; Chapter 5.

(6) (a) Pearson, R. G.; Dillon, R. L. *J. Am. Chem. Soc.* **1953**, *75*, 2439−2443.(b) Gordon, A. J.; Ford, R. A. *A Chemist's Companion. A. Handbook of Practical Data, Techniques, and References*; Wiley-Interscince: New York, 1972. (c) Bordwell, F. G.; Imes, R. H.; Steiner, E. C. *J. Am. Chem. Soc.* **1967**, *89*, 3905−3906.

TABLE 2. Conversion of β-Iodo γ-Sultones (8)[a] to Allenesulfonates (9)

	sultone	nucleophile	*T*, °C; solvent	time	product
1	**8b**	NaI 25 equiv	56 °C; DMSO	2 days	**9b**
2	**8b**	NaCN 2 equiv	RT; DMSO	~2 h	**9b**
3	**8b**	$CH_3C(O)SK$ 2 equiv	RT; DMSO	1 h	**9b**
4	**8c**	NaI 25 equiv	RT; DMSO	3.5 h	**9c**[b]
			RT; acetone	≤3.5 h	
5	**8d**	NaI 25 equiv	RT; DMSO	3 h	**9d**[b]
			RT; acetone	≤3 h	
6	**8e**	NaI 3 equiv	RT; DMSO	≤1 min	**9e**[b]
			RT; acetone	≤1 min	
7	**8e**	NaBr 5 equiv	RT; DMSO	≤1 min	**9e**
8	**8e**	NaN_3 2 equiv	RT; DMSO	1h 20 min	**9e**, subsequent decomposition
9	**8b**	KSCN 2 equiv	RT; DMSO	after18 h	no reaction
10	**8b**	$NaNO_2$ 2 equiv	RT; DMSO	after 2 h	no reaction
11	**8b**	Na_2S 1 equiv	RT; DMSO	<3 h	decomposition
12	**8c**	KSCN 2 equiv	RT; DMSO	after 5 days	no reaction
13	**7c**	NaI 25 equiv	RT; DMSO		decomposition

[a] The sultone concentration was ~0.05 ± 0.01 M. [b] The pure sodium allenesulfonate salts precipitated from the acetone solutions in quantitative yield.

SCHEME 3

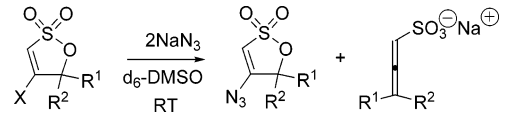
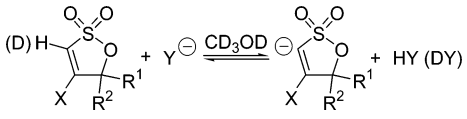


TABLE 3. Reaction of the β-Halo γ-Sultones[a] with NaN_3 (2 equiv) in DMSO

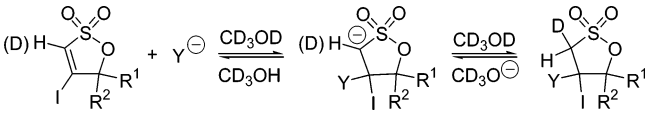
	β-halo γ-sultone	time (RT)	product (% yield)[b]
1	**7b**	1 h	**10b** (100)
2	**7c**	4 h	**10c** (100)
3	**8a**	1 h	**10a** (100)
4	**8b**	2 h	**10b** (100)
5	**8c**	12 days	**10c** (61) + **9c** (27) + **8c** (12)

[a] The sultone concentration was ~0.06 ± 0.01 M. [b] Products were isolated, and mixtures were separated.

SCHEME 4



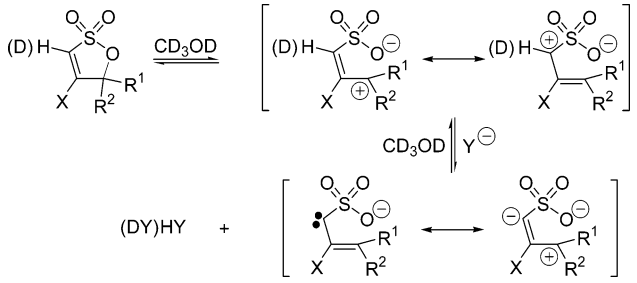
SCHEME 5



to a carbanion which expels the nucleophile at C_β (Scheme 5). However, such a pathway seems most unlikely. One of the two intermediate α-carbanions would be expected to expel the β-iodide, which is a much better leaving group than the added nucleophile (other than iodide). In fact, no displacement of the iodide was observed.

Another possibility might be ionization of the sulfonate function at C_γ to yield a zwitterion, whose cation moiety is an allyl carbenium ion. Deprotonation of the latter at C_α would produce an allyl carbene. Capture of a deuteron at C_α and collapse of the zwitterion at C_γ would complete the exchange process (Scheme 6). This mechanism also appears not to be operative, since one would certainly expect capture of the intermediate allyl carbenion species by the methanol solvent

SCHEME 6



(i.e., an SN_1 reaction), but no such solvolysis product is observed. Furthermore, assuming reasonably that in such a mechanism the ionization step would be rate-determining, the higher reactivity of the bromo derivatives as compared to the iodo ones, as well as the lack of exchange at ambient temperature of the α,β-unsaturated-γ,γ-dimethyl γ-sultone lacking a β iodine, **11c**, (Table 4, line 18), would seem incongruent.

The influence of C_γ alkyl substitution on the C_α−H exchange reaction is shown by comparison of the entries on lines 8, 11, and 15 in Table 4. Whereas the unsubstituted (**8a**) and the dimethyl-substituted (**8c**) β-iodo γ-sultones fully exchange C_α−H under acetate ion catalysis in 5 min, the reaction time for the monomethyl derivative (**8b**) is 1.5 h. The higher activation energy upon monomethyl substitution may be the result of an inductive effect and/or steric inhibition to solvation, while the reduction of the activation energy in the *gem*-dimethyl derivative **8c** is possibly a manifestation of an Ingold−Thorpe effect, since the formation of the anion is accompanied by changes in the ring angles. Interestingly, in the reaction of the 'soft' thioacetate nucleophile with **8c**, the halophilic elimination to give a fully substituted double bond preempts H−D exchange even in methanol solution (line 16, Table 4).

Reverting to the consideration of the simple overall C_α deprotonation−protonation mechanism (Scheme 4), without going into the details of possible hydrogen-bonded intermediate complexes, it must be recalled that, in contrast to the findings for $-CHNO_2$ groupings, proton transfer from $-CH-SO_2-$ is close to 'normal' in terms of the Eigen classification.[7] In an isoergonic reaction, it occurs with a rate constant within 2 orders of magnitude of diffusion control. This has been taken as

(7) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1−19.

TABLE 4. H−D Exchange of the γ-Sultones in CD_3OD

	γ-sultone (0.05 ± 0.01 M)	base[a]	$t_{1/2}$ (min) at ambient temperature	approximate k_2 (M^{-1} s^{-1})
1	**7b**	NaN_3, 2 equiv	≪1	
2	**7b**	NaN_3, 0.05 equiv	7.7	0.6
3	**7b**	$CH_3C(O)ONa$, 2 equiv	≪1	
4	**7b**	$CH_3C(O)SK$, 2 equiv	∼6	
5	**7c**	NaN_3, 2 equiv	≪1	
6	**7c**	$CH_3C(O)SK$, 2 equiv	∼1	
7	**8a**	NaN_3, 2 equiv	≪1	
8	**8a**	$CH_3C(O)$ ONa, 2 equiv	∼1	
9	**8b**	NaN_3, 2 equiv	≪1	
10	**8b**	Et_3N, 2 equiv	≪1	
11	**8b**	$CH_3C(O)$ ONa, 2 equiv	11.6	0.01
12	**8b**	$CH_3C(O)SK$, 2 equiv	58	0.002
13	**8b**	NaI, 2 equiv	115	0.001
14	**8c**	NaN_3, 2 equiv	≪1	
15	**8c**	$CH_3C(O)$ ONa, 2 equiv	∼1	
16	**8c**	$CH_3C(O)SK$, 2 equiv	∼25; only allenesulfonate formed; no H−D exchange	
17	**8e**	NaN_3, 2 equiv	≪1	
18	**11c**	NaN_3, 2 equiv	∼2300; 55 °C; No reaction at RT	

[a] The pK_a values in water at 25 °C for the conjugate acids of the bases are −5.2 for HI, 4.68 for HN_3, 3.33 for $CH_3C(O)SH$, 4.74 for $CH_3C(O)OH$, and 11.01 (at 18 °C) for Et_3NH^+. The pK_a value for MeOH is 15.5.

evidence that stabilization of a carbanion α to a SO_2 function is primarily electrostatic, and its formation involves little structural change due to charge delocalization. Alternatively, in terms of the Bernasconi formulation,[8] the carbanion stabilization in the transition state does not lag significantly behind the proton transfer. Though the intrinsic barrier to proton transfer from a $-CH-SO_2-$ group is, as indicated, very low, yet in an endergonic process of this type, the specific rate constant is reduced by a factor of $10^{\Delta pK_a}$, where ΔpK_a is the difference between the pK_a's of the conjugate acids of the bases between which the proton transfer is taking place,[7] and modified by the value of the relevant Brønsted coefficient.[9] Relating to the acidity scale in water, the pK_a of sulfones lacking additional activating groups is reported to be about 23,[6c] while that of hydrazoic acid and acetic acid (at 25 °C) is 4.59 and 4.76, respectively,[10] Though our observations are for methanol solution, it is abundantly clear that the rates of proton exchange found for compounds **7** and **8** are many orders of magnitude greater than those expected for simple sulfones. In fact, experimental findings for sulfones in methanol solution confirming this conclusion have been reported in the literature. Thus, 2-octyl-2-*d* phenyl sulfone in methanol at 100.6 °C in the presence of *methoxide* as base (pK_a of methanol = 15.5) exchanged its isotope with the second-order specific rate constant, $k_2 = 7.62 \times 10^{-4}$ M^{-1} s^{-1}.[11] The authors estimated that at 25 °C $k_2 \approx 3 \times 10^{-7}$ M^{-1} s^{-1}. Similarly, for 2-methyl-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide in CH_3OD solution in the presence of *methoxide* at 75.1 °C, k_2 of proton exchange is 1.79×10^{-4} M^{-1} s^{-1}.[12]

Clearly, compounds **7** and **8** possess structural features which contribute to the stabilization of the C_α-carbanion, and consequently the acidity of the $C_\alpha-H$, above and beyond the stabilization afforded by an $-SO_2-$ group, to an extent that very weak bases are capable of abstracting that proton and cause its rapid exchange. These features are the following. (1) C_α is trigonal and a $C(sp_2)$-H is more acidic than a $C(sp_3)$-H by more than 5 pK_a units. (2) It has been determined that the most stable conformation of a carbanion α to an SO_2 grouping is one in which the 'anion orbital' bisects the OSO angle.[13] In the present case, the $C_\alpha-H$ is already located in that position, and its abstraction does not involve significant conformational adjustment or restriction. (3) Compounds **7** and **8** are sultones, that is, sulfonate esters, rather than sulfones, and from the Table presented by Bordwell,[10b] it appears that $C_\alpha-H$ in a linear sulfonate esters is some 2−3.5 pK_a units more acidic on the DMSO scale than that in the analogous sulfone. In the present cases of the α,β-unsaturated five-membered ring sultones, the $C_\alpha-H$ and the S−O(−C) bonds of the sultones are fixed antiperiplanar to each other. The C_σ anion would therefore be expected to be stabilized by $sp_{2(C)}-\sigma^*_{(S-O)}$ overlap, in addition to the inductive effect of the third oxygen.[14] (4) The $C_\alpha-H$ and $C_\beta-X$ bonds are coplanar. The vicinal halogen is therefore expected to enhance $C_\alpha-H$ acidity by stabilization of the resultant C_α-carbanion by $sp_{2(C)}-\sigma^*_{(C-X)}$ overlap and by an inductive effect.[15] In fact, the more electronegative $C_\beta-Br$ is more effective than $C_\beta-I$ in enhancing the proton exchange (compare Table 4, lines 3 and 4 with lines 11 and 12).

It appears that it is the addition of all four effects to the ability of an $-SO_2-$ function to stabilize an α-carbanion which permits the observed proton exchange under the mild conditions described. Thus, as mentioned above, in the absence of a C_β halogen, **11c**, there is no exchange at ambient temperature. Neither does the γ-sultine **2b** show exchange under said conditions.

(8) (a) Bernasconi, C. F. *Acc. Chem. Res.* **198**7, *20*, 301−308. (b) Bernasconi, C. F. *Acc. Chem. Res.* **1992**, *25*, 9−16.

(9) Unknown, but probably in the region 0.85 ± 0.05; compare Bordwell, F. G.; Boyle, W. J.; Hautala, J. A.; Yee, K. C. *J. Am. Chem. Soc.* **1969**, *91*, 4002−4003, footnote 5.

(10) (a) On the DMSO scale, Bordwell[6] reports a pK_a value of 28.5 for dimethyl sulfone and of >31 for tetrahydrothiophene 1,1-dioxide, while Bordwell,[10b] quotes a value of 31.1 for dimethyl sulfone. The value for acetic acid is given as 12.3. (b) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456−463.

(11) Cram, D. J.; Scott, D. A.; Nielsen, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 8696−8707.

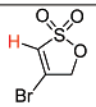
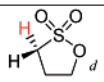
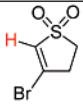
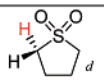
(12) Cram, D. J.; Roitman, J. N. *J. Am. Chem. Soc.* **1971**, *93*, 2225−2231.

(13) Cram, D. J. *Fundamental of Carbanion Chemistry (Organic Chemistry, Vol. 4*); Academic Press: New York, 1965; Chapter II.

(14) The two effects are of course interrelated.

(15) As for effect 3.

TABLE 5. Relative Proton Affinity (PA), Gas-Phase Basicity (GB), and Relative Protonation Free Energy in Methanol Solution (kcal/mol)

		ΔPA[a]	ΔGB[b]	ΔΔG[sol c]
No	**Compound Structure**	**mPW1PW91/6-311++ G(3df,2pd)**	**mPW1PW91/6-311++ G(3df,2pd)**	**PW1/DND**
7a		0.0	0.0	0.0
11a		11.6	13.4	10.4
12		19.0	20.5	16.3
13		7.8	8.2	5.1
14		20.4	21.3	13.8
15		26.6	28.3	21.3
16	Dimethyl sulfone	21.2	22.7	15.0

[a] PA = $-\Delta H_{prot}$. [b] GB = $-\Delta G_{prot}$. [c] Gas-phase − mPW1PW91/6-311++G(3df,2p)//mPW1PW91/6-31+G(d) and Cosmo continuum model (Methanol) with PW1/DND at PW1/DND gas-phase geometry. [d] Single conformation only.

To investigate the inherent (free of solvation effects) relative contributions of the above-mentioned factors to the stabilization of the α-carbanion, we turned to theoretical calculations. As reference point, we took the α-carbanion of the β-bromo γ-sultone **7a** and calculated the relative proton affinity (PA = $-\Delta H_{protonation}$) and gas-phase basicity (GB = $-\Delta G_{protonation}$) of the α-carbanions of the molecules listed in Table 5. All geometries were optimized employing the mPW91PW91 density functional with the 6-31+G(d) basis set. When these optimized geometries were used, single-point energy calculations were performed at the mPW91PW91/6-311++G(3df,2p)//mPW91PW91/6-31+G(d) level. All gas-phase calculations employed the Gaussian 03 program. The last column in Table 5 presents the calculated relative $-\Delta G$ of protonation in solution of dielectric constant 32.6, corresponding to methanol, using the COSMO continuum model (Accelrys Inc). Additional details of calculations, as well as coordinates for the neutral molecules and their anions are to be found in the Supporting Information. Calculations for dimethyl sulfone (**16**) are included in Table 5 for the purpose of "order of magnitude" comparison, as its pK_a in DMSO has been reported as 31.1.[10b]

Referring to the gas-phase data for the cyclic molecules in Table 5, the combined effect of factors (1) and (2) above is expressed by the difference [ΔGB(**12**) − ΔGB(**11a**)] = 7.1 kcal/mol, and by the difference [ΔGB(**15**) − ΔGB(**14**)] = 7.0 kcal/mol. In the anions of both **12** and **15**, the C_α has a distorted tetrahedral geometry, and the remaining C_α−H is out of 'the plane' of the ring, positioning the 'anion orbital' staggered between the O−S−O bonds.[16] Effect (3) finds expression in the differences [ΔGB(**13**) − ΔGB(**7a**)] = 8.2 kcal/mol, [ΔGB(**14**) − ΔGB(**11a**)] = 7.9 kcal/mol, and [ΔGB(**15**) − ΔGB(**12**)] = 7.8 kcal/mol. Effect (4), the contribution of a β-halogen, exemplified by that of the β-bromine, is given by [ΔGB(**11a**) − ΔGB(**7a**)] = 13.4 kcal/mol and by [ΔGB(**14**) − ΔGB(**13**)] = 13.1 kcal/mol. The near equality of the free energy values attributable to each one of the effects, even though arrived at from the comparison of different molecules, is impressive. Even more so is the near additivity of these values. Effects (1) + (2) + (3) are represented by [ΔGB(**15**) − ΔGB(**11a**)] = 14.9 kcal/mol, while addition (7.0/7.1 + 8.2/7.9/7.8) yields a value of 14.8−15.3 kcal/mol. For effect (1) + (2) + (4), represented by [ΔGB(**12**) − ΔGB(**7a**)] = 20.5 kcal/mol or [ΔGB(**15**) − ΔGB(**13**)] = 20.1 kcal/mol, addition (7.0/7.1 + 13.1/13.4) gives 20.1−20.5 kcal/mol. The combination of effects (3) + (4) is available from [ΔGB(**14**) − ΔGB(**7a**)] = 21.3 kcal/mol, while addition (8.2/7.9/7.8 + 13.1/13.4) leads to 20.9−21.6 kcal/mol. The sum of all four effects is given by [ΔGB(**15**) − ΔGB(**7a**)] = 28.3 kcal/mol, and addition (7.0/7.1 + 8.2/7.9/7.8 + 13.1/13.4) gives the range of 27.9−28.7 kcal/mol. It seems intuitively

(16) For **12**, the angles are (S−Cα−H) = 106.25°, (Cβ−Cα−H) = 112.79°. The torsional angles are (O−S−Cα−H) = 92.37°, (Cγ−Cβ−Cα−H) = −74.14°, (O′−S−Cα−H) = −20.98° (*O′*-sulfonyl oxygen), (O″−S−Cα−H) = −160.75° (*O″*-sulfonyl oxygen). For **15**, the angles are (S−Cα−H) = 107.14°, (Cβ−Cα−H) = 113.26°. The torsional angles are (Cδ−S−Cα−H) = 94.30°, (Cγ−Cβ−Cα−H) = −73.22°, (O′−S−Cα−H) = −21.80° (*O′*-sulfonyl oxygen), (O″−S−Cα−H) = −157.26° (*O″*-sulfonyl oxygen).

TABLE 6. Changes in Bond Lengths upon α-Carbanion Formation (Å)[a]

bond	7a	11a	12	bond	13	14	15
S−C_α	−0.030	−0.022	−0.129	S−C_α	−0.031	−0.019	−0.117
C_α−C_β	+0.002	+0.021	−0.012	C_α−C_β	0.000	+0.020	−0.011
C_β−C_γ	+0.012	+0.021	+0.022	C_β−C_γ	+0.014	+0.026	+0.027
C_γ−O	−0.012	−0.015	−0.021	C_γ−C_δ	−0.003	−0.007	+0.002
O−$S(O)_2$	+0.073	+0.080	+0.120	C_δ−$S(O)_2$	+0.034	+0.035	+0.052
S−O	+0.017	+0.019	+0.023	S−O	+0.016	+0.019	+0.022
sulfonyl	+0.017	+0.019	+0.019	sulfonyl	+0.018	+0.021	+0.022
C_β−Br	+0.070			C_β−Br	+0.080		

[a] For **16**, Δ S−C_α = −0.126 Å; Δ S−$C_{\alpha'}$ = +0.048 Å; Δ S−O = +0.026 Å.

reasonable that such additivity is evidence for a high degree of charge localization and would not pertain if the negative charge were highly delocalized into the $-SO_2-$ grouping. In any case, it is clear that of the four effects postulated above, it is the anion stabilizing effect of the vicinal halogen which is the dominant one.

The assumptions inherent in the solvation energy calculations make even relative values much less reliable than those of gas-phase calculations, especially in case of hydrogen-bonding solvents such as methanol. However, they remain informative. In the present case, the free energies of solvation of the neutral molecules in Table 5 all lie within the range of −11.3 (for **7a**) to −12.7 kcal/mol (for **11a**), while for the anions, the values range from −57.8 (for **7a** anion) to −66.6 kcal/mol (for **14** anion), as detailed in the Supporting Information (Table S2). The derived free energies of protonation in methanol solution listed in column 5 of Table 5 may be analyzed with regard to the contributions of the above-mentioned effects to anion stability, in the manner done for the gas-phase data. Not surprisingly, the values derived for a particular effect from two pairs of compounds are less precise varying by up to 1.7 kcal/mol. Thus, for factors (1) + (2), [$\Delta\Delta G^{sol}$(**12**) − $\Delta\Delta G^{sol}$(**11a**)] = 5.9 kcal/mol, while [$\Delta\Delta G^{sol}$(**15**) − $\Delta\Delta G^{sol}$(**14**)] = 7.5 kcal/mol. For effect (3), [$\Delta\Delta G^{sol}$(**13**) − $\Delta\Delta G^{sol}$(**7a**)] = 5.1 kcal/mol, [$\Delta\Delta G^{sol}$(**14**) − $\Delta\Delta G^{sol}$(**11a**)] = 3.4 kcal/mol, and [$\Delta\Delta G^{sol}$(**15**) − $\Delta\Delta G^{sol}$(**12**)] = 5.0 kcal/mol. For effect (4), [$\Delta\Delta G^{sol}$(**11a**) − $\Delta\Delta G^{sol}$(**7a**)] = 10.4 kcal/mol and [$\Delta\Delta G^{sol}$(**14**) − $\Delta\Delta G^{sol}$(**13**)] = 8.7 kcal/mol. However, if for each effect an average of its values is taken, near additivity remains. Thus, for effects (1) + (2) + (3), [$\Delta\Delta G^{sol}$(**15**) − $\Delta\Delta G^{sol}$(**11a**)] = 10.9 kcal/mol, while addition of averages gives 11.2 kcal/mol. For effects (1) + (2) + (4), [$\Delta\Delta G^{sol}$(**12**) − $\Delta\Delta G^{sol}$(**7a**)] = 16.3 kcal/mol and [$\Delta\Delta G^{sol}$(**15**) − $\Delta\Delta G^{sol}$ (**13**)] = 16.2 kcal/mol, while addition of averages yields 16.25 kcal/mol. For effects (3) + (4), [$\Delta\Delta G^{sol}$(**14**) − $\Delta\Delta G^{sol}$(**7a**)] = 13.8 kcal/mol, while addition of averages yields 14.05 kcal/mol. The sum of all four effects, given by [ΔGB(**15**) − ΔGB(**7a**)] = 21.3 kcal/mol and addition of averages lead to 20.75 kcal/mol. Predictably, solvation has but little influence on effects (1) + (2), and most influence on effect (3). Though the energy value of effect (4) is reduced, it remains dominant.

As the molecules under consideration are cyclic, a change in one of the geometric parameters of the ring, bond length or angle, necessarily induces a change in some others, and unless the change is large, one cannot be sure if it is of primary significance or if it is a secondary adjustment. Perusing the geometric changes accompanying the conversion of the neutral sultones and sulfones to their α-anions in Table 6, one finds the expected S−C_α bond lengthening to be much greater in the saturated structures, **12** and **15**, where C_α is sp^3 hybridized, than in the unsaturated structures where it is sp^2 hybridized, and in which the ring structure is more inflexible. In keeping with the analysis of the energy data, the other major changes are lengthening of the C_β−Br bonds and the O−$S(O)_2$ and C_δ−$S(O)_2$ bonds.

Experimental Section

General procedure for the preparation of γ-sultines, including characterization data for compounds **2a**−**c** were recently reported by us.[1a]

4-Iodo-1-oxa-2-thiaspiro[4.5]dec-3-ene 2-oxide (2d). (Yield 70%) Was purified by column chromatography using silica gel and hexane/ethyl acetate in the ratio 5:1, respectively, as eluent, and was obtained as a yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.89 (s, 1H), 2.14−1.95 (m, 2H), 1.90−1.82 (m, 1H), 1.81−1.72 (m, 5H), 1.52−1.48 (m, 1H), 1.31−1.17 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.9 (=**C**H−), 116.2 (=**C**−), 103.2 (−**C**−), 36.8 (−**C**H_2−), 35.5 (−**C**H_2−), 24.3 (−**C**H_2−), 21.7 (−**C**H_2−), 21.6 (−**C**H_2−). IR (neat): 1124, 1575, 2936 cm^{-1}. MS (CI/CH_4): *m*/*z* 299 (MH^+, 41%), 250 (6%), 171 (8%), 79 (100%). HRMS (elemental composition): calcd ($C_8H_{12}O_2SI$) 298.9603; found 298.9600.

4-Iodo-5-phenyl-5*H*-1,2-oxathiole 2-oxide (2e). (Yield 54%) The two diastereoisomers were separated by column chromatography using silica gel and hexane/ethyl acetate in the ratio 200:5, respectively, as eluent. The crystals were white needles.

For the first isomer (less polar), mp 105−106 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49−7.40 (m, 5H), 7.07 (d, *J* = 2.1 Hz, 1H), 6.03 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.6 (=**C**H−), 133.7 (=**C**− ipso), 129.8, 130.0, 128.8 (=**C**H−, Ph), 108.6 (=**C**−), 102.0 (−**C**H−). For the second isomer (more polar), mp 117−118 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46−7.42 (m, 3H), 7.27−7.24 (m, 2H), 7.13 (d, *J* = 2.1 Hz, 1H), 6.45 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.9 (=**C**H−), 133.4 (=**C**−, ipso), 130.2, 129.0, 128.2 (=**C**H−, Ph), 109.7 (=**C**−), 99.6 (−**C**H−). For the mixture of isomers, IR (neat): 1123, 1127 1574, 1578 cm^{-1}. MS (CI/CH_4): *m*/*z* 307 (MH^+, 0.8%), 306 (M^+, 0.7%), 258 ($(M-SO)^+$, 2%), 241 (3%). HRMS (elemental composition): calcd ($C_9H_8O_2SI$) 306.9290; found 306.9290.

Oxidation of γ-Sultines to γ-Sultones: General Procedure. To 20 mL of a cooled (0 °C) CH_2Cl_2 solution of the appropriate γ-sultine (5 mmol), a solution of *m*-CPBA (12.5 mmol) in 20 mL of CH_2Cl_2 was added dropwise with stirring. After a further 30 min at 0 °C, the reaction mixture was stirred for 24 h at ambient temperature. The CH_2Cl_2 solution was washed with aqueous solutions of KI/$Na_2S_2O_3$ (3 times), $NaHCO_3$ (3 times), and then with water. After drying ($MgSO_4$) and removal of the solvent, the products were recrystallized from ether or were separated by column chromatography using silica gel with hexane/ethyl acetate as eluent.

γ-Sultones **7b**,[1d] **7c**,[1c,d] and **11c**[1c] were reported previously.

4-Iodo-5*H*-1,2-oxathiole 2,2-dioxide (8a). (Yield 76%) Was obtained as a white solid upon silica gel chromatography, using hexane/ethyl acetate in the ratio 3:1, respectively, as eluent.

Mp 96−98 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12 (t, *J* = 2.1 Hz, 1H), 5.03 (d, *J* = 2.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$):

δ 130.2 (=**C**H−), 102.2 (=**C**−), 78.6 (−**C**H_2−). IR (neat): 1165, 1220, 1354, 1597, 3105 cm^{-1}. MS (CI/CH_4): *m/z* 246 (M^+, 100%), 182 ((M−SO_2)$^+$, 6%), 152 ((I−C≡C−H)$^+$, 33%), 127 (I^+, 27%), 119 ((M−I)$^+$, 55%). HRMS (elemental composition): calcd ($C_3H_3O_3SI$) 245.8848; found 245.8850.

4-Iodo-5-methyl-5*H*-1,2-oxathiole 2,2-dioxide (8b). (Yield 82%) Was obtained as a white solid after recrystallization from cold ether/pentane.

Mp 86−87 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04 (d, J = 2.0 Hz, 1H), 5.27 (qd, J = 7.0, 2.0 Hz, 1H), 1.68 (d, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.1 (=**C**H−), 110.1 (=**C**−), 86.8 (−**C**H−), 20.2 (−**C**H_3). IR (neat): 1165, 1218, 1342, 1591, 3094 cm^{-1}. MS (CI/CH_4): *m/z* 261 (MH^+, 26%), 260 (M^+, 95%), 245 ((M− CH_3)$^+$, 33%), 181 (($C_4H_6I^+$), 11%), 152 ((I−C≡C−H)$^+$, 38%), 133 ((M−I)$^+$, 100%), 127 (I^+, 15%). HRMS (elemental composition): calcd ($C_4H_5O_3SI$) 259.9004; found 259.9004.

4-Iodo-5,5-dimethyl-5*H*-1,2-oxathiole 2,2-dioxide (8c). (Yield 89%) Was obtained as a white solid after recrystallization from cold ether/pentane.

Mp 95−96.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.93 (s, 1H), 1.67 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.2 (=**C**H−), 116.3 (=**C**−), 94.7 (−**C**−), 26.9 (2×(−**C**H_3)). IR (neat): 1151, 1216, 1346, 1591 cm^{-1}. MS (CI/CH_4): *m/z* 274 (MH^+, 42%), 259 ((M− CH_3)$^+$, 100%), 86 (36%), 84 (58%). HRMS (elemental composition): calcd ($C_5H_7O_3SI$) 273.9161; found 273.9159.

4-Iodo-1-oxa-2-thiaspiro[4.5]dec-3-ene 2,2-dioxide (8d). (Yield 78%) Was obtained as a white solid upon silica gel chromatography, using hexane/ethyl acetate in the ratio 5:1, respectively, as eluent, of the cold ether soluble portion of the crude oxidation product.

Mp 114−115 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.95 (s, 1H), 1.99−1.67 (m, 9H), 1.31−1.18 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 130.6 (=**C**H−), 117.0 (=**C**−), 96.5 (−**C**−), 34.6 (−**C**H_2−), 23.9 (−**C**H_2−), 21.3 (−**C**H_2−). IR (neat): 1171, 1223, 1339, 1514 cm^{-1}. MS (CI/CH_4): *m/z* 314 (M^+, 2%), 187 (50%), 139 (100%). HRMS (elemental composition): calcd ($C_8H_{11}O_3SI$) 313.9474; found 313.9459.

4-Iodo-5-phenyl-5*H*-1,2-oxathiole 2,2-dioxide (8e). (Yield 82%) Was obtained as a white crystals after recrystallization from cold ether and washing with pentane.

Mp 149.5−150.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49−7.46 (m, 3H), 7.40−7.37 (m, 2H), 6.18 (d, J = 2.1 Hz, 1H), 6.02 (d, J = 2.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.4 (=**C**− ipso), 130.7 (=**C**H−), 130.7 (=**C**H−), 129.2 (=**C**H−), 128.1 (=**C**H−), 109.6 (=**C**−), 91.4 (−**C**H−). IR (neat): 1160, 1213, 1340, 1646 cm^{-1}. MS (CI/CH_4): *m/z* 322 (M^+, 11%), 241 (39%), 195 (21%), 131 (60%), 115 (100%). HRMS (elemental composition): calcd ($C_9H_7O_3SI$) 321.9161; found 321.9178.

Conversion of β-Iodo γ-Sultones (8) to Allenesulfonates (9). To a solution of the appropriate γ-sultone (~0.05 ± 0.01 M) in d_6-DMSO or d_6-acetone in an NMR tube was added the appropriate nucleophile (Table 2), and the reaction mixture was shaken. After the appropriate time at room temperature (except in one case, **8b** with NaI at 56 °C), determined by ^{1}H NMR, the pure sodium allenesulfonate salts were precipitated from the acetone solutions, washed with d_6-acetone, and dried in the air.

Sodium Buta-1,2-diene-1-sulfonate (9b, R = Na^+ Salt). (Yield 100%).

^{1}H NMR (300 MHz, d_6-DMSO): δ 5.86 (dq, J = 6.0, 3.0 Hz, 1H), 5.33 (qd, J = 7.2, 6.0 Hz, 1H), 1.63 (dd, J = 7.2, 3.0 Hz, 3H). ^{13}C NMR (150 MHz, d_6-DMSO): δ 201.3 (=**C**=), 101.4 (=**C**H−), 89.1 (=**C**H−), 21.1 (−**C**H_3).

Sodium 3-Methylbuta-1,2-diene-1-sulfonate (9c, R = Na^+ Salt). (Yield 100%) Was obtained as a white solid.

^{1}H NMR (600 MHz, CD_3OD): δ 5.94 (septet, J = 2.7 Hz, 1H), 1.79 (d, J = 2.7 Hz, 6H). ^{13}C NMR (150 MHz, CD_3OD): δ 201.2 (=**C**=), 103.4 (=**C**−), 98.5 (=**C**H−), 20.0 (2×(−**C**H_3)). MS (ES^-): *m/z* 147 (M^-, 100%). HRMS FB^- (elemental composition): calcd ($C_5H_7O_3S$) 147.0116; found 147.0121.

Sodium 2-Cyclohexylideneethylenesulfonate (9d, R = Na^+ Salt). (Yield 100%) Was obtained as a white solid.

^{1}H NMR (600 MHz, CD_3OD): δ 5.94 (quint, J = 1.8 Hz, 1H), 2.26−2.21 (m, 4H), 1.75−1.67 (m, 2H), 1.62−1.54 (m, 4H). ^{13}C NMR (150 MHz, CD_3OD): δ 198.1 (=**C**=), 110.3 (=**C**−), 98.3 (=**C**H−), 31.7 (2×(−**C**H_2−)), 28.0 (2×(−**C**H_2−)), 26.9 (−**C**H_2−). MS (ES^-): *m/z* 187 (M^-, 100%). HRMS FB^- (elemental composition): calcd ($C_8H_{11}O_3S$) 187.0429; found 187.0428.

Sodium 3-Phenylallene-1-sulfonate (9e, R = Na^+ Salt). (Yield 100%) Was obtained as a white solid.

^{1}H NMR (300 MHz, CD_3OD): δ 7.39−7.20 (m, 5H), ABq: 6.63 and 6.55 (d, J = 6.3 Hz, 1H each). ^{13}C NMR (75 MHz, CD_3OD): δ 205.3 (=**C**=), 134.0 (=**C**−, ipso), 129.7 (=**C**H−), 128.8 (=**C**H−), 128.5 (=**C**H−) (Ar), 104.0 (=**C**H−), 100.6 (=**C**H−). MS (ES^-): *m/z* 195 (M^-, 100%). HRMS FB^- (elemental composition): calcd ($C_9H_7O_3S$) 195.0116; found 195.0126.

Reaction of β-Halo γ-Sultones with NaN_3 (2 equiv) in DMSO. To a solution of the appropriate γ-sultone (~0.06 ± 0.01 M) in d_6-DMSO in an NMR tube at room temperature, was added sodium azide (2 equiv). The reaction mixture was shaken and kept at room temperature for the appropriate time, determined by ^{1}H NMR (Table 3). Then, methylene chloride was added, and the organic mixture was washed with water 10 times. After drying over anhydrous $MgSO_4$ and removal of the solvent under reduced pressure, the products were isolated and mixtures separated by column chromatography using silica gel with chloroform as eluent.

2,2-Dioxido-5*H*-1,2-oxathiol-4-yl azide (10a). (Yield 100%) Was obtained as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.43 (t, J = 1.8 Hz, 1H), 4.83 (d, J = 1.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.3 (=**C**−), 106.4 (=**C**H−), 69.2 (−**C**H_2−). IR (neat): 1171, 1288, 1347, 1617, 2129, 2164, 3104 cm^{-1}. MS (CI/CH_4): *m/z* 162 (MH^+, 70%), 119 (26%), 104 (100%), 103 (92%), 69 (64%). HRMS (elemental composition): calcd ($C_3H_4N_3O_3S$) 161.9973; found 161.9969.

4-Azido-5-methyl-5*H*-1,2-oxathiole 2,2-dioxide (10b). (Yield 100%) Was obtained as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.39 (d, J = 1.5 Hz, 1H), 5.06 (qd, J = 6.6, 1.5 Hz, 1H), 1.58 (d, J = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.2 (=**C**−), 106.0 (=**C**H−), 78.8 (−**C**H−), 18.5 (−**C**H_3). IR (neat): 1170, 1271, 1344, 1614, 2125, 2158, 3092 cm^{-1}. MS (CI/CH_4): *m/z* 176 (MH^+, 99%), 104 (55%), 84 (100%). HRMS (elemental composition): calcd ($C_4H_6N_3O_3S$) 176.0129; found 176.0130.

4-Azido-5,5-dimethyl-5*H*-1,2-oxathiole 2,2-dioxide (10c). (Yield 100%) Was obtained as a white solid.

Mp 93−94 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.29 (s, 1H), 1.61 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.4 (=**C**−), 105.4 (=**C**H−), 88.3 (−**C**−), 25.5 (2×(−**C**H_3)). IR (neat): 1154, 1248, 1326, 1614, 2150, 3085 cm^{-1}. MS (CI/CH_4): *m/z* 190 (MH^+, 3%), 86 (68%), 84 (100%). HRMS (elemental composition): calcd ($C_5H_8N_3O_3S$) 190.0278; found 190.0286.

H−D Exchange of the γ-Sultones in CD_3OD. To a solution of the appropriate γ-sultone (~0.05 ± 0.01 M) in CD_3OD in an NMR tube at room temperature (except in one case, **11c** at 55 °C) was added the appropriate base (Table 4), and the reaction mixture was shaken. After the appropriate time, determined by ^{1}H NMR, the solvent was removed under reduced pressure, and the products were isolated.

Computational Methods. All species were optimized employing the mPW91PW91 density functional[17] with the 6-31+G(d) basis set.[18] Frequency calculations were performed to analyze the stationary points on the potential energy surface, and these confirmed the location of minimum energy structures. Subsequently, single-point calculations were performed at the mPW91PW91/6-

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311++G(3df,2p)//mPW91PW91/6-31+G(d) level. Zero-point energy and thermal corrections were obtained by employing standard statistical mechanics expressions. These corrections were added to the electronic energy to obtain the proton affinity (PA) and gas-phase basicity (GB) at 298.15 K. All gas-phase calculations employed the Gaussian 03 program.[19]

The effect of solvent was accounted for via single-point calculations within the continuum approximation. Initially, the Polarizable Continuum Model (PCM)[20] was employed with the PBEPBE/6-31+G(d)[21] functional and UAKS (United Atom Kohn−Sham) atomic group radii as implemented in Gaussian 03. Additionally, the COSMO method[22] was employed in conjunction with the PW91PW91 density functional[23] and a double-ζ numerical basis set with *d*-functions (DND) as implemented in the DMol[3] program (Accelrys Inc).[24] A dielectric constant corresponding to methanol was employed (32.6). Both methods gave similar results.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra for all new compounds (**2d**,**e**, **8a**−**e**, **9b**−**e**, **10a**−**c**). Spectral data and ^{1}H NMR spectra for deuterated γ-sultones (α-D-**7b**, α-D-**7c**, α-D-**8a,** α-D-**8b**, α-D-**8c**, α-D-**8e**, α-D-**11c**). ^{1}H NMR spectra for known compounds **7b**, **7c**, and **11c**. Calculation data, including Cartesian coordinates, total energy, and number of imaginary frequencies for molecules of Table 5 and their anions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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