1 mmol) in $CHCl_3$ (1 mL) was set aside at room temperature for 7 days. Analysis by ^{31}P NMR of the crude reaction mixture showed the four isomers **16a**, **16b**, **16c**, and **16d** were formed in the ratio shown in the Table I. Purification of the mixture on a short pad of silica gel (eluant CH_2Cl_2–MeOH, 20:1) afforded 304 mg (97%) of a mixture of crystalline products. Isomers **16a** and **16c** can be isolated pure by repeated crystallization from ligroin. Anal. Mixture of isomers. Calcd for $C_{16}H_{20}NO_2P$: C, 69.00; H, 6.43; N, 4.47. Found: C, 68.84; H, 6.54; N, 4.75. IR (CCl_4): 3063, 3025, 2925, 2855, 1591, 1490, 1454, 1438, 1293, 1195 (vs), 1114 cm^{-1}.

16a: mp 155–156 °C (ligroin 100–150 °C). Anal. Calcd for $C_{18}H_{20}NO_2P$: C, 69.00; H, 6.43; N, 4.47. Found: C, 69.25; H, 6.56; N, 4.34. ^{31}P NMR: 36.17. ^1H NMR: 7.86–7.77 (m, 1 H), 7.58–7.45 (m, 1 H), 7.25–7.07 (m, 2 H), 4.70 (t, J = 8.4, H-3 isoxazoline numbering), 4.59 (ddd, J = 10.0, 7.8, 5.9, H-5 isoxazoline numbering), 3.33–2.51 (m, 6 H), 1.84 (d, J_{PH} = 13.0). ^{13}C NMR: 75.30 (J_{PC} = 86.0), 63.19, 47.76, 37.42, 28.05, 11.17 (J_{PC} = 70.4).

16b. ^{31}P NMR: 36.40. ^1H NMR: 4.78 (ddd, J = 10.3, 5.1, 3.2, H-5 isoxazoline numbering), 3.55 (t, J = 8.8, H-3 isoxazoline numbering), 1.88 (d, J_{PH} = 13.0, 3 H), other signals covered. ^{13}C NMR: 75.15 (J_{PC} = 86.8), 63.62, 47.76, 37.20, 28.61, 13.74 (J_{PC} = 69.4).

16c: mp 150–151 °C (ligroin 100–150 °C). Anal. Calcd for $C_{18}H_{20}NO_2P$: C, 69.00; H, 6.43; N, 4.47. Found: C, 69.30; H, 6.65; N, 4.34. ^{31}P NMR: 32.52. ^1H NMR: 7.77–7.65 (m, 1 H), 7.58–7.45 (m, 1 H), 7.25–7.00 (m, 1 H), 4.69 (t, J = 8.5, H-3 isoxazoline numbering), 4.49–4.36 (m, 1 H), 3.47–3.28 (m, 2 H), 3.12–2.60 (m, 4 H), 1.73 (d, J_{PH} = 13.2). ^{13}C NMR: 78.62 (J_{PC} = 81.1), 63.07, 49.78, 36.73, 28.17, 12.74 (J_{PC} = 72.0).

16d. ^{31}P NMR: 35.74.

X-ray Crystallography. Crystal data: **3a** ($C_{16}H_{16}NO_2P$) was recrystallized from ligroin in the orthorhombic system, space group *Pbca* with a = 7.823 (1) Å, b = 17.084 (3) Å, c = 22.211 (5) Å, Z = 8, V = 2968.5 (7) Å^3, and D_{calcd} = 1.223 mg/m^3. Intensity data were collected on a CAD4 diffractometer in the range $1 < \theta < 75°$ with graphite-monochromatized Cu Kα radiation (λ = 1.54178 Å) in the $\omega/2\theta$ scan mode, lattice constants refined by least-squares fit of 25 reflections in the θ range 21.9–27.4°, no absorption correction was applied. A total of 3486 integrated reflections were collected up to ($(\sin\theta)/\lambda$ = 0.6 Å^{-1}); $\omega/2\theta$ scan technique, scan width (1.1 + 0.14 tan θ)°; $0 < h < 9$; $0 < k < 21$; $0 < l < 27$; decline in intensities of three standard reflections (4,3,–3; 8,–2; 2,9,–2) 0.1% during 57.9 h. A total of 2733 reflections observed [$I > 3\sigma(I)$] were used to solve the structure by direct methods (by SHELX-86 program)[17] and to refine it by full-matrix least squares (by SHELX-76 program)[18] using F's; H atoms were found on a Fourier map and refined with isotropic thermal parameters; anisotropic thermal parameters were applied for all other atoms; refinement converged to R = 0.0555, R_w = 0.0702 with weight $w = 1.0/(\sigma^2(F) + 0.01441F^2)$, for 246 refined parameters; largest shift over esd in the last cycle 0.02; largest residual peak in final difference Fourier map 0.011 e Å^3. Scattering factors were from ref 19.

Acknowledgment. This work was supported by the Italian National Research Council (CNR) and the Polish Academy of Sciences (CPBP-01-13). Partial support from PR-II-10 is also acknowledged.

Supplementary Material Available: Tables of crystallographic experimental details—unit cell packing diagram, positional parameters, anisotropic temperature factors, hydrogen atom positional parameters, bond lengths, bond angles, and torsion angles (7 pages). Ordering information is given on any current masthead page.

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3-Oxo- and 3-Imino-4-substituted-1,2,5-thiadiazolidine 1,1-Dioxides: Synthesis, Spectral Properties, and Selected Chemistry

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A general synthesis for the preparation of 3-oxo- and 3-imino-4-substituted-1,2,5-thiadiazolidine 1,1-dioxides has been developed beginning with an aldehyde, metal cyanide, and sulfamide. The selected chemistry and spectral properties of these compounds are detailed, as well as an X-ray crystallographic structure of a representative member of each class of heterocyclic compound. 3-Imino-4-phenyl-1,2,5-thiadiazolidine 1,1-dioxide crystallizes in space group $P2_12_12_1$, with a = 5.156 (1) Å, b = 7.418 (2) Å, c = 24.407 (5) Å, and Z = 4. 4-(1'-Naphthyl)-3-oxo-1,2,5-thiadiazolidine 1,1-dioxide crystallizes in space group $P2_1/c$, with a = 19.018 (7) Å, b = 5.335 (1) Å, c = 11.544 (3) Å, β = 103.63 (2)°, and Z = 4.

Introduction

The diverse chemical reactivity and pharmacological properties of hydantoins (**1**) have commanded the interest of organic and medicinal chemists.[1] Unfortunately, little is known about the sulfur dioxide equivalent of 1, 3-oxo-1,2,5-thiadiazolidine 1,1-dioxides (**2**). The early description of the preparation of 4,4-diphenyl-3-oxo-1,2,5-thiadiazolidine 1,1-dioxide[2] and the recent articles by Unterhalt and Hanewacker on the synthesis of 2,4-disubstituted derivatives of **2**[3] are our major sources of knowledge for these compounds. The need for additional information is further magnified by the many useful biological properties (i.e., anticonvulsant,[4] hypoglycemic,[5] antihypertensive,[6] hist-

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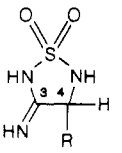
Table I. Physical and Selected Spectral Properties for 4-Substituted 3-Imino-1,2,5-thiadiazolidine 1,1-Dioxides 3



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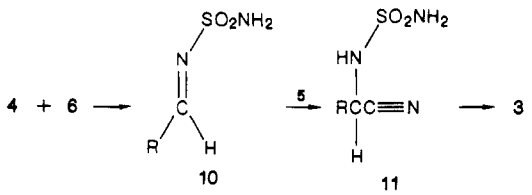
no.	R	yield,[a] %	mp,[b] °C (dec)	IR[c] C=N	IR[c] SO_2	^1H NMR[d] C(4)	^{13}C NMR[e] C(3)	^{13}C NMR[e] C(4)
3a	*n*-hexyl	40	199–200	1645	1360, 1110	4.13–4.15 (m)	171.18	61.13
3b	phenethyl	40	221–222	1665	1390, 1145	4.36 (dd, 8.8, 3.0)[f]	173.31[f]	62.56
3c	phenyl	35	272–273	1645	1360, 1135	5.32 (d, 4.7)	169.50	64.57
3d	4-methoxyphenyl	62	249–251	1640	1370, 1125	5.25 (d, 4.5)	169.87	64.08
3e	3,4,5-trimethoxyphenyl	58	272–274	1640	1365, 1125	5.25 (d, 3.0)	169.40	64.57
3f	1-naphthyl	26	231–233	1635	1375, 1140	6.03 (d, 6.0)	170.00	62.09
3g	2-naphthyl	35	246–248	1635	1365, 1135	5.53 (d, 2.0)	169.32	64.76
3h	2-thienyl	24	217–219	1650	1365, 1135	5.66 (d, 5.3)	169.25	60.32
3i	2-pyrrolyl	12	222–224	1650	1345, 1125	5.31 (s)	169.22	58.60

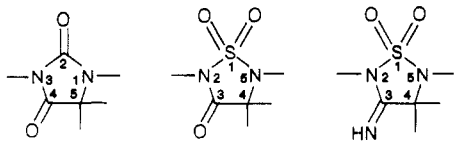
[a] Purified yields. [b] Melting (decomposition) points are uncorrected. [c] Infrared peak positions are recorded in reciprocal centimeters vs the 1601-cm^{-1} band in polystyrene and were taken in KBr disks. [d] ^1H NMR spectra were taken in Me_2SO-d_6 unless otherwise indicated. The number in each entry is the chemical shift value (δ) observed in parts per million relative to Me_4Si, followed by the multiplicity of the signal, followed by the coupling constant(s) in hertz. [e] ^{13}C NMR spectra were taken in Me_2SO-d_6 unless otherwise indicated. The number in each entry is the chemical shift value (δ) observed in parts per million relative to Me_4Si. [f] NMR spectrum taken in CD_3OD.

Scheme I



10 11

amine H_2-receptor antagonist,[7] herbicidal[8]) that have been observed for sulfamide-containing compounds.[9]

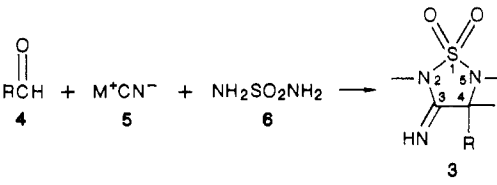


1 2 3

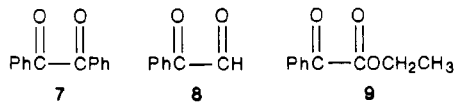
In this paper, we describe the first general route for the preparation of the *N,N'*-unsubstituted 3-oxo-1,2,5-thiadiazolidine 1,1-dioxides **2**, as well as the corresponding 3-imino analogues **3**. Key spectral properties for both **2** and **3** are presented along with the data obtained from the single-crystal X-ray structural determination of a representative member of each class of compound. Finally, selected chemistry for both 3-oxo (**2**) and 3-imino (**3**) 1,2,5-thiadiazolidine 1,1-dioxides is reported.

Results and Discussion

Synthesis of 3. The synthetic procedure adopted for the preparation of **3** was modeled after the Strecker synthesis of hydantoins.[10] Accordingly, an aqueous ethanolic solution of an aldehyde (**4**), sodium (potassium) cyanide (**5**), and excess sulfamide (**6**) was heated at reflux to generate the corresponding 3-imino-1,2,5-thiadiazolidine 1,1-dioxide adduct **3**. This procedure permitted the preparation of a wide range of 4-substituted alkyl and aryl derivatives of **3** in 12–62% yield (Table I). Use of the three α-keto substrates benzil (**7**), phenylglyoxal (**8**), and ethyl benzoylformate (**9**) in place of benzaldehyde gave **3c** in 20–48% yield. Formation of **3c** is consistent with previous studies by Schowen and co-workers,[11] who demonstrated that the cyanide-mediated cleavage of benzil furnished benzaldehyde and benzoic acid. Employment of the formaldehyde equivalents, paraformaldehyde, trioxane, and sodium formaldehyde bisulfite, as well as the ketones acetone and acetophenone, in this procedure proved unsuccessful.



4 5 6 3



7 8 9

Several potential mechanisms exist for the formation of **3**.[12] One of these pathways is depicted in Scheme I.

Synthesis of 2. The 3-imino-1,2,5-thiadiazolidine 1,1-dioxide adducts **3** served as convenient precursors for the preparation of the corresponding 3-oxo derivatives **2**. Treatment of **3** with ethanolic HCl gave the ring-opened

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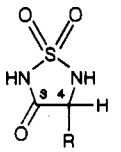
Table II. Physical and Selected Spectral Properties for 4-Substituted 3-Oxo-1,2,5-thiadiazolidine 1,1-Dioxides 2



2

no.	R	yield,[a] %	mp,[b] °C	IR[c] C=O	IR[c] SO_2	^1H NMR[d] C(4)	^{13}C NMR[e] C(3)	^{13}C NMR[e] C(4)
2a	phenethyl	51	168–169	1720	1365, 1170	4.10–4.13 (m)	171.96	60.62
2b	phenyl	54	215–217	1705	1370, 1150	4.73 (d, 5.1)	175.04	67.72
2c	1-naphthyl	45	175–176	1710	1340, 1155	6.18 (s)	170.61	62.09

[a] Purified yields from **3**. [b] Melting points are uncorrected. [c] Infrared peak positions are recorded in reciprocal centimeters vs the 1601-cm^{-1} band in polystyrene and were taken in KBr disks. [d] ^1H NMR spectra were taken in Me_2SO-d_6. The number in each entry is the chemical shift value (δ) observed in parts per million relative to Me_4Si, followed by the multiplicity of the signal, followed by the coupling constant(s) in hertz. [e] ^{13}C NMR spectra were taken in Me_2SO-d_6. The number in each entry is the chemical shift value (δ) observed in parts per million relative to Me_4Si.

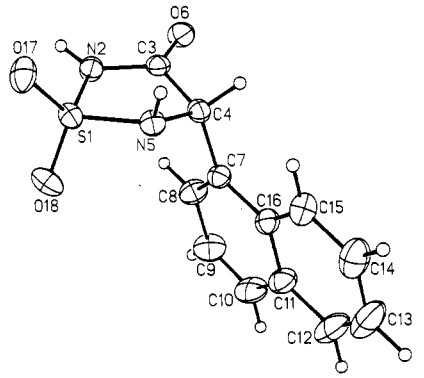


Figure 1. ORTEP view of compound **2c**, with atom labeling scheme. The thermal ellipsoids are 40% equiprobability envelopes, with hydrogens as spheres of arbitrary diameter.

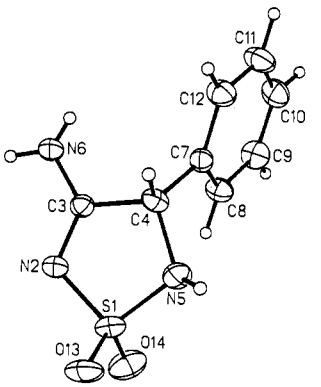
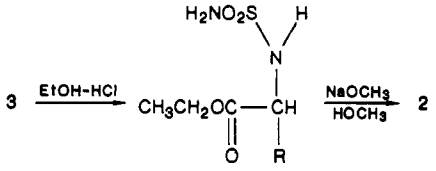


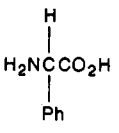
Figure 2. ORTEP view of compound **3c**, with atom labeling scheme. The thermal ellipsoids are 40% equiprobability envelopes, with hydrogens as spheres of arbitrary diameter.

ethyl ester **12**, which upon treatment with sodium methoxide yielded the 3-oxo derivative **2** in 45–54% overall yield (Table II). Several attempts (i.e., NEt_3, H_2O, heat; NaOH,



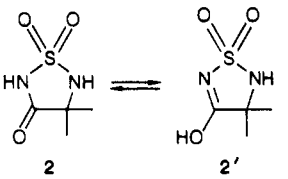
12

H_2O, heat; $NaNO_2$, HNO_3, H_2O) to convert **3** directly to **2** led either to no noticeable consumption of the starting material or to the formation of multiple products. Treatment of **3c** with aqueous 6 N HCl (reflux, 24 h) furnished phenylglycine (**13**) as the major product.

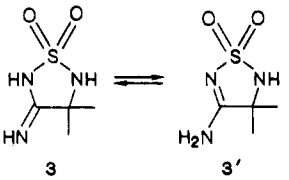


13

Spectral Studies. The key spectroscopic properties observed for **3** and **2** are presented in Tables I and II, respectively. Both sets of compounds exhibited characteristic absorption bands in the infrared spectrum at 1110–1170 cm^{-1} and 1340–1390 cm^{-1} for the sulfonyl group.[13] The imino stretching band in **3** was observed at 1635–1665 cm^{-1}, while the corresponding carbonyl band in **2** was detected at 1705–1720 cm^{-1}.[13] In the ^1H NMR spectra for **2** and **3**, a diagnostic signal was observed for the C(4) methine proton at δ 4.1–6.2.[14,15] In most instances this signal appeared as a doublet in DMSO-d_6, which collapsed to a singlet upon addition of D_2O. The corresponding N(5) proton appeared as a downfield doublet at δ 7.0–8.2. Both **2** and **3** can exist in two different tautomeric states (eq 1 and 2). The ^1H NMR data did not



(1)



(2)

permit us to determine which form predominated in solution. Typically, two distinct exchangeable protons were observed for **2** and three for **3**. The detection of three N–H

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Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for Compound 2c[a]

Bond Lengths			
S(1)–O(17)	1.417 (2)	S(1)–O(18)	1.417 (2)
S(1)–N(2)	1.652 (2)	S(1)–N(5)	1.624 (2)
O(6)–C(3)	1.208 (2)	N(2)–C(3)	1.355 (3)
N(2)–H(2)	0.879 (21)	N(5)–C(4)	1.494 (3)
N(5)–H(5)	0.828 (24)	C(3)–C(4)	1.525 (2)
C(4)–C(7)	1.515 (3)	C(4)–H(4)	0.986 (23)
Bond Angles			
O(17)–S(1)–O(18)	118.2 (1)	S(1)–N(2)–H(2)	122.2 (15)
O(18)–S(1)–N(2)	108.7 (1)	S(1)–N(5)–C(4)	108.5 (1)
O(18)–S(1)–N(5)	109.8 (1)	C(4)–N(5)–H(5)	111.5 (17)
S(1)–N(2)–C(3)	113.7 (1)	O(6)–C(3)–C(4)	125.1 (2)
C(3)–N(2)–H(2)	123.6 (15)	N(5)–C(4)–C(3)	105.6 (2)
O(6)–C(3)–N(2)	125.4 (2)	C(3)–C(4)–C(7)	112.8 (2)
N(2)–C(3)–C(4)	109.4 (2)	C(3)–C(4)–H(4)	105.8 (11)
N(2)–S(1)–N(5)	95.8 (1)	C(4)–C(7)–C(8)	121.4 (2)

[a] Standard deviation, σ for last digit, in parentheses.

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) for Compound 3c[a]

Bond Lengths			
S(1)–O(13)	1.450 (2)	S(1)–O(14)	1.434 (3)
S(1)–N(2)	1.626 (3)	S(1)–N(5)	1.648 (3)
N(2)–C(3)	1.302 (4)	N(5)–C(4)	1.482 (4)
N(5)–H(5)	0.920 (32)	N(6)–C(3)	1.316 (4)
N(6)–H(6A)	0.897 (31)	N(6)–H(6B)	0.725 (34)
C(3)–C(4)	1.523 (5)	C(4)–C(7)	1.524 (4)
C(4)–H(4)	1.200 (31)		
Bond Angles			
O(14)–S(1)–O(13)	114.7 (2)	N(5)–S(1)–N(2)	99.7 (1)
N(2)–S(1)–O(14)	108.9 (2)	C(4)–N(5)–S(1)	109.5 (20)
N(5)–S(1)–O(14)	111.5 (2)	H(5)–N(5)–C(4)	113.5 (20)
C(3)–N(2)–S(1)	108.9 (2)	H(6B)–N(6)–C(3)	114.9 (28)
H(5)–N(5)–S(1)	114.4 (20)	N(6)–C(3)–N(2)	122.4 (3)
H(6A)–N(6)–C(3)	115.5 (21)	C(4)–C(3)–N(6)	119.3 (3)
H(6B)–N(6)–H(6A)	129.6 (33)	C(7)–C(4)–N(5)	112.7 (3)
C(4)–C(3)–N(2)	118.3 (3)	H(4)–C(4)–N(5)	107.2 (15)
C(3)–C(4)–N(5)	103.4 (3)	H(4)–C(4)–C(7)	114.9 (14)
C(7)–C(4)–C(3)	111.6 (3)		

[a] Standard deviation, σ for last digit, in parentheses.

resonances for **3** is consistent with either **3** or **3′**, if hindered rotation exists for the exocyclic amino group in **3′**. Key signals detected in the ^{13}C NMR spectra for **2** and **3** included the resonances at 52.5–67.8 ppm and 169.2–175.1 ppm for the C(4) and C(3) carbon atoms, respectively.[15,16]

The X-ray crystallographic structures of **2c** and **3c** were determined in order to provide basic information concerning the solid-state structure of a representative member of both of these two heterocyclic systems. ORTEP views of compounds **2c** and **3c** are presented in Figures 1 and 2, while selected bond lengths and bond angles are listed in Tables III and IV. The X-ray crystallographic structure for **2c** indicates that the naphthyl derivative exists in the solid state as the 3-oxo tautomer. A distinctive feature in the molecular packing of this compound is the presence of mutual N(2)H···OC(3) hydrogen bonds between adjacent **2c** residues which form an eight-membered-ring hydrogen-bonded pair. Other intermolecular hydrogen bonds were also noted and are listed in Table 9 (supplementary material). Inspection of the X-ray crystallographic structure of the phenyl derivative **3c** indicates that this compound in the solid state exists as the 3-amino tautomer (i.e., **3′**). Of note, the racemic solution of compound **3c** underwent spontaneous resolution to form pure chiral crystals, a phenomenon that may be attributable to the

(16) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972 and references therein.

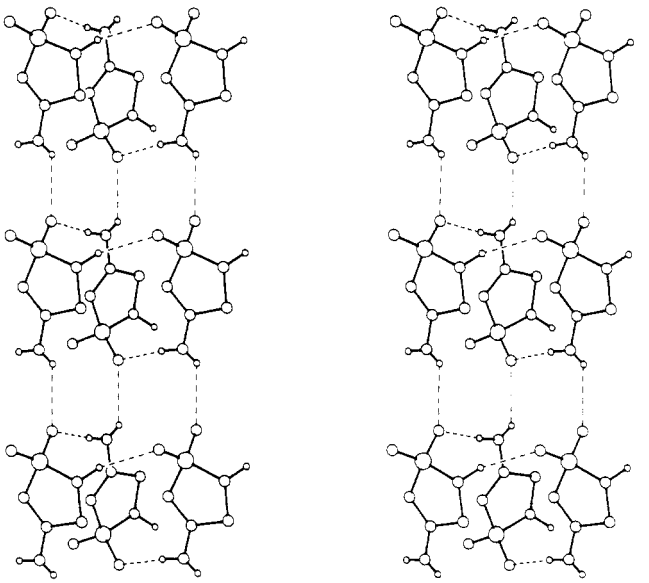
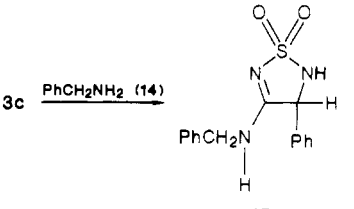


Figure 3. Stereoscopic view of the three-dimensional nature of the hydrogen bonding in compound **3c**, with phenyl groups omitted for clarity.

intricate hydrogen-bonding network that exists for this compound in the solid state (see Figure 3). Intermolecular hydrogen bonds were detected between all three amino protons and the two sulfonyl oxygen atoms (Table 14, supplementary material). Despite the differences in the preferred tautomeric forms for **2c** and **3c** in the solid state, notable similarities exist in the two structures. The bond length and bond angle data for both heterocyclic rings indicate that the N(5) nitrogen is largely sp^3 hybridized (sum of angles at N(5): for **2c**, 330°; for **3c**, 337°), while significant double-bond delocalization exists in both **2c** (sum of angles at N(2) = 360°, N(2)–C(3) = 1.36 Å, C(3)–O(6) = 1.21 Å) and **3c** (N(2)–C(3) = 1.30 Å, C(3)–N(6) = 1.32 Å).

Selected Chemistry. The reactivity profile exhibited by **3** with both water and ethanol prompted us to treat **3c** with benzylamine (**14**) (70–80 °C, 5 h). The major product isolated in this reaction has been identified as 3-(*N*-benzylamino)-4-phenyl-4,5-dihydro-1,2,5-thiadiazole 1,1-dioxide (**15**). A key feature in the ^1H NMR spectrum for this adduct was the appearance of a doublet (J = 4.7 Hz) for the benzylic protons at δ 4.38.



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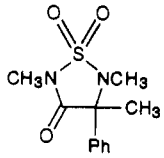
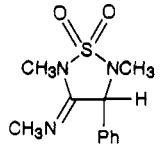
The final set of transformations examined for the 4-substituted phenyl adducts **2b** and **3c** was the determination of the reactivity of each substrate with excess methyl iodide and base (K_2CO_3, acetone). The product obtained from **2b** has been identified as the 2,4,5-trimethyl derivative **16**. A distinguishing feature in the ^1H NMR spectrum for this compound was the appearance of two resonances at δ 2.66 and 3.11 for the *N*-methyl groups and a singlet at δ 1.84 for the C(4) methyl group. The corresponding signals in the ^{13}C NMR spectrum were observed at 19.70, 24.81, and 24.85 ppm. These chemical shift values are in agreement with the proposed trisubstitution pattern.[14,15] The product obtained from the reaction of **3c**

with methyl iodide has been tentatively assigned as the nitrogen substituted trimethyl adduct **17** on the basis of the detection of three distinct peaks in the ^1H and ^{13}C NMR spectra for the methyl groups.[14,15] Moreover, these signals remained essentially unchanged as the temperature of the NMR probe was raised from 20 to 100 °C.[17]



16



17

Conclusions

An expedient route has been developed for the preparation of 3-oxo (**2**) and 3-imino (**3**) 4-substituted 1,2,5-thiadiazolidine 1,1-dioxides. The method is analogous to the Strecker synthesis of hydantoins and has proven useful for the synthesis of a wide variety of compounds. Key spectral properties and structural parameters for these novel heterocyclic systems have been ascertained. The pharmacological properties of both **2** and **3** are currently being investigated.

Experimental Section

General Methods. Infrared spectra (IR) were run on a Perkin-Elmer 283 spectrometer and calibrated against the 1601-cm^{-1} band of polystyrene. Absorption values are expressed in wavenumbers (cm^{-1}). Proton (^1H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were taken on Nicolet NT-300 and General Electric QE-300 NMR instruments. Chemical shifts (δ) are in parts per million (ppm) relative to Me_4Si, and coupling constants (J values) are in hertz. Low-resolution electron-impact mass spectral data (MS) were obtained at an ionizing voltage of 70 eV on a Bell and Howell 21-491 mass spectrometer at the University of Texas—Austin. Low-resolution chemical-ionization mass spectra were obtained on a Finnigan MAT TSQ-70 spectrometer using methane as the reagent gas at the University of Texas—Austin. High-resolution mass spectra were performed on a CEC 21-110B double-focusing magnetic-sector spectrometer at the University of Texas—Austin by Dr. John Chinn. Microanalyses were obtained from Spang Microanalytical Laboratory, Eagle Harbor, MI.

All glassware was dried before use. The solvents and reactants were of the best commercial grade available and were used without further purification. Thin- and thick-layer chromatography were run on precoated silica gel GHLF microscope slides (2.5 × 10 cm; Analtech No. 21521) or silica gel GHLF (20 × 20 cm; Analtech No. 11187).

General Procedure for the Preparation of 4-Substituted 3-Imino-1,2,5-thiadiazolidine 1,1-Dioxides 3. To a 70% aqueous ethanolic solution (20 mL) containing aldehyde **4** (10 mmol) and $NH_2SO_2NH_2$ (**6**) (20 mmol) was added NaCN (**5**) (11 mmol). The resulting solution was heated at reflux (6 h) and then concentrated to dryness in vacuo. An aqueous 1 N NaOH solution (10 mL) was added to the residue, and the solution was washed with ethyl acetate (2 × 10 mL) and diethyl ether (10 mL). The aqueous layer was then acidified (pH ~2) with a 1 N aqueous HCl solution, leading to the precipitation of a solid. The precipitate was filtered, dried, and recrystallized from ethanol to give **3**.

3-Imino-4-*n*-hexyl-1,2,5-thiadiazolidine 1,1-dioxide (3a): yield 0.88 g (40%); mp 199–200 °C; IR (KBr) 3380, 1645, 1360, 1110 cm^{-1}; ^1H NMR (DMSO-d_6) δ 0.87 (t, 3 H, J = 6.0 Hz), 1.26 (br s, 8 H), 1.49–1.53 (m, 1 H), 1.70 (br s, 1 H), 4.13–4.15 (m, 1 H), 7.01 (d, 1 H, J = 5.2 Hz), 7.80 (s, 1 H), 8.18 (s, 1 H); ^{13}C NMR (DMSO-d_6) 13.93, 22.01, 24.89, 28.19, 31.11, 32.75, 61.13, 171.18 ppm; MS (CI), 220 (P + 1).

Anal. Calcd for $C_8H_{17}N_3O_2S$: C, 43.81; H, 7.82; N, 19.16; S, 16.01. Found: C, 43.75; H, 7.96; N, 19.11; S, 16.08.

3-Imino-4-phenethyl-1,2,5-thiadiazolidine 1,1-dioxide (3b): yield 0.96 g (40%); mp 221–222 °C dec; IR (KBr) 3820, 1665, 1390, 1145 cm^{-1}; ^1H NMR (CD_3OD) δ 1.87–2.10 (m, 1 H), 2.12–2.17 (m, 1 H), 2.74 (t, 2 H, J = 8.0 Hz), 4.36 (dd, 1 H, J = 8.8, 3.0 Hz), 7.14–7.32 (m, 5 H); ^{13}C NMR (CD_3OD) 32.67, 36.67, 62.56, 127.15 (2 C), 129.53 (3 C), 142.07, 173.31 ppm; MS, m/e (relative intensity) 239 (12), 156 (32), 154 (21), 134 (43), 105 (45), 91 (17), 71 (100).

Anal. Calcd for $C_{10}H_{13}N_3O_2S$: C, 50.19; H, 5.47; N, 17.56; S, 13.40. Found: C, 50.17; H, 5.54; N, 17.60; S, 13.31.

3-Imino-4-phenyl-1,2,5-thiadiazolidine 1,1-dioxide (3c): yield 0.74 g (35%); mp 272–273 °C dec; IR (KBr) 3400, 1645, 1360, 1135 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.32 (d, 1 H, J = 4.7 Hz), 7.34–7.45 (m, 5 H), 7.53 (s, 1 H, exchangeable with D_2O), 7.69 (s, 1 H, exchangeable with D_2O), 8.27 (s, 1 H, exchangeable with D_2O); ^{13}C NMR (DMSO-d_6) 64.57, 127.63 (2 C), 128.40, 128.65 (2 C), 137.88, 169.50 ppm; MS, m/e (relative intensity) 146 (13), 105 (98), 104 (100), 103 (12), 78 (28), 77 (34); M_r 211.0412 (calcd for $C_8H_9N_3O_2S$, 211.0416).

Anal. Calcd for $C_8H_9N_3O_2S$: C, 45.48; H, 4.29; N, 19.89; S, 15.18. Found: C, 45.36; H, 4.26; N, 19.85; S, 15.22.

3-Imino-4-(4′-methoxyphenyl)-1,2,5-thiadiazolidine 1,1-dioxide (3d): yield 1.50 g (62%); mp 249–251 °C dec; IR (KBr) 3395, 1640, 1370, 1125 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.75 (s, 3 H), 5.25 (d, 1 H, J = 4.5 Hz), 6.95 (d, 2 H, J = 8.3 Hz), 7.34 (d, 2 H, J = 8.3 Hz), 7.48 (s, 1 H), 7.60 (d, 1 H, J = 4.5 Hz), 8.23 (s, 1 H); ^{13}C NMR (DMSO-d_6) 55.21, 64.08, 113.97 (2 C), 128.93 (2 C), 129.81, 159.27, 169.87 ppm; MS, m/e (relative intensity) 241 (23), 155 (20), 154 (20), 135 (100), 134 (96).

Anal. Calcd for $C_9H_{11}N_3O_3S$: C, 44.80; H, 4.60; N, 17.42; S, 13.29. Found: C, 44.76; H, 4.68; N, 17.36; S, 13.18.

3-Imino-4-(3′,4′,5′-trimethoxyphenyl)-1,2,5-thiadiazolidine 1,1-dioxide (3e): yield 1.75 g (58%); mp 272–274 °C dec; IR (KBr) 3390, 1640, 1365, 1125 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.65 (s, 3 H), 3.77 (s, 6 H), 5.25 (d, 1 H, J = 3.0 Hz), 6.82 (s, 2 H), 7.50 (s, 1 H), 7.72 (d, 1 H, J = 3.0 Hz), 8.26 (s, 1 H); ^{13}C NMR (DMSO-d_6) 55.81 (2 C), 59.98, 64.57, 104.72 (2 C), 133.22, 137.25, 152.89 (2 C), 169.40 ppm; MS, m/e (relative intensity) 301 (48), 195 (100), 180 (45), 178 (12), 150 (18), 149 (12), 137 (26), 125 (25); M_r 301.0740 (calcd for $C_{11}H_{15}N_3O_5S$, 301.0732).

Anal. Calcd for $C_{11}H_{15}N_3O_5S$: C, 43.85; H, 5.02; N, 13.95; S, 10.64. Found: C, 43.93; H, 5.09; N, 13.90; S, 10.60.

3-Imino-4-(1′-naphthyl)-1,2,5-thiadiazolidine 1,1-dioxide (3f): yield 0.68 g (26%); mp 231–233 °C dec; IR (KBr) 3400, 1635, 1375, 1140 cm^{-1}; ^1H NMR (DMSO-d_6) δ 6.03 (d, 1 H, J = 6.0 Hz), 7.38–8.00 (m, 8 H), 8.13 (d, 1 H, J = 6.0 Hz), 8.41 (s, 1 H); ^{13}C NMR (DMSO-d_6) 62.09, 123.41, 125.42, 126.01, 126.58, 128.65, 129.14, 131.08, 132.89, 133.54, 170.00 ppm. The remaining aromatic ^{13}C NMR resonance was not detected and is assumed to overlap one of the observed signals. MS: m/e (relative intensity) 261 (17), 200 (13), 155 (82), 154 (100), 153 (21), 127 (35), 94 (95).

Anal. Calcd for $C_{12}H_{11}N_3O_2S$: C, 55.20; H, 4.25; N, 16.08; S, 12.27. Found: C, 55.27; H, 4.26; N, 16.05; S, 12.35.

3-Imino-4-(2′-naphthyl)-1,2,5-thiadiazolidine 1,1-dioxide (3g): yield 0.91 g (35%); mp 246–248 °C dec; IR (KBr) 3395, 1635, 1365, 1135 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.53 (d, 1 H, J = 2.0 Hz), 7.51–7.58 (m, 4 H), 7.83 (d, 1 H, J = 2.0 Hz), 7.92–7.98 (m, 4 H), 8.31 (s, 1 H); ^{13}C NMR (DMSO-d_6) 64.76, 124.64, 126.53, 127.44, 127.57, 127.89, 128.51, 132.52, 132.72, 135.02, 169.32 ppm. The remaining aromatic ^{13}C NMR resonance was not detected and is assumed to overlap one of the observed signals. MS: m/e (relative intensity) 261 (35), 200 (23), 155 (100), 154 (77), 153 (29), 127 (40), 94 (83).

Anal. Calcd for $C_{12}H_{11}N_3O_2S$: C, 55.20; H, 4.25; N, 16.08; S, 12.27. Found: C, 54.86; H, 4.21; N, 15.98; S, 12.17.

3-Imino-4-(2′-thienyl)-1,2,5-thiadiazolidine 1,1-dioxide (3h): yield 0.52 g (24%); mp 217–219 °C dec; IR (KBr) 3440, 1650, 1365, 1135 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.66 (d, 1 H, J = 5.3 Hz), 7.01–7.71 (m, 3 H), 7.79 (s, 1 H), 7.81 (d, 1 H, J = 5.3 Hz), 8.41 (s, 1 H); ^{13}C NMR (DMSO-d_6) 60.32, 127.30 (2 C), 127.49, 127.66 (2 C), 140.91, 169.25 ppm; MS, m/e (relative intensity) 111 (100), 110 (56), 84 (8); M_r 216.9974 (calcd for $C_6H_7N_3O_2S_2$, 216.9980).

Anal. Calcd for $C_6H_7N_3O_2S_2$: C, 33.40; H, 3.25; N, 19.34; S, 29.51. Found: C, 33.15; H, 3.28; N, 19.24; S, 29.50.

(17) No noticeable reaction was observed upon treatment of **17** with either aqueous base (room temperature, 24 h) or excess benzylamine (150 °C, 24 h).

3-Imino-4-(2′-pyrrolyl)-1,2,5-thiadiazolidine 1,1-dioxide (3i): yield 0.24 g (12%); mp 222–224 °C dec; IR (KBr) 3390, 3320, 1650, 1345, 1125 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.31 (s, 1 H), 5.98 (s, 1 H), 6.02 (s, 1 H), 6.72 (s, 1 H), 7.40 (s, 1 H), 7.60 (s, 1 H), 8.28 (s, 1 H), 10.63 (s, 1 H); ^{13}C NMR (DMSO-d_6) 58.60, 106.99, 107.68, 118.59, 126.64, 169.22 ppm; MS, *m/e* (relative intensity) 200 (60), 134 (15), 95 (23), 94 (100), 93 (79).

Anal. Calcd for $C_6H_8N_4O_2S$: C, 35.99; H, 4.03; N, 27.98; S, 16.01. Found: C, 35.55; H, 4.19; N, 27.41; S, 16.09.

Preparation of 3-Imino-4-phenyl-1,2,5-thiadiazolidine 1,1-Dioxide (3c) from Benzil (7). Benzil (7) (1.01 g, 5 mmol), **5** (0.30 g, 5.5 mmol), and **6** (1.20 g, 12.5 mmol) were dissolved in a 70% aqueous ethanolic solution (10 mL). The solution was heated to reflux (3 h), then cooled to room temperature, and permitted to stand (16 h). The crystalline material that formed was filtered and recrystallized from ethanol to give 0.48 g (48%) of **3c**: mp 272–273 °C dec; IR (KBr) 3400, 1645, 1360, 1135 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.32 (s, 1 H), 7.32–7.45 (m, 5 H), 7.54 (s, 1 H), 7.69 (s, 1 H), 8.26 (s, 1 H); ^{13}C NMR (DMSO-d_6) 64.57, 127.63 (2 C), 128.40, 128.66 (2 C), 137.91, 169.51 ppm.

Anal. Calcd for $C_8H_9N_3O_2S$: C, 45.48; H, 4.29; N, 19.89; S, 15.18. Found: C, 45.56; H, 4.31; N, 19.87; S, 15.30.

Preparation of 3-Imino-4-phenyl-1,2,5-thiadiazolidine 1,1-Dioxide (3c) from Phenylglyoxal Hydrate (8). The preceding experiment was repeated by using phenylglyoxal hydrate (8) (0.76 g, 5 mmol) to give 0.20 g (20%) of **3c**: mp 272–273 °C dec; mmp 272–273 °C dec.

Preparation of 3-Imino-4-phenyl-1,2,5-thiadiazolidine 1,1-Dioxide (3c) from Ethyl Benzoylformate (9). Ethyl benzoylformate (9) (0.89 g, 5 mmol), KCN (0.36 g, 5.5 mmol), and $NH_2SO_2NH_2$ (0.96 g, 10 mmol) were dissolved in a 70% aqueous ethanolic solution (10 mL). The solution was heated to reflux (5 h), cooled to room temperature, and then acidified with concentrated aqueous HCl (pH 2.0). The solution was permitted to stand (2 h) at room temperature, and the solid that formed was filtered, washed with water and ethanol, and dried in vacuo to give 0.30 g (30%) of **3c**: 272–273 °C dec; mmp 272–273 °C dec.

General Procedure for the Conversion of 4-Substituted 3-Imino-1,2,5-thiadiazolidine 1,1-Dioxides 3 to Ethyl 2-Sulfamido-Substituted Esters 12. An ethanolic (35 mL) solution containing imino compound **3** (7.0 mmol) and concentrated HCl (15 mL) was heated to reflux (24 h), and then the volume was reduced to half of the original amount in vacuo. After the solution was cooled (0 °C), the crystalline material that precipitated was filtered, washed with water, and then dried in vacuo to give the corresponding ester **12**.

Ethyl 2-sulfamido-4-phenylbutanoate (12a): yield 1.15 g (62%); mp 94–96 °C; IR (KBr) 3320, 3225, 1705, 1355, 1140 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.20 (t, 3 H, J = 7.0 Hz), 1.87–1.93 (m, 2 H), 2.64–2.71 (m, 2 H), 3.80–3.84 (m, 1 H), 4.07–4.14 (m, 2 H), 6.63 (s, 2 H), 7.19–7.35 (m, 6 H); ^{13}C NMR (DMSO-d_6) 14.07, 31.20, 33.98, 55.04, 60.50, 126.00, 128.42 (3 C), 141.18 (2 C), 172.52 ppm; MS, *m/e* (relative intensity) 286 (4), 213 (36), 191 (41), 182 (14), 174 (19), 134 (29), 132 (26), 117 (100), 112 (19), 110 (35), 102 (43).

Anal. Calcd for $C_{12}H_{18}N_2O_4S$: C, 50.33; H, 6.36; N, 9.79; S, 11.20. Found: C, 50.48; H, 6.49; N, 9.88; S, 11.14.

Ethyl α-sulfamidophenylacetate (12b): yield 1.08 g (60%); mp 133–134 °C; IR (KBr) 3380, 3280, 3200, 1705, 1370, 1150 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.35 (t, 3 H, J = 7.0 Hz), 4.07–4.12 (m, 2 H), 5.01 (d, 1 H, J = 9.4 Hz), 6.75 (s, 2 H), 7.31–7.43 (m, 5 H), 7.73 (d, 1 H, J = 9.4 Hz); ^{13}C NMR (DMSO-d_6) 13.96, 59.16, 60.64, 127.47 (2 C), 128.07, 128.50 (2 C), 136.64, 170.99 ppm; MS, *m/e* (relative intensity) 186 (11), 185 (100), 168 (19), 106 (54), 104 (54), 79 (13), 77 (20); M_r 258.0682 (calcd for $C_{10}H_{14}N_2O_4S$, 258.0674).

Anal. Calcd for $C_{10}H_{14}N_2O_4S$: C, 46.46; H, 5.46; N, 10.85; S, 12.41. Found: C, 46.59; H, 5.54; N, 10.96; S, 12.58.

Ethyl α-sulfamido-1-naphthaleneacetate (12c): yield 1.12 g (52%); mp 104–105 °C; IR (KBr) 3320, 3260, 3220, 1715, 1380, 1145 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.10 (t, 3 H, J = 7.0 Hz), 4.06–4.19 (m, 2 H), 5.76 (d, 1 H, J = 9.0 Hz), 6.88 (s, 2 H), 7.48–7.99 (m, 7 H), 8.33 (d, 1 H, J = 9.0 Hz); ^{13}C NMR (DMSO-d_6) 13.92, 55.84, 61.08, 123.55, 123.66, 125.23, 125.39, 125.68, 128.69, 128.86, 130.68, 132.66, 133.52, 171.23 ppm; MS, *m/e* (relative intensity) 308 (27), 237 (26), 235 (100), 218 (35), 156 (65), 155 (32), 154 (91), 127 (53).

Anal. Calcd for $C_{14}H_{16}N_2O_4S$: C, 54.53; H, 5.23; N, 9.09; S, 10.50. Found: C, 54.69; H, 5.28; N, 9.11; S, 10.31.

Ethyl α-sulfamido-2-thiopheneacetate (12d): yield 0.48 g (26%); mp 106–107 °C; IR (KBr) 3360, 3260, 3200, 1710, 1355, 1150 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.20 (t, 3 H, J = 7.0 Hz), 4.16 (q, 2 H, J = 7.0 Hz), 5.23 (d, 1 H, J = 9.2 Hz), 7.00–7.50 (m, 3 H), 6.80 (s, 2 H), 7.83 (d, 1 H, J = 9.2 Hz); ^{13}C NMR (DMSO-d_6) 13.91, 55.02, 61.33, 126.23, 126.63, 126.97, 138.60, 170.09 ppm; MS, *m/e* (relative intensity) 264 (2), 191 (100), 183 (12), 174 (68), 112 (56), 111 (23), 110 (82).

Anal. Calcd for $C_8H_{12}N_2O_4S_2$: C, 36.35; H, 4.58; N, 10.60; S, 24.26. Found: C, 36.46; H, 4.68; N, 10.63; S, 24.17.

General Procedure for the Preparation of 4-Substituted 3-Oxo-1,2,5-thiadiazolidine 1,1-Dioxides 2. To a sodium methoxide solution [prepared by the addition of Na (0.23 g, 10 mmol) to methanol (30 mL)] was added ester **12** (10 mmol). The solution was heated at reflux (3 h) and then concentrated to dryness in vacuo. The residue was dissolved in water (10 mL), and the water solution was acidified (pH ~2.0) and then extracted with ethyl acetate (2 × 30 mL). The ethyl acetate solutions were combined, then washed with an aqueous saturated NaCl solution (3 × 30 mL), dried (Na_2SO_4), and concentrated in vacuo. The product was purified by flash column chromatography (methanol:chloroform:acetone = 1:3:5).

4-Phenethyl-3-oxo-1,2,5-thiadiazolidine 1,1-dioxide (2a): yield 2.07 g (83%); mp 168–169 °C; IR (KBr) 3400, 3260, 1720, 1365, 1170 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.86–1.94 (m, 1 H), 1.95–2.04 (m, 1 H), 2.67–2.73 (m, 2 H), 4.10–4.13 (m, 1 H), 7.05–7.30 (m, 6 H), 8.39 (br s, 1 H); ^{13}C NMR (DMSO-d_6) 31.13, 33.07, 60.62, 126.14, 128.42 (2 C), 128.50 (2 C), 140.61, 171.96 ppm; MS, *m/e* (relative intensity) 240 (37), 136 (79), 133 (11), 132 (40), 131 (20), 130 (11), 119 (13), 117 (11), 106 (15), 105 (100), 104 (34), 91 (76).

4-Phenyl-3-oxo-1,2,5-thiadiazolidine 1,1-dioxide (2b): yield 1.91 g (90%); mp 215–217 °C; IR (KBr) 3410, 3290, 3205, 1705, 1370, 1150 cm^{-1}; ^1H NMR (DMSO-d_6) δ 4.73 (d, 1 H, J = 5.1 Hz), 6.84 (d, 1 H, J = 5.1 Hz), 7.21–7.39 (m, 6 H); ^{13}C NMR (DMSO-d_6) 67.72, 126.66, 127.19 (2 C), 127.69 (2 C), 140.47, 175.04 ppm; MS, *m/e* (relative intensity) 169 (30), 105 (93), 104 (100), 78 (33), 77 (40); M_r 212.0264 (calcd for $C_8H_8N_2O_3S$, 212.0256).

Anal. Calcd for $C_8H_8N_2O_3S$: C, 45.27; H, 3.80; N, 13.20; S, 15.11. Found: C, 45.33; H, 3.89; N, 13.25; S, 15.22.

4-(1′-Naphthyl)-3-oxo-1,2,5-thiadiazolidine 1,1-Dioxide (2c). Utilizing the general procedure for the cyclization of **2**, the acidified aqueous solution obtained from **12c** was allowed to remain at 0 °C (3 h). The crystalline material that formed was filtered, washed with water, and then recrystallized from water to give 2.25 g (86%) of **2c**: mp 175–176 °C; IR (KBr) 3420, 3230, 1710, 1340, 1155 cm^{-1}; ^1H NMR (DMSO-d_6) δ 6.18 (s, 1 H), 7.50–8.50 (m, 8 H), 8.72 (br s, 1 H); ^{13}C NMR (DMSO-d_6) 62.09, 124.28, 125.37, 125.55, 126.04, 126.42, 128.51, 128.99, 131.09, 132.41, 133.52, 170.61 ppm; MS, *m/e* (relative intensity) 262 (18), 155 (54), 154 (100), 153 (15), 127 (28), 119 (13).

Anal. Calcd for $C_{12}H_{10}N_2O_3S$: C, 54.95; H, 3.84; N, 10.68; S, 12.23. Found: C, 54.86; H, 3.90; N, 10.63; S, 12.02.

Acid Hydrolysis of 4-Phenyl-3-imino-1,2,5-thiadiazolidine 1,1-Dioxide (3c). Compound **3c** (0.20 g, 0.95 mmol) was added to an aqueous 6 N HCl solution (30 mL) and heated to reflux (24 h). The solution was cooled to room temperature, the pH was adjusted to 6.2, and then the solution was permitted to stand at 0–5 °C (24 h). The crystalline material that formed was filtered and recrystallized from water to give 0.05 g (37%) of *dl*-phenylglycine (**13**): mp 290 °C subl; mmp 290 °C subl; ^1H NMR (DMSO-d_6 + trifluoroacetic acid) δ 4.99–5.03 (m, 1 H), 7.47–7.56 (m, 5 H), 8.76 (br s, 3 H); ^{13}C NMR (DMSO-d_6 + trifluoroacetic acid) 58.47, 130.14 (2 C), 130.96 (2 C), 131.60, 134.71, 171.81 ppm.

Reaction of 3-Imino-4-phenyl-1,2,5-thiadiazolidine 1,1-Dioxide (3c) with Benzylamine (14). A mixture of **3c** (0.21 g, 10 mmol) and **14** (3 mL, 27 mmol) was heated at 70–80 °C (5 h). A 6 N aqueous HCl solution (30 mL) was added to the solution, and then the solution was cooled to room temperature. The material that precipitated was filtered and recrystallized with ethanol to give 0.10 g (42%) of **15**: mp 198–200 °C; IR (KBr) 3315, 3215, 1600, 1350, 1145 cm^{-1}; ^1H NMR (DMSO-d_6) δ 4.38 (d, J = 4.7 Hz, 2 H), 5.43 (d, J = 4.8 Hz, 1 H), 7.14–7.44 (m, 10 H), 7.82 (d, J = 4.8 Hz, 1 H), 8.61 (m, 1 H); ^{13}C NMR (DMSO-d_6) 46.26, 64.27, 127.23 (4 C), 127.81 (2 C), 128.33 (2 C), 128.49, 128.65, 129.05,

Table V. Data Collection and Processing Parameters for Compounds 2c and 3c

	2c	3c
space group	$P2_1/c$, monoclinic	$P2_12_12_1$, orthorhombic
cell constants		
a, Å	19.018 (7)	5.156 (1)
b, Å	5.335 (1)	7.418 (2)
c, Å	11.544 (3)	24.407 (5)
β, deg	103.63 (2)	
V, Å^3	1138	934
molecular formula	$C_{12}H_{10}N_2O_3S$	$C_8H_9N_3O_2S$
fw	262.30	211.26
formula units/cell	$Z = 4$	$Z = 4$
density	$\rho = 1.53$ g cm^{-3}	$\rho = 1.50$ g cm^{-3}
abs coeff	$\mu = 2.72$ cm^{-1}	$\mu = 3.08$ cm^{-1}
radiation (Mo Kα)	$\lambda = 0.71073$ Å	$\lambda = 0.71073$ Å
collection range	$4° \le 2\theta \le 55°$	$4° \le 2\theta \le 65°$
scan width, deg	$\Delta\theta = 1.3 + (K\alpha_2 - K\alpha_1)$	$\Delta\theta = 1.4 + (K\alpha_2 - K\alpha_1)$
scan speed range	2.0–15.0° min^{-1}	3.0–20.0° min^{-1}
total data collected	2606	1977
independent data, $I > 3\sigma(I)$	2102	1674
total variables	173	141
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.034	0.042
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	0.033	0.034
weights	$w = \sigma(F)^{-2}$	$w = \sigma(F)^{-2}$

137.49, 137.82, 168.17 ppm; MS, m/e (relative intensity) 301 (16), 133 (19), 106 (75), 105 (23), 91 (100), 77 (22).

Anal. Calcd for $C_{15}H_{15}N_3O_2S$: C, 59.78; H, 5.02; N, 13.94; S, 10.64. Found: C, 59.61; H, 4.94; N, 13.88; S, 10.64.

Methylation of 4-Phenyl-3-oxo-1,2,5-thiadiazolidine 1,1-Dioxide (2b). A mixture of **2b** (0.42 g, 2 mmol), methyl iodide (1.68 g, 12 mmol), K_2CO_3 (4.14 g, 30 mmol), and acetone (30 mL) was stirred at room temperature (2 days). The solid was filtered, and the filtrate was concentrated to approximately half of the original volume in vacuo and then diluted with H_2O (50 mL). The material that precipitated was filtered, washed with H_2O, and dried to give 0.23 g (39%) of **16**: mp 118–120 °C (recrystallized in EtOH); IR (KBr) 1725, 1375, 1150 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.84 (s, 3 H), 2.66 (s, 3 H), 3.11 (s, 3 H), 7.43–7.51 (m, 5 H); ^{13}C NMR (DMSO-d_6) 19.70, 24.81, 24.85, 70.47, 126.66 (2 C), 128.91 (3 C), 136.19, 167.89 ppm; MS, m/e (relative intensity) 254 (29), 239 (63), 177 (22), 133 (88), 132 (62), 118 (100), 103 (26).

Anal. Calcd for $C_{11}H_{14}N_2O_3S$: C, 51.93; H, 5.55; N, 11.02; S, 12.61. Found: C, 51.96; H, 5.63; N, 10.94; S, 12.59.

Preparation of 2,5-Dimethyl-3-(*N*-methylimino)-4-phenyl-1,2,5-thiadiazolidine 1,1-Dioxide (17). Compound **3c** (0.21 g, 1 mmol), methyl iodide (1.42 g, 10 mmol), and K_2CO_3 (7.00 g, 50 mmol) were added to acetone (70 mL), and the mixture was stirred at room temperature (30 h). The solid was filtered, and the filtrate was concentrated to dryness in vacuo. The residue was dissolved in a minimum amount of acetone (~5 mL) and then diluted with H_2O (50 mL). The material that precipitated was filtered, washed with H_2O, and dried to give 0.16 g (64%) of **17**: mp 188–189 °C; IR (KBr) 1620, 1290, 1150 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.38 (s, 3 H), 2.67 (s, 3 H), 3.04 (s, 3 H), 5.61 (s, 1 H), 7.35–7.47 (m, 5 H); ^{13}C NMR (DMSO-d_6) 28.73, 37.75, 38.78, 68.10, 128.48 (2 C), 129.10, 129.16 (2 C), 133.63, 166.66 ppm; MS, m/e (relative intensity) 253 (22), 119 (57), 118 (100), 77 (13); M_r 253.0888 (calcd for $C_{11}H_{15}N_3O_2S$, 253.0885).

Anal. Calcd for $C_{11}H_{15}N_3O_2S$: C, 52.15; H, 5.97; N, 16.59; S, 12.66. Found: C, 52.03; H, 6.01; N, 16.46; S, 12.64.

X-ray Analyses of 2c and 3c. Single crystals of **2c** and **3c** suitable for X-ray analysis were both obtained from methanol. The crystals selected were mounted on glass fibers in random orientations, and the data were collected on a Nicolet R3m/V automatic diffractometer. The radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table V. Both structures were solved by use of the SHELXTL direct-methods program, which revealed the positions of all of the non-hydrogen atoms. The usual sequence of isotropic and anisotropic refinement was followed, after which the aromatic hydrogens were entered in ideal calculated positions and constrained to riding motion, with a single variable isotropic temperature factor. The remaining hydrogens were located in difference Fourier syntheses and allowed to refine independently, with a single variable isotropic temperature factor. In order to determine the correct absolute configuration of **3c**, the inverted structure was refined, and it showed a slightly larger R value (0.044). The Rogers test[18] was also performed and indicated conclusively at the 10σ level that the reported absolute configuration is preferred over its inverse. After all shift:esd ratios for structures **2c** and **3c** were less than 0.1, convergence was reached at the agreement factors listed in Table V. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density map for **2c** showed a maximum peak of approximately 0.2 e/Å^3, while the corresponding peak for **3c** was about 0.4 e/Å^3. All calculations were made by using Nicolet's SHELXTL PLUS (1987) series of crystallographic programs.

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Supplementary Material Available: Tables 6–9 and 11–14 giving a complete listing of atomic coordinates and equivalent isotropic displacement parameters, bond lengths, bond angles, and hydrogen-bonding parameters for compounds **2c** and **3c** (6 pages); Tables 10 and 15 giving a complete listing of observed and calculated structure factors for compounds **2c** and **3c** (16 pages). Ordering information is given on any current masthead page.

(18) Rogers, D. *Acta Crystallogr.* **1981**, *A37*, 734.