was added to the flask containing the trialkylborane (5 mmol), and the solution was then stirred for 1 h at room temperature. After the trialkylborate solution was cooled to −78 °C, iodine in THF (5.0 mL, 1 M) was added slowly to the vigorously stirred solution. Aliquots were withdrawn and quenched with sodium thiosulfate solution. The organic phase was analyzed by GC (10% DC 710, Chromosorb W, 6 ft × 0.25 in.) for the 1-alkene products.

Oxidation of Trialkylboranes. A 2-mL aliquot of the trialkylborane solution (~0.5 M) was delivered via syringe to a glassware assembly identical with that described above. The solution was cooled to 0 °C, 1 mL of 3 N NaOH was then added, followed by 1 mL of 30% H_2O_2. The mixture was stirred either at 50 °C for 1 h or at room temperature overnight. After the addition of K_2CO_3, the organic phase was separated and dried over anhydrous $MgSO_4$.

Oxidation of Dialkyliodoboranes. The iodinated reaction mixture was quenched with 3 mL of saturated sodium thiosulfate solution and warmed to 0 °C. The upper organic layer was transferred via a double-tipped needle to an identical glassware assembly. Oxidation was achieved by addition of 5 mL of 3 N NaOH and 5 mL of 30% hydrogen peroxide at 0 °C, and the resulting mixture was heated at 50 °C for 1 h. After addition of sodium thiosulfate and saturation of the mixture with K_2CO_3, the organic phase was separated and dried over K_2CO_3.

Acknowledgment. I thank Research Corp. for financial support.

Registry No. RR^1_2B (R = butyl; R^1 = cyclohexyl), 6917-84-6; RR^1_2B (R = *sec*-butyl; R^1 = cyclohexyl), 77123-47-8; RR^1_2B (R = isobutyl; R^1 = cyclohexyl), 6917-83-5; RR^1_2B (R = cyclohexyl; R^1 = butyl), 38103-70-7; RR^1_2B (R = cyclohexyl; R^1 = *sec*-butyl), 77123-48-9; RR^1_2B (R = cyclohexyl; R^1 = isobutyl), 77123-49-0; RR^1_2B (R = cyclohexyl; R^1 = 9-BBN), 53535-83-4; RR^1_2B (R = butyl; R^1 = 9-BBN), 23532-74-3; RR^1_2B (R = *sec*-butyl; R^1 = 9-BBN), 53317-06-9; RR^1_2B (R = isobutyl; R^1 = 9-BBN), 63942-77-8; $CH(CH_3)_2C(CH_3)_2BRR^1$ (R = butyl; R^1 = butyl), 42928-38-1; $CH(CH_3)_2C(CH_3)_2BRR^1$ (R = isobutyl; R^1 = butyl), 77136-28-8; $RCH{=}CH_2$ (R = butyl), 592-41-6; $RCH{=}CH_2$ (R = *sec*-butyl), 760-20-3; $RCH{=}CH_2$ (R = isobutyl), 691-37-2; $RCH{=}CH_2$ (R = cyclohexyl), 695-12-5; 1-vinyl-5-cyclooctanol, 81626-24-6; vinyl bromide, 593-60-2.

Ring Transformation of 1,3,4-Oxadiazole to *s*-Triazole-Fused Heterocycles. New Synthetic Route for Thiazolo[2,3-*c*]-*s*-triazole and 7*H*-*s*-Triazolo[3,4-*b*][1,3,4]thiadiazine

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s-Triazole-fused heterocycles have been synthesized by an intramolecular transformation of some 1,3,4-oxadiazole ketones with ammonia or hydrazine. The α-[(1,3,4-oxadiazol-2-yl)thio] ketone **2m** gave thiazolo[2,3-*c*]-*s*-triazole (**4m**), accompanied by a small amount of the hydrazide **9m** on treatment with ammonium acetate in acetic acid. Similar treatment of ketones **2a** and **2b** afforded only the hydrazides **9a** and **9b**, respectively. Ketones **2a–n** reacted with hydrazine hydrate in acetic acid to give 7*H*-*s*-triazolo[3,4-*b*][1,3,4]thiadiazines **5a–n**. However, ketones **2o–q**, with substituents α to the carbonyl group, could not be converted to the corresponding fused-ring systems. Mechanisms for these transformations are proposed.

s-Triazolo-fused heterocycles can be prepared by ring closure of hydrazino-substituted heterocycles with a carboxylic acid, cyanogen bromide, or carbon disulfide.[1] An alternative route involves reaction of a substituted *s*-triazole such as 4-amino-3-mercapto-1,2,4-triazole with a bifunctional compound.[2] Although *s*-triazoles can be prepared from 1,3,4-oxadiazoles and amines at elevated temperatures,[3] just as pyrroles are formed from furans and amines,[4] these ring transformations have been limited to the preparation of monocyclic systems. We have undertaken an investigation of the synthesis of *s*-triazolo-fused heterocycles by intramolecular ring closure of substituted 1,3,4-oxadiazoles (**2**) with ammonia or hydrazine. We here report new synthetic routes to a thiazolo[2,3-*c*]-*s*-triazole (**4m**) and the 7*H*-*s*-triazolo[3,4-*b*][1,3,4]thiadiazines (**5a–n**).

Table I. Yields and Melting Points of α-(1,3,4-Oxadiazol-2-yl)thio Ketones (2a–q)[a]

compd	R^1	R^2	R^3	yield, %	mp, °C[b]
2a	Ph	H	CH_3	95	97–98
2b	Ph	H	Ph	84	162–164
2c	4-ClC_6H_4	H	CH_3	76	145–146
2d	4-ClC_6H_4	H	Ph	95	170–172
2e	4-BrC_6H_4	H	CH_3	94	140–141
2f	4-BrC_6H_4	H	Ph	81	168–170
2g	2-pyridyl	H	CH_3	74	106–107
2h	2-pyridyl	H	Ph	89	145
2i	3-pyridyl	H	CH_3	63	115–117
2j	3-pyridyl	H	Ph	89	144–146
2k	4-pyridyl	H	CH_3	100	112–114
2l	4-pyridyl	H	Ph	79	155–157
2m	C_2H_5	H	CH_3	88	oil
2n	C_2H_5	H	Ph	84	69–71
2o	Ph	CH_3	Ph	62	135–137
2p	Ph	$(CH_2)_4$		84	108–110
2q	Ph	Ph	Ph	100	153–155

[a] All microanalyses were within 0.4% of the theoretical values. [b] All ketones except **2m** were recrystallized from EtOH. **2m** was purified on a silica gel column with $CHCl_3$ as the eluent.

Results and Discussion

Reactions of Ketones 2a,b,m with Ammonia. Mercapto ketones **2a–q** were prepared in high yields (Table

(1) (a) Potts, K. T.; Burton, H. R. *J. Org. Chem.* **1966**, *31*, 251. (b) Potts, K. T.; Hirsch, C. *Ibid.* **1968**, *33*, 143. (c) Potts, K. T.; Husain, S. *Ibid.* **1971**, *36*, 10. (d) Miller, G. W.; Rose, F. L. *J. Chem. Soc.* **1963**, 5642. (e) Gray, E. J.; Stevens, M. F. G. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1492. (f) Lovelette, C. A. *J. Heterocycl. Chem.* **1979**, *16*, 555. (g) Sasaki, T.; Ito, E. *Ibid.* **1981**, *18*, 1353.

(2) (a) Hoggarth, E. *J. Chem. Soc.* **1950**, 614. (b) *Ibid.* **1950**, 1579. (c) *Ibid.* **1952**, 4811. (d) Kanaoka, M. *Yakugaku Zasshi* **1956**, *76*, 1133; *Chem. Abstr*, **1957**, *51*, 3579.

(3) (a) Meyer, R. German Patent 574944, 1933; *Chem. Abstr.* **1933**, *27*, 4541. (b) Reid, J. R.; Heindel, N. D. *J. Heterocycl. Chem.* **1976**, *13*, 925.

(4) Jurjew, J. K.; Rakitin, P. M. *Ber.* **1936**, *69*, 2492.

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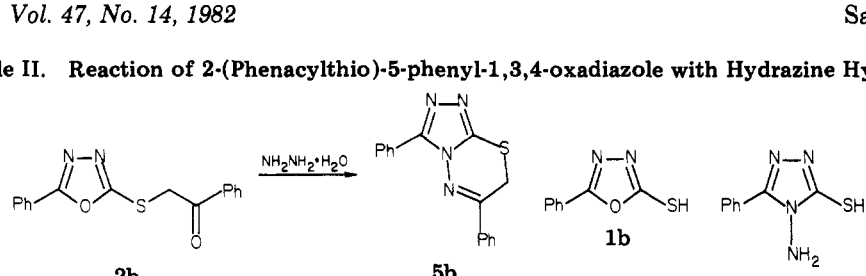
Table II. Reaction of 2-(Phenacylthio)-5-phenyl-1,3,4-oxadiazole with Hydrazine Hydrate

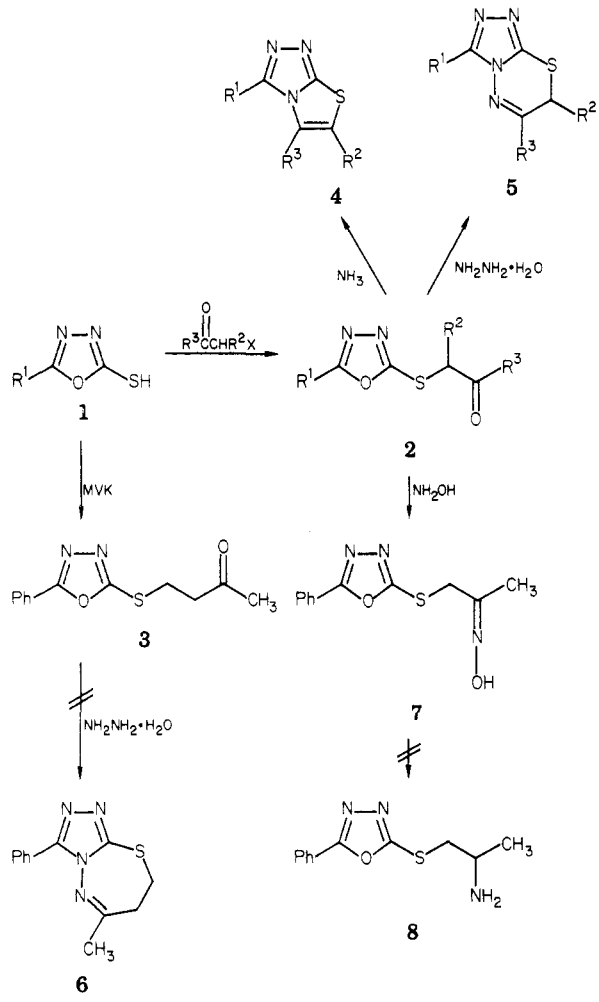


2b 5b 1b 13

equiv of $NH_2NH_2 \cdot H_2O$	solvent	temp	time	product (yield, %)
1	EtOH	reflux	4 h	**1b** (61)
10	neat	reflux	1 h	**13** (100)
2	AcOH	reflux	4 h	**5b** (79)
2	AcOH	room temp	8 day	**5b** (41)
1	HCl/EtOH[a]	reflux	5 h	**5b** (3)

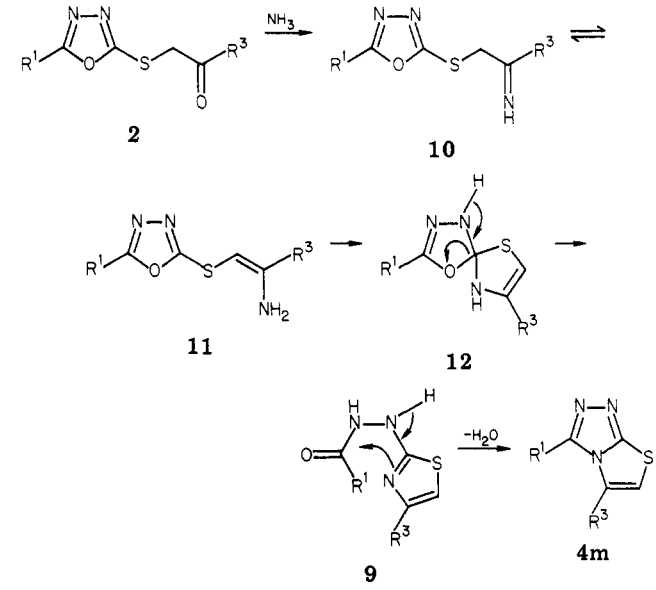
[a] One drop of concentrated HCl to 30 mL of ethanol.

Scheme I



1 2 3 4 5 6 7 8

Scheme II[a]



2 10 11 12 9 4m

[a] **a**, R^1 = Ph, R^3 = CH_3; **b**, R^1 = R^3 = Ph; **m**, R^1 = C_2H_5, R^3 = CH_3.

I) by reaction of the sodium salts of 5-substituted 2-mercaptooxadiazoles[5] with α-halo ketones (Scheme I). Their structures are in accord with IR and ^1H NMR spectra shown in Table IV. Attempts to effect ring closure of **2a** or **2b** to **4** by heating with excess ammonium acetate in EtOH or by treating with ammonia in refluxing acetic acid gave instead the thiazolyl hydrazides **9a** and **9b**, respectively, in 92–98% yields. The structure of **9a** was confirmed by comparison with the properties of an authentic sample prepared from 1-benzoylthiosemicarbazide[6] and chloroacetone.[7] Structure assignment of **9b** was based on elemental analysis and on the spectral data; IR spectra showed strong absorption at 1660 cm^{-1} (C=O) and around 3200 cm^{-1} (NHNH). The hydrazino function was also indicated by two D_2O-exchangeable signals in the ^1H NMR (δ 9.59 and 10.79).

The ketone **2m**, which has C_2H_5 rather than C_6H_5 at the 5-position of the oxadiazole ring, also gave only **9m** (51%) on treatment with ammonium acetate in refluxing EtOH but was converted to **4m** (33%) plus a little **9m** (8%) by treatment with ammonium acetate in refluxing acetic acid. The structure of **4m** was confirmed by comparison of its properties with those reported in the literature.[1c] The reaction path shown in Scheme II is proposed to account for the formation of **9** and **4**. Initially, condensation of the ketone function with ammonia gives **10**, which tautomerizes to **11**. Subsequent attack of the nitrogen of the enamine on the carbon–nitrogen double bond of the oxadiazole ring affords the spiro derivative **12**, which collapses to **9**. Under our reaction conditions, **9m** condenses to **4m**, whereas **9a** and **9b** are stable. These results agree with the report[1c] that condensation of 4-methyl-2-thiazolyl-

(5) (a) Young, R. W.; Wood, K. H. *J. Am. Chem. Soc.* **1955**, *77*, 400. (b) Ainsworth, C. *Ibid.* **1956**, *78*, 4475.

(6) Hoggarth, E. *J. Chem. Soc.* **1949**, 1163.

(7) Beyer, H.; Hohn, H.; Lassig, W. *Chem. Ber.* **1952**, *85*, 1122.

Table III. Yields and Melting Points of 7H-3,6-Disubstituted s-Triazolo[3,4-b][1,3,4]thiadiazines (5a-n)[a]

compd	R^1	R^3	yield, %	mp, °C
5a	Ph	CH_3	91	165-167[c]
5b	Ph	Ph	79	223-225[b] (Lit.[2c] 205-206)
5c	4-ClC_6H_4	CH_3	100	149-151[d]
5d	4-ClC_6H_4	Ph	95	261-263[b]
5e	4-BrC_6H_4	CH_3	94	156-160[d]
5f	4-BrC_6H_4	Ph	59	270 dec[b]
5g	2-pyridyl	CH_3	57	210-212[d]
5h	2-pyridyl	Ph	91	204-206[b]
5i	3-pyridyl	CH_3	61	158-160[d]
5j	3-pyridyl	Ph	74	232-234[b]
5k	4-pyridyl	CH_3	86	177-179[d]
5l	4-pyridyl	Ph	48	138 dec[b]
5m	C_2H_5	CH_3	52	95-97[e]
5n	C_2H_5	Ph	82	161-163[b]

[a] All microanalyses were within 0.4% of the theoretical values. R^2 = H. [b] Recrystallized from EtOH. [c] Recrystallized from CH_3CN. [d] Recrystallized from $CHCl_3$-Et_2O. [e] Purified on a silica gel column with 1:20 EtOH/$CHCl_3$ as the eluent.

hydrazine with propionic acid gives **4m**, whereas attempts to condense 4-methyl(or phenyl)-2-thiazolylhydrazine with benzoic acid to give **4a** or **4b** were unsuccessful. These authors were able to prepare **9a** and **9b** by another route and to close them to **4a** and **4b** with phosphoryl chloride.

Reaction of Ketones 2a-q with Hydrazine. The reaction of **2b** with hydrazine hydrate was examined in detail, with the results shown in Table II. Under neutral conditions the C-S bond was cleaved to give **1b** or with excess hydrazine to give **13**.[3b] Inasmuch as **5b** is stable on heating in acid or base, it appears that **13** is formed by reaction of **1b** with hydrazine rather than by hydrolysis of preformed **5b**. Reaction of **2b** with hydrazine hydrate in the presence of HCl gave **5b** in very low yield, whereas good yields of **5b** were obtained in acetic acid. Condensation of **2a-n** with hydrazine hydrate in refluxing acetic acid gave the corresponding triazolothiadiazines **5a-n** in good yields (Table III). On the other hand, ketones **2o-q**, which bear a substituent on the carbon α to the carbonyl group, did not give **5**: **2o** ($R^2 = CH_3$) gave intractable products; **2p** [$R^2 = (CH_2)_4$] cleaved to **1p**; *2q* ($R^2 = C_6H_5$) was inert to hydrazine hydrate in refluxing acetic acid.

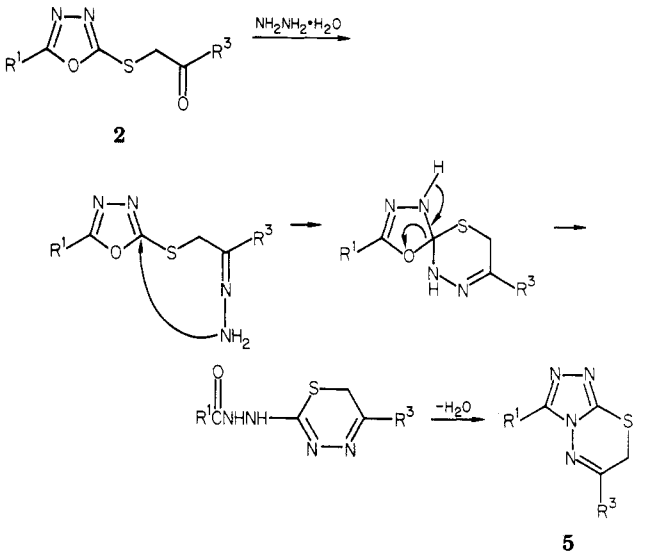
The structure of **5b** was confirmed by comparison with the properties of an authentic sample prepared from **13** and phenacyl bromide.[2c] Structure assignments of **5a** and **5c-n** were based on elemental analyses and on the spectral data shown in Table V (supplementary material); the ring closure was verified by the disappearance of the carbonyl absorption in the IR spectra and by the upfield shift of the methylene protons in the ^1H NMR. The reaction mechanism (Scheme III) is presumed to be similar to that proposed for the condensation with ammonia.

Other Approaches to Fused Triazole Systems. Michael addition[8] of **1a** to methyl vinyl ketone gave the oxadizole ketone **3** in 65% yield. Attempts to condense **3** to **6** (Scheme I) by using hydrazine hydrate in refluxing EtOH or acetic acid resulted in cleave back to **1a**.

We also attempted the preparation of amine **8**, which should be an intermediate to fused triazoles, by reduction of oxime **7**, obtained from **2a** and hydroxylamine. However, attempts to reduce **7** with Al-Hg, $LiAlH_4$, or Zn/HOAc were unsuccessful (Scheme I).

(8) Bakuzis, P.; Bakuzis, M. L. F. *J. Org. Chem.* **1981**, *46*, 235.

Scheme III



Experimental Section

Melting points were measured with a Yanagimoto micro-melting-point apparatus and are uncorrected. Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer. The ^1H NMR spectra were taken at room temperature with a JEOL C-60-HL spectrometer with tetramethylsilane as an internal standard. The IR spectra were taken with a JASCO IRA-1 spectrometer.

α-[(1,3,4-Oxadiazol-2-yl)thio] Ketones 2a-q. To a clear solution of 2-mercapto-1,3,4-oxadiazole[5] and an equimolar amount of NaOH was added an equimolar amount of α-halo ketone (chloroacetone, phenacyl bromide, desyl bromide,[9] 2-bromocyclohexanone,[10] or α-bromopropiophenone[11]) in one portion at room temperature. After the mixture was stirred for 12 h at room temperature, the product was filtered and recrystallized from ethanol, affording **2a-l** and **2n-q**. **2m** was extracted with chloroform from the reaction mixture. The organic layer was dried over anhydrous magnesium sulfate and concentrated to give a yellow oil, which was purified on a silica gel column with chloroform as the eluent. Yields and physical properties of **2a-q** are summarized in Table I and IV (supplementary material).

2-[(3-Oxobutyl)thio]-5-phenyl-1,3,4-oxadiazole (3). A solution of 2-mercapto-5-phenyl-1,3,4-oxadiazole (180 mg, 1.0 mmol), methyl vinyl ketone (0.08 mL, 1.0 mmol), triethylamine (0.03 mL, 0.2 mmol), and dry methanol (10 mL) was stirred for 12 h at room temperature. After removal of the solvent, washing the residue with water (ca. 20 mL) gave 160 mg (65%) of **3**. An analytical sample was obtained as colorless crystals by recrystallization from ethanol: mp 126-127 °C; IR (KBr) 1710 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.25 (s, 3 H, CH_3), 3.19 (d, J = 7.50 Hz, 2 H, CH_2), 4.39 (d, J = 7.50 Hz, CH_2), 7.32-8.01 (m, 5 H, Ar). Anal. Calcd for $C_{12}H_{12}N_2O_2S$: C, 58.05; H, 4.87; N, 11.28. Found: C, 57.96; H, 4.87; N, 11.36.

2-(4-Methylthiazol-2-yl)benzhydrazide (9a). From 2a and Ammonium Acetate. A solution of **9a** (230 mg, 1.0 mmol), ammonium acetate (770 mg, 10.0 mmol), and ethanol (20 mL) was heated under reflux for 2 h. After removal of solvent, washing the residue with water (ca. 10 mL) gave 210 mg (92%) of **9a**. An analytical sample was obtained as brown crystals by recrystallization from ethanol (mp 205-209 °C). Its spectral data were in good agreement with those of an authentic sample prepared from 1-benzoylthiosemicarbazide and chloroacetone.

From 1-Benzoylthiosemicarbazide and Chloroacetone. A mixture of 1-benzoylthiosemicarbazide[6] (500 mg, 2.6 mmol), chloroacetone (0.21 mL, 2.6 mmol), and dry ethanol (20 mL) was heated under reflux for 3 h. Removal of solvent from the resulting clear solution gave a colorless solid, which was dissolved in 30 mL

(9) Knoevenagel, E. *Ber.* **1888**, *21*, 1355.
(10) Plant, S. G. P. *J. Chem. Soc*, **1930**, 1595.
(11) Pampel, O.; Schmidt, G. *Ber.* **1886**, *19*, 2896.

of water. Insoluble products were removed by filtration and neutralization of the filtrate with saturated sodium acetate solution afforded 460 mg (77%) of **9a** as a colorless precipitate. An analytical sample was obtained as colorless crystals by recrystallization from ethanol: mp 213–215 °C; IR (KBr) 3230 (NH), 1660 (C=O) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 2.12 (d, J = 1.20 Hz, 3 H, CH_3), 6.35 (q, J = 1.20 Hz, 1 H, =CH), 7.37–8.25 (m, 5 H, Ph), 9.42 (s, 1 H, NH), 10.75 (s, 1 H, NH). Anal. Calcd for $C_{11}H_{11}N_3OS$: C, 56.63; H, 4.75; N, 18.01. Found: C, 56.83; H, 4.81; N, 18.28.

2-(4-Phenylthiazol-2-yl)benzhydrazide (9b). Compound **9b** was obtained similarly from the reaction of **2b** and ammonium acetate in ethanol: 98% yield; mp 203–205 °C (EtOH); IR (KBr) 3280 (NH), 1660 (C=O) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 7.22–8.17 (m, 11 H, Ph and =CH), 9.59 (s, 1 H, NH), 10.79 (s, 1 H, NH). Anal. Calcd for $C_{16}H_{13}N_3OS$: C, 65.06; H, 4.44; N, 14.23. Found: C, 64.89; H, 4.57; N, 14.27.

Treatment of 2m with Ammonium Acetate. In Ethanol. A solution of **2m** (370 mg, 2 mmol), ammonium acetate (1.5 g, 20 mmol), and ethanol (30 mL) was heated under reflux for 6 h. After removal of solvent, addition of water (10 mL) to the residue gave an oily product, which solidified on standing for 30 min at room temperature. Filtration gave 190 mg (51%) of **9m**, which was purified by recrystallization from ethanol: mp 187–190 °C; IR (KBr) 3270 (NH), 1660 (C=O) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 1.80 (t, J = 7.50 Hz, 3 H, CH_3), 2.15 (d, J = 1.20 Hz, 3 H, CH_3), 2.16 (q, J = 7.50 Hz, 2 H, CH_2), 6.22 (q, J = 1.20 Hz, 1 H, =CH), 9.10 (s, 1 H, NH), 9.94 (s, 1 H, NH). Anal. Calcd for $C_7H_{11}N_3OS$: C, 45.39; H, 5.99; N, 22.68. Found: C, 45.50; H, 6.14; N, 22.47.

In Acetic Acid. A solution of **2m** (370 mg, 2 mmol), ammonium acetate (160 mg, 2 mmol), and acetic acid (4 mL) was heated under reflux for 41 h. After addition of 20 mL of saturated brine solution, the resulting dark brown mixture was basified with 10% sodium hydroxide solution to pH 8 and extracted with chloroform (100 mL). The chloroform solution was dried over anhydrous magnesium sulfate and concentrated to give a dark brown oil, and chromatography on silica gel ($EtOH/CHCl_3$, 1/10) gave **9m** (30 mg, 8%) and **4m** (110 mg, 33%): mp 103–104 °C (lit.[1c] mp 96–97 °C); IR (KBr) 1602, 1510, 1480 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45 (t, J = 7.50 Hz, 3 H, CH_3), 2.52 (d, J = 1.20 Hz, 3 H, CH_3), 3.10 (q, J = 7.50 Hz, 2 H, CH_2), 6.50 (q, J = 7.50 Hz, 1 H, =CH).

Reaction of 2b with Hydrazine Hydrate. In Ethanol. A solution of **2b** (300 mg, 1 mmol), hydrazine hydrate (50 mg, 1 mmol), and ethanol (20 mL) was heated under reflux for 4 h. After removal of ethanol, the resulting yellow oil was dissolved in 20 mL of 2 N sodium hydroxide solution, and an insoluble dark yellow oil was separated by filtration. Neutralization of the filtrate with 2 N hydrochloric acid solution gave 110 mg (61%) of **1b** as a light yellow precipitate, which was recrystallized from ethanol; mp 220–223 °C[12] (lit.[5a] mp 219–220 °C).

(12) Spectral data are in good agreement with those of an authentic sample prepared according to the reported procedure.

Without Solvent. A mixture of **2b** (300 mg, 1 mmol) and hydrazine hydrate (500 mg, 10 mmol) was heated under reflux for 1 h. Removal of the excess hydrazine hydrate under reduced pressure gave a yellow oil, which solidified by the addition of 10 mL of 2 N hydrochloric acid solution, and filtration afforded 200 mg (100%) of **13**, mp 207–210 °C[12] (lit.[3b] mp 203–206 °C).

In Acetic Acid. A mixture of **2b** (300 mg, 1 mmol), hydrazine hydrate (100 mg, 2 mmol), and acetic acid (4 mL) was heated under reflux for 4 h. After removal of acetic acid, the residue was washed with 10 mL of water, filtered, and purified by recrystallization from ethanol to give 230 mg (79%) of **5b**. Its physical properties are summarized in Tables IV and V (supplementary material).

Similarly **5d,f,h,j,l,n** were obtained by the procedure employed for the synthesis of **5b**. **5a,c,e,g,i,k,m** were obtained by extracting the resulting residue with chloroform after basification to pH 8 with 2 N sodium hydroxide solution. The chloroform solution was dried over anhydrous magnesium sulfate and concentrated, followed by purification as listed in Table III. Yields and physical properties of **5a–n** are summarized in Table III and V.

α-[(5-Phenyl-1,3,4-oxadiazol-2-yl)thio]acetoxime (7). To a clear solution of hydroxylamine hydrochloride (90 mg, 1.2 mmol), potassium hydroxide (80 mg), and 50% aqueous ethanol (20 mL) was added **2a** (230 mg, 1.0 mmol) with stirring at room temperature. A white precipitate formed gradually, and after 5 h the solvent was removed. Washing the residue with 10 mL of water and filtration gave 240 mg (97%) of **7**. An analytical sample was obtained as colorless crystals by recrystallization from ethanol: mp 193–195 °C; IR (KBr) 3220 (OH) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 1.93 (s, 3 H, CH_3), 4.13 (s, 2 H, CH_2), 7.50–8.20 (m, 5 H, Ph), 10.94 (s, 1 H, OH). Anal. Calcd for $C_{11}H_{11}N_3O_2S$: C, 53.00; H, 4.45; N, 16.86. Found: C, 53.17; H, 4.41; N, 16.73.

Registry No. 1 (R_1 = Ph), 3004-42-0; 1 (R_1 = 4-ClC_6H_4), 23766-28-1; 1 (R_1 = 4-BrC_6H_4), 41421-19-6; 1 (R^1 = 2-pyridyl), 3690-47-9; 1 (R_1 = 3-pyridyl), 3690-46-8; 1 (R_1 = 4-pyridyl), 15264-63-8; 1 (R_1 = Et), 62999-57-9; **2a**, 81555-88-6; **2b**, 74087-90-4; **2c**, 81555-89-7; **2d**, 74087-97-1; **2e**, 81555-90-0; **2f**, 81555-91-1; **2g**, 81555-92-2; **2h**, 81555-93-3; **2i**, 81555-94-4; **2j**, 81555-95-5; **2k**, 81555-96-6; **2l**, 81555-97-7; **2m**, 81555-98-8; **2n**, 81555-99-9; **2o**, 81556-00-5; **2p**, 81556-01-6; **2q**, 81556-02-7; **3**, 81556-03-8; **4m**, 26542-56-3; **5a**, 81556-04-9; **5b**, 79074-65-0; **5c**, 81556-05-0; **5d**, 68469-09-0; **5e**, 81556-06-1; **5f**, 81556-07-2; **5g**, 81556-08-3; **5h**, 81556-09-4; **5i**, 81556-10-7; **5j**, 81556-11-8; **5k**, 56400-86-3; **5l**, 56400-87-4; **5m**, 24848-31-5; **5n**, 24848-29-1; **7**, 81556-12-9; **9a**, 36256-78-7; **9b**, 81556-13-0; **9m**, 81556-14-1; **13**, 22706-11-2; chloroacetone, 78-95-5; phenacyl bromide, 70-11-1; desyl bromide, 1484-50-0; 2-bromocyclohexanone, 822-85-5; α-bromopropiophenone, 2114-00-3; methyl vinyl ketone, 78-94-4; ammonium acetate, 631-61-8; 1-benzoylthiosemicarbazide, 5351-66-6; hydrazine, 302-01-2.

Supplementary Material Available: Tables IV and V containing infrared and NMR data for compounds **2a–q** and **5a–n** (5 pages). Ordering information is given on any current masthead page.