λ_{max} 358 nm (ε 5080), 282 (8800); ^{1}H NMR (CD_3CN) δ 4.00 (s, 3 H), 8.90 (s, 1 H), 8.93 (s, 1 H); ^{13}C NMR (Me_2SO-d_6, Cr(acac)) δ 148.72 (CH), 146.44 (CH), 118.76, 124.93, 153.85, 160.68; ^{13}C NMR [CD_3CN, Cr(acac)] δ 40.82 (CH_3), 148.44 (CH), 144.34 (CH).

8-Methyl-1,4-dithiino[3,4-*b*;3′,4′-*e*]diisothiazole-1-carbonitrile (27). A solution of tetraethylammonium cyanide (1.7 g, 0.01 mol) in acetonitrile (50 mL) was added over a 15-min period to a solution of **26** (3.3 g, 0.01 mol) in acetonitrile (100 mL) at 15 °C, and crude **27** (2.21 g, 98%) was isolated by filtration. Compound **27** was washed with acetonitrile and ether. Recrystallization from *n*-butyl chloride (or acetone) gave analytically pure **28**: mp 140–142 °C; IR (Nujol) 4.55, 6.21, 6.49 μm; ^{1}H NMR ($CDCl_3$) δ 3.45 (s, 3 H), 7.05 (s, 1 H), 8.47 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 39.71 (CH_3), 113.93 (CN), 123.20, 123.70, 126.99 (CH), 143.69 (CH), 156.04, 156.82. Anal. Calcd for $C_8H_5N_3S_4$: C, 35.4; H, 1.9; N, 15.5; S, 47.3. Found: C, 35.5; H, 2.2; N, 15.2; S, 47.2.

1,4-Dithiino[3,4-*c*;6,5-*c*]diisothiazole 4-Oxide (30).[38] A solution of trimethylsilyl nitrate[39] (2.8 g, 0.02 mol) in CH_2Cl_2 (20 mL) was added dropwise to a suspension of **18** (2.3 g, 0.01 mol) in CH_2Cl_2 (70 mL). The mixture was stirred at room temperature for 3 days and filtered. Recrystallization from ethanol gave 1.4 g (29%) of **24**: mp 183–185 °C; NMR (Me_2SO-d_6) δ 9.4 (s, 1 H), 10.22 (s, 1 H); mass spectrum, *m/e* 245.9070 (calcd *m/e* 245.9050). Anal. Calcd for $C_6H_2N_2S_4O$: C, 29.3; H, 0.8; N, 11.4. Found: C, 30.1; H, 1.2; N, 11.6.

1,4-Dithiino[3,4-*b*;3′,4′-*e*]diisothiazole 4,8-Dioxide (29).[40] A KelF vessel was charged with **18** (2.3 g, 0.01 mol), evacuated, and cooled in liquid N_2. HF (40 mL) was distilled directly in. The vessel was allowed to warm. When the HF had entirely melted, sodium nitrate (2.55 g, 0.03 mol) was added in one portion. The vessel was sealed and allowed to warm to room temperature. After the mixture was stirred for 7 h, the HF was allowed to evaporate under a gentle stream of nitrogen and then under aspirator vacuum to remove traces of HF. The remaining yellow solid was washed well with water, dried under vacuum, and recrystallized from Me_2SO, giving 2.68 g of product: mp >240 °C; IR (Nujol) 3.25, 6.91, 9.52 μm; ^{1}H NMR (Me_2SO-d_6) δ 10 (two peaks of equal intensity); mass spectrum, *m/e* 262. Anal. Calcd for $C_6H_2S_4N_2O_2$: C, 27.5; H, 0.8; S, 48.9; N, 10.7; mol wt 262. Found: C, 27.5; H, 1.1; N, 10.8; S, 48.7.

1,4-Dithiino[3,4-*b*;3′,4′-*e*]diisothiazole 4,4,8-Trioxide (31). A solution of **17** (5.0 g, 0.016 mol) in 5% NaOCl (200 mL) was heated at 65–67 °C for 3 h. The mixture was cooled and filtered, and the solid **31** was washed with H_2O, 95% EtOH, and ether to give 2.08 g (47%) colorless **31**. Recrystallization from a DMF–95% EtOH mixture gave analytically pure **31**: mp 235 °C dec; IR (KBr) 7.46, 8.62, 8.93, 9.09 μm; mass spectrum, *m/e* 277.8930 (calcd *m/e* 277.8948); the sample also showed traces of *m/e* 293.8848 (calcd *m/e* 293.8897), indicating the presence of trace amounts of the disulfone. Anal. Calcd for $C_6H_2N_2S_4O_3$: C, 25.9; H, 0.7; N, 10.1; S, 46.1. Found: C, 26.1; H, 1.0; N, 9.8; S, 45.7.

Registry No. **1**, 2448-55-7; **4**, 63419-80-7; **4** radical ion, 75083-00-0; **6**, 5466-54-6; **7**, 66232-78-8; **9**, 75083-01-1; **12**, 75083-02-2; **15**, 66393-25-7; **16**, 66232-81-3; **17**, 63419-82-9; **17** K salt, 66232-83-5; **17** NBu_4 salt, 63459-58-5; **17** amide, 75083-03-3; **17** methylamide, 75083-04-4; **17** dimethylamide, 63419-84-1; **17** phenylhydrazide, 75083-05-5; **17** *p*-methylphenylamide, 63419-90-9; **17** *p*-methoxyphenylamide, 63419-88-5; **17** *p*-nitrophenylamide, 63419-89-6; **17** *o*-nitrophenylamide, 63419-91-0; **17** methyl-*p*-nitrophenylamide, 63419-92-1; **17** methyl-*o*-nitrophenylamide, 63419-93-2; **17** dimethyl ester, 63419-85-2; **17** diethyl ester, 63419-86-3; **17** dibenzyl ester, 63419-87-4; **17** diphenyl ester, 75083-06-6; **18**, 63419-81-8; **18**·2HBr, 75083-07-7; **20**, 75082-98-3; **20** polymer, 75082-99-4; **21**, 75083-08-8; **22**, 75083-09-9; **24**, 75083-10-2; **25**, 75083-11-3; **26**, 75083-13-5; **27**, 75083-14-6; **29**, 75083-15-7; **30**, 75101-69-8; **31**, 75083-16-8; **41**, 63419-83-0; sulfur, 7704-34-9; 2-oxo-4,5-dicyano-1,3-dithiacyclopentene, 934-31-6; 3,4-bis(methylthio)isothiazole-5-carbonitrile, 75083-17-9; 3,4-dimercaptotoluene, 496-74-2; dichloromaleonitrile, 6613-48-5; dichloroquinoxaline, 2213-63-0.

(38) The authors thank Professor A. J. Arduengo, University of Illinois, for running this experiment.
(39) M. Schmidt and H. Schmidbauer, *Angew. Chem.*, 71, 220 (1959); L. Birkofer, M. Franz, *Chem. Ber.*, 105, 470 (1972).
(40) The authors thank Dr. Andrew E. Feiring of this department for running this experiment.

Reactions of Trimethylsilyl Azide with Heterocumulenes

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Trimethylsilyl azide (TMSA) reacted with aryl isocyanates to give arylcarbamoyl azides, 1-aryl-5(4*H*)-tetrazolinones, and/or 1-aryl-4-(arylcarbamoyl)-5(4*H*)-tetrazolinones, whose yields were dependent on the reaction conditions. The reaction between TMSA and benzoyl or thiobenzoyl isocyanates provides a facile method for the preparation of 5-aryl-3-hydroxy-1,2,4-oxadiazoles or -1,2,4-thiadiazoles, respectively. However, with phenyl or benzoyl isothiocyanate, 1-anilino-1,2,3,4-thiatriazole or benzoylcyanamide was obtained in low yield, respectively. TMSA reacted with carbodiimides to afford the corresponding 5-aminotetrazoles. Tetraphenylsuccinimide, *N*-(diphenylacetyl)tetraphenylsuccinimide, 1,3-bis(diphenylmethyl)urea, and/or benziloylamide were obtained from the reaction of TMSA with diphenyl ketene. The pathways for the formation of the above products are also described.

It is known that trimethylsilyl azide (TMSA) is a good reagent in organic syntheses. In analogy with organic azides, TMSA behaves as a 1,3-dipole toward acetylenes,[1] olefins,[2] and nitriles[2a,3] to give the corresponding cycloadducts. The reaction of TMSA with carboxylic acid chlorides,[4] anhydrides,[5] esters,[6] and lactones[6] provides a facile synthetic route to a variety of isocyanates which in some cases directly cyclized to heterocyclic compounds. It has also been reported that TMSA reacted with aliphatic aldehydes and epoxides to form the corresponding tri-

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(4) (a) H. R. Kricheldorf, *Synthesis*, 551 (1972); (b) J. H. McMillan and S. S. Washburne, *J. Org. Chem.*, 38, 2982 (1973).
(5) (a) H. R. Kricheldorf, *Chem. Ber.*, 105, 3958 (1972); (b) H. R. Kricheldorf and W. Regel, *ibid.*, 106, 3753 (1973); (c) S. S. Washburne, W. R. Peterson, Jr., and D. A. Berman, *J. Org. Chem.*, 37, 1738 (1972); (d) J. D. Warsen, J. H. McMillan, and S. S. Washburne, *ibid.*, 40, 743 (1975); (e) J. H. McMillan and S. S. Washburne, *J. Heterocycl. Chem.*, 12, 1215 (1975).
(6) H. R. Kricheldorf, *Chem. Ber.*, 106, 3765 (1973).

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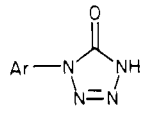
Table I. 1-Aryl-5(4*H*)-tetrazolinones (6)



	Ar	yield, %[a]	mp, °C[a]	IR (KBr), cm^{-1} NH	IR (KBr), cm^{-1} C=O	^{13}C NMR, δ[b] (C=O)	*m/e* (M$^+$)
6a	Ph	100 (76)	192-193 (189-190)	2400-3300	1710	150.1	162
6b	*p*-MeOC$_6$H$_4$	99 (76)	183-184 (181.5-182.5)	2400-3250	1710	150.3	192
6c	*p*-ClC$_6$H$_4$	93 (72)	210 (206-207)	2000-3300	1720	150.0	196, 198
6d	*p*-O$_2$NC$_6$H$_4$	83 (58)	227 (217-218)	2400-3300	1720	150.3	207

[a] Figures in parentheses are reported[9] yields and melting points, respectively. [b] Measured in Me$_2$SO-d_6.

methylsiloxy azides.[7] However, little attention has been drawn to the reaction of TMSA with heterocumulenes. In this paper we report the reactions of TMSA with heterocumulenes such as isocyanates, isothiocyanates, carbodiimides, and diphenylketene.

Results and Discussion

Reactions with Isocyanates. It has been reported that hydrazoic acid reacted with alkyl and aryl isocyanates to give the carbamoyl azides,[8] whereas the reaction of aluminum azide, generated in situ from sodium azide and aluminum chloride, with aryl isocyanates gave the corresponding 1-aryl-5(4*H*)-tetrazolinones in yields ranging from 58 to 76%.[9] Thus, we have first investigated the reaction of TMSA with aryl isocyanates (1) in order to compare with the above reactions.

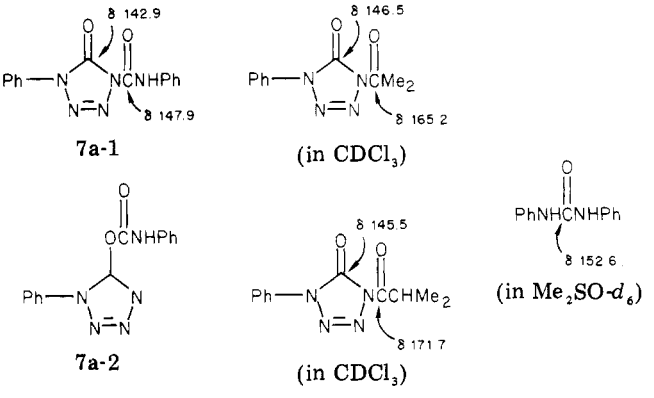
When TMSA was allowed to react with phenyl isocyanate (**1a**) and then the products were desilylated with water, phenylcarbamoyl azide (**3a**), 1-phenyl-5(4*H*)-tetrazolinone (**6a**), and/or its phenylcarbamoyl derivative **7a** were obtained; the yields were greatly dependent on the reaction conditions. In the reaction of TMSA with an equimolar amount of **1a** in dry benzene or without solvent at 50–60 °C for 24 h, **3a** or **3a**, **6a**, and **7a** were obtained in 57 or 21, 8, and 28% yields, respectively. On the other hand, the reaction of 2 molar amounts of TMSA with **1a** under reflux without solvent for 24 h afforded **6a** in quantitative yield. In the reactions of 2 molar amounts of TMSA with *p*-methoxyphenyl (**1b**), *p*-chlorophenyl (**1c**), and *p*-nitrophenyl isocyanate (**1d**) under similar conditions, the corresponding 1-aryl-5(4*H*)-tetrazolinones, **6b**, **c**, and **d**, were obtained in good yields.

The yields and physical and spectral data of 1-aryl-5-(4*H*)-tetrazolinones **6** are summarized in Table I. This method for the preparation of **6** is superior to the earlier method[9] in terms of both yields and the simple procedure.

The reaction of tetrazolinone **6a** with isocyanate **1a** in boiling benzene gave the phenylcarbamoyl derivative **7a** in 91% yield, whereas on being heated at 150 °C, **7a** reverted to **6a** and **1a**. Acylation of tetrazolinone **6a** generally occurs exclusively at the 4-*N*-position but O-acylation has been observed in up to 50% yield when the acylating agent was 2-methylpropanoyl chloride.[10] Thus, 1-phenyl-4-(phenylcarbamoyl)-5(4*H*)-tetrazolinone (**7a**-1) or 1-phenyl-5-[(phenylcarbamoyl)oxy]tetrazole (**7a**-2) is conceivable for the structure of **7a** (see Chart I).

On the basis of spectral data, however, it can be concluded that **7a** is **7a**-1 but not **7a**-2. The compound **7a**

Chart I



exhibited IR absorptions at 3260, 1760 (vs), and 1720 cm^{-1} (weak) and a ^{1}H NMR signal at δ 9.8–10.1 (1 H, br, NH). In particular, the IR spectrum is consistent with the structure **7a**-1 but not with the structure **7a**-2. The absorptions at 1760 and 1720 cm^{-1} correspond, respectively, to the side-chain C=O[11] and ring C=O[9] stretching vibrations in **7a**-1. The ^{13}C NMR spectrum also confirms the structure **7a**-1, showing two carbonyl carbon absorptions. On the basis of comparison with ^{13}C NMR data of analogous compounds as illustrated in Chart I, the signals at δ 142.9 and 147.9 in **7a**-1 are assignable to the ring C=O and side-chain C=O carbons, respectively. Two 4-acyltetrazolinones shown in Chart I were prepared by the reported method.[10]

The susceptibility of **7a**-1 to thermal dissociation is not unexpected since ureas derived from very weakly basic amines and phenyl isocyanate undergo thermal dissociation.[12]

It is evident that phenylcarbamoyl azide (**3a**) was formed through desilylation of its silylated compound **2a**. Arylcarbamoyl azides have proved resistant to both the Curtius rearrangement and base-induced cyclization to tetrazole derivatives.[8] In fact, **3a** was unchanged in refluxing benzene or toluene. On being heated in refluxing benzene, however, silylated compound **2a**, generated in situ from **3a** and trimethylchlorosilane in the presence of triethylamine, afforded **6a** in quantitative yield. The reaction of silylated compound **4a**, generated in situ from **6a**, with isocyanate **1a** in benzene at 50–60 °C afforded **7a**, whereas silylated compound **5a**, generated in situ from **7a**, gave **6a** on being heated in refluxing benzene.

Although attempts to isolate silylated compounds **2a**, **4a**, and **5a** were unsuccessful because of their labilities

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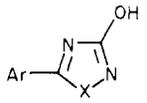
(11) A high C=O stretching absorption is typical in N-substituted carbamoylazoles [J. Denkosch, K. Schlogl, and H. Woidich, *Monatsh. Chem.*, **88**, 35 (1957)] as well as in azolides [H. A. Stabb, *Angew. Chem.*, **74**, 407 (1962)].
(12) R. A. Henry and W. M. Dehn, *J. Am. Chem. Soc.*, **71**, 2297 (1949).

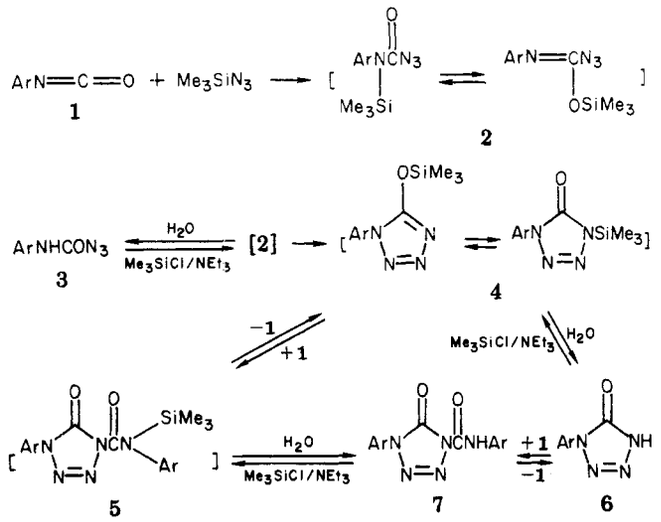
Table II. 5-Aryl-3-hydroxy-1,2,4-oxadiazoles (13) and -1,2,4-thiadiazoles (14)



	Ar	X	yield, %	mp, °C	IR (KBr), cm^{-1} [a] (azole ring)	^1H NMR, δ [b] (OH)	^{13}C NMR, δ [b] (azole C)	*m/e* (M^+)
13a	Ph	O	80	203-204 [c]	1615	12.2-13.5	173.0, 174.4	162
13b	*p*-$MeOC_6H_4$	O	65	217-218	1620 (sh), 1600	12.3-13.1	172.9, 174.4	192
13c	*p*-ClC_6H_4	O	83	223-224	1620 (sh), 1600	12.3-13.4	173.4, 173.9	196, 198
14a	Ph	S	85	208-209 [d]	1645	11.5-13.8	171.7, 186.9	178
14b	*p*-$MeOC_6H_4$	S	97	231-232	1650	12.3-12.7	171.6, 186.6	208
14c	*p*-ClC_6H_4	S	96	297-298	1645	12.2-13.3	171.5, 185.4	212, 214

[a] IR spectra exhibited broad absorption bands at 2000-3300 cm^{-1}. [b] Measured in Me_2SO-d_6. [c] Reported melting point 201-203 °C.[16] [d] Reported melting point 206 °C.[13]

Scheme I[a]



[a] a, Ar = Ph; b, Ar = *p*-$MeOC_6H_4$; c, Ar = *p*-ClC_6H_4; d, Ar = *p*-$O_2NC_6H_4$.

toward moisture, the pathway for the formation of **6** and **7** is illustrated in Scheme I on the basis of the above observations. The reaction proceeds via initial formation of silylated azide **2**. Subsequent cyclization of **2** to silylated tetrazolinone **4**, followed by reaction with isocyanate **1**, yields 1:2 adduct **5**. At a reaction temperature above 80 °C, 1:2 adduct **5** dissociates into **4** and **1**. Desilylation of **2**, **4**, and **5** with water gives stable products **3**, **6**, and **7**, respectively.

It has been reported that hydrazoic acid reacted with thiobenzoyl isocyanate to give pale red crystals formulated as 5-phenyl-2-(thiobenzoylcarbamoyl)-1,2,4-thiadiazolin-3-one which on recrystallization converted to 3-hydroxy-5-phenyl-1,2,4-thiadiazole in 34% yield.[13] As mentioned above, TMSA reacted with aryl isocyanates (**1**) to give different products from those in the reaction of hydrazoic acid. Contrary to the formation of 5-iminoimidazolidinedione derivatives from the reaction of trimethylsilyl cyanide with aryl isocyanates,[14] the cyanide reacted with thiobenzoyl isocyanates to give the 1,3,5-thiadiazepine-4,6-dione derivatives.[15] Thus, the reaction of TMSA with benzoyl (**8**) and thiobenzoyl isocyanates (**9**) was next investigated.

When TMSA was allowed to react with benzoyl isocyanate (**8a**) under reflux without solvent for 6 h and the reaction mixture was treated with ethanol, 3-hydroxy-5-phenyl-1,2,4-oxadiazole (**13a**) was obtained in good yield. Similarly, *p*-methoxybenzoyl (**8b**) and *p*-chlorobenzoyl isocyanates (**8c**) afforded the corresponding 3-hydroxy-1,2,4-oxadiazoles **13b** and **13c**, respectively, in fairly good yields. Previously **13a** was prepared in an overall yield of 32.5% by demethylation of 3-methoxy-5-phenyl-1,2,4-oxadiazole obtained from dimethyl *N*-benzoyliminothiolcarbonate and hydroxylamine.[16] Thus, the reaction of TMSA with isocyanates **8** provides a new route to 5-aryl-3-hydroxy-1,2,4-oxadiazoles **13**. Also, 5-(*p*-chlorophenyl)-3-(trimethylsiloxy)-1,2,4-oxadiazole (**12c**, mp 76–78 °C) as pale yellow crystals was isolated from the reaction of TMSA with **8c**.

TMSA reacted with thiobenzoyl (**9a**), *p*-methoxythiobenzoyl (**9b**), and *p*-chlorothiobenzoyl isocyanates (**9c**) in xylene at 120 °C to give the corresponding 5-aryl-3-hydroxy-1,2,4-thiadiazoles **14a–c**, respectively, in excellent yields after treatment of the respective reaction product with ethanol.

A possible pathway for the formation of **13** and **14** is outlined in Scheme II. In a similar manner as for **1**, TMSA adds to **8** or **9** to yield silylated tetrazole **10**. Subsequent elimination of nitrogen generates a presumed 1,3-dipole, **11**, which could exist in equilibrium with an acyl nitrene. Cyclization of **11** yields silylated 1,2,4-oxa(or thia)diazole **12** which gives stable **13** or **14** on desilylation. This process is somewhat analogous to that reported for the formation of 1,3,4-oxadiazoles by the reaction of a 5-substituted tetrazole and an acyl chloride in pyridine.[17] As an alternate pathway, particularly for the formation of **14**, it is not possible to exclude the process involving a 1,4-adduct **15** which could give **11**, because **9** exhibited high reactivity in 1,4-additions.[15]

Structural elucidation of **13** and **14** was accomplished on the basis of spectral data. The yields and physical and spectral data are summarized in Table II. It has been clarified that **13a** exists predominately in the hydroxy form.[16] No carbonyl absorption bands appeared in the IR spectra of the six compounds **13** and **14**. From this it is concluded that both **13** and **14** exist exclusively in the hydroxy form.

Reactions with Isothiocyanates. It has been reported that hydrazoic acid or sodium azide reacted with phenyl (**16**)[18] or benzoyl isothiocyanate (**17**)[19] to give 5-anilino-

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(16) A. R. Katritzky, B. Wallis, R. T. C. Brownlee, and R. D. Topsom, *Tetrahedron*, **21**, 1681 (1965).
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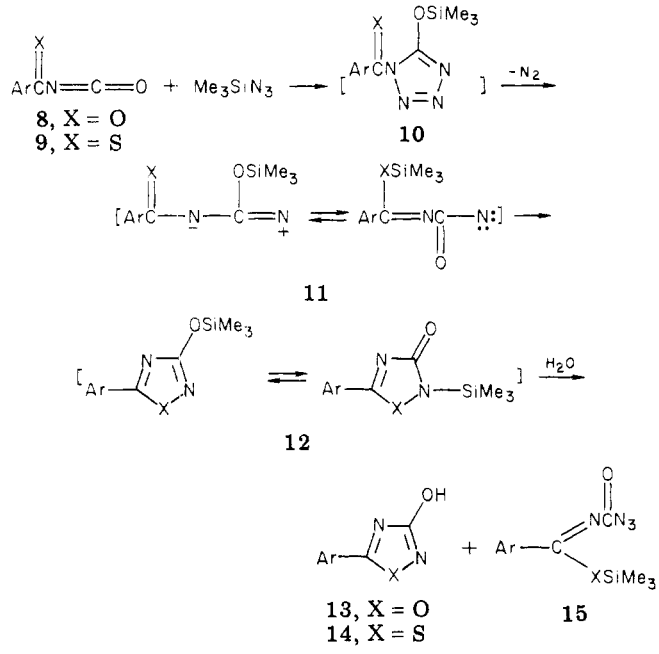
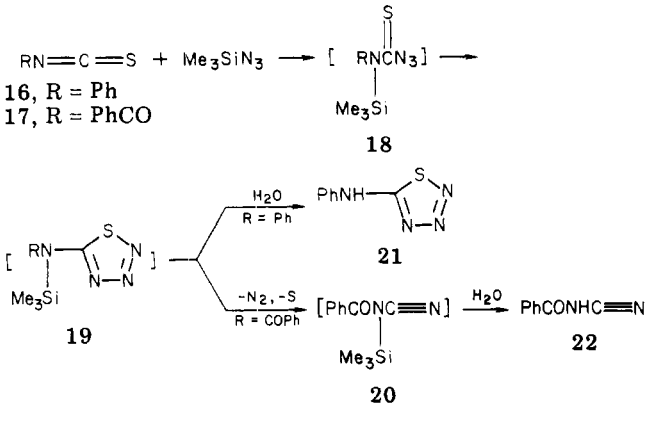
Scheme II[a]



[a] a, Ar = Ph; b, Ar = p-$MeOC_6H_4$; c, Ar = p-ClC_6H_4.

Scheme III



1,2,3,4-thiatriazole (21) or benzoylcyanamide (22), respectively, in good yields. Although cyclic products were not isolated from the reaction of phenyl isocyanate with tributyl(or phenyl)stannyl azide, the azide reacted with isothiocyanate 16 to afford 1-phenyl-4-(tributyl(or phenyl)stannyl)tetrazole-5-thione.[20] Thus, the reaction of TMSA with isothiocyanates 16 and 17 was investigated. However, the reactivity of TMSA toward the isothiocyanates was very low.

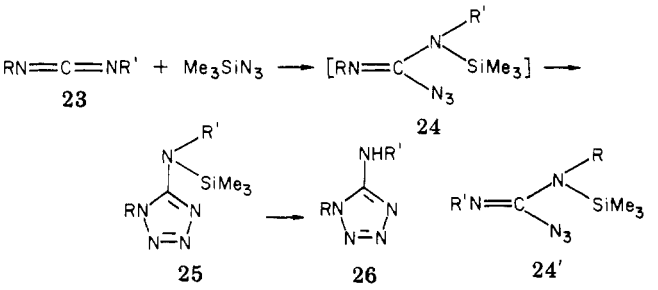
When TMSA was allowed to react with isothiocyanate 16 in dry benzene or without solvent at 50–60 °C for 24 or 40 h and the reaction mixture desilylated with water, thiatriazole 21 was obtained in 1.6 or 3.4% yield, respectively, together with recovery of 16. The reaction of TMSA with isothiocyanate 17 without solvent under reflux for 5 h gave a 23% yield of cyanamide 22 and small amount of sulfur, together with recovery of 17.

Structural elucidation of 21 and 22 was accomplished by identification with authentic samples.

The pathway for the formation of 21 and 22 is outlined in Scheme III. The reaction proceeds via initial formation of silylated azide 18, followed by cyclization of the azido group to a thiocarbonyl group in 18 to give silylated

(20) P. Dunn and D. Oldfield, *Aust. J. Chem.*, 24, 645 (1971).

Scheme IV[a]



[a] a, R = R′ = Ph; b, R = R′ = cyclohexyl; c, R = R′ = i-Pr; d, R = Ph, R′ = cyclohexyl; e, R = Ph, R′ = n-Bu.

1,2,3,4-thiatriazole 19. Under forcing reaction conditions, 19 (R = COPh) gives silylated cyanamide 20 with the elimination of both nitrogen and sulfur. Desilylation of both silylated compounds 19 and 20 gives stable 21 and 22, respectively.

Reactions with Carbodiimides. It has been demonstrated that the reaction of hydrazoic acid with symmetrical dialkylcarbodiimides, generated in situ from the corresponding N,N'-dialkylthiourea, afforded the 1-alkyl-5-(alkylamino)tetrazoles in 32–78% yields.[21] We have investigated the reaction of TMSA with carbodiimides.

When TMSA was allowed to react with N,N'-diphenylcarbodiimide (**23a**) in dry benzene at 50–60 °C for 48 h, a 1:1 adduct, 1-phenyl-5-[N-(trimethylsilyl)-anilino]tetrazole (**25a**), was obtained in 83% yield. Structural elucidation of **25a** was accomplished on the basis of spectral data and chemical conversion. Desilylation of **25a** with methanol afforded the known 5-anilino-1-phenyltetrazole (**26a**)[22] in quantitative yield. Under similar conditions TMSA reacted with N,N'-dicyclohexyl- (**23b**) and N,N'-diisopropylcarbodiimide (**23c**) to give directly the corresponding tetrazoles **26b** and **26c** in 76 and 29% yields, respectively.

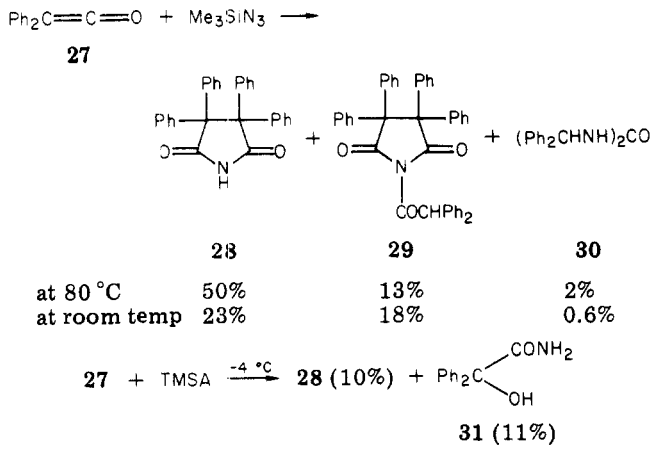
If an asymmetrical carbodiimide was employed, it would be expected to yield two isomeric tetrazoles. However, TMSA reacted with N-cyclohexyl-N'-phenyl- (**23d**) or N-n-butyl-N'-phenylcarbodiimide (**23e**) to give a sole isomeric tetrazole, **26d** or **26e**, respectively, in low yield. On the basis of ^1H NMR spectra which indicated the presence of an imino group coupled with an adjacent hydrogen, it was deduced that **26d** and **26e** are 5-(cyclohexylamino)-1-phenyl- and 5-(n-butylamino)-1-phenyltetrazole, respectively.

The pathway for the formation of **26** is outlined in Scheme IV. TMSA adds to carbodiimide **23** to yield silylated guanyl azide **24** in which the trimethylsilyl group is attached to the more basic nitrogen atom, but not **24′**. Subsequent cyclization of **24** to silylated 5-aminotetrazole **25**, followed by desilylation, gives final product **26**. The formation of **26d** and **26e** is not unexpected since it has been reported that cyclization of alkylphenylguanyl azides gave 5-(alkylamino)-1-phenyltetrazoles, which isomerized at 170–190 °C to the isomeric 1-alkyl-5-anilinotetrazoles.[23]

Reaction with Diphenylketene. Although TMSA did not react with diphenylketene-N-phenylimine, TMSA exhibited high reactivity toward diphenylketene (**27**). When TMSA was allowed to react with ketene **27**, generated in situ from azibenzil, in benzene under reflux or at room temperature, and then the reaction mixture

(21) D. F. Percival and R. M. Herbst, *J. Org. Chem.*, 22, 925 (1957).
(22) R. Stolle, *Ber. Dtsch. Chem. Ges.*, 52, 1289 (1922).
(23) W. G. Finnegan, R. A. Henry, and E. Lieber, *J. Org. Chem.*, 18, 779 (1953).

Scheme V

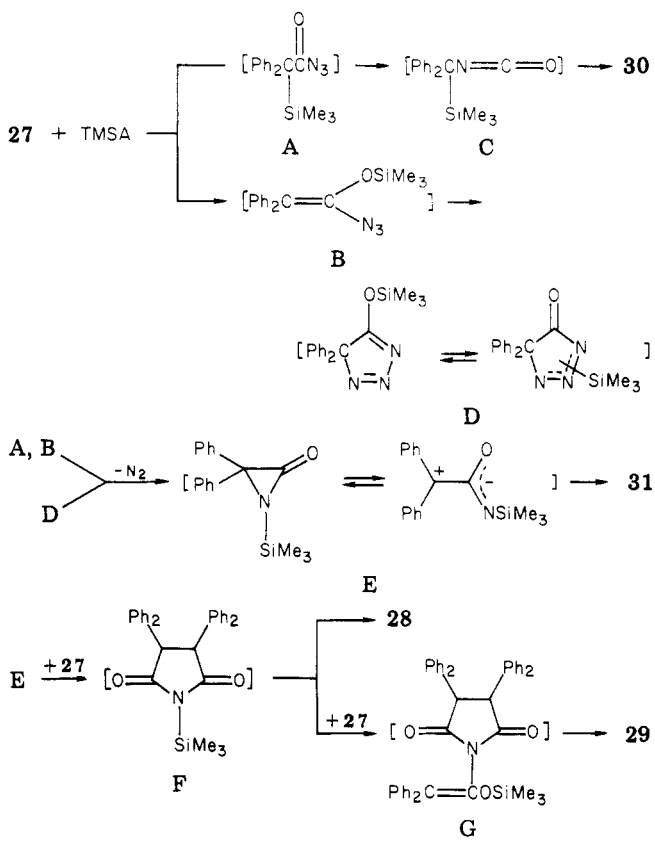


chromatographed on silica gel, tetraphenylsuccinimide (**28**) was obtained as the major product, accompanied by *N*-(diphenylacetyl)tetraphenylsuccinimide (**29**) and 1,3-bis(diphenylmethyl)urea (**30**) (Scheme V). The reaction at room temperature gave rise to an exotherm and evolution of gas. Furthermore, succinimide **28** and benziloylamide (**31**) were obtained from the reaction at −4 °C. Structural elucidation of the products was accomplished on the basis of spectral data.

This reaction may be characterized with regard to the formation of succinimide **28**, because hydrazoic acid reacts with **27** to give (diphenylmethyl)carbamoyl azide.[24] In addition, **28** has so far been obtained by ozonolysis of 5-oxo-6,6,7,7-tetraphenyl-6,7-dihydro-5*H*-pyrrolo[1,2-*a*]-imidazole.[25]

The pathway for this unique reaction can be explained as shown in Scheme VI. The reaction proceeds via initial formation of the trimethylsilyacyl azide A and *O*-trimethylsilyl azide B. Azide A partially undergoes the Curtius rearrangement to form isocyanate C, which gives urea **30**. On the other hand, azide B cyclizes to 1,2,3-triazole intermediate D and subsequent elimination of nitrogen gives α-lactam E which could exist in equilibrium with a 1,3-dipole. The isolation of **31** supports the generation of α-lactam E. Also, α-lactam E may be directly formed via cyclization of A or B with concurrent elimination of nitrogen. As depicted in Scheme VI, the formation of **28** can be readily interpreted by the cycloaddition of E to **27**.

Scheme VI



Experimental Section

Melting points were determined on a Yanagimoto micro melting point apparatus and were uncorrected. IR, NMR, and mass spectra were obtained on a JASCO IRA-1 spectrometer, Hitachi R-40 and JEOL SX-100 spectrometers, and a Hitachi RMS-4 spectrometer, respectively. IR spectra were taken in KBr disks, and mass specta were obtained at 70 eV. The usual precautions for protecting the reaction from moisture were taken in all reactions with TMSA.

Reaction of TMSA with Phenyl Isocyanate (1a). (i) A solution of TMSA (1.80 g, 15.6 mmol) and **1a** (1.86 g, 15.6 mmol) in dry benzene (5 mL) was stirred under nitrogen at 50–60 °C for 24 h. The solvent was evaporated in vacuo, and the residue was triturated with a small amount of water and then was extracted with ethyl ether to give 1,3-diphenylurea (0.495 g, 30%) as an insoluble product. The ether extract was evaporated in vacuo, and the residue was recrystallized from benzene–hexane to afford 1.45 g (57%) of phenylcarbamoyl azide (**3a**): mp 108–109 °C (lit.[26] mp 103–104 °C); IR 3300 (NH), 2150 (N_3), 1690 cm^{-1} (C=O).

(ii) A mixture of TMSA (1.62 g, 14 mmol) and **1a** (1.67 g, 14 mmol) was stirred under nitrogen at 50–60 °C for 24 h. The reaction mixture was triturated with a small amount of water, and then the resulting solid was well washed with ethyl ether to leave 1,3-diphenylurea (0.2 g, 13.5%). The ether washing was concentrated in vacuo, and several fractional recrystallizations of the residue from benzene-hexane and benzene gave 0.48 g (21%) of **3a**, 0.185 g (8%) of 1-phenyl-5(4*H*)-tetrazolinone (**6a**), and 0.55 g (28%) of 1-phenyl-4-(phenylcarbamoyl)-5(4*H*)-tetrazolinone (**7a**), respectively.

For **6a**: ^1H NMR (Me_2SO-d_6) δ 7.0–7.7 (m, 5 H), 8.2–8.3 (br, 1 H, NH); ^{13}C NMR (Me_2SO-d_6) δ 119.3, 127.4, 129.3, 134.9 (aromatic C), 150.1 (C=O).

For **7a**: mp 138–139 °C dec; IR 3260 (NH), 1760, 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 7.1–8.1 (m, 10 H), 9.8–10.1 (br, 1 H, NH); ^{13}C NMR (Me_2SO-d_6) δ 119.6, 120.2, 125.4, 128.6, 129.3, 129.6, 133.5, 135.6 (aromatic C), 142.9, 147.9 (C=O). Anal. Calcd for $C_{14}H_{11}N_5O_2$: C, 59.78; H, 3.94; N, 24.90. Found: C, 59.84; H, 4.03; N, 24.92.

(iii) After a mixture of TMSA (3.20 g, 27.8 mmol) and **1a** (1.68 g, 14 mmol) was refluxed for 24 h, excess TMSA was removed by distillation in vacuo. Recrystallization of the residue from benzene gave 2.56 g (100%) of **6a**. Under the same conditions TMSA reacted with *p*-methoxyphenyl (**1b**), *p*-chlorophenyl (**1c**), and *p*-nitrophenyl isocyanate (**1d**) to give the corresponding 1-aryl-5(4*H*)-tetrazolinones **6b–d**, respectively. The yields and some physical properties are lsited in Table I.

For **6b**: ^1H NMR (Me_2SO-d_6) δ 3.84 (s, 3 H), 7.0–7.3, 7.7–7.95 (each m, 2 H); ^{13}C NMR (Me_2SO-d_6) δ 55.4 (OCH_3), 114.5, 121.8, 127.1, 158.5 (aromatic C), 150.3 (C=O); mass spectrum, *m/e* 192 (M^+), 150 ($MeOC_6H_4NHCO^+$), 149 ($MeOC_6H_4NCO^+$, base peak), 121, 106.

For **6c**: ^1H NMR (Me_2SO-d_6) δ 7.4–8.1 (m); ^{13}C NMR (Me_2SO-d_6) δ 120.7, 129.4, 131.6, 133.1 (aromatic C), 150.0 (C=O); mass spectrum, *m/e* 198, 196 (M^+), 156, 154 ($ClC_6H_4NHCO^+$), 155, 153 ($ClC_6H_4NCO^+$, base peak), 127, 125, 113, 111.

(24) E. Oliveri-Mandala, *Gazz. Chim. Ital.*, **43**, 583 (1913).
(25) W. Rohr, R. Swoboda, and H. A. Staab, *Chem. Ber.*, **101**, 3491 (1968).
(26) T. Curtius and T. S. Hofman, *J. Prakt. Chem.*, **161**, 580 (1896).

For **6d**: ^{1}H NMR (Me_2SO-d_6) δ 7.6–8.6 (m); ^{13}C NMR (Me_2SO-d_6) δ 118.8, 125.4, 139.5, 145.6 (aromatic C), 150.3 (C=O); mass spectrum, m/e 207 (M^+), 165 ($NO_2C_6H_4NHCO^+$), 164 ($NO_2C_6H_4NCO^+$, base peak), 118, 106.

Conversion of Phenylcarbamoyl Azide (3a) to 1-Phenyl-5(4*H*)-tetrazolinone (6a). To a stirred solution of **3a** (1.0 g, 6.17 mmol) and trimethylchlorosilane (0.74 g, 6.82 mmol) in benzene (10 mL) was added a solution of triethylamine (0.623 g, 6.17 mmol) in benzene (5 mL) drop by drop at room temperature. The reaction mixture was refluxed for 24 h and then filtered to give 0.82 g (97%) of triethylammonium chloride. The filtrate was evaporated in vacuo, and recrystallization of the residue from benzene–hexane afforded 1.0 g (100%) of **6a**.

1-Phenyl-4-(phenylcarbamoyl)-5(4*H*)-tetrazolinone (7a). (i) A solution of tetrazolinone **6a** (0.5 g, 3 mmol) and isocyanate **1a** (0.73 g, 6.2 mmol) in benzene (10 mL) was refluxed for 24 h. The reaction mixture was evaporated in vacuo, and recrystallization of the residue from benzene afforded 0.79 g (91%) of **7a**.

(ii) To a stirred solution of carbamoyl azide **3a** (1.0 g, 6.17 mmol) and trimethylchlorosilane (0.74 g, 6.82 mmol) was added triethylamine (0.623 g, 6.17 mmol) drop by drop at room temperature. After the reaction mixture was stirred for 20 min, isocyanate **1a** (1.5 g, 12.6 mmol) was added drop by drop to the mixture, and then the reaction mixture was stirred at 50–60 °C for 24 h. Filtration gave 0.76 g (89%) of triethylammonium chloride. The filtrate was evaporated in vacuo, and recrystallization of the residue from benzene afforded 1.49 g (86%) of **7a**.

Conversion of 1-Phenyl-4-(phenylcarbamoyl)-5-(4*H*)-tetrazolinone (7a) to 1-Phenyl-5(4*H*)-tetrazolinone (6a). (i) In a flask was placed **7a** (0.5 g), and the flask was heated at 150 °C (bath temperature) for 30 min, during which time preheated nitrogen gas was introduced to remove the formed phenyl isocyanate. The residue was recrystallized from hexane–benzene to give 0.29 g (100%) of **6a**.

(ii) To a stirred solution of **7a** (0.7 g, 2.49 mmol) and trimethylchlorosilane (0.3 g, 2.74 mmol) in benzene (20 mL) was added a solution of triethylamine (0.252 g, 2.49 mmol) in benzene (5 mL) drop by drop at 40 °C. The reaction mixture was refluxed for 24 h and then filtered to give 0.32 g (93%) of triethylammonium chloride. The filtrate was concentrated in vacuo, and the residue was triturated with hexane (10 mL) to give unreacted **7a** (0.27 g, 38%). Aniline (1 mL) was added to the hexane solution to precipitate 1,3-diphenylurea (35 mg, 9.4%). The hexane filtrate was evaporated in vacuo, and recrystallization of the residue from hexane–benzene afforded **6a** (0.23 g, 57%).

Reaction of TMSA with Benzoyl Isocyanate (8a). TMSA (2.8 g, 24 mmol) was heated with **8a** (1.79 g, 12 mmol) under reflux for 6 h. The excess TMSA was removed by distillation in vacuo, and the residue was recrystallized from benzene–ethanol to give 1.57 g (80%) of 3-hydroxy-5-phenyl-1,2,4-oxadiazole (**13a**) as colorless prisms: ^{1}H NMR (Me_2SO-d_6) δ 7.5–7.9 (m, 3 H), 8.05–8.3 (m, 2 H), 12.2–13.5 (br, 1 H); ^{13}C NMR (Me_2SO-d_6) δ 123.9, 12 7.4, 129.3, 132.9 (aromatic C), 173.0, 174.4 (azole C); mass spectrum, m/e 162 (M^+), 121 ($PhCONH_2^+$), 105, 104 (base peak), 103, 77. Anal. Calcd for $C_8H_6N_2O_2$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.29; H, 3.82; N, 17.26.

Similarly, TMSA reacted with *p*-methoxybenzoyl isocyanate (**8b**) to give the corresponding 3-hydroxy-1,2,4-oxadiazole **13b**: ^{1}H NMR (Me_2SO-d_6) δ 3.91 (s, 3 H), 7.0–7.3, 7.9–8.1 (each m, 2 H), 12.3–13.1 (br, 1 H); ^{13}C NMR (Me_2SO-d_6) δ 55.5 (OCH_3), 114.8, 116.3, 129.3, 162.8 (aromatic C), 172.9, 174.4 (azole C); mass spectrum, m/e 192 (M^+, base peak), 149, 135, 134, 133. Anal. Calcd for $C_9H_8N_2O_3$: C, 56.25; H, 4.20; N, 14.58. Found: C, 56.20; H, 4.18; N, 14.39.

Reaction of TMSA with *p*-Chlorobenzoyl Isocyanate (8c). A mixture of TMSA (3.4 g, 29.5 mmol) and **8c** (2.7 g, 14.8 mmol) was refluxed for 6 h, and then the reaction mixture was evaporated in vacuo to leave 0.33 g (83%) of 5-(*p*-chlorophenyl)-3-(trimethylsiloxy)-1,2,4-oxadiazole (**12c**): mp 76–78 °C; yellow crystals; IR 2960, 2900, 1255, 1085, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.42 (s, 9 H), 7.4–7.55, 7.95–8.2 (each m, 2 H). A solution of **12c** (0.33 g) in ethanol (10 mL) was stirred at room temperature for 30 min and then evaporated in vacuo. Recrystallization of the residue from hexane–benzene afforded 2.42 g (100%) of the corresponding 3-hydroxy-1,2,4-oxadiazole **13c** as colorless needles: ^{1}H NMR (Me_2SO-d_6) δ 7.5–7.8, 7.9–8.2 (each m, 2 H), 12.3–13.4 (br, 1 H); ^{13}C NMR (Me_2SO-d_6) δ 123.0, 129.4, 129.8, 138.2 (aromatic C), 173.4, 173.9 (azole C); mass spectrum, m/e 198, 196 (M^+, base peak), 141, 140, 139, 138, 137, 113, 111. Anal. Calcd for $C_8H_5N_2O_2Cl$: C, 48.80; H, 2.54; N, 14.23. Found: C, 48.85; H, 2.62; N, 14.20.

Reaction of TMSA with Thiobenzoyl Isocyanate (9a). A solution of TMSA (1.2 g, 10.4 mmol) and 2-phenylthiazoline-4,5-dione[27] (1.0 g, 5.2 mmol) in xylene (5 mL) was stirred at 120 °C for 3 h, during which time the solution turned reddish violet and then yellow. The solution was evaporated in vacuo, and the residue was stirred with ethanol (5 mL) at room temperature for 15 min. The ethanol solution was concentrated in vacuo, and recrystallization of the residue from benzene–chloroform afforded 0.79 g (85%) of 3-hydroxy-5-phenyl-1,2,4-thiadiazole (**14a**) as colorless plates: ^{1}H NMR (Me_2SO-d_6) δ 7.4–8.3 (m, 5 H), 11.5–13.8 (br, 1 H); ^{13}C NMR (Me_2SO-d_6) δ 126.5, 129.4, 130.0, 132.2 (aromatic C), 171.7, 186.9 (azole C); mass spectrum, m/e 178 (M^+), 135, 104 (base peak), 103, 77.

Similar reactions of TMSA with *p*-methoxythiobenzoyl (**9b**) and *p*-chlorothiobenzoyl isocyanate (**9c**) afforded the corresponding 3-hydroxy-1,2,4-thiadiazoles **14b** and **14c**.

For **14b**: ^{1}H NMR (Me_2SO-d_6) δ 3.87 (s, 3 H), 6.9–7.2, 7.7–8.0 (each m, 2 H), 12.3–12.7 (br, 1 H); ^{13}C NMR (Me_2SO-d_6) δ 55.5 (OCH_6), 114.9, 122.9, 128.5, 162.6 (aromatic C), 171.6, 186.6 (azole C); mass spectrum, m/e 208 (M^+), 134 (base peak). Anal. Calcd for $C_9H_8N_2O_2S$: C, 51.92; H, 3.87; N, 13.46. Found: C, 51.94; H, 3.93; N, 13.40.

For **14c**: ^{1}H NMR (Me_2SO-d_6) δ 7.53–7.8, 7.9–8.1 (each m, 2 H), 12.2–13.3 (br, 1 H); ^{13}C NMR (Me_2SO-d_6) δ 128.1, 128.6, 129.4, 136.7 (aromatic C), 171.5, 185.4 (azole C); mass spectrum, m/e 214, 212 (M^+), 140, 139, 138 (base peak), 137, 113, 111. Anal. Calcd for $C_8H_5N_2OSCl$: C, 45.18; H, 2.35; N, 13.18. Found: C, 45.29; H, 2.41; N, 13.09.

Reaction of TMSA with Phenyl Isothiocyanate (16). A solution of TMSA (1.15 g, 10 mmol) and **16** (1.35 g, 10 mmol) in benzene (5 mL) was stirred under nitrogen at 50–60 °C for 24 h. The reaction mixture was concentrated in vacuo, and the residue was triturated with hexane to give crystals. Recrystallization of the crystals from benzene afforded 40 mg (1.6%) of 5-anilino-1,2,3,4-thiatriazole (**21**): mp 146–147 °C dec (lit.[18] mp 141 °C dec); colorless prisms; IR 3250–2400 cm^{-1}. The IR spectrum of **21** was identical with that of an authentic sample prepared by the reported method.[18] The hexane solution was evaporated in vacuo to leave 1.235 g (92%) of **16**.

A similar reaction of TMSA (1.15 g, 10 mmol) with **16** (1.35 g, 10 mmol) without solvent at 50–60 °C for 40 h afforded 60 mg (3.4%) of **21** together with recovery of 1.22 g (90%) of **16**.

Reaction of TMSA with Benzoyl Isothiocyanate (17). After a mixture of TMSA (2.3 g, 20 mmol) and **17** (1.63 g, 10 mmol) was refluxed for 5 h, excess TMSA was removed by distillation in vacuo. The residue was triturated with ether, and fractional recrystallizations of the resulting solid from ether and benzene afforded 5 mg of sulfur and 0.215 g (23%) of benzoylcyanamide (**22**): mp 142–143 °C dec (lit.[19] mp 132 °C dec); IR 3240, 2245, 1675 cm^{-1}; ^{1}H NMR (Me_2SO-d_6–$CDCl_3$) δ 7.3–8.1 (m, 5 H), 10.5–11.5 (br, 1 H); mass spectrum, m/e 146 (M^+). The IR spectrum of **22** was identical with that of an authentic sample prepared by the reported method.[19] The ether solution was evaporated in vacuo to leave 0.75 g (46%) of **17**.

Reaction of TMSA with *N,N'*-Diphenylcarbodiimide (23a). A mixture of TMSA (1.4 g, 12 mmol) and **23a** (1.12 g, 5.8 mmol) in benzene (2 mL) was stirred at 50–60 °C under nitrogen for 48 h. The reaction mixture was evaporated in vacuo, and the residue was triturated with hexane (5 mL) to give 1.48 g (83%) of 1-phenyl-5-[(*N*-trimethylsilyl)anilino]tetrazole (**25a**): mp 110–113 °C; colorless crystals; IR 2950, 2900, 1250, 845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.30 (s, 9 H), 6.7–7.4 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 1.10 ($SiCH_3$), 118.6, 125.1, 125.8, 125.9, 127.6, 129.2, 130.7, 134.4, 142.5 (aromatic C), 157.2 (C=N); mass spectrum, m/e 309 (M^+). The hexane filtrate was evaporated to leave **23a** (0.19 g, 8%).

After a solution of **25a** (1.48 g) in methanol (5 mL) was refluxed for 20 min, the solvent was removed in vacuo to leave crystals,

(27) It is known that on being heated in xylene at 120 °C, 2-arylthiazoline-4,5-diones generate the corresponding thiobenzoyl isocyanates [J. Goerdeler and H. Schenk, *Angew. Chem.*, **75**, 675 (1963)].

which on recrystallization from hexane–benzene afforded 1.10 g (98%) of 5-anilino-1-phenyltetrazole (**26a**): mp 166–167 °C (lit.[22] mp 161 °C); colorless needles; IR 2800–3300, 1610 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 118.6, 122.3, 125.2, 128.8, 129.9, 133.4, 139.9 (aromatic C), 152.5 (C=N); mass spectrum, *m/e* 237 (M^+). Anal. Calcd for $C_{13}H_{11}N_5$: C, 65.81; H, 4.67; N, 29.52. Found: C, 65.82; H, 4.64; N, 29.39.

Similarly, TMSA reacted with *N,N'*-dicyclohexylcarbodiimide (**23b**) or *N,N'*-diisopropylcarbodiimide (**23c**) to afford the corresponding tetrazole, **26b** or **26c**, in 76 or 29% yield, together with recovery of **23b** (24%) or **23c** (56%), respectively.

For **26b**: mp 200–201 °C; colorless needles; IR 3300, 2920, 2840, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–2.4 (m, 20 H), 3.5–3.85, 3.85–4.3 (each m, 1 H), 4.7–5.05 (br d, NH, *J* = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 25.0, 25.5, 31.9 33.2, 53.7, 55.3 (cyclohexyl C), 154.1 (C=N); mass spectrum, *m/e* 249 (M^+). Anal. Calcd for $C_{13}H_{23}N_5$: C, 62.61; H, 9.30; N, 28.09. Found: C, 62.74; H, 9.39; N, 27.88.

For **26c**: mp 166–167 °C (lit.[21] mp 160–161 °C); colorless needles; IR 3270, 2990, 2950, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31, 1.53 (each d, 6 H, *J* = 6 Hz), 4.07, 4.49 (each double q, 1 H, *J* = 6 Hz), 4.7–5.0 (br, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 21.7, 22.8, 46.5, 48.4 (isopropyl C), 154.2 (C=N); mass spectrum, *m/e* 169 (M^+). Anal. Calcd for $C_7H_{15}N_5$: C, 49.68; H, 8.93; N, 41.39. Found: C, 49.76; H, 8.97; N, 41.24.

Reaction of TMSA with *N*-Cyclohexyl-*N'*-phenylcarbodiimide (23d). A mixture of TMSA (1.3 g, 11.3 mmol) and **23d** (1.12 g, 5.8 mmol) in benzene (2 mL) was stirred at 50–60 °C under nitrogen for 72 h. The reaction mixture was worked up in a similar manner to that described above to give 0.14 g (10%) of 5-cyclohexylamino)-1-phenyltetrazole (**26d**), together with recovery of **23d** (0.95 g, 85%). Similarly, TMSA reacted with *N*-*n*-butyl-*N'*-phenylcarbodiimide (**23e**) to afford 5-(*n*-butylamino)-1-phenyltetrazole (**26e**) in 10% yield, together with recovery of **23e** (89%).

For **26d**: mp 121–122 °C (lit.[23] mp 120.5–121.5 C); colorless needles; IR 3220, 2930, 2850, 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–2.5 (m, 10 H), 3.6–4.1 (m, 1 H), 4.2–4.6 (br d, 1 H, NH, *J* = 7 Hz), 7.4–7.9 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 24.8, 25.4, 33.2, 53.5 (cyclohexyl C), 123.9, 124.9, 129.1, 129.7, 130.3, 133.3 (aromatic C), 153.9 (C=N); mass spectrum, *m/e* 243 (M^+). Anal. Calcd for $C_{13}H_{17}N_5$: C, 64.17; H, 7.04; N, 28.79. Found: C, 64.46; H, 7.04; N, 28.61.

For **26e**: mp 104–105 °C; colorless needles; IR 3230, 2950, 2930, 2860, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (t, 3 H, *J* = 6 Hz), 1.1–2.0 (m, 4 H), 3.48 (dt, 2 H, *J* = 5, 6 Hz), 4.7–5.1 (br t, 1 H, NH, *J* = 5 Hz), 7.4–7.8 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.7, 19.9, 31.5, 44.2 (butyl C), 123.8, 129.5, 130.0, 133.2 (aromatic C), 154.7 (C=N); mass spectrum, *m/e* 217 (M^+). Anal. Calcd for $C_{11}H_{15}N_5$: C, 60.80; H, 6.96; N, 32.24. Found: C, 60.66; H, 7.05; N, 31.94.

Reaction of TMSA with Diphenylketene (27). (i) A solution of TMSA (1.5 g, 13 mmol) and azibenzil (2.85 g, 12.8 mmol) in benzene (15 mL) was refluxed for 6 h. The reaction mixture was concentrated in vacuo, and the residue was chromatographed on silica gel with benzene and chloroform as eluents. From benzene elution, 0.34 g (13%) of *N*-(diphenylacetyl)tetraphenylsuccinimide (**29**) and 40 mg (2%) of 1,3-bis(diphenylmethyl)urea (**30**) were obtained, and the chloroform elution gave 1.28 g (50%) of tetraphenylsuccinimide (**28**) together with diphenylacetic acid (80 mg).

For **28**: mp 261–262 °C (lit.[25] mp 256–258 °C); colorless prisms; IR 3240, 1775, 1725, 1710 cm^{-1}; ^{13}C NMR (Me_2SO-d_6) δ 68.8 (quaternary C), 126.8, 127.2, 130.2, 139.5 (aromatic C), 177.5 (C=O); mass spectrum, *m/e* 403 (M^+). Anal. Calcd for $C_{28}H_{21}NO_2$: C, 83.35; H, 5.25; N, 3.47. Found: C, 83.10; H, 5.28; N, 3.34.

For **29**: mp 206–207 °C; colorless needles; IR 1800, 1750, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.94 (s, 1 H), 7.0–7.35 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 59.2 (tertiary C), 68.4 (quaternary C), 127.2, 127.4, 128.7, 128.7, 130.7, 136.1, 138.5 (aromatic C), 171.6, 174.3 (C=O); mass spectrum, *m/e* 597 (M^+). Anal. Calcd for $C_{42}H_{31}NO_3$: C, 84.40; H, 5.23; N, 2.34. Found: C, 84.30; H, 5.26; N, 2.46.

For **30**: mp 278–279 °C; colorless needles; IR 3320, 1630 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 5.94 (d, 2 H, *J* = 8 Hz), 7.0 (d, 2 H, NH, *J* = 8 Hz), 7.2–7.5 (m, 20 H); ^{13}C NMR (Me_2SO-d_6) δ 56.9 (tertiary C), 126.7, 128.2, 143.4 (aromatic C), 156.2 (C=O); mass spectrum, *m/e* 392 (M^+). Anal. Calcd for $C_{27}H_{24}N_2O$: C, 82.62; H, 6.16; N, 7.14. Found: C, 82.54; H, 6.17; N, 7.02.

(ii) TMSA (1.5 g, 13 mmol) was added to a solution of **27**, generated in situ from azibenzil (2.85 g, 12.8 mmol), in benzene (15 mL) at room temperature. After the reaction mixture was stirred at room temperature for 6 h, a workup similar to that above gave **28** (0.59 g, 23%), **29** (0.46 g, 18%), and **30** (15 mg, 0.6%).

(iii) TMSA (3.0 g, 26 mmol) was added to a solution of **27**, generated in situ from azibenzil (2.85 g, 12.8 mmol), in xylene (15 mL) at −4 °C for 3 h, and then the reaction mixture was allowed to stand overnight at room temperature. A workup of the reaction mixture similar to that above afforded 0.26 g (10%) of **28** and 0.32 g (11%) of benziloylamide (**31**), mp 154–156 °C (lit.[28] mp 154–155 °C).

Registry No. **1a**, 103-71-9; **1b**, 5416-93-3; **1c**, 104-12-1; **1d**, 100-28-7; **3a**, 940-38-5; **6a**, 5097-82-5; **6b**, 62442-51-7; **6c**, 3589-06-8; **6d**, 75430-97-6; **7a**, 75430-98-7; **8a**, 4461-33-0; **8b**, 4695-57-2; **8c**, 4461-36-3; **9a**, 3553-61-5; **9b**, 3553-62-6; **9c**, 3553-63-7; **12c**, 75430-99-8; **13a**, 21084-84-4; **13b**, 75431-00-4; **13c**, 21084-85-5; **14a**, 5378-17-6; **14b**, 75431-01-5; **14c**, 75444-53-0; **16**, 103-72-0; **17**, 532-55-8; **21**, 13078-30-3; **22**, 15150-25-1; **23a**, 622-16-2; **23b**, 538-75-0; **23c**, 693-13-0; **23d**, 3878-67-9; **23e**, 21848-95-3; **25a**, 75431-02-6; **26a**, 64287-36-1; **26b**, 73565-25-0; **26c**, 75431-03-7; **26d**, 66907-71-9; **27**, 525-06-4; **28**, 22270-82-2; **29**, 75431-04-8; **30**, 6744-64-5; **31**, 4746-87-6; TMSA, 4648-54-8; 2-phenylthiazoline-4,5-dione, 1628-53-1.

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Crystal Structure of 1,3,5-Trithiane 1-Oxide

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The conformation of 1,3,5-trithiane 1-oxide (**3**) observed in the crystal, as determined by single-crystal X-ray diffraction, has the sulfoxide oxygen axial. Previous studies involving proton and carbon nuclear magnetic resonance spectroscopy, as well as molecular mechanics calculations, indicated that the equatorial oxide is highly preferred in solution. Close C–H···O and S···O intermolecular contacts in the solid suggest that crystal packing is sufficiently strong to overcome the electrostatic destabilization of the axial conformation of **3**. Crystals of **3** conform to space group *Pnma* (D_{2h}^{16}, No. 62) with *a* = 19.179 (9), *b* = 7.044 (4), *c* = 4.629 (3) Å and *Z* = 4. The crystal structure was determined by the Patterson method. Least-squares refinement gave *R* = 0.046 for 833 reflections (493 independent data) whose intensities were measured by counter diffractometry using Cu Kα radiation.

Introduction

The conformational properties of six-membered cyclic sulfoxides have been examined by a variety of experimental techniques with most of the recent emphasis centered on nuclear magnetic resonance spectroscopy (both proton[1] and carbon[2] NMR) and X-ray crystallography.[3]

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