Thiadiaziridine 1,1-Dioxides: Synthesis and Chemistry

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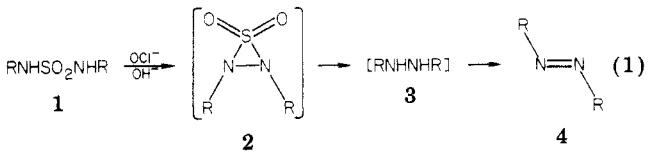
The synthesis and chemical reactions of a series of thiadiaziridine 1,1-dioxides (**2**) are described. The thermal stability is highly dependent on the R group and in one case (R = *tert*-octyl) it is postulated that the thermolysis initially produces a diradical intermediate which can be trapped or further fragments to give a nitrene. A temperature-dependent NMR study on the coalescence of the diastereotopic α-methyl protons of **2b** gives a $\Delta G^{\ddagger}$ = 20 kcal mol^{-1}.

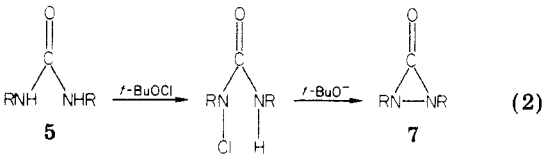
Three-membered-ring compounds containing one or two heteroatoms are well-known.[1] To date, however, only a few ring systems with no carbon atoms have been reported, trisilylcyclopropanes,[2] azadisilylcyclopropanes,[3] triphosphylcyclopropanes,[4] and oxadiaziridines[5] being four such examples.

In 1965 Ohme and co-workers[6,7] postulated thiadiaziridine 1,1-dioxides (**2**, eq 1) as intermediates in the alkaline–hypochlorite conversion of *N,N*-dialkylsulfamides (**1**) to dialkyldiazenes (**4**).



1 2 3 4 (1)

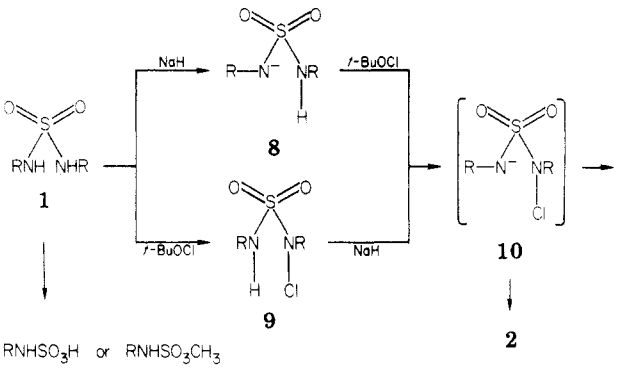
Studies directed toward formation of N–N bonds by Greene et al.[8,9] showed that the effect of strong bases on *N*-chloroureas (**6**) resulted in the formation of 2,3-diazacyclopropanones (diaziridinones, **7**; eq 2). The structures



5 6 7 (2)

and chemistry of these compounds have since been well characterized.[10-14] Comparison of the ring bond lengths with related small rings[12] indicates an unusually long N–N bond (1.601 Å) and short N–CO bonds (1.325 Å). Of all cases examined to date, except one,[11] diaziridinones were isolated only when both R groups were tertiary alkyl groups.

Scheme I[a]



[a] a, R = $(CH_3)_3C$; b, R = $(CH_3)_3CCH_2(CH_3)_2C$; c, R = adamant-1-yl.

By using nonaqueous conditions for sulfamides with tertiary alkyl groups, we were able to isolate thiadiaziridine 1,1-dioxides (**2**).[15-17] Since then the synthesis and isolation of other members of this system have been reported.[18-20]

X-ray data taken on *N,N'*-bis(1,1,3,3-tetramethylbutyl)thiadiaziridine 1,1-dioxide (**2b**) by Trefonas and Cheung[21] showed that the ring substituents had a trans configuration, and a comparison of the N–N bond length to related systems[12] showed it to be significantly longer (1.67 Å) than any analogous distance, even longer than that of the diaziridinone.

Results and Discussion

Synthesis. The preferred procedure for making thiadiaziridine 1,1-dioxides involves treating the dialkylsulfamides **1** with sodium hydride followed by treatment with *tert*-butyl hypochlorite. Earlier[17] we indicated that the

(1) (a) E. Schmitz, "Dreiringe mit Zwei Heteroatomen", Springer Verlag, New York, 1967; (b) A. R. Katritzky and S. M. Weeds, *Adv. Heterocycl. Chem.*, 7, 266 (1966).
(2) M. R. Ismail and H. J. Hoetzsch, French Patent Fr. 1 483 373 (1967).
(3) W. Fink, *Helv. Chim. Acta*, 46, 720 (1963); W. Fink, *Angew. Chem.*, 78, 803 (1966).
(4) K. Issleib and E. Fluck, *Angew. Chem.*, 78, 597 (1966).
(5) (a) S. S. Hecht and F. D. Greene, *J. Am. Chem. Soc.*, 89, 6761 (1967); (b) F. D. Greene and S. S. Hecht, *J. Org. Chem.*, 35, 2482 (1970); (c) J. Swigert and K. G. Taylor, *J. Am. Chem. Soc.*, 93, 7337 (1971).
(6) R. Ohme and E. Schmidt, *Angew. Chem., Int. Ed. Engl.*, 4, 433 (1965).
(7) R. Ohme and H. Preuschoff, *Justus Liebigs Ann. Chem.*, 713, 74 (1968).
(8) F. D. Greene and J. C. Stowell, *J. Am. Chem. Soc.*, 86, 3569 (1964).
(9) F. D. Greene, J. C. Stowell, and W. Bergmark, *J. Org. Chem.*, 34, 2254 (1969).
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(11) F. D. Greene and J. E. Pazos, *J. Org. Chem.*, 34, 2269 (1969).
(12) P. E. McGann, J. T. Groves, F. D. Greene, G. M. Stack, R. I. Majesté, and L. M. Trefonas, *J. Org. Chem.*, 43, 922 (1978).
(13) J. F. Pazos and F. D. Greene, *J. Am. Chem. Soc.*, 89, 1030 (1967).
(14) C. A. Renner and F. D. Greene, *J. Org. Chem.*, 41, 2813 (1976).
(15) J. W. Timberlake, M. L. Hodges, and K. Betterton, *Synthesis*, 632 (1972).
(16) J. W. Timberlake and M. L. Hodges, *J. Am. Chem. Soc.*, 95, 634 (1973).
(17) J. W. Timberlake, M. L. Hodges, and A. W. Garner, *Tetrahedron Lett.*, 3843 (1973).
(18) H. Quast and F. Kees, *Chem. Ber.*, 110, 1780 (1977).
(19) H. Quast and F. Kees, *Tetrahedron Lett.*, 1655 (1973).
(20) H. H. Chang and B. Weinstein, *J. Chem. Soc., Perkin Trans. 1*, 1601 (1977).
(21) L. M. Trefonas and L. D. Cheung, *J. Am. Chem. Soc.*, 95, 636 (1973).

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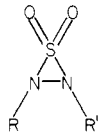
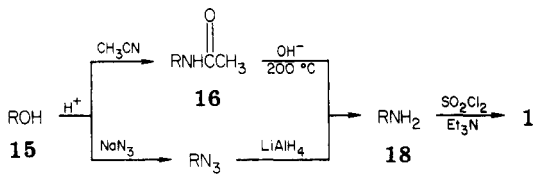
Table I. Substituents for Thiadiaziridine 1,1-Dioxides (2)



compd	R	R'
2a	$(CH_3)_3C$	$(CH_3)_3C$
b	$(CH_3)_3CCH_2C(CH_3)_2$	$(CH_3)_3CCH_2C(CH_3)_2$
c		
d	$(CH_3)_3C$	$(CH_3)_3CCH_2C(CH_3)_2$
e	$(CH_3)_3C$	
f	$C_6H_5C(CH_3)_2$	$C_6H_5C(CH_3)_2$
g	$(CH_3)_3CC(CH_3)_2$	$(CH_3)_3CC(CH_3)_2$
h	$CH_3(CH_2)_3C(CH_3)_2$	$CH_3(CH_2)_3C(CH_3)_2$
i	$CH_3(CH_2)_3C(C_2H_5)_2$	$CH_3(CH_2)_3C(C_2H_5)_2$
j	$C_6H_5CH_2C(CH_3)_2$	$C_6H_5CH_2C(CH_3)_2$
k	$C_6H_5C(CH_3)_2CH_2C(CH_3)_2$	$C_6H_5C(CH_3)_2CH_2C(CH_3)_2$

Scheme II



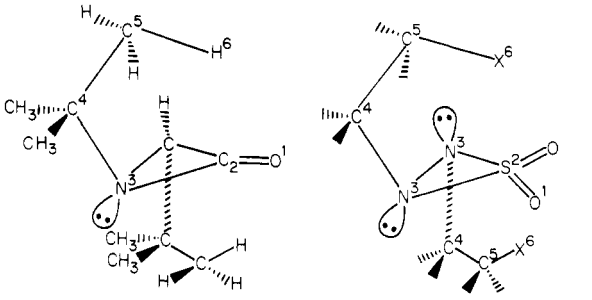
order of addition of reagents was not important for the bis(1,1,3,3-tetramethylbutyl)sulfamide (**1b**) but that the *N*-chloro-di-*tert*-butylsulfamide (**9a**, Scheme I) was converted mostly to sulfamide **1a** upon treatment with sodium hydride. Others[20] reported this same result for **9a**. However, a reinvestigation of this phenomenon shows that this is in error and that if **9a–c** are prepared at low temperature with careful purification, treatment with sodium hydride does indeed give the corresponding thiadiaziridine 1,1-dioxides in reasonable yields (40–80%). Care must be exercised, however, for at higher temperatures (i.e., room temperature) only the corresponding sulfamides are obtained, and prolonged treatment of sulfamide with hypochlorite in pentane leads to sulfamic acid (**11**) and in methanol to the ester **12**. These results are consistent with the intermediacy of **10**.

The unsymmetrically substituted thiadiaziridine 1,1-dioxides (**2d,e**, Table I; R = *tert*-butyl, R' = *tert*-octyl or adamantyl) required the synthesis of the corresponding sulfamide from the sulfamoyl chloride **14**. The latter was in turn prepared in situ from *tert*-butyl alcohol and chlorosulfonyl isocyanate (**13**) by thermal extrusion of carbon dioxide in refluxing hexane (eq 3).

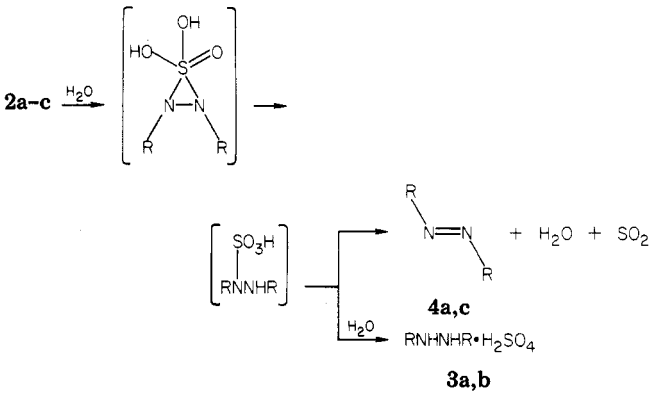
$$(CH_3)_3COH + \underset{\mathbf{13}}{OCNSO_2Cl} \rightarrow [(CH_3)_3COC(O)NHSO_2Cl] \xrightarrow[-CO_2]{\Delta,\ \text{hexane}} \underset{\mathbf{14}}{(CH_3)_3CNHSO_2Cl} \xrightarrow{R'NH_2} \underset{\mathbf{1d,e}}{(CH_3)_3CNHSO_2NHR'} \quad (3)$$

The synthesis of the symmetrical precursor sulfamides involves treatment of the prerequisite amines with sulfuryl chloride by using either triethylamine or pyridine as scavenger for the liberated HCl (Scheme II). The amine

Chart I



Scheme III



precursors for the sulfamides that were not commercially available were obtained via a Ritter or modified Ritter reaction (Scheme II), followed by hydrolysis of the amide or reduction of the azides. In some cases (see Experimental Section) the amides were resistant to normal hydrolysis and had to be cleaved in aqueous base at high temperature (220 °C), requiring sealing of the reaction mixture in a Monel metal autoclave. This procedure has interesting synthetic potential provided the substrates are thermally stable.

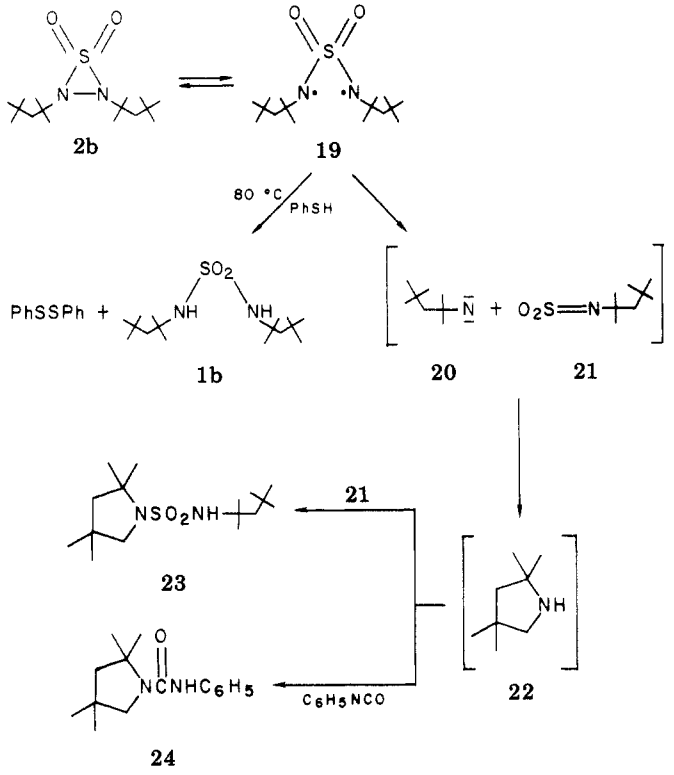
Among the thiadiaziridines that have been examined in detail, **2a–c**, the *tert*-butyl derivative **2a** is by far the least stable. Its stability is highly dependent on purity, and it decomposes after several days at room temperature or upon refluxing several hours in benzene to give SO_2 and di-*tert*-butyldiazene (or *N,N'*-di-*tert*-butylhydrazine hydrogen sulfate in the presence of moisture). The decomposition is not a kinetically discernible process and appears to be catalyzed by trace amounts of acid. For example, added HCl greatly enhances the rate. Conversely, the *tert*-octyl (**2b**) and adamantyl (**2c**) derivatives are quite stable and can be recovered unchanged after several hours of refluxing in toluene.

It is well-known that the stabilities of small ring compounds are enhanced by sterically bulky tertiary alkyl groups. For example, *tert*-butyl groups on the 1- and 3-positions of α-lactams (aziridinones) reduce nucleophilic attack and increase the thermal stability.[22] The decreased reactivity is predicted on the basis of the Newman rule of six (Chart I) which infers that the greater the number of atoms in the 6-position the greater will be the steric hindrance to addition.[23]

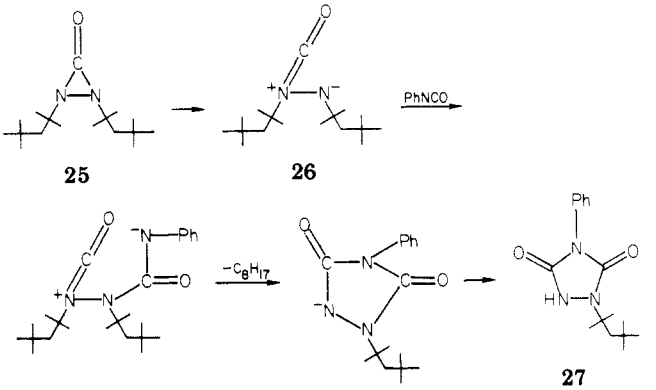
It has been shown[17] that the stability of thiadiaziridine 1,1-dioxides at room temperature greatly depends on the structure of the R group. In an effort to evaluate the magnitude of this steric stability aspect we synthesized a

(22) J. C. Sheehan and J. H. Beeson, *J. Am. Chem. Soc.*, **89**, 362 (1967).
(23) M. S. Newman, *J. Am. Chem. Soc.*, **72**, 4783 (1950).

Scheme IV



Scheme V



number of derivatives differing in the number of carbon atoms at the α- and γ-positions. (The α-position is defined as the carbon directly bonded to nitrogen.) It was hoped that a quantitative study of the ease of reactivity of each with water would give some indication of the importance of the steric bulk of the R group to ring stability. However, because of the different modes of reaction (Scheme III), only qualitative results were obtained which, at best, allow the compounds in Table I to be divided into three groups listed as follows in order of increasing stability: I = **2f** < II = **2a**,**d**,**e** < III = **2b**,**c**,**g**–**k**. With the exception of **2f**, compounds **2a**,**d**,**e** all have less sterically demanding groups than group III (**2b**,**c**,**g**–**k**) which indicates that substituents which are bulkier than *tert*-butyl enhance the stability. The compounds in group III are, within the limits of detection, similar in stability and thus preclude any interpretation of stability differences based on number of γ- or δ-carbon atoms.

Thermolysis of 2b. The thermal behavior of di-*tert*-octylthiadiaziridine 1,1-dioxide (**2b**) is illustrated in Scheme IV. Prolonged heating in benzene, toluene, or cumene gives rearranged sulfamide **23** as the only isolated product. In benzene with 2 equiv of thiophenol or with *tri*-*n*-butyltin hydride, di-*tert*-octylsulfamide (**1b**) was produced quantitatively along with, in the former case, an 85% isolated yield of diphenyl disulfide. In cumene at 75 °C the ratio of **23** to **1b** formed (by NMR) is 3.5:1, and in benzene with 1 equiv of thiophenol the ratio is 1:1.

These results are consistent with either the direct reaction of thiadiaziridine with these reducing agents or with the reversible formation of diradical **19** which can be trapped with these scavengers (thiophenol or cumene) at lower temperatures. As shown in Scheme IV, we prefer to use the latter mechanism as a working model although we have no direct evidence for diradical existence. In fact, all attempts to trap this "diradical" with reagents like tetracyanoethylene, 2,3-dimethylbutene, furan, dimethyl acetylenedicarboxylate, or diphenylketene were unsuccessful. Furthermore, unlike the diaziridinones studied by Greene,[19] thiadiaziridines fail to oxidize di-*tert*-butylhydrazine. However, the long N–N bond as determined by X-ray analysis[21] would support a weakened coordination, and NMR data (vida infra) as well as this chemical reactivity is consistent with the diradical interpretation.

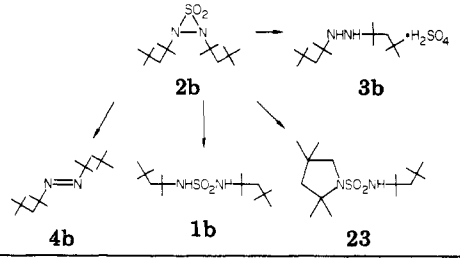
In the absence of scavengers (or in presence of relatively poor ones like cumene) the major product is rearranged sulfamide. While it is possible to conceive an intramolecular path for formation of sulfamide **23**, evidence that free pyrrolidine is produced comes from formation of urea **24** when thermolysis of **2b** is done in the presence of phenyl isocyanate. It is convenient to speculate that "diradical" **19** fragments to nitrene **20** and **21** and that C–H insertion of nitrene leads to pyrrolidine **22**. Such cyclizations of arylnitrenes and carbonylnitrenes are known, even though no substantiated alkylnitrene cyclization to pyrrolidine is known.[24] Studies on the chemistry of *tert*-octylnitrene are presently in progress to determine the nature of its reactivity. Therefore, while we have not been able to establish the existence of free nitrene, it most conveniently explains the product distribution.

As further evidence of the difference between the thiadiaziridine system and Greene's diaziridinones, di-*tert*-octyldiaziridinone was thermolyzed in the presence of phenyl isocyanate. Here again a difference in reactivity is observed as the major product is 1-*tert*-octyl-4-phenyl-3,5-triazolidinedione (**27**, Scheme V). Earlier work by Greene and co-workers on this system led them to postulate a dipolar intermediate (**26**) to explain several chemical reactions. By use of this intermediate the triazolidinedione product can readily be explained.

Chemical Reactivity of Thiadiaziridine 1,1-Dioxides. In toto, four structurally different products have been observed, depending on reagents and conditions. These are summarized in Table II for *N*,*N*′-bis(1,1,3,3-tetramethylbutyl)thiadiaziridine 1,1-dioxide (**2b**), which was chosen as the model rather than the *tert*-butyl derivative (**2c**) because it was felt that the larger, bulkier *tert*-octyl groups might show a greater selectivity toward electrophiles and nucleophiles. The first segment of the table bears this out as, under mild conditions, **2b** is stable toward both acids and bases. Under more rigorous conditions, **2b** is converted to *N*,*N*′-bis(1,1,3,3-tetramethylbutyl)diazene (**4b**). No attempt has been made to distinguish the mechanism for this reaction, and it is not clear whether hydrazine **3b** is an intermediate since it is known that oxidation of a hydrazine to an azo compound by oxygen is a facile process.[25] It is clear that under aqueous conditions **2b** is distinctly different from **2a**. The latter

(24) W. Lwowski, "Nitrenes", Wiley, New York, 1970, p 47–97.
(25) M. L. Heyman and J. P. Snyder, *Tetrahedron Lett.*, 2859 (1973); J. L. Miesel, *Tetrahedron Lett.*, 3847 (1974).

Table II. Summary of Chemical Reactivity of *N,N'*-Bis(1,1,3,3-tetramethylbutyl)thiadiaziridine 1,1-Dioxide (2b)



reagents	conditions[a]	products[b]
HOAC	24 h, 60 °C	NR
C_6H_5OH	48 h, 80 °C	NR
C_6H_5	4 h, 80 °C	NR
HCl	1 h, 50 °C, 3 M	NR
NaOH	2 M, 1 h, RT	NR
Cl_2	1 h, RT	NR
H_2O_2	3 h, 36 °C	NR
$KMnO_4$	3 h, 36 °C	NR
$(t\text{-BuNH-})_2$	2 h, 80 °C	NR
diphenylketene	24 h, RT	NR
$(MeO_2CC{\equiv})_2$	24 h, 60 °C	NR
HCl	12 M, 30 min, 60 °C	4b
HCl gas	30 min, 25 °C	4b
picric acid	24 h, RT	4b
NaOH	30 min, 80 °C	4b
$NaOCH_3$	30 min, 60 °C	4b
Cl_2	1 h, 50 °C	4b
t-BuOCl	3 h, 36 °C	4b
C_6H_5Cl	2 h, 25 °C	4b
$LiAlH_4$	1 h, 35 °C	4b + 1b (4:1)
C_6H_5SH	excess, 3 h, C_6H_6, reflux	1b
Bu_3SnH	24 h, RT	1b
H_2	24 h, RT, Pd/C, 50 psi	1b
$Nap^{-}\cdot$	140 h, RT	1b
CH_3MgI	2 h, 35 °C	1b
$C_6H_5CH_2MgCl$	2 h, 35 °C	1b
H_2O	THF or C_6H_5, 24 h, reflux	3b·H_2SO_4
cumene	24 h, reflux	23
cumene	24 h, 75 °C	23 + 1b (3.5:1)
PhNCO	72 h, 80 °C	23 + 24 (2.5:1)
$C_6H_5CH_3$	48 h, reflux	23
C_6H_5	72 h, reflux	23
C_6H_5SH	24 h, C_6H_6, reflux, 1 equiv	1b + 23 (1:1)

[a] RT = room temperature. [b] NR = no reaction.

has been observed to give either azo compound **4a** or hydrazine **3a**,[20] depending upon the conditions.

Radical trapping agents, as seen in the third group in Table II, give rise to sulfamide, presumably through diradical **19**. However, no adducts could be isolated from olefins, TCNE, diphenylketene, or acetylenedicarboxylate. Furthermore, di-*tert*-butylhydrazine was not efficient as a hydrogen donor to the diradical as was observed for di-*tert*-butyldiaziridinone.[9,10]

NMR Studies. Our original report on the NMR behavior of di-*tert*-octylthiadiaziridine 1,1-dioxide (**2b**) noted that the diastereotopic α-methyl groups were anisochromous in aromatic solvents. The same is true for the α-methyl signals of the 1,1-dimethyl-2-phenylethyl (**2j**) and 1,1,3-trimethyl-3-phenylbutyl (**2k**) derivatives. Additionally, the diastereotopic β-methylene and γ-methyl protons of **2k** are also anisochronous. The chemical shift differences ($\Delta\delta$) and the coalescence temperature for **2b,j,k** are 5.10 Hz and 99.0 °C, 4.20 Hz and 93 °C, and 10.50 Hz and 118 °C, respectively, for the α-methyl groups in diphenyl ether at 60 MHz. By employment of the equations of Gutowsky and Holm,[26] the approximate free energies of activation ($\Delta G^{\ddagger}$) for the coalescence phenomena are 20 ± 1 kcal mol^{-1} in each case. This value is somewhat higher than the 16-kcal mol^{-1} barrier determined by Greene et al. for di-*tert*-octyldiaziridinone.[9] For this reason, reexamination of the coalescence behavior of the diastereotopic probes of **2b** and **2k** (three sets of diastereotopic protons) in toluene-d_8 at 200 MHz was undertaken in order to assure that the coalescence behavior being observed was due to a chemical exchange process rather than to a simple chemical shift temperature dependence. For example, the 200-MHz NMR spectrum of **2b** shows α- and γ-methyl peaks at δ 0.974 (s, 9 H), 1.188 (s, 3 H), 1.298 (s, 3 H), respectively, and the AB pattern for the methylene protons at δ 1.442, 1.516, 1.683, and 1.758 (J_{AB} = 14.9 Hz, $\Delta\delta_{AB}$ = 46 Hz). A large temperature chemical shift dependence was noted for both **2b** and **2k** in toluene-d_8; e.g., the chemical shift of the α-methyls of **2b** was 1.243 at 25 °C and δ 1.308 at 102 °C. A priori, it would not be expected that a simple chemical shift temperature dependence of the α- and γ-methyl groups of **2k** would be the same; conversely, it is expected that the chemical exchange process for the α- and γ-methyl groups of **2k** would be identical. For **2k** at 27 °C in toluene-d_8 the chemical shift of the α- and γ-methyl groups are 37.8 and 77.4 Hz, respectively, at 200 MHz. Over the temperature range 27–97 °C, the chemical shift differences are reduced to 23.6 and 54.2 Hz, respectively, for the α- and γ-methyls. At higher temperatures, extensive decomposition of the sample occurs. Although coalescence cannot be reached at 200 MHz, treatment of the rate data below coalescence yields free energies of activation ($\Delta G^{\ddagger}$) for the α- and γ-methyl groups of 19.6 and 19.1 kcal/mol, respectively, indicating that the process being observed is one of chemical exchange. Similarly, the di-*tert*-octyl derivative **2b** does not exhibit coalescence at 200 MHz in the accessible temperature range because of decomposition (the greater field strength causes a greater chemical shift difference and hence requires a higher temperature for coalescence). $\Delta G^{\ddagger}$ (for all data below coalescence) is 20.3 kcal/mol.

Comparison of the current data with that for other diaziridines, e.g., 1,3-dimethyl-1,3-dibenzyldiaziridine ($\Delta G^{\ddagger}$ = 27.3 kcal mol^{-1}) and 1,3-dimethyl-3-benzyldiaziridine ($\Delta G^{\ddagger}$ = 26.3 kcal mol^{-1}),[27] reveals a significant lowering of the inversion barrier upon substitution of SO_2 for CR_2 and even greater lowering for CO substitution.[9] The exact reason for these dramatically different barriers to coalescence is unclear. However, the chemical reactivity of the thiadiaziridine 1,1-dioxides (trapping of diradical intermediates by thiophenol and cumene) and the long N–N bond distance (X-ray) are both consistent with the inversion occurring from a diradical or "virtual diradical" intermediate.

Experimental Section

Preparation of Amines. *tert*-Butylamine (**18a**), *tert*-octylamine (**18b**), and adamantylamine (**18c**) are commercially available (Aldrich). The other amines, **18f**,[28] **g**,[29] **h**,[30,31] **i**,[32] **j**,[33] **k**,[34]

(26) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).
(27) A. Mannschreck and W. Seitz, *Angew. Chem.*, **F1**, 224 (1969).
(28) A. C. Cope, J. T. Foster, and P. H. Towle, *J. Am. Chem. Soc.*, **71**, 3929 (1949).
(29) Z. J. Vejdelek and V. Tracka, *Experientia*, **15**, 215 (1959).
(30) O. S. Urbanskaya, *J. Gen. Chem. USSR (Engl. Transl.)*, **29**, 117 (1959).
(31) P. A. Zagorets, A. G. Shostarko, and A. M. Dodonov, *Khim. Vys. Energ.*, 378 (1972).

are known and were prepared from the corresponding alcohols by method A (alcohol to azide to amine)[35] or method B (alcohol to amide to amine).

Method A. Preparation of Azides. This is illustrated for 1-phenyl-1-methylethylamine (**18f**). To an ice bath cooled mixture of 33.8 g (0.25 mol) of 2-phenyl-2-propanol in 100 mL of 57% sulfuric acid and 100 mL of chloroform was added portionwise 48.8 g (0.75 mol) of sodium azide. The mixture was stirred for 48 h, poured into 500 mL of ice–water, and extracted with methylene chloride (2 × 100 mL). The combined chloroform and methylene chloride extracts were washed with water (2 × 100 mL), dried ($MgSO_4$), and concentrated in vacuo to give 31.2 g (80%) of crude azide identified by the absence of an OH stretch and the presence of an N_3 signal at 2100 cm^{-1} in the IR.

Similar treatment of 2-methyl-2-hexanol[36] (**15h**) and 3-ethyl-3-heptanol[31] (**15i**) gave the corresponding crude azides in 67% and 81% yields, respectively. They were identified by IR and used without further purification for fear of their explosive nature.

Reduction to Amine. To 7.6 g (0.20 mol) of lithium aluminum hydride in 250 mL of anhydrous ether was added 16.1 g (0.10 mol) of 2-phenyl-2-propyl azide in 50 mL of ether. The mixture was stirred for 12 h and refluxed for 1 h before the excess $LiAlH_4$ was destroyed by careful addition of water at 0 °C. The ether layer was dried ($MgSO_4$), concentrated in vacuo, and distilled to give 9.2 g (68%) of 2-phenyl-2-aminopropane (**18f**), bp 81–82 °C (10 mm) [lit.[28] bp 72–72 °C (8 mm)].

Similar treatment of azides **17h,i** from alcohols **15h,i** gave amines 1,1-dimethylpentylamine [**18h**: 88%; bp 125–126 °C (lit.[30] bp 124–127 °C)] and 1,1-diethylpentylamine [**18i**: 81%; bp 70–72 °C (16 mm) [lit.[31] bp 61–62 °C (11 mm)]].

Method B. Preparation of Amides. This is illustrated for 1,1-dimethyl-2-phenylethylamine (**18j**). 2-(Phenylmethyl)-2-propanol (15.0 g, 0.10 mol) was added portionwise to a solution of acetonitrile (4.5 g, 0.11 mol), glacial acetic acid (100 mL), and concentrated sulfuric acid (33 mL) cooled in an ice bath. The mixture was stirred at room temperature for 12 h, after which it was poured into 200 mL of ice–water and neutralized with solid sodium carbonate. The aqueous mixture was extracted with ether (4 × 100 mL), the extracts were dried ($MgSO_4$) and concentrated, and the residue was recrystallized from hexane to give 15.2 g of *N*-(1,1-dimethyl-2-phenylethyl)acetamide: mp 91–92.5 °C (lit.[37] mp 91–92 °C); NMR ($CDCl_3$) δ 1.23 (s, 6 H), 1.75 (s, 3 H), 2.98 (s, 2 H), 5.54 (br s, 1 H), 7.10–7.21 (m, 5 H); IR ($CHCl_3$) 3440, 3338, 1682, 1500 cm^{-1}.

Similar treatment of **15g** gave a 64% yield of *N*-(1,1,2,2-tetramethylpropyl)acetamide [**16g**, mp 115–116 °C (lit.[38] mp 111–112 °C)], and substitution of sodium cyanide for acetonitrile on **15k** gave a 75% yield of *N*-(1,1,3-trimethyl-3-phenylbutyl)-formamide [**16k**, mp 63–64 °C (from hexane) [lit.[34] mp 174 °C (0.27 mm)]].

Hydrolysis of Amides. A mixture of 250 mL of 23% aqueous potassium hydroxide solution and 19.1 g (0.1 mol) of *N*-(1,1-dimethyl-2-phenylethyl)acetamide was sealed in a Monel autoclave and heated to 200 °C for 24 h. After the mixture cooled, the combined ethereal extracts (2 × 100 mL) were dried ($MgSO_4$) and concentrated to give 11.4 g (77%) of the crude amine which was purified as the hydrochloride salt, mp 200–201 °C (lit.[32,33] mp 195–196 °C).

Similar treatment of acetamide **16g** and formamide **16k** gave 1,1,2,2-tetramethylpropylamine [**18g**, bp 120–122 °C (lit.[29] bp 121–122 °C)] and 1,1,3-trimethyl-3-phenylbutylamine [**18k**, bp 110–112 °C (1 mm) [lit.[34] 110–111 °C (1 mm)]] in 86% and 84% yields, respectively.

Preparation of Symmetrical Sulfamides. General Procedure. To 2 equiv of amine and 2 equiv of triethylamine in dichloromethane cooled to −10 °C was added 1 equiv of freshly distilled sulfuryl chloride. After the reaction was stirred for 4 h, the mixture was extracted with several portions of 5% hydrochloric acid to remove excess amines, and the organic layer was dried and concentrated to give the crude sulfamide. The following sulfamides were prepared in this fashion.

***N,N'*-Di-*tert*-butylsulfamide (1a)**: 66% yield; mp 141–142 °C (lit.[39] mp 140–141 °C).

***N,N'*-Bis(1,1,3,3-tetramethylbutyl)sulfamide (1b)**: 77% yield; mp 81–82 °C (hexane); NMR ($CDCl_3$) δ 1.04 (s, 18 H), 1.42 (s, 12 H), 1.62 (s, 4 H), 4.41 (s, 2 H); IR 3410, 3280, 1320, 1310, 1120 cm^{-1}.

Anal. Calcd for $C_{16}H_{36}N_2O_2S$: C, 59.93; H, 11.34; N, 8.73. Found: C, 60.07; H, 11.39; N, 8.63.

***N,N'*-Bis(adamant-1-yl)sulfamide (1c)**: 43% yield; mp 246–247 °C (lit.[40] mp 247–249 °C).

***N,N'*-Bis(1-methyl-1-phenylethyl)sulfamide (1f)**: 60% yield; mp 159–160.5 °C (EtOH); NMR (Me_2SO) δ 1.60 (s, 6 H), 3.29 (s, 1 H), 7.19–7.51 (m, 5 H); IR ($CHCl_3$) 1451, 1391, 1336 cm^{-1}.

Anal. Calcd for $C_{18}H_{24}N_2O_2S$: C, 65.04; H, 7.29; N, 8.42. Found: C, 64.94; H, 7.27; N, 8.36.

***N,N'*-Bis(1,1,2,2-tetramethylpropyl)sulfamide (1g)**: 48% yield; mp 174–175 °C (EtOH–H_2O); NMR ($CDCl_3$) δ 0.90 (s, 18 H), 1.38 (s, 12 H), 4.0 (s, 2 H); IR (CCl_4) 3410, 3300, 1310, 1130 cm^{-1}.

Anal. Calcd for $C_{14}H_{32}N_2O_2S$: C, 57.47; H, 11.03; N, 9.58. Found: C 57.71; H, 10.93; N, 9.59.

***N,N'*-Bis(1,1-dimethylpentyl)sulfamide (1h)**: 55% yield; mp 58–59 °C (EtOH–H_2O); NMR ($CDCl_3$) δ 0.89 (t, 3 H), 1.30 (s, 6 H), 0.70–1.52 (m, 6 H); IR (CCl_4) 3380, 3275, 2955, 2858, 1388, 1366, 1323, 1136 cm^{-1}.

Anal. Calcd for $C_{14}H_{32}N_2O_2S$: C, 57.48; H, 11.05; N, 9.56. Found: C, 57.21; H, 11.23; N, 9.42.

***N,N'*-Bis(1,1-diethylpentyl)sulfamide (1i)**: 64% yield; mp 89–90 °C (EtOH–H_2O); NMR ($CDCl_3$) δ 0.71–1.92 (m, 19 H), 3.87 (s, 1 H); IR (CCl_4) 3381, 3376, 2960, 2943, 2869, 1323, 1135 cm^{-1}.

Anal. Calcd for $C_{18}H_{40}N_2O_2S$: C, 61.98; H, 7.88; N, 11.58. Found: C, 61.81; H, 8.05; N, 11.58.

***N,N'*-Bis(1,1-dimethyl-2-phenylethyl)sulfamide (1j)**: 77% yield; mp 110–111 °C (EtOH–H_2O); NMR ($CDCl_3$) δ 1.32 (s, 6 H), 2.88 (s, 2 H), 4.02 (br s, 1 H), 7.21–7.36 (m, 5 H); IR (CCl_4) 3362, 3280, 3058, 1340, 1141 cm^{-1}.

Anal. Calcd for $C_{20}H_{28}N_2O_2S$: C, 66.63; H, 7.84; N, 7.77. Found: C, 66.83; H, 7.88; N, 7.95.

***N,N'*-Bis(1,1,3-trimethyl-3-phenylbutyl)sulfamide (1k)**: 55% yield; mp 78–79.5 °C (lit.[34] mp 79–80 °C).

Preparation of Unsymmetrical Sulfamides. *N*-*tert*-Butyl-*N'*-(1,1,3,3-tetramethylbutyl)sulfamide (1d). To 13.8 g (182 mmol) of *tert*-butyl alcohol in 100 mL of hexane was added 26.0 g (182 mmol) of chlorosulfonyl isocyanate in 50 mL of hexane at a rate fast enough to cause gentle refluxing. The mixture was heated at reflux for 1 h and cooled in an ice bath, and 1,1,3,3-tetramethylbutylamine (67.3 g, 0.364 mol) in 50 mL of hexane was added. The reaction was allowed to stir overnight at room temperature. After addition of water, the organic layer was washed with 5% hydrochloride acid (2 × 100 mL), dried ($MgSO_4$), and concentrated to give, after recrystallization (EtOH–H_2O), 21.1 g (44%) of sulfamide **1d**: mp 84–85 °C; NMR (CCl_4) δ 1.03 (s, 9 H), 1.33 (s, 9 H), 1.39 (s, 6 H), 1.51 (s, 2 H); ^{13}C NMR ($CDCl_3$ relative to Me_4Si) δ 29.2 (α-CH_3's), 31.7 (γ-CH_3's and γ-C), 55.4 (β-CH_2), 58.4 (α-C).

Anal. Calcd for $C_{12}H_{28}N_2O_2S$: C, 54.50; H, 10.67; N, 10.60. Found: C, 54.33; H, 10.58; N, 10.39.

***N*-*tert*-Butyl-*N'*-(adamant-1-yl)sulfamide (1e)** was prepared as in the procedure for **1d** in 45% yield: mp 166–168 °C (EtOH–H_2O); NMR ($CDCl_3$) δ 1.32 (s, 9 H), 1.55 (br s, 6 H), 1.96 (br s, 9 H), 4.13 (br s, 2 H).

Anal. Calcd for $C_{14}H_{26}N_2O_2S$: C, 58.71; H, 9.15; N, 9.78. Found: C, 58.58; H, 9.02; N, 9.60.

Preparation of *N*-Chlorosulfamides. *N*-Chloro-*N,N'*-di-*tert*-butylsulfamide (9a). *tert*-Butyl hypochlorite (2.7 g, 0.025 mol) in 25 mL of methanol was added dropwise to ice-bath-cooled solution of 5.2 g (0.025 mol) of *N,N'*-di-*tert*-butylsulfamide in 150 mL of methanol. After the mixture was stirred for 1 h at 0 °C,

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(38) J. Ritter and J. Kalish, *J. Am. Chem. Soc.*, **70**, 4049 (1948).
(39) J. C. Stowell, *J. Org. Chem. Soc.*, **32**, 2360 (1967).
(40) H. Quast and F. Kees, *Chem. Ber.*, **110**, 1780 (1977).

the solvent was removed (at 0 °C) under reduced pressure to yield 5.7 g (93%) of **9a**: mp 105–106 °C (pentane) (lit.[41] mp 98–100 °C); NMR ($CDCl_3$) δ 1.38 (s, 9 H), 1.50 (s, 9 H), 5.13 (s, 1 H); NMR (C_6H_6) δ 1.18 (s, 9 H), 1.41 (s, 9 H), 5.21 (s, 1 H).

Anal. Calcd for $C_8H_{19}ClN_2O_2S$: C, 39.59; H, 7.84; N, 11.55. Found: C, 39.85; H, 7.92; N, 11.60.

***N*-Chloro-*N*,*N*'-bis(1,1,3,3-tetramethylbutyl)sulfamide (9b)** was prepared in 91% yield by the same procedure as used for **9a**: mp 72–73 °C (EtOH); NMR (CCl_4) δ 1.06 (s, 18 H), 1.45 (s, 6 H), 1.58 (s, 6 H), 1.65 (s, 2 H), 1.83 (s, 2 H), 5.42 (s, 1 H).

Anal. Calcd for $C_{16}H_{35}ClN_2O_2S$: C, 54.16; H, 9.87; N, 7.90. Found: C, 54.51; H, 10.28; N, 7.86.

***N*-Chloro-*N*,*N*'-bis(adamant-1-yl)sulfamide (9c)** was prepared in 89% yield by the procedure used for **9a**; mp 152–155 °C (lit.[40] mp 153–155 °C).

Synthesis of Thiadiaziridine 1,1-Dioxides. Method 1. From Sulfamide. N,N'-Disubstituted sulfamide (1 equiv) was added over a period of 30 min to 1 equiv of NaH suspended in hexane (or pentane). The mixture was stirred and heated to reflux for 2 h and cooled to −30 °C and 1 equiv of *tert*-butyl hypochlorite in hexane was added dropwise. The solution was stirred for 3 h at this temperature and for 1 h at 0 °C, and cold ether was added. The organic layer was washed with 100 mL of water and dried ($MgSO_4$), and removal of the solvent under reduced pressure yielded the crude product.

Method 2. From *N*-Chloro-*N*,*N*'-disubstituted-sulfamide. To 1 equiv of the *N*-chloro-*N*,*N*'-disubstituted-sulfamide in dry tetrahydrofuran was added 1 equiv of NaH suspended in dry tetrahydrofuran, while the temperature was kept below −30 °C. The reaction mixture was stirred at this temperature for 2 h and at 0 °C for 1 h. Ice–water was added, and the organic layer was separated, washed with cold water, and dried ($MgSO_4$). Concentration yielded the crude product.

***N*,*N*'-Di-*tert*-butylthiadiaziridine 1,1-Dioxide (2a). Method 1.** *N*,*N*'-Di-*tert*-butylsulfamide (20.8 g, 0.10 mol), sodium hydride (2.4 g, 0.10 mol), and *tert*-butyl hypochlorite (10.9 g, 0.10 mol) gave 11.17 g (56%) of **2a**: mp 35.5–36 °C (EtOH, −50 °C); NMR (CCl_4) δ 1.35 (s); NMR (benzene) δ 1.10 (s); IR (CCl_4) 2970, 2925, 2860, 1475, 1455, 1340, 1230, 1190 cm^{-1}.

Anal. Calcd for $C_8H_{18}N_2O_2S$: C, 46.56; H, 8.81; N, 13.58. Found: C, 46.85; H, 8.93; N, 13.39.

Method 2. *N*-Chloro-*N*,*N*'-di-*tert*-butylsulfamide (1.21 g, 0.05 mol) and sodium hydride (0.12 g, 0.05 mol) gave 0.46 g (45%) of **2a** (mp 33.5–35 °C) spectrally identical with **2a** from above.

***N*,*N*'-Bis(1,1,3,3-tetramethylbutyl)thiadiaziridine 1,1-dioxide (2b)** was prepared in 90% yield. From 32.0 g (0.10 mol) of sulfamide, 2.4 g (0.1 mol) of sodium hydride, and 10.9 g (0.1 mol) of *tert*-butyl hypochlorite was obtained 28.6 g of **2b**: mp 49.5–50 °C (EtOH); NMR (CCl_4) δ 1.05 (s, 18 H), 1.40 (s, 12 H), 1.72 (s, 2 H), 1.75 (s, 2 H); NMR (benzene) δ 0.95 (s, 18 H), 1.18 (s, 6 H), 1.30 (s, 6 H), 1.57 (s, 2 H), 1.66 (s, 2 H); ^{13}C NMR ($CDCl_3$ relative to Me_4Si) δ 25.8 and 28.1 (α-CH_3's), 31.8 (α-CH_3's and γ-C), 54.8 (β-CH_2), 65.2 (γ-C).

Anal. Calcd for $C_{16}H_{34}N_2O_2S$: C, 60.38; H, 10.69; N, 8.81. Found: C, 60.13; H, 10.70; N, 8.79.

N-Chloro-*N*,*N*'-bis(1,1,3,3-tetramethylbutyl)sulfamide (**9b**; 7.1 g, 0.02 mol) and sodium hydride (0.48 g, 0.02 mol) gave 5.2 g (82%) of **2b** identical with the thiadiaziridine obtained above.

***N*,*N*'-Bis(adamant-1-yl)thiadiaziridine 1,1-dioxide (2c)** was prepared in 33% yield. From 2.0 g (5.5 mmol) of sulfamide **1c**, 0.264 g (5.5 mmol) of sodium hydride, and 0.595 g (5.5 mmol) of *tert*-butyl hypochlorite was obtained 0.65 g of **2c**: mp 173–174 °C (lit.[40] 173–174 °C); NMR (benzene) δ 1.44 (s, 6 H), 1.90 (s, 9 H).

N-Chloro-*N*,*N*'-bis(adamant-1-yl)sulfamide (**9c**; 1.99 g, 5 mmol) and sodium hydride (0.12 g, 5 mmol) gave 0.757 g (42%) of **2c** identical with the sample from above.

***N*-*tert*-Butyl-*N*'-(1,1,3,3-tetramethylbutyl)thiadiaziridine 1,1-dioxide (2d)** was prepared in 60% yield. From 5.0 g (18.9 mmol) of sulfamide **1d**, 0.92 g (18.9 mmol) of sodium hydride, and 2.12 g (18.9 mmol) of *tert*-butyl hypochlorite was obtained 3.0 g of **2d**: bp 106 °C (1.5 mm); NMR (CCl_4) δ 1.09 (s, 18 H), 1.33 (s, 4 H), 1.85 (d, 4 H).

Anal. Calcd for $C_{12}H_{26}N_2O_2S$: C, 54.92; H, 10.00; N, 10.68. Found: C, 55.10; H, 10.03; N, 10.39.

***N*-*tert*-Butyl-*N*'-(adamant-1-yl)thiadiaziridine 1,1-dioxide (2e)** was prepared in 85% yield. From 2.86 g (0.01 mol) of sulfamide **1e**, 0.24 g (0.01 mol) of sodium hydride, and 1.08 g (0.01 mol) of *tert*-butyl hypochlorite was obtained 2.42 g of **2e**: mp 65.5–66.5 °C (hexane); NMR ($CDCl_3$) δ 1.32 (s, 9 H), 1.57–1.80 (br s, 6 H), 1.82–2.04 (br s, 6 H), 2.06–2.30 (br s, 3 H).

Anal. Calcd for $C_{14}H_{24}N_2O_2S$: C, 59.12; H, 8.51; N, 9.85. Found: C, 59.25; H, 8.74; N, 9.78.

***N*,*N*'-Bis(1-methyl-1-phenylethyl)thiadiaziridine 1,1-dioxide (2f)** was prepared in 35% yield. From 1.66 g (5 mmol) of sulfamide **1f**, 0.12 g (5 mmol) of sodium hydride, and 0.54 g (5 mmol) of *tert*-butyl hypochlorite was obtained 0.65 g, after chromatography, of white solid tentatively identified as **2f**. The sample decomposed after being allowed to stand for 10 min and was only characterized by NMR ($CDCl_3$): δ 1.82 (d, 6 H), 7.15 (m, 5 H).

***N*,*N*'-Bis(1,1,2,2-tetramethylpropyl)thiadiaziridine 1,1-dioxide (2g)** was prepared in 33% yield. From 1.46 g (5 mmol) of sulfamide **1g**, 0.12 g (5 mmol) of NaH, and 0.54 g (5 mmol) of *tert*-butyl hypochlorite was obtained 0.47 g of **2g**: mp 76.5–77.5 °C (hexane); NMR ($CDCl_3$) δ 1.19 (s, 9 H), 1.22 (s, 6 H).

Anal. Calcd for $C_{14}H_{30}N_2O_2S$: C, 57.89; H, 10.41; N, 9.64. Found: C, 57.78; H, 10.64; N, 9.50.

***N*,*N*'-Bis(1,1-dimethylpentyl)thiadiaziridine 1,1-dioxide (2h)** was prepared in 53% yield. From 2.92 g (0.1 mol) of sulfamide **1h**, 0.24 g (0.01 mol) of NaH, and 1.08 g (0.01 mol) of *tert*-butyl hypochlorite was obtained, after chromatography, 1.72 g of **2h** as an oil: NMR (C_6H_6) δ 0.89 (t, 3 H), 1.15 (s, 3 H), 1.20 (s, 3 H), 1.04–1.55 (m, 6 H); IR ($CHCl_3$) 2940, 2887, 2735, 1603, 1461, 1370, 1351, 1144, 1075 cm^{-1}.

Anal. Calcd for $C_{14}H_{30}N_2O_2S$: C, 57.89; H, 10.41. Found: C, 57.44; H, 10.89.

***N*,*N*'-Bis(1,1-diethylpentyl)thiadiaziridine 1,1-dioxide (2i)** was prepared in 27% yield. From 3.48 g (0.01 mol) of sulfamide **1i**, 0.24 g (0.01 mol) of NaH, and 1.08 g (0.01 mol) of *tert*-butyl hypochlorite was obtained, after chromatography, an oil tentatively identified as **2i**: NMR ($CDCl_3$) δ 0.68–2.04 (m, 19 H); IR ($CHCl_3$) 2962, 2942, 2884, 1002, 1457, 1386, 1346, 1132, 1077 cm^{-1}.

***N*,*N*'-Bis(1,1-dimethyl-2-phenylethyl)thiadiaziridine 1,1-dioxide (2j)** was prepared in 63% yield. From 3.60 g (0.01 mol) of sulfamide **1j**, 0.24 g (0.01 mol) of NaH, and 1.08 g (0.01 mol) of *tert*-butyl hypochlorite was obtained 2.16 g of **2j**: mp 72.5–74 °C (pentane); NMR (C_6D_6) δ 1.08 (s, 6 H), 1.18 (s, 6 H), 2.77 (s, 4 H), 7.20–7.32 (m, 10 H); IR (CCl_4) 3080, 3060, 3022, 2967, 2925, 1349, 1140 cm^{-1}.

Anal. Calcd for $C_{20}H_{26}N_2O_2S$: C, 66.63; H, 7.83; N, 7.77. Found: C, 66.82; H, 7.59; N, 7.75.

***N*,*N*'-Bis(1,1,3-trimethyl-3-phenylbutyl)thiadiaziridine 1,1-dioxide (2k)** was obtained in 40% yield. From 4.44 g (0.01 mol) of sulfamide (**1k**), 0.24 g (0.01 mol) of NaH, and 1.08 g (0.01 mol) of *tert*-butyl hypochlorite was obtained 2.05 g of **2k**: mp 102.5–104 °C (EtOH–H_2O); NMR (CCl_4) δ 0.77 (s, 6 H), 1.38 (s, 6 H), 1.49 (s, 6 H), 2.11 (s, 4 H), 7.15–7.27 (m, 10 H); ^{13}C NMR ($CDCl_3$ relative to Me_4Si) δ 25.6, 27.5 (α-CH_3's), 30.6, 32.5 (γ-CH_3's), 37.8 (γ-C), 54.7 (β-CH_2), 65.2 (α-CH_3), 48.7, 48.9, 51.1, and 71.7 (aromatic); IR (CCl_4) 3086, 3059, 2972, 1602, 1466, 1389, 1191, 1145 cm^{-1}.

Anal. Calcd for $C_{26}H_{38}N_2O_2S$: C, 70.50; H, 8.63; N, 6.32. Found: C, 70.53; H, 8.29; N, 6.26.

Thermal Decomposition and Reactions of *N*,*N*'-Bis-(1,1,3,3-tetramethylbutyl)thiadiaziridine 1,1-Dioxide. In Refluxing Benzene. A solution of **2b** (0.8 g, 2.5 mmol) in 50 mL anhydrous benzene was heated to reflux for 72 h. An aliquot removed at 4 h showed no change by NMR. The solvent was evaporated under reduced pressure to yield 0.72 g (88%) of **23**: mp 98–99 °C (EtOH–H_2O); NMR ($CDCl_3$) δ 1.03 (s, 9 H), 1.12 (s, 6 H), 1.44 (s, 6 H), 1.47 (s, 6 H), 1.61 (s, 2 H), 1.74 (s, 2 H), 3.14 (s, 2 H), 3.98 (s, 1 H); ^{13}C NMR ($CDCl_3$ relative to Me_4Si) δ 28.1 (ring CH_3's), 29.0 (ring CH_3's), 29.1 (α-CH_3's), 31.7 (γ-CH_3's and γ-C), 35.4 (ring 3° C), 55.6 (β-CH_2), 57.0 (ring CH_2 farthest from N), 58.5 (γ-C), 61.5 and 65.1 (ring C's closest to N); IR (film) 3273, 2955, 1468, 1388, 1369, 1328, 1312, 1223, 1134, 1023, 1003 cm^{-1}.

(41) H. H. Chang and B. Weinstein, *J. Chem. Soc., Perkin Trans. 1*, 1601 (1977).

Anal. Calcd for $C_{16}H_{34}N_2O_2S$: C, 60.33; H, 10.76; N, 8.79. Found: C, 60.09; H, 10.66; N, 8.45.

In Refluxing Toluene. A solution of **2b** (0.8 g, 2.5 mmol) in 50 mL of toluene was heated to reflux for 48 h. An aliquot removed at 1 h showed no reaction by NMR. The solvent was removed, yielding 0.75 g (94%) of **23**.

In Refluxing Cumene. A solution of **2b** (0.8 g, 2.5 mmol) in 150 mL cumene was heated to reflux for 24 h. The cumene was evaporated under reduced pressure, yielding 0.68 g (85%) of **23**.

In Cumene at 75 °C. A solution of **2b** (0.8 g, 2.5 mmol) in 15 mL of cumene was heated to 75 °C and stirred for 24 h. The solvent was evaporated, and the NMR spectrum of the product showed a mixture of **23** and **1b** in a 3.5:1 ratio.

In Benzene with Excess Thiophenol. A solution of **2b** (1.0 g, 3.14 mmol) and thiophenol (0.8 g, 7.27 mmol) in 50 mL of benzene was heated to reflux for 4 h. The solvent was evaporated, and the residue was chromatographed on silica gel to yield 0.94 g (94%) of sulfamide **1b** and 0.58 g of diphenyl disulfide (85%): mp 59–60 °C (hexane) (lit.[42] mp 61 °C). A control experiment without **2b** gave no diphenyl disulfide.

In Benzene with 1 equiv of Thiophenol. A solution of **2b** (0.8 g, 2.5 mmol) and thiophenol (0.275 g, 2.5 mmol) in 50 mL of benzene was heated to reflux for 24 h. The solution was evaporated, and an NMR spectrum of the product showed a mixture of **1b** and **23** in a 1:1 ratio.

Reaction with Phenyl Isocyanate. A solution of **2b** (1.6 g, 5.0 mmol) and phenyl isocyanate (0.6 g, 5.10 mmol) in 50 mL of benzene was heated to reflux and stirred for 72 h. The solvent was evaporated and the residue passed through a silica gel column (ethyl acetate). The yellow band was collected, concentrated, and allowed to crystallize at −78 °C. The solid was filtered and recrystallized from hexane to give 0.26 g (21%) of **24**: mp 158.5–159.5 °C; NMR ($CDCl_3$) δ 1.18 (s, 6 H), 1.56 (s, 6 H), 1.79 (s, 2 H), 3.37 (s, 2 H), 7.32–7.46 (s, 5 H); IR (film) 3264, 2949, 1960, 1640, 1595, 1528, 1446, 1373, 1308, 1252, 1179 cm^{-1}.

Anal. Calcd for $C_{15}H_{22}N_2O$: C, 73.13; H, 9.00; N, 11.37. Found: C, 73.31; H, 9.39; N, 11.15.

The filtrate was concentrated, and the oily residue was recrystallized from hexane, sublimed at 122 °C (10 mm), and recrystallized from ethanol–water three times to yield 0.92 g (58%) of **23**.

Reaction with Tri-*n*-butyltin Hydride. A solution of **2b** (0.8 g, 2.5 mmol) and tri-*n*-butyltin hydride in 25 mL benzene was stirred at room temperature for 24 h. The NMR spectrum of the product showed that all of the starting material had been converted to the sulfamide **1b**.

Reaction with Phenol. A solution of **2b** and phenol (1:2 ratio) in 2 mL benzene was heated to 80 °C in an NMR tube for 48 h and analyzed. No change was observed.

Reaction with Acetic Acid. A solution of **2b** and acetic acid (1:2 ratio) in 2 mL benzene was heated to 60 °C in an NMR tube for 24 h and analyzed. No change was observed.

Reaction with Dimethyl Acetylenedicarboxylate. A solution of **2b** and dimethyl acetylenedicarboxylate (1:1 ratio) in 2 mL benzene was heated to 60 °C in an NMR tube for 24 h and analyzed. No change was observed.

Reaction with Diphenylketene. A solution of **2b** and diphenylketene[43] (1:1 ratio) in 2 mL benzene was stirred for 24 h at room temperature. The reaction mixture was analyzed, and no change was observed.

Reaction with *tert*-Butylhydrazine. A solution of **2b** and di-*tert*-butylhydrazine (1:1 ratio) in 2 mL of benzene was heated to 80 °C in an NMR tube for 24 h and analyzed. No change was observed.

Reaction with Water in Tetrahydrofuran. A solution of **2b** (0.8 g, 2.5 mmol) and water (0.36 g, 20 mmol) in 50 mL of tetrahydrofuran was heated to reflux for 24 h. The solvent was evaporated, yielding 0.91 g of white solid which was identified as the hydrazine hydrosulfate salt **3b**: mp 230–232 °C (EtOH); NMR (D_2O) δ 1.04 (s, 18 H), 1.44 (s, 12 H), 1.66 (s, 4 H).

Anal. Calcd for $C_{16}H_{38}N_2O_4S$: C, 54.20; H, 10.80; N, 7.90; S, 9.04. Found: C, 54.38; H, 11.20; N, 7.81; S, 9.09.

Reaction with Sodium Naphthalide. Naphthalene (6.25 g, 49 mmol) in 30 mL of dimethoxyethane under N_2 was cooled to −20 °C, and 1.25 g (47 mmol) of sodium was added. After the sodium dissolved, 1.5 g (47 mmol) of **2b** was added, and the mixture was stirred for 6 h. The mixture was poured into water and extracted with ether. The ether was dried ($MgSO_4$) and removed in vacuo to yield 1.34 g (89%) of sulfamide **1b**.

Reaction with Sodium Hydroxide. Stirring 318 mg (1.0 mmol) of **2b** with 10 mL of 2 N NaOH at 25 °C for 1 h and at 50 °C for 1 h gave only starting material. The same process with 6 N NaOH for 30 min at 80 °C gave 230 mg (90%) of **4b**.

Reaction with Sodium Methoxide. Stirring 318 mg (1.0 mmol) of **2b** in 10 mL of 2 N $NaOCH_3$ at 25 °C for 30 min at 60 °C for 30 min gave 227 mg (89%) of **4b**.

Reaction with Lithium Aluminum Hydride. Stirring 318 mg (1.0 mmol) of **2b** with 76 mg (2 mmol) of $LiAlH_4$ in 20 mL of ether at 35 °C for 1 h gave, after separation by chromatography, 178 mg (70%) of **4b** and 54 mg (17%) of **1b**.

Reaction with Hydrogen. A solution of 318 mg (1.0 mmol) of **2b** in 10 mL of acetic acid was hydrogenated in a Parr hydrogenator at 50 psi of H_2 on Pd/C for 24 h at 25 °C to give, after workup, 290 mg (91%) of **1b**.

Reaction with Hydrogen Peroxide. A solution of 318 mg (1.0 mmol) of **2b** in 10 mL of pentane was stirred at 36 °C for 3 h with 10 mL of 30% hydrogen peroxide. After workup 285 mg (90%) of **2b** was isolated.

Reaction with Potassium Permanganate. A solution of 318 mg (1.0 mmol) of **2b** in 10 mL of pentane was stirred for 3 h at 36 °C with 10 mL of 1 M $KMnO_4$. After workup, 289 mg (91%) of starting material was recovered.

Reaction with Picric Acid. Stirring 318 mg (1.0 mmol) of **2b** with 10 mL of 1 M picric acid in methanol for 24 h at 25 °C gave, after workup, 231 mg (91%) of **4b**.

Reaction with Chlorine. Chlorine was bubbled slowly through a solution of 318 mg (1.0 mmol) of **2b** in 25 mL of CCl_4 for 1 h at 25 °C. Workup gave 289 mg (91%) of starting material. A similar reaction conducted at 50 °C gave 223 mg (88%) of **4b**.

Reaction with Hydrochloric Acid. Stirring 318 mg (1.0 mmol) of **2b** with 10 mL of 3 M HCl for 1 h at 25 °C gave, after workup, 295 mg (93%) of recovered starting material. A similar reaction with 12 M HCl for 4 h at 25 °C gave 130 mg (51%) of **4b** and 126 mg of starting material; with 12 M HCl for 30 min at 60 °C there was isolated 218 mg (86%) of **4b**.

Reaction with Hydrogen Chloride. Stirring 318 mg (1.0 mmol) of **2b** in pentane and bubbling HCl gas slowly through the solution for 3 h gave 211 mg (83%) of **4b**.

Reaction with *tert*-Butyl Hypochlorite. A solution of 318 mg (1.0 mmol) of **2b** in 10 mL of pentane was stirred with 216 mg (2.0 mmol) of *tert*-butyl hypochlorite for 3 h at 36 °C. Workup gave 233 mg (92%) of **4b**.

Reaction with Phenyllithium. Stirring 318 mg (1.0 mmol) of **2b** with 2 mL of 1.6 M phenyllithium in 10 mL of hexane for 2 h at 25 °C gave, after workup, 213 mg (84%) of **4b**.

Reaction with Methylmagnesium Iodide. Stirring 318 mg (1.0 mmol) of **2b** with 10 mL of 0.2 M methylmagnesium iodide in ether for 2 h at 35 °C gave, after workup, 272 mg (85%) of **1b**.

Reaction with Benzylmagnesium Chloride. Stirring 318 mg (1.0 mmol) of **2b** with 10 mL of 0.2 M benzylmagnesium chloride in ether for 2 h at 35 °C gave 176 mg (55%) of **1b** and 104 mg (33%) of starting material.

Stability Studies. Approximately 200 mg of thiadiaziridine 1,1-dioxide was dissolved in 10 mL of a 90% THF/10% H_2O mixture, and this was stirred at room temperature. The progress of reaction was monitored by NMR by following the disappearance of starting material regardless of the course of reaction (see Results and Discussion). Those that reacted immediately or within a few minutes were classified as group I, those that were more than 50% decomposed within 1–3 h as group II, and those that were stable up to 4 h or more as group III.

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CHE78-02081) for funds used to purchase an NMR spectrometer.

Registry No. **1a**, 13952-67-5; **1b**, 6281-65-8; **1c**, 42399-75-7; **1d**, 50780-07-9; **1e**, 76613-17-7; **1f**, 76613-18-8; **1g**, 39198-31-7; **1h**, 76613-19-9; **1i**, 76613-20-2; **1j**, 76613-21-3; **1k**, 61455-16-1; **2a**, 40121-14-0; **2b**, 50780-12-6; **2c**, 42399-76-8; **2d**, 50780-13-7; **2e**, 76613-22-4; **2f**, 76613-23-5; **2g**, 76613-24-6; **2h**, 76613-25-7; **2i**, 76613-26-8; **2j**, 76613-27-9; **2k**, 76613-28-0; **3b**·H_2SO_4, 76613-30-4; **4b**, 39198-34-0; **9a**, 42028-71-7; **9b**, 76613-31-5; **9c**, 76613-32-6; **13**, 1189-71-5; **15a**, 75-65-0; **15f**, 617-94-7; **15g**, 594-83-2; **15h**, 2370-12-9; **15i**, 14202-62-1; **15j**, 100-86-7; **15k**, 5340-85-2; **16g**, 39198-35-1; **16j**, 5531-33-9; **16k**, 76613-33-7; **17f**, 32366-26-0; **17h**, 76613-34-8; **17i**, 76613-35-9; **18a**, 75-64-9; **18b**, 107-45-9; **18c**, 768-94-5; **18f**, 585-32-0; **18g**, 29772-54-1; **18h**, 2626-64-4; **18i**, 76613-36-0; **18j**, 122-09-8; **18j**·HCl, 1197-21-3; **18k**, 61455-15-0; **23**, 76613-37-1; **24**, 76613-38-2.

Interconversion of γ-Silyl α,β-Unsaturated Carbonyl Compounds and Siloxybutadienes by 1,5-Shifts of Silicon between Carbon and Oxygen

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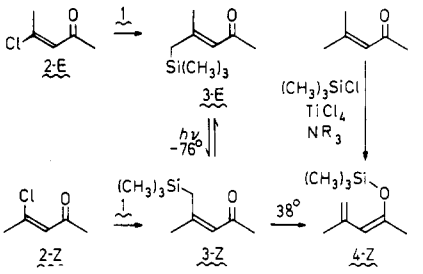
Reaction of lithium bis[(trimethylsilyl)methyl]cuprate (**1**) with (*E*)-4-chloro-3-penten-2-one (**2-E**) gives (*E*)-4-methyl-5-(trimethylsilyl)-3-penten-2-one (**3-E**). Photolysis of **3-E** at low temperature gives a 56:44 mixture of **3-E** and **3-Z**. Upon being warmed to 34 °C, **3-Z** undergoes a migration of silicon from carbon to oxygen to produce 2-methyl-4-(trimethylsiloxy)-2,4-pentadiene (**4-Z**). The reaction of **1** with methyl (*E*)-3-chloro-2-butenoate (**5-E**) leads to the formation of methyl (*E*)-3-methyl-4-(trimethylsilyl)-2-butenoate (**6-E**). Photolysis of **6-E** leads to a mixture of **6-E** and **6-Z**. Both **6-E** and **6-Z** are thermally stable and do not undergo silicon migration from carbon to oxygen for thermodynamic reasons. In fact, 1-methoxy-1-(trimethylsiloxy)-3-methyl-1,3-butadiene (**7**) undergoes a silicon migration from oxygen to carbon to give **6-Z**.

Several years ago we reported that β-acetoxy α,β-unsaturated carbonyl compounds react with lithium dialkylcuprate reagents to give γ-alkyl α,β-unsaturated carbonyl compounds.[1] Similar substitutions of alkyl groups for β-Cl, β-SR, and β-$OPO(OR)_2$ are known.[2] We decided to study the reactions of β-chloro α,β-unsaturated carbonyl compounds with $[(CH_3)_3SiCH_2]_2CuLi$ (**1**) in an attempt to generate γ-trimethylsilyl α,β-unsaturated carbonyl compounds. These compounds are of potential synthetic interest in light of the rich chemistry of allylsilanes.[3] In addition, the products are attractive precursors for the stereoselective generation of trimethylsiloxy-substituted butadienes via a 1,5-shift of silicon from carbon to oxygen. The use of oxygen-substituted dienes in Diels–Alder reactions has been shown to be of great synthetic utility by Danishefsky.[4]

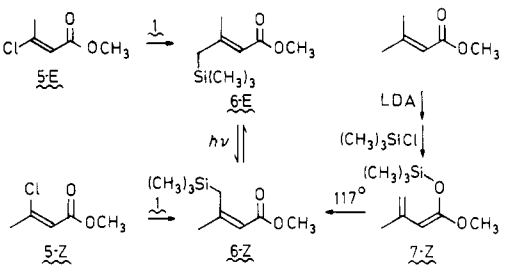
Results

Ketones. Although the synthesis of lithium bis[(trimethylsilyl)methyl]cuprate (**1**) had been previously reported by Lappert and by Brown,[5] its use as a reagent has not been mentioned. Solutions of $[(CH_3)_3SiCH_2]_2CuLi$ are stable at room temperature and are easily prepared by addition of 2 equiv of $(CH_3)_3SiCH_2Li$ to a suspension of CuI in ether or THF.

Scheme I



Scheme II



Reaction of **1** with (*E*)-4-chloro-3-penten-2-one[6] (**2-E**) proceeded rapidly at −15 °C to give (*E*)-4-methyl-5-(trimethylsilyl)-3-penten-2-one (**3-E**, Scheme I) in 51% isolated yield. Examination of the reaction mixture by gas chromatography showed a 74% yield of **3-E**. The stereochemistries of ketones **3-E** and **3-Z** are readily assigned on the basis of the deshielding of substituents cis to the carbonyl group. The allylic methyl group of **3-E** is cis to the ketone and is shifted downfield (δ 2.11) relative to the trans allylic group of **3-Z** (δ 1.65). Similarly, the cis CH_2Si

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