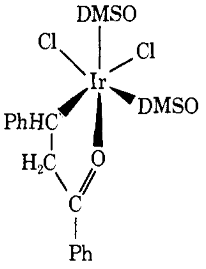
least-squares plane is less than 0.05 Å. Pertinent bond angles and distances are cited in the caption to Figure 1. The acyl group C(7)O(7) is coordinated through oxygen to Mn(1), similar to metal coordination of acyl groups observed in two previously reported structures, **5** (DMSO = dimethyl sulfoxide)[6] and **6**.[7] In the latter, the C═O and O→Mn bond distances of 1.23 and 2.06 (7) Å, respectively, compare favorably with the analogous parameters in **4** (see Figure 1). Metal-coordinated acyl groups have also been postulated in a number of other derivatives where their presence is associated with a characteristic band in the region 1495–1550 cm^{-1}.[8] Accordingly, in the ir spectrum of **4** we observe a strong absorption at 1460 cm^{-1} (surrounded by bands of lower intensity due to absorptions of the phenyl rings).



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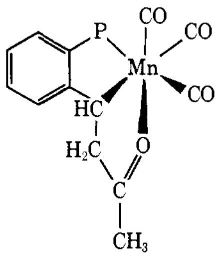

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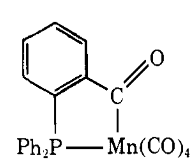
The other substances obtained in the reaction between **2** and **1** are as follows. The first band in the chromatographic separation proved to be **1**, either unreacted or formed by intramolecular metalation of **2** in competition with its reaction with **1** (or both). Under conditions in which the yield of **4** is optimized, approximately 25% of the initial weight of **1** is recovered. The third band is an orange compound, $C_{41}H_{28}Mn_2O_5P_2$ (**7**)[9] (yield 15–30%), formed by the loss of three CO groups from **4**. This transformation has been separately demonstrated by heating **4** to 170° where melting and gas evolution take place to form **7** essentially exclusively. This also accounts for the weakness of the ion peaks resulting from the loss of the first and second CO molecules in the mass spectrum of **4**.[3] The fourth band is another orange compound, $C_{61}H_{43}Mn_2O_7P_3$ (**8**), of low volatility obtained in 5–40% yield. It is analogous to **4** with a carbonyl on Mn(1) replaced by PPh_3. Both **7** and **8** display a strong absorption (1470 and 1460 cm^{-1}, respectively) indicating the presence of a metal-coordinated acyl group. The fifth and sixth chromatographic bands correspond to minor amounts (1–4% each) of compounds $Ph_2\overline{PC_6H_4Mn}(CO)_3L$ (**9**) and $Ph_2\overline{PC_6H_4C(O)Mn}(CO)_4$[2b] (**10**) which are also separately obtained in the treatment of **1** with Ph_3P or CO, respectively. The acyl group absorption for **10** is observed at 1610 cm^{-1}.

In the reaction of **1** with **3a**, we obtain $C_{27}H_{13}O_9PMn_2$ (**11**),[9] an analog of **4** in which $Ph_3P(1)$ is replaced by CO. This is accompanied by only trace amounts of the other derivatives in the reaction of **1** with **2** and also by $Mn_2(CO)_{10}$ (anywhere from 5 to 40% based on **3a**). Such decomposition is completely avoided using methylrhenium pentacarbonyl (**3b**) which results in **12**, an analog of **11** in which one of the two Mn atoms (as yet undetermined) is replaced by Re.



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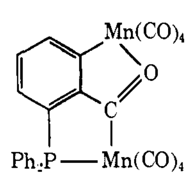

11

Repeating the above reactions with L = $P(p\text{-}FC_6H_4)_3$ or $P(p\text{-}CH_3C_6H_4)_3$ leads to analogous compounds; the rate of metalation for the tolyl rings is higher by about 25% while that for the fluoro-substituted rings is decreased by a similar amount compared to that observed for the phenyl groups, similar to what is found for the intramolecular aromatic metalation reaction.[10] A number of rearrangements must also accompany such substitution in order to account for the observed products. This is presently under investigation. The metalation reaction may also be extended to complexes of other transition metals containing aromatic rings activated by intramolecular metalation.[10]

Acknowledgment. We wish to thank the UCLA Computing Center for intramural support of a portion of the computing expenses in this work and Mr. Irwin Poliakoff for experimental assistance.

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[6] M. McPartlin and R. Mason, *J. Chem. Soc. A*, 2206 (1970).

[7] M. A. Bennett, G. B. Robertson, R. Watt, and P. O. Whimp, *J. Chem. Soc. D*, 752 (1971).

[8] See B. L. Booth and R. G. Hargreaves, *J. Chem. Soc. A*, 2766 (1969), and references cited therein.

[9] Satisfactory elemental and mass spectral analyses were obtained for this and other products mentioned below.

[10] See H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 72, 242 (1972), section II.C.4, and references cited therein, especially G. W. Parshall, *Accounts Chem. Res.*, 3, 139 (1970).

[11] Publication No. 3075.

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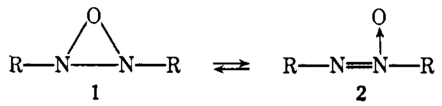
Thiadiaziridine 1,1-Dioxides. An Unusually Stable Strained Heterocyclic Ring System

Sir:

The literature on three-membered rings containing varying numbers of heteroatoms is extensive.[1] They present synthetic challenges and their chemistry is theoretically intriguing. To date, however, only one such ring system comprised entirely of heteroatomic units has been isolated and characterized.[1c,2] Oxadiaziridines are somewhat labile reverting to their valence isomers, azoxyalkanes (eq 1), at room temperature with half-lives of hours.[1c]



1 **2** (1)

We wish to report the second example (**4a,b**) of a three-membered heteroatomic ring system. These substituted thiadiaziridine dioxides were postulated as intermediates by Ohme,[3,4] Schmitz,[3] and Preuschhof[4]

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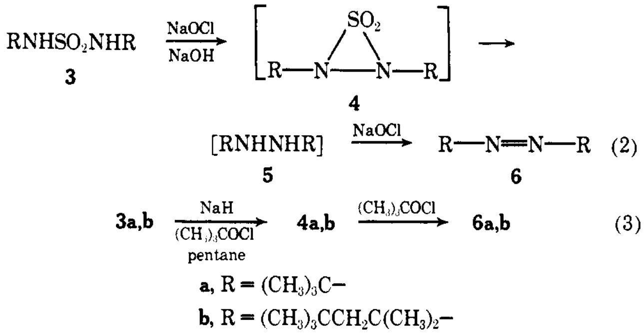
[1] (a) A. R. Katritzky and S. M. Weeds, *Advan. Heterocycl. Chem.*, 7, 226 (1966); (b) E. Schmitz, "Dreiringe mit Zwei Heteroatomen," "Springer-Verlag, New York, N. Y., 1967; (c) F. D. Greene and S. S. Hecht, *J. Org. Chem.*, 35, 2482 (1970), and references therein.

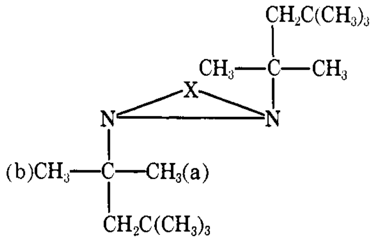
[2] (a) S. S. Hecht and F. D. Greene, *J. Amer. Chem. Soc.*, 89, 6761 (1967); (b) J. Swigert and K. G. Taylor, *ibid.*, 93, 7337 (1971).

[3] R. Ohme and E. Schmitz, *Angew. Chem., Int. Ed. Engl.*, 4, 433 (1965).

in their classic synthesis of azoalkanes (eq 2). However, the conditions of the reaction apparently preclude isolation. With slight modification of their procedure (eq 3) 2,3-di-*tert*-butylthiadiazirine 1,1-dioxide (**4a**) and bis(1,1,3,3-tetramethylbutyl)thiadiaziridine 1,1-dioxide (**4b**) have been prepared in 46 and 90% yields, respectively. Analyses and mass spectra of both are consistent with assigned structures, and X-ray analysis establishes a trans configuration for **4b**.[5] The nmr spectrum of **4a** is a sharp singlet at 1.32 ppm in CCl_4 and 1.12 ppm in benzene. For comparison the nmr of **3a** is a singlet at 1.32 ppm in CCl_4 and 1.21 ppm in benzene and for **6a** 1.17 ppm in CCl_4 and 1.21 ppm in benzene. The nmr of **4b** shows three singlets in CCl_4 at 0.96 (18 H), 1.12 (12 H), and 1.78 ppm (4 H).



An interesting, though not unique,[6] feature of the nmr spectrum of **4b** is the magnetic nonequivalence of the two methyl groups closest to the ring nitrogens (in benzene solvent $\Delta\delta$ = 8.5 Hz for a and b protons of **7**, in CCl_4 and $CHCl_3$ $\Delta\delta$ = 0). The coalescence temperature of 125° corresponds to a calculated ΔG^* = 21 kcal/mol for the "equivalence process."[7] This same behavior has been observed for di-*tert*-octyldiaziridinone (the methyl groups in eight coalescence at 40°, ΔG^* = 16 kcal/mol)[6] and has been ascribed to a slow inversion about both nitrogen bonds. However, the much higher coalescence temperature of **7** does not allow us to rule out competing mechanisms such as bond breaking, inversion, and bond re-formation, and, indeed, decomposition products can be observed to be slowly building up at these temperatures.



7, X = SO_2
8, X = CO

Both **4a** and **4b** display unexpected thermal and chemical stability and can be recovered unchanged from 2 *N* aqueous hydrochloric acid, 2 *N* aqueous sodium hydroxide, 2 *N* sodium methoxide in methanol, and 30% aqueous hydrogen peroxide. They are converted rapidly to 2,2′-dimethyl-2,2′-azopropane (**6a**) and 2,2′,4,4,4′,4′-hexamethyl-2,2′-azopentane (**6b**) with *tert*-butyl hypochlorite and slowly to the same products by chlorine in pentane. Compound **4a** undergoes pyrolysis in refluxing benzene with evolution of SO_2 to give a nearly quantitative yield of *trans*-2,2′-dimethyl-2,2′-azopropane (**6a**). Since *cis*-2,2′-dimethyl-2,2′-azopropane (**6a**) decomposes rapidly at 0° to hydrocarbon products without apparent isomerization to *trans*-**6a**,[8] it is probable that *trans*-**6a** arises directly from the diaziridine dioxide (**4a**). However, it is not known at this time whether this transformation involves the formation of an intermediate or is concerted, the observation being in accord with concerted nonlinear cheletropic elimination of SO_2.[9] These stereochemical results are similar to those obtained by Bordwell and coworkers for *cis*- and *trans*-2,3-diphenylthiirane 1,1-dioxides.[10] In contrast the di-*tert*-octyl compound **4b** is more stable than the di-*tert*-butyl analog and can be recovered unchanged after refluxing in toluene for 1 hr. It does decompose at temperatures above 130° but product analysis is complicated by the fact that one of the presumed products **6b** is also unstable at these temperatures ($t_{1/2}$(130°) = 63 min). This difference in thermal stability is not without precedence though it carries one exceptional feature. In recent years bulky substituents, commonly the tertiary butyl group, have been used to protect otherwise labile systems (diaziridinones,[6] diaziridinimines,[11] aziridinones,[12] cyclopropanones,[13] and α-lactones),[14] presumably impeding nucleophilic or electrophilic attack or adding hindrance to concerted ring opening. The difference in stability between **4a** (*tert*-butyl) and **4b** (*tert*-octyl) is significant and could prove to be general and extremely useful for synthesis of other small ring systems.

It is interesting to point out that the increasing size of substituent, which is apparently responsible for the stability of thiadiaziridine dioxides, results in decreasing stability in the corresponding azoalkanes. For example, Table I shows rate data for azoalkanes which indicate the *tert*-octyl group **6b** to have a large ground-

Table I. Rate Data for Azoalkanes, R—N═N—R

Compd	R	Rel rates, 100°	ΔG^*, kcal/mol, 100°	ΔS^*, eu
6a	$(CH_3)_3C$	1.0	36.2^a	16^a
6c	$(CH_3)_3CC(CH_3)_2$	12	34.3^b	8^b
6b	$(CH_3)_3CCH_2(CH_3)_2$	1300	30.8^b	4^b

[a] Taken from J. C. Martin and J. W. Timberlake, *J. Amer. Chem. Soc.*, **92**, 978 (1970). [b] Calculated from rates of decomposition determined at six different temperatures over a 30° range.

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(5) L. M. Trefonas and L. D. Cheung, *J. Amer. Chem. Soc.*, **95**, 636 (1973).

(6) F. D. Greene, J. C. Stowell, and W. R. Bergmark, *J. Org. Chem.*, **34**, 2254 (1969).

(7) It has been pointed out by a referee that the accuracy of calculation of ΔG^* from coalescence temperature measurements of this type is hard to determine; *cf.* G. Binsch, *Top. Stereochem.*, **3**, 122 (1968).

(8) T. Mill and R. S. Stringham, *Tetrahedron Lett.*, 1853 (1969).

(9) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Gmb H, Weinheim/Bergstr., Germany, 1970, p 152.

(10) F. G. Bordwell, J. M. Williams, E. B. Hoyt, and B. B. Jarvis, *J. Amer. Chem. Soc.*, **90**, 429 (1968).

(11) H. Quast and E. Schmitt, *Angew. Chem., Int. Ed. Engl.*, **8**, 449 (1969).

(12) (a) J. C. Sheehan and J. H. Beeson, *J. Amer. Chem. Soc.*, **89**, 362 (1967); (b) E. R. Talaty, A. E. Dupuy, and A. E. Cancienne, *J. Heterocycl. Chem.*, **4**, 657 (1967).

(13) J. F. Pazos and F. D. Greene, *J. Amer. Chem. Soc.*, **89**, 1030 (1967).

(14) R. Wheland and P. D. Bartlett, *ibid.*, **92**, 6057 (1970).

state steric destabilizing effect over both the *tert*-butyl (**6a**) and *tert*-heptyl (**6c**) azoalkanes.

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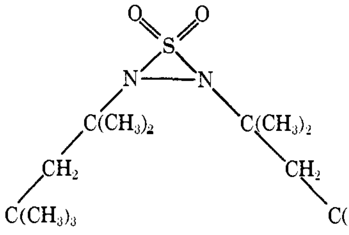
Crystal and Molecular Structure of Bis(1,1,3,3-tetramethylbutyl)thiadiaziridine 1,1-Dioxide

Sir:

We wish to report the first detailed structural information on a three-membered ring composed entirely of heteroatoms. Previously, oxadiaziridines[1,2] represented the only ring system made up solely of heteroatoms which had been isolated and characterized. A crystalline sample of a second and more stable three-membered ring system has now been prepared[3] and the structure of a substituted thiadiaziridine dioxide example (**1**) of this system is reported herein.



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The title compound crystallizes in the orthorhombic space group $Pca2_1$, with cell dimensions: $a = 14.811 \pm 0.001$, $b = 7.951 \pm 0.001$, and $c = 17.059 \pm 0.002$ Å. A complete set of three dimensional X-ray data was taken on a G.E. XRD-490 automated diffractometer system using Cu Kα radiation and stationary crystal–stationary counter techniques out to a 2θ limit of 120° ($d = 0.89$ Å). A total of 1012 reflections (58% of the 1754 measured) were considered observed based on our statistical criteria. The data were corrected for $\alpha_1 - \alpha_2$ splitting and absorption, followed by the usual $1/LP$ corrections.

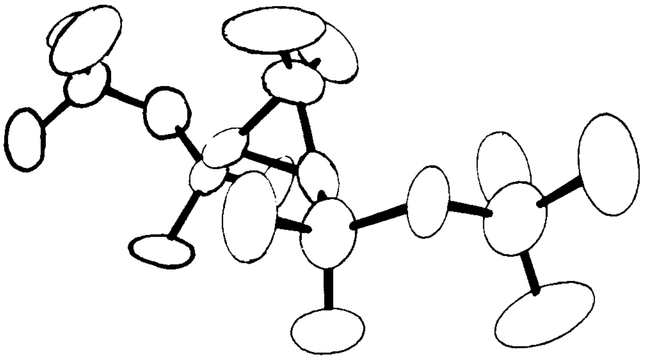

Figure 1. Projective view of bis(1,1,3,3-tetramethylbutyl)thiadiaziridine 1,1-dioxide.

The S–S vectors were identified on a Patterson map and used to phase the subsequent Fourier map (at a value of $R = 0.52$). Two additional peaks were found and assumed to be the oxygen atoms; the process was repeated ($R = 0.43$), and from that point on alternating least-squares and Fourier techniques resulted in all nonhydrogen atoms being identified ($R = 0.117$ for the final isotropic refinement). Conversion to anisotropic temperature factors followed by further least-squares refinements lowered the value of the reliability index to $R = 0.097$. The results, at this stage, are reported herein and are shown in Figure 1. Further work in locating the 34 hydrogen atoms and the final refinement of the structure are complicated by the relatively large thermal motion already evident in the nonhydrogens and the anticipated rotation of the methyl groups.

The trans configuration of the compound is unambiguously determined and substantiates the previous assumption based on chemical and nmr results. The large thermal motion of the atoms evident thus far obscures any trends in the bond distances of the two octyl side chains. The S–N average bond length of 1.62 Å is shorter than a value of 1.67 Å previously determined[4] for an analogous bond in a noncyclic system. The N–N bond (1.67 Å) is significantly longer than any analogous distance (for example, the 1.48-Å distance for the C–N bond in aziridine itself[5]) and is, in fact, bracketed between the values of 1.64 and 1.71 Å found for the admittedly lengthened[6,7] N–N bond in N_2O_4. Such lengthening may well be the only way that the NSN angle of 62° can be maintained at a value near 60°. For example, if one were to assume a "normal" N–N distance even as long as 1.48 Å and still maintain the present S–N distances, then the resultant NSN angle would be lowered to 52°. However, as a consequence of the ring maintaining this angle at the sulfur, the N–N bond is appreciably weakened. This conclusion suggests that the removal of the magnetic nonequivalence of the two methyl groups closest to the ring nitrogens in the nmr[3] may proceed through a bond breaking, inversion, and bond re-formation mechanism.

Acknowledgment. Partial support of this project by the National Science Foundation (GU-2632) is gratefully acknowledged.

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Conformation of Olefin–Iron Carbonyl Complexes from Long-Range Proton Magnetic Resonance Couplings

Sir:

Efforts to define the nature of diene–iron carbonyl complexes based upon pmr data have brought forth