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THE CHEMISTRY OF THIADIAZIRIDINE 1,1-DIOXIDES(III)[1,2]

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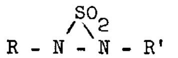
Since our original reports of the synthesis of thiadiaziridine 1,1-dioxides 1a,b,c, we have begun an investigation of their chemical reactivity[1-4] A preliminary report is outlined herein.



1a, R, R' = $(CH_3)_3C$-

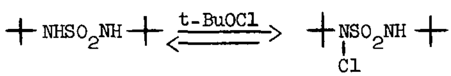
b, R, R' = $(CH_3)_3CCH_2C(CH_3)_2$-

c, R, R' = adamantyl

d, R = $(CH_3)_3C$-, R' = $(CH_3)_3CCH_2C(CH_3)_2$-

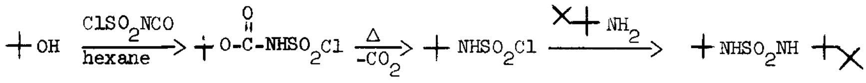
Compounds 1a (mp 35 5-36°), 1b (mp 49 5-50°), 1c (mp 169-170°), and 1d (bp 106°/1 5mm) are conveniently prepared by conversion of the dialkylsulfamide (2) to the sodium salt 3 followed by treatment with t-butylhypochlorite (equation 1) While the order of addition of reagents is not important in preparing 1b, the N-chloro derivative of the di-t-butylsulfamide (4a) is partially converted back to 2a upon treatment with sodium hydride (equation 2).

(1) $$\underset{\textbf{2}a,b,c,d}{RNHSO_2NHR'} \xrightarrow[\text{pentane}]{\text{NaH}} \underset{\textbf{3}a,b,c,d}{R\bar{N}SO_2NHR' \; Na^+} \xrightarrow{\text{t-BuOCl}} \left[\begin{array}{c} R\bar{N}SO_2NR' \\ Na^+ \quad Cl \end{array}\right] \longrightarrow \textbf{1}a,b,c,d$$

(2) 

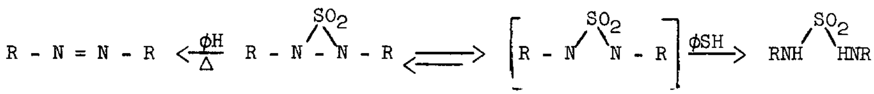
2a 4a

The syntheses of 2a-c have been described.[1,4] The preparation of 2d (equation 3) is an extension of a reaction studied by Hendrickson and Joffee[5] and, as modified, represents a new way of synthesizing unsymmetrical azoalkanes.[1]

(3) 

2d

The difference in thermal stability between 1a and 1b or 1c is striking. The t-butyl derivative (1a) decomposes quantitatively to 2,2'-dimethyl-2,2'-azopropane (5a) after 8-10 hours in refluxing benzene while 1b can be recovered from refluxing toluene.[3,6] Both 1a and 1b give quantitative yields of alkylsulfamides (2a,b) when heated in aromatic solvents with added thiophenol. This seems to indicate the formation of an equilibrium between thiadiaziridine and some diradical intermediate which can be trapped with an appropriate scavenger (equation 4). The unusually long nitrogen-nitrogen bond in 1b supports this contention.[7,8]

(4) 

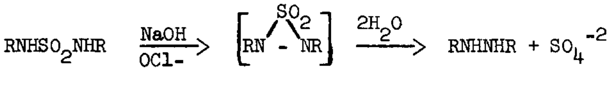
5a 1a,b 2a,b

Hydrolysis of 1a occurs slowly in an open container at room temperature in the solid state (and more rapidly in refluxing wet benzene) to 1,2-di-t-butylhydrazine hydrogen sulfate (6a, mp 178°). The hydrolysis of 1b in wet benzene is much slower and both 1b and 1c are stable for long periods at room temperature (equation 5). This transformation is not

(5) $$\text{1a} \xrightarrow{2H_2O} R-\overset{+}{N}HNH_2-R \quad \overset{-}{H}SO_4$$

6a

surprising and is consistent with the mechanism proposed by Ohme, Schmitz and Preuschhof (equation 6) in their synthesis of azoalkanes.[9,10]

(6) 

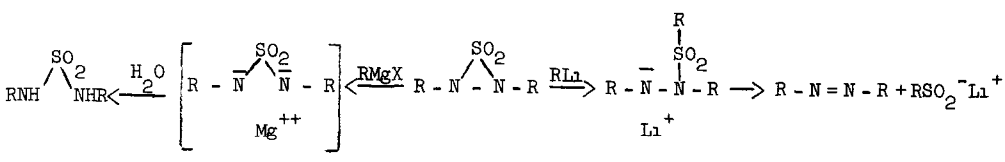
Additional chemical behavior displayed by thiadiaziridine dioxides is summarized for bis(1,1,3,3-tetramethylbutyl)thiadiaziridine 1,1-dioxide in Table 1

Table 1

Chemical Reactivity of Bis(1,1,3 3-tetramethylbutyl)thiadiaziridine 1,1-Dioxide

Reagent (equimolar)	Product
H_2O (benzene, reflux)	Hydrazine Salt (6a)*
H_2O_2 (dilute)[2]	N R
$KMnO_4$ (dilute)	N R
H_2 (HOAC, Pd/C 50 lb/in^2)	Sulfamide (2b)
$LiAlH_4$ (ether, 25°)	Azo (5b) + sulfamide (2b) in 4 1 ratio
Cl_2 (hexane, 50°)[2]	Azo (5b)
$(CH_3)_3COCl$ (pentane, 25°)	Azo (5b)
$NaOCH_3$ (3N CH_3OH, 60°)[2,11]	Azo (5b)
HCl (gas, pentane, 25°)	Azo (5b)
C_6H_5Li (hexane, 25°)	Azo (5b)
CH_3MgBr, $C_6H_5CH_2MgCl$ (ether, 25°)	Sulfamide (2b)
ϕ-SH (benzene, reflux)	Sulfamide (2b)

Of particular interest is the chemical reactivity of 1b towards lithium and Grignard reagents These reactions are illustrated in equation 7 and are probably the result of differences in nucleophilicity versus complexing ability of the reagents, although a complete mechanistic interpretation must await further experimental results

(7) 

* This reaction is reported for di-t-butylthiadiaziridine dioxide The products for di-t-octyl have not been completely identified

References

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3. J. W. Timberlake and M. L. Hodges, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973, Abstract No. 50.
4. H. Quast and F. Kees, Tetrahedron Lett., 1655 (1973). These authors have reported the synthesis of di-adamantylthiadiaziridine 1,1-dioxide (1c) and find it to be comparable to 1b in thermal stability; a result which we can also confirm. (cf. ref. 3).
5. J B. Hendrickson and I Joffee, J. Amer. Chem. Soc., 95, 4083 (1973).
6. B Weinstein (private communication) has confirmed our synthesis of 1a and has reported that sublimed samples are of slightly greater stability.
7. L. M. Trefonas and L. D Cheung, J. Amer Chem Soc , 95, 636 (1973).
8. It is hoped that additional x-ray studies on other thiadiaziridine derivatives will provide understanding to the differences in thermal stabilities.
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11. It was reported earlier, reference 2, that thiadiaziridine dioxides did not react with $NaOCH_3$ The reaction is slow, but does occur as shown in Table 1.

Acknowledgment

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