Distillation afforded 1.85 g (90%) of **7**,[2] bp 54.5–55.0° (20 mm) $\alpha^{23.5}{}_{\mathrm{D}}$ +12.5° (neat, 1 dm), and 3.48 g (92%) of trityl methyl ether,[7] bp 161–163° (0.8 mm). In most cases the trityl ether was not distilled.

The new cyclic ortho esters prepared are the following: 2-methoxy-2,4-dimethyl-1,3-dioxolane (**1**); D-(−)-2-methoxy-2,4,5-trimethyl-1,3-dioxolane (**2**); (*R*)-(−)-2-methoxy-4-phenyl-1,3-dioxolane (**3**); 2-methoxy-2,5,5-trimethyl-1,3-dioxane (**4**); and 2-methoxy-2-methyl-1,3-dioxepane (**5**). Analyses of these compounds are shown in Table III.

**Table III.** Analyses of New Compounds

| | | Analyses[a] | | | |
|---|---|---|---|---|---|
| | | C | | H | |
| Compd | Emp formula | Calcd | Found | Calcd | Found |
| **1** | $C_6H_{12}O_3$ | 54.6 | 54.6 | 9.1 | 8.9 |
| **2** | $C_7H_{14}O_3$ | 57.5 | 57.5 | 9.6 | 9.7 |
| **3** | $C_{11}H_{14}O_3$ | 68.0 | 67.9 | 7.2 | 7.3 |
| **4** | $C_8H_{16}O_3$ | 60.0 | 60.2 | 10.0 | 10.2 |
| **5** | $C_7H_{14}O_3$ | 57.5 | 57.7 | 9.6 | 9.8 |

[a] Analyses by M-H-W Laboratories, Garden City, Mich.

Recently, the substitution of trimethylsilyl chloride for trityl chloride has been shown to give similar results. A study of the stereochemical results in these reactions is now being made.[8]

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(7) C.-H. Wang, *J. Org. Chem.*, **28**, 2914 (1963).

(8) The use of $(CH_3)_3SiCl$ was demonstrated by Dr. Paul Tornstrom and is being studied by Dr. Dan Olson.

(9) Postdoctoral Fellow supported by Grant No. GP-12445X of the National Science Foundation.

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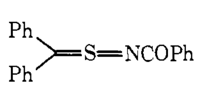
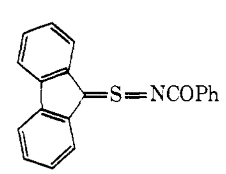
## Thione *S*-Imides. Preparation and Cycloaddition Reactions

*Sir:*

We wish to report the synthesis of the first representative system containing the functional group, $R_2C{=}S{=}NR'$ derived from a thione and to be designated as a thione *S*-imide. Such derivatives should exhibit electrophilic reactivity between thione ylides[1] ($R_2C{=}S{=}CR_2$) and thione *S*-oxides[2] ($R_2C{=}S{=}O$) for similar substitution, and the site (carbon *vs.* sulfur) of such electrophilic reactivity as well as stability would be a function of substituent choice in controlling the degree of contribution of the canonical structures, $C{=}S^{+}{-}N^{-} \leftrightarrow C^{+}{-}S{-}N^{-} \leftrightarrow {}^{-}C{-}S^{+}N$.[3] Consideration of such substitutent effects led to our selection of the thione *S*-imides, **1** and **2**, as an initial target with 1,3-dehydrohalogenation of a precursor $\alpha$-chlorosulfenamide as the ultimate synthetic step.[4]



**1**

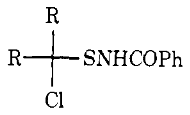


**2**

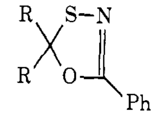
PhCONHSCl

**3**

The reaction of *N*-(trimethylsilyl)benzamide[5] with an excess of sulfur dichloride in THF solution at −30° afforded (80–85%) benzamide-*N*-sulfenyl chloride (**3**), mp 105–108° dec, ir ($CHCl_3$) 1670 (C=O) cm$^{-1}$.[6] Treatment of **3** with an equivalent of diphenyldiazomethane or diazofluorene in THF solution at −78° gave the requisite $\alpha$-chlorosulfenamides, **4a**, mp 114–117° dec, and **4b**, mp 114–116° dec. Triethylamine reacts rapidly with **4a** in THF solution at −78° without visible formation of a colored intermediate to yield an equivalent of triethylamine hydrochloride and 30% of the oxathiazole, **5a**, mp 118–120°. On the other hand, dehydrohalogenation of **4b** under the same conditions provided a deep red ($\lambda_{max}$ 484 nm) solution of **2**. Upon warming to *ca.* −30° the color of such solutions was discharged and 46% of the electrocylic closure product, 5-phenylspiro(fluorene-9,2′-[1,3,4]oxathiazole) (**5b**), mp 102–103° dec, could be isolated.[7] Both **5a** and **5b** were characterized by their absorption in the ir, ($CHCl_3$) 1605 (C=N), 1575 (C=C) cm$^{-1}$, and consistent mass spectra. Furthermore, upon standing at room temperature **5b** decomposed to give fluorenone, benzonitrile, and sulfur.



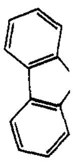
**4**



**5**

**a**, R = Ph—

**b**, R,R =



The electrophilic addition of dry HCl to **2** in THF solution at −78° results in the immediate re-formation of **4b**. Although the reactivity at −30° of **2** was not sufficient to compete against internal cyclization for the capture of nucleophiles such as ketene acetals, reaction with enamines or ynamines occurred readily at −78° in THF solution. With *N*-isobutenylpyrrolidine (**6a**) there was obtained (31%) a 1:1 adduct [mp 185–187° dec; ir ($CHCl_3$) 1635 (C=O), 1600 (C=C) cm$^{-1}$; nmr $\delta$ 7.47 (m, 13 H), 5.62 (s, 1 H), 3.23 (m, 4

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(1) M. Takaku, S. Mitamura, and H. Nozaki, *Tetrahedron Lett.*, 3651 (1969); R. M. Kellogg and S. Wassenaar, *ibid.*, 1987 (1970); R. M. Kellogg, S. Wassenaar, and J. Butler, *ibid.*, 4689 (1970).

(2) W. A. Sheppard and J. Diekmann, *J. Amer. Chem. Soc.*, **86**, 1891 (1964); B. Zwannenburg, L. Thijs, and J. Strating, *Tetrahedron Lett.*, 4461 (1969), and references cited therein.

(3) To illustrate this point a stable but apparently unreactive dithioester *S*-tosylimine has been reported: S. Tamagaki and S. Oai, *ibid.*, 1159 (1972).

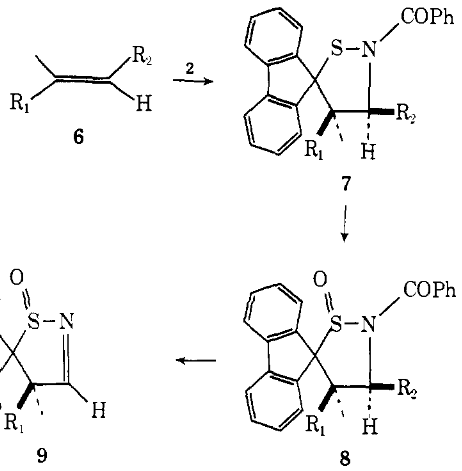
(4) The potential synthesis of a thione *S*-imide from the addition of a nitrene (or equivalent) to a thione has not been successful. For example, the thermal decomposition of benzenesulfonylazide in the presence of xanthione gives only the corresponding imine of xanthone: A. Schonberg and W. Urban, *J. Chem. Soc.*, 530 (1935). However, the dithio ester derivative reported in ref 3 was a result of the reaction of methanolic chloroamine-*t* with a trithione.

(5) N. Y. Derkach and N. P. Smetankina, *Zh. Obshch. Khim.*, **34**, 3613 (1964).

(6) Satisfactory (±0.3%) elemental analyses (C, H, N, S) have been obtained for all new isolated compounds.

(7) At −78° removal by filtration of the triethylamine hydrochloride and addition of hexane to the filtrate caused red needles of **2** to form. After collection at −78° the solid **2** obtained appeared to be stable at room temperature; however, the slightest amount of mechanical deformation of the crystals resulted in an instantaneous transformation to **5b**.

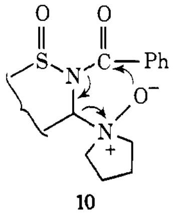
H), 1.76 (m, 4 H), 1.66 (s, 3 H), 0.58 (s, 3 H)] and from *N*-propenylpiperidine (**6b**) an analogous adduct [mp 159–161° (dec); ir ($CHCl_3$) 1637 (C=O), 1600 (C=C) $cm^{-1}$; nmr $\delta$ 7.46 (m, 13 H), 5.60 (d, $J$ = 8 Hz, 1 H), 3.17 (m, 5 H), 1.59 (bd s, 6 H), 0.56 (d, $J$ = 6.5 Hz, 3 H)].[8] The isothiazoline structures **7a** and **7b** have been assigned these adducts based on the above spectral evidence as well as the results of the following degradative sequence.[9] Oxidation of **6** with 1 equiv of *m*-chloroperbenzoic acid in $CH_2Cl_2$ solution at 30° provided (>50%) the *S*-oxides **8a** [mp 210–213° dec;



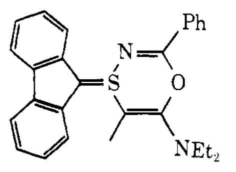
a, $R_1 = CH_3$; $R_2 = N(CH_2)_4$
b, $R_1 = H$; $R_2 = N(CH_2)_5$

ir ($CHCl_3$) 1665 (C=O), 1290 (S=O) $cm^{-1}$; nmr $\delta$ 7.61 (m, 13 H), 5.94 (s, 1 H), 3.31 (m, 4 H), 1.85 (s, 3 H), 1.80 (m, 4 H), 0.66 (s, 3 H)] and **8b** [mp 218–219° dec; ir ($CHCl_3$) 1665 (C=O), 1295 (S=O) $cm^{-1}$; nmr $\delta$ 7.60 (m, 13 H), 5.78 (d, $J$ = 8.5 Hz, 1 H), 3.32 (m, 5 H), 1.55 (s, 6 H), 0.77 (d, $J$ = 7.0 Hz, 3 H)]. The assignment of a cis relationship of $R_1$ and $R_2$ to the oxide function in **8b** rests upon the observed nmr downfield shift of the C-4 hydrogen relative to the **7b** system and the C-4, C-3 hydrogen coupling constant. The mass spectrum of **8a** displayed prominent fragment ions at *m/e* 240 and 206 corresponding to 1,5 and 3,4 bond cleavage. The action of an additional equivalent of *m*-chloroperbenzoic acid in $CH_2Cl_2$ solution at 30° resulted in the formation of the dihydroisothiazole **9a**; mp 168–169°; ir ($CHCl_3$) 1595 (C=N) $cm^{-1}$; nmr $\delta$ 7.46 (m, 9 H), 1.67 (s, 3 H), 0.96 (s, 3 H) with mass spectral ions at *m/e* 281 ($M^+$), 233 ($M^+$ − SO), and 206 ($M^+$ − HCNSO, base peak). This last oxidative elimination step may be the result of decomposition of an intermediate *N*-oxide (**10**).

Although **2** underwent 1,3-cycloadditions with enamines involving the CSN unit, a different system appeared to be important in reaction with ynamines. Addition of 1-(diethylamino)-1-propyne to THF solutions of **2** at −78° rapidly provided an unstable 1:1 adduct, mp 125–126° dec, which decomposed in solution at room temperatures or at the melting point to give benzonitrile. Structure **11** is tentatively assigned



**10**



**11**

to this adduct based on the observed ir [(KBr) 1590, 1525, and 1500 (C=C and C=N) $cm^{-1}$] which was transparent between 1600 and 2900 $cm^{-1}$. The ultraviolet spectrum in $CHCl_3$ was similar to fluorenethione *S*-oxide[2] but with a hypsochromic shift $\lambda_{max}$ ($\epsilon$) 310 (3980), 300 (4980), 277 (12,700), 263 (16,600), and 242 (28,800) nm. Nonequivalent *N*-ethyl groups were apparent in the nmr ($CDCl_3$, −30°): $\delta$ 7.58 (m, 13 H), 3.75 and 3.60 (q, $J$ = 7.3 Hz, 4 H), 2.72 (s, 3 H), 1.54 and 1.06 (t, $J$ = 7.3 Hz, 6 H).

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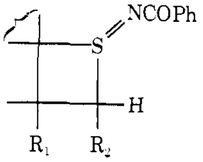
[8] All nmr spectra were recorded at 60 MHz in $CDCl_3$ solution.

[9] The possibility exists that 7 is the ultimate rearrangement product of a penultimate adduct, i, resulting from the action of 2 as a 1,2-dipolariphile. Assignment of a structure such as i to 7 is excluded on the observed C=O absorption at 1665 $cm^{-1}$ in the infrared. The frequency range observed for acyclic acyl iminosulfurans has been 1600–1540 $cm^{-1}$: H. Kise, G. F. Whitfield, and D. Swern, *J. Org. Chem.*, 37, 1121 (1972).



i

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## Photochemistry of Aminoboranes. Boron–Carbon Cleavage as a General Primary Photoprocess in Boron–Nitrogen Analogs of Stilbenes

*Sir:*

We wish to report that (*N*-methylanilino)phenylalkylboranes—isoelectronic boron–nitrogen analogs of stilbenes—undergo a general photochemical reaction that has little parallel in the solution-phase photochemistry of stilbenes or other alkenes. This new primary photoprocess is excited-state cleavage of a boron–alkyl bond.

For example, Pyrex-filtered ultraviolet irradiation of a deoxygenated 0.5 *M* solution of (methylphenylamino)benzylphenylborane[1] (**1a**, R = $PhCH_2$) in carbon tetrachloride at 35° led to nearly complete destruction of starting material and a mixture of products.[2] Analysis of a typical photolysis mixture, taken to *ca.* 80% conversion of **1a**, by a combination of vacuum-line and glpc techniques, revealed a complex mixture of photo-

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[1] Aminoboranes were synthesized by modifications of the general method of K. Niedenzu and J. W. Dawson, *J. Amer. Chem. Soc.*, **82**, 4223 (1960). Satisfactory spectral data and analyses were recorded for new compounds, the details to be reported in full later.

[2] Typical conversion times were *ca.* 30 hr for *ca.* 90% reaction of *ca.* 1 g of starting aminoborane, depending on the optics employed. The relatively long times required for high conversion were necessitated by the gradual accumulation of opaque polymeric material which greatly reduced the usable light absorbed by the aminoborane solution and made complete destruction of starting material difficult.