

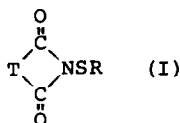
CHEMISTRY OF SULFUR COMPOUNDS-PART VIII<sup>1</sup>. A SELECTIVE AND NOVEL  
METHOD FOR THE PREPARATION OF N-(THIO)-N'-DIAMIDES

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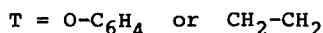
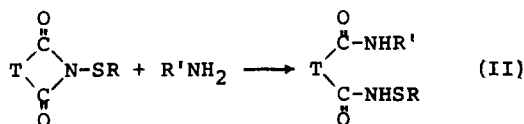
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In 1969, a work from this laboratory described the sulfenimides<sup>3</sup> of the following formula:



More recently we reported on the reaction of these sulfenimides with thiols to make disulfides<sup>4</sup> and with secondary amines to make N-thio-secondary amines<sup>1</sup>. We wish to report now on the reaction of these sulfenimides with primary amines. We have found that these amines react with (I) to give N-(thio)-N'-diamide (II):

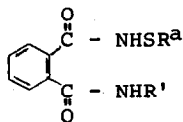


This reaction provides a novel route to a selective synthesis of a new class of compounds. In a typical example, 0.1 mole (10.1 g) of n-hexylamine is added at room temperature to a stirred solution of N-cyclohexylthiophthalimide (26.2 g, 0.1 mole in 200 cc benzene). After 15 minutes the mixture is filtered to recover a white solid which is washed with benzene and allowed to dry at room temperature, yield 27 g, MP 111-112°C. An additional 4 g of product is recovered by concentration of the filtrate. Anal. calc. for C<sub>20</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>S; C = 66.26%, H = 8.34%, N = 7.73%, S = 8.84%, found C = 66.85%, H = 8.23%, N = 7.46%, S = 8.32%. The nmr spectrum confirmed the structure of the diamide obtained; it showed two broad

different NH peaks of equal area at 7.1 $\delta$  and 7.9 $\delta$  (in CDCl<sub>3</sub>). Some of the compounds obtained as depicted in (II) are listed in Table 1.

Table 1

Diamides Obtained Via Primary Amine and Sulfenimides



<u>R</u>	<u>R'</u>	<u>MP, °C<sup>b</sup></u>
C <sub>6</sub> H <sub>11</sub>	n-C <sub>4</sub> H <sub>9</sub>	110-112°C
C <sub>8</sub> H <sub>15</sub>	n-C <sub>4</sub> H <sub>9</sub>	95-97 °C
C <sub>6</sub> H <sub>11</sub>	iso-C <sub>3</sub> H <sub>7</sub>	98-102°C
C <sub>6</sub> H <sub>11</sub>	CH <sub>3</sub>	137-138°C
C <sub>6</sub> H <sub>11</sub>	CH <sub>2</sub> =CHCH <sub>2</sub>	117°C
C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	165-170°C
C <sub>6</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>11</sub>	134-135°C
t-C <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	155-156°C
C <sub>6</sub> H <sub>5</sub>	C <sub>18</sub> H <sub>37</sub>	85-90 °C

<sup>a</sup> The C, H, N and S microanalyses were within acceptable limits.

All compounds were also identified by nmr.

<sup>b</sup> MP of unrecrystallized materials. Compounds decompose slowly at elevated temperature.

When a diamine such as 1,6 hexane diamine was reacted with N-cyclohexylthio-phthalimide in a molar ratio of 1 to 2, N,N'di-(cyclohexylthio)-N",N'''-hexamethylenediphthalamide was obtained (MP, 111-113°C). Anal. calcd. for C<sub>34</sub>H<sub>46</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>, C = 63.91%, H = 7.25%, N = 8.77%, S = 10.0; found, C = 64.80%, H = 7.31%, N = 8.56%, S = 9.61%.

Benzylamine and n-hexylamine reacted respectively with N-cyclohexylthio succinimide in a similar manner and gave N-benzyl, N'-(cyclohexylthio) succinamide (MP, 190-191°C) and N-cyclohexylthio-N'-(n-Hexyl)succinamide (MP, 123-124°C), Anal.

calcd. for  $C_{16}H_{30}N_2O_2S$ , C = 61.10%, H = 9.6%, N = 8.9%, S = 10.19%; found C = 60.61%, H = 9.54%, N = 8.95%, S = 10.14%.

An alternate route of synthesis of N-thio N'diamide could be achieved by reacting a sulfenyl chloride with an unsymmetrical primary diamide. However, one can easily imagine that the latter method, if successful, will produce a mixture of three possible products. The advantage of the novel synthesis described resides in yielding selectively a single and highly pure adduct.

Nmr Spectrum: The detailed studies will make the subject of a future communication. In a typical example N-benzyl-N'-t-(butylthio)phthalamide showed the following peaks (in  $CDCl_3$ ):  $(CH_3)_3C$ , s, 1.33 $\delta$ ;  $CH_2N$ , d, 4.9 $\delta$ , NHC, 7.1 $\delta$ ; NHS, 7.9 $\delta$ . After  $D_2O$  exchange the  $CH_2$  doublet became a singlet at 4.8 $\delta$ . The assignment of the peak at 7.1 $\delta$  to the NHC instead of the NHS was made by comparison with the nmr of N-methyl,N'methyl-phthalamide.

#### References

1. Part VII: see K. Boustany, Chimia, 1970 (II)
2. Contribution 13
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4. K. Boustany and A. B. Sullivan, Tetrahedron Letters, 1970, 3547.