1-d_5-Phenyl-2-d_5-phenyliminomaleimide. This compound was prepared from the d_{10}-phenyl derivative of **4**, as described in the above procedure: mp 136–137 °C; NMR (acetone-d_6) δ 7.05 (1 H, d, J = 6.0 Hz), 6.65 (1 H, d, J = 6.0 Hz); mass spectrum m/e 258 (M^+).

5-Anilino-1-phenylpyrrolid-2-one (7). A 50-mg sample of **4** was hydrogenated at room temperature and atmospheric pressure using Pd/C. After 12 h 2 molar equiv of H_2 was absorbed. The residue after evaporation of the solvent was crystallized (EtAc/petroleum ether): 38 mg of colorless crystals; mp 137–139 °C; NMR ($CDCl_3$) δ 6.4–7.6 (10 H, complex, multiplet), 5.65 (1 H, m), 4.10 (1 H, broad singlet, exchangeable), 1.7–2.8 (4 H, complex multiplet); ir ($CHCl_3$) 3410 (NH) and 1695 cm^{-1} (CO); uv λ_{max} (EtOH) 287 nm (ϵ 1700), 245 (12 500); mass spectrum m/e 252 (M^+, $C_{16}H_{16}N_2O$), 160 ($M^+ - C_6H_5NH$).

Phenylimino-*N*-phenylsuccinimide (8). **5** (250 mg, 1 mmol) and 50 mg of 10% Pd/C in ethyl acetate (15 ml) was hydrogenated at atmospheric pressure and room temperature. One molar equivalent of H_2 was absorbed after 5 h. The mixture was filtered through Celite, the solvent was evaporated, and the residue was twice crystallized from EtAc/petroleum ether: colorless, prismatic crystals; mp 139–140.5 °C; NMR ($CDCl_3$) δ 6.70–7.60 (10 H, complex multiplet), 2.70 (4 H, s); ir ($CHCl_3$) 1780 and 1665 cm^{-1}; mass spectrum m/e 250 (M^+, $C_{16}H_{14}N_2O$).

1,4-Dianilinobutane (9). To a solution of 200 mg of **8** in THF (20 ml) there was added portionwise $LiAlH_4$ (400 mg). The mixture was refluxed for 4 h, the solvent was evaporated, ether was added, and to the cooled mixture a 20% aqueous NaOH solution was added. The ether was decanted off, and the solid was triturated with portions of chloroform which were combined with the ether phase, dried (K_2CO_3), and evaporated. The residue was distilled with Kugelrohr (0.005 mm). The distillate (148 mg) was crystallized from ether–petroleum ether at 0 °C, crystals, mp 36–37 °C (lit.[10] mp 37 °C).

A 300-mg sample of **7** was reduced as described above, also yielding 1,4-dianilinobutane (65%).

Registry No.—**4**, 58966-81-7; **4** d_{10}-phenyl derivative, 58966-82-8; **5**, 58966-83-9; **5** d_{10} phenyl derivative, 58966-84-0; **6**, 58966-85-1; **7**, 58966-86-2; **8**, 58966-87-3; **9**, 13170-61-1; nitrosobenzene, 586-96-9; α-pyrone, 504-31-4; nitrosobenzene-d_5, 18628-43-8; benzene-d_6, 1076-43-3; 1,3-cyclohexadiene, 592-57-4.

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Reaction of Amines with Thiophthalimides. Anomalous Formation of a Thiooxamide[1]

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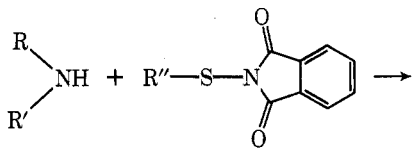
The reaction of various amines with thiophthalimides (**1**) has been shown to be a useful, general method for the preparation of sulfenamides **2**.[2a,b] The only observed exception to this behavior appears to be in the reaction of primary amines with thiophthalimides which have bulky groups. In these cases the nitrogen nucleophile reacts at the carbonyl carbon to give a ring-opened product (**3**).[2a,c] We have discovered an instance where the reaction of a primary amine with an unhindered thiophthalimide proceeds by an alternate route giving two



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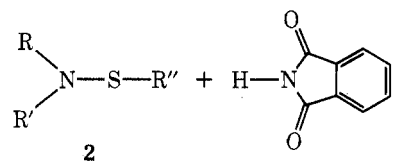

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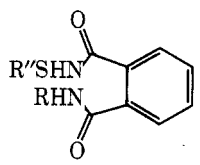

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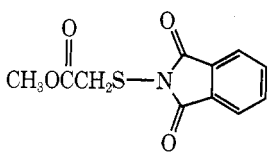

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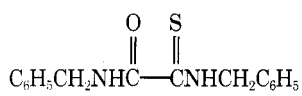
products which can be rationalized by an α-elimination process (vide infra).

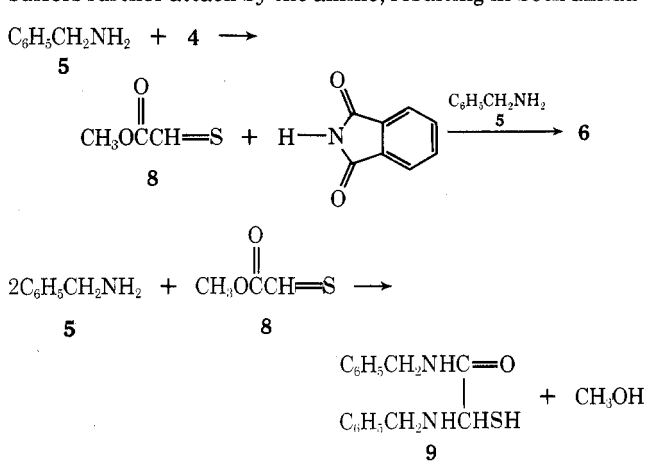
Thiophthalimide **4**[3] was treated with 2 equiv of benzylamine (**5**), the by-product phthalimide collected (69%), and the remaining material chromatographed to provide a mixture of unidentified components as well as two pure compounds.

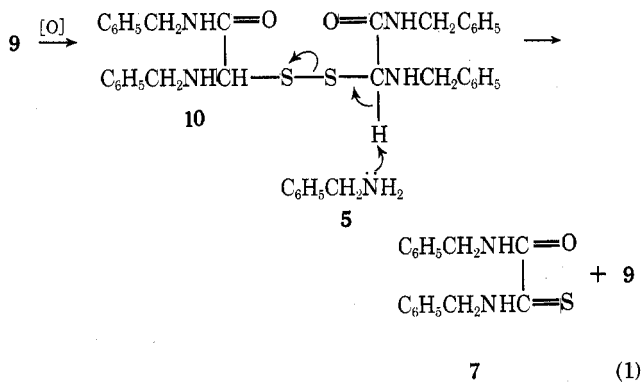
One of the latter products (**6**) was identified as *N*-benzylphthalamide (16% yield) (see Experimental Section). The other substance is a solid, mp 120–122 °C. It shows NMR ($CDCl_3$) δ 4.40 (d, 2 H), 4.75 (d, 2 H) (J = 6 Hz), 7.2 (s, 10 H), 8.38 (broad, 1 H), 9.71 (broad, 1 H). After treatment with $NaOD/D_2O$, the two high-field doublets collapsed to singlets and the low-field signals disappeared. Infrared, combustion, and MS analyses are consistent with thiooxamide **7** as the structure.



7

The formation of both **6** and **7** may be envisioned to arise via abstraction of an acidic methylene proton in **4** by benzylamine (**5**), thus eliminating phthalimide and generating the intermediate thioaldehyde **8**.[4a] The latter species probably suffers further attack by the amine, resulting in both amida-

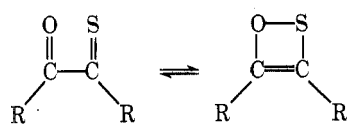




(1)

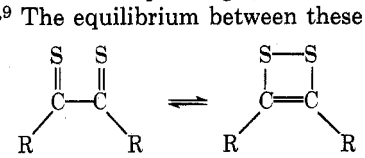
tion and addition to the thione function. The resulting thiol **9** may then be oxidized to the corresponding disulfide **10**,[4b] which in turn undergoes further proton abstraction, thereby displacing mercaptide ion and providing thiooxamide **7** (eq 1).

Compounds containing a thione moiety α to a carbonyl group have rarely been reported in the literature.[4a,7] Recently they have attracted attention[7d,g] because of possible interaction between the oxygen and sulfur atoms as shown below.



12 **13**

Although the existence of the 1,2-oxathiete structure **13** has not been firmly established,[7d,g] uv studies on the α-dithione **14** indicate that the corresponding 1,2-dithiete **15** is present in solution.[8,9] The equilibrium between these valence tau-



14 **15**

R = $(CH_3)_2NC_6H_5$—

tomers is affected by changes in solvent polarity, with formation of the cyclic form being favored by nonpolar media. To examine the possibility of a 1,2-oxathiete structure in solutions of **7**, uv spectra were recorded in solvents of disparate polarity. The spectrum in CH_2Cl_2 [λ_{max} 247 nm (ϵ 6800), 303 (6100), and 398 (40)] closely resembeled that reported for *N,N*-dimethylthiooxamide.[10] The spectra of **7** in 1:1 mixtures of ethanol–methylene chloride or cyclohexane–methylene chloride was not measurably different, indicating that an equilibrium of the type **12** ⇌ **13** is not operative to a significant extent.[11]

Experimental Section

Elemental analyses of compounds were obtained on a Hewlett-Packard Model 185 automatic CHN analyzer, or by Organic Microanalyses (Montreal, Canada). Infrared spectra were recorded on a Perkin-Elmer Model 257 grating spectrophotometer or on a Unicam SP 1000 instrument. A Unicam SP 800 spectrophotometer was used to obtain ultraviolet spectra. NMR spectra were determined on a Varian T-60 instrument. The high-resolution mass spectrum of **7** was recorded by Dr. J. R. Hoyland at the Battelle Memorial Institute (Columbia, Ohio) through the cooperation of Dr. J. P. Snyder, University of Copenhagen.

Reaction of Thiophthalimide 4 with Benzylamine. A solution containing 1.26 g (5 mmol) of thiophthalimide **4** and 1.07 g (10 mmol) of benzylamine in 50 ml of ether was stirred for 2 h at room temperature. After this time, phthalimide was filtered: 0.51 g (69%); mp 228–233 °C (lit.[12] 238 °C). The filtrate was evaporated to dryness to give a sticky, yellow solid which was chromatographed on a dry column of alumina. Elution with methylene chloride gave 0.38 g (27%) of **7**, mp 116–118 °C. Recrystallization from ethanol yielded yellow needles: mp 120–122 °C (lit.[7c] 118–119 °C); ir (KBr) max 3234, 1664, 1108, 1098, 1066, and 1023 cm^{-1}; mass spectrum, see Table I. Anal. Calcd for $C_{16}H_{16}N_2OS$: C, 67.6; H, 5.7; N, 9.9. Found: C, 67.6; H, 5.7; N, 9.8.

Further elution with ethyl acetate gave a white solid which was recrystallized from chloroform to give 0.21 g (16%) of *N*-benzylphthalamide **6**, mp 180–182 °C. A second recrystallization provided an analytical sample: mp 188 °C; NMR ($CDCl_3$) 4.60 (d, 2 H), 7.4 (m, 11 H), 8.07 ppm (s, 1 H); ir (KBr) 3365, 3300, 3185, 1642, 1595, 1540, 1420, 1095, 798, 750 cm^{-1}. Anal. Calcd for $C_{15}H_{14}N_2O_2$: C, 70.9; H, 5.6; N, 11.0. Found: C, 71.0; H, 5.6; N, 10.7.

While other compounds were produced in low yield, separation into pure components could not be achieved.

Table I. Mass Spectrum of Thiooxamide 7

m/e		% of base of	
Measured	Calcd	peak	Possible structure of ion
284.1030	284.0983	16.6	$C_6H_5CH_2NHCOCSNHCH_2C_6H_5$
193.0460	193.0436	64.7	$C_6H_5CH_2NHCSCONH$
149.0290	149.0299	6.7	$C_6H_5CH_2NCS$
106.0658	106.0657	63.8	$C_6H_5CH_2NH$
91.0561	91.0548	100.0	$C_6H_5CH_2$ or tropylium

Acknowledgment. We are grateful to the National Research Council of Canada for financial support of this work.

Registry No.—**4**, 42300-49-2; **6**, 58735-55-0; **7**, 20836-96-8; benzylamine, 100-46-9; phthalimide, 85-41-6.

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