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*N*-Benzoylthioamides (**1**) react with hydrazines and hydroxylamine to form 1*H*-1,2,4-triazoles and 1,2,4-oxadiazoles, respectively. A similar treatment of the *S*-methyl derivatives of **1** with amidines leads to 1,3,5-triazines. Ethyl *N*-benzoylthiocarbamate undergoes analogous reactions to yield the corresponding ethoxyheterocycles.

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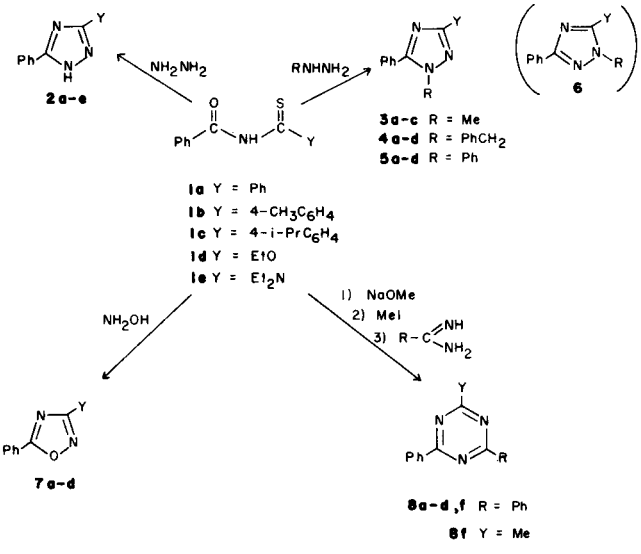
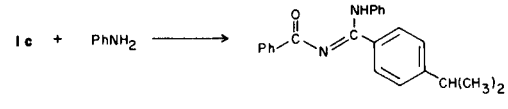
The reactions of *N*-ethoxycarbonylthioamides with hydrazines, hydroxylamines, and amidines involve nucleophilic attack at both thiocarbonyl and carbonyl groups and proceed with loss of hydrogen sulfide and ethanol to form substituted 1,2,4-triazolones, 1,2,4-oxadiazolones, and 1,3,5-triazinones, respectively (1,2). Analogous reactions of *N*-acylthioamides can be expected to result in loss of hydrogen sulfide and water and to yield the corresponding aromatic triazoles, oxadiazoles, and triazines in a straightforward manner. Surprisingly, very few examples of such reactions can be found in the literature. Thus, treatment of ethyl *N*-benzoylthiocarbamate with phenylhydrazine has been reported to lead to 3-ethoxy-1,5-diphenyl-1*H*-1,2,4-triazole (3). More recently, the reaction of *N*-acetylthiobenzamide with phenylhydrazine was found to yield 5-methyl-1,3-diphenyl-1*H*-1,2,4-triazole (4).

*N*-Acylthioamides have been prepared by the Friedel-Crafts reaction between toluene and benzoyl isothiocyanate (5), by acylation of thioamides (4), and by low-temperature treatment of acyl isothiocyanates with Grignard reagents (6). In our hands, the Friedel-Crafts method gave unsatisfactory yields (5-10% of purified product), but the low temperature reactions of benzoyl isothiocyanate with arylmagnesium bromides allowed the preparation of *N*-benzoylthioamides in reasonable yields (**1a**, 48%; **1b**, 48%; **1c**, 35%).

We have found that *N*-benzoylthioamides (**1a-c**) react readily with hydrazine to form 3,5-diaryl-1*H*-1,2,4-triazoles (**2a-c**) in very good yields. The structures assigned to these products are supported by spectral data (ir, nmr), as well as by the previously reported melting points for the known **2a** and **2b**. Analogous reactions of **1a-c** with methylhydrazine, benzylhydrazine, and phenylhydrazine lead to the corresponding 1,3,5-trisubstituted 1*H*-1,2,4-triazoles (**3a-c**, **4a-c**, and **5a-c**) in generally good yield. However, for such monosubstituted hydrazines, the possibility exists that reaction with **1** may occur in either of two orientations to yield either triazoles **3-5**, or their isomers **6**, or both. The proposed product structure (**3-5**) assumes attack on the thiocarbonyl of **1** by the primary amino group of the monosubstituted hydrazines and is supported by the following observations. (a) Treatment of




*N*-benzoyl-4-isopropylthiobenzamide (**1c**) with aniline results in evolution of hydrogen sulfide and formation of *N*-benzoyl-*N'*-phenyl-4-isopropylbenzamidine (**9**). (b) As mentioned earlier, *N*-acetylthiobenzamide is known to




**9**

react with phenylhydrazine in the above proposed manner to form 5-methyl-1,3-diphenyl-1*H*-1,2,4-triazole (4), which has been synthesized independently (7). (c) The isomeric 1,5-diphenyl-3-(4-methylphenyl)-1*H*-1,2,4-triazole (**5b**), mp 145-145.5°, (8) and 1,3-diphenyl-5-(4-methylphenyl)-1*H*-1,2,4-triazole (**6**, R = Ph, Y = 4-$CH_3C_6H_4$), mp 99.5-100°, (9) have been prepared by other investigators. The product of our reaction between **1b** and phenylhydrazine melts at 144.5-146.5°. (d) The proposed orientation is consistent with that observed for analogous reactions of *N*-ethoxycarbonylthioamides (1,2) and *N'*-acyl-*N,N*-dimethylamidines (10). In the latter case, the product structure was confirmed by x-ray diffraction analysis.

In a similar manner, *N*-benzoylthioamides (**1a-c**) react with hydroxylamine to form 3,5-diaryl-1,2,4-oxadiazoles

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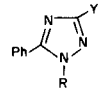
Table I

$^1H$-1,2,4-Triazoles



| Compound No. | R | Y | % Yield (a) | Mp °C (b) | Molecular Formula/ Weight | Elemental Analysis Calcd. (Found) C | H | N | $^1$H-Nmr (δ) (c) |
|---|---|---|---|---|---|---|---|---|---|
| **2a** | H | Ph | 96 | 191.5-192.5 (d) | $C_{14}H_{11}N_3$ 221.26 | | | | 7.5-7.7 (m, 6, ArH), 8.2-8.4 (m, 4, ArH), 14.6 (s, 1, NH) |
| **2b** | H | 4-$MeC_6H_4$ | 92 | 183-185 (e) | $C_{15}H_{13}N_3$ 235.29 | | | | 2.4 (s, 3, $CH_3$), 7.3-7.7 (m, 5, ArH), 8.0-8.3 (m, 4, ArH), 14.1-14.9 (bs, 1, NH) |
| **2c** | H | 4-*i*-$PrC_6H_4$ | 79 | 109-111.5 | $C_{17}H_{17}N_3$ 263.44 | 77.53 (77.46) | 6.51 (6.68) | 15.96 (16.06) | 1.2 (d, 6, $CH_3$), 2.9 (m, 1, CH), 7.3-7.7 (m, 5, ArH), 8.1-8.3 (m, 4, ArH), 13.9-15.3 (bs, 1, NH) |
| **2d** | H | EtO | 73 | 116.5-118 (f) | $C_{10}H_{11}N_3O$ 189.22 | 63.48 (63.44) | 5.86 (5.99) | 22.21 (22.28) | 1.4 (t, 3, $CH_3$), 4.4 (q, 2, $CH_2$), 7.3-7.5 (m, 3, ArH), 7.8-8.1 (m, 2, ArH), 12.8-14.1 (bs, 1, NH) |
| **2e** | H | $Et_2N$ | 52 | 159.5-161.5 | $C_{12}H_{16}N_4$ 216.29 | 66.64 (66.70) | 7.46 (7.45) | 25.90 (25.95) | 1.1 (t, 6, $CH_3$), 3.4 (q, 4, $CH_2$), 7.3-7.5 (m, 3, ArH), 7.8-8.0 (m, 2, ArH), 12.7 (s, 1, NH) |
| **3a** | Me | Ph | 51 | 81.5-82.5 (g) | $C_{15}H_{13}N_3$ 235.29 | 76.57 (76.45) | 5.57 (5.67) | 17.86 (17.82) | 3.9 (s, 3, $CH_3$), 7.3-7.5 (m, 6, ArH), 7.6-7.8 (m, 2, ArH), 8.0-8.2 (m, 2, ArH) |
| **3b** | Me | 4-$MeC_6H_4$ | 46 | 101-102.5 | $C_{16}H_{15}N_3$ 249.32 | 77.08 (77.11) | 6.06 (5.95) | 16.86 (16.87) | 2.3 (s, 3, $CCH_3$), 3.7 (s, 3, $NCH_3$), 6.9-7.4 (m, 7, ArH), 7.8-8.0 (m, 2, ArH) |
| **3c** | Me | 4-*i*-$PrC_6H_4$ | 51 | 92.5-93.5 | $C_{18}H_{19}N_3$ 277.37 | 77.95 (77.95) | 6.91 (6.76) | 15.15 (15.18) | 1.3 (d, 6, $CCH_3$), 2.9 (m, 1, CH), 3.9 (s, 3, $NCH_3$), 7.2 (d, 2, ArH), 7.3-7.5 (m, 3, ArH), 7.6-7.8 (m, 2, ArH), 8.0 (d, 2, ArH) |
| **4a** | $PhCH_2$ | Ph | 56 | 98.5-99.5 | $C_{21}H_{17}N_3$ 311.39 | 81.00 (80.88) | 5.50 (5.53) | 13.50 (13.57) | 5.4 (s, 2, $CH_2$), 7.1-7.7 (m, 13, ArH) 8.2-8.4 (m, 2, ArH) |
| **4b** | $PhCH_2$ | 4-$MeC_6H_4$ | 64 | 111.5-114.5 | $C_{22}H_{19}N_3$ 325.4 | 81.20 (81.27) | 5.89 (5.82) | 12.91 (12.79) | 2.3 (s, 3, $CH_3$), 5.4 (s, 2, $CH_2$), 7.2-7.7 (m, 12, ArH), 8.2 (d, 2, ArH) |
| **4c** | $PhCH_2$ | 4-*i*-$PrC_6H_4$ | 77 | 90.5-91.5 | $C_{24}H_{23}N_3$ 353.47 | 81.55 (81.50) | 6.56 (6.27) | 11.89 (12.00) | 1.2 (d, 6, $CH_3$), 2.9 (m, 1, CH), 5.3 (s, 2, $CH_2$), 7.2-7.5 (m, 12, ArH), 8.0-8.2 (m, 2, ArH) |
| **4d** | $PhCH_2$ | EtO | 61 | 66.5-68.5 | $C_{17}H_{17}N_3O$ 279.34 | 73.09 (73.27) | 6.13 (6.07) | 15.04 (14.98) | 1.3 (t, 3, $CH_3$), 4.3 (q, 2, $CH_2CH_3$), 5.4 (s, 2, $CH_2Ph$), 7.1-7.7 (m, 10, ArH) |
| **5a** | Ph | Ph | 71 | 102-104.5 (h) | $C_{20}H_{15}N_3$ 297.36 | | | | 7.2-7.8 (m, 13, ArH), 8.1-8.3 (m, 2, ArH) |
| **5b** | Ph | 4-$MeC_6H_4$ | 92 | 144.5-146.5 (i) | $C_{21}H_{17}N_3$ 311.39 | | | | 2.4 (s, 3, $CH_3$), 7.2-7.7 (m, 12, ArH), 8.2 (d, 2, ArH) |
| **5c** | Ph | 4-*i*-$PrC_6H_4$ | 94 | 149.5-151 | $C_{23}H_{21}N_3$ 339.44 | 81.38 (81.37) | 6.24 (6.25) | 12.38 (12.54) | 1.3 (d, 6, $CH_3$), 2.9 (m, 1, CH), 7.3-7.7 (m, 12, ArH), 8.3 (d, 2, ArH) |
| **5d** | Ph | EtO | 96 | 89.5-92.5 (j) | $C_{16}H_{15}N_3O$ 265.32 | | | | 1.4 (t, 3, $CH_3$), 4.4 (q, 2, $CH_2$), 6.9-7.6 (m, 10, ArH) |

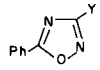
(a) Crude or recrystallized product with melting point lower than that of the analytically pure compound by not more than 5°. (b) Recrystallized from aqueous ethanol. (c) Determined in hexadeuteriodimethyl sulfoxide (**2a-e, 4d**), carbon tetrachloride (**3a-c, 5a-c**) and deuteriochloroform (**4a-c, 5d**). (d) Lit (14) mp 190°. (e) Lit (14) mp 189°. (f) Lit (15) mp 121°. (g) Lit (16) mp 85°. (h) Lit (9) mp 104-105°. (i) Lit (8) mp 145-145.5°. (j) Lit (3) mp 90°.

(**7a-c**) in very good yield. In this case too, the reaction may, in principle, occur in either of two different orientations. The structure proposed for the isolated oxadiazoles assumes attack on the thiocarbonyl group of **1** by the amino group of the reagent and is supported by the fact that **7a** and **7b** are known compounds which have been prepared by other methods.

The reaction of *N*-benzoylthioamides with amidines was found to proceed very sluggishly and to yield difficult to purify products. Better results were obtained when **1a-c** were first converted into their more reactive *S*-methyl derivatives, which, without prior isolation, were then treated with an amidine. Although triazines **8a-c** and **8f** were obtained in rather low yields, this can still be con-

Table II

1,2,4-Oxadiazoles

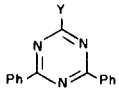


| Compound No. | Y | % Yield (a) | Mp °C (b) | Molecular Formula/ Weight | Elemental Analysis Calcd. (Found) C | H | N | $^1$H-Nmr (δ) (c) |
|---|---|---|---|---|---|---|---|---|
| **7a** | Ph | 83 | 107.5-108.5 (d) | $C_{14}H_{10}N_2O$ 222.25 | | | | 7.4-7.7 (m, 6, ArH), 8.1-8.4 (m, 4, ArH) |
| **7b** | 4-$MeC_6H_4$ | 89 | 101.5-102.5 (e) | $C_{15}H_{12}N_2O$ 236.24 | | | | 2.4 (s, 3, $CH_3$), 7.1-7.5 (m, 5, ArH), 7.8-8.1 (m, 4, ArH) |
| **7c** | 4-*i*-$PrC_6H_4$ | 85 | 62.5-64 | $C_{17}H_{16}N_2O$ 264.33 | 77.25 (77.27) | 6.10 (5.96) | 10.60 (10.62) | 1.4 (d, 6, $CH_3$), 3.0 (m, 1, CH), 7.3-7.6 (m, 5, ArH), 8.0-8.3 (m, 4, ArH) |
| **7d** | EtO | 46 | 46.5-47.5 (f) | $C_{10}H_{10}N_2O_2$ 190.20 | | | | 1.4 (t, 3, $CH_3$), 4.4 (q, 2, $CH_2$), 7.5-7.8 (m, 3, ArH), 7.9-8.2 (m, 2, ArH) |

(a) Crude or recrystallized product with melting point lower than that of the analytically pure compound by not more than 5°. (b) Recrystallized from aqueous ethanol. (c) Determined in deuteriochloroform (**4a**, **4b**, **4c**) and hexadeuteriodimethyl sulfoxide (**4d**). (d) Lit (17) mp 108°. (d) Lit (17) mp 107°. (f) Lit (18) mp 44.5-45°.

Table III

1,3,5-Triazines



| Compound No. | Y | % Yield (a) | Mp °C (b) | Molecular Formula/ Weight | Elemental Analysis Calcd. (Found) C | H | N | $^1$H-Nmr (δ) (c) |
|---|---|---|---|---|---|---|---|---|
| **8a** | Ph | 48 | 233.5-235.5 (d) | $C_{21}H_{15}N_3$ 309.37 | | | | 7.6-8.0 (m, 9, ArH), 8.6-8.8 (m, 6, ArH) |
| **8b** | 4-$MeC_6H_4$ | 37 | 197-200 (e) | $C_{22}H_{17}N_3$ 323.40 | | | | 2.5 (s, 3, $CH_3$), 7.5-7.9 (m, 8, ArH), 8.5-8.7 (m, 6, ArH) |
| **8c** | 4-*i*-$PrC_6H_4$ | 21 | 148.5-149.5 | $C_{24}H_{21}N_3$ 351.45 | 82.02 (82.24) | 6.02 (5.96) | 11.96 (11.96) | 1.3 (d, 6, $CH_3$), 3.0 (m, 1, CH), 7.3-7.6 (m, 8, ArH), 8.6-8.8 (m, 6, ArH) |
| **8d** | EtO | 57 | 99.5-102 | $C_{17}H_{15}N_3O$ 277.33 | 73.63 (73.77) | 5.45 (5.50) | 15.15 (15.20) | 1.4 (t, 3, $CH_3$), 4.5 (q, 2, $CH_2$), 7.3-7.5 (m, 6, ArH), 8.4-8.6 (m, 4, ArH) |
| **8f** | Me | 27 | 106-108 (f) | $C_{16}H_{13}N_3$ 244.30 | | | | 2.7 (s, 3, $CH_3$), 7.4-7.6 (m, 6, ArH), 8.5-8.8 (m, 4, ArH) |

(a) Crude or recrystallized product with melting point lower than that of the analytically pure compound by not more than 5°. (b) Recrystallized from toluene (**8a,b**), hexane (**8c**), cyclohexane (**8d**), and aqueous ethanol (**8f**). (c) Determined in trifluoroacetic acid (**8a,b**), carbon tetrachloride (**8c,d**), and deuteriochloroform (**8f**). (d) Lit (19) mp 232-233°. (e) Lit (19) mp 199-200°. (f) Lit (20) mp 107-108.

sidered a convenient approach to unsymmetrical, trisubstituted 1,3,5-triazines.

Following these results, it was decided to investigate analogous cyclization reactions leading to alkoxy and amino substituted 1*H*-1,2,4-triazoles, 1,2,4-oxadiazoles, and 1,3,5-triazines. The starting materials chosen, ethyl *N*-benzoylthiocarbamate (**1d**) and *N*-benzoyl-*N'*,*N'*-diethylthiourea (**1e**), are readily obtainable from benzoyl isothiocyanate by treatment with ethanol (11) and diethylamine (12), respectively. It was found that **1d** reacts smoothly with hydrazine, benzylhydrazine, phenylhydrazine, and hydroxylamine to yield the expected triazoles **2d**, **4d**, **5d** and oxadiazole **7d** in generally good yield. In the reaction with benzamidine, prior conversion of **1d** into its *S*-methyl derivative was found necessary for the formation of triazine **8d** to occur satisfactorily. On the other hand, thiourea **1e** proved too unreactive a starting material for most of the attempted cyclization reactions. The only satisfactory results were obtained when **1e** was first converted into its *S*-methyl derivative, which was then allowed to react with hydrazine to form triazole **2e** in moderate yield.

A brief investigation of the possibility of preparing 7-membered ring heterocycles from *N*-benzoylthioamides and 1,2-dinucleophilic reagents showed that 5-membered ring products are obtained instead, just as observed for

the corresponding reactions of *N*-ethoxycarbonylthioamides (13). Thus, treatment of **1b** with 1,2-diaminoethane yielded 2-(4-methylphenyl)-4,5-dihydroimidazole in 38% yield. Because heterocyclic compounds of this type can be prepared more conveniently from *N*-ethoxycarbonylthioamides (13), this investigation was not pursued further.

In conclusion, the reactions described in this paper allow convenient preparation of a number of heteroaromatic compounds in two steps from the readily available benzoyl isothiocyanate. For the second step, the reaction progress is followed readily by monitoring of the hydrogen sulfide evolution with lead acetate paper, product isolation is simple, and yields, although not always high, are in many cases very good.

## EXPERIMENTAL

*N*-Benzoylthiobenzamide (**1a**), *N*-Benzoyl-4-methylthiobenzamide (**1b**), and *N*-Benzoyl-4-isopropylthiobenzamide (**1c**).

A solution of arylmagnesium bromide prepared from 1.3 g (0.053 g-atom) of magnesium and 0.060 mole of aryl bromide in 100 ml of ethyl ether was added dropwise, over a period of 30 minutes, to a stirred solution of 8.15 g (0.050 mole) of benzoyl isothiocyanate in 400 ml of ethyl ether, under nitrogen, at −36 to −40°. After completion of the addition, the reaction product was hydrolyzed by the introduction of 300 ml of water followed by 50 ml of 2*N* sulfuric acid. The mixture was then stirred while warming up to room temperature, more ethyl ether (benzene for **1b**) was added to dissolve any insoluble material, and the crude product was isolated following separation of the layers, drying with calcium chloride of the organic solution, and distillation of the solvent under reduced pressure. After purification by recrystallization from ethyl acetate-petroleum ether (bp 63-75°), the following results were obtained.

Compound **1a**.

This compound was obtained in a yield of 5.8 g (48%), mp 115.5-118.5°, lit (6) mp 117-119°; ir: 3260-3100 (N-H), 1680 (C=O) $cm^{-1}$; nmr (DMSO-$d_6$): δ 7.3-7.8 (m, 8, ArH), 8.0-8.2 (m, 2, ArH), 12.6 (s, 1, NH).

Compound **1b**.

This compound was obtained in a yield of 6.1 g (48%), mp 133-136°, lit (5) mp 135-136°; ir: 3200-3100 (N-H), 1650 (C=O) $cm^{-1}$; nmr (DMSO-$d_6$): δ 2.3 (s, 3, $CH_3$), 7.2 (d, 2, ArH), 7.5-7.7 (m, 5, ArH), 7.9-8.1 (m, 2, ArH), 12.4 (s, 1, NH).

Compound **1c**.

This compound was obtained in a yield of 5.0 g (35%), mp 132-137°, raised to 135.5-137.5° by further recrystallization; ir: 3200-3100 (N-H), 1660 (C=O) $cm^{-1}$; nmr (DMSO-$d_6$): δ 1.2 [d, 6, $CH(CH_3)_2$], 2.9 [m, 1, $CH(CH_3)_2$], 7.3 (d, 2, ArH), 7.5-7.8 (m, 5, ArH), 7.9-8.1 (m, 2, ArH), 12.4 (s, 1, NH).

*Anal.* Calcd. for $C_{17}H_{17}NOS$: C, 72.05; H, 6.05; N, 4.94. Found: C, 72.20; H, 6.05; N, 4.95.

1*H*-1,2,4-Triazoles (**2a-e**, **3a-c**, **4a-d**, **5a-d**) (Table I).

The mixture resulting from the addition of 0.010 mole of **1a-d** to a solution of 0.012-0.020 mole of the hydrazine in 20 ml of ethanol was refluxed until the evolution of hydrogen sulfide had stopped (0.5-3.5 hours). After the reaction mixture had been cooled, addition of water followed by filtration yielded the crude product, which was recrystallized from aqueous ethanol.

For **3a-c**, after dilution with water, the reaction mixture was neutralized with acetic acid.

For **4a-d**, to the mixture of benzylhydrazine dihydrochloride, an equivalent amount of sodium acetate trihydrate, and ethanol, enough water was added to effect dissolution upon warming.

For **2e**, the procedure was modified as follows. To a stirred solution of sodium methoxide prepared from 0.28 g (0.012 g-atom) of sodium and 10 ml of methanol was added 2.36 g (0.010 mole) of **1e** and then 0.6 ml of methyl iodide. After further stirring for 2.5 hours, 40 drops of hydrazine was added and the resulting mixture was refluxed for 52 hours. Addition of water to the cooled reaction mixture followed by filtration yielded the product.

1,2,4-Oxadiazoles (**7a-d**) (Table II).

To a solution of 0.42 g (0.0060 mole) of hydroxylamine hydrochloride, 0.82 g (0.0060 mole) of sodium acetate trihydrate, 25 ml of ethanol, and enough water to effect dissolution upon warming was added 0.0050 mole of **1a-c** and the resulting mixture was refluxed until evolution of hydrogen sulfide was complete (2-3.5 hours). Following cooling and addition of water, filtration yielded the crude product, which was recrystallized from aqueous ethanol.

For **7d**, a mixture of 2.1 g (0.010 mole) of **1d**, 1.4 g (0.020 mole) of hydroxylamine hydrochloride, and 10 ml of pyridine was refluxed overnight (16 hours) and then treated as above.

1,3,5-Triazines (**8a-d,f**) (Table III).

To a stirred solution of sodium methoxide in methanol obtained from 0.28 g (0.012 g-atom) of sodium and 25 ml of methanol was added 0.010 mole of **1a-c** and, 10 minutes later, 0.6 ml of methyl iodide. After a further 15 minutes of stirring there was introduced a mixture obtained by the addition of 1.88 g (0.012 mole) of benzamidine hydrochloride to a solution of sodium methoxide in methanol prepared from 0.28 g (0.012 g-atom) of sodium and 25 ml of methanol. The resulting mixture was refluxed (14 hours for **8a**, **b**, 22 hours for **8c**), cooled, diluted with water, and filtered to yield the crude product.

For **8d**, sodium ethoxide and ethanol were used instead of sodium methoxide and methanol, and the reflux time was 18 hours.

For **8f**, thioamide **1a** and acetamidine hydrochloride were used following the general procedure given above, except that the reflux time was 48 hours.

Reaction of *N'*-Benzoyl-4-isopropylthiobenzamide (**1c**) with Aniline.

A mixture of 1.4 g (0.0050 mole) of **1c**, 5 ml of aniline, and 25 ml of ethanol was refluxed for 1.5 hour, cooled, and filtered to yield 1.4 g (82%) of *N*-benzoyl-*N'*-phenyl-4-isopropylbenzamidine (**9**), mp 196.5-201.5°. The pure compound was obtained by recrystallization from acetonitrile in the form of colorless crystals, mp 202-202.5°; ir: 3270 (N-H), 1625 (C=O) $cm^{-1}$; nmr (DMSO-$d_6$): δ 1.2[d, 6, $CH(CH_3)_2$], 2.9 [m, 1, $CH(CH_3)_2$], 7.1-7.5 (m, 10, ArH), 7.8-8.1 (m, 4, ArH), 10.2 (s, 1, NH).

*Anal.* Calcd. for $C_{23}H_{22}N_2O$: C, 80.67; H, 6.48; N, 8.18. Found: C, 80.52; H, 6.41; N, 8.27.

Reaction of *N*-Benzoyl-4-methylthiobenzamide (**1b**) with 1,2-Diaminoethane.

A mixture of 1.27 g (0.0050 mole) of **1b**, 0.50 g of 1,2-diaminoethane, and 10 ml of ethanol was refluxed until the evolution of hydrogen sulfide had stopped. It was then diluted with ethyl ether and extracted with three 25 ml portions of 6*N* hydrochloric acid. The aqueous extract was neutralized with 10% aqueous sodium hydroxide to yield a tan precipitate, recrystallization of which from benzene gave 0.30 g (38%) of 2-(4-methylphenyl)-4,5-dihydroimidazole, mp 181.5-182.5°, lit (22) ms 183°.

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