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# FACILE SYNTHESIS OF 2-BENZOYLIMINONAPHTHO[1,2-d]THIAZOLES

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**ABSTRACT:** Reaction of 1-naphthylamine with benzoyl chlorides and ammonium thiocyanate yielded N-benzoyl-N'-(naphthalene-1-yl) thioureas, which underwent oxidative cyclisation in the presence of phosphorous pentachloride and phosphorous oxichloride affording the title compounds.



It was reported[1-3] that naphtho[1,2-d]thiazoles and their derivatives possess diverse biological activities such as antihypertensive effect anticholinergic activity and antihistamine activity and diuretic activity. Substituted aryl thioureas exhibit potent antihypertensive activity and selective acute toxicities for rats[4-7]. 1-Naphthyl thiourea is marketed as a rodenticide. However, only few methods[8-12] are available for the synthesis of N-substituted thioureas and naphtho[1,2-d]thiazoles. We here in report a facile synthesis of substituted naphtho[1,2-d]thiazoles from N-benzoyl-N'-[naphthalene-1-yl]thioureas, prepared by the reaction of 1-naphthylamine with benzoyl chlorides and ammonium thiocyanate.

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As a representative case the reaction of 1-naphthylamine (**1a**) with benzoyl chloride (**2a**) and ammonium thiocyanate was carried out by refluxing in dry acetone. The crude product obtained was chromatographed over neutral alumina to obtain a pure compound m.p. 145-7° which showed the molecular ion peak at m/z 306 in its mass spectrum, the IR (KBr) spectrum displayed absorptions at 3210 $cm^{-1}$, 1665 $cm^{-1}$ and 1140 $cm^{-1}$ which are assigned for NH, C=O and C=S functions respectively. The $^1$H-NMR (DMSO-$d_6$) spectrum revealed signals at δ12.65 (s,1H,-NH,$D_2O$ exchangeable) δ9.15 (s,1H, NH $D_2O$ exchangeable) and δ 7.20-8.25 (m,12H, arom) Based on the foregoing spectral data, the compound was assigned N-benzoyl-N'-[naphthalene-1-yl]thiourea structure (**3a**).

N-Benzoyl-N'-[naphthalene-1-yl]thiourea (**3a**) was treated with phosphorous pentachloride in phosphorous oxichloride The usual work up followed by chromatography furnished a pale yellow coloured crystalline compound structure (**4a**), m.p. 155-7°. The compound showed the molecular ion peak at m/z 304 in its mass spectrum. The IR (KBr) spectrum displayed absorptions at 3300 $cm^{-1}$ (broad) due to NH and 1660 $cm^{-1}$ due to C=O functions. The $^1$H NMR (DMSO-$d_6$) spectrum revealed signals at δ8.6 (d,1H,H-9, arom), δ 6.8-7.7 (m,10H arom). Based on the foregoing spectral data, the compound was assigned 2-benzoyliminonaphtho[1,2-d]thiazole structure (**4a**). The fragmentation pattern of the compound is consistent with the assigned structure.

Following the above procedures, five substituted N-benzoyl-N'-[naphthalene-1-yl]thioureas (**3b-f**) and corresponding 2-benzoyl iminonaphtho[1,2-d]thiazoles (**4b-f**) were prepared (Table I & II).

**Table I - Physical data of N-benzoyl-N'-(naphthalene-1-yl)thiourea (3a-f)**

| Product No. | R' | R" | Yield (%) | M.P.[a] (°C) | Molecular formula ($M^+$) | IR (KBr) $cm^{-1}$ -NH | IR (KBr) $cm^{-1}$ C=0 | IR (KBr) $cm^{-1}$ C=S | $^1$H-NMR (δ ppm) |
|---|---|---|---|---|---|---|---|---|---|
| 3a | H | H | 70 | 145-7 | $C_{18}H_{14}N_2SO$ (306) | 3210 | 1665 | 1140 | 7.2-8.25 (m,12H,arom), 9.15 (s,1H,N'-H), 12.65 (s,1H, N-H). |
| 3b | $NO_2$ | H | 75 | 180-2 | $C_{18}H_{13}N_3SO_3$ (351) | 3300 | 1665 | 1145 | 7.3-8.4 (m,11H,arom), 9.20 (s,1H,N'-H), 12.75 (s,1H, N-H). |
| 3c | H | Cl | 78 | 162-4 | $C_{18}H_{13}N_2SOCl$ (340) | 3150 | 1670 | 1145 | 7.2-8.1 (m,11H,arom), 8.92 (s,1H,N-H), 12.65 (s,1H,N-H) |
| 3d | $NO_2$ | Cl | 60 | 178-9 | $C_{18}H_{12}N_3SO_3Cl$ (385) | 3180 | 1680 | 1140 | -- |
| 3e | H | $NO_2$ | 75 | 172-4 | $C_{18}H_{13}N_3SO_3$ (351) | 3240 | 1675 | 1140 | -- |
| 3f | H | $CH_3$ | 75 | 156-8 | $C_{19}H_{16}N_2SO$ (320) | 3200 | 1665 | 1150 | 2.1 (s,3H,-$CH_3$), 7.2-8.2 (m, 11H,arom), 9.23 (s,1H,-NH), 12.84 (s,1H,NH). |

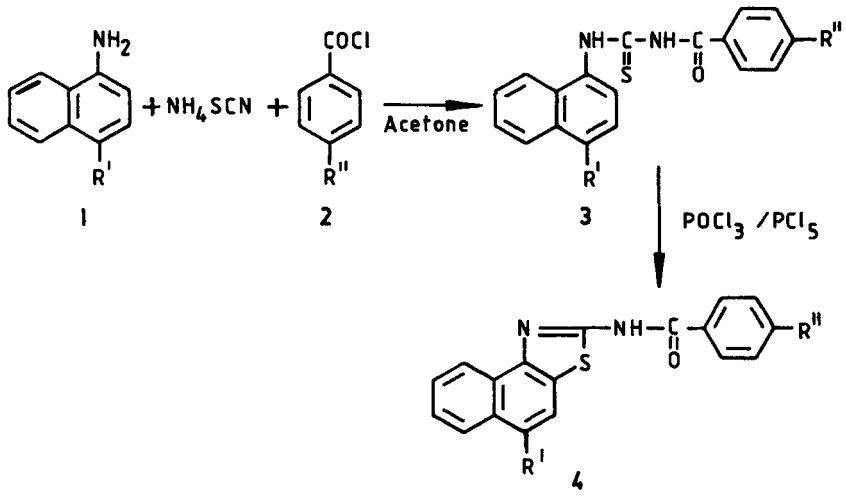
[a]Melting points are uncorrected.

**Table II - Physical data of aroyliminonaphtho[1,2-d]thiazole (4a-f)**

| Product No. | R' | R" | Yield (%) | M.P.[a] (°C) | Molecular formula ($M^+$) | IR (KBr) $cm^{-1}$ -NH | IR (KBr) $cm^{-1}$ C=0 | $^1$H-NMR (DMSO-$d_6$) ($\delta$ ppm) |
|---|---|---|---|---|---|---|---|---|
| 4a | H | H | 60 | 155-7 | $C_{18}H_{12}N_2SO$ (304) | 3300 | 1660 | 6.8-7.7 (m,10H,arom), 8.6 (d, 1H,periproton). |
| 4b | $NO_2$ | H | 65 | 152-4 | $C_{18}H_{11}N_3SO_3$ (349) | 3310 | 1665 | 7.4-8.4 (m,9H,arom), 8.6 (d, 1H, periproton). |
| 4c | H | Cl | 70 | 167-9 | $C_{18}H_{11}N_2SOCl$ (338) | 3325 | 1680 | 7.4-8.2 (m,9H,arom), 8.7 (d, 1H, periproton). |
| 4d | $NO_2$ | Cl | 65 | 162-4 | $C_{18}H_{10}N_3SO_3Cl$ (383) | 3250 | 1675 | -- |
| 4e | H | $NO_2$ | 70 | 156-8 | $C_{18}H_{11}N_3SO_3$ (349) | 3275 | 1675 | -- |
| 4f | H | $CH_3$ | 70 | 157-9 | $C_{19}H_{14}N_2SO$ (318) | 3150 | 1680 | 2.15 (s,3H,-$CH_3$), 7.25-8.15 (m,9H,arom), 8.65 (d,1H,periproton). |

[a] Melting points are uncorrected.

SCHEME




| | a | b | c | d | e | f |
|---|---|---|---|---|---|---|
| R' | H | $NO_2$ | H | $NO_2$ | H | H |
| R'' | H | H | Cl | Cl | $NO_2$ | $CH_3$ |



## EXPERIMENTAL PROCEDURE

**a) General procedure for the preparation of N-aroyl-N'-[naphthalene-1-yl]thiourea (3a-f)**

To a solution of ammonium thiocyanate (0.01 mol) in acetone, an equimolar quantity of aroylchloride was added dropwise with shaking. After heating the mixture on steam bath for 1 hr,

a solution of 1-naphthylamine (0.01 mol) in acetone was added and refluxed for 3-4 hours. The solvent was distilled off, the residue was treated with water and the solid that separated was filtered and dried. Chromatographic purification of the solid over a column of silica gel gave N-aroyl-N'-[naphthalene-1-yl]-thiourea in benzene fraction.

**b) Cyclisation of 3a-f**

N-Benzoyl-N'-[naphthalene-1-yl]thourea (0.01 mol) was refluxed in phosphorous oxichloride (15 ml) containing phosphorous pentachloride (0.01 mol) and the reaction was monitored by tlc. Later the reaction mixture was poured on to crushed ice. The solid that separated was filtered and purified by column chromatography, yielding the title compounds.

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