A Simple Method for the Synthesis of Thiobenzamides by Friedel–Crafts Reaction

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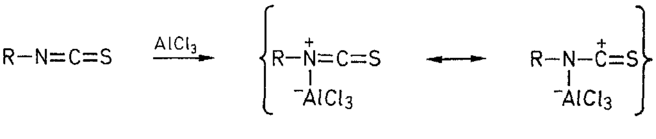
The reactions of substituted benzenes and phenols with aliphatic and aromatic isothiocyanates in a nitromethane solution of aluminum chloride give rise to the formation of the secondary thiobenzamides

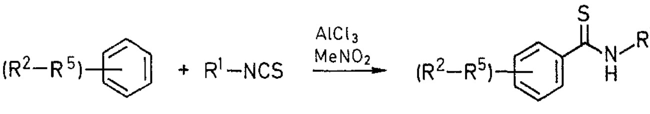
The Friedel–Crafts-type reaction of phenyl isothiocyanate with aromatic hydrocarbons was investigated first by Gattermann in 1892.[1,2] Only few reports[3-9] on similar reactions of aryl isothiocyanates with aromatic hydrocarbons and their functional derivatives were published later. In most cases, anhydrous aluminum chloride was used as the catalyst and the reactions were carried out in carbon disulfide, dichloroethane, or dichloromethane as well as without any solvent. Under these conditions, isolation and purification of the products were difficult.

In a previous paper,[10] we reported the synthesis of secondary thiophenecarbothioamides in a Friedel–Crafts reaction carried out in a nitromethane solution of aluminum chloride. Homogeneity of the reaction mixture simplified the procedure and markedly increased the yield. The same procedure was recently applied to the synthesis of thioamide derivatives of alkylthiophenes and alkyl-1-benzothiophenes.[11] According to our earlier suggestion,[10] the increased activity of isothiocyanates in the presence of aluminum chloride can be explained by the formation of complex of aluminum chloride with the isothiocyanate nitrogen atom.



The reaction with aromatic and heteroaromatic hydrocarbons proceeds in accord with the typical Friedel–Crafts reaction mechanism.

My present investigations concern the reactions of substituted benzenes and phenols with aliphatic and aromatic isothiocyanates in a nitromethane solution of aluminum chloride.



1 **2-16**

Unsubstituted benzene failed to react under such conditions and only traces of the thioamide derivative were detected by TLC when the reaction was performed with toluene. On the other hand, *tert*-butyl-, methoxy-, and di- and trimethylbenzenes reacted readily and the corresponding thioamides were isolated in fairly high yields (Table). Still better results were obtained with phenols, which reacted even at room temperature; almost pure products precipitated upon hydrolysis of the aluminum chloride complex. The substitution with the thioamide group occurred in the *para*-position with respect to the substituent activating the aromatic ring and in the case of alkylphenols, in the *para*-position to the hydroxy group. The formation of *ortho*-isomers was observed only with *para*-substituted phenols (Table, **16a** and **16b**).

Table. Thiobenzamides **2**–**16** Prepared

Product		Yield[a] (%)	mp (°C)[b] (solvent)	Molecular Formula[c] or Lit. mp (°C)	IR[d] ν(cm^{-1})	UV (EtOH)[e] λ_{max} (nm) (lgε)	^{1}H-NMR (DMSO-d_6/ HMDSO$_{int}$)[f] δ, J(Hz)
2[g]	$R^1 = C_6H_5$ $R^2 = 4\text{-}t\text{-}C_4H_9$	32	136–137 (heptane/ benzene)	$C_{17}H_{19}NS$ (269.4)	3172, 1520, 1340	271 (4.21), 313sh (3.94), 400 (2.70)	1.25 (s, 9H); 6.75–7.75 (m, 9H_{arom}); 8.95 (br s, 1H)
3	$R^1 = C_6H_5$ $R^2 = 2\text{-}CH_3$ $R^3 = 4\text{-}CH_3$	72	108–109[h] (benzene/ heptane)	$C_{15}H_{15}NS$ (241.4)	3176, 1532	308 (4.08), 390 (2.59)	2.5 (s, 6H); 7.13–8.25 (m, 8H_{arom}); 12.0 (br s, 1H)
4	$R^1 = C_6H_5$ $R^2 = 2\text{-}CH_3$ $R^3 = 4\text{-}CH_3$ $R^4 = 6\text{-}CH_3$	54	130–132 (CCl_4/ heptane)	$C_{16}H_{17}NS$ (254.4)	3204, 1524	309 (4.07), 384sh (2.15)	2.46 (s, 9H); 7.05–8.23 (m, 7H_{arom})
5a	$R^1 = C_6H_{11}$ $R^2 = 4\text{-}OCH_3$	80	103–105 (heptane)	$C_{14}H_{19}NOS$ (249.4)	3210, 1538	274 (4.24), 363sh (2.82)	1.2–2.55 (m, 11H); 4.6 (br s, 1H); 7.13 (d, 2H_{arom}, $J = 8$); 8.95 (d, 2H_{arom}, $J = 8$); 10.0 (d, 1H, $J = 8.5$)
5b	$R^1 = C_6H_5$ $R^2 = 4\text{-}OCH_3$	85	159–161 (benzene)	153–154[2]	3160br, 1520	294 (4.30), 400sh (2.79)	4.0 (s, 3H); 7.1–8.25 (m, 9H_{arom}); 11.75 (br s, 1H)
6	$R^1 = C_6H_5$ $R^2 = 3\text{-}Br$; $R^3 = 4\text{-}OCH_3$	54	214–215[h] (toluene)	$C_{14}H_{12}BrNOS$ (322.2)	3155, 1519	286 (4.23), 400sh (2.79)	4.1 (s, 3H); 7.25–8.43 (m, 8H_{arom}); 11.88 (s, 1H)
7	$R^1 = C_6H_5$ $R^2 = 4\text{-}OC_6H_5$	49	127–129.5 (octane/ CCl_4)	$C_{19}H_{15}NOS$ (305.4)	3164, 1528	283 (4.29), 400sh (2.63)	7.0–8.25 (m, 14H_{arom})
8a	$R^1 = CH_3$ $R^2 = 4\text{-}OH$	60	141–143 (H_2O)	C_8H_9NOS (167.2)	3316br, 1540, 1352	278 (4.18), 358sh (2.75)	3.3 (s, 3H); 6.95 (d, 2H_{arom}, $J = 8$); 7.95 (d, 2H_{arom}, $J = 8$); 10.1 (br s, 2H)
8b	$R^1 = C_2H_5$ $R^2 = 4\text{-}OH$	44	147–149 (benzene)	$C_9H_{11}NOS$ (181.3)	3168br, 1544, 1328	278 (4.22), 360sh (2.79)	1.42 (t, 3H, $J = 7$); 3.9 (q, 2H, $J = 7$); 7.0 (d, 2H_{arom}, $J = 8.5$); 7.93 (d, 2H_{arom}, $J = 8.5$); 10.12 (br d, 1H, $J = 8$)
8c	$R^1 = c\text{-}C_6H_{11}$ $R^2 = 4\text{-}OH$	50	138–140 (benzene)	$C_{13}H_{17}NOS$ (235.4)	3476, 3184, 1544, 1388, 1344	278 (4.22), 355sh (2.81)	1.13–2.38 (m, 11H); 4.63 (br s, 1H); 7.0 (d, 2H_{arom}, $J = 9$); 8.9 (d, 2H_{arom}, $J = 9$); 10.0 (br d, 1H, $J = 9$)
8d	$R^1 = C_6H_5$ $R^2 = 4\text{-}OH$	80	169–170 ($MeNO_2$)	164–165[4] 163–164[5]	3315, 3220br, 1527	301 (4.24), 394sh (2.78)	7.05 (d, 2H_{arom}, $J = 8.5$); 7.25–8.2 (m, 7H_{arom}); 10.4 (br s, 1H); 11.6 (s, 1H)
8e	$R^1 = 4\text{-}BrC_6H_4$ $R^2 = 4\text{-}OH$	85	208–210 ($MeNO_2$)	$C_{13}H_{11}BrNOS$ (308.2)	3232, 3150br, 1532	303 (4.34), 400sh (2.86)	7.08 (d, 2H_{arom}, $J = 9$); 7.7–8.2 (m, 6H_{arom}); 10.45 (br s, 1H); 11.7 (s, 1H)
9a	$R^1 = C_2H_5$ $R^2 = 2\text{-}CH_3$ $R^3 = 4\text{-}OH$	69	133–134 (toluene)	$C_{10}H_{13}NOS$ (195.3)	3252, 1544	270 (4.21), 353 (2.77)	1.43 (t, 3H, $J = 8$); 2.43 (s, 3H); 3.53 (q, 2H, $J = 7$); 6.7–7.38 (3H_{arom}); 9.75 (s, 1H); 10.2 (br s, 1H)
9b	$R^1 = c\text{-}C_6H_{11}$ $R^2 = 2\text{-}CH_3$ $R^3 = 4\text{-}OH$	60	195–197 ($MeNO_2$)	$C_{14}H_{19}NOS$ (249.4)	3248, 3096br, 1540	272 (4.18), 353 (2.64)	1.25–2.35 (m, 10H); 2.4 (s, 3H); 4.6 (br s, 1H); 6.7–7.3 (m, 3H_{arom}); 9.73 (s, 1H); 10.1 (br d, 1H, $J = 8$)
9c	$R^1 = C_6H_5$ $R^2 = 2\text{-}CH_3$ $R^3 = 4\text{-}OH$	77	184–186 (MeOH/ H_2O)	175–176[5]	3250, 3160, 1537	303 (4.12), 390 (2.76)	2.5 (s, 3H); 6.75–8.2 (m, 8H_{arom}); 9.88 (s, 1H); 11.8 (s, 1H)
9d	$R^1 = 4\text{-}ClC_6H_4$ $R^2 = 2\text{-}CH_3$ $R^3 = 4\text{-}OH$	75	186.5–188.5 ($MeNO_2$)	$C_{14}H_{12}ClNOS$ (277.8)	3240, 3190, 1548	294sh (4.18), 308 (4.18), 396 (2.76)	2.5 (s, 3H); 6.7–8.3 (m, 7H_{arom}); 9.9 (s, 1H); 11.9 (s, 1H)
10a	$R^1 = CH_3$ $R^2 = 2\text{-}CH_3$ $R^3 = 3\text{-}CH_3$ $R^4 = 4\text{-}OH$	77	196–198 ($MeNO_2$)	$C_{10}H_{13}NOS$ (195.3)	3296, 3156br, 1556	268 (4.18), 350 (2.76)	2.3 (d, 6H, $J = 3$); 3.28 (s, 3H); 6.95 (q, 2H_{arom}, $J = 9$); 9.65 (s, 1H); 10.2 (br s, 1H)
10b	$R^1 = C_2H_5$ $R^2 = 2\text{-}CH_3$ $R^3 = 3\text{-}CH_3$ $R^4 = 4\text{-}OH$	88	199.5–200.5 ($MeNO_2$)	$C_{11}H_{15}NOS$ (209.3)	3232, 3160sh, 1556	271 (4.16), 352 (2.73)	1.4 (t, 3H, $J = 7$); 2.3 (d, 6H, $J = 3$); 3.8 (q, 2H, $J = 8$); 6.95 (q, 2H_{arom}, $J = 9$); 9.63 (s, 1H); 10.2 (br s, 1H)
10c	$R^1 = c\text{-}C_6H_{11}$ $R^2 = 2\text{-}CH_3$ $R^3 = 3\text{-}CH_3$ $R^4 = 4\text{-}OH$	80	220–222 (toluene)	$C_{15}H_{21}NOS$ (263.4)	3232, 1522	273 (4.19), 352 (2.73)	1.13–2.4 (m, 16H); 4.5 (br s, 1H); 6.95 (q, 2H_{arom}, $J = 9$); 9.63 (s, 1H); 10.13 (br d, 1H, $J = 8$)
10d	$R^1 = C_6H_5$ $R^2 = 2\text{-}CH_3$ $R^3 = 3\text{-}CH_3$ $R^4 = 4\text{-}OH$	80	201–203 ($MeNO_2$)	$C_{15}H_{15}NOS$ (257.4)	3260, 3200, 3140, 1556	303 (4.20), 390 (2.81)	2.38 (d, 6H, $J = 9$); 6.83–8.25 (m, 7H_{arom}); 9.75 (s, 1H); 11.83 (s, 1H)
10e	$R^1 = 4\text{-}ClC_6H_4$ $R^2 = 2\text{-}CH_3$ $R^3 = 3\text{-}CH_3$ $R^4 = 4\text{-}OH$	89	257–260 (AcOH)	$C_{15}H_{14}ClNOS$ (291.8)	3220, 3180, 1544	293 (4.24), 303sh (4.23), 394 (2.81)	2.38 (d, 6H, $J = 8.5$); 6.9 (d, 1H_{arom}, $J = 8$); 7.25 (d, 1H_{arom}, $J = 8$); 7.65 (d, 2H_{arom}, $J = 9$); 8.22 (d, 2H_{arom}, $J = 9$); 9.75 (s, 1H); 11.9 (s, 1H)
11a	$R^1 = C_2H_5$ $R^2 = 3\text{-}CH_3$ $R^3 = 4\text{-}OH$ $R^4 = 5\text{-}CH_3$	64	164–166 ($MeNO_2$)	$C_{11}H_{15}NOS$ (209.3)	3280, 1544	283 (4.15), 358sh (2.83)	1.45 (t, 3H, $J = 6$); 2.4 (s, 6H); 3.95 (q, 2H, $J = 8$); 7.7 (s, 2H_{arom}); 9.05 (s, 1H); 10.0 (br s, 1H)

Table. (continued)

Product		Yield[a] (%)	mp (°C)[b] (solvent)	Molecular Formula[c] or Lit. mp (°C)	IR[d] ν(cm^{-1})	UV (EtOH)[e] λ_{max} (nm) (lgε)	^{1}H-NMR (DMSO-d_6/ HMDSO$_{int}$)[f] δ, J(Hz)
11b	$R^1 = c\text{-}C_6H_{11}$ $R^2 = 3\text{-}CH_3$ $R^3 = 4\text{-}OH$ $R^4 = 5\text{-}CH_3$	85	222–224 (AcOH)	$C_{15}H_{21}NOS$ (263.4)	3244, 3050br, 1548	282 (4.20), 358sh (2.87)	1.25–2.25 (m, 10H); 2.4 (s, 6H); 4.63 (br s, 1H); 7.6 (s, $2H_{arom}$); 9.0 (s, 1H); 9.8 (br d, 1H, $J = 9$)
11c	$R^1 = 4\text{-}ClC_6H_4$ $R^2 = 3\text{-}CH_3$ $R^3 = 4\text{-}OH$ $R^4 = 5\text{-}CH_3$	88	190–192 ($MeNO_2$)	$C_{15}H_{14}ClNOS$ (291.8)	3264, 3200sh, 3124, 1548	310 (4.32), 394sh (2.90)	2.4 (s, 6H); 7.5–8.1 (m, $6H_{arom}$); 11.6 (br s, 1H)
12a	$R^1 = C_2H_5$ $R^2 = 2\text{-}CH_3$ $R^3 = 4\text{-}OH$ $R^4 = 5\text{-}CH_3$	85	194–196 ($MeNO_2$)	$C_{11}H_{15}NOS$ (209.3)	3276, 3108br, 1540	271 (4.14), 350 (2.64)	1.38 (t, 3H, $J = 6$); 2.3 (d, 6H, $J = 7$); 3.8 (q, 2H, $J = 8$); 6.75 (s, $1H_{arom}$); 7.1 (s, $1H_{arom}$); 9.6 (s, 1H); 10.2 (br s, 1H)
12b	$R^1 = C_6H_5$ $R^2 = 2\text{-}CH_3$ $R^3 = 4\text{-}OH$ $R^4 = 5\text{-}CH_3$	97	187–189 ($MeNO_2$)	$C_{15}H_{15}NOS$ (257.4)	3248, 3150br, 1528	305 (4.15), 390 (2.75)	2.4 (d, 6H, $J = 11$); 6.8–8.2 (m, $7H_{arom}$); 9.7 (s, 1H); 11.8 (s, 1H)
13[g]	$R^1 = C_6H_5$ $R^2 = 2\text{-}OCH_3$ $R^3 = 4\text{-}OCH_3$	73	82–84 (MeOH/ H_2O)	$C_{15}H_{15}NO_2S$ (273.4)	3320, 1562	290sh (4.11), 313 (4.25), 390sh (2.87)	3.83 (d, 6H, $J = 8$); 6.33–8.65 (m, $8H_{arom}$); 10.8 (br s, 1H)
14a	$R^1 = c\text{-}C_6H_{11}$ $R^2 = 2\text{-}i\text{-}C_3H_7$ $R^3 = 4\text{-}OH$ $R^4 = 5\text{-}CH_3$	85	184–186 ($MeNO_2$)	$C_{17}H_{25}NOS$ (291.5)	3248, 3170, 1544	273 (4.17), 351 (2.56)	1.0–2.3 (m, 16H); 2.3 (s, 3H); 3.35 (quin, 1H, $J = 6$); 4.55 (br s, 1H); 6.95 (d, $2H_{arom}$, $J = 4$); 9.55 (s, 1H); 10.15 (br d, 1H, $J = 8$)
14b	$R^1 = C_6H_5$ $R^2 = 2\text{-}i\text{-}C_3H_7$ $R^3 = 4\text{-}OH$ $R^4 = 5\text{-}CH_3$	88	181–182 ($MeNO_2$)	$C_{17}H_{19}NOS$ (285.4)	3208br, 1544	305 (4.15), 387 (2.56)	1.43 (d, 6H, $J = 7$); 3.45 (quin, 1H, $J = 6$); 6.95 (s, $1H_{arom}$); 7.15 (s, $1H_{arom}$); 7.6 (q, $2H_{arom}$, $J = 7$); 8.15 (d, $2H_{arom}$, $J = 8$); 9.65 (s, 1H); 11.93 (s, 1H)
14c	$R^1 = 4\text{-}ClC_6H_4$ $R^2 = 2\text{-}i\text{-}C_3H_7$ $R^3 = 4\text{-}OH$ $R^4 = 5\text{-}CH_3$	86	169–170 ($MeNO_2$)	$C_{17}H_{18}ClNOS$ (319.9)	3252, 3180sh, 1540	298sh (4.15), 309 (4.20), 397 (2.73)	1.4 (d, 6H, $J = 7$); 2.3 (s, 3H); 3.4 (quin, 1H, $J = 6$); 6.93 (s, $1H_{arom}$); 7.15 (s, $1H_{arom}$); 7.65 (d, $2H_{arom}$, $J = 8$); 8.15 (d, $2H_{arom}$, $J = 8$); 9.7 (s, 1H); 12.0 (s, 1H)
15a	$R^1 = CH_3$ $R^2 = 2\text{-}CH_3$ $R^3 = 4\text{-}OH$ $R^4 = 5\text{-}i\text{-}C_3H_7$	89	144–146[h] (benzene)	$C_{12}H_{17}NOS$ (223.3)	3290, 3180, 1552	268 (4.13), 350 (2.75)	1.38 (d, 6H, $J = 6$); 2.37 (s, 3H); 6.8 (s, $1H_{arom}$); 7.2 (s, $1H_{arom}$); 9.7 (s, 1H); 10.2 (br s, 1H)
15b	$R^1 = C_2H_5$ $R^2 = 2\text{-}CH_3$ $R^3 = 4\text{-}OH$ $R^4 = 5\text{-}i\text{-}C_3H_7$	90	133–135[h] (benzene)	$C_{13}H_{19}NOS$ (237.4)	3300, 3148br, 1532	271 (4.16), 350 (2.75)	1.43 (t, 9H, $J = 7$); 2.38 (s, 3H); 3.38 (quin, 1H, $J = 6$); 3.82 (q, 2H, $J = 7$); 6.8 (s, $1H_{arom}$); 7.2 (s, $1H_{arom}$); 9.65 (s, 1H); 10.2 (br s, 1H)
15c	$R^1 = c\text{-}C_6H_{11}$ $R^2 = 2\text{-}CH_3$ $R^3 = 4\text{-}OH$ $R^4 = 5\text{-}i\text{-}C_3H_7$	86	182–183.5[h] (benzene)	$C_{17}H_{25}NOS$ (291.5)	3292, 3240sh, 1520	272 (4.19), 352 (2.79)	1.1–2.35 (m, 16H); 2.35 (s, 3H); 3.35 (quin, 1H, $J = 6$); 4.55 (br s, 1H); 6.78 (s, $1H_{arom}$); 7.18 (s, $1H_{arom}$); 9.6 (s, 1H); 10.05 (br d, 1H, $J = 8$)
15d	$R^1 = C_6H_5$ $R^2 = 2\text{-}CH_3$ $R^3 = 4\text{-}OH$ $R^4 = 5\text{-}i\text{-}C_3H_7$	88	175–176 (benzene)	$C_{17}H_{19}NOS$ (285.4)	3344, 3140, 3108, 1540	305 (4.20), 380 (2.85)	1.38 (d, 6H, $J = 7$); 2.45 (s, 3H); 3.38 (quin, 1H, $J = 6$); 6.83–8.2 (m, $7H_{arom}$); 9.75 (s, 1H); 11.77 (s, 1H)
15e	$R^1 = 4\text{-}ClC_6H_4$ $R^2 = 2\text{-}CH_3$ $R^3 = 4\text{-}OH$ $R^4 = 5\text{-}i\text{-}C_3H_7$	93	208–210 (MeOH/ H_2O)	$C_{17}H_{18}ClNOS$ (319.9)	3364, 3144, 3112, 1536	297sh (4.19), 310 (4.23), 395 (2.86)	1.4 (d, 6H, $J = 6$); 2.45 (s, 3H); 3.4 (quin, 1H, $J = 6$); 6.7 (s, $1H_{arom}$); 7.35 (s, $1H_{arom}$); 7.65 (d, $2H_{arom}$, $J = 8$); 8.2 (d, $2H_{arom}$, $J = 8$); 9.8 (s, 1H); 11.88 (s, 1H)
15f	$R^1 = 4\text{-}BrC_6H_4$ $R^2 = 2\text{-}CH_3$ $R^3 = 4\text{-}OH$ $R^4 = 5\text{-}i\text{-}C_3H_7$	92	201–203 (toluene)	$C_{17}H_{18}BrNOS$ (364.3)	3376, 3140, 3116, 1536	297sh (4.21), 311 (4.25), 397 (2.87)	1.4 (d, 6H, $J = 6$); 3.4 (quin, 1H, $J = 6$); 6.85 (s, $1H_{arom}$); 7.35 (s, $1H_{arom}$); 7.8 (d, $2H_{arom}$, $J = 8$); 8.18 (d, $2H_{arom}$, $J = 8$); 9.8 (s, 1H); 11.88 (s, 1H)
16a	$R^1 = c\text{-}C_6H_{11}$ $R^2 = 2\text{-}CH_3$ $R^3 = 3\text{-}CH_3$ $R^4 = 4\text{-}CH_3$ $R^5 = 6\text{-}OH$	60	159–160[h] (heptane/ CCl_4)	$C_{16}H_{23}NOS$ (277.4)	3336, 3280sh, 3176, 1524	276 (4.10), 346 (2.59)	1.25–2.45 (m, 19H); 4.58 (br s, 1H); 6.7 (s, $1H_{arom}$); 9.05 (s, 1H); 10.18 (br d, 1H, $J = 8$)
16b	$R^1 = C_6H_5$ $R^2 = 2\text{-}CH_3$ $R^3 = 3\text{-}CH_3$ $R^4 = 4\text{-}CH_3$ $R^5 = 6\text{-}OH$	64	128–132 (heptane/ CCl_4)	$C_{16}H_{17}NOS$ (271.4)	3360sh, 3280sh, 3160, 1536	306 (4.09), 385 (2.53)	2.33 (d, 9H, $J = 16$); 6.78–8.33 (m, $6H_{arom}$); 9.3 (s, 1H); 11.93 (s, 1H)

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[a] Yield of isolated product based on **1**.

[b] mp of purified product.

[c] Satisfactory microanalyses obtained: C ± 0.3, H ± 0.35, S ± 0.22.

[d] Recorded on a Specord M80 Infrared spectrophotometer in nujol and hexachlorobutadiene.

[e] Measured using Specord M40 UV spectrophotometer.

[f] Recorded at 80 MHz on a Tesla BS487C spectrometer.

[g] ^{1}H-NMR measured in $CDCl_3$/HMDSO$_{int}$.

[h] The crude products were column-chromatographed on a silica gel eluting with $CHCl_3$ or benzene/EtOAc 3/1.

The procedure is very simple and efficient. It yields readily isolable products which contain, however, trace amounts of the corresponding amides, as found in my earlier mass spectrometric investigations.[12] Column chromatography on silica gel has to be used in the preparation of analytical samples. The Friedel–Crafts-type reaction of isothiocyanates with reactive aromatic systems, carried out in a homogeneous solution of the reactants and aluminum chloride in nitromethane, may therefore be considered a general reaction and a valuable step in the synthesis of substituted benzylamines and benzoic acids which are hardly available by other methods.

Thiobenzamides 2-16; General Procedure:

The isothiocyanate (40 mmol) is added, at room temperature, to a stirred solution of anhydrous $AlCl_3$ (11.0 g, 80 mmol) in dry $MeNO_2$ (50 mL). The mixture is cooled with ice-water and the aromatic compound (42 mmol) is added in a single portion. A temperature increase is observed. The mixture is then stirred for 1 h at room temperature and left without stirring for 6 h or overnight. In the case of compounds **2–7**, the mixture is kept 2 h at 50–60 °C. The mixture is then poured onto crushed ice to decompose the aluminum complex; rapid crystallization of the thioamides occurs in most cases. The precipitate is isolated by suction, washed with H_2O (2 x 30 mL) and benzene (30 mL). When the thioamide does not precipitate sufficiently, the mixture is extracted with EtOAc (3 x 50 mL) and the extract washed with H_2O (3 x 100 mL), dried (Na_2SO_4 or $MgSO_4$), and evaporated under reduced pressure. The crude thiobenzamide is dissolved in EtOAc (50–100 mL) and passed under reduced pressure through a short column (10 x 2 cm) packed with Al_2O_3 (Brockmann II, neutral, standard) using EtOAc as eluent. Upon evaporation of the solvent, the residue is recrystallized from a suitable solvent (Table).

The reaction of phenols with isothiocyanates can be performed in a stoppered conical flask with magnetic stirring. The reaction is monitored by TLC (silica gel, benzene/EtOAc 4 : 1 or 3 : 1).

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