

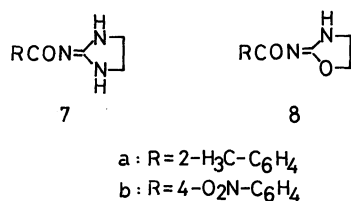
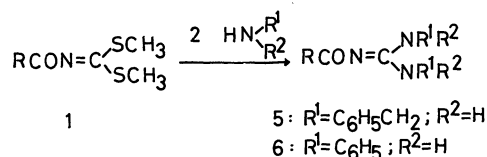
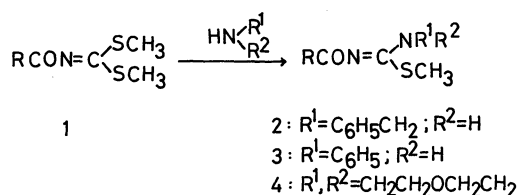
The Reaction of Dimethyl *N*-Benzoylcarbonimidodithioates with Amines

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Synopsis. 1-Substituted 3-benzoyl-2-methylisothio-ureas and 1,3-disubstituted 2-benzoylguanidines were synthesized from dimethyl *N*-benzoylcarbonimidodithioates and amines. From ethylenediamine and 2-aminoethanol, imidazolidine and oxazolidine derivatives were obtained respectively.

In recent years, α -oxoketene dithioacetals have been widely used for the preparation of heterocycles and intermediates in organic synthesis. However, relatively few studies have been reported on the reactions of the corresponding aza-analog *N*-acylcarbonimidodithioic acid dithioesters. In our continuing study of the reactions of amides with carbon disulfide,^{1,2)} we have previously reported the general synthesis of dimethyl *N*-aroylcarbonimidodithioates from aromatic amide, carbon disulfide, and sodium hydride.³⁾ The dithioesters reacted with hydrazine hydrate to give 3-aryl-5-methylthio-1*H*-1,2,4-triazoles in good yields.³⁾ Augustin *et al.* reported the syntheses of dimethyl *N*-cinnamoyl- and *N*-aroylcarbonimidodithioates, and their reactions with nucleophilic compounds.^{4–7)} Recently Potts *et al.* used diethyl *N*-benzoylcarbonimidodithioates and the potassium enolates of methyl ketones to prepare *N*-acyl- β -enamino ketones.⁸⁾

In this note, we wish to report the reactions of dimethyl *N*-benzoylcarbonimidodithioates **1** obtained from 2-methyl- and 4-nitrobenzamides with several amines. When equimolar mixtures of **1** and amines



(benzylamine, aniline, and morpholine) were heated in ethanol, 1-substituted 3-benzoyl-2-methylisothio-ureas **2–4** were obtained in good yields. Two moles of the amines (benzylamine and aniline) gave 1,3-

disubstituted 2-benzoylguanidines **5** and **6**. For the latter reactions it was necessary to heat in boiling xylene. Although early reports^{9,10)} described the preparation of compounds of these types (**2–6**), the method reported here is more convenient. From ethylenediamine and 2-aminoethanol, the cyclized compounds, 2-(benzoylimino)imidazolidines **7** and 2-(benzoylimino)oxazolidine **8** respectively, were obtained.

These results are similar to those of the reaction of α -oxoketene dithioacetals with amines¹¹⁾ and offer new possibilities in preparing heterocycles.

Experimental

1-Substituted 3-Benzoyl-2-methylisothio-ureas (**2–4**).

General Procedure. A mixture of dimethyl *N*-benzoylcarbonimidodithioate (**1**, 0.002 mol),³⁾ amine (benzylamine, aniline, or morpholine; 0.0022 mol), and ethanol (30–40 ml) was refluxed for 1–3 h. The solvent was then removed, and the residual solid was recrystallized.

1-Benzyl-2-methyl-3-(2-methylbenzoyl)isothiourea (2a): Recrystallized from ethanol; IR (KBr) 3160 m (NH) and 1590 vs. cm⁻¹ (C=O); UV (EtOH) λ_{max} 244sh (log ϵ 4.13), 249 (4.15), 255 (4.15), 262sh (4.22), and 282 nm (4.47); ¹H NMR (CCl₄) δ =2.55 (s, 3H, CH₃), 2.58 (s, 3H, CH₃), 4.55 (d, 2H, CH₂), 7.2–8.5 (m, 9H, C₆H₄ and C₆H₅), and 11.77 (br s, 1H, NH); MS *m/z* 298 (M⁺).

1-Benzyl-3-(4-nitrobenzoyl)-2-methylisothiourea (2b): Recrystallized from ethanol; IR (KBr) 3250 w (NH) and 1580 vs. cm⁻¹ (C=O); MS *m/z* 329 (M⁺).

2-Methyl-3-(2-methylbenzoyl)-1-phenylisothiourea (3a): Recrystallized from hexane–ethanol; IR (KBr) 1605 vs. cm⁻¹ (C=O); MS *m/z* 284 (M⁺).

2-Methyl-3-(4-nitrobenzoyl)-1-phenylisothiourea (3b): Recrystallized from ethanol; IR (KBr) 1615 m cm⁻¹ (C=O); MS *m/z* 315 (M⁺).

4-[2-Methylbenzoylimino(methylthio)methyl]morpholine (4a): Recrystallized from ethanol; IR (KBr) 1604 s cm⁻¹ (C=O); UV (EtOH) λ_{max} 240 (log ϵ 4.27) and 281 nm (4.23); MS *m/z* 278 (M⁺).

4-[Methylthio(4-nitrobenzoylimino)methyl]morpholine (4b): Recrystallized from ethanol; IR (KBr) 1630 s cm⁻¹ (C=O); MS *m/z* 309 (M⁺).

1,3-Disubstituted 2-Benzoylguanidines (**5** and **6**).

General Procedure. A mixture of **1** (0.002 mol), amine (benzylamine or aniline; 0.0044 mol), and xylene (30–40 ml) was refluxed for 5 h. In the case of **6a**, ethanol was used as the solvent. The solvent was removed, and the residual solid was recrystallized.

1,3-Dibenzyl-2-(2-methylbenzoyl)guanidine (5a): Recrystallized from ethanol; IR (KBr) 3295 vs. (NH) and 1615 vs. cm⁻¹ (C=O); MS *m/z* 357 (M⁺).

1,3-Dibenzyl-2-(4-nitrobenzoyl)guanidine (5b): Recrystallized from hexane–ethanol; IR (KBr) 3398 s (NH) and 1612 s cm⁻¹ (C=O); MS *m/z* 388 (M⁺).

1,3-Diphenyl-2-(2-methylbenzoyl)guanidine (6a): Recrystallized from ethanol; IR (KBr) 3380 m, 3250 s (NH), and 1680 vs. cm⁻¹ (C=O); UV (EtOH) λ_{max} 234sh (log ϵ 4.33) and 278 nm (4.42); MS *m/z* 329 (M⁺).

TABLE I. YIELDS AND ANALYTICAL DATA

Compound	Yield %	Mp $\theta_m/^\circ\text{C}$	Molecular formula	Found (Calcd) (%)			
				C	H	N	S
2a	97	71–72	$\text{C}_{17}\text{H}_{18}\text{N}_2\text{OS}$	68.40 (68.43)	6.14 (6.08)	9.50 (9.39)	10.44 (10.75)
2b	83	120–121	$\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_3\text{S}$	58.48 (58.35)	4.68 (4.59)	12.73 (12.76)	9.80 (9.73)
3a	66	71–72	$\text{C}_{16}\text{H}_{16}\text{N}_2\text{OS}$	67.43 (67.58)	5.73 (5.67)	9.59 (9.85)	11.12 (11.28)
3b	85	153–154 ^{a)}	$\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_3\text{S}$	57.25 (57.13)	4.18 (4.16)	13.37 (13.33)	10.25 (10.17)
4a	87	91–92	$\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$	60.66 (60.41)	6.52 (6.52)	10.10 (10.06)	11.26 (11.52)
4b	55	152–154	$\text{C}_{13}\text{H}_{15}\text{N}_3\text{O}_4\text{S}$	50.46 (50.48)	4.90 (4.89)	13.56 (13.58)	10.05 (10.37)
5a	78	146–147	$\text{C}_{23}\text{H}_{23}\text{N}_3\text{O}$	77.13 (77.28)	6.50 (6.49)	11.70 (11.76)	
5b	77	154–156	$\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_3$	67.73 (68.03)	5.29 (5.19)	14.26 (14.42)	
6a	57	134–135	$\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}$	76.49 (76.57)	5.87 (5.81)	12.76 (12.76)	
6b	84	145–147	$\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_3$	66.52 (66.66)	4.56 (4.48)	15.46 (15.55)	
7a	96	162–163	$\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}$	65.05 (65.01)	6.43 (6.45)	20.90 (20.68)	
7b	94	252–253 ^{b)}	$\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_3$	51.31 (51.28)	4.49 (4.30)	23.93 (23.92)	
8b	63	236–238	$\text{C}_{10}\text{H}_9\text{N}_3\text{O}_4$	51.05 (51.07)	3.90 (3.86)	17.93 (17.87)	

a) Lit,⁷⁾ mp 148–150 °C. b) Decomp.

1,3-Diphenyl-2-(4-nitrobenzoyl)guanidine (6b): Recrystallized from ethanol; IR (KBr) 3375 m (NH) and 1600 cm^{-1} (C=O); MS m/z 360 (M^+).

Imidazolidines 7 and Oxazolidine 8 were prepared from ethylene diamine and 2-aminoethanol respectively as has been described for the preparation of **2–4**.

2-(2-Methylbenzoylimino)imidazolidine (7a): Recrystallized from ethanol; IR (KBr) 3340 s (NH) and 1600 vs. cm^{-1} (C=O); UV (EtOH) λ_{max} 244 nm ($\log \epsilon$ 4.48); MS m/z 203 (M^+).

2-(4-Nitrobenzoylimino)imidazolidine (7b): Recrystallized from *N,N*-dimethylformamide-ethanol; IR (KBr) 3310 s (NH) and 1620 vs. cm^{-1} (C=O); MS m/z 234 (M^+).

2-(4-Nitrobenzoylimino)oxazolidine (8b): Recrystallized from *N,N*-dimethylformamide; IR (KBr) 3290 s (NH) and 1620 vs. cm^{-1} (C=O); MS m/z 235 (M^+).

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