

Interaction of 2-Aminobenzothiazoles with Benzoyl and *tert*-Butyl Isothiocyanates

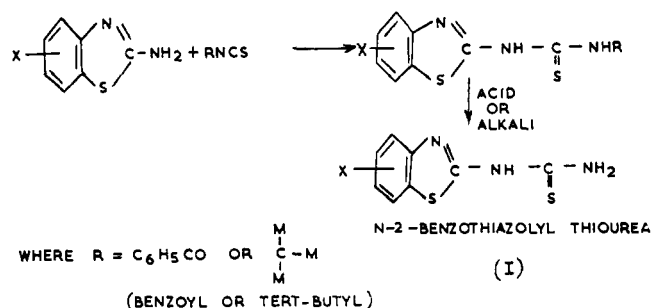
W. U. MALIK, P. K. SRIVASTAVA, and S. C. MEHRA

Department of Chemistry, University of Roorkee, Roorkee, India

Various 2-aminobenzothiazole derivatives have been condensed with benzoyl and *tert*-butyl isothiocyanates to give the corresponding *N*-benzoyl-(or *tert*-butyl)-*N'*-2-benzothiazolylthioureas. The reaction product of 2-aminobenzothiazole and benzoyl (or *tert*-butyl) isothiocyanate, on alkaline or acid hydrolysis, is *N*-2-benzothiazolylthiourea.

ALTHOUGH various *N*-aryl-*N'*-2-benzothiazolylthioureas have been prepared (5, 6) by the interaction of aryl isothiocyanates and 2-aminobenzothiazole derivatives, the reactions of benzoyl isothiocyanate and *tert*-butyl isothiocyanate with benzothiazole derivatives have not been investigated. In an effort to find new thiocarbamylating agents for amino compounds, the application of benzoyl (3, 4, 9) and *tert*-butyl (7, 10-12) isothiocyanates was studied.

In view of the reported ease and orderly disruption of the benzoyl and *o*-*tert*-butyl link in esters (1) and the *N*-*tert*-butyl link in amides (8), an investigation of thiocarbamylation by *tert*-butyl and benzoyl isothiocyanates appeared to be of great interest, since heterolysis of *N*-benzoyl-(or *tert*-butyl)-*N'*-2-benzothiazolylthioureas into the related *N*-2-benzothiazolylthioureas (I) can be effected smoothly.



Benzoyl- and *tert*-butyl isothiocyanates were condensed with different 2-aminobenzothiazoles with ease in solvents like petroleum ether, benzene, or ether. In many cases the reaction was exothermic and completed at room temperature, while in other cases heating for 1.5 to 5 hours was necessary. The expected *N*-benzoyl-(or *tert*-butyl)-*N'*-2-benzothiazolylthioureas were obtained in almost quantitative yields by evaporation of the solvent. The reaction product of 2-aminobenzothiazole and benzoyl (or *tert*-butyl) isothiocyanate was hydrolyzed with 10% alkali (or concentrated HCl in the case of the *tert*-butyl group) to give *N*-2-benzothiazolylthiourea (I).

EXPERIMENTAL PROCEDURE

Benzoyl isothiocyanate was prepared by the reaction of benzoyl chloride and ammonium thiocyanate in acetone (2). *tert*-Butyl isothiocyanate was prepared by the reaction of *tert*-butyl chloride and ammonium thiocyanate in the presence of zinc chloride (11).

A mixture of ammonium thiocyanate (27.4 grams), zinc chloride (10 grams), *tert*-butyl chloride (27.88 grams), and water (100 ml.) was shaken at intervals for 96 hours. The pale yellow upper layer consisting of *tert*-butyl thiocyanate and *tert*-butyl isothiocyanate was separated, washed repeatedly with water, and dried. It was then shaken with finely powdered anhydrous zinc chloride (5 grams) for 1 hour

Table I. Analytical Data on Benzothiazolylthioureas

(Benzoyl isothiocyanate used; solvent acetone)

Benzothiazoles	Compound Formed	Yield, %	M.P., °C.	Sulfur, %		Nitrogen, %	
				Found	Calcd.	Found	Calcd.
<i>N</i> -Benzoyl- <i>N'</i> -2-benzothiazolylthioureas Formed by Condensation of 2-Aminobenzothiazoles and Benzoyl Isothiocyanate							
2-Aminobenzothiazole	C ₁₅ H ₁₁ N ₃ S ₂ O ^a	70	133	20.31	20.44	13.40	13.42
2-ABT ^b (4-methyl)	C ₁₆ H ₁₃ N ₃ S ₂ O	75	126	19.39	19.57	12.79	12.84
2-ABT (5-methyl)	C ₁₆ H ₁₃ N ₃ S ₂ O	81	140	19.51	19.57	12.81	12.84
2-ABT (5-methoxy)	C ₁₆ H ₁₃ N ₃ S ₂ O ₂	50	152	18.58	18.65	12.01	12.25
2-ABT (6-methoxy)	C ₁₆ H ₁₃ N ₃ S ₂ O ₂	90	205	18.61	18.65	12.11	12.25
2-ABT (6-ethoxy)	C ₁₇ H ₁₅ N ₃ S ₂ O ₂	80	141	17.88	17.93	11.68	11.76
2-ABT (4-ethoxy)	C ₁₇ H ₁₅ N ₃ S ₂ O ₂	70	91	17.90	17.93	11.71	11.76
2-ABT (5-chloro)	C ₁₅ H ₁₀ N ₃ S ₂ OC1	50	120	18.38	18.42	12.11	12.08
2-ABT (6-chloro)	C ₁₅ H ₁₀ N ₃ S ₂ OC1	55	89	18.39	18.42	11.91	12.08
<i>N</i> - <i>tert</i> -Butyl- <i>N'</i> -2-benzothiazolyl Thioureas Formed by Condensation of 2-Aminobenzothiazole and <i>tert</i> -Butyl Isothiocyanate							
2-ABT	C ₁₂ H ₁₅ N ₃ S ₂	80	141	24.09	24.15	15.81	15.85
2-ABT (5-methyl)	C ₁₃ H ₁₇ N ₃ S ₂	84	162	22.88	22.94	15.11	15.05
2-ABT (6-chloro)	C ₁₂ H ₁₄ N ₃ S ₂ Cl	70	115	21.31	21.36	14.06	14.03
2-ABT (5-chloro)	C ₁₂ H ₁₄ N ₃ S ₂ Cl	50	121	21.29	21.36	13.96	14.03
2-ABT (6-ethoxy)	C ₁₄ H ₁₉ N ₃ S ₂ O	55	124	20.70	20.71	13.51	13.59
2-ABT (6-methoxy)	C ₁₃ H ₁₇ N ₃ S ₂ O	52	146	21.74	21.70	14.21	14.23

^a When hydrolyzed with alkali or acid produced *N*-2-benzothiazolylthiourea (I), m.p. 180° C. ^b Aminobenzothiazole.