

CYCLIZATION OF SUBSTITUTED 1,4-DIPHENYLTHIOSEMICARBAZIDES TO THIAZOLE DERIVATIVES

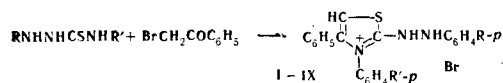
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Heating together substituted 1,4-diphenylthiosemicarbazides and ω -bromoacetophenone in ethanol gives new bases and quaternary salts of 2,3,4-substituted thiazole.

Among thiazole derivatives are known compounds of interest because of their physiological activities [1]. In developing research on derivatives of 1,4-diphenylthiosemicarbazide, it was of interest to synthesize and study new substituted thiazoles, prepared from the semicarbazides by heating with ω -bromoacetophenone. The literature describes the preparation of 2-arylhydrazinethiazoles, from monoarylthiosemicarbazide and its substitution products and α -halogenocarbonyl compounds [2,3]. We have prepared quaternary salts of 2,3,4-substituted thiazoles (I-IX) by heating the appropriate 1,4-diphenylthiosemicarbazide derivatives with ω -bromoacetophenone in ethanol for 5-8 hr.



It should be noted that in three cases the products were not quaternary salts, but 2,3,4 derivatives of the corresponding thiazole base (X-XII). The starting substituted 1,4-diphenylthiosemicarbazides were prepared from arylhydrazines and arylisothiocyanates [4,5]. The table gives the thiazole derivatives synthesized. They were crystalline, and had high melting points. They were purified by recrystallizing from ethanol.

EXPERIMENTAL

Quaternary salts of 2-(p-sulfonamidophenylhydrazo)-3-[N-(p-chlorophenyl)]-4-phenylthiazole (IV). 0.65 g ω -bromoacetophenone and 12 ml EtOH were added to 1.0 g 1-(p-sulfonamidophenyl)-4-(p-chlorophenyl)thiosemicarbazide. The mixture was heated on a water-

bath for 7 hr. The solid which separated on cooling was filtered off, and recrystallized from EtOH, mp 214° C, yield 0.93 g (62%).

Compounds I-IX were prepared similarly.

2-(Na salt p-sulfophenylhydrazo)-3-[N-(p-acetylamidophenyl)]-4-phenylthiazole (X). 0.4 g ω -bromoacetophenone and 20 ml EtOH were added to 1.0 g 1-(Na salt p-sulfophenyl)-4-(p-acetylamidophenyl)thiosemicarbazide. The whole was heated on a water-bath for 12 hr, the solid filtered off, and recrystallized from EtOH. It did not melt at 300° C. Yield 0.6 g (57%). Found: S 16.45; 16.40%. Calculated for $\text{C}_{23}\text{H}_{19}\text{N}_4\text{NaO}_6\text{S}_3$: S 16.97%.

2-(Na salt p-sulfophenylhydrazo)-3-[N-(p-sulfonamidophenyl)]-4-phenylthiazole (XI). Mp 282°-285° C (decomp). Yield 57%. Found: S 18.60; 18.63%. Calculated for $\text{C}_{21}\text{H}_{17}\text{N}_4\text{NaO}_5\text{S}_3$: S 18.32%.

2-(p-Tolylhydrazo)-3-[N-(p-nitrophenyl)]-4-phenylthiazole (XII). Mp 154°-155° C. Yield 64%. Found: S 7.91; 8.02%. Calculated for $\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_2\text{S}$: S 7.96%.

Compounds XI and XII were prepared similarly.

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Quaternary Salts of Thiazole Derivatives

Compound	R	R'	Mp, °C	Formula	S, %		Yield, %
					Found	Calculated	
I	NH ₂ SO ₂	C ₂ H ₅ COO	180-181	C ₂₄ H ₂₃ BrN ₄ O ₄ S ₂	11.59	11.61	72
II	NH ₂ SO ₂	C ₂ H ₅ O	196-198	C ₂₃ H ₂₃ BrN ₄ O ₃ S ₂	11.27	11.28	59
III	NH ₂ SO ₂	NO ₂	193	C ₂₁ H ₁₈ BrN ₄ O ₄ S ₂	11.54	11.53	60
IV	NH ₂ SO ₂	Cl	214	C ₂₁ H ₁₈ BrClN ₄ O ₂ S ₂	11.92	11.89	62
V	NH ₂ SO ₂	Br	221	C ₂₁ H ₁₈ Br ₂ N ₄ O ₂ S ₂	11.20	11.23	60
VI	NH ₂ SO ₂	CH ₃ O	191	C ₂₂ H ₂₁ BrN ₄ O ₃ S ₂	11.69	11.65	77
VII	NaSO ₃	C ₂ H ₅ O	170-172 (decomp)	C ₂₃ H ₂₁ BrN ₃ NaO ₄ S ₂	11.61	11.63	64
VIII	CH ₃	C ₂ H ₅ O	139	C ₂₄ H ₂₄ BrN ₃ OS	6.58	6.47	85
IX	CH ₃	C ₂ H ₅ COO	177-178	C ₂₅ H ₂₄ BrN ₃ O ₂ S	6.19	6.28	70

