

[A CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

Aryl Isothiocyanates and Ethyl Acetonedicarboxylate

BY DAVID E. WORRALL

It has been shown¹ that a piperidone is obtained by the action of *p*-tolyl isothiocyanate on ethyl acetonedicarboxylate. The product, which is readily methylated, may be converted into a benzothiazole derivative through the action of bro-

matic needles varying in amount from 3-8 g. All melted with decomposition. Tars were obtained with *o*-tolyl and β -naphthyl isothiocyanates. Prepared by short heating with methyl iodide in alcohol solution the sulfomethoxy derivatives separated as bright yellow slender needles. The benzothiazoles, yellow crystalline powders pre-

TABLE I
DERIVATIVES OF 2,4-DIOXO-5-CARBETHOXY-6-SULFOPIPERIDINE-3-THIOFORMO-

	M. p., °C.	Formula	Analyses, %			
			Calcd.		Found	
			C	H	C	H
(1-Phenyl) anilide	188-189	C ₂₁ H ₁₉ N ₂ O ₄ S ₂	59.1	4.2	59.0	4.1
6-Sulfomethoxy	148-149	C ₂₂ H ₂₀ N ₂ O ₄ S ₂	60.0	4.5	59.8	4.6
(1- <i>m</i> -Tolyl) <i>m</i> -toluide	125-126	C ₂₃ H ₂₂ N ₂ O ₄ S ₂	60.8	4.9	60.8	4.6
6-Sulfomethoxy	137-138	C ₂₄ H ₂₄ N ₂ O ₄ S ₂	61.5	5.1	61.8	5.0
(1- <i>p</i> -Anisyl) aniside	162-163	C ₂₃ H ₂₂ N ₂ O ₆ S ₂	56.8	4.5	56.4	4.7
6-Sulfomethoxy	152-153	C ₂₄ H ₂₄ N ₂ O ₆ S ₂	57.6	4.8	57.3	4.8
(1- <i>p</i> -Phenetyl) phenetide	195-197	C ₂₅ H ₂₃ N ₂ O ₆ S ₂	58.4	5.1	58.1	5.1
6-Sulfomethoxy	114-115	C ₂₆ H ₂₅ N ₂ O ₆ S ₂	59.1	5.3	58.8	5.5
(1- <i>p</i> -Bromo) <i>p</i> -bromoanilide	179-181	C ₂₁ H ₁₆ Br ₂ N ₂ O ₄ S ₂	43.2	2.8	43.0	2.8
6-Sulfomethoxy	152	C ₂₂ H ₁₅ Br ₂ N ₂ O ₄ S ₂	44.1	3.0	43.9	3.1

TABLE II
DERIVATIVES OF (2,4-DIOXY-5-CARBETHOXY-6-SULFOPIPERIDYL)-BENZOTHAZOLE

	Formula	Analyses, %			
		Calcd.		Found	
		C	H	C	H
(1-Phenyl)	C ₂₁ H ₁₆ N ₂ O ₄ S ₂	59.4	3.8	59.5	3.8
(1- <i>m</i> -Tolyl) 4 (or 6)-methyl	C ₂₃ H ₂₀ N ₂ O ₄ S ₂	61.1	4.4	60.8	4.3
(1- <i>p</i> -Anisyl) 5-methoxy	C ₂₃ H ₂₀ N ₂ O ₆ S ₂	57.0	4.1	56.8	4.2
(1- <i>p</i> -Phenetyl) 5-ethoxy	C ₂₅ H ₂₄ N ₂ O ₆ S ₂	58.6	4.7	58.2	4.8
(1- <i>p</i> -Bromo) 5-bromo	C ₂₁ H ₁₄ Br ₂ N ₂ O ₄ S ₂	43.3	2.4	43.6	2.5

mine. These reactions have been studied with phenyl isothiocyanate itself and some of the more common derivatives.

Experimental

To 0.1 g. mole of pulverized sodium suspended in ether was added 0.05 g. mole of the ester and then a similar amount of the isothiocyanate. After several hours the mixture, dissolved in water containing crushed ice, was carefully decomposed by addition to cold dilute hydrochloric acid. The pasty product using hot alcohol or alcohol-benzene mixture yielded yellow plates and pris-

cipitated from glacial acetic acid solution by the action of bromine, were thoroughly washed with alcohol and used directly for analysis. They may be crystallized from aniline. The melting points were too high to be recorded with a sulfuric acid-bath.

Summary

Several piperidones have been prepared by the interaction of representative aryl isothiocyanates with ethyl acetonedicarboxylate. The corresponding sulfomethoxy and benzothiazole derivatives were synthesized.

(1) Worrall, *THIS JOURNAL*, **61**, 2966 (1939).