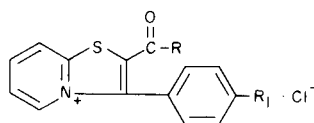


TABLE I
Thiazolo[3,2-*a*]pyridinium Chlorides



R	R ₁	M.p., °C (a)	Formula	Anal.	C, %	H, %	Cl, %	F, %	N, %	S, %
Cl	H	300	C ₁₄ H ₉ Cl ₂ NOS (b)	Calcd. Found	54.2 54.3	2.9 3.0	22.9 22.6		4.5 4.4	10.3 10.2
OH	H	180	C ₁₄ H ₁₀ ClNO ₂ S	Calcd. Found	57.6 57.6	3.5 3.5	12.2 12.2		4.8 4.8	11.0 11.2
OCH ₃	H	300	C ₁₅ H ₁₂ ClNO ₂ S	Calcd. Found	59.0 59.0	3.9 4.0	11.6 11.9		4.6 4.5	10.5 10.5
OC ₂ H ₅	H	183	C ₁₆ H ₁₄ ClNO ₂ S	Calcd. Found	60.1 59.7	4.4 4.4	11.1 11.1		4.4 4.3	10.0 10.0
Cl	F	300	C ₁₄ H ₈ Cl ₂ FNOS (b)	Calcd. Found	51.2 51.2	2.5 2.5	21.6 21.8	5.8 5.9	4.3 4.0	9.8 9.9
OH	F	190	C ₁₄ H ₉ ClFNO ₂ S	Calcd. Found	54.3 54.2	2.9 2.9	11.4 11.7	6.1 6.5	4.5 4.4	10.4 10.1
OCH ₃	F	230	C ₁₅ H ₁₁ ClFNO ₂ S	Calcd. Found	55.7 55.5	3.4 3.5	11.0 11.2	5.9 6.2	4.3 4.1	9.9 9.8
OC ₂ H ₅	F	190	C ₁₆ H ₁₃ ClFNO ₂ S	Calcd. Found	56.9 57.1	3.9 3.8	10.5 10.8	5.6 5.7	4.1 4.0	9.5 9.6
OC ₃ H ₇	F	208	C ₁₇ H ₁₅ ClFNO ₂ S	Calcd. Found	58.0 57.6	4.3 4.6	10.1 9.9	5.4 5.5	4.0 4.0	9.1 8.8
OC ₄ H ₉	F	208	C ₁₈ H ₁₇ ClFNO ₂ S	Calcd. Found	59.1 58.8	4.7 4.7	9.7 9.9	5.2 5.6	3.8 4.1	8.8 8.8
Cl	Cl	310	C ₁₄ H ₈ Cl ₃ NOS (b)	Calcd. Found	48.8 48.4	2.3 2.7	30.9 30.1		4.1 3.9	9.3 9.5
OH	Cl	215	C ₁₄ H ₉ Cl ₂ NO ₂ S	Calcd. Found	51.6 51.4	2.8 2.8	21.7 21.5		4.3 4.3	9.8 10.0
OC ₂ H ₅	Cl	180	C ₁₆ H ₁₄ Cl ₂ NO _{2.5} S (c)	Calcd. Found	52.9 52.6	3.9 3.8	19.5 20.0		3.9 3.8	8.8 8.8
Cl	NO ₂	285	C ₁₄ H ₈ Cl ₂ N ₂ O ₃ S (b)	Calcd. Found	47.3 46.4	2.3 2.6	20.0 19.7		7.9 7.8	9.0 8.8
OH	NO ₂	200	C ₁₄ H ₉ ClN ₂ O ₄ S	Calcd. Found	49.9 49.8	2.7 2.7	10.5 10.2		8.3 8.3	9.5 9.5

(a) Approximate decomposition points. In most samples, darkening and changes in the appearance of the crystals occurred at lower temperatures. (b) Crude product, analyzed as isolated without further purification. (c) Hemihydrate, Karl Fischer, 2.8%.

2-Chloroformyl-3-phenylthiazolo[3,2-*a*]pyridinium Chlorides.

A mixture of 0.1 mole of the cinnamic acid, 0.01 mole of pyridine, 0.5 mole of thionyl chloride and 100 ml. of toluene or chlorobenzene was heated at reflux temperature for 24-72 hours and filtered while hot to remove the insoluble 2-chloroformyl-3-phenylthiazolo[3,2-*a*]pyridinium chloride. The product was washed first with benzene and then with hexane, dried in a vacuum oven, and analyzed without further purification.

2-Carboxy-3-phenylthiazolo[3,2-*a*]pyridinium Chlorides.

Two grams of the 2-chloroformyl-3-phenylthiazolo[3,2-*a*]pyridinium chloride was heated to solution in about 40 ml. of

water and allowed to stand overnight in the cold room. The precipitate was filtered off and recrystallized from water containing a little 6*N* hydrochloric acid.

2-Carbalkoxy-3-phenylthiazolo[3,2-*a*]pyridinium Chlorides.

A mixture of the 2-chloroformyl-3-phenylthiazolo[3,2-*a*]pyridinium chloride and about 6 parts of the appropriate alcohol was heated to solution, allowed to stand at room temperature overnight, cooled and filtered. The product was generally analyzed without further purification.

2-Carboxy-3-phenylthiazolo[3,2-*a*]pyridinium Perchlorate.
A. From Cinnamic Acid.

A solution of 400 mg. of 2-carbethoxy-3-phenylthiazolo[3,2-a]-pyridinium chloride, prepared by the above procedure, in 20 ml. of water was treated with 0.2 ml. of 70% perchloric acid. The white precipitate which separated was filtered off and recrystallized from ethanol. The yield of 2-carbethoxy-3-phenylthiazolo[3,2-a]-pyridinium perchlorate, m.p. 204-206°, was 290 mg.; uv (methanol) 205 m μ (log ϵ 4.48); 234 (4.33); 314 sh (4.07); 323 (4.13); nmr δ 1.06 (3H, t, J = 7 Hz), 4.25 (2H, q, J = 7), 7.68 (5H, s), multiplets (4H) at 7.93, 8.49, 8.67, 8.94.

Anal. Calcd. for C₁₆H₁₄ClNO₆S: C, 50.1; H, 3.7; Cl, 9.2; N, 3.7; S, 8.4. Found: C, 49.8; H, 3.7; Cl, 9.1; N, 3.5; S, 8.3.

B. From 2-Mercaptopyridine.

Sodium (1.2 g., 0.05 mole) was dissolved in 90 ml. of absolute ethanol and 5.5 g. (0.05 mole) of 2-mercaptopyridine was added. The mixture was stirred for 30 minutes and 13.6 g. (0.05 mole) of ethyl α -bromobenzoylacetate was added in portions. Stirring was continued for 18 hours at room temperature and the precipitated salt was filtered off. The reaction mixture was concentrated and the residue was dissolved in 150 ml. of benzene and washed twice with water. The benzene layer was concentrated to 11.7 g. of dark brown oil. Tlc indicated a mixture of two major and three minor products. Attempts to purify by chromatography were only partially successful as some decomposition occurred during the process.

A sample of the above crude ethyl α -(2-pyridylthio)benzoylacetate was "purified" by thin layer chromatography on silica gel

plates using 9/1 heptane/THF. Band #3 was eluted with acetone and concentrated. A mixture of 600 mg. of this oil and 2 ml. of concentrated sulfuric acid was allowed to stand overnight at room temperature, poured into 50 ml. of cold ether and kept overnight in the cold room. The ether was decanted and the residue was dissolved in 5 ml. of water and treated with 4 ml. of 37% perchloric acid. An oil separated and gradually crystallized. The crystals were filtered, washed with water and dried in a vacuum oven. The yield was 389 mg., m.p. 160°. Recrystallization four times from ethanol resulted in pure 2-carbethoxy-3-phenylthiazolo[3,2-a]pyridinium perchlorate, m.p. 204-206°. This compound was identical to the previous sample by ir, uv and nmr.

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