$$4C_6 H_5 CH_2 CI + 3S$$
  $C_6 H_5$   $C_6 H_5$   $+ 2 H_2 S + 4 HCI$ 

The product of reaction of sulfur with p-chlorobenzyl bromide under the same conditions is the hitherto unknown compound tetrakis-p-chlorophenylthiophene (yield 25-30%). Found: C 63.51; H 3.20; S 6.23; Cl 26.79%. Calculated for C<sub>28</sub>H<sub>16</sub>Cl<sub>4</sub>S: C 63.87; H 3.05; S 6.09; Cl 26.99%.

Benzylidene chloride reacts with sulfur at 220-250° to give II (yield 51%)

This compound, also previously undescribed, melts at  $64^{\circ}$ . Found: C 68.5; H 3.54; S 13.28; Cl 14.23%. Calculated for  $C_{14}$  H<sub>9</sub>SCl: C 68.70; H 3.70; S 13.10; Cl 14.48%.

When sulfur reacts with benzylidene chloride at higher temperatures (250°-300°) III is formed, the yield exceeding 60% (m.p. 215°).

Benzylidene bromide reacts similarly with sulfur, but the yield of III is under 10%.

Unlike the mono- and dichloro-derivatives, benzotrichloride undergoes practically no reaction with sulfur when they are heated together for a long time at 225-240°.

16 October 1964

Institute of Organic Synthesis AS Latvian SSR, Riga

UDC 54.859 + 542.959

## SYNTHESIS OF PYRIMIDO[4,5-b][1,4]THIAZINE DERIVATIVES

## T. S. Safonova and M. P. Nemeryuk

Khimiya geterotsiklicheskikh soedinenii, Vol. 1, No. 1, p. 149, 1965

The pyrimido[4, 5-b][1, 4]thiazine system is practically uninvestigated, the only method described being the synthesis of certain 5H, 7H-pyrimido[4, 5-b][1, 4]thiazoles-6 (see [1, 2]). With a view to obtaining derivatives of the pyrimido[4, 5-b][1, 4]thiazine system, a study is being made of the reaction of 5-amino-6-mercaptopyrimidines with  $\alpha$ -halogenoketones.

Reacting 4-methoxy-5-amino-6-mercaptopyrimidine with  $\alpha$ -bromoacetophenone and its p-bromo derivative gives, respectively: 4-methoxy-6-phenyl- and 4-methoxy-6(p-bromphenyl)pyrimido[4, 5-b][1, 4]thiazines (I and II). Reaction of 2, 5-diamino-4-methyl-6-mercaptopyrimidine with chloroacetone,  $\alpha$ -chloroethylmethyl ketone, bromoacetophenone, and its p-bromo- and p-nitro derivatives gives the corresponding 2-amino-4-methyl-6-alkyl(aryl)pyrimido[4, 5-b][1, 4]-thiazines (III-VII).

4-Methoxy-6-phenylpyrimido[4, 5-b][1, 4]thiazine (I) m.p.  $176-178^{\circ}$  (from ethanol). Found: C 60, 84; H 4.51; N 16.23; S 12.43%.  $C_{13}H_{11}N_{3}OS$ . Calculated: C 60, 68; H 4.32; N 16.33; S 12.46%.

4-Methoxy-6-(p-bromphenyl)pyrimido[4, 5-b][1, 4]thiazine (II) m.p. 175-177° (from ethanol). Found: C 46.50; H 2.98; Br 23.80; N 12.55; S 9.66%.  $C_{18}H_{10}BrN_3OS$ . Calculated: C 46.44; H 2.99; Br 23.77; N 12.50; S 9.54%.

2-Amino-4, 6-dimethylpyrimido[4, 5-b][1, 4]thiazine (III) m.p.  $223-224^{\circ}$  (from dimethylformamide). Found: C 49.49; H 5.04; N 29.04; S 16.42%. C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>S. Calculated: C 49.45; H 5.20; N 28.83; S 16.50%.

2-Amino-4, 6, 7-trimethylpyrimido[4, 5-b][1, 4]thiazine (IV) m.p. 200-202.5° (from ethanol). Found: C 52.15; H 5.97; N 26.91; S 15.24%.  $C_9H_{12}N_4S$ : Calculated: C 51.89; H 5.80; N 26.90; S 15.39%.

2-Amino-4-methyl-6-phenylpyrimido[4, 5-b][1, 4]thiazine (V) m.p.  $281-282^{\circ}$  (from ethanol). Found: C 60.60; H 4.55; N 22.15; S 12.41%.  $C_{13}H_{12}N_4S$ . Calculated: C 60.91; H 4.72; N 21.86; S 12.51%.

2-Amino-4-methyl-6-(p-bromphenyl)pyrimido[4, 5-b][1, 4]thiazine (VI) m.p.  $240-242^{\circ}$  (from ethanol-dimethyl-formamide 2:1). Found: C 46.29; H 3.20; Br 23.62; N 16.91; S 9.67%. C<sub>13</sub>H<sub>11</sub>BrN<sub>4</sub>S. Calculated: C 46.57; H 3.08; Br 23.84; N 16.71; S 9.56%.

2-Amino-4-methyl-6-(p-nitrophenyl)pyrimido[4, 5-b][1, 4]thiazine (VII) m.p. >  $300^{\circ}$  (from dimethylformamide). Found: C 51.52; H 3.66; N 22.91; S 10.65%.  $C_{13}H_{11}N_5O_2S$ . Calculated: C 51.81; H 3.68; N 23.37; S 10.64%.

A paper on preparing I and its 4-hydrazino derivative appeared before this letter was sent to the Editor [3].

## REFERENCES

- 1. F. Rose, J. Chem. Soc., 3448, 1952.
- 2. M. Ishidate, H. Juki, Chem. Pharm. Bul., 8, 131, 1960.
- 3. E. Taylor, E. Garcia, J. Org. Chem., 29, 2121, 1964.

5 October 1964

Ordzhonikidze All-Union Chemical-Pharmaceutical Scientific Research Institute, Moscow