SATURATED NITROGEN-CONTAINING HETEROCYCLES

VI.* ALKYL-2-THIOPYRROLIDONES AND THEIR ACETYL DERIVATIVES

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A number of 5-alkyl-2-thiopyrrolidones and 1-methyl-5-alkyl-2-thiopyrrolidones were synthesized by the reaction of the corresponding pyrrolidones with phosphorus pentasulfide. The 5-alkyl-2-thiopyrrolidones were acylated.

Thioamides are finding broad application as accelerators for the vulcanization of rubber [2] and as corrosion inhibitors for metals [3]. Substances with chemotherapeutic activity [4] have also been detected among thioamides.

The literature contains very little material on the chemistry of thiopyrrolidones, which are cyclic amides of γ-aminothiocarboxylic acids. There is some information regarding the synthesis of only the simplest compounds of this type [5-8].

We accomplished the synthesis of the previously undescribed 5-alkyl-2-thiopyrrolidones (XIII-XVIII) and 1-methyl-5-alkyl-2-thiopyrrolidones (XIX-XXIV) via the method in [7, 8] by heating the corresponding pyrrolidones (I-XII) with phosphorus pentasulfide in a mixture of pyridine and xylene.

The 5-alkyl-2-thiopyrrolidones (XIII-XVIII) (Table 1) are low-melting substances that are quite soluble in methanol and ethanol. The lower homologs are quite soluble in water, but the solubility in water decreases as the size of the alkyl radical increases.

1-Methyl-5-alkyl-2-thiopyrrolidones (XIX-XXIV) (Table 2) were obtained in analogy with the nitrogen-unsubstituted thiopyrrolidones from the corresponding N-methyl-5-alkyl-2-pyrrolidones (VII-XII). Compounds XIX-XXIV are liquids with a characteristic odor and are quite soluble in alcohols.

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*See [1] for communication V.

TABLE 1. 5-Alkyl-2-thiopyrrolidones

Compound	R	Obtained from	Bp, °C (press., mm)	Mp, °C	Empirical formula	Found, %				Calc., %				Yield, %
						C	H	N	S	C	H	N	S	
XIII	C_3H_7	I	164 (2)	—	$C_7H_{13}NS$	58,6	9,1	9,8	22,5	58,8	9,2	9,8	22,4	70
XIV	C_4H_9	II	187 (2)	60—61	$C_8H_{15}NS$	61,3	9,5	8,8	20,3	61,20	9,6	8,9	20,4	75
XV	i-C_4H_9	III	178 (2)	63—64	$C_8H_{15}NS$	61,4	9,6	8,8	20,8	61,20	9,6	8,9	20,4	69
XVI	C_5H_{11}	IV	188 (2)	42—43	$C_9H_{17}NS$	63,4	10,1	8,3	18,2	63,21	10,0	8,2	18,8	76
XVII	i-C_5H_{11}	V	173 (2)	44—45	$C_9H_{17}NS$	63,4	9,8	8,4	18,6	63,21	10,0	8,2	18,8	70
XVIII	C_6H_{13}	VI	161 (2)	61—62	$C_{10}H_{19}NS$	64,4	10,2	7,8	16,9	64,9	10,4	7,6	17,3	62

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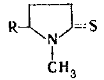
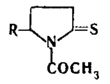
TABLE 2. N-Methyl-5-alkyl-2-thiopyrrolidones



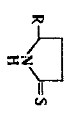
Compound	R	Obtained from	Bp, °C (pressure, mm)	n_D^{20}	Empirical formula	Found, %				Calc., %				Yield, %
						C	H	N	S	C	H	N	S	
XIX	C_3H_7	VII	123—125 (1)	1,5340	$C_8H_{15}NS$	61,4	9,6	8,6	20,8	61,2	9,6	8,9	20,4	80
XX	C_4H_9	VIII	133—136 (1)	1,5310	$C_9H_{17}NS$	63,1	9,9	8,6	18,2	63,2	10,0	8,2	18,8	50
XXI	i-C_4H_9	IX	132—135 (1)	1,5335	$C_9H_{17}NS$	63,4	10,2	8,9	18,6	63,2	10,0	8,2	18,8	65
XXII	C_5H_{11}	X	126—128 (1)	1,5380	$C_{10}H_{19}NS$	64,5	10,1	7,9	17,6	64,9	10,4	7,6	17,3	54
XXIII	i-C_5H_{11}	XI	133—134 (1)	1,5350	$C_{10}H_{19}NS$	64,5	10,3	7,8	17,4	64,9	10,4	7,6	17,3	50
XXIV	C_6H_{13}	XII	144—146 (1)	1,5410	$C_{11}H_{21}NS$	66,9	10,7	7,5	16,4	66,4	10,6	7,0	16,1	66

TABLE 3. N-Acetyl-5-alkyl-2-thiopyrrolidones



Compound	R	Obtained from	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D		Empirical formula	Found, %			Calc., %			Yield, %
						found	calc.		C	H	S	C	H	S	
XXV	C_3H_7	XIII	173—174 (2)	1,0715	1,5222	52,77	52,93	$C_9H_{15}NOS$	58,6	8,8	17,6	58,3	8,2	17,3	75
XXVI	C_4H_9	XIV	192—194 (2)	1,0473	1,5227	58,08	57,55	$C_{10}H_{17}NOS$	60,7	8,7	16,3	60,9	8,7	16,3	74
XXVII	i-C_4H_9	XV	194—195 (2)	1,0509	1,5232	57,59	57,58	$C_{10}H_{17}NOS$	61,0	8,4	16,8	60,9	8,7	16,3	73
XXVIII	C_5H_{11}	XVI	189—191 (2)	1,0425	1,5207	62,26	62,21	$C_{11}H_{19}NOS$	62,1	9,1	15,4	62,0	9,0	15,0	74
XXIX	i-C_5H_{11}	XVII	194—197 (3)	1,0447	1,5203	62,10	62,21	$C_{11}H_{19}NOS$	62,1	9,1	15,0	62,0	9,0	15,0	72
XXX	C_6H_{13}	XVIII	208—210 (3)	1,0319	1,5223	67,21	66,82	$C_{12}H_{21}NOS$	63,7	9,5	14,2	63,49	9,3	14,1	75

The IR spectra of the 5-alkyl-2-thiopyrrolidones contain primary and secondary amide bands at 1537 and 1285 cm^{-1}, which correspond to the stretching vibrations of the $>\text{N}-\overset{|}{\text{C}}=\text{S}$ grouping, and an absorption band at 3100 cm^{-1}, which corresponds to the stretching vibrations of the NH group; i.e., under normal conditions, the 5-alkyl-2-thiopyrrolidones are in the thiolactam form



XIII-XVIII

This is confirmed by the IR spectra of the 4-acetyl derivatives of the thiopyrrolidones, for which the frequency of the stretching vibration of the C=S group remains almost constant (1250 cm^{-1}), and an absorption band, which corresponds to the stretching vibrations of the C=O group, appears at 1700 cm^{-1}.

The 5-alkyl-2-thiopyrrolidones were acetylated by heating them at 90-100° with a twofold excess of acetic anhydride. The N-acetyl-5-alkyl-2-thiopyrrolidones (XXV-XXX) (Table 3) are yellow, mobile liquids with a characteristic odor and are quite soluble in organic solvents.

EXPERIMENTAL

The alkyl-substituted pyrrolidones – 5-propyl- (I), 5-butyl- (II), 5-isobutyl- (III), 5-amyl- (IV), 5-isoamyl- (V), 5-hexyl- (VI), N-methyl-5-propyl- (VII), and N-methyl-5-butyl-5-hexyl- (XII) – were obtained by known methods [9].

5-Propyl-2-thiopyrrolidone (XIII). A 3-g (0.013 mole) sample of phosphorus pentasulfide was added with stirring to a solution of 3 g (0.021 mole) of I in a mixture of 50 ml of anhydrous pyridine and 50 ml of xylene, and the mixture was refluxed at 115-120° for 1.5 h, during which it acquired a dark-red color. It was then cooled and filtered, and the solvent was evaporated. The residue was distilled at reduced pressure (Table 1). The other 5-alkyl-2-thiopyrrolidones (XIV-XVIII) (Table 1) were similarly obtained.

N-Methyl-5-propyl-2-thiopyrrolidone (XIX). Compound XIX (Table 2) was obtained by the reaction of 5 g (0.031 mole) of 1-methyl-5-propyl-2-pyrrolidone with 5 g (0.035 mole) of phosphorus pentasulfide in pyridine–xylene. The other 1-methyl-5-alkyl-2-thiopyrrolidones (XX-XXIV) (Table 2) were similarly obtained.

N-Acetyl-5-propyl-2-thiopyrrolidone (XXV). A 4-g (0.028 mole) sample of 5-propyl-2-thiopyrrolidone (XIII) was dissolved in 6 g (0.058 mole) of acetic anhydride. The mixture was heated at 90-100° for 2-2.5 h with subsequent distillation at reduced pressure to give XXV (Table 3). The other N-acetyl-5-alkyl-2-thiopyrrolidones (XXVI-XXX) (Table 3) were similarly obtained.

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