EXPERIMENTAL

2,2'-Polymethylene bis-(2-thiopseudouronium halides). The various 2,2'-alkylene *bis*-(2-thiopseudouronium halides) were prepared according to the procedure of Yale,[3] utilizing thiourea and the appropriate polymethylene dihalide, and have been previously reported.[4]

2,2'-Polymethylene bis-(2-thiopseudouronium nitrate). Method A. The nitrate salts were prepared from the corresponding isolated, and purified halide salts, by the procedure of Fishbein and Gallaghan[2] utilizing an aqueous solution of silver nitrate. The physical properties of the nitrate salt derivatives are shown in Table I.

Method B. The 2,2'-polymethylene *bis*-(2-thiopseudouronium nitrate) derivatives were prepared according to the method of Lane[5] by reacting thiourea with the corresponding polymethylene dinitrate.

2,2'-Polymethylene bis-(2-thiopseudouronium picrate). The picrate salts were prepared by heating the respective 2,2'-polymethylene *bis*-(2-thiopseudouronium halide) salt with a saturated alcoholic solution of picric acid, the technique being essentially that described by Cheronis.[6] The picrate salt derivatives were recrystallized from 60% ethanol and have been previously reported.[7]

Preparation of 2,2'-polymethylene bis-(1- or 3-nitro-2-thiopseudourea). Method A. Nitration of the nitrate salt. 2,2'-Decamethylene *bis*-(2-thiopseudouronium nitrate) (1.0 g., 0.0024 mole) was added with stirring to 3.5 ml. of concentrated sulfuric acid at 0–5° until the sample dissolved. To this mixture was added 1.7 ml. of fuming nitric acid (98%) at 0–10°. The temperature was allowed to rise to 17°, after which time the mixture was drowned in 15 g. of ice yielding 0.74 g. (81%) of product melting at 139–143°. One crystallization from acetone-alcohol (1:1) raised the m.p. to 145–147°.

Method B. Nitration of the picrate salt. 2,2'-Pentamethylene *bis*-(2-thiopseudouronium picrate) (2 g., 0.0028 mole) was made into a slurry by adding 6 g. of concentrated sulfuric acid at 10–20°; 2 ml. of fuming nitric acid (99%) then was added with stirring. The mixture was allowed to stand at 25° overnight, after which time the slurry was filtered through a sintered glass funnel. Repeated washings, with ether, (5 × 40 ml.), after the removal of the mixed acid filtrate, leached out the picric acid (1.2 g.) and left 0.2 g. of compound on the crucible. The mixed-acid filtrate was treated with 100 ml. of anhydrous ether-alcohol (1:1) causing the precipitation of an additional 0.3 g. of solid product. A total of 0.5 g. (56.2%) of product was collected melting at 145–155°. The crystallization from acetone-alcohol (1:1) raised the m.p. to 164–166°. A mixture melting point with a sample of 2,2'-pentamethylene *bis*-(1- or 3-nitro-2-thiopseudourea) was not depressed. The syntheses of the other 2,2'-polymethylene *bis*-(1- or 3-nitro-2-thiopseudourea) derivatives (Table II) were accomplished utilizing both Methods A and B as described above.

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Reactions of Long-Chain Amines. VI. Preparation of Thioureas*

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A general method of preparing monosubstituted ureas consists of heating the corresponding amine with urea.[1] The similar reaction, that of amines with thiourea, has not been reported as a means of preparing N-monosubstituted thioureas.[2] We have found, however, that it may be conveniently used to prepare N-alkylthioureas from primary long-chain aliphatic amines. Previously, the only route to these thioureas lay through reactions of alkyl isothiocyanates with ammonia.[3–7]

In the present procedure, the amine is heated with an excess of thiourea for a short time at approximately the melting point of thiourea. To avoid decomposition of the alkylthiourea, long reaction times are avoided.

We have also prepared a number of 1,3-disubstituted thioureas by reactions of long-chain amines with alkyl and aryl isothiocyanates. In addition, the preparation of a 1,3-dialkylthiourea from a long-chain amine and carbon disulfide is described.[8]

Yields and properties of all of these products are summarized in Table I.

EXPERIMENTAL

Reagents. The preparation of the long-chain amines has been described.[9] The isothiocyanates were commercial products.

Preparation of alkylthioureas from amine and thiourea (Method A). A mixture of the primary long-chain amine (one mole) and thiourea (two moles) is stirred and heated at 170–180° for 10–15 minutes. As soon as the mixture becomes homogeneous it is cooled rapidly. Recrystallization from benzene, Skellysolve C, or isopropyl alcohol yields the monoalkylthiourea.

From amine and isothiocyanate (Method B). A 10% excess of alkyl or aryl isothiocyanate is added at 25° to a solution of the amine in benzene or toluene. Filtration and recrystallization from benzene yields the pure disubstituted thiourea.

From amine and carbon disulfide (Method C). Carbon disulfide (one mole) is added in portions to a solution of the

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TABLE I

Substituted Alkylthioureas, $RNH\underset{\underset{S}{\|}}{C}NHR'$

R	R′	Method of preparation	Yield, %	M.P., °C.	Analyses Nitrogen Calc'd	Analyses Nitrogen Found
$C_{12}H_{25}$	H	A	45	103–103.8[a]	—	—
$C_{12}H_{25}$	CH_3	B	99	68–69	10.84	10.64
$C_{12}H_{25}$	C_2H_5	B	96	55–56	10.28	10.10
$C_{12}H_{25}$	C_4H_9	B	96	61–63	9.33	9.11
$C_{12}H_{25}$	$C_{12}H_{25}$	C	93	77–78[b]	—	—
$C_{12}H_{25}$	$CH_2{=}CHCH_2$	B	53	56–57.5	9.85	9.72
$C_{12}H_{25}$	C_6H_5	B	79	72–76[c]	—	—
$C_{18}H_{37}$	H	A	73	114.5–115.5	8.53[d]	8.76
$C_{18}H_{37}$	$CH_2{=}CHCH_2$	B	82	79–80.5	7.60	7.39
$C_{18}H_{37}$	C_6H_5	B	79	84–85	6.92	6.75

[a] Reported: m.p. 104–106°,[6] 106–107°.[4] [b] Reported: m.p. 69–70°,[4] 74.5–75°,[8] 76–78°.[6] [c] Reported: m.p. 69.5–69.8°,[8] 73–76°.[6] [d] *Anal.* Calc'd: C, 69.43; H, 12.27. Found: C, 68.89; H, 12.14.

amine (two moles) in toluene. The mixture is heated on the steam-bath overnight, cooled, and filtered to yield the dialkylthiourea.

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The Preparation of Secondary Aliphatic Amines from Schiff Bases Using Lithium Aluminum Hydride

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The preparation of unsymmetrical aliphatic secondary amines from the corresponding Schiff bases by catalytic hydrogenation[1,2] and by reduction with sodium and alcohol[3] has been described.

We have found that comparable yields of these amines are obtained more conveniently by the use of lithium aluminum hydride, which has been reported to reduce also aromatic[4] and alicyclic[5] Schiff bases. This method does not require a hydrogenation apparatus, and the product is easily purified by distillation of an ether filtrate after careful hydrolysis of the reaction measure. A recent paper[6] indicates that sodium borohydride may be equal or superior to lithium aluminum hydride in effecting such reductions as those described here.

The secondary amines which were prepared are listed in Table I, together with the primary amines from which they were derived and the yields which were obtained in single experiments.

TABLE I

Aliphatic Secondary Amines

Amine	Source	Yield, %
Methylbutyl[a]	Methylamine	55
Ethylpropyl	Propylamine	46
Propylbutyl	Propylamine	79
Propylisobutyl	Propylamine	71
Isopropylbutyl	Isopropylamine	72
Isopropylisobutyl[b]	Isopropylamine	78

[a] *α-Naphthylthiourea derivative*, m.p. 104°. *Anal.* Calc'd for $C_{16}H_{20}N_2S$: N, 10.29; Found: N, 10.31. [b] B.p. 110–111°, n_D^{25} 1.3993. *Anal.* Calc'd for $C_7H_{17}N$: N, 12.16; Found: N, 12.24. *α-Naphthylthiourea derivative*, m.p. 110°. *Anal.* Calc'd for $C_{18}H_{24}N_2S$: N, 9.33; Found: N, 9.38. British Patent 602,332, May 25, 1948, gives b.p. 109–112° for this compound prepared by catalytic hydrogenation of a mixture of acetone and isobutylamine.

EXPERIMENTAL

Schiff bases. These were prepared by the method described earlier.[2] Isopropylideneisobutylamine and butylidenemethylamine, which was prepared using 30% aqueous methylamine,[7] have been reported by Tiollais.[3] The Schiff bases were reduced immediately after distillation.

Secondary amines. The aldimine (0.3 mole) was added during one hour to a stirred solution of 11.4 g. (0.3 mole) of lithium aluminum hydride in 500 ml. of anhydrous ether under nitrogen. After another hour the mixture was hy-

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