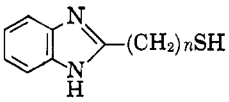
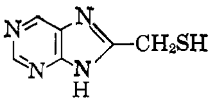


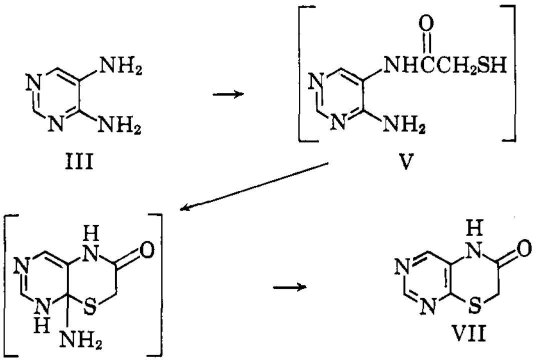
I, $n = 1$

II, $n = 2$



IV

When mercaptoacetic acid was used as reactant and solvent instead of the ester, the isolated product was shown to be not a purine but 5H-pyrimido[4,5-*b*][1,4]-thiazin-6(7H)-one (VII). Assignment of structure was made on the basis of analysis, strong amide carbonyl absorption in the infrared, and ultraviolet absorption dissimilar to that of purine-8-methanol. The formation of VII can be rationalized as a cyclization of the initially formed amide V by addition of —SH to —C(NH$_2$)=N— with loss of ammonia from the unstable intermediate VI. Cyclization resulted in effect from a novel displacement of the C-4 amino group by a mercaptoalkyl group, the more nucleophilic C-5 amino group being favored for amide formation and disfavored for displacement. The 2-amino-4-methyl derivative of this ring system had previously been obtained by acid-catalyzed cyclization of (2,5-diamino-6-methyl-4-pyrimidinylthio)acetic acid.[5]



III

V

VI

VII

Experimental

2-Benzimidazoleethanethiol (II).—A solution of freshly recrystallized *o*-phenylenediamine (2.00 g., 18.5 mmoles) and 3-mercaptopropionic acid (2.00 g., 19.2 mmoles) in 4 *N* hydrochloric acid (20 ml.) was refluxed for 1 hr., allowed to cool somewhat, and treated with decolorizing carbon. The colorless filtrate, diluted with methanol (10 ml.) and chilled to about 5°, was neutralized by the dropwise addition of cold concentrated ammonium hydroxide (8 ml.). The resulting white precipitate was collected and dried *in vacuo* over concentrated sulfuric acid and sodium hydroxide pellets. The crude product (1.88 g.) was extracted with cold 5% sodium hydroxide solution (38 ml.) with minimal exposure to air; addition of glacial acetic acid to the filtrate in the cold precipitated pure II as white crystals, which were collected under nitrogen and dried *in vacuo* over phosphorus pentoxide at 78°: yield 1.58 g. (48%), m.p. 168–169.5°, $\nu_{\max}^{\mathrm{KBr}}$ 2560 cm.$^{-1}$ (SH).

Anal. Calcd. for $C_9H_{10}N_2S$: C, 60.65; H, 5.66; N, 15.72; S, 17.99. Found: C, 60.54; H, 5.74; N, 15.41; S, 18.17.

5H-Pyrimido[4,5-*b*][1,4]thiazin-6(7H)-one (VII).—A solution of 4,5-diaminopyrimidine (2.00 g., 18.2 mmoles) in freshly distilled mercaptoacetic acid (20 ml.) was heated at 148–152° for 2 hr. The resulting red sirup was thoroughly triturated in two 20-ml. portions of benzene, which was removed by decantation. A solution of the residue in 1,2-dimethoxyethane (5 ml.), when stirred, deposited a yellow-tan powder, which was collected by filtration of the cooled mixture with the aid of a little cold methanol. A solution of the crude product in boiling methanol (300 ml.) was treated with decolorizing carbon (1.0 g.), filtered, and concentrated to 200 ml. Slow cooling produced 0.78 g. of colorless crystals, and a second crop of 0.23 g. was obtained from the filtrate concentrated to about 50 ml., yield 33%. For analysis, the combined crops were twice recrystallized from methanol, the final sample being dried *in vacuo* over phosphorus pentoxide at 78°: m.p. 295–300° dec. (capillary in aluminum block, from 260°); $\lambda_{\max}$ in mμ ($\epsilon \times 10^{-3}$), 217 (11.4), 242 (11.1), 302 (5.0), and 333 (sh) at pH 1, 213 (11.8), 242 (13.6), and 300 (6.3) at pH 7, 254 (13.8) and 297 (8.3) at pH 13; $\nu_{\max}^{\mathrm{KBr}}$ 3000–2500 (acidic NH) and 1680 cm.$^{-1}$ (amide CO, strong). The compound was homogeneous on a thin layer chromatogram [silica gel H (Merck), 9:1 $CHCl_3$–CH_3OH] viewed in ultraviolet light after spraying with aqueous Ultraphor solution.

Anal. Calcd. for $C_6H_5N_3OS$: C, 43.10; H, 3.01; N, 25.13; S, 19.18. Found: C, 42.90; H, 3.16; N, 25.12; S, 19.28.

Acknowledgment.—The authors are indebted to Dr. W. J. Barrett and his associates in the Analytical Chemistry Section of Southern Research Institute for the spectra and microanalyses reported.

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[5] F. L. Rose, *J. Chem. Soc.*, 3452 (1952).

The Addition of *t*-Butyl Chloride to Butadiene

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The cationic telomerization of butadiene with aliphatic halides is recorded in the literature[1-3] and has been studied extensively by Petrov and co-workers.[4-7] This reaction may be represented by the following generalized equations. With R = $(CH_3)_3C$– the lower

$$\mathrm{R{-}Cl} + n(\mathrm{CH_2{=}CH{-}CH{=}CH_2}) \longrightarrow \mathrm{R{-}(CH_2CH{=}CH{-}CH_2)_{\mathit{n}}Cl}$$

telomers (n = 1–3) were isolated and identified as straight-chain 1,4-addition compounds.[4,5]

We were particularly interested in getting high yields of pure 1-chloro-5,5-dimethyl-2-hexene, but none of the reported procedures appeared to be satisfactory. With the object of avoiding the formation of higher telomers, the influence of all reaction parameters, *i.e.*, catalyst, cocatalyst, temperature, time, and reactants ratio, on the conversion of starting materials and on the yields of chlorooctene and chlorododecadiene was investigated.

As may be seen from the results summarized in Table I, the telomerization of *t*-butyl chloride with butadiene was catalyzed by a number of Friedel–Crafts-type halides. Only mercuric chloride, antimony pentachloride, and antimony trichloride failed to show any efficiency.

The highest proportion of 1-chloro-5,5-dimethyl-2-hexene was obtained when zinc chloride and bismuth chloride were used as catalysts. Furthermore, it was found in two more experimental series not reported here in detail, that in order to obtain a good conversion, an amount of 0.9% (based on total weight of

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(1) I. G. Farben Ind., French Patent 824,909 (1938).

(2) W. H. Peterson and K. D. Detling, U. S. Patent 2,419,500 (1947).

(3) W. D. Niederhauser, U. S. Patent 2,689,873 (1954).

(4) A. A. Petrov and K. V. Leets, *Dokl. Akad. Nauk SSSR*, **95**, 285 (1954).

(5) A. A. Petrov and K. V. Leets, *Zh. Obshch. Khim.*, **26**, 1113 (1956).

(6) A. A. Petrov and T. V. Yakovleva, *Izv. Akad. Nauk SSSR Ser. Fiz.*, **23**, 1217 (1959).

(7) A. A. Petrov and Z. N. Kolyaskina, *Zh. Obshch. Khim.*, **30**, 1450 (1960)

TABLE I

TELOMERIZATION OF *t*-BUTYL CHLORIDE WITH BUTADIENE[a]

Cat.	Yield of products, % $n = 1$	$n = 2$	$n > 2$	Reactants conversion, %
$HClO_4$	..	..	100	21
$TiCl_4$	1	38	61	30
$AlCl_3$	9	6	85	60
$SnCl_4$	13	6	81	59
$ZnCl_2$	58	19	23	37
$BiCl_3$	60	22	18	64

[a] In these experiments, 0.45 mole of *t*-butyl chloride and 0.3 mole of butadiene in the presence of 0.5 g. of the halide catalyst were shaken for 5 days in pressure bottles at 20–25°.

reactants) zinc chloride or bismuth chloride and a reaction time of 120–130 hr. were necessary. A reaction time of more than 130 hr. at 20–25°, apart from being impractical, did not raise the conversion.

It has already been stated in the literature,[4,5] that concentrated hydrochloric acid suppresses the formation of high telomers. This is shown for the two most effective catalysts ($ZnCl_2$ and $BiCl_3$) in Table II.

TABLE II

INFLUENCE OF CONCENTRATED AQUEOUS HYDROCHLORIC ACID ON THE TELOMERIZATION OF *t*-BUTYL CHLORIDE AND BUTADIENE CATALYZED BY ZINC CHLORIDE AND BISMUTH TRICHLORIDE[a]

Cat.	Concd. HCl, ml.	Yield of products, % $n = 1$	$n = 2$	$n > 1$	$n > 2$	Reactants conversion, %
$ZnCl_2$	...	58	...	42	...	37
$ZnCl_2$	0.1	86	...	14	...	11
$ZnCl_2$	0.2	85	...	15	...	8
$ZnCl_2$	0.3	86	...	14	...	2
$ZnCl_2$	0.4	...	...	...	...	..
$BiCl_3$	...	60	22	...	18	64
$BiCl_3$	0.05	61	18	...	21	64
$BiCl_3$	0.1	62	19	...	19	60
$BiCl_3$	0.2	82	14	...	4	46
$BiCl_3$	0.3	83	13	...	4	38
$BiCl_3$	1.2[b]	80.5	12.9	...	2.9	51

[a] In these experiments, 0.45 mole of *t*-butyl chloride and 0.3 mole of butadiene were shaken in the presence of 0.5 g. of the halide catalyst at 20–25° for 120 hr. [b] See large-scale preparation in the Experimental part.

In both reactions, 1-chloro-5,5-dimethyl-2-hexene can be prepared in 80–85% yield. However, in the zinc chloride catalyzed reaction, this is only possible at a conversion of 11%, compared with a 40–50% conversion in the case of $BiCl_3$. It is evident from the results of Table II that, for the preparation of the lower telomers, $BiCl_3$ is the catalyst of choice. The influence of different *t*-butyl chloride–butadiene molar ratios on the telomer distribution in telomerizations catalyzed by $BiCl_3$ and aqueous HCl (in amounts of 0.9 and 0.2%, respectively, based on the total weight of reactants) is shown in Table III.

TABLE III

CONDENSATION OF *t*-BUTYL CHLORIDE AND BUTADIENE

Molar ratio[a]	Yield of products, % $n = 1$	$n = 2$	$n > 2$	Reactants conversion, %
1:2	34	23	43	89
1:1.5	39	19	42	84
1:1	59	21	20	78
1:0.63[b]	81	15	4	63
1:0.4	93	5	2	40

[a] Molar ratios of *t*-butyl chloride to butadiene. [b] See ref. 4.

From these results it may be seen that favorable conditions for the preparation of 1-chloro-5,5-dimethyl-2-hexene exist when the molar ratio of *t*-butyl chloride to butadiene lies in the range of 1.6 to 2.2.

The last reaction parameter investigated was the effect of temperature on the *t*-butyl chloride–butadiene conversions and telomer distribution. It was found that at 40° the results shown in Table II could be obtained after only 15–17 hr. The telomer distribution remained almost unaltered, as can be seen from an optimized up-scaled run described in the Experimental part.

The chlorooctene and chlorododecadiene obtained in this telomerization process are all-*trans* compounds as evidenced by their infrared spectra.

Experimental

A. **Small-Scale Runs.**—A 250-ml. glass pressure bottle was cooled to −10°, filled with the required amounts of reactants and catalysts, and shaken at room temperature for a certain number of hours. Excess butadiene was vented off and the brown liquid was decanted into water; the mixture was well shaken, the organic layer was washed until neutral with water, separated, dried with calcium chloride, and distilled. 1-Chloro-5,5-dimethyl-2-hexene distilled at 65–68° (25 mm.), n^{20}_{D} 1.4447 (lit.[4] b.p. 46–47° at 10 mm., n^{20}_{D} 1.4456). The remaining higher boiling material consisted of chlorododecadiene distilling at 55–57° (0.1 mm.), n^{20}_{D} 1.4658 (lit.[5] 68–73° at 2.5 mm., n^{20}_{D} 1.4643) and higher telomers.

B. **Large-Scale Preparation.**—A mixture of 440 g. (4.75 moles) of redistilled *t*-butyl chloride, 162 g. (3 moles) of butadiene, 5.4 g. of bismuth chloride, and 1.2 ml. of concentrated aqueous HCl was charged in a glass autoclave. The reaction mixture was heated to 40° and stirred at this temperature for 15 hr. At this point the manometer showed that the pressure in the reaction vessel had fallen to 1 atm. or less. The crude reaction mixture was neutralized with diethylamine and distilled over a 50-cm. Vigreux column. After a forerun of unreacted *t*-butyl chloride and dissolved butadiene, 1-chloro-5,5-dimethyl-2-hexene distilled at 65–68° (25 mm.) to give 306 g. (80.5% yield at 51% conversion) of a pure product; chlorododecadiene distilled at 55–57° (0.1 mm.) to give 49 g. (12.9% yield), followed by a small amount of higher boiling material (b.p. 60–120° at 0.1 mm.), 11 g., corresponding to a 2.9% yield.

Pyridines from Cyanogen-Like Compounds and Unsymmetrical Dienes[1]

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The synthesis of pyridines at 350–450° by the thermally initiated reaction of cyanogen-like compounds with 1,3-butadiene was reported in the preceding paper.[3] With unsymmetrical dienes, a route to a series of new pyridines is apparent; the relative amounts of the isomeric pyridines from each unsymmetrical

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[1] Abstracted in part from a thesis submitted by A. R. Monahan to Rensselaer Polytechnic Institute in partial fulfillment of the requirements for the Ph.D. degree, Aug. 1964.

[2] Union Carbide Fellow in Chemistry, 1963–1964.

[3] G. J. Janz and A. R. Monahan, *J. Org. Chem.*, **29**, 569 (1964).