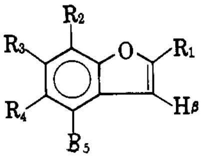
TABLE II.—BENZOFURAN DERIVATIVES WITH ONE FURAN HYDROGEN



Compd.					Band, cm.$^{-1}$,
R_1	R_2	R_3	R_4	R_5	Hβ
$COCH_3$	H	H	H	H^a	1135 (s)
$COOCH_3$	H	H	H	H	1143 (ms)
$COOCH_3$	H	H	OH	H^b	1152 (ms)
$COOCH_3$	H	H	OCH_3	H^b	1152 (ms)
$COOCH_3$	H	H	NH_2	H^c	1157 (s)
$COOCH_3$	H	H	$NHCOCH_3$	H^c	1152 (s)
$COOCH_3$	H	H	$COCH_3$	H^c	1126 (m)
$COOCH_3$	H	H	$C(CH_3)=NOH$	H^c	1163 (s)
$COOCH_3$	H	H	Cl	H^c	1122 (w)
COOH	H	H	C_2H_5	H^c	1142 (ms)
$CH(CH_3)_2$	H	H	$COCH_3$	H^c	1152 (ms)
$COH(CH_3)_2$	H	H	Cyclic ketal of $COCH_3$	H^c	1152 (ms)
$COOCH_3$	H	H	OH	$C_2H_5{}^b$	1152 (m) or 1131 (m)
$COOCH_3$	H	H	OH	$COCH_3{}^b$	1129 (m)
$C=CH_2CH_3$	H	OH	CONH	H^c	1142 (s)
$COOCH_3$	H	$OOCCH_3$	$COCH_3$	H^c	1136 (s)
$COOCH_3$	H	OH	Cyclic ketal of $COCH_3$	$H^{c,d}$	1156 (m) or 1129 (m)
$COOCH_3$	OCH_3	OCH_3	H	$H^{d,e}$	1165 (m) or 1135 (m)
$COOCH_3$	$COOCH_3$	H	H	$OCH_3{}^b$	1143 (m)
$COOCH_3$	NH_2	H	H	$OCH_3{}^b$	1172 (ms)
COOH	OH	H	H	$COCH_3{}^{b,f}$	1135 (s)
$COOCH_3$	$COCH_3$	H	C_2H_5	H^c	1136 (ms)
$COOCH_3$	OCH_3	H	NO_2	H^g	1125 (m)
$COOCH_3$	OCH_3	OCH_3	H	$OCH_3{}^{d,e}$	1149 (ms)
$COOCH_3$	OCH_3	OCH_3	H	$NH_2{}^g$	1157 (s)
$COOCH_3$	OCH_3	OCH_3	H	$NHCOCH_3{}^g$	1149 (s)
$COOCH_3$	OCH_3	OCH_3	H	$COCH_3{}^g$	1125 (s)
$COOCH_3$	OCH_3	OCH_3	H	$C(CH_3)=NOH^g$	1121 (s)
$COCH_3$	OH	OCH_3	OCH_3	H^h	1130 (s)
$COCH_3$	$OOCCH_3$	OCH_3	OCH_3	H^h	1134 (s)
$COCH_3$	OCH_3	OCH_3	OCH_3	H^h	1130 (s)
$COOCH_3$	OH	OCH_3	$COCH_3$	OH^e	1135 (s)
$COOCH_3$	$OOCCH_3$	OCH_3	$COCH_3$	OH^e	1149 (s)
$COOCH_3$	$OOCCH_3$	OCH_3	$COCH_3$	$OOCCH_3{}^e$	1138 (s)
COOH	OCH_3	OCH_3	$COCH_3$	$OCH_3{}^e$	1152 (s)
COOH	OCH_3	OCH_3	Br	$OCH_3{}^e$	1136 (s)
COOH	OCH_3	OCH_3	CH_3	$OCH_3{}^e$	1121 (s)
$COOCH_3$	OCH_3	OCH_3	CH_3	$OCH_3{}^{d,e}$	1150 (s)
$COCH_3$	$OOCCH_3$	OCH_3	$OOCCH_3$	$COCH_3{}^h$	1127 (m)
$COCH_2COCH_3$	$OOCCH_3$	OCH_3	$OOCCH_3$	$COCH_3{}^h$	1130 (m)

[a] J. I. Degraw and W. A. Bonner, *Tetrahedron*, **18**, 1295 (1962). [b] Footnote *a*, Table I. [c] Footnote *c*, Table I. [d] Spectrum run in carbon tetrachloride. [e] Footnote *e*, Table I. [f] Spectrum run as Nujol mull. [g] Footnote *b*, Table I. [h] Footnote *d*, Table I.

otherwise indicated. The preparation of the compounds listed in Tables I and II as previously unreported will be the subject of a later communication.

5H-Pyrimido[4,5-*b*][1,4]thiazin-6(7H)-one. The Product of a Novel Cyclization Reaction[1]

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Heteroaromatic-substituted alkanethiols, such as 2-benzimidazolemethanethiol (I), became of interest in a search for an effective heterocyclic modification of 2-aminoethanethiol as an antiradiation drug.[2] The reported[3] synthesis of I by the acid-catalyzed condensation of *o*-phenylenediamine and mercaptoacetic acid provided a good method for the synthesis of 2-benzimidazoleethanethiol (II) by a similar condensation in which 3-mercaptopropionic acid was used. The insolubility of 4,5-diaminopyrimidine (III) in ethyl mercaptoacetate, however, precluded the condensation expected to give the analogous purine-8-methanethiol (IV) under conditions suggested by Albert's synthesis of purine-8-methanol from III and ethyl glycolate.[4]

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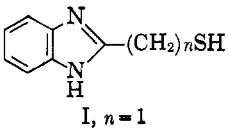
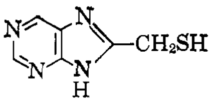
[1] This investigation was supported by the U. S. Army Medical Research and Development Command under Contract No. DA-49-193-MD-2028.

[2] (a) T. P. Johnston and A. Gallagher, *J. Org. Chem.*, **27**, 2452 (1962); (b) J. R. Piper and T. P. Johnston, *ibid.*, **28**, 981 (1963); (c) T. P. Johnston and A. Gallagher, *ibid.*, **28**, 1305 (1963).

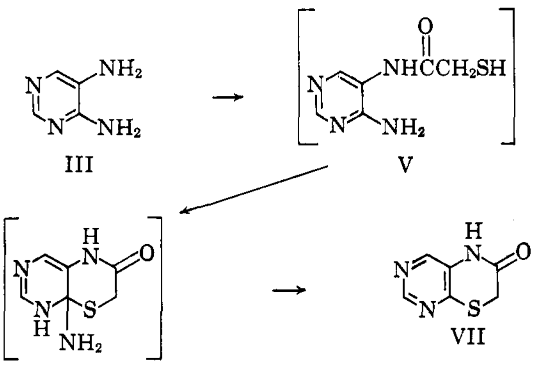
[3] G. K. Hughes and F. Lions, *J. Proc. Roy. Soc. N. S. Wales*, **71**, 209 (1938); *Chem. Abstr.*, **32**, 5830 (1938).

[4] A. Albert, *J. Chem. Soc.*, 2690 (1955).


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

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

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)