isothiourea hydrochloride in 300 ml. of 95% ethyl alcohol was added 28 g. (0.50 mole) of potassium hydroxide in approximately 50 ml. of water. The resulting mixture was allowed to stand for twenty-four hours at room temperature. Then the solvent was removed under reduced pressure on the steam-bath and water was added to dissolve the inorganic salts. On acidification of this solution with dilute hydrochloric acid, a semi-solid precipitate was formed. When this suspension was shaken with ether, the precipitate became crystalline. It was separated by filtration and was washed with water and ether. This product, m. p. 130–135°, weighed 23 g. but contained an insoluble impurity (which we could not recrystallize). The 2-benzylthio-4-benzylthiomethyl-6-hydroxypyrimidine was dissolved in hot ethyl alcohol and separated from the insoluble material by filtration. When cooled, the alcoholic filtrate deposited 17.5 g. of the pyrimidine, II, m. p. 140–144°. An additional 2 g. of product, m. p. 140–145°, was obtained by extraction of the preceding ether solution with 10% aqueous sodium hydroxide and acidification of the basic extract. Crystallization of the combined 19.5 g. (44.6%) of product from ethyl alcohol gave 18.2 g. (41.1%) of the pyrimidine, m. p. 144–147°. Further crystallization of the compound readily raised the melting point to 146–147°.

Anal. Calcd. for $C_{19}H_{18}N_2OS_2$: C, 64.40; H, 5.12; N, 7.97. Found: C, 64.46; H, 5.31; N, 7.99.

A small quantity (3.1 g.) of crude dibenzyl disulfide, m. p. 63–66°, was isolated from the ether extract.

2,6-Dihydroxy-4-benzylthiomethylpyrimidine (III).—A solution of 9.7 g. (0.027 mole) of 2-benzylthio-4-benzylthiomethyl-6-hydroxypyrimidine in 138.5 ml. of glacial acetic acid and 41.5 ml. of 20% hydrochloric acid was heated on the steam-bath for two and one-half hours, then cooled and neutralized with dilute ammonium hydroxide. The fine white crystals were separated by filtration; they weighed 6.8 g. (100%), m. p. 174–177°. Two crystallizations from ethyl alcohol gave 6.7 g. (98.7%) of 2,6-dihydroxy-4-benzylthiomethylpyrimidine, m. p. 182–183°. Further crystallization of the compound raised the melting point to 183–184°.

Anal. Calcd. for $C_{12}H_{12}N_2O_2S$: C, 58.06; H, 4.88; N, 11.28. Found: C, 58.42; H, 5.18; N, 10.83.

4-Methyl-6-hydroxypyrimidine.—To a solution of 4 g. of 2-benzylthio-4-benzylthiomethyl-6-hydroxypyrimidine dissolved in 60 ml. of water containing 0.60 g. of sodium hydroxide was added 55 ml. of Raney nickel suspension containing 55 g. of Raney nickel. The suspension was heated at 70–80° with vigorous stirring for one hour. The suspension was filtered and the residue washed with water. The filtrate was made neutral with dilute hydrochloric acid and the solution was evaporated on the steam-bath. The residue, after vacuum sublimation and crystallization of the sublimate from ethyl acetate, yielded 0.60 g. (48%) of 4-methyl-6-hydroxypyrimidine, m. p. 141–146°. Two crystallizations of the product from ethyl acetate raised its melting point to 148–149°. The compound is reported[10] to melt at 149–150°.

Anal. Calcd. for $C_5H_6N_2O$: C, 54.54; H, 5.45; N, 25.45. Found: C, 54.51; H, 5.74; N, 25.45.

2-Methylthio-4-methylthiomethyl-6-hydroxypyrimidine (IV).—To a suspension of 92.3 g. (0.333 mole) of S-methylisothiourea sulfate in 750 ml. of ethyl alcohol was added 69.7 g. (0.333 mole) of ethyl γ-bromoacetoacetate. Then 74.5 g. (1.33 mole) of potassium hydroxide in 200 ml. of water was added slowly with vigorous stirring; the stirring was continued at room temperature for three hours. The resulting suspension was allowed to stand for sixteen hours. The product was isolated in a manner similar to that described for compound II. Crystallization of the crude material from ethyl acetate yielded 14.2 g. (21.3%) of 2-methylthio-4-methylthiomethyl-6-hydroxypyrimidine, m. p. 147–149°. Several crystallizations of the product from ethyl acetate raised the melting point to 149.5–150.5°.

(10) Gabriel and Colman, *Ber.*, **32**, 2921 (1899).

Anal. Calcd. for $C_7H_{10}N_2OS_2$: C, 41.55; H, 4.98; N, 13.85. Found: C, 41.93, 41.69; H, 5.15, 4.84; N, 13.74.

2,6-Dihydroxy-4-methylthiomethylpyrimidine (V).—Hydrolysis of compound IV with 20% hydrochloric acid with or without the addition of glacial acetic acid gave 2,6-dihydroxy-4-methylthiomethylpyrimidine, m. p. 221–222°, in 65–70% yield. The product is easily crystallized from water.

Anal. Calcd. for $C_6H_8N_2O_2S$: C, 41.85; H, 4.68; N, 16.27. Found: C, 41.71, 41.57; H, 4.90, 5.06; N, 16.57.

2-Benzylthio-4-methyl-6-hydroxypyrimidine was prepared from 25.2 g. (0.125 mole) of S-benzylisothiourea hydrochloride and 16.25 g. (0.125 mole) of acetoacetic ester by a procedure similar to that used by Johns[11] for the preparation of 2-ethylthio-4-methyl-6-hydroxypyrimidine. After crystallization of the compound from alcohol, 8.0 g. (28%) of white, needle-like crystals, m. p. 176–178°, was obtained. A second crystallization from alcohol gave 7.0 g. (24%) of the pyrimidine, m. p. 176–178°.

Anal. Calcd. for $C_{12}H_{12}N_2OS$: C, 62.06; H, 5.17; N, 12.06. Found: C, 62.36; H, 5.35; N, 12.35.

The Reaction of Ethyl α-Bromoacetoacetate with S-Benzylisothiourea.—A solution of 26.2 g. (0.125 mole) of ethyl α-bromoacetoacetate and 50.6 g. (0.250 mole) of S-benzylisothiourea hydrochloride in 300 ml. of alcohol was treated with a solution of 28 g. (0.5 mole) of potassium hydroxide in 20 ml. of water. The resulting mixture was allowed to stand overnight. The precipitate which formed during this time was separated by filtration and washed well with water. Crystallization of this precipitate from dilute alcohol gave 20 g. (68%) of dibenzyl disulfide, m. p. 71°. A mixture with an authentic sample of dibenzyl disulfide[2] showed no depression in melting point.

The alcohol was distilled from the filtrate of the reaction mixture and the solution remaining was acidified with two normal hydrochloric acid. The oil which separated solidified on standing. It was crystallized from ethyl acetate to yield 8.0 g. (28%) of crude 2-benzylthio-4-methyl-6-hydroxypyrimidine, m. p. 160–170°. Several recrystallizations from dilute alcohol and from benzene gave 3.0 g. (10%) of the pure pyrimidine, m. p. 176–178°. A mixture with the 2-benzylthio-4-methyl-6-hydroxypyrimidine prepared above showed no depression in melting point.

(11) C. O. Johns, *Am. Chem. J.*, **40**, 348 (1908).

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Derivatives of 6-Methyl-5,6-dihydrophenanthridine

BY JACOB FINKELSTEIN AND SEYMOUR LINDER

During a study of synthetic anti-histaminics in 1945, recognizing the structural relationship between Antergan and 5,6-dihydrophenanthridine, it was decided to prepare N-substituted derivatives of the latter. Since the compounds were devoid of the desired pharmacological action, no further interest was developed. In view of the recent note by Huttrer[1] describing the 5,6-dihydrophenanthridine compound analogous to Antergan, we wish to record the preparation of 6-methyl-5,6-dihydrophenanthridine and a few N-derivatives (as well as a few chemical reactions of 6-methylphenanthridine).

Prior to Huttrer's note,[1] no catalytic reduction studies on the phenanthridine ring were reported.

(1) Huttrer, THIS JOURNAL, **71**, 4147 (1949).

Ritchie[2] was able to reduce 6-methylphenanthridine to its dihydro derivative with tin and hydrochloric acid in the same manner that Pictet and Ankersmit[3] reduced phenanthridine. Using catalytic reduction, it was found that under moderately low pressures at room temperature in the presence of platinum, 6-methylphenanthridine is readily reduced to its dihydro derivatives. The 6-methyl-5,6-dihydrophenanthridine was characterized by the preparation of its toluenesulfonamide.

If the reduction is carried out in acetic acid at 100° and 1000 lb. pressure, 6-methyloctahydrophenanthridine is obtained. This substance is a colorless crystalline compound melting at 57–58°, sublimes *in vacuo* at 110°, and forms a picrate. Tentatively, it is assumed that the ring vicinal to the nitrogen atom is reduced. In this connection it was interesting to observe that Albert, Brown and Duell[4] obtained hexahydrophenanthridine upon reduction of phenanthridone with sodium amalgam at 85° under carbon dioxide.

Following the procedure employed by Pictet and Patry[5] for the N-alkylation of 5,6-dihydrophenanthridine, the alkylation of 6-methyl-5,6-dihydrophenanthridine goes easily. On heating β-diethylaminoethyl chloride with the dihydro compound at 100°, 5-(β-diethylaminoethyl)-6-methyl-5,6-dihydrophenanthridine was obtained. For simple N-alkylations it was found that the preparation of a 5,6-dihydrophenanthridine was unnecessary. For example, 5-ethyl-6-methyl-5,6-dihydrophenanthridine was obtained by first preparing the ethyl *p*-toluenesulfonate quaternary salt followed by hydrogenation.

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Experimental

6-Methylphenanthridine can be obtained readily by the elegant method of Morgan and Walls[6] by dehydrating acetyl-*o*-xenylamine.

5-*p*-Toluenesulfonamido-6-methyl-5,6-dihydrophenanthridine.—A solution of 5 g. of 6-methylphenanthridine in 25 cc. of alcohol was reduced under 350 lb. pressure in the presence of platinum oxide. The initial drop in pressure was rapid and gradually slowed down until the reduction was completed. After filtering off the catalyst, the alcohol was removed by distillation and the residue treated with *p*-toluenesulfonyl chloride in aqueous alkali in the usual manner. The sulfonamide was purified by recrystallization from alcohol, m. p. 166–168°.

Anal. Calcd. for $C_{21}H_{19}NSO_2$: C, 72.18; H, 5.48; N, 4.01. Found: C, 72.16; H, 5.80; N, 4.00.

6-Methyloctahydrophenanthridine.—A solution of 20 g. of 6-methylphenanthridine in 55 cc. of acetic acid was hydrogenated at 100° and 1000 lb. pressure in the presence of platinum to completion. Approximately four moles of hydrogen were absorbed. After filtering and diluting with water, the solution was concentrated to a small volume *in vacuo* under nitrogen. Upon making alkaline with dilute sodium hydroxide, a precipitate was obtained. After purification by sublimation *in vacuo* at 110°, the product was obtained as long, colorless needles, m. p. 57–58°.

Anal. Calcd. for $C_{14}H_{19}N$: C, 83.55; H, 9.51; N, 6.95. Found: C, 83.17; H, 9.53; N, 6.92.

The picrate was prepared and recrystallized from hot methanol–butyl ether mixture, m. p. 137–138°.

Anal. Calcd. for $C_{14}H_{19}N\cdot C_6H_2OH(NO_2)_3$: C, 55.80; H, 5.16; N, 13.01. Found: C, 55.69; H, 5.02; N, 13.14.

5-(β-Diethylaminoethyl)-6-methyl-5,6-dihydrophenanthridine.—A mixture of 5 g. of 6-methyl-5,6-dihydrophenanthridine and 4 g. of β-diethylaminoethyl chloride was heated in a sealed tube at 100° for five hours. After cooling, dilute hydrochloric acid was added, and the unreacted phenanthridine was removed as its insoluble hydrochloride. The filtrate was made alkaline, and the resultant oil was extracted with ether and dried over potassium hydroxide. The dried ethereal solution was saturated with dry hydrogen chloride to obtain the salt; yield, 4 g. The compound was recrystallized from dioxane and dried *in vacuo* at 110°, m. p. 186–187°.

Anal. Calcd. for $C_{20}H_{26}N_2\cdot HCl\cdot{}^1/_2H_2O$: C, 70.67; H, 8.25; N, 8.24. Found: C, 70.43; H, 7.82; N, 8.49.

5-Ethyl-6-methyl-5,6-dihydrophenanthridine.—A mixture of 10 g. of 6-methylphenanthridine and 11 g. of ethyl *p*-toluenesulfonate was heated at 100° for three days. The melt was dissolved in 65 cc. of methanol and hydrogenated at room temperature under 1000 lb. pressure in the presence of platinum until one equivalent of hydrogen was absorbed. The methanol was removed by distillation and the residue treated with dilute sodium hydroxide. The precipitate was extracted with ether, dried, and the solution saturated with dry hydrogen chloride to produce the colorless hydrochloride; yield, 7.5 g. A small amount of 6-methylphenanthridine was separated when recrystallization from alcohol–ether was attempted. After removal, the alcohol–ether filtrate was concentrated and the residue made alkaline with ammonia. The oil was then extracted with ether, dried over potassium hydroxide, and saturated with hydrogen chloride. The hydrochloride now obtained was recrystallized from ethyl acetate–ether mixture, m. p. 148–149°.

Anal. Calcd. for $C_{16}H_{17}N\cdot HCl$: C, 73.98; H, 6.99; N, 5.39. Found: C, 73.70; H, 7.09; N, 5.21.

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(2) Ritchie, *J. Proc. R. S. N. S. W.*, **78**, 184 (1945).
(3) Pictet and Ankersmit, *Ber.*, **22**, 3339 (1889).
(4) Albert, Brown and Duell, *J. Chem. Soc.*, 1284 (1948).
(5) Pictet and Patry, *Ber.*, **35**, 2535 (1902).
(6) Morgan and Walls, *J. Chem. Soc.*, 2447 (1931).

Free-Radical Initiated Dimerizations

BY CHARLES E. FRANK AND ANGUS U. BLACKHAM[1]

A number of unsaturated compounds have been reported to yield largely dimers rather than higher molecular weight products when subjected to conditions favoring polymerization. Compounds of this type include methallyl chloride,[2] trichloroethylene[3a] and *sym*-dichloroethylene.[3b] Wilzbach, Mayo and Van Meter[4] recently determined the structure of methallyl chloride dimer, and suggested the following mechanism to account for the selective formation of this product.

(1) Abstracted from the thesis of A. U. Blackham submitted in partial fulfillment of the requirements for the M.S. degree at the University of Cincinnati. Presented at the Philadelphia Meeting of the A. C. S., April, 1950.
(2) Bauer and Gotz, U. S. Patent 2,338,893.
(3) (a) Mugden and Wimmer, U. S. Patent 2,161,078; (b) Bauer, U. S. Patent 2,267,712.
(4) Wilzbach, Mayo and Van Meter, THIS JOURNAL, **70**, 4069 (1948).