TABLE II

OXAZOLONE ADDITION PRODUCTS (VIII, X); ADDITION PRODUCTS (XII) OF 2-PHENYL-3,1-BENZOXAZ-4-ONE

Compound	Thil. R =	M.p.,[a] °C.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
VIIIa	C_6H_5	156	42	$C_{28}H_{23}NO_2S_2$	71.6	71.5	4.9	4.7	2.9	2.8	13.6	13.5
	$C_6H_4CH_3$-*p*	159	37	$C_{30}H_{27}NO_2S_2$	72.4	72.1	5.4	5.3	2.8	2.7	12.9	12.7
X	C_6H_5	234	88	$C_{50}H_{40}N_2O_4S_4$	69.8	69.6	4.6	4.5	3.3	3.1	14.9	14.7
	$C_6H_4CH_3$-*o*	229	71	$C_{54}H_{48}N_2O_4S_4$	70.7	70.6	5.2	5.2	3.1	3.0	14.0	13.9
	$C_6H_4CH_3$-*m*	181	69			70.7		5.0		2.9		13.7
	$C_6H_4CH_3$-*p*	232	86			70.4		5.0		2.8		14.0
XII	C_6H_5	169–170	33	$C_{20}H_{15}NO_2S$	72.1	71.9	4.5	4.4	4.2	4.1	9.6	9.4
	$C_6H_4CH_3$-*p*	124–125	15	$C_{21}H_{17}NO_2S$	72.6	72.5	4.9	4.7	4.0	3.8	9.2	9.0
	C_6H_5[b]	160–161	33	$C_{20}H_{15}NO_3$	75.7	75.5	4.7	4.5	4.4	4.4		

[a] Melting points are uncorrected. [b] Prepared from XI and phenol.

B. Terephthalylidene-bis-(2-phenyl-5-oxazolone) (IX)[17] and 2-Phenyl-3,1-benzoxaz-4-one (XI).[18]—The reactions between IX or XI and the thiols were carried out by substantially the procedure described under A(2).[19] N-Benzoylphenylanthranilate was prepared from XI and phenol.

The corresponding reaction products X and XII which were obtained as colorless crystals are listed in Table II. The derivatives of IX are easily soluble in benzene and alcohol, difficultly soluble in light petroleum, and insoluble in cold aqueous sodium hydroxide (10%); they give an orange color with concentrated sulfuric acid on standing. The derivatives of XI, N-benzoylmonophenyl- and N-benzoylmono-*p*-tolyl thioanthranilates (XIIa, b), are soluble in chloroform and benzene, but sparingly soluble in light petroleum; they give a yellow color with concentrated sulfuric acid.

C. Benzoxaz- (XIIIa) and N-Benzoylbenzoxaz-2-one (XIIIb).—XIIIa[20] or XIIIb,[21] heated with thiophenol and piperidine, was recovered almost unchanged.

Hydrolysis of Addition Products (VIIIb, X and XII).—A solution of 1 g. of VIIIb in 30 ml. of alcoholic potassium hydroxide (10%) was refluxed for a half-hour (water-bath). After cooling, the reaction mixture was poured onto crushed ice and acidified with dilute hydrochloric acid. The resulting solid was collected, washed with water and treated with carbonate solution. After recrystallization from light petroleum, the insoluble fraction gave colorless crystals, yield *ca.* 0.13 g., m.p. 43°, which were identified as *p*-thiocresol (m.p. and mixed m.p. and formation of a yellow lead salt). The carbonate solution, on acidification, gave colorless crystals which upon recrystallization from alcohol melted at 225°; they were identified as α-benzamidocinnamic acid (m.p. and mixed m.p.[22]). The acid, on boiling with acetic anhydride, was converted readily to the original oxazolone (VI) (m.p. and mixed m.p.).

X (R = $C_6H_4CH_3$-*p*) yielded *p*-thiocresol and an acid which could not be crystallized, but which was converted to the original oxazolone IX by acetic anhydride (m.p. and mixed m.p.). XIIa yielded colorless crystals which were identified as N-benzoylanthranilic acid (m.p. and mixed m.p.),[23] yield 89%, m.p. 180–181°. N-Benzoylanthranilate, prepared from XI and phenol, was hydrolyzed to the acid.

(17) P. Ruggli and O. Schetty, *Helv. Chim. Acta*, **23**, 721 (1940).

(18) G. Heller and G. Fiesselmann, *Ann.*, **324**, 118 (1902).

(19) XI and thiophenol were heated for 3 hours over a steam-bath without piperidine; the same reaction product in almost quantitative yield was obtained in the presence of piperidine with a heating period of a half-hour. The reaction of XI and *p*-thiocresol was carried out in the presence of piperidine.

(20) H. Lindemann and W. Schultheis, *Ann.*, **451**, 253 (1927).

(21) E. von Meyer, *J. prakt. Chem.*, **92**, 257 (1915).

(22) E. Erlenmeyer, *Ber.*, **33**, 2036 (1900).

(23) von A. Brüchner, *Ann.*, **113**, 205 (1890).

GIZA, CAIRO, EGYPT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Studies in the 10-Ethylphenothiazine System: Reductive Halogenation and N-Ethylation

BY HENRY GILMAN AND JOHN EISCH

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The action of hydrohalic acids on 10-ethylphenothiazine-5-oxide was studied. With hydrochloric acid 3-chloro-10-ethylphenothiazine was obtained in improved yield. Hydrobromic acid gave a compound which was shown to be 3-bromo-10-ethylphenothiazine; hydriodic acid produced 10-ethylphenothiazine and a salt of 10-ethylphenothiazine-5-oxide and hydriodic acid. That the mechanism of this reaction involves reduction of the sulfoxide group and electrophilic attack of free halogen was shown by the isolation of *p*-bromophenol from the interaction of hydrobromic acid and 10-ethylphenothiazine-5-oxide in the presence of phenol. The N-ethylation of phenothiazine-5-oxide was accomplished in low yield and phenothiazine-5-dioxide underwent no discernible ethylation.

The action of hydrochloric acid on various phenothiazine sulfoxides to yield chlorophenothiazines has been termed reductive chlorination. Page and Smiles[1] first observed this reaction with phenothiazine-5-oxide and hydrochloric acid. The product was found to be an isomorphic mixture of mono- and dichlorophenothiazines. A chloro-3-nitrophenothiazine also was reported from the action of hydrochloric acid on 3-nitrophenothiazine-5-oxide.[2] The analogous reaction with 10-methylphenothiazine-5-oxide led to a monochloro-10-methylphenothiazine in excellent yield.[1] Recently, this latter compound was shown to be the 3-chloro derivative.[3] Workers in these laboratories have applied successfully the reaction to 10-

(1) H. J. Page and S. Smiles, *J. Chem. Soc.*, **97**, 1112 (1910).

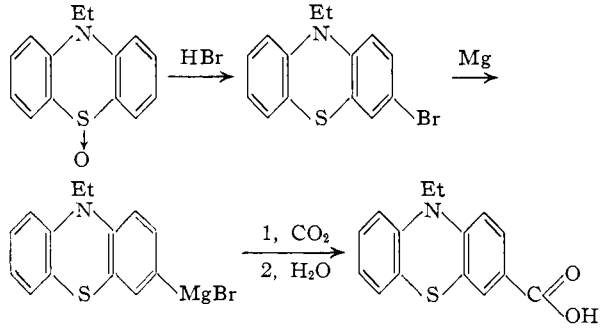
(2) F. Kehrmann and O. Nossekno, *Ber.*, **46**, 2809 (1913).

(3) A. C. Schmalz and A. Burger, THIS JOURNAL, **76**, 5455 (1954).

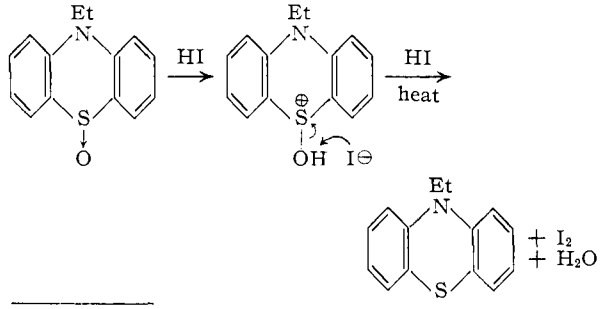
ethylphenothiazine-5-oxide and have shown that chlorine enters the 3-position also.[4]

Extension of this reaction to other hydrohalic acids has led to inconclusive results in the phenothiazine series. From the reaction of phenothiazine-5-oxide and fuming hydrobromic acid only a small amount of an impure bromophenothiazine was obtained.[1] Other workers report no isolable products with 10-methylphenothiazine-5-oxide and either hydrobromic or hydriodic acids, but interestingly enough found that hydrofluoric acid did reduce the sulfoxide group.[3]

In the present investigation the action of various hydrohalic acids on 10-ethylphenothiazine-5-oxide was evaluated. Both hydrochloric acid and hydrobromic acid were able to effect reductive halogenation, whereas hydriodic acid simply caused reduction. It was found that concentrated hydrohalic acids were inferior to more diluted acids in the reaction with 10-ethylphenothiazine-5-oxide. With concentrated acids a common side reaction seems to be cleavage of the sulfide linkage as evidenced by the hydrogen sulfide evolved in the course of the reaction. Also, intractable tars result from heating with concentrated acids. By use of diluted acid, hydrochloric acid gave a 77% yield of the previously reported 3-chloro-10-ethylphenothiazine.[4] Hydrobromic acid under similar conditions was found to give 44% of a monobromo-10-ethylphenothiazine. The bromine atom was shown to occupy the 3-position by the preparation and carbonation of the Grignard reagent to yield the known 10-ethylphenothiazine-3-carboxylic acid.[5] The action of hydriodic acid

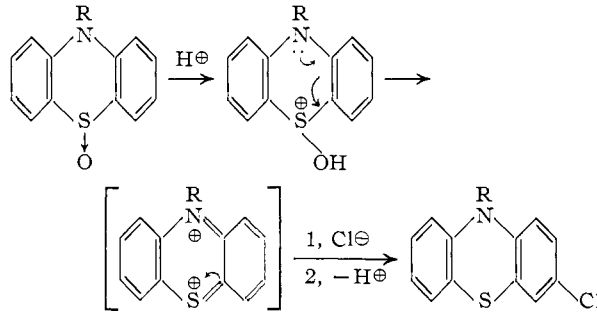


on 10-ethylphenothiazine-5-oxide produced 10-ethylphenothiazine and a substance which appears to be a salt of 10-ethylphenothiazine-5-oxide and hydriodic acid. Support for such a salt stems from the observations that the substance evolved iodine



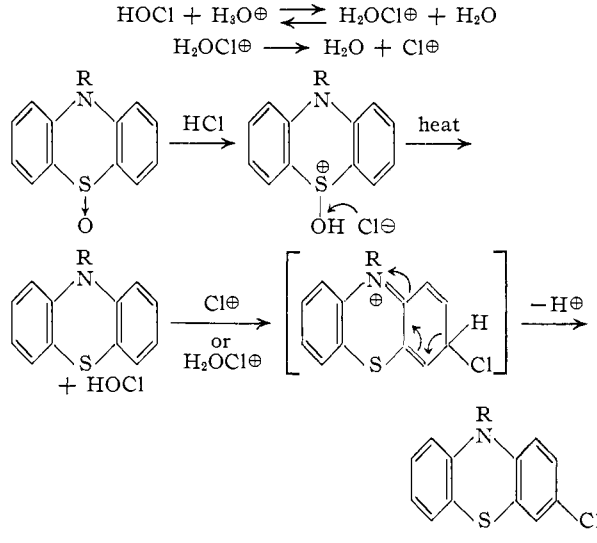
vapor upon moderate heating and yielded 10-ethylphenothiazine-5-oxide upon treatment with alkali. Suprisingly enough a small amount of iodoform resulted from the latter operation. Supposedly cleavage of the ethyl group occurs and this in turn is oxidatively halogenated by the hypoiodite ion. The latter must result from the small amount of free iodine in the product.

The mechanism for reductive halogenation proposed by its discoverers involves the rearrangement of *o*-quinonoid phenazothionium salts.[1] Present workers[3] in this field, accordingly, have expressed the course of the reaction thus



Isolation of phenazothionium salts from the reaction of hydrochloric acid with the sulfoxide has been considered as support for the above mechanism. However, the postulation of such highly charged intermediates seems undesirable.

The alternative mechanism also considered in the literature,[3] that is, the reduction of the sulfoxide grouping with the formation of one molar equivalent of chlorine (or hypochlorous acid) may be viewed in this manner

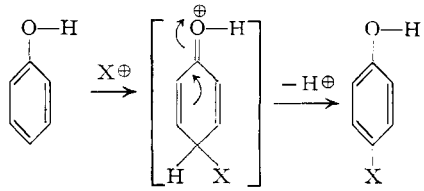


The two mechanisms proposed are nucleophilic and electrophilic attacks of chlorine, respectively, on the phenothiazine system. Moreover, if the second mechanism is operative, either free halogen or hypohalous acid should be present in the solvent. Therefore, by conducting the reaction in the presence of a third substance prone to electrophilic attack and isolating a halogenated derivative, it would be possible to eliminate the first mechanism.

(4) H. Gilman, R. K. Ingham, J. F. Champaigne, Jr., J. W. Diehl, and R. O. Ranck, *J. Org. Chem.*, **19**, 560 (1954).

(5) H. Gilman, P. R. Van Ess and D. A. Shirley, THIS JOURNAL, **66**, 1214 (1944).

The substance chosen to trap the halogen was phenol because of the ease of halogenation



When 10-ethylphenothiazine-5-oxide and hydrochloric acid were interacted in the presence of phenol, no chlorophenol could be isolated. However, with hydrobromic acid, 10-ethylphenothiazine-5-oxide and phenol, a 41% yield of *p*-bromophenol (as aryloxyacetic acid derivative) was obtained. To this may be added the isolation of 10-ethylphenothiazine in the case of hydriodic acid and 10-ethylphenothiazine-5-oxide. Thus, it seems clear that reductive halogenation proceeds by the electrophilic attack of halogen on the phenothiazine. With chlorine the reaction is so rapid that phenol cannot compete with the heterocycle. With bromine phenol can react at roughly the same rate as the heterocycle. Finally, iodine is unable to attack the heterocycle. This latter statement is borne out by the failure to isolate any iodo-10-ethylphenothiazine by the direct iodination of the heterocycle (*cf.* Experimental). However, by utilizing the sulfoxide group itself to remove the resulting hydrogen iodide, 10-ethylphenothiazine-5-oxide was iodinated in small yield to give 3-iodo-10-ethylphenothiazine.

The previously unknown 3-amino-10-ethylphenothiazine was obtained in low yield from the reaction of tin and hydrochloric acid with 3-nitro-10-ethylphenothiazine-5-oxide. Contrary to other studies,[6] it could be obtained pure, although it oxidized slowly in air.

The feasibility of obtaining the N-ethyl derivatives of phenothiazine-5-oxide and phenothiazine-5-dioxide by ethylation in liquid ammonia with sodamide and ethyl bromide was examined. Previous workers[4] always have ethylated phenothiazine and then oxidized the sulfide linkage. Contrasted with the 98–99% yield obtained in the ethylation of phenothiazine, phenothiazine-5-oxide was ethylated to the extent of 7% and phenothiazine-5-dioxide underwent no discernible ethylation under similar conditions. If the reaction is viewed as a nucleophilic attack of an amide ion on ethyl bromide, such results are understandable

$$>N^{\ominus} + Et{-}Br \longrightarrow >N{-}Et + Br^{\ominus}$$

With anions of comparable structure and nature nucleophilicity runs somewhat parallel with base strength. In addition, base strength is inversely proportional to the strength of the conjugate acid. Consequently, the series ammonia < phenothiazine < phenothiazine-5-oxide < phenothiazine-5-dioxide, represents a series of compounds having increasing acidity of the H-N< grouping. Thus, since phenothiazine-5-dioxide is the strongest acid, one would expect its anion to be the weakest base and thus the poorest nucleophile in the ethylation reaction.

Experimental[7]

Starting Materials.—The phenothiazine employed was that of the Eastman Kodak Co., practical grade, m.p. 184–185°. Following a published procedure[4] this was converted into 10-ethylphenothiazine in 98% yield, m.p. 105–106°. From the latter 10-ethylphenothiazine-5-oxide was prepared in 94% yield, m.p. 162–163°. The phenothiazine-5-oxide was that of the Matheson Co., m.p. 251–253°.

Ethylation of Phenothiazine-5-oxide.—According to published directions for the preparation of 10-ethylphenothiazine,[4] sodamide was prepared in liquid ammonia from 9.2 g. (0.40 g.-atom) of sodium. After 1.5 hours of stirring 64.5 g. (0.033 mole) of phenothiazine-5-oxide was added in portions. Little heat was evolved and the color was purple. After 2 hours 79.5 g. (0.729 mole) of ethyl bromide were dropped in by means of a funnel over 30 minutes. Stirring was continued for 8 hours and the ammonia was allowed to evaporate.

The residue was refluxed with 500 ml. of 95% ethanol and then filtered hot. Upon cooling 19.3 g. of phenothiazine-5-oxide was deposited, m.p. 230–235°. The original undissolved residue was boiled with 300 ml. of water, leaving 38.1 g. of light brown solid, m.p. 230–235°. Both solid fractions were combined and again washed with water. The product weighed 55.6 g. (86% recovery) and melted over the range 236–240°.

Dilution of the ethanolic mother liquor with water precipitated 10.0 g. of a tan solid melting over the range 136–142°. Recrystallization from dilute ethanol gave a mixture of white needles and brown solid. Mechanical separation of the white solid afforded 5.7 g., m.p. 160–162°. A mixture with authentic 10-ethylphenothiazine-5-oxide melted undepressed. The brown solid weighed 3.0 g., m.p. 230–235°. Thus, the ethylation reaction went to the extent of 6.9%, and 90.7% of the starting material was recovered.

Attempted Ethylation of Phenothiazine-5-dioxide.—Phenothiazine-5-dioxide was obtained in 71% yield from phenothiazine and 30% hydrogen peroxide in glacial acetic acid according to a procedure used for N-alkylphenothiazines.[4] Recrystallized from ethanol–dioxane it melted at 253.5–255.5°.

Analogous to the detailed procedure given above 29.2 g. (0.127 mole) of phenothiazine-5-dioxide, 3.2 g. (0.140 g.-atom) of sodium, 18.0 g. (0.165 mole) of ethyl bromide and 0.2 g. of ferric nitrate were interacted in 700 ml. of liquid ammonia. The solid reaction residue was refluxed with two 100-ml. portions of absolute ethanol. The residue of this extraction was boiled with 400 ml. of water and collected on a filter. This was 18.6 g. of the starting phenothiazine-5-dioxide, m.p. 251–254°. The preceding ethanolic extracts were concentrated stepwise to yield various fractions, all of which melted in the range 245–254°. The total recovery was 99% of the starting material.

3-Chloro-10-ethylphenothiazine.[4]—A mixture of 12.2 g. (0.050 mole) of 10-ethylphenothiazine-5-oxide and 50 ml. of 6 *N* hydrochloric acid was stirred for 30 minutes at room temperature. The dark red suspension was then refluxed for 1 hour. (A light pink-colored paste formed after 10 minutes.) The pink solid was collected and refluxed with 250 ml. of 95% ethanol (Norit). The filtered solution deposited 10.0 g. (77%) of white needles having a green cast, m.p. 116–117.5°. A mixture melting point with 3-chloro-10-ethylphenothiazine[4] was undepressed.

A run employing concentrated hydrochloric acid under the same conditions gave a lower yield (65%) of an impure product, melting over the range 95–105°. Evidence for cleavage of the sulfide linkage comes from the observed evolution of hydrogen sulfide in this case.

3-Bromo-10-ethylphenothiazine.—A mixture of 12.2 g. (0.050 mole) of 10-ethylphenothiazine-5-oxide, 25 ml. of 48% hydrobromic acid and 25 ml. of water was stirred for 30 minutes without heating and then for 1 hour at reflux. During the heating period a pink solid appeared in the dark red solution. (No odor of bromine could be detected.) The pink solid filtered from the cooled mixture weighed 15.8 g., m.p. 96–116°. Recrystallization from 95% ethanol (Norit) gave 6.9 g. (44%) of white needles, melting over the range 116–122°. By recrystallization from petroleum ether

(6) D. A. Shirley, unpublished thesis studies.

(7) All melting points are corrected.

(b.p. 60–70°) the melting point was raised to 123–124°. The compound gave a positive test for halogen.

Anal. Calcd. for $C_{14}H_{12}BrNS$: N, 4.57. Found: N, 4.57, 4.44.

10-Ethylphenothiazine-3-carboxylic Acid.—The Grignard reagent prepared from 0.40 g. (0.016 g.-atom) of magnesium turnings and 3.0 g. (0.01 mole) of x-bromo-10-ethylphenothiazine in ether under nitrogen was poured into a slurry of Dry Ice in dry ether. The solution remaining after the Dry Ice had evaporated was hydrolyzed with dilute hydrochloric acid. Two 50-ml. portions of ether were used to extract the mixture. The ether extracts were in turn shaken with two 50-ml. portions of 10% sodium hydroxide and the aqueous layer was separated. Acidification of the latter with dilute hydrochloric acid precipitated 1.0 g. (39%) of a lime-colored solid, m.p. 195–200°. Recrystallized from glacial acetic acid lime-colored platelets were formed, m.p. 198.0–199.5°. Admixed with authentic 10-ethylphenothiazine-3-carboxylic acid[5] it melted undepressed. Thus, in the original compound the bromine is in the 3-position.

Action of Hydriodic Acid on 10-Ethylphenothiazine-5-oxide.—A mixture of 12.2 g. (0.050 mole) of 10-ethylphenothiazine-5-oxide, 30 ml. of 47% hydriodic acid and 30 ml. of water formed a coherent, dark purple mass at room temperature. This was stirred for 20 minutes under reflux. The shiny, black solid which was collected by filtration weighed 14.1 g., m.p. 85–95° (no odor of iodine). This solid was extracted with four 100-ml. portions of ether. The unextracted brown solid (10.0 g.) upon mild heating in a crucible evolved iodine vapor. A sample suspended in water gave only a faintly positive test with starch paper, however.

Trituration of the brown solid with 50 ml. of 20% sodium hydroxide formed a light tan solid (strong odor of iodoform). Filtration of the mixture gave 6.8 g. (55%) of a tan solid melting over the range 150–160°. (Upon standing a small amount of lemon-colored iodoform was deposited by the filtrate.) Recrystallization from dilute ethanol (Norit) yielded stout white needles, m.p. 161–163°. Admixed with 10-ethylphenothiazine-5-oxide it melted undepressed.

The ether extracts of the original reaction mixture were dried over anhydrous sodium sulfate and the ether was removed. The solid residue was recrystallized from 95% ethanol (Norit) to yield 2.5 g. (22%) of white prisms, m.p. 106–107° and melting undepressed when admixed with authentic 10-ethylphenothiazine.

Reaction of Hydrobromic Acid with 10-Ethylphenothiazine-5-oxide in the Presence of Phenol.—A mixture of 6.1 g. (0.025 mole) of 10-ethylphenothiazine-5-oxide, 0.8 g. (0.0085 mole) of phenol, 13 ml. of 48% hydrobromic acid and 13 ml. of water was stirred at room temperature for 30 minutes. Then it was heated for 60 minutes at incipient reflux. At the end of this time an oil settled out of the red solution (a strong, burnt phenolic odor was noticed). The mixture was made alkaline with sodium hydroxide and thoroughly ground. The solid (6.3 g.) was filtered off, m.p. 86–92°. This was a mixture of 10-ethylphenothiazine and 3-bromo-10-ethylphenothiazine.

The colorless filtrate was treated with 2.0 g. (0.02 mole) of chloroacetic acid and the resulting solution was refluxed for 1 hour. The cooled solution was acidified with hydrochloric acid and extracted with 50 ml. of ether. The ether extract was washed with water and then extracted with 25 ml. of 5% sodium carbonate solution. Separation and acidification of the aqueous layer precipitated 0.6 g. (41%) of a cream-colored solid which melted at 154–157°. Two recrystallizations from hot water raised the melting point to 158–159°. An authentic specimen of *p*-bromophenoxyacetic acid was prepared according to general directions of Shriner and Fuson.[8] A mixture melting point with the above product was undepressed.[9]

Reaction of Hydrochloric Acid with 10-Ethylphenothiazine-5-oxide in the Presence of Phenol.—Following the directions given above for the run with hydrobromic acid in the presence of phenol, a mixture of 6.1 g. (0.025 mole) of 10-ethylphenothiazine-5-oxide, 0.8 g. (0.0085 mole) of phenol and 25 ml. of 6 *N* hydrochloric acid reacted and was worked up. No *p*-chlorophenoxyacetic acid was isolated, but only 0.7 g. (55%) of phenoxyacetic acid was obtained, m.p. 96–99°.

Attempted Iodinations of 10-Ethylphenothiazine.—The direct iodination of 10-ethylphenothiazine was attempted by several methods. Use of iodine and sodium bicarbonate led to a 95% recovery of the starting material, following the usual work-up.[10] When iodine and mercuric oxide were employed in chloroform solution,[11] a moderate quantity of 10-ethylphenothiazine-5-oxide was isolated. The action of iodine and nitric acid (to remove any hydrogen iodide)[12] on 10-ethylphenothiazine yielded only 3-nitro-10-ethylphenothiazine-5-oxide.

Iodination of 10-Ethylphenothiazine-5-oxide.—A solution of 20.9 g. (0.082 mole) of iodine and 20.0 g. (0.082 mole) of 10-ethylphenothiazine-5-oxide in 100 ml. of chloroform was refluxed for 60 hours. Washing of the dark chloroform solution with sodium bisulfite solution, drying over anhydrous sodium sulfate and removal of the solvent left a dark oil. This was dissolved in 100 ml. of ethanol (Norit) and allowed to cool. A cream-colored solid weighing 1.3 g. was collected, m.p. 110–123°. Recrystallized from ethanol and then from petroleum ether (b.p. 60–70°) it melted at 125–127°. The melting point was undepressed when admixed with authentic 3-iodo-10-ethylphenothiazine.[13]

3-Amino-10-ethylphenothiazine.—It has been observed that reduction of various 3-nitro derivatives of phenothiazines in order to obtain the 3-amino compounds would not give an isolable amine. The reason suggested for this failure was that such *para* diamines would be oxidized readily.[5] However, a small yield of 3-amino-10-ethylphenothiazine was realized in the following manner. To a mixture of 8.9 g. (0.031 mole) of 3-nitro-10-ethylphenothiazine-5-oxide, 20.0 g. (0.17 g.-atom) of granulated tin and 60 ml. of water was added 10 ml. of concentrated hydrochloric acid. Two more 10-ml. portions of acid were added after 10 minutes, whereupon the color of the solution turned a dark green. This color soon was replaced by a tan color. After 20 minutes of reflux a pale yellow oil settled out. The mixture was made alkaline and extracted with ether. After drying over anhydrous sodium sulfate the ether was removed and the solid recrystallized from 95% ethanol (Norit). Upon standing the filtered solution turned dark blue and shiny, light brown needles settled out, weighing 1.6 g. (22%), m.p. 139–140°. Another recrystallization from ethanol gave white needles, m.p. 139.5–141.0°.

A qualitative test for halogen was negative and for sulfur was positive.

Anal. Calcd. for $C_{14}H_{14}N_2S$: C, 69.38; H, 5.82; N, 11.56. Found: C, 69.32, 69.42; H, 5.90, 5.82; N, 11.39, 11.33.

An acetyl derivative was prepared and recrystallized from dilute ethanol as shiny, colorless platelets, m.p. 193.0–193.5°.

AMES, IOWA

(8) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 210.

(9) The interaction of the sulfoxide group with hydrohalic acids to give free halogen suggests that homogeneous, controllable halogenation might be effected by use of some water-soluble aliphatic sulfoxide and hydrohalic acids. The latter could be generated in the mixture or slowly introduced. The feasibility of this method for the halogenation of certain systems is currently being tested in these laboratories.

(10) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green, and Co., London, England, 1948, p. 619.

(11) V. Meyer and H. Kreis, *Ber.*, **17**, 1558 (1884).

(12) R. L. Datta and N. R. Chatterjee, THIS JOURNAL, **39**, 437 (1917).

(13) P. R. Van Ess, *Iowa State Coll. J. Sci.*, **12**, 164 (1938).