changed to brown. After 10 min. of stirring, Color Test I[9] was still strongly positive. The mixture was poured on a Dry Ice–ether slurry. Subsequent to the addition of water and ether, the mixture was filtered to give 2.95 g. (64%) of hexaphenyldisilane, m.p. 350–356° (mixed m.p.).

The layers of the filtrate were separated, the organic layer washed with dilute sodium hydroxide and water, dried with sodium sulfate, and the solvents removed. The addition of petroleum ether to the oily residue gave 0.35 g. (7%) of colorless crystals of triphenylsilanol, m.p. 152–154°. By distillation of the filtrate, 1.2 g. (32%) of diphenyl sulfide was recovered.

The aqueous layer had after acidification the pungent, characteristic odor of thiophenol. Ether extraction gave a yellow oil, from which by recrystallization from petroleum ether (b.p. 60–70°) 0.32 g. (29.5%) of benzoic acid, m.p. 120–121°, was isolated.

When in a second experiment, triphenylsilyllithium was allowed to react with diphenyl sulfide at −30° for 5 hr., the work-up by carbonation gave only traces of acidic material and traces of hexaphenyldisilane. Diphenylsulfide and triphenylsilanol were recovered in high yields.

Reaction of triphenylsilylpotassium with diphenyl sulfide.[24] A suspension of triphenylsilylpotassium in ether was prepared by cleaving 0.01 mole of hexaphenyldisilane with excess of sodium-potassium alloy.[25] A solution of 0.02 mole of diphenyl sulfide in 50 ml. of ether was added and the mixture stirred for 24 hr. The deep-brown reaction mixture was hydrolyzed. There was no insoluble solid formed. The ethereal solution was dried and the solvent removed by distillation. The yellow residue had the pungent odor of thiophenol. The crude product was dissolved in a mixture of benzene and petroleum ether (b.p. 60–70°) and cooled to give 3.5 g. (63%) of triphenylsilanol, m.p. 150–151°. Evaporation of the mother liquor gave a solid, melting at 225–229°. Three recrystallizations from a mixture of benzene and petroleum ether (b.p. 60–70°) yielded 0.2 g. (6%) of tetraphenylsilane, m.p. 233–235° (mixed m.p.).

Reaction of triphenylsilylpotassium with diphenyl sulfoxide.[24] A solution of 4.0 g. (0.02 mole) of diphenyl sulfoxide in 50 ml. of ether was added to a triphenylsilylpotassium suspension,[25] prepared from 0.01 mole of hexaphenyldisilane and excess sodium-potassium alloy in ether, containing the excess alloy. Heat was evolved and a white precipitate was formed. The reaction mixture was stirred for 45 min. at room temperature and subsequently hydrolyzed. A white ether-insoluble powder was filtered off (1.0 g.). This was recrystallized from dioxane to give 0.6 g. (12%) of hexaphenyldisilane,[26] m.p. 364–367°. The ethereal solution was evaporated to give a gummy residue, which was dissolved in benzene. On standing there was obtained 1.1 g. (21%) of hexaphenyldisiloxane, m.p. 227–229° (mixed m.p.). Evaporation of the mother liquor gave 1.3 g. of a solid, m.p. 225–232°. Recrystallization from benzene yielded 0.9 g. (27%) of tetraphenylsilane, m.p. 232–234° (mixed m.p.).

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AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Some New *N*-Substituted Phenothiazine Derivatives and Their 5-Oxides and 5,5-Dioxides

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Several new *N*-substituted phenothiazine derivatives were prepared by heating a mixture of phenothiazine and an aryl or heterocyclic halide in the presence of sodium carbonate and copper powder. Many of these derivatives were oxidized to sulfoxides and sulfones using hydrogen peroxide in ethanol and hydrogen peroxide in glacial acetic acid, respectively. In the preparation of the sulfoxides, the use of a high concentration of reactants was found to be advantageous. Complexes of phenothiazine and 10-(2-pyridyl)phenothiazine with boron trifluoride were investigated.

10-Phenylphenothiazine,[1] 10-(*n*-octadecyl)phenothiazine,[1] and several others have been prepared successfully by heating a mixture of phenothiazine and the appropriate organic halogen compound (usually the bromide or iodide) in the presence of sodium carbonate and copper powder. To denote such a process, the term "no-solvent" is used in this paper.

The no-solvent method has certain advantages over the other general techniques employed for *N*-alkylation of *N*-arylation (sealed tube reactions,[2] reactions employing a solvent such as benzene or xylene,[3] and reactions in anhydrous liquid ammonia[4]) in that temperatures can be reached which effect condensations that are not successful with milder conditions.

The preparation of 10-(2-pyridyl)phenothiazine by treating 10-sodiophenothiazine with 2-chloropyridine in liquid ammonia was unsuccessful.

(1) H. Gilman and D. A. Shirley, *J. Am. Chem. Soc.*, 66, 888 (1944). For general references and a survey on the chemistry of phenothiazine see the splendid article by S. P. Massie, *Chem. Revs.*, 54, 797 (1954).

(2) R. Dahlbom, *Acta Chem. Scand.*, 7, 879 (1953).

(3) H. Gilman, P. R. Van Ess, and D. A. Shirley, *J. Am. Chem. Soc.*, 66, 1214 (1944).

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

The reaction between 2-chloro- or 2-bromoypridine and 10-sodiophenothiazine in tetrahydrofuran[5] at room temperature also failed to give any product; nor was any 10-(2-pyridyl)phenothiazine obtained by heating a mixture of phenothiazine, 2-bromopyridine, potassium carbonate, and copper-bronze powder in kerosine (203°) for 50 hr. This latter reaction was patterned after the preparation of 9-(2-pyridyl)carbazole which was obtained in a yield of 13% by a similar manner.[6] When the no-solvent method was employed, a 62% yield of pure 10-(2-pyridyl)phenothiazine resulted. Likewise, 10-(2-quinolyl)phenothiazine could not be prepared from 2-chloroquinoline and 10-sodiophenothiazine in tetrahydrofuran,[5] but was obtained in a 43% yield using this no-solvent method with 2-chloroquinoline. 4,4′-Bis(10-phenothiazinyl)biphenyl was prepared in only a low yield from 4,4′-dibromobiphenyl, and the material which was obtained was quite impure.

The preparation of 10-[4-(7-chloroquinolyl)]phenothiazine was attempted but the excessive sublimation of one of the starting materials, 4,7-dichloroquinoline, even at relatively low temperatures did not make the reaction feasible.

In nearly all cases, an attempt was made to purify the crude material chromatographically on activated alumina since such a technique had been very successful on 10-ethylphenothiazine.[4] In no case was this method of purification adequate. To get pure material, recrystallization of the chromatographed material or distillation and recrystallization of the crude material was necessary.

As a means of getting some boron derivatives of phenothiazine for possible use in brain tumor therapy[7-9] both phenothiazine and 10-(2-pyridyl)-phenothiazine were treated with boron fluoride ethyl ether in benzene. The first of these gave a compound different from phenothiazine whose composition was not definitely established because of its high sensitivity to atmospheric conditions. In contrast to this was the complex between 10-(2-pyridyl)phenothiazine and boron trifluoride which was sufficiently stable to be recrystallized from absolute ethanol. It was unstable to water, however, hydrolyzing to 10-(2-pyridyl)phenothiazine.

Some of the *N*-substituted phenothiazines were oxidized to the monoxides by the use of hydrogen peroxide in refluxing ethanol, or to the dioxides by using hydrogen peroxide in hot glacial acetic acid. When 10-(2-pyridyl)phenothiazine was oxidized with hydrogen peroxide in glacial acetic acid using the conditions which were employed by Ochiai[10] for the preparation of pyridine-1-oxide, a compound whose sulfur analysis corresponded to the trioxide, 10-(1-oxo-2-pyridyl)phenothiazine-5,5-dioxide, was formed. The infrared spectrum of this compound showed absorption bands at 8.6μ and 8.8μ, characteristic of the sulfone, and another sharp absorption band at 12μ, which was not present in the spectra of either 10-(2-pyridyl)-phenothiazine or 10-(2-pyridyl)phenothiazine-5-oxide. This band was attributed to the *N*-oxide. When the trioxide was treated with iron in hot (100°) glacial acetic acid, a new compound, based on a change in melting point as well as the infrared spectrum, formed. The sulfur analysis on this material corresponded to that of 10-(2-pyridyl)-phenothiazine-5,5-dioxide. The infrared spectrum showed the sulfone absorption bands at 8.6μ and 8.8μ.

The oxidation of 10-phenylphenothiazine[1] to the sulfone gave a product melting at 211–211.5°. Finzi,[11] who carried out the oxidation with potassium permanganate in chloroform, reported a melting point of 204–205° for the sulfone.

Generally, the oxidations to the monoxides were run under conditions of greater concentration than is normally used.[12] This had previously been found to be advantageous in the preparation of several sulfoxides including 10-ethylphenothiazine-5-oxide,[4] 10-(*n*-decyl)phenothiazine-5-oxide,[5] and 10-(*n*-octadecyl)phenothiazine-5-oxide.[5] In the case of 10-phenylphenothiazine - 5 - oxide, a longer heating period than was previously used for this oxidation[1] was employed which greatly improved the yield. A good yield of 10-(2-pyridyl)phenothiazine-5-oxide is also reported.

As part of a general program designed to correlate scintillation activity with chemical structure,[13,14] the following compounds were screened as scintillator solutes: 10-phenylphenothiazine, 10-phenylphenothiazine-5-oxide and 5,5-dioxide, 10 - (2 - pyridyl)phenothiazine, 10 - (2-pyridyl)phenothiazine - 5 - oxide and 5,5 - dioxide, and 10 - (1 - oxo - 2 - pyridyl)phenothiazine-5,5-dioxide. All of these compounds had a relative pulse height of less than 0.10 when compared to 2,5-diphenyloxazole, which is assigned the arbitrary value of 1.00. The measurements were made in toluene at a concentration of 3 g./l.

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(14) H. Gilman, E. A. Weipert, R. O. Ranck, and F. N. Hayes, *J. Org. Chem.*, **23**, 628 (1958).

EXPERIMENTAL[15]

4,4'-Bis(10-phenothiazinyl)biphenyl. Twenty-four grams (0.12 mole) of phenothiazine, 15.6 g. (0.05 mole) of 4,4'-dibromobiphenyl, 12 g. (0.113 mole) of anhydrous sodium carbonate, and 1 g. (0.0159 g.-atom) of copper powder were stirred at a temperature of 150–210° for a period of 24 hr. An early low temperature was used to prevent excessive sublimation of the halogen compound. The temperature was gradually raised as the reaction progressed. After cooling to room temperature, the reaction mass was extracted with benzene, filtered to remove the insoluble material, and then reduced in volume. Twelve and one-half grams of material having a melting point range of 200–300° separated. This was recrystallized from benzene to give 5 g. (18%) of tan, amorphous material having a melting point range of 295–300° with decomposition. The material could not be purified further and gave a low sulfur analysis. The infrared spectrum did support the structure, however, showing characteristic *ortho* and *para* disubstitution bands at 13.5μ and 12.4μ respectively, and no absorption band characteristic of N—H.

10-(2-Pyridyl)phenothiazine. Twenty grams (0.1 mole) of phenothiazine, 23.7 g. (0.15 mole) of 2-bromopyridine, 12.5 g. (0.118 mole) of anhydrous sodium carbonate, and 1 g. (0.0159 g.-atom) of copper powder were stirred at reflux for 15 hr. After cooling to room temperature, the reaction mass was extracted with hot water to remove the soluble salts and was then aspirated to remove any unreacted 2-bromopyridine and water. The remaining solid was subjected to vacuum distillation. A portion of this material distilled at 170–175° (0.03 mm.) to give a viscous product which gradually solidified on standing. The material was recrystallized from an ethanol-water system to give 7.5 g. (27.1%) of cream colored crystals melting at 109–110°.

The undistilled portion of material was dissolved in benzene and was chromatographed on a column of activated alumina, the column being eluted with additional benzene. Evaporation of the solvent from the eluate left 19 g. (68.9%) of material having a melting point of 90–93°. This was recrystallized from an ethanol-water system to give 7.0 g. (25%) of cream colored, crystalline material melting at 107–108°.

The infrared spectrum confirmed the structure showing the characteristic absorption band at 6.35μ for the C=N and a weak absorption band at 13.4μ which is characteristic of *ortho* disubstitution. There was not N—H absorption band.

Anal. Calcd. for $C_{17}H_{12}N_2S$: S, 11.59. Found: S, 11.66, 11.48.

In another experiment starting with 0.3 mole of phenothiazine, 59 g. (71%) of material having a melting point of 107–108° was obtained by vacuum distillation of the crude material. Recrystallization of this from an ethanol-water system gave 51 g. (62%) of material melting at 108–109°.

10-(2-Quinolyl)phenothiazine. Twenty grams (0.10 mole) of phenothiazine, 24.5 g. (0.15 mole) of 2-chloroquinoline, 12 g. (0.113 mole) of anhydrous sodium carbonate, and 1 g. (0.0159 g.-atom) of copper powder were stirred at reflux (220–230°) for 48 hr. After cooling to room temperature, the mass was extracted with hot benzene. The extract was filtered and the benzene was stripped from the filtrate. The residue was subjected to vacuum distillation. Four grams of 2-chloroquinoline were recovered, but it was not possible to distill the main product. This undistilled portion was redissolved in benzene and was chromatographed on a column of activated alumina, the column being eluted with additional benzene. Eight fractions, all of which gave a viscous yellow oil after evaporation of the solvent from the eluate, were collected. These were combined and recrystallized from an ethanol-water system to give 14 g. (43%) of material having a melting point of 126–128°. The material was still quite colored (yellow) and believed to be somewhat impure. However, repeated recrystallizations failed to raise the melting point. The infrared spectrum supported the structure, showing characteristic absorption bands for 1,2,3,4-tetrasubstitution (12.4μ), *ortho* disubstitution (13.3 μ) and the C=N (6.3 μ). There was no N—H absorption band present.

Anal. Calcd. for $C_{21}H_{14}N_2S$: S, 9.82. Found: S, 10.35, 10.19.

10-Phenylphenothiazine-5-oxide. Twenty and one-half grams (0.075 mole) of 10-phenylphenothiazine[1] was dissolved in 500 ml. of refluxing absolute ethanol in an atmosphere of nitrogen.[16] Twenty-five milliliters (0.245 mole) of 30% hydrogen peroxide was added, and stirring was continued at reflux for 5 hr. Three hundred milliliters of the solvent was then removed by distillation and the remaining undistilled portion was poured into 925 ml. of water which had been preheated to 80°. Upon cooling to room temperature, 21.8 g. (100%) of white material melting at 172–173° crystallized. The reported[1] melting point for this compound is 170–171°.

10-(2-Pyridyl)phenothazine-5-oxide. Thirteen and eight-tenths grams (0.05 mole) of 10-(2-pyridyl)phenothiazine was dissolved in 333 ml. of refluxing absolute ethanol. The solution was kept in a nitrogen atmosphere and 17 ml. (0.167 mole) of 30% hydrogen peroxide was added, after which the reaction mixture was stirred at reflux for 5 hr. Two hundred milliliters of the solvent was removed by distillation and the remaining portion was poured into 620 ml. of water which had been preheated to 80°. Upon cooling, 10.3 g. of white needles having a melting point range of 129–133° and 3.4 g. of solidified oil drops melting over the range of 121–126° separated. These combined weights represent a crude yield of 94%. The two portions of crude material were crystallized from an ethanol-water system to give two fractions of material, the first weighing 5.5 g. (38%) and melting at 156–157° and the second weighing 4.5 g. (31%) and melting over the range of 125–132°. Recrystallization of the first fraction from this same solvent system gave material melting over the range of 120–158°.

All of the material was again combined and recrystallized from benzene to give a product melting at 157–158°, after showing some decomposition between 120–157°. Another recrystallization from a benzene–petroleum ether (b.p. 60–70°) system raised the melting point to 158.5–159.5° and still another one failed to change it.

The infrared spectrum indicated the presence of the sulfoxide with a weak absorption band at 9.4μ.

Anal. Calcd. for $C_{17}H_{12}N_2OS$: S, 10.97. Found: S, 10.62, 10.81.

10-Phenylphenothiazine-5,5-dioxide. Twenty and one-half grams (0.075 mole) of 10-phenylphenothiazine was dissolved in 440 ml. of glacial acetic acid at 80° to give a green solution. Twenty-three milliliters (0.225 mole) of 30% hydrogen peroxide was added, causing a change in color to red. The reaction was stirred at 80° for 1.5 hr. during which time the color changed to a light orange. Two hundred and fifty milliliters of solvent was removed by distillation under the partial vacuum provided by a water aspirator, the solution becoming dark red during this time. When the solution had cooled to room temperature, 19 g. (83%) of orange crystals melting over the range of 205–208° separated. An additional 2 g. (8.7%) of material having a melting point range of 190–200° was obtained upon dilution of the acetic acid filtrate with water. These two portions of material were combined and recrystallized from absolute ethanol to give 20 g. (87%) of orange colored material melting at 211–211.5°. Frinzi[11] reported a melting point of 204–205°.

The infrared spectrum showed bands at 8.6μ and 8.8μ which are characteristic of sulfones.

(15) All melting points reported herein are uncorrected.

(16) Studies in this laboratory have indicated that oxidations run in a nitrogen atmosphere sometimes give a product free of colored components.

Anal. Calcd. for $C_{18}H_{13}NO_2S$: S, 10.43. Found: S, 10.36, 10.81.

10-(1-Oxo-2-pyridyl)phenothiazine-5,5-dioxide. Thirteen and eight-tenths grams (0.05 mole) of 10-(2-pyridyl)phenothiazine was dissolved in 292 ml. of glacial acetic acid at 80° to give a deep yellow colored solution. Following the procedure of Ochiai for the preparation of pyridine-1-oxide,[10] thirty-one milliliters (0.3 mole) of 30% hydrogen peroxide was added and stirring was continued at 80° for 15 hr. During this time the solution became nearly colorless, and near the end of the heating time assumed a deep orange color. One hundred and eighty-five milliliters of the solvent was removed by distillation under the partial vacuum provided by a water aspirator. Refrigeration of the remaining acetic acid solution gave 16 g. (99%) of material melting over the range of 220–226°. Dilution of the filtrate with water gave an additional 2 g. (12.3%) of material melting at 225–227°. The two portions of material were combined and recrystallized from absolute ethanol to give 13 g. (80%) of cream colored, crystalline material melting at 232.5–234°. Another recrystallization from absolute ethanol failed to raise the melting point.

The infrared spectrum showed characteristic sulfone absorption bands at 8.6μ and 8.8μ as well as an absorption band at 12μ which was attributed to the *N*-oxide.

Anal. Calcd. for $C_{17}H_{12}N_2O_3S$: S, 9.88. Found: S, 9.88, 10.02.

10-(2-Pyridyl)phenothiazine-5,5-dioxide. Two and three-tenths grams (0.007 mole) of 10-(1-oxo-2-pyridyl)phenothiazine-5,5-dioxide, 2.2 g. (0.04 g.-atom) of iron powder, and 30 ml. of glacial acetic acid were stirred at 100° for 1 hr. The hot solution was filtered and was then diluted with water. Neutralization of the solution with sodium hydroxide caused the separation of a solid which was removed by filtration. This solid was extracted with ethanol and this extract was diluted with water and allowed to evaporate slowly. This caused the crystallization of 1.25 g. (57%) of white material having a melting point of 180–181°.

The infrared spectrum had the characteristic sulfone absorption bands at 8.6μ and 8.8μ but the absorption band at 12μ, which was present in the starting material, was absent.

Anal. Calcd. for $C_{17}H_{12}N_2O_2S$: S, 10.40. Found: S, 10.23, 10.40.

Phenothiazine: boron trifluoride complex. Seven and two-tenths grams (0.036 mole) of phenothiazine was dissolved in 250 ml. of benzene at 25° in an atmosphere of nitrogen. Four and one-half milliliters (0.036 mole) of boron fluoride ethyl ether was added over a 2-min. period. This caused a change in color from light yellow to dark red and the separation of a solid material. Slow evaporation of the solvent caused the separation of brown needles having a melting point of 158–160°. Other solids also separated. The needles gave a positive test for boron, but attempts to purify the material further failed because of its instability.

10-(2-Pyridyl)phenothiazine: boron trifluoride complex. Five and one-half grams (0.02 mole) of 10-(2-pyridyl)-phenothiazine was dissolved in 100 ml. of benzene in an atmosphere of nitrogen. Five milliliters (0.04 mole) of boron fluoride ethyl ether was added at room temperature over a period of 1 min. Immediately upon the addition of the boron compound a yellow solid separated. Agitation was continued for 3 hr., after which the solid was removed by filtration and dried. As the material dried, the color changed from yellow to white. Seven and one-half grams of product having a melting point range of 278–300° was obtained. The material was recrystallized from ethanol to give 4.4 g. (60% based on the nitrogen analysis) of material melting at 305–310° with preliminary softening at 295°. Another recrystallization from absolute ethanol failed to increase the melting point. Evaporation of the filtrate from the last crystallization to dryness left material having a melting point of 307–308° with preliminary softening at 240°.

Anal. Calcd. for $(C_{17}H_{12}N_2S)_2:(BF_3)_3$: N, 7.31. Found: N, 7.47.

Some of the compound was suspended in water at room temperature to determine the ease of hydrolysis. After being in contact for 12 hr., the solid was filtered off, dried, and examined. The material melted at 108–110° and showed no depression in melting point when admixed with an authentic sample of 10-(2-pyridyl)phenothiazine. Shorter periods of hydrolysis were not investigated.

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[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY AND THE RESEARCH AND DEVELOPMENT DIVISION, SMITH KLINE & FRENCH LABORATORIES]

Synthesis of 2-Aza- and 8-Chloro-2-aza-phenothiazine[1]

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The preparation of 2-azaphenothiazine and 8-chloro-2-azaphenothiazine and the intermediates involved in their syntheses is described. In addition, a preliminary attempt to prepare 3-azaphenothiazine by the Smiles rearrangement is reported.

The method for preparing phenothiazines by the ring closure (dehydrohalogenation) of diphenyl sulfide derivatives is well known.[2] This method has been successfully applied to the ring closure of pyridylphenyl sulfides in the synthesis of 2-azaphenothiazine (III) and 8-chloro-2-azapheno-

(1) These compounds were prepared at the Research Institute of Temple University under a contract with the Smith Kline & French Laboratories. (a) Research Institute of Temple University. (b) Smith Kline & French Laboratories.

(2) S. P. Massie, *Chem. Revs.*, **54**, 797 (1954).