*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 8.6$\mu$ and 8.8$\mu$ as well as an absorption band at 12$\mu$ 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 8.6$\mu$ and 8.8$\mu$ but the absorption band at 12$\mu$, 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.

*Acknowledgment.* We wish to thank Mr. E. Miller Layton, Jr., of the Ames Laboratory of the U. S. Atomic Energy Commission for the determination of the infrared spectra. We also wish to thank the Division of Biology and Medicine of the United States Atomic Energy Commission whose financial assistance has made a portion of this work possible. The results of the biological testing in brain tumor therapy will be reported by Dr. Otho D. Easterday of the Brookhaven National Laboratory.

AMES, IOWA

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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]

ANDREW J. SAGGIOMO,[1a] PAUL N. CRAIG,[1b] AND MAXWELL GORDON[1b]

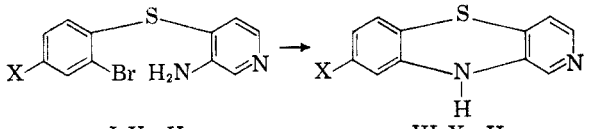
*Received July 14, 1958*

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).

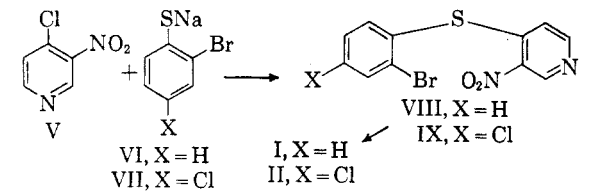


I, X = H
II, X = Cl

III, X = H
IV, X = Cl

thiazine (IV).[3] The cyclization of I in the presence of copper-bronze, or cuprous iodide, and sodium carbonate was accomplished in *N,N*-dimethylformamide, acetamide and in the absence of a solvent. The latter instance afforded the best yield and the purest product in the preparation of 2-azaphenothiazine (III). In contrast, the ring closure of II was conducted best in *N,N*-dimethylformamide.

The intermediates I and II were prepared by reduction of the sulfides formed from 4-chloro-3-nitropyridine (V)[4] and the sodium salts of *o*-



V

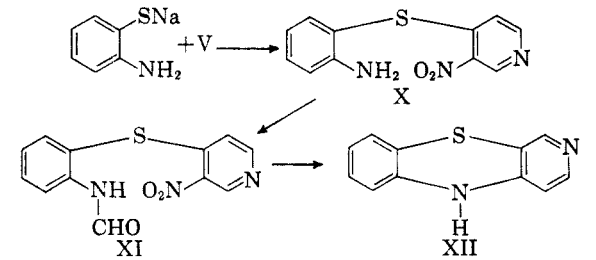
VI, X = H
VII, X = Cl

I, X = H
II, X = Cl

VIII, X = H
IX, X = Cl

bromothiophenol (VI)[5] and 2-bromo-4-chlorothiophenol (VII), respectively.

Since the intermediates were available, a preliminary attempt was made to prepare 3-azaphenothiazine (XII) by the Smiles rearrangement. In the presence of base the formamido derivative XI did not yield the expected product (XII).



X

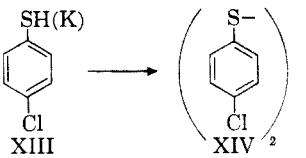
XI

XII

In addition, efforts to prepare the latter from the hydrochloride of *o*-aminothiophenol and V in the presence of sodium acetate followed by treatment with base according to the procedure utilized for 1-nitro-3-azaphenothiazine[6] also failed. The product isolated was demonstrated by mixed melting point to be the sulfide X.

In the course of preparing increasing amounts of the key intermediate *o*-bromothiophenol (VI) from *o*-bromoaniline according to reference 5, it was found that the yield of final product dropped off considerably. An investigation[7] was undertaken and the experimental conditions determined for producing larger quantities of VI in consistently good yields. 2-Bromo-4-chlorothiophenol (VII) was also prepared from the corresponding diazotized amine (obtained by bromination of *p*-chloroacetanilide) *via* the xanthate route.

Several methods were investigated in our efforts to prepare VII. The direct bromination of *p*-chlorothiophenol and its potassium salt (XIII) in



XIII

XIV [2]

carbon tetrachloride or dioxane produced, in almost quantitative yield, 4,4′-dichlorodiphenyldisulfide (XIV). The latter has also been obtained quantitatively by T. L. Fletcher, *et al.*,[8] in their recent attempt to brominate XIII by means of 48% hydrogen bromide in dimethyl sulfoxide. In addition, 2-bromo-4-chlorothiophenol was not isolated from the reaction between 2-bromo-4-chlorophenol and phosphorus pentasulfide. Farrington and Warburton[9] report the synthesis in low yield of 2-amino-4-chlorothiophenol, a possible precursor of VII. Our attempt to duplicate these results was unsuccessful.

## EXPERIMENTAL[10]

*4-Chloro-3-nitropyridine* (V). Pyridine was converted *via* pyridylpyridinium dichloride into 4-hydroxypyridine nitrate[11] and the latter nitrated to 4-hydroxy-3-nitropyridine.[12] Reaction with an equimolar quantity of phosphorus pentachloride in the presence of phosphorus oxychloride gave 4-chloro-3-nitropyridine (V).[4a] In the latter reaction it was found necessary during the last stages of the atmospheric distillation of phosphorus oxychloride to pass a nitrogen stream through the system in order to remove any excess phosphorus pentachloride. Various difficulties were encountered in subsequent reactions when V was contaminated with small quantities of phosphorus pentachloride which had been carried over during the final distillation.

(3) Upon conclusion of the work described herein, it was found that the synthesis of compounds III and IV was reported by Rhone-Poulenc, Belgian Patent 791,190 (Feb. 26, 1958); *Chem. Abstr.*, 52, 15597*d* (1958).

(4) (a) S. Kruger and F. G. Mann, *J. Chem. Soc.*, 2755 (1955). (b) T. Takahashi and K. Ueda, *Pharm. Bull. (Tokyo)*, 2, 34 (1954).

(5) G. Schwarzenbach and H. Egli, *Helv. Chim. Acta*, 17, 1176 (1934).

(6) V. A. Petrow and E. L. Rewald, *J. Chem. Soc.*, 591 (1945).

(7) The improved conditions described herein for preparing *o*-bromothiophenol were the result of a joint effort by A. J. Saggiomo, E. A. Nodiff, and S. Lipschutz of the R.I.T.U. laboratories.

(8) T. L. Fletcher, M. J. Namkung, and H. L. Pan, *Chem. & Ind. (London)*, 660 (1957).

(9) K. J. Farrington and W. K. Warburton, *Australian J. Chem.*, 8, 545 (1955).

(10) All melting and boiling points are uncorrected. Elemental analyses were obtained by the Research Analytical Section, Smith Kline & French Laboratories.

(11) E. Koenigs and H. Greiner, *Ber.*, 64, 1049 (1931); D. G. Leis and B. C. Curran, *J. Am. Chem. Soc.*, 67, 79 (1945).

(12) O. Bremer, *Ann.*, 529, 290 (1937).

*o-Bromothiophenol* (VI). *o*-Bromoaniline (258 g., 1.5 moles) was stirred with a solution of hydrochloric acid (264 ml. of concentrated acid in 942 ml. of water) and the suspension diazotized at 0°. The slightly orange diazonium solution was then added with a pipet beneath the surface of a stirred solution of 415 g. of potassium ethyl xanthate (Eastman White Label), in 755 ml. of water at 70–80°. Initial mild sputtering occurred. Heating was continued for 1 hr. after completion of the addition. The red oil which separated was washed with dilute base and then water. It was added in portions to a hot solution of 456 g. of potassium hydroxide in 346 ml. of water and 1040 ml. of ethanol. After refluxing for 21 hr. the mixture was diluted with ice water and made acidic with hydrochloric acid. The oil that formed was collected, washed with water, and dried over Drierite. Vacuum distillation gave *o*-bromothiophenol (80%) as a pale yellow oil, b.p. 90–93°/6 mm., $n_D^{28}$ 1.6298 (lit.[5,13] b.p. 96–98°/11 mm., $n_D^{24}$ 1.6321).

*2'-Bromophenyl-3-nitro-4-pyridylsulfide* (VIII). To *o*-bromothiophenol (189 g., 1.0 mole) in 300 ml. of absolute ethanol was added an aqueous solution of sodium hydroxide (1.0 mole in 50 ml. of water) and the solvent removed *in vacuo*. The anhydrous sodium salt in 750 ml. of absolute ethanol was then added dropwise to a stirred solution of 4-chloro-3-nitropyridine (V) (158 g., 1 mole) in 750 ml. of absolute ethanol at room temperature. The internal temperature was maintained at 40°. The reaction was then refluxed for 2 hr., filtered while hot, and the filtrate cooled. 2'-Bromophenyl-3-nitro-4-pyridylsulfide (282 g., 90%) was obtained as yellow crystals, m.p. 100–102°. The analytical sample from ethanol melted 101.5–102.5°.

*Anal.* Calcd. for $C_{11}H_7BrN_2O_2S$: N, 9.00. Found: N, 9.09.

*2'-Bromophenyl-3-amino-4-pyridylsulfide* (I). The preceding nitro-compound (VIII) (282 g., 0.907 mole) was added in portions to a stirred solution of stannous chloride dihydrate (880 g., 3.9 moles) in 780 ml. of concentrated hydrochloric acid at 50–60°. The addition was conducted so as to maintain an internal temperature of 50–60°. The stirred white suspension was then refluxed for 3 hr. after which time it was diluted with water. Neutralization of the reaction mixture with a hot concentrated solution of sodium hydroxide produced an oil which solidified upon cooling. The tan solid was washed well with water, filtered, and upon drying melted at 94–96° (243 g., 95%). The analytical sample from ligroin melted at 96–97°.

*Anal.* Calcd. for $C_{11}H_9BrN_2S$: C, 46.98; H, 3.23; N, 9.96. Found: C, 47.38, 47.54; H, 3.50, 3.34; N, 9.86.

*2-Azaphenothiazine* (III). An intimate mixture of 2'-bromophenyl-3-amino-4-pyridylsulfide (I) (52.5 g., 0.186 mole), anhydrous sodium carbonate (28.6 g., 0.27 mole), and cuprous iodide (9.37 g.), under prepurified nitrogen in a large sublimation apparatus, was placed in an oil bath at 180–190°. The molten mass was periodically stirred by means of a flat-edged glass stirring rod kept in position by a two-hole rubber stopper. A slow nitrogen stream was maintained over the reaction mass. It was found that 2 hr. 25 min. was required for cyclization. The mixture was then cooled to room temperature and the cold finger of the sublimation apparatus inserted. The crude product was sublimed at 220–230° at <1 mm. for 3 hr. Recrystallization of the yellow sublimate from benzene with Norit treatment gave golden yellow platelets of 2-azaphenothiazine (III) (24.2 g., 65%), m.p. 163.5–165°. This procedure has been successfully reproduced several times.

*Anal.* Calcd. for $C_{11}H_8N_2S$: C, 65.97; H, 4.03; N, 13.99. Found: C, 66.13; H, 4.09; N, 14.12.

When this reaction (*ca.* 0.5 mole) was conducted under nitrogen with mechanical stirring for 6 hr. at 180–200° a dark brown unsublimable product was obtained which was insoluble or only sparingly soluble in benzene, alcohol, and acetone.

(13) H. F. Wilson and D. S. Tarbell, *J. Am. Chem. Soc.*, **72**, 5200 (1950).

Several attempts were made to effect the ring closure in the presence of a solvent. A reaction (0.03 mole) conducted with copper-bronze powder in refluxing dimethylformamide for 16 hr. yielded mostly starting material. When the reaction was carried out for 43.5 hr. a dark green product was obtained which turned to a gum when filtered. It was insoluble in benzene and seemed to decompose upon attempted sublimation.

Acetamide was also employed as a solvent. A reaction (0.03 mole) maintained for 1.75 hr. at 180–190° in the presence of copper-bronze gave 0.5 g. 2-azaphenothiazine, m.p. 164–165°. However, the theoretical amount of silver bromide was obtained. Lowering the reaction time to 22 min. gave 0.1 g., of III and 40% silver bromide with a solution of $AgNO_3$.

Refluxing the reactants in dried dimethylaniline for 20 hr. under nitrogen in the presence of copper-bronze gave mostly starting material. After 49.5 hr., the aforementioned green gummy material was obtained from which III was not isolated.

*2-Bromo-4-chloroaniline*. *p*-Chloroacetanilide was brominated in the presence of sodium acetate in 70% acetic acid at 70° in 90% yield.[14] Hydrolysis with ethanolic potassium hydroxide produced 2-bromo-4-chloroaniline (95%) as buff-colored needles from benzene–petroleum ether, m.p. 68–69°.[15]

*2-Bromo-4-chlorothiophenol* (VII). 2-Bromo-4-chloroaniline was diazotized and the resulting diazonium solution treated as described under *o*-bromo-thiophenol to give VII (42%) as a pale yellow oil with a marked odor, b.p. 94–95° at 1.5 mm., $n_D^{30.5}$ 1.6413.

*Anal.* Calcd. for $C_6H_4BrClS$: C, 32.24; H, 1.80. Found: C, 32.75, 32.40; H, 2.23, 2.12.

*2'-Bromo-4'-chlorophenyl-3-nitro-4-pyridylsulfide* (IX). The reaction of the anhydrous sodium salt of 2-bromo-4-chlorothiophenol and V was conducted as described for VIII. The sulfide IX was obtained as yellow crystals from ethanol, m.p. 122.5–123.5°, in 72.5% yield.

*Anal.* Calcd. for $C_{11}H_6BrClN_2O_2S$: C, 38.22; H, 1.75; N, 8.11. Found: C, 38.08; H, 1.88; N, 7.97.

*2'-Bromo-4'-chlorophenyl-3-amino-4-pyridylsulfide* (II). The nitro compound IX was reduced in 50% yield by the same method used to prepare I. Recrystallization from benzene–petroleum ether gave II as white crystals, m.p. 90–91.5°.

*Anal.* Calcd. for $C_{11}H_8BrClN_2S$: C, 41.86; H, 2.55; N, 8.88. Found: C, 41.75; H, 2.56; N, 9.02.

*8-Chloro-2-azaphenothiazine* (IV). A mixture of 2'-bromo-4'-chlorophenyl-3-amino-4-pyridylsulfide (II) (37.8 g., 0.12 mole), anhydrous granular potassium carbonate (21.0 g., 0.151 mole), and copper-bronze powder (1.8 g.) was stirred in refluxing dimethylformamide (400 ml.) under a slow stream of prepurified nitrogen for 20 hr. $CO_2$ evolution was not apparent after this time. The contents of the flask were filtered and the filtrate thrown into water. A yellowish-green precipitate was collected, washed with several portions of water, and dried. Recrystallization from methanol gave 8-chloro-2-azaphenothiazine (IV) (17.3 g., 61.5%) as yellow crystals, m.p. 212.5–214°. A sample prior to recrystallization was sublimed twice at 200–210° at <0.1 mm. to give yellow microscopic needles, m.p. 213.5–214.5°.

*Anal.* Calcd. for $C_{11}H_7ClN_2S$: C, 56.29; H, 3.01; N, 11.94. Found: C, 56.17; H, 3.16; N, 12.17.

The above cyclization was also carried out in the absence of a solvent as described for 2-azaphenothiazine. Though some of the desired product was obtained, a better yield of 8-chloro-2-azaphenothiazine is obtained when the cyclization is conducted in dimethylformamide.

*Bromination of p-chlorothiophenol*. The bromination of *p*-chlorothiophenol and potassium *p*-chlorothiophenolate in

(14) G. Owen, *J. Chem. Soc.*, 123, 3392 (1923).

(15) F. D. Chattaway and K. J. P. Orton, *Ber.*, **33**, 2396 (1900).

carbon tetrachloride or dioxane produced in almost quantitative yield 4,4'-dichlorodiphenyldisulfide (XIV) as yellow plates from petroleum ether, m.p. 72–73°.

*Anal.* Calcd. for $C_{12}H_8Cl_2S_2$: C, 50.30; H, 2.82. Found: C, 50.58; H, 3.03.

*2'-Aminophenyl-3-nitro-4-pyridyl sulfide* (X). The reaction between the anhydrous salt of *o*-aminothiophenol and V was conducted in the same manner as described above for VIII. The sulfide X was obtained in 52% yield as yellow needles, m.p. 146–147°, after two recrystallizations from ethanol. Comparable yields were obtained with 1,4-dioxane as the reaction solvent.

*Anal.* Calcd. for $C_{11}H_9N_3O_2S$: C, 53.42; H, 3.67. Found: C, 53.57; H, 3.90.

*2'-Formamidophenyl-3-nitro-4-pyridyl sulfide* (XI). The above amino-sulfide (5.0 g., 0.02 mole) was refluxed for several hours with 10 times its weight of 90% formic acid. The solution upon dilution with water did not precipitate the formamido derivative. Neutralization of the mixture with sodium bicarbonate produced a gum. Recrystallization of the latter from benzene and then absolute ethanol yielded the formamido derivative (XI) (2.5 g., 45.5%), m.p. 146–147.5°. A mixture melting point with an authentic sample of the free amino-compound gave a large depression.

*Anal.* Calcd. for $C_{12}H_9N_3O_3S$: C, 52.35; H, 3.30. Found: C, 52.13; H, 3.12.

*Attempted Smiles rearrangement of 2'-formamidophenyl-3-nitro-4-pyridyl sulfide* (XI). An acetone solution of the formamido derivative was refluxed with a solution of potassium hydroxide in absolute ethanol for 2 hr. The reddish-brown solution was brought to dryness under vacuum. The residue was not soluble in most organic solvents. However, it was very soluble in alcohol and acidification of its aqueous solution produced a crude precipitate. No test for nitrite ion was obtained nor was 3-azaphenothiazine (XII) isolated. Indications seem to support the fact that a possible rearrangement to the potassium salt of the thiol may have occurred without the elimination of potassium nitrite.

*Acknowledgment.* The authors wish to express their deep appreciation to Drs. J. Wilson and C. Zirkle of Smith Kline & French Laboratories and to Mr. E. A. Nodiff for their valuable discussions related to this work.

PHILADELPHIA, PA.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MICHIGAN]

# The Effect of Some Substituents on the Thermal Breakdown of Diaryltetrazoles[1]

JOHN VAUGHAN AND PETER A. S. SMITH

*Received June 11, 1958*

Nine tetrazoles containing substituted phenyl, pyridyl, or quinolyl groups have been prepared from imidyl chlorides and aqueous sodium azide. All lost nitrogen when heated at 220–250°, to yield carbodiimides accompanied in some cases by benzimidazoles. The Schmidt reaction on acetophenone catalyzed by aluminum chloride in nitrobenzene solution gave 5-methyl-1-phenyltetrazole accompanied irreproducibly by large amounts of *N*-methyl-*N'*-phenylurea.

Tetrazoles have recently been found to break up when strongly heated to give carbodiimides accompanied in some cases by significant amounts of 2-arylarimidazoles.[2] If the reaction leading to imidazole could be made to occur more efficiently, it would be a useful synthetic route to benzimidazoles and perhaps their heterologs, such as the purine ring system. The reaction has now been explored with some representative tetrazoles bearing *p*-substituted phenyl, pyridyl, and quinolyl groups.

The required tetrazoles were prepared by a recently reported[2] modification of the von Braun-Rudolf synthesis from imidyl chlorides, using buffered aqueous sodium azide instead of anhydrous hydrogen azide solutions. This method was found to be generally successful, and to have some advantages in handling and in freedom from rearrangement products, but entailed separating the tetrazoles, formed in about 60% yields, from large amounts of the amides corresponding to the imidyl chlorides. Attempts to prepare 1-(8-quinolyl)-5-phenyl- and 1-(2,6-dimethyl-4-pyrimidyl)-5-*p*-chlorophenyltetrazole failed; this appeared to be due to difficulty in the reaction of the corresponding amides with phosphorus pentachloride.[3]

1,5-Diphenyltetrazole has already been found to give 12–14% of 2-phenylbenzimidazole when pyrolyzed, the remainder going to diphenylcarbodiimide; these results have now been confirmed. Since the two reactions occurring embody competition between one involving migration of a group from carbon to nitrogen, and one involving cyclization to a benzene ring without migration, it is of interest to examine the effect of substituents on the group that might migrate. A *p*-chloro substituent retards the migration of phenyl from C to N in the Beckmann rearrangement[4]; as would be expected from this, it also retarded carbodiimide formation relative to cyclization, and 1-phenyl-5-

(1) This work was supported by the U. S. Public Health Service, Contract No. C-2613.

(2) P. A. S. Smith and E. Leon, *J. Am. Chem. Soc.*, **80**, 4647 (1958).

(3) *Cf.* D. M. Hall, *J. Chem. Soc.*, 1603 (1948), for a report of similar difficulty.

(4) A. W. Chapman and F. A. Fidler, *J. Chem. Soc.*, 448 (1936).