are 1.3×10^{-4} (nitrobenzene, 80°), 4.7×10^{-4} (acetone, 25°), and 1.3 (water, 25°).

Experimental

Materials.—Salts were those described elsewhere,[1c] recrystallized three or more times and dried at room temperature and $\sim 10^{-4}$ mm. before use. Alkyl halides were commercial materials which were found homogeneous to gas chromatography.

Fused Salt Decomposition Products. A.—Salt samples (0.2–0.8 mmole) were heated in a glass-stoppered long-necked flask. After cooling, the salt was dissolved in 5 ml. of glacial acetic acid and the solution was titrated potentiometrically with 0.01 *N* $HClO_4$ in 99.9% dioxane.

B.—Salt samples (0.1–0.2 g.) were sealed in evacuated 3-ml. ampoules. After heating, the ampoules were opened at 0° and the salt was triturated with 2 ml. of pentane and filtered. The solid and ampoule were washed with four more portions of pentane, the filtrates being collected in 7 ml. of acetic acid. The pentane was evaporated from this mixture and the acetic acid solution was titrated with $HClO_4$.

C.—Sample tubes treated as in B were opened at −80° and 0.5 ml. of cyclooctane was added. The pulverized solid was allowed to settle and a 5-μl. sample of the supernatant liquid was chromatographed on a 2.5-m., 25% silicone 702 on 30–60-mesh firebrick column at 170°. Effluent peaks were identified by comparison with authentic specimens and determined by comparison of planimetrically determined peak areas with those given by standard solutions in cyclooctane when measured under the same conditions.

Equilibrium Constant Measurements.—The salt or salt mixture (*ca.* 1.0 mmole) and alkyl halide (*ca.* 0.04 mmole) were weighed into glass ampoules, sealed, equilibrated at 100 ± 0.5°, and rapidly quenched so that the salt crystallized instantly. The product was extracted with pure heptane and an aliquot of the heptane solution was analyzed gas chromatographically as described in the preceding section.

The Herz Reaction. The Formation and Hydrolysis of Herz Compounds

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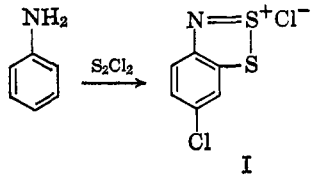
Evidence is given for the time sequence involved in the nuclear chlorination which occurs in certain Herz reactions. The previously unknown parent Herz compound, 1,3,2-benzothiazathiolium chloride, is synthesized and a new method for the synthesis of Herz compounds is given. A convenient method for the preparation and purification of some 3H-1,2,3-benzodithiazole 2-oxides is also present.

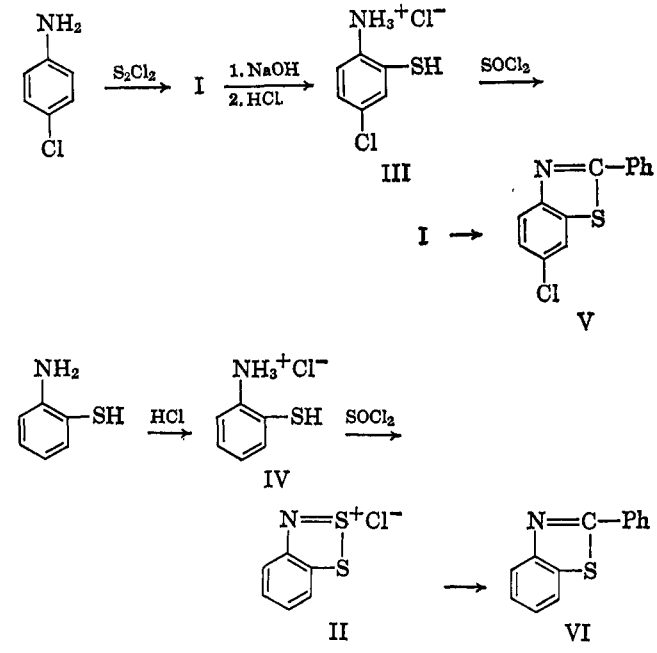
In spite of the fact that the reaction of aromatic primary amines with sulfur monochloride to give substituted 1,3,2-benzothiazathiolium chlorides (Herz compounds) has been known for a long time,[1,2] little is known about the mechanism of the reaction. For example, treatment of aniline with sulfur monochloride leads to the formation of 6-chloro-1,3,2-benzothiazathiolium chloride (I).[3,4] Attempts to alter the conditions of the Herz reaction to obtain this interesting heterocyclic system without the accompanying nuclear chlorination have been unsuccessful.[5,6] Consequently, one of the unresolved problems has been a determination of the point in the reaction sequence when nuclear chlorination occurs. This problem has now been partially answered by the synthesis of the previously unknown parent compound, 1,3,2-benzothiazathiolium chloride (II), and a study of its behavior with sulfur monochloride.



I

It had been suggested that substituted Herz compounds might be made by treating the appropriately substituted *o*-aminothiophenol with thionyl chloride, although no experimental work has ever been reported on this possibility.[7] To test this potential method of synthesis of Herz compounds, the hydrochlorides of 2-amino-5-chlorobenzenethiol (III) and 2-aminobenzenethiol (IV) were synthesized and treated with thionyl chloride in a manner illustrated by Scheme I.

SCHEME I

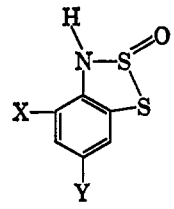


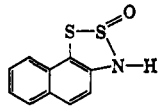
The conversion of the hydrochlorides to the Herz compounds (I and II) by treatment with thionyl chloride was accomplished in crude yields of 70 and 96%, respectively. Since Herz compounds decompose upon heating and are very difficult to purify, I and II were converted for the purpose of identification to the known

(1) R. Herz, *Chem. Zentr.*, **4**, 948 (1922).
(2) Cassella and Co., German Patent 360,690 (Oct. 6, 1922).
(3) W. König, *Ber.*, **61**, 2065 (1928).
(4) For further examples of the Herz reaction, see W. K. Warburton, *Chem. Rev.*, **57**, 1011 (1957).
(5) K. J. Farrington and W. K. Warburton, *Australian J. Chem.*, **8**, 545 (1955).
(6) K. J. Farrington and W. K. Warburton, *ibid.*, **9**, 480 (1956).
(7) Weinberg, *Ber.*, **63A**, 117 (1930).

TABLE I

3H-1,2,3-BENZODITHIAZOLE 2-OXIDES

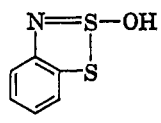


X	Y	M.p., °C. dec.	Yield,[a] %	Calcd., % C	H	Cl	S	Found,[b] % C	H	Cl	S	Ultraviolet spectral data[c] λ_{max}, mμ	log ε
H	H	123–124	49	42.08	2.94		37.45	42.14	3.11		37.35	208, 276	4.5, 3.25
H	Cl	113–114	47	35.03	1.96	17.24		34.91	1.95	17.37		214, 294	4.46, 3.37
Cl	Cl	129.5–130.5	44	30.01	1.26	29.53		30.21	1.39	29.70		222, 232 (s), 298, 307 (s)	4.43, 4.39, 3.35, 3.33
NO_2	OCH_3	163–164[d]	18									212, 307, 398	4.41, 3.57, 3.58
		144–145[e]	51	54.27	3.19			54.05	3.23			218 (s), 241, 262 (s), 289 302 (s), 343	4.34, 4.66, 4.01, 3.68, 3.59, 3.38

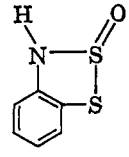
[a] Purified and based on the corresponding Herz compounds. [b] Microanalyses were made by Galbraith Laboratories, Inc., Knoxville, Tenn. [c] Ultraviolet spectra were taken with a DB Beckman spectrophotometer using 95% ethanol as solvent. [d] Ref. 10d, m.p. 162.5°, good analysis given. [e] Ref. 10e, m.p. 147.5°.

6-chloro-2-phenylbenzothiazole (V) and phenylbenzothiazole (VI) by the zinc salt method of Stephen and Wibberley.[8,9] These results indicate that not only can Herz compounds be made by this new method, but they also indicate that the reaction of IV with thionyl chloride proceeds without nuclear chlorination.

In a few instances it has been reported that Herz compounds (*e.g.*, I) can be hydrolyzed to give products[10] whose parent structure can be represented by two tautomeric forms, VII and VIII.[11] In view of the



VII

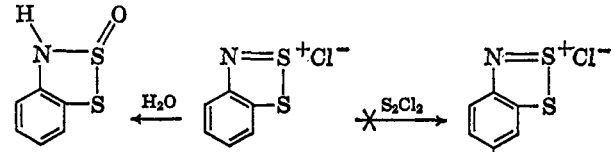


VIII

fact that only three of the hydrolysis products[10b,d,e] have been purified it was somewhat surprising that I, II, and 4,6-dichlorobenzothiazathiolium chloride readily underwent hydrolysis to give products in good yield which could be readily purified and which were fairly stable (see Table I). Consequently, these hydrolysis compounds were used as derivatives of the Herz compounds in subsequent reactions instead of the 2-phenylbenzothiazoles.

Because of the differences in the chemical and physical characteristics of Herz compounds and their hydrolysis products, the 3H-1,2,3-benzodithiazole 2-oxide structure (VIII) is favored over its tautomer (VII). One such difference is the visible and ultraviolet absorption spectra. The spectrum of VII would be expected to be somewhat like the spectrum of I or II. However, the actual spectra of the hydrolysis products are quite different from I or II spectra as they show a less intense absorption which occurs at much shorter wave lengths (see Table I and Experimental section). These spectra are much more consistent with a structure like VIII. Further work on the chemistry of these hydrolysis products is presently being carried on.

To determine the stage at which nuclear chlorination takes place in the Herz reaction, 1,3,2-benzothiazathiolium chloride (II) was treated with sulfur monochloride using the usual conditions for the Herz reaction. The starting material was recovered (92%) as was shown by the fact that hydrolysis gave only 3H-1,2,3-benzodithiazole 2-oxide (VIII) in 49% yield. It was of interest to learn if I could be formed by using a longer reaction time. This was tested by heating II with sulfur monochloride for 22 hr. (over seven times



VIII II I

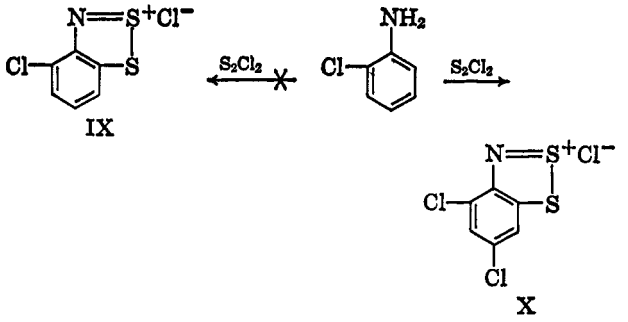
the usual reaction time). The product obtained appeared to have undergone extensive decomposition as indicated by its cinder-like appearance. Hydrolysis of these cinders gave a 14% yield of a product which when decolorized gave pure VIII. There is no evidence that I was formed even in very small amounts. These results indicate that sulfur monochloride will not chlorinate II and consequently it is very unlikely that structures like II can be an intermediate in the usual Herz reaction, where nuclear chlorination readily takes place if the position *para* to the amino group is occupied with a hydrogen. Thus, for example, 4-chlorobenzothiazathiolium chloride (IX) is not likely to be an intermediate in the reaction of *o*-chloroaniline

(8) F. F. Stephen and D. G. Wibberley, *J. Chem. Soc.*, 3338 (1950).

(9) Purification of the Herz compounds by recrystallization[10b,c] did not give satisfactory results.

(10) (a) A. W. Hixon and W. J. Cauwenberg, *J. Am. Chem. Soc.*, **52**, 2118 (1930); (b) J. F. Leaper, *ibid.*, **53**, 1891 (1931); (c) M. G. Ast and M. T. Bogert, *Rec. trav. chim.*, **54**, 917 (1935); (d) H. H. Fox and M. T. Bogert, *J. Am. Chem. Soc.*, **61**, 2013 (1939); (e) V. M. Zubarovskii, *J. Gen. Chem. USSR*, **17**, 613 (1947).

(11) M. K. Beszubez, *ibid.*, **17**, 681 (1947).



and sulfur monochloride to give 4,6-dichlorobenzothiazathiolium chloride (X).[12]

Experimental

6-Chloro-1,3,2-benzothiazathiolium Chloride (I).—A solution of 5.7 g. (0.045 mole) of *p*-chloroaniline in 7.0 ml. of anhydrous acetic acid was added to 25 ml. (42 g., 0.31 mole) of cold redistilled sulfur monochloride. This mixture was stirred for 3 hr. at room temperature, and then at 70–80° for 3 hr. After cooling to room temperature, the dark mixture was stirred with 50 ml. of dry benzene ($CaCl_2$) and then filtered. The Herz compound was washed with dry benzene and then dried *in vacuo* to give 9.3 g. (93%) of a yellow-brown solid which decomposed at 210–225°: ultraviolet spectrum, $\lambda_{max}^{CF_3COOH}$ 417 mμ (log ε 3.6) and 366 mμ (log ε 4.1).

6-Chloro-2-phenylbenzothiazole (V).—A mixture of 8.3 g. (0.037 mole) of I and 500 ml. of ice–water was vigorously stirred to give a red mixture. After making the mixture alkaline with 6 *M* NaOH, 5 g. of $NaHSO_3$ was added. After heating for 1 hr., the now greenish mixture was decolorized with Norit and filtered to give a nearly colorless filtrate which contained the sodium salt of 2-amino-5-chlorobenzenethiol. When the zinc mercaptide was precipitated by adding an excess of saturated zinc sulfate solution, acetic acid was added, and the mixture was filtered. A total of 2.65 g. (38%) of the dried zinc mercaptide was obtained.

To a suspension of 1.3 g. (0.0034 mole) of the zinc mercaptide in 40 ml. of anhydrous acetic acid was added 2.0 g. (0.014 mole) of benzoyl chloride. The resulting clear yellow solution was refluxed for 30 min. and then poured into 50 ml. of water. The tan precipitate which occurred was dissolved in methanol and decolorized with Norit, and the resulting colorless filtrate was heated and mixed with enough water to cause turbidity. A total of 1.25 g. (75%) of white needles were collected which had a melting point of 156–157°, lit.[13] m.p. 156.7°. V was also prepared in a similar yield from aniline by the same procedure, m.p. 153–155°. A mixture melting point of the 6-chloro-2-phenylbenzothiazole prepared by the two methods was 153–155°.

Synthesis of V by the Use of Thionyl Chloride.—A total of 9.7 g. (0.043 mole) of I was converted to a colorless alkaline solution of the sodium salt of 2-amino-5-chlorobenzenethiol in the same manner as described in the previous procedure. This solution was neutralized to pH 7 with 6 *M* acetic acid. The resulting mixture was extracted with four 100-ml. portions of ether. After drying the combined yellow ether extracts ($MgSO_4$), dry HCl gas was bubbled through the mixture until no more precipitation occurred. A total of 2.90 g. (34%) of white crystalline hydrochloride salt (III) was collected which melted at 209–211°.

A mixture of 1.63 g. (0.0083 mole) of III and 5 ml. (8 g., 0.07 mole) of thionyl chloride was gently refluxed with stirring for 30 min. Dry benzene (15 ml.) was added and stirring continued for 5 min. After filtering and washing with 100 ml. of benzene, the precipitate was dried *in vacuo* to give 1.30 g. (70%) of a yellow-green solid which decomposed at approximately 210°.

This product was converted into 6-chloro-2-phenylbenzothiazole (V) in the same manner as before. The melting point of this sample of V was 155–157°. A mixture melting point of this sample and that prepared by the other method was 156–157°.

2-Phenylbenzothiazole (VI).—Redistilled 2-aminobenzenethiol was converted to VI in an over-all yield of 47% by the method of Stephan and Wibberley.[8] The melting point of the colorless needles was 112–113°, lit.[14] m.p. 114°.

2-Aminobenzenethiol Hydrochloride (IV).—A solution of 25.0 g. (0.199 mole) of 2-aminobenzenethiol in 500 ml. of dry ether was saturated with dry hydrogen chloride gas. The dried, crystalline IV weighed 31.5 g. (98%). It readily sublimed upon heating but when heated rapidly it melted at 210–211° dec., lit.[15] m.p. 217° dec.

1,3,2-Benzothiazathiolium Chloride (II).—A total of 15.3 ml. (25 g., 0.21 mole) of thionyl chloride was added to 4.25 g. (0.0263 mole) of IV. Hydrogen chloride was immediately evolved, and the mixture turned orange. After refluxing the mixture gently for 30 min., it was mixed with dry benzene and filtered. The reddish orange precipitate was washed with dry benzene until the washings were colorless. The vacuum dried solid weighed 4.76 g. (96%) and decomposed at 190–196°. The n.m.r. spectrum of 120 mg. of II/ml. of CF_3COOH showed only a multiplet at τ 2.35.

II was converted to the corresponding zinc mercaptide in a 23% yield using the same procedure as before. A mixture of 1.0 g. (0.0032 mole) of the zinc mercaptide, 3.6 g. (0.026 mole) of benzoyl chloride, and 25 ml. of anhydrous acetic acid was refluxed for 30 min. After diluting this solution with 150 ml. of water, a light brown solid was collected and redissolved in ether. The ether solution was extracted with two 100-ml. portions of 5% $NaHCO_3$ and then dried ($MgSO_4$). After removal of the ether, a pale brown solid was collected and sublimed at 13 mm. to give 0.83 g. (62%) of white needles which melted at 113.5–114°. A mixture melting point with the 2-phenylbenzothiazole prepared by the other method showed no melting point depression.

3H-1,2,3-Benzodithiazole 2-Oxide (VIII).—A dark orange mixture of 1.20 g. (0.0063 mole) of II and 50 ml. of water was stirred until the reaction appeared to be complete (about 30 min.). After cooling to 0°, the purple mixture was filtered to give a light violet solid and a reddish filtrate. After drying, the crude product weighed 0.89 g. (83%) and melted at 121–124° dec. The crude product was purified by dissolving it in 20 ml. of methanol, decolorizing the purple solution with Norit, and precipitating the product from the light yellow filtrate by adding 80 ml. of water. A total of 0.53 g. (49%) of light yellow plates were obtained which melted at 123–124° dec.: infrared spectrum (KBr) (μ), 2.9 vw, 3.20 m, 6.34 w, 6.88 m, 7.20 m, 7.70 m, 7.92 m, 9.2 (broad) s, 10.85 w, 11.42 m, 11.72 m, 12.48, 13.50 w, 13.65 s, 14.06 m, 14.42 w. Analytical data and the ultraviolet spectrum are given in Table I.

6-Chloro-3H-1,2,3-benzodithiazole 2-Oxide.—When 1.53 g. (0.0068 mole) of I was hydrolyzed by the previous procedure, 1.11 g. (79%) of a purple-gray solid was obtained which upon purification gave 0.66 g. (47%) of light yellow needles which melted at 113–114° dec.: infrared spectrum (KBr) (μ), 2.9 vw, 3.20 m, 6.35 w, 6.83 s, 7.00 s, 7.31 m, 7.80 m, 7.96 w, 8.05 w, 8.70 m, 9.1 (broad) s, 11.40 m, 11.55 m, 11.65 m, 12.15 m, 12.45 s, 13.50 m, 14.25 m, 15.21 m.

4,6-Dichloro-3H-1,2,3-benzodithiazole 2-Oxide.—The Herz compound, 4,6-dichlorobenzothiazathiolium chloride (X), was made in 99% yield by treating 2,4-dichloroaniline with sulfur monochloride under the usual conditions. It is a reddish brown solid which decomposes at 218–230°. When 2.00 g. (0.0077 mole) of X was hydrolyzed, 1.65 g. (89%) of purple solid was collected. This was purified in the usual manner to give 0.81 g. (44%) of light yellow, small needles which melted at 129.5–130.5° dec.: infrared spectrum (KBr) (μ), 2.90 vw, 3.06 m, 6.40 m, 6.86 s, 7.08 vw, 7.20 m, 7.43 m, 7.83 m, 8.00 w, 8.40 w, 8.71 s, 9.00 m, 9.30 m, 11.32 m, 11.58 w, 11.72 m, 12.00 m, 12.40 m, 13.45 m, 14.22 m.

Reaction of 1,3,2-Benzothiazathiolium Chloride (II) with Sulfur Monochloride.—A total of 4.80 g. (0.0253 mole) of II was added all at once to a solution fo 25 ml. (38 g., 0.31 mole) of sulfur monochloride and 7 ml. of glacial acetic acid. After stirring at room temperature for 1 hr. and then at 60–80° for 3 hr., this dark mixture was cooled, mixed with 40 ml. of dry benzene, and filtered. The precipitate was washed with benzene and dried *in vacuo* to give 4.43 (92% yield) of an orange-brown solid.

A mixture of 1.84 g. (0.0097 mole) of this Herz compound was stirred with 50 ml. of water for 2 hr. The resulting brown solid weighed 1.45 g. (87%). This was purified from methanol and water in the usual manner to give 0.96 g. (58%) of light yellow plates which melted at 122.5–123.5° dec. This product gave no melting point depression when mixed with 1,2,3-benzodithiazole

(12) A. T. Blomquist and L. I. Diuguid, *J. Org. Chem.*, **12**, 718 (1947).
(13) M. T. Bogert and H. B. Corbitt, *J. Am. Chem. Soc.*, **48**, 783 (1926).
(14) M. T. Bogert and A. Stull, *ibid.*, **47**, 3078 (1925).
(15) Claasz, *Ber.*, **45**, 1031 (1912).

2-oxide (VIII), and the infrared spectra of the two samples were identical.

Attempted Nuclear Chlorination of II under More Drastic Conditions.—Sulfur monochloride (15 ml., 25 g., 0.19 mole) was added to a mixture of 3.0 g. (0.016 mole) of II and 4 ml. of glacial acetic acid. This mixture was stirred for 13 hr. at room temperature and then heated at 70–75° for 22 hr. Dry benzene was added to the resulting dark mixture, and the precipitate was collected by filtration. After washing and drying as before, 2.8 g. of dark cinders were obtained.

A mixture of 1.6 g. of these cinders was stirred with 50 ml. of water for 90 sec. The resulting orange solution was rapidly filtered from the dark insoluble material. After approximately 2 min., a light-colored solid began to separate out of the orange filtrate. After the mixture had been allowed to stand overnight, the precipitate was collected and dried to give 0.21 g. (14%) of light purple solid. After purifying as usual, 0.10 g. (7%) of light yellow plates were obtained which melted at 123–124° dec. The infrared spectrum of this product was identical with the spectrum of VIII.

The other Herz compounds and their hydrolysis products were made in a similar manner and the important experimental data for them is given in Table I.

Acknowledgment.—The authors gratefully acknowledge financial support by grants given under the National Science Foundation Undergraduate Education Program. We are indebted to Bernard J. Nist for the nuclear magnetic resonance spectra.

Cytosine 3-N-Oxide and Its Rearrangement on Acetylation[1]

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Cytosine and cytidine (I) have been oxidized to their N-oxides (II) by *m*-chloroperbenzoic acid. Acetylation of cytosine 3-N-oxide (IIa) resulted in a rearrangement to N^4-acetoxycytosine (III). This was proven by an unambiguous synthesis from 4-methylthiouracil (V).

A variety of purine N-oxides have been studied, some of which have chemotherapeutic[2,3] and oncogenic[4] activities, but until recently most of the known pyrimidine N-oxides have been either alkyl or alkoxy derivatives.[5] Pyrimidine N-oxides bearing only amino or hydroxy functions, or both, have just recently been reported.[6–9] Cramer[10–12] indicates that N-oxides of this type may be useful in determining the base sequence of polynucleotides.

In 1963 Cramer reported the direct oxidation of cytosine, cytidine, and cytidylic acid to the corresponding N-oxides using monoperphthalic acid.[6] However, the scale of those reactions was too small to permit isolation of pure products; identification was made on the basis of spectral data (Table I).

In our hands that method has not been successful, even on a larger scale, but we have accomplished the oxidation of cytosine and cytidine (I) to N-oxides (II), with the commercially available *m*-chloroperbenzoic acid. The product from the cytosine oxidation (IIa), obtained in 21% yield, was assumed to have the 3-N-oxide[13] structure on the basis of its similarity in spectrum to cytidine N-oxide. IIa was obtained as a monohydrate and, to exclude the possibility of a di-N-oxide, was reduced with Pd–C. The uptake of 1 equiv. of hydrogen and the isolation of cytosine confirmed this assumption.

Klötzer, in a very significant series of contributions, has reported total and unequivocal syntheses of several pyrimidine N-oxides,[7–9] including uracil 1- and 3-N-oxides[8] and cytosine 1- and 3-N-oxides.[9] We have now compared our cytosine N-oxide with Klötzer's cytosine 3-N-oxide, both paper chromatographically in several solvent systems and spectrally at three pH values, and established their identity.

Cytosine 3-N-oxide (IIa) is stable to alkali. From acid, it was recovered as its hydrochloride. Treatment of IIa with acetic anhydride in glacial acetic acid produced a compound which had an elemental analysis in agreement with a monoacetyl derivative, $C_6H_7N_3O_3$. Its ultraviolet absorption spectra indicated that the product was not an acetyl derivative of the N-oxide. The compound did not show any strong absorption in the 220–230-mμ region nor give a red-orange color with ferric chloride, as does cytosine 3-N-oxide.

From the spectral similarity of the product to that of N^4-acetylcytosine[14] and to N^4-hydroxycytidine derivatives,[15] and the slow production of a deep blue color with ferric chloride, a hydroxylamine was suspected. We have now established that this reaction had led to a rearrangement to N^4-acetoxycytosine (III). This conversion, IIa → III, is analogous to the Dimroth rearrangement which has recently been reviewed,[16] although the conditions employed are more nearly comparable with a reverse rearrangement reported by Ueda and Fox,[17,18] in which an aminomethyl group is rearranged to a ring N-methyl group.

(1) This investigation was supported in part by funds from the Atomic Energy Commission (Contract No. AT[30-1], 910) and from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service (Grant No. CA-03190-09).

(2) M. A. Stevens, A. Giner-Sorolla, H. W. Smith, and G. B. Brown, *J. Org. Chem.*, **27**, 567 (1962).

(3) G. Levin and G. B. Brown, *J. Med. Chem.*, **6**, 825 (1963).

(4) G. B. Brown and K. Sugiura, *Cancer Res.*, in press.

(5) D. J. Brown in "The Pyrimidines," Interscience Publishers, Inc., New York, N. Y., 1962, pp. 19, 128, 382.

(6) F. Cramer and H. Seidel, *Biochim. Biophys. Acta*, **72**, 157 (1963).

(7) W. Klötzer, *Monatsh. Chem.*, **95**, 265 (1964).

(8) W. Klötzer, *ibid.*, **95**, 1729 (1964).

(9) W. Klötzer, *ibid.*, **96**, 169 (1965).

(10) F. Cramer, F. Fittler, H. Kuntzel, and E.-A. Schäfer, *Z. Naturforsch.*, **18b**, 668 (1963).

(11) F. Cramer, K. Randerath, and E. A. Schäfer, *Biochim. Biophys. Acta*, **72**, 150 (1963).

(12) F. Cramer and H. Seidel, *ibid.*, **91**, 14 (1964).

(13) Cramer has also assigned his product the same structure but names it a 1-N-oxide.

(14) D. M. Brown, A. Todd, and S. Varadarajan, *J. Chem. Soc.*, 2384 (1956).

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