Oxidation of Dimercaptals to Tetrasulfones.—The cyclic dimercaptals and dimercaptol were oxidized to the corresponding tetrasulfones by the method of Drew.[8] The vanillin derivative could not be converted to the sulfone because of oxidative attack of the phenolic ring. The oxidation of the *p*-chlorobenzaldehyde derivative is typical.

A mixture of 4.068 g. of the cyclic dimercaptal from *p*-chlorobenzaldehyde and decamethylene dimercaptan in 200 ml. of chloroform was stirred with 272 ml. of a cold 0.417 *N* solution of monoperphthalic acid in ether. An additional 100 ml. of ether was added to increase the volume of solvent. After three days of stirring an additional 136 ml. of the monoperphthalic acid solution was added, and stirring was continued another three days. The reaction mixture was filtered and the precipitate washed repeatedly with 5% sodium bicarbonate solution and then water to remove phthalic acid. The white solid tetrasulfone after drying in a desiccator weighed 4.67 g. (96%). The sulfone was quite insoluble in common solvents. A sample was recrystallized repeatedly from a large volume of chloroform to give crystals, m.p. 166–170° dec.

Anal. Calcd. for $C_{34}H_{50}Cl_2O_8S_4$: C, 51.96; H, 6.41; S, 16.32. Found: C, 52.28; H, 6.53; S, 15.78.

The acetone cyclic dimercaptol gave a tetrasulfone, m.p. 213–218°. *Anal.* Calcd. for $C_{26}H_{52}S_4O_8$: C, 50.29; H, 8.44; S, 20.66. Found: C, 50.27; H, 8.75; S, 20.33.

The *m*-nitrobenzaldehyde cyclic dimercaptal gave a 93.3% yield of a tetrasulfone, m.p. 151–154° dec. *Anal.* Calcd. for $C_{34}H_{50}O_{12}N_2S_4$: C, 50.60; H, 6.24; S, 15.89; N, 3.47. Found: C, 50.70; H, 6.40; S, 15.48; N, 3.48.

Reaction of Heptamethylene Dithiol and Vanillin.—To a solution of 6.5 g. of heptamethylene dithiol and 6.02 g. of vanillin in 100 ml. of dioxane was added 20 ml. of dioxane saturated with dry hydrogen chloride. After 22 days no solid had crystallized. Evaporation of the solvent left a viscous liquid soluble in benzene but insoluble in methanol. This oil weighed 10.9 g. and had an inherent viscosity in benzene of only 0.03. It was not further investigated.

Reaction of Heptamethylene Dithiol and Acetone (By Eugene D. Vessel).—To a solution of 16.4 g. of heptamethylene dithiol and 5.8 g. of acetone in 80 ml. of dry dioxane was added 20 ml. of dioxane saturated with dry hydrogen chloride. The mixture was placed in a closed flask and stirred at room temperature for 8 days. Filtration gave 15.7 g. of crystals, m.p. 128–129°. From the mother liquors 3.5 g. of viscous material was obtained. On recrystallization from dioxane additional crystalline material (about 4–5 g.) was obtained until finally less than 0.5 g. of residual viscous polymeric material remained.

The crystals were recrystallized from benzene to give beautiful colorless plates, m.p. 129–129.5°.

Anal. Calcd. for $C_{20}H_{40}S_4$: C, 58.76; H, 9.86; S, 31.38; mol. wt., 408. Found: C, 58.73; H, 9.84; S, 31.47; mol. wt. Menzies–Wright b.p. elevation method[7] (av. of 3 runs), 415.5.

Reaction of Nonamethylene Dithiol and Acetone.—To a solution of 9.6191 g. of nonamethylene dithiol and 2.9039 g. of acetone in 40 ml. of dioxane was added 8 ml. of dioxane saturated with dry hydrogen chloride. The solution was stirred for 12 days at room temperature and then filtered to yield 5.57 g. (48%) of white crystals which proved to be the cyclic dimercaptol. After recrystallization from benzene the product melted at 128–129°.

Anal. Calcd. for $C_{24}H_{48}S_4$: C, 62.00; H, 10.41; S, 27.59; mol. wt., 464. Found: C, 62.00; H, 10.37; S, 27.20; Menzies–Wright b.p. elevation method[7] (av. of 3 runs), 437.

The infrared spectrum of this compound showed a C–SC band at 673 cm.$^{-1}$, $-(CH_2)_n-$ bands at 720 cm.$^{-1}$ and $(CH_3)_2$ bands at 1350, 1366 and 1379 cm.$^{-1}$ and aliphatic C–H at 2900 cm.$^{-1}$.

Ultraviolet Absorption Spectra of Cyclic Products.—The ultraviolet absorption of the cyclic dimercaptals and dimercaptols was taken in dioxane solution.

The results are listed in Table II.

TABLE II

Cyclic dimercaptal from	λ_{max}, mμ	log ε
Benzaldehyde and decamethylene dithiol	244[a]	3.50
m-Nitrobenzaldehyde and decamethylene dithiol	256	4.25
Vanillin and decamethylene dithiol	235	4.25
	285	4.01
p-Chlorobenzaldehyde and decamethylene dithiol	248[a]	3.72
Cyclic dimercaptol from		
Acetone and decamethylene dithiol	239	3.16
Acetone and nonamethylene dithiol	247	3.15

[a] Shoulders rather than peaks.

URBANA, ILL.

(8) H. F. Drew, Ph.D. Thesis, University of Minnesota, 1951, p. 52.

[CONTRIBUTION FROM THE MAYURBHANJA CHEMICAL LABORATORY, RAVENSHAW COLLEGE, UTKAL UNIVERSITY]

Synthesis of Isomeric Bromothiazolylamines and the Use of Their Mercurated Derivatives as Fungicides and Bactericides

BY G. N. MAHAPATRA

RECEIVED MAY 18, 1956

Fifteen isomeric bromothiazolylamines containing one, two or three bromine atoms have been synthesized. The relation between the position of bromine and biological activity has been studied. These bromothiazolylamines have been mercurated and the resulting compounds subjected to fungicidal and bactericidal assay with promising results.

In view of the antibacterial activity and other biological properties of 2-aminothiazoles and various N-substituted 2-amino thiazoles,[1-6] it was thought worthwhile to synthesize further N-substituted aminothiazoles. As the introduction of bromine into thiazolidone[7] and the thiazole[8] nucleus generally augments the antibacterial as well as antifungal activity, bromine has been introduced into these thiazole derivatives and the relation between the position of bromine in the molecules and their biological activity also has been studied.

Fifteen different phenyl-2-thiazolylamines having one, two or three bromine atoms at different positions of the molecule have been prepared.

(1) M. Perrault and D. Bovet, *Lancet*, **250**, 731 (1946); *C. A.*, **42**, 8969h (1948).

(2) Y. Tajika, Y. Nitta, J. Yomoda and H. Oya, *J. Pharm. Soc. Japan*, **71**, 709 (1951).

(3) D. Bovet, J. Bablet and J. Fournel, *Ann. Inst. Pasteur*, **72**, 105 (1946), *Semaine hopitaux Paris*, **37**, 8 (1945).

(4) C. W. Sondern and P. J. Breivogel, U. S. Patent 2,440,703, May 4 (1948); U. S. Patent 2,519,325, Aug. 15 ((1950).

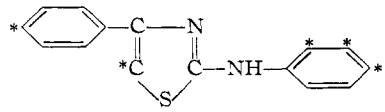
(5) Shigeya Saijo, *J. Pharm. Soc. Japan*, **72**, 1009 (1952).

(6) H. Erlenmeyer, U. S. Patent 2,400,689, May 21 (1946).

(7) M. K. Rout and G. N. Mahapatra, THIS JOURNAL, **77**, 2427 (1955).

(8) G. N. Mahapatra, *Nature*, **177**, 938 (1956).

There are five isomeric monobromo-, seven isomeric dibromo- and three isomeric tribromophenylthiazolylamines having a bromine atom either in the phenyl nucleus or in the thiazole ring, as marked in the following structure where the asterisk

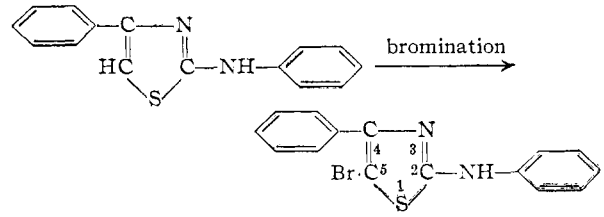


shows the positions of the bromine atoms in the molecule.

Of the five monobromothiazolylamines, four (which contain bromine atom in the phenyl rings as shown in the above figure) have been synthesized by the reaction of acetophenone with *o*-, *m*- or *p*-bromophenylthiourea or of *p*-bromoacetophenone with phenylthiourea by previously reported methods.[9,10] The fifth, with bromine directly attached to the thiazole nucleus at C-5, was prepared by brominating 2-phenylamino-4-phenylthiazole, prepared by condensing acetophenone with phenylthiourea by the above method. On addition of one equivalent of bromine to 2-phenylamino-4-phenylthiazole under controlled conditions, only one atom of bromine enters the molecule presumably at the C-5 of the thiazole nucleus.

This assumption is based upon evidence of Garreau,[11] Ganapathi and Venkataraman[12] and Mahapatra[13] that on bromination of 2-aminothiazole, where the C-4 is blocked by any substitution, bromine generally attaches to C-5, as the activity of this carbon atom in the thiazole nucleus is a maximum when there is a substitution at C-2.[14] The possibility that the bromine atom may instead enter the *para* position of the phenyl nucleus attached to the amino group at C-2 is discarded, as the bromo derivative so obtained would be identical with that prepared from *p*-bromophenylthiourea and acetophenone, which is not the case. Moreover such a bromo compound should couple with diazotized aniline forming an azo compound, where the azo group should enter the free C-5 position[15] of the thiazole nucleus. The monobromo compound does not undergo coupling with diazotized aniline, though before bromination it coupled in the usual manner. This indirectly confirms that the C-5 position of the thiazole nucleus is already occupied. Furthermore when the brominated compound is boiled with allyl alcohol and concd. hydrochloric acid for 8 hours,[16] the bromine is replaced by hydrogen, thus liberating the bromine free compound. This indirectly supports the conclusion that the bromine atom is attached to the thiazole nucleus, not to the phenyl nucleus.

The possibility of the bromine atom entering the phenyl nucleus attached to C-4 of the thiazole nucleus is also discarded by the same arguments as given above.



Of the seven dibromo derivatives, three have been prepared by condensing *p*-bromoacetophenone with *o*-, *m*- and *p*-bromophenylthioureas in the usual manner. The remaining four have been prepared by brominating monobromo derivatives prepared by direct synthesis, as mentioned above. The position of the second bromine atom in these four cases is assumed to be at C-5 of the thiazole nucleus and the position can be confirmed by the arguments given above.

The three tribromo derivatives have been prepared by direct bromination of the three dibromo compounds directly synthesized as stated above. The third bromine atom is assumed to be on the fifth carbon atom of the thiazole nucleus.

In view of the pronounced antibacterial[17] as well as antifungal[18] action of organomercurials and the recent report of mercurated derivatives of the thiazole compounds[19,20] as good fungicides, these fifteen isomeric bromothiazolylamines have been mercurated with mercuric acetate, to form acetoxymercuric compounds. It has been assumed on the basis of the earlier work[21,22] that the acetoxymercuric group enters the aryl nucleus attached to the amino group at C-2, at the *para* position (with respect to –NH group) of the aryl nucleus and that if the *para* position is blocked the substitution occurs at the *ortho* position. When the mercurated derivative of 2-phenylamino-4-phenylthiazole is treated with potassium perbromide solution,[23] the acetoxymercuri group is removed and is replaced by a bromine atom, and the resulting compound is found to be identical in melting point and other physical and chemical properties to 2-*p*-bromophenylamino-4-phenylthiazole, directly synthesized from *p*-bromophenylthiourea and acetophenone.

The preparation of different phenylthioureas required for the synthesis of thiazoles, the preparation of different arylaminothiazoles and lastly the bromination and mercuration of these arylaminothiazoles have been illustrated by giving one example in each case in the Experimental. The an-

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(15) G. N. Mahapatra and M. K. Rout, communicated to the *J. Indian Chem. Soc.*

(16) Y. Garreau, *Compt. rend.*, **230**, 448 (1950); *C. A.*, **44**, 6853f (1950).

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(22) G. N. Mahapatra and M. K. Rout, *J. Indian Chem. Soc.*, **31**, 933 (1954).

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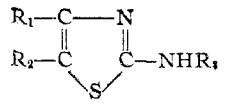
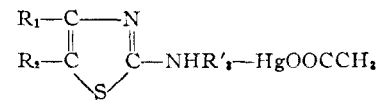
TABLE I



Bromophenylthiazolylamines



Acetoxymercuri derivatives

Compound	R_1	R_2	R_3	M.p., °C.	Yield, %	Sulfur, % Calcd.	Sulfur, % Found	Bromine, % Calcd.	Bromine, % Found	M.p., °C.	Yield, %	Mercury, % Calcd.	Mercury, % Found
1	*p*-BrC_6H_4–	H	C_6H_5–	104	70	9.67	9.21	24.17	24.51	240	71	33.95	33.61
2	C_6H_5–	H	*p*-BrC_6H_4–	122	75	9.67	9.93	24.17	24.39	249	82	33.95	34.09
3	C_6H_5–	H	*m*-BrC_6H_4–	87	70	9.67	9.15	24.17	23.88	195	75	33.95	34.31
4	C_6H_5–	H	*o*-BrC_6H_4–	114	72	9.67	9.41	24.17	23.98	243	63	33.95	33.69
5	C_6H_5–	Br	C_6H_5–	116	65	9.67	9.33	24.17	24.33	281–282 d.	72	33.95	33.71
6	*p*-BrC_6H_4–	H	*p*-BrC_6H_4–	133–134	72	7.80	7.36	39.02	39.52	244	85	29.94	29.39
7	*p*-BrC_6H_4–	H	*m*-BrC_6H_4–	96	81	7.80	7.53	39.02	38.75	213	67	29.94	30.15
8	*p*-BrC_6H_4–	H	*o*-BrC_6H_4–	103	65	7.80	7.99	39.02	38.79	231	61	29.94	29.40
9	*p*-BrC_6H_4–	Br	C_6H_5–	102	78	7.80	8.35	39.02	39.49	215	73	29.94	30.37
10	C_6H_5–	Br	*p*-BrC_6H_4–	117	69	7.80	7.59	39.02	39.36	252–253	78	29.94	29.81
11	C_6H_5–	Br	*m*-BrC_6H_4–	132	72	7.80	8.32	39.02	38.63	186	67	29.94	30.19
12	C_6H_5–	Br	*o*-BrC_6H_4–	156	65	7.80	7.21	39.02	39.51	118	65	29.94	29.39
13	*p*-BrC_6H_4–	Br	*p*-BrC_6H_4–	162	71	6.54	7.09	49.08	48.81	206	63	26.80	26.53
14	*p*-BrC_6H_4–	Br	*m*-BrC_6H_4–	225–226	79	6.54	6.13	49.08	49.53	195–196	71	26.80	27.27
15	*p*-BrC_6H_4–	Br	*o*-BrC_6H_4–	113–114	82	6.54	6.89	49.08	49.31	177	69	26.80	27.19

alytical data on these bromophenylthiazolylamines and their mercurated derivatives are given in Table I.

Experimental

1. Preparation of Different Arylthioureas.—Phenylthiourea[24] was obtained by the action of alcoholic ammonia on phenyl isothiocyanate prepared from aniline by the method of Dains, Brewster and Olander.[25] *o*-, *m*- and *p*-bromophenylthioureas have been prepared by boiling *o*-, *m*- and *p*-bromoaniline hydrochloride with ammonium thiocyanate,[26] respectively.

***m*-Bromophenylthiourea** which is a new compound, has melting point 138°, and forms colorless glistening crystalline plates.

Anal. Calcd. for $C_7H_7N_2SBr$: Br, 34.63; S, 13.85. Found: Br, 34.81; S, 13.53.

2. Preparation of 2-*p*-Bromophenylamino-4-phenylthiazole.—Nine grams of *p*-bromophenylthiourea was mixed with 4 g. of acetophenone in the presence of 6 g. of iodine and heated for 24 hours on a water-bath with a condenser and then for another period of 12 hours without the condenser. The reaction mixture was then treated with ether and kept overnight to remove unreacted ketone and iodine. The ether was removed and the mixture was boiled with water to dissolve any unreacted products. Then the reaction product was treated with strong aqueous ammonia to liberate the base. The product was finally crystallized from alcohol; yield 75%, m.p. −122°. *Anal.* Calcd. for $C_{15}N_2SH_{11}Br$: C, 54.38; H, 3.32; S, 9.67; Br, 24.17. Found: C, 54.81; H, 3.63; S, 9.93; Br, 24.39.

Dry benzene was taken as the condensing medium when all the starting materials were solids.

3. Bromination of 2-*p*-Bromophenylamino-4-phenylthiazole.—Three and one-half grams of the above thiazole derivative was treated with 2 cc. of concentrated hydrobromic acid and the hydrobromide salt thus formed was dissolved in 30 cc. of glacial acetic acid and the mixture stirred and well cooled under ice, so that its temperature was between 0–3°; 2 g. of bromine dissolved in 15 cc. of acetic acid, was added dropwise. The whole was stirred for another hour after addition. The excess acetic acid was distilled out under reduced pressure. Then the residue was treated with water and was made alkaline with concentrated ammonia. The free amino base liberated was recrystallized from ethanol; yield 69%, m.p. −117°. *Anal.* Calcd. for $C_{15}N_2SH_{10}Br_2$: S, 7.80; Br, 39.02. Found: S, 7.59; Br, 39.36.

4. Mercuration of 4-Phenyl-2-phenylamino-5-bromothiazole.—The thiazole compound (1 g.) was dissolved in 20 cc. of ethanol–acetic acid solution (50–50%). A solution of mercuric acetate (1.3 mole) in water acidified with dilute acetic acid was then added. Precipitate appeared in some cases after 1–2 hours. The reaction mixture was kept overnight and then filtered and the residue was washed thoroughly with hot water, dilute alcohol and finally with dilute acetic acid; yield 72%, m.p. −281–282° dec. *Anal.* Calcd. for ($C_{17}N_2SBrO_2H_{11}Hg$): Hg, 33.95. Found: Hg, 33.71.

Fungicidal Test.—For fungicidal assay the method of Montgomery and Moore[27] was used. *Piricularia Orizae* Cav, the causative organism of the *rice blast*, was used as the test fungus. The brominated phenylthiazolylamines containing bromine in the thiazole nucleus showed the maximum activity, inhibiting the spore germination completely at a concentration of 30 p.p.m., while compounds having bromine in the two phenyl moiety were active in a concentration of 90 p.p.m. All the tribromo and a few dibromo derivatives containing a bromine atom in the thiazole nucleus showed a little enhanced fungicidal activity.

All the fifteen mercurated compounds showed an excellent fungicidal activity, while those having one of the bromine atoms in the thiazole nucleus showed the highest activity, inhibiting the spore germination completely at a concentration of 1–2 p.p.m.

Bactericidal Test. The Rideal-Walker serial drop dilution method[28] was used for the comparative antibacterial activity. The bactericidal activity was measured in terms of maximum effective dilution (M.E.D.). The test organism was a 24-hour culture of *Staphylococcus aureus*. The brominated derivatives containing one bromine atom in the thiazole nucleus showed maximum activity in 1:10,000 dilution, while compounds having the bromine atom in the phenyl nucleus of the molecule showed an activity at a concentration of only 1:4000. The mercurated compounds, especially when they contained one of the bromine atoms in the thiazole nucleus, showed a very high degree of activity, being active in 1:100,000 dilution.

Acknowledgment.—The author is highly grateful to Dr. M. K. Rout, Reader in Chemistry, for his kind interest and necessary guidance and to Mr. S. Y. Padmanavan, the mycologist of the Central Rice Research Institute, Cuttack, for

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(25) F. B. Dains, R. Q. Brewster and C. P. Olander, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 447.

(26) Ph De Clermont and E. Wehrlin, *J. Chem. Soc.*, **31**, 70 (1877); *Compt. rend.*, **88**, 347 (1877).

(27) H. B. S. Montgomery and M. H. Moore, *J. Pomol & Hort Sci.*, **15**, 253 (1938).

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supplying the culture of the test fungus to carry out the fungicidal work in this Laboratory and lastly to the Board of Scientific and Industrial Research, Government of Orissa, for a research grant.

CUTTACK-3, INDIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

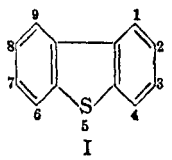
Nitration of 1-Hydroxythianthrene and of 1-Hydroxythianthrene-5,10-tetroxide

BY HENRY GILMAN AND DHAIRYASHEEL R. SWAYAMPATI

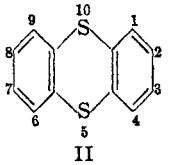
RECEIVED SEPTEMBER 24, 1956

1-Hydroxythianthrene was prepared in greatly improved yield by a modification of an earlier procedure. The treatment of the phenol with nitric acid (sp. gr. 1.2) in glacial acetic acid at reflux temperature resulted in the formation of 2,4-dinitro-1-hydroxythianthrene-5(or 10)-oxide in 61–65% yield. Reduction of the sulfoxide with hydrogen bromide gave 2,4-dinitro-1-hydroxythianthrene from which the same sulfoxide was regenerated by oxidation with the nitric acid. 1-Hydroxythianthrene-5,10-tetroxide reacted with nitric acid (sp. gr. 1.5) to give a fair yield of 2,4-dinitro-1-hydroxythianthrene-5,10-tetroxide.

Dibenzothiophene (I) can be nitrated with nitric acid to give a mixture of 2-nitrodibenzothiophene and dibenzothiophene-5-oxide.[1] The sulfoxide, dibenzothiophene-5-oxide, can also be nitrated to yield 3-nitrodibenzothiophene-5-oxide.[2] This capacity of dibenzothiophene and dibenzothiophene-5-oxide of being nitrated is not shared by thianthrene (II) or any of its oxides.



I



II

Treatment of thianthrene with dilute nitric acid (sp. gr. 1.2) in glacial acetic acid at reflux temperature results in the formation of thianthrene-5-oxide in very good yields.[3–8] Nitric acid has also been used in the preparation of thianthrene-5,10-dioxide,[5,7] thianthrene-5,5,10-trioxide[4,7] and thianthrene-5,10-tetroxide.[8–11] Nitric acid (sp. gr. 1.5) oxidizes II to the tetroxide.[3,7,8,12] If II is dissolved in fuming nitric acid and the solution repeatedly evaporated to dryness, a quantitative yield of thianthrene-5,10-tetroxide is obtained. The action of a mixture of nitric and sulfuric acids does not proceed beyond oxidation of II to the tetroxide.[13] Even where a number of methoxyl[5,7] or methyl[6,7,9,10,12] groups are present, the treatment with nitric acid proceeds in the same manner as with the parent substance II.

The present investigation deals with the nitration of thianthrene and some of its derivatives. Our attempts of nitrating II by dissolving it in nitric acid (sp. gr. 1.5) at −10° and at −30° were unsuccessful and resulted in the formation of the α-form[14] of thianthrene-5,10-dioxide. Subsequently, 1-hydroxythianthrene (III) was selected as a promising derivative for nitration in the thianthrene system. This phenol has been prepared[15] by metalating thianthrene with *n*-butyllithium and oxidizing the thianthrenyllithium with oxygen in the presence of *n*-butylmagnesium bromide. The yield of the phenol, however, was only 2.5%. By suitably modifying the procedure, particularly in the working up of the reaction mixture, we were able to obtain the product in 46% yield. 1-Thianthreneoxyacetic acid and its ethyl ester were prepared as derivatives which may have activity as plant hormones.

The presence of the hydroxyl group was found to make the thianthrene molecule very susceptible to nitration. In an attempt of preparing a monosulfoxide of III by the usual treatment with the dilute nitric acid in glacial acetic acid at reflux temperature for 30 minutes, we obtained, instead, a dinitro-1-hydroxythianthrene-5(or 10)-oxide (IV) in 61% yield. Reduction of IV with hydrogen bromide gave a dinitro-1-hydroxythianthrene (V), which upon treatment with the dilute nitric acid in glacial acetic acid at reflux temperature for 15 minutes gave a product which was identical with IV. The infrared spectrum of V showed, among others, an absorption band at 13.4μ, characteristic of 1,2-substitution, which meant that one of the two benzene rings was only disubstituted. The dinitration, therefore, occurred in the same benzene ring which carried the hydroxyl group. The two nitro groups must have been substituted in the 2,4- positions in view of the powerful *ortho–para* directing influence of the phenolic hydroxyl group in electrophilic reactions. Hence the structure of V must be 2,4-dinitro-1-hydroxythianthrene and that of IV, 2,4-dinitro-1-hydroxythianthrene-5(or 10)-oxide. Whether the sulfoxide group in IV was in the 5- or in the 10-position could not be established with any amount of certainty. The conversion of V to IV, upon oxidation, is interesting in view of the fact that an isomer of IV in which the oxygen atom of the sulfoxide group is on the sulfur atom different from that in IV was equally pos-

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