of 10–28% of mercury salt and 50–60% of hydrofluoric acid was used. Some runs employed 0.25 mole of the chloride and as much as 200% excess hydrofluoric acid. The successful preparation of 9,9-difluorofluorene is described in detail below.

Five-tenths mole (117 g.) of 9,9-dichlorofluorene was dissolved in 200 cc. of chlorobenzene and 0.37 mole (100 g.) of mercuric chloride was now added. Hydrogen fluoride next was bubbled into the stirred solution at a temperature of 30°. After thirty minutes no apparent reaction had occurred so the temperature was raised. At 70° the solution turned a very dark green but in contrast to the large amount of heat liberated when mercuric oxide and hydrofluoric acid are used this reaction showed little evidence of heat evolution. The temperature did not exceed 81° and the time of reaction was one and one-half hours.

The solution was washed with water and sodium carbonate solution, treated with Darco and distilled at 1–5 mm. The first fraction 55–115° (5 mm.), weighed 6 g. and was chlorobenzene. The second fraction, 115–130° (3 mm.), weighed 20 g. It was a light yellow, viscous oil. The third fraction, 125–135° (3 mm.), weighed 13 g. and came over as a yellow oil that solidified in the receiver. On standing overnight fraction 2 had changed to a thick tarry mass with gas bubbles and yellow crystals held in suspension. Some pressure was evidenced and fumes of hydrogen chloride and hydrogen fluoride were evolved when the container was unstoppered. A somewhat similar but much less pronounced effect was observed in fraction 3.

The yellow crystals were separated and recrystallized from ligroin, m. p. 47–48°. They contained fluorine but no chlorine.

Anal. Calcd. for $C_{13}H_8F_2$: F, 18.8; mol. wt., 202.2. Found: F, 17.9; mol. wt., 195.

From the decomposed material, fluorenone was isolated. Probably unstable 9,9-fluorochlorofluorene was the principal product in fraction 2.

Summary

9,9-Difluorofluorene has been prepared by treating 9,9-dichlorofluorene with hydrogen fluoride in the presence of mercuric chloride. It is somewhat unstable. Evidence has been found for the transitory existence of 9-chloro-9-fluorofluorene.

Mercuric chloride and hydrogen fluoride form a fluorinating agent that is especially useful in the preparation of the less stable fluorides.

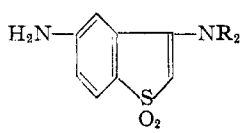
CINCINNATI 21, OHIO RECEIVED DECEMBER 6, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Studies in the Thianaphthene Series.[1] II. Aminothianaphthene-1-dioxides[2]

BY F. G. BORDWELL AND C. J. ALBISETTI, JR.[3]

In a previous paper[4] the synthesis of a sulfanilamide vinylog in which the sulfamyl group was separated from the aromatic ring by a vinyl group was described. As an extension in our synthesis of molecules with chemical characteristics similar to sulfanilamide, but with different stereochemical relationships of the functional groups, the synthesis of 3,5-diaminothianaphthene-1-dioxide (I, R = H) was undertaken. This molecule is a vinylog of sulfanilamide in which the sulfonyl and amino portions of the sulfamyl group have been separated by a vinyl group.



I

It is also noteworthy because of its relationship to bis-(4-aminophenyl) sulfone, a compound which has aroused considerable interest because of its high bacteriostatic activity. Recently 2,8-diaminodibenzothiophene-5-dioxide and 2,8-diaminothiaxanthene-5-dioxide, which are closely related to I, have been synthesized for pharmacological testing.[5]

The simplest approach to I appeared to be nitration of 5-nitrothianaphthene, oxidation of the sulfur atom and reduction of the nitro groups.

The preparation of 5-nitrothianaphthene by decarboxylation of 5-nitro-2-thianaphthenecarboxylic acid[6] has been described by Fieser and Kennelly.[7] Our yields of 5-nitro-2-thianaphthenecarboxylic acid from crude 2-chloro-5-nitrobenzaldehyde were about 25%; which compares well with the 28% yield reported by Fieser and Kennelly[7] using pure 2-chloro-5-nitrobenzaldehyde, but is considerably lower than the maximum yield of 45% reported by Fries and his co-workers.[6] The decarboxylation was carried out by a slight modification of the method of Fieser and Kennelly,[7] which was found to be more convenient.

Nitration of 5-nitrothianaphthene to give a pure dinitrothianaphthene was not easy, since it was found that a third nitro group entered the molecule almost as readily as did the second nitro group. By carrying out the nitration with an equivalent amount of potassium nitrate in sulfuric acid at 0–5° for one hour a dinitrothianaphthene, m. p. 171°, was isolated in 46% yield. This compound is very probably 3,5-dinitrothianaphthene since the 3-position is known to be the most active

(1) For the first paper in this series see Bordwell and Albisetti, THIS JOURNAL, **70**, 1558 (1948).

(2) A preliminary account of this work was given at the One Day Technical Meeting of the Chicago Section of the American Chemical Society, January 24, 1947.

(3) Du Pont Predoctoral Fellow, 1946–1947. Present address: du Pont Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware. Abstracted from the Ph.D. dissertation of C. J. Albisetti, Jr., August, 1947.

(4) Bordwell, Colbert and Alan, THIS JOURNAL, **68**, 1778 (1946).

(5) Neumoyer and Amstutz, *ibid.*, **69**, 1920, 1925 (1947).

(6) Hemmecke, Dissertation, Braunschweig, 1929; Fries, Heering, Hemmecke and Siebert, *Ann.*, **527**, 83 (1936).

(7) Fieser and Kennelly, THIS JOURNAL, **57**, 1611 (1935).

position in the thianaphthene nucleus toward ordinary substitution.[8]

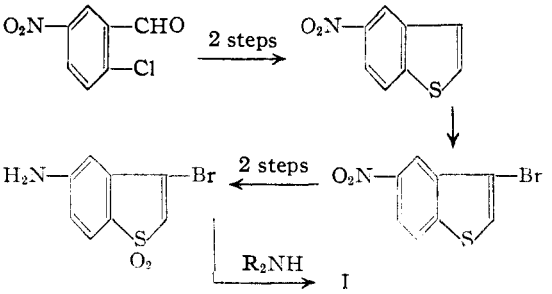
The sulfur atom in 3,5-dinitrothianaphthene was not oxidized by either 30% hydrogen peroxide in acetic acid–acetic anhydride or by sodium dichromate and sulfuric acid. The electron withdrawing effect of the 3-nitro group is responsible for the resistance of the sulfur atom to oxidation, since 5-nitrothianaphthene was readily oxidized to 5-nitrothianaphthene-1-dioxide by 30% hydrogen peroxide in acetic acid–acetic anhydride, but 3-nitrothianaphthene and 3,5,7-trinitrothianaphthene[9] were not oxidized under similar conditions.

No difficulty should be experienced in oxidizing the sulfur atom in 3,5-diacetamidothianaphthene, but attempts to obtain this compound were unsuccessful. In reductions of 3,5-dinitrothianaphthene using palladium on charcoal in the presence of acid the requisite hydrogen was absorbed but no pure products could be isolated. Similar results were obtained in attempted reductive acetylations using hydrogen and palladium catalyst and acetic anhydride in benzene solution. Reduction with tin and hydrochloric acid gave a crystalline tin salt, but attempts to liberate the amine from this salt or to acetylate it according to the method of Hemmecke[6] gave impure materials. Hemmecke[6] was unable to prepare 3-aminothianaphthene in a pure state. Apparently the 3-aminothianaphthenes, like the aminothiophenes, exist to a considerable extent in the imino form, and are very susceptible to oxidation and hydrolysis.

No difficulty is encountered in isolating and purifying aminothianaphthenes in which the amino group is in the benzenoid ring.[6] The nitro group in 5-nitrothianaphthene was reduced by the method of Fieser and Kennelly[7] and the 5-aminothianaphthene produced was converted to 5-(2-diethylaminoethylamino)-thianaphthene for pharmacological testing.[10] In a similar manner 5-aminothianaphthene-1-dioxide was prepared from 5-nitrothianaphthene-1-dioxide.

Synthesis of molecules of type I was finally accomplished by an alternate route. The bromine atom in 3-bromothianaphthene-1-dioxide has been found to be readily replaced by alkylamino groups[1]; therefore, 5-nitrothianaphthene was brominated to 3-bromo-5-nitrothianaphthene and the latter oxidized to 3-bromo-5-nitrothianaphthene-1-dioxide. The bromination of 5-nitrothianaphthene required considerably more vigorous conditions than are necessary for bromination of thianaphthene itself; a 64% yield of 3-bromo-5-nitrothianaphthene was obtained by treating 5-nitrothianaphthene with excess bromine in a refluxing carbon tetrachloride solution for seventy-two hours. The structure of the bromination product was proved by removal of the nitro group by reduction and deamination. The resulting bromothianaphthene was shown to be the 3-derivative by oxidation to 3-bromothianaphthene-1-dioxide.

Refluxing 3-bromo-5-nitrothianaphthene-1-dioxide in alcoholic solution with excess piperidine for thirty minutes gave a 94% yield of 3-(1-piperidino)-5-nitrothianaphthene-1-dioxide. A 94% yield of 3-diethylamino-5-nitrothianaphthene-1-dioxide was obtained in a similar reaction using diethylamine instead of piperidine. Reduction of the nitro group in these compounds could not be accomplished in acid solution without hydrolysis of the 3-alkylamino group.[1] It was, therefore, found to be more convenient to prepare compounds of type I by reduction of 3-bromo-5-nitrothianaphthene-1-dioxide to 3-bromo-5-aminothianaphthene-1-dioxide, which was then coupled with the desired amine. By this procedure 3-diethylamino-5-aminothianaphthene-1-dioxide (I, R = Et) was obtained in good yield. The preparation of 3,5-diaminothianaphthene-1-dioxide I(R = H) could no doubt be accomplished by the reaction of 3-bromo-5-aminothianaphthene-1-dioxide with ammonia according to the procedure used for 3-aminothianaphthene-1-dioxide,[1] but it was felt that 3-diethylamino-5-aminothianaphthene-1-dioxide would serve as well for pharmaceutical testing.



Acknowledgment.—We wish to express our appreciation to the du Pont Company for the fellowship which supported this work. A generous supply of *o*-chlorobenzaldehyde was furnished by the Heyden Chemical Corporation; the 60% sodium sulfide was furnished by the Hooker Electrochemical Company; and the thianaphthene was donated by the Texas Company.

Experimental[11,12]

5-Nitrothianaphthene-2-carboxylic Acid.—This compound was prepared from 2-chloro-5-nitrobenzaldehyde

(8) Fries and co-workers (ref. 6) reported the isolation of a dinitrothianaphthene, m. p. 171°, and a trinitrothianaphthene, m. p. 196°, by nitration of 3-nitrothianaphthene. At present we have under way an investigation of the nitration of thianaphthene, and we hope to be able to isolate the compounds reported by Fries, *et al.*, for comparison with those melting at the same temperature which were obtained by nitration of 5-nitrothianaphthene.

(9) The structure of this compound was not established, but its preparation by nitration of 5-nitrothianaphthene leaves little doubt as to the orientation of the nitro groups.

(10) Block, Lehr and Erlenmeyer, *Helv. Chim. Acta.*, **28**, 1406 (1945), have recently reported 5-aminothianaphthene to be one of the most active of the thirty-seven compounds tested *in vitro* against the tubercle bacillus.

(11) Microanalyses were by Mrs. Margaret Ledyard, Mrs. Nelda Mold and Miss Patricia Craig.

(12) All melting points were taken on a Fisher melting point block and are uncorrected.

essentially by the procedure described by Hemmecke[6] and by Fries, *et al.*,[6] except that the sodium disulfide was prepared and added in a 50% alcoholic solution.

5-Nitrothianaphthene.—A well-stirred mixture of 80 g. (0.36 mole) of 5-nitrothianaphthene-2-carboxylic acid, 400 ml. of quinoline and 20 g. of copper powder was gradually heated to the reflux temperature and the solution was stirred and allowed to reflux for thirty minutes. The mixture was cooled, poured onto 2 kg. of crushed ice and acidified with 18% hydrochloric acid. The suspension was cooled overnight and filtered. The air-dried solids were extracted with one 1.5-liter portion and three 500-ml. portions of boiling acetone (in one experiment a soxhlet extraction apparatus was used). The acetone was clarified with 5 g. of carbon (Norit A) and concentrated to 300 ml. by distillation. On cooling 43 g. (66.7%) of 5-nitrothianaphthene separated from the solution as a light tan powder, m. p. 149–150°.

5-(2-Diethylaminoethylamino)-thianaphthene.—This compound was prepared from 5-aminothianaphthene[7] by a procedure similar to that used by Gilman and Avakian[13] for the attachment of the γ-diethylaminopropylamino side chain on 2-aminodibenzothiophene. The product, obtained in 57% yield, was a yellow oil, b. p. 168–171° at 0.5 mm., which darkened on exposure to air.

Anal. Calcd. for $C_{14}H_{20}N_2S$: C, 67.70; H, 8.12. Found: C, 67.87; H, 7.90.

5-Nitrothianaphthene-1-dioxide.—To a warm mixture of 18.0 g. (0.1 mole) of 5-nitrothianaphthene in 100 ml. of acetic acid, 70 ml. of 30% hydrogen peroxide was added at such a rate as to keep the reaction from becoming too vigorous. A further 20 ml. of 30% hydrogen peroxide in 100 ml. of acetic acid was then added and the reaction mixture heated on the steam-bath for three hours. The hot solution was diluted to the point of turbidity and allowed to cool. The product was separated by filtration and purified by crystallization from 300 ml. of alcohol. There was obtained 13.8 g. (65.5%) of material melting at 164°. Further crystallization from alcohol raised the m. p. to 166°.

Anal. Calcd. for $C_8H_5NO_4S$: C, 45.48; H, 2.39. Found: C, 45.71; H, 2.62.

5-Aminothianaphthene-1-dioxide.—This compound was prepared in 44% yield from 5-nitrothianaphthene-1-dioxide by the procedure described by Fieser and Kennelly for reducing 5-nitrothianaphthene. After several crystallizations from 60% alcohol the material melted at 178°.

Anal. Calcd. for $C_8H_7NO_2S$: C, 53.02; H, 3.90. Found: C, 52.96; H, 4.12.

3,5-Dinitrothianaphthene.—To 120 ml. of concd. sulfuric acid stirred at 0–5° was slowly added 10.8 g. (0.06 mole) of carefully purified 5-nitrothianaphthene. To this was added, dropwise, a solution of 6.06 g. (0.06 mole) of potassium nitrate in 120 ml. of sulfuric acid. After being stirred for one hour at 0–5°, the mixture was poured onto ice. Crystallization of the product from 1 l. of a 1:1 benzene–Skellysolve C mixture gave 6.2 g. (46%) of 3,5-dinitrothianaphthene, m. p. 163–166°. Several crystallizations from alcohol gave pale yellow needles, m. p. 171°.

Anal. Calcd. for $C_8H_4N_2O_4S$: C, 42.87; H, 1.80. Found: C, 42.95; H, 1.89.

Unless carefully purified 5-nitrothianaphthene was used in the above method the conversion to 3,5-dinitrothianaphthene was low. 5-Nitrothianaphthene was essentially unchanged when 9.0 g. in 60 ml. of acetic acid was treated with a mixture of 5 ml. of water and 5 ml. of fuming nitric acid (d. 1.49) and the solution boiled for twenty minutes and diluted. This method has been used by Fries and Hemmecke[14] for the preparation of 3-nitrothianaphthene from thianaphthene. Similarly, treatment of a solution of 4.5 g. of 5-nitrothianaphthene in 40 ml. of acetic acid (d. 1.47), stirring the mixture at 40° for two hours and allowing to stand at room temperature for eighteen hours, did not bring about nitration. Except for the longer length of time and the more dilute reaction mixture used in the present experiment, these are the conditions used by Cullinane, Davies and Davies[15] for the successful nitration of dibenzothiophene.

3,5,7-Trinitrothianaphthene.—In another attempt to prepare 3,5-dinitrothianaphthene 1.8 g. (0.01 mole) of 5-nitrothianaphthene was added slowly to 36 ml. of fuming nitric acid at 0–5° over a period of thirty minutes. The mixture was held at this temperature and stirred for two hours and was then diluted. There was obtained 0.9 g. (33%) of material, m. p. 195–196°. After crystallization from 1-butanol the material melted at 196°.

Anal. Calcd. for $C_8H_3N_3O_6S$: C, 35.70; H, 1.12. Found: C, 35.73; H, 1.29.

Dinitration of 5-nitrothianaphthene also occurred by reaction at about 0° when 10 g. of material was added to a cold mixture of 100 ml. of concd. sulfuric acid and 100 ml. of fuming nitric acid (d. 1.49) and the mixture stirred while cold for two hours and diluted.

Attempted Oxidation of 3-Nitrothianaphthenes.—An attempt to oxidize 3,5-dinitrothianaphthene with sodium dichromate in the presence of sulfuric acid in acetic acid solution, according to the method described for dibenzothiophene[16] was unsuccessful. Hydrogen peroxide (30%) in acetic acid had no effect on 3,5-dinitrothianaphthene, and a refluxing solution of 30% hydrogen peroxide, acetic acid and acetic anhydride was likewise ineffective in attempts to convert 3-nitro-[14] and 3,5,7-trinitrothianaphthenes to the corresponding 1-dioxides.

3-Bromo-5-nitrothianaphthene.—A mixture of 7.2 g. (0.04 mole) of carefully purified 5-nitrothianaphthene, 19.2 g. (0.12 mole) of bromine and 800 ml. of chloroform was refluxed for seventy-two hours. The cooled solution was washed with aqueous sodium carbonate, dried over anhydrous sodium carbonate and concentrated. A total of 7.8 g. of material was obtained in three crops. On purification from ethanol 6.6 g. (64%) of material melting at 170–171° was obtained. A sample purified for analysis separated from ethanol in short, pale-yellow needles, m. p. 170.5–171°.

Anal. Calcd. for $C_8H_4NO_2SBr$: C, 37.22; H, 1.56. Found: C, 37.41; H, 1.87.

5-Amino-3-bromothianaphthene.—Reduction of 5-nitro-3-bromothianaphthene with stannous chloride and concd. hydrochloric acid was effected in 75% yield. The product was purified by crystallization from Skellysolve B, the last trace of pink color being removed with the aid of activated alumina. The compound was obtained as fine colorless needles, m. p. 84°.

Anal. Calcd. for C_8H_6NSBr: N, 6.14. Found: N, 6.18.

Proof of Structure of 5-Amino-3-bromothianaphthene.—Deamination was accomplished by diazotization and treatment with ethanol in the presence of copper powder.[17] Steam distillation of the product from an alkaline solution gave a yellow oil, which was oxidized with 30% hydrogen peroxide in acetic acid–acetic anhydride solution to a yellow solid. The purified compound melted at 181–182°, and a mixed melting point with 3-bromothianaphthene-1-dioxide[1] showed no depression.

3-Bromo-5-nitrothianaphthene-1-dioxide.—Oxidation of 3-bromo-5-nitrothianaphthene was accomplished in 74% yield by the method used for the preparation of 3-bromothianaphthene-1-dioxide.[1] The product was a cream-colored solid, m. p. 185–187°. Crystallization from ethanol gave material melting at 190–191°.

Anal. Calcd. for $C_8H_4NO_4SBr$: C, 33.12; H, 1.39. Found: C, 33.09; H, 1.53.

(13) Gilman and Avakian, THIS JOURNAL, **68**, 1514 (1946).

(14) Fries and Hemmecke, *Ann.*, **470**, 1 (1929).

(15) Cullinane, Davies and Davies, *J. Chem. Soc.*, 1435 (1936).

(16) Gilman, Jacoby and Pacevitz, *J. Org. Chem.*, **3**, 120 (1938).

(17) Baker, Albisetti, Dodson, Lappin and Riegel, THIS JOURNAL, **68**, 1534 (1946).

3-(1-Piperidino)-5-nitrothianaphthene-1-dioxide.—A 94% yield of this compound was obtained within thirty minutes by the reaction of 3-bromo-5-nitrothianaphthene-1-dioxide with a two molar excess of piperidine in refluxing ethanol solution. After crystallization from ethanol it melted at 197–198° (with dec.).

Anal. Calcd. for $C_{13}H_{14}O_4N_2S$: N, 9.53. Found: N, 9.29.

In a similar manner a 94% yield of **3-diethylamino-5-nitrothianaphthene-1-dioxide**, m. p. 210°, was obtained.

Anal. Calcd. for $C_{12}H_{14}O_4N_2S$: N, 9.92. Found: N, 9.74.

3-Bromo-5-aminothianaphthene-1-dioxide.—Reduction of 3-bromo-5-nitrothianaphthene-1-dioxide in ethanol solution was brought about in 81% yield using stannous chloride and concd. hydrochloric acid, according to the method of Fries, *et al.*[6] The product, m. p. 233°, was obtained as yellow needles by crystallization from ethanol.

Anal. Calcd. for $C_8H_6O_2NSBr$: N, 5.38. Found: N, 5.46.

3-Diethylamino-5-aminothianaphthene-1-dioxide.—By refluxing a mixture of 0.65 g. (0.0025 mole) of 3-bromo-5-aminothianaphthene-1-dioxide, 0.55 g. (0.0075 mole) of diethylamine and 10 ml. of ethanol for one hour, there was obtained 0.44 g. (70%) of a cream-colored solid, m. p. 180–184°. Purified four times by crystallization from ethanol, the material melted at 194°.

Anal. Calcd. for $C_{12}H_{16}O_2N_2S$: C, 57.11; H, 6.39. Found: C, 56.65; H, 6.43.

Summary

1. 3-Bromo-5-nitrothianaphthene was obtained in the bromination of 5-nitrothianaphthene. From the nitration of 5-nitrothianaphthene a dinitro- and trinitrothianaphthene were isolated, which are believed to be 3,5-dinitro- and 3,5,7-trinitrothianaphthene.

2. The electron attracting power of a nitro group in the 3-position of several thianaphthenes was found to be strong enough to prevent oxidation of the sulfur atom under the usual conditions.

3. 3-Diethylamino-5-aminothianaphthene-1-dioxide, which is a vinylog of N,N-diethyl sulfanilamide, and is closely related to bis-(4-aminophenyl)-sulfone has been prepared.

EVANSTON, ILLINOIS RECEIVED JANUARY 17, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

The Decomposition of Dibutylchloramine

BY GEORGE F WRIGHT

It has recently been found that aliphatic secondary amines can be nitrated in organic acid anhydrides when a chloride catalyst is present[1]; further, that the formation of the nitramine proceeds *via* the chloramine. Unsatisfactory yields of certain nitramines have been attributed to the instability of this intermediate.[2] It thus seemed worthwhile to re-investigate the stability of chloramines. Dibutylchloramine, which was chosen for this study, has been found to decompose to complex mixtures. Partial identification of these mixtures indicates that extensive intramolecular chlorination has taken place.

Chlorine, which has been reported as a product when chloramines are treated with excess hydrogen chloride,[3] was obtained in 68% yield from dibutylchloramine, I, in methanol. The expected dibutylammonium chloride, IV, was produced in 55% yield. It is not unreasonable to assume that this decomposition proceeds by formation from I of dibutylchloramine hydrochloride, II, which decomposes spontaneously in excess of hydrogen chloride to dibutylammonium chloride, IV.

The spontaneous decomposition of dibutylchloramine yielded dibutylammonium chloride released by reaction I → V. No chlorine was evolved. A liquid could be distilled out of the tar left when electropositive chlorine had disappeared, but this liquid showed a peculiar instability. Immediately after distillation a hydrochloride began to precipitate, but ceased after a certain amount had appeared. After redistillation the precipitation was resumed approximately to the same extent as before.

This distillate is considered to be a mixture of VI, VIII, X and XI which is formed by the action of chlorine released by initial decomposition of I. It is thought that the mixture loses hydrogen chloride until the basicity is reduced by hydrochloride formation, and that this loss is resumed after removal from the hydrochloride by distillation. The aldimine structure of the mixture has been confirmed by alkaline decomposition in presence of *p*-bromobenzenesulfonyl chloride to give the bromosulfonyl derivatives of monobutylamine.

Monobutylamine as its hydrochloride also was formed when the hydrochloride of the mixture was treated with methanol. The aldehydic fraction remaining after precipitation of the salt with ether was unstable, so it was treated with phenylhydrazine hydrochloride in ethanol. A distinctive blood-red color appeared which faded when the hydrochloride of ethylglyoxal precipitated. The color change is remindful of that which occurs when dichloroacetaldehyde is converted to glyoxal osazone.[4] Since the color change does not occur when ethylglyoxal is treated with phenylhydrazine, this hydrochloride, which is convertible to the known osazone,[5] is probably formed from

(1) Wright, *et al.*, *Can. J. Res.*, **26B**, 89, 257 (1948).

(2) K. K. Carroll and G. F Wright, *ibid.*, **26B**, 271 (1948).

(3) Houben, "Die Methoden der organischen Chemie," 3rd ed., Vol. 4, Georg Thieme, Leipzig, 1941, p. 569.

(4) G. Oddo and G. Cusmano, *Gazz. chim. ital.*, **41**, [II], 246 (1911).

(5) L. Wolff, *Ann.*, **288**, 20 (1895); E. Kolshorn, *Ber.*, **37**, 2476 (1904).