TABLE V

DI(AMINOTHIATRIAZOLES)

R[a]	Functional Positions	% Yield	M.P[b]	Formula	N Calcd.	N Found	S Calcd.	S Found
C_6H_4	1,4	80	180	$C_8H_6N_8S_2$	40.33	40.25	23.00	22.90
C_6H_4	1,3	82	162	$C_8H_6N_8S_2$	40.33	40.30	23.00	22.85
$C_{13}H_{10}$[c]	4,4′	86	148	$C_{15}H_{12}N_8S_2$	30.43	30.10	17.39	17.20

[a] New compound. [b] With detonation. [c] Diphenylmethane.

25 ml. of dimethylformamide, cooled to 5°, and agitated by a magnetic stirring bar. There was then added 4 ml. of 4 *N* hydrochloric acid and 0.4 g. (0.006 mole) of sodium nitrite in 5 ml. of water over a 10-min. period. A yellow-green solid precipitated immediately. The reaction was maintained at 5–10° for 20 min. The crude product, 0.51 g. (80%), was recovered as a greenish powder, detonating at 160°. Recrystallization was effected by dissolving in 15 ml. of dimethylformamide, decolorizing with charcoal, filtering, and then diluting with ethanol. A light tan powder, detonating at 180° was obtained. The di(aminothiatriazoles) are listed in Table V.

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[13] E. Lieber and J. Ramachandran, *Can. J. Chem.*, **37**, 101 (1959).

Formation of Quinoxalone Dye in the Color Photographic Coupling Reaction

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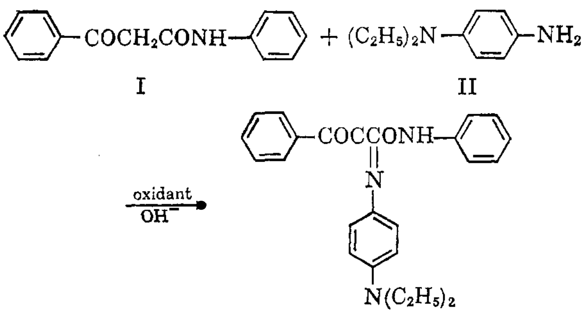
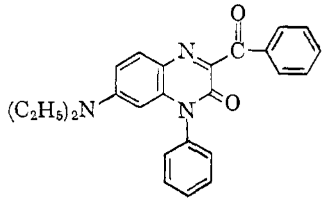
A large class of the compounds ("couplers") giving yellow color photographic image dyes contain the grouping, —$COCH_2CONH$—.[1] Reaction of the oxidized *p*-phenylenediamine derivative developing agent at the activated methylene group of such a coupler gives azomethine dye, as shown.



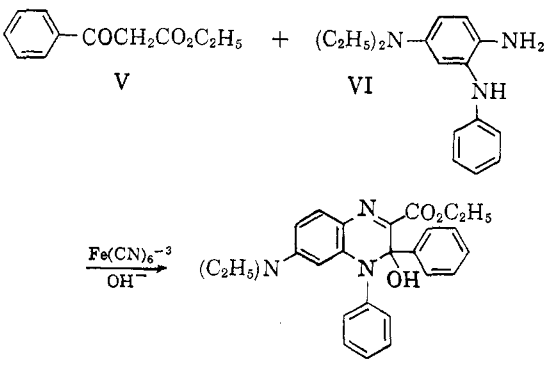
I II III

When couplers of this class react with oxidized color developing agents in dilute solution, it is often observed[2] that, in addition to the azomethine dye, a yellow dye of another type is produced. This dye differs from the azomethine dye in its fluorescence, smaller value of λ_{max}, and greater slope of the absorbance *vs.* λ curve on the long wave length side of λ_{max}. The present communication gives a proof of structure or a representative of this type of dye and evidence for a mechanism by which it forms.

On the basis of the fluorescence and absorption spectra, it was suggested[3] several years ago that the fluorescent, yellow dyes formed along with the yellow azomethine dyes are quinoxalones. For example, I and II would give IV. Structure IV has now been verified by means of the following alternative synthesis:



IV



V VI VII

Irradiation of the yellow pseudo base, VII, in solution converts it to IV, identical with the fluorescent dye obtained from I and II.

The oxidative condensation of dicarbonylmethylene compounds with *p*-phenylenediamines having a monosubstituted amino group *ortho* to the unsubstituted amino group has been described by Schmidt *et al.*[4] The products are yellow in the presence of alkali and magenta under neutral or weakly acidic conditions. The new dye VII shows this typical behavior. Schmidt *et al.*[4] proposed that in the magenta form the dyes have a quinoxalinium structure, whereas in the yellow form they exist as the corresponding pseudo bases (1,2-

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[1] P. W. Vittum and A. Weissberger, *J. Phot. Sci.*, **2**, 81 (1954).

[2] G. H. Brown, private communication.

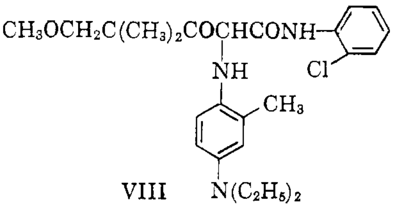
[3] P. W. Vittum, private communication.

[4] W. A. Schmidt, V. Tulagin, J. A. Sprung, R. C. Gunther, R. F. Coles, and D. E. Sargent, *Ind. Eng. Chem.*, **45**, 1726 (1953).

dihydro-2-quinoxalinols). This structural assignment is supported by the earlier results of Kehrmann and Falke.[5] Their quinoxalinium compounds having substituted amino groups in the 7-position are magenta and give yellow, fluorescent (in solution) pseudo bases.

The conversion of VII to IV takes place when solutions are exposed to radiant energy within the wave-length region, 350–450 mμ. This region corresponds to the long wave length absorption band of VII. Reaction occurs in acetone, acetonitrile, benzene, and cyclohexane. Not all of the VII is converted to IV. Other products are formed, too. The fraction of the photoreacted VII going to IV increases as the intensity of irradiation is decreased. There is little or no reaction in the dark, even in refluxing acetonitrile. The mechanism of the photoreaction is under investigation. It is hoped that the results of this study may be reported at a later date.

Consider now the steps leading to formation of quinoxalone dye in an oxidative condensation reaction such as that of I with II. An intermediate in the formation of azomethine dye by this reaction is the leuco form of the dye. A leuco dye (VIII) of this type has been synthesized. When VIII is oxidized with dichloroquinone, both azomethine and quinoxalone dye are formed. The latter dye is recognized by its analysis, characteristic fluorescence, and absorption spectrum, and by the fact that close to the theoretical four equivalents of oxidant are consumed in its formation. It is inferred that, in oxidative condensation reactions such as that of I with II, the leuco dye is a precursor of both the azomethine and quinoxalone dyes. Dichloroquinone does not oxidize the azomethine dye to the quinoxalone dye, showing that the former dye is not an intermediate in the formation of the latter. Therefore, branching in the reaction path must occur either at the leuco-dye stage, or, as seems more likely, at a stage intermediate between the leuco dye and azomethine dye. For example, the leuco dye may undergo a single-electron transfer reaction with the oxidant, giving a dye semiquinone which either undergoes ring closure, leading, on further oxidation, to quinoxalone dye, or is oxidized to azomethine dye.



VIII

Experimental

Ethyl 6-Diethylamino-3,4-dihydro-3,4-diphenyl-3-hydroxy-2-quinoxalinecarboxylate (VII).—To 15 ml. of ethyl benzoylacetate (V) (Eastman Grade) and 900 ml. of methanol was added an alkaline slurry of 3-anilino-N^1,N^1-diethyl-*p*-phenylenediamine (VI), prepared by dissolving 15 g. of sodium carbonate monohydrate in a solution of 2.1 g. (0.006 mole) of the sulfuric acid salt of VI[6] in 300 ml. of water. To the stirred mixture was added during 20 min. a solution of 9.0 g. of potassium ferricyanide in 120 ml. of water. Stirring was continued for 5 min. After the mixture was filtered, it was chromatographed on Florisil.[7] The product was very strongly absorbed and had the magenta color of the quinoxalinium ion. The column was washed with 50% aqueous methanol. The product was eluted as the yellow pseudo base first with acetone and finally with a mixture of 90 parts acetone, 10 parts triethylamine, and 4 parts water. The residue from the evaporated eluate was dissolved in benzene, washed with water, and dried over sodium sulfate. This solution was passed through a column of Florisil,[7] which was then washed with acetone. The product was eluted using the 90:10:4 acetone–triethylamine–water mixture. Evaporation of the eluate gave a partly crystalline, dark-colored residue (*ca.* 0.6 g.), which was crystallized three times from cyclohexane. The yellow, nonfluorescent crystals (0.27 g.) give green-fluorescing solutions in organic solvents; m.p. 114–117° dec. This value was determined as follows: The sample on the Fisher-Johns hot stage was heated during 5 min. to within 5° of initial melting. Rate of heating was then 1°/min. until melting started, when the rate was reduced to 0.5°/min. When the crystals are dropped on a preheated stage (Kofler Heizbank, Reichert Co., Austria), the lowest temperature at which rapid melting occurs is *ca.* 130°.

Anal. Calcd. for $C_{27}H_{29}O_3N_3$: C, 73.1; H, 6.6; N, 9.5. Found: C, 73.2; H, 6.3; N, 9.5.

Visible and ultraviolet spectra in acetonitrile (*ca.* 2.5 × 10^{-5} *M* in potassium hydroxide): 303 mμ (peak, log ε 3.96); 408 mμ (peak, log ε 4.32). Infrared spectrum in Nujol mull: broad hydroxyl band at 3230 cm.$^{-1}$; single carbonyl band at 1700 cm.$^{-1}$ (ester).

3-Benzoyl-7-diethylamino-1-phenyl-2(1)-quinoxalone (IV).—(1). To a stirred solution of 1.6 g. of potassium hydroxide, 0.24 g. of benzoylacetanilide,[8] and 2.8 g. of *N*,*N*-diethyl-*p*-phenylenediamine monohydrochloride (Eastman Grade) in 250 ml. of methanol was added, all at once, a solution of 1.4 g. of potassium ferricyanide in 50 ml. of water. After 4 min., 2 ml. of glacial acetic acid was added. The crude product was precipitated by addition of 1 l. of water, separated by filtration, and washed with water. This procedure was repeated once on the same scale and once on twice this scale. The dried products were combined, dissolved in benzene, and chromatographed on Florisil.[7] Mixtures of benzene and acetone were used as eluting solvent. The azomethine dye, which was readily separated from IV on the column, was discarded. Separation of IV from 4,4′-bis(diethylamino)azobenzene, which is formed as a by-product in the reaction, was not clean. Therefore, the contaminated IV was chromatographed again. The crude IV (0.4 g.) was crystallized from acetone. The residue from the mother liquor was crystallized from ethanol and combined with the crystallized product. This combination was crystallized from acetone. The yellow crystals (0.13 g.) fluoresce green; m.p. 192–193°.

Anal. Calcd. for $C_{25}H_{23}O_2N_3$: C, 75.5; H, 5.8; N, 10.6. Found: C, 75.0; H, 5.9; N, 10.6.

Visible and ultraviolet spectra in acetonitrile: 228 mμ (peak, log ε 4.61); 255 mμ (shoulder, log ε 4.26); 294 mμ (shoulder, log ε 3.79); 427 mμ (peak, log ε 4.43). Infrared spectrum in potassium bromide pressing: two carbonyl bands at 1650 cm.$^{-1}$ and 1675 cm.$^{-1}$.

(2). A solution of 0.050 g. of VII in 500 ml. of benzene in a 15- × 9.5-in. dish was exposed to General Electric Co. Cool

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[5] F. Kehrmann and E. Falke, *Helv. Chim. Acta*, **7**, 981 (1924).

[6] Prepared by R. Bent, of these laboratories, using the method of J. C. Arcos and J. A. Miller, *J. Am. Chem. Soc.*, **77**, 3128 (1955).

[7] Floridin Co., Tallahassee, Fla.

[8] C. J. Kibler and A. Weissberger, *Org. Syntheses*, **25**, 7 (1945).

White fluorescent bulbs at a level of *ca.* 20 ft.-candles. After 160 min., all of the VII had disappeared from the solution. Evaporation of the benzene gave 0.045 g. of a brown-yellow, largely crystalline residue, which was crystallized twice from ethanol. The yellow crystals (6.2 mg.) fluoresce green; m.p. 192–193°. The ultraviolet, visible, and infrared spectra are identical with those for the IV prepared by method 1.

The precursors (IX–XIV) of the leuco dye, VIII, were synthesized by Lee J. Fleckenstein of these laboratories.

Methoxypivalic acid (IX) was prepared by a procedure similar to that described for the preparation of methoxyacetic acid;[9] b.p. 105–110° (5.5 mm.); $n^{25}\text{D}$ 1.4199. This compound has been prepared previously and characterized analytically at the Tennessee Eastman Co.[10]

Ethyl Methoxypivalate (X).—A mixture of 57.3 g. (0.434 mole) of IX, 70 ml. of absolute ethanol, 170 ml. of benzene, and 1.5 ml. of concd. sulfuric acid was refluxed for 18 hr. in a flask equipped with a short Vigreux column surmounted by a Dean-Stark trap and reflux condenser. The mixture was cooled, washed several times with saturated sodium carbonate solution, dried over potassium carbonate, and distilled to give 55.4 g. (80%) of X; b.p. 161–165°; $n^{25}\text{D}$ 1.4060.

Anal. Calcd. for $C_8H_{16}O_3$: C, 60.0; H, 10.0. Found: C, 60.3; H, 9.7.

(Methoxypivalyl)acetonitrile (XI) was prepared from X by the general procedure of Eby and Hauser.[11] From 15.9 g. (0.69 g.-atom) of sodium, 600 ml. of liquid ammonia, 28.3 g. (0.69 mole) of acetonitrile, and 55.2 g. (0.345 mole) of X, there was obtained 42.7 g. (80%) of XI; b.p. 109–112° (1.3 mm.); $n^{25}\text{D}$ 1.4400.

Anal. Calcd. for $C_8H_{13}NO_2$: C, 61.9; H, 8.4; N, 9.0. Found: C, 61.6; H, 8.7; N, 8.9.

Methyl (Methoxypivalyl)acetate (XII).—A solution of 42.6 g. (0.275 mole) of XI in 250 ml. of absolute methanol was cooled in an ice bath and saturated with gaseous hydrogen chloride. After standing 16 hr. at room temperature, the mixture was concentrated to dryness under reduced pressure at room temperature. To the residue was added 200 ml. of benzene, 150 ml. of water, and 3 drops of concd. hydrochloric acid. The mixture was refluxed for 2 hr. and cooled. The phases were separated, and the aqueous phase was extracted twice with benzene. The extracts were added to the original organic phase, washed with saturated salt solution, and dried over sodium sulfate. The solution was concentrated at atmospheric pressure, and the residue was distilled under reduced pressure through a short Vigreux column to yield 29.1 g. (56%) of XII; b.p. 87–94° (1.4 mm.); $n^{25}\text{D}$ 1.4398.

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.5; H, 8.5. Found: C, 57.7; H, 8.6.

2′-Chloro-2-(methoxypivalyl)acetanilide (XIII).—A mixture of 7.82 g. (0.061 mole) of *o*-chloroaniline, 11.3 g. (0.060 mole) of XII, and 150 ml. of xylene was heated at the boiling point for 3 hr. in a flask equipped with a distillation head. During this time, 75 ml. of distillate was collected. The hot mixture was filtered into 300 ml. of heptane, and the solution was refrigerated. There was obtained 5.5 g. of white crystals; m.p. 51–56°. By concentrating and refrigerating the mother liquors, two additional crops of crystals (6.5 g.) were obtained. The three crops were combined and recrystallized from ether to give 11 g. (65%) of XIII as heavy white prisms; m.p. 50–56°.

Anal. Calcd. for $C_{14}H_{18}O_3NCl$: C, 59.2; H, 6.3; N, 5.0; Cl, 12.5. Found: C, 59.6; H, 6.4; N, 5.3; Cl, 12.9.

2,2′-Dichloro-2-(methoxypivalyl)acetanilide (XIV).—A solution of 10.85 g. (0.0382 mole) of XIII in 100 ml. of chloroform was cooled in an ice bath, and a solution of 5.54 g. (0.041 mole) of sulfuryl chloride in 35 ml. of chloroform was added, with stirring, over a period of 65 min. The mixture was stirred at room temperature for an additional 35 min., then concentrated under reduced pressure at room temperature to a white, crystalline solid. The solid was washed with a little petroleum ether, collected by filtration, dried, and recrystallized from hexane containing a small amount of ethanol to give 10.5 g. (87%) of XIV as large, colorless prisms; m.p. 90–94°.

Anal. Calcd. for $C_{14}H_{17}O_3NCl_2$: C, 52.8; H, 5.3; N, 4.4; Cl, 22.3. Found: C, 52.8; H, 5.2; N, 4.4; Cl, 22.7.

2′-Chloro-2-(4-diethylamino-2-methylanilino)-2-(methoxypivalyl)acetanilide (VIII).—In a closed vessel fitted with inlet and outlet tubes were placed 1.83 g. of XIV and 3.50 g. of N^1,N^1-diethyl-3-methyl-*p*-phenylenediamine monohydrochloride (Kodak Color Developing Agent CD-2). The vessel was swept with nitrogen, and 7 ml. of nitrogen-swept dimethylformamide was introduced, followed 2 min. later by 9.3 ml. of nitrogen-swept 10% methanolic potassium hydroxide solution. Nitrogen was passed through the mixture for 2 min. and then over the mixture while it was held at 32° for 100 min. After adding 125 ml. of nitrogen-swept, 85% aqueous methanol, the solution was cooled in an ice bath and seeded with crystals of VIII from a previous, small-scale experiment. The mixture was stirred with nitrogen for 30 min., and then 15 ml. of nitrogen-swept water was added. After an additional 30 min., the crystals of VIII were filtered off in air and washed with air-saturated 80% methanol, 50% methanol, and with water. The light yellow product was dried over calcium chloride in a nitrogen-filled desiccator; weight, 2.18 g. The product was crystallized three times from methanol, all operations, including drying, being carried out under nitrogen. The very pale yellow crystals (1.1 g.) melt at 84–86°.

Anal. Calcd. for $C_{25}H_{34}O_3N_3Cl$: C, 65.3; H, 7.5; N, 9.1; Cl, 7.7. Found: C, 65.1; H, 7.1; N, 9.3; Cl, 7.6.

Oxidation of Leuco Dye VIII to Azomethine and Quinoxalone Dyes.—The VIII used in this experiment was prepared as described above but was not recrystallized. The VIII (2.36 g.) was dissolved in 150 ml. of warm (*ca.* 40°), nitrogen-swept methanol to which 0.5 ml. of 10% methanolic potassium hydroxide solution had been added. The solution was stirred, and a solution of 2.45 g. of 2,5-dichloro-*p*-benzoquinone (Eastman Grade) in 27 ml. of warm acetone was added all at once. After 5 min., the solution was cooled to 25°, and 300 ml. of water was added. The product was extracted into benzene, and the solution was washed with water. The benzene was allowed to evaporate. The residue was redissolved in a little benzene and chromatographed on Florisil.[7] Mixtures of benzene and acetone were used for elution. The crude azomethine dye, 2′-chloro-2-(4-diethylamino-2-methylphenylimino)-2-(methoxypivalyl)acetanilide, weighed 1.65 g. It was crystallized from methanol, chromatographed on Florisil,[7] and crystallized from methanol; orange crystals, m.p. 113–114°.

Anal. Calcd. for $C_{25}H_{32}O_3N_3Cl$: C, 65.6; H, 7.0; N, 9.2; Cl, 7.7. Found: C, 65.6; H, 7.3; N, 9.5; Cl, 8.0.

Visible spectrum in methanol: 442 mμ (peak, log ε 4.19).

The crude quinoxalone dye, **1-(2-chlorophenyl)-7-diethylamino-3-(methoxypivalyl)-5-methyl-2(1)-quinoxalone,** after one crystallization from 90% aqueous methanol, weighed 0.35 g. It was chromatographed again on Florisil[7] and crystallized from 85% aqueous methanol and from cyclohexane; yellow, green-fluorescing crystals; m.p. 128–129°.

Anal. Calcd. for $C_{25}H_{30}O_3N_3Cl$: C, 65.9; H, 6.6; N, 9.2; Cl, 7.8. Found: C, 65.6; H, 6.8; N, 9.3; Cl, 7.7.

Visible spectrum in methanol: 434 mμ (peak, log ε 4.44)

Equivalents of Oxidant Consumed in the Oxidation of VIII.—The chloro-*p*-benzoquinone used as oxidant in this experiment was prepared by oxidizing chlorohydroquinone (Eastman Organic Chemicals) with potassium dichromate in aqueous sulfuric acid. The crude product was crystallized four times from 50% aqueous ethanol.

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[9] T. L. Gresham, J. E. Jansen, F. W. Shaver, J. T. Gregory, and W. L. Beers, *J. Am. Chem. Soc.*, **70**, 1004 (1948).

[10] K. C. Brannock, private communication.

[11] C. J. Eby and C. R. Hauser, *J. Am. Chem. Soc.*, **79**, 723 (1957).

Reactions of the chloroquinone and VIII were carried to completion in a mixture of 12.5 ml. of methanol and 5.0 ml. of water. In each reaction, 4.16×10^{-7} moles of VIII was used. The amounts of the dyes produced were determined spectrophotometrically. Results are shown in Table I.

TABLE I

OXIDATION OF LEUCO DYE VIII BY CHLOROQUINONE

Chloroquinone Used, Moles $\times 10^7$	Azomethine Dye Produced, Moles $\times 10^7$	Quinoxalone Dye Produced, Moles $\times 10^7$	Theoretical Chloroquinone Consumption, Moles $\times 10^7$
6.7	1.15	2.5_5	6.2_5
5.0	0.75	2.0	4.7_5
3.8	0.55	1.5_5	3.6_5
2.2	0.35	0.9	2.1_5

The last column gives the total amount of oxidant needed to produce the azomethine and quinoxalone dyes of the second and third column, on the assumption that 1 mole (two oxidation equivalents) of the oxidant is used for the formation of 1 mole of the azomethine dye and 2 moles (4 oxidation equivalents) for the formation of 1 mole of the quinoxalone dye. The correctness of these assumptions is indicated by the agreement between the figures of columns 1 and 4.

Observations on the Formation of Piperidine Hydrochloride from Chloroform and Piperidine

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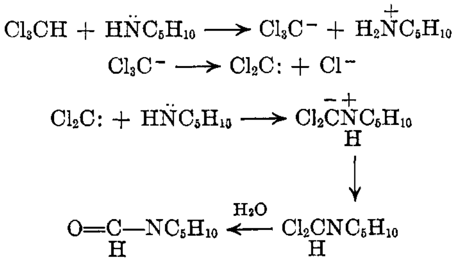
Received October 16, 1961

The formation of piperidine hydrochloride from the reaction of chloroform and piperidine, with or without a strong base, has been reported by several workers.[2,3] The same product has also been observed in reactions that yield chloroform, when piperidine is present in the reaction mixture, but no effort has been made by previous investigators to establish the source of piperidine hydrochloride.[4,5] Since we are currently investigating similar reactions, we were interested in studying the conditions which lead to the formation of piperidine hydrochloride. Secondary amines have been shown to react with chloroform in the presence of potassium *t*-butoxide to yield amides.[6] Under these conditions, a dichlorocarbene has been shown to be an intermediate.[7]

It is the purpose of this communication to show that chloroform is sufficiently acidic to react with an organic base such as piperidine ($k = 1.2 \times 10^{-3}$)[8] to yield piperidine hydrochloride and *N*-dichloromethylpiperidine, which is instantaneously hydrolyzed to *N*-formylpiperidine. The extent to which this reaction takes place is very small in the absence of a strong base. Equimolecular amounts of piperidine and chloroform yield piperidine hydrochloride and *N*-formylpiperidine to the extent of 1%, after they are allowed to stand together for several days. The presence of *N*-formylpiperidine, as one of the products of the reaction between chloroform and piperidine in the absence of strong bases, has not been previously detected by chemical means since it is not easily identified when formed in minute amounts. We found that *N*-formylpiperidine could be easily detected when no particular attempts were made to keep the reaction mixture anhydrous. However, when precautions were taken to exclude moist air from the reaction mixture, no *N*-formylpiperidine could be detected by gas-liquid chromatography. This observation could be ascribed to the fact that if a dichlorocarbene were an intermediate in this reaction, *N*-dichloromethylpiperidine would be formed and under anhydrous conditions this compound could not be hydrolyzed to *N*-formylpiperidine. On the other hand, the observation could mean that the reaction between chloroform and piperidine proceeds *via* a free radical mechanism, as in the photolysis of diazomethane or ketone, which is believed to yield the methylene diradical.[9] To eliminate the last possibility, similar experiments were carried out, one in the absence of air and light, another in the presence of an inhibitor such as hydroquinone. These conditions did not appear to modify the course of the reaction to any great extent. The addition of hydroquinone to the reaction mixture appears to facilitate the reaction since under these conditions piperidine hydrochloride is obtained in 3% yield. This may be attributed to the increase in the polarity of the medium.

In view of these findings, it is concluded that the reaction between chloroform and piperidine proceeds *via* an ionic mechanism probably similar to that proposed by Saunders and Murray for related reaction.[10]



$$Cl_3CH + H\ddot{N}C_5H_{10} \longrightarrow Cl_3C^- + H_2\overset{+}{N}C_5H_{10}$$

$$Cl_3C^- \longrightarrow Cl_2C{:} + Cl^-$$

$$Cl_2C{:} + H\ddot{N}C_5H_{10} \longrightarrow Cl_2\overset{-}{C}\underset{H}{\overset{+}{N}}C_5H_{10}$$

$$\big\downarrow$$

$$O{=}\underset{H}{C}{-}NC_5H_{10} \xleftarrow{H_2O} Cl_2\underset{H}{C}NC_5H_{10}$$

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[1] To whom all inquiries should be addressed.

[2] J. Busz and A. Kekulé, *Ber.*, **20**, 3246 (1887).

[3] F. B. Ahrens, *ibid.*, **27**, 2090 (1894).

[4] Y. Ursy and M. Paty, *Compt. rend.*, **252**, 3812 (1961).

[5] M. M. Joullié, Ph.D. thesis, University of Pennsylvania (1953).

[6] M. Saunders and R. W. Murray, *Tetrahedron*, **6**, 88 (1959).

[7] W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

[8] Y. N. Sheinker and E. M. Peresleni, *Zhur. Fiz. Khim.*, **32**, 2112 (1958).

[9] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, 1959, p. 750.

[10] M. Saunders and R. W. Murray, *Tetrahedron*, **11**, 1 (1960).