Used qualitatively the test is very sensitive. By looking through the depth of a test-tube of solution against a white background and comparing with a control tube of alkaline picrate solution, the detection of very small amounts of cyanide is made possible. In the 25-cc. volume used in the test one in ten million (CN) is very easily distinguished, one in twenty million (CN) is quite distinct and one in fifty million is distinguished definitely but with more difficulty.

I wish to thank Dr. A. L. Tatum for the suggestion and direction of this research.

Summary

1. A method for the quantitative determination of cyanide in amounts of the order of 0.1 mg. within 1% error is described. The method depends on the formation of a reddish-brown color which occurs when cyanide is added to an alkaline picrate solution.

2. The effects of time and temperature on the development of the color are discussed.

3. The presence of certain reducing substances which cause the development of a red color in alkaline picrate solutions may invalidate the method. The concentration of such substances necessary to be an interfering factor is indicated.

4. Used qualitatively the test is sensitive to one part of cyanide (CN) in fifty million.

CHICAGO, ILLINOIS, AND ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND THE WALKER CHEMICAL LABORATORY OF RENSSELAER POLYTECHNIC INSTITUTE]

THE FORMATION OF PYRROLINES FROM GAMMA-CHLOROPROPYL AND CYCLOPROPYL KETIMINES[1]

BY JOHN B. CLOKE

RECEIVED AUGUST 24, 1928 PUBLISHED APRIL 5, 1929

In a long, interesting paper appearing in 1923 de Booseré[2] reported the isolation of ethyl cyclopropyl ketimine and its hydrochloride with several other products following the action of magnesium ethyl bromide on γ-chlorobutyronitrile. The mechanism indicated by him for the origin of the ketimine follows closely an earlier one formulated by Bruylants[3] for an entirely analogous reaction. The equations follow.

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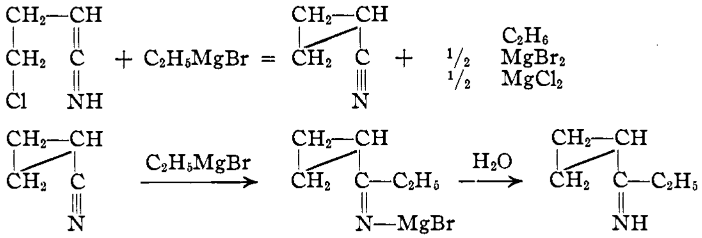
[1] This paper is constructed from the first part of a dissertation to be presented by John B. Cloke to the University of Chicago in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] De Booseré, *Bull. soc. chim. belg.*, **32**, 26–51 (1923).

[3] Bruylants, *Bull. sci. acad. roy. belg.*, **12**, 1082–1084 (1908).



Ketimines react normally with water to give the corresponding ketone and ammonia, as follows: R—C(=NH)—R′ + H_2O = R—CO—R′ + NH_3. Ordinarily this change is greatly accelerated by acids. Until de Booseré's paper appeared, qualitative reports concerning the rate of this reaction, notably by Mignonac,[4] indicated that it increases as the substituted groups become more aliphatic in character, although no purely aliphatic ketimines have thus far been recorded.

In striking contrast with the generalization of Mignonac, de Booseré reported that his ethyl cyclopropyl ketimine hydrochloride does not appear to be altered either by cold water or even by the action of hot water for several minutes. This observation appeared especially notable in view of a further statement that the compound is decomposed by hot sodium hydroxide solution giving ammonia and an odor analogous to that of ethyl cyclopropyl ketone. The identity of the latter compound appeared to be established conclusively by the formation, but with some difficulty, of its semicarbazone.

In view of the striking resistance to hydrolysis reported for the ethyl cyclopropyl ketimine hydrochloride as opposed to the great sensitivity of its phenyl analog,[5] Professor Julius Stieglitz instituted four years ago a physico-chemical investigation of the ketimines as a class in order to ascertain precisely the relationship existing between their structure, their stability in water and their strength as bases. This line of attack, it was supposed, might connect the striking stability of the ethyl cyclopropyl ketimine hydrochloride with the presence of a large percentage of the enamic tautomer in the equilibrium $—C(=NH)—CH< \rightleftharpoons —C(NH_2)=C<$.[6] Although evidence of this type has been collected for certain ketimines, the investigation by redirecting attention to the preparation of the cyclopropyl ketimines has shown that the stable supposed

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[4] Mignonac, *Compt. rend.*, 170, 936–938 (1920).

[5] Bary, *Bull. soc. chim. belg.*, 31, 404 (1922).

[6] The determination of sensitiveness to hydrolysis has been made the basis of a study of ketimine–quinoid–amine tautomerism of phenolic derivatives of benzophenone by J. Stieglitz and J. B. Culbertson (Doctorate "Dissertation," University of Chicago, 1927). Thus the tautomerism $HO—C_6H_3(OH)—C(=NH_2^+)C_6H_5 \rightleftharpoons O=C_6H_3(OH)=C(NH_3^+)—C_6H_5$ reveals itself in the rate of saponification of the ketimine as well as in color and other relations (J. S.).

ethyl cyclopropyl ketimine hydrochloride is in reality the isomeric 2-ethylpyrroline salt, which is perfectly stable in water. In addition the writer has also found that the real cyclopropyl ketimine hydrochlorides also undergo a molecular rearrangement to the pyrroline salts, whereby the unstable triatomic ring is opened and a new stable five-atom ring is closed.

The Formation of 2-Phenylpyrroline from γ-Chlorobutyronitrile.—In an attempt to prepare phenyl cyclopropyl ketimine by an extension of the reaction which de Booseré claimed gave ethyl cyclopropyl ketimine, γ-chlorobutyronitrile was treated with magnesium phenyl bromide. The addition product was decomposed by both the acetic acid–ammonia and the ice–ammonium chloride methods as described by Moureu and Mignonac,[7] and also by liquid ammonia as developed by the writer. The evaporation of the dry filtered ether solutions obtained by the foregoing methods on the water-bath gave mainly solid 2-phenylpyrroline hydrochloride accompanied by a variable amount of the free base and other products. It is to be noted that the evaporation and heating on the water-bath led to a chemical change, since the solid hydrochloride is insoluble in ether.

The Origin of the 2-Phenylpyrroline Hydrochloride.—It is clear that the 2-phenylpyrroline hydrochloride resulted from the rearrangement of phenyl γ-chloropropyl ketimine. Thus, in the first place, theory would indicate that magnesium phenyl bromide would react normally with γ-chlorobutyronitrile, $Cl—(CH_2)_3—CN$, to give the bromomagnesium derivative of phenyl γ-chloropropyl ketimine, $Cl—(CH_2)_3—C(=NMgBr)C_6H_5$, which by careful decomposition as indicated above would yield the free ketimine, $Cl—(CH_2)_3—C(=NH)C_6H_5$, with certain by-products. It is well known, however, that compounds of the type of the aforementioned ketimine show a general tendency toward internal condensation. Thus, by analogy with the behavior of β-chloro-ethyl imidobenzoate[8] and γ-chloropropyl imidobenzoate,[9] it would be expected that phenyl γ-chloropropyl ketimine would rearrange into 2-phenyl-Δ^1-pyrroline hydrochloride. If, however, the Δ^2 structure, which has been assigned by Gabriel and Colman[10] to the pyrroline hydrochloride finally obtained, is correct, the rearrangement of the ketimine into this compound could be readily understood by assuming the ketimine to be in equilibrium with its enamic tautomer,[11] also called an isoketimine,[12] and that the latter

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[7] Moureu and Mignonac, *Compt. rend.*, **156**, 1801–1806 (1913); *Ann. chim.*, [9] **14**, 322–359 (1920).

[8] Wislicenus and Körber, *Ber.*, **35**, 164–168 (1902).

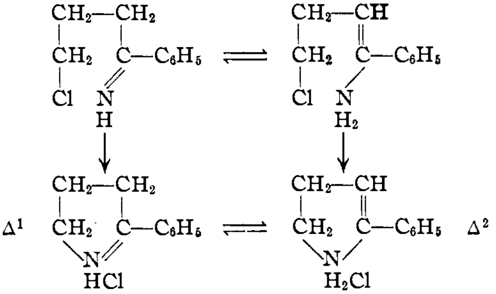
[9] F. A. Keniston, "Thesis," Rensselaer Polytechnic Institute.

[10] Gabriel and Colman, *Ber.*, **41**, 517–518 (1908).

[11] Compare Thorpe and Best, *J. Chem. Soc.*, **95**, 1506 (1909).

[12] Moureu and Mignonac, *Ann. chim.*, **14**, 352 (1920).

then undergoes ring closure. These two possibilities and also a third involving a Δ^1–Δ^2 tautomerism are shown by the following equations[13]



In order to substantiate the foregoing theory, namely, that the action of magnesium phenyl bromide on γ-chlorobutyronitrile gives phenyl γ-chloropropyl ketimine as an intermediate product, which then rearranges into the phenylpyrroline hydrochloride, an attempt was made to isolate and identify the ketimine.

Phenyl γ-Chloropropyl Ketimine.—On account of certain concurrent and consecutive reactions associated with the formation of the bromomagnesium derivative of phenyl γ-chloropropyl ketimine, and because of the unstable character of the ketimine itself, it was not found possible by the method used to isolate the ketimine in a sufficiently pure state to establish its identity positively by analysis. That this compound was formed, however, is clear from the facts, first, that the bromomagnesium derivative, whose composition closely approximated the theoretical values, gave phenyl γ-chloropropyl ketone on hydrolysis, and, second, that the impure ketimine hydrochloride, which was actually separated, gave in one experiment a velocity constant for its reaction with water at 0° whose value, *viz.*, $k_v = 0.36 \pm$, was in complete harmony with the estimated order of reactivity, $k_v = 0.371$. The latter value was calculated upon the basis of an extensive comparative study of imido ester and ketimine stability which is being carried out in these Laboratories.

The Origin of the Free 2-Phenylpyrroline.—The free 2-phenylpyrroline, which is formed in connection with all three decomposition methods, doubtless results from several concurrent and consecutive reactions. In the first place the free base is obtained with ammonium chloride by the action of ammonia on its hydrochloride, which is formed as described above. In the second place the free pyrroline would result from the decomposition of its N-bromomagnesium derivative, which appears to be formed to some extent. In addition a very small portion of the free

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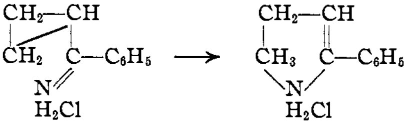
[13] Since Gabriel presented no critical evidence for the Δ^2 structure which he adopted, work is being continued on this phase of the problem in conjunction with the synthesis of other pyrrolines and related compounds.

base, which is obtained in connection with the ice–ammonium chloride decomposition method, would be formed by the action of ammonia on the hydrolysis product of the ketimine, namely, the ketone.

The Formation of 2-Phenylpyrroline Hydrochloride from Phenyl Cyclopropyl Ketimine Hydrochloride.—When it was found that phenyl cyclopropyl ketimine apparently could not be obtained directly from γ-chlorobutyronitrile, the original method followed by Bary for the preparation of this compound was employed. In studying the hydrochloride of this ketimine it was found that it melted fairly sharply at about 104–105°, but that it resolidified almost immediately, giving a compound melting from 195–200°. This change was found to be occasioned primarily by the rearrangement of the ketimine hydrochloride into the isomeric pyrroline salt as a result of the rupture of the cyclopropyl ring, as follows



All other cyclopropyl and cyclobutyl ketimine hydrochlorides thus far investigated behave in the same manner.[14]

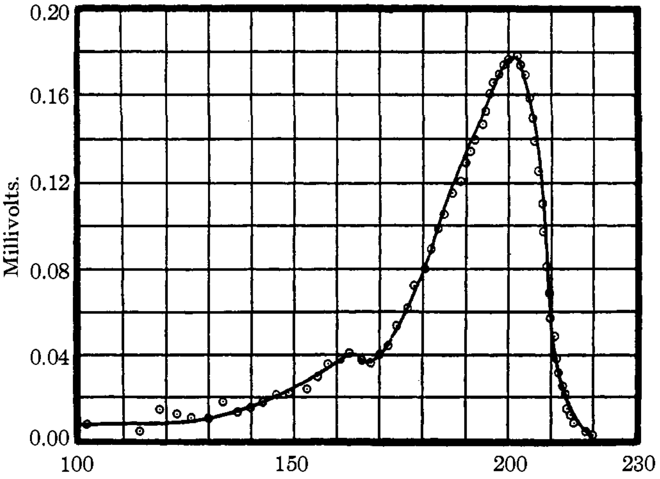


Fig. 1.

The Formation of 2-Phenylpyrroline from Phenyl Cyclopropyl Ketimine.—Although the discovery of the rearrangement of phenyl cyclopropyl ketimine hydrochloride into the isomeric pyrroline salt indicated that the free ketimine base would rearrange similarly, the experimental

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[14] Baer, Robbins and Van Wyck, "Theses," Rensselaer Polytechnic Institute.

confirmation of this reaction came accidentally as the result of the distillation of a quantity of the free ketimine, which contained some chlorine compound, probably hydrochloride, as an admixture.

In order to avoid future loss of ketimine, comparative measurements were made to ascertain the effect of temperature and the presence of the hydrochloride on the sensitivity of the compound to rearrangement. On account of the scarcity of ketimine and in view of the fact that the ring rupture liberates heat, a differential chromel–constantan thermocouple was employed for the work. One leg of the thermocouple was immersed in the sample and the other in an equal amount of liquid petrolatum. The two tubes were then heated uniformly in a bath and simultaneous minute readings were taken on the thermometer and potentiometer.

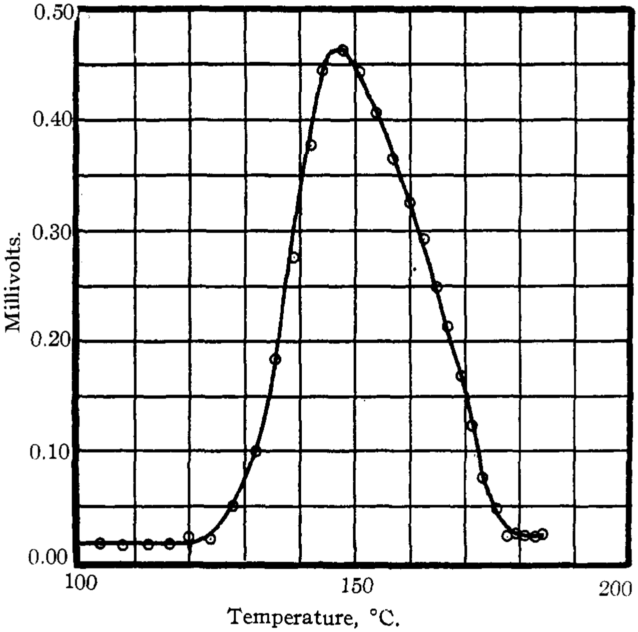

Fig. 2.

Figure 1 represents the effect of heating on the free ketimine, the heating being started at 91°. Exactly the same type of curve was obtained in the case of a second run which was started at 26°. Fig. 2 shows the catalytic effect produced by the addition of 0.0027 g. of the hydrochloride to 0.3483 g. of the free base. The same type of curve was given by the substitution of the same weight of the isomeric pyrroline salt for the ketimine hydrochloride but the maximum reached was somewhat lower, as would be expected. Ketimine free from all traces of hydrochloride would doubtless show a somewhat greater thermal stability than that indicated by Fig. 1.

The greater sensitivity of the phenyl cyclopropyl ketimine hydrochloride to rearrangement as compared with the free base is in complete harmony with the work of several investigators,[15] who have found that the cyclopropyl ring has an increased tendency to rupture in the presence of hydro-halogen acid.

Although practically all of the ketimine is converted into the pyrroline under the conditions mentioned above, other reactions occur. The most obvious of these is the probable formation of ammonia and diphenylcyclopropylcyclopropylidene ketisoketimine, the latter of which would probably undergo ring ruptures analogous to those previously described.

Experimental Part

Preparation of Nitriles.—Cyclopropyl cyanide, $\overline{\mathrm{CH_2—CH_2—CH}}\mathrm{—CN}$, was prepared by the action of sodium hydroxide on γ-chlorobutyronitrile, $\mathrm{Cl—CH_2CH_2CH_2—CN}$, which was obtained from trimethylene chlorobromide, $\mathrm{Cl—CH_2CH_2CH_2—Br}$, and potassium cyanide.

The trimethylene chlorobromide was made both by the action of moist hydrogen bromide gas on allyl chloride, $\mathrm{CH_2{=}CH—CH_2Cl}$,[16] according to the procedure described by Bruylants,[17] and also by the refluxing of trimethylene chlorohydrin,[18] $\mathrm{Cl—CH_2CH_2CH_2OH}$, while it was stirred with 48% hydrobromic acid according to the general procedure described by Kamm and Marvel.[19] This latter procedure is much to be preferred. The writer also succeeded in preparing the chlorobromide in one operation from trimethyleneglycol, $\mathrm{HO—CH_2—CH_2—CH_2—OH}$, by several methods, but the yields were comparatively unsatisfactory.

γ-Chlorobutyronitrile was prepared by Henry's method,[20] with the exception that 1.1 mole of potassium cyanide per mole of chlorobromide was found to be slightly more advantageous; moreover, the time of refluxing was increased and the nitrile and alcohol were distilled under diminished pressure.

The cyclopropyl cyanide was obtained by the action of powdered sodium hydroxide on γ-chlorobutyronitrile.[21] The reaction is quite violent and considerable ammonia is given off, the latter resulting from the hydrolysis of the nitriles by the water formed during the reaction. On account of the value of the cyclopropyl cyanide, several methods were studied for minimizing the hydrolysis. The admixture of powdered calcium oxide was of apparent value, but still better results were obtained by the use of anhydrous aluminum oxide, suggested by Dr. F. W. Schwartz. Subsequently it was found that sodamide works quite well. Although still better results may possibly be obtained by employing some of the technique developed by Nicolet and Sattler,[15] for the preparation of this compound, the following typical procedure for the sodium hydroxide–aluminum oxide method is given as a matter of record.

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[15] Compare Nicolet and Sattler, THIS JOURNAL, **49**, 2066–2068 (1927).

[16] Coffey and Ward, *J. Chem. Soc.*, 119, 1305 (1921).

[17] Bruylants, *Bull. sci. acad. roy. belg.*, **12**, 1085–1094 (1908).

[18] Hultman, Davis and Clarke, THIS JOURNAL, **43**, 369 (1921).

[19] Kamm and Marvel, *ibid.*, **42**, 307 (1920).

[20] Gabriel, *Ber.*, **23**, 1771 (1890).

[21] Henry, *Bull. sci. acad. roy. belg.*, [3] **36**, 34 (1898).

A mixture of 40 g. of powdered sodium hydroxide and 15 g. of freshly dehydrated powdered aluminum oxide was introduced into a 250-cc. distilling flask connected with an efficient water condenser. A weight of 75 g. of γ-chlorobutyronitrile was then added all at once and the mixture well shaken, giving a uniform paste. The flask and contents were then heated in an oil-bath to about 154°, when a vigorous reaction occurred, necessitating the removal of the oil-bath. When the intensity of the reaction had subsided somewhat, the bath was returned and its temperature gradually raised to about 275°. Finally the receiver and distillate were replaced by a second receiver, when the application of diminished pressure gave a small additional quantity of distillate. The total distillate was washed once with water and then dried. Several similar runs were combined and fractionated with the aid of a special Vigreaux–Hempel column of small diameter and about two feet long, giving results similar to those reported by Bruylants and Stassens,[22] the main fraction boiling from 133–134° at 749 mm.

The Formation of 2-Phenyl Pyrroline, $C_6H_5—\overbrace{C{=}CH—CH_2—CH_2—NH}$, **from γ-Chlorobutyronitrile.**—Magnesium phenyl bromide was prepared from 8.4 g. of magnesium (2.42 mole), 56 g. of bromobenzene (2.5 mole) and 150 cc. of absolute ether, the procedure employed by Moureu and Mignonac being used.[23] To this ether solution 15 g. (1 mole) of γ-chlorobutyronitrile (b. p. 78–80° at 12 mm.), dissolved in its own volume of ether, was added slowly and with stirring. At the end of about nine minutes crystals separated out, accompanied by vigorous ebullition of the ether. The heating and stirring were then continued for four hours. During this time the material, which was originally crystalline and white, turned dark slowly and took on an amorphous appearance. The mass was then washed with anhydrous ether, when the residue was treated with 24 cc. of glacial acetic acid dissolved in 100 cc. of ether. Stirring and heating on the water-bath were then continued for ten hours, when the mixture was allowed to stand. At this point the yellowish residue was collected on a filter, washed with ether, suspended in more dry ether and then treated with a current of dry ammonia gas for several hours. The ether solution resulting was filtered from the residue (B), and distilled on the water-bath, leaving in the flask a yellowish solid, which was found to be the hydrochloride of a base. Up to this point the writer supposed that he was preparing phenyl cyclopropyl ketimine, but the appearance of the solid showed that some different change had taken place.

Since the residue (B), which was collected on a filter following the action of the ammonia, was found to contain undecomposed organomagnesium derivative, this was decomposed with shaved ice and ammonium chloride; the mixture was then extracted with ether and the ether solution dried over anhydrous sodium sulfate. The dry filtered solution was then evaporated under diminished pressure at a temperature below 0°, leaving a few cc. of a brownish oil. This liquid, contained in a flask, was then heated in a water-bath, when solidification occurred mainly in the vicinity of 85°, although a considerable fraction in this case failed to change.

The two hydrochloride residues thus obtained were dissolved in dry chloroform, the solution treated with dry ammonia gas and, after filtration, the chloroform was distilled off, leaving an oil, which gave about 5 g. of substance boiling between 117–125° at 12 mm. This product was later combined with similar material, which was obtained in the course of a second run not greatly different from the foregoing, and the mixture distilled, giving a liquid boiling for the most part at 124° at 15 mm. (In a subsequent run by a somewhat simplified procedure 8.5 g. of base, b. p. 125–125.5° at 15.5–16 mm., was obtained.) The distillate was colorless at first but it slowly developed a reddish

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[22] Bruylants and Stassens, *Bull. sci acad. roy. belg.*, [5] **7**, 702–719 (1921).

[23] Moureu and Mignonac, *Ann. chim.*, **14**, 336 (1920).

tint on standing. It was identified as 2-phenylpyrroline from a study of its hydrochloride.

The hydrochloride was obtained by the action of carefully dried hydrogen chloride gas on a solution of the free base in dry ether. The precipitated hydrochloride was collected on a filter, washed with dry ether and then left overnight in a desiccator containing sodium hydroxide and calcium chloride. The compound was recognized as 2-phenylpyrroline hydrochloride upon the basis of its stability in water, even on boiling, its chlorine content and its conversion into the characteristic picrate and the chloroplatinate of the base. The hydrochloride dissolves readily in chloroform, alcohol and water, but it is practically insoluble in ether and only slightly soluble in carbon tetrachloride.

Anal. Subs., 0.0454: 2.46 cc. 0.1 *N* $AgNO_3$. Calcd. for $C_{10}H_{12}NCl$: Cl, 19.52. Found: 19.24. *Anal.* of chloroplatinate. Subs., 0.0931: Pt, 0.0258. Calcd. for $C_{20}H_{24}N_2Cl_6Pt$: Pt, 27.87. Found: Pt, 27.71.

Isolation of Impure Phenyl γ-Chloropropyl Ketimine, $C_6H_5—C(=NH)—CH_2—CH_2—CH_2—Cl$.—An ether solution of magnesium phenyl bromide was prepared from 6.76 g. of magnesium (1.29 mole) and 44.8 g. of bromobenzene (1.33 mole). To this was added 22 g. of γ-chlorobutyronitrile (1 mole) dissolved in its own volume of ether; crystallization occurred as usual. The mixture was then heated for two hours on the water-bath and allowed to stand for twelve hours. At this time the precipitate was brought onto a filter, washed three times with anhydrous ether, decomposed with shaved ice and ammonium chloride, extracted four times with ether and the ether solution finally dried over anhydrous sodium sulfate. Two portions of this solution were next removed with the hope of being able to separate the free ketimine from the first portion and its hydrochloride from the second.

Free Base.—The ether was removed from portion No. 1 by evaporation under diminished pressure at less than room temperature. Since solid began separating as the result of a reaction almost as soon as the ether was removed, samples of the brownish liquid were taken immediately.

Anal. Calcd. for $C_{10}H_{12}NCl$: N, 7.71; Cl, 19.52. Found: 5.73; 16.12.

The amount of acid neutralized by the residue also was only in qualitative accord with the ketimine theory.

Hydrochloride.—A current of dry air was aspirated through the second ether portion in order to remove any ammonia. Pure dry hydrogen chloride gas was next passed into the cold ether solution, giving a yellow viscous mass which adhered to the flask tenaciously. The ether was poured off, the residue dissolved in dry chloroform and reprecipitated with dry ether, giving the same kind of viscous product as before. However, by repeating this procedure several times a product was finally obtained which solidified when rubbed with a glass rod. This solid hydrochloride, which was brought on a filter in dry air, was impure, as was shown by its melting incompletely in the vicinity of 85–88°, and also by its analysis.

Anal.[24] Calcd. for $C_{10}H_{13}NCl_2$: N, 6.42; Cl, 32.52. Found: N, 8.10; Cl, 32.40.

The most significant property of this hydrochloride was its remarkable rate of reaction with water at 0°. The procedure followed for the measurements was the same in principle as that developed by Stieglitz and Derby for the imido-ester hydrochlorides.[25] In the following table Col. 2 gives

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[24] The writer is indebted to Mr. F. A. Keniston for these Cl and N determinations.

[25] Derby, *Am. Chem. J.*, **39**, 439–441 (1908).

the cc. of $N/10$ sodium hydroxide neutralized by the ketimine hydrochloride in 10 cc. of solution, containing 10.9 g. per liter, at the end of times t_1, t_2..... The constant k is calculated from the expression for a monomolecular reaction

$$k = \frac{2.303}{t_2 - t_1} \log \frac{v_1}{v_2}$$

where v_1, v_2 represent the cc. of $N/10$ sodium hydroxide in Col. 2, and the correction of t_1, t_2 from seconds to minutes is made.

TABLE I

DECOMPOSITION OF PHENYL γ-CHLOROPROPYL KETIMINE HYDROCHLORIDE

Time from start, sec.	30	76	145	180	
Vol. of $N/10$ NaOH, cc.	3.35	2.50	1.96	1.16	
k	..	0.386	0.280	0.425	Av. 0.363

Relatively large experimental errors were unavoidable on account of the exceedingly high reaction rate of the compound.

Analysis of Bromomagnesium Derivative of the γ-Chloropropyl Phenyl Ketimine, $(ClCH_2CH_2CH_2)(C_6H_5)C{=}NMgBr$.—Magnesium phenyl bromide was added to γ-chlorobutyronitrile as previously described, but without any subsequent heating. A portion of the carefully washed crystalline mass was analyzed after several hours' exposure in a vacuum desiccator at 50°.

Anal. Subs., 0.1233: MgO, 0.0178. Subs., 0.03132: cc. of $N/100$ HCl, 9.85. Calcd. for $C_{10}H_{11}NClBrMg$: Mg, 8.54; N, 4.91. Found: Mg, 8.71; N, 4.40.

Previous analytical results indicate that the compound crystallizes with a molecule of ether.

Phenyl γ-Chloropropyl Ketone, $C_6H_5{-}CO{-}CH_2CH_2CH_2Cl$.—The above magnesium compound was decomposed with aqueous hydrochloric acid and the mixture extracted with ether. The ether solution was dried over calcium chloride and then treated with dry hydrogen chloride gas in order to precipitate any 2-phenylpyrroline as hydrochloride, some of this being obtained. After standing for a day the ether was removed from the filtered solution, leaving an oily residue. This was fractionated several times through a short column, giving a nitrogen-free oil which boiled mainly from 130–133° at 4 mm.

Anal. Subs., 0.1689: AgCl, 0.1256. Calcd. for $C_{10}H_{11}OCl$: Cl, 19.42. Found: Cl, 18.40.

Several further rectifications gave a liquid of boiling point 120–121° at 3 mm.; d_4^{20}, 1.149; n_D^{20}, 1.55433.

Anal. Calcd. for $C_{10}H_{11}OCl$: Cl, 19.42. Found: Cl, 16.79.

The lower chlorine content was probably occasioned by the loss of hydrogen chloride accompanied by the formation of phenyl cyclopropyl ketone.

Semicarbazone of Phenyl γ-Chloropropyl Ketone.—The semicarbazone separated out after a day in the form of colorless crystals melting at 136–137°. Prolonged heating leads to some decomposition, possibly to carbamyl-1-phenyl-3-tetrahydropyridazine.[26] The semicarbazone was analyzed according to Pregl's micro methods.

Anal. Subs., 9.98 mg.: N_2, 1.500 cc. (as measured at 16°, 765.9 mm.). Subs., 14.70 mg.: AgCl, 8.90 mg. Calcd. for $C_{11}H_{14}ON_3Cl$: N, 17.53; Cl, 14.80. Found: N, 17.54; Cl, 14.98.

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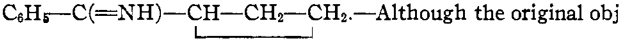
[26] Compare Wohlgemuth, *Ann. chim.*, [9] **2**, 454 (1914).

The Formation of 2-Phenylpyrroline from Phenyl γ-Chloropropyl Ketone.—Hielscher's preparation of 2-methylpyrroline by the action of ammonia on methyl γ-bromopropyl ketone[27] led Wohlgemuth[28] to attempt the extension of the reaction. He found, however, that the interaction of ammonia and γ-chloro-*n*-butyl ethyl ketone gave methyl cyclopropyl ethyl ketone, that is, methyl-1-propionyl-2-cyclopropane. He was unable to identify any pyrroline. The writer, on the other hand, has been partially successful in a similar case, as described below.

Phenyl γ-chloropropyl ketone was treated with an excess of cold alcoholic ammonia for three weeks. The solution was dried over anhydrous sodium sulfate, filtered and the alcohol completely removed by evaporation at ordinary temperatures under diminished pressure after the addition of a little ether. The residue was dissolved in dry ether, treated with a slight excess of dry hydrogen chloride and allowed to stand until the 2-phenyl pyrroline hydrochloride had completely precipitated. The solid, obtained in about 10% yield, was identified as 2-phenylpyrroline hydrochloride upon the basis of its melting point and the formation of the picrate. The ether was removed from the remaining solution leaving an oily residue, apparently composed of the unchanged original ketone mixed with phenyl cyclopropyl ketone.

Since bases, in general, tend to form cyclopropyl derivatives from γ-chloropropyl compounds, it follows that any free pyrroline base, for example 2-phenylpyrroline, must not be distilled in the presence of a γ-chloropropyl ketone such as the γ-chloropropyl phenyl ketone, which is a by-product of one method previously described for the preparation of pyrrolines. The heating results in the formation of the pyrroline hydrochloride which condenses in the flask neck.

The Formation of 2-Phenylpyrroline from Phenyl Cyclopropyl Ketimine, $C_6H_5—C(=NH)—CH—CH_2—CH_2$.—Although the original object in the preparation of the phenyl cyclopropyl ketimine was to obtain the pure free base and its hydrochloride for certain physico-chemical measurements, lack of precise knowledge regarding the stability of the ketimine at that time led to the accidental synthesis of the isomeric pyrroline.



Phenylmagnesium bromide was prepared from 14.6 g. of magnesium (1.46 mole), 94.2 g. of bromobenzene (1.5 mole) and 250 cc. of anhydrous ether. To this solution 26.8 g. (1.0 mole) of cyclopropyl cyanide (b. p. 133–134° at 749 mm.), dissolved in its own volume of ether, was added over an interval of four minutes. After remaining quiescent for six minutes a light grey or slate-colored precipitate separated from the solution, occasioning such vigorous boiling of the ether that prompt cooling in water was necessary in order to prevent the expulsion of the mixture through the condenser. The ketimine was next liberated from the well-washed bromomagnesium derivative by the action of shaved ice and ammonium chloride; it was immediately separated by several extractions with ether, the extract being dried at once with calcium chloride followed by anhydrous sodium sulfate. By treating this solution with dry hydrogen chloride the ketimine was precipitated in the form of its hydrochloride, which was then dissolved in hot, dry chloroform and reprecipitated by ether as beautiful white crystals containing a molecule of chloroform. With the expectation of obtaining the pure free base and its hydrochloride for the physico-chemical measurements, the crystals containing the added chloroform were dissolved in warm chloroform; the solution was treated with an excess of dry ammonia gas, following which the precipitated ammonium chloride was removed by filtration and the chloroform by distillation on the water-bath. Since the free ketimine thus obtained was slightly colored, it was erro-

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[27] Hielscher, *Ber.*, 31, 277 (1898).

[28] Wohlgemuth, *Ann. chim.*, [9] 2, 441 (1914).

neously decided to risk the distillation process in order to obtain a colorless product, but during the attendant heating under diminished pressure the ketimine rearranged into the isomeric pyrroline, as was conclusively demonstrated by the study of the hydrochloride described below. The rearrangement appeared to be accompanied by a peculiar color change associated with more vigorous boiling. About 90% of the ketimine was obtained as the pyrroline; the brownish-red residue was not examined.

In passing it may be noted that, although an excess of dry ammonia gas was employed in the foregoing procedure, a number of crystals of the hydrochloride of some base collected in the neck of the Claisen flask at the end of the distillation. These together with the excessive temperature, as was learned later, were responsible for the sensitivity of the ketimine to rearrangement. The crystals softened at 67° and melted from 71–73°. The nature of this compound, of which only a few milligrams was obtained, may be cleared up in connection with work on other pyrrolines.

2-Phenylpyrroline Hydrochloride.—The distilled 2-phenylpyrroline, obtained as described above, was dissolved in dry ether, treated with dry hydrogen chloride and the salt removed by filtration.

Anal. Subs., 12.08 mg.: cc. $N/100$ HCl, 6.62. Subs., 0.4366: cc. $N/10$ $AgNO_3$, 23.96. Calcd. for $C_{10}H_{12}NCl$: N, 7.71; Cl, 19.52. Found: N, 7.67; Cl, 19.46. *Anal.* of chloroplatinate. Subs., 8.00 mg.: Pt, 2.23 mg. Calcd. for $C_{20}H_{24}N_2Cl_6Pt$: Pt, 27.87. Found: Pt, 27.87.

Phenyl Cyclopropyl Ketimine.—The ketimine which was employed in securing data for Figs. 1 and 2 was obtained by the evaporation of the ether at less than room temperature from a filtered dry ether solution obtained as described in the preceding section on the formation of 2-phenylpyrroline from phenylcyclopropyl ketimine with the single exception that the Grignard reagent was prepared in an atmosphere of dry hydrogen.

The Formation of 2-Ethylpyrroline Hydrochloride from γ-Chlorobutyronitrile.—By the action of magnesium ethyl bromide on γ-chlorobutyronitrile, de Booseré, as stated previously, obtained the hydrochloride of a base, identified by him as ethyl cyclopropyl ketimine. This compound, which distilled from 160–170° (14–16 mm.), was very deliquescent and was apparently unattacked by water. When treated with sodium hydroxide solution, however, it was stated to decompose into ammonia and ethyl cyclopropyl ketone, the presence of the latter being inferred upon the basis of odor and the formation of the semicarbazone. The free base, which was obtained from the hydrochloride, boiled from 127–128° at 759 mm. Although it appeared clear that the base was actually 2-ethylpyrroline,[29] in spite of the behavior with semicarbazide, the reaction has been reinvestigated.

Magnesium ethyl bromide was prepared from 8.4 g. of magnesium, 39 g. of ethyl bromide and 145 cc. of ether. To this solution 15 g. of γ-chlorobutyronitrile dissolved in its own weight of ether was added, no permanent separation of solid occurring. The solution was then allowed to simmer gently for half a day, at which time the greenish-yellow liquid was poured into water containing ammonium chloride and the solution extracted with ether. Since distillation of the dried ether extract failed to give a constant-boiling fraction, the combined non-ethereal fractions were treated with alcoholic ammonia for a day, at which time the alcoholic solution was neutralized with anhydrous hydrogen chloride. The ammonium chloride was removed by filtration and the filtrate distilled, giving a substance which passed over mainly at 166° (18 mm.) and which solidified on cooling. The compound was so deliquescent that no accurate melting point could be determined by the capillary tube method, values being obtained ranging from 87–101°, these being surprisingly close to the melting point of the real ethyl cyclo-

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[29] Dennstedt, German Patent 127,086; *Chem. Zentr.*, [1] 338 (1902).

propyl ketimine hydrochloride. Recrystallization from acetic anhydride and dry ether gave nice crystals but these deliquesced immediately when exposed to the outside air. The compound, like that of de Booseré, was not apparently altered either by hot or cold water. When treated with sodium hydroxide, an odor was at once developed which, indeed, resembled that of a mixture of ammonia and ethyl cyclopropyl ketone, as previously reported. That this was an olfactory error was shown by the fact that an alcoholic solution of the hydrochloride gave a precipitate with alcoholic platinic chloride, which, after resolution in boiling alcohol and reprecipitation by anhydrous ether, was found to be the chloroplatinate of 2-ethylpyrroline, m. p. 179–180° with decomposition.

Anal. of chloroplatinate. Subs., 9.33 mg.: Pt, 3.00 mg. Calcd. for $C_{12}H_{24}N_2Cl_6Pt$: Pt, 32.35. Found: Pt, 32.15.

Dennstedt, who first prepared the chloroplatinate in an impure form, found that it melted in the vicinity of 170°.

That the hydrochloride is not hydrolyzed to ammonia and ketone when distilled with a base was shown by the separation of the same chloroplatinate from an aqueous distillate, which was obtained by distilling the hydrochloride with aqueous sodium hydroxide.

The Formation of 2-Ethylpyrroline Hydrochloride from Ethyl Cyclopropyl Ketimine Hydrochloride.—Ethyl cyclopropyl ketimine was prepared from magnesium ethyl bromide and cyclopropyl cyanide by the acetic acid–ammonia process of Moureu and Mignonac. During the work certain unexpected difficulties arose which necessitated the exposure of the mixture to the outside air for a short time. Since this led to some hydrolysis of the very sensitive ketimine, the pure compound will be described later. Semi-quantitative work relating to its stability, however, shows that it is very rapidly hydrolyzed by water to give the ketone and ammonia. A portion of the ketimine was heated in a sealed tube up to 185° in order to learn how sensitive it is to rearrangement. No pyrroline, however, was separated.

A small amount of the impure ketimine was converted into its hydrochloride. This melted between 101–103°, decomposing shortly afterward. From a portion heated to 130° the chloroplatinate of the 2-ethylpyrroline was obtained.

Anal. of chloroplatinate. Subs., 7.33 mg.: Pt, 2.36 mg. Calcd. for $C_{12}H_{24}N_2Cl_6Pt$: Pt, 32.35. Found: Pt, 32.19.

In passing it may be added that the real ethyl cyclopropyl ketimine hydrochloride is decomposed normally by water, although it is more stable than was expected. This is being investigated further.

The writer is indebted to Professor Julius Stieglitz, under whose direction the work was undertaken, for criticism, inspiration and advice, and to President P. C. Ricketts and Professor A. W. Davison for their aid in providing materials and equipment.

Summary

1. 2-Phenylpyrroline can be obtained as a result of the action of magnesium phenyl bromide on γ-chlorobutyronitrile. By the procedure described most of the pyrroline is initially obtained in the form of its hydrochloride, which results from the rearrangement of phenyl γ-chloropropyl ketimine.

2. By heating phenyl cyclopropyl ketimine hydrochloride above its melting point it rearranges into 2-phenylpyrroline hydrochloride.

3. 2-Phenylpyrroline is formed by the action of heat on phenyl cyclopropyl ketimine. Curves are given which show the effect of temperature and the presence of the ketimine hydrochloride on the stability of the ketimine base.

4. The facts enumerated in 1, 2 and 3, together with a general study of ketimine stability, have led to the proof that de Booseré's so-called ethyl cyclopropyl ketimine hydrochloride, which is described as remarkably stable toward hydrolysis, is in reality a pyrroline derivative. The true ethyl cyclopropyl ketimine hydrochloride is sensitive to hydrolysis, as are the other true ketimine hydrochlorides.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE NEW JERSEY AGRICULTURAL EXPERIMENT STATION]

PROCESSES INVOLVED IN THE DECOMPOSITION OF WOOD WITH REFERENCE TO THE CHEMICAL COMPOSITION OF FOSSILIZED WOOD[1]

BY SELMAN A. WAKSMAN AND KENNETH R. STEVENS

RECEIVED OCTOBER 1, 1928 PUBLISHED APRIL 5, 1929

Our information concerning the chemical processes involved in the decomposition (or so-called "decay") of wood, fossilization being merely a type of decomposition, is very meager. The question as to whether decomposition, which is never complete and which results only in a partial reduction in the bulk of woody substance, consists in the gradual utilization by microörganisms (fungi and bacteria) of all the chemical constituents of wood or whether certain complexes are decomposed more readily than others, has aroused considerable discussion. The nature of the processes involved in the decomposition of wood and other plant substances has found special application in connection with the recently proposed theories of the origin of coal and peat, largely centering upon the role of celluloses and lignins in this process.

It is commonly assumed that the disintegration of wood consists, first, in the chemical simplification of the various constituents from a greater to a lesser complexity, finally leading to their transformation into carbon dioxide, ammonia, water and, under anaërobic conditions, also into hydrogen and methane. The assumption that a number of intermediary substances are formed in this process has never been sufficiently substantiated.

Investigations reported elsewhere[2] on the decomposition of plant residues by microörganisms brought out the fact that the water-soluble plant constituents are the first to be attacked, long before the hemicelluloses

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[1] Journal series paper of the New Jersey Agricultural Experiment Station, Department of Soil Chemistry and Bacteriology.

[2] S. A. Waksman and F. G. Tenney, *Soil Science*, **24**, 275–284 (1927); **26**, 155–171 (1928).