

liquid products from each of the above tests were distilled to 260° to separate unconverted di-butylbenzene and lower boiling fractions. The residual fraction boiling above 260° solidified on cooling to room temperature and was extracted with hot 80% alcohol to separate phenanthrene (solubility 5 g. per 100 cc.) from any anthracene present which is comparatively insoluble in dilute alcohol. After one recrystallization from the hot, dilute alcohol the phenanthrene had a melting point of 100° which was not lowered when mixed with an authentic sample.

The residue from the extraction with dilute alcohol was a dark gummy oil in which no anthracene could be detected.

TABLE III
DEHYDROGENATION OF *p*-DI-*n*-BUTYLBENZENE
Catalyst A; temperature, 500°

Space velocity	0.38	0.20
Yields, wt. % of charge		
Total liquid fraction	70.2	53.8
Toluene	0.5	0.3
Paraffins 110–120°	1.4	1.0
Aromatics 120–150°	4.6	3.3
Aromatics 150–175°	6.1	4.6
Aromatics 175–200°	8.6	6.5
Aromatics 200–260°	27.6	20.7
Phenanthrene	17.6	14.3
Residue	3.8	3.1
Gas	11.0	20.0
Carbon	18.8	26.2
Wt. % phenanthrene in liq. frac.	25.1	26.6

The composition of the gas from the 0.2 space velocity test in mole % was: H₂, 74.4%; CH₄, 7.0%; C₂H₄, 0.5%; C₂H₆, 7.0%; C₃H₆, 1.1%; C₃H₈, 7.1%; and C₄, 2.9%.

Dehydrogenation of Bibenzyl.—A 25 wt. % bibenzyl-75% benzene solution was passed over Catalyst B at 550°, atmospheric pressure, and 1 space velocity during a reaction period of one hour. The recovered liquid products amounted to 95.4 wt. % of the total charge from which a

mixture of stilbene and isostilbene was separated by distillation. Stilbene was identified as α -stilbene dibromide, melting point 237°. Toluene was identified as symmetrical trinitrotoluene, melting point 80°. The gas contained 92.3 mole % hydrogen and 7.7% paraffins having a carbon index of 1.21. The following yields were obtained as weight per cent. of the bibenzyl charged: stilbene, 43.1%; benzene, 9.1%; toluene, 26.8% unreacted bibenzyl and unidentified lower boiling hydrocarbons, 2.5%; gas, 4.0%; and catalyst deposit, 14.5%. No detectable quantity of phenanthrene was found in the reaction products.

Acknowledgment.—Appreciation is expressed to Mr. M. W. Cox for assistance in the experimental work.

Summary

The action of chromia-alumina on benzene, toluene, *n*-butylbenzene, *p*-di-*n*-butylbenzene, phenyl *n*-propyl ketone and bibenzyl at 500–600° has been investigated.

Biphenyl and anthracene were formed from benzene and toluene, respectively, without the formation of detectable amounts of other aromatics.

Naphthalene yields of 51–55 wt. % per pass were obtained from *n*-butylbenzene.

Similar dehydrogenations with *p*-di-*n*-butylbenzene gave phenanthrene yields of 14–18 wt. % per pass. Anthracene was not formed in any appreciable amount.

Dehydrogenation of phenyl *n*-propyl ketone resulted in the formation of naphthalene which at 600° amounted to 34 wt. % per pass.

Dehydrogenation of bibenzyl resulted in the formation of stilbene without the formation of phenanthrene or anthracene.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Preparation of 4-Methylquinolines

BY KENNETH N. CAMPBELL AND IRWIN J. SCHAFFNER^{1,2}

In the course of other work in progress in this Laboratory, large amounts of quininic acid were needed. The methods described in the literature³ for the preparation of this substance are both expensive and laborious, and involve a large number of steps. It seemed to us that if 6-methoxyepidine could be obtained in good yields in one step from *p*-anisidine by the Doebner-Miller reaction, and then oxidized to quininic acid, a

great saving in time and materials would be effected.

Many workers have used the Doebner-Miller reaction to prepare 4-alkylquinolines, but the yields have, in general, been low. In some cases the required α,β -unsaturated ketone has been used directly,⁴ but as these substances are not readily available they are frequently generated in the reaction mixture. Thus a mixture of a methyl ketone and an aldehyde may be used,⁵ but the results are not satisfactory; the yield of lepidine by this procedure was around 4%.^{5b}

(1) This paper is abstracted from the dissertation submitted by Mr. Schaffner in partial fulfillment of the requirements for the Ph.D. degree, June, 1944. This paper was presented before the Organic Division of the American Chemical Society at the New York meeting, September, 1944.

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(3) (a) Ainley and King, *Proc. Roy. Soc. (London)*, **125B**, 60 (1930); (b) Rabe, *et al.*, *Ber.*, **64**, 2493 (1931); (c) Thielepape, *ibid.*, **73**, 1440 (1939); (d) Halberkann, *ibid.*, **64**, 3090 (1921); (e) Kaufmann, *ibid.*, **46**, 1831 (1913).

(4) (a) Blaise and Maire, *Bull. soc. chim.*, (4) **3**, 658, 667 (1908); (b) Prill and Walter, U. S. Patent 1,806,584 (1931); C. A., **25**, 3668 (1931).

(5) (a) Beyer, *J. prakt. Chem.*, (2) **33**, 393 (1886); (b) Mikeska, Stewart and Wise, *Ind. Eng. Chem.*, **11**, 456 (1919); Mikeska, *THE JOURNAL*, **43**, 2396 (1920); (c) Palkin and Harris, *Ind. Eng. Chem.*, **14**, 704 (1922).

In other cases^{4a,6} a β -chloroalkyl ketone has served as the source of unsaturated ketone; this modification suffers from the fact that such chloro ketones are not easily available. β -Hydroxyalkyl ketones frequently have been used,⁷ sometimes fair yields of the 4-alkylquinolines have been obtained.

Few workers have used oxidizing agents in the Doebner-Miller reaction in spite of its close similarity to the Skraup reaction. In those cases^{6a,7a} where an oxidizing agent has been used an improvement in yield has been noted; thus Kenner and Statham^{6a} obtained a 40% yield of lepidine from methyl β -chloroethyl ketone by using stannic chloride or ferric chloride. Utermohlen⁸ recently has described a good method for the preparation of quinaldines in which *m*-nitrobenzenesulfonic acid is used as oxidizing agent.

Another factor which may contribute to the generally low yields obtained in the Doebner-Miller reaction is the high acidity of the reaction medium. Most workers have carried the reaction out in the presence of a large excess of concentrated hydrochloric acid or alcoholic hydrogen chloride; some have used concentrated sulfuric acid in a technique similar to that of the Skraup reaction. These strenuous conditions may well cause extensive polymerization of the unsaturated ketone. In those cases where milder conditions have been used^{7b} the yields seem to be better.

We have made a detailed study of the preparation of 4-methylquinolines by the Doebner-Miller reaction, and have found that good yields can be obtained by the use of mild conditions, an oxidizing agent and a condensing agent. Methyl vinyl ketone was used in the earlier part of the work, but as it is unstable and cannot be kept for any length of time without considerable loss by polymerization, a search was made for a more suitable derivative. This was found in 1,3,3-trimethoxybutane, which is readily available from vinylacetylene.⁹ The trimethoxy compound is stable in the absence of hydrogen ion, but in the presence of acid it readily loses the methoxyl groups in a stepwise manner.¹⁰ 4-Methoxy-2-butanone, which can be obtained from the trimethoxy compound by acid hydrolysis, can also be used in place of methyl vinyl ketone in the Doebner-Miller reaction.

Whether trimethoxybutane and methoxybutanone react themselves with the primary aromatic amine, or whether they are first degraded to methyl vinyl ketone is not known at present.

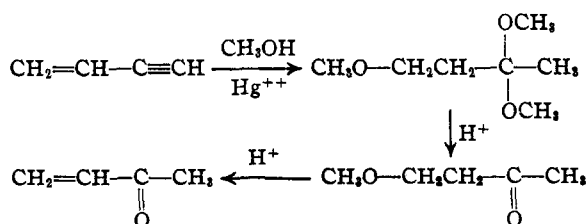
(6) (a) Kenner and Statham, *Ber.*, **90**, 16 (1936); (b) British Patent 283,577 (1927); *C. A.*, **22**, 4132 (1928); (c) German Patent, 518,291 (1927); *C. A.*, **25**, 2442 (1931); (d) U. S. Patent 1,804,045 (1931); *C. A.*, **25**, 3668 (1931).

(7) (a) Prill and Walter, German Patent, 505,320 (1928); *C. A.*, **26**, 479 (1932); (b) Tseou Heo Feo, *Bull. soc. chim.*, (5) **2**, 90 (1935); (c) Manske, Marion and Leger, *Can. J. Research*, **20B**, 133 (1942).

(8) Utermohlen, *J. Org. Chem.*, **8**, 544 (1943).

(9) Killian, Hennion and Nieuwland, *This Journal*, **56**, 1786 (1934); U. S. Patent 2,140,713 (1938).

(10) Norris, Verbanck and Hennion, *ibid.*, **60**, 1159 (1938).



We are now investigating the mechanism of the reaction.

In a basic experiment it was found that a 28% yield of lepidine could be obtained by heating methyl vinyl ketone or trimethoxybutane with a mixture of aniline and aniline hydrochloride in methyl or ethyl alcohol. The yield was raised to 48-55% by use of the calculated amount (2 moles) of ferric chloride; this substance appears to be a specific oxidizing agent, as others, such as nitrobenzene, *p*-nitrophenol and arsenic acid, did not give satisfactory results. *m*-Nitrobenzenesulfonic acid also can be used but the yields are not as high as with ferric chloride. Attempts were made to use gaseous oxygen in the presence of a small amount of ferric chloride as "carrier" but the yields by this process were lower.

In later work it was found that the yield could be raised to 72% by using all the amine in the form of its hydrochloride, and adding a small amount of zinc chloride as condensing agent. Phosphorus pentoxide and boron fluoride are also effective condensing agents.

The method works well with other primary aromatic amines; for example, 4,6-dimethylquinoline was obtained in 65% yield from *p*-toluidine, and 6-methoxylepidine in 52% yield from *p*-anisidine.

We are now investigating the oxidation of 6-methoxylepidine and other substituted lepidines to the corresponding quinoline-4-carboxylic acids, and expect to report the results shortly.

Experimental

Reagents.—The amines used in this work were Eastman Kodak Co. Practical Grade, and in most cases were not purified. The methyl vinyl ketone was prepared in two ways: from formaldehyde and acetone¹¹ and by hydration of vinylacetylene^{12,13}; this is by far the better method. 1,3,3-Trimethoxybutane was made by the catalytic addition of methanol to vinylacetylene,⁹ but no excess of vinylacetylene was used. The material after careful fractionation through a Fenske-Whitmore column had b. p. 69° (30 mm.), *n*_D²⁰ 1.4095. 4-Methoxy-2-butanone was prepared from trimethoxybutane by the method of Killian, Hennion and Nieuwland,⁹ except that the distillation was carried out under reduced pressure to avoid resinification.

Preparation of Lepidine.—The best method was as follows: a 2-liter, 3-neck flask was fitted with a mercury-seal stirrer, dropping funnel, reflux condenser and thermometer. The flask was charged with 80.8 g. of aniline hydrochloride (0.625 mole), 270 g. (1 mole) of ferric chloride hexahydrate, 10 g. of anhydrous zinc chloride and 450 ml. of 95% alcohol. The mixture was heated on a water-

(11) Wohl and Prill, *Ann.*, **440**, 143 (1924).

(12) U. S. Patent 1,967,225 (1934); *C. A.*, **28**, 5834 (1934).

(13) We wish to thank the Jackson Laboratory of the du Pont Co. for furnishing this and certain other chemicals.

bath to an inside temperature of 60–65°, and 0.5 mole of trimethoxybutane, methyl vinyl ketone or 4-methoxy-2-butanone was added dropwise over a period of one and one-half to two hours. The mixture was then refluxed for two hours, and allowed to stand overnight. Most of the alcohol was removed by distillation, the residue was made alkaline, with cooling, with 25% sodium hydroxide and steam distilled, preferably with superheated steam. The distillate was extracted with ether, the extracts dried over potassium carbonate and distilled from a Vigreux-type Claisen flask. In a typical run there was obtained 53 g. of lepidine, b. p. 87–89° (1–2 mm.), n_D^{20} 1.6190–1.6194. This is a 73% yield. In order to show that this material was substantially free of aniline, a 100.3-g. sample (n_D^{20} 1.6179–1.6198) was fractionated through a 10-plate Fenske-Whitmore column. There were obtained 1.3 g. of aniline (b. p. 52° (3 mm.), n_D^{20} 1.5863), 1.9 g. of intermediate fraction (b. p. 52–98° (3 mm.), n_D^{20} 1.6078) and 89.6 g. of lepidine, (b. p. 99–99.5° (3 mm.), n_D^{20} 1.6191–1.6197). The liquid held up by the column packing weighed 7.0 g., and was substantially pure lepidine, n_D^{20} 1.6193.

The middle cut in the above distillation had the following physical constants: b. p. 259–260° (752 mm.), m. p. 8–9°, n_D^{20} 1.6197, d_4^{20} 1.0832, M_R obs. 46.41, M_R calcd. 45.11. It yielded a picrate, m. p. 212°, a methiodide, m. p. 173–174°, and a sulfate, m. p. 223–225°.

A large number of variations in the preparation of lepidine were tried; these are summarized in Table I.

TABLE I
PREPARATION OF LEPIDINE

Solvt.	Aniline, moles	Aniline-HCl, moles	Ketone, ^a moles	Oxid. agent	Condensing agt.	Lepidine, %
Abs. alc.	1.7	0.86	0.86 MVK	28
Abs. alc.	1.0	.5	.5 TMB	30
Abs. alc.	1.0	.5	.5 MVK	Nitrobenzene	...	26
Abs. alc.	1.0	.5	.5 TMB	zene	...	28
Abs. alc.	0.74	.37	.37 MVK	Naphthalene	...	19
Abs. alc.	.5	.25	.25 MVK	p-Nitrophenol	...	30
Abs. alc.	1.0	.5	.5 MVK	FeCl ₃ ·6H ₂ O	...	49
Abs. alc.	1.0	.5	.5 TMB	FeCl ₃ ·6H ₂ O	...	60
Abs. alc.	..	.75	.25 MVK	FeCl ₃ ·6H ₂ O	...	70
95% alc.	..	.75	.25 MVK	FeCl ₃ ·6H ₂ O	...	65
95% alc.	..	1.5	.5 MVK	FeCl ₃ ·6H ₂ O	ZnCl ₂	73
95% alc.	..	0.63	.5 MVK	FeCl ₃ ·6H ₂ O	ZnCl ₂	72
95% alc.	..	.63	.5 TMB	FeCl ₃ ·6H ₂ O	ZnCl ₂	73
95% alc.	..	.63	.5 MeB	FeCl ₃ ·6H ₂ O	ZnCl ₂	70
95% alc.	..	.63	.5 TMB	H ₂ AsO ₄	ZnCl ₂	23
95% alc.	..	.63	.5 TMB	FeCl ₃ ·6H ₂ O	BF ₃	47
95% alc.	..	.63	.5 TMB	FeCl ₃ ·6H ₂ O	P ₂ O ₅	36
95% alc.	..	.63	.5 TMB	m-Nitrobenzene SO ₂ H ^b	ZnCl ₂	40

^a MVK = methyl vinyl ketone, TMB = trimethoxybutane, MeB = 4-methoxy-2-butanone. ^b The sodium salt was used, together with twice the theoretical amount of concentrated hydrochloric acid to liberate the sulfonic acid.

Preparation of 6-Methoxylepidine.—This was obtained in 52% yield from 0.625 mole of *p*-anisidine hydrochloride, 1 mole of ferric chloride hexahydrate, 10 g. of zinc chloride, 450 ml. of 95% alcohol and 0.5 mole of methyl vinyl ketone or trimethoxybutane. Since methoxylepidine is not easily volatile with steam, it is necessary to use steam superheated to 225–250°. As an alternative method of isolation, the basic solution can be evaporated to dryness under reduced pressure. The last traces of water can be removed by adding alcohol and again evaporating. The dry, hard residue is broken up and thoroughly and repeatedly triturated with benzene or ether. The dried extracts are then distilled.

The 6-methoxylepidine isolated by distillation is the anhydrous form, b. p. 121–123° (2 mm.), m. p. 28–32°.

It is easily converted to the hydrate, m. p. 52°, by treatment with water, dilute alcohol or exposure to moist air. The 6-methoxylepidine hydrate so obtained did not depress the melting point of a sample prepared by the method of Ainley and King.¹⁴ In order to show that the 6-methoxylepidine prepared by the Doebner-Miller reaction was substantially free of *p*-anisidine, a 52.9-g. portion was refluxed with 50 g. of acetic anhydride and 250 ml. of glacial acetic acid. There was recovered 51.3 g. of 6-methoxylepidine hydrate, m. p. 50–52°.

Several variations were tried in the preparation of 6-methoxylepidine; these are summarized in Table II.

TABLE II
PREPARATION OF 6-METHOXYLEPIDINE^a

Anisidine-HCl, moles	Ketone, ^b moles	Oxidizing agent	Condensing agent	Yield of 6-MeO-lepidine, %
0.313	0.25 TMB	3.5
.313	.25 TMB	...	ZnCl ₂	12.7
.313	.25 TMB	FeCl ₃ ·6H ₂ O	ZnCl ₂	52
.313	.25 MVK	FeCl ₃ ·6H ₂ O	ZnCl ₂	50
.63	.5 TMB	FeCl ₃ (0.2 mole) + O ₂	ZnCl ₂	35
.63	.5 TMB	K ₂ Fe(CN) ₆ (0.2 mole) + O ₂	ZnCl ₂	5

^a 95% alcohol was used as solvent; similar results are obtained with absolute alcohol or 99% methanol. ^b TMB = trimethoxybutane, MVK = methyl vinyl ketone.

Preparation of Other 4-Methylquinolines.—These were all prepared in the same way from 0.313 mole of the amine hydrochloride, 0.5 mole of ferric chloride hexahydrate, 5 g. of zinc chloride, 225 ml. of 95% alcohol and 0.25 mole of the ketone component. Most of the products were isolated by distillation with superheated steam.

4,6-Dimethylquinoline was made from *p*-toluidine hydrochloride and methyl vinyl ketone. There was obtained 8.7 g. of recovered *p*-toluidine and 25.6 g. (65%) of 4,6-dimethylquinoline, b. p. 103–105° (2–3 mm.), n_D^{20} 1.6070–1.6093. Redistillation yielded a colorless oil, b. p. 104–105° (2 mm.), n_D^{20} 1.6100, d_4^{20} 1.0577, M_R obs. 51.51, M_R calcd. 49.7. This compound gave a picrate, m. p. 235–237°, a methiodide, m. p. 235–239°, and a hydrochloride, m. p. 262–264°. The index of refraction and density of this compound have not previously been reported. Ewins and King¹⁴ found b. p. 140–141° (2 mm.), picrate m. p. 236–237°.

2,4-Dimethylquinoline was obtained in 24.2 g. yield (61.6%) from aniline hydrochloride and 3-penten-2-one.¹⁵ It boiled at 104.5–105.5° (4 mm.), n_D^{20} 1.6075, d_4^{20} 1.0558, M_R obs. 51.44, M_R calcd. 49.7. The picrate melted at 193°, the methiodide at 254–256° and the hydrochloride at 265–267°. Manske, Marion and Leger¹⁶ report a melting point of 196° for the picrate.

8-Chlorolepidine, m. p. 107–107.5°, was obtained in 23% yield from *o*-chloroaniline hydrochloride and trimethoxybutane. The compound is difficultly volatile with superheated steam, and this probably accounts for the low yield.

5,6-Benzolepidine was prepared from β -naphthylamine hydrochloride and trimethoxybutane. The crude material (37 g., 77%), m. p. 95–98°, contained a small amount of naphthylamine and was purified by treatment with acetic anhydride, followed by recrystallization from alcohol or hexane. The purified product weighed 28 g. (58%) and melted at 100–101°. It gave a picrate, m. p. 231–232°, and a hydrochloride, cream-white crystals, m. p. 214–215°. Knorr¹⁶ and Gibson¹⁷ have previously prepared 5,6-benzolepidine in poor yield by distillation of 2-hydroxy-5,6-benzolepidine with zinc dust. They reported a melting point of 91–92° for the free base, and

(14) Ewins and King, *J. Chem. Soc.*, **108**, 104 (1913).

(15) Grignard and Fluchaire, *Ann. chim.*, (10) **9**, 10 (1928).

(16) Knorr, *Ber.*, **17**, 844 (1884).

(17) Gibson, *et al.*, *J. Chem. Soc.*, **139**, 2247 (1926).

230–231° for the picrate. That the compound obtained in the present work was 5,6-benzolepidine and not the linear isomer was shown by the color of its hydrochloride and by the fact that it did not react with maleic anhydride.¹⁸

Summary

1. A modification of the Doebner–Miller reaction has been developed for the preparation of 4-methylquinolines from methyl vinyl ketone.

2. The yields have been improved by the use

(18) Johnson and Mathews, *THIS JOURNAL*, **66**, 210 (1944).

of mild conditions, oxidizing agents and condensing agents.

3. A new synthesis of 4-methylquinolines from 1,3,3-trimethoxybutane has been found.

4. The method has been applied to the preparation of the following substances: lepidine, 6-methoxylepidine, 8-chlorolepidine, 5,6-benzolepidine, 4,6-dimethylquinoline and 2,4-dimethylquinoline.

NOTRE DAME, INDIANA

RECEIVED OCTOBER 5, 1944

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Structure of Leucenol. I

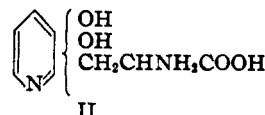
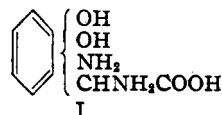
BY ROGER ADAMS, STANLEY J. CRISTOL, ARTHUR A. ANDERSON AND ALFRED A. ALBERT

Leucaena is a genus of tree similar to acacia and mimosa, one of the most common of which is *Leucaena glauca* benth. It is small, leguminous and native to tropical America, now widely distributed in southern Asia and neighboring islands. The leaves and seeds are reported to be a valuable fodder for cattle, but cause an irritation of the skin when ingested by horses.¹

Mascre² isolated an optically inactive crystalline solid, m. p. 287°, by aqueous extraction of ground *Leucaena glauca* seed and named this substance leucenol. Its empirical formula was shown to be $(C_8H_8O_2N)_x$ and further experimental evidence demonstrated that it was an α -amino acid and contained a phenolic hydroxyl.

Mimosine, a substance with very similar properties to leucenol, was isolated from the sap of the sprouts and roots of *Mimosa pudica* benth by Renz.³ This compound has the same empirical formula, $(C_8H_8O_2N)_x$, gives similar reactions and solubilities to those described by Mascre for leucenol, but has a different melting point (228°) and is optically active. Renz, on the basis of titrations in water and in ethanol, suggested the formula $C_{16}H_{20}O_4N_4$, although no molecular weight data could be obtained due to the insolubility of mimosine in organic solvents. It would appear to us that mimosine may be an optically active form of leucenol.

Mimosine was also described by Nienburg and Tauböck,⁴ who repeated similar tests to those of Renz and in addition isolated a copper salt having the analysis $C_8H_8O_4N_2Cu \cdot 2H_2O$. From these data, the authors concluded that the formula of mimosine was $C_8H_{10}O_4N_2$ and speculated on two possible structures (I) and (II). They concluded that structure I was not possible for a substance that would titrate one equivalent of base to a phenolphthalein end-point and therefore that



structure II, a dihydroxypyridylalanine, was the more likely formulation.

The objective in this investigation was the elucidation of the structure of leucenol. The isolation and purification of leucenol by the method of Mascre² was tedious and a continuous extraction of the ground seed with 90% ethanol was found to be more satisfactory. The product, recrystallized from water, melted at 291° with decomposition (Maquenne block). The empirical formula and other reactions described by Mascre were confirmed; a Van Slyke determination showed half the nitrogen to be primary amino, the ninhydrin test indicated an α -amino acid and the color with ferric chloride or Folin reagent a phenolic hydroxyl.

The chemical study of leucenol is hampered by its insolubility in practically all organic solvents except methanol and ethanol. It can be recovered unchanged from dilute acid or base solutions by adjusting the pH so that it is just acidic to brom cresol green (pH range, 3.8–5.4).

A difference in basicity of the two nitrogen atoms was demonstrated by the formation of monobasic salts with hydrochloric, hydrobromic and hydriodic acid. Treatment of leucenol with methanolic hydrogen chloride resulted in the formation of the dihydrochloride of the methyl ester of leucenol, indicating that both nitrogen atoms in this derivative were sufficiently basic to form salts. The ester gave a red-violet coloration with aqueous ferric chloride, showing the phenolic hydroxyl still to be present but, as expected, the ninhydrin test was negative.

Attempts to synthesize simple derivatives other than the methyl ester failed or resulted in non-crystalline products, e. g., acetylation, benzoylation, catalytic hydrogenation under various conditions, formation of a β -naphthalene sulfonate or a

(1) Anon., Dept. Agr. Ceylon, Leaflet No. 7 (1918); C. A., **13**, 1108 (1919).

(2) Mascre, *Compt. rend.*, **204**, 890 (1937).

(3) Renz, *Z. physiol. Chem.*, **244**, 153 (1936).

(4) Nienburg and Tauböck, *ibid.*, **247**, 80 (1937).