AN INVESTIGATION OF THE SYNTHESIS OF "PIRYLENE"

Thesis by

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TABLE OF CONTENTS.

Preparation of the Mixed Bases

TABLE OF CONTENTS (CONT.)

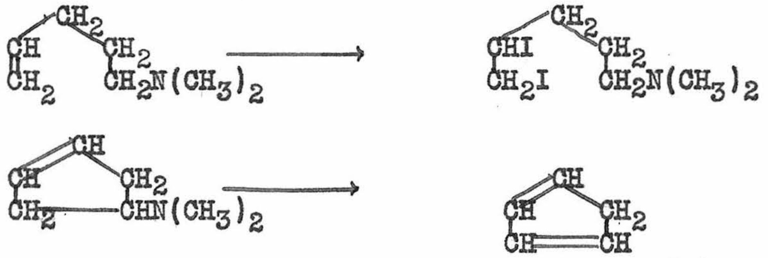
I wish to thank Dr. Edwin R. Buchman for suggesting the problem and also Mr. Herbert Sargent for permission to include certain results obtained in his investigations.

AN INVESTIGATION OF THE SYNTHESIS OF "PIRYLENE."

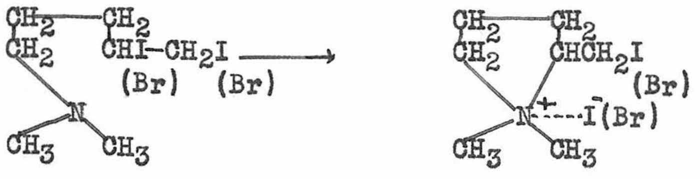
Theoretical Part.

I. Historical Review of the Synthesis of Pirylene.(1)

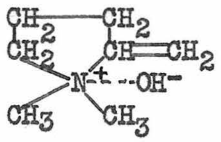
In 1888 Ladenburg(2) obtained by the Hofmann degradation of piperidine the so-called "dimethylpiperidine" $CH_2{=}CH(CH_2)_3N(CH_3)_2$. Iodine was added to the double bond of this compound and on treatment with silver oxide a tertiary base $C_5H_7N(CH_3)_2$ called dimethylpiperidein was produced. The quaternary salt was formed which, on treatment with alkali, yielded trimethylamine and a hydrocarbon, C_5H_6, of unknown structure, which was called pirylene. Ladenburg's interpretation of the reactions was as follows:



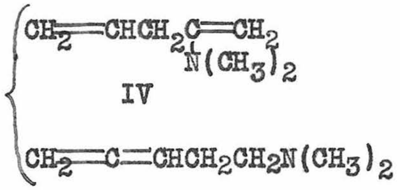
As a result of the investigations of Merling,(3) Roser(4) and Willstatter,(5) it was shown however that the first addition product (I) of iodine or bromine with "dimethylpiperidine" goes over by rearrangement into a pyrrolidine derivative (II) which by treatment with alkali or silver oxide is converted to the base (III). This last compound on distillation leads to a product, dimethylpiperidine, with two different possible formulas:



I II



III



$$CH_2{=}CHCH_2\underset{N(CH_3)_2}{C}{=}CH_2$$

IV

$$CH_2{=}C{=}CHCH_2CH_2N(CH_3)_2$$

V

Willstatter obtained salts of (III) and assumed the ring opening led to the structure (IV). He did not consider the possibility of (V) and paid little attention to pirylene.

In 1928 von Braun and Teuffert(1) tried to clarify the relation between dimethylpiperidein and pirylene. The statements of Willstatter in regard to the base (III) and its salt were confirmed for the most part. Evidence on the structure of dimethylpiperidein was obtained by catalytic reduction, 4H being added to produce homogeneous n-amyldimethylamine. As a result dimethylpiperidein was shown to have a straight chain. (IV) was thus eliminated as a possible structure and the structure (V) accepted since the index of refraction indicated two cumulative double bonds.

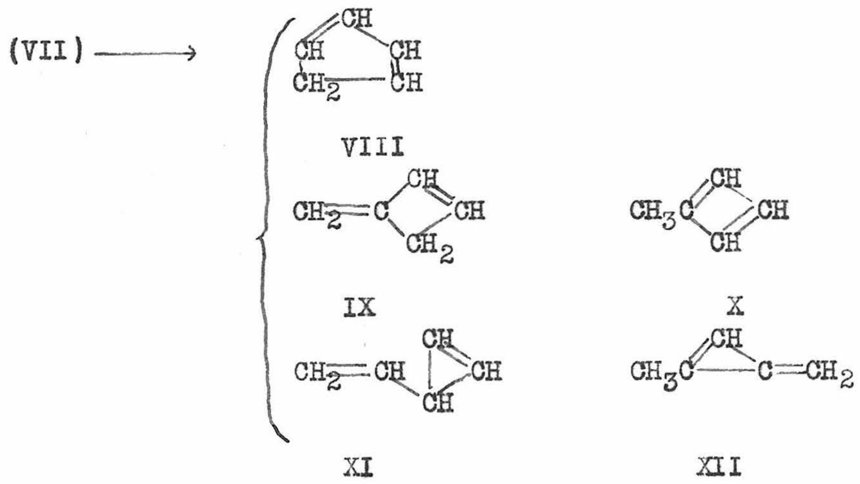
$$(V) \longrightarrow \quad CH_2{=}C{=}CHCH_2CH_2N(CH_3)_3OH$$

(VI)

$$\longrightarrow \quad CH_2{=}C{=}CHCH{=}CH_2$$

(VII)

The formulation of (VII) as pirylene would follow from (V) but von Braun found that the addition of hydrogen showed two and not three double bonds. It was therefore assumed that (VII) went over by rearrangement into a five-, four- or three-membered ring.



Cyclopentadiene (VIII) was eliminated, being a known compound with different properties than those of pirylene. Methylcyclobutadiene (X) was considered improbable because it had been shown by Willstätter and Waser(6) that cyclobutadiene is unstable and decomposes at higher temperatures into acetylene. The molecular refraction found for pirylene was somewhat higher than calculated for (X) and also (XI) but agreed well with the values for (IX) and (XII). (IX) was considered the more likely being a simpler transition from (VII). Only acetic acid and oxalic acid could be obtained from pirylene by oxidation which did not help in choosing between (IX) and (XII) since each of these could give rise to both those acids.

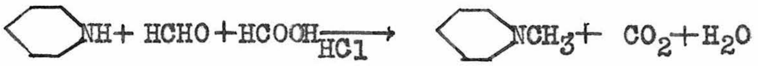
II. Purpose and Outline of the Investigation.

In February 1939, under the direction of Dr. E. R. Buchman, I commenced the synthesis of pirylene. Our aim was to clarify aspects of the synthesis which had not been completely investigated or had been ignored by the previous workers, and also, incidentally, to prepare some pirylene for electron diffraction studies.

The synthesis was accomplished following essentially the original procedure of Ladenburg. Certain important modifications were introduced which permitted the obtaining of larger yields of a number of intermediates. Also a careful study of the reaction leading to the formation of dimethylpiperidein revealed that a single compound was not produced here and this finding led us to investigate the separation and nature of the products formed.

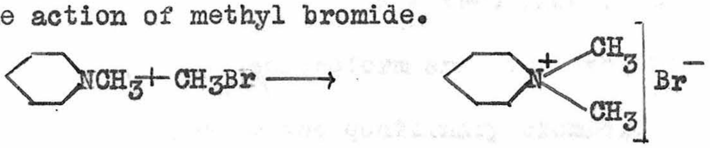
III. Preparation of the Quaternary Pyrrolidinium Bromide.

Piperidine was methylated by(7) means of formaldehyde and formic acid in the presence of hydrochloric acid.



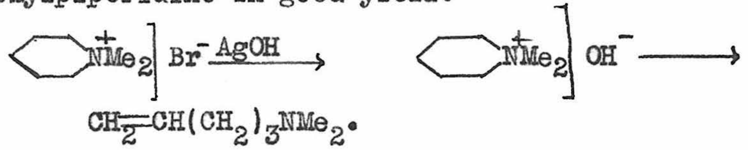
This reaction gave methylpiperidine accompanied by varying amounts of dipiperidyl methane and in some cases the product was contaminated by unmethylated starting material. It was found that dipiperidyl methane on further treatment with the same methylating agents (HCHO and HCOOH) went over smoothly to methyl piperidine. It is therefore desirable to insure complete methylation of the piperidine by heating the reaction mixture and adding fresh reactants (HCHO and HCOOH) until CO_2 evolution is reduced to the rate from a blank experiment (HCHO+HCOOH alone). Under these conditions a good yield of methylpiperidine can result.

Dimethylpiperidinium bromide was formed from methylpiperidine by the action of methyl bromide.



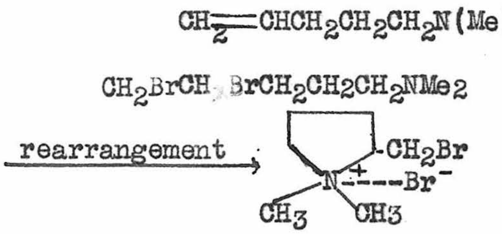
This reaction has not been described in the literature and has the advantage that the relatively cheap methyl bromide may be substituted for methyl iodide. The reactants were combined at -45°, the reaction taking place as the temperature was slowly allowed to rise.

Treatment of the quaternary bromide with silver oxide and distillation of the resultant base over KOH[9] gave the so-called "dimethylpiperidine" in good yield.



$CH_2{=}CH(CH_2)_3NMe_2$.

The reaction of bromine with dimethylpiperidine goes in two steps to form the product obtained by Willstätter.[5]



$CH_2{=}CHCH_2CH_2CH_2N(Me)_2 + Br_2 \longrightarrow$

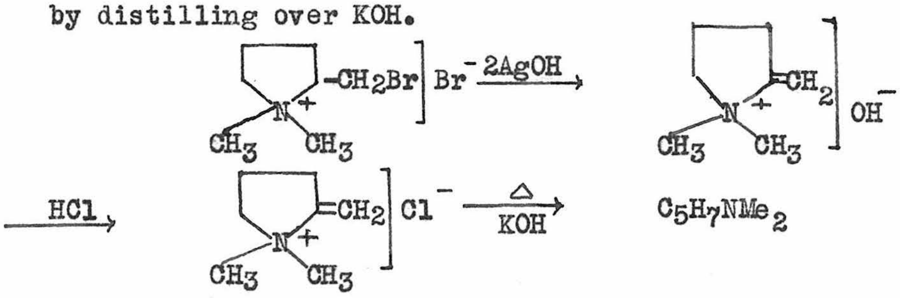
$CH_2BrCHBrCH_2CH_2CH_2NMe_2$

rearrangement

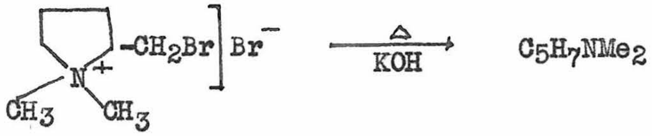
The reaction was carried out in chloroform solution from which the expected quaternary salt precipitates in quite good yield. It was found that in addition to the expected quaternary salt the reaction gave considerable amounts of a by-product which when purified had a melting point of $158.2 - 158.7^{\circ}$. It could be shown from analytical results and other data that this compound is a hydrobromide of the base formed by adding one mole of bromine to the unsaturated base i.e. $CH_2BrCHBrCH_2CH_2CH_2NMe_2 \cdot HBr$. When this compound is liberated as a free base from its salt with alkali it is obtained as a chloroform and ether soluble heavy oil which quickly isomerizes to the quaternary bromide.

IV. Degradation of the Quaternary Bromide.

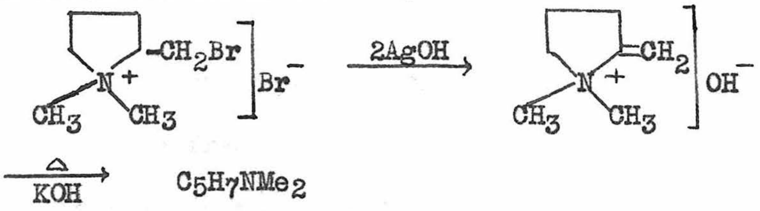
As mentioned above dimethylpiperidein ($C_5H_7NMe_2$) has been obtained by various investigators all of whom regarded it as essentially a single compound. In our experiments the degradation of the quaternary bromide was carried out by three methods each producing a mixture of isomeric bases. By the first method the bromide was converted to the quaternary base with silver oxide which also removed bromine from the side chain. The chloride was formed with HCl and the degradation carried out by distilling over KOH.



By the second method the bromide in a small amount of water was distilled directly over KOH.



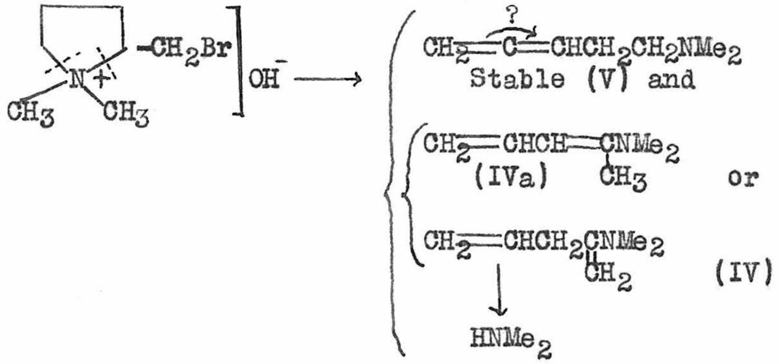
By the third method the bromide was treated with two moles of silver oxide forming the bromine free unsaturated ammonium hydroxide which was distilled over KOH.



From the standpoint of yield the second method proved superior. It required fewer and less costly reagents and in our experience can be used equally well with large and small batches. The degradation product, consisting of isomeric $C_5H_7NMe_2$ bases, was purified by vacuum distillation. A 50-60% yield of material boiling at 54 -65° at 40 mm. was obtained.

V. The Nature of the Isomeric Bases.

Various facts indicated that we were dealing with a mixture of bases and that these bases have the structure (IV) and (V) (or some structure closely related to these by rearrangement of double bonds). For one of these bases, the stable one, formula (V) was made probable by showing that the carbon atoms in the C_5H_7 radical are arranged in a straight chain. The other base has little stability in the presence of hydrolytic agents and apparently decomposes in both acidic and basic solutions, particularly on heating, to give dimethylamine. This base presumably has the structure (IV) or (IVa), the double bond α β to the nitrogen atom being in accord with the observed easy splitting off of dimethylamine.



VI. The Separation and Salts of the Isomeric Bases.

The mixture of bases was converted to diliturates (10) which were recrystallized from hot water. The diliturates separated into a difficultly soluble fraction and an easily soluble fraction which was also quite soluble in alcohol. Recrystallization of the difficultly water soluble fraction from hot water gave a pure diliturate which was found to be dimethylamine diliturate.

The easily soluble diliturate fractions were found to be substantially the diliturate of the stable base. Recrystallization from an ethyl alcohol-water mixture or from ethyl alcohol alone in every case gave needles of m.p. 159-161°. Regeneration of the base from the diliturate with sodium hydroxide gave the free base, boiling point 64-65°/49mm., d_4^{25} 0.800, picrate m.p. 100.5-101°.

The methiodide of the stable base is formed by treating the pure base, isolated as described above, with methyl iodide. This methiodide, m.p. 247-248°d, in contrast to statements in the literature (von Braun), is quite stable in aqueous or alcoholic solutions. When pure it can be easily recrystallized from hot water in which it is rather difficultly soluble in the cold. It can also be isolated from the mixed methiodides obtained directly from the mixed bases.*

VII. Catalytic Reduction of the Quaternary Salt of the Stable Base.

Reduction of this quaternary salt should give normal amyltrimethylammonium salt provided the stable base has the straight chain formula (V) postulated. The quaternary iodide and others of its type were found impossible to reduce with the method used, the iodide ion interfering with catalytic hydrogenation. However, conversion to the corresponding chloride

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*From the mixed methiodides was also isolated the isomeric methiodide presumably corresponding to (IV) or (IVa). The amounts of this substance were however insufficient for further examination. Also present in the quaternary salt mixture from the mixed bases is tetramethylammonium salt derived from (IV) (or (IVa)) via dimethylamine.

gave an equally suitable material which could be hydrogenated. The reduced product was shown identical with n-amyltrimethylammonium chloride by conversion to two solid crystalline derivatives, the bromide and picrate, and comparison of these (mixed melting points) with material of known structure. This result, incidentally, confirms the work of von Braun who, it will be recalled, reduced $C_5H_7NMe_2$ and demonstrated the identity of the product with n-amyldimethylamine. Evidently von Braun had a $C_5H_7NMe_2$ base which was nearly pure (V) (or a closely related substance). It is not surprising that he obtained only the stable isomer since under his conditions the unstable isomer may have been destroyed without his having been able to detect its presence.

VIII. The Formation of Pirylene.

The degradation of $C_5H_7NMe_3I$ to pirylene was carried out as described by Ladenburg.(2) Pirylene agreed in properties with the literature description.(1)

$$C_5H_7NMe_3I \xrightarrow[KOH]{\Delta} C_5H_6 + Me_3N + KI + H_2O$$

IX. A suggested Structure of Pirylene

Electron diffraction pictures of pirylene were taken by Schomaker in this laboratory. The results indicate that pirylene contains no ring. It will be recalled that von Braun's preferred structures (see p. 3 above) each contain a ring. There was possibly some error in his hydrogenation of the hydrocarbon. It may well be that pirylene has a straight chain. Comparison of the physical constants of methylvinylacetylene(11) and pirylene(1) show close agreements.

Pirylene:

b. 60°; d^{19}_{4}, 0.7443; n^{19}_{D}, 1.4505;

M_R (found) 23.88.

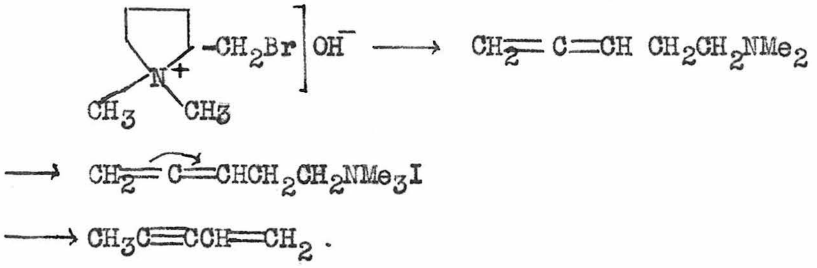
1-Methyl-2-vinylacetylene:

b_{760} 59.2°; d^{20}_{4}, 0.7401; n^{20}_{D}, 1.4496;

M_R (found) 23.94

Jacobson and Carothers(11) report that methylvinylacetylene polymerized on long standing. We found that pirylene polymerizes on long standing (see p. 24).

The methylvinylacetylene structure might arise as follows:



In view of the above considerations we suggest the identity of methylvinylacetylene and pirylene.

Experimental Part.

N-Methylpiperidine. (7) (8) - 557 g. of piperidine were mixed with 1000 g. 37% aqueous formaldehyde in a 5 l. round bottomed flask in an ice bath. 653 cc. of 12 N. aqueous HCl was added slowly with continued ice cooling and then 1000 g. of 85% aqueous formic acid was added. The flask was fitted with a reflux condensor (ground glass joint) to the top of which was attached a tube by means of which evolved CO_2 could be recovered over water. The refluxing was continued several hours until the gas evolution was slow. The rate of evolution was compared to the rate from a blank of proportionate amounts of formaldehyde, formic acid and hydrochloric acid. The mixture was transferred to an erlenmeyer and while cooling with an ice bath excess saturated aqueous NaOH was added and then NaOH pellets. The mixture was filtered through sinter~~r~~ed glass with mild suction and the filtrate was separated, to give an aqueous phase and a base phase. The aqueous phase and the precipitate were washed with Et_2O and the washings combined. NaOH pellets were added to the base phase which was then distilled over sodium, collecting the main fraction between 100 and 110°. Yield about 63% theory. The higher boiling residue was remethylated using the same procedure with proportionate amounts of the methylating agents. The yield was further increased by distilling the ether washings. In other runs unmethylated piperidine was found in the main fraction necessitating remethylation. The presence of piperidine can be tested for by the addition of CS_2 which precipitates this base but not a tertiary amine.

Dimethylpiperidinium iodide. - An ether solution of methylpiperidine was treated with excess CH_3I and the quaternary iodide was deposited. After filtering the iodide was washed with Et_2O and recrystallized from 95% ethyl alcohol.

Dimethylpiperidinium bromide. - 124 g. of methylpiperidine dissolved in 1240 cc. of anhydrous ether in a 2 l. erlenmeyer was cooled to -50° in an alcohol-solid carbon dioxide bath and about 170 g. of methyl bromide was added. The temperature was allowed to rise slowly to 0° and the mixture was placed in the cold room and then allowed to stand at room temperature (total length of time at 0° - room temperature at least 4 days). After filtering and drying, 235 g. of the quaternary bromide were obtained. Yield, 96.7% theory.

"Dimethylpiperidine."(9) - 200 g. of dimethylpiperidinium bromide in aqueous solution was treated with about 20% excess AgOH and the mixture was filtered through sintered glass with suction, the precipitate being washed with a little water and the washings combined with the filtrate. The filtrate was transferred to an open dish and evaporated down on a steam bath. The residue was combined with 100 g. KOH and a little water and distilled. The distillate was saturated with NaOH and separated giving 109 g. of crude base. The base was dried over NaOH pellets and distilled over sodium. There was 5.5 g. of forerun to 112° and a main fraction $112-118^\circ$ of 94.3 g. and a small residue. Yield 81% theory.

N,N-Dimethyl-α-bromomethylpyrrolidinium bromide. (5) - 50 g. of "dimethylpiperidine" dissolved in 350 cc. of dry (recently distilled) chloroform were placed in a 2 l. three necked flask fitted with a dropping funnel and a stirrer and placed in an ice bath. 70 g. of bromine dissolved in 500 cc. of chloroform were added from the dropping funnel drop by drop with stirring. After the addition of all the bromine the temperature was allowed to rise slowly. Too rapid heating can result in a violent formation of the quaternary salt by rearrangement so the temperature must be kept low until the salt is formed. The mixture was filtered with suction and the precipitate dried in a vacuum dessicator to give 101.5 g. (84%) of bromide. This salt was recrystallized by dissolving in about 230 cc. hot 90% EtOH and letting stand in the cold room. After filtering and drying, 83.3 g. (69% theory overall) of quaternary bromide of m.p. 228.5-230° were obtained. Samples were recrystallized to constant m.p. 232°d. The yield can be increased by evaporation down and recrystallizing the alcoholic mother liquors.

N,N-Dimethyl-δ,ε-dibromoamylamine hydrobromide, $CH_2BrCHBrCH_2CH_2CH_2NMe_2HBr$.- This substance is a by-product of the synthesis of the above paragraph. The chloroform mother liquor was distilled and the residue recrystallized from 90% EtOH and the crystals pressed on tile and recrystallized. Such a sample was recrystallized from ethyl alcohol using norite and was easily brought to a constant melting point of 158.2-158.7°.

Anal. Calcd. for $C_7H_{16}NBr_3$: C, 23.75; H, 4.56; N, 3.96; Br. -22.58.

Found: C, 24.15; H, 4.62; N, 3.98; Br, -23.32.

The addition of sodium picrate to an aqueous solution of the hydrobromide gave a picrate which on recrystallization from ethanol melted at 105-105.3°.

Preparation of the Mixed Bases $C_5H_7NMe_2$ (so-called dimethylpiperidein). First Method. - 20.3 g. of the quaternary bromide was dissolved in water and treated with AgOH made from 30 g. $AgNO_3$ (about 20% escess). The mixture was shaken a few times, filtered through sinterred glass and the filtrate was neutralized to litmus with HCl, and evaporated on a steam bath. The resulting crystalline deliquescent mass was transferred with a little water to a 50 cc. distilling flask containing 20 g. of KOH pellets and distilled. It was necessary to treat strongly to complete the decomposition. Sodium hydroxide was added to distillate and the phases were separated with a separatory funnel. The base phase was distilled over sodium. The forerun, mostly 130-135°, was about 0.5 g.; the main fraction, 135-144°, 2.0 g.; and a small higher boiling fraction and residue. Yield, 24.3% theory.

Second Method. - 91 g. of the quaternary bromide, 56 g. KOH pellets and 100 cc. H_2O were combined in a 250 cc. distilling flask and distilled using an oil bath. The bath was heated gradually to 265° and kept there until no more oil came over. KOH was added to the distillate which was separated giving 33 g. of crude base. The base was distilled at 40 mm. pressure.

The forerun, 4.0 g., being collected to 54°; the main fraction, 25.4 g., 54-65°; and a higher boiling fraction of about 1 g. to about 70°. The small residue was discarded. Most of the main fraction was from 58° to 64° and in other runs the range for the main fraction was 54-64°. Cloudiness in the main fraction suggested the presence of water so the fraction was redistilled at 40 mm. to give 22.8 g. base coming over in the range 56-67°. There was a small forerun of 0.5 g. and about 1 g. free flowing residue. Yield 61.6% theory from the quaternary bromide. The yields for the other runs using essentially this method varied from 50% to 65.8% theory.

Third Method. - 20 g. of the quaternary bromide were dissolved in H_2O and treated with AgOH (from 27.4 g. $AgNO_3$ - 20% excess). The mixture was stirred and filtered through sinterred glass. The filtrate was transferred to a distilling flask containing 20 g. KOH and distilled until no more base came over. KOH was added to the distillate and the base phase was separated, dried over KOH and distilled. There was 0.4 g. of forerun to 135°; 3.3 g. main fraction, 135-141°; 0.5 g. of a fraction, 141-144°; and a residue. Yield 40.5% theory. The mixed bases in a stoppered flask invariably precipitated a dark oily water soluble phase on standing for a few hours.

Purification and Properties of the $C_5H_7NMe_2$ Mixture. Diliturates. - The diliturates were prepared by adding an equivalent amount or a slight excess of base to a saturated hot water solution of dilituric acid. Diliturates from the mixed bases were recrystallized from hot water and were separated into a difficultly soluble fraction and an easily soluble fraction which was also quite soluble in alcohol. The difficultly soluble fraction was recrystallized from hot water to a pure diliturate (identified as dimethylamine diliturate). Its solubility coincided exactly with that found for a known sample of dimethylaminediliturate, 36.6 mg./10 cc. of water at 23°. The melting points were above 275°.

Anal. Calcd. $C_6H_{10}N_4O_5$: C, 33.03; H, 4.62.

Found: C, 33.32; H, 4.75.

Treatment of the diliturate with excess alkali and distilling the liberated base into a small amount of water resulted in an aqueous dimethylamine solution which gave a picrate, m.p. 157-157.5°. An authentic sample of dimethylamine picrate melted at the same point and the mixed melting point was not depressed.

The diliturate fractions easily soluble in water, substantially the diliturate of the stable base, when recrystallized from ethyl alcohol-water mixture or from EtOH alone, gave the same substance. This diliturate crystallized well in needles m.p. 156-161°. The analysis of the substance was not entirely satisfactory, due perhaps to the presence of difficultly removable water of crystallization, but there can be no doubt of its essential composition. For regeneration of the pure base see below (p. 19).

<u>Methiodides.</u> - The formation of mixed methiodides from mixed bases was in one case carried out by mixing 22.8 g. of the bases $C_5H_7NMe_2$ with 50 cc. CH_3OH in a flask cooled with an ice bath and adding 33.5 g. CH_3I. Some heat was developed so the reaction was

controlled by shaking in the ice bath. The mixture was allowed to stand about one hour at room temperature and was then cooled, filtered and the precipitate washed with CH_3OH to give 20.5 g. dry white crystals. In this and other cases the first crop of crystals deposited was found to be almost entirely the methiodide of the stable base together with another substance, presumably a difficultly water soluble quaternary iodide, perhaps partly amorphous since some solutions containing it were difficult to crystallize and giving upon treatment of aqueous solutions with sodium picrate, a non-crystalline sticky picrate insoluble in water and alcohol.* Also there is evidence (see below, p. 21) that Me_4NI** is present. The separation of the by-products from the methiodide of the stable base was not too easily accomplished. Recrystallization several times from water gave a pure quaternary salt m.p. 259°d, which with sodium picrate gave a pure picrate.

Anal. Calcd. for $C_8H_{16}NI$: C, 37.96; H, 6.37; N, 5.53.

Found: C, 38.33; H, 6.60; N, 5.57.

Possibly the best method of obtaining the pure quaternary halide of the stable base was found by converting the insoluble mixed methiodides to picrates from which the picrate of the $C_5H_7NMe_3$ base was easily separated by extracting it with ethyl alcohol and recrystallizing, m.p. 112.5-113°. As mentioned above the picrate

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*This by-product may be in part the result of some sort of Diels-Alder reaction of a quaternary iodide with itself or its isomer.

** Formed from $HNMe_2 + CH_3I$.

of the by-product is quite insoluble in alcohol. The purified picrate was treated with halogen acid in aqueous suspension, the picric acid removed with ethyl acetate and the aqueous solution evaporated to obtain pure quaternary salt.

The use of picrates can be applied in the same way to isolating the isomeric methiodide corresponding to the unstable base. This isomeric methiodide is contained for the most part, presumably, in the CH_3OH mother liquors after the methiodides have been formed and the first crop of crystals deposited. The mother liquors also contain (besides small quantities of the insoluble C_5H_7 methiodide) salts of presumably quaternary bases which give oily insoluble picrates such as were mentioned above. The separation of the isomeric methiodide by recrystallization was a long, tedious procedure with considerable loss, but material was obtained which gave the proper analytical figures. However, the conversion to picrates, separation from the alcohol insoluble sticky picrates and regeneration with halogen acid gave satisfactory results. A quaternary iodide was obtained which, on recrystallization from ethanol-isopropyl ether using norite and then from ethyl alcohol, had a m.p. 227-228°d. and solubility properties similar to the other isomer. An oily picrate was formed which solidified in the icebox and has not been further investigated because of its low melting point and the consequent difficulty of purification.

Anal. Calcd. for $C_8H_{16}NI$: C, 37.96; H, 6.37; N, 5.53.

Found: C, 37.59; H, 6.62; N, 5.68.

The Pure, Stable $C_5H_7NMe_2$ Base. - This base would be prepared from the pure diliturate. Regeneration was easily brought about by treatment with sodium hydroxide, steam distilling, extracting with ether, drying with potassum hydroxide and distilling in vacuo. The base boiled at 64-65°/49 mm. and had d_4^{25} 0.800.

Anal. Calcd. for $C_7H_{13}N$: C, 75.60; H, 11.79.

Found: C, 75.89; H, 12.10.

The pure base on standing remains clear. (The dark material precipitated from mixed bases on standing therefore owes its origin to the unstable isomer).

With ethereal picric acid the base forms a picrate which crystallizes from ethanol-isopropyl ether in well formed cubes m.p. 100.5-101°.

Anal. Calcd. for $C_{13}H_{16}N_4O_7$: C, 45.88; H, 4.74; N, 16.47.

Found: C, 46.35; H, 4.86; N. 16.25.

With methyl iodide the methiodide was formed. It was recrystallized from hot water, m.p. 247-248°d. (The difference in melting point between that observed here and that given above was probably due to a difference in the rate of heating in the melting point apparatus). With sodium picrate the methiodide in aqueous solution, formed a picrate, m.p. 112.5-113° from ethanol.

Thus the base has been characterized by a diliturate, a picrate, a methiodide and a quaternary picrate.

Reduction of the Quaternary Salt of the Stable Base and Identification of the Product. - The catalyst used in the reductions was prepared as follows: 1/2 ml. of 10% $PdCl_3$ (in H_2O HCl) was placed with 1 gram of freshly ignited norite in 100 ml. of distilled H_2O. The mixture was shaken with H_2 at 30 lbs. pressure for 10 minutes, filtered with mild suction and washed with C.P. methanol. 5 g. of the quaternary iodide and the above catalyst in methyl alcohol were shaken for two hours under 37 lbs. pressure of H_2 without any absorbtion of hydrogen. The catalyst was filtered out and shaken with 20 g. mesityl oxide in methyl alcohol for 1/2 hour at 37 lbs. pressure of H_2 with no reaction. With the same mixture using fresh calalyst the pressure dropped to 20 lbs. in 15 minutes.

Some quaternary chloride was prepared by adding an aqueous solution of the iodide (not entirely pure) to a 30% excess of AgCl, filtering and evaporating the filtrate on a steam bath. The salt was found to be very hygroscopic. It was dried in a vacuum dessicator and hydrogenated using the same procedure as with the iodide. Roughly 2 moles of hydrogen were added. The catalyst was filtered off and the filtrate evaporated down and dried.

The reduced product was identified as a salt of $n\text{-}C_5H_{11}NMe_3$ base by conversion into both the picrate and the bromide and these derivatives were then compared with authentic samples as described below. It was found that each derivative had the same melting point as the corresponding known compound and that the mixed melting points were not depressed. The bromide was made by treating a sample of chloride with excess Ag_2O, filtering, adding excess HBr and evaporating to dryness. The product was separable into two parts by means of a difference in solubility in ethanol.

The alcohol insoluble portion had no melting point, gave a picrate which melted above 270° and on heating with KOH evolved a volatile base having an odor similar to that of NMe_3. Analysis of this alcohol insoluble quaternary bromide indicated that it was substantially pure Me_4NBr (see p. 17). The alcohol soluble bromide after recrystallization from alcohol-isopropyl ether melted constantly at 181-181.5°. Its aqueous solution treated with sodium picrate gave a picrate m.p. 93.2-94° (mixed m.p. 93.4-94°).

<u>n-Amyltrimethylammonium bromide and picrate.</u> - 5 g. n-amyl bromide and 6.8 g. (25% excess) 36% NMe_3 in benzene were placed in a tube which was then sealed and kept in boiling water for 24 hours. The product was filtered with mild suction, washed with anhydrous ether and dried in a vacuum dessicator. Yield, 4.58 g. which was 65.8% theory. The bromide was crystallized twice from absolute EtOH to a m.p. of 181-181.5°. Its aqueous solution with sodium picrate gave an oily picrate which solidified when placed in the icebox and did not melt again at room temperature. It was washed with water, dried and recrystallized from ethanol-isopropyl ether coming down in prisms m.p. 93.5-93.8°.

<u>Reduction of "Trimethylpiperidinium chloride."</u> - The methiodide was formed by dissolving 11.2 g. of "dimethylpiperidine" in an equal volume of absolute EtOH, cooling in an ice bath, and adding 16.32 g. CH_3I (15% excess) slowly in small portions. The product was filtered with mild suction, washed with anhydrous Et_2O, dried in a

vacuum dessicator (yield about 100%) and recrystallized from not absolute EtOH to give 14 g. of iodide m.p. 220-2°. Yield 55.4% theory.

The quaternary chloride was formed by treating an aqueous solution of the iodide with a 50% excess of AgCl, filtering and evaporating the filtrate on a steam bath. The salt was found to be very hygroscopic. On treatment with sodium picrate it gave an oily picrate which became crystalline on standing. Recrystallized from ethanol-isopropyl ether it had m.p. 98.5-99°. It was found that it did not depress the melting point of the $C_5H_{11}NMe_3$ picrate to any great extent. The maximum depression was obtained with about 10% $C_5H_9NMe_3$ picrate added to the other (mixed m.p. 90.5-92°). Other examples have been noted in which picrates of similarly constituted structure did not depress the melting point of each other when mixed.

Just as with $C_5H_7NMe_3I$ the quaternary iodide of dimethylpiperidine could not be reduced catalytically, therefore the chloride was reduced, following the procedures given above for the $C_5H_7NMe_3$ salt. The reduced product was converted to the picrate which was compared by means of melting points and mixed melting points and found identical with an authentic sample of $C_5H_{11}NMe_3$ picrate.

<u>Characterization of Quaternary Salts.</u> - Some attempts were made to work out a general procedure for characterizing quaternary salts of the type found in this research. It was difficult to get

get easily crystallizable salts having a reproducible melting point. The iodides melt with decomposition and the chlorides are hygroscopic. Precipitation of the quaternary salts from aqueous solution is not easily done: sodium S-benzylthiosulphate, potassium thiocyanate, sodium styphnate and sodium picrolonate were tried without success. The picrates are low melting and quite soluble in many solvents. There were indications in the literature that Reinecke salt might be useful. Experiments were carried out which showed that this agent may be satisfactory. An impure Reinecke salt produced large precipitates with aqueous solutions of the quaternary salts but these precipitates were in all cases mixtures being definitely separable into alcohol soluble and alcohol insoluble material. The alcohol soluble material can be recrystallized from alcohol and in the case of the n-amyltrimethylammonium bromide derivative gave after several recrystallizations a substance of m.p. 159.5-160°. The formation of more than one compound may have been due to impurities in the Reinecke salt used. A highly purified Reinecke salt might form useful derivatives.

Pirylene. - 19.5 g. $C_5H_7NMe_3I$ (MeOH insoluble methiodide mixture) together with 9.0 g. KOH dissolved in a small amount of H_2O in a 50 cc. distilling flask were distilled using an oil bath. The receiver was tightly fitted to the end of the condenser, there being an outlet attached to a rubber tube from the top of the receiver and the receiver was in an ice bath. A two phase distillate was collected. The oil bath was carried to 150° for the first fraction and a second fraction was collected when the bath was 150-250°. The first fraction was acidified, and the oil phase separated with a small separatory funnel. The second fraction had only an aqueous phase. Sodium was added to the oil which was put, lightly stoppered, in the cold room. A final distillation was carried out over sodium and 1.98 g. of material boiling in the range 54-59° (mostly 58°) was collected. Yield, 39% theory. On standing over a period of months the material polymerized to a gum.

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