

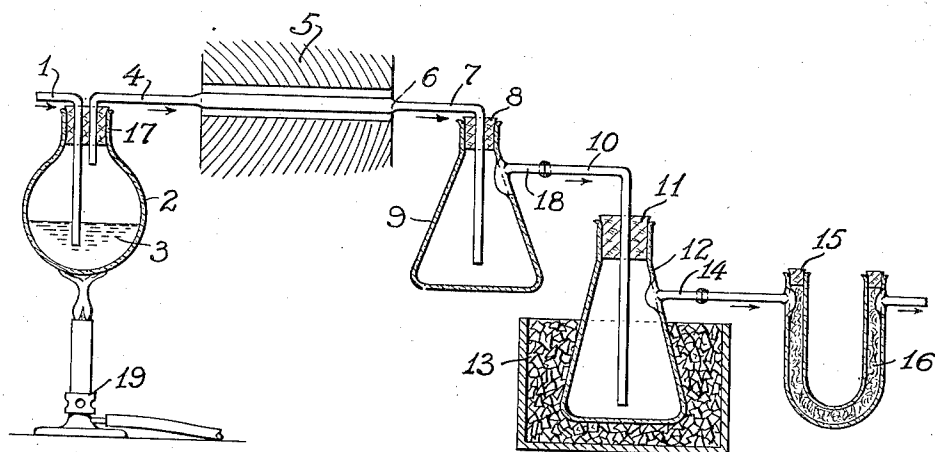
April 8, 1941.

J. R. BAILEY ET AL

2,237,541

PYROLYSIS OF NITROGEN BASES

Filed June 26, 1937



INVENTORS
J.R. Bailey & Raymond Mahan

BY *Philip Subkow*
ATTORNEY.

UNITED STATES PATENT OFFICE

2,237,541

PYROLYSIS OF NITROGEN BASES

James R. Bailey and Raymond Mahan, Austin, Tex., assignors to Union Oil Company of California, Los Angeles, Calif., a corporation of California

Application June 26, 1937, Serial No. 150,637

2 Claims. (Cl. 260—290)

This invention relates to pyrolysis of nitrogen bases and to a method for the production of pyridine, quinoline and pyrrole and their alkylated homologs. More specifically the invention relates to a method for the production of pyridine and quinoline homologs from complex basic nitrogen compounds.

We have discovered that certain nitrogen containing compounds found in petroleum, coal tar, shale oil, oil obtained by pyrolysis of such protein material as cotton seed meal and more specifically, California asphalt-base petroleum, can be converted into other nitrogenous compounds by our process of pyrolysis.

According to our invention, nitrogen containing compounds such as pyridines, isopyridines, and polynuclear bases containing condensed ring systems or mixtures of crude nitrogen bases of analogous structure, such as the crude bases obtained from petroleum distillates, are subjected to treatment with heat or with heat in the presence of a suitable catalyst and at suitable pressure, to form inter alia simpler pyridines or quinolines. The reactions induced by our process may comprise dehydrogenation, ring cleavage, dealkylation, and the like, or combinations of these reactions, but in general the effect is to increase the aromaticity of the bases so treated. Aromatic bases, which comprise pyridines and quinolines, are characterized, in contradistinction to non-aromatic or hydro-aromatic bases, by a high refractive index for a given molecular weight, by a relatively high carbon to hydrogen ratio, and by the preferential solution of their hydrochlorides in water in the presence of chloroform. According to the character of base or bases taken for treatment and the conditions of pyrolysis our process may result in either lower boiling simple molecules or in higher boiling molecules, but in any case our process converts non-aromatic or hydroaromatic bases into aromatic bases or into bases of more aromatic character.

It is, therefore, an object of our invention to produce simpler pyridines and quinolines from nitrogenous bases by pyrolysis of the latter with a suitable catalyst under suitable conditions of temperature and pressure. It is a further object of our invention to increase the aromaticity of such bases by such treatment.

The figure is illustrative of one form of apparatus which may be employed in carrying out our invention. Referring to the figure, container 2 is a flask for holding the crude nitrogen base material for treatment. This flask is pro-

vided with a two hole stopper 17. Through one of the holes in stopper 17 there is inserted a tube 1 which extends downward into the flask 2 and terminates beneath the surface of the crude nitrogen base material 3. The other hole of stopper 17 is also provided with a tube 4 one end of which terminates in the vapor space of flask 2. The other end of tube 4 is connected with Jena glass tube 6 which is positioned within the heating space of furnace 5. The Jena glass tube employed in the figure is 24 inches long and ½ inch inside diameter with approximately 12 inches of this tube exposed to direct heat of the furnace 5. The other end of tube 6 is connected to tube 7 which passes through the single hole cork or stopper 8 into separating flask 9. Tube 7 terminates within about 1½ inches from the bottom of flask 9. Flask 9 is provided with a side tube 18 directly underneath stopper 8. The side tube 18 connected to tube 10 passes through the one hole stopper 11 fitted to flask 12. Tube 10 terminates about 1½ inches from the bottom of flask 12. In order to maintain flask 12 cool it is immersed in beaker or jar 13 which is filled with ice. The side tube 14 of flask 12 is connected with U-tube 15 which is filled with glass wool 16 moistened with concentrated sulphuric acid.

In carrying out the pyrolysis of nitrogen base material according to our invention, flask 2 was charged with a measured quantity of nitrogen base material having the formula $C_{16}H_{25}N$ and believed to be methylated dihydroisopyridine. This material was derived from kerosene bases in the 275–280° C. boiling range as follows: The crude bases were dissolved in an equal volume of 6NHCl and the hydrochlorides extracted with a volume of chloroform equal to the volume of the bases. The non-aromatic or hydroaromatic base hydrochlorides passed into the chloroform layer and on distilling the chloroform from the crude hydrochlorides, the $C_{16}H_{25}N.HCl$ precipitated in crystalline form and was obtained free of impurities by crystallizing from acetone. The $C_{16}H_{25}N$ base is obtained pure on neutralizing the $C_{16}H_{25}N.HCl$ with caustic alkali. This base had a boiling point at 746 mm. of 278.2° C., a density (20/4) of .9391 and a refractive index (n_{20}^D) of 1.5129. Furthermore this base is colorless, odorless, optically inactive, slightly soluble in water and very soluble in organic solvents. A more complete description of this base may be found together with the method of isolation in the Journal of the American Chemical Society, volume 53, page 1007.

Natural gas was admitted into tube 1 and forced into flask 2 beneath the surface of the nitrogen base stock 3. The content 3, of flask 2 was heated by means of burner 19 in order to facilitate passage of the base vapors into tube 6. The natural gas, laden with the vapors of the crude nitrogen base material was thus passed through tube 4 into tube 6 positioned within the heating zone of furnace 5. Here the temperature of the nitrogen base material was raised to approximately 700° C. The heated material in tube 6 was then sent via line 7 into detarring flask 9 where heavy fractions formed during the pyrolysis of the crude stock in tube 6 were separated. The gases or vapors in flask 9 were then led through line 10 into flask 12 which was cooled by immersion in ice bath 13. Flask 12 functions as a condenser and liquefies the major portion of the products contained in the vapors passing to this flask. The materials which are not condensed in flask 12 pass via tube 14 to sulphuric acid scrubber where any basic substances present are collected.

As a result of this experiment a portion of the crude stock contained in flask 2 was converted into pyridine bodies in pyrolytic zone 6 and collected in flask 12. The yield of pyridines obtained by this experiment was found to be 10% of the theoretical yield based upon the quantity of charging stock sent or transferred from flask 2 through the pyrolytic zone 6.

The same experiment was repeated using $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ as catalyst in pyrolysis tube 6. This catalyst was prepared by neutralizing Na_2SiO_3 to a pH value of 6 or 7 with a water solution of $\text{Al}_2(\text{SO}_4)_3$. As a result of this neutralization $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ separated in a white, grainy condition. The granular $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ was thoroughly washed with water and then thoroughly dried for a period of 2 hours. The dried material was then heated at 700° C. for a period of 5 hours with the result that a grainy, porous material was obtained.

Using the above catalyst, $\text{C}_{16}\text{H}_{25}\text{N}$ as the charging stock, natural gas as the carrier and a temperature of 700° C. in the pyrolysis tube 6 a yield of pyridines equal to 70% of theoretical, based on the raw stock treated, was obtained. In other words, pyrolysis of 50 grams of the $\text{C}_{16}\text{H}_{25}\text{N}$ base with the aluminum catalyst yielded 11 grams of pyridines and 20 grams of the original base. This crude mixture was purified as follows: The crude material was thoroughly sulphited with SO_2 at 20–25° C. The sulphited mass was then heated at 100° C. for a period of two hours to drive off a portion of the contained SO_2 . As a result of driving off a portion of the SO_2 (which is known as degassing) some of the original base layered out and was decanted away. Caustic was then added to the aqueous layer and the oil liberated by this treatment was recovered and picrated to a crystalline salt. This salt was recrystallized from water twice and once from dilute ethyl alcohol. The purified crystals obtained were long slender yellow needles having a melting point of 146–148° C. From the analytical data obtained from this picrate the formula $\text{C}_8\text{H}_{11}\text{N}$ was derived.

In a further experiment using the same temperature, catalyst, base, etc., but using a longer heating zone, 100 grams of the $\text{C}_{16}\text{H}_{25}\text{N}$ base was pyrolyzed to 48 grams of $\text{C}_8\text{H}_{11}\text{N}$ base. This yield of $\text{C}_8\text{H}_{11}\text{N}$ was around 91.2% of the theoretical.

While we have described the use of an

aluminum oxide catalyst as an aid in the pyrolysis of the crude nitrogen base material to pyridine we do not wish to limit ourselves to this catalyst since we have found that other dehydrogenating catalysts such as molybdenum oxide and chromium oxide may also be used.

Three crude nitrogen base fractions containing no pyridines having boiling point ranges within 0.5° C. of 200°, 210° and 220° C., respectively, recovered from kerosene extract by acid extraction were separately pyrolyzed as follows:

Seventy five grams of each of the above bases were pyrolyzed at 700° C. in the presence of $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ catalyst, using natural gas as the base carrier, as described in connection with the figure. The time employed to pass the 75 gram samples of the crude bases through the pyrolyzing zone was 1½ hours.

The distillates obtained by these three pyrolytic experiments were collected and examined.

From the distillate obtained by the pyrolysis of the 75 gram sample of 200° C. boiling point crude base there was recovered 5.3 grams of pyridines having a boiling point of 205° C. at 746 mm. and a refractive index of (n_{25}/D) 1.5010; 7.1 grams of pyridines having a boiling point of 216° C. at 746 mm. and a refractive index of (n_{25}/D) 1.5024; and 18.6 grams of pyridines having a boiling point of 224° C. at 746 mm. and a refractive index of (n_{25}/D) 1.5030. The total yield of pyridines in this case was therefore 31.0 grams and the total percent recovery on the weight basis of charging stock and pyridine recovered was 41%.

From the distillate obtained by the pyrolysis of the 75 gram sample of 210° C. boiling point crude base there was recovered 6.7 grams of pyridines having a boiling point of 214° C. at 746 mm. and a refractive index of (n_{25}/D) 1.5040; 20.1 grams of pyridines having a boiling point of 228° C. at 746 mm. and a refractive index of (n_{25}/D) 1.5060; and 6.0 grams of pyridines having a boiling point of 234° C. at 746 mm. and a refractive index of (n_{25}/D) 1.5132. The yield of pyridines in this experiment was 32.8 grams or 44% of the weight of the crude base charged into the pyrolysis tube.

From the 220° C. boiling point crude base there was obtained 9.7 grams of pyridines having a boiling point of 228° C. at 746 mm. and a refractive index of (n_{25}/D) 1.5022; 21 grams of pyridines having a boiling point of 238° C. at 746 mm. and a refractive index of (n_{25}/D) 1.5126, and 3.8 grams of pyridines having a boiling point of 246° C. at 736 mm. and a refractive index of (n_{25}/D) 1.5148. The total yield of pyridines in this experiment was therefore 34.5 grams or 45.5% of the weight of the crude base pyrolyzed.

A further pyrolysis experiment was performed upon a 100 gram sample of crude nitrogen bases having a boiling point of 275° C. and composed approximately of 85% non-aromatics and 15% aromatics. These bases were derived from kerosene bases of 275–280° C. boiling point range. These bases were pyrolyzed at 700° C. in the presence of the $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ catalyst, using natural gas as the base carrier. The distillate collected as a result of the pyrolysis was examined and found to contain 20 grams of mixed quinolines and pyridines with an initial boiling point of 225° C. at 746 mm. and a refractive index of (n_{25}/D) 1.5025 and 30 grams of unreacted charging stock. This was a yield of 29% based on the pyrolyzed charging stock.

Furthermore 50 grams of a crude non-aromatic base having a boiling point of 275° C. was pyrolyzed as described above in the presence of $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ catalyst at 700° C. using natural gas as the carrier for the crude bases. From the distillate collected from the pyrolysis tube there was obtained 11 grams of pyridines having a boiling point of 180° C. which picrated nicely indicating a simple mixture.

In another experiment crude kerosene bases boiling between 270° and 280° C. were dissolved in aqueous hydrochloric acid and extracted with chloroform. The chloroform extracted the non-aromatic or hydro-aromatic base hydrochlorides from which free bases were obtained by evaporation of the chloroform and treatment of the salts with caustic alkali. These free bases were then condensed with an excess of phthalic acid anhydride, whereby 78% formed phthalones. The residual 22%, comprising non-aromatic or hydro-aromatic bases uncondensable with phthalic anhydride, and which had a refractive index (n_{25}/D) of 1.5123 was then pyrolyzed at 700° C. over an $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ catalyst. From a charge of 115 cc., 53.0 cc. of acid soluble condensate were obtained. This condensate was then fractionally distilled to give cuts ranging in boiling point from 172° C. to 293° C. The fractions boiling below 200° C. were found to be pyridines, while the fractions boiling from 200° to 293° C. were found to be mixtures of quinolines and pyridines together with a small quantity of unchanged original material. Only the lowest boiling fraction (172° C.) was found to have a refractive index

(n_{25}/D) 1.4962 lower than the material pyrolyzed (boiling point 270° C., n_{25}/D 1.5123). The remainder of the fractions had refractive indices (n_{25}/D) ranging from 1.5232 to 1.5844.

The catalysts used in our process should be capable of effecting dehydrogenation. We find that difficultly reducible metallic oxides are suitable for this purpose, particularly the mixed oxides of aluminum and silicon. Contact masses such as pumice are also effective. We observe but little pyrolytic action at temperatures lower than 400° C., whereas at 700° C. substantial pyrolysis was obtained. Higher temperatures are also suitable, but excessively high temperatures which induce complete pyrolysis or degradation of the organic nitrogen compounds should be avoided.

It is to be understood that the disclosures here made are to be considered as illustrative and not as limiting except as required by the state of the prior art.

We claim:

1. A method of treating nitrogen bases having the general formula $\text{C}_{16}\text{H}_{25}\text{N}$ and derived from petroleum distillates, which comprises conducting the vapors of said bases at a temperature of about 700° C. over a contact mass composed of complex salts of oxides of aluminum and silicon, collecting the products of reaction, and recovering pyridines therefrom.

2. A method according to claim 1 in which the nitrogen base vapors are borne by a carrier gas.

JAMES R. BAILEY.
RAYMOND MAHAN.