48. **Takeo Iida:** Studies on the Components of the Fushun Shale Oil. II.[1]
2,3,5-Trimethylpyrrole from the Crude Gasoline.*

*(Pharmaceutical Faculty, University of Toyama**)*

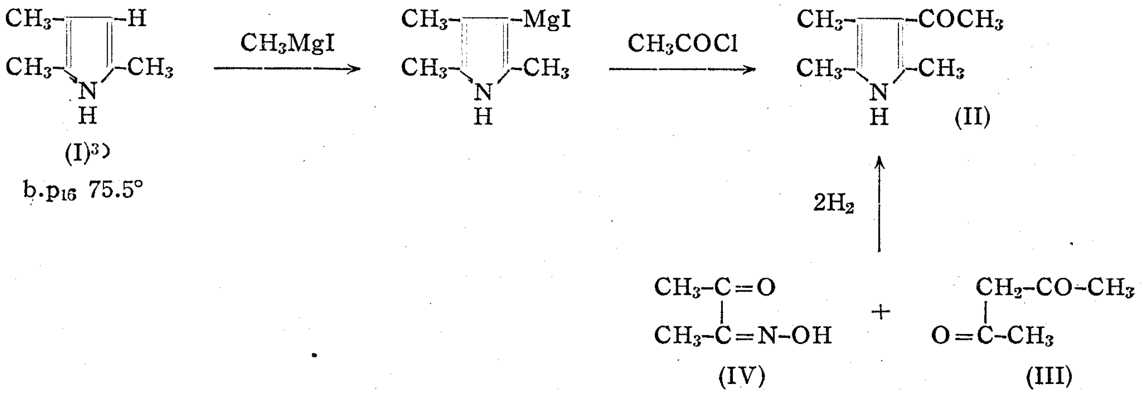
In the previous paper, Iida and Tanaka[1] reported that the crude gasoline of the Fushun shale oil contains fatty acid nitriles as one of neutral nitrogen compounds. It was also stated that the gasoline also contains some pyrroles as another neutral nitrogen components. Later, the author was able to prove the presence of 2,3,5-trimethylpyrrole (I) in the crude gasoline as the derivative of 2,3,5-trimethyl-4-acetylpyrrole (II).

Before washing, the crude shale gasoline was distilled under a reduced pressure. The faint yellow distillate, b.p. 120~200°, was washed quickly with diluted sulfuric acid and sodium hydroxide solution successively to remove the basic and acidic oils, and the neutral oil was shaken with a small amount (about 2~3 v% of the oil) of 60% sulfuric acid. By this treatment, components which give positive Ehrlich reaction and pine-plinter test were transferred into the sulfuric acid layer. The acid solution was poured into ice water, and an oil containing pyrrole compounds was recovered. This oil is designated as the "pyrrole oil". The pyrrole oil might be a complex mixture containing presumably furan compounds besides pyrroles, since it was separated into two parts by alumina chromatography; the upper part containing the substances that color red with Ehrlich's reagent and the lower, blue. The pyrrole oil was fractionated under a reduced pressure in hydrogen stream. The results are shown in the following:

Distillate	b.p$_{17}$ °C	Weight of the distillate (g.)
a	60~70	35.0
b	70~85	11.8
c	85~100	20.7
d	100~120	13.3

Some trials to oxidize with chromic acid and to diazotize each portion of the distillates failed. However, 2,3,5-trimethylpyrrole was identified by introducting acetyl group which was expected to stabilize the pyrrole nucleus. The distillate (b) was treated with Grignard reagent and with acetyl chloride, and white crystals, m.p. 206°, thereby formed was undepressed on admixture with an authentic specimen of 2,3,5-trimethyl-4-acetylpyrrole[2], prepared by the Fischer's method[3].

The attempt to prepare 2,3,5-trimethyl-4-acetylpyrrole by the Friedel-Crafts reaction between the distillate (b) and acetyl chloride gave a poor yield.



---

* The author's unpublished work since 1944 is published here because of the work of R.A. Van Meter and others (Anal. Chem., **24**, 1759 (1952)). ** 5 Okuda, Toyama (飯田武夫).

1) T. Iida, M. Tanaka; J. Pharm. Soc. Japan, **64**, 162(1944). 2) H. Fischer: Hoppe-Seyler's Z. physiol. Chem., **77**, 197(1915). 3) H. Fischer: "Die Chemie des Pyrrols", 44.

The author wishes to acknowledge his indebtedness to Prof. Dr. E. Ochiai for his constant guidance during this study.

Experimental

Separation of the pyrrole oil from crude gasoline—The crude gasoline, b.p. 120∼200°, which was obtained by the topping distillation of crude shale oil, is a brown oil with ill odor, and turns into colorless transparent oil by distilling under a reduced pressure. However, after several hours of standing in open air the oil changes to deep red-brown so that it is necessary to wash the oil as rapidly as possible. The neutral oil, which was obtained by washing the crude gasoline with excess of 10% sodium hydroxide solution and 20% sulfuric acid to remove acid and basic substances, was washed with 60% sulfuric acid (2∼3 v% of the oil), until the components of the gasoline which give positive Ehrlich test, were transferred almost completely into the sulfuric acid layer and the gasoline (containing nitrile compounds) gave only a faint coloration with the Ehrlich reagents. The acid extract was poured into ice-water, diluted to the extent of 10∼20% sulfuric acid, and the pyrrole oil was separated. The ether solution of this oil was shaken with alkali for neutralization and after drying, it was distilled fractionally under a reduced pressure. The results are shown in the table. The yield of the pyrrole oil from 20 kg. of crude gasoline was about 100 g.

Oxidation with chromic acid—5.6 g. of CrO_3 dissolved in 12 cc. of water was added dropwise, slowly under vigorous stirring, keeping the temperature at about 5∼10°, to a solution of 1.4 g. of the pyrrole oil distillate (a) in 40 cc. of 60% sulfuric acid. The reaction mixture which was dark brown in the beginning, changed to greenish color and became transparent in the end. The reaction mixture was cooled in an ice bath for 3∼4 hours, allowed to stand overnight, and was poured on ice, the resulting solution amounting to 90 cc. This solution was extracted with 300 cc. of ether in five portions, the ethereal extract was washed with potassium carbonate solution to remove organic acids, and after drying, the ether was evaporated to dryness, leaving a trace of white crystalline residue. This substance resembled alkylmaleinimide by sublimation and by its solubility in solvents, but further investigation was impossible due to its poor yield.

Catalytic hydrogenation of pyrrole azo compound—To a solution of *p*-diazobenzenesulfonic acid (8 g.) in 30% sulfuric acid (200 cc.), 4 g. of the pyrrole oil distillate (a) was gradually added under stirring at 4°. Fine cinnabar crystals precipitated, which were found assembled in a ball at one center under the microscope observation and yellow long thread-like crystals were obtained from a solution of *p*-diazobenzenesulfonic acid. These crystals are unstable and on standing change to mud-brown in color within a few hours, that it is necessary to filter rapidly under suction. The precipitate was washed with water and then with ether, and dried on a porous plate. On hydrogenation of the crystalline powder here obtained (ca. 6 g.) in the presence of 30% palladium-charcoal, 400 cc. of hydrogen was absorbed rapidly and the cinnabar solution in the beginning turned to faint yellow through crimson yellow. The palladium-charcoal was filtered off, the filtrate was evaporated under a reduced pressure, and the residue was extracted with methanol. The methanol residue was a yellow syrupy resin, and attempts to crystallize failed.

Separation of 2,3,5-trimethyl-4-acetylpyrrole by Grignard reagent—On adding the ethereal solution of freshly distilled pyrrole oil distillate (b) (6 g.) to methylmagnesium iodide (prepared from 1.2 g. of magnesium and 7.0 g. of methyl iodide), light yellow transparent pyrrole-magnesium iodide was produced under evolution of methane. The reaction was completed by stirring at a room temperature for one hour. When acetyl chloride (4 g.) dissolved in ether was added dropwise to the Grignard reagent, chilled in an ice bath, yellowish red precipitate separated, which turned to cinnabar, viscous mass on stirring at a room temperature for 2 hours. The ethereal reaction mixture turned to reddish brown transparent solution after stirring with 20∼30 g. of ice. The ethereal solution was washed with diluted hydrochloric acid and dilute alkali, the solvent was removed, and distilled with steam to remove volatile oils. The residue was extracted with ether to give a dark brown crystalline mass, from which 0.5 g. of white crystals, m.p. 206°, were obtained by dissolving it in alcohol-ethyl acetate mixture, decolorized with activated charcoal, and recrystallized several times. The crystals were sublimable, and although they give negative result with Ehrlish's test in the cold, color slightly scarlet in the hot, and dissolve readily in acetone and alcohol, and less soluble in cold benzene, rather more in the hot. The results of elementary analysis were identical with those of trimethylacetylpyrrole. *Anal.* Calcd. for $C_9H_{13}ON$: C, 71.5; H, 8.6; N, 10.6; Mol. Wt., 151. Found: C, 71.3; H, 8.46; N, 10.1; Mol. Wt., 138.4.

The melting point showed no depression on admixture with synthetic 2,3,5-trimethyl-4-acetylpyrrole.

Separation of 2,3,5-trimethyl-4-acetylpyrrole by the Friedel-Crafts reaction—Powdered anhydrous aluminum chloride (2 g.) and acetyl chloride (1.8 g) were added rapidly to the solution of the pyrrole distillate (b) (2 g.) in carbon disulfide (20 cc.). On refluxing the solution on a steam bath, vigorous reaction occurred evolving hydrogen chloride. After one hour's heating, carbon disulfide was removed to give a reddish product, which was steam-distilled to recover the unreacted material (1 g.). The steam-distillation residue was treated in the same way to give 0.1 g. of white crystals, m.p. 206°, giving no depression of the melting point when admixed with authentic 2,3,5-trimethyl-4-acetylpyrrole.

Synthesis of 2,3,5-trimethyl-4-acetylpyrrole—Acetylacetone (IV) (1.4 g.) and isonitrosomethyl ethyl ketone (III) (1.4 g.) were dissolved together in 30 cc. of glacial acetic acid, and catalytically hydrogenated using 0.1 g. of 40% palladium-charcoal, absorbed 240 cc. of hydrogen rapidly. After the catalyst was filtered off, the filtrate was distilled under a reduced pressure to remove the acetic acid, the residue was dissolved in ether, and the ether solution was washed with diluted acid and dilute alkali solution. The crystalline ether residue was recrystallized from ethyl acetate-alcohol mixture to white needles, m.p. 206°.

Summary

2,3,5-Trimethylpyrrole obtained from the Fushun shale oil gasoline was identified through 2,3,5-trimethyl-4-acetylpyrrole, m.p. 206°, prepared by the Grignard reagent and then of acetyl chloride on the pyrrole oil extracted from the neutral shale gasoline by washing it with 60% sulfuric acid.

(Received May 21, 1953)

---

49. **Takeo Iida* and Minoru Tanaka**:** Studies on the Components of the Fushun Shale Oil. III. Nitriles from the Crude Light Oil.

(Pharmaceutical Faculty, University of Toyama)*

In the earlier paper[1], it was reported that the crude gasoline of the Fushun shale oil contains aliphatic nitriles (capro-, enantho-, and caprylo-nitriles) as its neutral nitrogen components to the extent of 0.5 %. Using the same procedure as that previously employed by the present authors[1], the research on the crude light oil[2] was continued and it was found that the light oil also contains caprylo-, pelargo-, capro-, hendecano- and lauro-nitriles to the total amount of about 2 %. The physical properties of these acids and their derivatives are listed in Table I.

This investigation was carried out under the continued guidance of Prof. Dr. E. Ochiai to whom the authors express their heartfelt and profound gratitude.

Experimental

Preparation of the neutral oil—Three kg. of the faint yellow crude light oil, which is freshly distilled in vacuum, was washed with 10% caustic soda, then successively with 20% and 60% sulfuric acid to remove the acid oil (5%), basic oil (4.5%), and the pyrrole oil[3] (1.5 %), and the neutral oil (82%) was obtained.

Saponification of the nitriles—The neutral oil (about 2.4 kg.) was heated with an air condenser for 12 hours at about 200°. Heating was continued until the evolution of gaseous ammonia ceased.

Separation of fatty acids—After saponification the mixture was cooled to a room temperature, and the resulting potassium soap was extracted with hot water. The aqueous extract was stirred with benzene to remove mechanically the small amount of contaminated neutral oil and then made acidic. The crude brown fatty acids were obtained.

Esterification and refining of the crude fatty acids—The crude fatty acids were boiled with 5% methanolich ydrochloric acid for 2∼3 hours on a water bath converting them to the methyl esters,

---

* 5 Okuda, Toyama (飯田武夫).

** Niizu, Niigata-ken (田中 実).

[1] T. Iida, M. Tanaka: J. Pharm. Soc. Japan, 64, 162(1944).

[2] This name is given to the 200∼280° fraction of the crude shale oil obtained by the low-temperature carbonisation of Fushun oil shale in Manchuria.

[3] Neutral oil extracted with 60 % sulfuric acid contains a large amount of pyrrole compounds.