

was immersed in a 70° water bath for 10 min. and a solution of 3.8 g. of titanium tetrachloride, diluted with dry heptane to a volume of 12.2 ml., was added in small amount over a 5-min. period, using a hypodermic syringe. The bottle was vented from time to time in order to relieve the pressure. The reaction bottle was then tumbled for 30 min. at 70°, after which time 42.3 ml. of triisobutylaluminum-heptane solution and 75 ml. of freshly distilled styrene were added. The bottle was then tumbled in a 70° water bath for 24 hr. After the bottle was cooled to room temperature, the contents were poured into methanol. Hydrochloric acid was added to dissolve the inorganic materials, and the mixture allowed to stand for 16 hr. The polymer was collected and then suspended in acetone containing hydrochloric acid. The polymer was washed by decantation several times with a fresh acetone and subsequently boiled in acetone for 18 hr., to give a 72% yield of polystyrene having an inherent viscosity of 4.42, a melting point of 230°, and extremely high crystallinity.

KODAK RESEARCH LABORATORIES  
COMMUNICATION NO. 1922  
ROCHESTER, N. Y.

## An Improved Synthesis of 3-Methylpyrrole<sup>1</sup>

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Received December 16, 1957

The simple compound 3-methylpyrrole is only very poorly characterized in the chemical literature. Earlier methods of synthesis<sup>2-7</sup> gave either low yields, small amounts of impure material, or an inseparable mixture of isomers.

The present paper reports the synthesis of pure 3-methylpyrrole in 37.8% yield starting with potassium phthalimide by condensation of aminoacetone with diethyl oxalacetate and subsequent hydrolysis and decarboxylation of the product, 2-carboxy-3-carbethoxy-4-methylpyrrole, essentially by the method of Piloty and Hirsch.<sup>2</sup> Our contribution consists in the development of a new method for the *in situ* synthesis of aminoacetone (hydrolysis of *N*-acetylphthalimide) and in the improvement of the subsequent steps, as well as in a more complete characterization of 3-methylpyrrole.

(1) This investigation was performed as a part of American Petroleum Institute Research Project 52 on *Nitrogen Constituents of Petroleum*, which is conducted at the University of Kansas in Lawrence, Kan., and the Bureau of Mines Experiment Stations in Laramie, Wyo., and Bartlesville, Okla.

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## EXPERIMENTAL

*N*-Acetylphthalimide. An intimate mixture of 250 g. of potassium phthalimide with 200 g. of 1-chloropropanone was added to a 2-l., three necked round bottomed flask fitted with a mechanical stirrer and a reflux condenser. The mixture was heated gently by means of a heating mantle until reaction began; the heat was then withdrawn and the reaction allowed to proceed to completion at room temperature. The solid product was recrystallized from water to yield 269 g. (98.2%) of colorless needles of *N*-acetylphthalimide, m.p. 116.0–116.8°, 122.9–123.5° after recrystallization from water (reported<sup>8</sup> 124°).

2-Carboxy-3-carbethoxy-4-methylpyrrole. A solution made from 150 ml. of concentrated hydrochloric acid and 75 ml. of water was added to 50.0 g. of crude *N*-acetylphthalimide in a 500-ml., one necked round bottomed flask fitted with a reflux condenser. The solution was heated at reflux for 4 hr., cooled and brought to pH 1.5 by addition of 30% aqueous sodium hydroxide solution and filtered to remove the phthalic acid that precipitated. The filtrate was then added slowly to a solution of 45 g. of diethyl oxalacetate sodium salt in 400 ml. of water while the temperature was maintained at 75° and the pH at 5 by periodic addition of small amounts of sodium hydroxide solution.

The mixture was then cooled and the precipitate removed by filtration. The pH of the filtrate was brought to 8 by the addition of further sodium hydroxide solution and the resulting solution heated at 75° for 30 min., reacidified with dilute hydrochloric acid, and cooled. Filtration afforded a second crop of 2-carboxy-3-carbethoxy-4-methylpyrrole to bring the total yield of product, m.p. 195.7–196.8° (reported<sup>3</sup> 196°), to 25.5 g. (52.8%).

3-Carboxy-4-methylpyrrole. A solution of 440 g. of potassium hydroxide in 1250 ml. of water was added to 67 g. of 2-carboxy-3-carbethoxy-4-methylpyrrole and the mixture refluxed for 24 hr. The solution was brought to pH 9 with concentrated sulfuric acid, cooled, and filtered. The filtrate was then acidified, cooled, and filtered to afford a quantitative yield (42.5 g.) of 3-carboxy-4-methylpyrrole, m.p. 152.6–153.7° (reported<sup>3</sup> 149°).

3-Methylpyrrole. A total of 22.0 g. of finely powdered 3-carboxy-4-methylpyrrole was placed in a 200-ml. round bottomed flask fitted for distillation. The flask was heated gently with a free flame until no more liquid distilled. The distillate was taken up in ether, the solution dried over anhydrous magnesium sulfate and redistilled to yield 10.6 g. (73.1%) of pure 3-methylpyrrole, b.p. 142–143° (740 mm.)  $n_D^{20}$  1.4970,  $n_D^{25}$  1.4949.

*Anal.* Calcd. for C<sub>6</sub>H<sub>7</sub>N: C, 74.0; H, 8.7; N, 17.3. Found: C, 74.0; H, 8.8; N, 17.3.

The absorption bands in the infrared spectra of 3-methylpyrrole and 2-methylpyrrole<sup>9</sup> are compared in Table I and the respective infrared spectra of 12.25% solutions in chloroform taken with a Perkin Elmer Model 21 double beam spectrophotometer in 0.05 mm. sodium chloride cells are shown in Figs. 1 and 2.

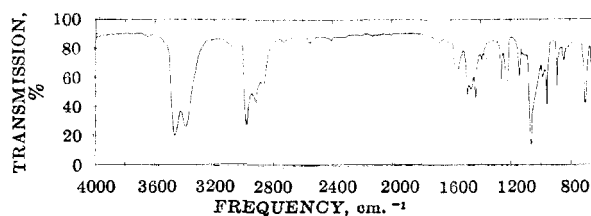


Fig. 1. Infrared spectrum of 3-methylpyrrole

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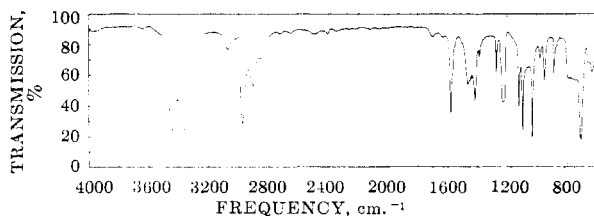


Fig. 2. Infrared spectrum of 2-methylpyrrole

TABLE I  
ABSORPTION BANDS IN INFRARED SPECTRA OF  
3-METHYLPYRROLE AND 2-METHYLPYRROLE<sup>a</sup>

3-Methyl- pyrrole	2-Methyl- pyrrole	3-Methyl- pyrrole	2-Methyl- pyrrole
3462 vs	3441 vs	1390 vw	1386 vw
3390 vs	3362 vs	1375 vw	1375
3080 sh	3072 w	1259 m	1259
2981 vs	2971 vs	1218 <sup>b</sup> m	1230 <sup>b</sup> s
2915 s	2904 m	1139 m	1130 s
2862 m	2850 w (sh)	1097 <sup>b</sup>	1097 <sup>b</sup> vs
2730 vw	2730	1061 vs	1061
2550 vw	2550	1030 <sup>b</sup>	1030 <sup>b</sup> vs
1700	1700 vw	980 w	980 w
1672 vw	1672	956 m	951 m
1635	1635 vw	889 m	889 m
1570 <sup>b</sup> w	1577 <sup>b</sup> s-vs	879	879 sh
1556 <sup>b</sup> w-m	1550 <sup>b</sup>	790 <sup>b</sup>	790 <sup>b</sup> m
1490 <sup>b</sup> m-s	1490 <sup>b</sup>	700 s	704 vs
1463 m	1463 m	660	660 sh
1432 m-s	1418 m-s	633	633 w

<sup>a</sup> Values are frequencies in cm.<sup>-1</sup>; s = strong, m = medium, w = weak, vs = very strong, sh = shoulder. <sup>b</sup> Principal differences.

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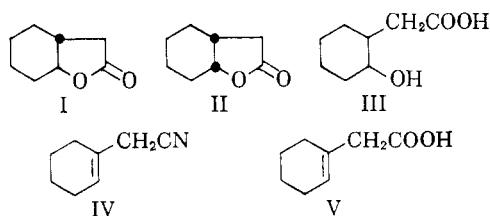
## Preparation of *cis*-2-Hydrocyclohexane-acetic Acid Lactone

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Received January 13, 1958

The *trans*-lactone (I) of 2-hydroxycyclohexane-acetic acid is easily obtainable from diethyl sodiomalonate and cyclohexene oxide. However, the *cis*-lactone (II) has only been obtained indirectly by hydrolysis of I to the *trans*-acid (III), followed by oxidation to the corresponding ketoacid and catalytic hydrogenation to a mixture of the acids III, containing 84% of the *cis*-isomer. The latter lactonized spontaneously to II. The over-all yield of II, based on cyclohexene oxide, was 38%.<sup>1</sup>

It has now been found that II is obtained in about 30% yield by one-step reaction of the readily accessible 1-cyclohexene-1-acetonitrile<sup>2</sup> (IV) with concentrated hydrochloric or hydrobromic acid in boiling glacial acetic acid. The determination of the



composition of the lactone obtained was based on the fact observed by Newman and Vanderwerf<sup>1</sup> that I yields on dissolution in aqueous sodium hydroxide and subsequent acidification the *trans*-acid III, while the *cis*-acid III, obtained under these conditions from II, cyclizes spontaneously again to II.

The mechanism of this stereospecific reaction very probably does not consist of initial hydration of the double bond and subsequent attack of the hydroxy group on the nitrile triple bond. In this case it would have to lead to a mixture of I and II and should not markedly depend on the nature of the acid employed. In fact sulfuric acid, for example, does not bring about the conversion of IV to II. The first step in the production of the lactone II is the formation of the unsaturated acid (V); it can be isolated when the reaction is interrupted after a shorter time than that required for the formation of the lactone. The hydrolysis of the nitrile function is obviously not a simple acid-catalyzed reaction, but is brought about by an addition of the acid to the C≡N bond and is influenced also by the anion of the acid. Therefore, the order of the rates of the reaction of IV with the acids employed is: hydrobromic > hydrochloric > sulfuric acid; this is also the order of the nucleophilicities of the anions.

The cyclization step, which follows the formation of the acid V, is not the rate controlling one, since the acid V is cyclized smoothly in the presence of either hydrobromic or sulfuric acid.

## EXPERIMENTAL

*Reaction of hydrobromic acid with 1-cyclohexene-1-acetonitrile IV. General procedure.* To 20 g. of IV in 80 ml. of glacial acetic acid, 140 ml. of concentrated hydrobromic acid was added and the mixture was refluxed for the desired period of time, after which water was added and the product extracted with benzene. The benzene layer was washed with 5% aqueous sodium carbonate solution. The acidic products, obtained by acidification of the washings, were extracted with benzene and distilled. 1-Cyclohexene-1-acetic acid (V) distills at 155–158° (20 mm.) and melts at 37°.<sup>3</sup> Some bromine-containing acids were also observed after longer reaction periods. They boiled at 170–190° (20 mm.), but have not been obtained in pure form.

The neutral products remaining in the benzene layer can be separated by fractionation. The nitrile IV distills at 120° (20 mm.); the lactone II boils at 145–148° (20 mm.).

The obtained lactone consisted of the *cis*-product II. In one case only was a small amount of the *trans*-isomer I found.

In order to determine the content of I and II in the lactone, the neutral products obtained after evaporating

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