

METALATION OF PYRROLE, 1-METHYLPYRROLE, AND 1-PHENYLPYRROLE WITH *n*-BUTYLLITHIUM

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In continuation (1, 2) of a program of study of the metalation of simple heterocyclic types with *n*-butyllithium, we have undertaken an examination of pyrrole and its 1-methyl and 1-phenyl derivatives. There is considerable information in the literature on the chemistry of 1-pyrrolypotassium and 1-pyrrolymagnesium halides. In general the potassium compound reacts at ordinary temperature to produce 1-substituted types (3) while the Grignard reagent yields 2-substituted derivatives. 1-Pyrrolymagnesium halide and its reactions have been investigated very extensively by Oddo and co-workers [(see reference (4) and many earlier papers)].

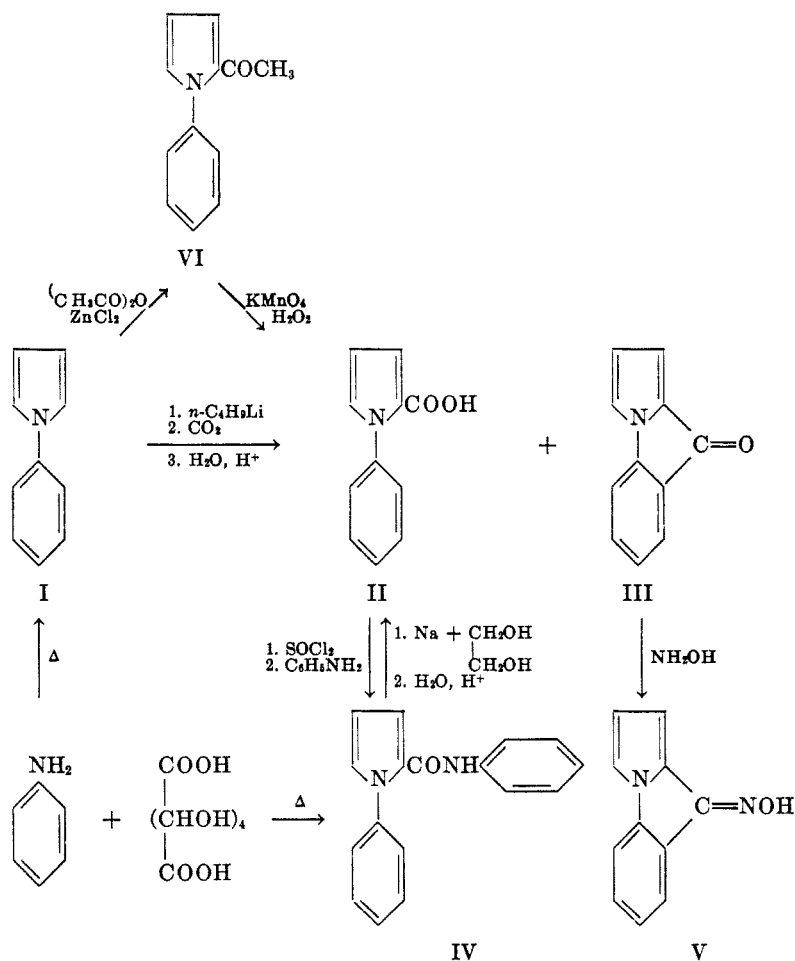
The reaction of pyrrole and excess *n*-butyllithium gave, upon subsequent carbonation, pyrrole-1-carboxylic acid in 34% yield. The failure of the 1-pyrrolylithium, first formed with one equivalent of *n*-butyllithium, to undergo additional metalation is similar to the behavior of indole (1) but in striking contrast to carbazole (5) and phenothiazine (6). The use of a slight excess of pyrrole with *n*-butyllithium resulted in metalation in only 14% yield based on the *n*-butyl bromide from which the *n*-butyllithium was prepared.

This lack of reactivity of pyrrole toward C-metalation is quite different from the behavior of the 1-methyl derivative. When 1-methylpyrrole was treated with a slight excess of *n*-butyllithium, followed by carbonation, the 1-methylpyrrole-2-carboxylic acid was formed in 42% yield based on *n*-butyl bromide. Use of a three-fold excess of *n*-butyllithium caused formation of only 1-methylpyrrole-2,5-dicarboxylic acid in 58% yield based on 1-methylpyrrole. The structures of the two acids obtained from the metalation of 1-methylpyrrole are indicated by the well-known tendency of metalation by alkylolithium compounds to occur at positions adjacent to heterocyclic oxygen, sulfur, and nitrogen atoms and by the comparison of the melting points of the metalation acids or esters and amides with recorded values from the literature (7-9).

The metalation of 1-phenylpyrrole (I) was undertaken in order to compare the reactivity of the pyrrole and benzene rings toward *n*-butyllithium. The metalation of 1-phenylindole (I) shows preferred substitution in the pyrrole ring of indole, but 9-phenylcarbazole substitutes in the N-phenyl group (10, 11). In experiments in which 1-phenylpyrrole was treated with an equivalent quantity of *n*-butyllithium, a monocarboxylic acid (II), m.p. 187-188°, was formed subsequent to carbonation, in about 20% yield. The only monocarboxylic acid derivative of 1-phenylpyrrole recorded in the literature is the 2-carboxylic acid reported to melt with decarboxylation at 166° (12). The acid isolated here melts

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without loss of carbon dioxide, but heating above its melting point for a short time causes loss of carbon dioxide leaving a residue of 1-phenylpyrrole. The structure of the carboxylic acid (II) from metalation was indicated to be the 2-carboxylic acid by several lines of evidence. The acid from metalation was converted to its methyl ester, m.p. 86–87°, and to the anilide (IV), m.p. 136–137°. These melting points compare favorably with literature values (12) given for the corresponding derivatives of the 2-carboxylic acid, m.p. 88° and m.p. 136° respectively. Pictet and Steinman (12) obtained their anilide of 1-phenylpyrrole-2-carboxylic acid as one of the products of pyrolysis of aniline and mucic acid. Its structure is indicated by the method of formation. We repeated this work and obtained the anilide, m.p. 136–137°, which was identical (mixture m.p.) with the sample obtained from the metalation acid; and its hydrolysis produced the acid, m.p. 187–188°, instead of the reported m.p. 166°.



1-Methylpyrrole has been acylated to form 1-methyl-2-acetylpyrrole (13, 14). The action of acetic anhydride and zinc chloride on 1-phenylpyrrole produced

a monoacetyl derivative (VI) which on oxidation was converted to 1-phenylpyrrole-2-carboxylic acid identical with the samples produced by metalation and ring closure.

Metalation of 1-phenylpyrrole with about three moles of *n*-butyllithium to one of the pyrrole did not yield any dicarboxylic acid subsequent to carbonation. Instead there was obtained, in addition to some monocarboxylic acid, a bright yellow compound which contained a carbonyl group and which was indicated by analysis and molecular weight determination to be 5-ketopyrrolo[1,2-*a*]indole (III). This compound would arise from dimetalation of 1-phenylpyrrole in the 2- and 2'-positions followed by intramolecular ketone formation with carbon dioxide. Ketones are commonly formed as by-products from the action of reactive organometallic compounds on carbon dioxide, but in this case the cyclic ketone is the only product isolated from dimetalation. This is undoubtedly due to the favorable steric arrangement of functional groups after one molecule of carbon dioxide has reacted. A similar situation was encountered in the dimetalation of 1-phenylindole (1), although here it was possible also to isolate some of the dicarboxylic acid.

Several substituted anilines were condensed with mucic acid to produce new correspondingly substituted 1-phenylpyrroles. In general the presence of electron-withdrawing groups on the aniline molecule did not allow ring closure to the substituted pyrrole.

The compounds mentioned above as well as some additional derivatives were submitted to the Eli Lilly Company for evaluation of possible chemotherapeutic activity and we should like to acknowledge this help. For example hydrazides of all carboxylic acids were examined for antitubercular activity. The results of these tests will be reported elsewhere.

EXPERIMENTAL²

Metalation of pyrrole. To a solution of *n*-butyllithium, prepared (15) from 27.4 g. (0.2 mole) of *n*-butyl bromide, in 100 ml. of ether was added slowly 17.3 g. (0.25 mole) of pyrrole³ dissolved in 20 ml. of ether. The reaction mixture was stirred and heated under reflux for one hour and then poured onto a slurry of ether and crushed excess solid carbon dioxide. After evaporation of the carbon dioxide, the mixture was hydrolyzed with excess water, and the ether layer was separated and extracted with several portions of water. The combined aqueous portions were acidified with hydrochloric acid and the precipitated white solid was collected, dried, and recrystallized twice from a mixture of ether and petroleum ether. The yield was 1.4 g. of acid, m.p. 118–118.5°, corresponding to 14% based on the *n*-butyl bromide used. The neutralization equivalents found for the product were 110 and 116; the calculated value for a pyrrolemonocarboxylic acid is 111. Pyrrole-1-carboxylic acid has been reported to melt at 95° by Tschelinzeff and Maxoroff (3), the 2-acid at 207° (16), and the 3-acid at 161–162° (17). Later work (18) has shown that the 161–162° melting "3-acid" is a second crystalline modification of the 2-acid and that the 3-acid actually melts (19) at 148°.

The acid obtained above was converted to its amide in 41% yield. The amide melted at

² All elementary analyses were performed by the Galbraith Microanalytical Laboratory of Knoxville, Tennessee. All melting and boiling points are uncorrected.

³ The pyrrole and *N*-methylpyrrole used in this research were provided through the courtesy of the E. I. du Pont de Nemours and Co.

165–166° which agrees with the value of 166° reported for the amide of pyrrole-1-carboxylic acid by Tschelinzeff and Maxoroff (3). Pyrrole-2-carboxamide melts at 176.5° (20) and the amide of the 3-acid is apparently unknown. It is proposed that our metalation acid, m.p. 118–118.5°, is a second crystalline modification of the pyrrole-1-carboxylic acid.

Metalation of pyrrole (0.05 mole) with the *n*-butyllithium prepared from 0.20 mole of *n*-butyl bromide followed by carbonation and work-up as described above produced the pyrrole-1-carboxylic acid in 34% yield.

Metalation of 1-methylpyrrole. To 100 ml. of an ethereal solution of *n*-butyllithium prepared from 27.4 g. (0.20 mole) of *n*-butyl bromide was added a solution of 20.3 g. (0.25 mole) of 1-methylpyrrole in 20 ml. of ether. The mixture was stirred and heated under reflux for 20 hours after which it was carbonated as described above. Recrystallization of the white acid product was from 20% aqueous ethanol and there was obtained 10.5 g. (42%) of 1-methylpyrrole-2-carboxylic acid melting at 135–136°. The neutralization equivalent was determined at 125 and 126 and the calculated value is 125. Bell (8) and Fischer (7) report 135° for the m.p. of this compound.

The *methyl ester* was prepared in normal fashion by mixing an ethereal solution of the acid with an ethereal solution of excess diazomethane. The ester was formed in 84% yield, b.p. 95–98°/28 mm., n_D^{25} 1.5177.

Anal. Calc'd for $C_7H_9NO_2$: N, 10.07. Found: N, 10.18.

The *hydrazide* of 1-methylpyrrole-2-carboxylic acid was prepared from the methyl ester and hydrazine hydrate. The product melted at 123° and was obtained in 51% yield. During the course of this research this compound was reported (21) and its m.p. was described as 119–121°.

Metalation of 1-methylpyrrole with a 3.0 to 3.5 *molar* excess of *n*-butyllithium and a reaction time of 12 hours allowed formation of an acid which sublimed without melting at 270–275°. The neutral equivalent was found to be 85 in two determinations. The calculated value for 1-methylpyrrole-2,5-dicarboxylic acid is 86.5. The yield was 58%.

The *dimethyl ester* was prepared in 76% yield by the action of excess methanol and concentrated sulfuric acid. It melted at 80–80.5° as compared to a value of 80–81° reported by Tschelinzeff and Maxoroff (9).

The *dihydrazide* was prepared in 45% yield from the dimethyl ester. It melted at 292–293°.

Anal. Calc'd for $C_7H_{11}N_4O_2$: C, 42.63; H, 5.62; N, 35.52.

Found: C, 42.52; H, 5.71; N, 35.50.

The mono- and di-carboxylic acids from the above metalation reactions were essentially uncontaminated by other acidic materials. However, when amounts of *n*-butyllithium in between the amounts recorded above were used, mixtures of mono- and di-carboxylic acids resulted.

1-Phenylpyrrole. The method of preparation of 1-phenylpyrrole used in this research is given below in some detail, since in our hands it was superior to the published procedures (22–24).

Aniline (233 g., 2.5 moles) was heated to 85° in a large evaporating dish on a steam-cone and 252 g. (1.2 moles) of mucic acid was added. The mixture was stirred and 12 ml. of water was added whereupon the aniline mucate rapidly solidified. The salt was placed in a 2-l. round-bottomed flask equipped with a downward air condenser 1 inch in diameter and was heated on a Woods' metal bath. The bath temperature was raised to 360° and the major portion of the distillate was collected at a bath temperature of 360°. The distillate was collected in 1 l. of dilute (1:4) hydrochloric acid. The acid was decanted and the residue was subjected to steam-distillation with 3 l. of distillate being collected. The white 1-phenylpyrrole was separated from the distillate, dried, and distilled to yield 114 g. (33%), b.p. 124–127°/22 mm., m.p. 58–58.5°. Recrystallization from 70% aqueous ethanol raised the m.p. to 60–61°. The yields varied between 31 and 38% in four runs. The residue in the steam-distillation flask was extracted with cold chloroform and crystallized from 70% aqueous ethanol to yield 24.4 g. of *sym*-diphenylurea, m.p. 239°.

1-m-Tolylpyrrole, b.p. 253–257°/745 mm. was prepared in similar manner and 22% yield from *m*-toluidine and mucic acid.

Anal. Calc'd for $C_{11}H_{11}N$: N, 8.91. Found: N, 8.90.

1-p-Methoxyphenylpyrrole, b.p. 174–180°/23 mm., m.p. 112–113° was prepared in similar manner and 32% yield.

Anal. Calc'd for $C_{11}H_{11}NO$: N, 8.09. Found: N, 8.08.

It was not found possible by this procedure to prepare the corresponding substituted *N*-phenylpyrrole from the following derivatives of aniline: methyl anthranilate, *m*-aminoacetophenone, *o*-bromoaniline, and *p*-bromoaniline.

Metalation of 1-phenylpyrrole (I). To a solution of 14.3 g. (0.10 mole) of 1-phenylpyrrole in 100 ml. of ether was added an ether solution of *n*-butyllithium containing 0.113 mole of organolithium reagent (25). The mixture was stirred for eight hours at room temperature, carbonated, and hydrolyzed in the usual manner. The ether layer was washed with water and the aqueous layer plus the washings acidified with dilute hydrochloric acid to precipitate 4.0 g. of light brown solid, m.p. 170–172°. Evaporation of the ether layer gave a solid which after recrystallization yielded 3.0 g. of 1-phenylpyrrole. The brown acidic material was recrystallized once from a large volume of hot water to yield 3.0 g., m.p. 183–184°. A second recrystallization from 70% ethanol with charcoal treatment gave a white acid, m.p. 184–185°. Analyses and neutralization equivalent indicated that the product was a mono-carboxylic acid (II). The yield of product of m.p. 183–184° was 14%. The m.p. of 1-phenylpyrrole-2-carboxylic acid is given by Pictet and Steinman (12) as 166°. This is the only isomer known.

Anal. Calc'd for $C_{11}H_9NO$: C, 70.58; H, 4.85; N, 7.48; Neut. eq., 187.

Found: C, 70.32; H, 4.80; N, 7.54; Neut. eq., 189.

The *methyl ester* was prepared in 81% yield from the crude acid, m.p. 170–172°, above. It melted at 86–87°. Pictet and Steinman report m.p. 88° for methyl 1-phenylpyrrole-2-carboxylate. Saponification of the ester produced in 76% yield a sample of the carboxylic acid, m.p. 187–188°.

The *anilide (IV)* of the carboxylic acid was prepared in quantitative yield by the action of thionyl chloride and aniline. It melted at 136–137° which is in agreement with the literature value (12) for the anilide of the 2-acid.

The *hydrazide* was prepared from the methyl ester in 67% yield. It melted at 172–173°.

Anal. Calc'd for $C_{11}H_{11}N_2O$: N, 20.88. Found: N, 21.01.

The metalation of 1-phenylpyrrole with two equivalents of *n*-butyllithium for a period of 14 hours at reflux temperature followed by carbonation produced different products. Evaporation of the ether layer from a typical run using 27.3 g. (0.19 mole) of 1-phenylpyrrole gave a yellow oil which was distilled to yield a fraction boiling at 208–212°/30 mm. This solidified on cooling and was recrystallized from petroleum ether to give 1.5 g. of a bright yellow solid, m.p. 121–122°. The product showed a positive 2,4-dinitrophenylhydrazine test for a carbonyl group. Elemental analyses indicated it to correspond in structure to 5-ketopyrrolo[1,2-*a*]indole (III) or a di-(1-phenyl-2-pyrryl) ketone. A molecular weight determination by the Menzies method showed a value of 143, not a satisfactory check with the calculated value for III of 169 but rather strong evidence against the di-(1-phenyl-2-pyrryl) ketone structure.

Anal. Calc'd for $C_{11}H_7NO$: C, 78.09; H, 4.17; N, 8.25.

Found: C, 78.24; H, 4.11; N, 8.19.

An *oxime derivative (V)* produced by the method of Bachmann and Boatner (26) in 36% yield melted at 192–193°.

Anal. Calc'd for $C_{11}H_9N_2O$: C, 71.72; H, 4.38; N, 15.21.

Found: C, 71.96; H, 4.55; N, 15.35.

The aqueous layer from hydrolysis of the original reaction mixture precipitated no carboxylic acid on acidification, but instead a blue oil. This was separated and extracted with ether to leave a blue solid which was of indistinct melting point, amorphous, soluble in aqueous base, and insoluble in water and organic solvents. It could not be further purified or characterized, but it appeared to be polymeric in nature.

In several experiments it was attempted to convert 1-phenylpyrrole-2-carboxylic acid (II) to the ketone III by action of Friedel-Crafts type catalysts on the acid chloride of II.

No product could be isolated corresponding in properties to III or to the yellow ketone described above.

In other metalation experiments under essentially the same conditions some monocarboxylic acid was isolated. For example from 14.3 g. (0.1 mole) of 1-phenylpyrrole and 0.2 mole of *n*-butyllithium there was obtained 2.7 g. of monocarboxylic acid, 3.7 g. of the acidic blue material, and 0.12 g. of the cyclic ketone. When a five-fold excess of *n*-butyllithium was used, the blue material increased in quantity and no monocarboxylic acid was isolated in two runs. No dicarboxylic acid was isolated in any of the experiments.

Isolation of the anilide of 1-phenylpyrrole-2-carboxylic acid from the pyrolysis of aniline mucate. One-half mole of aniline mucate prepared as described above was heated in a Claisen flask at 240° for 1½ hours. The mixture then was distilled and the fraction boiling at 120–280°/26 mm. was extracted with cold chloroform which removed the 1-phenylpyrrole and the anilide. The extract was steam-distilled to remove the chloroform and 1-phenylpyrrole. The residue was recrystallized two times from dilute ethanol to yield 11.4 g. (8.7%) of the anilide, m.p. 136–137°. This procedure was adapted from the rather scanty directions available from Pictet and Steinman (12). A mixture m.p. between this compound and the anilide prepared from the metalation acid showed no depression.

The anilide was saponified with sodium in ethylene glycol at 150–170° for 11 hours. The acid obtained was identical with the metalation acid.

Acetylation of 1-phenylpyrrole. A solution of 27.2 g. (0.20 mole) of anhydrous zinc chloride in 200 ml. of ether was added to 100 ml. of an ethereal solution containing 28.6 g. (0.20 mole) of 1-phenylpyrrole and 20.4 g. (0.20 mole) of acetic anhydride. The mixture was stirred at room temperature for one hour, after which the dark red material was added to excess ice-water. The ether layer was separated after completion of the hydrolysis and washed with dilute sodium carbonate solution and with water. Distillation produced three fractions: (a) 10.0 g., b.p. 116–164°/13 mm.; (b) 9.2 g., b.p. 164–170°/13 mm.; (c) 3.1 g., b.p. 170–196°/13 mm. The (b) fraction gave a positive test for the carbonyl group with 2,4-dinitrophenylhydrazine and was extracted with petroleum ether. The extracts, when cooled in a solid carbon dioxide-acetone bath precipitated a white solid, m.p. 44–46°. Repetition of the latter operation several times produced 6.0 g. (16%) of ketone, m.p. 57–58°. This compound showed a sharp depression of m.p. when mixed with 1-phenylpyrrole. Analyses indicated the product to be a monoacetyl-1-phenylpyrrole.

Anal. Calc'd for C₁₂H₁₁NO: C, 77.81; H, 5.99; N, 7.56.

Found: C, 77.59; H, 6.14; N, 7.60.

The *oxime*, m.p. 116–117°, was prepared in 64% yield.

Anal. Calc'd for C₁₂H₁₂N₂O: N, 13.99. Found: N, 13.93 and 13.89.

Oxidation of 2-acetyl-1-phenylpyrrole to 1-phenylpyrrole-2-carboxylic acid (7). Four g. (0.022 mole) of 2-acetyl-1-phenylpyrrole was finely powdered and suspended in 300 ml. of water and a solution of 7.0 g. of potassium permanganate in 250 ml. of water was added dropwise at room temperature over a period of one hour. The mixture then was heated to 70° and stirred for a second hour. The mixture was filtered, and the filtrate concentrated to 100 ml., cooled, and the precipitated solid removed by filtration and washed on the filter with dilute aqueous potassium hydroxide solution. The combined filtrates were acidified with hydrochloric acid and extracted several times with ether. The combined extracts were evaporated to yield 2.7 g. of a semi-solid which was warmed on a steam-bath for 15 minutes with 10 ml. of 30% hydrogen peroxide. The mixture then was filtered and the filtrate was cooled to form 0.7 g. (17%) of carboxylic acid which melted at 185–186° after one recrystallization from ethanol and water. A mixture m.p. with the metalation acid showed no depression.

1-(o-Carbomethoxyphenyl)-2,5-dimethylpyrrole. The condensation of anthranilic acid and acetylacetone was carried out in accordance with the procedure of Hazelwood and Hughes (27). The 1-(*o*-carboxyphenyl)-2,5-dimethylpyrrole, m.p. 119–120°, was obtained in 66% yield. The acid (10 g.) was esterified by mixing an ethereal solution with a solution of excess diazomethane in ether. The ester was distilled to yield 8.5 g. (80%) of pure product, b.p. 177–179°/35 mm.

Anal. Calc'd for $C_{14}H_{15}NO_2$: N, 6.11. Found: N, 6.05.

The *hydrazide* was prepared in 63% yield from the above ester. It melted at 118.5–119°.

Anal. Calc'd for $C_{13}H_{15}N_3O$: N, 18.33. Found: N, 18.25 and 18.32.

SUMMARY

The metalation of pyrrole with *n*-butyllithium followed by carbonation gave only the 1-carboxylic acid even in the presence of excess organometallic.

Metalation of 1-methylpyrrole with equivalent amounts of *n*-butyllithium produced 1-methylpyrrole-2-carboxylic acid in 42% yield while the use of excess organolithium reagent allowed formation of 1-methylpyrrole-2,5-dicarboxylic acid in 58% yield.

The metalation of 1-phenylpyrrole produced 1-phenylpyrrole-2-carboxylic acid in 20% yield when an equivalent quantity of metalating agent was used and a cyclic ketone, 5-ketopyrrolo[1,2-*a*] indole in the presence of excess organolithium compound.

Acylation of 1-phenylpyrrole with acetic anhydride and zinc chloride formed 2-acetyl-1-phenylpyrrole.

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