were used in the gaseous state by passing them directly into the alcohol–catalyst mixture. The other acetylenes were used in the liquid state.

**Action of Methanol on Ethylacetylene.**—The catalyst was prepared by heating together momentarily 5 g. of red mercuric oxide, 2 ml. of $(C_2H_5)_2O·BF_3$ and 2 ml. of methanol. To this was added two moles (64 g.) of methanol. The mixture was placed in a 2-liter 3-necked flask equipped with an inlet tube for ethylacetylene, a mercury sealed motor driven stirrer, and a liquid ammonia reflux condenser.[5] Ethylacetylene was passed directly into the reaction mixture maintained at 40°; after stirring for two hours the contents of the flask was mixed with 5 g. of anhydrous potassium carbonate and fractionated at 100 mm. Forty grams of 2,2-dimethoxybutane was obtained.

**Action of Methanol on Propylacetylene.**—One-half mole (34 g.) of propylacetylene was added slowly with constant stirring to one and one-quarter moles of methanol (40 g.) containing the usual catalyst. The temperature of the reaction mixture was not allowed to rise above 35°. The procedures for the preparation and purification of 2,2-dimethoxypentane and heptane are analogous to that already described[1] by the authors for 2,2-dimethoxyhexane.

**Proof of the Structure of 2,2-Dimethoxyheptane.**—Hydrolysis of 2,2-dimethoxyheptane with dilute mineral acid yielded methyl alcohol and methyl *n*-amyl ketone, b. p. 149–150°. The latter was identified by its semicarbazone, m. p. 120–121°.

## Summary

1. A series of 2,2-dimethoxyalkanes has been prepared from various alkylacetylenes with methanol in the presence of mercuric oxide and boron fluoride.

2. The ketals obtained from methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl acetylenes are described.

3. With monohydric alcohols other than methanol, no ketals have been isolated by this method.

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[5] Vaughn and Pozzi, *J. Chem. Ed.*, **8**, 2433 (1931).

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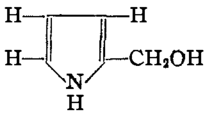
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

# Synthesis of Pyrrole Alcohols and their Derivatives

BY MILLARD S. TAGGART AND G. HOLMES RICHTER

Although the higher complex pyrrole alcohols are known in great variety, the first member of the series has not been prepared. Mingoia[1] attempted to prepare 2-pyrrolecarbinol by the action of formaldehyde on pyrrylmagnesium bromide and obtained a substance which seemed to be the diether of the 2,3 or 2,5 glycol. Tschelinzeff and Maxorow,[2] and many others, condensed formaldehyde with pyrrole and obtained several products which were considered as derivatives of the unknown 2-pyrrylcarbinol (I)



I

We have carefully repeated these experiments and have been able to isolate the previously unknown alcohol; however, the structure of the alcohol obtained in both cases was not the 2 isomer as expected, but the 1 isomer. This was demonstrated by preparing the unknown 2-pyrrylcarbinol by reduction of 2-pyrrylaldehyde. This alcohol had entirely different physical properties. Additional proof of structure was afforded by preparing the 1-carbinol by the reaction of chloromethyl acetate with potassium pyrrolate and subsequent hydrolysis of the ester to the alcohol; this alcohol and its derivatives correspond in all respects to the alcohol obtained by condensing formaldehyde with either pyrrole or pyrrylmagnesium bromide. The determination of the number of active hydrogens by the method of Tschugaeff and Zerewitinoff also indicated that the latter was the 1 isomer as only one active hydrogen was found, whereas, if the 2 isomer were produced, two active hydrogens would be present. Several derivatives and homologs of these alcohols were prepared and are described in the experimental part.

## Experimental

**1. Reaction of Pyrrylmagnesium Bromide with Formaldehyde.**—The Grignard solution was prepared from 9 g. of magnesium, 40.7 g. of ethyl bromide and 200 cc. of dry ether; 25 g. of pyrrole was then added to form the Grignard reagent of pyrrole. Formaldehyde, by heating 16 g. of paraformaldehyde, was passed into the solution until the contents became quite dark. The product was treated with ammonium chloride, the aqueous layer saturated with potassium carbonate and extracted with

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[1] Mingoia, *Gazz. chim. ital.*, **62**, 844 (1932).

[2] Tschelinzeff and Maxorow, *J. Russ. Phys.-Chem. Soc.*, **48**, 748 (1916).

ether. The extract was distilled *in vacuo* and 1 g. of the N-pyrrylmethyl alcohol was obtained; b. p. 65–75° at 1 mm. The crude material will decompose readily at higher temperatures with the evolution of a gas and the production of a black pitch. The material was converted into the phenylurethan of m. p. 111–112°.

*Anal.* Calcd. for $C_{12}H_{12}O_2N_2$: H, 5.60; C, 66.63. Found: H, 5.65; C, 67.10.

2. **Reaction of the Pyrrylmagnesium Bromide with Butyric Aldehyde.**—This experiment was carried out like the above; on distillation in a sausage flask a small amount of the alcohol, b. p. 60–80° at a pressure less than 0.2 mm., was obtained. The material was converted into the phenylurethan, m. p. 109–110°.

*Anal.* Calcd. for $C_{15}H_{18}O_2N_2$: H, 7.03; C, 69.72. Found: H, 7.16; C, 69.40.

3. **Reaction of Pyrrole with Formaldehyde.**—One-half gram of calcium hydroxide, 10 cc. of ethyl alcohol and 11 g. of 40% formaldehyde were mixed and treated with 10 g. of pyrrole. After three hours the solution was saturated with potassium carbonate and extracted with ether. On distillation 3 g. of the N-pyrrylcarbinol was obtained: b. p. 45.5–51° at 1.5 mm.; $d_4^{20}$ 1.0738; $n_D^{20}$ 1.5208.

*Anal.* Calcd. for $C_5H_7ON$: H, 7.27; C, 61.81. Found H, 7.53; C, 61.81.

This material is much purer than that obtained by the Grignard reaction above. The substance is very sensitive to heat; if the temperature of the oil-bath goes above 90°, a very rapid decomposition will take place. It is soluble in water and ether in all proportions. From its aqueous solution it is precipitated immediately by mineral acids, the stability toward alkali is greater, although hot alkali will slowly resinify the material.

The Tschugaeff–Zerewitinoff test gave active hydrogen: calcd. for N-pyrrylcarbinol, 1; found, 0.86.

The phenylurethan of this alcohol melted at 111–112°; a mixed melting point determination with phenylurethan obtained from the alcohol by Grignard reaction gave no depression.

*Anal.* Calcd. for $C_{12}H_{12}O_2N_2$: H, 5.59; C, 66.63; N, 12.96. Found: H, 5.86; C, 66.63; N, 12.74.

4. **N-Pyrrylmethyl Acetate.**—Seventy-five grams of potassium pyrrolate, prepared in the usual way, was suspended in a small amount of dry ether and treated with 73 g. of monochloromethyl acetate in 50 cc. of ether. The reaction flask must be cooled during the addition. The ester was washed with water, dried over magnesium sulfate and distilled; 17.5 g. of the pure product was obtained, b. p. 59–63.5° at 3 mm., $d_4^{20}$ 1.0916, $n_D^{20}$ 1.4907.

*Anal.* Calcd. for $C_7H_9O_2N$: H, 6.52; C, 60.40. Found: H, 7.15; C, 59.84.

5. **Hydrolysis of N-Pyrrylmethyl Acetate.**—Sixteen grams of the ester was hydrolyzed with 10 g. of potassium hydroxide in 30 cc. of water. The temperature must not be permitted to go above 55–60°. As soon as a homogeneous solution was obtained the alcohol was extracted with ether. The material was distilled and analyzed. The physical properties were identical with those observed for the alcohol produced by the condensation of pyrrole with formaldehyde.

*Anal.* Calcd. for $C_5H_7ON$: H, 7.27; C, 61.81. Found: H, 7.74; C, 61.50. Active hydrogen by Tschugaeff–Zerewitinoff method: calcd., 1.0; found, 0.76.

This alcohol gave a phenylurethan of m. p. 111–112°; mixed melting point with phenylurethan of the alcohol from condensation of pyrrole with formaldehyde was 111–112°.

*Anal.* Calcd. for $C_{12}H_{12}O_2N_2$: N, 12.97. Found: N, 13.39.

6. **Reaction of Potassium Pyrrolate with Monochloromethyl Ether.**—Sixty-five grams of potassium pyrrolate suspended in 200 cc. of dry ether was treated with 50 g. of monochloromethyl ether in an equal volume of ether. The product was washed with water, dried and distilled, the bulk of the material boiling at 65–67° at 7 mm.: $d_4^{20}$ 1.0400, $n_D^{20}$ 1.4761. Analysis for C, H, N gave the empirical formula $C_8H_{13}O_2N$; 5 g. of a higher boiling fraction of b. p. 75–77.5° at 4 mm. gave the analysis C, 60.96; H, 8.47. Since about half of the original pyrrole was recovered, two moles of the chloride apparently reacted with one of the salt to give the di-ether and a small amount of the tri-ether.

7. **Synthesis of 2-Pyrrylmethyl Alcohol.**—Seven and one-half grams of α-pyrrylaldehyde was mixed with 50 cc. of water and treated with 375 g. of 1% sodium amalgam. The mixture was permitted to stand for several days, then the tarry materials removed by filtration. The aqueous solution was extracted repeatedly with ether; on concentrating the ether the alcohol crystallized out. The crude product was recrystallized from *n*-propyl alcohol and obtained as snow white crystals of m. p. 117.5–118°. The material is very soluble in water and alcohol, less soluble in ether. It is much more stable than the isomeric N-pyrrylmethyl alcohol.

*Anal.* Calcd. for $C_5H_7ON$: C, 61.81; H, 7.27; N, 14.4. Found: C, 61.95; H, 7.08; N, 14.1.

## Summary

1. The condensation of formaldehyde with pyrrole or pyrrylmagnesium bromide yields N-pyrrylcarbinol.

2. The synthesis of the 2-pyrrylcarbinol was accomplished by the reduction of the 2-pyrrylaldehyde.

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