I desire to express my hearty thanks to Professor Hata for the interest which he has kindly taken in this work.

## Summary

5-Acetamino-6-hydroxy-, 5-acetamino-8-hydroxy-, 7-iodo-5-acetamino-8-hydroxy- and 7-acetamino-5-methyl-8-hydroxyquinoline have been prepared and characterized.

TOKYO, JAPAN

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

# THE REDUCTION OF NAPHTHALENE BY ALKALI METALS IN LIQUID AMMONIA[1]

BY CHARLES BUSHNELL WOOSTER AND FRANK B. SMITH

RECEIVED JULY 26, 1930 PUBLISHED JANUARY 12, 1931

The reaction between sodium and naphthalene in liquid ammonia solution was first investigated by Lebeau and Picon[2] and the products which they obtained at 15° were sodium amide and tetrahydronaphthalene. These facts are equally open to two different interpretations.

I. It may be assumed that the naphthalene was reduced by nascent hydrogen generated by a reaction between the alkali metal and the solvent.

$$4Na + 4NH_3 \longrightarrow 4NaNH_2 + 4(H) \quad (1)$$

$$4(H) + C_{10}H_8 \longrightarrow C_{10}H_{12} \quad (2)$$

This hypothesis is analogous to that advanced by Kekulé, Kolbe, von Baeyer and others[3] to explain reductions of organic substances with sodium amalgam and water.

II. The formation of tetrahydronaphthalene may also be attributed to a solvolytic action of the solvent upon an organo-alkali compound which was formed as an intermediate product.

$$C_{10}H_8 + 4Na \longrightarrow C_{10}H_8Na_4 \quad (3)$$

$$C_{10}H_8Na_4 + 4NH_3 \longrightarrow C_{10}H_{12} + 4NaNH_2 \quad (4)$$

This assumption is analogous to an alternative theory of amalgam reduction recently proposed by Willstätter, Seitz and Bumm.[4]

This reaction, therefore, is of especial interest as a test case for indicating the possibilities of wider application of the two general hypotheses.

Dipotassium[5] and dilithium[6] derivatives of naphthalene have been pre-

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[1] Paper presented at the Cincinnati meeting of the American Chemical Society, September, 1930.

[2] Lebeau and Picon, *Compt. rend.*, **158**, 1514 (1914).

[3] (a) Kekulé, *Ann. Suppl.*, **1**, 129 (1861); (b) Herrmann, *Ann.*, **132**, 75 (1864) (an account of work done in Kolbe's laboratory); (c) von Baeyer, *ibid.*, **269**, 145, 170, 174 (1892).

[4] Willstätter, Seitz and Bumm, *Ber.*, **61**, 871 (1928).

[5] Berthelot, *Ann.*, **143**, 98 (1867); *Ann. Suppl.*, **5**, 370 (1867); *Ann. chim.*, [4] **12**, 157, 205 (1867).

[6] Schlenk and Bergmann, *Ann.*, **463**, 83 (1928).

pared by the action of alkali metals on the pure hydrocarbon at elevated temperatures and on its solutions in organic solvents at room temperature, respectively, but thus far no similar derivatives containing a higher proportion of alkali metal have been reported. Preliminary observations indicated the formation of a compound between potassium and the hydrocarbon in liquid ammonia at lower temperatures, and, accordingly, a more detailed study of the reaction under these conditions was undertaken.

## Experimental Part

**Ratio of Sodium and Potassium to Naphthalene.**—It is an evident consequence of the second hypothesis outlined above that the maximum amount of sodium entering into reaction must bear a definite relation to the quantity of naphthalene used, whereas no such restriction is demanded by the first hypothesis. In attempting to determine the number of sodium atoms which react with a molecule of naphthalene, considerable experimental difficulties were encountered. It was equally difficult to titrate a known amount of sodium with naphthalene or a known amount of naphthalene with sodium because the reaction does not go to completion with ease. If an excess of sodium were used, titration with ammonium bromide to the disappearance of the blue color of the free metal would lead to erroneous results, since ammonium bromide would also react with a sodium compound of naphthalene. Advantage was taken of the fact that ammonium bromide reacts with free sodium to liberate hydrogen, whereas no hydrogen would be formed in its reaction with a sodium compound of naphthalene. This method was open to a possible source of error, since the hydrogen evolved might itself react with naphthalene or its reduction products, thus making the apparent sodium ratio too high. If ethyl bromide were used instead, the ethane evolved would not react with naphthalene or its reduction products, but the reaction between ethyl bromide and the organo-alkali compound might also generate gaseous products and indicate too low a sodium ratio.[7] However, if the same value were obtained by both methods, it would seem reasonable to suppose that these possible sources of error are merely hypothetical.

The apparatus employed was similar to that previously described.[8] It was found necessary, however, to alter the design of the reaction tube in order to promote complete reaction. The gaseous ammonia was admitted through an inlet at the very bottom of

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[7] Another possibility requiring consideration is that of gas formation between ethyl bromide and the sodium amide resulting from Reaction 1 or 4. However, ethyl bromide reacts but slowly with sodium amide in liquid ammonia at −40° and even in the more rapid reaction at room temperature, only small amounts of ethylene are formed [Picon, *Bull. soc. chim.*, **35**, 979–81 (1924)]. It may be expected, therefore, that ethylene would not be evolved in quantities too large to be removed by solution in the water over which the gases were collected.

[8] Wooster, THIS JOURNAL, **51**, 1859 (1929).

the reaction tube to insure vigorous stirring and the top of the reaction tube was fitted with a ground-in dropping funnel which permitted liquids or solutions to drip directly into the agitated reaction mixture.

The sodium was cut under petroleum ether, weighed under "Nujol," washed with petroleum ether, placed in the bottom of the reaction tube and ammonia condensed upon it. A suitable amount of pure, dry naphthalene was dissolved in a small quantity of dry toluene and the solution added slowly with vigorous stirring to the sodium solution after which the reaction mixture was stirred slowly with a stream of ammonia gas for a period of several hours. In Experiments 1 and 2, dry ammonium bromide was then added and the evolved gas collected over water. The greenish color of the reaction mixture was slowly discharged and gave way to a bright transparent red, after which no more gas was evolved upon further addition of ammonium bromide, although the red color eventually disappeared. The collected gas was dried and characterized by its density as hydrogen. In Experiments 3 and 4, pure, dry ethyl bromide was used instead of ammonium bromide to dissipate the free sodium. The procedure and observations were analogous to those just described except that the gas collected was found by its density to be ethane. In experiments using potassium instead of sodium, it was found that the amount of gas liberated by the action of ammonium bromide depended somewhat on the length of time the reaction was allowed to proceed. If sufficient time elapsed, the reaction mixture eventually turned red before ammonium bromide was added, and the action of this reagent did not result in the formation of any gas. This behavior is apparently due to a slow ammonolysis of the excess potassium, since hydrogen is evolved during the process. In Experiments 5 and 6 no ammonium bromide was added and hydrogen was collected from the very beginning of the reaction until the red color appeared, when the evolution of gas ceased. The results of these experiments appear in Table I.

TABLE I

RATIO OF SODIUM AND POTASSIUM TO NAPHTHALENE

| No. | Metal, g. | $C_{10}H_8$, g. | Gas, cc. | Na or K consumed, atoms/mole of $C_{10}H_8$ |
|---|---|---|---|---|
| 1 | 0.4585 (Na) | 0.5609 | 35.65 ($H_2$) | 3.83 |
| 2 | 2.6411 (Na) | 2.9468 | 315.1 ($H_2$) | 3.77 |
| 3 | 2.0620 (Na) | 2.3040 | 181.0 ($C_2H_6$) | 4.09 |
| 4 | 1.6240 (Na) | 1.6628 | 204.1 ($C_2H_6$) | 4.04 |
| 5 | 1.6158 (K) | 1.0037 | 128.4 ($H_2$) | 3.81 |
| 6 | 1.4161 (K) | 0.9021 | 114.4 ($H_2$) | 3.70 |

It seems evident from the first four values in column five that only four atoms of sodium per molecule of naphthalene react regardless of the quantity of excess metal present and (within reasonable limits) of the time elapsed, the somewhat low values obtained in the first two experiments being doubtless due to the presence of small amounts of hydrogen in the ammonia, incident to the previous drying of this solvent with sodium. This is decidedly in favor of the second mechanism, outlined in the introduction, and it may be concluded that the four sodium atoms primarily add to a molecule of naphthalene.

The last two values in column five indicate that approximately four equivalents of potassium per mole of naphthalene reacted without the formation of gaseous products. Although in this case the gradual ammonolysis of the potassium[9] prevents a discrimination between the two mechanisms on the basis of the quantitative results, the formation of the characteristic transparent red solution strongly suggests the presence of an organo-alkali compound.

**Identification of the Product of Hydrolysis of the Sodium Derivative.**—Although the evidence presented above indicates that four atoms of sodium react with each molecule of naphthalene, it does not indicate which positions the sodium atoms enter. Accordingly, the hydrolysis product of the sodium compound was prepared and its properties studied for the purpose of identification.

Twenty-three grams of sodium was dissolved in liquid ammonia in a large Dewar flask equipped with a mechanical stirrer;[10] 30 g. of naphthalene, or slightly less than one molecule to every four atoms of sodium, was then added slowly in ether solution and the reaction mixture stirred for twenty-four hours. Ammonium bromide was added in excess and after the ammonia had been allowed to evaporate, the Dewar flask was washed out with water. The oil which separated was taken up in ether and the aqueous solution extracted with this solvent. The combined ethereal extracts were dried over sodium hydroxide and evaporated on a water-bath leaving a yellow oil which was carefully distilled *in vacuo*. A colorless, highly refractive oil boiling at 50–55° under less than 1 mm. pressure constituted the main reaction product. This substance did not react with solutions of bromine in carbon tetrachloride at room temperature and the reaction which occurred upon heating with liquid bromine was accompanied by the evolution of hydrobromic acid. These facts distinguish the product from the dihydronaphthalenes and, accordingly, it was compared with a carefully distilled sample of commercial tetralin. Both substances, independently and when mixed, boiled at 207–207.5° under 753 mm., and the density of both was $0.965 \pm 0.0005$ at 25°. Since tetralin has been demonstrated to be 1,2,3,4-tetrahydronaphthalene,[11] the four sodium atoms must add in the 1,2,3,4 positions.

**Observations Indicating Ammonolysis.**—When the residue from the evaporation of ammonia from the sodium and naphthalene reaction mixture was heated by surrounding the evacuated reaction tube with a steam jacket, a liquid distilled and collected in drops on the cool upper walls of the tube. This circumstance indicates the formation of tetrahydronaphthalene by ammonolysis at higher temperatures and accounts for the fact that Lebeau and Picon were able to obtain this substance directly from the interaction of sodium and naphthalene.

It remained to be determined whether in liquid ammonia at its boiling point the tetrasodium tetrahydronaphthalene was entirely stable or whether it was partly ammonolyzed. The following observation suggested the latter to be the case. When oxygen was passed through the reaction mixture the presence of nitrite ions in the residue could be shown by a qualitative test with potassium iodide, hydrochloric acid and carbon

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[9] This action may well be ascribed to the catalytic influence of the potassium amide formed in the ammonolysis of the potassium compound of naphthalene [unpublished observations of one of the authors (C. B. W.)]. Sodium amide exerts a similar influence upon the ammonolysis of sodium [Kraus, THIS JOURNAL, **29**, 1569 (1907)], but this reaction is too slow to interfere with the experiments described.

[10] This apparatus has been previously described [Wooster and Mitchell, *ibid.*, **52**, 691 (1930)].

[11] Schroeter, *Ann.*, **426**, 83 (1922).

disulfide. This proves the presence of sodium amide in the original solution since it is oxidized under these conditions with formation of sodium nitrite.[12]

**Quantitative Study of the Ammonolysis.**—Although it is true that the occurrence of ammonolysis would result in an increase in weight of the reaction residue, this fact does not serve as a basis for a suitable method of attacking the problem under consideration. Apart from the errors introduced by the volatility of the products, it is evident that the increase in weight exhibited by the contents of a reaction tube which has been evacuated after it has attained room temperature will be determined by the state of equilibrium characteristic of the residue at room temperature and not of the solution in liquid ammonia at its boiling point. If, on the other hand, the tube is evacuated at the temperature of boiling ammonia, the equilibrium may be displaced during the evaporation of the solvent and the result may also be influenced by the weight of solvent retained as ammonia of crystallization.

Consequently, a method of analysis was sought which could be applied directly to the liquid ammonia solutions. No such method was found which was capable of precision, but a procedure was developed which provided approximate values of the degree of ammonolysis. This procedure was based upon a study of the products formed in oxidizing the reaction mixture. Rengade,[12] by leading oxygen into solutions of cesium, potassium and sodium amides in liquid ammonia, found oxidation to take place according to the equation,

$$2MNH_2 + 1^1/_2O_2 = MOH + MNO_2 + NH_3 \quad (M = Cs, K \text{ or } Na) \qquad (5)$$

The oxidation of metallic sodium in liquid ammonia yields the peroxide, $Na_2O_2$.[13]

According to Kraus and Rosen[14] sodium peroxide and triphenylmethyl peroxide may be obtained by the oxidation of sodium triphenylmethide in liquid ammonia. It is reasonable to suppose that the sodium or potassium in combination with naphthalene would also be oxidized to the peroxide. Thus if a reaction mixture contained sodium amide, a sodium hydronaphthalene and free sodium, the inorganic oxidation products should be sodium nitrite, sodium hydroxide and sodium peroxide. Since the oxidation of the materials in solution is reasonably rapid, and since both the organo-alkali compound and the alkali metal amide are simultaneously attacked and destroyed, displacement of the ammonolytic equilibrium would be minimized, and it might be expected that a determination of the amounts of nitrite and peroxide formed would furnish an approximate estimate of the degree of ammonolysis.

[12] Rengade, *Ann. chim. phys.*, **11**, 348 (1907).

[13] Kraus and Whyte, THIS JOURNAL, **48**, 1781 (1926).

[14] Kraus and Rosen, *ibid.*, **47**, 2739 (1925).

The sodium peroxide was separated from sodium nitrite by treating the ice-cold aqueous solution of the residue left after oxidation and subsequent evaporation of the ammonia, with an ice-cold solution of barium chloride, as described by Schrader.[15] The precipitate of barium peroxide was separated by filtration, washed, dried and analyzed. The filtrate was then analyzed for nitrite ions.

The method of nitrite analysis used was that developed by Gerlinger,[16] in which the nitrite solution is boiled with a concentrated solution of ammonium chloride in an atmosphere of carbon dioxide, and the nitrogen evolved is collected over potassium hydroxide solution. The amount of nitrite is calculated from the amount of nitrogen liberated, according to the equation

$$NH_4Cl + MNO_2 \longrightarrow MCl + 2H_2O + N_2 \qquad (6)$$

A method of peroxide determination was developed in which the solid barium peroxide was added to a strong solution of potassium iodide, strong hydrochloric acid added, and the liberated iodine titrated with standard thiosulfate solution. Calculations were based on the equation

$$BaO_2 + 4HCl + 2KI + 2Na_2S_2O_3 \longrightarrow 2H_2O + BaCl_2 + 2KCl + 2NaI + Na_2S_4O_6 \qquad (7)$$

In order to determine how nearly quantitatively potassium and sodium amides were oxidized under the conditions of the experiments, potassium was converted to the amide, oxidized and the products analyzed. Sodium was converted partially to the amide, the mixture of amide and free metal oxidized and the products analyzed. (The extent of the ammonolysis was in each case determined by collecting the hydrogen formed.) The results are indicated in Table II, where all amounts are given in milliatoms or millimoles.

TABLE II

OXIDATION OF SODIUM AND POTASSIUM AMIDES

| No. | Metal | Amount | Amide formed | Nitrite Found | Nitrite Calcd. | Peroxide Found | Peroxide Calcd. |
|---|---|---|---|---|---|---|---|
| 1 | Potassium | 26.5 | 25.6 | 10.6 | 12.8 | None | None |
| 2 | Potassium | 31.3 | 30.3 | 12.8 | 15.2 | None | None |
| 3 | Sodium | 47.7 | 30.2 | 12.0 | 15.1 | 0.14 | 17.5 |

In the following experiments a slight excess over four atoms of alkali metal was allowed to react with each molecule of naphthalene. In the case of potassium, the excess metal was converted to the amide before oxidation. Excess sodium was left as free metal before oxidation. The results of several experiments are summarized in Tables III and IV, where all corrected values are calculated by the use of the data in Table II. All quantities are given in milliatoms or millimoles.

The corrected amount of sodium amide formed by ammonolysis of the organo-alkali compound is given in column six. In the experiment re-

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[15] Schrader, *Z. anorg. Chem.*, **108**, 44 (1919).

[16] Gerlinger, *Z. angew. Chem.*, **50**, 1250 (1901).

TABLE III

OXIDATION OF SODIUM COMPOUND, FREE SODIUM AND SODIUM AMIDE

| No. | Sodium | $C_{10}H_8$ | Nitrite | Amide<br>Found | Corr. | Peroxide | Free metal | Sodium compound |
|---|---|---|---|---|---|---|---|---|
| 1 | 43.06 | 10.07 | 12.46 | 24.92 | 31.15 | 9.05 | 2.78 | 9.03 |
| 2 | 57.23 | 14.00 | 17.82 | 35.64 | 44.05 | 9.39 | 1.23 | 9.38 |

corded in Table II very little peroxide was obtained from the oxidation of the free metal; accordingly the major portion of the peroxide obtained in these oxidations was ascribed to the oxidation of the organo-alkali compound, as may be seen upon examination of column nine. The results indicate that of the four sodium atoms which are known to react with naphthalene, 3.09 and 3.15 are converted into sodium amide by the solvent while 0.90 and 0.67 atoms appear definitely to remain in combination with the naphthalene.

TABLE IV

OXIDATION OF POTASSIUM COMPOUND AND POTASSIUM AMIDE

| | | | | Amide | | | | |
|---|---|---|---|---|---|---|---|---|
| No. | Potassium | $C_{10}H_8$ | Nitrite | Found | Corr. | From excess | From ammonolysis | Peroxide |
| 1 | 27.4 | 6.5 | 7.9 | 15.8 | 18.8 | 1.4 | 17.4 | 0.4 |
| 2 | 27.1 | 6.5 | 8.4 | 16.6 | 19.8 | 1.1 | 18.7 | .5 |

The values in column eight represent the amounts of potassium amide presumably resulting from ammonolysis of tetrapotassium tetrahydronaphthalene. They correspond to 2.68 and 3.04 molecules per molecule of naphthalene, respectively. As no free metal was present during the oxidation in these experiments, the peroxide[17] could only result from the oxidation of an organo-alkali compound. Thus the existence of peroxide in the oxidation products together with the observation of the characteristic red color, previously noted, constitute definite evidence of the presence of an organo-alkali compound in the reaction mixture. Furthermore, the approximate correspondence between the results given in Tables III and IV indicates that the reaction between potassium and naphthalene is not essentially different from that which takes place when sodium is used.

## Discussion

The evidence presented in this paper shows that the reduction of naphthalene with sodium in liquid ammonia takes place through the intermediate formation of a 1,2,3,4-tetrasodium addition product which is

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[17] The low values for the peroxide given in the table may to a large extent be ascribed to the fact that potassium peroxide is capable of further oxidation under the conditions of these experiments and that the higher oxides so formed might escape notice in the analytical procedure employed. In contrast to these low peroxide values, but in agreement with the amounts of amide formed, the general behavior of alkali metal amides in liquid ammonia suggests that the potassium compounds would be less susceptible to ammonolysis than the corresponding sodium compounds.

approximately three-fourths ammonolyzed even in solution at −33.5°. This confirms the mechanism derived by an extension to this case of the theory proposed by Willstätter, Seitz and Bumm[4] to explain amalgam reductions.

It is of interest to note that of the compounds which were also found by Lebeau and Picon[18] to be reduced to hydro derivatives with formation of sodium amide: anthracene,[19] phenanthrene, biphenyl,[20] stilbene and phenylethylene[21] have been found to yield addition products with the alkali metals or with organo-alkali compounds, whereas the compounds which failed to undergo such a reduction (amylene, benzene, toluene, cymene, terpinene, terpinoline, carvene, terebene, $\alpha$-pinene and menthene) have not as yet been found capable of adding the alkali metals, although several have been specially investigated with this point in view.[22] This coincidence cannot fail to suggest that these other reductions observed by Lebeau and Picon proceed by means of a mechanism similar to that just demonstrated to operate in the reduction of naphthalene.

It is perhaps also worth mention that whereas catalytic reduction of naphthalene always yields a tetrahydro or more highly hydrogenated derivative,[23] the reducing action of sodium in alcohol[24] may also yield a dihydro derivative in which the additional hydrogen atoms occupy the same positions (1,4) as do the alkali metal atoms in the dilithium and dipotassium addition products which have been prepared. Here again the postulate of an intermediate organo-alkali compound in the reduction process is in harmony with the evidence available.

## Summary

1. It has been shown that the reduction of naphthalene with sodium in liquid ammonia takes place through the intermediate formation of a 1,2,3,-4-tetrasodium addition product, which is approximately three-fourths ammonolyzed even in solution at −33.5°.

2. The reaction with potassium apparently follows essentially the same course as that with sodium.

3. These facts confirm the mechanism derived by extending to this reaction the theory proposed by Willstätter, Seitz and Bumm to explain reductions of organic compounds with sodium amalgam and water.

4. Certain facts have been pointed out which suggest a similar mecha-

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[18] Lebeau and Picon, *Compt. rend.*, **157,** 223 (1913); *ibid.*, **159,** 70 (1914).

[19] Schlenk and Bergmann, *Ann.*, **463,** 98–227 (1928).

[20] Schlenk and Bergmann, *ibid.*, **463,** 2–97 (1928).

[21] Ziegler, Crossmann, Kleiner and Schäfer, *ibid.*, **473,** 1 (1929).

[22] Unpublished observations of one of the authors (C. B. W.).

[23] (a) Leroux, *Compt. rend.* **139,** 673 (1904); *Ann. chim.*, [8] **21,** 465, 466 (1910). (b) Sabatier and Senderens, *Compt. rend.*, **132,** 1257 (1901).

[24] Bamberger and Lodter, *Ber.*, **20,** 1703 (1887).

nism for the reduction of other aromatic compounds by sodium in liquid ammonia and for the reduction of naphthalene by sodium in ethyl alcohol.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF IOWA STATE COLLEGE]

# SYNTHESIS OF SOME NEW COMPOUNDS IN THE PYRROLE AND PYRROLIDINE SERIES

BY LYMAN C. CRAIG WITH R. M. HIXON

RECEIVED JULY 28, 1930 PUBLISHED JANUARY 12, 1931

A previous paper[1] reported the preparation of pyrrolidine, N-phenylpyrrolidine and N-cyclohexylpyrrolidine. In extending the series for the contemplated study of insecticidal action and physical properties, the benzyl, methyl, butyl and *p*-tolyl derivatives were desired.

The aliphatic N-substituted derivatives can be prepared by the general method of Britton[2] or by addition of RX to the free base. Contrary to the literature[3] the yield by the latter method is low due to the formation of the quaternary derivative. The general method to be recommended for the preparation of N-substituted derivatives where R is a saturated aliphatic radical is to prepare the N-substituted pyrrole and reduce it catalytically as pyrrole was reduced. The presence of excess acid is necessary for a successful reduction. Substitution on the nitrogen appears to stabilize the ring toward polymerization by acid, eliminating the difficulty encountered with the carbon substituted derivatives.[4] J. P. Wibaut[5] reduced methylpyrrole catalytically with Adams and Shriner catalyst in glacial acetic acid, but his reduction required large amounts of catalyst and shaking for a long period of time. If alcohol acidified with hydrochloric acid is used as a solvent, the reduction requires only 0.2 g. of catalyst and is complete in three hours. The same catalyst may be used several times. N-Methylpyrrole has also been reduced successfully to N-methylpyrrolidine by passing its vapor over palladium[6] at 160°.

Tadeus Reichstein[7] gave a method for the characterization of N-substituted pyrroles by the use of a diazo reaction. Reduction can also be used for this purpose since the yield is practically quantitative and the resulting pyrrolidine derivative can easily be identified as the picrate.

In the N-butylpyrrole synthesis the formation of the substituted acid

[1] Craig and Hixon, THIS JOURNAL, **52**, 804 (1930).

[2] E. C. Britton, U. S. Patent 1,607,605, Nov. 23, 1926.

[3] Schlinck, *Ber.*, **32**, 952 (1899); Ciamician and Magnaghi, *ibid.*, **18**, 2079 (1885).

[4] Anderson and McElvain, THIS JOURNAL, **51**, 887 (1929).

[5] Wibaut, *Rec. trav. chim.*, **44**, 1101–5 (1925); Dejong and Wibaut, *ibid.*, **49**, 237 (1930).

[6] Zelinsky and Jerjew, *Ber.*, **62**, 2589 (1929).

[7] Reichstein, *Helv. Chim. Acta*, **10**, 387 (1927).