of furans and for the preparation of new and hitherto inaccessible types, particularly iodofurans. Attention is directed to essential differences in reactivities between α- and β-substituted furans.

AMES, IOWA
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

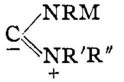
Attempts to Prepare Some Nitrogenous Derivatives of Divalent Carbon[1]

BY DENNISTOUN WOOD, JR., AND F. W. BERGSTROM

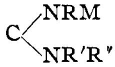
Introduction

The Nef formula for hydrocyanic acid, HN=C, represents, according to Franklin,[2] an ammono (meta) carbonous acid, and it was indeed found that many of its chemical properties are in harmony with this view.[3] Granting the existence of an ammonometacarbonous acid—at least in the form of its esters, the isocyanides—it appears not unreasonable to anticipate the existence of derivatives of ammonoorthocarbonous acid, $C(NH_2)_2$, in which at least three of the hydrogen atoms are replaced by alkyl or aryl groups.

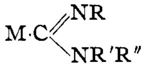
In casting about for a method of synthesizing this class of compounds, we were interested by Scheibler's announcement[4] of the preparation of carbon monoxide diethylacetal, $C(OC_2H_5)_2$, (a diethyl aquocarbonite) which may be made from ethyl formate as a starting material. On the basis of analogy, it would logically follow that the esters of ammono orthocarbonous acid might similarly be prepared from substituted formamidines, $H{\cdot}C({=}NR)NR'R''$, that is, from esters of an ammonoformic acid, $H{\cdot}C({=}NH)NH_2$. To this end it was first desired to prepare metallic salts of a number of substances of this type, which would correspond to one or more of the structures[5]



$$\overset{-}{C}\begin{cases}NRM\\ \overset{+}{N}R'R''\end{cases}$$



$$C\begin{cases}NRM\\ NR'R'\end{cases}$$



$$M{\cdot}C\begin{cases}{=}NR\\ NR'R''\end{cases}$$

(M is a monovalent metal)

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(1) Abstracted from the doctoral dissertation of Dennistoun Wood, Jr., Stanford University, 1930.

(2) Franklin, *J. Phys. Chem.*, **27**, 167–186 (1923).

(3) It is of course recognized at the present time that this tautomer represents only a very minor proportion of ordinary hydrocyanic acid.

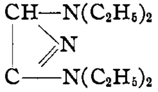
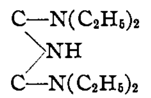
(4) Scheibler, *Ber.*, **59**, 1022–1032 (1926); **60**, 554–557 (1927); *Z. angew. Chem.*, **40**, 1072–1081 (1927).

(5) Within the past few years an increasing tendency has been noted to discard the older ideas of divalent carbon and ascribe to substances of this class formulas in which the carbon and nitrogen are united by three conventional non-polar single bonds and by one electrovalency, as in $^{-}C{\equiv}O^{+}$. (a) Langmuir, THIS JOURNAL, **41**, 903 (1919); (b) Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Co., New York, 1923, p. 127; (c) Sugden, "The Parachor and Valency," Routledge and Sons, 1930, p. 171; (d) Hammick, New, Sidgwick and Sutton, *J. Chem. Soc.*, 1876–1887 (1930); (e) Lindemann and Wiegrebe, *Ber.*, **63**, 1650 (1930). Pauling [*Proc. Natl. Acad. Sci.*, **18**, 294 (1932); THIS JOURNAL, **54**, 1000–1001 (1932)] regards carbon monoxide as a resonance mixture of the two forms, $^{-}C{\equiv}O^{+}$ and $C{=}O$, of which the first is the more important.

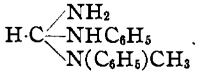
and which could be converted, by the action of alkyl halides, etc., into nonionic compounds that would show the reaction of derivatives of divalent carbon.

Unfortunately, we were unable to obtain salts of the carbonous form of any of the trisubstituted formamidines examined, because of the pronounced tendency of metallic amides in liquid ammonia to add to the parent compound to form substances which are very probably derivatives of ammono orthoformic acid, $H \cdot C(NH_2)_3$.

Preliminary Experiments

As an introduction to this investigation, a number of fruitless attempts were made to prepare carbon monoxide diethylacetal according to Scheibler's directions, but we are forced to conclude with Arbuzov[6] that the preparation offers insuperable difficulties. We were likewise unable to prepare a specimen of Pinner's compound,[7] $(C_{10}H_{21}N_3 \cdot HCl)_2 \cdot PtCl_4$, to the base of which he ascribed the formula,  $\begin{array}{l} CH{-}N(C_2H_5)_2 \\ \mid \quad \rangle N \\ C{-}N(C_2H_5)_2 \end{array}$ a structure which might conceivably be  $\begin{array}{l} C{-}N(C_2H_5)_2 \\ \quad \rangle NH \\ C{-}N(C_2H_5)_2 \end{array}$

Attempts to prepare dipotassium carbonite, $C(OK)_2$, and potassium ethyl carbonite, $C(OK)(OC_2H_5)$, in liquid ammonia by the action of potassium amide upon formic acid and ethyl formate, respectively, failed. In the latter case, mixtures were obtained which were composed of the potassium salts of the products of ammonolysis of the ester.[8]

Diphenylmethylformamidine, $C_6H_5N{=}CH{-}N(CH_3)C_6H_5$.—The alkali and alkaline earth amides fail to convert diphenylmethylformamidine in liquid ammonia solution to salts of the "carbonous" modification, but yield instead salts which may be formulated as derivatives of an ammono-orthoformic acid,  $H \cdot C \begin{cases} NH_2 \\ NHC_6H_5 \\ N(C_6H_5)CH_3 \end{cases}$. Hydrolysis of these salts produces methylaniline as well as the original diphenylmethylformamidine and smaller quantities of unidentified solid reaction products. Neither aniline nor methylamine was obtained. It may be remarked that liquid ammonia itself does not decompose diphenylmethylformamidine.

Diphenylmethylformamidine was prepared from methylaniline and formanilide:[9] specific gravity, 1.095 24°/0°; b. p. 335–340°, uncorr., at 760 mm. (215.5–6.5° at 24 mm.) with slight decomposition; viscous golden-yellow oil, solidifying to a glass at −78°; picrate, golden-yellow crystals from alcohol, m. p. 152–2.5° (dec.) uncorr.

The reaction between calcium amide and diphenylmethylformamidine will serve as an illustration of the method by which the data in Table I were obtained. In the two

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(6) Arbuzov, *Ber.*, **64**, 698–700 (1931); *cf.* Adickes, *ibid.*, **60**, 272–277 (1927); **63**, 3012–3027 (1930); Scheibler, *ibid.*, **64**, 2914–2916 (1931).

(7) Pinner, *ibid.*, **16**, 1650–1651 (1883); **17**, 179–182 (1884); "Die Imidoaether und ihre Derivative, Oppenheim, Berlin, p. 103–104 (1902).

(8) Titherley, *J. Chem. Soc.*, **81**, 1522 (1902), has reported his inability to prepare a sodium salt of ethyl formate in benzene.

(9) Wheeler and Johnson, *Am. Chem. J.*, **20**, 859 (1898).

legs of a liquid ammonia reaction tube[10] were placed, respectively, 4.4 g. (1 mol) of diphenylmethylformamidine and 1.0 g. of metallic calcium (1.2 atoms) together with a coil of iron wire to serve as a catalyst for the conversion of the metal to amide. This having been accomplished, the liquid ammonia solution of the diphenylmethylformamidine was washed over into the calcium amide leg, whereupon most of this material dissolved. After standing for several days, the solution was carefully decanted from the unused calcium amide into the clean leg of the reaction tube, then concentrated and refrigerated at −78° (carbon dioxide snow–acetone) until yellow crystals appeared. These were freed of mother liquor, and then recrystallized. The specimen was prepared for analysis in the usual manner, after heating in a vacuum at 75° to remove ammonia. The product solidified to a glassy yellow froth. Nitrogen was estimated by the Kjeldahl method, calcium was weighed as sulfate, the specimen having previously been dissolved in dilute hydrochloric acid. Diphenylmethylformamidine, recovered from the solution, was identified by its boiling point in a known vacuum, and by the preparation and analysis of its chloroaurate. Methylaniline, formed at the same time, was identified by its specific gravity, by the reaction of its hydrochloric acid solution with sodium nitrite, and by the preparation and analysis of tetranitromethylaniline (mixed m. p. determined). There was also obtained a solid amorphous substance, which yielded a picrate, m. p. 146.5° (dec.) uncorr. The other salts were prepared in the same manner, and the products of hydrolysis similarly identified.

TABLE I

DERIVATIVES OF DIPHENYLMETHYLFORMAMIDINE[a,b]

Metallic amide, mols used	Analysis, % Metal	Analysis, % N	Calculated, % Metal	Calculated, % N	Probable structure[e]
$Ca(NH_2)_2$ (1.2)	13.2	16.7	15.1	15.8	PhNHCH(NCa)R
$Ba(NH_2)_2$[b] (1.2)	38.3	11.4	37.9	11.6	PhNHCH(NBa)R
$Ba(NH_2)_2$[b] (1.75)	45.7	11.0	47.9	9.8	PhNBa($^1/_2$)CH(NBa)R
$Ba(NH_2)_2$[b] (1.75)	44.9	10.8			
$NaNH_2$ (8.7)	19.4	15.4	17.0	15.5	$PhNHCH(NNa_2)R$
KNH_2[c] (excess)	Deep red solution, could crystallize nothing				
$AgNH_2$[d] (1)	48.6	8.8	48.9	9.5	$PhNHCH(NAg_2)R$

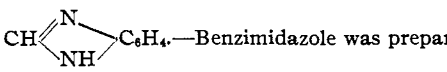
[a] One mol proportion of diphenylmethylformamidine in each of these expts.

[b] One part of diphenylmethylformamidine dissolves in two parts of liquid ammonia at 20°. This solution separates into two phases on cooling to −40°, as do the solutions of the two barium salts.

[c] No N_2 or H_2 liberated in this reaction. Another derivative of formic acid, formamide, does liberate hydrogen in reacting with an excess of potassium amide. Miss R. V. Fulton, Dissertation, Stanford University, 1925.

[d] $AgNH_2$ itself was not used. One mol proportion of AgI was slowly added to an ammonia solution of 1.5 mol proportions of diphenylmethylformamidine and 1 mol proportion of KNH_2 at 0°. Dark gray cryst. meal, after removal of NH_3 at 100°. Precipitation of the compound at higher temperatures gave mixtures containing $AgNH_2$.

[e] Ph = C_6H_5, R = $-N(CH_3)C_6H_5$.

Benzimidazole,  $CH\begin{matrix}\diagup N \diagdown \\ \diagdown NH \diagup\end{matrix}C_6H_4$.—Benzimidazole was prepared from *o*-phenylenediamine and formic acid[11] while the *o*-phenylenediamine was made by reducing *o*-nitroaniline.[12] The salts of benzimidazole were prepared as were the salts of diphenyl-

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(10) Franklin, THIS JOURNAL, **27**, 831–833 (1905); **35**, 1460–1462 (1913); *J. Phys. Chem.*, **15**, 511–517 (1911), and other articles.

(11) Wundt, *Ber.*, **11**, 826–827 (1878).

(12) Hinsberg and König, *ibid.*, **28**, 2947 (1895).

methylformamidine (see Table II). An excess of amide was used in each case. Benzimidazole was recovered from the products of hydrolysis of the salt.

TABLE II

SALTS OF BENZIMIDAZOLE[a]

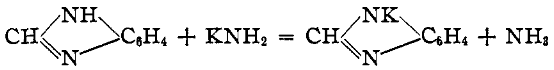
Metallic salt	Heated in a vacuum at ()°	Analyses, % Metal	Analyses, % N	Calculated, % Metal	Calculated, % N	Formula
Na	20	18.1	21.0	16.4	20.0	$C_7H_5N_2Na$
Li	20	4.38		4.39		$C_7H_5N_2Li \cdot 2NH_3$
	20	4.25				
	90	4.69		4.92		$C_7H_5N_2Li \cdot NH_3$
	200	5.14		5.24		$C_7H_5N_2Li \cdot {}^1/_2NH_3$
Ba	23	35.0		35.4		$(C_7H_5N_2)_2Ba \cdot NH_3$
	97	37.8		37.0		$(C_7H_5N_2)_2Ba$
K	Salt extremely soluble, could not be crystallized.					

[a] Sodium amide is soluble to the extent of about 1 g. per liter in liquid ammonia at room temperatures. If the calculated amount of free sodium amide in the solution of the salt is taken into consideration, the Na and N analyses are reduced approximately to the theoretical values.

All of the salts listed in the table were readily soluble in ammonia, with the exception of the barium salt. This was freed from the excess barium amide by repeated extractions with ammonia.

Benzimidazole in liquid ammonia solution at −33° reacted with excess sodium metal to yield 1.002 equivalents of hydrogen, proving the formation of a monosodium salt alone. At room temperatures, 0.920 equivalent of hydrogen was liberated, indicating the formation of small amounts of reduction products, although only benzimidazole could be recovered on hydrolysis.[13]

Evidence for the existence of a monopotassium salt of benzimidazole was obtained by determining the loss in weight of ammonia that occurred in the reaction between potassium amide and benzimidazole.[14]

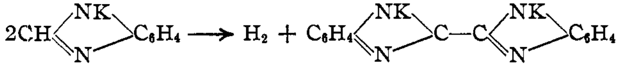


(1)

Experimental

Reaction I.—0.4243 g. benzimidazole (1 mol), 4 mol proportions of KNH_2, tube evacuated at 20°. 0.0468 g. NH_3 lost (0.766 mol).

Reaction II.—0.8722 g. benzimidazole (1 mol), 2.15 mol proportions of KNH_2, tube evacuated at 20, 88, 190–5°. NH_3 loss in mols, respectively, 0.837, 1.036, 1.345. In addition, 0.502 mol H_2 was obtained during evacuation at 190–195°. Because of the simultaneous evolution of ammonia at this temperature, the reaction is more complex than the following equation indicates.[15]



(not isolated)

Reaction III.—Monopotassium benzimidazole, prepared without excess potassium amide, may be heated in a vacuum to 260° with only slight discolorization. Most of

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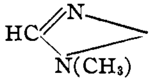
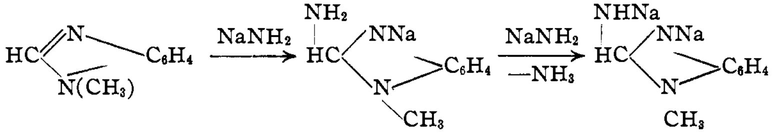
[13] Bamberger and Lorenzen [*Ann.*, **273**, 270, 277 (1893)] were unable to reduce benzimidazole to dihydrobenzimidazole.

[14] Bergstrom, THIS JOURNAL, **53**, 4068–4070 (1931).

[15] *Cf.* the instability of HCOONa when heated with excess NaOH. Merz and Weith, *Ber.*, **15**, 1507–1513 (1882); German Patents abstracted in *Chem. Zentr.*, II, 777 (1903); II, 367 (1905).

the benzimidazole can be recovered unchanged. Potassium benzimidazole is soluble in dry *n*-butylamine.

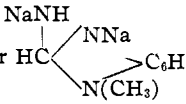
N-Methylbenzimidazole,  $HC\langle{}^{N}_{N(CH_3)}\rangle C_6H_4$.—N-methylbenzimidazole is a neutral ester of ammonoformic acid. Treated in liquid ammonia solution with sodium amide, there is formed a salt which is probably an ammono-orthoformate.

 (2)

Hydrolysis yields the original N-methylbenzimidazole. That this substance partakes of the aldehydic nature of formic acid is demonstrated by its reduction of a liquid ammonia solution of silver iodide to metallic silver in the presence of potassium amide (no reaction occurs in the absence of KNH_2).

N-Methylbenzimidazole was prepared by several methods, that of Skraup[16] being by far the best. The compound is pale yellow when hot, but colorless when cold. It rapidly darkens in contact with the air, and may be supercooled as much as 70° without immediate crystallization. It is very soluble in liquid ammonia at room temperatures, although it may be crystallized at −78°.

Sodium amide dissolves, to the extent of over two equivalents, in a liquid ammonia solution of N-methylbenzimidazole with the evolution of a slight amount of heat, no nitrogen or hydrogen being produced in the reaction. Cooling to −78° causes the slow precipitation of thick yellow crystals but supercooling is very persistent. Repeated recrystallizations are necessary to secure a homogeneous product, the contamination presumably being by a more soluble salt, richer in sodium. Prior to analysis, the salt was dried in a vacuum at 50–70°, being thereby obtained as a pale yellow powder.

Anal. Calcd. for  $HC(NaNH)\langle{}^{NNa}_{N(CH_3)}\rangle C_6H_4$: Na, 23.9; N, 21.8. Found: Na, 25.6, 28.4, 27.8; N, 24.1, 23.8, 24.9;[17] Na, 26.6 dried in a vacuum at 20°; the same, dried in a vacuum at 100°, Na, 27.4.

That the reaction roughly follows the course of equation (2) is indicated by a determination of the loss of ammonia during the reaction.[14] One mole (0.7169 g.) of N-methylbenzimidazole was treated with 3.6 mol proportions of sodium amide. The total loss of ammonia was 0.935 mol (tube evacuated at 23°) and 1.052 mol (tube evacuated at 65–70°). Hydrolysis of this salt as well as of the others described here gives the original N-methylbenzimidazole without the formation of methylamine.

Potassium amide reacts with N-methylbenzimidazole in liquid ammonia to produce a dark red solution, from which nothing can be crystallized. N-Methylbenzimidazole may be recovered unchanged by hydrolysis of the mixture. Neither calcium amide nor metallic magnesium dissolves in a liquid ammonia solution of N-methylbenzimidazole.

Summary

1. This paper reports a number of experiments designed to prove or

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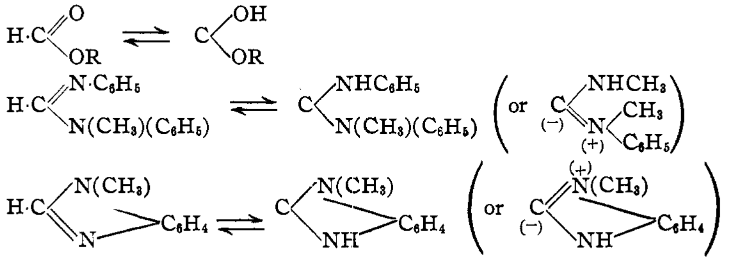
[16] Skraup, *Ann.*, **419**, 72 (1919).

[17] The average of the first three of these analyses is higher than the calculated by N, 2.5, Na, 4.0. The ratio, 2.5/4.0, is very nearly that of N to Na in $NaNH_2$, an impurity which was concentrated during the repeated crystallizations.

disprove the existence of the tautomerism between the derivatives of formic acid and carbonous acid represented in the equations



It was hoped that the hydrogen atoms in the "carbonous acid" formulas on the right would be sufficiently acidic to react with the metallic amides in liquid ammonia to form salts which would clearly show the reactions of derivatives of divalent carbon. No such expectations were realized, because of the more pronounced tendency of the metallic amides to add to the double bond between the carbon and nitrogen, of compounds represented by the two lower formulas in the left-hand column.

2. Ethyl formate is not converted to a potassium salt by the action of potassium amide in liquid ammonia, nor is formic acid converted to a dipotassium salt.

3. Only one hydrogen atom of benzimidazole can be replaced by a metal in liquid ammonia, in agreement with the accepted formula.

STANFORD UNIVERSITY, CALIFORNIA

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The Composition of Lemon Albedo Pectin[1]

BY CATHERINE M. BRIDGHAM AND C. G. KING

Substances containing sugars combined with uronic acids have lately been found to occur widely, comprising the chief structural material of plant gums, mucilages, hemicelluloses, pectins, bacterial gums, etc. Their biological and industrial importance clearly justifies intensive study of their chemical nature. The recent identification of vitamin C as a six-carbon sugar acid[2] has added to the interest in this group of substances. Lemon pectin has become an important commodity in the recovery of by-products from the citrus fruit industry.

Identification of Structural Units.—Fresh lemon albedo (white portion of peel) was partially purified by alcohol and ether extraction, after which the pectin was ex-

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[1] This paper is based upon a thesis submitted by Catherine M. Bridgham to the Graduate School of the University of Pittsburgh in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Waugh and King, *J. Biol. Chem.*, **97**, 325 (1932); *Science*, **75**, 357 (1932); *ibid.*, **76**, 630 (1932); Svirbely and Szent-Gyorgi, *Biochem. J.*, **26**, 865 (1932); *Nature*, **129**, 576 (1932).