On the Mechanism of the Conversion of 6-Chloropyrido[2,3-*b*]pyrazine into 1*H*-Imidazo[4,5-*b*]pyridine by Potassium Amide in Liquid Ammonia (1,2)

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The synthesis of a number of 2-R_1, 3-R_2-6-X-pyrido[2,3-*b*]pyrazines (**1**) is reported and their reaction with potassium amide in liquid ammonia investigated. Ring contraction into a 2-R-1*H*-imidazo[4,5-*b*]pyridine was found to occur with X = Cl, R_1 = H, R_2 = C_6H_5 (**1b**); X = Cl, R_1 = R_2 = C_6H_5 (**1c**); X = Cl, R_1 = H, R_2 = *t*-C_4H_9 (**1d**). Besides ring contraction, an increasing amount of dechlorination of **1** was found: **1a**, 20%; **1b**, 30%; **1d**, 40%; **1c**, 60%; **1g**, 95%. **1e** (X = Cl, R_1 = *t*-C_4H_9, R_2 = H) yields the unreactive anionic σ-adduct at C-3 *i.e.*, 3-amino-2-*t*-butyl-6-chloro-3,4-dihydropyrido[2,3-*b*]pyrazine. The ring contraction only proceeds with X = Cl. **1b** (X = F) gives an amino-defluorination, **1b** (X = Br) exclusively undergoes reductive debromination. The ring contraction of **1a** (X = Cl, R_1 = R_2 = H) is investigated by ^{15}N- and ^{13}C-labelling. It is concluded that the conversion into 1*H*-imidazo[4,5-*b*]pyridine proceeds *via* the reactive anionic σ-adduct at C-2, under exclusive elimination of C-2.

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Introduction.

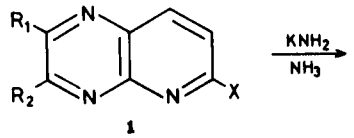
Extensive investigation on the behaviour of 2-X-4,6,7-triphenylpteridines (X = Cl, H, SCH_3) towards potassium amide in liquid ammonia has shown (2-4) that this ring system can undergo *i* a ring contraction into a purine derivative in case of X = H, SCH_3 (initiated by attack of amide to the pyrazine ring carbon atoms, followed by expulsion of - mainly - C-7) and *ii* a nucleophilic substitution at C-2 (X = Cl, SCH_3) which process takes place by initial attack of amide to C-4 [S_N(ANRORC)-mechanism]. In order to be more informed about the general scope of the contraction of the pyrazine ring we directed our attention to the behaviour of the pyrido-[2,3-*b*]pyrazine derivatives towards potassium amide in liquid ammonia. It was found that, in contrast to pteridine, pyrido[2,3-*b*]pyrazine (**2a**) is stable in a dilute solution of potassium amide in liquid ammonia; however its 6-chloro derivative (**1a**, X = Cl) was recently found (2) to undergo two different reactions: dechlorination into **2a** and ring contraction into 1*H*-imidazo[4,5-*b*]pyridine (**3a**, X = H). Thus the formation of **3a** involves ring contraction with a simultaneous dehalogenation.

In this paper we wish to present the results of a more detailed study with a number of differently substituted 6-halogenopyrido[2,3-*b*]pyrazines (**1**) on the mode of formation of both products **2** and **3**. Therefore we studied first the influence of alkyl (methyl, *t*-butyl) or aryl (phenyl), (9,10-phenanthro) groups present in the pyrazine ring on both reactions as well as the influence of different halogeno atoms at position 6 of **1**. Furthermore we investigated by means of ^{13}C- and ^{15}N labelling the mechanism (2) of the ring contraction of **1a** (X = Cl) into **3a** (X = H).

Results and Discussion.

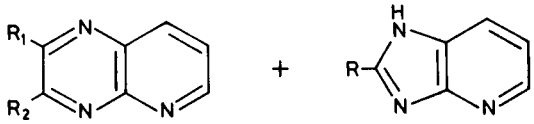
The Influence of Substituents in the Pyrazine Ring of the Pyrido[2,3-*b*]pyrazine (**1**, X = Cl).

The choice of the substituents (alkyl and aryl groups was mainly determined by the availability of the diketones or keto-aldehydes. Condensation with 6-chloro-2,3-diaminopyrimidine gives the desired pyrido[2,3-*b*]pyrazine derivatives (**1**, X = Cl). The preparation of the compounds **1a**, **1c** and **1g** (X = Cl) by this method have already been described.



1

	R_1	R_2
a	H	H
b	H	C_6H_5
c	C_6H_5	C_6H_5
d	H	*t*-C_4H_9
e	*t*-C_4H_9	H
f	CH_3	CH_3
g	Phenanthro (9,10)	



2 **3**

	R_1	R_2
a	H	H
b	H	C_6H_5
c	C_6H_5	C_6H_5
d	H	*t*-C_4H_9
e	Phenanthro (9,10)	

	R
a	H
b	C_6H_5
c	*t*-C_4H_9

With phenylglyoxal monohydrate only the 3-substituted isomer was formed (**1b**, X = Cl). A mixture of 3- and 2-substituted isomers (**1d** and **1e**) was obtained when the condensation was performed with *t*-butylgluoxal hemi-

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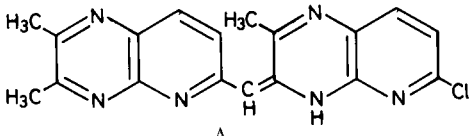
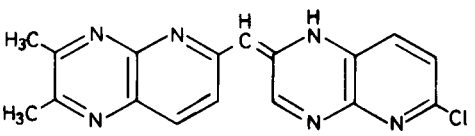
hydrate. By chromatography on silica gel this mixture could easily be separated. Reaction with biacetyl gives in good yield the dimethyl derivative **1f**. These results parallel those obtained in the formation of the pteridine analogues (5) from keto-aldehydes or diketones with 4,5-diaminopyrimidines. The reactivity of the compounds **1b-1g** (X = Cl) towards potassium amide in liquid ammonia was found in several verses to be rather different from that of **1a** (X = Cl).

A phenyl substituent attached to C-3 (**1b**) has almost no influence on the occurrence of dechlorination and ring contraction. The dechlorination product 3-phenylpyrido-[2,3-*b*]pyrazine (**2b**) and the ring contraction product 2-phenyl-1*H*-imidazo[4,5-*b*]pyridine (**3b**) were formed in nearly the same ratio (**2b**/**3b** = 1/3) as obtained from the conversion of **1a** into **2a** and **3a**. 6-Chloro-2,3-diphenyl-pyrido[2,3-*b*]pyrazine (**1c**, X = Cl) yielded mainly dechlorinated material **2c**; the ring contraction, giving rise to the formation of 2-phenyl-1*H*-imidazo[4,5-*b*]pyridine (**3b**) took place to only a small extent. Also in the reaction of 6-chloro-2,3-[phenanthro(9,10)]pyrido[2,3-*b*]pyrazine (**1g**, X = Cl) with potassium amide in liquid ammonia almost quantitatively the dechlorinated material **2e** was formed. A completely anomalous behaviour towards potassium amide was featured with 6-chloro-2,3-dimethylpyrido[2,3-*b*]pyrazine (**1f**). Compound **1f** underwent a fast reaction into a red coloured product to which we tentatively assigned structure **A** or **B**, probably resulting from initial deprotonation of the 3-CH_3 group and a subsequent attack of the anion formed, on C-6 of a second molecule **1** (6). The structure assigned was based on the following evidence: The ^{1}H nmr spectrum showed the presence of three methyl groups at δ 2.74, δ 2.69 and δ 2.52 ppm, a singlet at δ 5.81 ppm (=CH) and two pair of doublets at δ 7.88 and 8.73 ppm (J = 9 Hz) and at δ 7.77 and δ 7.11 ppm (J = 8 Hz). These doublets refer to AB groups in the pyridine rings.

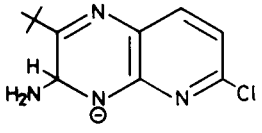


A



B

A strikingly different reaction pattern is observed with the isomeric 2-*t*-butyl-6-chloropyrido[2,3-*b*]pyrazine (**1e**, X = Cl) and 3-*t*-butyl-6-chloropyrido[2,3-*b*]pyrazine (**1d**, X = Cl). Whereas **1d** showed a completely parallel behaviour as **1b** - two reaction products *i.e.*, **2d** and **3c** are formed - **1e** appeared to be completely stable under the reaction conditions. The complete inertness of the chloro atom of **1d** towards amide ions - even no dechlorination could be detected - was possibly due to formation of the negatively charged 1:1 σ-adduct **4**, which species would be deactivated for a nucleophilic attack. Attempts to detect 4 by pmr spectroscopy were very successful. A solution of **1e** (X = Cl) in liquid ammonia, containing potassium amide, showed a pair of doublets at δ 6.99 (1H) and at δ 5.76 ppm (1H), and a singlet at δ 4.90 ppm (1H). This singlet shows an upfield shift of Δδ 4.1 ppm when compared with a solution of **1e** (X = Cl) in deuteriochloroform, indicating the presence of a sp^3 tetrahedral centre in **4**.



4

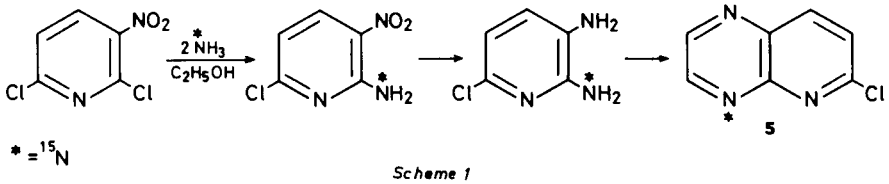
From the results of the above described experiments strong arguments can be taken, that the ring contraction of **1** into **3** only proceeds *via* elimination of C-2, since in cases where this position is free or not heavily blocked the ring contraction is the main process.

The Effect of the Nature of the Halogen Atom in the Pyrido[2,3-*b*]pyrazines (**1**, X=F, Br).

In order to study the effect of the nature of the halogen atom on the possible formation of the compounds **2** and **3** we studied the reactivity of the 2,3-diphenyl-6-X-pyrido[2,3-*b*]pyrazines (**1c**, X = F, X = Br). Compound **1c** (X = F) was prepared from **1c** (X = Cl) by a halogen-exchange with potassium fluoride in hot DMSO. Compound **1c** (X = Br) was synthesized by the action of phosphoryl bromide on 2,3-diphenylpyrido[2,3-*b*]-pyrazin-6-one. 6-Bromo-2,3-diphenylpyrido[2,3-*b*]pyrazine (**1c**, X = Br) appeared to undergo only reductive debromination; thus it reacts quite analogous as the compound **1c** (X = Cl). 2,3-Diphenyl-6-fluoropyrido[2,3-*b*]pyrazine, **1c** (X = F), exclusively undergoes amino-defluorination into 6-amino-2,3-diphenylpyrido[2,3-*b*]pyrazine. Neither defluorination into **2c**, nor any ring contraction product could be isolated from the reaction mixture. These results indicate that only the 6-chloro substituent is able to induce a ring contraction of the pyrido[2,3-*b*]pyrazine ring system into 1*H*-imidazo[4,5-b]pyridine derivatives.

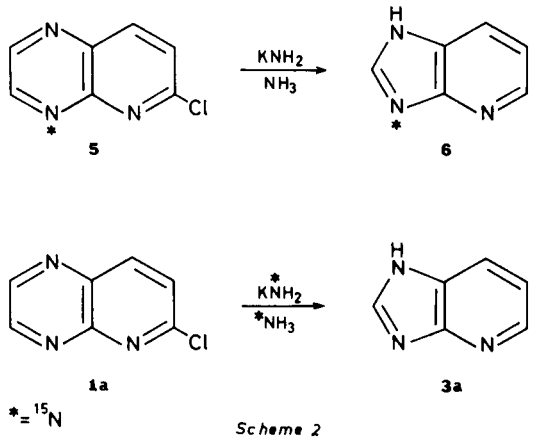
Study of the Mechanism of the Ring Contraction of **1a** into **3a** by ^{15}N- and ^{13}C Labelling Experiments.

6-Chloro[^{15}N-4]pyrido[2,3-*b*]pyrazine (**5**) was synthesized as outlined in scheme 1.



Scheme 1

This scheme was in principle based on the reactions described earlier (7). On reaction of **5** with potassium amide, the 1*H*-imidazo[4,5-*b*]pyridine (**6**) was found to contain by mass spectrometric determination the same excess of ^{15}N label as **5** (Table). In a complementary experiment **1a** (X = Cl) was reacted with ^{15}N labelled potassium amide. Compound 3a did not contain any excess of ^{15}N label (Scheme 2).



Scheme 2

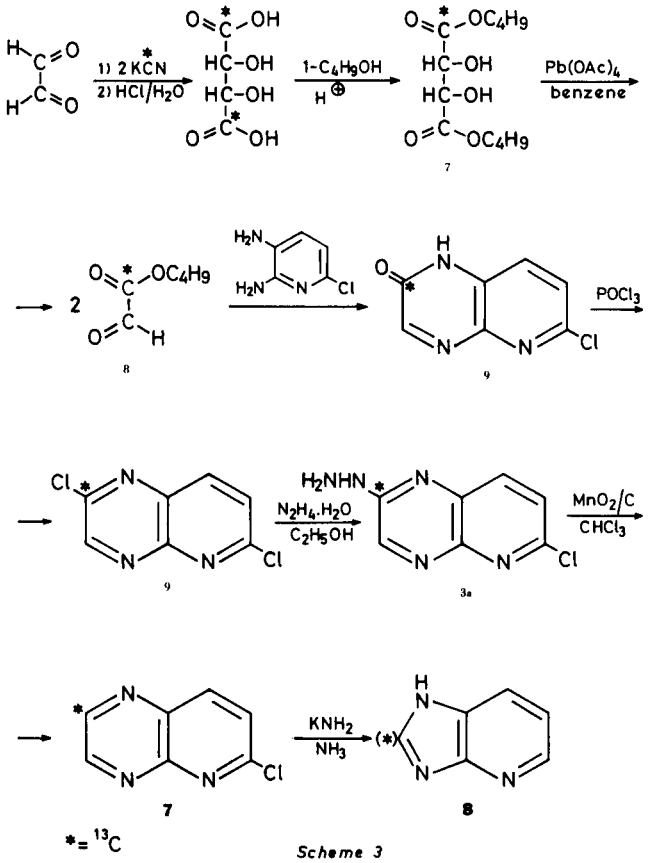
These experiments indicate that in the ring contraction of **1a** (X = Cl) into **3a** the nitrogen atom of the amide ion is not incorporated in **3a** and that both N-1 and N-4 of **1a** are present in **3a**. Although experiments with substituted pyrido[2,3-*b*]pyrazines indicate a strong preference for an expulsion of C-2 during the ring contraction, we wanted to prove that also with the parent substance **1a** (X = Cl) C-2 is exclusively expelled during the ring contraction. Therefore we synthesized 6-chloro-[^{13}C-2]pyrido[2,3-*b*]pyrazine (**9**), as is outlined in Scheme 3. By quantitative mass spectrometric and ^{13}C nmr measurements the enrichment of ^{13}C at C-2 was established (see Table).

Table

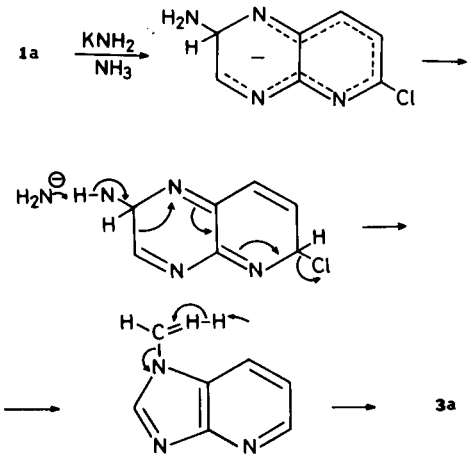
Results of the ^{15}N- and ^{13}C Labelling Experiments

% excess of	comp.; %	comp.; %
^{15}N-4	**5**; 7.0	**6**; 7.0
$^{15}NH_2/^{15}NH_3$; 6.7	**1a**; 0.0	**3a**; 0.0
^{13}C-2	**9**; 5.7	**3a**; 0.2

After allowing **9** to react with potassium amide in liquid ammonia we found that in the isolated 1*H*-imidazo[4,5-*b*]pyridine (**3a**) no excess of ^{13}C label could



Scheme 3

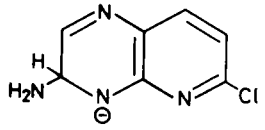


Scheme 4

be detected (see Table).

This means that also in the ring contraction of the parent substance **1a** (X = Cl) into **3a** C-2 is expelled exclusively. The mechanism to explain these results involves an initial addition of amide ion at C-2. From this σ-adduct a further rearrangement, leading to **3a** can be presented (see Scheme 4).

We want to point out that although it has been unequivocally proved that the ring contraction involves a reactive σ-adduct at C-2, these experiments do not exclude that in a solution of **1a** (X = Cl) in liquid ammonia containing potassium amide, a small concentration of a stable adduct at C-3 (**10**) is present.



10

EXPERIMENTAL

Amination Procedure.

The pyrido[2,3-*b*]pyrazine derivatives (1.0 mmole) were allowed to react with 4 equivalents of potassium amide, dissolved in 50 ml. of liquid ammonia, at -33°, for a period of one hour. Glc analysis (glass column, 180 cm, 2.1 g., chromosorb W-HP 100-120 + 10% OV-275, at 250°) of the reaction products of **1a** (X = Cl) showed a reaction time of 1 hour to give optimum yields. In general 20-30% of starting material was recovered.

Synthesis of the Pyrido[2,3-*b*]pyrazines.

The following compounds were synthesized according to procedures described in the literature: 6-chloropyrido[2,3-*b*]-pyrazine (**1a**) (8), pyrido[2,3-*b*]pyrazine (**2a**) (9), 1*H*-imidazo-[4,5-*b*]pyridine (**3a**) (10), 2-phenyl-1*H*-imidazo[4,5-*b*]pyridine (**3a**) (11), 6-chloro-2,3-diphenylpyrido[2,3-*b*]pyrazine (**1c**) (12), 2,3-diphenylpyrido[2,3-*b*]pyrazine (**2c**) (13), 6-chloro-2,3-[phenanthro (9,10)]pyrido[2,3-*b*]pyrazine (**2e**) (12), 3-phenylpyrido-2,3-*b*]pyrazine (**2b**) (13), 6-chloro-2,3-diaminopyridine (7).

6-Chloro-3-phenylpyrido[2,3-*b*]pyrazine (**1b**).

6-Chloro-2,3-diaminopyridine (0.76 g., 5.0 mmoles) and 0.75 g. (5.1 mmoles) of phenylglyoxal monohydrate were dissolved in 50 ml. of boiling ethanol. To the hot solution were added 50 ml. of water, whereupon **1b** crystallized, m.p. 147-149°.

Anal. Calcd. for $C_{13}H_8ClN_3$: C, 64.40; H, 3.34; Found C, 64.90; H, 3.14.

2,3-Diphenyl-6-fluoropyrido[2,3-*b*]pyrazine (**1c**, X = F).

Two g. of potassium fluoride (stored at 110°) was added in one portion to a solution of 0.5 g. of **1c** (X = Cl) in dry DMSO (5 ml.). The mixture was heated for 10 minutes under vigorous stirring. To the cooled contents of the flask 20 ml. of water were added. The organic material was extracted with chloroform, concentrated and recrystallized from hexane, to give a slightly yellow coloured compound in 50% yield, m.p. 142-143°.

Anal. Calcd. for $C_{19}H_{21}FN_3$: C, 75.73; H, 4.01; Found C, 75.53, H, 4.12.

6-Bromo-2,3-diphenylpyrido[2,3-*b*]pyrazine (**1c**, X = Br).

2,3-Diphenylpyrido[2,3-*b*]pyrazin-6-one (16) was reacted by the standard procedure with phosphoryl bromide. The crude material was recrystallized from hexane to yield (70%) slightly yellow needles, m.p. 164-165°.

Anal. Calcd. for $C_{19}H_{12}BrN_3$: C, 63.00; H, 3.34; Found C, 63.26; H, 3.11.

2- and 3-*t*-butyl-6-chloropyrido[2,3-*b*]pyrazines (**1e, 1d**).

Equimolar amounts of *t*-butylglyoxal hemihydrate and 6-chloro-2,3-diaminopyridine were dissolved in boiling ethanol. The solvent was removed *in vacuo* after allowing to reach room temperature. The solid obtained was chromatographed on silica gel, eluent chloroform. Compound **1d**, isolated in 80% yield, was found to have the higher mobility. The yield of **1e** varied from 10-20%. **1d** (X = Cl), m.p. 133-134° (ethanol/water).

Anal. Calcd. for $C_{11}H_{12}ClN_3$: C, 59.59; H, 5.46; Found C, 59.88; H, 5.20.

6-chloro-2,3-dimethylpyrido[2,3-*b*]pyrazine (**1f**).

The slightly coloured solid obtained after the reaction of 6-chloro-2,3-diaminopyridine with biacetyl in ethanol, was purified by column chromatography (silica gel, chloroform) and by recrystallization from hexane, m.p. 176-178°, yield 80%.

Anal. Calcd. for $C_9H_8ClN_3$: C, 55.82; H, 4.16; Found C, 55.95; H, 4.06.

The Dimer **A** (or **B**).

Compound **1f** was allowed to react for 5 minutes with potassium amide in liquid ammonia. The red coloured product was obtained in quantitative yield and recrystallized from ethanol, m.p. 229-230°.

Anal. Calcd. $C_{18}H_{15}ClN_6$: C, 61.62; H, 4.31; Found C, 61.30; H, 4.20.

3-*t*-Butylpyrido[2,3-*b*]pyrazine (**2d**).

Condensation of 2,3-diaminopyridine and *t*-butylglyoxal hemihydrate in ethanol afforded **2d** in quantitative yield. The compound was found to be a liquid, b.p. 194° dec. and was analyzed as the picrate, m.p. 141-142°.

Anal. Calcd. $C_{17}H_{16}N_6O_7$: C, 49.03; H, 3.87; Found C, 49.22, H, 3.60.

2-*t*-Butylimidazo[4,5-*b*]pyridine (**3c**).

The mixture of products, obtained after the reaction of **1d** (X = Cl) with potassium amide in liquid ammonia, was purified by column chromatography on silica gel. When eluted with chloroform, fractions were obtained containing **2d**. Compound **3c** was eluted with ethyl acetate. Recrystallization from acetone gave m.p. 200° subl., 220° dec.

Anal. Calcd. for: $C_{10}H_{12}N_3$: C, 68.94; Found C, 68.74; H, 6.81.

6-Chloropyrido[2,3-*b*]pyrazin-2-one.

To a solution of 6-chloro-2,3-diaminopyridine (1.52 g., 10 mmoles) in 30 ml. of ethanol was added freshly distilled 1-butylglyoxalate (1.43 g., 1.1 eq.). The mixture was stirred while standing for 2 days at room temperature. The product was collected by filtration and washed with ethanol and ether to obtain 1.65 g. (90%) of yellowish-brown crystals. These could be recrystallized from water using charcoal, to a colourless micro-crystalline material, m.p. 220° subl., 275° dec.

Anal. Calcd. for $C_7H_4ClN_3O$: C, 46.30; H, 2.22; Found C, 46.19; H, 2.49.

2,6-Dichloropyrido[2,3-*b*]pyrazine.

To 2.6 g. (20 mmoles) of thoroughly dried 6-chloropyrido-[2,3-*b*]pyrazin-2-one were added 160 ml. of phosphoryl chloride. The mixture was refluxed under the exclusion of moisture till all the solid material had disappeared. Phosphoryl chloride 120 ml. was removed in vacuo. To the remaining slightly yellow-green syrup was added 300 g. of ice, and the excess of phosphoryl chloride was carefully decomposed. The acidic solution was extracted with 3 portions of 50 ml. of ether and the combined etherial layers were washed with water and sodium bicarbonate, dried and concentrated *in vacuo*. The remaining slightly coloured solid was purified by column chromatography on silica gel (eluent dichloromethane) and recrystallized from ethanol:water to yield 2.6 g. (90%) of colourless needles, m.p. 163° dec.

Anal. Calcd. for $C_9H_3Cl_2N_3$: C, 42.03; H, 1.51; Found: C, 42.22; H, 1.46.

6-Chloro-2-hydrazinopyrido[2,3-*b*]pyrazine.

To 2.0 g. (10 mmoles) of 2,6-dichloropyrido[2,3-*b*]pyrazine, dissolved in 120 ml. of ethanol, were slowly added under vigorous stirring 2.0 g. (4 eq.) of hydrazine hydrate at room temperature. After 30 minutes, hte mixture was refluxed for 2 hours. The contents of the reaction flask were cooled and the solid removed by filtration. It could not be recrystallized. By reaction with 2,4-dinitrobenzaldehyde in ethanolic solution an intensively yellow coloured 2,4-dinitrophenylhydrazone was obtained, m.p. 170° dec.

Anal. Calcd. for $C_{14}H_8ClN_7O_4$: C, 44.99; H, 2.16; Found C, 45.02; H, 2.27.

6-Chloropyrido[2,3-*b*]pyrazine (**1a**, X = Cl).

To a suspension of the above described hydrazino compound (1.9 g., 10 mmoles) in 100 ml. of chloroform was added freshly prepared manganese dioxyde on carbon catalyst (**2g**) in small portions at room temperature, under vigorous stirring. After the addition had been completed, the solvent was refluxed for 2 hours. The suspension was filtered, while still hot, over hyflo supercel. The solid material was extracted with hot chloroform (100 ml.). The combined filtrates were dried on magnesium sulphate, filtered and the solvent was removed in vacuo. Thus pure **1a** (X = Cl) could be obtained in a yield of 70%. The product was recrystallized from water and proved to be identical with an authentic specimen by its m.p., mixed m.p. and pmr spectrum.

Synthesis of the ^{15}N- and ^{13}C Labelled Compounds.

6-Chloro[^{15}N-4]pyrido[2,3-*b*]pyrazine (**5**).

This compound was prepared as described in the literature for the unlabelled compound (7,8). The required 6-chloro[^{15}N-2]-2,3-diaminopyridine was obtained *via* the reduction of [^{15}N-2]-amino-6-chloro-3-nitropyridine as described in the literature for the unlabelled specimen (7). The latter could be readily obtained by the amino-dechlorination of 2,6-dichloro-3-nitropyridine with ethanolic ammonia containing $^{15}NH_3$, following the procedure already described for the unlabelled material (7).

Di-1-butyl[di^{13}C-2,3]tartrate (**7**).

To a solution of a mixture of 4.6 g. potassium cyanide (71 mmoles) and 0.5 g. potassium (^{13}C) cyanide (7.6 mmoles) in water (20 ml.) and acetonitrile (5 ml.), cooled to -8°, are added dropwise 7 ml. of a 30% solution of glyoxal in water. The temperature is not allowed to rise above -5°. After the addition has been completed the solution is allowed to reach room temperature and 10 ml. of concentrated hydrochloric acid was added dropwise. To the resulting colourless solution 45 ml. of concentrated hydrochloric acid are added in one portion and the mixture kept at 70° for 2 hours. The solvents are removed in vacuo and the remaining solid is dried at 70°C. To the dry solid 40 ml. of 1-butanol and 3 drops of concentrated sulphuric acid are added. The mixture is refluxed for 1 hour and distilled azeotropically to remove the water and the excess of 1-butanol. The cooled residue is diluted with ether and washed with a solution of sodium bicarbonate in water. The ethereal layer is dried over magnesium sulphate and concentrated in vacuo. The ethereal layer is dried over magnesium sulphate and concentrated in vacuo. The remaining crude di-1-butyl tartrate is distilled in vacuo, b.p. 136°, 0.4 mm Hg. The yield of pure material is 6.0 g. (29%).

1-Butyl[^{13}C-2]blyoxalate (**8**).

Six g. (23 mmoles) of **7** were dissolved in 25 ml. of dry benzene in an atmosphere of nitrogen. Under vigorous stirring 11.5 g. (1.1 eq.) of lead tetraacetate were added in small portions. The temperature was not allowed to rise above 30°. After the addition had been completed, the stirring was continued for 1 hour. The organic material was isolated by filtration and the benzene and acetic acid were removed in vacuo in an atmosphere of nitrogen. The product distilled at 55-65°, 13 mm Hg, yield 4.8 g. (80%).

6-Chloro[^{13}C-2]pyrido[2,3-*b*]pyrazine (**9**).

This compound was prepared *via* the route described for the unlabelled material. All ^{13}C labelled compounds were proved to be identical with the unlabelled specimens, by comparing their physical and chemical properties.

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