Anal. Calcd. for $C_7H_{14}BrNO$: Br, 38.41. Found: 38.17, 38.11.

1-Methyl-4-piperidone methobromide hydrate (XIIIa). The methobromide (XIII) was dissolved in water and precipitated by addition of acetone. The resulting solid melted when introduced into a bath at 150°.

Anal. Calcd. for $C_7H_{16}BrNO_2$: Br, 35.34. Found: Br, 35.29, 35.30.

1-Methyl-1,2,5,6-tetrahydro-3-pyridyl methyl ether (VIII). A solution of 32 g. of 3-hydroxypyridine (VII) and 21 g. of sodium methoxide in 150 ml. of methanol was treated with 100 g. of methyl iodide. The mixture was heated under reflux for 7 hr., cooled, and 26 g. of sodium borohydride was added portionwise. The solvent was removed by distillation, and water was added to the residue. Potassium carbonate was added to the aqueous solution, and ether was used for extraction. After drying over potassium carbonate, the ether solution was concentrated, and the residual oil was distilled under reduced pressure to give 12.93 g. (40%) of 1-methyl-1,2,5,6-tetrahydro-3-pyridyl methyl ether (VIII), b.p. 60–63°/11 mm., n_D^{24} 1.4663.

Anal. Calcd. for $C_7H_{13}NO$: C, 66.09; H, 10.30. Found: C, 66.13; H, 10.63.

The *picrate* was prepared in ethanol, m.p. 119–120°. The molecular weight determined by the ultraviolet absorption method[18] was 354; the calculated value is 356.

Anal. Calcd. for $C_{13}H_{16}N_4O_8$: C, 43.82; H, 4.53, Found: C, 44.19; H, 4.48.

1-Methyl-3-piperidone (VI). A solution of 12.9 g. of VIII in 40 ml. of 48% hydrobromic acid was heated under reflux for 6 hr. The solution was neutralized and extracted with ether. The ether solution was concentrated, and the residue was distilled under reduced pressure to give 10.7 g. of 1-methyl-3-piperidone (VI), b.p. 65–70°/15 mm., n_D^{26} 1.4535; lit.[11] b.p. 63–64°/13 mm., n_D^{25} 1.4559. Addition of anhydrous hydrogen chloride to a solution of the 1-methyl-3-piperidone in ether gave 12.00 g. of 1-methyl-3-piperidone hydrochloride hydrate, m.p. 105–108°; lit.[11] m.p. 110–111°.

Anal. Calcd. for $C_6H_{14}ClNO_2$: Cl, 21.15; Found: Cl, 21.19, 21.02.

1-Methyl-3-piperidone hydrobromide (IX). A solution of 10.8 g. of VIII in 33 ml. of hydrobromic acid was heated under reflux for 8 hr. and evaporated to dryness under reduced pressure to give an oily residue which crystallized on treatment with acetone. The solid was isolated by filtration to give 15.9 g. of IX, m.p. 103–106°.

Anal. Calcd. for $C_6H_{12}BrNO$: Br, 41.18. Calcd. for $C_6H_{14}BrNO_2$: Br, 37.68. Found: Br, 38.02, 37.99.

Anhydrous 1-methyl-3-piperidone hydrochloride (III). A sample of the hydrate IV was heated under reduced pressure. The residue, III, melted at 138–141°.

Anal. Calcd. for $C_6H_{12}ClNO$: Cl, 23.70. Found: 23.39.

Anhydrous 1-methyl-3-piperidone methobromide (XIV). A solution of 1-methyl-3-piperidone (VI) and methyl bromide in ether deposited the methobromide (XIV) m.p. 175–179°, on standing.

Anal. Calcd. for $C_7H_{14}BrNO$: Br, 38.41. Found: Br, 37.97, 38.14.

1-methyl-3-piperidone methobromide hydrate (XIVa). A solution of the salt XIV was treated with acetone to precipitate 1-methyl-3-piperidone methobromide hydrate (XIVa) which melted on introduction into a bath at 150°.

Anal. Calcd. for $C_7H_{16}BrNO_2$: Br, 35.34. Found: Br, 35.29.

DURHAM, N. H.

(18) K. C. Cunningham, W. Dawson, and F. S. Spring, *J. Chem. Soc.*, 2305 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BROOKLYN COLLEGE]

Synthesis of 2,6-Disubstituted Pyrazines and Related Derivatives

DAVID M. SHAREFKIN

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A number of 2,6-disubstituted pyrazines and related derivatives have been prepared. A new procedure for the preparation of 7-methyllumazine is described. 7-Methyllumazine has been cleaved to furnish both 6-methyl-2-pyrazinol and 2-amino-6-pyrazinol was coupled to furnish a new series of azopyrazine dyes. These azopyrazine dyes were reduced in acid solution to furnish 5-amino-6-methyl 2-pyrazinols.

7-Methyllumazine (2,4-dihydroxypyrimido-4,5-6-pyrazine) (I) is readily cleaved by alkali.[1] The products are 2-amino-6-methyl-3-pyrazinoic acid (II) and 2-hydroxy-6-methyl-3-pyrazinoic acid (III). These carboxylic acids are readily decarboxylated to the 2-amino- (IV) and the 2-hydroxypyrazines (XII). The conventional approach to lumazine synthesis involving the condensation of a 4,5-diaminopyrimidine with an α,β-dicarbonyl compound[2,3] gives brown gelatinous products. A fine, yellow, crystalline 7-methyllumazine is obtained here by condensation in acid solution of 5,6-diaminouracil with stabilized methylglyoxal (30% solution).[4] This procedure furnished practically quantitative yields of micro crystalline 7-methyllumazine and also permitted quantitative detection of α-dicarbonyl compounds in quantities as low as 5 γ per ml. equivalent to 2 γ of methyl glyoxal.[5]

Owing to the paucity of 2,6-disubstituted pyrozines, it was of interest to investigate further the preparation of compounds of this class. In approaching this problem, the method of Weijlard and coworkers for the conversion of 7-methyllumazine into 2-amino-6-methylpyrazine (IV) was used. Efforts to prepare 2,6-diaminopyrazine through a

(1) J. Weijlard, M. Tishler, and A. E. Erickson, *J. Am. Chem. Soc.*, **67**, 802 (1945).

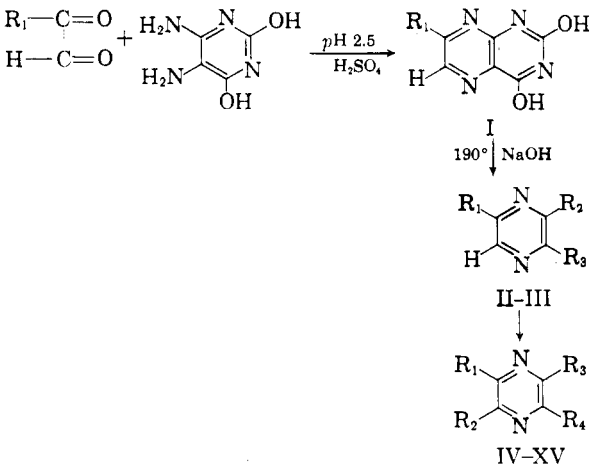
(2) (a) R. Kuhn and W. Cook, *Ber.*, **70**, 761 (1937); (b) J. Ganapti, *J. Indian Chem. Soc.*, **14**, 627 (1937).

(3) E. C. Taylor, R. B. Garland, and C. F. Howell, *J. Am. Chem. Soc.*, **78**, 210 (1956).

(4) Methyl glyoxal 930% stabilized solution was obtained from Carbide and Carbon Chemicals Co. 30 2. 42nd St., New York, N. Y.

(5) L. Sattler and F. W. Zerban, *Ind. Eng. Chem.*, **41**, 1401 (1949).

Curtius-Schmidt reaction on 2-acetamido-6-pyrazinoic acid (IV) proved unsuccessful.[6] No attempt was made here to try a Hofmann reaction on 2-carboxamido-6-acetamidopyrazine (IX) in view of the known resistance of carboxamidopyrazines to such degradations.[7] Although tetralin served as an excellent high boiling decarboxylating medium for converting 2-amino-6-methyl-3-pyrazinoic acid (II) to 2-amino-6-methylpyrazine (IV), it did not serve to decarboxylate 2-amino-3-bromo-6-pyrazinoic acid (XI) to the desired 2-amino-3-bromopyrazine even under more strenuous conditions. If decarboxylation had been successful it would have been possible to prepare it by ammonolysis to the known 2,3-diaminopyrazine for authenticity.[7b]



	R_1	R_2	R_3	R_4
I.	CH_3			
II.	CH_3	NH_2	COOH	H
III.	CH_3	OH	COOH	H
IV.	CH_3	NH_2	H	H
V.	CH_3	NHAc	H	H
VI.	COOH	NHAc	H	H
VII.	COOH	NH_2	H	H
VIII.	$COOCH_3$	NHAc	H	H
IX.	$CONH_2$	NHAc	H	H
X.	COOH	NHAc	Br	H
XI.	COOH	NH_2	Br	H
XII.	CH_3	OH	H	H
XIIIa.	CH_3	ONa	H	p-$NaSO_3SC_6H_5N{=}N-$
XIIIb.	CH_3	ONa	H	p-$NO_2C_6H_4N{=}N-$
XIV.	CH_3	OH	H	NH_2
XV.	CH_3	$=N-NHC_6H_3(NO_2)_2$	H	NH_2

Although Weijlard *et al.*[1] have stated that 7-methyllumazine (I) by alkaline cleavage conditions would furnish 2-amino-6-methyl-3-pyrazinoic acid exclusively by heating at 170° for 20 hr., it was found possible by doubling the heating time and raising the temperature to 190° to also produce 2-hydroxy-6-methyl-3-pyrazinoic acid (III).[8] From it in turn 6-methyl-2-pyrazinol (XII) could be obtained by decarboxylation in either 80% sulfuric acid at 180° or in boiling tetralin solution at 205°. No attempt was made to produce 6-methyl-2-pyrazinol (XII) exclusively under these conditions since a separation of the two products after decarboxylation was successful.

Derivatives of 6-methyl-2-pyrazinol (XII) could not be made by acetylation or benzoylation in pyridine solution due to keto-enolization of the 2-hydroxy group with the adjacent ring nitrogen. This has been noted also by others in the failure of 2-pyrazinol to acetylate.[9]

A new series of azo coupled pyrazine dyes (XIII a,b) was formed by coupling 6-methyl-2-pyrazinol with diazotized aromatic amines. Aqueous solutions of these dyes are yellow to orange in acid solution and orange to red in alkali solution.

Vigorous reduction of one of these pyrazinol dyes (XIIIa) with stannous chloride split the azo linkage to yield the original aromatic amine and the aminated pyrazinol, 5-amino-6-methyl-2-pyrazinol (XIV). The 5-amino-6-methyl-2-pyrazinol was isolated as its sodio salt and derivatized by means of 2,4-dinitrophenylhydrazine as the insoluble orange hydrazone (XV).

Ultraviolet absorption maxima and minima were determined and were considered as representative for 2,6-disubstituted pyrazines. The absorption curves of the 5-azo coupled pyrazolinate dyes were continued into the near infrared region to obtain values for absorption due to the azobenzene linkage as well as that of the substituted pyrazine ring.

EXPERIMENTAL

Preparation of 7-methyllumazine (I). Fifty grams of uracil 5,6-diamino sulfate (5,6-diamino-2,4-dihydroxypyrimidine)[10] were suspended in 1400 ml. of water. Then 130 ml. of methyl glyoxal, 30% aqueous solution, were added and followed by 60 ml. of 10% sulfuric acid to *p*H 2.5. The mixture was boiled for 2 hr. or until the volume was reduced to 950 ml. The mixture was made alkaline with sodium hydroxide to *p*H 9.5 and then cooled to 2°. After 2 hr. in the ice bath, the fine crystals were filtered, washed once with ice water, and air dried. The light yellow crystals were very soluble in water. An aqueous solution of 7-methyllumazine

(6) D. M. Sharefkin and P. E. Spoerri, *J. Am. Chem. Soc.*, **73**, 1637 (1951).

(7) (a) P. E. Spoerri and A. E. Erickson, *J. Am. Chem. Soc.*, **60**, 400 (1938); (b) R. C. Ellingson and R. L. Henry, *J. Am. Chem. Soc.*, **71**, 2798 (1949).

(8) R. G. Jones, *J. Am. Chem. Soc.*, **71**, 78 (1949).

(9) I. Krems and P. E. Spoerri, *Chem. Revs.*, **40**, 2, April, 1947.

(10) M. T. Bogert and D. Davidson, *J. Am. Chem. Soc.*, **55**, 1668 (1933).

was strongly fluorescent in sunlight. The average yield was 38 g. or 98%.

Since the members of the lumazines cannot be distinguished because of a lack of melting points within the series, ultraviolet absorption spectrograms were made in the range of 220 mμ to 400 mμ for both acid and alkaline solutions of 7-methyllumazine.

Preparation of 2-amino-6-methylpyrazine (IV). 7-Methyllumazine was cleaved in strong alkaline solution at 170° for 20 hr. to furnish 2-amino-6-methyl-3-pyrazinoic acid.[1] Fifteen g. of the crude acid (II) were suspended in 250 ml. of dry tetralin and refluxed at 205° for 30 min. during which time the solid dissolved. The solution was cooled and extracted with small portions of 10% hydrochloric acid until the acid extract was no longer yellow colored. The combined acid extracts were washed with petroleum ether to remove traces of tetralin and then made alkaline with 20% sodium hydroxide. Several extractions with ether were necessary to remove the amine. The combined ether extracts were dried, reduced in volume to produce 8 g. of yellow crystalline solid, m.p. 124–125°, or 78%.

Preparation of 2-acetamido-6-methylpyrazine (V). 2-Amino-6-methylpyrazine (IV) (10.9 g.) was added to a solution of 14 ml. of acetic anhydride in 60 ml. of glacial acetic acid. The mixture was stirred on the steam bath for 3 hr. When cooled, ether was added to precipitate the acetylated compound. After filtration, the filtrate was treated with a small volume of acetyl chloride to obtain a second crop of the white solid. The total weight after crystallization from absolute methanol was 11 g. or 64%, m.p. 168–169°.

Anal. Calcd. for $C_7H_9ON_3$: N, 27.871. Found: N, 27.94.

Preparation of 2-acetamido-6-pyrazinoic acid (VI). Eight grams of 2-acetamido-6-methylpyrazine (V) were dissolved in a solution of 12 g. of magnesium sulfate in 600 ml. of warm water. The solution was heated to 75° and 16.5 g. of potassium permanganate was added in small portions. The temperature was kept at 85° until discharge of the color. The mixture was filtered hot and the residue washed twice with boiling water. The combined filtrates were reduced in volume to 200 ml. and *p*H adjusted to 2.5 with dilute sulfuric acid. After cooling in the ice bath 5.4 g. of white solid was obtained. The solid was recrystallized from boiling water also adjusted to *p*H 2.5 with dilute sulfuric acid, to yield 5 g. of the 2-acetamido-6-pyrazinoic acid, m.p. 173°.

Anal. Calcd. for $C_7H_7O_3N_3$; C, 46.42; N, 23.22. Found: C, 46; 51; N, 27.04, 27.71.

The discrepancy in the nitrogen analysis was believed due to irregularity in the behavior of the substance during combustion. Two different samples prepared at different times gave the same analytical anomalies. Its precursor, 2-acetamido-6-methyl pyrazine (V) and its derivatives, the 6-methyl ester (VIII) and the 3-bromo pyrazines (X) and (XI) gave analytical results which were in agreement with the calculated values.

Preparation of 2-amino-6-pyrazinoic acid (VII). One-half gram of 2-acetamido-6-pyrazinoic acid (VI) were suspended in 10 ml. of 3*N* hydrochloric acid and boiled for 20 min. The solution was decolorized with Norit and then made *p*H 6.5 by addition of solid sodium bicarbonate. The solution was extracted with 100 ml. of ether in 5 portions. The combined extracts were dried and concentrated to produce 0.25 g. of bright yellow crystals of the amino acid, m.p. 120–121°. Acetylation of the yellow crystals produced a white solid which gave a mixed melt at 173°, identical with that of the 2-acetamido-6-pyrazinoic acid (VI).

Attempted Curtius-Schmidt reaction on 2-acetamido-6-pyrazinoic (VI). In an attempt to prepare 2,6-diaminopyrazine by a modified Curtius reaction, 0.26 g. of sodium azide was added over a 3-hr. period to a solution of 0.197 g. of 2-acetamido-6-pyrazinoic acid in 4 ml. of concentrated sulfuric acid containing 1.5 g. of trichloroacetic acid. The reaction was maintained at 60° with continuous stirring, cooled, and poured onto 10 g. of crushed ice. After making alkaline with sodium hydroxide, the mixture was extracted with three 25-ml. portions of ether. The combined ether extracts were dried over anhydrous sodium sulfate and the ether solution concentrated. The yellow solid which formed on cooling of the other concentrate melted at 120° and was the 2-amino-6-pyrazinoic acid as shown by its indicator test as a B_wP_w, and by the formation of an acetylated derivative, the 2-acetamido-6-pyrazinoic acid (VI), which melted at 173°.

Preparation of 2-acetamido-6-carbomethoxy pyrazine (VIII). To 3 g. of 2-acetamido-6-pyrazinoic acid (VI) suspended in 30 ml. of absolute methanol there were added 1 g. of anhydrous sodium sulfate and 0.2 ml. of concentrated sulfuric acid. After 3 hr. of refluxing, Norit was added and the mixture filtered hot. The solution was reduced in volume to 15 ml. and the acidity adjusted to *p*H 2.5 with a few drops of 10% sodium hydroxide. After cooling, 2.4 g. of fine crystals were collected and dried, m.p. 159°.

Anal. Calcd. for $C_8H_9O_3N_3$: N, 21.50. Found: N, 21.56.

Preparation of 2-acetamido-6-carboxamido pyrazine (IX). A hot solution of 0.3 g. of 6-carbomethoxy pyrazine (VIII) in 10 ml. of absolute methanol was poured into 15 ml. of 28% ammonia and heated until the total volume was reduced to 10 ml. The solution was then cooled to obtain a white solid which after washing with methanol and drying did not melt over 300°.

Anal. Calcd. for $C_7H_8O_2N_4$: N, 31.00. Found: N, 31.06.

Preparation of 2-acetamido-3-bromo-6-pyrazinoic acid (X). To a solution of 1.6 g. of 2-acetamido-6-pyrazinoic acid (VI) in 20 ml. of warm acetic acid, 0.6 ml. of bromine were added dropwise over a 30-min. period. The clear red solution was poured over 20 g. of crushed ice to produce a heavy precipitate. A sample recrystallized from 10 ml. of absolute methanol yielded white needles, m.p. 173°.

Anal. Calcd.: for $C_7H_6O_3Br$: N, 16.16. Found: N, 15.84.

Preparation of 2-amino-3-bromo-6-pyrazinoic acid (XI). To a solution of 3 g. of 2-acetamido-3-bromo-6-pyrazinoic acid (X) in 600 ml. of hot water there was added 10 ml. of concentrated hydrochloric acid. The solution was boiled for 15 min., filtered, and then evaporated slowly to 30 ml. The solid obtained on cooling was filtered and dried to yield, 2.1 g. of a white solid m.p. 152–153°. After recrystallization from ethanol, the solid melted 153–154°.

Anal. Calcd.: for $C_5H_4O_2N_3Br$: N, 19.20. Found: N, 19.05.

Attempted decarboxylation of 2-amino-3-bromo-6-pyrazinoic acid (XI). One gram of 2-amino-3-bromo-6-pyrazinoic acid (XI) was added to 10 ml. of dry tetralin and the mixture refluxed at 205° for 30 min. Norit was added to the hot solution, and filtered. Crystals formed on chilling the filtrate in the ice bath. The filtered crystals were washed with petroleum ether and dried, m.p. 153–154°. The material recovered was the unchanged 2-amino-3-bromo-6-pyrazinoic acid.

Preparation of 6-methyl-2-pyrazinol (XII). A suspension of 37.4 g. of 7-methyllumazine (I) in a solution of 37 g. of sodium hydroxide in 190 ml. of water was prepared. This mixture was sealed into a steel bomb tube and heated at 180–190° for 50 hr. After cooling, the solution was filtered to remove a slight sediment. There was a very strong odor of ammonia from the tube. The solution was reduced in volume of 100 ml. and then made *p*H 2.5 with hydrochloric acid to precipitate a mixture of 2-amino-6-methyl-3-pyrazinoic acid (II) and 2-hydroxy-6-methyl-3-pyrazinoic acid.

There was no attempt made to separate the mixture of the crude acids at this point. Separation was considered more effective after decarboxylation of the two acids by heating 12.5-g. portion of the crude acids in 40 ml. of 80% sulfuric acid at 180° for 10 min. The acid solution was poured onto 250 g. of crushed ice and then made alkaline with 50% sodium hydroxide. Ether extraction removed a small amount (3.5 g.) of 2-amino-6-methylpyrazine (IV).

The solution was adjusted to *p*H 6.8 and then extracted with 2.4 l. of ethyl acetate in 6 portions. The combined extracts were dried over anhydrous sodium sulfate and reduced in volume to 200 ml. Cooling produced shining platelets

of the yellow 6-methyl-2-pyrazinol (XII). Recrystallization from anhyd. ethyl acetate furnished 4.4 g. of the yellow platelets, m.p. 240°.

Anal. Calcd. for $C_5H_6N_2O$: N, 25.44. Found: N, 25.80.

Preparation of azo coupled compounds of 6-methyl-2-pyrazinol (XIII). *A. Disodio salt of 6-methyl-5-azobenzenesulfonate-2-pyrazinolate* (XIIIA). Two ml. of 6*N* sodium hydroxide solution were added to a suspension of 1.8 g. (0.01*M*) of sulfanilic acid in 15 ml. of water. Solution was obtained on warming. Then 0.7 g. of sodium nitrite was added and the solution cooled to room temperature. Then this solution was poured into a mixture of 1.3 ml. of concentrated sulfuric acid, 26 g. of ice, and 20 ml. of water, and allowed to stand for 30 min. After which, a solution of 1.6 g. (0.01*M*) of 6-methyl-2-pyrazinol (XII) in 20 ml. of water and 10 drops of 20% sodium hydroxide was added to the diazotized sulfanilic acid. The reaction mixture was stirred for 5 min., after which 10% sodium hydroxide was added to make *p*H 6. After an orange precipitate had formed, 30 ml. of saturated sodium chloride solution was added and the mixture cooled for 10 min. Filtration produced 2.1 g. of orange yellow solid. The solid was recrystallized from 125 ml. of distilled water at 95°, to give 2 g. of bright yellow solid. Aqueous solutions are colored red in acid and orange red in alkaline solution. The solid did not melt up to 300°.

Anal. Calcd. for $C_{11}H_8O_4N_5SNa_2$: N, 16.38. Found: N, 15.01, 15.31.

B. Sodio salt of 6-methyl-5-p-nitrobenzeneazo-2-pyrazinol (XIIIB). A suspension of 1.4 g. of *p*-nitroaniline in 5 ml. of concentrated hydrochloric acid was prepared. Solution was obtained by heating to 80°. On cooling to room temperature, 10 g. of ice and a solution of 0.8 g. of sodium nitrite were added. To the diazotized *p*-nitroaniline, a solution of 1.3 g. of 6-methyl-2-pyrazinol (XII) in 20 ml. of water and 10 drops of 20% sodium hydroxide was added with stirring. The reaction mixture stood for 10 min. and then a solution of 0.6 g. of anhydrous sodium acetate in 2 ml. of water was added. After 15 min., the solid was filtered, washed with ice water, and dried. The dried solid was digested with a small amount of benzene to remove unchanged *p*-nitroaniline. For analysis, a sample was recrystallized from 95% ethanol; no m.p. up to 300°.

Anal. Calcd. for $C_{11}H_8O_5N_5Na$: N, 24.90. Found: N, 24.73.

Preparation of 5-amino-6-methyl-2-pyrazinol (XIV). To a solution of the disodio salt of 5-azobenzenesulfonate 6-methyl-2-pyrazinolate (XIIIA) in 60 ml. of water at 85°, there was added a solution of 8 g. stannous chloride in 20 ml. of concentrated hydrochloric acid. The mixture was warmed until the dye color was lost. Then the mixture was cooled in an ice salt bath until there was no further precipitation of sulfanilic acid. After filtration of the sulfanilic acid, sodium hydroxide solution (20%) was added to precipitate stannic oxide. The filtrate was evaporated to dryness on the steam bath and then extracted with absolute methanol, 300 ml. in 3 portions. The alcoholic extracts were combined and reduced in volume to 25 ml. Cooling to 0°, produced a light tan solid. The solid was recrystallized from absolute methanol to yield 0.5 g. of pale yellow solid (62%), which did not melt up to 300°.

Anal. Calcd. for $C_5H_6ON_3Na$: C, 40.81; H, 4.11. Found: C, 41.11; H, 4.22.

Preparation of 5-amino-6-methyl-2-(2,4-dinitrophenylhydrazone) pyrazinone (XV). A saturated solution of 2,4-dinitrophenylhydrazine in 2*M* hydrochloric acid–methanol was added dropwise to a solution of 1.5 g. of 5-amino-6-methyl-2-pyrazinol (XIV) until precipitation was complete. The yellow orange micro crystals were recrystallized from hot methanol-water to yield 2 g. of product. The hydrazone gave a dark red color on addition of 2*M* alcoholic potassium hydroxide solution indicating the aromatic nature of the pyrazine ring. The hydrazone was dried, m.p. 125°.

Anal. Calcd. for $C_{11}H_{11}O_4N_7$: C, 45.32; H, 3,63. Found: C, 45.56; H, 3.44.

ULTRAVIOLET ABSORPTION MAXIMA AND MINIMA

	Max., Mμ	Min., Mμ
7-Methyllumazine (I) acid solution	325	270
7-Methyllumazine (I) sodio salt	275,342	255,292
2-Acetamido-5-methylpyrazine (V)	300	260,400
6-Methyl-2-pyrazinol (XII)	250	324,410
2-Amino-3-bromo 6-pyrazinoic acid (XI)	243,340	285,400
5-Amino-6-methyl 2-pyrazinol (XIV)	253	236,360
5-Benezenesulfonate-6-methyl-2-pyrazinolate disodio salt (XIIA)	362	260
5-Benzenesulfonate-6-methyl-2-pyrazinolate disodio salt (XIIIA) at *p*H 11	410	700

BROOKLYN 10, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OKLAHOMA]

Chromatographic Separation of Nitration Products of Ester-Blocked 2-Hydroxybiphenyl[1]

J. C. COLBERT AND D. PAUL DENNY

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Nitration of the benzenesulfonate of *o*-hydroxybiphenyl yields 2′- and 4′-mononitro derivatives. Hydrolysis of these esters and nitration of the resulting mononitrohydroxybiphenyls lead to mononitro and dinitro substitution in the phenolic ring. A satisfactory separation of the nitrohydroxybiphenyls has been accomplished by chromatographic methods.

The direction of entering nitro groups to positions in the nonphenolic ring of the hydroxybiphenyls by the "ester block" method has been reported by Bell and Kenyon,[2] Hazlet *et al.*[3,4] and others. In addition to the 4′-mononitro derivative,

(1) Abstracted from a thesis submitted by D. Paul Denny to the faculty of the University of Oklahoma in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1957.

(2) F. Bell and J. Kenyon, *J. Chem. Soc.*, 129, 3044 (1926).

(3) S. E. Hazlet, G. Alliger, and R. Tiede, *J. Am. Chem. Soc.*, **61**, 1447 (1939).

(4) S. E. Hazlet, L. C. Hensley, and H. Hass, *J. Am. Chem. Soc.*, **64**, 2449 (1942).