[CONTRIBUTION FROM THE METCALF LABORATORIES, BROWN UNIVERSITY]

Cyclization of Aminoalkylaminoalkanols to Piperazines with a Raney Nickel Catalyst[1]

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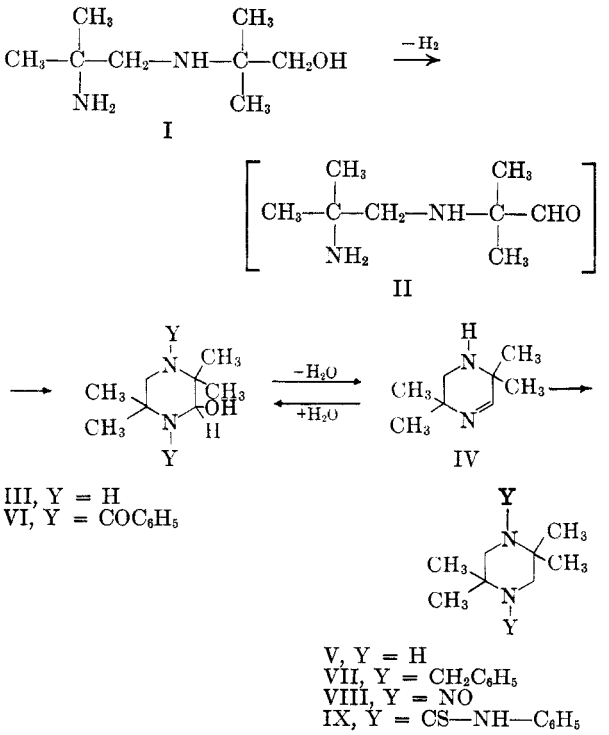
Catalytic cyclization of 5-amino-2,2,5-trimethyl-3-aza-1-hexanol with Raney nickel gave 2,2,5,5-tetramethyl-2,3,4,5-tetrahydropyrazine in 79% yield. This compound is a Schiff base or a pseudo base in aqueous solution and is easily reduced catalytically, and with nitrous acid, phenyl isothiocyanate, and picric acid in hydroxylic solvents. The source of hydrogen in these last three reactions has not been definitely established but it appears to come from the solvent in one case and may arise from disproportionation in the other two. Cyclization of 5-amino-2-ethyl-3-aza-1-heptanol gave 2,5-diethylpiperazine (25%) and 2,5-diethylpyrazine (8%).

Kitchen and Pollard[3] obtained piperazine in 32% yield by the cyclization of N-(2-hydroxyethyl)-ethanediamine in the presence of Raney nickel simply by distilling the product away from the catalyst at atmospheric pressure. When the same procedure was applied to the homolog, 5-amino-2,2,5-trimethyl-3-aza-1-hexanol (I), an unsaturated compound, 2,2,5,5-tetramethyl-2,3,4,5-tetrahydropyrazine (IV) was formed in 79% yield instead of the expected piperazine (V). The tetrahydropyrazine is readily reduced with a Raney nickel catalyst in a closed system[4] as well as with platinum at one atmosphere of hydrogen. Furthermore, this compound (IV) apparently removes hydrogen from alcohol solvents (see below) and disproportionates to the piperazine (V) with two other reagents.



I

II

III, Y = H
VI, Y = COC_6H_5

IV

V, Y = H
VII, Y = $CH_2C_6H_5$
VIII, Y = NO
IX, Y = CS—NH—C_6H_5

Success in isolating IV and a derivative of III amplifies the probability that the Kitchen and Pollard cyclization proceeds by the successive steps: dehydrogenation, cyclic dehydration, hydrogenation. In the present case, the process stops at compound IV.

The tetrahydropyrazine (IV) was identified by reduction to the known piperazine (V)[5] and comparison with an authentic sample.[6] There appears to be a facile equilibrium in aqueous solution between the tetrahydropyrazine (Schiff base) and the pseudo base structure (III). The free base, IV, isolated by distillation and sublimation was a partial hydrate which could not be obtained completely anhydrous. Drying the compound over solid potassium hydroxide for three months gave the tetrahydropyrazine nearly free of water. Infrared spectra of this compound showed a medium C=N band at 6.03 μ (in carbon tetrachloride). The same band is given by 2,2,5,5-tetramethyl-2,5-dihydropyrazine. The dihydrochloride of IV crystallizes as a monohydrate but still exhibits the C=N band at 6.33 μ (in Nujol).

On the other hand, a Schotten-Baumann reaction on the cyclization product gave a dibenzamide of structure VI. The evidence that the dibenzamide was a derivative of III rather than of II is as follows. Reduction of VI with a large excess of lithium aluminum hydride gave a 76% yield of 1,4-dibenzyl-2,2,5,5-tetramethylpiperazine (VII). A similar example of removal of a hydroxy group by lithium aluminum hydride has been reported by de Mayo and Rigby,[7] who obtained quinoline from the reduction of carbostyril. Neither the C—H stretching band of the aldehyde group in the 3.7 μ region nor the aldehyde carbonyl at 5.8 μ were visible in the infrared spectrum of VI. However, there was a weak band at 2.94 μ which could be interpreted as

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(3) Kitchen and Pollard, *J. Am. Chem. Soc.*, **69**, 854 (1947).

(4) Plante and Clapp, *J. Org. Chem.*, **21**, 86 (1956).

(5) McElvain and Pryde, *J. Am. Chem. Soc.*, **71**, 326 (1949).

(6) The authors are indebted to Prof. S. M. McElvain for a sample of 2,2,5,5-tetramethylpiperazine.

(7) deMayo and Rigby, *Nature*, **166**, 1075 (1950).

an O—H stretch and a strong band at 6.17 μ (amide carbonyl). The compound (VI) would not form an oxime, phenylhydrazone, 2,4-dinitrophenylhydrazone, nor a semicarbazone and oxidation with alkaline permanganate did not give the expected dibenzamido acid. Instead a trace of 2-benzamido-2-methylpropanoic acid resulted. Hydrolysis of VI in 18% hydrochloric acid gave back the hydrochloride of IV in 97% yield, establishing the fact that no rearrangement had occurred in forming the dibenzamide.

An attempt to prepare an O-acetyl derivative of compound VI resulted in a 41% yield of 1,4-dibenzamido-2,2,5,5-tetramethylpiperazine. This probably arises from a disproportionation reaction though the necessary accompanying product was not identified.

The 2,2,5,5-tetramethyl-2,3,4,5-tetrahydropyrazine (IV) showed unexpected ability to remove hydrogen from hydroxylic solvents at room temperature. When a reduction was carried out on the hydrochloride of IV with Adams' platinum catalyst in methanol or aqueous ethanol under one atmosphere of hydrogen, an 86% yield of 2,2,5,5-tetramethylpiperazine (V) was obtained although only 30% of the theoretical amount of hydrogen was adsorbed. When the reduction was carried out in dioxane, an uptake of one mole of hydrogen was observed. Isolation of the tetrahydropyrazine in the reducing atmosphere in which it is formed is also surprising since addition of one mole of hydrogen to 2,2,5,5-tetramethyl-2,5-dihydropyrazine in ethanol or dioxane gave only 2,2,5,5-tetramethylpiperazine (V) (35 and 30% yields, respectively).

Three other reactions of the tetrahydropyrazine IV gave unusual results. Nitrosation of IV in aqueous solution was accompanied by reduction to give a 60% yield of 1,4-dinitroso-2,2,5,5-tetramethylpiperazine (VIII). Clearly this product could not have arisen wholly from disproportionation of IV since the yield in that circumstance could not exceed 50%. 2,2,5,5-Tetramethylpiperazine was nitrosated under the same conditions to the extent of 74%.

Similarly, in absolute ethanol, both 2,2,5,5-tetramethyl-2,3,4,5-tetrahydropyrazine (IV) and 2,2,5,-5-tetramethylpiperazine (V) gave the same phenylthiourea, N,N'-bis-(phenylthiocarbamido)-2,2,5,5-tetramethylpiperazine (IX) in yields of 25% and 94%, respectively. The yield of the saturated phenylthiourea from the tetrahydropyrazine is sufficiently small to be accounted for by a disproportionation. When the bisphenylthiourea was prepared from the tetrahydropyrazine in anhydrous toluene, in which case all of the phenylthiourea would have had to be formed by disproportionation of the tetrahydropyrazine, 11.5% of the theoretical amount of the phenylthiourea was formed.

Attempts to prepare the picrate of the tetrahydropyrazine in ethanol resulted in the formation of 2,2,5,5-tetramethylpiperazine picrate.

An attempt to synthesize the tetrahydropyrazine (IV) from the triamine, 1,5-diamino-2,2,5-trimethyl-3-aza-hexane, with Raney nickel at atmospheric pressure failed. In a closed system, however, with dipentene as solvent at 160°, the tetrahydropyrazine formed in 17% yield. (Compare Martin and Martell).[8]

A similar catalytic cyclization of 5-amino-2-ethyl-3-aza-1-heptanol gave 2,5-diethylpiperazine in 25% yield and 2,5-diethylpyrazine in 8% yield. These products may arise entirely by disproportionation of an unstable tetrahydropyrazine, a reasonable assumption in the light of the results just described for the isomeric diamino alcohol.

EXPERIMENTAL[9]

Cyclodehydration of 5-amino-2,2,5-trimethyl-3-aza-1-hexanol. 5-Amino-2,2,5-trimethyl-3-aza-1-hexanol (38.8 g.)[10] prepared by the reduction of 5-nitro-2,2,5-trimethyl-3-aza-1-hexanol[11] was placed in a 500-ml. round-bottomed flask with 10 g. of Mozingo's catalyst,[12] wet with ethanol. A 12"-column carrying a nichrome spiral packing and an external heating jacket was attached and set for distillation. The ethanol was quickly distilled and then 36.5 g. of distillate, b.p. 100–170°, was collected while the column temperature was maintained at 120°. Part of the distillate quickly crystallized and was recrystallized from 100 ml. of petroleum ether (b.p. 30–40°). The yield was 8.2 g. of 2,2,5,5-tetramethyl-2,3,4,5-tetrahydropyrazine; m.p. 72–76°. By treating the remaining distillate with dilute hydrochloric acid and evaporating on the steam-bath, 30.5 g. of 2,2,5,5-tetramethyl-2,3,4,5-tetrahydropyrazine dihydrochloride monohydrate was obtained. The total yield as tetrahydropyrazine was 79%. The more soluble unreacted 5-amino-2,2,5-trimethyl-3-aza-1-hexanol (19%) remained as the hydrochloride after evaporation to dryness.

A satisfactory analysis was not obtained on the tetrahydropyrazine itself. The compound is volatile and hygroscopic, and absorbs carbon dioxide readily. It could not be purified by sublimation alone. After three recrystallizations from pentane, 2,2,5,5-tetramethyl-2,3,4,5-tetrahydropyrazine melted sharply at 83–84° and the infrared spectrum showed a medium C=N band at 6.03 μ in carbon tetrachloride.

Anal. Calc'd for $C_8H_{16}N_2O$: C, 68.52; H, 11.50; N, 19.98. Found: C, 66.52, 67.60; H, 12.29, 12.30; N, 19.77.

Although the analysis is unsatisfactory, 75–85% of the water must have been removed since the monohydrate or compound III would analyze as follows:

Anal. Calc'd for $C_8H_{18}N_2O$: C, 60.03; H, 11.28; N, 17.73.

2,2,5,5-Tetramethyl-2,3,4,5-tetrahydropyrazine dihydrochloride monohydrate was recrystallized from a mixture of 95% ethanol and acetone, m.p. 167–169° dec. When absolute ethanol was substituted for the 95% ethanol, only an oil was obtained.

Anal. Calc'd for $C_8H_{20}Cl_2N_2O$: C, 41.56; H, 8.72; N, 12.12; Cl, 30.68. Found: C, 41.60, H, 8.64, N, 12.20, 12.46; Cl, 30.4.

2,2,5,5-Tetramethylpiperazine (V). 2,2,5,5-Tetramethyl-2,3,4,5-tetrahydropyrazine dihydrochloride monohydrate

(8) Martin and Martell, *J. Am. Chem. Soc.*, **70**, 1817 (1948).

(9) Melting points given to tenths of a degree are corrected. Boiling points are uncorrected. Microanalyses by S. M. Nagy, Microchemical Laboratory, Massachusetts Institute of Technology, Cambridge, Mass.

(10) Johnson, *J. Am. Chem. Soc.*, **68**, 12, 14 (1946).

(11) Senkus, *J. Am. Chem. Soc.*, **68**, 10 (1946).

(12) Mozingo, *Org. Syntheses*, **21**, 15 (1941).

(18 g.) was dissolved in 250 ml. of 50% ethanol, and 0.5 g. of platinum oxide was added. Reduction with hydrogen at one atmosphere resulted in a hydrogen uptake of 695 ml., approximately 30% of the theoretical. After evaporation to dryness and neutralization with base, an ether extraction gave 9.5 g. (86%) of 2,2,5,5-tetramethylpiperazine; m.p. 80–84°. The piperazine was identified by conversion to the dibenzamide; m.p. 268–270°. A mixture m.p. with an authentic sample[6] was taken; m.p. 270–272°.

2,2,5,5-Tetramethyl-2,5-dihydropyrazine. The method of Conant and Aston[13] gave a 29% yield of 2,2,5,5-tetramethyl-2,5-dihydropyrazine. Controlled oxidation of 2-amino-2-methyl-1-propanol is somewhat easier to carry out though the results are not better. An ice-cold solution of 47.1 g. of 2-amino-2-methyl-1-propanol and 133 g. of sulfuric acid in 150 ml. of water was prepared and a solution of 52 g. of potassium dichromate in 500 ml. of water was slowly added with stirring. Cooling was continued one-half hour and then the solution was allowed to come to room temperature overnight. The solution was made strongly basic and extracted with ether. The ether was dried with solid potassium hydroxide and then was evaporated. The residue was recrystallized from hexane giving 10 g. (27%) of 2,2,5,5-tetramethyl-2,5-dihydropyrazine; m.p. 78–82°.

Attempted partial reduction of 2,2,5,5-tetramethyl-2,5-dihydropyrazine. One gram of 2,2,5,5-tetramethyl-2,5-dihydropyrazine in 50 ml. of absolute ethanol was allowed to absorb 200 ml. (one equivalent) of hydrogen in the presence of 0.1 g. of platinum oxide at one atmosphere. The reduced platinum was removed by centrifugation and the solution was treated with ethanolic hydrogen chloride. The solvent was evaporated on the steam-bath and the hydrochloride was converted to a benzamide. Recrystallization from absolute ethanol gave 0.86 g. (35%) of 1,4-dibenzamido-2,2,5,5-tetramethylpiperazine; m.p. 270–272°. A mixture m.p. with an authentic sample of this compound gave no depression.

After it was recognized that the tetrahydropyrazine (IV) could remove hydrogen from ethanol in the presence of platinum, the partial reduction was repeated in dioxane. A yield of 30% of the dibenzamido derivative just described was obtained.

1,4-Dibenzamido-2,2,5,5-tetramethyl-6-hydroxypiperazine (VI). 2,2,5,5-Tetramethyl-2,3,4,5-tetrahydropyrazine dihydrochloride monohydrate (100 mg.) was converted to 150 mg. (78%) of 1,4-dibenzamido-2,2,5,5-tetramethyl-6-hydroxypiperazine by the standard Schotten-Baumann procedure; m.p. 232–234°. An analytical sample was sublimed at 200° (0.4 mm.); m.p. 234.4–235.0°.

Anal. Calc'd for $C_{22}H_{26}N_2O_3$: C, 72.10; H, 7.15; N, 7.65. Found: C, 72.07; H, 7.21; N, 7.49.

The dibenzamide (183 mg.) was refluxed with 15 ml. of 18% hydrochloric acid for eight hours. After cooling, benzoic acid was removed by filtration and one extraction with ether. Evaporation of the solution gave 112 mg. (97%) of the dihydrochloride monohydrate of 2,2,5,5-tetramethyl-2,3,4,5-tetrahydropyrazine; m.p. 166–170° dec. A mixture m.p. with an authentic sample showed no depression.

An attempt to prepare an O-acetyl derivative of compound VI failed. Acetic anhydride (5 g.) containing a few drops of pyridine was refluxed for 16 hours with 0.63 g. of 1,4-dibenzamido-2,2,5,5-tetramethyl-6-hydroxypiperazine. By cooling in ice, 0.25 g. (41%) of 1,4-dibenzamido-2,2,5,5-tetramethylpiperazine was obtained from the reaction mixture; m.p. 270–273°. A gummy residue remaining in the acetic anhydride solution was not identified.

1,4-Dibenzyl-2,2,5,5-tetramethylpiperazine (VII). 1,4-Dibenzamido-2,2,5,5-tetramethyl-6-hydroxypiperazine (2.25 g.) was dissolved in 50 ml. of refluxing tetrahydrofuran. To this solution a slurry of 5 g. of lithium aluminum hydride in 50 ml. of tetrahydrofuran was added. The mixture was allowed to stand overnight and then was worked up in the usual way. The suspension of lithium aluminate obtained from the decomposition was extracted with ether, and the ethereal solution was dried with potassium hydroxide. Saturation of the anhydrous ether solution with dry hydrogen chloride gave 1.86 g. of 1,4-dibenzyl-2,2,5,5-tetramethylpiperazine dihydrochloride. From the *hydrochloride*, 1.39 g. (70%) of 1,4-dibenzyl-2,2,5,5-tetramethylpiperazine was obtained; m.p. 164.4–165.4°.

Anal. Calc'd for $C_{22}H_{30}N_2$: C, 81.90; H, 9.38; N, 8.69. Found: C, 81.80; H, 9.40; N, 8.65.

The *hydrochloride* also was converted to the *picrate* with aqueous picric acid. After four recrystallizations from a large volume of absolute ethanol, an analytical sample was obtained, m.p. 211.0–212.9°.

Anal. Calc'd for $C_{34}H_{36}N_8O_{14}$: C, 52.30; H, 4.65; N, 14.35. Found: C, 52.06; H, 4.72; N, 14.44.

1,4-Dinitroso-2,2,5,5-tetramethylpiperazine (VIII). One gram of 2,2,5,5-tetramethyl-2,3,4,5-tetrahydropyrazine was dissolved in 7.3 ml. of 10% hydrochloric acid. The solution was cooled to 0°, and a cold solution of 1.04 g. of sodium nitrite in 10 ml. of water was added slowly with stirring and cooling. The mixture was allowed to stand at 0° for 15 minutes, and then the temperature was allowed to rise to 25°. The pale green crystals were filtered and recrystallized from absolute ethanol. The yield of 1,4-dinitroso-2,2,5,5-tetramethylpiperazine was 0.86 g. (60%); m.p. 210–212°.

Using the same amounts of reagents as above, 1,4-dinitroso-2,2,5,5-tetramethylpiperazine was prepared from 1.0 g. of 2,2,5,5-tetramethylpiperazine. After recrystallization from absolute ethanol, the yield was 1.04 g. (74%); m.p. 211–212°. A mixture m.p. on these dinitrosopiperazines showed no depression. Conant and Aston[13] report a m.p. of 208–210° for 1,4-dinitroso-2,2,5,5-tetramethylpiperazine.

N,N'-Bis-(phenylthiocarbamido)-2,2,5,5-tetramethylpiperazine (IX). 2,2,5,5-Tetramethylpiperazine (0.45 g.) was dissolved in 20 ml. of absolute ethanol and 2 ml. of phenyl isothiocyanate was added. The solution was warmed on the steam-bath for one-half hour, cooled, and filtered. The white needles were washed liberally with carbon tetrachloride and were recrystallized from absolute ethanol. The yield of N,N'-bis-(phenylthiocarbamido)-2,2,5,5-tetramethylpiperazine was 1.22 g. (94%); m.p. 138–139°.

Anal. Calc'd for $C_{22}H_{28}N_4S_2$: C, 63.98; H, 6.84; N, 13.59. Found: C, 64.14; H, 6.83; N, 13.33.

When 0.78 g. of 2,2,5,5-tetramethyl-2,3,4,5-tetrahydropyrazine was treated in the same manner as described above, a yield of 0.56 g. (24%) of N,N'-bis-(phenylthiocarbamido)-2,2,5,5-tetramethylpiperazine was obtained. In anhydrous toluene, 1.07 g. of 2,2,5,5-tetramethyl-2,3,4,5-tetrahydropyrazine gave 0.35 g. (11.5%) of N,N'-bis-(phenylthiocarbamido)-2,2,5,5-tetramethylpiperazine. Mixture m.ps. on these bis-phenylthioureas showed no depression.

2,2,5,5-Tetramethylpiperazine picrate. An ethanol solution of 2,2,5,5-tetramethyl-2,3,4,5-tetrahydropyrazine (0.1 g.) was treated with a saturated solution of picric acid in ethanol. A quantitative yield of the reduced piperazine picrate was obtained and was recrystallized from a large volume of alcohol-water. The picrate blackened at 260° and detonated at about 275°. The picrate prepared from 2,2,5,5-tetramethylpiperazine itself behaved in the same way.

Anal. Calc'd for $C_{20}H_{24}N_8O_{14}$: C, 40.01; H, 4.03; N, 18.65. Found: C, 40.29; H, 4.13; N, 18.71.

1,5-Diamino-2,2,5-trimethyl-3-azahexane. In a stainless steel autoclave, 41 g. of 2,2-dimethylethylenimine[14] was placed with 71 g. of isobutylenediamine[11] and 5 g. of ammonium chloride. The reaction mixture was heated at 100° for 23 hours. Fractionation of the contents of the autoclave gave 39 g. (42%) of 1,5-diamino-2,2,5-trimethyl-3-azahexane, b.p. 85–87° (10 mm.). An analytical sample was obtained by redistillation in an atmosphere of nitrogen, b.p. 80–82° (8 mm.), $n^{25}D$ 1.4493, and d^{25}_4 0.8605.

(13) Conant and Aston, *J. Am. Chem. Soc.*, **50**, 2783 (1928).

(14) Cairns, *J. Am. Chem. Soc.*, **63**, 871 (1941).

Anal. Calc'd for $C_8H_{21}N_3$: C, 60.33; H, 13.29; N, 26.38; MR_D, 49.47. Found: C, 60.31; H, 13.48; N, 26.44; MR_D, 49.58.

A 26% yield of this same triamine was obtained as a second product in the ammonolysis of 2,2-dimethylethylenimine with liquid ammonia in earlier work.[15] This was reported as polymer and was not further identified at that time.

The *benzamide* derivative of the triamine was prepared by the standard Schotten-Baumann procedure. Recrystallization from 95% ethanol gave an analytical sample, m.p. 201.8–202.4°. A sublimed sample gave a lower m.p.

Anal. Calc'd for $C_{29}H_{33}N_3O_3$: C, 73.86; H, 7.05; N, 8.91. Found: C, 74.01; H, 7.12; N, 8.96, 9.03.

Cyclodeammonation of 1,5-diamino-2,2,5-trimethyl-3-azahexane. When 1,5-diamino-2,2,5-trimethyl-3-azahexane was subjected to the same cyclization conditions used previously for 5-amino-2,2,5-trimethyl-3-aza-1-hexanol, none of the tetrahydropyrazine could be isolated. However, in a closed system in the presence of a hydrogen carrier, dipentene, a 17% yield of 2,2,5,5-tetramethyl-2,3,4,5-tetrahydropyrazine was obtained. Freshly distilled dipentene (200 ml.), 10 g. of Mozingo's catalyst,[12] and 48.5 g. (0.31 m.) of 1,5-diamino-2,2,5-trimethyl-3-azahexane were sealed in an 1850-ml. stainless steel bomb and heated at 160° with shaking for 22 hours. After cooling, the contents of the bomb were subjected to fractional distillation. A water extraction of the fraction of b.p. 55–65° (13 mm.), which was largely dipentene, gave 7.2 g. (17%) of 2,2,5,5-tetramethyl-2,3,4,5-tetrahydropyrazine, by acid titration. The compound was identified by the m.p. of the hydrochloride, 166–169°, and by conversion to the benzamide previously described, m.p. 234–236°. The second fraction, b.p. 80–85° (13 mm.) contained 5.0 g. (18.5%) of isobutylenediamine, identified as the benzamide, m.p. 180–181°, by comparison with an authentic sample.[15] A third fraction, b.p. 95–103° (13 mm.), gave 6.2 g. (12.5%) of unreacted starting compound, and a residue of 9.2 g. was not identified.

(15) Clapp, *J. Am. Chem. Soc.*, **70**, 184 (1948).

Cyclization of 5-amino-2-ethyl-3-aza-1-heptanol. 5-Amino-2-ethyl-3-aza-1-heptanol[15] was subjected to the cyclization described above for the isomeric diamino alcohol. The 2,5-diethylpiperazine was precipitated from the distillate by the addition of petroleum ether (b.p. 30–40°) in 25% yield, m.p. 87–88°.[15] It was identified by conversion to the benzamide; m.p. 167–169°,[15] the phenylthiourea; m.p. 240–244°,[16] and the benzenesulfonamide; m.p. 187–188°. Recrystallization of this last derivative from ethanol-chloroform gave an analytical sample; m.p. 188.2–190.4°.

Anal. Calc'd for $C_{20}H_{26}N_2S_2O_4$: C, 56.85; H, 6.21; N, 6.63. Found: C, 57.07; H, 6.44; N, 7.13.

After removal of the diethylpiperazine, a Schotten-Baumann reaction was carried out on the remaining distillate and the reaction mixture was subjected to steam-distillation. The 2,5-diethylpyrazine in the steam-distillate was determined by conversion to the picrate by shaking with aqueous picric acid. The yield of yellow needles was 9.2 g. (8%); m.p. 93°.[17]

When the aqueous distillate was cold, the pyrazine remained in solution but when it was warmed to room temperature, an oil separated. This decreasing solubility in hot water is characteristic of pyrazine. A small portion of the solution was converted to the mercuric chloride addition compound; m.p. 166–168° dec. Kolshorn[17] reported m.p. 168° dec.

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(16) Clapp, *J. Am. Chem. Soc.*, **73**, 2584 (1951).

(17) Kolshorn, *Ber.*, **37**, 2478 (1904).