β-phenylpropionamide,[11] m. p. 100–100.5°, the mixture melted at 100.5–101°.

Phenylmethylcarbinol and Ammonium Polysulfide.—Phenylmethylcarbinol (3.0 g.) and ammonium polysulfide (15 g.) were heated four hours at 210 ± 5° in a pressure tube. The solid material was removed by filtration and the mother liquor was extracted with ether from which there was obtained more of the product. The crude product (wt. 1.6 g., 48% yield, crude) was recrystallized once from water to give white plates, m. p. 156.5–157°, undepressed when mixed with an authentic sample of phenylacetamide.

Styrene and Ammonium Polysulfide.—Styrene (3.0 g.) and ammonium polysulfide (15 g.) were heated four hours at 210 ± 5° in a pressure tube. The crude product, isolated as above, weighed 1.64 g. (49% yield, crude); after recrystallization from water it melted at 156–157°, undepressed when mixed with an authentic sample of phenylacetamide.

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[11] Conrad, *Ann.*, **204**, 174 (1880); Hofmann, *Ber.*, **18**, 2740 (1885).

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RECEIVED AUGUST 23, 1945

Preparation of 6-Methylpyrazine-2-carboxylic Acid

BY FREDERICK LEONARD AND PAUL E. SPOERRI

In the course of our studies on pyrazine carboxylic acids it was of interest to prepare the 6-methylpyrazine-2-carboxylic acid. The related acid, 5-methylpyrazine-2,3-dicarboxylic acid, obtained by the oxidation of 2-methylquinoxaline had been described by Böttcher in 1913.[1] By considerable modification of Böttcher's oxidation procedure, followed by decarboxylation, we have been able to prepare the desired 6-methylpyrazine-2-carboxylic acid in satisfactory yields.

The mono carboxylic acid melted sharply at 138° with decomposition. Since Stoehr[2] found that 5-methylpyrazine-2-carboxylic acid melts at 200°, the substance we obtained can only be the isomeric 6-methylpyrazine-2-carboxylic acid.

Experimental

5-Methylpyrazine-2,3-dicarboxylic Acid.—Twenty-eight and eight-tenths grams of 2-methylquinoxaline was dissolved in 2400 cc. of water containing 8 g. of potassium hydroxide. To this solution at 50°, a solution of 176 g. of potassium permanganate in 1600 cc. of water, preheated to 50°, was added dropwise with good stirring. The addition took about two and one-half hours. The mixture was heated for an additional hour, 50 cc. of alcohol was added and heating continued for a half hour more. The filtrate from the manganese dioxide was concentrated to about 1 liter, made alkaline with concentrated ammonia, and a solution of 142 g. of calcium nitrate tetrahydrate in 200 cc. of water added. After the mixture had been digested on a steam-bath for one hour, the calcium oxalate was filtered off and washed with water. The combined filtrate and washings were made acid to congo red with 1:1 nitric acid and precipitated with a solution of 68 g. of silver nitrate in 200 cc. of water. The precipitated silver salt was filtered by suction and washed with water. It was suspended in water, acidified with acetic acid and treated with hydrogen sulfide at 60° with constant stirring for one and one-half hours. The silver sulfide was filtered off and washed. The combined filtrate and washings were partially decolorized with Norit A and evaporated to dryness *in vacuo* to yield 11 g. (39% yield) of 5-methylpyrazine-2,3-dicarboxylic acid, m. p. 163–164°. Recrystallized from an alcohol-ether mixture, the compound melted at 174–175°. It titrated as a strong acid and had a neutral equivalent of 93.0 (determined by potentiometric titration); calcd. 91.1. Aqueous solutions of this acid gave deep wine red colorations with ferrous sulfate.

Anal. Calcd. for $C_7H_6O_4N_2$: C, 46.15; H, 3.32; N, 15.36. Found: C, 46.40; H, 3.69; N, 14.33.

S-Benzylthiuronium salt prepared according to Donleavy[3]; m. p. 203–204°, after recrystallization from aqueous alcohol.

Anal. Calcd. for $C_{23}H_{26}O_4N_6S_2$: C, 53.65; H, 5.09; N, 16.34; S, 12.45. Found: C, 53.40; H, 5.09; N, 16.65; S, 12.10.

6-Methylpyrazine-2-carboxylic Acid.—One gram of 5-methylpyrazine-2,3-dicarboxylic acid was placed in a vacuum sublimation apparatus and was decarboxylated by heating to 175–185° at 1 mm. with simultaneous sublimation to yield 0.6 g. (82%) of 6-methylpyrazine-2-carboxylic acid, m. p. 135–140°. After two resublimations at 100–110° (1 mm.) the compound melted sharply at 138–140° (turbid melt which became clear at 144 with the evolution of a gas). Neutral equivalent by potentiometric titration was 136; calcd. 138. The ferrous sulfate color test gave orange coloration.

Anal. Calcd. for $C_6H_6O_2N_2$: C, 52.19; H, 4.38; N, 20.29. Found: C, 52.31; H, 4.21; N, 20.21.

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[1] Böttcher, *Ber.*, **46**, 3084 (1913).

[2] Stoehr, *J. prakt. Chem.*, [2] **47**, 480 (1893).

[3] Donleavy, THIS JOURNAL, **58**, 1004 (1936).

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RECEIVED OCTOBER 5, 1945

Interaction Energies and Thermochemical Data

BY JOHN R. LACHER[1]

Recently Aston, *et al.*,[2] have been able to calculate empirically the height of potential barriers hindering internal rotation. They assumed that the barrier was due to a repulsion between hydrogen atoms. Urey and Bradley,[3] in discussing the normal vibrations of carbon tetrachloride and similar compounds, found it necessary to assume the existence of repulsive forces between the atoms situated at the corners of a tetrahedron. These latter forces were in addition to those directed along and perpendicular to the chemical bonds. H. A. Stuart,[4] V. Deitz,[5] R. Serber,[6] and E. Mack[7] have already indicated that interaction energy due to the repulsion (and in some situations certainly due to the attraction) of certain groups should be taken into account in the interpretation of thermochemical data. It is desired here to illustrate and develop this idea further in connection with groups arranged tetrahedrally

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[2] J. G. Aston, S. Isserow, G. J. Szasz and R. M. Kennedy, *J. Chem. Phys.*, **12**, 336 (1944).

[3] H. C. Urey and C. A. Bradley, Jr., *Phys. Rev.*, **38**, 1969 (1931).

[4] H. A. Stuart, *ibid.*, **38**, 1372 (1938).

[5] V. Deitz, *J. Chem. Phys.*, **3**, 58, 436 (1935).

[6] R. Serber, *ibid.*, **3**, 81 (1935).

[7] E. Mack, Jr., *J. Phys. Chem.*, **41**, 221 (1937).