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).

RESEARCH LABORATORIES
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RENSSELAER, NEW YORK
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).

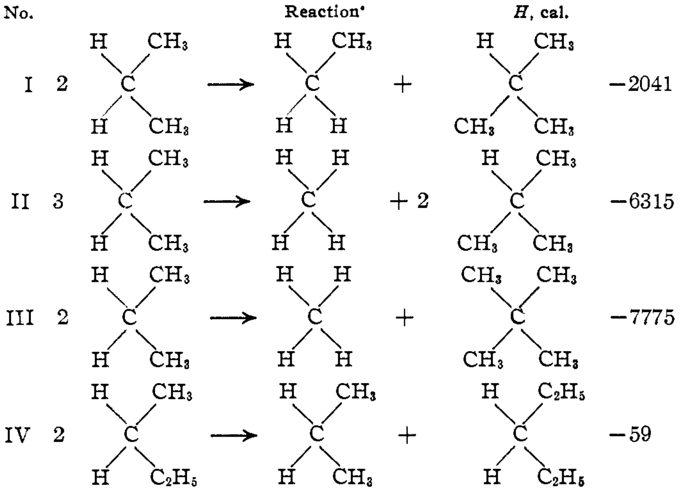
[4] H. A. Stuart, *ibid.*, **38**, 1372 (1938).

[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).

about a central carbon atom. Accordingly the heats of the following reactions were calculated from the data of Rossini.[8] In these reactions the number of carbon–carbon and carbon–hydrogen bonds remains unchanged. There has taken place merely a redistribution of hydrogen atoms, methyl, and ethyl groups about a central carbon atom. The heats of the first three reactions are in the ratio of one, three and four. This may be interpreted by assigning a repulsion to the hydrogen atoms and methyl groups arranged about the central carbon atom and by assuming that the repulsive forces are directed along the six edges of a tetrahedron. The net effect in reaction I is the conversion of two hydrogen–methyl interactions into a hydrogen–hydrogen and a methyl–methyl interaction. In reactions II and III the number of hydrogen–methyl conversions is simply three and four times as many as for I. This result may be summarized as



$$2H\cdot CH_3 \longrightarrow H\cdot H + CH_3\cdot CH_3;\ \Delta H = -2030 \pm 100 \text{ cal.}$$

In reaction IV, the net effect is the conversion of two methyl–ethyl repulsions into one methyl–methyl and one ethyl–ethyl. Since the heat effect is zero, we may write

$$2CH_3\cdot C_2H_5 \longrightarrow CH_3\cdot CH_3 + C_2H_5\cdot C_2H_5 \qquad \Delta H \sim 0$$

The composition of equilibrium mixtures of tetraethyl and tetramethyl lead is determined, according to Calingaert and Beatty,[9] merely by the external symmetry numbers of the molecules involved. Stearn[10] pointed out that this means that the heat of the redistribution reaction must be zero.

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RECEIVED SEPTEMBER 21, 1945

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[8] F. D. Rossini, *Chem. Rev.*, **27**, 1 (1940).

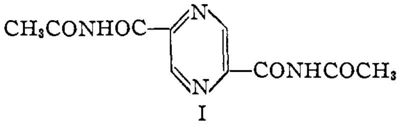
[9] Calingaert and Beatty, THIS JOURNAL, **61**, 2748 (1939).

[10] Stearn, *ibid.*, **62**, 1630 (1940).

Syntheses in the Pyrazine Series. Preparation of 2,5-Dicyanopyrazine and the Diacetyl Diamide of Pyrazine Dicarboxylic Acid-2,5

BY IRVING J. KREMS AND PAUL E. SPOERRI

Since Braun[1] and Tscherniac had reported that phthalic acid diamide undergoes a semi-dehydration to the amido nitrile when treated with acetic anhydride, we subjected the diamide of pyrazine dicarboxylic acid-2,5[2] to the same treatment. No change was detected after four hours; after forty-eight hours of refluxing, crystals of the diacetyl diamide (I) were obtained.



I

When a suspension of the diamide in nitrobenzene was treated with phosphorus pentoxide, the dinitrile was produced in low yield.

Experimental

Pyrazine Dicarboxylic Acid-2,5.[3]—Since the yields were quite poor the conditions of the permanganate oxidation of 2,5-dimethylpyrazine were modified. The results showed that the yield was independent of the permanganate concentration between two and twenty per cent., and the time of addition of the oxidizing solution between one and thirty-six hours, but was favored by an increase in *p*H. An oxidation of the insoluble mercuric chloride double salt instead of the free base indicated no protection to the pyrazine nucleus.

Twenty-seven grams of dimethylpyrazine[4,5] was dissolved together with 5 g. of potassium hydroxide in 150 ml. of water and warmed on the steam-bath in a 2,000 ml. three-necked round-bottom flask fitted with a separatory funnel, thermometer, condenser and stirrer. A hot solution of 158 g. of potassium permanganate in 760 ml. of water was added slowly over a period of one hour with stirring, the temperature being kept at 75°. Stirring was maintained for another half hour at the same temperature, after which the mixture was allowed to cool and stand overnight. The precipitate was filtered off and washed several times with hot water. The filtrate was evaporated to small volume, acidified with dilute nitric acid, and allowed to stand for one hour. The free diacid was filtered off, washed thoroughly with hot water, dissolved with hot dilute ammonium hydroxide and reprecipitated with dilute nitric acid. The precipitate was filtered off and dried *in vacuo* over sulfuric acid; yield 1.68 g., m. p. 253° (seal cap).

The Diacetyl Diamide of Pyrazine Dicarboxylic Acid 2,5 (I).—One-half gram of the diamide of pyrazine dicarboxylic acid-2,5[2] and 15 ml. acetic anhydride were placed in 50 ml. flask fitted with a two-foot length of glass tubing as an air condenser. Care was taken to eliminate moisture, and the air condenser was fitted with a calcium chloride tube. The mixture was refluxed for forty-eight hours at the end of which time it had turned completely black. It was allowed to cool, and then was placed in the ice chest for twenty-four hours. The resultant crystals were filtered

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[1] Braun and Tscherniac, *Ber.*, **40**, 2710 (1907).

[2] Spoerri and Erickson, THIS JOURNAL, **60**, 400 (1938).

[3] Stoehr, *Ber.*, **24**, 4108 (1892).

[4] Étard, *Compt. rend.*, **92**, 460, 795 (1881).

[5] Stoehr, *J. prakt. Chem.*, [2] **43**, 156 (1891); **47**, 439 (1893).