[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Constitution of Pyromellitic, Mellophanic and Prehnitic Acids

BY LEE IRVIN SMITH AND GORDON D. BYRKIT

No proof of the constitution of the three isomeric benzene tetracarboxylic acids has apparently been offered in which they have been converted into compounds of known orientation. Numerous syntheses have made it certain that pyromellitic acid is the 1,2,4,5-tetracarboxylic acid. Such procedures in the case of the 1,2,3,4- and the 1,2,3,5-acids, however, have led to conflicting results.[1] The purpose of the investigation presented in this paper has been to make the orientation of these other two acids certain by converting one of them to a compound of known orientation. The importance of such a structure proof is apparent from the wide use of these acids as reference compounds.

Baeyer[2] separated "isopyromellitic acid" into these two isomeric acids, naming one of them prehnitic acid, and determining the orientation of this acid as 1,2,3,5.

Jacobsen[3] oxidized the hydrocarbon resulting from the action of sodium and methyl iodide on bromomesitylene, and obtained a tetrabasic acid having the properties of Baeyer's mellophanic acid. Tohl[4] prepared prehnitene from pentamethylbenzene by means of the Jacobsen reaction, and on oxidizing this hydrocarbon, obtained an acid having the properties of Baeyer's prehnitic acid.

In 1910, Carré[5] treated mesitylmagnesium bromide with paraformaldehyde, and the resulting carbinol, on oxidation, gave an acid agreeing in properties with Baeyer's mellophanic acid. Bamford and Simonson,[6] using almost the same series of reactions, prepared a tetrabasic acid softening at 240° and melting at 252°, which gave a tetramethyl ester melting at 108–109°. These are the properties of Baeyer's prehnitic acid. In addition, Bamford and Simonson, by oxidizing 1,4-dimethylnaphthalene, succeeded, after much difficulty, in isolating from the reaction mixture an acid sintering at 225° and melting at 238°, which gave a tetramethyl ester melting at 133–135°; these are the properties of Baeyer's mellophanic acid.

Hence from the work of Jacobsen, Tohl and Carré, it appears that Baeyer had assigned incorrect orientations to these two acids, and that

---

[1] The 1,2,3,4-acid has usually been called mellophanic (but sometimes prehnitic acid) and assigned the melting point 238° (225–241°). Conversely, the 1,2,3,5-acid has usually been called prehnitic (sometimes mellophanic) and assigned melting points varying between 237 and 262° (usually about 250°).

[2] Baeyer, *Ber.*, **2**, 94 (1869); **4**, 273 (1871); *Ann. Suppl.*, **7**, 20 (1870); *Ann.*, **166**, 325, 628 (1873).

[3] Jacobsen, *Ber.*, **17**, 2517 (1884).

[4] Tohl, *ibid.*, **21**, 904 (1888).

[5] Carré, *Compt. rend.*, **151**, 151 (1910).

[6] Bamford and Simonson, *J. Chem. Soc.*, **97**, 1904 (1910).

mellophanic acid should be 1,2,3,5 and prehnitic acid 1,2,3,4; while from the work of Bamford and Simonson, the orientation as Baeyer originally assigned it is correct and prehnitic acid is the 1,2,3,5, while mellophanic acid is the 1,2,3,4.

The results of our investigation are in agreement with those of Bamford and Simonson. Mesitylene carboxylic acid, prepared both by their method and by the haloform reaction, gave identical products agreeing in properties with their acid. Part of this sample was oxidized to the 1,2,3,5-acid, which was the same as theirs. Part of it was nitrated, the oxidation completed and the dinitrotetracarboxylic acid decarboxylated. Since the resulting product was *m*-dinitrobenzene, the carboxyl groups certainly occupied the 1-, 2-, 3- and 5-positions. This makes it certain that the acid melting at 237–250°, Baeyer's prehnitic acid (tetramethyl ester melting at 108–109°), is the 1,2,3,5-acid. Since, in addition to this, it is possible to decarboxylate diaminopyromellitic acid to *p*-phenylenediamine, the third acid melting at 238° (240°) Baeyer's mellophanic acid (tetramethyl ester melting at 133–135°) must be the 1,2,3,4-acid.

We consider the constitution of these acids now made certain by this agreement with and extension of the work of Bamford and Simonson. It is difficult to explain the result of Jacobsen, Tohl and Carré, but the suggestion of Bamford and Simonson that prehnitene is 1,2,3,5-tetramethylbenzene cannot be accepted, since all the many syntheses of isodurene, as well as its reactions, indicate that isodurene is the 1,2,3,5-tetramethylbenzene. With regard to the nomenclature, however, we propose the following change: Since the constitution of prehnitene is known to be 1,2,3,4-tetramethylbenzene, it is essential to clarity that benzene-1,2,3,4-tetracarboxylic acid be known as prehnitic acid. Likewise mellophanic acid must be the term applied to benzene-1,2,3,5-tetracarboxylic acid.

Experimental Part

I. Pyromellitic Acid Series

Acetylpseudocumene.—The method of Maxwell and Adams[7] was used; b. p. 114–116° (7 mm.).

Durylic Acid.—The haloform reaction described by Mills[8] and investigated by Fuson[9] was used with the following modifications. The reaction mixture was refluxed for five hours and excess bromine discharged by sodium bisulfite. The unchanged acetylpseudocumene as well as bromoform and carbon tetrabromide were extracted with ether. The purification of the sodium salt gave very satisfactory results provided the gelatinous material not dissolved by alkali was carefully filtered off. Crystallization of the sodium salt from acetone was omitted but the acid obtained melted at the same temperature given by Mills (148–149°).

Pyromellitic Acid.—The acid obtained by the method of Mills[8] by the oxidation of durylic acid sintered at 235°, melted at 270–272°.

---

(7) Maxwell and Adams, THIS JOURNAL, **52**, 2969 (1930).

(8) Mills, *J. Chem. Soc.*, **101**, 2191 (1912).

(9) Fuson, *et al.*, THIS JOURNAL, **52**, 3269 (1930); **53**, 1985, 3494, 4097 (1931).

Dinitrodurylic Acid.—This was obtained from durylic acid by the method of Nef.[10] An acid melting at 212.5–214.5° (corr.) was obtained through the following purification. The crude acid was suspended in a small amount of water and dilute sodium hydroxide added to faint alkalinity. The solution was warmed and the undissolved material (trinitropseudocumene) filtered off. The filtrate was acidified, the acid filtered off and washed with water. It was dissolved in the minimum amount of 95% alcohol, *slightly* warmed. Sufficient water was added to begin precipitation and then alcohol to redissolve. After standing *uncovered* overnight, the crystals were filtered off, allowed to effloresce in air for two hours and then dried in the oven at 60°.[11]

Dinitropyromellitic Ester.—The oxidation of dinitrodurylic acid and esterification of the dinitropyromellitic acid was done according to Nef[10] except that the latter acid need not be isolated. To a hot solution of 10 g. of the purified calcium salt of dinitropyromellitic acid in 200 cc. of water was added hot ammonium oxalate solution containing a little ammonia until precipitation was just complete. The calcium oxalate was filtered off and to the hot filtrate was added a hot solution of silver nitrate as long as precipitation occurred. The silver salt was filtered off and dried at 100°; yield 18 g. or 97.8%.

This silver salt was converted to the ester as described by Nef[10] by refluxing with ethyl bromide in dry ether, yellow crystals of m. p. 127–128°.

Diaminopyromellitic Ester.—Nef's directions[10] for the reduction of dinitropyromellitic ester with zinc and acetic acid were used. On pouring the reaction mixture into water, a yellow solid was precipitated which changed quickly to a brilliant scarlet; m. p. 133–134°.

Decarboxylation.—0.4 g. of potassium hydroxide and 1.0 g. of diaminopyromellitic ester were dissolved in 25 cc. of 95% alcohol and refluxed four hours. The solution was evaporated to dryness, mixed with an equal weight of soda lime and dry distilled; 0.25 g. (93%) of a yellow solid distilled over; m. p. 136–137°. Mixed with *p*-phenylenediamine (m. p. 136–137°), there was no depression of the melting point.

The diacetyl derivative of the yellow solid was prepared according to the directions of Mulliken[12] with acetic anhydride. The product melted at 302–303° and mixed with known diacetyl-*p*-phenylenediamine (m. p. 303–304°), showed no depression of the melting point.

II. The 1,2,3,5-Series

Mesitylene Carboxylic Acid.—Mesitylmagnesium bromide was carbonated by passing a stream of pure, dry, carbon dioxide through the ethereal solution overnight. The reaction mixture was worked up in the usual way. The crude acid was recrystallized from the minimum amount of carbon tetrachloride; yield 37 g. (53.7%) taking into account the recovery of 16 g. of bromomesitylene; m. p. 151–152°.

Acetylmesitylene.—This was prepared by the method of Meyer and Molz.[13]

Mesitylene Carboxylic Acid from Acetylmesitylene.—In the case of acetylmesitylene, hypobromite gave an ω,ω,ω-tribromoacetylmesitylene which was not hydrolyzed by the alkali used.[9] Houben and Fischer[14] obtained a quantitative yield on hydrolyzing ω,ω,ω-trichloroacetylmesitylene by boiling two hours with 40% alkali. By this method, however, the tribromo compound gave rise to considerable tar and only 16% yield of the acid. The product melted at 145–147° and mixed with mesitylene carboxylic acid prepared by the Grignard method it melted at 148.5–150°.

---

(10) Nef, *Ann.*, **237**, 1 (1887).

(11) Gissmann, *ibid.*, **216**, 200 (1883).

(12) Mulliken, "Identification of Pure Organic Compounds," Vol. II, p. 112.

(13) Meyer and Molz, *Ber.*, **30**, 1271 (1897).

(14) Houben and Fischer, *ibid.*, **63B**, 2458 (1930).

Benzene-1,2,3,5-tetracarboxylic Acid.—This was prepared in precisely the same way as pyromellitic acid, oxidizing mesitylene carboxylic acid instead of durylic acid; m. p. 238–253°.

Benzene-1,2,3,5-tetramethyl Carboxylic Ester.—One gram of the acid was suspended in 100 cc. of ether and treated with the diazomethane from 3 cc. of nitroso methylurethan. The yellow color slowly faded, but not much gas was evolved. Two more similar portions of diazomethane were added, the solution then filtered and the filtrate evaporated. The residue was crystallized twice from methyl alcohol; m. p. 107–109°.

Dinitromesitylene Carboxylic Acid.—This was prepared according to Nef's[10] directions for dinitrodurylic acid and purified as described above for dinitrodurylic acid. The yield was 27 g. (87.1%) from 20 g. of mesitylene carboxylic acid; m. p. 231–232°.

Dinitrobenzene-1,2,3,5-tetracarboxylic Acid.—Four grams of dinitromesitylene carboxylic acid was dissolved in a solution of 10 g. of potassium carbonate in 400 cc. of water, 14.5 g. of potassium permanganate was added, and the mixture heated on the steam-bath until the color faded (four days). Then 0.5 g. of potassium permanganate was added and the heating continued two more days. The slight color was discharged by sodium bisulfite and the manganese dioxide filtered off and washed. The filtrates were combined, concentrated and acidified, then extracted several times with ether and the ether evaporated. The residue was dissolved in water and treated with excess barium carbonate and filtered. Alcohol was added to the cold filtrate slowly with stirring until, on standing an hour, additional alcohol caused no further precipitation.[15] The barium salt was filtered off, dissolved in water and excess of 50% sulfuric acid added. Without filtering, the mixture was extracted several times with ether. The extracts were evaporated to dryness on the steam-bath and finally dried in a vacuum desiccator over concentrated sulfuric acid for several days; yield, 1 g. (12%); m. p. 216–218°. The acid contains three molecules of water of crystallization.

Anal. Calcd. for $C_{10}H_4O_{12}N_2{\cdot}3H_2O$: C, 30.15; H, 2.51. Found: C, 29.9; H, 2.59. Loss of H_2O at 110°, found, 2.97, 3.04 moles. *Anal.* of anhydrous acid, $C_{10}H_4O_{12}N_2$: Calcd. C, 34.88; H, 1.16. Found: C, 35.1; H, 1.16.

Decarboxylation of Dinitrobenzene-1,2,3,5-tetracarboxylic Acid.—2.0 grams of the acid, 4 g. of quinoline and 0.4 g. of copper chromite[16] were heated at 160° for four hours, then at 210° for two hours.[17] The mixture was taken up in 10 cc. of ether, washed with dilute hydrochloric acid and water. The ether on evaporation left 0.65 g. (65%) *m*-dinitrobenzene; m. p. 79–82°. This was recrystallized from alcohol; yield 0.5 g.; m. p. 85.5–86.5°. Mixed with known *m*-dinitrobenzene (m. p. 85–86°) it melted at 85–86°.

Summary

By relating two of them to compounds of known orientation, it has been shown that of the three isomeric benzene tetracarboxylic acids, the one melting at 270–272° is the 1,2,4,5-acid, the one melting at 238–253° is the 1,2,3,5-acid while the one melting at 238° (240°) by elimination must be the 1,2,3,4-acid. It is suggested that these compounds should be called pyromellitic, mellophanic and prehnitic acids, respectively.

MINNEAPOLIS, MINNESOTA

RECEIVED JUNE 30, 1933
PUBLISHED OCTOBER 6, 1933

---

(15) The calcium salt of this acid is precipitated from water by alcohol as an oil even in the cold. By precipitating the barium salt in the cold, the salt is obtained as a solid.

(16) Connor, Folkers and Adkins, THIS JOURNAL, **54**, 1138 (1932).

(17) Reichstein, Grüssner and Zschokke, *Helv. Chim. Acta*, **15**, 1066 (1932).