[Contribution from the Division of Industrial and Cellulose Chemistry, McGill University, and the Pulp and Paper Research Institute of Canada]

Separation of Benzene Hexa-, Penta- and the Three Isomeric Tetracarboxylic Acids and their Methyl Esters[1]

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Certain published information about the above acids was checked and used to separate them systematically by means of barium salts insoluble at *p*H 10 and by means of the varying degree to which they were esterified by hot 3% methanolic hydrogen chloride. Somewhat more advantageous preparations were found for benzene penta- and 1,2,3,4-tetracarboxylic acids. The acidic, crystalline ester of the 1,2,3,5-isomer proved to be a trimethyl ester, and not the dimethyl derivative previously reported.

The drastic oxidation of graphite, coals, wood lignin and similar materials frequently produces mixtures of the higher benzenecarboxylic acids that are hard to separate, particularly when the amounts available are limited. Howard and his collaborators,[2] who studied this problem, noted that continuous extraction of these strong organic acids from aqueous salt solution with ether required a week to recover 80%, and that the necessity of carrying out the extraction at a *p*H in the neighborhood of 1 had not always been observed. They preferred a recovery based on the electrodialysis of the alkaline oxidation liquor. The precipitation of individual acids as insoluble barium,[3,4] silver or lead[5] salts from a special synthesis has been frequently used, and mixed barium or calcium salts have been separated into crude fractions soluble or insoluble in dilute acetic acid or water.[2,6] Although mellitic acid could be isolated from the others as a sparingly soluble, neutral ammonium salt,[2,7a] such separations were usually carried out with difficulty by the fractional crystallization of the neutral methyl esters. The high boiling points of these esters also made their fractionation difficult, even in a molecular still of the sublimation type.[8]

While the structures of benzenehexacarboxylic (mellitic), pentacarboxylic and 1,2,4,5-tetracarboxylic (pyromellitic) acids were definitely established at an early date, there was some confusion between those of the 1,2,3,5 and the 1,2,3,4-isomers. The proper structures were conclusively established in 1933 by Smith and his collaborators who reviewed the earlier work.[4,9] They also called attention to the fact that the current assignments of the trivial names "mellophanic acid" and "prehnitic acid" to the 1,2,3,4- and 1,2,3,5-isomers, respectively, should be reversed in order to conform with the name "prehnitene" given to 1,2,3,4-tetramethylbenzene. Regard for clarity suggests that the use both of "mellophanic" and "prehnitic" should be discontinued.[10] All five acids are usually prepared, but in very variable yield, by the drastic oxidation of aromatic substances appropriately substituted by carbon, but not by oxygen, atoms.[11] The methods used in the Experimental portion were of a standard nature and employed hot alkaline potassium permanganate as the oxidant. The use of diacetylmesitylene and of an improved preparation of 1-methyl-4-bromonaphthalene as the precursors of benzenepentacarboxylic and of 1,2,3,4-tetracarboxylic acid, respectively, appeared to be convenient innovations. Since α-keto aromatic acids and oxalic acid tend to be produced in oxidations with alkaline permanganate, in all cases the crude products were boiled with concentrated nitric acid. Trial confirmed the presumption that all the benzenecarboxylic acids discussed were stable to both these oxidants,[7a] but that oxalic acid was readily destroyed during the digestion with nitric acid. The melting points observed for pure, recrystallized samples (Table I) agreed well with published data except in the case of pyromellitic acid, which had to be corrected from 275° at most[12] to 281–283°. The formation of anhydrides renders the values sensitive to large variations in the rate of heating.

The fact that all the acids were freely soluble in the lower alcohols as well as in water suggested that they might be quantitatively extracted from aqueous solution by butanol. In accord with the partition coefficients (Table I) pyromellitic and benzene-1,2,3,5-tetracarboxylic acids were recovered almost completely in two manual operations with equal volumes of aqueous solution and butanol, but the others would have required a continuous extraction with the risk of forming esters. Further attempts at isolating the mixed acids in this way were therefore abandoned. Qualitative tests then showed that benzene-1,2,3,4- and 1,2,3,5-tetracarboxylic acids were precipitated from dilute aqueous solution by the addition of barium chloride,[13,14] the latter acid probably as the hydrated salt $(C_{10}H_5O_8)_2Ba\cdot 3H_2O$,[14] but that solutions of the other three acids remained clear. A preliminary adjustment of the *p*H to about 10, however, caused precipitations corresponding to at least 90% recovery of all five acids from approximately 0.4% solu-

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(1) Abstracted from a Ph.D. Thesis submitted by D. E. Read, October, 1949.

(2) B. Juettner, R. C. Smith and H. C. Howard, This Journal, **59**, 236 (1937).

(3) W. H. Mills, *J. Chem. Soc.*, **101**, 2191 (1912).

(4) L. I. Smith and E. J. Carlson, This Journal, **61**, 288 (1939).

(5) O. Jacobsen, *Ber.*, **17**, 2576 (1884).

(6) F. Fischer, H. Schrader and A. Friedrich, *Ges. Abhandl. Kenntnis Kohle*, **6**, 1, 21 (1921).

(7) (a) B. Juettner, This Journal, **59**, 208 (1937); (b) *ibid.*, **59**, 1472 (1937).

(8) G. Schultz and H. C. Howard, *ibid.*, **68**, 991 (1946).

(9) L. I. Smith and G. D. Byrkit, *ibid.*, **55**, 4305 (1933).

(10) "Prehnitic acid," for example, was the 1,2,3,4-isomer in the 1917 and 1927 Decennial Indices of *Chemical Abstracts*, in references (4), (9) and (14). The name was used for the 1,2,3,5-isomer in the Decennial Indices for 1937 and 1947, and in ref. (13).

(11) O. Diels, *Ber.*, **75**, 1406 (1942), however, described an elegant synthesis of hexamethyl mellitate by the polymerization of dimethyl acetylenedicarboxylate.

(12) H. Meyer and K. Steiner, *Monatsh.*, **35**, 391 (1914). This interesting article reviews early research on mellitic acids.

(13) L. F. Fieser and Mary A. Peters, This Journal, **54**, 4347 (1932).

(14) H. Bamford and J. L. Simonsen, *J. Chem. Soc.*, **97**, 1904 (1910).

TABLE I

BENZENE POLYCARBOXYLIC ACIDS AND METHYL ESTERS

Carboxylic acid	M.p., °C.	Partition[a]	Recovery as Ba salt, %[b]	Neutral esters m.p., °C. (cor.)	Acid esters		
					OCH$_3$	COOH	M.p. (cor.), °C.
Hexa	289–292	0.24	94.5	186–187[e]	5	1	141–144[c]
Penta	239–244	0.78	98.5	149–150[f]	Indefinite	Indefinite	174–176
Tetra							
1,2,4,5-	281–283	2.4	105.8[d]	143–144[g]	..	..	......
1,2,3,5-	243–247	5.1	102.3	111–116[h]	3	1	192–193
1,2,3,4-	241–244	1.45	92.2	130–131[k]	2	2	171–172

[a] Between equal volumes of water and *n*-butanol near 20°. To ±10% when water = 1. [b] Samples, 0.2 g., in 55 cc. of 0.5% potassium hydroxide at 60° mixed with 10 cc. of 10% barium chloride dihydrate. Precipitate collected after several hours and dried at 105°. Results corrected for blanks. [c] Quoted from ref. 18b. [d] Possibly a hydrate. [e] Previous m.p. 188° (ref. 11) and 182–184° (ref. 18b). [f] Previous m.p. similar; W. P. Campbell, M. D. Soffer and T. R. Steadman, THIS JOURNAL, **64**, 425 (1942). [g] Previous m.p. similar (ref. 27); L. F. Fieser and W. P. Campbell, THIS JOURNAL, **60**, 2635 (1938). [h] Previous m.p. 107–109° (ref. 9), 108–109° (ref. 14), 110–111° (ref. 16). [k] Previous m.p. similar (ref. 4, 13, 14.)

tions (Table I). Since the results were not significantly changed when the solutions were made up in 10% potassium chloride instead of in water, and were improved to at least 98% of theory when more concentrated solutions were used, it appeared that the acids could be isolated in this way from the salt-laden liquors resulting from an oxidation with alkaline potassium permanganate. Although the strontium salts were equally insoluble at *p*H 10, the barium salts were preferred because of the ease with which the barium ion could subsequently be eliminated as sulfate. Oxalic acid, of course, was also precipitated quantitatively under the same conditions.

The complete esterification of the pure benzenepolycarboxylic acids with diazomethane[2,15] gave in all cases nearly quantitative yields of the neutral methyl esters which were purified to the highest attainable melting point. The latter (Table I) agreed well with published values except in the case of tetramethyl benzene-1,2,3,5-carboxylate which softened at 111° and melted sharply at 116°, instead of at 107–109°.[9,14,16] These crystalline esters were well suited for purposes of identification.

Meyer and Sudborough[17] noticed that mellitic acid was not esterified by methanol saturated with hydrogen chloride at room temperature, although Meyer[18b] prepared an acidic pentamethyl ester and much of the neutral hexamethyl ester by heating a solution of mellitic acid in 30 cc. of concentrated sulfuric acid with 12 cc. of methanol at 120–125°. The inefficiency of methanol with a hydrogen chloride or a sulfuric acid catalyst at room temperature, and of 3% methanolic hydrogen chloride at the boiling point, was confirmed during the present work. As was expected,[17] pyromellitic acid gave high crude yields of the neutral tetramethyl ester under all three conditions of esterification, but a dibasic diester resulted from the 1,2,3,4-isomer. This partial esterification gave a crystalline product only when 3% methanolic hydrogen chloride was used; although the crude yield was good, the pure substance was isolated in small amount. The melting point of the pure diester remained at 171–172° and could not be increased to 176–177°, as recorded for a sample that had not been recrystallized.[17] Although Bamford and Simonsen[14] prepared an acidic *triethyl* ester by the action of boiling ethanolic hydrogen chloride on benzene-1,2,3,5-tetracarboxylic acid, they claimed that cold methanolic hydrogen chloride produced only a dibasic dimethyl ester, m.p. 191°. A repetition of the latter preparation confirmed this melting point at 192–193° but showed that the ester in question contained three, and not two methoxy groups. This correction completed the data (Table I) of Meyer and Sudborough to show that carboxyl groups located between two others in the ortho positions were sterically hindered and could not be esterified by acid alcohols in the conditions used. Although this theory suggested that benzenepentacarboxylic acid would yield a tribasic dimethyl ester, no record of such a preparation was found, no definite product resulted with methanol containing sulfuric acid, and the hydrogen chloride catalysts gave only a small amount of crystalline material, m.p. 174–176°. Analyses suggested that the crystals were a mixture of mono- and diester, and the larger portion of the product was a glass.

Consideration of the crude yields and melting points of the partial esterifications (Table II) made it clear that methanol containing sulfuric acid was less certain in its action than boiling 3% methanolic hydrogen chloride, which was the reagent of choice. It was also clear from Table I that the partial esterification of a mixture of all five benzenepolycarboxylic acids, followed by the extraction of a slightly alkaline aqueous solution of the product with ether, would separate the neutral tetramethyl ester of pyromellitic acid. This step was accomplished with an over-all recovery of at least 77%. Adjustment of the residual alkaline liquor to *p*H 2 then made it possible to extract the three acidic esters with ethyl acetate and to recover the unesterified mellitic acid from the aqueous layer in at least 44% yield. Although the three partial esters in the remaining mixture contained ester–carboxyl ratios of 1 to 2:4 to 3, 3:1 and 2:2, 0.2% solutions of all three in water had *p*H values of 2.4, 2.4 and 2.7, respectively, and potentiometric titrations gave very similar plots of the type characteristic of strong organic acids. A separation based on differences in ionic strength therefore appeared impractical.

The high ester–carboxyl ratio of 3:1 possessed by the partial ester of benzene-1,2,3,5-tetracarboxylic acid, however, made it possible to recover 75.5% from aqueous solution in a crude, and 61% in a

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(15) R. C. Smith, R. C. Tomarelli and H. C. Howard, THIS JOURNAL, **61**, 2398 (1939).

(16) W. P. Campbell and D. Todd, *ibid.*, **61**, 1291 (1940).

(17) V. Meyer and J. J. Sudborough, *Ber.*, **27**, 1580 (1894).

(18) (a) V. Meyer, *ibid.*, **29**, 1413 (1896); (b) *Monatsh.*, **25**, 1211 (1904).

pure, condition, by two extractions with equal volumes of ether. Only 28 and 11.7%, respectively, of the diester of the 1,2,3,4-isomer and the ester of benzene pentacarboxylic acid were extracted in the same conditions. These two esters could be recovered from the mother liquors of the recrystallizations and from the aqueous residue as a mixture melting over the range 110 to 150°, but no simple method was found to separate the components in a pure condition.

Experimental

Materials.—The following compounds were purified until each gave the m.p., b.p. or refractive index quoted in the literature.

Mesitylene (1,3,5-trimethylbenzene), prepared from acetone,[19] when condensed with 1 mole of acetic anhydride in presence of 2.2 moles of anhydrous aluminium chloride, gave a 77% yield of pure acetomesitylene.[20] When the amounts of anhydride and aluminium chloride were doubled, the same method gave a 43% yield of crude diacetomesitylene, b.p. 204° (70 microns). Recrystallization from a ligroin solution by rapid cooling in solid carbon dioxide left 34% with m.p. 43–45°. The recorded m.p. was 46°.[18a] Bromomesitylene[21] gave a Grignard reagent which on carbonation yielded 57% of recrystallized mesitoic acid.[22]

Pseudocumene (1,2,4-trimethylbenzene) occurred in a fraction, b.p. 165–172°, obtained from a commercial hydrocarbon, "Solvent R."[23] After purification by means of the crystalline sulfonic acid derivative,[24] the pseudocumene was acetylated as described for acetomesitylene to 5-acetopseudocumene, b.p. 139–141° (20 mm.). Oxidation of the methyl ketone group in acetopseudocumene with alkaline hypobromite[5,9] yielded 55% of recrystallized durylic acid, which was purified to the correct m.p. 147–149.5°, by means of the sodium salt. Commercial 1-methylnaphthalene after rectification had the correct b.p. 110.5–111° (10 mm.) and n^{20}D 1.6135.

Oxidations with Alkaline Potassium Permanganate.—A solution or suspension of the substance in hot dilute potassium hydroxide was treated with successive increments of the permanganate until the reduction became exceedingly slow. A few cc. of ethanol was then added to reduce any unused oxidant; filtration removed the sludge of precipitated manganese dioxide, and after the filtrate and washings had been concentrated to a convenient volume they were acidified, usually with hydrochloric acid, to decompose the carbonate present. The liquors were then usually adjusted to *p*H 10 and while hot and efficiently stirred were mixed with an excess of a hot 10% solution of barium chloride dihydrate. The precipitated barium salts were recovered a little later and were dried at 55° *in vacuo*. A solution of the barium salt in about 10 volumes of hot 3 *N* hydrochloric acid was then mixed with the exact amount of 3 *N* sulfuric acid to precipitate all barium as sulfate. Concentration of the filtrate, sometimes almost to dryness, and cooling caused the crystallization of the crude benzenepolycarboxylic acid, which was freed from any oxalic acid by being boiled for two hours in 5 to 10 volumes of concentrated nitric acid. Recrystallizations from the same liquid, and then from the minimum quantity of hot water, were continued until the m.p. of the product remained constant and the neutralization equivalent was correct.

Mellitic Acid.—The sample,[25] on recrystallization from hot concentrated nitric acid melted correctly at 289–292°.[12]

Anal. Calcd. for $C_{12}H_6O_{12}$: neut. equiv., 57.0. Found: neut. equiv., 58.8, 58.8.

Benzenepentacarboxylic Acid.—Diacetomesitylene, 25 g., was kept as a molten suspension at 50° in 300 cc. of 3.3% potassium hydroxide while 80 g. of solid potassium permanganate was added in 10–15-g. portions during one hour. Further oxidation in 1200 cc. of 2.5% potassium hydroxide at 70–90° took about 50 hours and consumed a further 144 g. of permanganate. Since the barium salt from this oxidation gave the product as a yellow powder, 33.8 g., instead of the expected white crystals, the crude benzene pentacarboxylic acid was reoxidized for seven hours with an excess of alkaline permanganate. Decomposition of the resulting barium salt, 63.4 g., gave 26.2 g. of the acid, which after being boiled in concentrated nitric acid, yielded a total of 19.1 g. (51%) of white crystals. Several recrystallizations, each from 100 cc. of hot nitric acid, left 16.7 g. of pure material, m.p. 229–234° with decomposition or the formation of anhydrides. The recorded[26] m.p. was 228–230° for an air-dry sample and 238° for an anhydride.

Anal. Calcd. for $C_{11}H_6O_{10}$: neut. equiv., 59.6. Found: neut. equiv., 62.6, 62.4.

Pyromellitic Acid.—The oxidation of 15 g. of durylic acid with alkaline permanganate[3] yielded 60 g. of hydrated barium pyromellitate and 19.5 g. (70%) of crude pyromellitic acid. Repeated recrystallizations from nitric acid and from water failed to alter the m.p. from 281–283°. Published values include 242.5° (for a dihydrate) and 275°,[27] 265–268°,[5] 270–272°[9] and 273–275°.[12]

Anal. Calcd. for $C_{10}H_6O_8$: neut. equiv., 63.5. Found: neut. equiv., 63.6, 63.4.

Benzene-1,2,3,5-tetracarboxylic Acid.—A 50-g. sample of mesitoic acid dissolved in 240 cc. of 1.5 *N* potassium hydroxide was oxidized at 70–90° with a total of 6 l. of 5% potassium permanganate. After filtration and concentration to 2 l., the barium salt, 170 g., was precipitated from slightly acid solution instead of from one at *p*H 10. This salt yielded 62.4 g. (78%) of benzene-1,2,3,5-tetracarboxylic acid as crude, hydrated crystals; m.p. 236–253°; neut. equiv., 73.5, 74.0. Recrystallization from hot nitric acid gave the anhydrous product, m.p. 243–247°, previous values being 238–253°[9] and 238–240°.[14]

Anal. Calcd. for $C_{10}H_6O_8$: neut. equiv., 63.5. Found: neut. equiv., 63.0, 63.6.

1-Methyl-4-bromo- and 1-Methyl-4-carboxy-naphthalene.—A published procedure[28] for the bromination of the methylnaphthalene was modified by substituting carbon tetrachloride for the carbon disulfide used as a solvent, and by keeping the temperature close to 0°. These changes increased from 55 to 75% the yield of 1-methyl-4-bromonaphthalene; b.p. 155–157° (8 mm.), n^{20}D 1.6505, and stable to boiling alcoholic sodium ethylate.

Carbonation of the Grignard complex of the above bromo derivative in the manner described[28] yielded 23% of 1-methyl-4-carboxynaphthalene, with the correct m.p. 174–176°, after recrystallization from hot toluene.

Benzene-1,2,3,4-tetracarboxylic Acid.—A 43-g. sample of 1-methyl-4-carboxynaphthalene was substituted for the 50 g. of naphthalene-1,4-dicarboxylic acid whose oxidation with alkaline permanganate was described elsewhere.[4] The barium salts (free of carbonate) weighed 35.8 g. and yielded 12.4 g. (22%) of once recrystallized product. Further recrystallization from 100 cc. of hot nitric acid left the m.p. at 241–244°, previous values being 236–238°,[4] 241° with sintering at 215°[5] and 238°.[14]

Anal. Calcd. for $C_{10}H_6O_8$: neut. equiv., 63.5. Found: neut. equiv., 63.8, 63.5.

As previously noted,[4] the crystals acquired a deep purple color after exposure to light, and reverted to white when recrystallized.

Stability to Oxidants (a) Alkaline Permanganate.—Weighed samples of about 0.2 g. were boiled under reflux for six hours with 45 cc. of 2% potassium permanganate–1% potassium hydroxide solution. After reducing the permanganate with ethanol, removing the manganese dioxide and any carbonate, the acids were recovered at *p*H 10 as the barium salts on tared, sintered glass crucibles. A blank

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(19) R. Adams and R. W. Hufferd, "Organic Syntheses," Coll. Vol. I, Second Ed., John Wiley and Sons, Inc., New York, N. Y., 1944. p. 341.

(20) C. R. Noller and R. Adams, This Journal, **46**, 1889 (1924).

(21) L. I. Smith, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 95.

(22) R. P. Barnes, *Org. Syntheses*, **21**, 77 (1941).

(23) The authors are indebted to the Barrett Division, Allied Chemical and Dye Corporation, for the gift of this solvent.

(24) L. I. Smith and O. W. Cass, This Journal, **54**, 1603 (1932).

(25) The authors thank Drs. J. A. Bilton and G. H. Segall, of Canadian Industries, Limited, McMasterville, Que., for the gift of this sample.

(26) C. Friedel and J. M. Krafts, *Ann. chim. phys.*, [6] **1**, 473 (1884).

(27) F. Feist, *Ber.*, **44**, 135 (1911).

(28) F. Meyer and A. Sieglitz, *ibid.*, **55**, 1835 (1922).

containing no sample gave a barium salt weighing 0.1334 g. When corrected for this blank, the data corresponded to recoveries between 87.5 and 106.3% in all cases.

(b) Acid Permanganate.—Samples, 0.10 g., dissolved in 250 cc. of 2 *N* sulfuric acid at 50°, failed to decolorize 0.2-cc. volumes of 0.12 *N* potassium permanganate in 20 minutes, or in conditions used for the quantitative oxidation of oxalic acid.

(c) Concentrated Nitric Acid.—With the exception of mellitic acid, 0.2-g. samples dissolved readily and completely when boiled for two hours with 20 cc. of the nitric acid. No brown oxides of nitrogen were evolved. The remaining small amount of nitric acid was removed by solid potassium hydroxide in a vacuum desiccator and the residues were dried to constant weight. Recoveries of the unchanged acids were quantitative in all five cases.

Oxalic acid dihydrate, 1.005 g., was boiled for one-half hour with 10 cc. of the nitric acid. The dry residue, 0.19 g., when similarly treated with another 10 cc. of the nitric acid, left a residue of only 0.012 g., dried to constant weight.

Esterifications. (a).—Samples, 0.5 g., of the acids dissolved in 20 cc. of anhydrous methanol were esterified by adding an ethereal solution of the diazomethane produced from 2 g. of nitrosomethylurea and 6 cc. of 40% potassium hydroxide. The products from a single methylation were not quite pure, even after two crystallizations from aqueous methanol. After a second methylation followed by recrystallizations, methoxyl contents were within 0.2% of theory and melting points had reached the constant values noted in Table I. Crude yields were practically quantitative.

(b).—Samples, 0.5 g., were dissolved in 10-cc. volumes of anhydrous methanol containing 10 drops of concentrated sulfuric acid. The solutions were heated under reflux for about 16 hours and then were adjusted to *p*H 8 by the addition of saturated sodium bicarbonate. The neutral ester of pyromellitic acid was extracted at this *p*H by four 30-cc. volumes of ether. The other samples were adjusted to *p*H 1–2 with dilute hydrochloric acid and the products were removed by extracting four times with 30-cc. volumes of ethyl acetate. After being dried over anhydrous sodium sulfate, the combined extract from each sample was evaporated and dried to constant weight in a vacuum desiccator over phosphoric anhydride.

(c).—The 0.5-g. samples dissolved slowly in 30–40% methanolic hydrogen chloride[17] and the mixtures were shaken for an hour before being kept at room temperature for 12 hours. Recovery of the esters was as described in (b).

(d).—Samples, 0.5 g., in 3% methanolic hydrogen chloride were heated under reflux for six hours and the esters were recovered as in (b).

The yields and melting points of the crude products are in Table II.

Partial Methyl Esters of the Benzenepolycarboxylic Acids.—Mellitic acid by method (b) gave no ester which could be extracted from the aqueous methanol solution by ether or ethyl acetate. Barium mellitate was recovered in 94.5% yield by adjusting the aqueous residue from *p*H 1 to *p*H 10 and adding excess barium chloride solution.

The melting point of the product from benzenepentacarboxylic acid by method (b) was not substantially changed after several recrystallizations from acetone and petroleum ether. That from method (c) after several recrystallizations gave a small yield of crystals, m.p. 174–176° (cor.) undepressed by admixture with a similar small crop from method (d). The composition suggested a readily hydrolyzable mixture of partial esters.

TABLE II

PARTIAL METHYLATION OF BENZENEPOLYCARBOXYLIC ACIDS[a]

	Methylating agent					
Poly-carb-oxylic acid	MeOH–H_2SO_4[b] M.p., °C.	%	30–40% MeOH–HCl[b] M.p., °C.	%	3% MeOH–HCl[c] M.p., °C.	%
Hexa	No esterification					
Penta	120–124	100	165–173	64–93	142–150	91–101
Tetra						
1,2,4,5	141–144	99	139–142	64–94	133–137	96
1,2,3,5	187–195	99	183–193	86–95	189–194	98
1,2,3,4	110–135	99	170–180	70–80	161–165	98

[a] Yields and melting points of crude products. [b] At room temperature for 12–16 hours. [c] At reflux temperature for 6 hours.

Anal. Calcd. for $C_6H(COOH)_3(COOCH_3)_2$: OCH_3, 19.0; neut. equiv., 108.7. Calcd. for $C_6H(COOH)_4(COOCH_3)$: OCH_3, 10.0; neut. equiv., 78. Found: OCH_3, 14.2, 14.3; neut. equiv., 117.

The addition of ligroin to the mother liquors from these recrystallizations precipitated a viscous yellow oil that could not be crystallized.

Neutral tetramethyl pyromellitate, m.p. 143–144° (cor.) undepressed by admixture with an authentic sample, was obtained by recrystallizing the corresponding crude esters from aqueous methanol. Esterification methods (a), (b), (c) and (d) gave the same result.

Benzene-1,2,3,5-tetracarboxylic acid by methods (b), (c) and (d) gave partial esters all of which, when recrystallized from 30% aqueous methanol several times, gave fine needles, m.p. 192–193° (cor.).

Anal. Calcd. for $C_6H_2COOH(COOCH_3)_3$: OCH_3, 31.4; neut. equiv., 296. Found: OCH_3, 31.2, 31.2; neut. equiv., 306, 303. This ester therefore contained three methyl groups and not two, as previously reported.[14]

Benzene-1,2,3,4-tetracarboxylic acid by method (b) on recrystallization from acetone–ligroin yielded a stiff gum which softened over a wide range up to 130°. The products from methods (c) and (d) on recrystallization acquired the m.p. 171–172° (cor.), when heated at a rate of about 3° a minute. When heated at less than 2° a minute, the crystals softened near 170° with evolution of gas but did not completely melt below 180°. The previous m.p. was 176–177°.[17]

Anal. Calcd. for $C_6H_2(COOH)_2(COOCH_3)_2$: OCH_3, 22.0; neut. equiv., 141. Found: OCH_3, 21.5, 21.7; neut. equiv., 143, 144.

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