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HIGH PURITY PREPARATION OF THE BENZENE CARBOXYLIC ACIDS GIVING SOLID, NEUTRAL METHYL ESTERS*

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Abstract—The preparation and purification of the nine benzene carboxylic acids giving solid, neutral methyl esters and of these esters are described. By acid hydrolysis of these esters the corresponding benzene carboxylic acids are prepared in a high state of purity and in quantitative yields. The purities of the acids which have no definite melting-points were checked by reference to the material balances of the hydrolyses of the esters in conjunction with the elementary analyses of the acids. Corrected melting-points are given for the esters. Data in the literature are also examined and criticised in the light of the present results.

INTRODUCTION

BENZENE carboxylic acids appear frequently in structural studies as degradation products from the oxidation of many aromatic substances, both natural and synthetic. It is well known, for example, that oxidation of coals, lignins, rosin, and similar materials results in the production of mixtures of these acids.[1,2] Although the structures of these acids were definitely established at an early date, there has been some confusion between those of the 1-2-3-4-and 1-2-3-5-isomers. Baeyer, who discovered these two acids,[3] named them "mellophanic acid" for the 1-2-3-4-isomer and "prehnitic acid" for the 1-2-3-5-compound. Due to the fact that the accepted name for the 1-2-3-4-tetramethylbenzene is "prehnitene" this nomenclature was unfortunate and was the origin of several contradictory investigations for establishing the true structures of these two acids. Bamford and Simonsen,[4] Freund and Fleischer,[5] and more recently Smith and co-workers[6,7] conclusively established the constitution of both acids, confirming Baeyer's structures and refuting the objections of Jacobsen.[8] Smith and Birkyt[6] proposed reversing the original assignments in order to use the name "prehnitic" for the acid derived from "prehnitene" (1-2-3-4-tetramethylbenzene). Roy and Howard[9] have supported this proposal which is also favoured here. Read and Purves[10] have suggested discontinuing the use of both trivial names.

In spite of the laboratory importance of these acids in structural studies and of the commercial importance of some of them, particularly the lower members, very

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[1] H. C. Howard *Chemistry of Coal Utilization* (H. H. Lowry, editor), Chapter 18. John Wiley & Sons, Inc., New York (1945).

[2] F. González-Sánchez *Combustibles (Zaragoza)* **14,** 3 (1954).

[3] A. v. Baeyer *Ann.* **141,** 271 (1867); *Ibid.* **7,** suppl., 1 (1870).

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

[5] M. Freund and K. Fleischer *Ann.* **411,** 14 (1916).

[6] L. I. Smith and G. D. Byrkit *J. Amer. Chem. Soc.* **55,** 4305 (1933).

[7] L. I. Smith and E. J. Carlson *J. Amer. Chem. Soc.* **61,** 288 (1939).

[8] O. Jacobsen *Ber. Dtsch. Chem. Ges.* **17,** 2516 (1884).

[9] A. N. Roy and H. C. Howard *J. Amer. Chem. Soc.* **74,** 3239 (1952).

[10] D. E. Read and C. B. Purves *J. Amer. Chem. Soc.* **74,** 116 (1952).

little is known about the properties of this series of acids as a whole. This lack of data on the benzene carboxylic acids became apparent to the author during the course of an investigation dealing with the study of the acid mixtures obtained by oxidation of coal.[11] While there are already methods for the preparation of these acids in a crude condition, no systematic work describing their preparation and purification to a high degree of purity can be found, except in connection with the lowest members. This may be due partly to the fact that with the exclusion of the benzoic acid, the remaining eleven benzene carboxylic acids have no true melting points. The acids form anhydrides, and decompose or sublime near or at the melting temperatures. Reported m.p.s. vary therefore widely as shown in Table 1, which is a representative compilation of recorded m.p.s of these acids and their neutral, methyl esters. Because of this, it is impossible to follow by the rise in m.p. the purification of these acids by crystallisation. The neutral, methyl esters of benzoic, *o*-phthalic and trimellitic (1-2-4) acids are liquid. The remaining nine esters of the benzene carboxylic acids are solid. Small variations are found in the m.p.s reported by different authors (Table 1).

Under these circumstances, it did appear convenient to undertake a study to develop methods of preparation and purification of the benzene carboxylic acids and

TABLE 1. M.P. OF THE BENZENE CARBOXYLIC ACIDS AND THEIR NEUTRAL, METHYL ESTERS

	Acid, m.p., °C	Ester, m.p., °C
Benzoic	122·43[c]; 122·305[d]; 122·375[e]; 122·45[f]	Liq.
Phthalic (1–2)[a]	Subl. 200–208[g]	Liq.
Isophthalic (1–3)	Subl. without melting, 348 ?[g]	67–68[s′]; 68[n]; 64–65[t′]; 66–67[u′]; 71[v′]
Terephthalic (1–4)	Subl. without melting	140[w]; 140–141[x′]; 141–142[y′]; 140[z′]; 140·8[a′]; 140·5–141[b″]
Hemimellitic (1-2-3)	190 dec.[h,i]; 197[i]; 190[k]	100[i,c″]; 101–102[d″]
Trimellitic (1-2-4)[b]	216–219[l]; 221[m]; 215–217 o.c., 229–234 c.c.[n]; 235[o]; 228[p,q,r]; 228 dec.[s,t,u]; 215[k]; 220–235[v]; 210[w]; 217–220[x]	Liq.
Trimesic (1-3-5)	345–350[y]; 375–380[z]; 380[a′]; 360[b′,c′]; 379[d′]	143[e″]; 143–144[w,f″,g″]; 142[c′,d′]
Prehnitic (1-2-3-4)	215 soft.–238[l]; 241 dec.[e′]; 238 dec.[f′]; 238–242 dec. o.c., 264–267 dec. c.c.[g′]; 236–238[h′]; 241–244[j′]	133–135[j′]; 129[g″,h″]; 129–130[i″]; 130–131[i′,j″]; 131–133[h′]; 132[k″]
Mellophanic (1-2-3-5)	240 soft.[l,e′,f′,j′]; 250[l]; 253–262[e′]; 252[f′]; 238–253[k′]; 263–266[l′]; 243–247[i′]	108–109[f′]; 107–109[k′]; 110–111[l″]; 111–116[i′]
Pyromellitic (1-2-4-5)	264[l]; 265–268[m′]; 273–275[n′]; 275[o′]; 260 soft.–279[p′]; 270–272[k′]; 276[l′]; 281–283[i′]	138[i]; 141·5[o′]; 141[m″]; 142[n″]; 143–144[i′,o′,o″]
Benzene pentacarboxylic	228–230[q′]; 238[s′,r′]; 229–234 anh. or dec.[i′]	146–147[n″]; 148·2[p″]; 149–150[i′,q″]
Mellitic (exa)	288 c.c.[n′]; 288–292[i′]	187[r″]; 187 – 188[s″]; 182 – 184[c″]; 188[t″]; 186–187[i′]

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[11] F. González-Sánchez *Combustibles* (*Zaragoza*) **15**, 273, 361 (1955).

their neutral methyl esters, and also to determine for both acids and esters properties hitherto unknown or not well defined, which could be used in the future for a better characterisation of these compounds. In the present paper, which is the first of a series dealing with the above objectives, the preparation and purification of the benzene carboxylic acids giving solid, neutral methyl esters and of these esters are described. Corrected m.p.s are also given for these nine solid esters.

EXPERIMENTAL

Solid, neutral, methyl esters

Starting materials for the preparation of the nine solid esters were the impure esters or the corresponding acids. When acids were used, they were dissolved in anhydrous methanol or ether or mixtures of both and esterified totally with an excess of ethereal diazomethane. Purification of the esters was accomplished by repeated crystallisation in reagent grade methanol. The esters were crystallised until constant m.p. and then, at least, three times more. Special precautions were taken to prevent contamination of samples or solutions by dust or other impurities. Elementary analyses are shown in Table 2.

Benzene carboxylic acids giving solid, neutral methyl esters

The nine benzene carboxylic acids which give solid, neutral methyl esters were prepared from the corresponding esters by acid hydrolysis, as follows: To 100 ml

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Footnotes to Table 1

[a] Phthalic anhydride melts at 131·6°C[c]. [b] Trimellitic anhydride melts at 162[r]; 163[x,u'']; 162·5–163·5[v'']; 165–167[w'']; 166°C[x'']. [c] Burriel-Marti, *Bull. Soc. Chim. Belg.* **39**, 590 (1930). [d] Jessup, Green, *J. Res. Nat. Bur. Stand.* **13**, 469 (1934). [e] Schwab, Wichers, *Ibid.* **34**, 333 (1945). [f] Landolt-Börnstein, *Physikalisch-Chem. Tabellen* Erg. IIIa, Table 84. [g] (Ref. 13). [h] Graebe, Bossel, *Ann.* **290**, 206 (1896). [i] Graebe, Leonhardt, *Ibid.* **290**, 218 (1896). [j] Dziewonski, *Ber. Dtsch. Chem. Ges.* **46**, 2156 (1913). [k] Mousseron, Nguyen-Phuoc-Du, *Bull. Soc. Chim. Fr.* 91 (1948). [l] (Ref. 3). [m] Freund, Fleischer, *Ann.* **373**, 321 (1910); *Ibid.* **402**, 54 (1914). [n] Wegscheider, Perndanner, Auspitzer, *Monatsh.* **31**, 1253 (1910). [o] Fleischer, Seifert, *Ann.* **422**, 312 (1921). [p] Ekstrand, *J. Prakt. Chem.* (2), **43**, 428 (1891). [q] Ruzicka, de Graaf, Hosking, *Helv. Chim. Acta* **14** 233 (1931). [r] Mills, Nodder, *J. Chem. Soc.* **119**, 2094 (1921). [s] Morgan, Coulson, *Ibid.* 2551 (1929). [t] Maxwell, Partington, *Trans. Faraday Soc.* **32**, 775 (1936). [u] Feist, *Ann.* **496**, 102 (1932). [v] Huebner, Jacobs, *J. Biol. Chem.* **169**, 211, (1947). [w] Reppe, Sweckendiek, *Ann.* **560**, 104 (1948). [x] Fernholz, *Ibid.* **568**, 63 (1950). [y] Fusco, Palazzo, Chiavarelli, Bovet, *Gazz. Chim. Ital.* **78**, 511 (1948). [z] Graebe, Krafft, *Ber. Dtsch. Chem. Ges.* **39**, 2509 (1906). [a'] Ullmann, Uzbachian, *Ibid.* **36**, 1798 (1903). [b'] Gastaldi, Cherchi, *Gazz. Chim. Ital.* **45**, II, 251 (1915). [c'] Schorger, *J. Amer. Chem. Soc.* **39**; 2671 (1917). [d'] Sodi-Pallares, Martínez-Garza, *Arch. Inst. Cardiol. Mex.* **17**, 833 (1947). [e'] (Ref. 5). [f'] (Ref. 4). [g'] Schroeter, *Ber. Dtsch. Chem. Ges.* **57**, 2023 (1924). [h'] (Ref. 7). [i'] (Ref. 10). [j'] Doebner, *Ann.* **311**, 143 (1900). [k'] (Ref. 6). [l'] Maxwell, Partington, *Trans. Faraday Soc.* **32**, 778 (1936). [m'] (Ref. 8). [n'] Meyer, Steiner, *Monatsh.* **35**, 391, 475 (1914). [o'] Feist, *Ber. Dtsch. Chem. Ges.* **44**, 135 (1911). [p'] Fleischer, Seifert, *Ann.* **422**, 272 (1921). [q'] Schroeter, Weitzenboeck, Witt, *Monatsh.* **29**, 246, 249, 749 (1908). [r'] Wolff, *Ann.* **322**, 387 (1902). [s'] von Baeyer, *Ber. Dtsch. Chem. Ges.* **31**, 1404 (1898). [t'] Aschan, *Ann.* **387**, 1 (1911). [u'] Stark, Garben, *Ber. Dtsch. Chem. Ges.* **46**, 663 (1913). [v'] Hieber, *Ann.* **439**, 97 (1924). [w'] Schwanert, *Ibid.* **132**, 269 (1864). [x'] Mulliken, *Method* I, 85 (1904). [y'] Zelinski, Glinka, *Ber. Dtsch. Chem. Ges.* **44**, 2, 305 (1911). [z'] Cohen, Pennington, *J. Chem. Soc.* **113**, 57 (1918). [a''] Bogert, Harris, *J. Amer. Chem. Soc.* **41**, 1676 (1919). [b''] Weissberger, Williams, *Z. Physik. Chem.* (B), **3**, 367 (1929). [c''] Meyer, *Monatsh.* **25**, 1205 (1904). [d''] Meyer, Wesche, *Ber. Dtsch. Chem. Ges.* **50**, 452 (1917). [e''] Piutti, *Ibid.* **20**, 539 (1887). [f''] van der Zanden, de Vries, *Rec. Trav. Chim.* **67**, 998 (1948). [g''] Warnat, *Ber. Dtsch. Chem. Ges.* **58B**, 2768 (1925). [h''] Spath, Holter, Posega, *Ibid.* **61B**, 322 (1928). [i''] Fieser, Peters, *J. Amer. Chem. Soc.* **54**, 4347 (1932). [j''] Ruzicka, Seidel, Brugger, *Helv. Chim. Acta* **30**, 2168 (1947). [k''] Ruzicka, Brugger, Egli, Ehmann, Goldberg, *Ibid.* **15**, 1496 (1932). [l''] Campbell, Todd, *J. Amer. Chem. Soc.* **61**, 1291 (1940). [m''] Farmer, Ingold, *J. Chem. Soc.* **119**, 2001 (1921). [n''] Ruzicka, Schinz, Meyer, *Helv. Chim. Acta* **6**, 1077 (1923). [o''] Fieser, Campbell, *J. Amer. Chem. Soc.* **60**, 2635 (1938). [p''] Fischer, Schrader, Treibs, *Ges. Abhandl. Kenntnis Kohle* **5**, 259 (1920). [q''] Campbell, Soffer, Steadman, *J. Amer. Chem. Soc.* **64**, 425 (1942). [r''] Kraut, Busse, *Ann.* **177**, 273 (1875). [s''] Pechmann, *Ber. Dtsch. Chem. Ges.* **31**, 502 (1898). [t''] Diels, *Ibid.* **75B**, 1452 (1942). [u''] Fichter, Stenzl, Beglinger, *Helv. Chim. Acta* **21**, 375 (1938). [v''] Schultze, *Ann.* **359**, 129 (1908). [w''] Spath, Kuffner, *Ber. Dtsch. Chem. Ges.* **64B**, 371 (1931). [x''] Smith, Tomarelli, Howard, *J. Amer. Chem. Soc.* **61**, 2398 (1939).

of 2-3N hydrochloric acid in a 250 ml round bottom, necked flask, amounts of about 0·3–0·6 g of the purified esters, exactly weighed to the nearest 0·1 mg, were added, and the mixture boiled gently under reflux for 24 hr. Prior to removing the condenser, this was washed internally with small portions of distilled water. The contents of the flask were filtered quantitatively to a weighed 150 ml beaker. The flask was washed several times with small amounts of hot distilled water and the washings added to the beaker. The hydrochloric acid was removed on the steam bath, with addition of small portions of water to prevent concentration. After evaporation to dryness, the beaker and its content were dried to constant weight at 105°C and the amount of acid determined. No special precautions had to be taken and the acids were further purified by several recrystallisations from water or 1 : 1 hydrochloric acid. Elementary analyses of the acids are shown in Table 2.

TABLE 2. MICROANALYSES OF THE PURIFIED BENZENE CARBOXYLIC ACIDS AND NEUTRAL METHYL ESTERS

Compound	Acid				Ester			
	Carbon, %		Hydrogen, %		Carbon, %		Hydrogen, %	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
1-2	57·83	57·90	3·64	3·67	61·85	61·81	5·19	5·22
1-3	57·83	57·80	3·64	3·70	61·85	61·83	5·19	5·26
1-2-3	51·44	51·46	2·88	2·89	57·14	57·19	4·80	4·79
1-3-5	51·44	51·38	2·88	2·95	57·14	57·11	4·80	4·74
1-2-3-4	47·26	47·29	2·38	2·44	54·20	54·25	4·55	4·58
1-2-3-5	47·26	47·32	2·38	2·35	54·20	54·21	4·55	4·54
1-2-4-5	41·39[a]	41·24[a]	3·47[a]	3·55[a]	54·20	54·13	4·55	4·58
Penta	44·31	44·26	2·03	2·04	52·18	52·21	4·38	4·34
Exa	42·12	42·16	1·77	1·83	50·71	50·81	4·26	4·21

[a] Analysed as hydrate (+2H_2O).

Melting points

These were determined in a modified Hershberg apparatus.[12] The apparatus was provided with a mechanical stirrer mounted on a ball-bearing assembly to keep the liquid moving at a rapid rate and with a Bureau of Standards, certified, total-immersion thermometer. Corrected m.p.s for the nine purified solid esters were calculated from the uncorrected ones by means of the usual formula, $\Delta = K.n. (T_{obs.} - t_{stem})$. Uncorrected and corrected m.p.s were determined on the purified samples and are shown in Table 3. The m.p.s observed are in general somewhat higher than those previously reported (Table 1). In particular, the m.p. of the 1-2-3-5-ester was raised from 107–111° to 115·6–116·4° (cor.), confirming recent observations of Read and Purves[10] who quoted 111–116°. Comparison of the m.p. of benzoic acid (compare

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[12] E. B. Hersberg *Industr. Engng. Chem. (Anal.)* 8, 312 (1936).

this with most exact values reported in Table 1) and the esters suggests that the lower temperatures starting the melting ranges found for the latter may possibly be the absolute m.p.s of these esters.

TABLE 3. M.P.S OF THE SOLID, NEUTRAL METHYL ESTERS

Ester	M.p., °C (uncorr.)	M.p., °C (corr.)
1-3	67·6–68·1	67·8–68·3
1-4	139·1–139·9	141·0–141·8
1-2-3	100·9–101·4	101·6–102·1
1-3-5	143·3–144·0	145·3–146·0
1-2-3-4	129·6–130·3	131·1–131·8
1-2-3-5	114·5–115·3	115·6–116·4
1-2-4-5	141·7–142·5	143·6–144·4
Penta	147·8–148·6	149·8–150·6
Exa	186·1–186·9	189·7–190·5
Benzoic acid[a]	121·2–121·9	122·4–123·1

[a] Bureau of Standards certified benzoic acid, for comparison.

As already indicated the nine benzene carboxylic acids studied have no true m.p.s. It is therefore impossible to check their purity or to follow their purification by crystallisation, by means of the melting characteristics.

In Table 4, material balances of the hydrolyses of eight of the nine esters are shown. Due to the low solubility of the terephthalic acid, the amount of ester hydrolysed was too small to permit a reliable balance; the hydrolysis was otherwise normal. Although it was difficult to visualise at first the hydrolysis of insoluble esters with m.p.s higher than the temperatures of boiling of the aqueous solutions, in practice the method developed worked out satisfactorily. Hydrolyses were complete, no side reactions, such as decarboxylation, were found and no impurities are

TABLE 4. BALANCES OF THE HYDROLYSES

Acid	Ester hydrolysed g	Acid	
		Calc. g	Recovd. g
1-3	0·2628	0·2248	0·2248
1-2-3	0·4419	0·3682	0·3679
1-3-5	0·5665	0·4720	0·4718
1-2-3-4	0·3370	0·2761	0·2759
1-2-3-5	0·3118	0·2554	0·2549
1-2-4-5	0·5964	0·4886	0·4892
Penta[a]	0·9275	0·7509	0·7504
Exa	0·5492	0·4408	0·4404

[a] Prepared in two batches.

introduced. On examination of Table 4, it is easily seen that the differences between the amounts of acid calculated and recovered are very small and the mean deviation for the eight cases is only ±0·08%, referred to calc. acid.

Microanalyses of both the purified acids and esters are shown in Table 2. These analyses were performed by an independent laboratory. An examination of the elementary analyses of carbon and hydrogen of eighteen closely related compounds, shows that values found for both carbon and hydrogen are within ±0·08% of the calc. ones, except carbon for mellitic ester and hydrogen for pyromellitic acid which deviate, respectively, by 0·11 and −0·15%. Mean deviations among the values found and calculated are: Esters: C, ±0·046% and H, ±0·037%; Acids: C, ±0·057% and H, ±0·046%, giving an overall mean deviation of about ±0·05%. These statistical results point to a high degree of purity of the esters and acids prepared, particularly, when they are considered in conjunction with the results of the hydrolyses and with the m.p.s found. In addition to these quantitative checks, the purified products were further examined qualitatively for impurities by means of the polarizing and stereoscopic microscopes. No impurities were found. On the basis of method used, of experimental results, and of the foregoing discussion it is believed that the prepared samples of the above nine acids and their esters are of a high purity, of the order of 99·5–99·9%.

Some errors have appeared in the literature in connection with the 1-2-3-4- and 1-2-3-5-benzene carboxylic acids. Huntress and Mulliken[13] describe the 1-2-3-4-benzene tetracarboxylic acid as having a hydrate. This acid does not form any hydrate; it is the 1-2-3-5-isomer which gives a hydrate,* so that the four hydrates of this series of acids are those of the 1-2-3, 1-2-3-5, 1-2-4-5 and penta compounds. If other hydrates, such as a mono attributed to the 1-3-5-acid, exist they must be very unstable under normal conditions. This was checked by several means including infra-red and X-ray work. The benzene pentacarboxylic hydrate is a pentahydrate; the other three are dihydrates. The stability of these hydrates, except that of the pyromellitic acid and to some extent that of the hemimellitic acid, is low. It is therefore strongly recommended that the acids be examined in an anhydrous condition, except the pyromellitic acid which is difficult to dehydrate. Smith and Carlson[7] and more recently Read and Purves[10] have pointed out that the neutral, methyl ester of 1-2-3-4-benzene carboxylic acid or the acid itself develop a purple colour when exposed to light. This property has also been mentioned by Huntress and Mulliken.[13] Highly purified samples of this acid and its ester prepared from coal have been exposed to light for several years by the author without developing a purple colour. The change in colour observed by those workers may probably be caused by some impurity being produced in their particular synthesis and which is difficult to eliminate on purification.

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* This error appears originally in Beilstein-IX (p. 997), where some of the properties of the 1-2-3-5-benzene carboxylic acid are described under the 1-2-3-4-isomer and vice versa. Interchange of names (and even errors) appear also in other books, abstract journals and articles as pointed out in refs. 10 and 13.

[13] E. H. Huntress and S. P. Mulliken *Identification of Pure Organic Compounds* (*Order I*) p. 121. John Wiley & Sons, Inc., New York (1941).

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