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Thermal Transformation of Alkali Salts of Aromatic Carboxylic Acids. IV.[1] Reaction of Potassium and Sodium Salts of Alkyl- and Phenylbenzoic Acids[2]

Yasuhiko Dozen

Government Industrial Research Institute, Osaka, Ikeda-shi, Osaka

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The cadmium halides-catalyzed thermal transformation of potassium and sodium salts of isomeric methyl- and phenylbenzoic acids has been investigated. Potassium *o*-toluate gave toluene, 3-methylphthalic, and 4-methylisophthalic acids, whereas sodium *o*-toluate gave toluene, 3-, and 4-methylphthalic acids, as the main products. In the reaction of potassium *m*- and *p*-toluates, both of them gave toluene, 5-methylisophthalic, and 4-methylphthalic acids, whereas the sodium salt of these acids gave toluene and 4-methylphthalic acid, as the main products. Potassium and sodium isomeric dimethylbenzoates gave xylenes and dimethylphthalic acids, *e. g.*, 3, 4- and 4, 5-dimethylphthalic acids from 2, 3- or 3, 4-dimethylbenzoates, 3, 5-dimethylphthalic acid from 2, 4-dimethylbenzoate, and 3, 6-dimethylphthalic acid from 2, 5-dimethylbenzoate. In the case of *o*-phenylbenzoate, potassium salt gave biphenyl, *m*- and *p*-phenylbenzoic, and biphenyl-*p, p'*-dicarboxylic acids, but sodium salt gave biphenyl, *m*- and *p*-phenylbenzoic, and 4-phenylphthalic acids. Sodium *p*-phenylbenzoate gave biphenyl and 4-phenylphthalic acid, but potassium *p*-phenylbenzoate was stable under the conditions used. These results may be interpreted by the ortho-, meta-, and para-directed disproportionation for the potassium salts and ortho-directed one for the sodium salts. These dibasic acid salts produced were decarboxylated to monocarboxylates, which then underwent further disproportionation.

In the earlier papers of this series,[3,4] it has been reported that sodium *o*-toluate gave 3-methylphthalic acid and *m*- and *p*-toluates gave 4-methylphthalic acid upon heating in the presence of a catalyst (cadmium halide) under the pressure of carbon dioxide; a small amount of 2-methylterephthalic acid was detected by infrared spectroscopy in the reaction product of potassium *o*-toluate, but attempts to isolate it failed.[4] Ogata *et al.*[5] reported that potassium *o*-toluate gave 2-methylterephthalic acid, while potassium *o*-phenylbenzoate gave *p*-phenylbenzoic and biphenyl-*p, p'*-dicarboxylic acids. Biphenyl-*p, p'*-dicarboxylic acid has been prepared from potassium salt of diphenic acid by Raecke and Schirp.[6]

A detailed study of these reactions may lead to a better understanding of the difference in orientation between potassium and sodium salts of aromatic carboxylic acids in the disproportionation. The materials chosen for this study were isomeric toluic, dimethylbenzoic, and phenylbenzoic acids.

Results and Discussion

Reaction of Toluates. Table 1 shows the reaction products from potassium and sodium *o*-toluates. Both potassium and sodium salts gave the same products. 4-Methylisophthalic acid was isolated in the present investigation, and 2-methylterephthalic acid was isolated by Ogata *et al.*,[5] but these acids could not be separated by vapor-phase chromatography. 3-Methylphthalic acid in the reaction of sodium *o*-toluate has been isolated as acid anhydride.[4] The formation of toluene, 3-methylphthalic, 4-methylisophthalic, and 2-methylterephthalic acids may be explained by the ortho-, meta-, and para-directed disproportionation of *o*-toluate. *m*-Toluic acid may be produced by the decarboxylation of the vicinal carboxyl group to the methyl group of 3-methylphthalic and 2-methylterephthalic acids because of the steric hindrance. The *m*-toluate thus formed may be converted to 4-methylphthalic acid and toluene by the disproportionation. A trace of benzoic acid was observed by the vapor-phase chromatography, but discussion based on the present data is

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[1] Part III: Y. Dozen and S. Fujishima, *Yuki Gosei Kagaku Kyokaishi (J. Soc. Org. Syn. Chem. Japan)* **25**, 155 (1967).

[2] This paper was presented in part at the 4th Hokkaido Meeting of the Chemical Society of Japan, July, 1965.

[3] Y. Dozen and H. Shingu, Japanese Pat. 457862 (1965).

[4] Y. Dozen and H. Shingu, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **67**, 581 (1964); *Bull. Gov. Ind. Res. Inst. Osaka,* **15**, 202 (1964).

[5] Y. Ogata, M. Hojo, M. Morikawa and J. Maekawa, *J. Org. Chem.*, **27**, 3373 (1962).

[6] B. Raecke and H. Schirp (to Henkel & Cie G. m. b. H.), German Pat. 953071 (1956); Brit. Pat. 790375 (1958); U. S. Pat. 2823228 (1958).

TABLE 1. REACTION PRODUCTS OF *o*-TOLUATE (mol%)[a]

Product	From potassium salt	From sodium salt
Toluene[b]	21.6	5.6[c]
Benzoic acid	Trace	Trace
o-Toluic acid	39.6	16.4
m-Toluic acid	1.1	12.8
3-Methylphthalic acid[b]	11.0	1.6
4-Methylphthalic acid[b]	1.4	3.0
4-Methylisophthalic and/or 2-methylterephthalic acid[b]	9.8	1.6

a) At 360°C for 1 hr
b) Based on the disproportionation.
c) A significant amount of toluene was lost during the isolation.

premature. The yields of toluene given in the tables are not accurate because of the loss by vaporization during the isolation.

Table 2 shows the reaction products from potassium and sodium *m*-toluates. In the reaction of potassium salt, 4-methylphthalic and 5-methylisophthalic acids were obtained as the main products, and 3-methylphthalic and 4-methylisophthalic and/or 2-methylterephthalic acids were produced as minor products. This result may also be explained in terms of the ortho-, meta- and para-directed disproportionation of *m*-toluate. The small yield of 3-methylphthalic acid may be attributed to the steric hindrance at the ortho position to the methyl group. The para-directed carboxylation to the carboxyl group will be prevented by the same steric effect as in the formation of 3-methylphthalic acid. A trace of benzoic acid was observed by the vapor-phase chromatography.

On the other hand, sodium *m*- toluate gave only the ortho-directed disproportionation products, *e. g.*, 3- and 4-methylphthalic acids. The yield of 3-methylphthalic acid, however, was reduced by the steric hindrance.

The reaction products from potassium and sodium *p*-toluates are shown in Table 3. In the reaction of potassium salt at 380°C for 3 hr, 94.5% of *p*-toluic acid and 0.2% of 4-methylphthalic acid were obtained. At 400°C for 1 hr 4-methylphthalic and 5-methylisophthalic acids were obtained as the main products, while 3-methylphthalic and 4-methylisophthalic and/or 2-methylterephthalic acids were produced as the minor products. The 4-methylphthalate produced is decarboxylated to *m*- and *p*-toluates.[4] The formation of 3-methylphthalic and 5-methylisophthalic acids may be explained by the ortho- and meta-directed disproportionation of *m*-toluate. A trace of *m*-toluic acid was observed by studying the infrared spectrum after the esterification and distillation of the *p*-toluic acid fraction. It seems that the formation of 5-methylisophthalate from *m*-toluate is quite rapid. A trace of benzoic acid was observed by vapor-phase chromatography.

TABLE 2. REACTION PRODUCTS OF *m*-TOLUATE(mol%)[a]

Product	From potassium salt	From sodium salt
Toluene[b]	31.8	17.0
Benzoic acid	Trace	—
m-Toluic acid	50.6	39.8
3-Methylphthalic acid[b]	1.0	5.4
4-Methylphthalic acid[b]	7.2	32.2
4-Methylisophthalic and/or 2-methylterephthalic acid[b]	1.6	—
5-Methylisophthalic acid[b]	4.4	—

a) At 380°C for 1 hr
b) Based on the disproportionation.

The entity of the carboxylating agent in the disproportionation of carboxylates can be explained by the complex formation of aromatic carboxylate and the cadmium ion.[7]

TABLE 3. REACTION PRODUCTS OF *p*-TOLUATE (mol%)

Product	From potassium salt[a]	From sodium salt[b]
Toluene[c]	39.0	6.2
Benzoic acid	Trace	—
p-Toluic acid	24.9	73.1
3-Methylphthalic acid[c]	0.1	—
4-Methylphthalic acid[c]	17.2	15·2
4-Methylisophthalic and/or 2-methylterephthalic acid[c]	8.6	—
5-Methylisophthalic acid[c]	16.1	—

a) At 400°C for 1 hr
b) At 385°C for 3 hr
c) Based on the disproportionation.

Reaction of Dimethylbenzoates. Sodium 2, 3-dimethylbenzoate gave 93% of *o*-oxylene, 10% of 3, 4- and 4, 5-dimethylphthalic acids, and 12% of 3, 4-dimethylbenzoic acid at 355°C for 4 hr. 3, 4-Dimethylbenzoic acid may be produced by the decarboxylation of the vicinal carboxyl group to the methyl group of 3, 4-dimethylphthalate obtained by the disproportionation, and the 3, 4-dimethylbenzoate thus produced may be disproportionated to 4, 5-dimethylphthalate.

Table 4 shows the reaction products of potassium and sodium 3, 4-dimethylbenzoates. Potassium 3, 4-dimethylbenzoate was disproportionated to 3, 4- and 4, 5-dimethylphthalates and *o*-xylene. The yield of 3, 4-dimethylphthalate was lower

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[7] a) Y. Ogata and K. Sakamoto, *Chem. & Ind. (London)*, **1964**, 749. b) Y. Ogata and K. Sakamoto, *ibid.*, **1964**, 2012. c) Y. Ogata and K. Nakajima, *Tetrahedron*, **21**, 2393 (1965).

TABLE 4. REACTION PRODUCTS OF 3, 4-DIMETHYLBENZOATE[a]

Run No.	Condition		Product (mole %)					
	Temp. °C	Time hr	*o*-Xylene[b]	3, 4-Dimethylbenzonic acid	2, 3-Dimethylbenzonic acid	3, 4-Dimethylphthalic acid[b] (A)	4, 5-Dimethylphthalic acid[b] (B)	B/A
From potassium salt								
1	355	1	9.6	71.5	0.2	3.2	10.8	3.4
2	380	1	44.2	38.8	0.6	2.2	7.2	3.5
From sodium salt								
3	300	1	—	94.6	—	—	—	—
4	335	1	34.6	54.1	—	4.2	31.8	7.6
5	360	1	36.2	51.7	—	4.4	34.2	7.8
6[c]	380	1	3.8	89.7	0.1	0.9	9.4	10.7
7	380	1	46.4	46.2	—	4.0	32.8	8.2
8[d]	380	1	44.2	49.3	—	5.2	27.8	5.3
9	380	6	41.2	40.7	—	4.6	39.0	8.5
10	400	1	44.2	48.0	—	4.2	26.8	6.4
11	435	1	77.4	22.9	—	2.2	24.2	11.0

a) Condition: Dimethylbenzoate 0.10 mol, alkalicarbonate 5.0 g, CdF_2 1.0 g, initial pressure of CO_2 30 kg/cm^2 gauge.
b) Based on the disproportionation.
c) Sodium carbonate and cadmium fluoride were not used.
d) Three grams of cadmium fluoride were added.

than that of 4, 5-isomer by the steric hindrance of the methyl group. A trace of *m*-toluic acid (retention time, 3.2 min), an unknown product (retention time, 4.2 min), and 2, 3-dimethylbenzoic acid were observed by vapor-phase chromatography.

Sodium 3, 4-dimethylphthalate gave *o*-xylene, 3, 4-, and 4, 5-dimethylphthalic acids as shown in Table 4. In the absence of the catalyst (run 6), the yield of dimethylphthalic acids was lower than that in the presence of the catalyst. The quantities of the catalyst, however, did not alter the yields of dimethylphthalic acids (compare runs 7 and 8). The yields of the dimethylphthalic acids were unchanged by longer heating (runs 7 and 9). It seems that the equilibrium state is presented in this reaction. The high ratio of 4, 5- to 3, 4-dimethylphthalic acid obtained at a high temperature (435°C) (B/A in Table 4) indicates that the ortho carboxyl group to the methyl group of 3, 4-dimethylphthalate is considerably decarboxylated to 3, 4-dimethylbenzoic acid.

Potassium 2, 4-dimethylbenzoate gave 26.4% of *m*-xylene, 2% of 3, 5-dimethylbenzoic acid, 21.0% of 3, 5-dimethylphthalic acid, and 49% of unaltered 2, 4-dimethylbenzoic acid at 350°C for 0.5 hr. Sodium 2, 4-dimethylbenzoate also gave 50% of *m*-xylene, 4.0% of 3, 5-dimethylphthalic, and 31.4% of 2, 4- and 3, 5-dimethylbenzoic acids at 335°C for 0.5 hr. However, at 360°C for 1 hr, 3, 5-dimethylbenzoic acid was the sole product (17.4%). These results can also be explained by the disproportionation of 2, 4-dimethylbenzoate to *m*-xylene and 3, 5-dimethylphthalate, and by the decarboxylation of 3, 5-dimethylphthalate to 3, 5-dimethylbenzoate.

In the reaction of potassium 2, 5-dimethylbenzoate at 345°C for 0.5 hr, 9.2% of *p*-xylene, 88.7% of unaltered 2, 5-dimethylbenzoic acid, and 1.4% of 3, 6-dimethylphthalic acid were obtained. Sodium 2, 5-dimethylbenzoate gave 16.8% of *p*-xylene and a mixture of 2, 5-dimethylbenzoic and 3, 6-dimethylphthalic acids at 340°C for 0.5 hr. At 360°C for 2 hr, 104% of *p*-xylene and 10.2% of 3, 6-dimethylphthalic anhydride were produced. This acid anhydride was isolated by the acidification of the hot alkaline solution of the product with hydrochloric acid. The direct formation of the 3, 6-dimethylphthalic anhydride may be interpreted in terms of the instability of the sterically-hindered dimethylphthalic acid. Alder, Brachel and Kaiser[8] reported that 3, 6-dimethylphthalic acid was converted to acid anhydride by melting it for a short time. It has also been reported by Parker and Goldbladt[9] that sterically-hindered 3-methyl-6-isopropylphthalic and 3, 4, 6-trimethylphthalic anhydrides are obtained by the acidification of the aqueous alkaline solution of these acids with hydrochloric acid.

Reaction of Sodium *p*-Ethyl- and *p*-*n*-Propylbenzoates. Sodium *p*-ethylbenzoate gave 64% of ethylbenzene, 26% of 4-ethylphthalic acid,

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8) K. Alder, H. v. Brachel and K. Kaiser, *Ann.*, **608**, 195 (1957).

9) E. D. Parker and L. A. Goldbladt, *J. Am. Chem. Soc.*, **72**, 2156 (1950).

and 17% of unaltered *p*-ethylbenzoic acid at 390°C for 5 hr. At 355°C for 5 hr, 95% of the starting material was recovered.

In the reaction of sodium *p*-*n*-propylbenzoate at 385°C for 5 hr, 91% of *n*-propylbenzene, 11.4% of dicarboxylic acid, and 18.4% of unaltered *p*-*n*-propylbenzoic acid were obtained. This dibasic acid has an acid value of 502 (calcd for propylphthalic acid: 539), but attempts to isolate it as acid anhydride after treatment with acetic anhydride failed.

Reaction of Phenylbenzoates. The synthesis of biphenyl-*p*, *p*′-dicarboxylic acid by the thermal transformation of potassium salt of diphenic acid has been reported by Raecke and Schirp.[6] This reaction was checked in the present investigation; 27.7% of biphenyl, 44.5% of biphenyl-*p*, *p*′-dicarboxylic acid, and 9.3% of *p*-phenylbenzoic acid were isolated from the reaction at 395°C for 2 hr. In the reaction of sodium salt of diphenic acid at 360°C for 0.5 hr, 29.6% of biphenyl, and small amounts of biphenyl-*p*, *p*′-dicarboxylic, *o*-, *m*- and *p*-phenylbenzoic acids were obtained.

Potassium *p*-phenylbenzoate was stable at 390°C for 3 hr, and 86.2% of the starting material and a trace of polycarboxylic acid were obtained. Sodium *p*-phenylbenzoate, on the other hand, gave 33.6% of biphenyl, 2% of 4-phenylphthalic acid, and 76.0% of the starting material at 380°C for 5 hr.

Small amounts of *p*-phenylbenzoic and biphenyl-*p*, *p*′-dicarboxylic acids have been obtained by Ogata *et al.*[5] from potassium *o*-phenylbenzoate. By the reexamination of this reaction at 365°C for 1 hr, 116.8% of biphenyl and small amounts of biphenyl-*p*, *p*′-dicarboxylic and *p*-phenylbenzoic acids were isolated. At 335°C for 0.5 hr, 39.0% of biphenyl and 67.7% of the starting material were obtained. Sodium *o*-phenylbenzoate, on the other hand, gave 101.8% of biphenyl, 23.2% of *o*-, *m*- and *p*-phenylbenzoic acids (*p*-isomer was the main product), and 4% of 4-phenylphthalic acid at 360°C for 3 hr.

These results show that the ortho carboxyl group to the phenyl group is thermally unstable and easily decarboxylated to biphenyl. The free phenyl ring in biphenylcarboxylate was carboxylated to produce the biphenyl-*p*, *p*′-dicarboxylate in the reaction of potassium *o*-phenylbenzoate. In the reaction of sodium salt, the free phenyl ring was not attacked and phthalic acid was obtained. The formation of biphenyl-*p*, *p*′-dicarboxylate from potassium *o*-phenylbenzoate may be explained by the disproportionation of *p*-phenylbenzoate. The formation of *m*- and *p*-phenylbenzoates from *o*-phenylbenzoate may be explained by the decarboxylation of the phenyldicarboxylates which were produced by the ortho-, meta- and para-directed disproportionation, as has been shown in the reaction of *o*-toluates.

Experimental[10]

Materials. *o*- *m*- and *p*-Toluic acids were prepared by the method of the earlier paper.[4] 2, 3- and 3, 4-Dimethylbenzoic acids were synthesized by the method of Birch *et al.*[11] from 2, 3- and 3, 4-dimethylnitrobenzenes; mp 144—145°C (ethanol) (lit., mp 144°C[12]) and 165.5—166.5°C (ethanol) (lit., mp 166°C[13]) respectively. 3, 4-Dimethylbenzoic acid was also prepared by the sodium hypochlorite oxidation of the 3, 4-dimethylacetophenone[14] obtained by the acetylation of *o*-xylene with acetic anhydride and aluminum chloride.[15,16] 2, 4- and 2, 5-Dimethylbenzoic acids were syntheiszed by the sodium hypochlorite oxidation of the corresponding acetophenones prepared from *m*- and *p*-xylenes; mp 125—126°C (50% aqueous alcohol) (lit., mp 125—126°C[17]) and 133—134°C (50% aqueous alcohol) (lit., mp 132°C[18]) respectively. *N*-Ethynlailine prepared by the method of Rice and Kohn[19] from aniline, ethanol, and Raney nickel well rearranged to *p*-ethylaniline using anhydrous cobaltous chloride.[20] *p*-Ethylaniline was converted to *p*-ethylbenzoinitrile by the Sandmeyer reaction, and the nitrile was hydrolyzed with sulfuric acid to give *p*-ethylbenzoic acid; mp 112—113°C (aqueous alcohol) (lit., mp 110—111°C[21] and 113.5°C[22]). *p*-*n*-Propylbenzoic acid was prepared by the same procedure as that used for the synthesis of *p*-ethylbenzoic acid; mp 141.5—142.5°C (alcohol) (lit., mp 142.5°C[23]). *o*-Phenylbenzoic acid was obtained by the alkaline fusion of fluorenone[24] prepared by the potassium dichromate oxidation of fluorene[25]; mp 112—113°C (50% aqueous alcohol) (lit., mp 110—111°C[24] and 113.5—114.5°C[26]). *p*-Phenylbenzoic acid was synthesized by the chromic acid oxidation of *p*-methylbiphenyl[27] (mp 46—47°C), which had been prepared

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10) All melting points are corrected. The yields of hydrocarbons and dibasic acids except for diphenic acid, are based on the disproportionation. Vapor-phase chromatography, infrared spectra, and micro analysis were performed using a Shimadzu G. C.-1B and a Hitachi Infrared Spectrophotometer EPI SII (in Nujol), and a Yanagimoto C. H. N. Corder MT-I apparatus respectively.

11) S. F. Birch, R. A. Dean, F. A. Fidler and R. A. Lawry, *J. Am. Chem. Soc.*, **71**, 1364 (1949).

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14) A. M. Van Arendonk and M. E. Cupery, *J. Am. Chem. Soc.*, **53**, 3184 (1931).

15) C. R. Noller and R. Adams, *ibid.*, **46**, 1889 (1924).

16) G. A. Olah, M. E. Moffatt, S. J. Kuhn and B. A. Hardie, *ibid.*, **86**, 2198 (1964).

17) O. Jacobsen, *Ber.*, **11**, 18 (1878).

18) O. Jacobsen, *ibid.*, **14**, 2111 (1881).

19) R. G. Rice and E. J. Kohn, *J. Am. Chem. Soc.*, **77**, 4052 (1955).

20) W. J. Hickinbottom, *J. Chem. Soc.*, **1927**, 64.

21) R. Fittig and J. König, *Ann.*, **144**, 291 (1867).

22) K. Kindler, *ibid.*, **452**, 102 (1927).

23) K. Kindler, *Ber.*, **69**, 2792 (1936).

24) R. Fittig and E. Ostermeyer, *Ann.*, **166**, 374 (1873).

25) J. Schmidt and H. Wagner, *Ber.*, **43**, 1797 (1910).

26) M. Wagner and K. Döring, *ibid.*, **36**, 881 (1903).

27) W. Dietrich, *Helv. Chim. Acta*, **8**, 154 (1925).

from *p*-toluidine and benzene28); mp 224—225°C (benzene) (lit., mp 224°C27) and 228°C29)). Diphenic acid was obtained from anthranylic acid30); mp 228—229°C (lit., mp 225—228°C31)). The syntheses of the other authentic samples for the identification have been reported in a previous paper.30)

General Method. An aromatic carboxylic acid was neutralized with aqueous potassium (or sodium) hydroxide to pH 7.0—7.5. The solution was evaporated to dryness and further dried under a vacuum (*ca.* 5 mmHg) at 150—180°C. This alkali carboxylate (0.1—0.2 mol) was mixed with potassium (or sodium) carbonate (5 g) and cadmium fluoride (1.0—1.5 g). The mixture was dried under a vacuum (5 mmHg) at 150—180°C, charged in a rotary autoclave (160 m*l*, 60 rpm), and allowed to react under the pressure of carbon dioxide (initial pressure of 30—40 kg/cm^2 gauge). The warm-up period was *ca.* 1 hr. After cooling, the reaction product was extracted with ether (Soxhlet) to remove the hydrocarbon. The extract was evaporated to give toluene, xylenes, ethylbenzene, *n*-propylbenzene, or biphenyl (identified by means of a study of the infrared spectrum). The ether-insoluble substance was dissolved in hot water (300—400 m*l*); the solution was neutralized with hydrochloric acid to pH 6—7, treated with active carbon, and further acidified to pH 1. The precipitate was filtered while hot and dried (Acid I). The aqueous solution was extracted twice with ether (each 200 m*l*). The ether solution was dried over anhydrous calcium chloride and evaporated to give the acid (Acid II). Acids I and II were esterified with diazomethane, and the ester was analyzed by vapor-phase chromatography (25% Silicone DC 550 on 30—60 mesh Shimalite, 4 mm × 1.5 m; column temperature, 190°C; and flow rate of He, 80 m*l*/min). The retention times (min) of the authentic methyl esters were as follows: benzoate (1.8), *o*-toluate (2.7), *m*-toluate (3.2), *p*-toluate (3.4), 2, 3-dimethylbenzoate (4.8), 3, 4-dimethylbenzoate (5.7), 2, 4-dimethylbenzoate (4.4), 2, 5-dimethylbenzoate (4.7), 3, 5-dimethylbenzoate (5.0), 3-methylphthalate (15.2), 4-methylphthalate (17.1), 2-methylterephthalate (17.5), 4-methylisophthalate (18.5), 5-methylisophthalate (20.4), 2, 3-dimethylphthalate (26.4), 3, 4-dimethylphthalate (30.0), 3, 5-dimethylphthalate (22.4), 3, 6-dimethylphthalate (23.5), *o*-phenylbenzoate (23), *m*-phenylbenzoate (45), and *p*-phenylbenzoate (48).

Identification of 4-Methylisophthalic Acid. The Acid I fraction (8.9 g) obtained from the reaction of potassium *o*-toluate (18.7 g) at 360°C for 1 hr was converted to methyl ester with methanol and sulfuric acid, and the ester was distilled to collect the dibasic acid fraction (bp 122°C/3.5 mmHg, 0.9 g). This fraction was chilled to precipitate the colorless crystals, and then, after recrystallization from methanol, 50 mg of dimethyl 4-methylisophthalate were obtained; mp 75.0—77.0°C. It was identified by a mixed melting point with an authentic sample31) (76.0—77.0°C) and by comparing the infrared spectra.

Identification of 5-Methylisophthalic Acid. A) The Acid I fraction (12.5 g) obtained from the reaction of potassium *m*-toluate (25.0 g) at 380°C for 1 hr was esterified with methanol and sulfuric acid, and the ester was distilled. The dibasic acid fraction (bp 133°C/3.5 mmHg, 1.5 g) was chilled to precipitate colorless crystals, and these crystals were recrystallized from methanol to give dimethyl 5-methyl-isophthalate; mp 90.5—95.5°C (0.1 g). This ester was identified by a mixed melting point with an authentic sample31) (92.5—97.5°C) and by comparing the infrared spectra.

B) The Acid I fraction (5.1 g) obtained from the reaction of potassium *p*-toluate (24.2 g) at 400°C for 1 hr gave dimethyl 5-methylisophthalate (0.1 g, mp 92.5—96.5°C) by the treatment described in A).

Identification of 3, 4- and 4, 5-Dimethylphthalic and 3, 4-Dimethylbenzoic Acids. *A) From the Reaction of Sodium 2, 3-Dimethylbenzoate (12.2 g) at 355°C for 4 hr.* The Acid I fraction (1.2 g, mp 161.5—164.5°C) was identified by a mixed melting point with authentic 3, 4-dimethylbenzoic acid and by comparing the infrared spectra. The Acid II fraction (1.4 g) was refluxed with 10 m*l* of acetic anhydride for 0.5 hr, and the acetic anhydride was evaporated under a vacuum. The residue was extracted with petroleum benzine. After the evaporation of the solvent, 0.45 g of 3, 4-dimethylphthalic anhydride was obtained; this was recrystallized from petroleum benzine (mp 113—115°C (lit., mp 126°C32) and 125—127°C33))).

Found: C, 68.40; H, 4.56%. Calcd for $C_{10}H_8O_3$: C, 68.18; H, 4.58%.

The infrared spectrum shows acid anhydride bands at 1833 and 1761 cm^{-1}.

The insoluble substance in petroleum benzine was 4, 5-dimethylphthalic anhydride; 0.3 g, mp 205—207.5 °C (lit., mp 208—209°C34)). It was identified by a mixed melting point with the sample obtained from sodium 3, 4-dimethylbenzoate and by comparing the infrared spectra.

B) From the Reaction of Sodium 3, 4-*Dimethylbenzoate (12.2 g) at 370°C for 5 hr.* The Acid II fraction (2.8 g) was treated with acetic anhydride, and the product was recrystallized from petroleum benzine - benzene (1 : 2 vol) to give 1.9 g of 4, 5-dimethylphthalic anhydride; mp 207—208°C (lit., mp 208—209°C34)). Found: C, 68.49; H, 4.65%.

The infrared spectrum has anhydride bands at 1845 and 1763 cm^{-1}. Dimethyl 4, 5-dimethylphthalate has a melting point of 51—52°C (methanol).

The petroleum benzine - benzene solution was evaporated to dryness, and the residue was recrystallized from petroleum benzine to give crude 3,4-dimethylphthalic anhydride; mp 96—107°C. This anhydride (10.6 g) obtained from the several experiments was esterified with methanol and sulfuric acid, and the ester was distilled under a vacuum to collect the bp 141.5—143°C (5 mmHg) fraction (3.4 g). This fraction was chilled to give colorless crystals of dimethyl

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3, 4-dimethylphthalate; mp 49.0—51.5°C (lit., mp 57°C[35]).

Found: C, 65.00; H, 6.41%. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35%.

This ester was soluble in the available organic solvents. When this ester was mixed with dimethyl 4, 5-dimethylphthalate, liquefaction occurred even at room temperature.

Identification of 3, 5-Dimethylphthalic and 3, 5-Dimethylbenzoic Acids. The Acid II fraction (2.7 g) obtained from the reaction of sodium 2, 4-dimethylbenzoate (35.0 g) at 335°C for 0.5 hr was treated with acetic anhydride and evaporated to dryness under a vacuum. The residue was recrystallized twice with ligroin to give 3,5-dimethylphthalic anhydride; mp 111—113°C (lit., mp 114—115.5°C[36] and 115—116°C[37]), 0.7 g Found: C, 67.87; H, 4.28%.

The infrared spectrum has acid anhydride bands at 1835 and 1773 cm^{-1}.

The Acid I fraction (2.0 g) obtained from the reaction of sodium 2, 4-dimethylbenzoate (34.5 g) at 360°C for 1 hr was recrystallized from aqueous alcohol to give 3, 5-dimethylbenzoic acid; mp 164.5—166.5°C, 0.9 g. It was identified by a mixed melting point with an authentic sample[31] and by comparing the infrared spectra.

Identification of 3, 6-Dimethylphthalic Acid. The Acid I fraction (1.8 g) obtained from the reaction of sodium 2, 5-dimethylbenzoate (34.5 g) at 360°C for 3 hr gave fiber-like crystals of 3, 6-dimethylphthalic anhydride; mp 141°C. Recrystallization from ligroin gave a substance with a mp of 142—142.5°C (lit., mp 143°C[38]) (0.8 g). Found: C, 68.28; H, 4.44%.

The infrared spectrum has acid anhydride bands at 1849 and 1764 cm^{-1}.

Identification of 4-Ethylphthalic Acid. The Acid II fraction (1.4 g) obtained from the reaction of sodium *p*-ethylbenzoate (10.1 g) at 390°C for 5 hr was treated with acetic anhydride, and then the product was recrystallized twice from petroleum benzine to give 4-ethylphthalic anhydride; 0.5 g, mp 75.5—77.0°C (lit., mp 76—77°C[39]). Found: C, 68.41; H, 4.67%.

The infrared spectrum has acid anhydride bands at 1846 and 1766 cm^{-1}.

Identification of Diphenyl-*p*, *p*'-dicarboxylic and *p*-Phenylbenzoic Acids. *A) From the Reaction of Potassium Salt of Diphenic Acid (50.0 g) at 395°C for 2 hr.* The Acid I fraction (20.1 g) was extracted with ether (Soxhlet). The ether-insoluble substance (16.2 g) was esterified with methanol and sulfuric acid to give dimethyl biphenyl-*p*, *p*'-dicarboxylate; mp 213.5—214.5°C (methanol) (lit., mp 212—213°C[6]). The ether extract was evaporated, and the residue (2.9 g) was esterified with methanol and sulfuric acid to give methyl *p*-phenylbenzoate mp 112—116°C (methanol) (lit., mp 117.5°C[40]).

B) From the Reaction of Sodium Salt of Diphenic Acid (31.9 g) at 360°C for 0.5 hr. The Acid I fraction (4.9 g) was esterified with methanol and sulfuric acid. The ester was extracted with methanol, and the methanol-insoluble substance was recrystallized from ethyl acetate to give 0.05 g of dimethyl biphenyl-*p*, *p*'-dicarboxylate; mp 214—215°C. The methanol solution was distilled under a vacuum; the distillate was identified as a mixture of methyl *o*-, *m*- and *p*-phenylbenzoates by an examination of the infrared spectrum and by vapor-phase chromatography.

C) From the Reaction of Potassium o-Phenylbenzoate (24.0 g) at 365°C for 1 hr. The Acid I fraction (2.0 g) was esterified with methanol and sulfuric acid, and the ester was extracted with methanol. The methanol-insoluble ester gave dimethyl biphenyl-*p*, *p*'-dicarboxylate; mp 214—215°C (ethyl acetate). From the methanol solution, 0.2 g of methyl *p*-phenylbenzoate was isolated; mp 114—117°C.

Identification of 4-Phenylphthalic Acid. *A) From the Reaction of Sodium p-Phenylbenzoate (8.5 g) at 380°C for 5 hr.* The Acid II fraction (0.1 g) was treated with acetic anhydride, and the product was recrystallized from petroleum benzine - benzene to give 4-phenylphthalic anhydride; mp 140—141°C (lit., mp 138—139°C[41] and 141—142°C[42]).

Found: C, 75.49; H, 3.55%. Calcd for $C_{14}H_8O_3$: C, 75.00; H, 3.60%.

The infrared spectrum has acid anhydride bands at 1853 and 1773 cm^{-1}.

B) From the Reaction of Sodium o-Phenylbenzoate (22.0 g) at 360°C for 3 hr. The Acid I fraction (4.6 g) was esterified with methanol and sulfuric acid, and the ester was distilled (bp. 136—160°C/3 mmHg). A study of the infrared spectrum and vapor-phase chromatography showed that this fraction consisted of a mixture of methyl *o*-, *m*- and *p*-phenylbenzoates. By chilling this fraction, methyl *p*-phenylbenzoate was isolated; 1.8 g, mp 113—115°C (methanol). The Acid II fraction (0.5 g) was treated with acetic anhydride, and the product was recrystallized from petroleum benzine to give 4-phenylphthalic anhydride; mp 132—136°C. It was identified by a mixed melting point with the sample obtained from the reaction of sodium *p*-phenylbenzoate (133—139°C) and by a comparison of the infrared spectra.

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