STUDIES ON THE DERIVATIVES OF BENZOYLBENZOIC ACIDS.

By Mosuke HAYASHI, Sinzô TURUOKA, Ikuo MORIKAWA, and
Hirochika NAMIKAWA.

Received October 31st, 1935. Published March 28th, 1936.

One of the authors has reported an isomeric change of halogenohydroxybenzoyltoluic acids under the influence of concentrated sulphuric acid⁽¹⁾. They now wish to report further studies on the other derivatives of benzoylbenzoic acid.

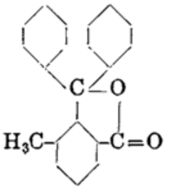
I. Condensation of 3-Methylphthalic Anhydride with Benzene. When 3-methylphthalic anhydride was condensed with benzene, one substance, m.p. 116–117° (A), from the part insoluble in ammonia and two benzoyltoluic acids, m.p. 171–172° (B) and m.p. 126.5–127.5° (C), from the part soluble in ammonia were isolated. The analytical data of the first substance (A) corresponded to the empirical formula $C_{21}H_{16}O_2$, and it may be 1-methyl-2,3-dibenzoylbenzene (III) or diphenylmethylphthalide (I or II).

Benzoyltoluic acids (B and C) remained unaltered on being treated with concentrated sulphuric acid at room temperature. But when isomeride B was treated with concentrated sulphuric acid at 100–105°, an isomeric change

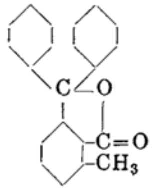
---

(1) *J. Chem. Soc.*, **1927**, 2516; **1930**, 1513, 1520,1524.

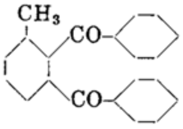
occurred, and isomeride C was obtained from the part soluble in ammonia. From the reason that stereoisomerides can not exist owing to their constitutions in this case, we must consider that benzoyltoluic acid B or C may have the formula IV or V and the action of concentrated sulphuric acid on isomeride B gives rise to position isomeric change. From this evidence, the isomeric phenomenon of the other benzoylbenzoic acid derivatives, which have already been reported in the previous papers,(1) should be a position isomeric change.



I

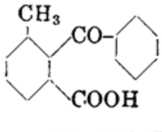


II



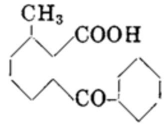
III

m.p. 116–117° (A)



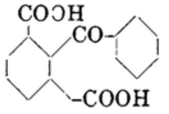
m.p. 171–172° (B)

IV



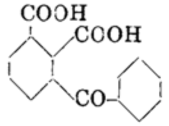
m.p. 126.5–127.5° (C)

V



m.p. 255–256° (D)

VI



Air dried, m.p. 121–125–146° (E)
Anhydrous, m.p. 140–141° (foam.)

VII

The diphenylketone dicarbonic acids, which were obtained by oxidizing benzoyltoluic acids B and C with potassium permanganate, melted at 255–256° (D) and at 121–125–146° (air dried) (E) respectively. Since diphenylketone-2,6-dicarbonic acid melts at 260°(2) and diphenylketone-2,3-dicarbonic acid at 100–130–140–183°(3), substances D and E would be diphenylketone-2,6-dicarbonic acid (VI) and diphenylketone-2,3-dicarbonic acid (VII); and accordingly benzoyltoluic acids B and C would be 2-benzoyl-3-methylbenzoic acid (IV) and 2-benzoyl-6-methylbenzoic acid (V), respectively.

On assuming that the equilibrium of 3- and 6-isomeride in concentrated sulphuric acid solution would be much the same as in the cases of 2-benzoyl-3-methylbenzoic acid and the halogenohydroxytoluic acids, the halogenohydroxybenzoyltoluic acids which have been reported in the previous papers would have formulæ as shown in Table 1.

---

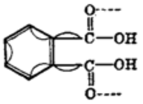
(2) Graebe and Leonhardt, *Ann.*, **290** (1896), 232.

(3) Graebe and Leonhardt, *ibid.*, 230.

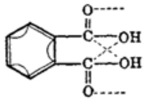
Table 1.

Original	Corrected
2-(5′-Chloro-2′-hydroxybenzoyl)-3(or 6)-methylbenzoic acid, m.p. 238–239°(4)	2-(5′-Chloro-2′-hydroxybenzoyl)-3-methylbenzoic acid
2-(5′-Chloro-2′-hydroxybenzoyl)-6(or 3)-methylbenzoic acid, m.p. 171–171.5°(5)	2-(5′-Chloro-2′-hydroxybenzoyl)-6-methylbenzoic acid
2-(5′-Bromo-2′-hydroxybenzoyl)-3(or 6)-methylbenzoic acid, m.p. 246–246.5°(6)	2-(5′-Bromo-2′-hydroxybenzoyl)-3-methylbenzoic acid
2-(5′-Bromo-2′-hydroxybenzoyl)-6(or 3)-methylbenzoic acid, m.p. 163.5–164°(7)	2-(5′-Bromo-2′-hydroxybenzoyl)-6-methylbenzoic acid
2-(3′-Chloro-4′-hydroxybenzoyl)-3(or 6)-methylbenzoic acid, m.p. 198–199°(8)	2-(3′-Chloro-4′-hydroxybenzoyl)-3-methylbenzoic acid
2-(3′-Chloro-4′-hydroxybenzoyl)-6(or 3)-methylbenzoic acid, m.p. 188.5–189°(9)	2-(3′-Chloro-4′-hydroxybenzoyl)-6-methylbenzoic acid
2-(4′-Chloro-2′-hydroxybenzoyl)-3(or 6)-methylbenzoic acid, m.p. 219.5–220.5°(10)	2-(4′-Chloro-2′-hydroxybenzoyl)-3-methylbenzoic acid
2-(4′-Chloro-2′-hydroxybenzoyl)-6(or 3)-methylbenzoic acid, m.p. 177.5–178°(11)	2-(4′-Chloro-2′-hydroxybenzoyl)-6-methylbenzoic acid
2-(2′-Chloro-4′-hydroxybenzoyl)-3(or 6)-methylbenzoic acid, m.p. 218–218.5°(12)	2-(2′-Chloro-4′-hydroxybenzoyl)-3-methylbenzoic acid
2-(2′-Chloro-4′-hydroxybenzoyl)-6(or 3)-methylbenzoic acid, m.p. 201–202°(13)	2-(2′-Chloro-4′-hydroxybenzoyl)-6-methylbenzoic acid

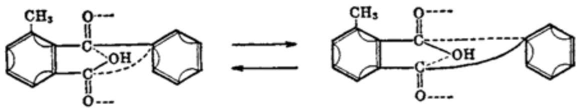
Now that we consider that the formula of phthalic acid is IX instead of VIII, the above-mentioned phenomena and also the reaction of ammonia on acid chloride of alkyl 3- or 4-methylphthalate(14) and on acid chloride of methyl 3- or 4-nitrophthalate(15) may be conveniently illustrated as shown below.



VIII



IX



---

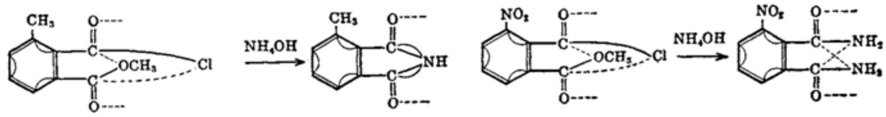
(4) (5) (6) (7) *J. Chem. Soc.*, **1927**, 2516; *ibid.*, **1930**, 1514.

(8) (9) *J. Chem. Soc.*, **1930**, 1521.

(10) (11) (12) (13) *J. Chem. Soc.*, **1930**, 1526.

(14) See pp. 187, 193.

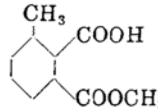
(15) See pp. 191, 200; *J. Soc. Chem. Ind., Japan*, **36** (1933), 203B.



II. Condensation of Acid Chlorides of Methyl 3- and 4-Methylphthalates with Benzene. The methyl ester of benzene-1,2,3-tricarbonic acid, which was obtained by oxidizing methyl 3-methylphthalate (F), m.p. 114.5–115°, with potassium permanganate, melted with decomposition at 193–194°(16). When acid chloride of methyl 3-methylphthalate (F) was condensed with benzene, 2-benzoyl-3-methylbenzoic acid (IV) and substance A (I, II or III) were obtained, but 2-benzoyl-6-methylbenzoic acid (V) could not be isolated. From these facts, it is highly probable that methyl 3-methylphthalate (F), m.p. 114.5–115°, may be 1-methyl 3-methylphthalate (X). Therefore, ethyl 3-methylphthalate (G), m.p. 86–87°, would be also 1-ethyl 3-methylphthalate (XI).

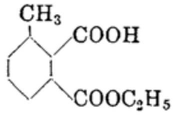
Benzoyltoluic acid, which was obtained by condensing acid chloride of methyl 4-methylphthalate (H), m.p. 89–90°, with benzene, melted at 136–138° and was proved to be identical with 2-benzoyl-5-methylbenzoic acid (XXII)(17). Therefore, methyl 4-methylphthalate (H), m.p. 89–90°, may be 2-methyl 4-methylphthalate (XII).

On treating acid chloride of 1-methyl or 1-ethyl 3-methylphthalate and of 2-methyl 4-methylphthalate with conc. aqueous ammonia, 3-methylphthalimide (XIV), m.p. 188.5-189°(18) and 4-methylphthalimide (XV), m.p. 194.5-195°(19), were obtained, respectively(20).



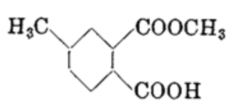
m.p. 114–115° (F)

X



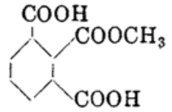
m.p. 86–87° (G)

XI



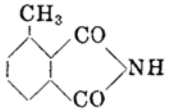
m.p. 89–90° (H)

XII



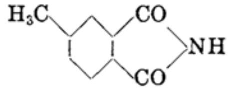
m.p. 203–205°(decomp.)

XIII



m.p. 188.5–189°

XIV



m.p. 194.5–195°

XV

---

(16) *Ann.*, **290** (1896), 226: 2-methyl ester of benzene-1,2,3-tricarbonic acid (XIII), m.p. 203–205° (decomp.).

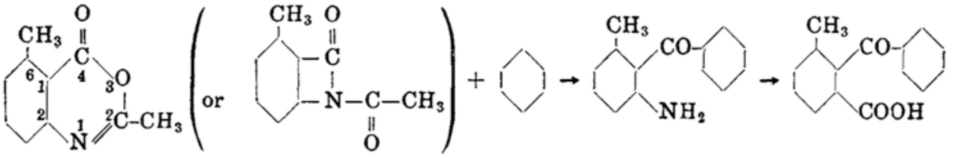
(17) *J. Chem. Soc.*, **1930**, 1518: 2-benzoyl-4 (or 5)-methylbenzoic acid (E), m.p. 145–145.5°, and also see p. 189 and 197.

(18) *Ber.*, **25** (1892), 2107; **40** (1907), 4413: m.p. 183-184°, 187°.

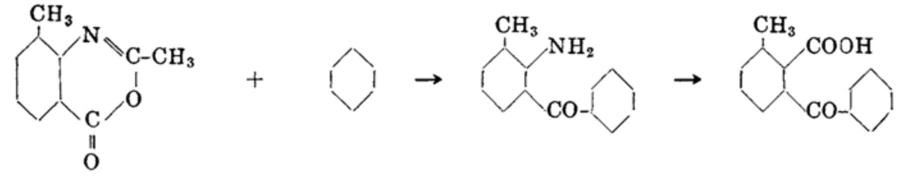
(19) *Monatsh.*, **12** (1891), 627: m.p. 196°.

(20) Compare p. 193.

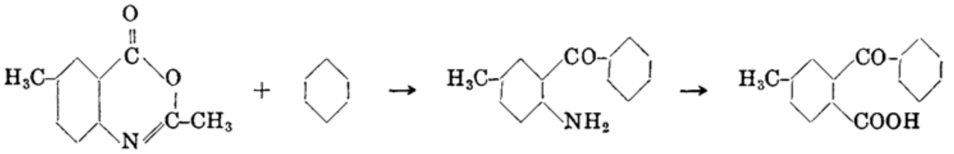
III. An Attempt to determine the Constitutions of Benzoyltoluic Acids. As far as the authors are aware, a condensation of methyl-2-oxo-4-(toluoxazine-3,1)-derivatives with aromatic hydrocarbons or with their derivatives in the presence of aluminium chloride has not been reported. This synthesis was attempted to determine the constitutions of benzoyltoluic acids by schemes shown below. The results were not very satisfactory, yields of amino-diphenylketones being very poor.



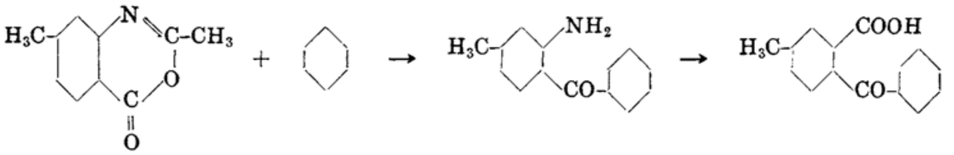
XVI



XVII



XVIII XX XXI



XIX XXII

2-Amino-5-methyldiphenylketone (XX) had been already prepared by Chattaway and Lewis(21), Esselen and Clarke(22), and Hanschke(23). 2-Benzoyl-4-methylbenzoic acid (XXI), which was derived from 2-amino-5-methyldiphenylketone, melted at 149–150° and was proved to be identical with 2-

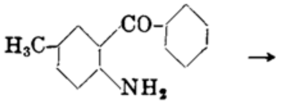
---

(21) *J. Chem. Soc.*, **85** (1904), 594.

(22) *J. Am. Chem. Soc.*, **1914**, 321.

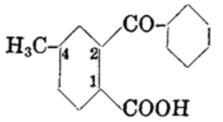
(23) *Ber.*, **32** (1899), 2021.

benzoyl-(5 or 4)-methylbenzoic acid (D), m.p. 150-150.5°.(24) Therefore 2-benzoyl-(4 or 5)-methylbenzoic acid(17) (E), m.p. 145–145.5°, should be 2-benzoyl-5-methylbenzoic acid (XXII).



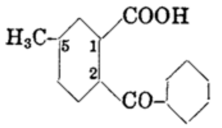
m.p. 64–64.5°

XX



m.p. 149–150° (150–150.5°)
[2-Benzoyl-5(or 4)-methylbenzoic Acid (D)]
2-Benzoyl-4-methylbenzoic Acid

XXI



m.p. 145–145.5°
[2-Benzoyl-4(or 5)-methylbenzoic Acid (E)]
2-Benzoyl-5-methylbenzoic Acid

XXII

By analogy the authors propose the corrections of the interpretations given in the paper, "A New Isomerism of Halogenohydroxybenzoyltoluic Acids" as shown in Table 2.

Table 2.

Original	Corrected
2-(5′-Chloro-2′-hydroxybenzoyl)-5(or 4)-methylbenzoic acid (A), m.p. 239.5–240.5°(25)	2-(5′-Chloro-2′-hydroxybenzoyl)-4-methylbenzoic acid (A)
2-(5′-Chloro-2′-hydroxybenzoyl)-4(or 5)-methylbenzoic acid (B), m.p. 227.5–228.5°(26)	2-(5′-Chloro-2′-hydroxybenzoyl)-5-methylbenzoic acid (B)

IV. **Condensation of 3-Methylphthalic Anhydride with Phenol.** When 3-methylphthalic anhydride was condensed with phenol, two hydroxybenzoyltoluic acids were obtained; one melted at 220–221° (K) and the other at 197–198° (L). When these two acids were separately treated with concentrated sulphuric acid at room temperature, an isomeric change occurred, and hydroxybenzoyltoluic acid, m.p. 141–142° (K′) from the former (K), and hydroxybenzoyltoluic acid, m.p. 183–184° (L′) from the latter (L), were produced. The four acids K, K′, L, and L′ exhibit absorption bands with heads at λ 3300 and ca. 2500, 3310 and ca. 2500, 2875, and 2880 Å, respectively.

2-(2′-Hydroxybenzoyl)-benzoic acid (XXIII)(27), m.p. 171–171.5°, and 2-(4′-hydroxybenzoyl)-benzoic acid (XXIV)(28), m.p. 212–213°, have absorption bands with heads at λ 3310 and ca. 2500, and 2880, respectively. Reasoning

---

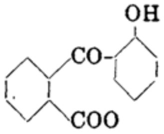
(24) *J. Chem. Soc.*, **1930**, 1518.

(25) (26) *J. Chem. Soc.*, **1930**, 1516.

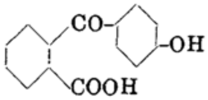
(27) (28) Ullmann and Schmidt, *Ber.*, **52** (1919), 2100, 2106.

from the great similarity of these absorption bands, K or K′ should have formula XXV or XXVI which has the hydroxy-group in the *o*-position to the carbonyl-group, and L or L′ should have formula XXVII or XXVIII which has the hydroxy-group in the *p*-position to the carbonyl-group.

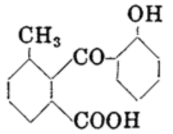
On taking into account the case of benzene, K, K′, L, and L′ would be 2-(2′-hydroxybenzoyl)-3-methylbenzoic acid (XXV), 2-(2′-hydroxybenzoyl)-6-methylbenzoic acid (XXVI), 2-(4′-hydroxybenzoyl)-3-methylbenzoic acid (XXVII) and 2-(4′-hydroxybenzoyl)-6-methylbenzoic acid (XXVIII) respectively.



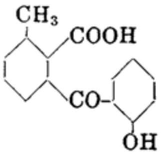
m.p. 171–171.5°
XXIII



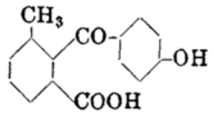
m.p. 212–213°
XXIV



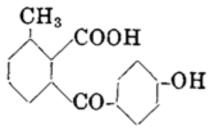
m.p. 220–221° (K)
XXV



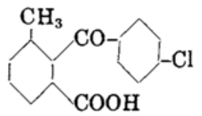
m.p. 141–142° (K′)
XXVI



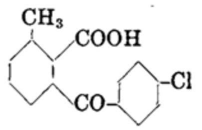
m.p. 197–198° (L)
XXVII



m.p. 183–184° (L′)
XXVIII



m.p. 175.5–176°
XXIX



XXX

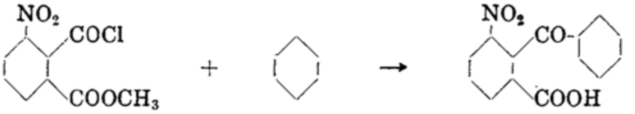
V. Condensation of 3-Methylphthalic Anhydride with Chlorobenzene. On taking into account of the general rule, chlorobenzoyltoluic acid, m.p. 175.5–176°, which was obtained by condensation of 3-methylphthalic anhydride with chlorobenzene, should have formula XXIX or XXX, and may be 2-(4′-chlorobenzoyl)-3-methylbenzoic acid (XXIX) from the analogy with the case of benzene, but an isomeric change in concentrated sulphuric acid solution was not clear.

VI. Condensation of 3-Nitrophthalic Anhydride with Benzene. When 3-nitrophthalic anhydride was condensed with benzene, W. Lawrance(29) obtained two 2-benzoylnitrobenzoic acids, one melted at 217–221° and the other at 140–158–161° (decomp.) (or 157–160°), and concluded that the former is "6-benzoyl-2-nitrobenzoic acid" (XXXII) and the latter is "2-benzoyl-3-nitrobenzoic acid" (XXXI). The present authors, however, could isolate only one benzoylnitrobenzoic acid (M), m.p. 236–237°. When acid chloride of

---

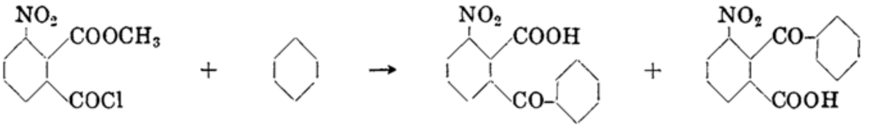
(29) *J. Am. Chem. Soc.*, **42** (1920), 1874.

1- or 2-methyl 3-nitrophthalate was condensed with benzene(30), only isomeride M was isolated in the case of 1-methyl ester, and a small amount of isomeride M and a comparatively larger amount of isomeride N, m.p. 160–161°, in the case of 2-methyl ester. The present authors' experimental result support that isomerides M and N may be 2-benzoyl-3-nitrobenzoic acid (XXXI) and 2-benzoyl-6-nitrobenzoic acid (XXXII), respectively, not coincident with Lawrance's conclusions.



XXXI

m.p. 236–237° (M)



m.p. 160–161° (N) m.p. 236–237° (M)

XXXII XXXI

On treating acid chloride of 1- or 2-methyl 3-nitrophthalate with conc. ammonia, diamide of 3-nitrophthalic acid, m.p. 204–204.5° (decomp.), was obtained in both cases(31).

Experimental.

I. **Condensation of 3-Methylphthalic Anhydride with Benzene.** Anhydrous aluminium chloride (15.4 g.) was gradually added to a solution of 3-methylphthalic anhydride (7.7 g.) in benzene (70 c.c.) with constant stirring, and then the mixture was gradually heated, boiled after 1.5 hours' heating, and maintained at a boiling state until the evolution of hydrogen chloride had almost ceased (about 2 hours). The brown coloured mass(32) was treated with aqueous sodium carbonate, a substance (10.7 g., 94%), m.p. 128–156°, was obtained from the soluble portion, and a substance (4.2 g.), m.p. 109–113°, from the insoluble portion. On fractionally crystallising the former from glacial acetic acid, two fractions were isolated. The less soluble crystals (4.3 g.) melted at 163–170° and the more soluble ones (1.1 g.) at 123–128°. The residue (4.8 g.), from which nothing definite could be isolated by further recrystallisation, melted at 100–160°.

Substance A (I, II *or* III). The substance, m.p. 109–113°, crystallised from alcohol in colourless needles (Found: C, 84.26; H, 5.49; M, in camphor by Rast's method, 314, 303. Calculated for $C_{21}H_{16}O_2$: C, 83.97; H, 5.37%; M, 300.1). It melts at 116–117°, and

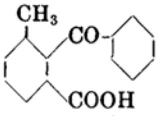
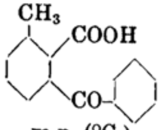
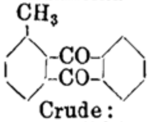
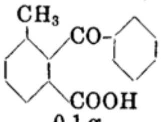
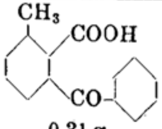
---

(30) Compare Lawrance, *ibid.*, **42** (1920), 1875.

(31) Compare p. 186, 200.

(32) From the filtrate, crude 3-methylphthalic acid (0.5 g.), m.p. 149–150° (decomp.), was recovered by extraction with ether.

Table 3.

Sample	Condition			Soluble part in ammonia					Insoluble part in ammonia
				Before recrystallisation			After recrystallisation		
	H_2SO_4 100% (c.c.)	Temp. (°C.)	Hours	m.p. (°C.)	Mixed with		 m.p. (°C.)	 m.p. (°C.)	 Crude: m.p. (°C.)
					3-isomeride m.p. (°C.)	6-isomeride m.p. (°C.)			
 0.1 g.	2	room temp.	15	155–165	164–169	—	—	—	—
0.5 g.	3	70–75	$\frac{3}{4}$	119–146 0.43 g.	145–164	113–125	157–165	?	169.5–172 0.05 g.
0.5 g.	2.5	100–105	$\frac{2}{3}$	121–125.5 0.35 g.	120–162	122–127.5	?	125.5–127 0.31 g.	167–171.5 0.1 g.
0.5 g.	2.5	100–105	$1\frac{1}{2}$	121–124° 0.23 g.	117–156	121–125.5	?		168.5–172 0.2 g.
 0.31 g.	1.6	100–105	$\frac{3}{4}$	122–125° 0.2 g.	—	122–127	—	—	168–171 0.1 g.
Residue m.p. 100–160°, 4.8 g. m.p. 125–153°, 0.7 g.	25	100–105	$\frac{1}{2}$	110–120 4.4 g.	—	—	—	126.5–127.5 1.6 g.	— 0.83 g.

is soluble to some extent in glacial acetic acid, and appreciably in alcohol. This substance is not soluble in dilute caustic alkali, and dissolves in conc. sulphuric acid to a faintly yellow solution.

2-Benzoyl-3-methylbenzoic acid (B). When the material, m.p. 163-170°, was recrystallised several times from glacial acetic acid, fine colourless crystals, m.p. 171-172°, were obtained (Found: C, 74,85; H, 5.29. Calculated for $C_{15}H_{12}O_3$: C, 74.97; H, 5.04%). It is easily soluble in alcohol and appreciably soluble in glacial acetic acid. The solution in conc. sulphuric acid is faintly yellow. Its methyl ester melts at 106.5–107.5°.

2-Benzoyl-6-methylbenzoic acid (C). Fine colourless crystals, m.p. 126.5–127.5°, were obtained from the substance, m.p. 123-128°, by several crystallisations from glacial acetic acid (Found: C, 74.90; H, 5.43%). The solubilities of this acid are generally similar to, but greater than, those of the isomeric acid (B). Its methyl ester melts at 122.5–123°.

The results, which were obtained when 2-benzoyl-3- or 6-methylbenzoic acid was treated with conc. sulphuric acid, are given in Table 3.

Diphenylketone-2,6-dicarbonic acid (D). 2-Benzoyl-3-methylbenzoic acid (0.88 g.) was boiled with 1% potassium permanganate solution (184 c.c.) for 27 hours. The solution was concentrated and acidified with hydrochloric acid; a substance (ca. 1 g.), m.p. 249–255°, was obtained. On recrystallising from glacial acetic acid, it melted at 255–256° (Found: C, 66.60; H, 3.93. Calculated for $C_{15}H_{10}O_5$: C, 66.65; H, 3.73%).

Diphenylketone-2,3-dicarbonic acid (E). Diphenylketone-2,3-dicarbonic acid, which was obtained by oxidizing the 2-benzoyl-6-methylbenzoic acid with potassium permanganate, melted at 100–125–176–186°. It was recrystallised from acetic acid or from water; fine colourless crystals, which melted with foaming at 121–125–146°, were obtained (Found for air-dried material: loss at 100–105°/28 mm., 6.30; C, 62.53; H, 4.29. Calculated for $C_{15}H_{10}O_5.H_2O$: H_2O, 6.25; C, 62.48; H, 4.20%). Its anhydrous form melts with foaming at 140–141° (Found for anhydrous material: C, 66.73; H, 3.90. Calculated for $C_{15}H_{10}O_5$: C, 66.65; H, 3.73%).

II. Condensation of Acid Chloride of Methyl 3- and 4-Methylphthalate with Benzene. (a) *Preparation of alkyl 3- and 4-methylphthalates.* As far as the authors are aware, alkyl 3- and 4-methylphthalates have not been prepared; they synthesised these esters as summarised in Table 4. These results are not in agreement with v. Meyer's theory of esterification(33).

1-Methyl 3-methylphthalate (F) (0.3 g.) was boiled with 1% potassium permanganate solution (70 c.c.) for 12 hours. The solution was concentrated and acidified with hydrochloric acid; a substance, m.p. 188–207° (decomp.), was obtained. On recrystallising from acetic acid, it melted with decomposition at 193–194° (0.15 g.).

(b) *3- and 4-Methylphthalimide.* 1-Ethyl or 1-methyl 3-methylphthalate (G or F) was boiled with thionyl chloride (5 parts) for 15–30 minutes. The excess of thionyl chloride was removed by distillation under reduced pressure. On treating the residue with an excess of conc. ammonia 3-methylphthalimide (XIV), melting at 188.5–189° after recrystallisation in both cases, was obtained (Found: N, 8.99. Calculated for $C_9H_7O_2N$: N, 8.69%).

4-Methylphthalimide (XV), which was prepared by much the same method as in the case of 3-methylphthalic acid, melted at 194.5–195° (Found: C, 67.09; H, 4.57; N, 8.92; 8.64. Calculated for $C_9H_7O_2N$: C, 67.06; H, 4.38; N, 8.69%).

---

(33) *Ber.*, **27** (1897), 1585; also compare *Ber.*, **27** (1894), 510, 3146; **28** (1895), 182, 1254, 1468; **29** (1896), 1401.

Table 4.

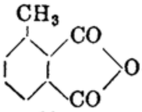
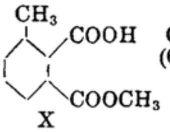
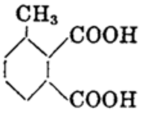
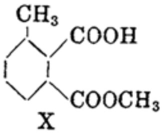
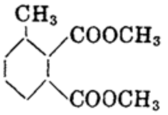
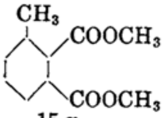
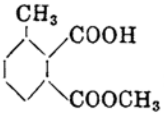
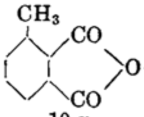
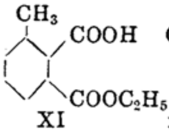
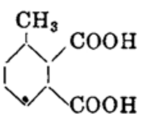
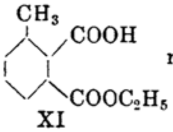
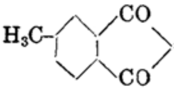
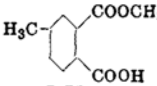
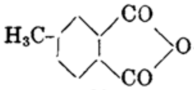
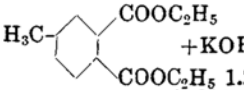
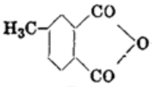
Materials	Condition	Crude product	Pure product
 $+CH_3OH$ 19 g. 100 c.c.	boil 5 h.	Air-dried: m.p. 74–89° (22.3 g., 89.5%) Anhydrous: m.p. 109–114°	 X Air-dried: $C_{10}H_{10}O_4 \cdot H_2O$ (6.3 g., 27.7%) Anhydrous: m.p. 114.5–115° (F)
 $+CH_3OH+HCl$ gas 20 g. 200 c.c.	boil $^1/_2$ h.	Soluble part in Na_2CO_3: anhydrous, m.p. 101–111.5° (2.95 g., 11.3%)	 X Anhydrous: m.p. 114.5–115° (F)
		Insoluble part in Na_2CO_3: b.p. ca. 165–169°/21 mm. (15.6 g., 60.7%)	 b.p. 167–169°/21 mm.
 $+KOH+C_2H_5OH$ 15 g. 5 g. 70 c.c.	boil 5 h.	Soluble part in NaOH: anhydrous, m.p. 107–112°	 Recrystallisation three times from acetic acid: anhydrous, m.p. 109–112° (3.25 g.), mixed m.p. with (F) 109–114°
 $+C_2H_5OH$ 10 g. 200 c.c.	boil 2 h.	Air-dried: m.p. 71–80° (5.4 g., 38.8%) Anhydrous: m.p. 77–82°	 XI Air-dried: $C_{11}H_{12}O_4 \cdot H_2O$, m.p. 75–85° (4 g.) Anhydrous: m.p. 86–87° (G)
 $+C_2H_5OH+HCl$ gas 4 g. 40 c.c.	boil 1 h.	Soluble part in NH_4OH: air-dried, m.p. 69–82° (0.63 g., 12%) Anhydrous: m.p. 73–83°	 XI Anhydrous: m.p. 86–87° (G)
		Insoluble part in NH_4OH	Diester
 $+CH_3OH$ 10 g. 100 c.c.	boil 2 h.	Anhydrous: m.p. 85–90° (5.1 g., 42.6%)	 XII Air-dried: $C_{10}H_{10}O_4 \cdot H_2O$ Anhydrous: m.p. 89–90° (H) (4.7 g., 39.3%)

Table 4. (*Concluded*)

Materials	Condition	
 $+C_2H_5OH$ 20 g. 200 c.c.	boil 2 h.	Pure ethyl monoester could not be isolated
 $+KOH$ $+C_2H_5OH$ 1.2c.c. (0.834g./1c.c.) 4.6 g. 30c.c.	boil 1 h.	
 $+C_2H_5OH+$ conc. H_2SO_4 5 g. 20 c.c. 5 c.c.	boil 1 h.	Diester, b.p. ca. 193–195°/27 mm. (4.6 g.)

(c) *Condensation.* When acid chloride of 1-methyl 3-methylphthalate (ca. 6 g.) was condensed with benzene (120 c.c.) in the presence of anhydrous aluminium chloride (4.5 g.), crude substance A (I, II or III)(34) (ca. 0.9 g.) and 2-benzoyl-3-methylbenzoic acid(35) (ca. 1.3 g.) were isolated but 2-benzoyl-6-methylbenzoic acid could not be separated.

Aluminium chloride (0.8 g.) was added to a solution of acid chloride of 2-methyl 4-methylphthalate (ca. 0.5 g.) and benzene (5 c.c.), and the mixture was boiled for 30 minutes. The product soluble in ammonia, on recrystallising from acetic acid, melted at 136–138° and was proved to be identical with 2-benzoyl-5-methylbenzoic acid(17).

III. **An Attempt to determine the Constitutions of Benzoyltoluic Acids.** (a) **Preparation of methyl-2-oxo-4-(toluoxazine-3,1).** *6-Methyl-2-acetoanthranil* (XVI). When 2-amino-6-methylbenzoic acid (9 g.) was boiled with acetic anhydride (50 c.c.) for one hour and distilled fractionally under reduced pressure, 6-methyl-2-acetoanthranil (7 g., 86%; b.p. 145–150°/10 mm.) was obtained. It crystallised from a mixed solvent of benzene and petroleum ether in a colourless crystalline substance, m.p. 84° (Found: C, 68.47; H, 5.40. Calculated for $C_{10}H_9O_2N$: C, 68.54; H, 5.18%).

3-Methyl-2-acetoanthranil (XVII). After a solution of 2-amino-3-methylbenzoic acid (30 g.) in acetic anhydride (150 c.c.) was boiled for one hour, some acetic anhydride was distilled and the solution cooled; 3-methyl-2-acetoanthranil (31 g., 89%), m.p. 135–136°, separated, 2 acetylamino-3-methylbenzoic acid (3 g., 7.8%), m p. 193–195° (foaming), being recovered from the filtrate on treating with water. The former was recrystallised from benzene mixed with petroleum ether, m.p. 136–137° (Found: N, 8.02%).

After recrystallisation from glacial acetic acid, 2-acetylamino-3-methylbenzoic acid melted with foaming at 196.5–197° (Found: N, 7.01. Calculated for $C_{10}H_{11}O_3N$: N, 7.25%).

5-Methyl-2-acetoanthranil (XVIII). On treating 2-amino-5-methylbenzoic acid with acetic anhydride (5 parts.), 5-methyl-2-acetoanthranil (70%, m.p. 123–124°) and 2-acetyl-

---

(34) See p. 191.

(35) See p. 193.

amino-5-methylbenzoic acid (30%, m.p. 177–187°) were obtained. The former crystallised from benzene in almost colourless needles (Found: N, 8.17%). The latter, on several recrystallisations from acetic acid or alcohol, showed m.p. 179–190°(36) and had no water of crystallisation (Found: N, 7.38%).

4-Methyl-2-acetoanthranil (XIX). This substance was prepared by the same method as in the above cases and melted at 102–103° (Found: N, 7.85%).

(b) **Condensation of acetoanthranil with benzene.** Acetoanthranil (50 g.) was dissolved in benzene (300 c.c.) and aluminium chloride (91 g.) gradually added with constant stirring and then the mixture boiled for 14 hours, the evolution of hydrogen chloride being very slight. The reaction mixture, after distillation in steam as usual and the addition of an excess of alkali, was extracted several times with ether, and the ethereal extract was evaporated. The resinous substance was dissolved in a small amount of alcohol, and hot dilute hydrochloric acid added; the brownish resinous substance that separated was removed. On evaporation of the alcoholic solution, a substance, m.p. 160° (decomp.), separated in 5.7% yield (5.5 g.). After the addition of alkali to the filtrate and being washed with a small amount of alcohol, substance (2 g., 3.3%, m.p. about 106°) was obtained.

2-Phenylaminodiphenylketone. After neutralisation, the former crystallised from alcohol in colourless crystals, m.p. 121.5–122° (Found: N, 5.16. Calculated for $C_{19}H_{15}ON$: N, 5.13%). It dissolves easily in ether, benzene, and glacial acetic acid. Its hydrochloride melts with decomposition at 165–167° and is hydrolysed readily in water (Found: N, 4.59. Calculated for $C_{19}H_{15}ON \cdot HCl$: N, 4.52%).

2-Aminodiphenylketone. The latter was recrystallised from alcohol; yellow long hexagonal plates, m.p. 109–110°, were obtained (Found: N, 7.08. Calculated for $C_{13}H_{11}ON$: N, 7.11%). Its hydrochloride (colourless needles) dissolves easily in water and melts with decomposition at 179–180° (Found: N, 6.07. Calculated for $C_{13}H_{11}ON \cdot HCl$: N, 5.99%).

(c) **Condensation of 3-methyl-2-acetoanthranil with benzene.** *2-Phenylamino-3-methyldiphenylketone.* 3-Methyl-2-acetoanthranil (20.3 g.) was condensed with benzene (150 c.c.) in the presence of aluminium chloride (34.1 g.), and the subsequent treatment and the separation of the reaction product were carried out as in the case of acetoanthranil. In this case, 2-phenylamino-3-methyldiphenylketone (yield as hydrochloride, 5.6 g.), m.p. 123-123.5°, was only separated (Found: N, 4.88. Calculated for $C_{20}H_{17}ON$: N, 4.88%). Its hydrochloride melts with decomposition at 166–168–173° (Found: N, 4.54. Calculated for $C_{20}H_{17}ON \cdot HCl$: N, 4.33%).

(d) **Condensation of 5-methyl-2-acetoanthranil with benzene.** 5-Methyl-2-acetoanthranil (7.3 g.), benzene (50 c.c.), and aluminium chloride (15 g.) were boiled for 22 hours with constant stirring. On treating the reaction product as in the case of acetoanthranil, crude 2-phenylamino 5-methyldiphenylketone (1.9 g., 15.9%; m.p. 159–161°), and crude 2-amino-5-methyldiphenylketone (0.1 g., 1.1%) were separated.

2-Phenylamino-5-methyldiphenylketone. It crystallised from alcohol in colourless fine needles, m.p. 163.5° (Found: C, 83.47; H, 6.26; N, 4.74. Calculated for $C_{20}H_{17}ON$: C, 83.58; H, 5.97; N, 4.88%).

2-Amino-5-methyldiphenylketone (XX). After recrystallising from alcohol, it melted at 62–63°, and was proved to be identical with Chattaway and Lewis' 2-amino-5-methyldiphenylketone(21), m.p. 64–64.5°.

---

(36) Miller and Meyer, *Ber.*, **24** (1891), 1914; "Beilsteins Handbuch," 3 Ed., II, 1333: m.p. 193-194°.

(e) **The determination of constitution of 2-benzoyl-5 (or 4)-methylbenzoic acid (D)(37).** 2-Amino-5-methyldiphenylketone, which was prepared by Chattaway and Lewis' method from *p*-toluidine and benzoyl chloride, melted at 64–64.5° (Found: N, 6.78. Calculated for $C_{14}H_{13}ON$: N, 6.58%). The diazotized solution of 2-amino-5-methyldiphenylketone (20 g.) was added to a well agitated potassium cuprous cyanide solution at 40°, the mixture was then boiled for about ten minutes, and an oily substance (α) (18 g.) was isolated by means of ether. On keeping a long time in a vacuum desiccator, a small amount of crystals, which melted at 189–190° after being recrystallised from benzene mixed with alcohol, was obtained (Found: N, 3.48. Calculated for $C_{28}H_{23}O_2N$(38): N, 3.46%). The oily substance, filtered from these crystals was distilled several times under reduced pressure; a clear, almost colourless, viscous oil, b.p. 192–195°/19 mm., which contained no nitrogen, was obtained.

The above-mentioned substance (α) was refluxed with 20% hydrochloric acid (10 parts) for 10 hours; a sticky substance thus obtained was extracted with ether, and the ethereal solution was treated with dilute aqueous ammonia. On acidifying the ammoniacal solution with hydrochloric acid, a very small amount of crude 2-benzoyl-4-methylbenzoic acid, m.p. 144–148°, was obtained. After recrystallising from acetic acid, it melted at 149–150°, and at 149–150° or at 130–138° when it was mixed with a specimen of 2-benzoyl-5-(or 4)-methylbenzoic acid (D)(37), m.p. 150–150.5°, or of 2-benzoyl-4-(or 5)-methylbenzoic acid (E)(17), m.p. 145–145.5°. Therefore 2-methyl-5-(or 4)-methylbenzoic acid (D) should be 2-benzoyl-4-methylbenzoic acid.

Diphenylketone-2,5-dicarbonic acid, which was obtained from 2-benzoyl-4-methylbenzoic acid by oxidizing with potassium permanganate, melted at 291–292°.

(IV) **Condensation of 3-Methylphthalic Anhydride with Phenol.** Anhydrous aluminium chloride (20 g.) was added to a solution of 3-methylphthalic anhydride (10 g.) and phenol (7 g.) in acetylene tetrachloride (50 c.c.), and the mixture was heated at 130° until the evolution of hydrogen chloride had nearly ceased (about 3.5 hours). On repeated crystallisation from glacial acetic acid, two fractions were isolated from the part soluble in aqueous sodium carbonate. One melted at 212–217° (4.5 g.) and the other at 85–101° (8 g.).

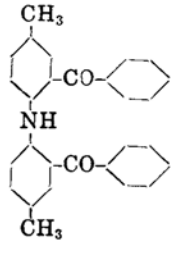
2-(2′-Hydroxybenzoyl)-3-methylbenzoic acid (K). The former crystallised from acetic acid in colourless rhombic crystals (Found: C, 70.20; H, 4.89. Calculated for $C_{15}H_{12}O_4$: C, 70.29; H, 4.72%). It melts at 220–221° and dissolves in alkali to a faintly yellow solution.

2-(4′-Hydroxybenzoyl)-3-methylbenzoic acid (L). The latter was recrystallised three times from glacial acetic acid, a substance (3.4 g.), m.p. 195–197°, being separated. On further recrystallisation from glacial acetc acid, colourless plates, m.p. 197–198°, were

---

(37) *J. Chem. Soc.*, **1930**, 1518.

(38)



obtained (Found: C, 70.21; H, 4.84%). It dissolves in alkali to an almost colourless solution.

2-(2′-Hydroxybenzoyl)-6-methylbenzoic acid (K′). A solution of 2-(2′-hydroxybenzoyl)-3-methylbenzoic acid (0.8 g.) in sulphuric acid (100%, 10 c.c.) was kept for 15 hours at room temperature; on pouring the product into ice-water, a precipitate (0.74 g., m.p. 122–138°) separated. It crystallised from glacial acetic acid in faintly yellow prisms (0.5 g.) (Found: C, 70.49; H, 4.97%). It melts at 141–142° and dissolves in alkali to a faintly yellow solution.

2-(4′-Hydroxybenzoyl)-6-methylbenzoic acid (L′). After a solution of 2-(4′-hydroxybenzoyl)-3-methylbenzoic acid (0.9 g.) in 100% sulphuric acid (9 c.c.) had been kept for 15 hours at room temperature, the isolated product (0.84 g., m.p. 140–146.5°) crystallised from glacial acetic acid in colourless fine crystals, m.p. 183-184° (Found: C, 70.22; H, 4.95%). It dissolves in alkali to an almost colourless solution.

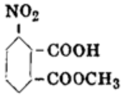
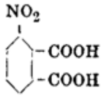
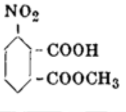
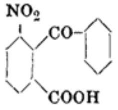
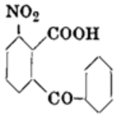
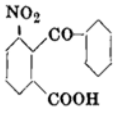
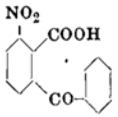
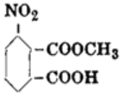
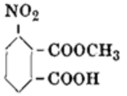
(V) **Condensation of 3-Methylphthalic Anhydride with Chlorobenzene.** 3-Methylphthalic anhydride (10 g.) was condensed with chlorobenzene (50 c.c.) in the presence of anhydrous aluminium chloride (20 g.). A substance (9.2 g.), m.p. 158–162°, was obtained from the part insoluble in ammonia and chlorobenzoyltoluic acid (10 g.), m.p. 162–169°, from the part soluble in ammonia. On recrystallising the latter from glacial acetic acid, faintly yellow 2-(4′-chlorobenzoyl)-3-methylbenzoic acid was obtained (Found: C, 65.43; H, 4.22. Calculated for $C_{15}H_{11}O_3Cl$: C, 65.56; H, 4.04%). It melts at 175.5–176°.

The authors have examined the ultra-violet absorption curves of alcoholic solutions of the above-mentioned substances (Table 5).

Table 5.

Substance	Maxima of absorption bands, Å	
1-Methyl-2,3-dibenzoylbenzene (A), m.p. 116–117°	2830,	2670
2-Benzoyl-3-methylbenzoic acid (B), m.p. 171–172°	2830,	2650
2-Benzoyl-6-methylbenzoic acid (C), m.p. 126.5–127.5°	2830,	2650
Diphenylketone-2,6-dicarbonic acid (D), m.p. 255-256°	2820,	2650
Diphenylketone-2,3-dicarbonic acid (E), m.p. 140–141° (foam.)	2820,	2650
1-Methyl 3-methylphthalate (F), m.p. 114.5–115°	2830,	2670
1-Ethyl 3-methylphthalate (G), m.p. 86–87°	2830,	2660
2-(2′-Hydroxybenzoyl)-3-methylbenzoic acid, m.p. 220–221° (K)	3300,	ca. 2500
2-(4′-Hydroxybenzoyl)-3-methylbenzoic acid, m.p. 197–198° (L)	2875	
2-(2′-Hydroxybenzoyl)-6-methylbenzoic acid, m.p. 141–142° (K′)	3310,	ca. 2500
2-(4′-Hydroxybenzoyl)-6-methylbenzoic acid, m.p. 183–184° (L′)	2880	
2-(2′-Hydroxybenzoyl)-benzoic acid,(27) m.p. 171–171.5°	3310,	ca. 2500
2-(4′-Hydroxybenzoyl)-benzoic acid,(28) m.p. 212–213°	2880	
2-(4′-Chlorobenzoyl)-3-methylbenzoic acid, m.p. 175.5–176°	ca. 2510	

Table 6.

		AlCl$_3$	Conditions of conden-sation		Substance recovered from water solution. 	Precipitate	Fraction soluble in ammoina (γ)			Fraction insoluble in ammonia (β)	
(g.)	(c.c.)	(g.)	(°C.)	hrs.		(g.)					
50	250	32.5	-80 boil	5½ ½	9 g. m.p. 206–209° (decomp.)	—	2.6 g. m.p. 148–158–	0.2 g. m.p. 200–210°–	not isolated	4.6 g. m.p. 210–230°	not isolated
10	50	9	-70 boil	1 5	—	10.2	—	0.4 g. m.p. 220–224°	not isolated	← combined	not isolated
10	120	6	55–60	6	—	10.8	—	not isolated			
14	100	17	-80 boil	1 5	—	—	—	0.2 g. m.p. 229–234°	not isolated	0.15 g. m.p. 210–230°	not isolated
10	50	6	-80 boil	1 5	—	—	—	0.1 g. m.p. 200–220°	not isolated	← combined	not isolated
											
20	200	24	-80 boil	1 4½	—	—	—	0.2 g. m.p. 228–230°	3 g.(39) m.p. 155–160°	not isolated	
50	250	32.5	-80 boil	7 ½	13.9 g. m.p. 207–215° (decomp.)	—	0.3 g. m.p. 134–140°	0.2 g. m.p. 225–230°	—	4.7 g. m.p. 223–230°	0.5 g. m.p. 148°152°
10	50	6	-80 boil	1 5	—	—	—	—	0.6 g. m.p. 146–158°	—	—

(39) On recrystallisation from glacial acetic acid, 2-benzoyl-6-nitrobenzoic acid (N) melted at 160–161° (Found: N, 5.38. Calculated for $C_{14}H_9O_5N$: N, 5.17%).

(VI) **Condensation of 3-Nitrophthalic Anhydride with Benzene.** 3-Nitrophthalic anhydride (50 g.) was dissolved in benzene (300 c.c.), aluminium chloride (75 g.) was added with constant stirring, and the mixture heated slowly and boiled in the course of 40 minutes. After 5 hours' boiling, the product was mixed with ice-water and, after the addition of hydrochloric acid (90 c.c.), distilled in steam. The residue was extracted with aqueous ammonia, the ammoniacal extracts were freed from ammonia, cooled, and the resinous substance that separated was removed. On acidification of the filtrate, a sticky precipitate (27.3 g.) separated. This substance was dissolved in glacial acetic acid and treated with animal charcoal, the substance (2 g.), m.p. 220–228°, thus obtained was recrystallised from glacial acetic acid; faintly yellow rhombic crystals (Found N, 5.27. Calculated for $C_{14}H_9O_5N$: N, 5.17%). 2-Benzoyl-3-nitrobenzoic acid (M) melts at 236–237°. When this acid was heated with 100% sulphuric acid (10 parts) at 100–105° for 45 minutes or kept for 17 hours at room temperature, no isomeric change occurred.

Condensation of acid chloride of 1- or 2-methyl 3-nitrophthalate with benzene. To a solution of acid chloride of 1- or 2-methyl 3-nitrophthalate in benzene, aluminium chloride was added, and the mixture boiled. On treating the product as usual, an insoluble part (β) in ammonia and an ammoniacal solution (γ) were obtained. The latter (γ) was boiled with animal charcoal, and acidified with hydrochloric acid; the resinous substance thus precipitated was recrystallised fractionally from acetic acid or purified by preparing its barium salt. The former (β) was extracted several times with boiling alcohol, and the alcoholic solution was boiled with 50% KOH solution. The fraction soluble in alkali was recrystallised fractionally from acetic acid. Their results are given in Table 6.

Diamide of 3-nitrophthalic acid. On treating acid chloride of 1-methyl 3-nitrophthalate (m p. 97.5–99.5°)(40) or 2-methyl 3-nitrophthalate (m.p. 95–97°)(41) with an excess of conc. ammonia and recrystallising from alcohol, colourless fine crystals were obtained in each case (Found: N, 20.21. Calculated for $C_8H_7O_4N_3$: N, 20.10%). They melt with decomposition at 204–204.5°(42).

Department of Colour Chemistry and Dyeing,
Tokyo University of Engineering.

---

(40) *J. Chem. Soc.*, **109** (1916), 234: m.p. 97–99°.
(41) *J. Chem. Soc.*, **109** (1916), 234: m.p. 95–97°.
(42) *J. Am. Chem. Soc.*, **23** (1901), 747: m.p. 200–201° (decomp.).