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Syntheses of All Isomers of Naphthalenetricarboxylic Acids

Yasuhiko DOZEN

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

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All the fourteen isomers of naphthalenetricarboxylic acids have been synthesized by the oxidation of trimethylnaphthalenes, dimethylacetonaphthones, dimethylnaphthoic acids, methylnaphthalenedicarboxylic acids, β-(dimethylnaphthoyl)propionic acid, or β-(acenaphthoyl)propionic acids with aqueous sodium bichromate or potassium ferricyanide. Most of these naphthalenetricarboxylic acids, acid anhydrides, and trimethyl esters are new compounds.

During the course of studies on the thermal transformation of alkali salts of naphthalenecarboxylic acids,[1] we realized the necessity of naphthalenetricarboxylic acids for comparison with possible intermediates in the reaction. However, only a limited number of these acids have been reported. Naphthalene-1,4,5-,[2,3] 1,3,8-,[3] and 1,2,8-[3,4] tricarboxylic acids have been prepared by the oxidation of acetylacenaphthenes or cyclohexylacenaphthenes. 1,2,5-[5-7] and 1,2,7-Isomers[8,9] have been synthesized from the corresponding trimethylnaphthalenes. 1,2,4-Tricarboxylic acid is obtained by the oxidation of 1-methylnaphthalene-3,4-dicarboxylic acid.[10] It has been reported that 1-acetyl-2,6-dimethylnaphthalene

1) a) Raecke, *Angew. Chem.*, **70**, 1 (1958). b) E. McNelis, *J. Org. Chem.*, **30**, 1209 (1965). c) J. W. Patton and M. O. Son, *ibid.*, **30**, 2869 (1965). d) Y. Dozen, This Bulletin, **41**, 664 (1968). e) J. Ratusky, *Chem. Ind.* (London), **1970**, 1347. f) M. Matsuoka, T. Kitao, and K. Konishi, *Kogyo Kagaku Zasshi*, **74**, 77 (1971).

2) C. Graebe and P. Haas, *Ann. Chem.*, **327**, 95 (1903).

3) N. G. Sidorova and F. M. Saidova, *Zhur. Obshch. Khim.*, **33**, 2213 (1963); *Chem. Abstr.*, **59**, 13899 g (1963).

4) L. F. Fieser and J. Cason, *J. Amer. Chem. Soc.*, **61**, 1740 (1939).

5) I. M. Heibron and D. G. Wilkinson, *J. Chem. Soc.*, **1930**, 2551.

6) L. Ruzicka and J. R. Hosking, *Helv. Chim. Acta*, **13**, 1402 (1934).

7) C. W. Brandt and L. G. Neubauer, *J. Chem. Soc.*, **1939**, 1037.

8) L. Ruzicka, H. W. Huyser, M. Pfeifer, and C. F. Seidel, *Ann. Chem.*, **471**, 37 (1929).

9) L. Ruzicka and A. G. VanVeen, *Rec. Trav. Chim. Pays-Bas*, **48**, 1023 (1929).

10) K. Alder and R. Schmitz-Josten, *Ann. Chem.*, **595**, 29 (1955).

gives 1,2,6-tricarboxylic acid,[11] but the position of the acetyl group in this acetyldimethylnaphthalene is doubtful.[12,13]

The suitable oxidation procedure of methyl and acetyl groups in naphthalene derivatives with aqueous sodium bichromate has been developed for methylnaphthoic acid,[14] dimethylnaphthalenes,[14] and methylacetonaphthone.[15] Methods for synthesizing the fourteen isomers of trimethylnaphthalene to be oxidized to naphthalenetricarboxylic acids have been reported by some workers,[16-18] but it is not easy to synthesize them all.

In this paper, we wish to report appropriate synthetic methods and the properties of all the fourteen isomers of naphthalenetricarboxylic acid.

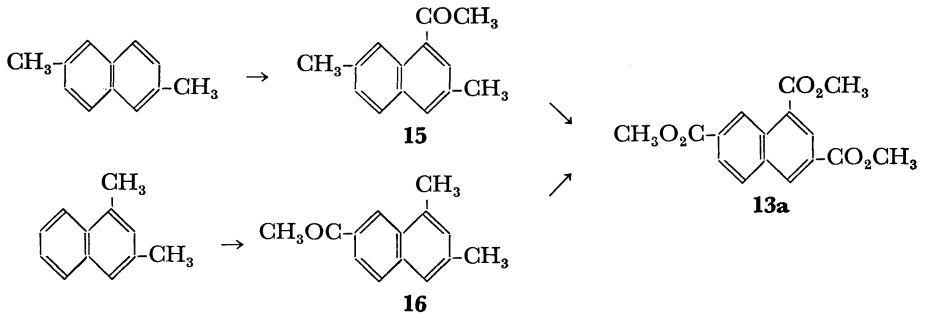
Results and Discussion

The preparative methods of naphthalenetricarboxylic acids given so far can be classified into three groups: (1) carboxylation of bromodimethylnaphthalenes by the Grignard reaction, (2) acylation of dimethylnaphthalenes or acenaphthene and (3) cyclization of the methyl- or dimethylphenylbutyric acid derivatives to the naphthalene ring.

1-Bromo-2,4-, 2,3-, 2,6-, and 4,6-dimethylnaphthalenes were prepared by the method of Arnold and Liggett[19] from 1,3-, 2,3-, 2,6-, and 1,7-dimethylnaphthalenes. The orientation for the bromination of these dimethylnaphthalenes has been reported by Kim *et al.*[20] Bromodimethylnaphthalenes were carboxylated to the corresponding dimethylnaphthoic acids by the Grignard reaction with carbon dioxide and then were oxidized with aqueous sodium bichromate to 1,2,4-, 1,2,3-, 1,2,6-, and 1,4,6-naphthalenetricarboxylic acids (Table 3, **2**, **1**, **4**, and **14**).

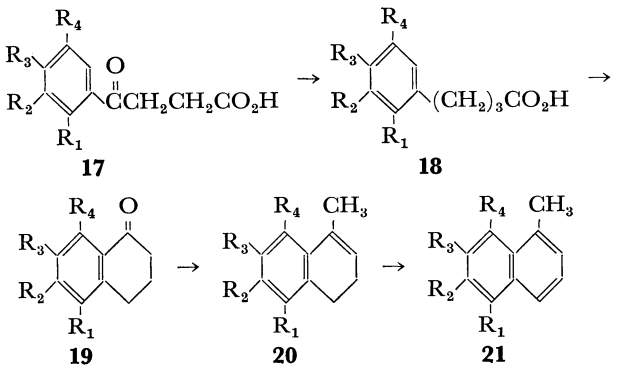
It has been reported that 2,6-dimethylnaphthalene gives 1-acetyl-2,6-dimethylnaphthalene (mp 70—71°C) by the Friedel-Crafts acetylation reaction in carbon disulfide,[12,13] and the acetyl compound is oxidized with aqueous hypochlorite solution to 2,6-dimethyl-1-naphthoic acid (mp 203—204°C)[13] which is further oxidized with dilute nitric acid to naphthalene-1,2,6-tricarboxylic acid (mp of trimethyl ester: 139—140°C).[11] We prepared 2,6-dimethyl-1-naphthoic acid with mp 173—174°C by the Grignard reaction on 1-bromo-2,6-dimethylnaphthalene. The trimethyl naphthalenetricarboxylate obtained from this compound had mp 141—142°C. On the other hand, trimethyl naphthalenetricarboxylate(**13a**) obtained by the aqueous bichromate oxidation of acetyl-2,6-dimethylnaphthalene(**15**) had mp 172.5—173.5°C. The results indicate that the acetyl group in acetyl-2,6-dimethylnaphthalene(**15**) is not located in the position given in literature. The structure of this acetyl compound was confirmed to be 1-acetyl-3,7-dimethylnaphthalene(**15**) from the fact that both trimethyl naphthalenetricarboxylates(**13a**) obtained by the aqueous bichromate oxidation of acetyl-2,6-dimethylnaphthalene(**15**) (mp 70—71°C) and of acetyl-1,3-dimethylnaphthalene(**16**) (mp 96.5—97.5°C), in which the acetyl group should be located in 7-position as shown in Scheme 1, were the same compound.

β-(5-Acenaphthoyl)propionic acid which had been prepared by the Friedel-Crafts reaction of acenaphthene and succinic anhydride[21] was oxidized to naphthalene-1,4,5-tricarboxylic acid (Table 3, **8**) with aqueous sodium bichromate, but β-(3-acenaphthoyl)propionic acid[21] gave benzene-1,2,3-tricarboxylic acid (Table 3, **6**). On the other hand, β-(3-acenaphthoyl)propionic acid could be oxidized with aqueous potassium ferricyanide to naphthalene-1,2,8-tricarboxylic acid. Naphthalene-2,3,6-tricarboxylic acid(Table 3, **10**) was obtained by the aqueous sodium bichromate oxidation of β-[2-(6,7-dimethylnaphthoyl)]propionic acid prepared by the Friedel-Crafts reaction of 2,3-dimethylnaphthalene and succinic anhydride.[22]



Scheme 1.

11) S. M. Maker, H. F. Bassilios, and A. Y. Salem, *J. Chem. Soc.*, **1958**, 2437.
12) E. Clar, H. Wallenstein, and R. Avenarius, *Ber.*, **62**, 950 (1929).
13) K. Dziewonski, K. Stec, and P. Zagata, *Bull. intern. acad. polon. sci., Classe sci. math. nat.*, **1938A**, 324; *Chem. Abstr.*, **33**, 1713[3] (1939).
14) L. Friedman, D. L. Fishel, and H. Shechter, *J. Org. Chem.*, **30**, 1453 (1965).
15) H. Frischkorn and E. Schinzel, German P. 1291329 (1969); Brit. P. 1173704 (1969).
16) L. Ruzicka, J. R. Hosking, L. Ehman, J. Jensen, and T. Lien, *Helv. Chim. Acta*, **13**, 1411 (1930).
17) L. Ruzicka and L. Ehman, *ibid.*, **15**, 140 (1932).
18) W. Ried and H. Boden, *Chem. Ber.*, **91**, 1354 (1958).
19) R. T. Arnold and R. W. Liggett, *J. Amer. Chem. Soc.*, **64**, 2875 (1942).
20) J. B. Kim, C. Chen, J. K. Krieger, K. R. Judd, C. C. Simpson, and E. Berliner, *ibid.*, **92**, 910 (1970).
21) L. F. Fieser and M. A. Peters, *ibid.*, **54**, 4347 (1932).
22) R. D. Hawarth and F. M. Bolam, *J. Chem. Soc.*, **1932**, 2248.

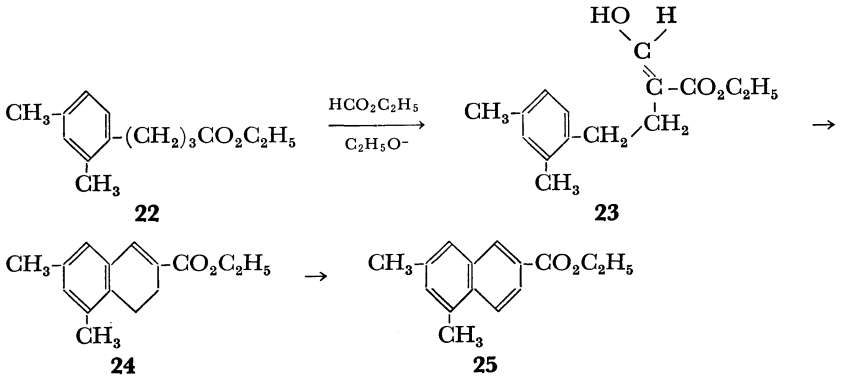


a. 2,3,5-Trimethylnaphthalene: $R_2=R_3=CH_3$ and $R_1=R_4=H$
b. 1,3,5-Trimethylnaphthalene: $R_1=R_3=CH_3$ and $R_2=R_4=H$
c. 1,2,5-Trimethylnaphthalene: $R_1=R_2=CH_3$ and $R_3=R_4=H$
d. 1,3,8-Trimethylnaphthalene: $R_2=R_4=CH_3$ and $R_1=R_3=H$

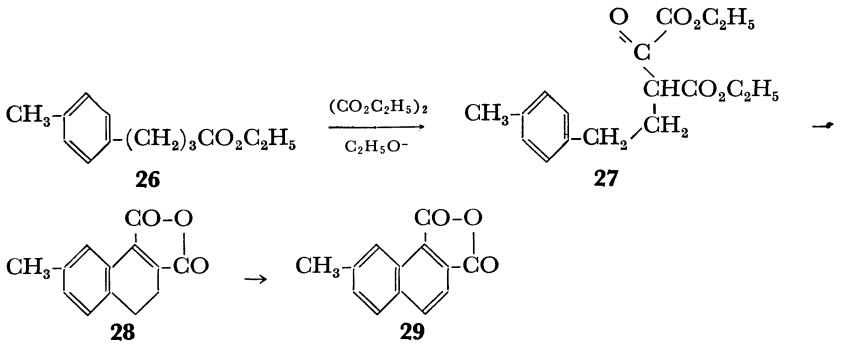
Scheme 2.

γ-(3,4- or 2,4-Dimethylphenyl)butyric acid(**18a** or **b**) was prepared by the Clemmensen reduction of β-(3,4- or 2,4-dimethylbenzoyl)propionic acid(**17a** or **b**) synthesized from *o*- or *m*-xylene with succinic anhydride.[23] After ring closure of these γ-dimethylphenylbutyric acids(**18a**, **b**) to dimethyltetralones(**19a**, **b**) with polyphosphoric acid,[24,25] the dimethyltetralones were converted into 1,6,7- and 1,5,7-trimethyl-3,4-dihydronaphthalenes(**20a** and **b**) by the Grignard reaction with methylmagnesium iodide and then dehydrogenated to 2,3,5- and 1,3,5-trimethylnaphthalenes(**21a** and **b**) with sulfur as shown in Scheme 2. These trimethylnaphthalenes gave the corresponding naphthalenetricarboxylic acids (Table 3, **9** and **11**). Methyl β-(2,3- or 3,5-dimethylbenzoyl)propionate was obtained by the reaction of 3-bromo-*o*-xylene or 5-bromo-*m*-xylene and β-carbomethoxypropionyl chloride by the method of Dauben and Tilles,[26] who reported on the synthesis of methyl benzoyl- and toluylpropionates. The methyl β-(dimethylbenzoyl)propionates were hydrolyzed to the corresponding free acids(**17c** and **d**) and then converted into 1,2,5- and 1,3,8-trimethylnaphthalenes (**21c** and **d**) by a similar reaction route. These trimethylnaphthalenes gave naphthalene-1,2,5- and 1,3,8-tricarboxylic acids (Table 3, **3** and **7**).

Ethyl 5,7-dimethyl-3,4-dihydronaphthalene-2-carboxylate(**24**) was prepared by the reaction of ethyl γ-(2,4-dimethyl)butyrate (**22**) and ethyl formate in the presence of sodium ethoxide followed by the ring closure with phosphoric acid - sulfuric acid mixture as shown in Scheme 3. This reaction route has been reported on the synthesis of ethyl 6,7-dimethoxy-3,4-dihydronaphthalene-2-carboxylate[27] and ethyl 7-methyl-2-naphthoate.[28] Dihydro compound(**24**)



Scheme 3.



Scheme 4.

23) E. de B. Barnett and F. G. Sanders, *ibid.*, **1933**, 434.
24) H. R. Snyder and F. X. Weber, "Organic Syntheses" Coll. Vol. III, 798 (1955).
25) R. P. Evans and J. C. Smith, *J. Chem. Soc.*, **1954**, 798.
26) W. G. Dauben and H. Tilles, *J. Org. Chem.*, **15**, 785 (1950).
27) H. L. Holmes and L. W. Trevoy, "Organic Syntheses" Coll. Vol. III, 300 (1955).
28) W. Adcock and P. R. Wells, *Aust. J. Chem.*, **18**, 1357 (1965),

was dehydrogenated with sulfur to ethyl 5,7-dimethylnaphthalene-2-carboxylate(**25**), hydrolyzed to free acid and then oxidized to naphthalene-1,3,6-tricarboxylic acid (Table 3, **12**).

Ethyl α-carbethoxy-γ-(*p*-methylphenyl)butyrate(**27**) was synthesized by the reaction of γ-(*p*-methylphenyl)butyrate(**26**) and diethyl oxalate in the presence of sodium ethoxide. This compound was cyclized with sulfuric acid to 7-methyl-3,4-dihydronaphthalene-1,2-dicarboxylic anhydride(**28**) and then dehydrogenated with sulfur to 7-methylnaphthalene-1,2-dicarboxylic anhydride(**29**) as shown in Scheme 4. The preparative method has been reported on the naphthalene-1,2-dicarboxylic anhydride.[29,30]

An attempt to prepare 5-methylnaphthalene-3,4-dihydro-1,2-dicarboxylic anhydride from γ-(*o*-methylphenyl)butyrate by a similar method failed. 7-Methylnaphthalene-1,2-dicarboxylic anhydride gave naphthalene-1,2,7-tricarboxylic acid (Table 3, **5**).

The melting points and analytical data of trimethyl naphthalenetricarboxylates are summarized in Table 1. The esters were hydrolyzed with potassium hydroxide in aqueous ethanol to give free acids, and some of them were dehydrated with acetic anhydride to the corresponding acid anhydrides. Melting points, analytical data, and infrared absorption bands of carbonyl group of naphthalenetricarboxylic acid monoanhydrides are shown in Table 2. In the cases of naphthalene-1,2,8-, 1,3,8-, and 1,4,8-tricarboxylic acids, 1,8-anhydrides were directly obtained by acidification of hot alkaline solution of the corresponding acids.[31]

Table 1. Melting points and analytical data of trimethyl naphthalenetricarboxylates

	Position	Mp (°C) Obsd.	Mp (°C) Ref.	Analytical data[a] Found (%) C	H
1a	1,2,3-	88.5— 89.5	—	63.41	4.77
2a	1,2,4-	119.5—120.5	120[b]	63.40	4.68
3a	1,2,5-	89.0— 89.5	90—91[c] 89[d]	63.46	4.66
4a	1,2,6-	141.0—142.0	139—140[e]	63.58	4.70
5a	1,2,7-	153.0—154.0	153—154[f] 152—153[g]	63.99	4.70
6a	1,2,8-	92.5— 93.5	—	64.04	4.68
7a	1,3,8-	110.5—111.5	—	63.47	4.29
8a	1,4,5-	126.0—127.0	—	63.52	4.77
9a	2,3,5-	128.0—128.5	—	63.43	4.66
10a	2,3,6-	124.5—125.5	—	63.68	4.88
11a	1,3,5-	128.0—129.0	—	63.45	4.70
12a	1,3,6-	194.5—195.5	—	63.62	4.70
13a	1,3,7-	172.5—173.5	—	63.55	4.67
14a	1,4,6-	135.0—136.0	—	63.48	4.70

a) Calcd for $C_{16}H_{14}O_6$: C, 63.58; H, 4.67%. b) Ref. 10. c) Ref. 6, p. 1411. d) Ref. 5. e) Ref. 11. f) Ref. 13. g) Ref. 9.

Experimental[32]

2,3-, 2,4-, 2,6-, and 4,6-Dimethyl-1-naphthoic Acids. 2,3-, 1,3-, 2,6-, and 1,7-Dimethylnaphthalenes were brominated by the method of Arnold and Liggett[19] to give 1-bromo-

Table 2. Physical properties and analytical data of naphthalenetricarboxylic acid monoanhydrides

	Position	Mp (°C) Obsd.	Mp (°C) Ref.	Analytical data[a] Found (%) C	H	Infrared spectrum ν_{CO} (cm^{-1})
2b	1,2,4-	292—293	—	64.79	2.06	1851, 1794, 1701
3b	1,2,5-	277—278	270[b] 270—272[c]	64.46	2.13	1848, 1770, 1759, 1683
4b	1,2,6-	>300	298—300[d]	64.21	2.09	1840, 1792, 1775, 1691
5b	1,2,7-	>300	—	64.86	2.07	1861, 1794, 1695
6b	1,2,8-	298.5—299.5	297.5—298.5[e] 295—297[f]	64.81	1.87	1775, 1742, 1734, 1689
7b	1,3,8-	289—290	287—288[f]	64.28	2.06	1774, 1737, 1693
8b	1,4,5-	273.5—274.5	273—274[f] 273—275[g] 274—275[h]	64.72	2.09	1770, 1737, 1703
9b	2,3,5-	>300	—	64.10	2.06	1843, 1831, 1780, 1676
10b	2,3,6-	288.5—289.5	—	64.22	2.10	1852, 1788, 1695

a) Calcd for $C_{13}H_6O_5$: C, 64.47; H, 2.50%. b) Mp of free acid: Ref. 7. c) Mp of free acid: Ref. 5. d) Mp of free acid: Ref. 11. e) Ref. 4. f) Ref. 3. g) A. A. Morton, J. B. Davidson, T. R. P. Gibb, Jr., E. L. Little, E. E. Clarke, and A. G. Green, *J. Amer. Chem. Soc.*, **64**, 2250 (1942). h) H. E. Nürsten and A. T. Peters, *J. Chem. Soc.*, **1950**, 2389.

29) L. F. Fieser and E. B. Hershberg, *J. Amer. Chem. Soc.*, **57**, 1851 (1935); E. B. Hershberg and L. F. Fieser, "Organic Syntheses" Coll. Vol. II, 194 (1948).

30) E. B. Hershberg and L. F. Fieser, *ibid.*, Coll. Vol. II, p. 423 (1948).

31) Naphthalene-1,8-dicarboxylic acid gives anhydride by recrystallization from nitric acid(S. G., 1,4): C. Graebe and E. Gfeller, *Ber.*, **25**, 653 (1892).

32) Infrared spectroscopy and micro analysis were performed with a Hitachi Infrared Spectrophotometer EPI-S2 (in Nujol) and a Yanagimoto C. H. N. Corder MT-1 apparatus, respectively. The methyl ester of the carboxylic acid was synthesized by the reaction of the silver salt of carboxylic acid and methyl iodide.

2,3-dimethyl-, 1-bromo-2,4-dimethyl-, 1-bromo-2,6-dimethyl-, and 1-bromo-4,6-dimethylnaphthalenes.

2,3-Dimethyl-1-naphthoic acid was prepared by the Grignard reaction of 1-bromo-2,3-dimethylnaphthalene[19]: 52% yield, mp 170—171°C (lit, mp 167—168°C[19]).

1-Bromo-2,4-dimethylnaphthalene gave 2,4-dimethyl-1-naphthoic acid by a similar method; 55% yield, mp 165.5—167.0°C (aqueous EtOH). Found: C, 78.02; H, 6.01%. Calcd for $C_{13}H_{12}O_2$: C, 77.96; H, 6.04%.

1-Bromo-2,6-dimethylnaphthalene gave 2,6-dimethyl-1-naphthoic acid (46.3%) and 2,6-dimethylnaphthalene (24.3%). The acid had mp 173—174°C(aqueous EtOH). Found: C, 77.64; H, 6.02% (the acid reported to have mp 203—204°C[11,13,33] should be assigned to 3,7-dimethyl-1-naphthoic acid). Methyl 2,6-dimethyl-1-naphthoate: mp 89.5—90.5°C (MeOH). Found: C, 78.23; H, 6.73%. Calcd for $C_{14}H_{14}O_2$: C, 78.49; H, 6.58%.

1-Bromo-4,6-dimethylnaphthalene gave 4,6-dimethyl-1-naphthoic acid; 59% yield, mp 196.5—197.0°C (benzene). Found: C, 78.02; H, 6.23%.

Acetylation of 2,6- and 1,3-Dimethylnaphthalenes. 2,6-Dimethylnaphthalene was acetylated with acetic anhydride and anhydrous aluminum chloride in carbon disulfide by the method of Clar, Wallenstein, and Avenarius[12] giving a fraction of bp 151—157°C/4 mmHg in 64.5% yield. This fraction which solidified partly was filtered and recrystallized from ethanol to give 3,7-dimethyl-1-acetonaphthone(**15**); mp 70—71°C(lit, mp 70—71°C).[11-13] This was reported to be 2,6-dimethyl-1-acetonaphthone. 3,7-Dimethyl-1-acetonaphthone (10 g) was oxidized with aqueous sodium hypobromite solution at room temperature for 20 hr to give 1.6 g of 3,7-dimethyl-1-naphthoic acid; mp 202—203°C (aqueous EtOH) (lit, mp 204—205°C[34]) or with aqueous sodium bichromate to naphthalene-1,3,7-tricarboxylic acid (Table 3, **13**). The tricarboxylic acid (2.0 g) was recrystallized from 50 m*l* of acetic anhydride, washed with benzene and dried. The infrared spectrum of this compound has no acid anhydride band.

1,3-Dimethylnaphthalene (37.7 g, 0.242 mol) in 50 m*l* of nitrobenzene was added to a solution of 19.4 g (0.248 mol) of acetyl chloride and 34 g (0.248 mol) of anhydrous aluminum chloride in 80 m*l* of nitrobenzene under chilling with ice-water. Stirring was continued for 2 hr at room temperature and then 2 hr at 60°C. After treatment in the usual manner, 1,3-dimethyl-7-acetonaphthone(**16**) which boiled at 152—159°C/3 mmHg was collected; mp 96.5—97.5°C (EtOH), 56.5% yield(37 g). Found: C, 84.74; H, 7.27%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.11%. The ketone gave naphthalene-1,3,7-tricarboxylic acid (Table 3, **13'**). The trimethyl ester(mp 172.5—173.5°C) was identified to be the same compound by means of mixed melting point and comparison of the infrared spectra with the sample obtained from 3,7-dimethyl-1-acetonaphthone (**15**).

Succinoylation of Acenaphthene and 2,3-Dimethylnaphthalene. β-(3- and 5-Acenaphthoyl)propionic acids were synthesized by the method of Fieser and Peters[21] from acenaphthene and succinic anhydride.

β-[2-(6,7-Dimethylnaphthoyl)]propionic acid was prepared by a modified method of Hawarth and Bolam.[22] 2,3-Dimethylnaphthalene (40.0 g, 0.256 mol) was added to a solution of 78 g (0.58 mol) of anhydrous aluminum chloride and 26.0 g (0.26 mol) of succinic anhydride in 250 m*l* of nitrobenzene under chilling with ice-water. Stirring was carried out overnight at room temperature. The reaction product was treated and purified by a similar method to that in the synthesis of β-(5-acenaphthoyl)propionic acid[21] to give 17.0 g (37%) of β-[2-(6,7-dimethylnaphthoyl)] propionic acid; mp 183.5—184.5°C. Recrystallization from methanol gave mp 184.0—185.0°C (lit, mp 179—180°C[22]).

2,3,5- and 1,3,5-Trimethylnaphthalenes. γ-(3,4- and 2,4-Dimethylphenyl)butyric acid[23] (**18a** and **b**) were cyclized with polyphosphoric acid (200 m*l* of 85% phosphoric acid and 240 g of phosphorus pentoxide)[24,25] to give 6,7- and 5,7-dimethyltetralones (**19a** and **b**); 89% yield, bp 128—130°C/4 mmHg and 90% yield, bp 137°C/5.5 mmHg, respectively. The dimethyltetralones were converted into 1,6,7- and 1,5,7-trimethyl-3,4-dihydronaphthalenes (**20a** and **b**) by the Grignard reaction with methylmagnesium iodide and then dehydrogenated with sulfur at 210°C for 8 hr to give 2,3,5- and 1,3,5-trimethylnaphthalenes (**21a** and **b**); bp 131—131.5°C/11 mmHg (lit, bp 138°C/12 mmHg[17]) and bp 115—116°C/5.5 mmHg, mp 42.5—44.5°C (lit, mp 43°C[16]), respectively.

1,3,8- and 1,2,5-Trimethylnaphthalenes. 4-Acetamido-*m*-xylene[35] was nitrated by a modified method of Haller, Adams, and Wherry.[36] 4-Acetamido-*m*-xylene (100 g, mp 129.5—130.5°C) in 100 m*l* of glacial acetic acid was dropped into 200 m*l* of fuming nitric acid (S. G., 1.52) under stirring at 10°C for 3 hr and further stirred for 20 min. The reaction mixture was poured into 1 *l* of water, filtered, washed with water and finally recrystallized from 500 m*l* of ethanol to give 5-nitro-4-acetamido-*m*-xylene; 70—79% yield, mp 175—176°C (lit, mp 172°C[35]). The compound was deaminated to 5-nitro-*m*-xylene,[36] reduced to 5-amino-*m*-xylene by the Béschamp reduction, brominated to 5-bromo-*m*-xylene by the method of Zanten and Nauta,[37] and then made to react with β-carbomethoxypropionyl chloride to give methyl β-(3,5-dimethylbenzoyl)propionate by the method of Dauben and Tilles[26]; 25.6% yield, bp 153—160°C/2 mmHg. The ester was hydrolyzed to β-(3,5-dimethylbenzoyl)propionic acid(**17d**); 70.3% yield, mp 117—118°C(aqueous EtOH). Found: C, 69.42; H, 7.28%. Calcd for $C_{12}H_{12}O_3$: C, 69.21; H, 7.74%. The Clemmensen reduction of the above keto-acid gave γ-(3,5-dimethylphenyl)butyric acid(**18d**) (95% yield, mp 60—61°C). 1,3,8-Trimethylnaphthalene(**21d**) was then prepared in a similar way *via* 6,8-dimethyltetralone(**19d**) and 1,6,8-trimethyl-3,4-dihydronaphthalene(**20d**); mp 45.5—46.5°C (MeOH) (lit, mp 48°C[5]).

Methyl β-(2,3-dimethylbenzoyl)propionate was prepared from 3-bromo-*o*-xylene[37] in a similar way to that described above; 21—24% yield; bp 145—148°C/2 mmHg. The free acid (**17c**) had mp 100.5—101.5°C (EtOH); 69—72% yield. Found: C, 69.63; H, 7.38%. 1,2,5-Trimethylnaphthalene(**21c**) was then synthesized by a similar way as described above *via* γ-(2,3-dimethylphenyl)butyric acid (**18c**) (mp 109.5—110.5°C from benzene), 5,6-dimethyltetralone(**19c**) (mp 58—59°C) and 1,5,6-trimethyl-3,4-dihydronaphthalene(**20c**); bp 132—134°C/4 mmHg (lit, bp 147—148°C/11 mmHg[16]).

5,7-Dimethyl-2-naphthoic Acid. Into a solution of sodium ethylate prepared from 7.0 g of sodium sand and 17 m*l* of absolute ethanol in 150 m*l* of dry ether, a mixture of 42.0 g (0.191 mol) of ethyl γ-(2,4-dimethylphenyl)butyrate (**22**)[23] and 21.0 g (0.284 mol) of ethyl formate in 100 m*l* of dry ether was added under stirring and chilling with ice-

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34) F. G. Baddar, I. M. Dwidar, and M. Gindy, *J. Chem. Soc.*, **1959**, 1005.
35) W. Willgerodt and F. Schmierer, *Ber.*, **38**, 1473 (1905).
36) H. L. Haller, E. Q. Adams, and E. T. Wherry, *J. Amer. Chem. Soc.*, **42**, 1840 (1920).
37) B. van Zanten and W. T. Nauta, *Rec. Trav. Chim. Pays-Bas*, **97**, 1216 (1960).

salt bath for 20 min and stirred at room temperature for 50 hr. The reaction mixture was worked up as described by Holmes and Trevoy[27] to give 3,4-dihydro-5,7-dimethyl-2-naphthoate (**24**) in 36—40% yield (15.7—17.5 g), bp 163—165°C/2.5 mmHg, mp 75.5—76.5°C. The dihydro compound (52 g, 0.226 mol) was dehydrogenated with 7.5 g (0.234 atom) of sulfur at 240°C for 3 hr to give 44.1 g of ethyl 5,7-dimethyl-2-naphthoate (**25**); bp 165—175°C/3 mmHg. Crystallization three times from 50 m*l* portions of ethanol gave 18.7 g of pure ethyl ester; mp 57.5—58.5°C. Found: C, 79.09; H, 7.27%. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06%. The ester(20 g) was hydrolyzed with potassium hydroxide in aqueous ethanol for 30 hr to give 17.4 g of 5,7-dimethyl-2-naphthoic acid in 99% yield, mp 206.5—207.5°C (EtOH). Found: C, 78.09; H, 6.12%. Calcd for $C_{13}H_{12}O_2$: C, 77.97; H, 6.04%. Methyl 5,7-dimethyl-2-naphthoate had mp 70.0—71.0°C (MeOH). Found: C, 78.54; H, 6.66%. Calcd for $C_{14}H_{14}O_2$: C, 78.49; H, 6.58%.

7-Methylnaphthalene-1,2-dicarboxylic Anhydride. Diethyl oxalate (57.5 g, 0.393 mol) in 100 m*l* of dry ether was added to a solution of sodium ethylate prepared from 6.3 g (0.274 atom) of sodium sand and 13 g of absolute ethanol in 100 m*l* of dry ether, during the course of 30 min at room temperature and 53.5 g (0.260 mol) of ethyl γ-(*p*-methylphenyl)butyrate (**26**) in 50 m*l* of dry ether was then added for 5 min. After stirring for 30 hr at room temperature, the product was worked up as described by Fieser and Hershberg[29] to give 27.9 g (50.2%) of 3,4-dihydro-7-methylnaphthalene-1,2-carboxylic anhydride (**28**); mp 138—140°C (from petroleum benzine-benzene). Found: C, 73.00; H, 4.64%. Calcd for $C_{13}H_{10}O_3$: C, 72.88; H, 4.67%. The dihydro compound (21 g, 0.10 mol) was dehydrogenated with 3.2 g (0.10 atom) of sulfur at 200—250°C for 3 hr to give 13.7 g of 7-methylnaphthalene-1,2-dicarboxylic anhydride (**29**). Crystallization three times from benzene(active carbon) gave mp 161.5—163.5°C. The anhydride (26 g) was dissolved in aqueous sodium hydroxide solution by heating to remove trace of hydrogen sulfide, treated with active carbon and reprecipitated with hydrochloric acid. The acid (20.7 g) was treated with 80 m*l* of acetic anhydride at 150°C for 1 hr to give pure 7-methylnaphthalene-1,2-dicarboxylic anhydride (16.7 g); mp 164.5—165.5°C, ν_{CO}: 1842 and 1768 cm^{-1}. Found: C, 73.64; H, 3.45%. Calcd for $C_{13}H_8O_3$: C, 73.56; H, 3.82%. Dimethyl ester: mp 88—89°C (MeOH). Found: C, 69.42; H, 5.52%. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46%.

Sodium Bichromate Oxidation. Dimethylnaphthalenecarboxylic acids, methylnaphthalenedicarboxylic acid, dimethylacetonaphthones, β-(acenaphthoyl)propionic acid, β-(dimethylnaphthoyl)propionic acid and trimethylnaphthalenes were oxidized with aqueous sodium bichromate at

Table 3. Conditions and products of sodium bichromate oxidation

	Material: Naphthalene	g (mol)	$Na_2Cr_2O_7 \cdot 2H_2O$ g (mol)	Conditions[a] Water m*l*	Temp. °C	Time hr	Product: Naphthalene tricarboxylic acid Position	g (%)
1	1-Carboxy-2,3-dimethyl-[b]	13.0 (0.065)	60 (0.22)	180	260± 5	5	1,2,3-	5.0[c] (25)
2	1-Carboxy-2,4-dimethyl-	12.5 (0.063)	57 (0.19)	150	270±10	5	1,2,4-	12.5 (77)
3	1,2,5-Trimethyl-	9.4 (0.055)	75 (0.25)	150	270±10	21	1,2,5-	0.5 (3)
4	1-Carboxy-2,6-dimethyl-	11.0 (0.055)	55 (0.18)	100	270±10	5	1,2,6-	11.3 (79)
5	1,2-Dicarboxy-7-methyl-	12.5 (0.059)	24 (0.08)	100	265±10	6	1,2,7-	6.8 (44)
6	β-(3-Acenaphthoyl)propionic acid	12.0 (0.047)	75 (0.25)	150	265± 5	6	—[e]	
7	1,3,8-Trimethyl-	3.4 (0.02)	25 (0.083)	75	255± 5	19	1,3,8-	2.2[d] (46)
8	β-(5-Acenaphthoyl)propionic acid	11.2 (0.044)	75 (0.25)	150	280± 5	5	1,4,5-	5.9[d] (55)
9	2,3,5-Trimethyl-	9.0 (0.053)	72 (0.24)	150	270± 5	18	2,3,5-	8.7 (63)
10	β-[2-(6,7-dimethylnaphthoyl)]propionic acid	10.0 (0.039)	70 (0.23)	150	270± 5	6	2,3,6-	7.9 (78)
11	1,3,5-Trimethyl-	8.5 (0.05)	70 (0.23)	150	275± 5	18	1,3,5-	9.6 (74)
12	2-Carboxy-5,7-dimetyl-	8.0 (0.04)	36 (0.12)	100	260± 2	6	1,3,6-	9.9 (95)
13	1-Acetyl-3,7-dimethyl-	9.0 (0.046)	60 (0.22)	150	275± 5	18	1,3,7-	10.9 (92)
13'	7-Acetyl-1,3-dimethyl-	8.0 (0.044)	60 (0.22)	150	275± 5	19	1,3,7-	10.2 (89)
14	1-Carboxy-4,6-dimethyl-	5.0 (0.025)	22.5 (0.075)	100	265± 5	5	1,4,6-	6.0 (92)

a) 300 m*l* Autoclave used as reaction vessel. b) 400 m*l* Autoclave used. c) Separated as methyl ester.
d) Separated as acid anhydride. e) Trimethyl hemimellitate.

250—280°C under autogeneous pressure (*ca.* 30—40 kg/cm²). Sodium bichromate was used 1.3—1.5 times excess per methyl or methylene group. Methylnaphthalenecarboxylic acids, dimethylnaphthoylpropionic acid and acenaphthoylpropionic acids were dissolved in equimolar amount of aqueous sodium hydroxide and oxidized. The reaction mixture was filtered at 70—80°C, and the filtrate was neutralized with hydrochloric acid to pH≃6, treated with active carbon and then acidified with hydrochloric acid to give naphthalenetricarboxylic acids. The reaction conditions and products are summarized in Table 3.

In the cases of naphthalene-1,2,3- and 1,2,5-tricarboxylic acids (Table 3, **1** and **3**), the reaction product was filtered, acidified with nitric acid, neutralized with sodium hydroxide to pH≃9 and treated with active carbon. Excess silver nitrate was then added in order to isolate the carboxylic acid as silver salt owing to the high solubility of these acids in water. The silver salts were converted into trimethyl naphthalenetricarboxylates with methyl iodide. The ester obtained from the 1,2,5-trimethylnaphthalene was dissolved in methanol, chromatographed through the alumina column and eluted with methanol. The eluted solution was evaporated and the residue was recrystallized from methanol to give 0.6 g of trimethyl hemimellitate; mp 100.5—101.5°C. It was identified by means of the mixed melting point and comparison of the infrared spectra with the authentic sample. The mother liquors were evaporated to dryness and the residue (4.5 g) was extracted with 15 m*l* of hot ligroin. After cooling of the ligroin solution, trimethyl naphthalene-1,2,5-tricarboxylate was isolated; 0.4 g, mp 89.0—89.5°C (MeOH).

From the oxidation product of β-(3-acenaphthoyl)propionic acid(Table 3, **6**), trimethyl hemimellitate (mp 101—102°C; 0.2 g) was isolated by a similar treatment to that in the case of 1,2,5-trimethylnaphthalene. The mother liquors gave 1.3 g of impure product; mp 83—93°C.

Potassium Ferricyanide Oxidation of β-(3-Acenaphthoyl)-propionic Acid. β-(3-Acenaphthoyl)propionic acid (5.4 g), 82 g of potassium hydroxide, 470 g of potassium ferricyanide, and 1200 m*l* of water were allowed to react at 60°C for 74 hr. A solution of 24 g of potassium hydroxide, 90 g of potassium ferricyanide, and 200 m*l* of water was added at 24 hr intervals. The product was cooled, acidified with hydrochloric acid and filtered. The filtrate was extracted fifteen times with 300 m*l* portions of ether. The ether was evaporated to give 3.5 g of naphthalene-1,2,8-tricarboxylic acid; mp 288—290°C.

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