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Thermal Transformation of Alkali Salts of Aromatic Carboxylic Acids. V.[1] Reaction of Potassium and Sodium Salts of Naphthoic Acids

Yasuhiko DOZEN

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

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The cadmium fluoride-catalyzed thermal transformation of potassium and sodium salts of naphtoic acids has been investigated. At the initial reaction stage both potassium and sodium α-naphthoate gave naphthalene and naphthalene-1, 2- and 1, 3-dicarboxylates, which were converted to naphthalene-2, 3- and 2, 6-dicarboxylates. The products composition, however, differed between potassium and sodium salts. Potassium β-naphthoate gave naphthalene and naphthalene-1,2- and 2, 3-dicarboxylates, which were then further converted to naphthalene-2, 6-dicarboxylate. On the other hand, sodium β-naphthoate gave naphthalene and naphthalene-1, 2- and 2, 3-dicarboxylates. In the presence of potassium cyanate, potassium α- and β-naphthoates gave a high yield of naphthalene-2, 6-dicarboxylate. The mechanism of the reaction was discussed.

Raecke[2,3] found that potassium α- and β-naphthoates gave naphthalene-2, 6-dicarboxylate in the presence of a catalyst under carbon dioxide pressure and under heating at a high temperature. The reaction conditions have been studied by Yamashita, Enomoto, Ebisawa, and Kato,[4] and

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[1] Part IV: Y. Dozen, This Bulletin, **40**, 1218 (1967).

[2] B. Raecke (to Henkel & Cie, G. m. b. H.), German Pat. 953072 (1956); Brit. Pat. 744721 (1956); U. S. Pat. 2823231 (1958).

[3] B. Raecke, *Angew. Chem.*, **70**, 1 (1958).

[4] J. Yamashita, K. Enomoto, H. Ebisawa and S. Kato, *Yuki Gosei Kagaku Kyokaishi (J. Soc. Org. Syn. Chem. Japan)*, **20**, 501 (1962).

TABLE 1. REACTION PRODUCTS OF α-NAPHTHOATE

Run No.	Condition		Product (mol%)								
	Temp. °C	Time hr	Naphthalene[a]	Naphthoic acid		Naphthalene dicarboxylic acid[a]				
				α-	β-	1,2-	2,3-	1,3-	2,6-	2,7-
From potassium salt										
1	325	1	22	78	—	10	1	—	—	—
2	345	1	53	35	12	0.6	1.4	12	4	—
3	385	1	79	—	24	—	8	—	34	—
4[b,c]	370	1	99	—	27	—	—	—	47	—
5[b,c]	370	4	100	—	10	—	—	—	64	—
From sodium salt										
6	290	1	33	61	—	10	5	6	0.3	0.2
7	320	1	63	8	19	24	28	1	4	2
8[c]	345	1	73	—	21	—	23	—	6	—
9	385	1	66	—	20	12	24	—	7	—
10	385	3	61	—	21	—	25	1	9	—

a) The yield was based on the disproportionation of naphthoate.
b) Potassium cyanate (7.0 g) was added.
c) The acid II fraction (see Experimental part) was not treated for the large contamination with the resinous substance.

TABLE 2. REACTION PRODUCTS OF β-NAPHTHOATE

Run No.	Condition		Product (mol%)					
	Temp. °C	Time hr	Naphthalene[a]	Naphthoic acid		Naphthalene dicarboxylic acid[a]		
				α-	β-	1,2-	2,3-	2,6-
From potassium salt								
1[b]	380	1	11	—	80	—	18	—
2	430	2	31	—	34	Trace	9	43
3[b,c]	380	1	26	—	68	—	6	14
4[b,c]	380	4	25	—	43	—	5	44
5[c]	395	10	31	—	30	1	4	78
From sodium salt								
6	385	1.5	38	—	58	4	30	—
7	445	1.5	30	—	48	Trace	33	—
8	445	5	33	—	44	Trace	29	—
9[b,d]	450	5	28	—	44	—	37	—

a) The yield was based on the disproportionation of naphthoate.
b) The acid II fraction (see Experimental part) was not treated for the large contamination with the resinous substance.
c) Potassium cyanate (7.0 g) was added.
d) Zink chloride instead of cadmium fluoride was added.

an improvement of the reaction apparatus has been reported by Dorschner, Markworth, and Plenz.[5]

In the previous paper,[1] it has been reported that potassium methylbenzoates gave *o*-, *m*-, and *p*-directed disproportionation products, while sodium methylbenzoates gave an *o*-directed one. It was also observed in 1965 that sodium β-naphthoate gave naphthalene-2, 3-dicarboxylate. At that time, similar results were reported by McNelis,[6] and Patton and Son.[7] This paper will report the results of more detailed studies of the difference in orientation between potassium and sodium salts of naphthoic acids in the disproportionation.

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[5] O. Dorschner, H. Markworth and J. Plenz (to Metallgeselschaft A.-G.), German Pat. 1155770 (1963).

[6] E. McNelis, *J. Org. Chem.*, **30**, 1209 (1965).

[7] J. W. Patton and M. O. Son, *ibid.*, **30**, 2869 (1965).

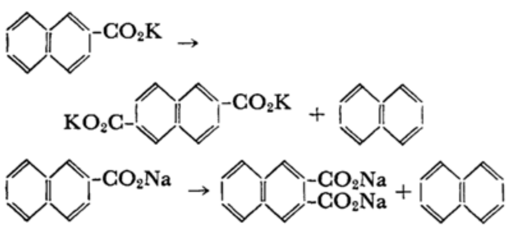

Table 1 shows the reaction products from potassium and sodium salts of α-naphthoic acid. Both salts, in each case, gave naphthalene and naphthalene-1, 2- and 1, 3-dicarboxylates as the primary product at a low temperature. With a rise in the temperature, however α-naphthoate disappeared, and β-naphthoate, naphthalene-2, 3-, 2, 6-, and 2, 7-dicarboxylates were produced. The potassium salt gave the 2, 6-isomer predominantly, while the sodium salt gave the 2, 3-isomer as the main product.

In the presence of potassium cyanate and potassium carbonate, potassium α-naphthoate gave a higher yield of naphthalene-2, 6-dicarboxylate than in the absence of potassium cyanate. This may be explained in terms of direct carboxylation with potassium carbonate, as has been reported in the reactions of potassium benzoate, potassium carbonate, and potassium cyanate.[8]

Table 2 shows the reaction products from potassium and sodium salts of β-naphthoic acid. Potassium β-naphthoate gave naphthalene-2, 3-dicarboxylate at low temperatures and 2, 6-isomer at high temperatures. In the presence of potassium cyanate, the yield of 2, 6-isomer was increased. On the other hand, sodium β-naphthoate gave naphthalene-2, 3-dicarboxylate selectively.

These results indicate that α-naphthoate is disproportionated to naphthalene-1, 2- and 1, 3-dicarboxylates in the initial stage of the reaction, and then a thermally-unstable α-carboxyl group of these acids is decarboxylated or cross-disproportionated to β-naphthoate. Thermally-stable naphthalene-2, 3- and 2, 6-dicarboxylates may be produced by the disproportionation of β-naphthoate or by the cross-disproportionation of β-naphthoate and another carboxylate, as shown in Chart 1. The facts that potassium β-naphthoate gave naphthalene-2, 3- and 2, 6-dicarboxylates, and that sodium β-naphthoate was converted to naphthalene-2, 3-dicarboxylate, may be explained in terms of the difference in thermal stability between the potassium and sodium salts of naphthalene-2, 3-dicarboxylate.

McNelis[6] reported the decarboxylation-recarboxylation mechanism for the reaction of potassium β-naphthoate to naphthalene-2, 6-dicarboxylate. In the reaction of potassium benzoate, a similar mechanism has been discussed by Furuyama[9] using deuterated or radioactive benzoate. In the reaction of potassium phthalates and benzoate under an atmosphere of radioactive carbon dioxide, it has been reported by Riedel and Kienitz[10] that the quantity of $^{14}CO_2$ incorporated into the molecules of benzene carboxylates was lower than the calculated value. This reaction was further investigated by Ratusky and Sorm[11] in a thin-layer state of carboxylates with perfect mixing; there results suggest the decarboxylation-recarboxylation mechanism.

When the decarboxylation - recarboxylation mechanism is involved in the reaction, the α-hydrogen of the naphthalene ring, which is more reactive than the β-hydrogen, will be abstracted by the carbanion which is produced by the decarboxylation of β-naphthoate, and α-naphthoate

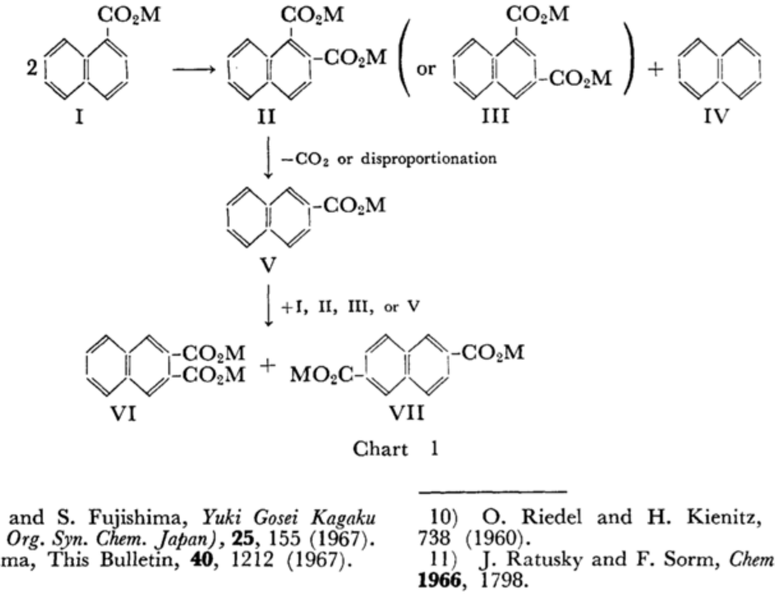

Chart 1

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[8] Y. Dozen and S. Fujishima, *Yuki Gosei Kagaku Kyokaishi (J. Soc. Org. Syn. Chem. Japan)*, **25**, 155 (1967).
[9] S. Furuyama, This Bulletin, **40**, 1212 (1967).
[10] O. Riedel and H. Kienitz, *Angew. Chem.*, **72**, 738 (1960).
[11] J. Ratusky and F. Sorm, *Chem. & Ind. (London)*, **1966**, 1798.

will be obtained as the reaction product. α-Naphthoate, however, could not be detected in the reaction product of the β-naphthoate (see Table 2). This fact may be explained by the intermolecular disproportionation mechanism.

Experimental[12]

Materials. α-Naphthoic acid was prepared by the Grignard reaction of α-bromonaphthalene[13]; mp 161—162°C (benzene). β-Naphthoic acid was synthesized by the hypobromite oxidation of β-acetylnaphthalene,[14] which had been prepared by the Friedel-Crafts reaction of naphthalene and acetyl chloride[15]; mp 183—184°C (EtOH).

General Method. A naphthoic acid was neutralized with aqueous potassium (or sodium) hydroxide to pH 7.0—7.5. The solution was then evaporated to dryness and further dried under a vacuum (*ca.* 5 mmHg) at 150—180°C. The alkali salt of naphthoic acid (15.0 g) was mixed with cadmium fluoride (1.0 g) and potassium (or sodium) carbonate (5.0 g). The mixture was dried under a vacuum (*ca.* 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 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 naphthalene, which was identified by means of its melting point. The ether-insoluble substance was dissolved in hot water (500 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 evaporated to dryness, and the residue was extracted with ethanol to give an acidic substance (Acid II).[16]

Analysis. Each fraction of Acid I and II (1—2 g) was converted to silver salt, and the salt was esterified with methyl iodide in benzene. After the evaporation of the solvent, the residue was dissolved in chloroform and analyzed by vapor-phase chromatography. α- and β-Naphthoates were analyzed with 25% Silicone DC 550 on Shimalite (30—60 mesh; 4 mmϕ × 1.5 m; column temperature, 190°C; flow rate of He, 50 m*l*/min), and naphthalene dicarboxylates were determined with 15% Silicone DCHV Grease on Celite 545 (Nishio Kogyo Co., Ltd.) (40—60 mesh; 4 mmϕ × 1.5 m; column temperature, 220°C; flow rate of He, 50 m*l*/min). The retention times of the authentic samples are shown in Fig. 1. The analytical data of the esters derived from an authentic mixture of α-naphthoic (24.8 wt%), β-naphthoic (26.7%), naphthalene-2, 3-dicarboxylic (23.5%), and 2, 6-dicarboxylic (25.0%) acids gave 21.8, 29.5, 23.4 and 25.4 wt% respectively.

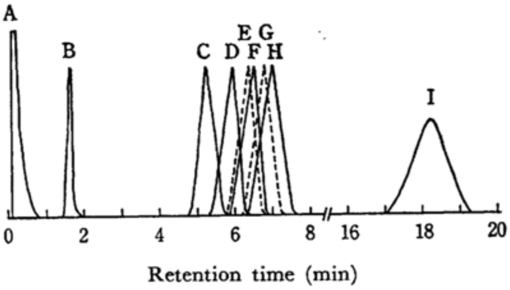

Fig. 1. Vapor-phase chromatogram of methyl esters of naphthalene carboxylic acids.

15% silicon DCHV grease on celite 545
column temperature, 220°C
flow rate of He, 50 m*l*/min

A	Solvent ($CHCl_3$)
B	α- and β-Naphthoates
C	1, 2-Dicarboxylate
D	2, 3-, 1, 4- and 1, 8-Dicarboxylates
E	1, 3- and 1, 5-Dicarboxylates
F	1, 7-Dicarboxylate
G	2, 6- and 1, 6-Dicarboxylates
H	2, 7-Dicarboxylate
I	1, 3, 5-Tricarboxylate

Identification of the Reaction Products. *Naphthalene-2, 6-dicarboxylic Acid.* The dimethyl ester obtained from the reaction product of potassium β-naphthoate (430°C for 1.5 hr) or α-naphthoate (Table 1, run 5) was recrystallized from ethyl acetate or benzene to give dimethyl naphthalene-2, 6-dicarboxylate; mp 189.0—189.5°C (lit., mp 187—188°C[17]).

Naphthalene-2, 3-dicarboxylic Acid. The reaction products of sodium β-naphthoate (445°C for 1.5 hr) were extracted with ether (Soxhlet, 8 hr); the insoluble substance (1.5 g) was then treated with acetic anhydride to give 0.9 g of naphthalene-2, 3-dicarboxylic anhydride; mp 245—246°C (lit., mp 246°C[18]).

Found: C, 72.59; H, 2.74%. Calcd for $C_{12}H_6O_3$: C, 72.72; H, 3.05%.

The infrared spectrum had acid anhydride bands at 1841 and 1764 cm^{-1}.

Naphthalene-1, 2-dicarboxylic Acid. The ester of the Acid II fraction obtained by the reaction of potassium α-naphthoate (Table 1, run 7) was recrystallized from methanol to give dimethyl naphthalene-1, 2-dicarboxylate (mp 78—82°C), which was identified by a mixed-melting-point determination and by a comparison of the infrared spectra with those of an authentic sample (see the next paragraph).

Naphthalene-1, 3-dicarboxylic Acid. The ester obtained from the reaction product of potassium α-naphthoate Table 1, run 2) was distilled to remove the methyl naphthoates. The residue had all the peaks of the infrared spectrum appearing in dimethyl naphthalene-1, 3-dicarboxylate, but all attempts to isolate it failed.

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[12] All melting points are corrected. Vapor-phase chromatography, infrared spectroscopy, and micro analysis were performed using a Shimadzu G. C-1B, a Hitachi Infrared Spectrophotometer EPI-SII (in Nujol), and a Yanagimoto C. H. N. Corder MT-1 apparatus respectively.

[13] H. Gilman, N. B. St. John and F. Schulze, "Organic Synthesis," Coll. Vol. II, p. 425 (1948).

[14] M. S. Newman and H. L. Holmes, *ibid.*, p. 428.

[15] T. Immediate and A. R. Day, *J. Org. Chem.*, **5**, 516 (1940).

[16] This fraction was more or less contaminated with a resinous substance.

[17] M. Freund and K. Fleischer, *Ann.*, **402**, 68 (1913).

[18] H. Meyer and K. Bernhauer, *Monatsch.*, **53/54**, 750 (1929).

Synthesis of Dimethyl Naphthalene Dicarboxylates as the Standard Sample of the Vapor-phase Chromatography.[19] *1, 2-Isomer.* 1, 2-Dicyanonaphthalene (mp 190.5—191.5°C; lit., mp 190°C[20]) was synthesized by the method of Brandbrook and Linstead[20] from 2-aminonaphthalene-1-sulfonic acid (Tobias Acid), and the nitrile was hydrolyzed to naphthalene-1, 2-dicarboxylic acid. The dimethyl ester had a melting point of 84—85°C (MeOH) (lit., mp 85°C[20]).

1, 3-Isomer. Brandbrook and Linstead[20] have reported that they prepared naphthalene-1, 3-dicarboxylic acid (mp 267—268°C) by the hydrolysis of 1, 3-dicyanonaphthalene (mp 179°C), which had been synthesized by the reaction of sodium 3-cyanonaphthalene-1-sulfonate and potassium ferrocyanide. The physical constants of these substances as prepared by the following route, however, differ from those reported by Brandbrook and Linstead.

A) 2, 4-Dibromo-1-naphthylamine (mp 115—117°C (EtOH); lit., mp 116—118°C[21]), which had been prepared by the method of Consden and Kenyon,[21] was converted to 1, 3-dibromonaphthalene (mp 61—62°C (EtOH); lit., mp 64°C[22]) by the method of Meldra.[22] The dibromonaphthalene (6.1 g, 0.021 mol), cuprous cyanide (5.0 g, 0.056 mol), and dimethyl formamide (30 m*l*) were heated at 180—185°C for 4 hr by a method similar to that of Friedman and Shechter[23] to give 1, 3-dicyanonaphthalene (0.8 g); mp 226.5—227.5°C (EtOH).

Found: C, 81.11; H, 3.48; N, 15.44%. Calcd for $C_{12}H_6N_2$: C, 80.87; H, 3.39; N, 15.72%.

The dinitrile was hydrolyzed with aqueous sulfuric acid to give naphthalene-1, 3-dicarboxylic acid (0.7 g); mp>300°C. The methyl ester has a melting point of 105—106°C (EtOH).

Found: C, 69.12; H, 4.73%. Calcd for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95%.

B) 1, 3-Dimethylnaphthalene (bp 100°C/4 mmHg; lit., bp 129°C/9 mmHg[24]) was prepared by the method of Balaban and Barabas[24] from acetyl acetone and benzyl magnesiumchloride. A mixture of dimethylnaphthalene (7.2 g), sodium bichromate (22 g), and water (40 m*l*) was heated at 250—260°C for 22 hr in an autoclave by a method similar to that of Friedman, Fishel, and Shechter[25] to give naphthalene-1, 3-dicarboxylic acid. The dimethyl ester had a melting point of 104.5—105.5°C. It was identified by a mixed-melting-point determination and by a comparison of the infrared spectrum with that of the sample obtained in A).

1, 4-Isomer. Naphthalene-1, 4-dicarboxylic acid was prepared from 1, 4-dicyanonaphthalene (mp 207.5—208.5°C (EtOH); lit., mp 208°C[20]), which had been prepared by the method of Brandbrook and Linstead[20] from 1-aminonaphthalene-4-sulfonic acid (Naphthionic Acid). The dimethyl ester had a melting point of 65—66°C (dil. AcOH) (lit., mp 67°C[20]).

1, 5-Isomer. 1, 5-Dicyanonaphthalene was synthesized from disodium naphthalene-1, 5-disulfonate and potassium ferrocyanide by a method similar to that of Brandbrook and Linstead[20]; mp 263—264°C (EtOH) (lit., mp 263°C[20]). The dinitrile was converted to the corresponding acid, which gave dimethyl naphthalene-1, 5-dicarboxylate (mp 116—117°C (EtOH); lit., mp 119°C[20]).

1, 6-Isomer. 1, 6-Dicyanonaphthalene was prepared by the method of Brandbrook and Linstead[20] from 1-aminonaphthalene-6-sulfonic acid (1, 6-Cleve's Acid); mp 210—211°C (EtOH) (lit., mp 211°C[20]). The nitrile was hydrolyzed to acid. The dimethyl ester had a melting point of 97—98°C (aq. MeOH) (lit., mp 98°C[20]).

1, 7-Isomer. 1, 7-Dicyanonaphthalene was prepared from 1-aminonaphthalene-7-sulfonic acid (1, 7-Cleve's Acid); mp 166—167°C (EtOH) (lit., mp 167°C[20]). The nitrile was hydrolyzed to acid, which gave dimethyl naphthalene-1, 7-dicarboxylate (mp 89—90°C (aq. EtOH); lit., mp 90°C[20]).

1, 8-Isomer. Dimethyl naphthalene-1, 8-dicarboxylate was prepared from naphthalic acid; mp 102—103°C (MeOH) (lit., mp 104°C[20]).

2, 3-Isomer. Naphthalene-2, 3-dicarboxylic anhydride, which had been obtained by the reaction of sodium β-naphthoate, was converted to dimethyl naphthalene-2, 3-dicarboxylate; bp 191—192°C/6 mmHg, mp 48—50°C (lit., mp 47°C,[20] 50—51°C[26]).

2, 6-Isomer. Dimethyl naphthalene-2, 6-dicarboxylate was prepared from the corresponding dicarboxylic acid, which had been obtained by the reaction of potassium β-naphthoate; mp 189.0—189.5°C.

2, 7-Isomer. 2, 7-Dicyanonaphthalene was obtained by the reaction of disodium naphthalene-2, 7-disulfonate and potassium ferrocyanide by a method similar to that of Brandbrook and Linstead[20]; mp 264°C (AcOH) (lit., mp 267°C[20]). The nitrile was hydrolyzed to an acid, which gave dimethyl naphthalene-2, 7-dicarboxylate (mp 135—136°C (EtOH); lit., mp 135°C[20]).

The author is indebted to Professor Haruo Shingu, Kyoto University, for his help and encouragement, and to (Mrs.) Shizu Fujishima of our laboratory for her assistance in the microanalysis.

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[19] The ester of the carboxylic acid was synthesized by the reaction of the silver salt of the carboxylic acid and methyl iodide.

[20] E. F. Brandbrook and R. P. Linstead, *J. Chem. Soc.*, **1936**, 1739.

[21] R. Consden and J. Kenyon, *J. Chem. Soc.*, **1935**, 1594.

[22] R. Meldra, *Ber.*, **12**, 1963 (1879).

[23] L. Friedman and H. Shechter, *J. Org. Chem.*, **26**, 2522 (1961).

[24] A. T. Balaban and A. Barabas, *Chem. & Ind. (London)*, **1967**, 404.

[25] L. Friedman, D. L. Fishel and H. Shechter, *J. Org. Chem.*, **30**, 1453 (1965); "Oxidation in Organic Chemistry," Part A, K. B. Wiberg Ed., Academic Press, New York (1965), p. 90.

[26] D. N. Burge and N. L. Allphin, *Chem. Eng. Data*, **8**, 458 (1963).