Reactions of Aromatic Carboxylates. II.[1] The Henkel Reaction
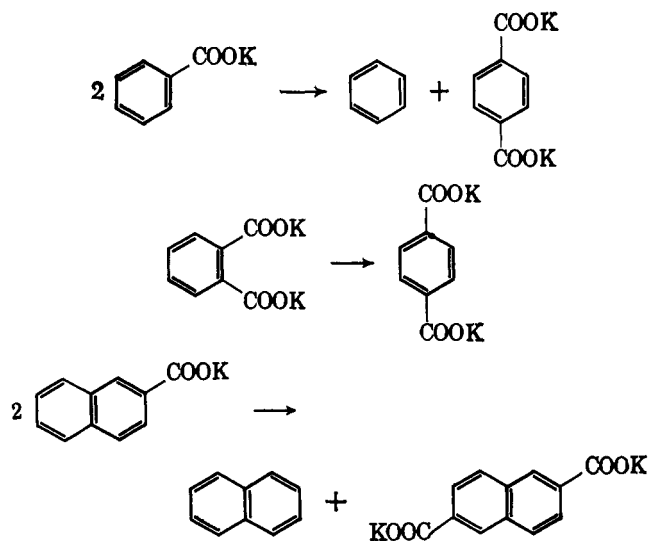
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The Henkel reaction of alkali metal salts of naphthalene acids is reported. The salts of 1-naphthoic acid, 2-naphthoic acid, 1,3-NDCA (naphthalene-1,3-dicarboxylic acid), 2,3-NDCA, 1,6-NDCA, 1,8-NDCA, and 2,7-NDCA and mixtures containing all other diacid salts afford the naphthalene-2,6-dicarboxylate as the principal product. Reaction variables, the detection of intermediate acids, and physical state of reactants and their mechanistic implications are discussed. An intermolecular mechanism is supported; contentions for an intramolecular mechanism are examined.

During the past decade, the cognoscenti of industrial chemistry have observed with interest the development of the Henkel reaction, which is the thermal rearrangement or disproportionation of aromatic carboxylates of alkali metals to symmetrical aromatic dicarboxylates. This reaction, sometimes referred to as the Raecke process, is usually carried out in an inert atmosphere between 350 and 500° in the presence of catalytic quantities of cadmium salts. The first results of studies on this reaction were reported by Raecke and co-workers at Henkel et Cie. in 1952.[2] Strong emphasis was placed on the process variables of the benzenecarboxylates, since the principal product is terephthalic acid, a valuable component for polyester derivatives. Several important reactions exemplifying this process are listed below.

$$2 \text{ (benzoate, COOK)} \longrightarrow \text{(benzene)} + \text{(terephthalate, COOK/COOK)}$$

$$\text{(phthalate, COOK/COOK)} \longrightarrow \text{(terephthalate, COOK/COOK)}$$

$$2 \text{ (2-naphthoate, COOK)} \longrightarrow \text{(naphthalene)} + \text{(naphthalene-2,6-dicarboxylate, KOOC/COOK)}$$

In the naphthalene series, our prime concern in this paper, potassium 1- and 2-naphthoate disproportionate to dipotassium naphthalene-2,6-dicarboxylate,[2] which is also the product of the rearrangement of dipotassium naphthalene-1,8-dicarboxylate. Similar reactions apply to the carboxylates of furan, thiophene, pyrrole, and pyridine. Potassium is the cation used most often in the Henkel reaction. Rubidium and cesium are quite satisfactory, whereas sodium and lithium give much lower yields at temperatures higher than the usual range of 400–450°. Henkel chemists found that 2–10 mole % cadmium, and sometimes zinc, is the preferred catalyst concentration. The reaction is carried out under pressure, usually with carbon di-oxide, between 10 and 140 atm. With certain notable exceptions, lower pressures give lower yields, as does replacement of carbon dioxide with nitrogen. Water, hydrogen, acids, and oxygen are poisons.

The mechanism of the Henkel reaction has been the focus of no little controversy.[3,4] It is the purpose of this paper to resolve some apparent contradictions and to present certain cogent data aimed at a resolution of the reaction mode. Toward this end, the naphthalene series serves as a model for certain mechanistic generalities.

Experimental

Salt Preparation.—The naphthoic acid or the naphthalenedicarboxylic acid was added to an aqueous solution of potassium hydroxide with stirring. The base concentration was equivalent to the added acid. After filtration, the salt solution was stripped on a steam bath in a Rinco evaporator at water pump pressure. The salt was washed with ether and then dried for at least 24 hr. at 100° (0.1 mm.). After drying, the free-flowing salt was checked for residual acid and water by means of an infrared spectrum.

Bomb Preparation.—The salt and catalyst were weighed separately and mixed intimately with a spatula. If the humidity was high, then weighings, mixing, and bomb loading were done in an air-conditioned room. Upon securing the bomb head, the bomb containing the reactants was evacuated to 0.1 mm. and heated overnight at 150°. Cooling and introduction of gas followed. The control thermocouple was placed against the bomb bottom. There was no rocking. The bomb was heated to temperature and then heating was discontinued. This system was not outfitted with an internal thermocouple. Work with a 300-ml. bomb with an internal thermocouple showed internal to bottom differences of 10–50°. This was caused, no doubt, by the position of the internal thermocouple in the reactants, and reflected the local heating within the unagitated bomb. The designation YY refers to a method of heating whereby the bomb bottom was heated to the stated temperature, at which point heating was discontinued. From the heating charts of these experiments, the reaction time is estimated to be 20 to 30 min. Since the outer diameter and length of the 50-ml. bomb was equal to the 300-ml. bomb, the metal volume of the smaller bomb was larger and higher temperatures were required to obtain comparable yields on the same starting materials. Unless stated otherwise, the experiments reported in this paper were carried out in a 300-ml. bomb. All yields are based on charged starting material.

Work-Up.—Gas samples were taken prior to bleeding off the gas. The bomb and its head were washed with 300 ml. of ether. The ether wash solution was filtered and stripped to give the naphthalene-bearing residue. The ether-insoluble material was treated with water and filtered. The residue contained carbon and cadmium carboxylates. The water solution was acidified to give a precipitate, which was filtered and dried. The acid filtrate was extracted with 300 ml. of ether to give any water-soluble acids which may have been present. The ether-washed water was evaporated to give the dry salts if a soluble

(1) Part I: E. McNelis, *J. Org. Chem.*, **28**, 3188 (1963).
(2) The basic review article is due to B. Raecke, *Angew. Chem.*, **70**, 1 (1958).
(3) Y. Ogata, M. Tsuchida, and A. Muramoto, *J. Am. Chem. Soc.*, **79**, 6005 (1957).
(4) J. Ratusky and F. Šorm, *Collection Czech. Commun.*, **24**, 2553 (1959).

cadmium determination was needed. The dried acid precipitate was treated first with ethyl ether (125 ml.) to give a solution containing largely monoacids. The acid cake was further washed with methanol (125 ml.) to obtain mixed diacids and monoacids. The remaining acid cake was naphthalene-2,6-dicarboxylic acid (NDCA). Infrared spectra on all fractions were taken. For the reactions of barium salts, the usual work-up required modification, because most of the barium carboxylates are insoluble in water. The insoluble barium salts were subjected to an exchange reaction with potassium carbonate solution, which gave soluble potassium carboxylates and insoluble barium carbonate. The soluble salts were then acidified to give the mixed acids.

Analyses.—Analyses on the various acids were accomplished by the use of infrared spectra. Those diacids of the naphthalene series which have been studied have characteristic spectra in the fingerprint region. Low solubility prohibited the use of solvents for the spectra, so they were determined in a Nujol mull. For example, the important bands that are peculiar to 2-naphthoic acid are at 11.0, 11.5, 12.0 and 12.8 μ. The bands strongly characteristic of 2,6-NDCA are at 10.9 and 12.1 μ.

For the determination of mixtures of acids, the acids were esterified and analyzed by vapor phase chromatography using a 300-cm. column of SE 52 silicone oil (6%) on Chromosorb 2 at 220°. Fractions were isolated and submitted for infrared analysis for a further isomer determination.

Carbon Dioxide Evolution.—A 50-ml. Minilab flask was fitted with two Claisen adapters to afford a thermocouple inlet, a nitrogen inlet, and a gas exit. The exit led consecutively to a Dewar trap, a Drierite tube, an Ascarite (8–20 mesh) tube, and a bubbler tube. The unit was swept with nitrogen. The nitrogen valve was shut; the Ascarite tube was closed and weighed. The remaining portion of the unit was evacuated to 0.1 mm. and heated to 150° to remove traces of water in the salts. Upon resumption of a nitrogen sweep, the Ascarite tube was reconnected and the temperature was raised to the desired level.

Results and Discussion

The experimental findings of this investigation in conjunction with literature results can best be interpreted in light of an intermolecular mechanism (Scheme I). The reaction path of the naphthoate involves a primary act of decarboxylation to a naphthalene anion (C). If the reactant is a naphthalenedicarboxylate (B), the intermediate is a substituted naphthoate anion (E). These types of anions are extremely strong bases since their parent acids are aromatic hydrocarbons. They are capable of abstracting a proton from a neighboring naphthalene ring. If the anion is derived from a naphthoate, it will abstract a proton to become naphthalene. If it is derived from a naphthalate, it will abstract a proton to become a naphthoate. Carboxylation by liberated carbon dioxide or added carbon dioxide takes place along with proton abstraction. The combination of decarboxylation, proton abstraction, and carboxylation leads to the formation of a salt mixture, from which the most thermally stable isomer survives in greatest yield.

For the naphthalene nucleus, the most stable isomer is the naphthalene-2,6-dicarboxylate if the cation is an alkali metal; for the benzene nucleus the correspondingly stable salt is the terephthalate. The latter point has been well demonstrated by Raecke.[2] Tables I and II show that naphthalene-2,6-dicarboxylate is the product of Henkel reactions of the 1,6 isomer, the 2,7 isomer, the 2,3 isomer, and the 1,3 isomer in addition to the 1,8 isomer.[2] Furthermore, a mixture of salts of naphthalene-1,2-dicarboxylic acid and its 1,4 isomer[5] afforded a 74% yield of the 2,6 isomer under

TABLE I
HENKEL REACTION OF DIACIDS[a]

Reactant	Catalyst (5 mole %)	Temp., °C.	Pressure of CO₂, p.s.i.	Yield of 2,6-NDCA, mole %
K₂ 1,3-NDCA	CdF₂	530[b]	750	47
K₂ 1,6-NDCA	CdCl₂	475[c]	300	78
K₂ 2,3-NDCA	CdCl₂	475[c]	300	70
K₂ 2,7-NDCA	CdCl₂	475[c]	300	69

[a] Heating method YY. [b] Reaction run in 50-ml. bomb. [c] Reaction run in 300-ml. bomb.

TABLE II
HENKEL REACTION OF MIXED NAPHTHALENEDICARBOXYLATES[a]

Catalyst[b]	% yield of 2,6-NDCA[c]
CdF₂	67
ZnO	49
CdO	67

[a] The mixed acids were prepared by the carbogen oxidation[6] of a dimethylnaphthalene concentrate whose composition was as follows: 2,6-DMN (dimethylnaphthalene) and 2,7-DMN, 26.1%; 1,6-DMN, 1,7-DMN, and 1,3-DMN, 42.6%; 2,3-DMN and 1,4-DMN, 16.8%; 1,5-DMN and 1,2-DMN, 6.1%; 1,8-DMN, 1.2%; 2-ethyl- and 1-ethylnaphthalene, 4.9%; other aromatics, 2.3%. The composition of the acids paralleled the hydrocarbon values. A 300-ml. aminco bomb heated to 500° (method YY) with 300 p.s.i. of CO₂ was used. [b] 5 mole %. [c] No other diacids were detected.

Henkel reaction conditions. Clearly there is no ring barrier to these isomerizations. The 1,5 and 1,7 isomers were not available in pure form, but their arrangement to the 2,6 isomer is presumed on the basis of experiments wherein mixed naphthalenedicarboxylates containing these isomers gave high selectivity for the 2,6 isomer and neither of these two isomers were detected in the reaction products.

The 2,6 isomer generalization does not apply to certain salts of alkaline earth metals. Barium 1-naphthoate disproportionates to naphthalene and a mixture of naphthalene-1,2-dicarboxylate and its 1,8 isomer. The yield of diacids was 65%, 70% of which was the 1,2 isomer. Barium 2-naphthoate behaved similarly to give a 44% yield of naphthalene-2,3-dicarboxylate and a 14% yield of its 1,2 isomer.

Contrary to some older work of Šorm[4] and in agreement with later work of his colleagues,[7] we have found that the symmetrical dicarboxylate is not the sole product if the reaction is run below optimum conditions. In the rearrangement of dipotassium naphthalene-2,3-dicarboxylate, other isomers such as the 1,2, the 1,6, and the 2,7 are formed along with 2-naphthoic acid and triacid. This result is shown in Table III. Similar results are displayed for the cesium 2-naphthoate, sodium 2-naphthoate, and the potassium 1-naphthoate disproportionation. It should be noted that these are minimum values; other diacid intermediates may have been formed, but the analytical method (v.p.c. of ester) precluded a sharp separation of all ten isomers.

The intermolecular mechanism is further substantiated by the radioactivity studies of Šorm[4] who showed that the benzoate disproportionation in a radioactive CO₂ atmosphere afforded radioactive terephthalate

(5) These acids were formed from the corresponding dihydro compounds prepared by the sodium naphthalene carbonation reaction of J. F. Walker and N. D. Scott [*J. Am. Chem. Soc.*, **60**, 951 (1938)].

(6) E. S. Roberts and L. J. Christman, Belgian Patent 599,413 (Jan. 23, 1961).

(7) M. Kraus, K. Kochloefl, K. Satinek, L. Beranek, M. Hauda, and V. Bazant, *Chem. Prumysl*, **12** (37), No. 10, 529 (1962).

SCHEME I

THE INTERMOLECULAR MECHANISM OF THE HENKEL REACTION
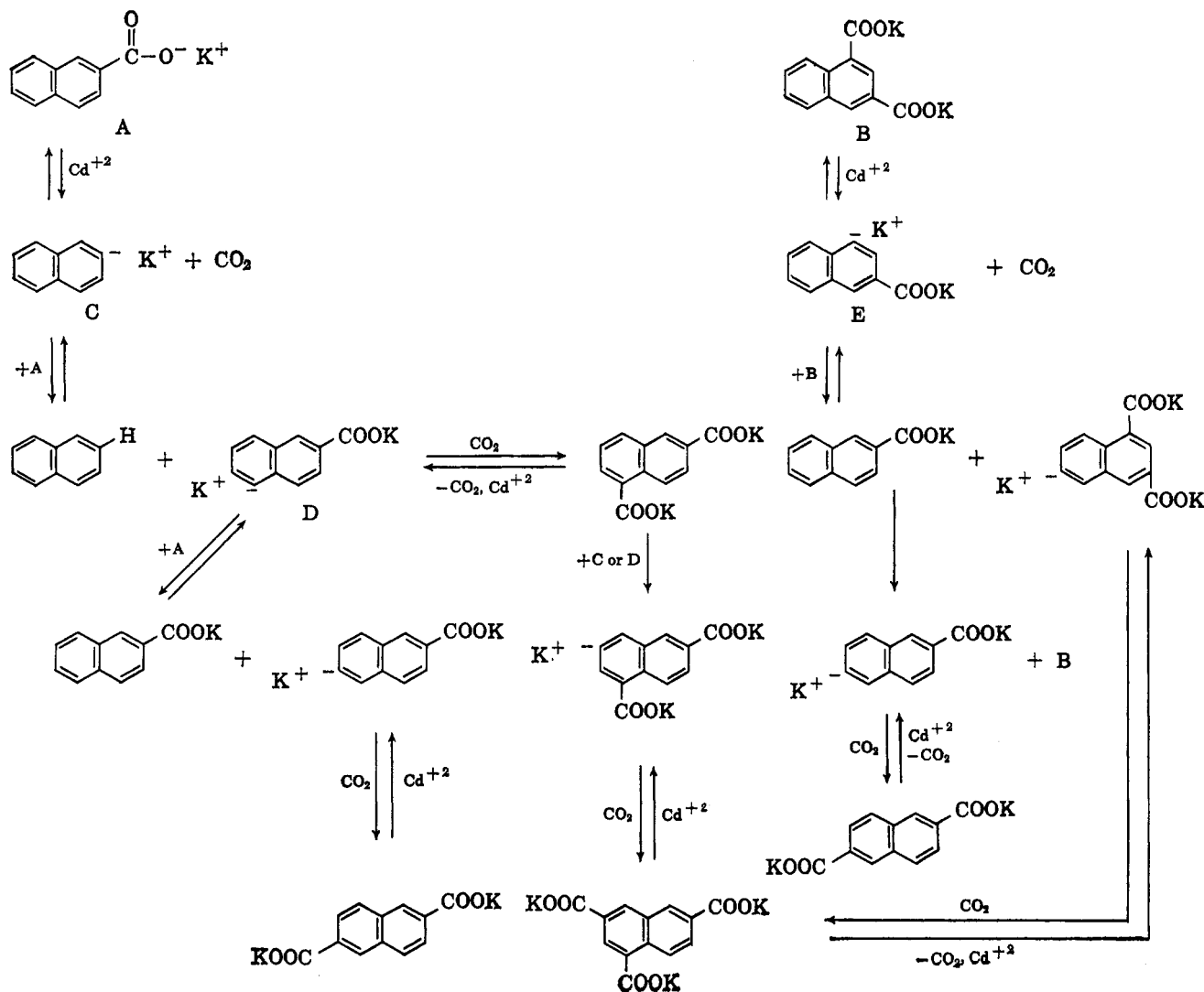
TABLE III

INTERMEDIATE FORMATION IN THE HENKEL REACTION

| | % yield of products and intermediates | | | |
Reactant	K_2 2,3- NDCA[a]	Cs 2-naph- thoate[b]	Na 2-naph- thoate[c]	K 1-naph- thoate[d]
2,6-NDCA	38.6	38.4	4.6	5.9
Naphthalene	2.2	37.5	36.0	32.4
1,2-NDCA	1.2	1.4	0.3	3.2
2,3-NDCA	...	2.5	4.0	2.0
1,3-NDCA	0.7	1.2	...	0.9
1,7-NDCA	...	1.3	...	0.9
1,6-NDCA	1.1	1.2	0.6	1.5
2,7-NDCA	0.6	3.1	...	1.8
Triacids	3.4	1.1	0.8	7.5
2-Naphthoic	14.0	...	...	17.3
1-Naphthoic	...	...	...	15.3

[a] Dipotassium naphthalene-2,3-dicarboxylate (10 mmoles) with 5 mole % CdF_2 at 450° (YY) and 300 p.s.i. of CO_2. [b] Cesium 2-naphthoate (10 mmoles) with 10 mole % $CdCl_2$ at 410° (YY) and 100 p.s.i. of CO_2. [c] Sodium 2-naphthoate (10 mmoles) with 30 mole % $CdCl_2$ at 410° (YY) and 300 p.s.i. of CO_2. [d] Potassium 1-naphthoate (10 mmoles) with 10 mole % $CdCl_2$ at 300° (1 hr.) in a nitrogen atmosphere.

and radioactive recovered benzoate. A similar result was obtained with the phthalate reaction. This latter result was confirmed by Riedel and Kienitz.[8]

Later, Goodman[9] found that radioactive potassium phthalate reaction in the presence of dipotassium naphthalene-1,8-dicarboxylate gave radioactive terephthalate as well as radioactive naphthalene-2,6-dicarboxylate.

Ogata's findings[10] that the isophthalate "rearrangement" is second order in isophthalate is consistent with the disproportionation character of the intermolecular mechanism.

The liberation of carbon dioxide in the initial step and the necessity for subsequent carboxylation require that carbon dioxide be present in the reaction mixture either trapped in the melt or superimposed if the reaction mixture is nonmolten. As shown in Table IV, a pressurized system is necessary to decrease coking and to increase yields in a nonmolten system such as potassium 2-naphthoate. The replacement of carbon dioxide with nitrogen in the 2-naphthoate reaction decreased the yield of naphthalene-2,6-dicarboxylate to 12%. Thermal isomerization of potassium o-phthalate in a nitrogen atmosphere[11] gave rise to lower amounts of terephthalate and a

(8) O. Riedel and H. Kienitz, Angew. Chem., 72, 738 (1960).

(9) I. Goodman, ibid., 74, 607 (1962).

(10) Y. Ogata and K. Sakamoto, Chem. Ind. (London), 749 (1964).

(11) J. Nelles and R. Streicher, Z. Chem., 3, 188 (1963).

TABLE IV

EFFECT OF PRESSURE AND CATALYSTS ON THE HENKEL
REACTION OF POTASSIUM 2-NAPHTHOATE

Temp., °C.[a]	Initial CO_2, p.s.i.	Catalyst (5 mole %)	% yield of 2,6-NDCA
500	50	CdF_2	49
470	50	CdF_2	61
450	50	CdF_2	32
500	750	CdF_2	58
500	300	CdF_2	83
500	150	CdF_2	69
500	50	CdF_2	49
530[c]	1000	CdF_2	51
530[c]	1000	$CdCl_2$	75
530[c]	1000	$CdCl_2$[b]	55
530[c]	1000	CdI_2	54
530[c]	1000	ZnF_2	50
500	300	ZnO	71
500	300	CdO	78
500	300	$BaCl_2$	15
500	300[d]	CdF_2	12

[a] Method YY: heating bomb (300 ml.) bottom to stated temperature and discontinuing heating. [b] 10 mole %. [c] Reactions run in 50-ml. bomb. [d] Reaction run under nitrogen pressure.

variety of precoking products such as fluorene, terphenyl, fluorene, and 9-phenylfluorene.

Quantitative decarboxylation (Table V) was examined as a possible probe into the nature of the Henkel reaction. This procedure pointed out the fact that carbon dioxide evolution from a salt is not a satis-

TABLE V

DECARBOXYLATION OF CARBOXYLATES[a]

Salt (10 mmoles)	CO_2 evolved, mg.
Potassium 1-naphthoate[b]	2
Potassium 1-naphthoate	40
Cesium 1-naphthoate[b]	10
Cesium 1-naphthoate	37
Potassium 2-naphthoate[b]	2.5
Potassium 2-naphthoate	53
Cesium 2-naphthoate	45
Sodium 2-naphthoate	49
Cadmium 2-naphthoate[b,c]	291
Dipotassium 2,6-NDCA	14
Dicesium 2,6-NDCA	35
Dipotassium 2,7-NDCA	20
Potassium benzoate	33

[a] At 300–305° for 1 hr. with a nitrogen sweep and 1 mmole of $CdCl_2$ catalyst. [b] No catalyst. [c] 5 mmoles.

factory measure of its ability to undergo a Henkel reaction. For example, potassium 1-naphthoate was found to evolve as much carbon dioxide as cesium 1-naphthoate (Table VI). The yields of products

TABLE VI

COMPARISON OF 1-NAPHTHOATES[a]

	Potassium 1-naphthoate[b]	Cesium 1-naphthoate[b]
Evolved CO_2, mg.	40	37
Naphthalene, mg.	414	434
Ether-soluble acids, mg.	459	122
Methanol-soluble acids, mg.	153	295
2,6-NDCA, mg.	98	450
Yield of 2,6-NDCA, %	9	42
Water-soluble acids, mg.	365	39

[a] Reacted at 300–305° for 1 hr. in a nitrogen stream. [b] 10 mmoles of salt with 1 mmole of cadmium chloride.

of these reactions, however, are not the same. The yield of naphthalene-2,6-dicarboxylic acid was 42% for the cesium salt and 9% for the potassium salt. An isomer equilibration reaction is clearly much faster than the diffusion of the evolved carbon dioxide and gaseous naphthalene through the melt to the surface where their escape is dependent on the high surface tension of the melt. This effect of the physical state of the reaction mixture is further underlined by the observation that molten potassium 1-naphthoate evolved the same amount of carbon dioxide *in vacuo* as with a nitrogen sweep. The nonmolten cesium naphthalene-2,6-dicarboxylate evolves as much carbon dioxide as does the molten cesium 1-naphthoate. In the 2-naphthoate system the same observations prevail. The sodium salt (nonmolten) evolves 49 mg. of CO_2 and 221 mg. of naphthalene; the potassium salt (nonmolten) evolves 53 mg. of CO_2 and 318 mg. of naphthalene. No naphthalene-2,6-dicarboxylate was formed in the sodium example, whereas a yield of 25% 2,6-NDCA was obtained in the potassium case. Other investigators[12,13] have reported similar high yields of stable symmetrical dicarboxylates at low pressures from molten systems such as potassium o-phthalate.

The function of cadmium in the intermolecular scheme is to facilitate decarboxylation. Moderate yields of terephthalate or 2,6-naphthalenedicarboxylate, however, can be obtained without catalysts. Raecke has shown that cesium benzoate and rubidium benzoate without catalysts give 65% and 47% yields,[14] respectively, of terephthalate in addition to the observation that potassium o-phthalate without catalyst affords a 57% yield of terephthalate.[15] We obtained a 39% yield of 2,6-naphthalenedicarboxylate from cesium 2-naphthoate without a catalyst. The ionic size of cesium and the concomitant charge density reduction facilitate electron movement to the ring in the decarboxylation step. This same factor aids in a cationic exchange between catalyst and carboxylate prior to decarboxylation in catalyzed systems. A remarkable decrease in reaction temperature was observed for cesium 2-naphthoate with catalyst (Table VII). In addition to the optimum effect for catalysts, indicated in Table IV, it should be noted (Table V) that cadmium 2-naphthoate evolved 66% of its available carboxyl groups. The presence of organocadmium products in this reaction was inferred by the observation of a cadmium mirror and mass spectral analyses of ether-soluble products which displayed strong peaks at 254 (binaphthyl) and 282 (dinaphthyl ketone). Consequently, although present evidence is consistent with associating cadmium primarily with decarboxylation, the exact mode of this catalysis is obscured by side reactions.

For his intermolecular mechanism, Šorm[4] has postulated for the o-phthalate reaction that the anion from an initial decarboxylation of o-phthalate isomerizes presumably through proton shifts to an anion, which gives terephthalate upon carboxylation. This is,

(12) (a) Y. Ogata, M. Tsuchida, and A. Muramoto, *J. Am. Chem. Soc.* **79**, 6005 (1957); (b) Y. Ogata, M. Tojo, and M. Morikawa, *J. Org. Chem.* 2082 (1960).

(13) J. Yamashita, K. Enomoto, H. Ebisawa, and S. Kato, *Yuki Gosei Kagaku Kyokai Shi*, **20**, 507 (1962).

(14) B. Raecke, U. S. Patent 2,823,230 (Feb. 11, 1958).

(15) B. Raecke, British Patent 747,204 (March 28, 1956).

TABLE VII

CESIUM 2-NAPHTHOATE WITH CADMIUM CHLORIDE[a]

Temp., °C.	CO₂, p.s.i.		2,6-NDCA, % yield	Naphthalene, mg.	Residue, mg.
	Charged	Max.			
400[b]	200	425	76	437	114
400[c]	300	680	82	598	112
425[c]	300	700	76	558	131
450[c]	300	735	66	684	177

[a] Ten mmoles of salt with 5 mole % catalyst. [b] For 0.5 hr. [c] Method YY: heating bomb (300 ml.) bottom to stated temperature and discontinuing heating.

untenable in the light of the intermediate findings. Further, if this suggestion were valid in the naphthalene series, a ring barrier would prevail and the most stable isomer derivable from naphthalene-2,3-dicarboxylate would be naphthalene-1,4-dicarboxylate. This is not the case since the 1,3 isomer and the 2,3 isomer as well as a 1,2–1,4 isomer mixture are converted to the 2,6 isomer.

An important mechanistic scheme is Ogata's intramolecular mode involving π-complexes.[12] This proposal grew out of Ogata's finding that radioactive
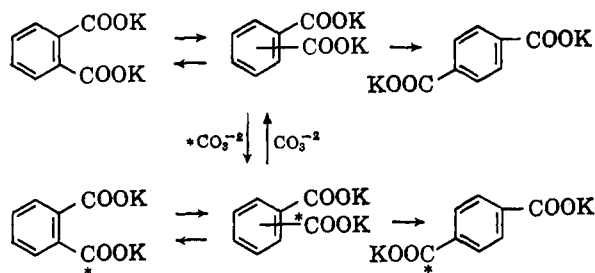
terephthalate is formed in small amounts in the o-phthalate and the benzoate reactions when radioactive potassium carbonate or cadmium carbonate were in the reaction mixture. These results would argue against a decarboxylation–recarboxylation reaction mode which predicts that radioactivity should have been found to a greater extent in the terephthalate, provided that the carbonates decompose extensively to their oxides and carbon dioxide at reaction conditions. This proviso is incorrect. Cadmium carbonate

decomposes at 510° according to differential thermal analysis[16]; potassium carbonate does not decompose to an appreciable extent[17] below 500°. The fact that some radioactivity is found in terephthalate and unreacted o-phthalate might be explained by a small amount of such decompositions. For the lack of clear-cut data on this point, the π-complex mechanism might appear to be a solution. In this mechanism, however, no mention is made of the fate of the displaced hydrogen in the position that the carboxyl will occupy. Such an exchange is without precedent. Furthermore, this incompletely delineated proposal ignores the very real possibility that there is a carbonate–gaseous carbon dioxide exchange. That carbonates in general do exchange with gaseous carbon dioxide at a rapid rate between 350 and 400° has been shown by Shushunov and Zateev.[18] The carbon dioxide arises from the decarboxylation of the phthalate and exchanges with the radioactive carbonate. The radioactive gas can then be incorporated by reaction with an aromatic anion formed by decarboxylation. Consequently, the intramolecular reaction mechanism is without valid argumentation.

(16) C. N. R. Rao, S. R. Yoganarasimhan, and M. P. Lewis, Can. J. Chem., 38, 2359 (1960).
(17) D. Janjic, E. Briner, and H. Pillard, Helv. Chim. Acta, 38, 349 (1955)
(18) V. A. Shushunov and B. G. Zateev, Zh. Fiz. Khim., 30, 321 (1956).

The Synthesis and Stereochemistry of Octahydrophenanthrenes. II[1,2]

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The addition of ethyl acrylate to the diene I gave, after saponification, 1,2,3,9,10,10aβ-hexahydro-7-methoxy-2α-phenanthrenecarboxylic acid (III). This acid was converted into its isopropyl ester IX, which, upon hydroboration and oxidation, gave the B/C cis (XIV) and the B/C trans (XXV) octahydro-7-methoxy-4-oxo-2-phenanthrenecarboxylic acids. The B/C cis keto acid XIV could be converted into the other possible B/C cis stereoisomer XVII. All possible isomeric nonlactonizing and lactonizing acids and lactones of this series were prepared, and their stereochemistry was established. In the B/C trans series, the lactones with ring C in the chair and with ring C in the boat conformation, have been prepared (XII and XXVII). N.m.r. spectroscopy provided additional proof for the stereochemistry of the compounds of this series.

In continuation of the work on the octahydrophenanthrene-1-carboxylic acids,[2] the synthesis and stereochemical studies of several new C-2-, C-4-, and C-7-substituted octahydrophenanthrene derivatives is now described.

The starting material for the preparation of the derivatives was 3,4-dihydro-6-methoxy-1-vinylnaphthalene (I).[4a,b] The reaction of I with methyl vinyl