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Transcarboxylation of Naphthalene using the Alkali Metal Salts of Benzene Carboxylic Acids under Carbon Dioxide Pressure

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Cadmium iodide–catalyzed transcarboxylation (Eq. 1) of naphthalene (**1**) using alkali metal of benzene carboxylic acids (**2a–c**) has been investigated at 400℃ under the pressure of carbon dioxide (80 atm). In the reaction of **1** with potassium benzoate (**2a**) gave dipotassium 2,6-naphthalenedicarboxylate (**3a**) in a high selectivity (80 - 90%) together with benzene (**4**). Activity of catalysts, particularly of cadmium halide was examined in detail. The addition of cesium halide as co-catalyst to cadmium catalytic system increased the yield of **3a**. The catalytic activity of the halide anion increased in the order; $F^- < Cl^- < Br^- < I^-$. The reactivity of **2a** as transcarboxylating agent (donor) was also compared with that of dipotassium phthalate (**2b**) and terephthalate (**2c**), and the reaction mechanism was discussed.

KEY WORDS: Transcarboxylation / 2,6-Naphthalenedicarboxylate / Carbon dioxide / Cadmium iodide / Alkali metal

INTRODUCTION

A general description of the Henkel reaction can be found in articles by Reacke[1] and Sherwood[2]. Examples of the Henkel reaction are the formation of a terephthalate salt (**2c**) by the disproportionation of alkali metal benzoates (**2a**) at high temperature in the presence of certain catalysts. The reaction is not confined to the benzene series; other aromatic systems behave similarly. In the naphthalene series, Reacke[1] reported that a potassium 1-naphthoate (**5**) and 2-naphthoate (**6**) disproportionates to dipotassium 2,6-naphthalenedicarboxylate (**3a**). McNelis[3] discussed the mechanism of the disproportionation of potassium **6** to **3a** and naphthalene (**1**). On the other hand, Patton and Son[4] and Dozen[5] reported that sodium salt **5** and **6** could be transformed to 2,3-naphthalenedicarboxylate (**3b**). These reaction are usually carried out by heating the starting carboxylate under the pressure of CO_2 at 350 - 450℃ in the presence of a catalytic amount of cadmium salts or sometimes zinc salts.

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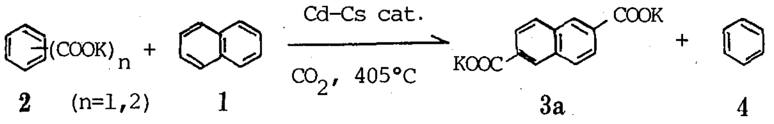
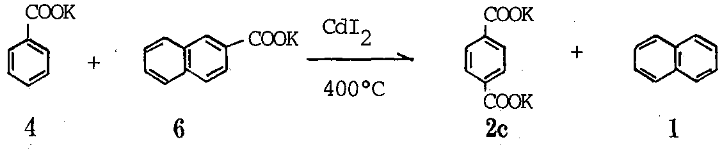
2,6-Naphthalenedicarboxylic acid has attracted attention because it is often used as a component of high-performance polymer. For example, poly (ethylene naphthalenedicarboxylate) is known for its heat resistance and high modulus[7]. Consequently, at present much efforts are being made to get the high and selective yield of **3 a**. Recently, the rearrangement of dipotassium 1,8-naphthalenedicarboxylate to **3 a** was reported by Mitamura et al[8]. Moreover, though they have published the transcarboxylation between **1** and dipotassium phthalate (**2 b**) to give **3 a** in the naphthalene dispersion medium (Eq. 1), there has been no detailed report on it[9].

Concerning mixed transcarboxylation of potasium **2 a** and **6** to **2 c** using cadmium iodide (CdI_2) was already known (Eq. 2)[10].



(Eq. 1)



(Eq. 2)

In order to examine the above mentioned reaction (Eq. 2), prior to this study, we have attempted the reaction of potassium **2 a** (2 mmol) and **6** (0.5 mmol) in the presence of CdI_2 (0.25 mmol) under pressure of CO_2 (100 atm) at 400℃ in naphthalene dispersion medium, and it was found that naphthalenedicarboxylate (**3**) containing 90% of **3 a** was obtained in 83.5% at 80% conversion based on the charged **6**. It indicates that the **6** is transcarboxylated through **2 a** in contrast with the mixed transcarboxylation (Eq. 2). This result prompted us to study the present transcarboxylation. From the more detailed investigation of the transcarboxylation, it was found that the course of the reaction was much more complicated than would appear from the overall scheme as shown Eq. 1.

In the present paper, further study of cadmium catalyzed-transcarboxylation is described, and a reasonable mechanism is discussed further.

EXPERIMENTAL

Materials: Alkali metal salts of benzenecarboxylic acids were prepared as follows; the benzenecarboxylic acid was neutralized with aqueous alkali metal hydroxide to pH 7-7.5. The solution was then evaporated to dryness and futher dried under vacuum (ca. 5 mmHg) at 150-180℃. CdI_2, CsI, and **1** were obtained commercially, which were used after being further dried. In order to analyze the products in the reaction mixture, some naphthalenecarboxylic acids were prepared as follows. The **3 a, 3 b, 5** and **6** were commercially available. Other dicarboxylic acids, such as the 2,4-, 1,2-, 1,4-, 2,5-, and 2,7- isomers, were prepared by oxidation of the corresponding dimethylnaphthalenes[11].

Reaction Procedure: The potassium salt of benzenecarboxylic acid (2 mmol), CdI_2 (0.25 mmol), CsI (0.25 mmol), and **1** (20 mmol) were mixed intimately in a mortar. The mixed powder charged into a shaking type autoclave (40 ml), was dried under a vacuum at room temperature for 1 h, and CO_2 (60 atm) was charged into the autoclave. The mixture was thereafter heated to 400℃, the warming-up period was ca. 20 min, it was then maintained at the desired temperature for 2.5 h. The pressure increased to 80 atm at the reaction temperature. After cooling, the reaction product was extracted with ether to remove **1** and benzene (**4**). The ether-insoluble substances were dissolved in water. The aqueous solution was acidified (pH 1) to give free acids, which was sufficiently extracted with enough ether, and then subjected to the following product analysis.

Analyses: For the determination of mixtures of acids, the acids were esterified into the corresponding methyl esters with diazomethane. These esters were analyzed by GC using *trans*-stilbene as the internal standard at 250℃ (column: Apiezon grease L on uniport HP). The ether-soluble substance was also analyzed by GC using biphenyl as the internal standard at 140-200℃ (column: OV-1701 capillary column 0.25 ㎜× 50 m).

RESULTS AND DISCUSSION

Effect of Catalysts on the Transcarboxylation of Potassium Benzoate: First, in order to evaluate the transcarboxylation of **1** using potassium **2 a**, experiments were carried out with various catalytic systems in naphthalene dispersion medium under CO_2 (80 atm) at 400℃ (Table 1). When **2 a** was heated without a catalyst nearly 90% of **2 a** recovered (Run 1).

The reaction was largely dependent on the catalyst cation species as well as the anion species. Of all the catalyst metals investigated, cadmium iodide (CdI_2) was the most effective and then its catalytic activity was improved by the addition of cesium iodide (CsI) as a co-catalyst (Runs 2 and 3); while zinc salt was less effective (Run 9).

The influence of the anion species of cadmium and cesium salts on the yield of dipotassium naphthalenedicarboxylate (**3**) was unexpectedly large; halogen anions were most effective, and the decreasing order of the effectiveness was $I^- > Br^- > Cl^- > F^-$ (Runs 3-6). Cadmium and cesium carbonate were unsatisfactory (Runs 7 and 14). Ogata et al.[12] reported a similar observation that the increasing order of the catalytic activity was $CdCl_2 < CdBr_2 < CdI_2$ in the isomerization of dipotassium **2b** to **2c**. Although the reason for the remarkable catalytic effect of the iodide is still obscure, it is interesting to note a observation that addition of iodine (0.39 m mol) into the above system (Run 3) was harmful and facilitated unfavorable decomposition of **2 a**; the loosening of the carbon-carbon bond between a carboxyl group and an aromatic nucleus seems to be facilitated in the presence of iodide just as in the

Table 1. Investigation of various catalytst[a)]

Run	Catalysts	Yield/mol %[b)]			
		3	NTC	**6**	Select. of **3a**[c)]
1	none	0	0	trace	
2	CdI_2	8.5	0.8	1.1	79.1
3	CdI_2-CsI	12.9	1.4	1.4	78.3
4	$CdBr_2$-CsI	8.1	1.0	1.2	70.0
5	$CdCl_2$-CsI	5.2	0.5	1.0	60.6
6	CdF_2-CsI	3.7	0	1.7	55.7
7	$CdCO_3$-CsI	3.5	trace	0.9	73.0
8	$Cd(AcO)_2$-CsI	0.9	0.8	1.5	17.5
9	ZnI_2-CsI	1.8	0	1.7	39.4
10	SnI_2-CsI	trace	0	1.4	—
11	PbI_2-CsI	0.2	0	0.9	5.8
12	CdI_2-CsCl	7.2	0.6	1.5	76.8
13	CdI_2-CsBr	9.9	1.6	1.4	71.4
14	CdI_2-Cs_2CO_3	8.6	0.6	1.5	88.9
15	CdI_2-RbI	9.0	0.6	1.3	74.9
16[d)]	CdI_2-KI	3.3	0.2	1.1	68.5

a) Conditions: **1**=19−20 mmol, Potassium benzoate(**2a**) 2.0 mmol, Catalyst=0.24−0.25 mmol. CO_2=79−84 atm at reaction temperature, 400℃, 2.5 h, b) Based on the charged **2a**, **3**: Total naphthalenedicarboxylate, **3a**: 2,6-Naphthalenedicarboxylate, NTC: Naphthalenetricarboxylate, **6**: 2-Naphthoate, c) **3a**/(**6**+**3**+NTC)×100, d) Donor is phthalate(**2b**) (2 mmol).

decarboxylation process.

Using the CdI_2–CsI mixed catalyst, we examined the various effects of the reaction conditions on the yield of **3 a**. In the transcarboxylation, **3 a** was a main product if the reaction was run at optimum conditions, other isomers such as 2,3-(**3 b**), 2,4- (**3 c**), and 2,7-dicarboxylate (**3 d**) were obtained as minor products along with **6** and some naphthalenetricarboxylate (NTC) isomers.

Study of Various Transcarboxylating Agents (Donors): The efficiency of various substrates as the donor on the transcarboxylation are summarized in Table 2. The examination was conducted by using CdI_2–CsI mixed catalyst. Table 2 (Runs 1–3) shows that **2 a**, **2 b** and **2 c** can be easily transcarboxylated to give **3** in good yield similarly. In contrast with the reaction using **2 a–c**, tripotassium salt of trimellic acid was more less active as donor (Run 4). Other substrates such as potassium 4-toluate and potassium 4-chlorobenzoate were not performed by this procedure (Runs 5 and 6). Thus, aromatic compounds having acidic hydrogen of alkyl groups or halogen atom seem to bring about the decarboxylation of itself or products to lower the yields because these substrates were not recovered at all in each case. In addition, **1** was not carboxylated by the potassium salt of furan-2-carboxylic acid (Run 7) and picolinic acid (Run 8). Furthermore, when potassium salts of aliphatic acids, such as acetic acid, malonic acid, and oxalic acid, were used as a donor, these were not effective at all (Runs 9-11). Besides, the reaction using potassium phenolate was failed (Run 13). Therefore, the transcarboxylation seems to be limited to those alkali metal salts of benzenemono- and dicarboxylic acids.

Table 2. Various salts as transcarboxylating agent (donor)[a)]

Run	Donors	Yield/mol %[b)]			
		3	NTC	**6**	select. of **3a**[c)]
1	K-benzoate	12.9	1.4	1.4	78.3
2	K_2-phthalate	8.6	1.5	1.4	70.3
3	K_2-terephthalate	13.8	0.5	0.9	87.7
4	K_3-trimellitate	0.3	0	0.2	—
5	K-4-toluate	2.4	0	1.3	46.3
6	K-4-Cl-benzoate	0.4	0	0.6	—
7	K-furan-2-carboxylate	0			
8	K-α-picolinate	0.3	0	0.2	—
9	AcOK	trace			
10	K_2-maronate	trace			
11	K_2-Oxalate	0			
12[d)]	K-2-naphthoate	18.2	2.7	12.5	70.0
13	K-phenolate	trace			

a) Conditions : Donor=2 mmol, **1**=19−20 mmol, CdI_2=CsI=0.24−0.25 mmol, CO_2=75−84 atm at reaction temp., 400℃, 2.5 h. b) Based on the charged amount of donor. c) **3a**/(**6a**+**3**+NTC)×100, d) 2-naphthoate=0.485 mmol. Other and abbreviations are the same as those in Table 1.

Table 3. Effect of alkali metal salts of benzoic acid as donor[a)]

M	(MP/℃)	Yield/mol %[b)]			
		3	NTC	**6**	Select. of **3a**[c)]
Li	(344−346)	1.1	0	5.9	5.1
Na	(431−432)	5.9	0.2	7.5	25.4
K	(422−424)	12.9	1.4	1.4	78.3
Rb	(417−419)	10.6	0.8	0.7	83.3
Cs	(407−408)	18.8	2.9	1.5	73.5

a) Conditions are identical to those described in Table 1. b), c) and abbreviations are the same as those in Table 1.

Comparison of Alkali Metals: Table 3 shows the results of the transcarboxylation with various alkali metal benzoate. The reaction was also carried out using the CdI_2–CsI mixed catalyst at 400℃ for 2.5 h. Cesium benzoate was the most effective on the yield, and rubidium and potassium salts were next effective. In each case, these salts gave **3 a** as a main product; whereas sodium and lithum benzoate gave much poor yields, and the selectivities of **3 b** and **3 c** varied. The selectivities of **3 b** and **3 c** were 20% and 35% for the lithium salt, and 40% and 3 % for the sodium salt, respectively. The order of the effectiveness of the alkali metals on the selectivity for **3 a** was Rb>K>Cs≫Na≫Li.

Those differences may be depend on the thermal stability among these alkali metal salts of **3** isomers.

The Effect of the Initial Amount of **1** and **2 a**: The effect of the initial amount of **1** and **2 a** on the yield of transcarboxylated products are summarized in Table 4 and 5. It was found that the yield and selectivity of **3 a** depended on the amount of

Table 4. Effect of the amount of naphthalene(**1**) as molten solvent[a)]

Run	**1**	Yield/mol %[b)]			
	mmol	**3**	NTC	6	select. of **3a**[c)]
1	4.688	0.7	0	0.2	——
2	9.645	0.8	0.3	0.3	——
3	14.584	4.7	1.6	1.0	55.8
4	18.865	12.9	1.4	1.4	78.3
5	28.933	13.9	0.9	2.5	80.6

a) Conditions are identical to those described in Table 1 without amount of **1**. b), c) and abbreviations are the same as those in Table 1.

Table 5. Effect of the amount of K-benzoate(**2**)[a)]

Run	**2a**	Results/mol %[b)]			
	mmol	**3** (mmol)	NTC	**6**	Select. of **3a**[c)]
1	0.4886	9.9 (0.0479)	3.0	3.8	48.5
2	0.9823	16.3 (0.1601)	1.7	1.3	82.3
3	1.9360	12.9 (0.2498)	1.4	1.4	78.3
4	2.9178	7.7 (0.2347)	0.8	0.9	76.3

a) Conditions are identical to those decribed in Table 1 without amount of K-benzoate. b), c), and abbreviations are the same as those in Table 1.

1 and **2 a**. When the amount of **1** was less than about 10 mmol, the yield was very low, and the reproducibility of the reaction was very poor (Table 4). These findings indicate that a large exess of **1** form the dispersion medium, and hence the liquid **1** promotes both heat and mass transfer in the reaction region, resulting in the improvement of the reaction.

The yield of **3** was increased with the amount of **2a** (Table 5). The maximum yield was obtaind at about 1 mmol, and then decreased with more amount in the present conditions. When the amount of **2 a** was over about 2 mmol, the formation of **2 c** increased considerably (30% based the **2 a**). These results suggest that the disproportionation of **2 a** to **2 c** took place preferably at higher concentration of **2 a**.

The Effect of Catalyst Ratio CsI/CdI_2 and Behavior: In order to optimize the transcarboxylation and to examine the functions of both CdI_2 and CsI in the reaction, several control experiments were carried out using **2 b** as initial donor. The results are shown in Figure la–b and Table 6. As shown in Figure la, at constant amount of CdI_2 (0.25 mmol), the yield and selectivity of **3 a** were largely dependent upon the ratio of Cs/CdI_2, reaching a maximum at 1.6 ratio. On the other hand, a different tendency are seen with the amount of CdI_2 increasing at a constant amount of CsI (0.25 mmol). The addition of CdI_2 to the mixture is favorable to the present reaction, and the yield and selectivity of **3 a** increase with increasing CdI_2 ratio to CsI as shown in Figure 1 b. In the absence of CdI_2, the transcarboxylation and transformation of **2 b** to **2 c** did not proceed at all, but much more amount of **2 a** (62.8%) resulting from the decarboxylation of **2 b** was observed.

The comparative results of the transcarboxylation using the three donors (**2 a**–

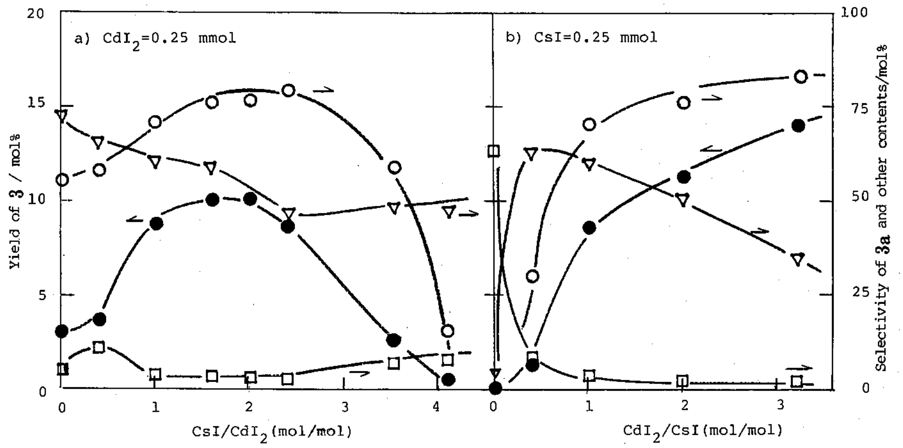


Fig. 1. Effect of ratio of charge mole ratio CsI/CdI_2 and CdI_2/CsI.
Conditions : K_2-phthalate(**2b**)=2 mmol, Naphthalene(**1**)=20 mmol, K_2-phthalate (**2b**)=2 mmol, CO_2=80 atm, 400℃, 2.5h. ● : yield of **3**(based on the charged **2b**), ○ : Selectivity of **3a**, ▽ : **2c**, □ : **2a**.

Table 6. Behavior of CdI_2 and CsI on the transcarboxylation[a)]

Initial donars	CdI_2 mmol	CsI mmol	Products distribution/%[b)] 3	2a	2c	2b	4
K-benzoate (**2a**)	0	0	0	90.4	0	1.2	3.2
	0	0.25	0	54.9	0.2	1.4	35.2
	0.25	0	8.5	1.8	22.9	0.2	67.1
	0.25	0.25	12.9	3.5	15.6	0.8	68.2
K_2-phthalate (**2b**)	0	0	0	40.8	1.5	31.3	18.5
	0	0.25	0	62.8	3.5	16.6	14.6
	0.25	0	3.1	6.5	68.1	0.9	18.4
	0.25	0.25	8.6	3.5	59.0	1.0	27.8
K_2-tere-phthalate (**2c**)	0	0	0	0	98.2	0	0
	0	0.25	0	0	88.0	0	0
	0.25	0	6.1	0.2	74.7	0.1	14.5
	0.25	0.25	13.8	0.4	68.5	0.1	23.6

a) Donor=2 mmol, Naphthalene=19−20 mmol, CO_2=75−80 atm at reaction temp. 400℃, 2.5 hr. b) Based on the charged donor. **4** : Benzene, **3** : Total naphthalenedicarboxylate

c) with and without CdI_2 and/or CsI are summarized in Table 6. In the absence of the both catalysts, the reaction did not occur at all in each case. While **2 a** and **2 c** were little changed, **2 b** was transformed to **2 a** considerably. In the system of the sole presence of CsI, no transcarboxylation occurred, but the decarboxylation of **2 a** and **2 b** was considerably enhanced even under CO_2 pressure (80 atm). However, **2c** was not decarboxylated to **2 a** in that system. The reaction was only initiated by the addition of CdI_2 in each case. The disproportionation of **2 a** and the rearrangment of **2 b** to **2 c** also proceeded by CdI_2 catalyst. The activity of Cd–catalyst was remarkably stimulated by adding CsI. These results indicate that CsI functions as

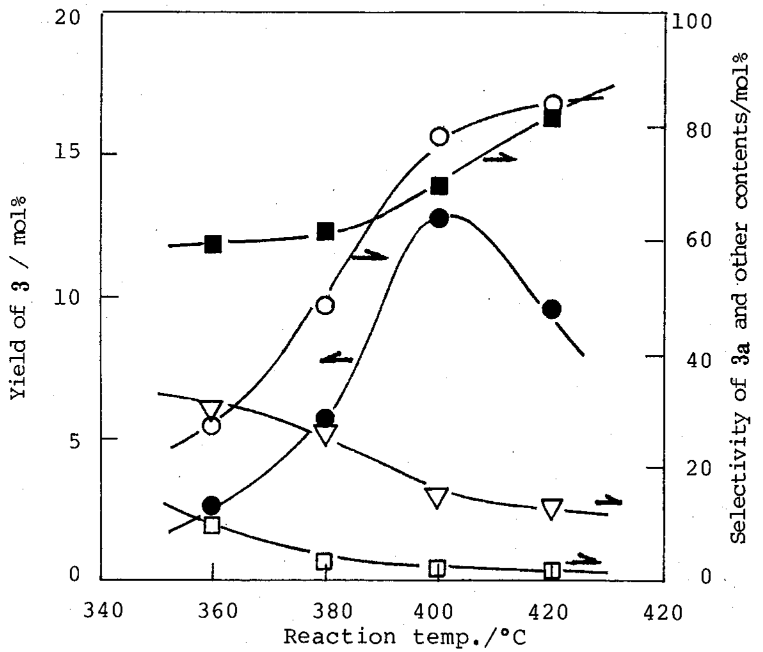


Fig. 2. Effect of reaction temperature.
Conditions: K-benzoate(**2a**), **1** = 20 mmol, $CdI_2 = CsI = 0.25$ mmol, $CO_2 = 75-80$ atm, 2.5 h. ●: yield of **3**, ○: Selectivity of **3a**, ▽: **2c**, □: **2a**, ■: **4**.

promoter of decarboxylation of the donor, while CdI_2 induces not only the decarboxylation of the donor, but also the transcarboxylation.

Effect of the Temperature: Figure 2 shows the effect of reaction temperature on the transcarboxylation using **2 a** as the donor under 80 atm CO_2. No reaction did not take place below 350℃. At low temperature (360℃), the yield of **3** was only 2.7%, 71% of which was **3 a**, and the formation of **6** was higher than that of **3**. An increase in the reaction temperature resulted in the increase in the yield and the selectivity of **3 a**, but decreased significantly above 420℃. However, the selectivity of **3 a** increased with temperature. On the other hand, the amount of **2 c** resulting via disproportionation of **2 a** decreased gradually, and the formation of **4** increased with temperature. The low yield of **3** at high temperature may be due to the decarboxylation of the donor.

Effect of CO_2 Pressure: Figure 3 shows the CO_2 pressure dependence on the transcarboxylation using **2 b** as the donor. The yield and selectivity of the desired product, **3 a**, are remarkably sensitive to the pressure. It should be noted that the pressurization of the system with CO_2 is essential to cause the reaction because no reaction occurred by replacement of CO_2 with Argon (1 atm). The yield and selectivity of **3 a** increased with the initial increase in CO_2 pressure, but nearly reached a maximum as the pressure increased to ca. 110 atm and decreased thereafter. The amount of **2 c** resulting from the reactions via the rearrangement of **2 b**, however, increased slightiy with the pressure. At higher pressure, the strongly adverse effect

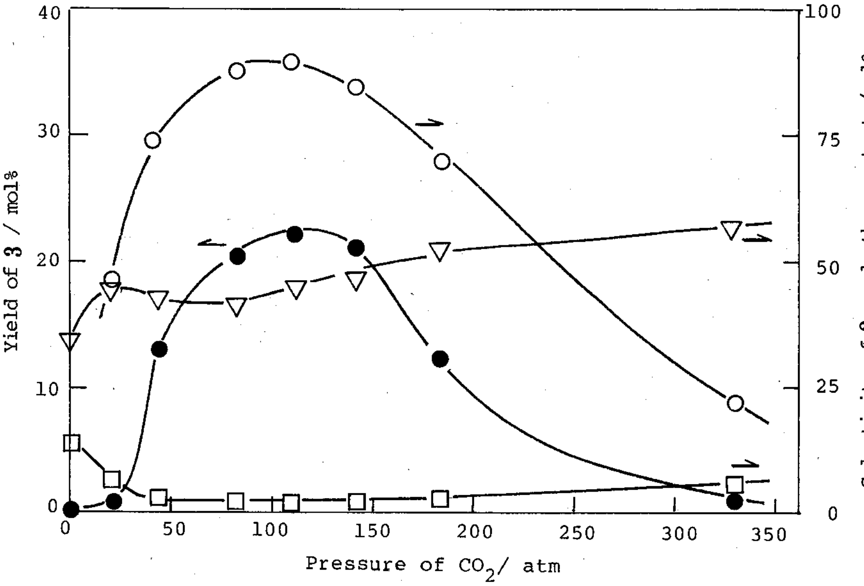


Fig. 3. Effect of CO_2 pressure.
Conditions: **2b**=2 mmol, **1**=20 mmol, CdI_2=CsI=0.50 mmol, 400℃, 2.5 h, ●: yeld of **3**, ○: Selectivity of **3a**, ▽: **2c**, □: **2a**.

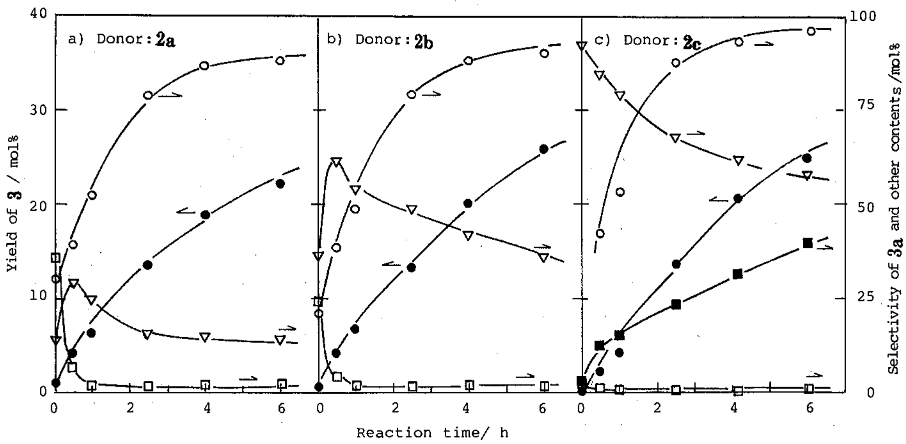
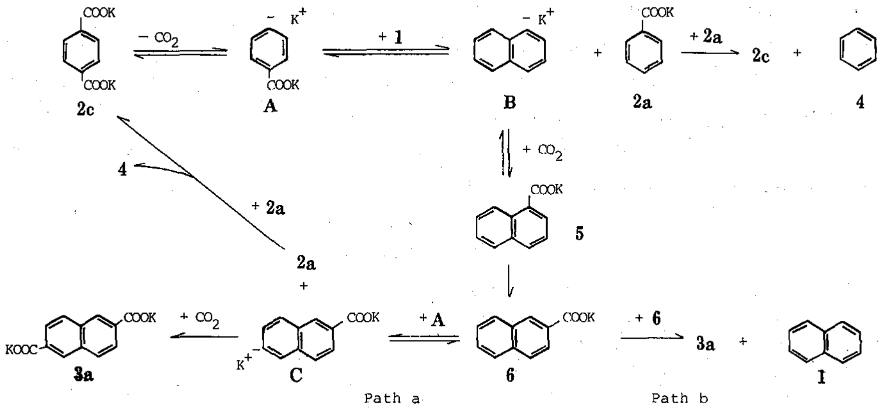


Fig. 4. Time-dependent product yields on the trascarboxylation.
Conditions: Donor=2 mmol, **1**=20 mmol, Cd_2I=CsI=0.25 mmol, CO_2=75−80 atm, 400℃. ●: yield of **3**, ○: Selectivity of **3a**, ▽: **2c**, □: **2a**, ■: **4**.

is presumed to arise not only from the inhibition of the decarboxylation of a key donor (**2c**), but also from the Cd(II) species which could be saturated by a greater number of CO_2 molecules, rendering the Cd–catalyst less electrophilic and therefore less susceptible to the transcarboxylation.

The Time-Dependent Product Distributions: In order to grasp the behavior of the donors, the reaction was carried out comparatively by using **2a**, **2b**, and **2c** as



Scheme 1

a donor under the same conditions. Figure 4 a–c show the effect of reaction time on the product distribution in each case. In both cases of **2 a** and **2 b** (Fig. 4 a–b), **2 c** was produced in preference to **3** at the earlier stage. The amount of **2 c** reached a maximum (ca. 30 min) and then it decreased with the prolonged reaction time, and the yield and selectivity of **3 a** increased in the same manner. It should be also noted that a small amount of **2 a** remains at the steady state. Thus, the reaction includes the rapid disproportionation or the rearrangement of them to **2 c**, i. e., almost all of them already disappeared during the warming-up stage (ca. 20 min). In the case of **2 c** as the donor (Fig. 4c), **3** was gradually increased along with decreasing **2 c** in a similar manner to the above mentioned, and the rate of formation of **3** was almost identical to the above cases. These results implies that the **2 c** plays an important role as the key donor in the reaction.

Mechanistic Aspects: Although the mechanism of the transcarboxylation is not fully understood yet, the reasonable discussion can be made on the basis of the knowledge known about the accepted mechanisms of aromatic carboxylates of alkali metals to aromatic dicarboxylates.[3, 5, 6, 13]

We propose the cross intermolecular decarboxylation–recarboxylation mechanism for the reaction as depicted in Scheme I.

The reaction would begin with the decarboxylation of donor (**2 c**) to form an anion **A**. The anion **A** is expected to act as an extremely strong base since this parent acid is an aromatic hydrocarbon. This is capable of abstracting a proton from a neighboring naphthalene ring to afford the naphthalene anion **B** and **2 a**. The former will react with CO_2 to give primarily the product, **5**, which then isomerizes to the thermally more stable **6**. The latter is disproportionated rapidly to give **2 c** and **4**. The naphthoate **6** then is disproportionated to the most stable isomer **3 a** (path b). An alterative possible path for the formation of **3 a** from **6** involves a direct carboxylation via electrophilic addition of the liberated or added CO_2 to the naphthoate anion (C), which arises through a proton abstraction of **6** by the anion **A** (path a). This combination of decarboxylation, proton abstraction, and carboxylation mechanism had been proposed in the Henkel reaction[3]. As shows in Table 2 (Run 12), the disproportionation of **6** to **3 a** was not so extremely favorable as expected. Also, as shown in Figure 3, a pressurized system is necessary to perform the reaction. These facts could rule out the possibility that the disproportionation (path b) is a main path. Thus, it is probable that the target product **3 a** is formed mainly through the recarboxylation of **C** (path a).

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