TRANSCARBOXYLATION REACTIONS OF SALTS OF ORGANIC ACIDS. XX.*

THE USE OF MIXED TRANSCARBOXYLATIONS IN THE MECHANISTIC STUDY OF TRANSCARBOXYLATION REACTIONS

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A method for mechanistic study of transcarboxylation reactions of salts of aromatic carboxylic acids was proposed consisting in a mixed transcarboxylation in the presence of a salt of aromatic carboxylic acid with known transcarboxylation mechanism.

The transcarboxylation of the salts of aromatic carboxylic acids[1] was regarded by some authors as an intramolecular[2-4], whereas by others as an intermolecular process[5-11]. On the basis of further studies the concept of an intramolecular rearrangement was abandoned and the intermolecular mechanism was accepted, assuming in some cases formation of a transition complex of the reacting salts with the catalyst[12-17] or a direct terephthalate formation without any intermediates[12-14]. This mechanism, though very similar to the mechanism of ionic decarboxylation-recarboxylation proposed by us, has a weak point in the assumption of a "sandwich-type" complex between the salt and the catalyst. Following reasons speak against this assumption: *1.* the transcarboxylation takes place even without a catalyst, *2.* when only traces of catalyst are present, this mechanism would require an excellent mobility of molecules; this is not guaranteed in cases of some salts which are difficult to melt, particularly in the stage of solidification of the reaction mixture. On the other hand, the best explanation is offered by an intermolecular ionic decarboxylation-recarboxylation mechanism combined with an intermolecular transprotonation[7,8,18,19], as shown by us earlier.

In our preliminary communication on carboxylation of salts of various aromatic carboxylic acids with potassium naphthalene carboxylates[20,21], as well as in a communication on similar reactions of salts of heterocyclic carboxylic acids[22] we have pointed out that the analogous mechanism of transcarboxylation of the salts of carboxylic acids containing different aromatic nuclei could be used as a method for studying the transcarboxylation reaction of acids for which this mechanism was not yet determined. For this study we have chosen transcarboxylations of potassium salts of the two simplest aromatic carboxylic acids where the reaction proceeds relatively smoothly and affords a uniform end-product, *i.e.* the transcarboxylation of potassium

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benzene and naphthalene carboxylates. The transcarboxylation path for benzene carboxylates may be described by equations (A) and (B)[7,8,18,19,24], the latter being non-reversible[18,19,24]. Analogously, the transcarboxylations of potassium naphthalene carboxylates may be described by equations (C) and (D)[9,23], the latter again being non-reversible[24]. The path and mechanism of both reactions is similar and in both cases the end-product crystallizes from the reaction mixture and therefore the transcarboxylation of a mixture of salts of both acids could be expected[20,21] to yield a product which is thermally most stable and has the best crystallization ability. We have found that *e.g.* in the mixed transcarboxylation of an equimolar mixture of potassium benzoate and α-naphthoate the benzoate is carboxylated in more than 90% by α-naphthoate to give potassium terephthalate and naphthalene (Table I, experiment 1, equation (E)). Similarly, the benzoate is carboxylated also by salts of other naphthalene mono- or dicarboxylic acids, the most complete carboxylation being achieved if the ratio of benzene nuclei to carboxylate groups in the reaction reaction mixture is 1 : 2 (Table I, *e.g.* experiments 1, 2, 9) (equation (E) and (F)). With other ratios, the transcarboxylation follows in part the path (B) or (C), (D).
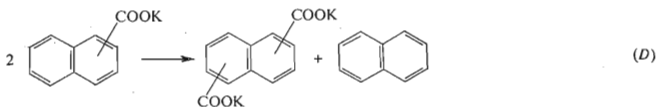

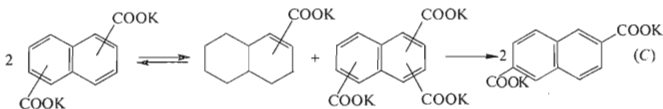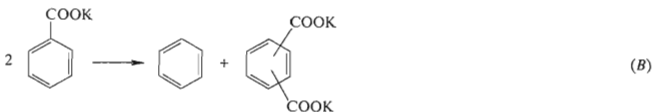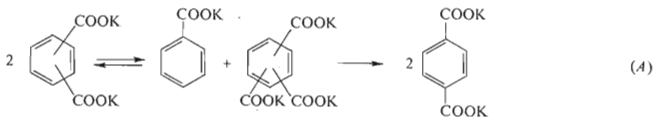$$(A)$$

$$(B)$$

$$(C)$$

$$(D)$$

TABLE I

Composition of the Reaction Mixtures (%) in Carboxylations of Potassium Benzoate by Potassium Naphthalene Carboxylates

No	Starting compounds[a,b]	B[c]	Na[c]	BK$_x$[c]	NaK$_x$[c]	TK$_2$[c]
1	α-NaK + BK	5·5	94·5	94·1	5·9	81
2	β-NaK + BK	9·4	90·6	90·7	9·3	78
3	1,2-NaK$_2$ + 2 BK	24·2	74·8	84·8	15·2	74
4	1,4-NaK$_2$ + 2 BK	25·0	75·0	83·5	16·5	75
5	1,5-NaK$_2$ + 2 BK	22·5	77·5	85·0	15·0	77
6	1,6-NaK$_2$ + 2 BK	27·0	73·0	81·5	18·6	73
7	1,8-NaK$_2$ + 2 BK	30·8	69·2	77·2	22·5	70
8	2,3-NaK$_2$ + 2 BK	28·5	71·5	82·0	18·0	76
9	Mixture of NaK$_x$[d] + x BK	6·5	93·5	92·5	7·5	77
10	2,6-NaK$_2$ + 2 BK	50·2	49·8	69·0	31·0	61
11	2,7-NaK$_2$ + 2 BK	38·0	62·0	71·0	29·0	62

[a] Abbreviations: B benzene; BK benzoate; TK$_2$ terephthalate; IK$_2$ isophthalate; PK$_2$ phthalate; TsK$_3$ trimesate; TlK$_3$ trimellitate; HeK$_3$ hemimellitate; BK$_2$ a mixture of benzene dicarboxylates; BK$_x$ a mixture of benzene carboxylates; Na naphthalene; α- and β-NaK α- and β-naphthoate, respectively; 1,2-, 1,4-, 1,5-, 1,6-, 1,8-, 2,3-NaK$_2$, 1,2-, 1,4-, 1,5-, 1,6-, 1,8- and 2,3-naphthalenedicarboxylate, respectively; NaK a mixture of α- and β-naphthoate; NaK$_2$ a mixture of naphthalene dicarboxylates; NaK$_3$ a mixture of naphthalene tricarboxylates; NaK$_x$ a mixture of naphthalene carboxylates. [b] The reaction was carried out using the indicated molar ratio of reactants; temperature 385—400°C; time 10 min; catalyst 10% (wt/wt) of CdI$_2$. [c] The mol % of reaction products were calculated separately for hydrocarbons and for salts of carboxylic acids. [d] Mixture of NaK$_x$: 33% α-NaK, 33% β-NaK, 15% 1,8-NaK$_2$, 15% 2,3-NaK$_2$, 10% 1,2-NaK$_2$, and 5% 2,6-NaK$_2$.
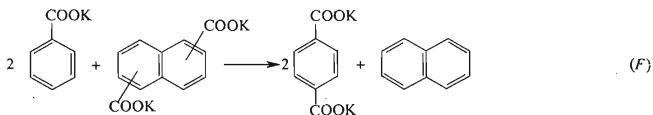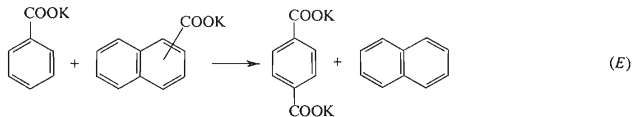

$$(E)$$

$$(F)$$

TABLE II

Composition of the Reaction Mixtures (mol %) in the Initial Stage of Carboxylation of Benzoate with Potassium α-Naphthoate[a,b]

| Products	Experiment No (min)				
	1 (0·5)	2 (1)	3 (2)	4[c] (0·5)	5[d] (9)
B	5	7·4	5·5	5	5
Na	95	94·6	94·5	95	95
BK	28·5	10·8	3·3	45·4	50·6
TK$_2$	2·2	53·1	71·2	0·1	0·05
IK$_2$	8·9	7·6	5·35	0·4	0·1
PK$_2$	14·3	5·5	4·7	2·0	0·1
TsK$_3$	0·65	1·4	0·95	—	—
TlK$_3$	3·05	2·0	1·4	—	—
HeK$_3$	traces	0	0	—	—
NaK	25·3	10·8	5·5	35·3	46·0
NaK$_2$	17·1	8·7	7·55	17·0	3·0
NaK$_3$	1·5	—	—	traces	—

[a] Abbreviations and footnotes[a,b] same as in Table I, but for the reaction time; [c] 350—360°C; [d] 270°C.

The carboxylation of potassium benzoate is also incomplete if a very stable naphtalene carboxylate, *e.g.* potassium 2,6-naphthalenedicarboxylate, is used as reagent. In such case transcarboxylation of two molecules of benzoate takes place to a considerable extent, giving rise to terephthalate and benzene according to equations (B) and (A), the path (B) being non-reversible, so that the 2,6-naphthalene-dicarboxylate cannot carboxylate the arising benzene[24]. The resulting reaction mixture thus contains benzene, naphthalene, potassium terephthalate and 2,6-naphthalene-dicarboxylate (Table III, experiment 29). Similar results are obtained in the mixed transcarboxylation of potassium benzoate and 4,4'-biphenyldicarboxylate (Table III, experiment 30), although the reaction with potassium salts of other biphenylcarboxylic acids proceeds normally giving potassium terephthalate (Table III, experiment 8, 9).

The carboxylation of benzoate with naphthalene carboxylates (*e.g.* the mixed transcarboxylation of potassium benzoate and α-naphthoate) may, in principle, proceed in three ways: *1.* direct transcarboxylation of carboxylate group from the naphthoate to the benzoate molecule (equation (G)) giving rise to naphthalene and benzene carboxylates which, on further transcarboxylation according to (A), afford potassium terephthalate, *2.* simultaneous transcarboxylation of benzoate (equations (B) and (A)) and naphthoate (equations (D) and (C)) followed by carboxylation

of benzene with naphthalene carboxylates, and *3*. primary transcarboxylation of naphthoate to naphthalene and naphthalene dicarboxylates according to (*D*), followed by carboxylation of benzoate with a mixture of naphthalene carboxylates (*e.g.* (*H*)), affording naphthalene and benzene dicarboxylates which give terephthalate according to (*A*).

The carboxylation of potassium benzoate with α-naphthoate proceeds principally according to the alternative *3* (*cf.* Table II) as evidenced by the following results: *1*. the benzene: naphthalene ratio remains practically constant during the whole reaction (experiments 1—3), *2*. as we have shown previously[24], the hydrocarbon once formed in the reaction is not carboxylated, *3*. in the first period of the carboxylation reaction there is a substantial decrease of α-naphthoate and, on the other hand, a significant amount of naphthalene dicarboxylates and tricarboxylates is formed (experiments 4, 5), *4*. the transcarboxylation temperature of potassium α-naphthoate is known[20] to be lower than that of potassium benzoate, and therefore the former reacts sooner than the latter.

$$(G)$$

$$(H)$$
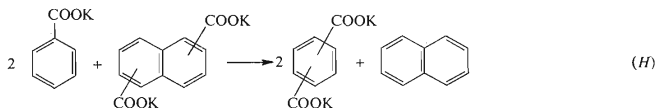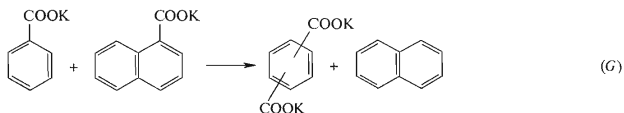
The analysis of the experimental results shows that the fission of the C—C bond between the naphthalene ring and the carboxylate group, as well as the transprotonation between naphthoate molecules and carbanions in the mixed transcarboxylation, is easier than the same reaction of benzene derivatives. These results, however, also lead to the identical mechanism of transcarboxylation of potassium benzene and naphthalene carboxylates (Table I, II).

Analogously to the already mentioned transcarboxylation of an equimolar mixture of potassium benzoate and α-naphthoate, mixed transcarboxylations of benzoate with salts of other aromatic acids were carried out. In all cases except for the markedly anomalous reaction of potassium benzoate with α-picolinate (Table III, experiment 4), the benzoate acted preponderantly as an acceptor of carboxylate groups. Thus, potassium benzoate is carboxylated smoothly also by β-naphthoate, naphthalene dicarboxylates (Table I, experiments 2—11, and Table III, experiments 2 and 3), further by 9-anthracenecarboxylate (equation (*I*)), 9-phenanthrenecarboxylate (equation (*K*)) and 1-pyrenecarboxylate (Table III, experiments 14, 15, 15a). Similarly, potassium benzoate is carboxylated by the salts of heterocyclic carboxylic acids, as *e.g.* potassium 2-furancarboxylate, 2-pyrrolecarboxylate, 2-thiophenecarboxylate

TABLE III

Composition of the Reaction Mixtures in Mixed Transcarboxylations of the Potassium Salts of Aromatic Carboxylic Acids

| No	Starting compounds[a,b]	Hydrocarbons (mol %)		Acids (mol %)	
1	BK + α-NaK	B : Na	(5 : 95)	BH_x : NaH_x	(95 : 5)
2	BK + β-NaK	B : Na	(10 : 90)	BH_x : NaH_x	(90 : 10)
3	2 BK + 1,8-NaK$_2$	B : Na	(31 : 69)	BH_x : NaH_x	(77 : 23)
4	BK + α-PicK	B : Pyr	(53 : 47)	BH_x : $PyrH_x$	(50 : 50)
5	BK + NicK	B : Pyr	(27·5 : 72·5)	BH_x : $PyrH_x$	(70 : 30)
6	BK + isoNicK	B : Pyr	(25·5 : 74·5)	BH_x : $PyrH_x$	(75 : 25)
7	2 BK + 3,4-PyrK$_2$	B : Pyr	(38 : 62)	BH_x : $PyrH_x$	(69 : 31)
8	BK + 2-BiphK	B : Biph	(20 : 80)	BH_x : $BiphH_x$	(84 : 16)
9	2 BK + 2,2′-BiphK$_2$	B : Biph	(25 : 75)	BH_x : $BiphH_x$	(78 : 22)
10	BK + α-FurK	B : Fur	(10 : 90)	BH_x : $FurH_x$	(92 : 8)
11	BK + α-PyrroleK	B : Pyrrole	(15 : 85)	BH_x : $PyrroleH_x$	(87 : 13)
12	BK + α-ThiophK	B : Thioph	(10 : 90)	BH_x : $ThiophH_x$	(90 : 10)
13[c]	BK + PyrazineK	B : Pyrazine	(19 : 81)	—	
14[d]	BK + AntK	B : Ant	(4 : 96)	BH_x : $AntH_x$	(90 : 10)
15[d]	BK + PhenK	B : Phen	(16 : 84)	BH_x : $PhenH_x$	(80 : 20)
15a[d]	BK + PyreneK	B : Pyrene	(10 : 90)	BH_x : $PyreneH_x$	(85 : 15)
16	α-NaK + α-PicK	Na : Pyr	(90 : 10)	NaH_x : $PyrH_x$	(15 : 85)
17	α-NaK + NicK	Na : Pyr	(70 : 30)	NaH_x : $PyrH_x$	(33 : 67)
18	α-NaK + isoNicK	Na : Pyr	(77 : 23)	NaH_x : $PyrH_x$	(28 : 72)
19	α-NaK + 2-BiphK	Na : Biph	(40 : 60)	NaH_x : $BiphH_x$	(55 : 45)
20	α-NaK + α-FurK	Na : Fur	(12 : 88)	NaH_x : $FurH_x$	(85 : 15)
21	α-NaK + α-PyrroleK	Na : Pyrrole	(31 : 69)	NaH_x : $PyrroleH_x$	(70 : 30)
22	α-NaK + α-ThiophK	Na : Thioph	(32 : 68)	NaH_x : $ThiophH_x$	(74 : 26)
23	β-NaK + α-Pick	Na : Pyr	(81 : 19)	NaH_x : $PyrH_x$	(24 : 76)
24	β-NaK + NicK	Na : Pyr	(71 : 29)	NaH_x : $PyrH_x$	(30 : 70)
25	β-NaK + isoNicK	Na : Pyr	(72·5 : 27·5)	NaH_x : $PyrH_x$	(29 : 71)
26[c]	AntK + PhenK	Ant : Phen	(49·5 : 50·5)	—	
27[c]	α-NaK + AntK	Na : Ant	(31·5 : 69·5)	—	
28[c]	α-NaK + PhenK	Na : Phen	(23·5 : 76·5)	—	
29	2 BK + 2,6-NaK$_2$	B : Na	(50·2 : 49·8)	BH_x : NaH_x	(52 : 48)
30	2 BK + 4,4′-BiphK$_2$	B : Biph	(53 : 47)	Bh_x : $BiphH_x$	(59 : 41)

[a] Abbreviations: BK benzoate; α-, β-NaK, α-, β- naphthoate; α-PicK, NicK and isoNicK α-pico-linate, nicotinate and isonicotinate, respectively; 3,4-PyrK$_2$ 3,4-pyridinedicarboxylate; 2-BiphK and 2,2′-BiphK$_2$ 2-biphenylcarboxylate and 2,2′-biphenyldicarboxylate, respectively; α-FurK, α-PyrroleK, α-ThiophK, PyrazineK, AntK and PhenK pyromucate, α-pyrrolecarboxylate, α-thiophenecarboxylate, pyrazinecarboxylate, 9-anthracenecarboxylate and 9-phenanthrene-carboxylate, respectively; BH_x, NaH_x, $PyrH_x$, $BiphH_x$, $FurH_x$, $PyrroleH_x$ and $ThiophH_x$ a mix-ture of benzene, naphthalene, pyridine, biphenyl, furan, pyrrole and thiophene carboxylic acids. The reactions were carried out in millimolar amounts in sealed ampoules, catalyst CdI_2 (3% Cd^{2+} per weight of the salts), CO_2 pressure 3 atm, temperature: No 1—15 400—410°C, No

and pyrazinecarboxylate (Table III, experiments 10—13). The situation is somewhat more complicated in the case of pyridine carboxylic acids even though here too the carboxylation of benzoate in principle takes place (Table III, experiments 4—7).


$$(I)$$

$$(K)$$
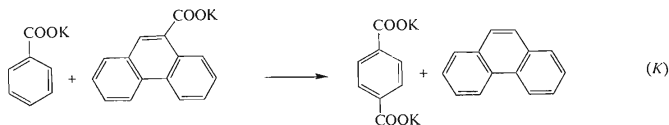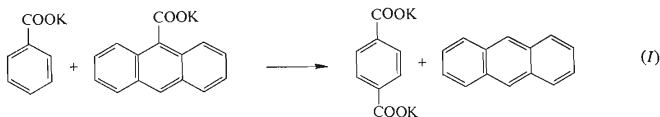
The ratio of benzene and pyridine, as well as of the corresponding carboxylic acids, seems to indicate that the benzoate is carboxylated only to a small extent. This is particularly marked in the transcarboxylation of a mixture of potassium benzoate and α-picolinate (Table III, experiment 4). This weak carboxylating effect of pyridine carboxylates, particularly of α-picolinate, is due to the ability of pyridine carboxylates (similarly to potassium α-naphthoate in a mixture with potassium benzoate) to react mutually at a substantially lower temperature than the benzoate. However, contrary to the naphthalene carboxylates, the arising mixture of pyridine carboxylates is thermally considerably unstable and undergoes destruction reactions, and therefore it is unable to carboxylate quantitatively the potassium benzoate. This reacts then in a non-reversible reaction to benzene and terephthalate according to equations (B) and (A) misrepresenting thus partly the path of the mixed transcarboxylation. The mixed transcarboxylation of benzoate and o-biphenyl carboxylates is also complicated: in this case the predominant carboxylation of benzoate is accompanied by a cyclisation reaction of o-biphenyl carboxylates leading to fluorenone and fluorenone carboxylates[25,26]. These competitive reactions depicted in equations (L) and (M) reduce thus the yield of the carboxylation of benzoate (Table III, experiments 8, 9).

16—22 380—390°C, No 23—25 390—400°C, time: No 1—15, 10 min, No 16—25 12 min. [b]The reactants were taken into reaction in the ratio indicated. [c]In No 13, 26—28 the ratio of acids was not determined due to low accuracy in their isolation. [d]In No 14—15a the ratio of acids suffers from great error. Due to very low volatility of methyl anthracene, phenanthrene and pyrene carboxylates the determination of this ratio was carried out by a combination of vapour phase chromatographic analysis and the differential weighing after distilling off methyl benzene carboxylates in high vacuum.

$$(L)$$

$$(M)$$
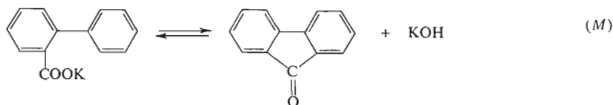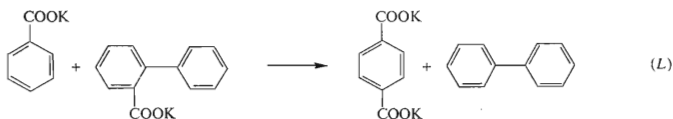
The mixed transcarboxylations of α- and β-naphthoates with pyridine carboxylates which take place at lower temperatures result in a smooth and unequivocal transfer of carboxylate groups from naphthoates to pyridine monocarboxylates (Table III, experiments 16—18, 23—25), giving thus further evidence that the above-mentioned complications in mixed transcarboxylations of benzoate and pyridine carboxylates (particularly potassium α-picolinate) are mainly due to a low thermal stability of pyridine carboxylates. On the other hand, the transcarboxylation of a mixture of potassium α-naphthoate and 2-biphenylcarboxylate gives roughly equal amounts of naphthalene and biphenyl, and naphthalene and biphenyl carboxylic acids (Table III, experiment 19). Similar result is obtained in mixed transcarboxylation of potassium 9-anthracenecarboxylate with 9-phenanthrenecarboxylate (Table III, experiment 26). However, if α-naphthoate is allowed to react with 9-anthracenecarboxylate or 9-phenanthrenecarboxylate, the reaction in both cases results in the carboxylation of the α-naphthoate with these carboxylates. Thus, the α-naphthoate acts here as an acceptor of carboxylate groups (Table III, experiments 27, 28). Similarly, in the mixed transcarboxylations of α-naphthoate with potassium 2-furan-, 2-pyrrole- and 2-thiophenecarboxylates the carboxylation of the α-naphthoate in all cases predominates (Table III, experiments 20—22). These examples show that naphthalene monocarboxylates act in some cases as a donor (e.g. equations (E)—(H), (N)) whereas in other cases they are rather an acceptor of carboxylate groups (e.g. equations (O), (P)).

Summing up all the results we may outline the limitations of the use of mixed transcarboxylations in the study of transcarboxylation mechanism of aromatic carboxylic acids salts. This method is applicable to such transcarboxylations where the transfer of carboxylate groups from molecules of one acid to another is as complete as possible, and it is immaterial whether the transcarboxylation of the salts of both acids is simultaneous or not. The method is not suitable for cases where some of the acids reacts only to a limited extent, e.g. in the reaction of benzoate with 2,6-naphthalenedicarboxylate or with 4,4'-biphenyldicarboxylate (Table III, experiments 29, 30), or where salt of some acid is of low thermal stability, as e.g. in the reaction of benzoate with potassium α-picolinate (Table III, experiment 4). It may be combined with the method of mixed transcarboxylations of deuterium-labelled and non-labelled acids containing different aromatic nuclei[25,26], or, with mixed transcarboxylations of salts containing ^{14}C-labelled carboxylate groups[27].

(N)

(O)

(P)
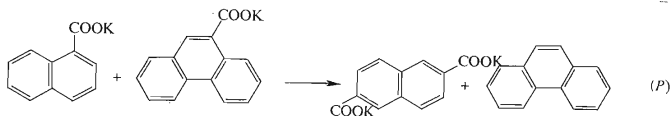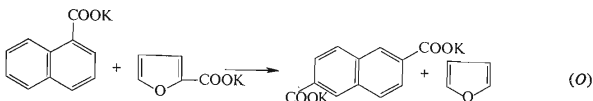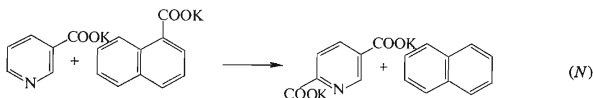
EXPERIMENTAL

Starting acids: Potassium salts were prepared by neutralisation of aqueous solutions (or suspensions) of the acids with KOH (phenolphthalein), evaporation to dryness, powdering the salts and drying at 110—150°C/0·01 Torr. α-Naphthoic acid was prepared from α-bromonaphthalene[28]; m.p. 161°C (lit.[28] m.p. 159—161°C). β-Naphthoic acid was prepared by oxidation of 2-acetyl-naphthalene[29]; m.p. 183—184°C (lit.[29] m.p. 181—183°C). 1,2-Naphthalenedicarboxylic acid was isolated as the main product of the transcarboxylation reaction of barium α-naphthoate[9], m.p. 173—175°C (water), reported[30] m.p. 175°C; dimethyl ester m.p. 83—84°C (reported[30] m.p. 85°C). 1,4-Naphthalenedicarboxylic acid was obtained by oxidation of 1-methyl-4-acetyl-naphthalene with aqueous sodium dichromate at 250°C; m.p. 300—310°C (reported[30] m.p. above 300°C, 309°C lit.[31]), dimethyl ester m.p. 64—66°C (reported[30] m.p. 67°C). 1,5-Naphthalenedicarboxylic acid was prepared from 1,5-dibromonaphthalene[32] by a Grignard reaction[33], m.p. 310—320°C (reported[30] m.p. above 300°C lit.[33], 320—322°C lit.[35]); dimethyl ester m.p. 114—117°C (reported[30] m.p. 119°C, 114—115°C lit.[33], 114—115°C lit.[34], 113—114°C lit.[35]). 1,6-Naphthalenedicarboxylic acid was obtained by hydrolysis of 1,6-dicyanonaphthalene which in turn was prepared from 1,6-naphthalenedisulphonic acid[36] according to a modified method of King and Wright[37], m.p. 305—312°C (reported[38] m.p. 310°C); dimethyl ester m.p. 96—97°C (reported[30] m.p. 97—98°C, 98°C lit.[39]). A mixture of 1,4- and 1,5-naphthalenedicarboxylic acids was prepared by oxidation of a mixture of 1,4- and 1,5-bis(chloroethyl)naphthalene[40] with aqueous sodium dichromate in the presence of sodium hydrogen carbonate solution at 250°C. 1,7-Naphthalenedicarboxylic acid was prepared by hydrolysis of 1,7-dicyanonaphthalene[30], m.p. 290—295°C (dec.) (reported[41,42] m.p. 265°C, 294—296°C (dec.) lit.[43]); dimethyl ester m.p. 87—89°C (reported[30] m.p. 90°C, 86—87°C lit.[43]). 2,7-Naphthalenedicarboxylic acid was obtained by heating dimethyl 2,7-naphthalenedisulphonate[36] with sodium cyanide and subsequent hydrolysis of the resulting 2,7-dicyanonaphthalene[37] with sulphuric acid. M.p. 320 to 325°C (reported[44] m.p. above 300°C); dimethyl ester m.p. 135°C (reported[30,45] m.p. 137°C, 128—131°C lit.[39]). 2,3-Naphthalenedicarboxylic acid was a Koch-Light product, m.p. 233—240°C

(dec.), (reported[46] m.p. 239—241°C (dec.)); dimethyl ester m.p. 44—46°C (reported[30] m.p. 47°C). 2,6-Naphthalenedicarboxylic acid was prepared from potassium α-naphthoate by a transcarboxylation reaction; m.p. above 325°C (reported[30] m.p. above 300°C), dimethyl ester melted at 192°C (reported[30] m.p. 186°C). 9-Phenanthrenecarboxylic acid was prepared by hydrolysis of 9-cyanophenanthrene[48,49]; m.p. 257·5—258·5°C (reported[50] m.p. 250°C); potassium salt m.p. 270—273°C.

9-*Anthracenecarboxylic acid*: Lithium (1·3 g) was added under nitrogen to a solution of n-butyl chloride (10 ml) in ether (50 ml) and the stirred mixture was refluxed for 2 h. A solution of 9-bromoanthracene (11 g) in ether (25 ml) was then added under nitrogen to the stirred solution. The stirred yellow suspension of the formed 9-lithiumanthracene was refluxed under nitrogen for 10 min and an excess of solid carbon dioxide was added under constant stirring. Violent reaction occured and the mixture thickened. Under continuous stirring the mixture was treated with methanol (40 ml) and water (150 ml). The aqueous layer was separated, washed with ether (2 × 100 ml), acidified with HCl and the yellow precipitate filtered, washed with water and dried, yielding 6·7 g (71%) of the product, m.p. 211—213°C. Recrystallisation from acetic acid gave 5·0 g (53%) of material melting at 213·5—215°C (reported[47] m.p. 211—216°C).

1-*Pyrenecarboxylic acid*: Lithium (1·1 g) was added under nitrogen to a solution of n-butyl chloride (4·9 ml) in ether (40 ml) and the mixture was refluxed for 2 h under stirring. Another portion of n-butyl chloride (3·5 ml) in ether (20 ml) was added and the mixture was refluxed for another 2 h. The stirred mixture was then treated with 1-bromopyrene[51] (8·5 g) in ether (50 ml) and refluxed under stirring for 30 min. An excess of solid CO_2 was added, the mixture diluted with water (150 ml), the aqueous layer separated, extracted with ether (2 × 100 ml) and acidified with HCl. The precipitate was filtered, washed with water and dried, giving thus 3·5 g (47·5%) of product, m.p. 258·5—263°C, of 98·5% purity (titration with 0·1M-NaOH). Potassium salt: m.p. 345—375°C (blackening). The preparation and physical constants of α-picolinic, nicotinic, isonicotinic, 3,4-pyridinedicarboxylic, 2,5-pyridinedicarboxylic, 2-furancarboxylic, 2,5-furancarboxylic, 2-thiophenecarboxylic, 2,5-thiophenedicarboxylic, 2-pyrrolecarboxylic, and 2,5-pyrroledicarboxylic acids and their methyl esters are described in ref.[22]; 2-biphenylcarboxylic, 4-biphenylcarboxylic, 2,2′-biphenyldicarboxylic and 4,4′-biphenyldicarboxylic acids, together with their methyl esters are described in ref.[26].

Transcarboxylation reactions. Potassium benzoate: Reaction of a mixture of potassium benzoate (32 g) and CdI_2 (1·6 g) (425°C, 30 min) afforded after isolation 16·2 g (97·6%) of a mixture of benzene carboxylic acids containing 14·3 g (86·2%) of terephthalic acid. The yield of benzene was 5 g (64%); some benzene was lost during the evaporation of ether which was used for extraction of benzene from the reaction mixture.

Potassium α-naphthoate: Reaction (390°C, 30 min) of a mixture of potassium α-naphthoate (42·0 g, 0·2 mol) and CdI_2 (2·0 g) afforded 12·5 g (97·5%) of naphthalene which was isolated by extraction of the reaction mixture with ether. The mixture of salts of naphthalene carboxylic acids was dissolved in hot water (1000 ml), filtered while hot and the hot filtrate was acidified with HCl. The precipitated 2,6-naphthalenedicarboxylic acid was filtered while hot, washed with hot water (200 ml) and dried at 130°C/0·1 Torr to a constant weight: yield 18·8 g (88·0%). The cooled filtrate deposited further portion of acids which were filtered off and the filtrate was extracted with ether, the ethereal layer dried and taken down. The total amount of naphthalene carboxylic acids was 19·9 g (92·5%); this amount contained 17·8 g (89·5%) of 2,6-naphthalenedicarboxylic acid (Table IV, experiment 1).

Potassium β-naphthoate: Reaction (410°C, 45 min) of a mixture of potassium β-naphthoate (42·0 g; 0·2 mol) and CdI_2 (2 g) gave 12·3 g (96·0%) of naphthalene, and a mixture of naphthalene

carboxylic acids (19·4 g; 90·0%) containing 17·2 g (79·5%) of 2,6-naphthalenedicarboxylic acid (Table IV, experiment 2).

Potassium 1,5-naphthalenedicarboxylate: Reaction (45 min, 415—420°C) of a mixture of potassium 1,5-naphthalenedicarboxylate (29·2 g; 0·1 mol) and CdI$_2$ (1·5 g) afforded 0·5 g of naphthalene (3·9% calculated for decarboxylation) and a mixture of naphthalene carboxylic acids (19·65 g; 91·0%) containing 17·6 g (81·5%) of 2,6-naphthalenedicarboxylic acid (Table IV, experiment 5). The potassium salts of 1,2-, 1,4-, 1,8-, 2,3- and of a mixture of 1,4- and 1,5-naphthalenedicarboxylic acids were analogously subjected to the transcarboxylation reaction and the analyses of the corresponding reaction mixtures are given in Table IV (experiments 3,4,8,9,12). The transcarboxylations of potassium 1,6-, 1,7-, 2,6- and 2,7-naphthalenedicarboxylates were carried out in millimolar amounts in sealed glass ampoules (pressure CO$_2$ 3 atm) placed in an electrically heated quartz tube[8,19]. The composition of the corresponding reaction mixtures is listed in Table IV (experiments 6,7,10,11).

TABLE IV

Composition of the Reaction Mixtures in Transcarboxylation of Potassium Naphthalene Carboxylates with CdI$_2$ as Catalyst (5% per weight of salts)

No	Starting compounds[a,b]	Temp. °C	Time min	CO$_2$ pressure atm	Yield, %		Composition of the mixture of acids[e]			
					naphthalene[c]	acids[d]	NaH	NaH$_2$	2,6-NaH$_2$	NaH$_3$
1	α-NaK	390	30	50	97·5	92·5	2·5	4·8	89·5	3·0
2	β-NaK	410	45	50	96·0	90·0	5·2	11·3	79·5	4·1
3	1,2-NaK$_2$	415—420	45	50	3·3	91·8	4·9	8·1	81·5	6·0
4	1,4-NaK$_2$	415	45	50	4·2	88·6	7·2	10·8	78·5	4·6
5	1,5-NaK$_2$	415—420	45	50	3·9	91·0	6·8	7·2	81·5	4·4
6	1,6-NaK$_2$	415	20	3	5·6	87·0	6·6	9·9	75·6	7·7
7	1,7-NaK$_2$	415	20	3	7·0	85·0	8·4	13·1	74·8	3·9
8	1,8-NaK$_2$	415	45	50	4·0	88·5	5·6	11·3	79·8	3·5
9	2,3-NaK$_2$	415	45	50	4·6	86·7	5·2	8·5	82·7	4·0
10	2,6-NaK$_2$	420	45	3	4·0	89·9	2·0	3·5	93·6	1·0
11	2,7-NaK$_2$	415	20	3	6·5	86·5	8·8	9·7	76·5	5·8
12	1,4, 1,5-NaK$_2$	415	45	50	4·9	88·6	4·6	7·1	83·0	5·1

[a]Abbreviations see Tables I—III; 1,7-, 2,6-, 2,7-NaK$_2$ 1,7-, 2,6-, 2,7-naphthalenedicarboxylate; NaH mixture of α- and β-naphthoic acids, NaH$_2$ mixture of naphthalene dicarboxylic acids except for 2,6-naphthalenedicarboxylic acid; 2,6-NaH$_2$ 2,6-naphthalenedicarboxylic acid; NaH$_3$ a mixture of naphthalene tricarboxylic acids. [b]Experiments No 1—4, 8, 9, 12 were carried out in an autoclave with 0·1—0·2 mol of reactants, experiments No 5—7, 10, 11 in a glass ampoules with 1 mmol. [c]The yield of naphthalene in experiments 1 and 2 is given in mol% calculated for disproportionation of naphthoates, the yield of naphthalene in No 3—12 is given in mol% calculated for complete decarboxylation of naphthalene dicarboxylates. [d]The yield of acids in No 1 and 2 is given in mol% calculated for the disproportionation, in No 3—12 calculated for transcarboxylation. [e]mol%, calculated for 100% of the mixture of acids.

Mixed transcarboxylation of potassium α-naphthoate and *benzoate*: A mixture of potassium benzoate (16·0 g; 0·1 mol), potassium α-naphthoate (21·0 g; 0·1 mol) and $CdCl_2$ (1 g; 1·6% Cd^{2+} per weight of the salts) was heated to 420°C for 30 min under CO_2 (50 atm). Extraction with ether afforded 11·5 g (90·0%) of naphthalene and 0·3 g (3·85%) of benzene (during the isolation procedure a part of the hydrocarbons, particularly of the volatile benzene, was lost). The mixture of salts was dissolved in hot water (1 000 ml), the solution filtered while hot, the filtrate acidified with HCl, the precipitate filtered, washed with hot water (300 ml) and dried at 110°C/0·1 Torr till the constant weight (14·2 g). The precipitate contained a mixture of terephthalic acid and 2,6-naphthalenedicarboxylic acid in molar ratio 9 : 9. Upon cooling, the filtrate deposited further product (*A*) which was filtered (0·5 g). The filtrate was basified and evaporated to 50 ml, acidified with HCl and extracted with ether. The ethereal solution was dried and evaporated to dryness affording thus a further amount of acids (*B*) (1·2 g). Both acidic portions (*A* + *B*) were combined and analysed by vapour phase chromatography as methyl esters. The mixture contained benzene dicarboxylic and naphthalene dicarboxylic acids in molar ratio 9 : 1, the content of terephthalic acid being 2%. The overall yield of the acids was 15·9 g with molar ratio benzenedicarboxylic acids : naphthalenedicarboxylic acids 91 : 9, the yield of terephthalic acid being 80·4 mol % (calculated for complete transfer of the carboxylate group from α-naphthoate to benzoate).

Mixed transcarboxylation of potassium benzoate and α-naphthoate on a micro scale. A mixture of potassium benzoate (160·0 mg; 1·0 mmol), potassium α-naphthoate (210 mg; 1 mmol) and CdI_2 (20 mg) was heated in a sealed ampoule to 390°C for 15 min under CO_2 (3 atm). After cooling, the volatile products (benzene, naphthalene) were freezed out into tip of the ampoule at −78°C which was then sealed off and set aside. The residual hydrocarbons were rinsed from the ampoule with a small amount of ether (3 . 1 ml), the extract was combined with the main portion of hydrocarbons and the ratio of hydrocarbons was determined by vapour phase chromatography. The mixture of salts was dissolved in hot water (10 ml), the carbonised portions were filtered off and the filtrate was acidified with HCl. The precipitate was filtered while hot, washed with hot water (2 ml) and dried to a constant weight. It consisted of terephthalic and 2,6-naphthalenedicarboxylic acids (139 mg, 84% calculated on terephthalic acid). The filtrate was cooled and the further portion of the precipitated acids was filtered off. The filtrate thus obtained was made alkaline (phenolphthalein), evaporated to a small volume (about 3 ml), acidified with HCl, extracted with ether (3 . 10 ml), the ethereal layer dried and taken down affording thus further amount of acids. All the acidic portions were combined (162 mg; 97·5% calculated for terephthalic acid) and converted into their methyl esters by treatment with ethereal diazomethane. After evaporation of ether the esters were analysed by vapour phase chromatography using an internal standard. The molar ratio benzene: naphthalene was 5 : 95, benzene carboxylic acids: naphthalene carboxylic acids 93 : 7. Other mixed transcarboxylations were carried out in an analogous manner and their results are listed in Tables I—III.

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