TRANSCARBOXYLATION REACTIONS OF SALTS OF ORGANIC ACIDS. XVI.*

TRANSCARBOXYLATION OF THE SALTS OF HETEROCYCLIC CARBOXYLIC ACIDS

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The course of transcarboxylation reactions of the salts of heterocyclic carboxylic acids was investigated. On the basis of the incorporation of radionuclide ^{14}C into the molecule of these acids, the dependence of the composition of the reaction mixture on the reaction time and the mixed transcarboxylations, an intermolecular ionic mechanism was proposed for these reactions.

Similarly as in the case of salts of benzene- or naphthalene carboxylic acids heating at an elevated temperature brings about transcarboxylations, the same is true of salts of heterocyclic carboxylic acids[1]. However, in contrast to acids containing a benzene or naphthalene nucleus, where a single end-product is formed during the reaction, in the case of heterocyclic acids a mixture is formed with a greater or lesser predominance of one acid only. Thus, for example, on transcarboxylation of pyridine carboxylates the formed product is 2,5-pyridinedicarboxylic acid salt, in the case of thiophene, or furan, or pyrrole carboxylates the salts of 2,5-thiophene-, or 2,5-furan-, or 2,5-pyrroledicarboxylic acids are formed. In addition to this these reactions give rise to an appreciable amount of by-products and carbonised material. The very complex mixture of intermediary products formed during the reaction, as well as their difficult analysis, make the study of the reaction mechanism very difficult.

As we have shown earlier during the study of the mechanism of transcarboxylation of the most simple representative of aromatic carboxylic acids, *i.e.* during the transformation of potassium benzene carboxylates, this reaction takes place *via* a complex mixture of intermediates. Nevertheless, it leads to a single end-product, *i.e.* potassium terephthalate[2-9].

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From the experimental results it followed that the transcarboxylation reaction of benzene carboxylates takes place through a mechanism of intermolecular ionic decarboxylation-recarboxylation combined with a splitting off and addition of protons in many repeated cycles. This mechanism is in better agreement with the experimental results found[2-9] than the mechanism of intramolecular rearrangement proposed by some other authors[10-12]. A similar mechanism[13] was also proposed for the transcarboxylation of naphthalene carboxylic acids salts, which is in agreement with the mechanism proposed by McNelis[14], except for the first stage of the disproportionation of naphthalene monocarboxylates, of which we have proved unambiguously — in contrast to McNelis — that this is an irreversible reaction[15].

The appreciable complexity of the final reaction products after transcarboxylation of the salts of heterocyclic carboxylic acids possessing a less symmetrical aromatic nucleus than benzene, and in some instances containing even an acid hydrogen in its nucleus, led us to a closer study of the mechanism of these reactions. In order to determine the mechanism we made use of three methods: *1.* the method of incorporation of radionuclide ^{14}C from the reaction atmosphere $^{14}CO_2$ into the molecules of carboxylic acids salts[7,15], *2.* a modified (simplified) method of the dependence of the composition of the reaction mixtures on the reaction time[7,8], and *3.* the methods of mixed transcarboxylation with acid salts for which the transcarboxylation mechanism was determined earlier[16,17]. The results of the study of the transcarboxylation mechanism are summarised according to single heterocyclic acids.

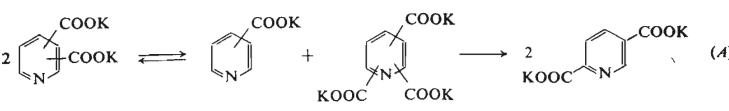
Pyridine Carboxylic Acids

Using the method of incorporation of radionuclide ^{14}C from the reaction atmosphere $^{14}CO_2$ into the carboxylate groups of the salts of acids we found that the incorporation takes place very rapidly until the equilibration of ^{14}C between carboxylate groups and $^{14}CO_2$ in the reaction atmosphere is complete, and that it is complete already in the initial stage of the reaction when the final composition of the reaction mixture with predominating 2,5-pyridinedicarboxylic acid is not yet formed (Table I, experiments 12, 14). After reaction the final product, 2,5-pyridinedicarboxylic acid, contains such an amount of incorporated ^{14}C as would correspond to the above mentioned ratio of carboxylate groups and $^{14}CO_2$ in the reaction atmosphere (Table I, experiments 1, 3, 5, 7, or 2, 4, 6, 8). If the transcarboxylation reaction does not take place, as for example in the absence of a catalyst, the incorporation of ^{14}C into the molecules of the acid does not take place either (Table I, experiments 11, 13). All these experimental results correspond fully to the results of similar incorporation experiments carried out with the salts of benzene-[7,15] or naphthalene carboxylic acids[13] and they show that on transcarboxylation an ionic splitting off of the carboxylate groups from the pyridine carboxylic acid salts takes place.

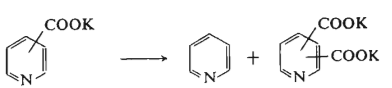
The determination of the dependence of the reaction mixture composition on the reaction time, which was made use of successfully during the determination of the mechanism of the transcarboxylation reactions of benzene carboxylic acids salts[7-9],

was complicated in the case of pyridine carboxylic acids by the difficult analysis of the very complex reaction mixtures (three pyridine mono-, six di-, and six tricarboxylic acids). Therefore, for the sake of simplicity, only the sum of pyridine mono- and tricarboxylic acids was determined analytically, while in the case of dicarboxylic acids only the final or the starting acids were determined, whereas other dicarboxylic acids were determined only as a sum. From the experiments 1–6 in Table II it follows clearly that on transcarboxylation of pyridine carboxylates a decomposition takes place initially to a mixture of pyridinemono- and tricarboxylates, from which pyridine carboxylates are formed again in subsequent stages of the reaction (equation (*A*)). This represents a similar course as in the transcarboxylations of benzene dicarboxylic acids salts.

From Table III (experiments 1–17) it also follows that the transcarboxylation reactions of pyridine monocarboxylates take place in a similar manner as the reaction of potasium benzoate (equation (*B*) for the first step and equation (*A*) for the second). The only difference is that during these reactions the fraction of carbonised material is substantially larger. It is important to note that pyridine formed on disproportionation during the first step (equation (*B*)) is formed almost in quantitative yield and that partial destruction of the reaction mass takes place only in the subsequent reaction step (equation (*A*)). Here too, in analogy to potassium benzoate or both naphthoates, the first step reactions (equation (*B*)) are irreversible, while second step reactions (equation (*A*)) are reversible.



(*A*)



(*B*)

In view of the fact that the determination of the mechanism of transcarboxylation reactions of pyridine carboxylic acids salts according to the preceding method was rather difficult, we utilised a simpler method, *i.e.* mixed transcarboxylation with potassium benzoate or naphthoate. According to this reaction, mixtures of equimolar amounts of pyridine monocarboxylic acid salt and potassium benzoate or naphthoate are allowed to react[17]. This method is based on the assumption that the mechanism of transcarboxylation of the salts of various aromatic acids is identical and that a transfer of the carboxylate groups between the acids with various aromatic nuclei may therefore take place. In this reaction the salt of that acid crystallises out which

TABLE I

Transcarboxylation Reactions of the Salts of Heterocyclic Carbocylic Acids in $^{14}CO_2$ Atmosphere

Experiment No[a]	Starting compounds[b]	Temp. °C	Time min	Products	Yield of acids[c] %	Radio-activity[d] %
1	2 PicK	390	20	2,5-$PyrH_2$ + pyridine	46	65
2	2 PicK	390	20	2,5-$PyrH_2$ + pyridine	53	95 (4·1)
3	2 NicK	390	20	2,5-$PyrH_2$ + pyridine	50	65
4	2 NicK	390	20	2,5-$PyrH_2$ + pyridine	59	94 (4·0)
5	2 iNicK	390	20	2,5-$PyrH_2$ + pyridine	47	65
6	2 iNicK	390	20	2,5-$PyrH_2$ + pyridine	57	95 (4·1)
7	2,3-$PyrK_2$	400	25	2,5-$PyrH_2$	43	63
8	2,3-$PyrK_2$	400	25	2,5-$PyrH_2$	51	95·5 (3·9)
9	2 FurK	380	20	2,5-$FurH_2$ + furan	40	67
10	2 FurK	380	20	2,5-$FurH_2$ + furan	59	94 (4·0)
11	2 PicK	390	5	2 PicH	—	0
12	2 PicK	390	1	$PyrH_x$ + pyridine	—	62
13	2 NicK	390	5	2 NicH	—	0
14	2 NicK	390	1	$PyrH_x$ + pyridine	—	63
15	2 FurK	380	5	2 FurH	—	0
16	2 FurK	380	1	$FurH_x$ + Fur	—	62
17	2 ThiK	390	20	2,5-$ThiH_2$ + thiophene	53	65
18	2 PolK	390	20	2,5-$PolH_2$ + pyrrole	49	64
19	2 ThiK	390	5	2 ThiH	—	0
20	2 PolK	390	5	2 PolH	—	0

[a] Abbreviations: PicK potassium picolinate, NicK potassium nicotinate, iNicK potassium isonicotinate, 2,3-$PyrK_2$ potassium 2,3-pyridinedicarboxylate, FurK potassium 2-furancarboxylate, ThiK potassium 2-thiophenecarboxylate, PolK potassium 2-pyrrolecarboxylate, 2,5-$PyrH_2$ 2,5-pyridinedicarboxylic acid, 2,5-$FurH_2$ 2,5-furandicarboxylic acid, PicH picolinic acid, FurH 2-furancarboxylic acid, $PyrH_x$ or $FurH_x$ mixtures of pyridine- or furan carboxylic acids, resp. 2,5-$ThiH_2$ or 2,5-$PolH_2$ 2,5-thiophene- or 2,5-pyrroledicarboxylic acids, resp., ThiH or PolH 2-thiophene- or 2-pyrrolecarboxylic acids, respectively. Experiments 1—16 are from a paper ref.[13]. [b] Starting salts of acids were taken into reactions in millimolar amounts, as indicated by symbols; the molar ratio of carboxyl groups in salts of acids to $^{14}CO_2$ was 1 : 25 in experiments 2, 4, 6, 8, and 10, while in other experiments it was 2 : 1, experiments 11, 13, and 15 were carried out without a catalyst, the others in the presence of 10% of CdI_2 (the basis of calculation was the weight of the salt). [c] The purity of the mentioned acids was about 85—90%, the difference from 100% represented other isomeric acids. [d] Specific radioactivity of the acids per mmol in percents of the specific radioactivity of $^{14}CO_2$ (per mmol) taken into the reaction. The values in brackets mean the percentage of radionuclide ^{14}C incorporated in the carboxyls of the acids relative to the initial amount of $^{14}CO_2$.

is thermally most stable and the crystallisation ability of which is greatest. From Table IV (experiments 1–3) it follows that the salts of pyridine carboxylic acids carboxylate potassium benzoate under formation of potassium terephthalate and pyridine, while potassium naphthalene carboxylates carboxylate pyridine monocarboxylates under formation of naphthalene and a mixture of pyridine carboxylates in which the 2,5-isomer predominates (Table IV, experiments 4–6).

In order to corroborate the ionic character of the transcarboxylation reactions of pyridine carboxylic acids salts we carried out these reactions in the presence of water. We found that the protons set free from water brought about a relatively smooth decarboxylation of salts to pyridine (Table V, experiments 1–3). Thus, the reaction is similar to the decarboxylations of the salts of benzene- or naphthalene carboxylic acids during their transcarboxylation in the presence of substances liberating protons[4,7].

TABLE II

Composition of the Reaction Mixtures During the Transcarboxylation of the Salts of Pyridine dicarboxylic Acids

Exp. No	Time min	Pyridine[b]	Carbonized fraction[c]	Acids[d], %				
				PyrH	$PyrH_2$	$PyrH_3$	2,3-$PyrH_2$[e]	2,5-$PyrH_2$[e]
			Potassium 2,3-pyridinedicarboxylate[a]					
1	0·5	—	—	3	traces	2	95	—
2	1	traces	—	7	3	6	81	—
3	2	3	7	19	12	21	40	6
4	4	5	11	26	22	24	—	8
5	8	7	19	10	25	9	—	43
6	12	8	28	6	30	7	—	56
			Potassium 2,5-pyridinedicarboxylate[a]					
7	2	—	—	3	6	2	—	85
8	4	3	4	5	7	4	—	83
9	16	4	9	6	12	3	—	78

[a] The starting salts were taken into the reaction in millimolar amounts, temp. 390–400°C; catalyst 10% CdI_2 per weight of salts, pressure of CO_2 in ampoule 3 atm; [b] weight percents of the whole reaction mixture; [c] weight percents of the solid fractions of the reaction mixture; [d] molar percents in relation to the mixture of acids alone; [e] experimental error about ±10%. PyrH mixture of three isomeric pyridinemonocarboxylic acids, $PyrH_2$ mixture of pyridinedicarboxylic acids, $PyrH_3$ mixture of pyridinetricarboxylic acids.

From all the experimental results mentioned above it follows clearly that the mechanism of transcarboxylation of pyridine carboxylic acids salts is similar to that of the reaction of benzene- or naphthalene carboxylic acids and that it is an ionic intermolecular decarboxylation-recarboxylation connected with the splitting off and the addition of protons on the heterocyclic nucleus. Also, all reactions are repeated in multiple cycles. Thus for example, in the case of potassium 3,4-pyridinedicarboxylate equation (*C*) applies for decarboxylation leading to a carbanion and

TABLE III

Composition of the Reaction Mixtures on Transcarboxylation of Pyridine monocarboxylic Acids Salts

Exp. No	Time min	Pyridine[b]	Carbonized fraction[c]	Acids[d], %			
				PyrH	$PyrH_2$	$PyrH_3$	2,5-$PyrH_2$[e]
			Potassium picolinate[a]				
1	0·5	6	—	89	8	traces	—
2	1	20	traces	78	12	4	2
3	2	63	4	39	45	9	7
4	4	84	15	16	42	6	36
5	8	11	20	9	33	7	49
6	12	93	27	11	29	6	54
			Potassium nicotinate[a]				
7	0·5	5	—	90	4	—	—
8	1	15	2	74	18	3	3
9	2	54	6	40	44	10	6
10	4	85	14	15	46	6	34
11	8	92	21	9	31	9	47
12	12	93	29	8	27	9	52
			Potassium isonicotinate[a]				
13	0·5	4	1	88	5	—	—
14	1	17	3	75	16	4	2
15	2	52	7	44	37	9	9
16	4	86	13	19	43	7	32
17	8	90	22	12	29	9	46

[a] Identical as in Table II; [b] molar percents of the theoretical yield of disproportionation; [c] weight percents of the solid fraction of the reaction mixtures; [d] molar percent in relation to the mixture of acids only; [e] experimental error ± 10%.

TABLE IV

Transcarboxylation of Mixtures of Heterocyclic Carboxylic Acids Salts

Exp. No	Starting compounds[a]	Products				
		hydrocarbons[b]	ratio mol %	acids		ratio mol %
1	BK + PicK	B : pyridine	50 : 50	BH_x	: $PyrH_x$	50 : 50
2	BK + NicK	B : pyridine	27 : 73	BH_x	: $PyrH_x$	75 : 25
3	BK + iNicK	B : pyridine	25 : 75	BH_x	: $PyrH_x$	76 : 24
4	α-NaK + PicK	Na : pyridine	93 : 7	NaH_x	: $PyrH_x$	10 : 90
5	α-NaK + NicK	Na : pyridine	79 : 21	NaH_x	: $PyrH_x$	20 : 80
6	α-NaK + iNicK	Na : pyridine	84 : 16	NaH_x	: $PyrH_x$	15 : 85
7	BK + FurK	B : furan	10 : 90	BH_x	: $FurH_x$	90 : 10
8	α-NaK + FurK	Na : furan	12 : 88	NaH_x	: $FurH_x$	85 : 15
9	BK + ThiK	B : thiophene	10 : 90	BH_x	: $ThiH_x$	90 : 10
10	α-NaK + ThiK	Na : thiophene	42 : 58	NaH_x	: $ThiH_x$	55 : 45
11	BK + PolK	B : pyrrole	15 : 84	HB_x	: $PolH_x$	85 : 15
12	α-NaK + PolK	Na : pyrrole	25 : 75	NaH_x	: $PolH_x$	75 : 25

[a] Abbreviations: The same as in Table I and II; ThiK potassium 2-thiophenecarboxylate, PolK potassium 2-pyrrolecarboxylate, BH_x, NaH_x, $PyrH_x$, $FurH_x$, $ThiH_x$, $PolH_x$ mixture of benzene, naphthalene, pyridine, furan, thiophene, or pyrrole carboxylic acids; the starting salts of acids were taken into reaction in millimolar amounts as is indicated by symbols; reaction temperature 400°C; catalyst CdI_2 10%; pressure of CO_2 in ampoules 3 atm; reaction time 10 min; [b] mixture of hydrocarbons and heterocycles.

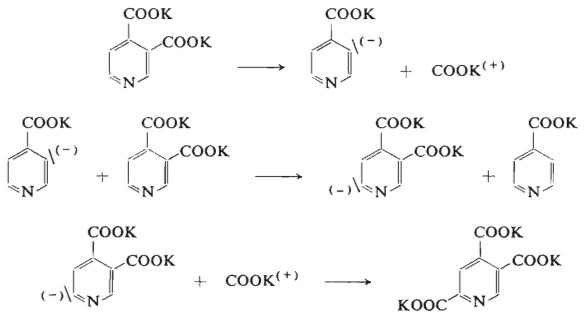
TABLE V

Heating of the Salts of Heterocyclic Carboxylic Acids in the Presence of Water

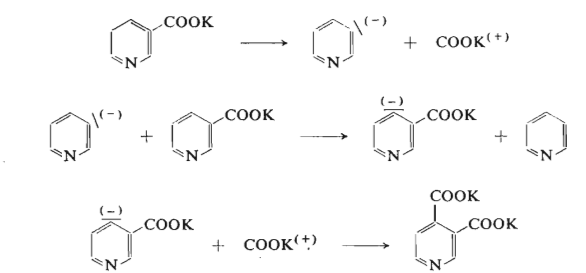
Exp. No	Starting compounds[a]	Products			
		heterocycle[b]	%	acid[c]	%
1	PicK	pyridine	93	$PyrH_x$	6
2	NicK	pyridine	88	$PyrH_x$	8
3	i NicK	pyridine	89	$PyrH_x$	9
4	FurK	furan	90	$FurH_x$	4
5	ThiK	thiophene	93	$ThiH_x$	4
6	PolK	pyrrole	91	$PolH_x$	6

[a] Abbreviations same as in Table I—IV; the salts of the starting acids were taken into reaction in millimolar amounts; temp. 400—410°C; time 15 min; pressure CO_2 3 atm; catalyst CdI_2 10% (per weight of the salts); [b] percents calculated for complete decarboxylation; [c] percents calculated on the basis of the weight of the starting salt.

a carboxylate cation, equation (*D*) for transprotonation, and equation (*E*) for reverse carboxylation of the corresponding carbanion.



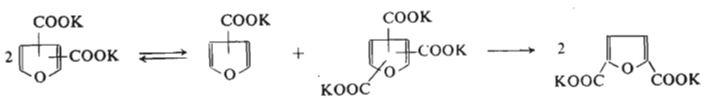
For the transcarboxylation of potassium nicotinate decarboxylation equation (*F*) applies, further transprotonation equation (*G*) leading to pyridine, which is, in analogy to potassium benzoate or naphthoate, an irreversible equation, finally, carboxylation equation (*H*) which leads to the formation of the corresponding potassium pyridine carboxylate.



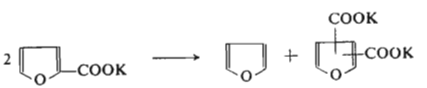
Furan Carboxylic Acids

The same methods which were employed for the determination of the mechanism of transcarboxylation of pyridine carboxylic acids salts were also used in the case of the reactions of furan carboxylic acids salts. From Table I (experiments 9, 10, 15, 16) it follows that the incorporation of the radionuclide ^{14}C from the atmosphere

of $^{14}CO_2$ into carboxylate groups of furan carboxylic acids takes place in the same manner as in the case of the salts of benzene, naphthalene, or pyridine carboxylic acids. The transcarboxylation of these salts in the presence of substances liberating protons, for example water or inorganic acids, results in a smooth decarboxylation under formation of furan (Table V, experiment 4). When the course of transcarboxylation was followed (Table VI, experiments 1–5) it was observed that during the reaction of furan carboxylic acids salts similar reactions take place as in the case of transcarboxyliations of the salts of benzene, naphthalene, or pyridine carboxylic acids, leading to the formation of a mixture of furan carboxylic acids in which the 2,5-isomer predominated (equations (*I*), (*K*)).

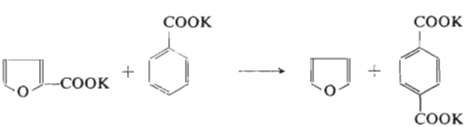


(*I*)

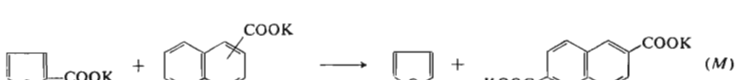


(*K*)

During the transcarboxylations of furan carboxylic acids in mixtures with the salts of benzene or naphthalene carboxylic acids the transfer of the carboxylate group from the furan nucleus to the benzene or naphthalene nucleus takes place according to equations (*L*) and (*M*) (Table IV, experiments 7, 8).



(*L*)

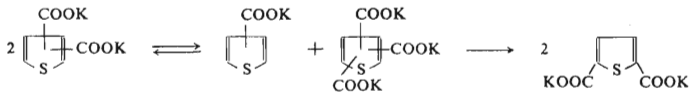


(*M*)

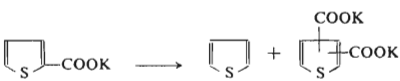
Thiophene Carboxylic Acids

The analysis of the experimental results obtained on studying the mechanism of the transcarboxylation of thiophene carboxylic acids salts by the above mentioned

methods (Table I, experiments 17, 18; Table VII, experiments 1 – 5) shows that the reaction also takes place by intermolecular decarboxylation-recarboxylation according to equations (*N*) and (*O*).

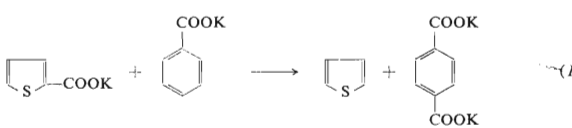


(*N*)



(*O*)

Transcarboxylation of thiophene carboxylic acids salts in mixtures with the salts of benzene or naphthalene carboxylic acids takes place in the first case under an unambiguous transfer of the carboxylate group into the benzene nucleus, while in the second case the group is only partly transferred to the naphthalene nucleus (Table IV, experiments 9, 10), according to the equations (*P*) and (*R*).



(*P*)

(*R*)

Pyrrole Carboxylic Acids

Pyrrole carboxylic acids have a special position among the investigated heterocyclic acids because they carry an acid hydrogen in their nucleus on the nitrogen atom. However, it was shown that the transcarboxylation reactions of their salts take place in a similar manner to that of the salts of the above discussed acids, *i.e.* by ionic, intermolecular decarboxylation-recarboxylation (Table I, experiments 18, 20; Table V, experiment 6; Table VIII, experiments 1 – 5) according to equations (*S*) and (*T*).

TABLE VI

Composition of the Reaction Mixtures (%) in Transcarboxylations of the Salts of Furan Carboxylic Acids

Exp. No	Starting compounds[a]	Time min	Furan[b]	Carbonized fraction[c]	Acids[d]			
					FurH	$FurH_2$	$FurH_3$	2,5-$FurH_2$
1	FurK	1	5	—	90	4	—	traces
2	FurK	4	47	8	40	20	9	32
3	FurK	12	85	20	9	32	3	54
4	2,5-$FurK_2$	4	2[e]	traces	2	4	—	90
5	2,5-$FurK_2$	16	6[e]	7	6	7	—	85
6	$FurK_x$	16	11[e]	14	10	27	6	57

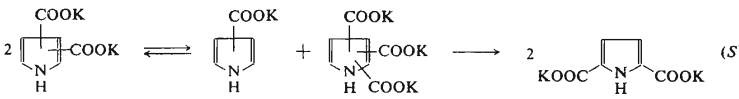
[a] Abbreviations are the same as in Table I, FurH mixture of furan monocarboxylic acids, $FurH_2$ mixture of furan dicarboxylic acids, $FurH_3$ mixture of furan tricarboxylic acids, $FurK_x$ mixture of potassium salts of furanmono-, di-, and tricarboxylic acids. Initial salts were taken into reaction in millimolar amounts; temp. 370–380°C; catalyst 10% CdI_2 per weight of the salts; pressure of CO_2 3 atm; [b] molar percents per theoretical yield of the reaction; [c] weight percents per solid fraction of the reaction mixture; [d] molar percents related only to the mixture of acids; [e] weight percents per total reaction mixture.

TABLE VII

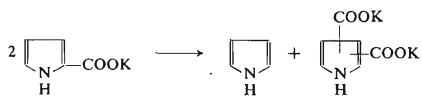
Composition of the Reaction Mixtures (%) in Transcarboxylations of the Salts of Thiophene Carboxylic Acids

Exp. No	Starting compounds[a]	Time min	Thiophene[b]	Carbonized fraction[c]	Acids[d]			
					ThiH	$ThiH_2$	$ThiH_3$	2,5-$ThiH_2$
1	2 ThiK	1	3	—	92	6	—	—
2	2 ThiK	4	35	6	45	24	8	22
3	2 ThiK	12	84	15	10	29	4	58
4	2,5-$ThiK_2$	4	2[e]	—	1	5	—	93
5	2,5-$ThiK_2$	16	8[e]	5	5	8	—	86
6	$ThiK_x$	16	10[e]	13	9	26	6	58

[a–e] Same as in Table VI. Abbreviations: ThiK potassium 2-thiophenecarboxylate, 2,5-$ThiK_2$ potassium 2,5-thiophenedicarboxylate, ThiH, $ThiH_2$, $ThiH_3$ mixture of thiophenemono-, di-, and tricarboxylic acids; 2,5-$ThiH_2$ 2,5-thiophenedicarboxylic acid; $ThiK_x$ mixture of potassium salts of thiophene mono-, di-, and tricarboxylic acids.

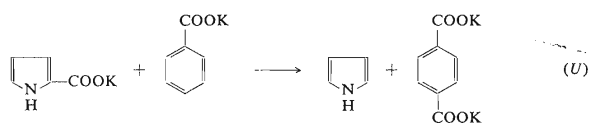


(S)

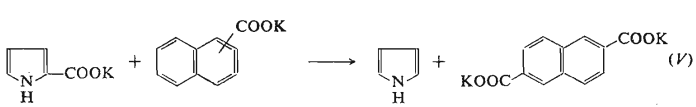


(T)

When transcarboxylated in mixtures with the salts of benzene or naphthalene monocarboxylic acids the transfer of the carboxylate group from the pyrrole nucleus to the benzene or naphthalene nuclei (Table IV, experiments 11, 12) takes place according to equations (*U*) and (*V*). Thus, it can be stated that the transcarboxylation of the salts of acids with a heterocyclic nucleus in the molecule takes place *via* rather complex reaction products, following the same mechanism as in the case of the transcarboxylation of the salts of benzene or naphthalene carboxylic acids, *i.e.* by intermolecular decarboxylation-recarboxylation combined with the splitting off and the addition of protons. Lower yields of the final products are caused both by a lesser thermal stability of the heterocyclic acids salts, and by the lower crystallisation ability of the end products.



(U)



(V)

EXPERIMENTAL

Compounds Used

α-Picolinic acid was prepared by oxidation of α-picoline according to Singer and McElvain[18], m.p. of hydrochloride 210°C (lit.[18] 210—212°C); m.p. 138°C (lit.[19] 137—139°C). Nicotinic acid, m.p. 235—237°C (lit.[20] 236—237°C); methyl ester m.p. 38°C. Isonicotinic acid, m.p. 312—316°C (lit.[20] 315—316°C). 3,4-Pyridinedicarboxylic acid was prepared according to

TABLE VIII

Composition of the Reaction Mixtures (%) in Transcarboxylations of the Salts of Pyrrole Carboxylic Acids

Exp. No	Starting compounds[a]	Time min	Pyrrole[b]	Carbonized fraction[c]	Acids[d]			
					PolH	$PolH_2$	$PolH_3$	2,5-$PolH_2$
1	2 PolK	1	4	—	95	4	—	—
2	2 PolK	4	29	8	49	30	6	13
3	2 PolK	12	81	25	9	34	5	53
4	2,5-$PolK_2$	4	4[e]	3	3	9	—	89
5	2,5-$PolK_2$	16	10[e]	8	8	12	—	80
6	$PolK_x$	16	11[e]	12	10	29	7	55

[a–e] Same as in Table VI but for the reaction temperature: 360–370°C. Abbreviations: PolK potassium 2-pyrrolecarboxylate, 2,5-$PolK_2$ potassium 2,5-pyrroledicarboxylate, PolH, $PolH_2$, $PolH_3$ mixture of pyrrolemono-, di-, and tricarboxylic acids; 2,5-$PolH_2$ 2,5-pyrroledicarboxylic acid.

Ahrens[21], m.p. 262–264°C (lit.[21] m.p. 264–268°C). 2,5-Pyridinedicarboxylic acid was prepared according to Meyer and Staffen[22], m.p. 252–255°C (lit.[22] m.p. 254°C); dimethyl ester m.p. 160–163°C (lit.[22] m.p. 164°C). 2-Furancarboxylic acid was prepared according to Wilson[23], m.p. 123–130°C (lit.[23] m.p. 125–132°C, 134°C lit.[24]). 2-Thiophenecarboxylic acid was prepared on oxidation of 2-acetylthiophene with chlorite[25], m.p. 123–125°C (lit.[25] m.p. 126°C). 2-Pyrrolecarboxylic acid was prepared by condensation of pyrrole potassium and carbon dioxide, m.p. 178°C (decomp.) (lit.[26] m.p. 192°C (decomp.); methyl ester m.p. 69–70°C (lit.[27] m.p. 73°C). 2,5-Furandicarboxylic acid, prepared on heating of mucic acid with sulfuric acid[28], does not melt up to 325°C (lit.[29] does not melt up to 320°C); dimethyl ester m.p. 107–111°C (lit.[28] m.p. 112°C). 2,5-Thiophenedicarboxylic acid does not melt up to 350°C (lit.[30]); dimethyl ester m.p. 144–146°C (lit.[30] m.p. 146–147°C). 2,5-Pyrroledicarboxylic acid, decomposes (blackening) at about 250°C (lit.[31] decomp. at 260°C); dimethyl ester m.p. 129–131°C (lit.[26] m.p. 132°C).

A mixture of furan carboxylic acids of the approximate composition: 25% furanmono-, 60% furandi-, and 15% furantricarboxylic acids, was obtained from the acidified solution of the transcarboxylation mixture of the salts of furan carboxylic acids after filtration off of the main fraction of 2,5-furandicarboxylic acid. Its analysis was carried out in the form of methyl esters by gas chromatography. After its transformation to a mixture of potassium salts it was used as the starting material for transcarboxylation reactions.

A mixture of thiophene carboxylic acids (approx. 23% thiophenemono-, 65% thiophenedi-, 12% thiophenetricarboxylic acids) was obtained and analysed in a similar manner as the preceding mixture.

The mixture of pyrrole carboxylic acids (composition: 27% pyrrolemono-, 58% pyrroledi-, and 15% pyrroletricarboxylic acids) was prepared and analysed as in the two preceding cases.

Potassium salts of corresponding acids were prepared by dissolution of the acid in a potassium hydroxide solution (analytical grade) and neutralisation (phenolphthalein); the solution was evaporated to dryness and the solid residue was powdered and dried at 150°C/0·01 Torr. The

catalyst was added to the samples in the form of finely ground CdI_2 and it was thoroughly mixed with the acid salt. The amount of the catalyst made 10% of the weight of the initial material. The esters of the acids were prepared either using an ethereal diazomethane solution or on treatment with a methanolic hydrogen chloride solution.

Procedure and the Analysis of the Reaction Mixture

The experiments were carried out in sealed ampules applying the method described earlier[7,13]. The amount of single samples was 1—2 mmol and the quantity of the catalyst (CdI_2) was 10% of the weight of the salts. The working up of the reaction mixture was carried out in a similar manner as described earlier[7,13]. Mixtures of the hydrocarbon and the heterocycle were isolated by freezing them out into the tip of the ampoule at −78°C, setting aside the tips, and the residual hydrocarbon was rinsed from the reaction ampoule 5 times with 0·2 ml of ether, both fractions were combined and the ether evaporated; in the case of mixed transcarboxylations the sample was analysed by gas chromatography using the corresponding internal standard. Only when a mixture of furan and naphthalene was analysed the procedure was changed because of the big diference in their boiling points and the too low boiling point of furan. From the weighed reaction mixture furan was distilled off and naphthalene was then weighed differentially. The analysis of the mixture of acids was carried out both by gas chromatography of their methyl esters[7,13,17] and by paper chromatography combined with UV spectrometry, or by a combination of both methods[17].

Experiments with the incorporation of radionuclide ^{14}C from the $^{14}CO_2$ atmosphere into the molecules of corresponding acids during the transcarboxylation of their salts were carried out with the salts of acids applied in a very thin layer on the carrier[7,13] in an amount of approx. 1/2 mmol. The reaction mixture was analysed by a method described earlier[7,13].

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