TRANSCARBOXYLATION REACTIONS OF SALTS OF ORGANIC ACIDS. XVIII.*
THE ANOMALOUS COURSE OF TRANSCARBOXYLATION OF SALTS OF BIPHENYL CARBOXYLIC ACIDS

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The mechanism of the anomalous course of transcarboxylation of salts of biphenyl carboxylic acids was studied. Experimental findings obtained by methods used previously in mechanistic studies of transcarboxylations of benzene- and naphthalene carboxylic acids salts, together with the results of mixed transcarboxylation and deuterium exchange, proved that the transcarboxylation of salts of biphenyl carboxylic acids is an intermolecular ionic decarboxylation-recarboxylation process which is combined with intermolecular transprotonation. Besides these reactions, a reversible intramolecular cyclisation reaction affording fluorenone derivatives takes place.

Transcarboxylation reactions of salts of biphenyl carboxylic acids were studied by Raecke[1,2] who obtained from potassium diphenate in a low yield (10%) the salt of the expected 4,4'-biphenyldicarboxylic acid, together with other, not identified biphenyl carboxylic acids. A similar reaction of potassium 2-biphenylcarboxylate is mentioned by Ogata and coworkers[3] who isolated 4,4'-biphenyldicarboxylic acid, and 4- and 3-biphenylcarboxylic acids (0·02%, 1·1% and 0·8%, respectively), together with starting 2-biphenylcarboxylic acid (16·2%) and a great amount of biphenyl (102%, based on disproportionation). These unexpected results indicate a decarboxylation, rather than a disproportionation, reaction of the 2-biphenylcarboxylate. Dozen[4] who repeated the reaction under the same conditions as Raecke[1,2], obtained a relatively high yield of 4,4'-isomer (45%); however, this yield may be due to the presence of other biphenyl carboxylic acids in the mixture[5,6].

The great inconsistency of the results described in the literature, the complicated reaction course and mixtures, and particularly the formation of fluorenone derivatives in the transcarboxylation of the salts of biphenyl dicarboxylic acids led us to perform a more detailed mechanistic investigation of these reactions. As we have shown[7-10], following fundamental conditions must be satisfied in order to enable a smooth path of transcarboxylation reactions of salts of aromatic carboxylic acids: *1.* The salts of the reacting acids must be able to form carbanions by splitting off carboxylate groups or protons, *2.* Proton-releasing compounds must not be present in the reaction

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mixture, 3. The end product must be thermally stable and must exhibit a great crystallization ability in order not to decompose during the reaction and to crystallize out of the reaction mixture.

All these conditions are satisfied e.g. for benzene or naphthalene carboxylic acids[7-13], whereas e.g. in the case of salts of toluic acids[3,4,14,15] or heterocyclic carboxylic acids[16] the lower yields of end products are due to their lesser thermal stability and lower crystallization ability. In accord with the literature[2-4], we have found that transcarboxylation of biphenyl carboxylic acids salts does not lead to the anticipated thermally stable and crystallizable 4,4'-biphenyldicarboxylate (Table I, experiments 8, 9) but to a very complicated mixture of acids in which no acid predominates. Theoretically, three isomeric biphenyl monocarboxylic, twelve dicarboxylic and twenty four tricarboxylic acids can arise and, therefore, their isolation from the complex reaction mixture is difficult. Thus, for example, from the product of transcarboxylation of potassium 2-biphenylcarboxylate, we isolated all three biphenyl monocarboxylic acids, of the biphenyl dicarboxylic acids the 2,3-, 2,4-,

TABLE I

Transcarboxylation Reactions of Salts of Biphenyl Carboxylic Acids[a]

No	Starting compounds[b]	T, °C	Time min	Neutral, %		Acids[e], %				
				Σ^c	ratio Biph : Fl	Σ^d	BiphH	BiphH$_2$	4,4'-BiphH$_2$	BiphH$_3$
1	2-BiphK	390	4	86·2	88 : 12	69	30	70	tr.	tr.
2	2-BiphK	390	120	98·0	95 : 5	64	27	71	2	tr.
3	3-BiphK	400	15	25·0	100 : 0	75	68	29	1	—
4	4-BiphK	400	15	19·0	100 : 0	81	77	18	2	—
5	2,2'-BiphK$_2$	390	10	15·7	89 : 11	68	15	78	7	1·5
6	2,2'-BiphK$_2$	400	120	6·0	97 : 3	77	14·5	72	11	2·5
7	3,3'-BiphK$_2$	430	30	8·0	100 : 0	80	7·5	84·5	5	—
8	4,4'-BiphK$_2$	435	30	6·25	100 : 0	89	0·5	2	98	—
9	4,4'-BiphK$_2$	435	60	7·0	100 : 0	86	1	2·5	96	—

[a] Abbreviations: 2-, or 3-, or 4-BiphK potassium 2-, or 3-, or 4-biphenylcarboxylate, respectively; 2,2'-, or 3,3'-, or 4,4'-BiphK$_2$ potassium 2,2'-, or 3,3'-, or 4,4'-biphenyldicarboxylate, respectively; 4,4'-BiphH$_2$ 4,4'-biphenyldicarboxylic acid; Biph biphenyl; Fl fluorenone; BiphH mixture of biphenyl monocarboxylic acids; BiphH$_2$ or BiphH$_3$ mixture of biphenyl di- or tricarboxylic acids, respectively. [b] The reaction was carried out in millimolar amounts in sealed ampoules, pressure CO$_2$ 3 atm. catalyst CdI$_2$ (3% Cd^{2+} per weight of the salts). [c] w% of the mixture of biphenyl and fluorenone (in experiments 1 and 2 based on the disproportionation of 2-biphenylcarboxylate). [d] w% (in experiments 1 and 2 based on the disproportionation of 2-biphenylcarboxylate). [e] Molar percents, based on the mixture of acids. The hydrocarbons, as well as the acids (as methyl esters) were analyzed by gas chromatography.

2,5-, 2,6-, 3,4- and 3,5-isomers, further small amount of 4,4′-, 3,3′- and 2,2′-biphenyl dicarboxylic acids, and a small quantity of five unidentified acids which — according to their retention times on vapour phase chromatogram — are biphenyl dicarboxylic acids. Only very small amount of biphenyl tricarboxylic and fluorenone carboxylic acids was found and it was not possible to separate and identify them; the sum (less than 10%) of the latter was determined by infrared spectrometry (Table II).

TABLE II

Composition of the Reaction Mixtures (%) in Transcarboxylations of Potassium 2-Biphenyl-carboxylate and Potassium 2,2′-Biphenyldicarboxylate

Products[a]	2-BiphK	2,2′-BiphK$_2$	2,2′-BiphK$_2$[b]
Biphenylcarboxylic acids[f]			
2-	3·9	2·5	3·5
3-	4·1	5·6	6·7
4-	4·2	7·4	9·8
2,2′-	2·1	18·5	7·4
3,3′-	4·0	7·6	5·7
4,4′-	0·9	6·5	17·2
2,3-	12·0	4·7	6·8
2,5-	10·3	3·4	4·6
2,6-	2·0	2·5	3·5
3,4-	17·0	4·6	4·7
3,5-	12·6	5·7	4·8
Unidentified acids[h]	14·5	16·6	17·8
Tricarboxylic acids	5·0	4·5	3·3
Fluorenone carboxylic acids	8·1	7·5	3·5
Others			
Biphenyl + fluorenone	113·0[c]	10·0[d]	21·8[d]
Biphenyl[e]	89·0	79·2	98·3
Fluorenone[e]	11·0	20·8	1·7
Carbonized fraction[g]	19·5	13·6	9·6

[a] Abbreviations and reaction conditions see Table I; temperature 390—400°C; time 10 min; the reaction mixtures were analysed by gas chromatography and IR spectroscopy. [b] The reaction was carried out in an autoclave with 0·1 mol 2,2′-BiphK$_2$; time 120 min; pressure CO_2 50 atm. Molar percents based on: [c] biphenyl and on disproportionation, [d] biphenyl and on decarboxylation. [e] The content of biphenyl and fluorenone in their mixture. [f] The acids in the reaction mixture. [g] w%, based on the starting compounds. [h] Sum of 2,3′-, 2,4′-, 3,4′- and 2,4-biphenyldicarboxylic acids.

A closer analysis of the reaction mixtures revealed that their composition depends on whether the carboxyl groups of the starting biphenyl carboxylic acids are attached to one or to both benzene nuclei of the biphenyl system. In the first case the intermolecular transfer of carboxylate groups takes place only on the same benzene ring on which these groups are attached, whereas in the second case certain amount of biphenyl carboxylates having carboxyls on both benzene rings of biphenyl system arises, in addition to isomers with carboxyls on one benzene ring. As an example we may mention the different results of transcarboxylation of potassium 2,2'-biphenyldicarboxylate (diphenate) and potassium 2-biphenylcarboxylate. The first compound gives, besides the biphenyl dicarboxylates (equation (B)), also a small amount of potassium 4,4'-biphenyldicarboxylate (equation (A)) (Table II) whereas the 2-biphenylcarboxylate affords no 4,4'-biphenyl dicarboxylate giving only a complex mixture of biphenyl carboxylates in which isomers with carboxyls attached only to one benzene ring of the biphenyl system predominate (equation (C)) (Table II). Moreover, this reaction affords besides biphenyl a certain (variable) amount of cyclic ketone fluorenone $(10-20\%)$ as a product of reversible cyclisation side-reaction which is enabled by the favourable steric situation in the molecule of potassium 2-biphenylcarboxylate (equation (D)), (Table II). This cyclisation takes place to a small extent also in the above-mentioned transcarboxylation of potassium diphenate and affords fluorenone carboxylic acids. According to infrared spectroscopy, their content in the reaction mixture is $5-10\%$ (Table II).
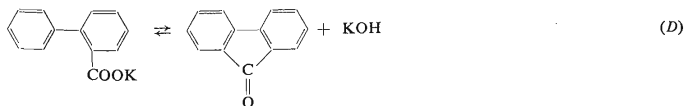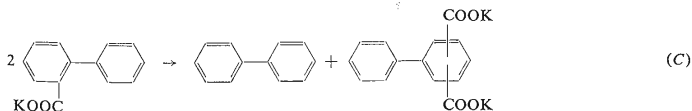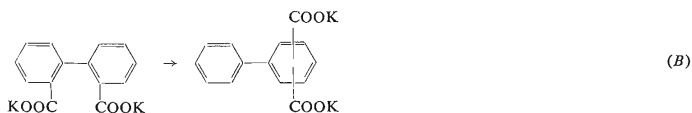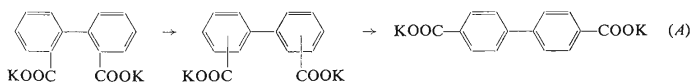
In view of the mentioned complex course of transcarboxylation reactions of biphenyl carboxylates, it was of interest to know whether the mechanism of these reactions is analogous to the mechanism of transcarboxylation of other aromatic carboxylic acids salts, *i.e.* whether it is an intermolecular ionic decarboxylation-recarboxylation process which is combined with an intermolecular transprotonation, or rather an intramolecular cyclic transcarboxylation between benzene rings of the biphenyl system, accompanied with formation of fluorenone and its carboxy derivatives.

We made use of methods similar to methods employed in determination of mechanism of transcarboxylations of benzene- or naphthalene carboxylic acids salts and, further, a new simple method of transcarboxylation of biphenyl monocarboxylates in a mixture with potassium benzoates or naphthoates[13], or mixed deuterium exchange between benzoate-d_5 and non-labelled biphenyl carboxylates[17].

Using the method of radionuclide ^{14}C incorporation from the $^{14}CO_2$ atmosphere into carboxylate groups of biphenyl carboxylic acids salts, we have found that the amount of the incorporated ^{14}C corresponds to the statistical exchange of $^{14}CO_2$ for non-radioactive carbon dioxide liberated from the carboxylate groups of the salts (Table III, experiments 1—5). Thus, the incorporation of ^{14}C into molecules of biphenyl carboxylates is analogous to that in transcarboxylations of salts of benzene or naphthalene carboxylic acids in the $^{14}CO_2$ atmosphere[7,8].

Because transcarboxylation of biphenyl carboxylates results in a complex mixture of acids instead of giving a homogeneous end product, the mono-, di- and tricarboxylic acids were determined only as sums. In the case of the transcarboxylation of biphenyl monocarboxylates, also the volatile part (*i.e.* biphenyl and fluorenone) was analysed. From the experiments it follows

TABLE III

Incorporation of Radionuclide ^{14}C from the Reaction Atmosphere $^{14}CO_2$ into Carboxyl Groups of the Salts of Biphenyl Carboxylic Acids in the Transcarboxylation Reactions

No	Starting compound[a]	Products, %		4,4′-BiphH$_2$[d]
		Biph[c]	BiphH$_x$[c]	
1	2 2-BiphK[b]	95	74 (63)[e]	traces
2	2 2-BiphK	—	88 (0)[e]	—
3	2,2′-BiphK$_2$[b]	20	72 (62)	11 (64)[e]
4	2,2′-BiphK$_2$	—	82 (0)	—
5	4,4′-BiphK$_2$[b]	—	—	92 (0)[e]

[a] Abbreviations: The same as in Table I; DifH$_x$ mixture of biphenyl carboxylic acids. Temperature 400°C; time 15 min. Starting compounds were taken into reactions in millimolar amounts, as indicated by symbols. The molar ratio of $^{14}CO_2$ to carboxylate groups was 1 : 2, *i.e.* one $^{14}CO_2$ to two equivalents of potassium 2-biphenylcarboxylate or one equivalent of potassium 2,2′-biphenyldicarboxylate. [b] Catalyst CdI$_2$, 3% wt/wt Cd^{2+} based on the weight of the salts. [c] In the experiment 1, the yield (%) is based on the disproportionation of 2-biphenylcarboxylate; in the experiment 3 the percents (wt/wt) are based on decarboxylation. [d] wt%. [e] Specific radioactivity in percents relative to the radioactivity of $^{14}CO_2$ taken into the reaction.

TABLE IV

Composition of the Reaction Mixtures in Mixed Transcarboxylations of Potassium Benzoate or α-Naphthoate with Potassium 2-Biphenylcarboxylate or 2,2′-Biphenyldicarboxylate

No	Starting compounds[a]	Ratio of mol %	
		hydrocarbons	acids
1	BK + 2-BiphK	B : Biph (20 : 80)	BH_x : $BiphH_x$ (84 : 16)
2	2 BK + 2,2′-BiphK$_2$	B : Biph (25 : 25)	BH_x : $BiphH_x$ (78 : 22)
3	α-NaK + 2-BiphK	Na : Biph (40 : 60)	NaH_x : $BiphH_x$ (55 : 45)
4	2 α-NaK + 2,2′-BiphK$_2$	Na : Biph (48 : 52)	NaH_x : $BiphH_x$ (50 : 50)

[a] Abbreviations: BK potassium benzoate, α-NaK potassium α-naphthoate, B benzene, Na naphthalene, BH_x or NaH_x mixture of benzene or naphthalene carboxylic acids, respectively; other abbreviations and reaction conditions see Table I; temperature: experiments 1,2 400–410°C, experiments 3,4 380–390°C, time: experiments 1,2 10 min, experiments 3,4 12 min. Starting compounds were taken into reaction in the ratio indicated by symbols.

TABLE V

Composition of Deuterated Products in Mixed Transcarboxylations of Potassium Salts

The reaction was carried out in millimolar amounts in sealed ampoules at 400°C and at a CO_2 pressure 3 atm, catalyst CdI$_2$ (3% Cd^{2+} relative to the weight of the salts), time 10 min. Products were analysed by mass spectrometry of the methyl esters of the acids. Benzene was formed in negligible amount.

Mixture	Products, %					
	d_0	d_1	d_2	d_3	d_4	d_5
Equimolar mixture of benzoate-d_5 and 2-biphenylcarboxylate						
Benzoic acid	0·70	10·22	28·10	36·45	20·60	3·93
Benzenedicarboxylic acids	11·55	23·45	35·00	24·50	5·50	—
Biphenyl	25·38	33·80	24·02	12·06	3·68	1·05
Biphenylcarboxylic acids	8·63	24·40	33·80	23·50	7·30	1·94
Biphenyldicarboxylic acids	10·15	27·45	32·70	21·90	4·60	3·20
2 Equivalents of benzoate-d_5 and 1 equivalent of 2,2′-biphenyldicarboxylate						
Benzoic acid	2·0	8·5	27·0	34·5	22·4	5·5
Benzenedicarboxylic acids	9·5	24·5	35·4	22·0	6·0	—
Biphenyl[a]	5·2	9·0	11·0	15·0	15·1	14·0
Biphenylcarboxylic acids[b]	4·1	7·2	13·1	17·0	16·1	14·2
Biphenyldicarboxylic acids[c]	6·2	9·2	13·3	18·6	16·4	15·3

[a] d_6 10·1; d_7 8·1; d_8 5·1; d_9 4·5; d_{10} 3·0. [b] d_6 12·0; d_7 8·3; d_8 6·0; d_9 2·0; [c] d_6 10·0; d_7 7·1; d_8 3·9.

(Table I) that in the transcarboxylation of biphenyl dicarboxylates complicated disproportionation reactions take place giving rise to a complex mixture of acids. An appreciable amount of these acids has the carboxyl attached only to one benzene ring of the biphenyl system; the reaction affords relatively small amount of the expected 4,4′-biphenyldicarboxylate, although this derivative is thermally stable and its crystallization ability is considerable. According to the experiments 8 and 9 in Table I, this derivative practically does not enter transcarboxylation reactions. In addition to compounds already mentioned, the transcarboxylation of *ortho*-substituted biphenyl carboxylates gives fluorene (10—20%) and fluorenone carboxylates (less than 10%) (Table II and Table I, experiments 1, 2, 5, 6).

The potassium salts of biphenyl monocarboxylic acids were subjected to mixed transcarboxylation with an equimolar amount of potassium benzoate or α-naphthoate. In the first case, the benzoate is relatively smoothly carboxylated by the action of potassium 2-biphenylcarboxylate (Table IV, experiments 1, 2), whereas in the second case the reaction mixture contains approximately equimolar amounts of naphthalene, biphenyl, and naphthalene carboxylic and biphenyl carboxylic acids (Table IV, experiments 3, 4). Moreover, the results are complicated by the fact that salts of *ortho*-biphenyl carboxylic acids afford, in addition to the mixture of biphenyl carboxylic acids, fluorene and fluorenone carboxylic acids as products of a cyclisation side-reaction. In spite of this, the mentioned experimental results show that the transcarboxylations of biphenyl carboxylates proceed by an intermolecular ionic transcarboxylation between biphenylcarboxylate molecules.

A further interesting problem was the question of the transcarboxylation reactivity of carboxyl-substituted and carboxyl-unsubstituted benzene rings in a biphenyl. Since we had previously shown that transcarboxylation is directly connected with transprotonation we attempted to differentiate the reactivity of both benzene rings in 2-biphenylcarboxylate using the deuterium–protium exchange. We therefore carried out a transcarboxylation of an equimolar mixture of the deuterium-labelled benzoate and the non-labelled 2-biphenylcarboxylate. From the results we may infer that this exchange takes place mainly on one of the benzene rings of biphenyl (Table V). The small amount of biphenylmonocarboxylate-d_5 and biphenyldicarboxylate-d_4 or -d_5 can be ascribed with some degree of probability to a reversible cyclisation side-reaction which gives fluorenone from 2-biphenylcarboxylate (equation *D*), or to a certain, though low, transprotonation (and hence also transcarboxylation) reactivity of the second (unsubstituted) benzene ring in biphenyl (Table V). The difference between the reactivity of substituted and unsubstituted benzene rings in biphenyl system is shown by an intercomparison of exchange reactions in transcarboxylations of the mixtures: potassium benzoate-d_5 and 2-biphenylcarboxylate, and potassium benzoate-d_5 and 2,2′-biphenyl dicarboxylate (Table V). In the latter reaction a smooth exchange occurs on both benzene rings. This different behaviour of deuterium exchange between benzoate-d_5 and diphenate, and between benzoate-d_5 and 2-biphenylcarboxylate proves that in the case of 2-biphenylcarboxylate the exchange takes place preferentially on the carboxyl-substituted benzene ring of the diphenyl system. These experiments prove the difference in transprotonation reactivity of carboxyl-substituted and carboxyl-unsubstituted benzene rings in biphenyl system. Further, they prove that transprotonation, and hence also transcarboxylation, of biphenyl carboxylates proceeds by an intermolecular mechanism between individual molecules of biphenyl carboxylates, and not by an intramolecular transfer within the biphenyl carboxylate molecule.

The experimental results of all methods mentioned above allow to explain the anomalous course of intermolecular migration of carboxylate group from one benzene ring of biphenyl system to another in the transcarboxylation reaction of biphenyl carboxylates, and thus also to explain the formation of salts of biphenyl carboxylic

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$$(F)$$

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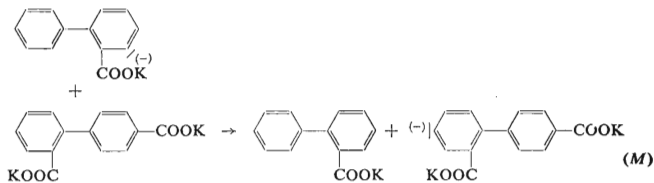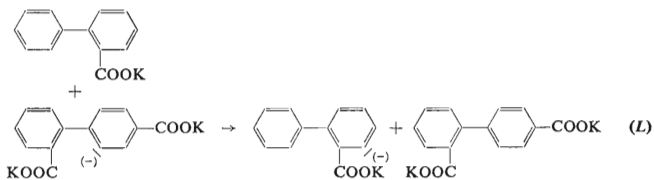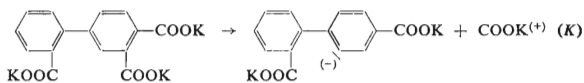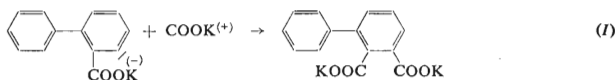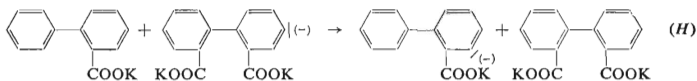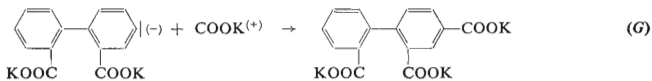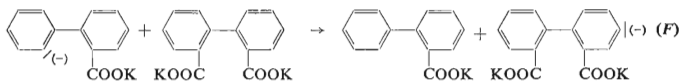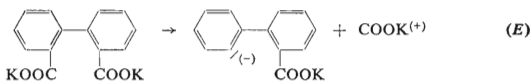
acids with carboxyl groups attached only to one benzene ring of the biphenyl system. This explanation rests first of all in lower reactivity of that benzene ring of biphenyl which is not substituted with carboxylate groups. Under this assumption, it follows from the intermolecular ionic mechanism that the carboxylate groups are successively transferred from one benzene ring of biphenyl to another. As an example we may mention the mechanism of transcarboxylation of potassium diphenate (2,2'-biphenyldicarboxylate) (the equations $(E) - (P)$ show only one of the whole series of possible reactions)
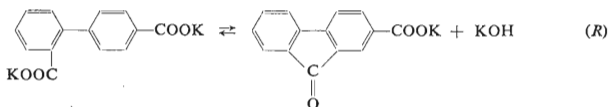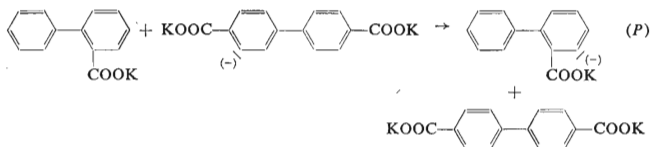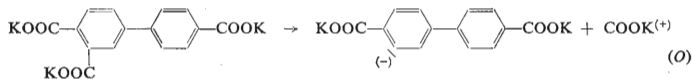
In the first reaction step, *i.e.* in the decarboxylation of diphenate (equation (E)), as well as in the second step, *i.e.* the removal of proton from the yet unreacted diphenate by the formed carbanion to give a biphenyl monocarboxylate (equation (F)), a molecule of biphenyl carboxylate is formed in which one of the benzene rings of the biphenyl system is devoid of carboxylate group. This stabilizes the ring to such an extent that an analogous reaction of this biphenyl monocarboxylate with another

carbanion results in removal of proton from that benzene ring on which the carboxylate group remained (equation (H)); thus, subsequent addition of a carboxylate cation may give rise to a biphenyl carboxylate with both carboxyl groups attached to the same benzene ring of the biphenyl system (equation (J)). It is evident from the above equations that the 4,4'-biphenylcarboxylate can arise from a diphenate only by the following reaction sequence: decarboxylation, transprotonation and recarboxylation (equations (E), (F), and (G)), new decarboxylation of the formed biphenyl tricarboxylate (equation (K)) followed by transprotonations (equations (L) and (M)), further recarboxylation of the corresponding carbanion (equation (N)), new decarboxylation of the tricarboxylate (equation (O)) and, finally, a transprotonation (equation (P)).

The equations describing the formation of 4,4'-biphenyldicarboxylate from potassium diphenate show that the probability of its formation is relatively low (disregarding the possible, though low, reactivity of the carboxyl-unsubstituted benzene rings, and at the same time assuming an equal reactivity of all carbons of the carboxyl-substituted benzene ring). On the other hand, all examples of the mentioned equations show a great preference for the formation of biphenyl carboxylates with carboxyls only on one benzene ring of biphenyl, this fact being in accord with experimental results (Table II). It must be born in mind, that potassium 4,4'-biphenyldicarboxylate exhibits a great thermal stability and crystallization ability and that it may crystallize out of the reaction mixture and thus shift the reaction equilibrium (Table I, experiments 8, 9). However, contrary to these factors favourable for the formation of the 4,4'-isomer, there are factors which are unfavourable: the formation of great amount of isomeric biphenyl carboxylates which act as fusing agents, the formation of side-products, *i.e.* fluorenone, fluorenone carboxylates, and decarboxylation products, further the substantially lowered reactivity of the carboxyl-unsubstituted benzene ring of the biphenyl system which acts against the formation of the 4,4'-isomer, and the transcarboxylation reactivity (though small) of the 4,4'-biphenyldicarboxylate itself (Table I, experiments 8 and 9), which practically returns this compound into the reaction. All these possibilities show the great complexity of transcarboxylation reactions of biphenyl carboxylates and the difficulty of formation of 4,4'-isomer in these reactions.

Finally, a side-reaction accompanying transcarboxylations of o-biphenyl carboxylates deserves comment. It is the formation of fluorenone and fluorenone carboxylates from 2-biphenylcarboxylate and o-biphenyldicarboxylate, respectively, by a cyclisation reaction, under formation of potassium hydroxide (equations (D) and (R)). This reaction is analogous to the preparation of fluorenone from diphenic or o-phenylbenzoic acids or to the preparation of fluorenone carboxylic acids from o-biphenyldicarboxylic acids by their heating with sulphuric acid. This cyclization side reaction of o-biphenylcarboxylates is reversible because the formed potassium hydroxide is capable of splitting fluorenone[52] and fluorenone carboxylates[36,37,40,41,50,51]

to 2-biphenylcarboxylate and to the corresponding biphenyl dicarboxylates, respectively. This is in accord with the fact that the amount of fluorenone in the reaction mixture decreases in the later phases of the reaction (Table II and Table I, experiments 1, 2, 5, 6). However, in addition to this cleavage reaction, another reaction may take place: it is the neutralization of the arising potassium hydroxide with carbon dioxide from the reaction atmosphere which affords potassium hydrogen carbonate and this — as a proton releasing agent — may cause the decarboxylation of the biphenylcarboxylate molecules. This reaction is indicated by the high content of biphenyl in the reaction mixtures resulting from transcarboxylations of biphenyl mono- as well as dicarboxylates (Table II and Table I, experiments 1, 2, 5, 6). According to the analyses of the reaction mixtures, it seems that in transcarboxylations both these reactions to a certain extent take place.

The cyclisation which affords fluorenone and fluorenone carboxylates is a reversible reaction, and the reverse reaction (cleavage) acts against the transfer of carboxylate groups from one benzene ring of biphenyl to another. It is known that the cleavage of fluorenone carboxylates by potassium hydroxide gives mainly biphenyl dicarboxylates with carboxylate groups on both benzene rings of biphenyl, thus partly supporting the 4,4'-biphenyldicarboxylate formation. This reversible cyclisation — cleavage reaction is also the cause of the partial exchange of deuterium for protium on the carboxyl-unsubstituted benzene ring of biphenyl in the mixed transcarboxylation of benzoate-d_5 and 2-biphenyldicarboxylate (besides a certain, low, transcarboxylation reactivity of the carboxyl-unsubstituted benzene ring of the biphenyl system).

All the equations mentioned above show a very complicated course of the thermal reaction of salts of biphenyl carboxylic acids, even though the basic mechanism of the main reaction — transcarboxylation — is simple and analogous to the mechanism of transcarboxylation of salts of other aromatic carboxylic acids. The mentioned main reaction is accompanied by reversible cyclisations which afford fluorenone and its carboxy derivatives. These reactions are made possible by specific structural properties of biphenyl carboxylic acids.

EXPERIMENTAL

Starting and Reference Compounds

2-Biphenylcarboxylic acid was prepared by fusion of fluorenone with potassium hydroxide; m.p. 114°C (lit.[18] m.p. 110—111°C, 115°C lit.[19], 114—115°C lit.[20], 110—111°C lit.[21]); its potassium salt was obtained by neutralisation with potassium hydroxide solution (phenolphthaleine) and by drying at 105°C/0·01 Torr; its methyl ester was prepared by esterification with diazomethane[21], liquid[18], b.p. 100°C/0·01 Torr (reported[18] b.p. 308°C/760 Torr).

3-Biphenylcarboxylic acid: The methyl ester was prepared by heating of methyl *m*-iodobenzoate with iodobenzene in the presence of copper powder in a sealed ampoule at 260°C for 5 hours, according to a modified method of Ullmann and Löwenthal[22]. From the formed mixture of biphenyl, methyl 3-biphenylcarboxylate and dimethyl 3,3'-biphenyldicarboxylate, the lower-boiling fraction (biphenyl, non-reacted iodobenzene and methyl *m*-iodobenzoate) was distilled off, and

the residue was chromatographed of a neutral alumina column (activity II). 3-Biphenylcarboxylic acid was obtained from its ester by saponification with potassium hydroxide, m.p. 159°C (lit.[23] m.p. 160°C, 160—161°C lit.[20,24]). Its potassium salt was prepared by neutralisation with potassium hydroxide (phenolphthalcine) and dried at 110°C/0·01 Torr. Methyl ester was obtained by treatment with diazomethane[20,24], b.p. 99—103°C/0·01 Torr.

4-Biphenylcarboxylic acid was a Koch-Light product, m.p. 223°C, reported[25] m.p. 224°C; its potassium salt and methyl ester, m.p. 115°C (lit.[26] m.p. 117·5°C, 117—118°C lit.[24], 116—117°C lit.[20,21]) were obtained by procedures analogous to the preceding experiments.

2,2'-Biphenyldicarboxylic acid was a Koch-Light product, m.p. 226—228°C (lit.[27] m.p. 228 to 229°C, 225—228°C lit.[28]); potassium salt and dimethyl ester (m.p. 73°C, reported[29,30] m.p. 73—74°C) were prepared analogously to the preceding experiments.

Fluorenone-4-carboxylic acid was prepared by heating 2,2'-biphenyldicarboxylic acid with concentrated sulphuric acid according to Underwood and Kochmann[30]; its methyl ester melted at 138°C (reported[30] 139°C).

3,3'-Biphenyldicarboxylic acid: Dimethyl ester m.p. 102—104°C (lit.[22] m.p. 104°C, 105—106°C lit.[31]) was obtained by heating of methyl *m*-iodobenzoate with copper powder to 265°C for 6 hours[22,31]. The acid, m.p. 350—355°C (lit.[22] m.p. 356—357°C and >300°C lit.[31]) and its potassium salt were prepared in the same manner as described for 3-biphenylcarboxylic acid.

4,4'-Biphenyldicarboxylic acid was prepared from benzidine[32], its dimethyl ester, m.p. 212°C (lit.[33] m.p. 212—213°C, 214°C lit.[34], and 218°C lit.[35]), and potassium salt were obtained as described above.

2,3'-Biphenyldicarboxylic acid was prepared by fusion of fluorenone-1-carboxylic acid with potassium hydroxide according to Fittig and coworkers[36,37], m.p. 215—218°C (water), (lit.[36] m.p. 216°C, 219—221°C lit.[38]). Its dimethyl ester was prepared by treatment with diazomethane, m.p. 68 to 70°C (methanol), reported[37] m.p. 69·5°C; it was prepared also in a mixture with dimethyl esters of 2,2'-biphenyldicarboxylic and 3,3'-biphenyldicarboxylic acids by heating an equimolar mixture of methyl *o*-iodobenzoate and methyl *m*-iodobenzoate with copper powder to 265°C for 5 hours. In this case, the mixture was not separated into individual isomers and served only as standard for gas chromatography.

Fluorenone-1-carboxylic acid was obtained by heating 2,3-biphenyldicarboxylic acid with concentrated sulphuric acid to 50°C for 15 minutes[39], m.p. 192—194°C (dilute ethanol) (reported[39] m.p. 192°C and 196—197°C, lit.[38]).

2,4'-Biphenyldicarboxylic acid was prepared from fluorenone-2-carboxylic acid by fusion with potassium hydroxide at 200—220°C; m.p. 257—262°C (reported[41] m.p. 251—252°C, 264·5—265·5°C lit.[40]). Its dimethyl ester was obtained as a mixture with dimethyl esters of 2,2'-biphenyldicarboxylic and 4,4'-biphenyldicarboxylic acids by heating of an equimolar mixture of methyl *o*- and *p*-iodobenzoates with copper powder to 260—265°C for 5 hours. The mixture of esters was used as standard in gas chromatography. For identification, the dimethyl 2,4'-biphenyldicarboxylate was isolated in the following manner. First, from the mixture of the three esters the 4,4'-isomer was separated by two subsequent treatments with a ten-fold amount of boiling methanol in which this isomer is insoluble. Then, from the methanolic solution of the remaining two isomers, the 2,4'-isomer was separated by chromatography on neutral alumina (activity II). The dimethyl 2,4'-biphenyldicarboxylate melted at 82°C (reported[40] m.p. 83°C) and the corresponding acid, obtained by saponification, had m.p. 259—261°C.

Dimethyl 2,3-biphenyldicarboxylate was prepared by a reaction of diazonium salt of dimethyl 3-aminophthalate with benzene in an alkaline medium[39]; m.p. 91—92°C (light petroleum). reported[39] m.p. 94°C. Hydrolysis of the ester afforded the acid, m.p. 179°C (reported[39] 181°C),

Methyl 3,4'-biphenyldicarboxylate was obtained in a mixture with 3,3'- and 4,4'-isomers by heating of an equimolar mixture of methyl *m*- and *p*-iodobenzoates with copper powder in the same manner as described for the 2,4'-isomer. The ester mixture was used as standard for gas chromatography.

Dimethyl 3,4-biphenyldicarboxylate was prepared by a reaction of dimethyl phthalate with diazotised aniline in alkaline medium[39]; this procedure afforded also the 2,3-isomer. The 3,4-isomer was isolated by crystallization of sodium salts[42]. The acid melts at 188—190°C (reported[42] m.p. 189·2—190·1°C, 193—194°C lit.[43]); the dimethyl ester was obtained from the acid by treatment with diazomethane; m.p. 60—61°C (reported[43] m.p. 62°C).

Dimethyl 3,5-biphenyldicarboxylate was prepared by a reaction of dimethyl isophthalate (60 g) with a solution (80 ml) of diazotised aniline (from 20 g of aniline) in a solution of sodium hydroxide (20 g) in water (65 ml), methanol (150 ml) and dioxan (150 ml) under intensive stirring for 20 hours at room temperature. Fractionation of the reaction mixture afforded 10 g of the crude ester, b.p. 140—190°C/0·1 Torr, which was contaminated with a small amount of the other two isomers. A purification gave the dimethyl ester m.p. 90—93°C (methanol) (reported[44] m.p. 93—94°C). The acid was obtained by saponification of the dimethyl ester with potassium hydroxide, m.p. >315°C (acetic acid) (reported[45] m.p. >310°C).

2,4-Biphenyldicarboxylic acid was prepared by a reaction of diazotised dimethyl 4-aminoisophthalate (from 21 g of ester) with benzene (100 ml) in an alkaline medium, with subsequent hydrolysis of the crude ester with potassium hydroxide, similarly as the 2,3-isomer. M.p. 242 to 244°C (reported[46] m.p. 245—246°C, 245°C lit.[47]).

Fluorenone-2-carboxylic acid was obtained by heating 2,4-biphenyldicarboxylic acid with concentrated sulphuric acid to 150°C; m.p. 179—180°C (reported[46,47] m.p. 181°C).

2,5-Biphenyldicarboxylic acid was prepared by a reaction of diazotised dimethyl aminoterephthalate (from 21 g of the ester) with benzene (100 ml) in an alkaline medium, followed by hydrolysis of the crude ester with potassium hydroxide, similarly as in the preparation of 2,3- or 2,4-isomers; m.p. 274—276°C (aqueous methanol) (reported[47] m.p. 277—278°C).

Fluorenone-3-carboxylic acid was obtained by heating 2,5-biphenyldicarboxylic acid with sulphuric acid; m.p. 282—284°C (reported[47] m.p. 285°C).

2,6-Biphenyldicarboxylic acid was prepared from diphenic acid via fluorenone-4-carboxylic acid[30,48,49] (m.p. 220°C; reported[46] m.p. 222°C); its fusion with potassium hydroxide[50,51] at 200—220°C afforded, after isolation[51] from the reaction mixture, the product melting at 278—280°C (reported[51] m.p. 281—282°C). *Fluorenone* was prepared according to Huntress and coworkers[52]; m.p. 81—83°C (reported[52] m.p. 83·5—84·5°C). *Potassium benzoate-d₅* was obtained by an exchange reaction between potassium benzoate and deuterium oxide, according to a modified method of Brown and Garnett[53] described by us previously[54]. Deuterium content: 95·6%, mass spectrum: d_5 79·7%, d_4 18·7%, d_3 1·6%, d_2–d_0 0%.

General Procedure

The starting potassium salts of the carboxylic acids were prepared by neutralisation (phenolphthaleine) of their aqueous solutions with potassium hydroxide; the solution was evaporated to dryness and the residue was powdered and dried at 150°C/0·01 Torr. Cadmium iodide (3% Cd^{2+} calculated on the weight of the salt) was used as catalyst. The transcarboxylations were carried out according to[8]. The formed hydrocarbons were isolated by freezing them out into the tip of the ampoule, the tip was then set aside and the residual hydrocarbons were extracted from the mixture of salts with ether and the ether was taken down. Both fractions were combined and

analyzed by gas chromatography. The acids were isolated by the following procedure: the salts were dissolved in water (to give about 3% solution), the catalyst and impurities were filtered off, and the hot solution acidified with hydrochloric acid to pH 1. The insoluble acids were filtered off, the remaining acids extracted from the filtrate with ether and the extract taken down. Both acidic portions were combined and esterified with diazomethane to give a mixture of methyl esters which was analysed on a gas-chromatograph Chrom 2 (ČSSR) using tetrakis(cyanoethoxy)butane[8] or silicone F. X. 1150[6]. The mass spectra were taken on a Soviet instrument MX-1303 (Academy of Sciences, USSR), the IR-spectra were recorded on a spectrophotometer Zeiss UR-10.

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