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INITIATED DECARBOXYLATION OF MERCURIC SALTS OF CYCLOALIPHATIC CARBOXYLIC ACIDS WITH CONDENSED CYCLES *

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Summary

Under the action of either acyl peroxides or UV irradiation in the medium of organic solvents, mercuric *endo*-2-camphanecarboxylate (I), ketopinoate (II, *d,l*- and *l*-isomers), and 1-adamantoate (III) undergo smooth reaction of initiated decarboxylation (ID) to form bornylmercury, 7,7-dimethyl-2-oxobicyclo[2,2,1]heptylmercury and 1-adamantylmercury compounds, respectively. These were mostly isolated as halogenides (chlorides or bromides) in about 65—92% yields. ID of acylate I proceeds without retention of the organic radical configuration, whereas ID of (*l*-2) occurs without racemization to yield an optically active organomercurial.

The reaction of initiated decarboxylation of mercuric acylates (eq. 1) is a convenient route to preparation of alkyl- and cycloalkylmercury salts.

$$(RCO_2)_2Hg \xrightarrow{initiation} RHgO_2CR + CO_2 \quad (1)$$

G.A. Razuvaev and coworkers were the first to describe this reaction in 1954 [1]. It was shown to proceed via a chain free-radical mechanism; acyl peroxides, UV irradiation, and electric current may serve as initiators. So far, reaction 1 has been comprehensively studied for a large number of mercury salts of aliphatic, aromatic, heterocyclic, and monocyclic cycloaliphatic carboxylic acids (for a review see ref. 2). The initiated decarboxylation of mercury cycloalkanoates, whose organic radical is a condensed cycloaliphatic system, has been described for some examples of salts of camphenonic [3] and (briefly) ketopinic [4] acids.

In the present work we have investigated the decarboxylation of mercuric *endo*-2-camphanecarboxylate (I), ketopinoate (II, *d,l*- and *l*-isomers), and

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* Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

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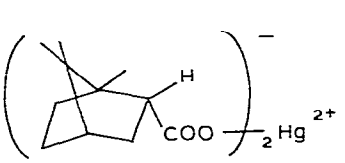
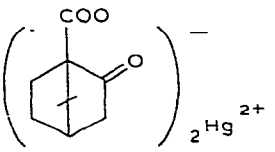
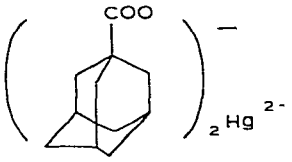
1-adamantoate (III) under the action of acyl peroxides and UV irradiation.



(I)



(IIa, d,l – isomer, IIb, l – isomer)



(III)

In the absence of initiator, salts I—III did not undergo decarboxylation when heated in boiling benzene; only a side reaction of the solvent mercuration to phenylmercury compounds occurred (Table 1, runs 1, 7, 18). On the contrary, in the presence of either peroxide initiators or UV irradiation acylates I—III were smoothly decarboxylated to form related cycloalkylmercury salts in preparative yields.

Decomposition of acylate I initiated either by UV irradiation or by benzoyl peroxide afforded a 65—67% yield of organomercurial: the bornylmercury salt (runs 4—6). 3 mmol of benzoyl peroxide were effective for practically complete decomposition of 10 mmol of this acylate. A decrease in the amount of peroxide down to 1—2 mmol (runs 3 and 4) led to incomplete decomposition of the initial acylate and reduced yields of the bornylmercury salt.

The *endo*-2-camphanecarboxylic acid peroxide showed an essentially lower initiating activity toward acylate I: with 3 mmol of this peroxide approximately one half of the starting acylate remained unreacted; the yield of bornylmercury compound was only 5% (run 2). The benzene mercuration to a phenylmercury salt dominated in the process.

The bornylmercury compound formed in the initiated decarboxylation of acylate I comprised a mixture of stereoisomeric *endo*- and *exo*-forms, i.e. the reaction proceeds without retention of configuration of the starting acylate. This is in good agreement with the data [5] on initiated decarboxylation of stereoisomeric mercury cycloalkanoates, and with a free-radical character of the reaction.

Comparatively low yields (28—33%, runs 9, 10, 16) of the organomercurial product of decarboxylation, 7,7-dimethyl-2-oxobicyclo[2,2,1]heptylmercury, were obtained when decomposition of acylates IIa,b was initiated by either benzoyl peroxide or UV irradiation in benzene. A still lower yield (8%) was registered with ketopinoyl peroxide as initiator (run 14). The low initiative activity of this peroxide is due to its slow decomposition at the boiling point of benzene, so that the predominant part of the starting mercuric acylate was expended in the side reaction of solvent mercuration. A combined application of ketopinoyl peroxide and UV irradiation (runs 8, 15) allowed reduction of the reaction time and enhancement of the yield of cycloalkylmercury product up to 38—40% along with a decrease of mercuration product yields. However, for the preparative synthesis of the 7,7-dimethyl-2-oxobicyclo[2,2,1]heptylmercury compounds the technique proposed earlier by us of conducting the reaction in a small volume of boiling propylacetate proved more effective. Under these conditions the yields of the organomercurial were about 80 and

92% at mol ratios of acylate : ketopinoyl peroxide of 1 : 0.5 and 1 : 1, respectively (runs 12, 13, 17).

The data in Table 1 show the reactivity of acylates IIa and IIb as being approximately equal.

The 7,7-dimethyl-2-oxobicyclo[2,2,1]heptylmercury compound formed from acylate IIb is optically active, i.e. decarboxylation of the acylate occurs without racemization. As we have previously shown [4] the retention of optical activity resulted from a rigid bridge structure of the intermediate radical, 7,7-dimethyl-2-oxobicyclo[2,2,1]heptyl, which in turn excludes racemization of an asymmetric carbon tetrahedron via a plane transition state.

The initiated decarboxylation of acylate III proceeded readily: 1 mmol of benzoyl peroxide was effective for a reasonably complete decomposition of 10 mmol of acylate, the yield of organomercurial product of decarboxylation, an adamantylmercury salt, being 54% (run 20). An increase in benzoyl peroxide amount up to 5 mmol caused a decrease of adamantylmercury product yields, along with simultaneous elevation in yields of the side product from the interaction of acylate and peroxide, a phenylmercury compound (run 22).

The photolysis of acylate III terminated in less than 2 h, with the adamantylmercury product yield reaching 61% (run 23). Still higher yield, 79%, was obtained from the reaction initiated by the peroxide, generating 1-adamantyl radicals (run 19). Tert-butylperoxyadamantoate was employed in this work as an adamantyl radical source instead of the known unstable 1-adamantanecarboxylic acid peroxide [6]. Neither isomerisation nor rearrangement of adamantane nuclei was observed during the reaction course, which is in good agreement with reported data [6—9].

The data obtained here indicate that the initiated decarboxylation of acylates I—III follows the general rules found earlier [2] for mercuric alkanoates and cycloalkanoates. The reaction is suitable for preparative synthesis of organomercurial derivatives of condensed alicycles.

Experimental *

The carboxylic acids were synthesised by the techniques described: the *endo*-2-camphanecarboxylic acid was synthesised from bornyl chloride via a Grignard reagent with subsequent isomerisation with thionyl chloride [10]; *l*- and *d,l*-ketopinic acids were obtained from *l*- and *d,l*-camphor, respectively [11]; 1-adamantanecarboxylic acid resulted from the treatment of 1-bromoadamantane with formic acid in oleum [12]. The constants of the acids synthesized were in accord with those in literature. Mercuric salts of the cited acids were prepared from their sodium salts and mercuric nitrate. Mercuric *endo*-2-camphanecarboxylate (I): m.p. 233—234°C. Found: Hg, 35.65, 35.52. $C_{22}H_{34}HgO_4$ calcd.: Hg, 35.65%. Mercuric *d,l*-ketopinoate (IIa): m.p. 209—210°C. Found: Hg, 35.71, 35.82, $C_{20}H_{26}HgO_6$ calcd.: Hg, 35.62%. Mercuric *l*-ketopinoate (IIb): m.p. 245—248°C (decomp.). Found: Hg, 35.72, 35.60, $C_{20}H_{26}HgO_6$ calcd.: Hg, 35.62%. Mercuric 1-adamantoate (III): m.p. 255—267°C. Found: Hg, 35.82, 35.78 $C_{22}H_{30}HgO_4$ calcd.: Hg, 35.87%. *d,l*- and

* Yu.A. Dzhomidava and T.A. Rubakha assisted in carying out the runs.

TABLE 1

INITIATED DECARBOXYLATION OF 10.0 mmol OF MERCURIC *endo*-2-CAMPHANECARBOXYLATES (I), KETOPINOATES (IIa,b) AND 1-ADAMANTOATE (III) IN BOILING SOLVENTS

Run No.	Initiator (mmol)	Solvent (ml)	Reaction time (min)	Yields of reaction products (mmol)					
				Cycloalkyl-mercury compound	Phenyl-mercury compound	Mercuric salt	Mercurous salt	Hg	CO_2
		Mercuric *endo*-2-camphanecarboxylate (I)							
1 [a]	Absence	Benzene, 100	360	0.0	0.98	0.99	0.0	0.0	0.0
2	KKP [b], 3.0	Benzene, 200	45	0.53 [c]	4.14	4.94	0.0	0.0	3.44
3	BP [d], 1.0	Benzene, 200	360	4.89	3.85	1.12	0.0	0.03	6.8
4	BP, 2.0	Benzene, 200	360	6.30	2.44	1.16	0.0	0.06	8.81
5	BP, 3.0	Benzene, 200	510	6.70	3.0	0.22	0.0	0.0	9.5
6	UV irradiation	Benzene, 175	90	6.47	0.0	0.56	1.14	0.65	9.5
		Mercuric *d*, *l*-ketopinoate (IIa)							
7 [e]	Absence	Benzene, 100	360	0.0	3.48	1.5	Trace	0.0	0.0
8	*d*, *l*-KPP [f] 2.0, UV irradiation	Benzene, 175	360	3.98 [g]	2.21	0.69	1.32	0.47	5.52
9	BP, 3.0	Benzene, 200	420	2.87	3.78	0.51	1.38	0.0	6.26
10	UV irradiation	Benzene, 175	300	3.36	1.85	0.64	1.91	0.28	4.70
11	*d*, *l*-KPP, 3.0	PrOAc, 20	390	5.2	—	4.13	0.11	0.43	6.44
12	*d*, *l*-KPP, 5.0	PrOAc, 20	420	8.02	—	1.16	Trace	0.80	11.25
13	*d*, *l*-KPP, 10.0	PrOAc, 20	480	9.22	—	0.09	Trace	0.69	19.00

		Mercuric *l*-ketopinoate (IIb)							
14	*l*-KPP, 5.0	Benzene, 200	960	0.82 [h]	6.65	0.69	0.87	0.0	2.58
15	*l*-KPP, 2.0, UV irradiation	Benzene, 175	360	3.79	1.98	1.12	1.48	0.13	4.97
16	BP, 3.0	Benzene, 200	420	3.24	4.15	0.56	0.98	0.04	6.50
17	*l*-KPP, 5.0	PrOAc, 20	420	8.0	—	0.85	Trace	1.14	9.40
		Mercuric 1-adamantoate (III)							
18 [i]	Absence	Benzene, 100	360	0.0	0.8	4.21	0.0	0.0	0.0
19	BPA [j], 5.0	Benzene, 200	30	7.95 [k]	0.0	Trace	0.85	0.35	11.4
20	BP, 1.0	Benzene, 200	180	5.45	1.75	Trace	0.66	0.98	8.32
21	BP, 3.0	Benzene, 200	360	5.45	2.18	Trace	0.30	1.25	11.2
22	BP, 5.0	Benzene, 200	360	4.28	3.25	Trace	Trace	2.10	13.8
23	UV irradiation	Benzene, 175	50	6.10	Trace	Trace	1.52	0.48	8.3
24	UV irradiation	Benzene, 175	100	5.0	Trace	Trace	1.22	2.45	10.02
25	UV irradiation	Heptane, 175	180	0.8	—	4.47	1.33	2.04	4.13
26	UV irradiation	Heptane, 175	300	2.62	—		0.12	6.9	10.8

[a] 2.0 mmol of acylate I were employed in run 1. [b] KPP = the *endo*-2-camphanecarboxylic acid peroxide. [c] Bornylmercury salt in runs with acylate I, a mixture of *endo*- and *exo*-isomers. [d] BP = benzoyl peroxide. [e] 5.0 mmol of acylate IIa were used. [f] KPP = ketopinic acid peroxide, *d*, *l*-, or *l*-isomers. [g] *d*, *l*-7,7-dimethyl-2-oxobicyclo-[2,2,1]heptylmercury salt in runs with acylate IIb. [i] 5.0 mmol of acylate III were used in run 18. [j] BPA = tert-butylperoxyadamantoate. [k] 1-Adamantylmercury salt in runs with acylate III.

l-ketopinoyl peroxides were prepared as in ref. 13, tert-butylperoxy-1-adamantoate as in ref. 6, benzoyl peroxide according to ref. 14, and benzene solution of the *endo*-2-camphanecarboxylic acid peroxide in analogy with ref. 15. The peroxides were analysed iodometrically as in ref. 16. IR spectra were recorded using an UR-20 spectrophotometer, the circular dichroism curves were obtained from J-20 spectropolarimeter (Jasco, Japan).

Reactions of mercuric acylates with peroxides

Runs were made in a 200 ml three-necked flask equipped with a stirrer, dropping funnel and reflux condenser connected with a burette for gas storage.

Reaction of mercuric endo-2-camphanecarboxylate (I) with endo-2-camphanecarboxylic acid peroxide. To a boiling mixture of 5.63 g (10.0 mmol) of acylate I and 170 ml of benzene was poured, while stirring, a solution of 1.086 g (3.0 mmol) of peroxide in 30 ml of benzene. The mixture was heated and stirred until gas evolution ceased (45 min). The solvent was then distilled off and the residue was dissolved in ethanol. An aqueous solution of KBr was added and the mixture was heated on a steam bath. The alcohol was removed and the precipitate of organomercurial bromides was filtered off. The amount of unreacted I was determined from the filtrate by precipitation with hydrogen sulfide; 1.15 g (4.94 mmol) of HgS were obtained. The bromide residue was recrystallized from heptane to afford 1.48 g (4.14 mmol) of phenylmercury bromide, m.p. 280° C, and 0.22 g (0.56 mmol) of a mixture of *endo*- and *exo*-isomers of bornylmercury bromide, m.p. 177—178° C, a mixed sample with authentic compound prepared by the published method [17] melted without depression. The IR and PMR spectra of both samples of bornylmercury bromides were identical.

Reactions of acetylate I with benzoyl peroxide were carried out analogously.

Reaction of mercuric l-ketopinoate with l-ketopinoyl peroxide. a) In benzene. To a boiling mixture of 5.63 g (10.0 mmol) of mercuric acylate and 180 ml of benzene was quickly added a solution of 1.81 g (5.0 mmol) of *l*-ketopinoyl peroxide in 20 ml of benzene. The mixture was heated and stirred until gas evolution ceased (16 h). The solvent was removed, the residue was dissolved in ethanol. An aqueous solution of KCl was then added and the mixture was heated in a bath. The alcohol was distilled off and precipitated chlorides were separated; under the action of hydrogen sulfide 0.16 g (0.69 mmol) of HgS were isolated from the filtrate. The chloride precipitate was washed with hot acetic acid. An insoluble portion was a calomel, 0.41 g (0.87 mmol) yield. The acetic acid was removed from the extract, and the residue was recrystallised from acetone and aqueous ethanol to give 2.08 g (6.65 mmol) of phenylmercury chloride, m.p. 249° C, along with 0.3 g (0.82 mmol) of *l*-isomer of 7,7-dimethyl-2-oxobicyclo[2,2,1]heptylmercury chloride. After chromatography on silica gel L 40/100 (eluent chloroform) the substance had a m.p. 201° C, $[\theta]_{max}$ 60.0×10^2 at λ_{max} 298 nm (in alcohol), and was identical to that described in ref. 4. b) In propylacetate. To a boiling mixture of 10.0 mmol of acylate (IIb) and propylacetate was rapidly added a suspension of 5.0 mmol of *l*-ketopinoyl peroxide in the same solvent (total amount of propylacetate was 20 ml). The mixture was heated and stirred until gas evolution ceased (7 h). The precipitated mercury was separated, the solvent was removed, the

residue was dissolved in alcohol, aqueous KCl was added and the mixture was heated. The precipitate obtained was crystallised from acetone and ethanol to obtain 2.98 g (8.02 mmol) of the *l*-isomer of 7,7-dimethyl-2-oxobicyclo[2,2,1]-heptylmercury chloride, m.p. 201°C. Circular dichroism parameters: in ethanol $[\theta]_{max}$ 60.0 × 10^2 at λ_{max} 298 nm; in dioxane $[\theta]_{max}$ 61.6 × 10^2 at λ_{max} 303 nm. The substance was identical to the one described earlier [4].

Reaction of mercuric 1-adamantoate (III) with tert-butylperoxyadamantoate in benzene. 5.58 g (10.0 mmol) of acylate III, 1.26 g (5.0 mmol) of tert-butylperoxyadamantoate and 200 ml of benzene were used. The reaction time was 30 min. Precipitated mercury was isolated from the reaction mixture (0.07 g, 0.35 mg-at). Benzene was distilled off, the residue was extracted with hexane using a Soxhlet apparatus. 4.08 g (7.95 mmol) of 1-adamantylmercury adamantoate were obtained, m.p. 217—218°C. Found: Hg, 38.57, 38.7 $C_{21}H_{30}HgO_2$ calcd.: Hg, 38.98%. 1.03 g (2.0 mmol) of this substance was dissolved in 50 ml of acetone and a solution of KCl (1 g) in aqueous acetone was added. Two hours later the precipitate was separated; after reprecipitation with hexane from acetone the 1-adamantylmercury chloride was obtained, m.p. 195—199°C (sublim.). Found: Hg, 55.0, 54.4 $C_{10}H_{15}ClHg$ calcd.: Hg, 54.03. IR spectrum (cm^{-1}): 670w, 815m, 955m, 975m, 1040s, 1108m, 1292s, 1350m, 1455s, doublet 2860, 2920s. The aqueous filtrate after organomercurial chloride separation was acidified; 1-adamantanecarboxylic acid was obtained, m.p. 181°C.

Reaction of acylate III with benzoyl peroxide was conducted in an analogous manner.

Photoreactions of acylates I—III were carried out in a flask equipped with a stirrer and reflux condenser connected to a gas burette. A PRK-4 lamp served a UV light source. Using a quartz tube the lamp was immersed into a reaction mixture. The reaction products were examined in analogy with the above methods.

Experimental results are given in Table 1.

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