CONCLUSIONS

1. By the action of the $Na_2S_2O_8$—$CuCl_2$ system, alkanoic acids RR'CHCH(R")CH_2COOH convert into γ-lactones $RR'\overline{CCH(R'')CH_2C(O)O}$ with high regioselectivity.

2. A reaction mechanism was proposed, including the formation from alkanoic acids of alkylcarbonyloxyl radicals, their rearrangement with 1,5-migration of the H atom into 3-carboxylalkyl radicals, and oxidative cyclization of the latter into γ-lactones.

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CYCLOKETONIZATION AND LINEAR POLYKETONIZATION OF α,ω-DICARBOXYLIC ACIDS.

COMMUNICATION 7. PREPARATION AND REACTIONS OF ZINC SALTS OF UNBRANCHED DICARBOXYLIC ACIDS

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Ketonization of Mn and Cd salts of dicarboxylic acids of composition C_6 and higher is a complex process including two main reactions, namely, cycloketonization and linear polyketonization, and two secondary reactions, namely, crotonic condensation of cyclopentanone and cyclohexanone on MnO [1, 2] and crotonic condensation of the polyketodicarboxylic acids formed during linear polyketonization in the presence of CdO [2-4]. The investigation of the ketonization of Zn salts of dicarboxylic acids was intended to elucidate the generalness and specific differences of the mechanism of ketonization of dicarboxylic acid salts with different cations and also the possibility of elucidating the yields of cycloalkanones due to inhibition of linear polyketonization and secondary reactions. The data [5-7] on the ketonization of Zn salts of dicarboxylic acids are very contradictory.

In the present paper, we have studied the ketonization of Zn salts of adipic, pimelic, suberic, azelaic, and sebacic acids. The reaction was carried out according to [8] with due regard for the improvements mentioned in [4] and [9]. To obtain Zn salts of dicarboxylic

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TABLE 1. Ketonization of C_6-C_{10} Dicarboxylic Acids in the Presence of Zinc

Starting acid	Amount, g	Zn compound, g		Reaction products and their yield, %			
		ZnO	$5ZnO \cdot 2CO_2 \cdot 4H_2O$	liquid condensate	cycloalkanone	condensation products	linear polyketodicarboxylic acid
Adipic	5,0	2,8	–	86,1	66,7	19,4	–
	5,0	–	3,9	72,7	46,9	26,8	–
	3,0	–	11,6	40,6	11,6	29,0	–
Pimelic	3,0	1,5	–	87,3	69,6	17,7	–
	3,0	–	2,5	84,0	72,0	12,0	–
Suberic	6,0	2,8	–	69,7	69,7	–	13
	6,0	–	3,9	58,0	58,0	–	41
	3,0	–	9,6	56,0	56,0	–	21
Azelaic	5,0	2,2	–	2,0	2,0	–	85
	5,0	–	3,9	3,0	3,0	–	85
Sebacic	5,0	2,0	–	<1	<1	–	75
	5,0	–	2,8	<1	<1	–	75
	3,0	–	8,4	<1	<1	–	50

acids, we used technical-grade ZnO and basic zinc carbonate ($5ZnO \cdot 2CO_2 \cdot 4H_2O$). The obtained results of the decomposition of Zn salts are reproduced well and are comparable with the data of pyrolysis of the same dicarboxylic acids in the presence of Mn and Cd carbonates [1, 2].

In the presence of the studied Zn compounds, the primary yields* of five- and six-membered cycloalkanols were just as high (87-88%) as with Mn salts [1-4]. Their final yield was 20-40% lower because of consumption in the secondary reaction of crotonic condensation.

Cycloheptanone from suberic acid in the presence of ZnO was obtained in significantly higher yield (70%) than could be achieved previously (58%), even on the specially prepared radioactive ThO_2 catalyst specially recommended for this purpose [10]. The high efficiency of ZnO in this reaction and the possibility of its use in technical form without any additional treatment enable us to recommend the dicarboxylic acid ketonization method based on the use of this catalyst for preparative synthesis of cycloheptanone under laboratory conditions.

The decomposition of azelaic and sebacic acids in the presence of ZnO and basic Zn carbonate gave primarily the reaction products of linear polycondensation. The yield of cyclooctanone was 2-3%, 10 and 5 times as great as in the reactions with Mn and Cd salts, respectively. Therefore, the search for new cations for the pyrolysis of azelaic acid should be continued.

Like the corresponding Mn salts, the residues in the tube after isolation of CO_2 and ketone from the C_8-C_{10} acids were Zn salts of polyketodicarboxylic acids. Their structure was confirmed as in [1]. The values of the atomic ratios of H to C calculated according to the data of elemental analysis for the obtained polyketodicarboxylic acids were in good agreement with the theoretical values in all the cases: for suberic, azelaic, and sebacic acids, we found 1.63, 1.73, and 1.78, respectively, and calculated 1.71, 1.75, and 1.78, respectively.

From Zn salts of adipic and pimelic acids giving ketones tending to undergo crotonic condensation, we obtained cycloalkylidenecycloalkanones and also, apparently, solid products of their condensation with the starting acids. The yield of the solid products was 1-7%. These solid products were not investigated in greater detail.

Thus, in the presence of compounds of all three studied elements (Cd, Mn [1, 2], and Zn), there was competition between the two main routes of ketonization (cycloketonization and linear polycondensation); in the case of the lower members of the series of studied dicarboxylic acids, the cycloketonization reaction predominated; in the case of adipic acid, cycloketonization predominated with significant subsequent crotonic condensation (see Table 1). In the case of higher dicarboxylic acids, linear polyketonization predominated. On the whole, the reaction proceeded in three easily distinguishable steps with different temperature ranges

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*Taking into account the ketone that entered into the secondary reaction of crotonic condensation (Table 1).

for each of them: salt formation (150-220°C), ketonization (290-360°C), and pyrolysis of the salts of the polyketodicarboxylic acids (>350-400°C in relation to the nature of the cation).

CONCLUSIONS

1. Just as in the presence of manganese and cadmium compounds, ketonization of dicarboxylic acids in the presence of zinc compounds occurs by two competing routes (cycloketonization and linear polyketonization). In the case of adipic and pimelic acids, a secondary reaction of crotonic condensation of the resulting ketones also occurs.

2. Zinc oxide catalyzes efficiently the cycloketonization of suberic acid to cycloheptanone, making it possible to obtain it in such a way in the highest yield described in the literature (70%).

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POLYSULFONYLETHYLENES.

COMMUNICATION 1. SYNTHESIS OF TETRAKIS(ALKYL,ARYL)SULFONYLETHENES*

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Tetrasulfonylethylenes (TSE) constitute a class of ethylenes with an electron-deficient C=C bond. The presence of four strong electron-acceptor groups should make the TSE highly active in various nucleophilic processes.

The TSE were unknown before our research, in spite of numerous attempts to prepare them. Thus, the photochemical oxidation of tetra(alkyl,aryl)thioethenes produced a complex mixture whose major components were dithiooxalates and disulfides [2, 3]. Oxidation of tetratolylthioethene [4] and 1,1-di(methylsulfonyl)-2,2-di(methylthio)ethene [5] by 30% H_2O_2 in acetic acid produced on heating only ditolyl- and dimethylsulfonylmethane, respectively. Oxidation of more complex tetrathioethenes such as tetrahydrotetrathiofulvalenes by m-chloroperbenzoic acid in CH_2Cl_2 was unsuccessful, and the use of H_2O_2 in acetic acid [4, 5] also resulted in splitting the molecule [6].

In spite of the claims in [7] (see the experimental section), the oxidation of tetrakis-(2 chloroethylthio)ethene (I) by 30% H_2O_2 in acetic acid actually forms di(2-chloroethyl)-sulfonylmethane (III) as well and not the tetrasulfone (II):

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*For preliminary discussion, see [1].

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