5,5′-BIS(1-AZA-2-CYCLOHEPTANONE) AND 5,5′-ISOPROPYLIDENE-BIS(1-AZA-2-CYCLOHEPTANONE) AND THEIR COPOLYMERIZATION WITH ε-CAPROLACTAM*

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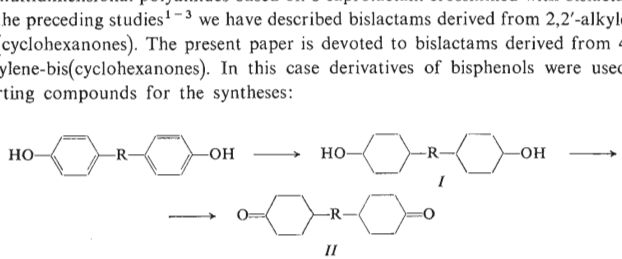
Both 5,5′-bis(1-aza-2-cycloheptanone) and 5,5′-isopropylidene-bis(1-aza-2-cycloheptanone) were prepared by stepwise syntheses starting with derivatives of 4,4′-bis(phenol). The second mentioned compound was separated in two isomeric forms; both isomers form stabile monohydrates. It was proved that none of the described bislactams is able to homopolymerise at 260°C in the presence of water or of ε-aminocaproic acid. Their behaviour in copolymerizations with ε-caprolactam was followed.

In the II paper of this series[1] we have concerned ourselves with the preparation of multidimensional polyamides based on ε-caprolactam crosslinked with bislactams. In the preceding studies[1-3] we have described bislactams derived from 2,2′-alkylene-bis(cyclohexanones). The present paper is devoted to bislactams derived from 4,4′-alkylene-bis(cyclohexanones). In this case derivatives of bisphenols were used as starting compounds for the syntheses:



SCHEME 1

a: R = $>C(CH_3)_2$; *b*: R denotes single covalent bond.

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Dialcohol *Ia* was oxidized to diketone *IIa* by several methods. The highest yields (84·5%) were obtained when sodium bichromate was used as an oxidizing agent in the mixture of glacial acetic acid and sulphuric acid and in the presence of 20 molar excess of 2-butanone (it was found that the dependence of the yield of diketone *IIa* on the concentration of 2-butanone proceeds through maximum). In the absence of 2-butanone the yields of only 64–71% are obtained as it is reported by Hopff and coworkers[4]. Similarly as in the ref.[4] the oxidation with sodium bichromate in sulphuric acid was not successful. The newly developed preparative method for diketone *IIa* which is based on catalytic dehydrogenation of dialcohol *Ia* with Adkins' catalyst gives high yields (87·5%). The reaction is performed in decalin at its boiling point. The yields quoted may be influenced by the purity of the starting dialcohol *Ia*; the dehydrogenation is inhibited namely by the traces of epichlorhydrin which comes in from the crystallisation of dialcohol *Ia*. Five to ten-times excess of decalin, used as a solvent, does not practically influence the yield, but in its absence the yields fall down below 25%, and also the purity of the product is impaired. At higher temperatures (above 200°C) and in the absence of the solvent, the dehydration reactions become more important. After the crystallisation the diketone *IIa*, prepared by the described methods, has m.p. 160°C (in ref.[4] m.p. 135°C is quoted for crude product).

Dialcohol *Ib* was oxidized with bichromate in the presence of 2-butanone, or with chromium(VI) oxide, but the yields did not exceed 55%.

Dioxime *IIIa* was prepared in 96% yield (ref.[4] quotes 66%) by the generally used method, *i.e.* by the reaction of diketone *IIa* with hydroxylamine hydrochloride in the presence of bicarbonate in methanol. M.p. 224–225°C quoted in ref.[4] corresponds to crude dioxime *IIIa*; m.p. of the crystallized product is 236–238°C.

According to patent literature[5], bislactam *IVa* can be prepared by Schmidt's reaction in the presence of concentrated hydrochloric acid in 79% yield. Hopff and coworkers[4] repeated this method and obtained only 69% yield; with the aid of polyphosphoric acid they increased the yield to 80%. The highest yields (95%) are obtained by Beckmann's rearrangement in polyphosphoric acid. In all these preparations they obtained bislactam *IVa* which had m.p. 216°C. In contrast to the mentioned paper[4] we have succeeded to isolate by fraction crystallization from the products of Schmidt's and of Beckmann's reactions, keeping the same reaction conditions and obtaining the similar yields, two isomers of bislactam *IVa*; isomer A having m.p. 213–215°C, which is evidently identical with bislactam isolated by Hopff and coworkers[4] and isomer B having m.p. 238–240°C. Both isomers were always obtained in the ratio of about 1 : 1. Furthermore, we have found that both isomers, in contrast to most of other lactams, excluding 2-pyrrolidone[6], give stable monohydrates.

The presence of water was, besides the elemental analysis, also proved by Fisher's method and by thermogravimetrical analysis. The conductometric titration revealed that none of the isomers contains $—NH_2$ or —COOH groups, the presence of which could be due to a partial hydrolysis of bislactam. Water is very tightly bound in the molecule of bislactam; the spontaneous dehydration takes place at the temperatures higher than 130°C and pressure lower than 1 Torr. The difference in the melting points of both compounds after dehydration give the evidence that we are dealing with two isomers.

The existence of two isomers of bislactam *IVa* can be explained either by diastereoisomery or atropoisomery. The real dimensions of the unit cell of the isomer A determined by the X-ray diffraction method are in compliance with the supposition that water is most probably bound intramolecularly. Hydrogen bonds between water molecule and amide group block any rotation and therefore the atropoisomery is in this case more probable. From the study of models follows, that bislactam *IVa* can form two isomers which differ in the symmetry of the molecule. One isomer which has twofold axis of symmetry forms monoclinic crystals and the second which has no axis of symmetry and therefore it should form triclinic crystals. X-ray structural analysis has proved that the hydrate of isomer A forms monoclinic crystals. (The dimensions of the unit cell: $a = 15{\cdot}17$ Å; $b = 10{\cdot}67$ Å; $c = 11{\cdot}50$ Å; $\beta = 123°C$; $V = 1560$ Å^3; the unit cell is formed by four molecules.)

Bislactam *IVb* was prepared by Schmidt's reaction of diketone *IIb* in polyphosphoric acid. Only one product was isolated and its elemental analysis corresponded to anhydrous bislactam. Therefore, the atropoisomery of bislactame *IVa* seems to be anomalous, and can be due to the presence of isopropylidene bridge which turns both lactame cycles into the positions which are suitable for the hydrate formation, *i.e.* for the formation of the bridge amide–water–amide. From the study of models also follows that this possibility of bridge formation does not exist for other described bislactams.

Hopff and coworkers[4] quote, that at 250°C and in the presence of catalysts 5,5'-isopropylidene-bis(1-aza-2-cycloheptanone) is not able to undergo neither the hydrolytic nor the anionic polymerization. Unfortunately, it is not quite clear whether the authors have not polymerized bislactam which contained crystal water. If yes, then the negative polymerization results would not be suprising, because in this instance the formation of oligomers soluble in water can be expected. We have shown that none of the isomers of bislactam *IVa*, which was dried under the conditions which secured total removal of crystal water, is able to undergo hydrolytic polymerization at 260°C, even if the period of heating is prolonged. Molecular weight of the product after, *e.g.* 70 hours of heating at 260°C, (in the presence of 2 mol % of ε-aminocaproic acid) determined by vapour pressure osmometry, corresponded to the mixture of monomer and dimer (molecular weight 440). Analogously, we have found that also bislactam *IVb* is not, under the similar conditions, able to polymerize, even if we have got to admit in this case, that the polymerization conditions were not quite correct because of a high melting point of this bislactame (monomer was at first melted at 295°C and then placed into the thermostat at 260°C).

The unability of the mentioned bislactams to undergo homopolymerization is probably somehow connected with the position of amide bonds in the molecule. It is well known, that γ-substituted ε-caprolactams exhibit substantially lower polymerization activity, than ε- or α-substituted ε-caprolactams[7,8]. If we take into our consideration a general decrease of polymerization activity with increasing size and branching of the substituent and also the fact that γ-isopropyl-ε-caprolactam is not able to polymerize[7–9], then the polymerization inactivity of bislactams' *IVa* and *IVb* is not suprising.

In contrast to homopolymerization, the bislactams *IVa* and *IVb* are able to copolymerize with ε-caprolactam. With increasing concentration of these bislactams

the equilibrium content of the copolymer is decreasing (see Table I). This decrease can be expected because of the unability of these lactams to undergo homopolymerization, but it can also be influenced by the fact that nonpolymerizable lactams can act as an inert dilution agent, as it is known that equilibrium content of lactam polymers decreases with increasing content of dilution agent[10,11]. Only at copolymers with low content of bislactam (up to 2% mol) the course of copolymerization is identical with the course of homopolymerization of ε-caprolactam under the analogous conditions. The equilibrium monomer–copolymer is attained after 12–24 hours in case of bislactam *IVa* and after 24–48 hours in case of bislactam *IVb*. No differences were found in the copolymerization of both isomers of bislactam *IVa*.

TABLE I

Copolymere Content After 96 Hours of Copolymerization of ε-Caprolactam with Bislactams *IV* at 260°C in the Presence of 2 mol % of ε-Aminocaproic Acid

$[IV]_0$ Initial concentration of bislactam (mol %).

$[IV]_0$	*IVa*-A	*IVa*-B	*IVb*	$[IV]_0$	*IVa*-A	*IVa*-B	*IVb*
0·1	88·5[a]	88·5	89·6	3·0	88·1	87·8	87·9
0·2	—	88·9	89·2	10·0	80·2	81·6	87·9
0·5	—	88·3	88·5	30·0	67·0	68·3	—
1·0	89·5	88·2	88·9	50·0	51·8	54·3	—
2·0	88·9	88·5	88·7	90·0	0	0	—

[a] After 72 hours.

In Table II are also quoted the results which were obtained at the copolymerization of ε-caprolactam with both isomers of bislactam *IVa* in the form of their hydrates. With regard to an increasing content of water with increasing concentration of bislactam in the reaction mixture, the decrease of the equilibrium content of the copolymer is sharper, when compared with the change of polymer content at the copolymerization with dehydrated isomers; the higher value of extractable portion is most probably due to the drop of molecular weight and the increasing content of oligomers. On the other hand, the rate of copolymerization is increasing with increasing concentration of the hydrate of bislactam *IVa*. Though, *e.g.* while at the concentration up to 12·7 mol % the equilibrium monomer–copolymer is attained between 6–48 h, at the concentration of 22·2–32·6 mol % it is attained as early as after 6 h. From these results it can be concluded that the cited authors[4] have used for their copolymerization bislactam *IVa* in its hydrated form, also the quoted[4] lower crosslinking efficiency of this bislactam supports this conclusion. The quoted lower critical crosslinking

efficiency in case of the hydrate can be attributed to the presence of water and to the decrease of molecular weight of the main chain. The viscosity of the solution of the copolymers soluble in *m*-cresol increases with increasing concentration of bislactam and the content of the copolymer. The bislactam incorporates into the chain in the early stages of copolymerization, as it is indicated by unusually high values of Huggins' constants of the copolymer solution[12,13] having $[\eta]$ lower than 1·5 dl/g, in comparison to linear poly(ε-caprolactam). These viscometric data indicate relatively

TABLE II

Copolymerization of ε-Caprolactam with Monohydrates of Isomers A and B of Bislactam *IVa* at 260°C in the Presence of 2 mol % of ε-Aminocaproic Acid

$[IV]_0$ Initial concentration of bislactam (mol %), *t* polymerization time (h), [c] copolymer content.

$[IV]_0$	*t*	For isomer A		For isomer B	
		[c]	η_{red}	[c]	η_{red}
0·4	5	80·1	1·5	80·3	1·4
	10	87·6	1·6	87·4	1·6
	20	89·0	2·0	90·6	1·8
	30	89·0	2·0	89·9	1·7
	50	88·8	1·9	89·7	1·7
	90	89·4	1·8	89·3	1·6
0·8	5	78·2	1·6	80·3	1·4
	10	85·0	1·7	88·4	1·6
	20	88·1	2·1	89·6	1·9
	30	88·2	2·8	90·5	2·3
	50	89·2	2·1	89·8	2·3
	90	89·4	2·1	89·5	2·4
1·2	5	79·0	1·4	80·6	1·4
	10	86·0	2·4	86·3	2·3
	20	87·4	3·4	88·6	2·9
	30	89·6	3·9	90·1	3·2
	50	90·2	3·1	90·2	3·9
	90	90·0	2·6	90·2	4·5
4·1	96	85·8	[a]	85·5	[a]
12·7	96	—	—	77·8	[a]
22·2	96	64·3	[a]	—	—
32·6	96	44·5	[a]	—	—

[a] Copolymer insoluble in *m*-cresol.

high rate of copolymerization, which is in accord with known higher rate of polymerization of γ-substituted ε-caprolactams, in contrast to the polymerizations of ε-substituted derivatives[14,15].

In Table I and II are summarised results which show quite clearly the decrease of η_{red} with time at the samples with longer copolymerization time. As the polymer solution did not contain any insoluble gel particles, therefore this relatively small decrease of η_{red} can be attributed either to degradation or to structural changes which were caused by a different rate of incorporation of both lactams into the copolymer at the early stages of the reaction and followed by transamidation reactions leading to redistribution of bislactam *IVa* units in the chain of the branched copolymer.

The observed critical crosslinking efficiency, in spite of the unability of bislactams *IVa* and *IVb* to homopolymerize, is practically identical with that of bislactams derived from 2,2′-alkylene-bis(cyclohexanones) which exhibit high homopolymerization ability. With regard to this relatively high crosslinking efficiency of bislactams *IVa* and *IVb* the above mentioned decrease of the equilibrium content of the copolymer with increasing content of bislactam would not be an obstacle in practical applications, because at the concentrations sufficient for crosslinking, *i.e.* up to 2 mol %, the equilibrium monomer–copolymer is still identical with the equilibrium monomer–polymer of poly(ε-caprolactam).

The differences in crosslinking efficiency of bislactam *IVb* (lower than 1 mol %) and *IVa* are not surprising, as among bislactams derived from 2,2′-alkylene-bis(cyclohexanone) the highest crosslinking efficiency exhibited 7,7′-bis(1-aza-2-cycloheptanone), *i.e.* the monomer in which both lactam cycles are directly connected. On the other hand the bislactams whose caprolactam cycles are connected through, *e.g.* methylene or ethylidene bridge, exhibited, similarly as bislactam *IVa*, relatively lower crosslinking efficiency[1]. The differences in crosslinking efficiency due to the type of the bridge can be attributed to the differences in sterical possibilities of bislactam molecules in the cyclic and the chain form.

EXPERIMENTAL

Melting points were determined on a Kofler block; the data were not corrected. Infrared spectra were run on a Zeiss UR 10 apparatus. Crystallographic data were determined by X-ray diffraction method.

Syntheses

4,4′-Isopropylidene-bis(cyclohexanol) (Ia). Dialcohol *Ia* was prepared by hydrogenation of 4,4′-isopropylidene-bis(phenol) using Raney-Ni as a catalyst at the temperature of 150—170°C and the pressure of 100 atm in the presence of commercial grade methylcyclohexanol. Cool reaction mixture was after dilution with methanol treated in the usual way[4]. After crystallisation from epichlorhydrine dialcohol *Ia* having m.p. 144—146°C (ref.[4] 110—140°C) was obtained.

4,4′-Isopropylidene-bis(cyclohexanone) (*IIa*)

a) Solution of 2·4 g (0·01 mol) of dialcohol *Ia* in 100 ml of benzene and 18 ml of 2-butanone was dropwise added, under continuous stirring, to the solution of 10·45 g (0·035 mol) of sodium bichromate in the mixed solvent containing 22·5 ml of conc. sulphuric acid, 12·5 ml of glacial acetic acid and 200 ml of water cooled down to 0°C. After 5 h of stirring in thermostated bath kept at 30°C the reaction mixture was extracted with ether; after washing (water, diluted sodium hydroxide, water) and drying of the extract, ether was distilled off and 2 g (84·5%) of diketone *IIa* having m.p. 160°C (cyclohexane) (ref.[4] 135°C) was obtained.

b) The mixture of 7·2 g (0·03 mol) of dialcohol *Ia* which was recrystallised from acetone and dried for 8 hours at 20°C/15 Torr, and of 40 ml of decalin and 1·25 g of Adkins' catalyst was heated up to the boiling point. When the evolution of hydrogen slowed down (evolution was followed volumetrically) another portions of catalyst were added (several times) so that the total amount of added catalyst was 5 g. The catalyst was then filtered off at 40—50°C and the filtrate cooled down; 6·2 g (87·2%) of diketone *IIa* having m.p. 160°C (ethanol or water) was obtained. For $C_{15}H_{24}O_2$ (236·3) calculated: 76·22% C, 10·24% H; found: 76·02% C, 10·61% H. Dioxime *IIIa*, m.p. 236—238 (methanol) (ref.[4] 224—225°C). For $C_{15}H_{26}N_2O_2$ (266·4) calculated: 67·63% C, 9·84% H; found: 67·88% C, 9·81% H.

5,5′-*Isopropylidene-bis*(1-*aza-cycloheptanone*) (IVa). Bislactam *IVa* was prepared according to ref.[2] by Schmidt's reaction of diketone *IIa* in hydrochloric acid or in polyphosphoric acid; the respective yields were 92·5% and 90%; Beckmann's rearrangement of dioxime *IIa* yielded 89% (in sulphuric acid) or 82·5% (in polyphosphoric acid). Crude bislactam was fractionally crystallised from 2-butanone. The portion soluble in 2-butanone yielded after partial evaporation and crystallization from water hydrate of isomer A, m.p. 213—215°C, the portion insoluble in 2-butanone yielded after crystallization from 2-propanol or from water hydrate of isomer B, m.p. 238—240°C. Both isomers were in all cases obtained in the approximate ratio of 1 : 1. Infrared spectrum of isomers A and B ($CHCl_3$): 1 675, 3 230, 3 300, 3 425 cm^{-1}. For $C_{15}H_{26}N_2O_2 . H_2O$ (284·5) calculated: 63·33% C, 9·92% H, 9·85% N; found for isomer A: 63·33% C, 9·86% H, 10·17% N; found for isomer B: 63·69% C, 10·03% H, 9·75% N. The content of water determined by Fisher's method: 0·92 mol H_2O/mol of isomer A. Differential thermography: the loss of crystal water of isomer A hydrate takes place at 130°C/1 Torr. M.p. of isomer A is 233—7°C, and of isomer B is 240—3°C.

4,4′-*Bis*(*cyclohexanol*) (Ib). Dialcohol *Ib* was prepared analogously as dialcohol *Ia* by hydrogenation of 4,4′-bis(phenol) (Bayer) under the similar conditions. After crystallisation from water dialcohol *Ib* had m.p. 138—142°C.

4,4′-Bis(cyclohexanone) (*IIb*)

a) Diketone *IIb* was prepared by the procedure quoted under *a*) for the preparation of diketone *IIa* in 25% yield; the only exclusion was, that instead of the solution an emulsion was dosed, because of a low solubility of dialcohol *Ib* in benzene and 2-butanone. The yields could be increased (55%) by the addition of acetanhydride to the reaction mixture (100 ml/mol of dialcohol *Ib*).

b) A suspension of 10 g (0·051 mol) of dialcohol *Ib* in 25 ml of acetic acid and 25 ml of acetanhydride was slowly dropwise added to the oxidation mixture (7 g, 0·07 mol of chromium trioxide and 40 ml of acetanhydride) cooled down to 15°C. The reaction mixture was at this temperature stirred for 12 hours and then both acetic acid and acetanhydride were removed by repeated distillation; each time 100 ml of chloroform and 100 ml of methanol was added. Glass-like

distillation residue was crushed and extracted with 250 ml of benzene in a Soxhlet extractor. A brown product obtained from the extract yielded after crystallization from cyclohexane 5·35 g (47%) of diketone *IIb*, m.p. 115—119°C.

5,5'-Bis(1-aza-2-cycloheptanone) (IVb). Bislactam *IVb* was prepared by Schmidt's reaction of diketone *IIb* in polyphosphoric acid by the procedure described in ref.[2] in 90% yield. M.p. 288·5—289·5°C (water or 2-propanol). Infrared spectrum (KBr): 1670, 3070, 3210, 3310 cm^{-1}. $C_{12}H_{20}N_2O_2$ (224·3) calculated: 64·25% C, 8·99% H, 12·49% N; found: 64·45% C, 9·10% H, 12·38% N.

Polymerization

Polymerizations and copolymerizations with ε-caprolactam were performed in evacuated sealed glass ampoules in the presence of 2 mol % of ε-aminocaproic acid at 260 ± 0·5°C by the generally used technique[16]. Monomers were prior to polymerization dried for 12 hours at 50°C/1 Torr; both isomers of bislactam *IVa* were freed from crystal water by an additional drying for 2 hours at 150°C/1 Torr. Copolymer content was determined by a repeated extraction of dry polymers with boiling water by the usual procedure[13]. Viscosity measurements of selected soluble copolymers were performed in *m*-cresol at the concentration of 0·4 g/100 ml at 25 ± 0·005°C in a Ubbelohde viscometer fitted with a capillary No II, by the usual technique[13]. In experiments in which the polymerization of bislactam *IVb* was attempted, the reaction mixture was in an ampoule at first melted at 295°C and then immediately transferred to a polymerization bath.

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