

# Synthesis of Mixed Bisamides of Cyclic *ortho*-Dicarboxylic Acids

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**Abstract**—A procedure was developed for preparation of bisamides of cyclic *ortho*-dicarboxylic acids by acylation of *m*- or *p*-phenylenediamine in acetone solution at room temperature simultaneously with two different anhydrides of cyclic or aromatic *ortho*-dicarboxylic acids; another process consisted in treating an anhydride of aromatic or cyclic dicarboxylic acid with monoamide of *cis*-4-cyclohexene-1,2-dicarboxylic acid in dimethylformamide at room temperature.

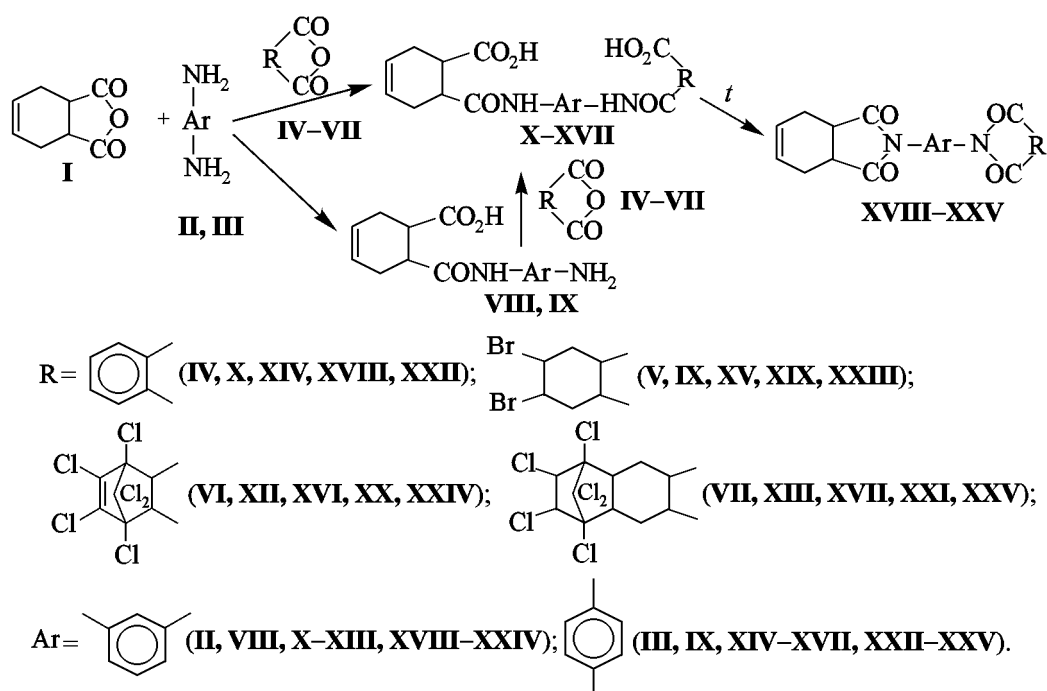
Amidoacids from aromatic and cyclic *ortho*-dicarboxylic acids serve as excellent monomers for preparation of heat-resistant polyamides [1].

Symmetrical bisamides were prepared before [2] by acylation of aromatic diamines with anhydrides of cyclic *ortho*-dicarboxylic acids. The ready formation of bisamides shows that acylation of both amino groups in *m*- and *p*-phenylenediamines occurs with similar rates.

We describe here a procedure for preparation of mixed bisamides where the ratio of reactants,

mixing order, and character of solvent play significant role.

A simultaneous mixing of acetone solutions containing equimolar quantities of *m*- or *p*-phenylenediamine (**II**, **III**) anhydride of *cis*-4-cyclohexene-1,2-dicarboxylic acid (**I**), and also anhydrides of phthalic (**IV**), *trans*-4,5-dibromocyclohexane-1,2-dicarboxylic (**V**), 1,4,5,6,7,7-hexachloro[2.2.1]hept-5-ene-2,3-dicarboxylic (**VI**) or 1,2,3,4,11,11-hexachlorotricyclo-[6.2.1.0<sup>5,10</sup>]undec-2-ene-7,8-dicarboxylic (**VII**) acids in acetone medium at room temperature results in formation of mixed bisdiamides **X–XVII**.



Characteristics and elemental analyses of bisamides **X–XVII** and bisimides **XVII–XXV**

Compd. no.	Yield, %	mp, °C (from benzene)	$R_f$	Found, %			Formula	Calculated, %			$M$		Acid number		
				C	H	Hlg		N	H	Hlg	N	found	calcd.	found	calcd.
<b>X</b>	97	299	0.39	64.38	4.65	–	6.60	64.70	4.90	–	6.86	405.5	408.0	270.1	275.8
<b>XI</b>	99	315	0.41	46.00	4.02	27.26	4.82	46.15	4.20	27.97	4.90	566.6	572.0	196.8	197.8
<b>XII</b>	97	321	0.46	43.58	2.48	33.20	4.00	43.34	2.85	33.75	4.44	629.5	631.0	176.8	177.5
<b>XIII</b>	97	348	0.50	47.21	3.42	30.20	4.00	47.30	3.50	31.9	4.00	684.2	685.0	162.4	163.3
<b>XIV</b>	99	281	0.41	65.00	4.79	–	6.80	64.08	5.83	–	6.80	405.0	408.0	274.6	275.8
<b>XV</b>	98	301	0.42	46.00	4.03	27.27	4.60	46.15	4.20	27.97	4.90	566.8	572.0	196.8	197.8
<b>XVI</b>	98	296	0.43	43.61	2.66	33.18	4.10	43.74	2.85	33.75	4.44	630.0	631.0	177.0	177.5
<b>XVII</b>	97	334	0.51	47.21	3.48	30.88	4.00	47.30	3.50	31.09	4.09	684.0	685.0	162.8	163.5
<b>XVIII</b>	94	306	0.69	70.08	4.00	–	7.21	70.97	4.30	–	7.53	370.2	372.0		
<b>XIX</b>	96	220	0.58	49.33	3.00	29.71	4.98	49.62	3.61	30.10	5.26	531.0	532.0		
<b>XX</b>	96	230	0.70	46.01	2.10	35.61	4.44	46.38	2.35	35.80	4.70	370.0	372.0		
<b>XXI</b>	95	306	0.69	49.25	2.89	32.41	4.01	49.92	3.08	32.82	4.31	647.8	649.0		
<b>XXII</b>	79	230	0.73	70.51	3.92	–	7.04	70.97	4.30	–	7.53	370.2	372.0		
<b>XXIII</b>	99	194	0.67	49.07	2.71	29.22	4.88	49.62	3.01	30.10	5.26	528.4	532.0		
<b>XXIV</b>	96	202	0.68	45.91	2.11	35.48	4.32	46.38	2.35	35.80	4.70	594.4	595.0		
<b>XXV</b>	88	308	0.71	49.69	3.21	32.66	4.14	50.23	2.48	33.02	4.34	643.6	645.0		

Bisamides **X–XVII** were also obtained by reaction of monoamides **VIII** or **IX** with anhydrides **IV–VI** or **VII** in DMF at room temperature. Since monoamides **VIII**, **IX** are insoluble in acetone, their reaction with anhydrides **IV–VI** or **VII** occurs only in DMF that ensures homogeneity of the medium. The developed procedure provides a possibility to obtain any mixed bisamides by acylation of *m*- or *p*-phenylenediamine varying the order of anhydride addition and the solvent.

The proof of the structure of mixed bisamides **X–XVII** was performed by transformation thereof into bisimides **XVIII–XXV** by heating the respective amides in DMF for 5–6 h at boiling (152°). The characteristics of bisamides **X–XVII** and bisimides **XVIII–XXV** are given in the table.

The structure of the mixed bisamides is also confirmed by IR spectra containing the stretching bands of C=C bonds at 1660, 1610 cm<sup>-1</sup> and of amide group at 3290, 3220 cm<sup>-1</sup>. The stretching vibrations of the carboxy group appear as a strong shoulder at 1720 cm<sup>-1</sup>. The band at 2600 cm<sup>-1</sup> indicates that the carboxy group is linked to the adjacent amide group by an intramolecular hydrogen bond. The presence of carboxy group in compounds **X–XVII** was also proved by measuring the acid numbers.

## EXPERIMENTAL

IR spectra of bisamides **X–XVII** were recorded on spectrophotometer UR-20 from mulls in mineral oil [3]. The acid numbers were determined by potentiometric titration with the use of LPM-60M device by procedure [4]. The purity of compounds was checked by TLC on silica gel of L5/40μ grade, eluent benzene–dichloroethane–acetic acid, 4:1.5:1 (by volume), visualizing of spots under UV irradiation [5]. Molecular weight was determined by cryoscopy in camphor [6].

Anhydride of *cis*-4-cyclohexene-1,2-dicarboxylic acid was obtained as in [7], anhydride of *trans*-4,5-dibromocyclohexane-1,2-dicarboxylic along procedure [8], anhydride of 1,4,5,6,7,7-hexachloro[2.2.1]hept-5-ene-2,3-dicarboxylic acid was prepared by method [9], anhydride of 1,2,3,4,11,11-hexachlorotricyclo-[6.2.1.0<sup>5,10</sup>]undec-2-ene-7,8-dicarboxylic acid by method [10].

**Synthesis of *cis*-4-cyclohexene-1,2-dicarboxylic acid monoamides **VIII**, **IX**.** To a solution of 0.1 mol of anhydride **I** in 20 ml of acetone was added at vigorous stirring a solution of 0.1 mol of *meta*-**(II)** or *para*-**(IV)** phenylenediamine in 100 ml of acetone.

The separated crystals were filtered off, washed with acetone, and dried.

***cis*-4-Cyclohexene-1,2-dicarboxylic acid *N*-(*m*-aminophenyl)amide (**VIII**).** Yield 99%. mp 189°C (from benzene). *R*<sub>f</sub> 0.30. Found, %: C 64.05; H 5.91; N 10.21. C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>. Calculated, %: C 64.62; H 6.15; N 10.77.

***cis*-4-Cyclohexene-1,2-dicarboxylic acid *N*-(*p*-aminophenyl)amide (**IX**).** Yield 98%. mp 202°C (from benzene). *R*<sub>f</sub> 0.31. Found, %: C 63.91; H 5.88; N 10.29. C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>. Calculated, %: C 64.62; H 6.15; N 10.77.

**Synthesis of mixed bisamides **X–XVII**.** (a) To a solution of 0.1 mol of anhydride (**I**) and 0.1 mol of anhydride **IV–VI** or **VII** in 300 ml of acetone at room temperature while vigorous stirring was added solution of 0.1 mol of *meta*-**(II)** or *para*-**(IV)** phenylenediamine in 50 ml of acetone. The mixture was left standing for 12 h till crystals precipitated. The precipitate was filtered off, washed with acetone, dried, and analyzed. The characteristics of bisamides **X–XVII** are given in table.

(b) To a vigorously stirred solution of 0.1 mol of monoamide **VIII** or **IX** in 300 ml DMF was gradually added at room temperature 0.1 mol of anhydride **IV–VII** dissolved in 50 ml of DMF. The mixture was left standing for 12 h. The precipitated crystals were filtered off, dried, and recrystallized from benzene. Yield of bisamides **X–XVII** 96–99%. Characteristics of compounds **X–XVII** prepared along procedures (a) and (b) are identical.

**Synthesis of mixed bisimides **XVIII–XXV**.** A mixture of 0.1 mol of mixed bisamide **X–XVII** and 200 ml of DMF was heated to 152°C for 5–6 h. The cooled mixture was poured into ice water at stirring. The separated crystals were filtered off, washed with distilled water, and recrystallized from methanol. Yield of bisimides **XVIII–XXV** 79–96%, their characteristics are given in table.

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