SYNTHESIS OF ISOMERIC DIIMIDES OF

N,N'-ALKYLENEBISASPARTIC AND

BISMETHYLASPARTIC ACIDS

T. V. Sheremeteva, T. A. Kalinina,V. P. Sklizkova, G. N. Larina,and N. A. Romashina

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Previously we have proposed a simple method for the preparation of the diimides of alkylenebisaspartic acids [1, 2], which is based on the addition of primary and secondary diamines to the double bond of unsaturated cyclic imides in the absence of moisture, for example:



It was reported that two stereoisomeric diimides are formed only when piperazine is used as the diamine component. The theory was expressed that one of the reasons for the isomerism of the diimides is the isomerism of the substituted piperazine ring. As it was, this phenomenon was corroborated at the



Fig. 1. Infrared spectra of reaction products: Ia and Ib) diethylene-N',N"-bismethylasparagine-(Nmethyl)diimide; IIa and IIb) N',N"-xylylene-bisasparagine-(N-methyl)diimide; IIIa and IIIb) N',N"hexamethylene-bisasparagine-(N-methyl)diimide; IV) N-methylcitraconimide.

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TABLE 1

Compound	Mp, ℃	Found/Calculated,%			Empirical	Dihydrochlo- ride, Cl found	Tetramide, N, found
		C	н	N	formula	/calculated	/calculated
Ia	201-202	$\frac{57,16}{57,14}$	$\frac{7,08}{7,14}$	$\frac{16,57}{16,67}$	$C_{16}H_{24}N_4O_4$	$\frac{17,20}{17,36}$	
lь	247-248	$\tfrac{57,24}{57,14}$	$\frac{7,34}{7,14}$	$\frac{16,67}{16,67}$	C ₁₆ H ₂₄ N ₄ O ₄	$\frac{17,80}{17,36}$	
Ha	125—127	$\frac{60,67}{\overline{60,34}}$	$\frac{6,56}{6,14}$	$\frac{15,76}{15,64}$	C18H22N4O4	$\frac{15,71}{16,30}$	
IIb	168—170	$\left \frac{60,41}{60,34}\right $	$\frac{6,20}{6,14}$	$\frac{15,68}{15,64}$	$C_{18}H_{22}N_4O_4$	$\frac{15,80}{16,30}$	$\frac{19,65}{20,00}$
IIIa	74,5—75,5	$\frac{57,12}{56,80}$	$\frac{8,10}{7,92}$	$\frac{15,26}{10,56}$	$C_{16}H_{26}N_4O_4$	$\frac{17,45}{17,27}$	$\frac{21,20}{21,01}$
IIIb	114—115	$\frac{57,10}{56,80}$	$\frac{7,96}{7,92}$	$\frac{16,42}{16,56}$	$C_{16}H_{26}N_4O_4$	$\frac{17,40}{17,27}$	$\frac{20,96}{21,01}$

start of the present investigation, since when studying the reaction of piperazine with the N-methylimide of citraconic acid, in the absence of moisture, the reaction product immediately separated easily into two isomers.



However, in subsequent work with hexamethylenediamine and p-xylylenediamine, a careful carrying out of the experiment also led to the isolation of two stereoisomeric diimides in each case, the formation of which can be explained by the genesis of two asymmetric carbon atoms when diamines add to the double bond of imides (see Table 1). It is postulated that one of the isomers is the meso form, while the other is a racemic mixture of the dd' and ll' forms. In each case the isomeric diimides have the same elemental composition, corresponding to the addition of one molecule of the diamine to two molecules of the unsaturated imide. The IR spectra of the isomers are identical, and in them can be distinctly seen absorption bands at 1700 and 1780 cm⁻¹, which are characteristic for the stretching vibrations of C=O in a five-membered imide ring, while an absorption band at 1645 cm⁻¹, corresponding to the C=C of a double bond (this band is distinctly seen in the spectrum of the starting N-methylcitraconimide), is absent (Fig. 1). The presence of two amine groups in each diimide was proved by preparing the dihydrochlorides. The addition was proved by the NMR spectrum.

EXPERIMENTAL METHOD

Preparation of Diethylene-N',N"-bismethylasparagine-(N-methyl)diimide (Ia) and (Ib). To a stirred solution of 25 g of N-methylcitraconimide in 20 ml of absolute methanol was added in drops a solution of 8.6 g of piperazine in 40 ml of absolute methanol. After 15-20 h the obtained precipitate was filtered. We obtained 20.3 g (60%) of (I). The product was separated into two products by fractional recrystallization from methanol: (Ia), with mp 201-202°C, and (Ib), with mp 247-248°.

Preparation of N',N"-Xylylene-bisasparagine-(N-methyl)diimide (IIa) and (IIb). To a stirred solution of 34 g of N-methylmaleimide in 20 ml of absolute methanol was added in drops a solution of 20.8 g of pxylylenediamine in 40 ml of absolute methanol. A precipitate began to deposit within several minutes. The solution was heated and stirred for 1 h. After 16 h the obtained precipitate was filtered. The yield of product was 49.18 g (91%). The product was separated into two products by fractional recrystallization from methanol: 19.32 g of (IIa) with mp 125-127°, and 29.86 g of (IIb) with mp 168-170°.

Preparation of Tetramide of Product (IIb). An excess of alcoholic methylamine solution was added to the diimide. After 2 days the obtained tetramide was filtered and then recrystallized from methanol; mp 231-232°.

<u>Preparation of N',N"-Hexamethylene-bisasparagine-(N-methyl)diimide (IIIa) and (IIIb)</u>. To a stirred solution of 42.84 g of N-methylmaleimide in 20 ml of absolute toluene was added 22.39 g of hexamethylene-diamine in a mixture of 50 ml of absolute toluene and 35 ml of absolute methanol. After 3-4 h the obtained precipitate was filtered, washed with cold toluene, and dried in a vacuum oven at 50°. We obtained 30.23 g (46.3%) of product (IIIb) with mp 111-112°. After two recrystallizations from acetone, mp 114-115°. To the mother liquor was added 100 ml of diethyl ether; the precipitate represented 23.07 g (35.3%) of product (IIIa). After two recrystallizations from an CCl₄, mp 74.5-75.5°.

<u>Preparation of Tetramide of Product (IIIa)</u>. An excess of aqueous methylamine was added to 2 g of diimide (III) and the mixture left to stand for 2 days. Removal of the excess solvent resulted in the deposition of a white crystalline precipitate. We obtained 2.14 g (93%) of the tetramide. After recrystallization from water, mp 182-183°.

<u>Preparation of Tetramide of Product (IIIb)</u>. An excess of aqueous methylamine solution was added to 2 g of diimide (IIIb). The precipitate failed to dissolve completely. After 2 days the precipitate was filtered. We obtained 2.1 g (91.2%) of the tetramide. After recrystallization from water, mp 204-205°.

CONCLUSIONS

When piperazine, p-xylylenediamine and hexamethylenediamine are reacted with the imides of citraconic and maleic acids in the absence of moisture the amines add to the double bond of the imide rings. Two stereoisomeric diimides of the corresponding alkylenebisaspartic and methylbisaspartic acids are formed here.

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