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With the object of the further development of investigations carried out in our laboratory on the study of the relation of the stability of a five-membered imide ring to the identity of the substituent on the nitrogen [1], we have studied the reactions of various amines with N-substituted succinimide (I) and citraconimide (II):



These reactions were found to provide a convenient method for the preparation of various N-substituted succinamides and citraconamides of general formula



in which R' = alkyl or aryl and R" = alkyl. The products were very pure and were obtained in high yield.

At present there is scarcely any information in the literature on the preparation of diamides of dicarboxylic acids having different substituents on the nitrogen atoms. The generally known methods of synthesizing the amides of monocarboxylic acids from their acid chlorides and esters lead in this case to mixtures of difficultly separable products.

The well studied decyclization of dicarboxylic anhydrides, lactones, and lactams with amines with formation, respectively, of dicarboxylic monoamides, hydroxy acid amides, and amino acid amides prompted us to plan the use of the decyclization of cyclic imides with amines as a method of synthesizing substituted dicarboxylic diamides. The use of different combinations of substituted imides and amines may make it possible to obtain dicarboxylic diamides with different substituents in the amide groups:



in which R' = alkyl or aryl and R'' = alkyl (the N may carry a second R'').

Literature references on this question are confined to indications of the possibility of obtaining succinamides by treating succinimide with alcoholic ammonia in a sealed tube at $100-105^{\circ}$ [2] or with aqueous benzylamine solution [3], and to work on the decyclization of N-substituted quinolinimides with amines [4].

Succinamides
f Substituted
ynthesis of
TABLE 1. S

ľ	Reactants		Yield,	M.p.		Found,	%	Molecular		Calc.,	20
Product	Imide	Amine	60	ړ ا	C	H	z	formula	υ	H	N
N-Methylsuccinamide	Succinimide	Methylamine	11,5	158	46,19	7,68	21,58	C5H10N2O2	46,16	7,69	21,53
N-Cyclohexylsuccinamide	Succinimide	Cyclohexylamine	9,7	190	60,22	9,10	13,73	$C_{10}H_{18}N_2O_2$	60,60	9,10	14,10
N, N'-Dimethylsuccin-	N-Methylsuccinimide	u.۵ g Methylamine	4,45	176,5	50,11	8,37	19,48	$C_6H_{12}N_2O_2$	50,00	8,33	19, 45
amıde N-Methyl-N'-phenylsuccin-	5 g N-Phenylsuccinimide	1.55 g Methylamine	1,93	202	63,63	7,00	13, 99	$C_{11}H_{14}N_2O_2$	64,00	6,80	13, 58
amide N,N-Dimethyl-N'-phenyl-	3.5 g N-Phenylsuccinimide	0.67 g Dimethylamine	2,04	154	65, 25	7,36	12,46	$C_{12}H_{16}N_2O_2$	65,45	7,27	12, 72
succinamide N.N'-Dicvclohexvlsuccin-	3.5 g N-Cvclohexvlsnccin-	1 g Cvclohevvlamine	4	238	68,56	10,01	9,87	$C_{16}H_{28}N_2O_2$	68,50	10,01	10,00
amide	imide 3.62 g	2.16 g			_				_	_	

TABLE 2. Synthesis of Substituted Citraconamides

- Ψ ₀	Z	17,95 12,51
Calc.	н	7,69 6,90 8,63
	υ	53,85 67,24 64,28
Molecular	formula	C ₇ H ₁₈ N ₂ O ₂ C ₁₃ H ₁₆ N ₂ O ₂ C ₁₂ H ₂₀ N ₂ O ₂
10	z	17,87 17,87 12,08 12,63
o und, °	Н	7,64 6,97 9,17
Ц. 	ö	53,40 67,25 64,31
M.D	°C	138 (decomp.) 180–181 (decomp.) 165–166 (decomp.)
, Yield,		11,81 4,74 4,61
	Amine	Methylamine 4.8 g Dimethylämine 2 g Methylamine 1.55 g
Reactants	Imide	N-Methylcítraconimide 17.8 g N-Phenylcítraconimide 6.3 geftracon- imide 0.64 g
Product		N, N [*] - Dimethylcitracon- amide N, N-Dimethyl-N [*] -phenyl- citraconamide N-Cyclohexyl-N [*] -methylcitra- conamide

As stated above, as starting substances in this investigation we selected N-substituted succinimides and citraconimides. The reactions between substituted succinimides and amines were carried out under mild conditions: standing in the cold of solutions or suspensions of the imides and amines in methanol. We carried out the reactions of succinimide with methylamine, succinimide with cyclohexylamine, N-methylsuccinimide with methylamine, N-phenylsuccinimide with methylamine, N-phenylsuccinimide with dimethylamine, and N-cyclohexylsuccinimide with cyclohexylamine.

Under analogous conditions in a medium of aqueous methanol we prepared substituted citraconamides. We carried out the reactions of N-methylcitraconimide with methylamine, N-phenylcitraconimide with dimethylamine, and N-cyclohexylcitraconimide with methylamine.

It must be pointed out that in the case of citraconic derivatives the reaction medium is of determining significance, for when its character is changed the course of the reaction changes. Thus, when the reaction of N-methylcitraconimide with methylamine is carried out in a nonpolar solvent (dry toluene), N,N-dimethylcitraconimide is obtained only as a by-product; the main reaction product, which is isomeric to this, is at present being investigated. The effect of the medium on the course of the reaction is being studied.

EXPERIMENTAL

The reactions were carried out in a conical flask with a ground stopper. A 25-30% solution or suspension of the imide in methanol was cooled to $3-5^\circ$, and a 60-70% solution of the amine in methanol, cooled to a temperature of from -5 to -10° , was added. The reaction mixture was left in ice water for 3-4 h and then at room temperature for 12-16 h. Cooling was then applied, and the precipitated crystals were filtered off on a Schott filter. By strong cooling of the filtrate a further amount of the product was isolated. The crystalline products obtained were purified by recrystallization—succinic derivatives from ethanol and citraconic derivatives from a mixture of benzene and methanol.

The results are summarized in Tables 1 and 2.

SUMMARY

1. Succinimide and its alkyl and aryl derivatives, and also the alkyl and aryl derivatives of citraconimide, react with alkylamines in the cold with opening of the ring.

2. A method was developed for the synthesis of N,N'-dialkyl, N-alkyl-N-aryl, and N,N,N'-trialkyl dicarboxylic diamides (succinamides and citraconamides). It permits the preparation of diamides having different substituents in the amide groups.

3. Nine previously undescribed compounds were synthesized.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-tocover English translations appears at the back of this issue.