

REACTIONS OF AMIDINES WITH OXALYL CHLORIDE. II

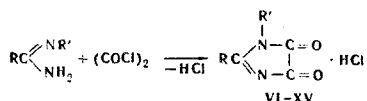
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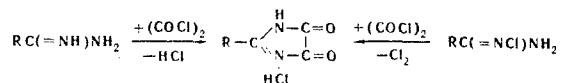
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Unsubstituted, N-alkyl(aryl)- and N-chloroamidines react with oxalyl chloride to form imidazolidine-4,5-diones. The hydrochlorides of 1-aryl-2-alkyl(aryl)imidazolidine-4,5-diones decompose thermally to give N-arylimidoyl isocyanates which change immediately to 4-quinazolones.

Further studies of the reactions of N-alkyl(aryl)amidines with oxalyl chloride have shown that the initial products of the reactions are the imidazolidine-4,5-dione hydrochlorides and not the imidoyloxamoyl chlorides reported earlier [1].

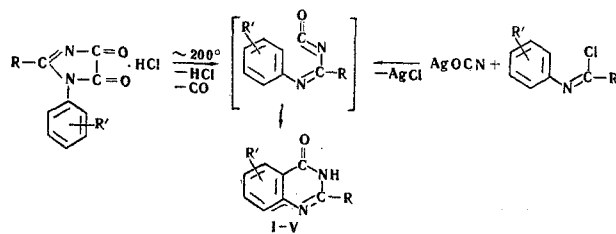


Unsubstituted amidines react similarly with oxalyl chloride and give the hydrochlorides VI and XIII. The same compounds are obtained from the reaction between oxalyl chloride and N-chloroamidines.



Hydrochlorides of the imidazolidine-4,5-diones VI-XV are colorless crystalline materials, many of which are sparingly soluble in the usual organic solvents. Hydrochlorides of the 1-aryl-2-alkyl(aryl)imidazoli-

dine-4,5-diones decompose on heating to their melting points with the evolution of HCl and CO and are converted into 4-quinazolones (method A, Table 1). The decomposition of the 1-aryl-2-alkyl(aryl)imidazolidine-4,5-diones takes place, apparently, with the intermediate formation of the imidoyl isocyanates [1]. In separate experiments with N-arylimidoyl chlorides and silver cyanate, only the 4-quinazolones were obtained. Intermediate products of these reactions, undoubtedly, were the imidoyl isocyanates [3], which confirms the correctness of the proposed reaction sequence.



Under the same conditions, the hydrochloride of 1-(α -naphthyl)-2-phenylimidazolidine-4,5-dione gives 2-phenyl-7,8-benzo-4-quinazolone (V). It has not as yet been possible to isolate individual compounds from the thermal decomposition of 1-alkyl-2-alkyl(aryl)imidazolidine-4,5-diones.

EXPERIMENTAL

Imidazolidine-4,5-diones (VI-XV, Table 2) were obtained from the corresponding amidines and oxalyl chloride by the method previously described [1]. Compounds VI and XIII did not show depressions

*For part I, see [1].

Table 1
4-Quinazolones

Com- pound	Name	Method of prepa- ration	Mp, °C (crystal solvent)	Empirical formula	Found, %		Calc., %		Yield, %
					C	H	C	H	
I	2-Trichloromethyl-6-methoxy-4-quinazolone	A	198-200 (methanol + water)	C ₁₀ H ₇ Cl ₃ N ₂ O ₂	41.29	2.43	40.91	2.40	92
II	2-Trichloromethyl-6-chloro-4-quinazolone	A	243-244 (acetone + water)	C ₉ H ₄ Cl ₄ N ₂ O	36.48	1.34	36.27	1.35	90
III	2-Phenyl-4-quinazolone	A, B	236-237** (benzene)	C ₁₄ H ₁₀ N ₂ O	—	—	—	—	90*
IV	2-Phenyl-6-methyl-4-quinazolone	B	255-257 (benzene)	C ₁₅ H ₁₂ N ₂ O	76.13	5.20	76.26	5.12	30
V	2-Phenyl-7,8-benzo-4-quinazolone	A, B	311-313 (nitromethane)	C ₁₈ H ₁₂ N ₂ O	79.20	4.52	79.39	4.43	79*

*Yields are based on compounds obtained by method A.

**According to the literature [2], mp 235-236° C.

Table 2
Imidazolidine-4,5-diones

Compound	R	R'	Mp, °C (crystal solvent)	Empirical formula	Found, % Cl	Calc., % Cl	Yield, %
VI	CCl ₃	H	194 (decomp.) ^{2*}	C ₄ H ₂ Cl ₄ N ₂ O ₂	56.20	56.30	82 ^{1*}
VII	CCl ₃	CH ₃	156—158 (benzene + + petroleum ether)	C ₅ H ₄ Cl ₄ N ₂ O ₂	53.01	53.33	72
VIII	CCl ₃	<i>n</i> -C ₄ H ₉	107—109 CCl ₄	C ₈ H ₁₀ Cl ₄ N ₂ O ₂	45.88	46.04	70
IX	CCl ₃	C ₆ H ₅ CH ₂ CH ₂	151—152 CCl ₄	C ₁₂ H ₁₀ Cl ₄ N ₂ O ₂	39.58	39.83	87
X	CCl ₃	C ₆ H ₅	188 (decomp.) ^{3*}	—	—	—	99
XI	CCl ₃	<i>p</i> -ClC ₆ H ₄	191 (decomp.) ^{2*}	C ₁₀ H ₅ Cl ₅ N ₂ O ₂	49.39	48.91	93
XII	CCl ₃	<i>p</i> -CH ₃ OC ₆ H ₄	185 (decomp.) ^{2*}	C ₁₁ H ₈ Cl ₄ N ₂ O ₃	39.99	39.61	94
XIII	C ₆ H ₅	H	192 (decomp.) ^{2*}	C ₉ H ₇ ClN ₂ O ₂	17.03	16.84	60 ^{4*}
XIV	C ₆ H ₅	C ₆ H ₅	177 (decomp.) ^{3*}	—	—	—	99
XV	C ₆ H ₅	α -C ₁₀ H ₇	174 (decomp.) ^{2*}	C ₁₉ H ₁₃ ClN ₂ O ₂	10.45	10.53	89

^{1*}Yield from corresponding N-chloroamidine, 93%. ^{2*}The compound was purified by washing with benzene, CCl₄, and benzene and ether. ^{3*}See [1]. ^{4*}Yield from corresponding N-chloroamidine, 82%.

in mixed melting points with those obtained from the reaction between the N-chloroamidines and oxalyl chloride.

4-Quinazolones (I-V). **A.** The 4-quinazolones were obtained by thermal decomposition of the hydrochlorides of 1-aryl-2-alkyl(aryl)-imidazolidine-4,5-diones [1]. **B.** To a solution of 0.05 mole of the N-arylimidazolyl chloride in 80 ml of anhydrous benzene was added 7.5 g (0.05 mole) of silver cyanate. The mixture was stirred vigorously for 3-4 hr. After cooling the reaction mixture, the solid was filtered off with suction. The 4-quinazolone was extracted from the residue with benzene. Yield 20-30%. Compounds III and V, obtained by method A, did not depress the melting points of samples obtained using method B.

REFERENCES

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