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NOVEL PREPARATION OF 1,2,4-OXADIAZOLES FROM N-BENZOYLAMIDINES[1)]

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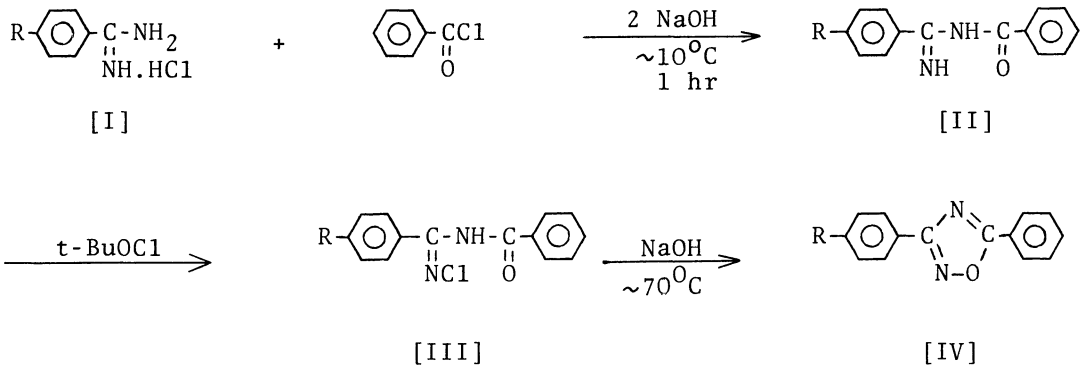
A new efficient procedure for the conversion of N-benzoylamidines with t-butyl hypochlorite and sodium hydroxide to 1,2,4-oxadiazoles has been devised.

In a previous communication,[2)] we have reported that the thermolysis of acyl derivatives of N-benzimidoyl-S,S-dimethylsulfilimine gives rise to 1,2,4-oxadiazoles.

In this communication, we wish to report on the preparation of 1,2,4-oxadiazoles [IV] from N-benzoyl-N'-chlorobenzamidines [III].



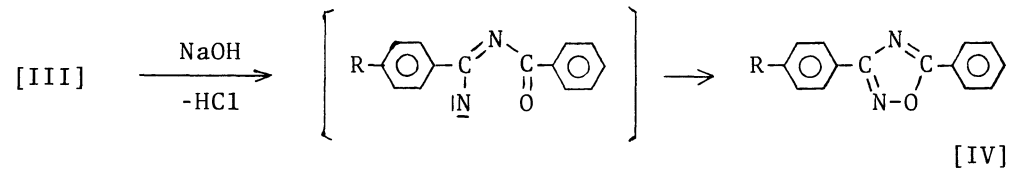
[I] [II] [III] [IV]

Benzoyl derivatives of [I] were easily obtained by the reaction of [I] with benzoyl chloride in the presence of two equivalents of 2N sodium hydroxide.

3,5-Diphenyl-1,2,4-oxadiazole was prepared in good yield by the following procedure. To a stirred suspension of N-benzoylbenzamidine (1.12 g, 5 mmol) in ethanol was gradually added dropwise t-butyl hypochlorite (0.60 g, 5.5 mmol) at 0~5°C. After the mixture had been stirred at the same temperature for 30 minutes, 4 ml of 2N sodium hydroxide was added. When the mixture was warmed at 70°C, white needle-like crystals began to appear. After 5 minutes, the mixture was cooled, and then precipitate was separated by filtration to give 0.77 g of IVa, mp 108°C. IVa was

obtained further by the addition of water (10 ml) to the filtrate, 0.11 g, mp 105~106°C. The total yield was 80%. Recrystallization from aqueous ethanol gave a pure product, mp 108°C. The structure was confirmed by elemental analysis, IR and mass spectra. By the same procedure, N-benzoyl-p-toluamidine was converted to the corresponding 1,2,4-oxadiazole [IVb].

This interesting ring formation may proceed via a nitrene intermediate as proposed by Moriarty et al.[3] and us.[2]



[IV]

Table1. Physical Properties of [II], [III], and [IV]

Compd	R	Yield (%)	Mp (°C)	IR (cm^{-1}) νNH	Anal (Calcd %) C	H	N	Cl
IIa	H	74	98 (98)[4]	3150 3300 3350	-	-	-	-
IIb	Me	82	129~130	3150 3250 3350	75.79 (75.61)	5.97 (5.92)	11.64 (11.76)	-
IIIa	H	-	98	3300	- -	- -	- -	12.90 (13.70)
IIIb	Me	-	129~130	3200	-	-	10.24 (10.27)	13.96 (13.00)
IVa	H	80	108 (108)[5]	absent	75.74 (75.66)	4.56 (4.54)	12.67 (12.60)	-
IVb	Me	46	103~104 (103)[6]	absent	76.26 (76.25)	5.02 (5.12)	11.92 (11.86)	-

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