

# Synthesis of New *N,N'*-Bis(*O*-Nitrophenoxycarbonyl) Diamines

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**Abstract:** The reaction between *bis(o*-nitrophenyl) carbonate and diamine gives a mixture of both cyclic urea and *N,N'*-*bis(o*-nitrophenoxycarbonyl) diamine. In order to obtain *N,N'*-*bis(o*-nitrophenoxycarbonyl) diamine various reaction conditions were employed. The desired products were isolated by column chromatography in yields between 20% and 90% depending on the diamine used.

**Keywords:** *N,N'*-*bis(o*-nitrophenoxycarbonyl) diamine, *bis(o*-nitrophenyl) carbonate

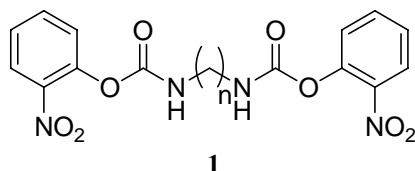
## 1. Introduction

In recent years there has been considerable interest shown in the replacement of phosgene [1] in organic synthesis with non-toxic compounds, especially, highly reactive organic carbonates which can be manufactured using phosgene-free routes.

*Bis(o*-nitrophenyl) carbonate [2], has been under our study since 2001 when we noticed from literature data that in spite of its high reactivity it had been neglected in favour of its much less reactive *p*-isomer which had been used as phosgene substitute for synthesis of carbonates [3], carbamates and ureas [4] and as a coupling reagent for the preparation of various active esters [5].

In these last seven years we demonstrate that *bis(o*-nitrophenyl) carbonate DoNFC could be a feasible alternative reagent to phosgene. It has been successfully utilized for the synthesis of *o*-nitrophenyl carbamates [6,7,8], symmetrical or unsymmetrical disubstituted ureas [7,9,10], imidazolidinones and oxazolidinones [11,12].

We wish to report here the results obtained when *bis(o*-nitrophenyl) carbonate is treated with diamines in order to obtain *N,N'*-*bis(o*-nitrophenoxycarbonyl) diamines.



## 2. Experimental

Melting points were determined on a Boetius apparatus (Carl Zeiss Jena). The IR spectra were recorded in KBr pellet for solid compounds and the reaction monitoring was carried out in thermostated silicon cells of 0.137 mm thickness on a Jasco FT/IR-430 instrument. TLC analyses were carried out on pre-coated plates of silica gel 60 F<sub>254</sub>(Merk). To visualize spots the plates were exposed under a UV 254 lamp. *Bis(o*-nitrophenyl)carbonate **1** was

obtained by the method described [2a]. All reagents were purchased from chemical suppliers and used without further purification

**General Procedure for the Preparation of *N,N'*-*bis(o*-nitrophenoxycarbonyl) diamines.** A solution of compound **1** (0.2 g, 0.657mmoli) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was mixed at 5°C or room temperature with a solution of diamine (0.313 mmoli) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The reaction mixture was kept under stirring until no diamine was detected by TLC (eluent: CHCl<sub>3</sub> : Ac = 5 : 1, developer p-dimethylaminobenzaldehyde). Removal of the solvent under reduced pressure gave a yellow solid which was purified by column chromatography, eluting with CHCl<sub>3</sub> : Ac = 5 : 1. The solvent was removed from the fractions which contain the desired product and the residue was triturated with petroleum ether.

***N,N'*-*bis(o*-nitrophenoxycarbonyl)-ethane-1,2-diamine **1a**.** Obtained in 71% yield as a white solid; mp = 117-119°C; IR (KBr, cm<sup>-1</sup>): 3346i, 1712i, 1531m, 1347m, 1347m, 1220m, 976.

***N,N'*-*bis(o*-nitrophenoxycarbonyl)-propane-1,2-diamine **1b**.** Obtained in 52% yield as a white solid. Mp 108-110°C; IR (KBr, cm<sup>-1</sup>): 3324m, 3076, 2943, 1713i, 1530i, 1347m, 1222, 820.

***N,N'*-*bis(o*-nitrophenoxycarbonyl)-propane-1,3-diamine **1c**.** Obtained in 93% yield as a white solid. Mp 137-139°C; IR (KBr, cm<sup>-1</sup>): 3317m, 3047, 2941, 1715i, 1521i, 1352m, 1221, 784.

***N,N'*-*bis(o*-nitrophenoxycarbonyl)-butane-1,4-diamine **1d**.** Obtained in 93% yield as a white solid. Mp 142-144°C; IR (KBr, cm<sup>-1</sup>): 3359m, 2950, 2866, 1729i, 11520i, 1349m, 1217m, 781.

***N,N'*-*bis(o*-nitrophenoxycarbonyl)-hexane-1,6-diamine **1e**.** Obtained in 89% yield as a white solid. Mp 132-134°C; IR (KBr, cm<sup>-1</sup>): 3326m, 2937, 2853, 1715i, 1522i, 1346m, 1213m, 786.

***N,N'*-*bis(o*-nitrophenoxycarbonyl)-piperazine **1f**.** Obtained in 92% yield as a white solid. Mp 223-225°C; IR (KBr, cm<sup>-1</sup>): 2933, 2875, 1714i, 1526i, 1344m, 1213m, 738.

### 3. Results and discussion

It has been noticed that when *bis(o*-nitrophenyl) carbonate was reacted with diamine at molar ratio 1 : 1 = carbonate diamine, cyclic ureas (imidazolidinones) were obtained [12].

To obtain *N,N'*-*bis(o*-nitrophenoxycarbonyl) diamines (called also shorter "dicarbamates") a molar ratio 2.5:1 DoNFC : diamine was first employed, but a mixture of both cyclic urea and *N,N'*-*bis(o*-nitrophenoxycarbonyl) diamine resulted at room temperature. In literature data [13] had been also mentioned that the direct conversion of diamines with short chain to diisocyanates occurred in low yield because of the cyclization byreaction.

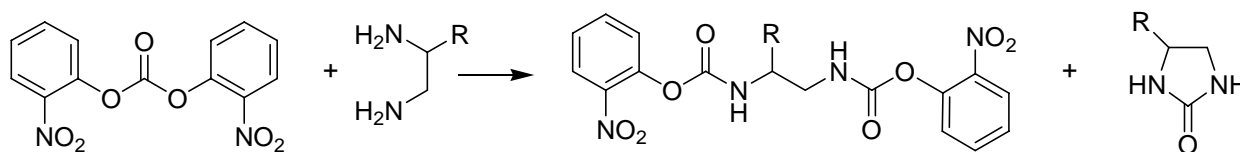
In order to avoid the cyclisation, the molar ratio DoNFC : diamine was further increased. The reaction between *bis(o*-nitrophenyl) carbonate and ethylenediamine (EA) was studied by FTIR spectroscopy at various molar ratio. As could be seen in Figure 1, *bis(o*-nitrophenyl) carbonate which has the carbonyl stretching band at 1796  $\text{cm}^{-1}$  forms with ethylenediamine at molar ratio DoNFC : EA = 1 : 1.1 cyclic urea (imidazolidine) with the carbonyl absorption band at 1713  $\text{cm}^{-1}$ . At higher molar ratio DoNFC : EA a new carbonyl stretching band appears at 1754  $\text{cm}^{-1}$  which belong to the *N,N'*-*bis(o*-nitrophenoxycarbonyl)-ethane-1,2-diamine but also the band characteristic to cyclic urea can be seen in spectrum. Even at molar ration DoNFC : EA = 10 : 1 the cyclic urea

can be noticed, but as the Figure 1 display increasing of molar ratio more than 2.5 : 1 does not bring the rise of dicarbamate percent.. The desired product was finally isolated from reaction mixture by column chromatography separation in 50% yield. Because the reaction between *bis(o*-nitrophenyl) carbonate and ethylenediamine is fast at room temperature the cyclization takes place before the both amine groups to be *o*-nitrophenoxycarbonylated. To avoid this by side reaction, which happen after one amine group reacted with DoNFC, the reaction was carried out at lower temperature. In this case an increase of the *N,N'*-*bis(o*-nitrophenoxycarbonyl)-ethane-1,2-diamine yield to 70% was noticed.

The reaction of DoNFC with 1,2-propilenediamine has been studied also by IR spectroscopy (Figure2) and has been noticed that the cyclic product is obtained in approximately 60% both at 2.5 : 1 and at 4 : 1 molar ratio, in this case the byproduct being obtained even in higher percent. With decreasing of the temperature to 5°C the yield in desired product is improved only with 10%.

Other diamines used are presented in Table 1. They reacted with DoNFC similar to ethylenediamine forming both dicarbamates and cyclic ureas but the proportion in dicarbamate rose with the increasing of carbon chain of diamine.

From 1,3-propilenediamine has been obtained the corresponding dicarbamate in 50% yield at room temperature and in 93% at 5°C.



Scheme 1

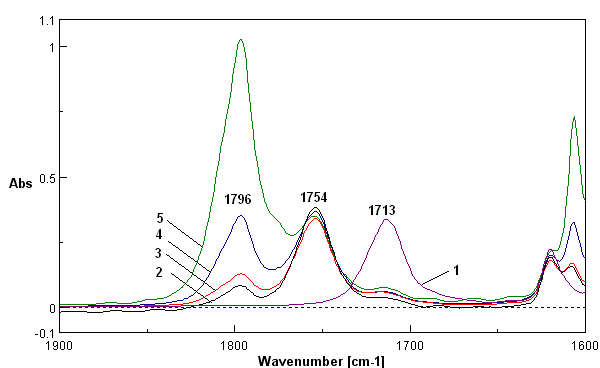


Figure 1. Reaction of DoNFC with ethylenediamine. Study on the reaction using FTIR at different molar ratios.  
DoNFC:EA 1) 1:1,1; 2) 2,5:1; 3) 3:1; 4) 4:1; 5) 10:1

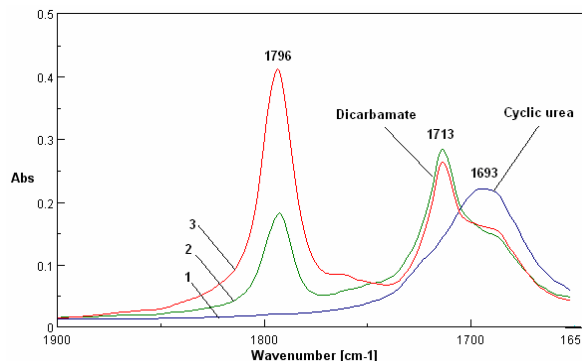
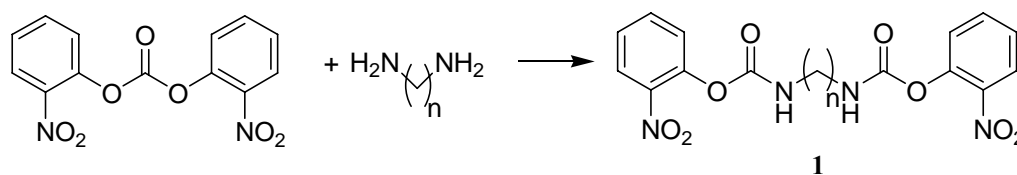


Figure 2. Reaction of DoNFC with 1,2-propilenediamine. Study on the reaction using FTIR at different molar ratios.  
DoNFC: 1,2-propilenediamine 1) 1:1,1; 2) 2,5:1; 3) 4:1



Scheme 2

TABLE I. Preparation of *N,N'*-bis(*o*-nitrophenoxycarbonyl) diamines

Diamine (1)	Molar ratio DoNFC : 1	Time, Temperature	Yield (%)
	2.5:1	3h, r.t.	50a
	2.1:1	1h, 5°C	71a
	2.5:1	3h, r.t.	40a
	2.1:1	1h, 5°C	51a
	2.5:1	5h, r.t.	50a
	2.1:1	1h, 5°C	93a
	2.5:1	5h, r.t.	56a
	2.1:1	1h, 5°C	93a
	2.1:1	3h, r.t.	69b
	2.1:1	1h, 5°C	89a
	2.1:1	1h, r.t.	92a
a) Column chromatography separation. b) Precipitation from reaction mixture			

1,4-Butyldiamine and 1,6-hexyldiamine formed with DoNFC their dicarbamates in 56% and 69% yields at room temperature and in 93% and 89% at 5°C.

The best results have been obtained with piperazine where the yield was 90% at room temperature.

#### 4. Conclusions

A new class of compounds has been obtained from bis(*o*-nitrophenyl) carbonate and aliphatic diamines. The products were isolated from reaction mixture where they are obtained alongside cyclic ureas by column chromatography separation in yields between 20% and 90% depending on the diamine used.

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