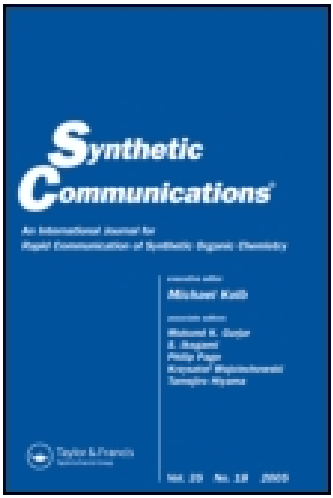

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Synthesis of New Active o-Nitrophenyl Carbamates

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Published online: 17 Dec 2010.

To cite this article: Monika Simon , Carol Csunderlik , Livius Cotarca , Miron Teodor Căproiu , Ion Neda , Maria Cristina Turoczi & Raffaella Volpicelli (2005) Synthesis of New Active o-Nitrophenyl Carbamates, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 35:11, 1471-1479, DOI: 10.1081/SCC-200057986

To link to this article: http://dx.doi.org/10.1081/SCC-200057986

Synthetic Communications®, 35: 1471–1479, 2005

ISSN 0039-7911 print/1532-2432 online
DOI: 10.1081/SCC-200057986

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Abstract: A very high-yielding reaction of *bis*(*o*-nitrophenyl) carbonate with aliphatic amines under mild conditions has been developed. The resulting *o*-nitrophenyl carbamates were characterized by IR, ^{1}H-NMR, ^{13}C-NMR, and elemental analysis.

Keywords: *o*-Nitrophenyl carbamates, bis(*o*-nitrophenyl) carbonate, phosgene-free carbonylations, triphosgene

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INTRODUCTION

Many carbamates are biologically active or represent key intermediates for the synthesis of biologically active compounds.[1–3] They are usually prepared by addition of an amine to a chloroformate[4] or alternately by addition of a hydroxy compound to an isocyanate[5] or to an *N*-substituted carbamoyl chloride.[6] However, the aforementioned methods share a common disadvantage: toxic phosgene is used as the starting material. Recently, there is a tendency to use nonphosgenation methods to obtain this class of compounds. Therefore, highly reactive organic carbonates have been preferred as phosgene substitutes in the synthesis of carbamates.[7–9] In particular, *bis*(*p*-nitrophenyl) carbonate has been extensively used in peptide synthesis as a coupling reagent for the preparation of various biologically active esters[10] and in the synthesis of carbonates,[11] carbamates, and ureas[9] as an efficient alternative to phosgene.

While investigating the reactivity of several active carbonates by theoretical calculations, we found that *bis*(*o*-nitrophenyl) carbonate could be a valid alternative reagent to phosgene.[12] Literature precedent, describing the synthesis of various carbonates[11] and polycarbonates[13] by transesterification reactions, reported *bis*(*o*-nitrophenyl) carbonate among the key examples. Howevew, no account on its reactivity toward nucleophiles was mentioned. In the recent studies, showed that *bis*(*o*-nitrophenyl) carbonate displays an enhanced reactivity toward *N*-nucleophiles with respect to *bis*(*p*-nitrophenyl) carbonate.[14] Our aim consisted in seeking viable synthetic conditions to obtain *o*-nitrophenyl carbamates by using stable and nontoxic *bis*(*o*-nitrophenyl) carbonate.[15,16]

RESULTS AND DISCUSSION

In this article, we report the reaction of *bis*(*o*-nitrophenyl) carbonate with various amines as a simple and convenient method for the synthesis of new biologically active *o*-nitrophenyl carbamates. Johnston et al. have reported the synthesis of one *o*-nitrophenyl carbamate as a key intermediate for synthesis of antitumor active ingredients *N*-(2-fluoroethyl)-*N*-nitrosoureas.[17] Their strategy consisted of combining *o*-nitrophenyl chloroformate with the corresponding amine to furnish the *o*-nitrophenyl carbamate. However, the instability of *o*-nitrophenyl chloroformate, which undergoes uncontrolled decomposition during purification by vacuum distillation, represents a great disadvantage of this method.

Our route toward the synthesis of variously substituted *o*-nitrophenyl carbamates consisted of treating stable and nontoxic *bis*(*o*-nitrophenyl) carbonate (D*o*NFC) with primary and secondary amines. In turn, the starting material D*o*NFC was efficiently obtained following a recent literature procedure,

which consisted of reacting triphosgene with *o*-nitrophenol in dichloromethane in the presence of triethylamine.[16]

Reactions of *bis*(*o*-nitrophenyl) carbonate (D*o*NFC) with primary amines proceeded smoothly, furnishing the desired carbamates in 85–95% isolated yield (Scheme 1, Table 1). A typical reaction occurred at ambient temperature, in dichloromethane, at a molar ratio 1:1.3 of carbonate–amine, going to completion within 5–10 min. No traces of disubstituted ureas were observed when the products were examined by thin-layer chromatography.

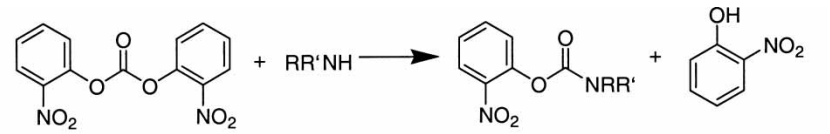
Secondary amines required longer reaction times. Reaction with dibenzylamine was completed after 2 days at molar ratio 1:1.3 of carbonate–amine and in 90 min at molar ratio of 1:2.1. Diisobutylamine completely converted *bis*(*o*-nitrophenyl) carbonate in the corresponding carbamate only after 5 days at a molar ratio of 1:2.5.

The products were isolated by column chromatography (on silica gel, eluent: dichloromethane) and characterized by IR, elemental analysis, and ^{1}H- and ^{13}C-NMR. Selected data are reported in Table 1.

Reactivity studies on the reaction of D*o*NPC and D*p*NPC toward propylamines (*n*PrA and *iso*PrA) in terms of yield and reaction time were executed (Table 2). It was noticed that *bis*(*p*-nitrophenyl) carbonate (D*p*NFC) reacted at least six times slower when compared with *bis*(*o*-nitrophenyl) carbonate (D*o*NPC) (Table 2).

It is also known from literature data that the *N*,*N*-dibenzyl-*p*-nitrophenyl carbamate has been obtained only after 2 days from *bis*(*p*-nitrophenyl) carbonate,[9] using the same molar ratio of 1:2.1 (carbonate–amine) we used in the reaction between *bis*(*o*-nitrophenyl) carbonate and *N*,*N*-dibenzylamine. Once again, this fact confirms that *bis*(*o*-nitrophenyl) carbonate is much more effective than its p-isomer.

As can be seen from Table 1, the *N*-alkyl-*o*-nitrophenyl carbamates present two carbonyl-stretching bands in solid state. The similar *N*-alkyl-*p*-nitrophenyl carbamates have only one carbonyl stretching band. *N*,*N*′-dicyclohexylurea has been obtained when *bis*(*o*-nitrophenyl) carbonate was allowed to react with an excess of amine (1:2.1 ratio) (Scheme 2). The product was separated from the reaction medium by precipitation and had the carbonyl stretching band at 1626 cm^{-1}. This fact also confirms that both of the two carbonyl stretching bands belong to the carbamate group.



(R′) = *n*Pr(H); *i*Pr(H); *n*Bu(H); *i*Bu(H); *s*Bu(H); *i*Pn(H); *c*-C_6H_{11}(H); Bz(H); *i*Bu(*i*Bu); Bz(B

Scheme 1.

Table 1. Synthesis of *o*-nitrophenyl carbamates

Entry	R(R′)	Yield[a] (%)	Mp (°C)	Molecular formula	Calculated/found %C; %H; %N	$\nu_{C=O}$ (cm^{-1})
1	*iso*-Propyl(H)	90	141–143	$C_{10}H_{12}N_2O_4$	53.57; 5.36; 12.5	1748
				224.2	53.72; 5.51; 11.90	1707
2	*n*-Propyl(H)	89	49–51	$C_{10}H_{12}N_2O_4$	53.57; 5.36; 12.5	1750
				224.2	54.18; 5.69; 11.85	1715
3	*n*-Butyl(H)	85	39–41	$C_{11}H_{14}N_2O_4$	55.46; 5.88; 11.76	1744
				238	54.92; 6.20; 11.23	1716
4	*iso*-Butyl(H)	91	56–58	$C_{11}H_{14}N_2O_4$	55.46; 5.88; 11.76	1750
				238	55.38; 5.95; 11.53	1716
5	*sec*-Butyl(H)	88	55–57	$C_{11}H_{14}N_2O_4$	55.46; 5.88; 11.76	1747
				238	55.08; 6.33; 10.95	1711
6	*iso*-Pentyl(H)	90	54–56	$C_{12}H_{16}N_2O_4$	57.14; 6.35; 11.11	1752
				252.3	56.70; 6.52; 10.48	1716
7	*c*-C_6H_{11}(H)	95	144–146	$C_{13}H_{16}N_2O_4$	59.10; 6.00; 10.61	1748
				264.3	59.37; 5.92; 10.10	1714
8	$CH_2C_6H_5$(H)	93	81–83	$C_{14}H_{12}N_2O_4$	61.76; 4.41; 10.29	1728
				272	61.88; 4.33; 10.03	1709
9	*iso*-Butyl(*iso*-Butyl)	70	Oil	$C_{15}H_{22}N_2O_4$	61.22; 7.48; 9.52	1731
				294	60.60; 7.18; 9.33	
10	$CH_2C_6H_5(CH_2C_6H_5)$	85	67–70	$C_{21}H_{18}N_2O_4$	69.61; 4.97; 7.74	1707
				362.4	69.43; 5.06; 7.72	

[a]After column chromatography separation and trituration with petroleum ether.

Table 2. Comparative study for the synthesis of *N*-propyl-nitrophenyl carbamates using D*o*NPC and D*p*NPC

Entry	Carbonate	Amine	Time (min)	Yield (%)
1	D*o*NFC	*n*-PrA	~5	89
2	D*o*NFC	*iso*-PrA	~10	90
3	D*p*NFC	*n*-PrA	60	92
4	D*p*NFC	*iso*-PrA	90	89

In summary, *o*-nitrophenyl carbamates could be easily obtained in mild conditions and high yields. The attained results demonstrate on the one hand the high reactivity of *bis*(*o*-nitrophenyl) carbonate and on the other hand the possibility of efficiently synthesizing new and known active carbamates using a novel and mild procedure.

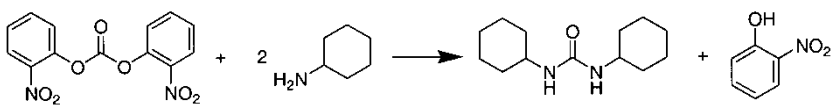
EXPERIMENTAL

Melting points were determined on Boetius apparatus (Carl Zeiss Jena). The IR spectra were recorded in KBr pellet for the solid compounds with a Jasco FT/IR-430 instrument. TLC analyses were carried out on precoated plates of silica gel 60 F_{254} (Merck). To visualize spots, the plates were exposed under a UV 254 lamp. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker DPX at 200 MHz. Elemental analysis was carried out on a Vario EL instrument.

Preparation of Carbamates

The following procedure for preparation of *N-iso*-propyl-*o*-nitrophenyl carbamate is representative of the general method used for synthesis of the carbamates.

N-iso-Propyl-*o*-nitrophenyl carbamate. A solution of *bis*(*o*-nitrophenyl) carbonate (0.506 g, 1.665 mmol) in CH_2Cl_2 (10 mL) was mixed in a 50-mL flask at room temperature with iso-propylamine (0.2 mL, 2.164 mmol). After the consumption of carbonate (TLC analysis, silica; eluent: dichloromethane),



Scheme 2.

the reaction mixture was transferred to a separating funnel and washed with 1 M of HCl solution (5 mL). The organic layer was separated, dried with anhydrous $MgSO_4$, filtered, and the solvent removed by evaporation in vacuo to 1–2 mL volume. The solution was separated by column chromatography on silica gel using dichloromethane as eluent. More polar *o*-nitrophenol was first isolated (Rf = 0.82), followed by the carbamate (Rf = 0.43). The title compound was isolated as a white solid, which was further triturated with petroleum ether to yield 0.336 g of product (90%). Mp 80–82°C; $\nu_{max}(KBr)/cm^{-1} = 1748$; 1707 (C = 0); δ_H (200 MHz; $CDCl_3$) 1.13 (d, 6H), 3.8 (m, 1H), 5 (NH), 7.25 (m, 2H), 7.55 (t, 1H), 7.95 (d, 1H); δ_C (200 MHz; $CDCl_3$) 23 ($2CH_3$), 44 (CH), 125.46 (CH), 125.54 (CH), 126 (CH), 134 (CH), 142 (C), 144 (C), 152 (C).

N-n-Propyl-*o*-nitrophenyl carbamate. Obtained in 89% yield as a white solid. Mp 49–51°C; $\nu_{max}(KBr)/cm^{-1} = 1750$; 1715 (C = O); δ_H (200 MHz; $CDCl_3$) 0.9 (t, 3H), 1.5 (m, 2H), 3.2 (c, 2H), 5.2 (NH), 7.25 (m, 2H), 7.55 (t, 1H), 7.95 (d, 1H); δ_C (200 MHz; $CDCl_3$) 11 (CH_3), 22.5 (CH_2), 44 (CH_2), 125.5 (CH), 125.53 (CH), 126 (CH), 134 (CH), 142 (C), 144 (C), 153 (C).

N-n-Butyl-*o*-nitrophenyl carbamate. Obtained in 85% yield as a white solid. Mp 53–55°C; $\nu_{max}(KBr)/cm^{-1} = 1744$; 1716 (C = O); δ_H (200 MHz; $CDCl_3$) 0.87 (t, 3H), 1.35 (s, 2H), 1.5 (p, 2H), 3.21 (c, 2H), 5.2 (NH), 7.25 (m, 2H), 7.55 (t, 1H), 7.95 (d, 1H); δ_C (200 MHz; $CDCl_3$) 14 (CH_3), 19.5 (CH_2), 31.7 (CH_2), 41 (CH_2), 125.5 (CH), 125.53 (CH), 126 (CH), 134 (CH), 142 (C), 144 (C), 153 (C).

N-iso-Butyl-*o*-nitrophenyl carbamate. Obtained in 91% yield as a white solid. Mp 56–58°C; $\nu_{max}(KBr)/cm^{-1} = 1750$; 1716 (C = O); δ_H (200 MHz; $CDCl_3$) 0.96 (d, 6H), 1.85 (m, 1H), 3.1 (t, 2H), 5.3 (NH), 7.25 (m, 2H), 7.55 (t, 1H), 7.95 (d, 1H); δ_C (200 MHz; $CDCl_3$) 20 (CH_3), 28.6 (CH), 48.8 (CH_2), 125.48 (CH), 125.53 (CH), 126 (CH), 134 (CH), 142 (CH), 144 (C), 153 (C).

N-sec-Butyl-*o*-nitrophenyl carbamate. Obtained in 88% yield as white solid. Mp 55–57°C; $\nu_{max}(KBr)/cm^{-1} = 1747$; 1711 (C = O); δ_H (200 MHz; $CDCl_3$) 0.9 (t, 3H), 1.15 (d, 3H), 1.5 (p, 2H), 3.61 (s, 1H), 5 (NH), 7.25 (m, 2H), 7.55 (t, 1H), 7.95 (d, 1H); δ_C (200 MHz; $CDCl_3$) 10 (CH_3), 20.5 (CH_3), 29.5 (CH_2), 49 (CH), 125.48 (CH), 125.53 (CH), 126 (CH), 134 (CH), 142 (C), 144 (C), 152.5 (C).

N-iso Penthyl-*o*-nitrophenyl carbamate. Obtained in 90% yield as white solid. Mp 54–56°C; $\nu_{max}(KBr)/cm^{-1} = 1752$; 1716 (C = O); δ_H (200 MHz; $CDCl_3$) 0.9 (d, 6H), 1.4 (c, 2H), 1.6 (m, 1H), 3.2 (c, 2H), 5.1 (NH), 7.2 (m, 2H), 7.55 (t, 1H), 7.95 (d, 1H); δ_C (200 MHz; $CDCl_3$) 22 ($2CH_3$), 25.5 (CH), 38.5 (CH_2), 40 (CH_2), 125.48 (CH), 125.53 (CH), 126 (CH), 134 (CH), 142 (C), 144 (C), 153 (C).

N-Ciclohexyl-*o*-nitrophenyl carbamate. Obtained in 95% yield as a white solid. Mp 144–146°C; $\nu_{max}(KBr)/cm^{-1} = 1748$; 1714 (C = O); δ_H (200 MHz; $CDCl_3$) 1.2 (m, 6H), 2 (m, 4H), 3.5 (p, 1H), 5 (NH), 7.25 (m, 2H), 7.55 (t, 1H), 7.95 (d, 1H); δ_C (200 MHz; $CDCl_3$) 24.6 (CH_2), 25.4 (CH_2), 30 (CH_2), 33 (CH_2), 50 (CH), 125.48 (CH), 125.53 (CH), 126 (CH), 134 (CH), 142 (C), 144 (C), 153 (C).

N-Benzyl-*o*-nitrophenyl carbamate. Obtained in 93% yield as a white solid. Mp 81–83°C; $\nu_{max}(KBr)/cm^{-1} = 1728$; 1709 (C = O); δ_H (200 MHz; $CDCl_3$) 4.35 (d, 2H), 5.5 (NH), 7.25 (m, 2H), 7.52 (t, 1H), 7.93 (d, 1H); δ_C (200 MHz; $CDCl_3$) 45.5 (CH_2), 125.52 (CH), 125.6 (CH), 126.15 (CH), 127.59 (CH), 127.74 (CH), 128.77 (CH), 134.5 (CH), 137.5 (C), 142 (C), 144.3 (C), 153.3 (C).

N,*N*-Diisobutyl-*o*-nitrophenyl carbamate. Obtained in 70% yield as a pale yellow oil. $\nu_{max}(KBr)/cm^{-1} = 1731$ (C = O); δ_H (200 MHz; $CDCl_3$) 0.96 (dd, 12H), 2.1 (m, 2H), 3.25 (dd, 4H), 7.3 (m, 2H), 7.6 (t, 1H); 8.05 (d, 1H); δ_C (200 MHz; $CDCl_3$) 19.94 (CH_3), 20.05 (CH_3), 26.7 (CH), 27.39 (CH), 55.25 (CH_2), 55.72 (CH_2), 125.35 (CH), 125.40 (CH), 125.71 (CH), 134.21 (CH), 142.3 (CH), 144.86 (C), 153.5 (C).

N,*N*-dibenzyl-*o*-nitrophenyl carbamate. A solution of bis(o-nitrophenyl) carbonate (0.506 g, 1.665 mmol) in CH_2Cl_2 (10 mL) was mixed in a 50-mL flask at room temperature with dibenzylamine (0.67 mL, 3.498 mmol). When TLC analysis (silica; eluent: dichloromethane) indicated the carbonate consumption, the reaction mixture was treated with 1 M of HCl solution (5 mL). The dibenzylamine chlorohydrate precipitated and was filtered off. The organic layer was separated, dried with anhydrous $MgSO_4$, filtered, and the solvent removed by evaporation in vacuo until 1–2 mL solution remained. This solution passed down a silica column using dichloromethane as eluent. The solvent was removed from the fractions that contain carbamate and the residue was triturated with petroleum ether yielding 0.512 g of white solid ($\eta = 85\%$). Mp 67–70°C; $\nu_{max}(KBr)/cm^{-1} = 1707$ (C = O); δ_H (200 MHz; $CDCl_3$) 4.56 (s, 2H), 4.6 (s, 2H), 7.35 (m, 2H), 7.65 (t, 1H), 8.12 (d, 1H); δ_C (200 MHz; $CDCl_3$) 49.52 (CH_2), 49.85 (CH_2), 125.46 (CH), 125.7 (CH), 126.14 (CH), 127.6 (CH_2), 127.7 (CH), 128.16 (CH), 128.7 (CH), 134.5 (CH), 136.2 (C), 136.34 (C), 142 (C), 144.8 (C), 153.7 (C).

N-iso-Propyl-*p*-nitrophenyl carbamate. The procedure is similar to that for *o*-nitrophenyl carbamates. At column chromatography separation, the *p*-nitrophenyl carbamate came out first (Rf = 0.42), followed by *p*-nitrophenole (Rf = 0.19). Obtained in 89% yield as white solid. Mp 141–143°C; (lit. 144–147)[9]. $\nu_{max}(KBr)/cm^{-1} = 1713$ (C = O); δ_H (200 MHz; $CDCl_3$) 1.25 (d, 6H), 3.95 (m, 1H), 4.95 (NH), 7.33 (d, 2H), 8.25 (d, 2H); δ_C

(200 MHz; $CDCl_3$) 23 ($2CH_3$), 44 (CH), 123 (2CH), 125 (2CH), 143 (C), 155 (C), 156 (C). Anal. calcd. for $C_{10}H_{12}N_2O_4$: C, 53.57; H, 5.36; N, 12.5. Found: C, 53.73; H, 5.52; N, 12.12.

N-*n*-Propyl-*p*-nitrophenyl carbamate. Obtained in 92% yield as white solid. Mp 104–106°C; (lit. 106–108[9]). $\nu_{max}(KBr)/cm^{-1} = 1709$ (C = O); δ_H (200 MHz; $CDCl_3$) 0.95 (t, 3H), 1.6 (m, 2H), 3 (c, 2H), 4.9 (NH), 7.33 (d, 2H), 8.25 (d, 2H); δ_C (200 MHz; $CDCl_3$) 11 (CH_3), 23 (CH_2), 44 (CH_2), 123 (2CH), 125 (2CH), 143 (C), 155 (C), 156 (C). Anal. calcd. for $C_{10}H_{12}N_2O_4$: C, 53.57; H, 5.36; N, 12.5. Found: C, 53.96; H, 5.21; N, 12.03.

N,*N*′-Dicyclohexylurea. A solution of *bis*(*o*-nitrophenyl) carbonate (0.506 g, 1.665 mmol) in CH_2Cl_2 (10 mL) was mixed in a 50–mL flask at room temperature with cyclohexylamine (0.4 mL, 3.4965 mmol). After TLC analysis (silica; eluent: dichloromethane) indicated that no carbamate remained, the precipitate formed was filtered and washed with dichloromethane. The crystalline product yielded 0.28 g (75%). Mp 227–227°C; (lit. 228,[9] 229–230[18]) $\nu_{max}(KBr)/cm^{-1} = 1626$ (C = O) (lit. $\nu_{C=O}$ (KBr)/$cm^{-1} = 1635$).[9]

ACKNOWLEDGMENTS

M.S., C.C., M.T.C., and M.C.T. thank CNCSIS for financial support (Grant A, Cod CNCSIS 475/18/2000).

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