Synthesis of a New Chiral Carbamate: 2-nitrophenyl(1R,2S)-(1,2-diphenyl-2-hydroxyethyl)carbamate

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A new attractive chiral compound was obtained by treating bis(o-nitrophenyl)carbonate with (1S,2R)-(+)-2-amino-1,2-diphenylethanol. The reaction was carried out in dichloromethane at room temperature and the product, 2-nitrophenyl (1R,2S)-(1,2-diphenyl-2-hydroxyethyl)carbamate, was isolated after 1h in high yield by column chromatography and characterized by melting point, IR, ^{1}H- and ^{13}C-NMR spectroscopy.

Keywords: bis(o-nitrophenyl)carbonate, (1S,2R)-(+)-2-amino-1,2-diphenylethanol, 2-nitrophenyl (1R,2S)-(1,2-diphenyl-2-hydroxyethyl)carbamate

Many physiologically active compounds with applications in the pharmaceutical and agrochemical industries have been identified among carbamate derivatives [1]. For this reason various methods are available for preparation of different types of carbamates [1,2].

Bis(*o*-nitrophenyl)carbonate [3], which has already proved to be a feasible substitute of phosgene in the synthesis of symmetrical and unsymmetrcal ureas [4], bis-ureas [5], carbonates [6], polycarbonates [7] and oxazolidinones [8], can also be an alternative in obtaining carbamates [9]. A fast, high-yielding synthesis of new 2-nitrophenyl carbamates under mild conditions has recently been reported [9b].

In this paper we wish to present the synthesis of a new chiral carbamate, 2-nitrophenyl (*1R,2S*)-(1,2-diphenyln-2-hydroxyethyl)carbamate, with potential applications in asymmetric synthesis.

Experimental part

The reaction was monitored in thermostated silicon cells of 0.137 mm thickness on a Jasco FT/IR-430 instrument with a resolution of 1 cm^{-1}.

A solution of bis(*o*-nitrophenyl)carbonate (0.1019 g) in 10 ml CH_2Cl_2 was prepared and the spectrum of this solution was recorded. To this solution (*1S,2R*)-(+)-2-amino-1,2-diphenylethanol (0.0694 g) dissolved in 10 mL CH_2Cl_2 was added and the spectrum of this solution was recorded. The spectra were recorded at different time intervals, the first at 5 min and the last at 1 hour after mixing the reagents (fig. 1).

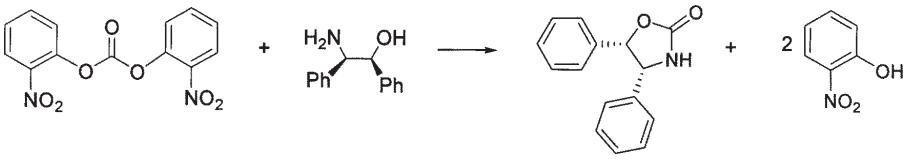
The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker DPX spectrometer at 200 MHz and 50 MHz, respectively.

Method for obtaining the carbamate

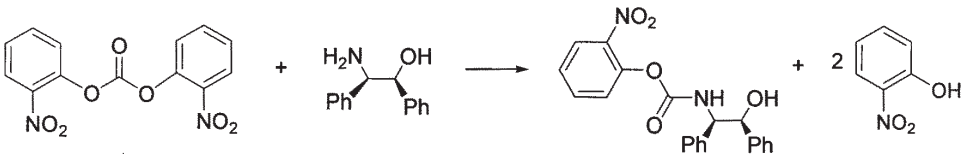
To a solution of bis(*o*-nitrophenyl)carbonate (0.1019 g, 0.358 mmol, 1.1 eq) in 10 mL CH_2Cl_2 a solution of (*1S,2R*)-(+)-2-amino-1,2-diphenylethanol (0.0694 g, 0.32 mmol) in 3 mL CH_2Cl_2 was added. The reaction was maintained under stirring at room temperature for 1 hour. The crude product was purified by column chromatography, using CH_2Cl_2 as eluent until the complete elution of 2-nitrophenol, followed by CH_2Cl_2:EtOAc 1:1. The compound was isolated as a white solid. Yield 0.114 g (95%). Mp 135-137°C; IR (KBr pellet, cm^{-1}): 3346.8m (ν_{NH}), 1714 ($\nu_{C=O}$), ^{1}H-NMR ($CDCl_3$/DMSO-d_6, 200 MHz, ppm): 4.8 (d, NH), 5.13 (s , 2H), 7.19 (s, 10H), 7.32 (t, 1H), 7.58 (t, 1H), 7.71 (d, 1H), 7.96(d, 1H); C ^{13}C-NMR ($CDCl_3$/DMSO-d_6, 50MHz, ppm): 60, 88 (CH), 75.42 (CH), 125.1, 125.4, 125.87, 126.65, 127.1, 127.21, 127.49, 127.68, 128.27, 134.3 (C), 137.93 (C), 141.24 (C), 144.11 (C), 154 (C=O).

Results and discussions

Our purpose was to obtain (*4R,5S*)-diphenyl-2-oxazolidinone by a new method [8b] which consists in treating (*1S,2R*)-(+)-2-amino-1,2-diphenylethanol with bis(*o*-nitrophenyl)carbonate (scheme 1). The reaction was monitored by IR spectroscopy and it was observed that after adding the solution of aminoalcohol to the carbonate solution, the valence vibration band of the carbonate carbonyl group at 1798 cm^{-1} started to decrease, and a new band emerged and increased in time at 1756 cm^{-1}. After one hour at room temperature it was found that the reaction was complete, as the IR spectrum of the reaction mixture was no longer changing in time (fig. 1). Column chromatography was employed to isolate the product obtained, which was initially characterized by melting point and IR spectroscopy.



Scheme 1



Scheme 2

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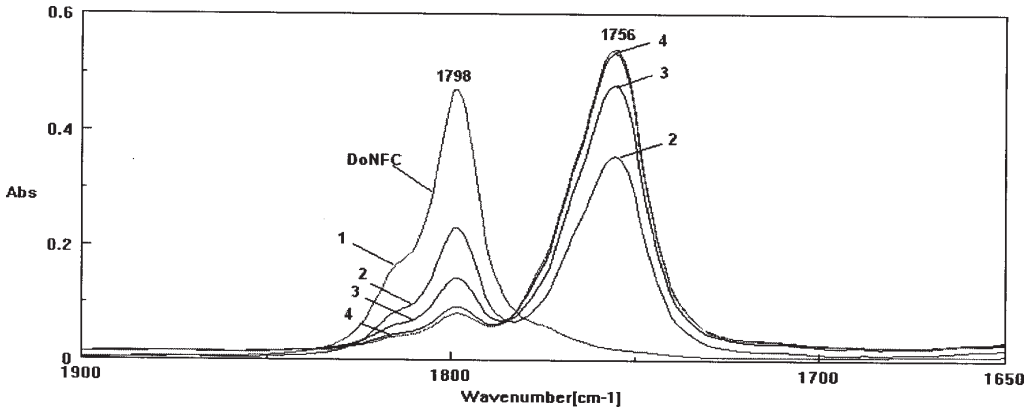

Fig. 1. The variation of C=O valence vibration bands:
1) DoNFC, CH_2Cl_2;
2) 5 min after mixing the reactants;
3) 30 min after mixing the reactants;
4) 1h after mixing the reactants

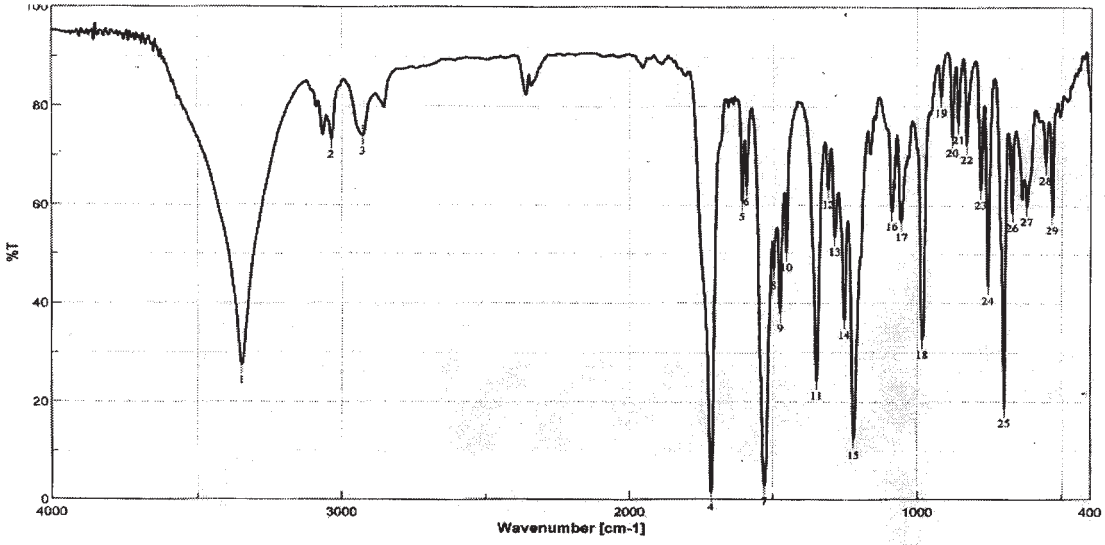

Fig. 2. IR spectrum of isolated compound: 2-nitrophenyl (*1R,2S*)-(1,2-diphenyl-2-hydroxyethyl)carbamate

Result of Peak Picking

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1:	3346.85	27.6113	2:	3035.41	73.3869	3:	2927.41	74.1640	4:	1714.41	1.6877
5:	1607.38	60.8315	6:	1591.95	63.9272	7:	1530.24	2.9347	8:	1498.42	46.8864
9:	1476.24	38.2033	10:	1455.03	50.4679	11:	1350.89	24.4860	12:	1309.43	63.3345
13:	1286.29	53.6507	14:	1253.50	36.8055	15:	1221.68	12.3312	16:	1087.66	58.9061
17:	1055.84	56.7407	18:	984.48	32.7933	19:	916.99	82.0023	20:	878.42	73.9426
21:	857.20	76.5194	22:	828.28	72.4996	23:	780.06	63.2659	24:	754.99	43.7306
25:	700.03	18.8792	26:	671.11	58.5153	27:	620.00	59.8429	28:	554.43	68.2816
29:	532.26	58.1750									

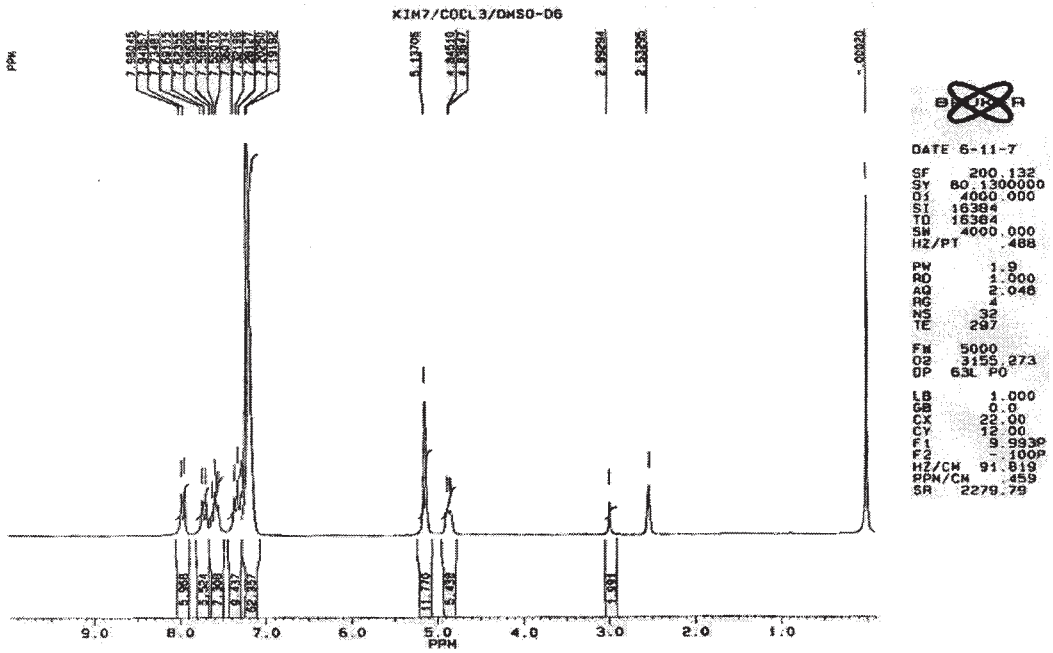

Fig. 3. ^{1}H-NMR spectrum of the isolated compound: 2-nitrophenyl (*1R,2S*)-(1,2-diphenyl-2-hydroxyethyl)carbamate

It was observed that the melting point and the IR spectrum differed from the results reported in the literature for the oxazolidinone[10]. Thus, our product melts in the range 135-137 °C, while the desired oxazolidinone melts at 232.5-233.5 °C[10]. The most significant band in the IR spectrum is the valence vibration of the carbonyl group, which appears at 1714 cm^{-1} for our compound and at 1765 cm^{-1} for oxazolidinone[10]. These results demonstrate that the isolated compound is only the intermediate, 2-nitrophenyl (*1R,2S*)-(1,2-diphenyl-2-hydroxyethyl) carbamate (scheme 2).

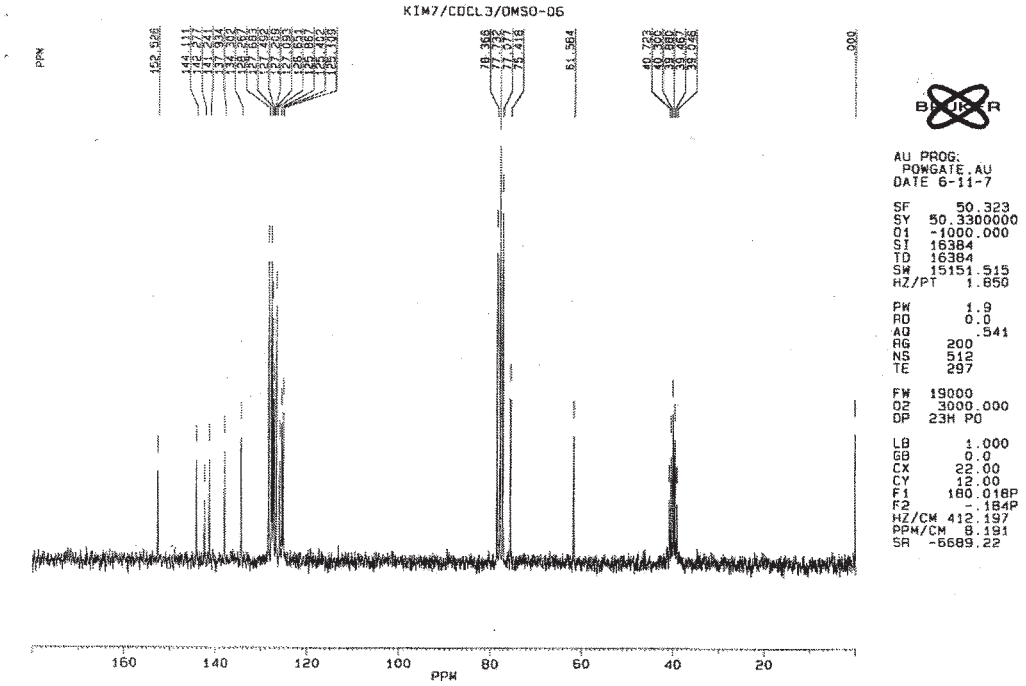

Fig. 4. ^{13}C-NMR spectrum of the isolated compound: 2-nitrophenyl (*1R,2S*)-(1,2-diphenyl-2-hydroxyethyl)carbamate.

The intermediate was characterized by ^{1}H-NMR spectroscopy (fig. 3) and in the spectrum the aromatic protons of the 2-nitrophenyl were identified by their specific chemical shifts, which shows in addition that the product did not cyclize. The two aliphatic protons have the same chemical shift, their signal appearing as a singlet at 5.13 ppm. In the ^{13}C-NMR spectrum (fig. 4) the shifts of the aliphatic carbon atoms at 60 and 88 ppm, carbonyl carbon at 154 ppm and of the tetrasubstituted carbon atoms of the aromatic nuclei can be easily identified.

Conclusions

It was found that the reaction of (*1S,2R*)-(+)-2-amino-1,2-diphenylethanol with bis(*o*-nitrophenyl)carbonate in the absence of the catalyst [8b] stops at the intermediate (carbamate) stage.

A new chiral compound was obtained by the reaction of bis(*o*-nitrophenyl)carbonate and (*1S, 2R*)-(+)-2-amino-1,2-diphenylethanol. This compound has potential applications in asymmetric synthesis.

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