2-ARYLOXY-ALKYLPHENYLCARBAMATES

Cornelia Cercasov *, D. Spantulescu, Ancuta Ciurea and G. Constantinescu

Seven new carbamates were synthetized. The structures of the compounds **1-8** were confirmed by means of spectral data. They have not a special antiinflammatory or antibacterial effect.

Introduction

Carbamates have many biological properties and interesting applications as raw materials in some polyuretan syntheses.

There are some papers, which reported syntheses of various uretans starting by aryloxyalcohols and aromatic isocyanates [1÷4], using different ways. We synthetized 7 new carbamates using a particular way, starting by related aryloxyethanols and phenylisocyanate. Their structures were confirmed by spectral data. Some preliminary biological tests do not emphasize a relevant biological activity, yet.

Materials and Methods

Melting points were determined using a *Boetius* apparatus and are uncorrected.

The IR spectra were made in KBr pellets on an *IR-71 KZJ* apparatus.

^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ at 400MHz, 100MHz respectively using a *Jeol-Lambda 400* apparatus.

MS-spectra were recorded using a *JEOL GCMate* apparatus, EI type.

Purity degree for each synthetized substance was determined by TLC using as elution system a mixture of petroleum ether: ethyl ether: dichloromethane: ethyl acetate (7.5: 1: 2: 1 in volumes) and fluorescent silicagel as stationary phase. The spots were revealed using UV light (λ=250 nm).

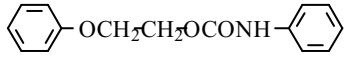
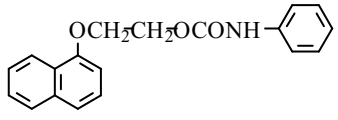
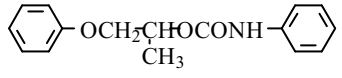
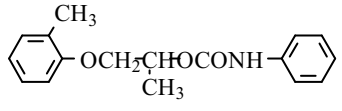
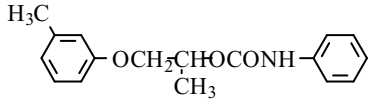
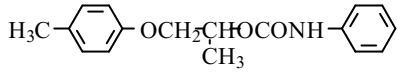
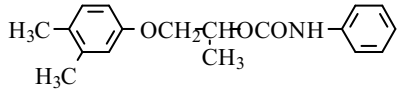
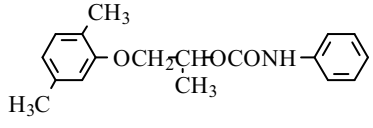
General procedure for the synthesis of carbamates 1-8

A solution of 1mMole 2-aryloxyethanol (or 1-Methyl-2-aryloxyethanol) and 1mMole phenylisocyanate in *n*-hexane was refluxed for 2 hours. The reaction was monitorized through TLC until the reactants are consumed. After cooling, the carbamate crystallizes and it is filtered. The carbamate is recrystallized from the apropriate solvent (see Table 1).

* Department of Organic Chemistry, Faculty of Chemistry, University of Bucharest, 90-92 Sos. Panduri, 76233 Bucharest - 5, Romania

The phenoxyetanol and the naphtoyethanol, used as raw materials, were synthetized from phenols and ethylencarbonate, catalyzed by KI, using the Katzschmann's similar procedure [5]. Substitued phenoxypropanols, used as raw materials, were synthetized from phenols and propenoxyde, catalyzed by KCl, using the Spasov & co way [6]. All aryloxyalcohols were purified by law pression distillation and their purity was confirmed by chromatography and spectral data [a].

Table 1. Physical characteristics of the synthetized carbamates

No	Compound	Yield [b] (%)	M.p. (°C) and recryst. solvent	R_f	Reference
1		27	96-97 $CHCl_3$:*n*-hexane	0,850	[7]
2		51.4	139-140 CH_2Cl_2	0,805	new compound
3		34	85-86 *n*-hexane	0,800	new compound
4		15,6	132-133 *n*-hexane	0,833	new compound
5		41,5	65-66 CH_2Cl_2: *n*-hexane	0,819	new compound
6		29,4	96-97 *n*-hexane	0,799	new compound
7		33,3	97-98 *n*-hexane	0,833	new compound
8		40,9	100-101 *n*-hexane	0,819	new compound

[a] data included in Project reports of the Contract 612/1996 « β-Aryloxyalcohols and derivats », supported by Research & Technology Ministry, performed by the authors

[b] yields calculated after recrystallization

Results and Discussions

The IR spectra validate the expected stuctures, by the specifical absorptions of carbamate function and the unchanged absorptions of the aryloxy function (see Table 2). In the IR spectra of all carbamates **1**-**8**, absorptions in the 2250÷2390 cm^{-1} and 3420÷3440 cm^{-1} domains, typical for isocyanate, respectively hydroxyde function, are absent. New absorptions are present in the 1710÷1725 cm^{-1} domain that is characteristic [2÷4] for carbamate (urethan) group.

A small variance of the absorptions of CH_2 and C_{ar}-O-CH_2 was noticed, due to the substitution effect of the aryl ring.

Table 2. IR Absorptions of the carbamates

Comp.	ν_{CO} (cm^{-1})	δ_{NH} (cm^{-1})	ν_{COCar} (cm^{-1})		ν_{Ar} (cm^{-1})	ν_{NH} (cm^{-1})	ν_{CH2} (cm^{-1})	
			as	**sim**			**as**	**sim**
1	1690	1520	1235	1070	680,720,920,1445,1495,1590	3270,3020	2960	2830
2	1677	1515	1225	1065	670,720,910,1430,1500,1575	3280,3020	2920	2800
3	1670	1520	1217	1095	670,730,910,1430,1475,1575	3210,2980	2880	2710
4	1682	1520	1222	1075	690,730,880,1430,1485,1580	3220,3075	2980	2880
5	1670	1522	1230	1105	680,725,915,1430,1485,1585	3180,3120	3000	2900
6	1680	1525	1227	1105	680,730,920,1430,1505,1587	3250,3040	2980	2920
7	1682	1530	1215	1065	682,727,910,1425,1495,1587	3260,3060	3020	2880
8	1672	1507	1180	1020	665,710,772,1420,1470,1580	3220,3060	3000	2890

The MASS spectra of the chosen substances (see Table 3) may be explained by an easy and rapid fragmentation of the molecule at the C_{ar}-O-C_{aliph} bond level, resulting an aryloxy ion (m/z=93 for **1** and **3**, respectively 144 for **2**, 107 for **6**) or the related phenol (m/z= 94 for **1** and **3**, respectively 145 for **2**, 108 for **6**) and a rest containing the aliphatic chain, the carbamate function and the other phenyl ring (m/z=164 for **1** and **2**, respectively 178 for **3** and **6**). The others peaks result as effect of the fragmentation of this rest.

Table 3. Mass spectra of the carbamates

Comp.	Relative abundance /(m/z)
1	63/5,2; 64/6; 65/33; 66/7,4; 77/73,9; 78/6,5; 79/3; 91/19,8; 92/28,3; **93/19,4**; 94/28; 95/3,3; 103/2,4; 107/4; 119/25,1; 120/78,7; 121/10,8; 129/3,4; 137/17,7; 138/6,6; 163/5,4; **164/100**; 165/36,4; 166/3,4; **257/31,4**; 258/5,7
2	63/9,9; 64/11,3; 65/17,3; 77/38,6; 89/7,5;91/20,8; 92/30,6; 93/58; 115/69,1; 116/33,9; 119/47,4; 120/79; 121/6,9; 126/6,9; 127/28,3; 128/9,2; 143/7; **144/91,8**; **145/12,2**; 154/12,3; 163/8,8; 164/100; 165/50,9; 178/5,1; 188/32,6; **307/38,2**; 308/8,5
3	60/20,4; 63/4,1; 64/4,8; 65/25,7; 66/7,5; 77/64,6; 78/8,1; 79/9; 91/13,4; 92/16,7; **93/22,4**; **94/30,6**; 95/9,8; 105/5; 106/3,9; 107/33,7; 108/6,6; 119/22,3; 120/41,4; 121/4,2; 132/2,6; 133/6,7; 134/79,9; 135/18,1; 137/7,2; **178/100**; 179/25,5; **271/26,7**; 272/5,3
6	53/5,7; 60/46,6; 63/7,6; 64/7,6; 65/46,1; 66/8,2; 77/58,4; 78/18,9; 79/21,3; 89/5,2; 90/6,5; 91/83,8; 92/39,6; 93/35,1; 105/8,3; 106/8; **107/54,5**; **108/60,8**; 109/11,7; 119/33; 120/94,7; 121/37; 122/6,9; 132/7,7; 133/14,8; 134/21; 143/8,3; 148/66,7; 149/17,5; 160/7,8; 166/6,7; 177/8,1; **178/100**; 179/68; 180/6,4; **285/49,9**; 286/10,4

The RMN spectra of the compound **1-8** was obtained. The ^{1}H and ^{13}C NMR spectra also validate the structure of the synthetized compounds. No special behaviour was observed.

Table 4. ^{1}H-NMR Chemical shifts of the carbamates 1-8 - δ, ppm -

Comp.	ArO-							OCH_2	CHR	R	>NH	-NHAr		
	H2	*H3*	*H4*	*H5*	*H6*	*H7*	*H8*					*H2,H6*	*H3,H5*	*H4*
1	6,93 dq	7,29 td	6,97 tt	7,29 td	6,93 dq	-	-	4,41 t	4,52 t	-	6,76 s	7,37 t	7,30 t	7,06 t
2	6,75 d	7,34 t	7,43 d	7,78 dd	7,47 td	7,45 m	8,29 dd	4,31 t	4,63 t	-	6,79 s	7,37 d	7,27 t	7,05 t
3	6,93 dq	7,28 td	6,96 tt	7,28 td	6,93 dq	-	-	4,06 d	5,26 qt	1,40 d	6,67 s	7,37 d	7,30 t	7,06 tt
4	2,15 s CH_3(2)	7,05 m	6,79 dt	7,05 m	6,72 d	-	-	3,96 m	5,23 m	1,36 d	6,60 s	7,30 d	7,22 t	6,98 tt
5	6,75 s	2,32 s CH_3(3)	6,78 d	7,16 t	6,72 d	-	-	4,04 m	5,25 m	1,42 d	6,67 s	7,37 d	7,30 t	7,06 t
6	6,73 dt	6,98 dd	(CH_3) 2,19 s	6,98 dd	6,73 dt	-	-	3,93 dd	5,16 qt	1,33 dd	6,63 s	7,29 d	7,21 td	6,97 td
7	2,18 s CH_3(2)	7,00 d	6,68 d	2,30 s CH_3(5)	6,63 s	-	-	4,03 m	5,30 m	1,44 d	6,61 s	7,38 d	7,30 t	7,06 dt
8	6,65 d	2,14 s CH_3(3)	2,11 s CH_3(4)	6,95 d	6,58 dd	-	-	3,94 d	5,17 m	1,34 dd	6,60 s	7,30 d	7,22 t	6,98 tt

Table 5. ^{13}C-NMR Chemical shifts of the carbamates 1-8 - δ, ppm -

Comp.	ArO-										CH_3 arom.	CHR	R alif.	OCH_2	OCO	-NHAr			
	C1	*C2*	*C3*	*C4*	*C5*	*C6*	*C7*	*C8*	*C9*	*C10*						*C1*	*C2, C6*	*C3, C5*	*C4*
1	158,31	114,46	129,48	121,14	129,48	114,46	-	-	-	-	-	63,47	-	66,02	153,26	137,62	118,68	128,95	123,46
2	154,20	104,81	125,69	120,74	127,41	126,47	125,30	121,96	125,53	134,46	-	63,50	-	66,49	153,36	137,62	118,76	129,01	123,55
3	158,48	114,54	129,43	121,04	129,43	114,54	-	-	-	-	-	69,73	16,77	69,98	152,93	137,76	118,61	128,94	123,34
4	156,59	126,96	137,76	120,73	126,75	110,97	-	-	-	-	16,13	69,86	16,89	70,17	152,97	137,76	118,63	129,03	123,43
5	158,56	115,48	139,55	121,90	129,21	111,38	-	-	-	-	21,46	69,86	16,83	70,00	152,89	137,77	118,59	129,03	123,41
6	156,46	114,48	129,89	130,32	129,89	114,48	-	-	-	-	20,42	69,86	16,82	70,28	152,92	137,79	118,61	128,99	123,38
7	156,49	123,78	130,43	121,24	136,55	112,07	-	-	-	-	15,70 21,43	69,96	16,89	70,18	152,98	137,79	118,64	129,04	123,42
8	156,72	116,27	137,81	123,39	129,28	111,45	-	-	-	-	18,77 19,98	69,95	16,83	70,22	152,92	137,75	118,56	129,02	123,39

There is not an important ^{13}C NMR shifts difference between the carbons of the methylene groups linked at the aryloxy rest and the carbons direct linked with the carbamate group. The ^{13}C NMR chemical shifts of the carbon from carbamate group are almost constant: 152.9 for the compounds **3**-**8** containing isopropylidene group and 153.3 for the compounds **1**, **2** containing ethylidene group (see Tables 4 and 5).

Biological activity of carbamates. A biological research of the compounds 1÷8 may be useful, because many of the carbamates have a biological activity. Some preliminary antibacterial and antiinflammatory tests did not emphasize a special effect of these compounds.

Conclusions

Seven new compounds were synthetized and characterized. The synthesis way offers a medium yield, and it can be improved by a better crystallization of the final compounds.

The preliminary biological tests do not provide an interesting behaviour of the compounds **1-8**.

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