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Synthesis and Properties of *N*-Hydroxymethylcarbamates and Their Derivatives

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SUMMARY:

The dicarbamates **3a–d** were synthesized by the method of Kraft. Their reaction with formaldehyde in the presence of alkali or acid afforded in one case the mono-*N*-hydroxymethyl derivative **4** and with **3a–c** the *N*,*N'*-bis(hydroxymethyl) derivatives **5a–c**. These were transformed into the corresponding *N*,*N'*-bis(alkoxymethyl) derivatives **6a–f** by reaction with alcohols at pH 2,2. The reaction of the *N*-hydroxymethylcarbamates with urea afforded urea derivatives of type **9** and **10**.

ZUSAMMENFASSUNG:

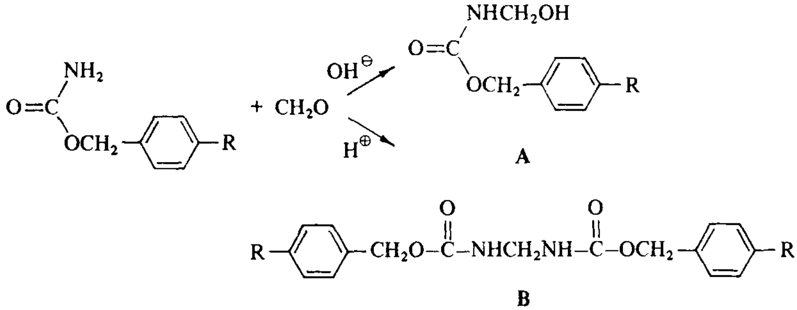
Die Dicarbamate **3a–d** wurden nach der Methode von Kraft dargestellt. Ihre Reaktion mit Formaldehyd in Gegenwart von Alkali oder Säure lieferte in einem Fall das Mono-*N*-hydroxymethyl-Derivat **4** und mit **3a–c** die *N*,*N'*-Bis(hydroxymethyl)-Derivate **5a–c**. Diese wurden durch Reaktion mit Alkoholen bei pH 2,2 in die entsprechenden *N*,*N'*-Bis(alkoxymethyl)-Derivate **6a–f** übergeführt. Die Reaktion von *N*-Hydroxymethylcarbamaten mit Harnstoff führte zu den Harnstoffderivaten vom Typ **9** und **10**.

Introduction

Carbamates react with formaldehyde to give carbamate-formaldehyde resins which are superior to urea- or melamine-formaldehyde resins as crease-resistant finish agents in the textile industry.

In the previous paper[1], it was reported that alkali-catalyzed reactions of *p*-substituted *O*-benzyl carbamates with formaldehyde yield *N*-hydroxymethyl derivatives (**A**). Acid catalysis affords *p*-substituted benzyl esters of *N*,*N'*-methylene dicarbamates (**B**).

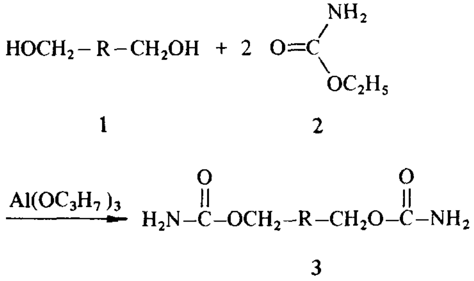
The present paper deals with the synthesis of dicarbamates, their *N*,*N'*-bis(hydroxymethyl) derivatives and their reactions with alcohols or urea.



R=Cl,Br,NO_2,H,OCH_3

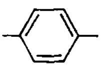
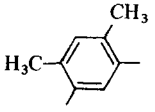
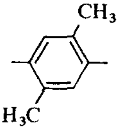
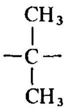
Synthesis and characterization of dicarbamates

The dicarbamates (**3a–d**) were prepared from bis(hydroxymethyl) derivatives (**1a–d**) and *O*-ethyl carbamate (**2**) by the method of Kraft[2)] and characterized by elemental analysis (s. Exp. Part, Tab. 3) and by their IR and NMR spectra (Tab. 1).



$$HOCH_2-R-CH_2OH + 2\ O{=}C(NH_2)(OC_2H_5) \xrightarrow{Al(OC_3H_7)_3} H_2N-\overset{\displaystyle O}{\overset{\|}{C}}-OCH_2-R-CH_2O-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2$$

1 **2** **3**

1,3	a	b	c	d
R				 $-C(CH_3)_2-$

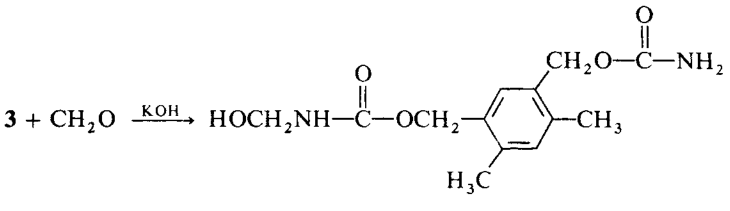
Synthesis and characterization of N-hydroxy- and N-alkoxyderivatives of dicarbamates

The reaction of *O*,*O*-methylene-(4,6-dimethyl-1,3-phenylene)methylene dicarbamate (**3b**) with paraformaldehyde and catalytic amounts of 6 N potas-

Tab. 1. IR and NMR data of dicarbamates

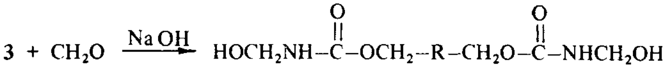
Compound	Wave numbers in cm^{-1}			δ-Values in ppm			
	$\nu_{(NH_2)}$	$\nu_{(C=O)}$	$\delta_{(NH_2)}$	Phenyl	$—NH_2$	$—CH_2O—$	$—CH_3$
O,O'-Methylene-1,4-phenylenemethylene dicarbamate (**3a**)	3430—3230	1700	1620	7,27	6,5	4,93	—
O,O'-Methylene-(4,6-dimethyl-1,3-phenylene)-methylene dicarbamate (**3b**)	3427—3207	1687	1605	7,22 7,02	6,5	4,93	2,23
O,O'-Methylene-(2,5-dimethyl-1,4-phenylene)-methylene dicarbamate (**3c**)	3460—3180	1693	1610	7,10	6,5	4,93	2,23
O,O'-Isopropylidene dicarbamate (**3d**)	3427—3207	1708	1615	—	6,4	3,7	0,85

sium hydroxide affords the mono-*N*-hydroxymethyl derivative (**4**) in ≈8% yield:



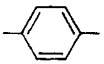
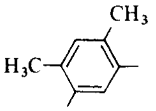
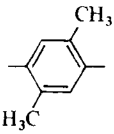
4

3a, b, and **c** react with formaldehyde in the presence of sodium hydroxide to give the *N*,*N*′-bis(hydroxymethyl) derivatives (**5a–c**).



$$3 + CH_2O \xrightarrow{NaOH} HOCH_2NH-\overset{O}{\overset{\|}{C}}-OCH_2-R-CH_2O-\overset{O}{\overset{\|}{C}}-NHCH_2OH$$

5

5	a	b	c
R			

The mono-*N*-hydroxymethyl derivative **4** was characterized by its elemental analysis (s. Exp. Part) and its spectral data. It shows IR absorption bands at 1610 and 1530 cm^{-1} characteristic of ν_{NH_2} and $\nu_{CN} + \delta_{NH}$ (Fig. 1a). Its NMR spectrum (Fig. 1b) indicates the presence of NH_2-protons ($\delta = 6{,}55$ ppm) and the NH-proton ($\delta = 7{,}85$ ppm).

The *N*,*N*′-bis(hydroxymethyl) derivatives **5a–c** were also characterized by their elemental analyses (s. Exp. Part, Tab. 4) and their spectral data.

E.g. in the IR spectrum of the reaction product of **3a** with formaldehyde (**5a**) the absorptions at 3430—3230 and 1620 cm^{-1} of the dicarbamate have

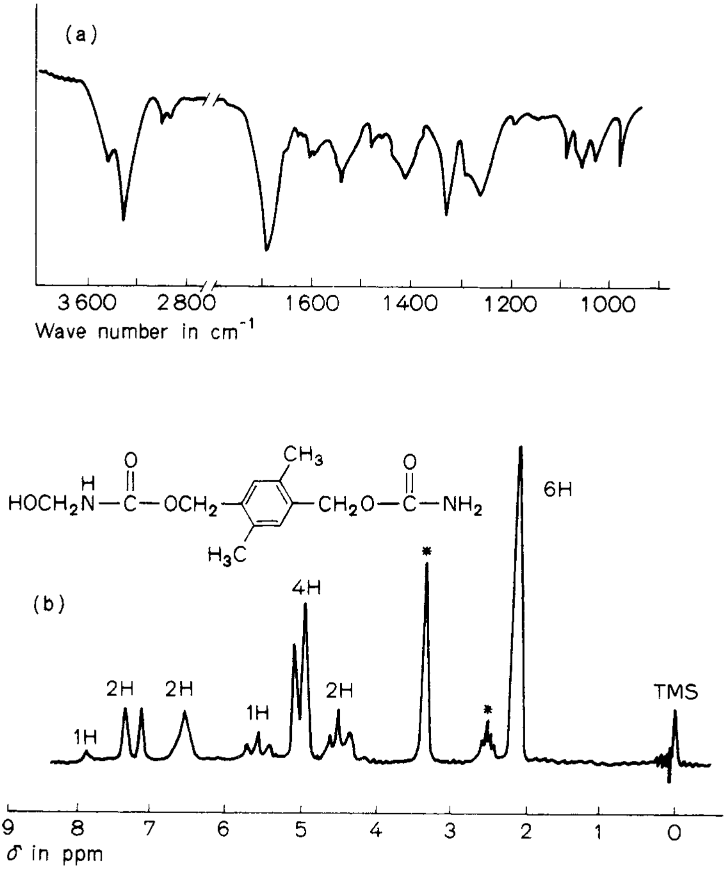


Fig. 1. (a) IR (in KBr) and (b) NMR spectra (in DMSO-d_6) of **4**. Absorptions due to solvent impurities are marked by an asterix

disappeared and new bands were observed at 3317 (ν_{NH}/ν_{OH}) and 1530 cm^{-1} ($\nu_{CN}+\delta_{NH}$). The NMR spectrum of **5a** indicates the presence of the NH-proton ($\delta=7{,}8$ ppm) and of the OH-proton ($\delta=5{,}5$ ppm).

The IR and NMR data of the *N*,*N*′-bis(hydroxymethyl) derivatives are summarized in Tab. 2.

Compounds **5a–c** react with alcohols at pH 2,2 to give the corresponding *N*,*N*′-bis(alkoxymethyl) derivatives **6a–f**).

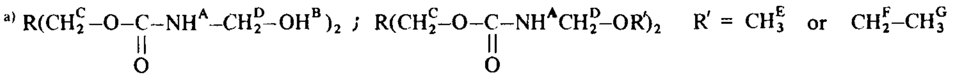
The elemental analyses (s. Exp. Part, Tab. 4) and spectroscopic data of **6a–f** confirm their structure. E.g. in the IR spectrum of the reaction products

Tab. 2. IR and NMR data of *N*,*N*′-bis(hydroxymethyl) and *N*,*N*′-bis(alkoxy methyl) derivatives of dicarbamates

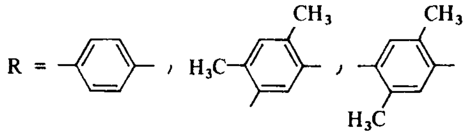
Compound	Wave numbers in cm^{-1}				δ-Values in ppm$^{a)}$							
	$\nu_{NH,OH}$* ν_{NH}	$\nu_{C=O}$	ν_{CN} $+\delta_{NH}$	ν_{COC}	A	Phenyl	B	C	D	E*F	G	CH_3 in phenyl
O,*O*′-Methylene-1,4-phenylenemethylene di(*N*-hydroxymethylcarbamate) (**5a**)	3317*	1695	1530	—	7,68 −7,9	7,29	5,37 −5,6	5,0	4,32 −4,45	—	—	—
O,*O*′-Methylene-(4,6-dimethyl-1,3-phenylenemethylene) di(*N*-hydroxy-methylcarbamate) (**5b**)	3250*	1690	1530	—	7,65 −7,88	7,02 −7,23	5,38 −5,6	4,92	4,33 −4,55	—	—	2,24
O,*O*′-Methylene-(2,5-dimethyl-1,4-phenylenemethylene) di(*N*-hydroxymethylcarbamate) (**5c**)	3407* 3297*	1685	1545	—	7,63 −7,84	7,07	5,35 −5,52	4,94	4,32 −4,53	—	—	2,22
O,*O*′-Methylene-1,4-phenylenemethylene di(*N*-methoxymethylcarbamate) (**6a**)	3240	1685	1540	1130	8,04 −8,25	7,37	—	5,08	4,4 −4,5	3,15*	—	—
O,*O*′-Methylene-1,4-phenylenemethylene di(*N*-ethoxymethylcarbamate) (**6b**)	3280	1695	1530	1110	8,02 −8,25	7,42	—	5,1	4,45 −4,51	3,27 −3,63	0,98 −1,22	—

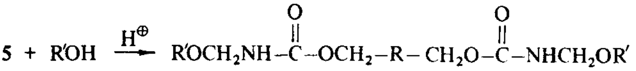
Tab. 2. Continued.

Compound	Wave numbers in cm^{-1}				δ-Values in ppm[a)]							
	$\nu_{NH,OH}$* ν_{NH}	$\nu_{C=O}$	ν_{CN} $+\delta_{NH}$	ν_{COC}	A	Phenyl	B	C	D	E*F	G	CH$_3$ in phenyl
O,O'-Methylene-(4,6-dimethyl-1,3-phenylenemethylene) di(*N*-methoxymethylcarbamate)(**6c**)	3220	1690	1530	1128	8,0 −8,23	7,10 −7,31	—	5,06	4,4 −4,5	3,2*	—	2,3
O,O'-Methylene-(4,6-dimethyl-1,3-phenylenemethylene) di(-*N*-ethoxymethylcarbamate)(**6d**)	3290	1728	1530	1102	7,95 −8,16	7,05 −7,26	—	5,03	4,42 −4,53	3,26 −3,62	0,97 −1,21	2,27
O,O'-Methylene-(2,5-dimethyl-1,4-phenylene methylene) di(*N*-methoxymethylcarbamate)(**6e**)	3320	1728	1530	1130	8,03 −8,22	7,2	—	5,12	4,42 −4,54	3,17*	—	2,27
O,O'-Methylene-(2,5-dimethyl-1,4-phenylenemethylene) di-(*N*-ethoxymethylcarbamate) (**6f**)	3297	1702	1547	1102	7,93 −8,2	7,18	—	5,04	4,42 −4,53	3,38 −3,65	0,98 −1,22	2,25

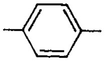
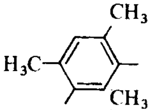
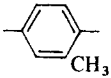
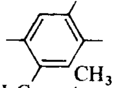
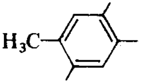
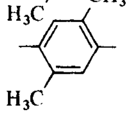


[a)] $R(CH_2^C{-}O{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}NH^A{-}CH_2^D{-}OH^B)_2$; $R(CH_2^C{-}O{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}NH^A CH_2^D{-}OR')_2$ $R' = CH_3^E$ or $CH_2^F{-}CH_3^G$





$$5 + R'OH \xrightarrow{H^{\oplus}} R'OCH_2NH-\overset{O}{\overset{\|}{C}}-OCH_2-R-CH_2O-\overset{O}{\overset{\|}{C}}-NHCH_2OR'$$

6	R	R'	6	R	R'
a		CH_3	d		C_2H_5
b		C_2H_5	e		CH_3
c		CH_3	f		C_2H_5

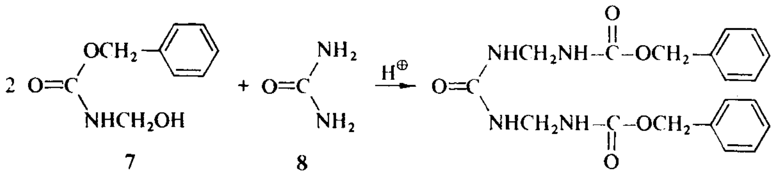
of **5a** with methanol the absorption at 3317 has disappeared and new bands were observed at 3240 (ν_{NH}) and 1130 cm^{-1} (ν_{COC}).

The NMR spectrum of **6a** indicates the presence of the OCH_3-protons ($\delta = 3{,}15$ ppm).

The IR and NMR data of the *N*,*N'*-bis(alkoxymethyl) derivatives are shown in Tab. 2.

Reaction of N-hydroxymethylcarbamates with urea

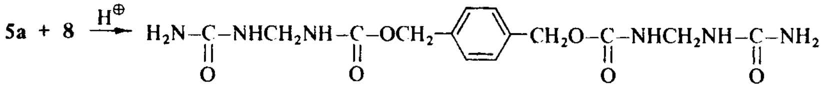
O-Benzyl *N*-hydroxymethylcarbamate (**7**) reacts with urea (**8**) in dioxane/water at pH 1,0 to afford *O*,*O'*-dibenzyl (ureylene-*N*,*N'*-dimethylene)dicarbamate (**9**). Its NMR and IR spectrum (Fig. 2) show the absorptions according to structure **9**. The NMR-spectrum indicates the presence of some impurity.



7

8

9



$$\mathbf{5a} + \mathbf{8} \xrightarrow{H^{\oplus}} H_2N-\underset{O}{\underset{\|}{C}}-NHCH_2NH-\underset{O}{\underset{\|}{C}}-OCH_2-C_6H_4-CH_2O-\underset{O}{\underset{\|}{C}}-NHCH_2NH-\underset{O}{\underset{\|}{C}}-NH_2$$

10

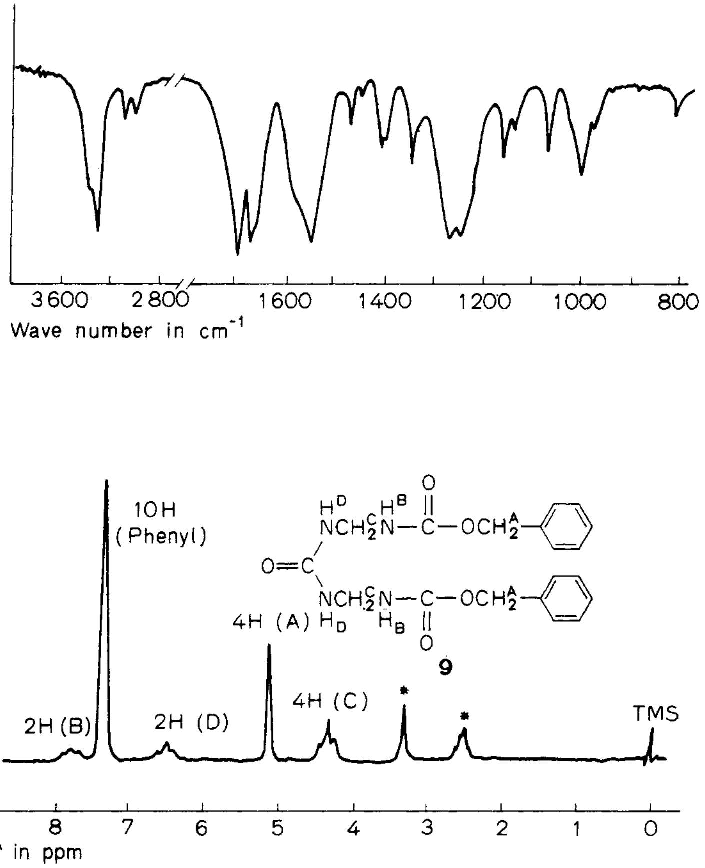


Fig. 2. (a) IR (in KBr) and (b) NMR spectra (in DMSO-d_6) of **9**

Methylene-1,4-phenylenemethylene di(*N*-ureidomethylcarbamate) (**10**) was obtained reacting **5a** with **8** under acidic conditions at 60°C with 33% yield. In contrast to **9** NH_2 absorptions are observed in the IR and NMR spectrum (Fig. 3), which confirm the structure together with the elemental analysis.

Experimental Part

Materials: O-Ethylcarbamate of commercial grade was recrystallized from benzene. 4-Hydroxymethylbenzyl alcohol (**1a**), 3-hydroxymethyl-4,6-dimethylbenzyl alcohol (**1b**),

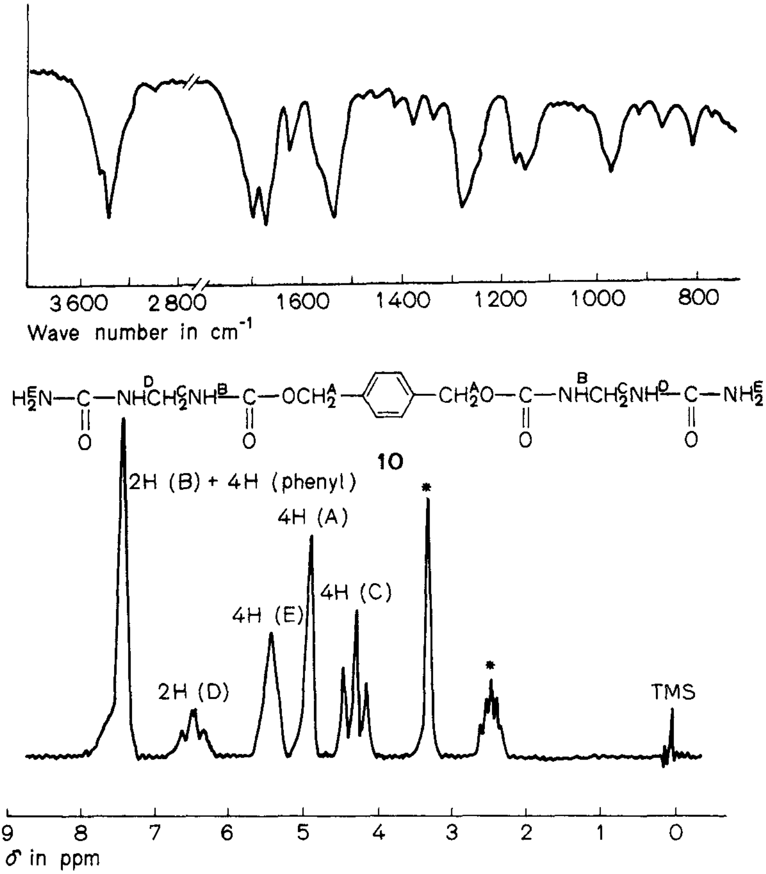


Fig. 3. (a) IR (in KBr) and (b) NMR spectra (in DMSO-d_6) of **10**

4-hydroxymethyl-2,5-dimethylbenzyl alcohol (**1c**), and 2,2-dimethyl-1,3-propandiol (**1d**) were recrystallized from methanol. Paraformaldehyde of commercial grade was used as formaldehyde source.

Dicarbamates: The carbamates were prepared by the method of Kraft[2]. The analytical data and mp are given in Tab. 3.

Reaction of the dicarbamates with formaldehyde

O,O′-Methylene-(4,6-dimethyl-1,3-phenylene)methylene carbamate N-hydroxymethylcarbamate (**4**): 0,5 cm^3 of 6 N KOH were added to a mixture of *O,O′*-methylene-(4,6-dimethyl-1,3-phenylene)methylene dicarbamate (**3b**) (3,8 g; 15 mmol), paraformaldehyde (0,6 g; 20 mmol), dioxane (30 cm^3), and water (15 cm^3).

After the mixture was stirred and heated at 70 °C for 30 min, 200 cm^3 of water were added and the solid formed after a stirring time of 2 h was recrystallized from methanol/water. White powder; mp 140—142 °C. Yield: 0,38 g (8 %). A test with Tollens' reagent was positive.

$C_{13}H_{18}N_2O_5$ (282,3) Calc. C 55,19 H 6,52 N 9,78
Found C 55,30 H 6,45 N 9,92

N,N'-Bis(hydroxymethyl) dicarbamates: The reactions of **3a–c** with formaldehyde were carried out in the presence of sodium hydroxide. The analytical data are given in Tab. 4.

Reaction of dicarbamates with alcohols

As a typical example the reaction of **5a** with methanol is described.

Tab. 3. Results of elemental analyses and mp of the carbamates

Compound	Elemental analysis				mp in °C
3a	Calc.	C 53,56	H 5,40	N 12,50	
	Found	C 53,70	H 5,53	N 12,36	211—213
3b	Calc.	C 57,12	H 6,41	N 11,10	199—200
	Found	C 57,38	H 6,40	N 11,12	
3c	Calc.	C 57,12	H 6,41	N 11,10	226—228
	Found	C 57,16	H 6,40	N 10,93	
3d	Calc.	C 44,19	H 7,43	N 14,73	158—159
	Found	C 44,12	H 7,28	N 14,54	

O,O'-Methylene-1,4-phenylenemethylene di(N-methoxymethylcarbamate) (**6a**): The mixture of **5a** (2,84 g; 10 mmol) and methanol (80 cm^3; large excess) was stirred at 60 °C and pH 2,2 for 10 min. Then it was poured into a large amount of ice/water. The solid was filtered and recrystallized from methanol. White powder; mp 111—113 °C. Elemental analysis s. Tab. 4.

The values of the elemental analyses and mp of other *N,N'*-bis(alkoxymethyl) dicarbamates are summarized in Tab. 4.

Reaction of dicarbamates with urea

O,O'-Dibenzyl-(ureylene-N,N'-dimethylene) dicarbamate (**9**): A mixture of *O*-benzyl *N*-hydroxymethylcarbamate (**7**) (3,0 g; 170 mmol), urea (0,5 g; 8 mmol), dioxane (30 cm^3) and water (15 cm^3) was stirred at 30 °C in the presence of sulfuric acid (6 N-H_2SO_4; pH 1,0) for 1 h and then 200 cm^3 of cold water were added. The solid was filtered and recrystallized from methanol. White powder; mp 213—215 °C. Yield: 0,2 g (3 %).

Tab. 4. Results of elemental analyses and mp of *N*,*N'*-bis(hydroxymethyl) dicarbamates and *N*,*N'*-bis(alkoxymethyl) dicarbamates

Compound		Elemental analysis			mp in °C
5a	Calc.	C 50,69	H 5,68	N 9,86	172—173
	Found	C 50,94	H 5,84	N 9,66	
5b	Calc.	C 53,85	H 6,47	N 8,97	145,5—147
	Found	C 53,67	H 6,68	N 8,82	
5c	Calc.	C 53,85	H 6,47	N 8,97	129—130
	Found	C 54,10	H 6,35	N 9,26	
6a	Calc.	C 53,84	H 6,45	N 8,97	111—113
	Found	C 53,91	H 6,29	N 9,12	
6b	Calc.	C 56,46	H 7,10	N 8,23	120—121,5
	Found	C 56,45	H 7,04	N 8,32	
6c	Calc.	C 56,45	H 7,12	N 8,23	125—127
	Found	C 56,31	H 6,95	N 8,52	
6d	Calc.	C 57,60	H 7,41	N 7,91	108—109
	Found	C 57,82	H 7,45	N 7,72	
6e	Calc.	C 56,45	H 7,12	N 8,23	133,5—135
	Found	C 56,22	H 7,04	N 8,25	
6f	Calc.	C 57,60	H 7,41	N 7,91	120,5—121,5
	Found	C 57,84	H 7,49	N 7,70	

Negative reaction with Tollens' and Ehrlich's reagent.
$C_{19}H_{22}N_4O_5$ (386,5) Calc. C 59,09 H 5,74 N 14,50
Found C 58,80 H 5,88 N 14,79

Methylene-1,4-phenylenemethylene di(N-ureidomethylcarbamate) (**10**): A mixture of **5a** (1,4 g; 5 mmol), urea (3 g; 500 mmol), dioxane (30 cm^3), and water (10 cm^3) was stirred at 60°C in the presence of sulfuric acid (6 N H_2SO_4, 1,3 cm^3) for 1 h and then 100 cm^3 of cold water were added. The solid was filtered and reprecipitated from DMSO. White powder; mp 223—224°C. Yield: 0,6 g (33%). Negative reaction with Tollens' and positive reaction with Ehrlich's reagent.

$C_{14}H_{20}N_6O_6$ (368,4)	Calc.	C 45,64	H 5,48	N 22,82
	Found	C 45,71	H 5,58	N 22,62

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(1) S. Takeuchi, M. Kinoshita, K. Kō, M. Imoto, Makromol. Chem. **157**, 63 (1972)
(2) W. M. Kraft, J. Am. Chem. Soc. **70**, 3569 (1948)