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REACTIVITY OF MONOPHENOLS TOWARDS HYDROXYMETHYLCAPROLACTAM

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Abstract. Unsymmetrical methylene compounds were obtained in HCl-catalyzed melt-condensation of various monophenols and N-methylolcaprolactam. The electron withdrawing influence of the substituent used causes great deactivation to further substitution in the phenolic ring followed by parallel formation of N,N′-methylenedicaprolactam.

^{1}H methylene chemical shifts from 100 MHz ^{1}H NMR spectra were used for product interpretation. Conjugation in the amide group, intramolecular H-bond, effective electronegativity of nitrogen, strong complexing power of pyridine (NMR solvent), and the influence of *ortho*-hydroxyl and -methyl effects are the main phenomena considered in ^{1}H chemical shift assignment.

Key words: monophenols, methylolcaprolactam, methylene compounds, ^{1}H chemical shift, hydroxyl and methyl effects.

INTRODUCTION

The hydroxymethylation reaction of monophenols has been mostly studied in the presence of an alkaline catalyst for the stabilization of the methylol stage [1]. A mechanism satisfying the condensation reactions in all conditions includes the intramolecular dehydration of methylol or its dimeric anhydro form by the formation of quinone methide intermediates [2]. Quinone methides are in formal equilibrium with their zwitteronic carbonium form with higher probability of *para*-species. They show a high reactivity to electrophiles and nucleophiles. In accordance with this, the condensation is promoted in the presence of an acid catalyst by benzylic carbonium ion formation and in the presence of an alkaline catalyst through the strongly nucleophilic methylol phenoxide ion [3, 4].

Differently, the presence of an alkaline catalyst causes the release of formaldehyde from methylolcaprolactam at a rate dependent on the reactivity of

the co-reagent. The Mannich-type condensation, leading to unsymmetrical methylene compounds [5] in our case, can be regarded according to Hellmann [6] as an amidomethylation reaction. This reaction occurs as electrophilic substitution in substrates by equilibrium carbonium–imonium ion formed through the addition of proton and subsequent dehydration. Methylolcaprolactam as a monofunctional reagent enables to study acid-catalyzed substitution in the phenolic ring without further condensation. There is a great difference in comparison with the phenol–formaldehyde reaction.

The ^{1}H NMR study of the HCl-catalyzed resorcinol or 5-methylresorcinol/N-methylolcaprolactam reaction has shown the great nucleophilic potential of the resorcinolic compound in all available positions [7]. The obtained clear C4 favoured substitution is well known in resorcinol–formaldehyde reaction [8]. Because of the ring deactivating influence of the substituent the next stage occurs, according to the electron density, preferably as C2,4 disubstitution.

The HCl-catalyzed reaction of N-methylolcaprolactam with phenol and its methyl derivatives was the object of this study. ^{1}H NMR spectroscopy was used for rate evaluation and for product analysis.

EXPERIMENTAL

Materials

N-methylolcaprolactam (MCL) was synthesized from caprolactam (CL) and 37% aqueous solution of formaldehyde (FA) (molar ratio 1/1) in boiling benzene with continual removal of water. After distillation of benzene MCL was recrystallized from diethyl ether (m.p. 67.3 °C, content of methylol groups 6.91 mekv/g). Reagent grade vacuum-redistilled phenol (Ph) and *o*- and *p*-cresols (Cr) were recrystallized twice from petrol ether or hexane (m.p.: Ph 40.9, *o*-Cr 34.7, and *p*-Cr 30.9 °C). Reagent grade 2,4- and 3,4-xylenol (Xy) (The British Drug Houses Ltd.), 2,5- and 3,5-Xy (Schuchardt, München), 2,6-Xy (Koch-Light Lab. Ltd.) were redried in vacuum (m.p. ~28, 64.5, 74.5, 68, and 49 °C, respectively).

Studied systems

Most co-condensation reactions were carried out in the melt at 80 °C with molar ratio of phenolic compound/MCL/HCl 1/1/0.001. If there were two aromatic *o*- and *p*-positions available, experiments with molar ratio 1/2/0.002 were added. The reactions 3,5-Xy/MCL/HCl and Ph/MCL/HCl 1/1/0.0005 at 70 °C were also performed. In case of reactions with Ph a reduced quantity of MCL (0.25/1 and 0.5/1) was also used. Otherwise, the reaction product 1/1/0.001 was used for further co-condensation, adding MCL by 0.5 mole to final molar ratio of MCL/Ph 3/1 and increasing at the same time the quantity of HCl (0.01 mole) and the temperature of melt-condensation (100 °C).

Some pure monosubstituted compounds were isolated from reaction mixtures by treating with different solvents. For example, from the reaction mixture Ph/MCL/HCl 1/0.5/0.01, after removal of free Ph with water, *o*-isomer (m.p. 113.5 °C) was crystallized by the solution in diethyl ether. From the soluble part, *p*-isomer (m.p. 134.5 °C) was crystallized by treating with benzene. Other monosubstituted compounds were obtained from reaction mixtures 1/1/0.001. *o*-Isomers of *p*-Cr and 2,4-Xy were crystallized from diethyl ether (m.p. 102.5 and 124 °C, respectively) and *p*-isomer of 2,6-Xy from acetone (m.p. 133 °C). *o*-Isomer of *o*-Cr was crystallized from methanol (m.p. 135.5 °C) and after that *p*-isomer was crystallized from benzene (m.p. 149.5 °C). The insoluble part of the reaction product in acetone consists of *p*-isomer of 2,5-Xy (m.p. 183.5 °C). Treatment with diethyl ether was used to crystallize the *o*-isomer (between OH and CH_3) of 3,4-Xy (m.p. 182 °C).

The isolated pure monosubstituted compounds of *o*-Cr and *p*-Cr were used also as reagents for additional melt-condensation at 80 °C with molar ratio of compound/MCL/HCl 1/1/0.001.

Analysis

100 MHz ^{1}H NMR spectra were recorded to follow the reaction rate and to ascertain the product composition and the structure of the separated compounds. ^{1}H chemical shifts for 12–15% samples in deuterated pyridine (Py), chloroform, and acetone were measured from internal hexamethyldisiloxane and calculated from tetramethylsilane. Quantitative changes in molar concentrations during the reaction were calculated from integral intensities of methylene signals for methylol and dimethylene ether derivatives of CL and for unsymmetrical methylene compounds and N,N′-methylenedicaprolactam. For quantitative determination of the intensities of proton signals we used the average of three parallel integrals calculated with regard to the proton signal intensity of —$(CH_2)_3$— of CL (e.g., 1.64 ppm in $CDCl_3$) unchanged during the reaction. The parallel integral values in the region necessary for quantitative calculation (1.64–5.02 ppm in $CDCl_3$) do not differ more than ±2% from one another. The different ^{1}H chemical shifts from methylene linked to nitrogen make it possible to calculate the quantity of bound and free CL. The time dependence of the molar amounts of the initial components, intermediates, and final products bases on the FA balance for any analysed moment of reaction. For the phenols used in co-condensation reactions and for pure compounds separated also aromatic and methyl ^{1}H chemical shifts and the molar ratio of corresponding protons were estimated.

RESULTS AND DISCUSSION

The course of the reaction of MCL with phenols is complicated yet quite similar for different phenols. As an example, the time dependence of the molar content of the components of the reaction mixture Ph/MCL/HCl 1/1/0.001 is

presented in Fig. 1. The first-step formation of an equilibrium mixture of MCL and its dimeric ether form (DECL) is the fastest reaction in the system. The resolution of ^{1}H methylene signals for MCL and DECL in Py (5.15 and 4.93 ppm, respectively) allowed us to estimate the proportion of the ether form to be 54–63% in systems with different phenols. In addition, the forms of bound FA are in equilibrium with free FA. The latter makes up about 12–22% for different systems in the initial stage of the reaction. The reaction proceeds by electrophilic substitution with amidomethyl carbonium ion, which forms during the reaction from the equilibrium mixture of MCL and DECL. The pure amidomethylation reaction occurs, but differently from the reaction with resorcinols [7] the lower reactivity of phenols promotes parallel homocondensation of MCL as well.

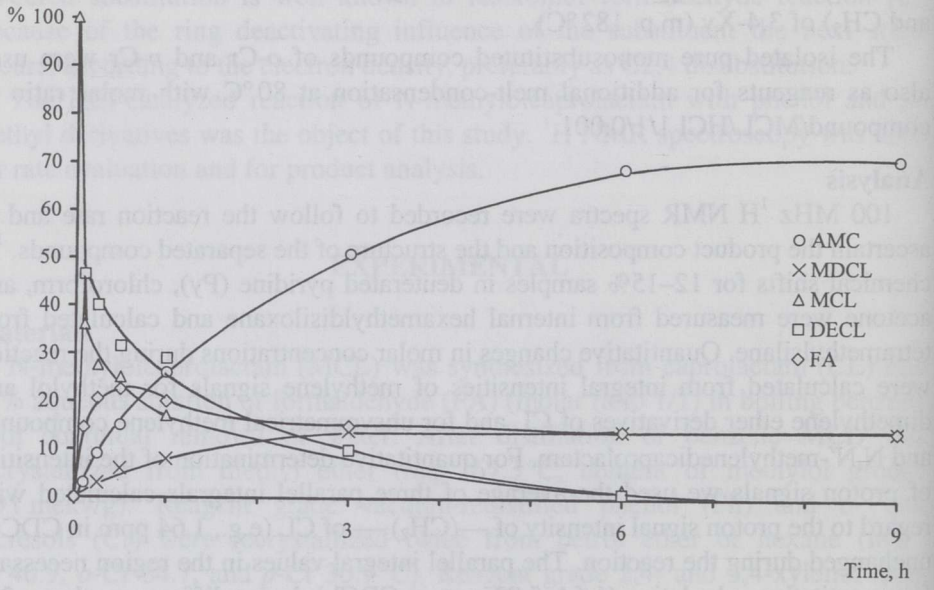


Fig. 1. Time dependence of the molar content of the components in the reaction of phenol/ N-methylolcaprolactam/HCl 1/1/0.001 (80 °C). AMC, unsymmetrical methylene compound; MDCL, N,N'-methylenedicaprolactam; MCL, N-methylolcaprolactam; DECL, dimeric ether of caprolactam; FA, formaldehyde.

The final products of the reaction are unsymmetrical methylene compounds of phenols and CL (AMC) and N,N'-methylenedicaprolactam (MDCL). It is obvious (Table 1) that the molar distribution of methylene between compounds in different systems depends on the reactivity of the phenolic compound, and it correlates quite well with the well-known reactivity of different phenols with FA [1, 9]. Although the complicated reaction mechanism of the melt-condensation of the above-mentioned reagents does not permit a precise characterization of reaction kinetics, the time dependence of AMC formation in different systems supports reactivity conception (Figs. 2 and 3). Because of two *meta*-methyl groups in 3,5-Xy the

highest rate and quantitative yield of AMC were obtained even at a lower temperature (70°C) and at half the acid amount. The lowest reaction rate with monofunctional 2,4- and 2,6-Xy is explained by the presence of two *ortho*- and *para*-methyl groups. At the same time the higher relative rate of monosubstitution leads to the best AMC yield per one reactive position in this case.

Table 1

Composition of reaction products of methylolcaprolactam with different phenols

Phenol	Molar ratio Ph/MCL/HCl	Methylene molar distribution,%		Methylene molar distribution in Ar-CH_2-CL, %		
		Ar-CH_2-CL	CL-CH_2-CL	Monosubstituted		Disubstituted
				ortho-	*para*-	
Phenol	1/1/0.001	70	15	41	22	37
p-Cresol	1/1/0.001	72	14	57	–	43
	1/2/0.002	40	30	57	–	43
o-Cresol	1/1/0.001	74	13	32	51	17
	1/2/0.002	40	30	25	40	35
2,4-Xylenol	1/1/0.001	59	20.5	100	–	–
2,6-Xylenol	1/1/0.001	57	21.5	–	100	–
2,5-Xylenol	1/1/0.001	86	7	26	48	26
	1/2/0.002	64	18	18	32	50
3,4-Xylenol	1/1/0.001	88	6	26 (2-) 42 (6-)	– –	32
	1/2/0.002	64	18	16 (2-) 26 (6-)	– –	58
3,5-Xylenol	1/1/0.0005	100	0	38	24	38

This study presents four examples of phenols with equal bifunctionality. In comparison with the above-mentioned 2,4- and 2,6-Xy the exclusion of one methyl group (*o*- or *p*-Cr) causes a higher rate of AMC formation. The inclusion of one additional *meta*-methyl group (2,5- or 3,4-Xy) promotes the substitution in these phenols in comparison with cresols. The yield of AMC (and MDCL) (Table 1) correlates quite well with the rate of their formation. In case of monosubstitution, *para*-substitution is favoured (*o*-Cr or 2,5-Xy) in comparison with *ortho*-substitution. The same is valid in the hydroxymethylation reaction as well [1].

Monosubstitution has a strong deactivating influence on further substitution. It is a difference in comparison with the hydroxymethylation reaction where only

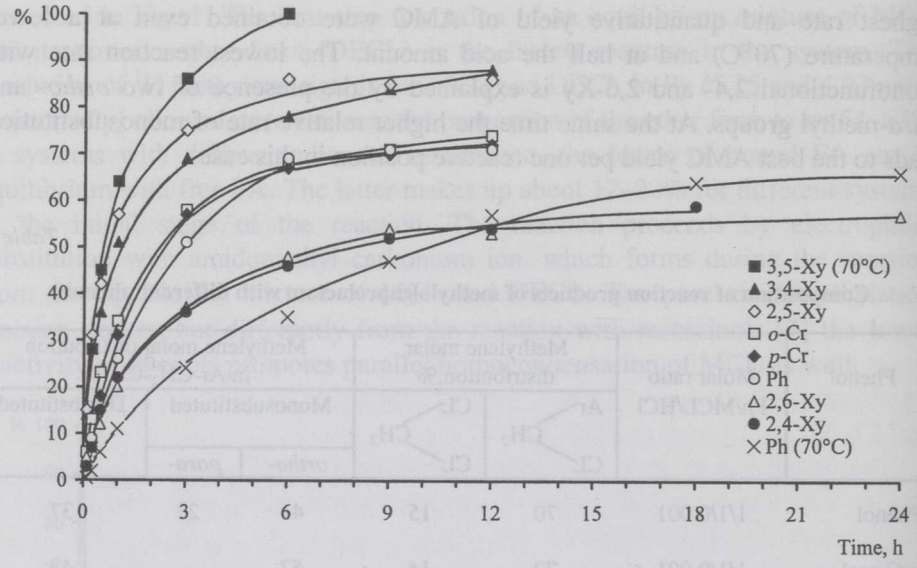


Fig. 2. Time dependence of the formation of unsymmetrical methylene compounds in the reactions of phenolic compound/N-methylolcaprolactam/HCl 1/1/0.001 (80 °C, Ph and 3,5-Xy/MCL/HCl 1/1/0.0005 at 70 °C). See Table 1 for phenols.

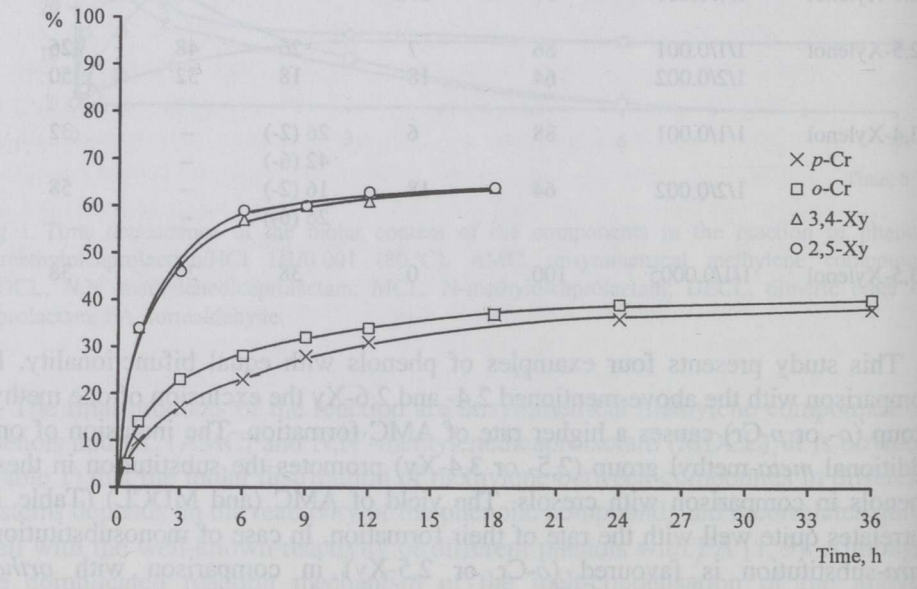


Fig. 3. Time dependence of the formation of unsymmetrical methylene compounds in the reactions of phenolic compound/N-methylolcaprolactam/HCl 1/2/0.002 (80 °C). See Table 1 for phenols.

para-substitution has this effect [1]. This means that in our case the electron withdrawing role of the substituent appears also in the *ortho*-position due to a different situation for the intramolecular H-bond formation between phenolic hydroxyl and the substituent groups. The smaller amount of MCL (1/1 mixture) promotes the AMC formation (Table 1). An excess of MCL does not increase substantially the yield of AMC (*o*-Cr and *p*-Cr). The low relative disubstitution rate in phenols gives preference to the homocondensation of MCL. The higher reactivity of 2,5- and 3,4-Xy is responsible for the increase in the proportion of disubstituted AMC (2/1 mixtures) over 50% but the rate of disubstitution in phenols remains below the rate of MCL homocondensation.

Formation of disubstituted AMC shows that 2,6-compounds (*p*-Cr or 3,4-Xy) are formed in greater amounts in comparison with 4,6-compounds (*o*-Cr or 2,5-Xy). Besides that, 3,4-Xy is the only example where two free *ortho*-positions are available in different environments. The substitution in position 6 is preferred as the *meta*-methyl group, analogically to hydroxyl group, promotes *para*-substitution in comparison with *ortho*-substitution. The stability of the whole *p*/*o* (*o*/*o* in 3,4-Xy) substitution ratio and that of monosubstitution during the reactions allow us to conclude that both monosubstituted AMC are equally used up for the formation of disubstituted derivatives.

Because of different reaction conditions the condensation of pure mono-AMC of *o*-Cr (*ortho*- and *para*-) and *p*-Cr with MCL (AMC/MCL/HCl 1/1/0.001) quite surprisingly leads only to quantitative homocondensation of the added MCL. This supports excellently the idea of a strong deactivating effect of the substituent used on the further substitution.

In all cases studied where MDCL is the reaction by-product an equivalent quantity of free FA is released (cf. Fig. 1). Free FA subsequently prefers to separate from the system because of the above-mentioned deactivating effect. This means that no hydroxymethylation followed by polycondensation reaction happens with the phenolic substrate. ^{1}H NMR analysis is quite sensitive to assign the typical signals ensued from the last reaction. Among others the lack of the most expected signal for *p*, *p*'-methylenes (3.8 ppm in Py) remains no doubt in the proposed mechanism. The possibility of other reaction products is excluded also because of the presence of CL quantitatively in the bound form up to the end of the reaction. The typical signal for methylene linked to nitrogen of CL appears in the region of 3.15–3.30 ppm in Py depending on the phenol used and the position of substitution. However, no signal can be found of the same methylene for free CL (3.01 ppm in Py).

Two trifunctional phenols differing greatly in reactivity (Ph and 3,5-Xy) were used in this study. In the case of 3,5-Xy only the equimolar reaction can be analysed due to solubility problems of AMC in NMR solvents. Quantitative calculations were made using spectra in $CDCl_3$ (Table 1). The insoluble part in Py (also in acetone) consists of the preferably formed *ortho*-isomer of AMC. A greater amount of disubstituted AMC causes insolubility also in $CDCl_3$.

Table 2

Composition of phenol–methylolcaprolactam reaction products

Characteristic	Molar ratio of MCL/Ph/HCl							
	0.25/1/0.001	0.5/1/0.01	1/1/0.0005	1/1/0.001	1.5/1/0.01	2/1/0.01	2.5/1/0.01	3/1/0.01
	Temperature and time							
	80°/0.5 h	80°/0.5 h	70°/36 h	80°/12 h	80°/3 h	80°/3 h	100°/6 h	100°/6 h
Distribution of —CH_2—, molar %								
C2*	69	59	43	41	34	18	16	13
C4*	31	23	18	22	21	12	9	7
C2,4*	–	7	22	16	21	22	25	29
C2,6*	–	11	17	21	24	32	31	26
C2,4,6*	–	–	–	–	–	16	19	25
ortho/para	2.2	2.7	2.4	2.3	2.2	2.5	2.5	2.4
AMC, moles	0.25	0.5	0.72	0.70	0.98	1.18	1.34	1.44
AMC in addition, moles	–	–	–	–	0.28	0.20	0.16	0.10
AMC, %	100	100	72	70	65	59	54	48
MDCL, moles	–	–	0.14	0.15	0.26	0.41	0.58	0.78

* The compounds are characterized by the position of substitution in the phenolic ring.

Similar rates of the reactions of Ph and cresols with MCL (Fig. 2) and the same yield of AMC (Tables 1 and 2) in the equimolar mixture were obtained in spite of different functionalities. *Ortho*-substitution is preferred due to two aromatic free *ortho*-positions. Only mono-AMC formation occurs in case of a great excess of Ph (1/0.25). Despite the use of more drastic reaction conditions for further condensation of the 1/1 reaction product with MCL, the advancing of the reaction reduces the relative consumption of MCL for AMC formation. 2,6-Disubstitution is slightly preferred in spite of the possibility of the 2,4-isomer formation from both monosubstituted AMCs. Similar attraction of Ph and cresols to the AMC formation (2/1 reactions) can be concluded from the equal consumption of MCL per one reactive aromatic position (~0.4 moles). This means that the deactivating influence of the substituents in Ph has decreased, causing a smaller proportion of monosubstituted AMC in products. In this case not more than a half of MCL is spent for AMC formation (3/1 reaction) in comparison with nearly quantitative one in case of resorcinols [5].

^{1}H NMR assignments are reported in three solvents (Table 3). ^{1}H chemical shift (δ) of unsymmetrically substituted methylene in different environments is the main characteristic for the interpretation of reaction products (mixtures and separated pure compounds). The values of δ for $CDCl_3$ and acetone solutions are quite similar in most cases. The intramolecular H-bond between phenolic hydroxyl and methylol group is revealed in a great *ortho*-effect [10] due to effective electronegativity of oxygen linked to methylene.

In our case the diminished electronegativity of nitrogen because of conjugation in the amide group followed by the formation of H-bond between the phenolic hydroxyl and the carbonyl group of enhanced electronegativity gave the opposite effect and the signals of *ortho*- in comparison with *para*-methylene appeared in the upper field ($CDCl_3$). Py is not used very often as δ values in Py are strongly affected by the mutual orientation between phenolic hydroxyl and Py nitrogen. We sometimes prefer Py for this useful phenomenon, as it leads to better resolution of ^{1}H signals, mainly in the presence of additional methyl effects. The signals in Py solution appear usually in a lower field (Table 3). Naturally, the effect is more pronounced in case of *ortho*-substitution because of the decomposition of the intramolecular H-bond. It can be concluded that in Py solution δ depends only on the position of substitution (*ortho* or *para*), but in $CDCl_3$ solution even more sensitively on the number of substitution (Fig. 4). In case of the absence of other substituent *ortho*-effects quite similar methylene δ values were obtained for *para*-substituted AMC, especially in Py solution (Ph, *o*-Cr, 2,6-Xy). The additional *ortho*-methyl effect causes the appearance of the same *para*-methylene signal in a lower field (2,5-Xy, 3,5-Xy).

A great difference between solvents exists in the δ assignment for *ortho*-substituted AMC. Quite constant δ values were obtained in $CDCl_3$ (4.35–4.41 ppm), only the falling of the substituent between hydroxyl and methyl groups causes an additional downfield δ shift (3,4-Xy, 3,5-Xy). *Ortho* to

hydroxyl electron donating methyl group strongly changes the orientation situation in Py solution, reducing the electronegativity of nitrogen (CL) and leading to an upfield shift of the signal (*o*-Cr, 2,4-Xy). ^{1}H methylene chemical shift for *ortho*-substituted AMC from 2,5-Xy is in accordance with others considering the opposite influence of two methyl effects.

Table 3

Methylene ^{1}H signals of unsymmetrical co-condensates of phenols and caprolactam

Phenol	Compound*	^{1}H signal, ppm from TMS		
		C_5D_5N	$CDCl_3$	$(CD_3)_2CO$
Phenol	C2	4.65	4.41	4.44
	C4	4.56	4.47	4.50
	C2,4 C2	**	4.36	**
	C4	**	4.46	**
	C2,6	**	4.52	**
	C2,4,6; C2,6	**	4.49	**
	C4	**	4.41	**
p-Cresol	C2	4.58	4.37	4.37
	C2,6	4.61	4.47	4.45
o-Cresol	C2	4.43	4.40	4.40
	C4	4.56	4.44	4.40
	C2,4	**	4.36**	4.38**
2,6-Xylenol	C4	4.57	4.41	4.38
2,4-Xylenol	C6	4.40	4.36	4.35
2,5-Xylenol	C4	4.62	4.50	4.44
	C6	4.59	4.53	4.51
	C4,6 C4	4.71	**	4.58
	C6	4.65	4.58	4.49
3,4-Xylenol	C2	4.97	4.62	4.62
	C6	4.54	4.35	4.34
	C2,6 C2	4.95	4.76	4.69
	C6	4.49	4.41	4.40
3,5-Xylenol	C2	4.80	4.51	***
	C4	4.65	4.61	***

* The compounds are characterized by the position of substitution in the phenolic ring.
** Signals overlap.
*** Not determined.

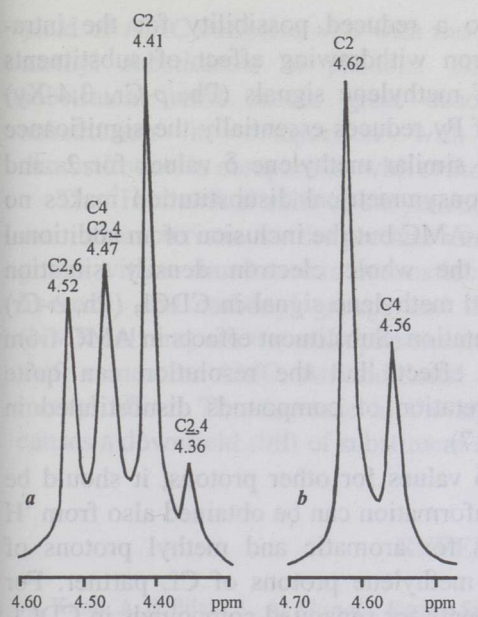


Fig. 4. ^{1}H NMR spectra of reaction mixture phenol/N-methylolcaprolactam/HCl 1/1/0.001 (80 °C, 12 h) in $CDCl_3$ (*a*) and pyridine-d_5 (*b*). The signals are marked here and in Figs. 5–7 by the position of substitution in the phenolic ring.

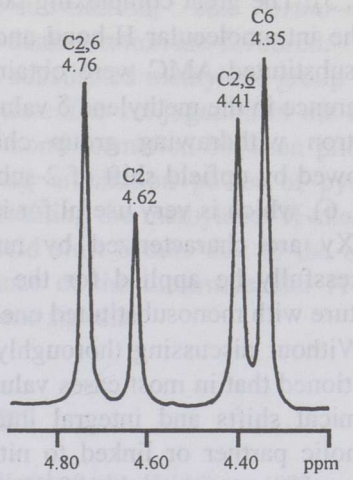


Fig. 5. ^{1}H NMR spectrum of the reaction mixture 3,4-xylenol/N-methylolcaprolactam/HCl 1/2/0.002 (80 °C, 18 h) in $CDCl_3$.

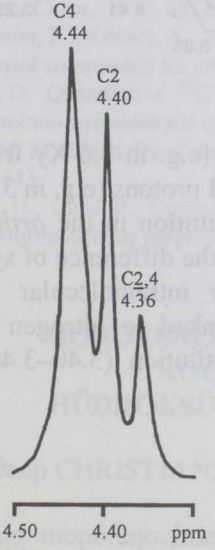


Fig. 6. ^{1}H NMR spectrum of the reaction mixture *o*-cresol/N-methylolcaprolactam/HCl 1/2/0.002 (80 °C, 36 h) in $CDCl_3$.

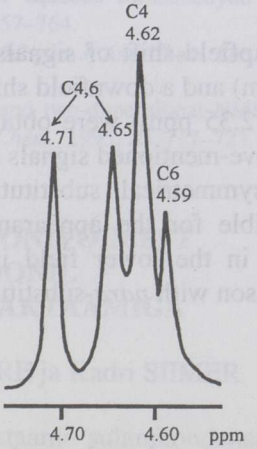
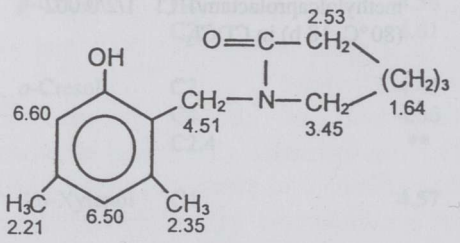
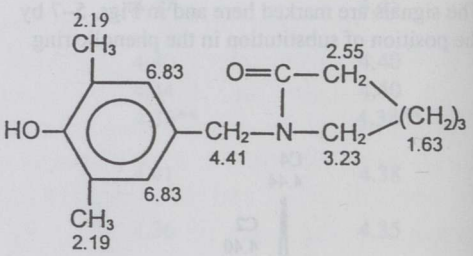


Fig. 7. ^{1}H NMR spectrum of the reaction mixture 2,5-xylenol/N-methylolcaprolactam/HCl 1/2/0.002 (80 °C, 18 h) in pyridine-d_5.

In case of 2,6-disubstitution due to a reduced possibility for the intramolecular H-bond formation the electron withdrawing effect of substituents increases, causing a downfield shift of methylene signals (Ph, *p*-Cr, 3,4-Xy) (Fig. 5). The great complexing power of Py reduces essentially the significance of the intramolecular H-bond and more similar methylene δ values for 2- and 2,6-substituted AMC were obtained. Nonsymmetrical disubstitution makes no difference in the methylene δ value for 4-AMC but the inclusion of an additional electron withdrawing group changes the whole electron density situation followed by upfield shift of 2-substituted methylene signal in $CDCl_3$ (Ph, *o*-Cr) (Fig. 6), which is very useful for interpretation. Substituent effects in AMC from 2,5-Xy are characterized by multiple effects but the resolution can quite successfully be applied for the interpretation of compounds disubstituted in mixture with monosubstituted ones (Fig. 7).

Without discussing thoroughly the δ values for other protons, it should be mentioned that in most cases valuable information can be obtained also from ^1H chemical shifts and integral intensities for aromatic and methyl protons of phenolic partner or linked to nitrogen methylene protons of CL partner. For illustration, two examples of ^1H assignments for separated compounds in $CDCl_3$ solution are presented.





An upfield shift of signals of aromatic protons (e.g. in 2,6-Xy from 6.94 to 6.83 ppm) and a downfield shift of signals of methyl protons (e.g. in 3,5-Xy from 2.22 to 2.35 ppm) were obtained due to the substitution in the *ortho*-position. The above-mentioned signals show unambiguously the difference of symmetrical or nonsymmetrical substitution in phenols. The intramolecular H-bond is responsible for the appearance of a signal of linked to nitrogen methylene protons in the lower field in case of *ortho*-substitution (3.40–3.46 ppm) in comparison with *para*-substitution (3.20–3.25 ppm).

CONCLUSIONS

HCl-catalyzed melt-condensation of various monophenols with hydroxymethylcaprolactam leads to unsymmetrical methylene compounds (AMC) and N,N'-methylenedicaprolactam in different proportions. The formation rate and

yield of AMC correlate well with the position and number of electron donating methyl substituents in phenols. The electron attracting influence of the substituent used causes great deactivation to further substitution. *Para*-substitution in comparison with *ortho*-substitution, and *ortho–ortho*-disubstitution in comparison with *ortho–para*-disubstitution are favoured.

The ^{1}H chemical shift of unsymmetrically substituted methylene group is the main characteristic for the product interpretation. The conjugation in the amide group with a simultaneous intramolecular H-bond formation between phenolic hydroxyl and carbonyl groups and the strong orientation power of pyridine (NMR solvent) are the main phenomena determining the methylene ^{1}H chemical shift values for AMC. An additional downfield shift occurs due to the *ortho*-methyl effect. The decrease in the significance of the intramolecular H-bond causes a downfield shift of substituent methylene signals.

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MONOFENOOLIDE REAKTSIOONIVÕIMEST KOOSKONDENSATSIOONIL HÜDROKSÜMETÜÜLKAPROLAKTAAMIGA

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Erinevate monofenoolide ja metüloolkaprolaktaami sulamkondensatsioonil saadi happelise katalüsaatori manulusel mittesümmeetrilised metüleenühendid. Kasutatud asendaja elektronatraktiivne loomus põhjustas fenoolse tuuma

deaktiveerumise edasise asenduse suhtes. Sellest tingituna toimus osaliselt ka metüloolkaprolaktaami omakondensatsioon.

Reaktsiooniproduktide struktuuri interpreteerimiseks määrati 100 MHz TMR spektritest metüleenrühmade ^{1}H keemilised nihked. Viimaste väärtus olenes eelkõige konjugatsioonist amidorühmas, sisemolekulaarsest vesiniksidemest, lämmastiku aatomi elektronegatiivsusest, püridiini (TMR lahusti) tugevast kompleksimoodustusvõimest ning hüdroksüül- ja metüülrühma *orto*-efektist.