NEW PHOSGENE-FREE PROCEDURE FOR PREPARATION OF METHYL N-PHENYLCARBAMATE AND DIMETHYL DIPHENYLMETHANE DICARBAMATE AS IMPORTANT PRECURSORS FOR PRODUCING ISO- AND DIISOCYANATES

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Methyl N-phenylcarbamate was prepared by reductive carbonylation of nitrobenzene in the presence of methanol and a new catalytic system composed of sulfur, vanadium pentoxide and a base – alkoxides of alkali metals or hydroxides of alkali metals or alkali earths – in good yields. Reaction mechanism of this process is discussed. Diphenylmethane dicarbamates were obtained by acid-catalyzed condensation of methyl N-phenylcarbamate with formaldehyde. Concentrated and dilute sulfuric acids, dilute hydrochloric acid, a mixture of hydrochloric and sulfuric acids, and bentonite were the catalysts investigated. The influence of the catalyst used, the molar ratio of methyl N-phenylcarbamate (MPC) to formaldehyde, temperature and reaction time of yields of dimethyl 4,4'-diphenylmethane dicarbamate and its higher homologues was examined. The condensation products were analysed by high-performance liquid chromatography on reversed phases (RP-HPLC) with a favourable chemically bonded octadecyl stationary phase and a mixed mobile phase water–methanol.

Alkyl N-phenylcarbamates and their condensation products with methylenation agents are important precusors for preparation of iso- and diisocyanates, which are valuable intermediates in the production of polyurethane. Polymeric esters of aromatic carbamic acids as diphenylmethane dicarbamates, mainly dimethyl 4,4'-diphenylmethane dicarbamate (MDDC) and related higher homologues of polymethylene polyphenyl carbamates (PMPPC) are of rising importance for preparation of commercially valuable diphenylmethane diisocyanate (MDI) and mixtures of diisocyanates and polyisocyanates (PMPPI) by thermal cleavage of the corresponding esters of polymeric carbamic acids[1].

Aiming to eliminate the dangerous phosgene, progressive procedures avoiding this strongly toxic chemical for the synthesis of MDI have recently been worked out. Search for new effective methods for preparation of isocyanates, MDI and polyisocyanates led to progressive procedures based on the reductive carbonylation of aromatic nitro compounds[2-6], oxidative carbonylation of aromatic amines[7,8] (Fig. 1), or most recently

to carboxylation of secondary aromatic amines[9,10] yielding either isocyanates[2–4] or carbamates[5–10]; these were condensed with methylenation agents to dicarbamates[11–16] and thermally cleaved to diisocyanates[11].

The most representative agents for introducing the methylene grouping especially suitable for condensation of alkyl N-phenylcarbamates are formaldehyde[11], formaldehyde oligomers as e.g. paraformaldehyde[12] or trioxane[13] and acetals as formaldehyde dimethyl acetal[14], formaldehyde diethyl acetal[15] and formaldehyde thioacetal[16].

Representative protic acid catalysts are concentrated and dilute acids[11,12], hydrochloric acid[17], superacids[18], Lewis acids[19], heteropolyacids[16] and strongly sulfonated polyaromatic ion exchangers[13,15].

Alkyl N-phenylcarbamates are most preferably analysed by separation methods as high-performance liquid[20,21] and mainly gas chromatographies[22,23]. Only few papers[24,25] deal with the analysis of condensation products of alkyl N-phenylcarbamates (mostly ethyl N-phenylcarbamate), where high-performance liquid chromatography on normal or reversed phases (HPLC or RP-HPLC) were employed.

This paper concerns *a*) the phosgene-free preparation of methyl N-phenylcarbamate by reductive carbonylation of nitrobenzene by carbon monoxide in methanol and analysis of carbonylation products by GLC; *b*) the acid-catalyzed condensation of methyl N-phenylcarbamate with formaldehyde and analysis of the condensation products by RP-HPLC.

EXPERIMENTAL

Chemicals

Nitrobenzene (Lachema, Brno), chemically pure 0.4 wt. % maximum water content; methanol (Lachema, Brno), p.a. grade, 0.25 wt. % maximum water content was rectified on a 30-theorethical plates column operating at a 5 : 1 reflux ratio. The resulting water content was lower than 0.03 wt. %. Carbon monoxide contained 0.5 vol. % hydrogen, 0.05 vol. % oxygen, 1.34 vol. % nitrogen and 0.1 vol. % carbon dioxide. Sulfur (Lachema, Brno), chemically pure, m.p. 120 °C, b.p. 444.6 °C. Sodium acetate, anhydrous (Lachema, Brno), vanadium pentoxide (Lachema, Brno), phenyl isocyanate (Merck Schuchard, Germany), formaldehyde (37% aqueous solution stabilized with 1 wt. % methanol, Chemko, Strážske), 4,4'-MDI (Desmodur 44 Bayer, Germany), Bentonite (Jelšový Potok, Czechoslovakia). Methyl N-phenylcarbamate and dimethyl 4,4'-diphenylmethane dicarbamate (4,4'-MDDC) were prepared according to refs[23,26] and ref.[27], respectively.

Methyl N-Phenylcarbamate by Reductive Carbonylation of Nitrobenzene

Nitrobenzene (0.81 mol), powdered sulfur (0.31 mol), methanol (3.84 – 6.24 mol) and vanadium pentoxide as a catalyst were placed into a stainless rotatory digester (1 l volume) equipped with a heating coil. The amount of methanol depended on that of sodium methoxide (10 wt. %) as cocatalyst; totally 6.24 mol of methanol was in the experiment. Besides of sodium methoxide also sodium or potassium acetate or their mixtures, solid powdered sodium or potassium hydroxide and their mixtures with calcium oxide or magnesium hydroxide were applied as cocatalysts. Carbon monoxide was pressed into the autoclave to 14 MPa,

stirring (180 rpm) and heating were started. After the temperature reached 150 °C the reaction was carried out for 4 h, the vessel content was worked up, weighted and analysed by GLC.

Determination of Methyl N-Phenylcarbamate in the Carbonylation Product of Nitrobenzene by GLC

Methyl N-phenylcarbamate and the carbonylation products of nitrobenzene were analysed using CHROM-4 (Laboratorní přístroje, Praha) apparatus equipped with a flame-ionizing detector[23,26] at following conditions: stainless capillary column (2.5 m × 3 mm), stationary phase 5% XE-60 over Chromaton NAW (0.16 – 0.20 grain size), carrier gas – nitrogen of flow rate 24 ml min^{-1}, inlet pressure 0.30 kPa at 140 °C, flow rates of hydrogen and air 48 and 450 ml min^{-1}, respectively. For analysis 1 μl of isopropanolic solution of methyl N-phenylcarbamate or carbonylation product were injected.

Acid-Catalyzed Condensation of Methyl N-Phenylcarbamate with Formaldehyde

Concentrated sulfuric acid being the catalyst. Aqueous formaldehyde (35 wt. %, 44 mmol) was added dropwise during 50 min to the stirred mixture of methyl N-phenylcarbamate (208 mmol), sulfuric acid (96 wt. %, 100 mmol) and hexane (35 ml). Water present in the mixture was removed by azeotropic distillation at the same time, while stirring was continued for 80 min. The remaining hexane was distilled off, heptane (35 ml) was added, the mixture was heated to 97 – 98 °C and stirred for 20 min. Heptane was distilled off, methanol (30 ml) was added and the methanolic solution of sulfuric acid was removed by pressure filtration and washed with methanol (2 × 30 ml). The solid was dried, weighted and analysed by RP-HPLC.

Dilute sulfuric acid as catalyst. Aqueous formaldehyde (35 wt. %, 44 mmol) and sulfuric acid (43 wt. %, 175 mmol) were added dropwise to a stirred and to 82 – 83 °C heated mixture of methyl N-phenylcarbamate or the carbonylation product (31 mmol) and sulfuric acid (43 wt. %, 1.05 mol) during 45 min. After further 60 min the mixture was filtered, the solid was washed with distilled water (3 × 100 ml), dried, weighted and analysed.

Dilute hydrochloric acid as catalyst. The above procedure was employed applying hydrochloric acid (18 wt. %, 1.59 mol) for dissolving of MPC and 133 mmol for dilution of formaldehyde; dropping time 15 min, additional stirring time 15 min.

Mixture of hydrochloric and sulfuric acids as catalyst. The mixture of methyl N-phenylcarbamate (31 mmol), hydrochloric acid (18 wt. %, 1.44 mol), sulfuric acid (25 wt. %, 82 mmol), temperature 100 °C; formaldehyde (35 wt. %, 31 mmol), hydrochloric acid (18 wt. %, 120 mmol), sulfuric acid (25 wt. %, 7 mmol); dropping time: 15 min, additional stirring: 15 min.

Bentonite as catalyst[28]. A mixture of methyl N-phenylcarbamate, bentonite and an inert solvent were heated with stirring to the required temperature; formaldehyde was introduced under concurrent removal of water by azeotropic distillation together with a part of the inert solvent. The inert solvent was then distilled off, acetone dissolving all reaction components was added, the mixture was filtered and the filtrate was worked up.

Determination of Methyl N-Phenylcarbamate and Dimethyl 4,4'-Diphenylmethane Dicarbamate in the Condensation Product of Methyl N-Phenylcarbamate and the Carbonylation Product with Formaldehyde by RP-HPLC

The above-mentioned compounds were separated from the remaining components of the mixture by RP-HPLC using the isocratic elution mode. A direct method was applied for calibration.

Analysis conditions: high-resolution liquid chromatograph (Laboratorní přístroje, Praha), column *a*) 150 × 3.3 mm i.d. packed with Separon CGC, 5 μm grain size; *b*) 250 × 4.2 mm i.d., Separon SGX C_{18}, 5 μm grain size.

Mobile phase: methanol–water 6 : 4 (v/v), flow rate 0.3 ml min^{-1}; detector UV_{254}; injected amount 5 μl of methanolic solution, chart drive 0.15 cm min^{-1}.

Chemicals: methanol p.a. grade, commercially available, distilled water; standards of methylphenylurethane, diphenylurea and dimethyl 4,4'-diphenylmethane dicarbamate were twice crystallized from heptane, petroleum ether or methanol, the purified substance content was higher than 99.2 wt. %. No satisfactory resolution of the mixture under investigation was achieved with the mobile phase methanol–water 7 : 3 (cf. Table I); diphenylurea did not separate from dimethyl 4,4'-diphenylmethane dicarbamate as required. Aniline, which was not anticipated in the sample analysed, eluted closely after methyl N-phenylcarbamate. Better resolution afforded methanol–water 6 : 4 (v/v); a shorter column was used aiming to shorten the time needed for analysis.

Content of constituents in samples (in wt. %) was calculated according to Eq. (*1*),

$$c = (A_s R_F 100) / n , \qquad (1)$$

where c is the substance content, A_s the peak area of the compound determined in the sample, R_F the response factor of the given compound, n the amount of samples.

TABLE I
Retention times of compounds at specified conditions: methanol per water ratio, carrier liquid flow (ml min^{-1}) and the column packing (A Separon CGC; B Separon SGX C_{18})

Compound	Conditions		
	7 : 3; 0.4; B	6 : 4; 0.3; B	6 : 4; 0.3; A
Methyl N-phenylcarbamate	11.3	12.0	6.0
Aniline	11.7	–	–
Diphenylurea	15.3	18.7	10.3
Nitrobenzene	16.0	–	10.0
Dimethyl 4,4'-diphenylmethane dicarbamate	15.3	22.7	13.0

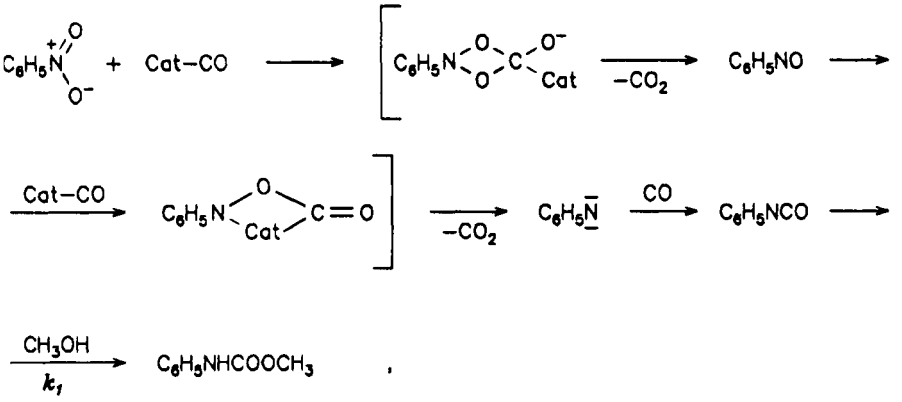
RESULTS AND DISCUSSION

Catalytically Activated Reductive Carbonylation of Nitrobenzene to Methyl N-Phenylcarbamate

A high conversion and selectivity to methyl N-phenylcarbamate was succeeded to achieve on reductive carbonylation of nitrobenzene with carbon monoxide in the presence of methanol and components of a new catalytic system[29] (Table II).

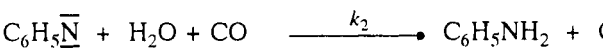
$$C_6H_5NO_2 + 3\ CO + CH_3OH \xrightarrow[70\text{–}240\ °C,\ 3\text{–}30\ MPa]{\text{catalyst}} C_6H_5NHCOOCH_3 + 2\ CO_2 \qquad (2)$$

As far as the reaction mechanism is concerned, we suppose – in accordance with the literature[30–32] – that reduction of nitrobenzene to phenylnitrene took place. We assume that the first step in the mechanism is associated with formation of carbonyl sulfide, a catalyst, which lowers its stability due to the influence of sodium acetate[33] or alkali metal methoxide or hydroxide to form a complex with nitrobenzene followed by decarboxylation leading to phenylnitrene.



(3)

The later reacted with carbon monoxide to yield phenyl isocyanate and with methanol to furnish methyl N-phenylcarbamate. Phenylnitrene can react with water to produce aniline



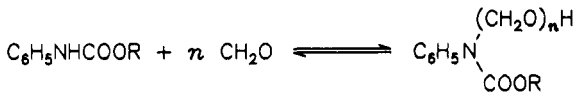
(4)

where $k_1 << k_2$.

This conception is also backed by our findings that a positive effect is encountered in the presence of oxygen[34] and vanadium pentoxide in the reaction system.

Condensation of Methyl N-Phenylcarbamate with Formaldehyde

The condensation mechanism for aromatic carbamates with methylenation agents has so far not been elucidated. It is supposed[35] that during condensation a compound was produced on reaction of aromatic carbamates with formaldehyde

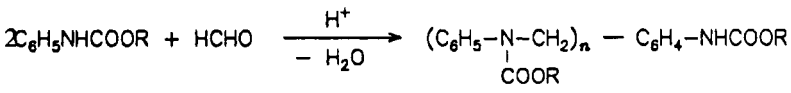


(5)

where $n \geq 1$.

In addition to MDDC also higher homologues – PMPPC and eventually a lot of by-products – can be formed during condensation as a result of the kind of the catalyst, methylenation agent, concentration of reagents in the solvent, temperature and time; consequently, the mechanism and kinetics of condensation can be rather complicated.

Condensation of alkyl N-phenylcarbamate with formaldehyde can give, in addition to the principal isomer with a secondary nitrogen – 4,4'-MDDC – also 2,4'- and 2,2'-isomers in 10 to 20 times lesser extent[36]. Further isomers possessing a tertiary nitrogen and having the carbamate nitrogen bonded through the methylene bridge (N-benzyl derivatives) can originate under the same conditions



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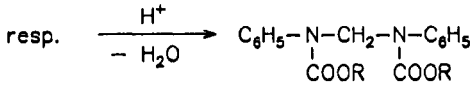
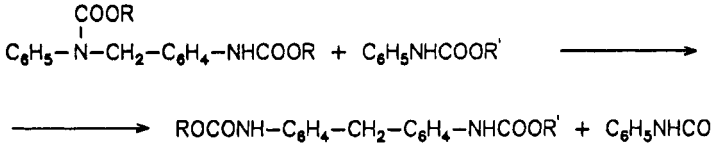


(7)

where $n \geq 1$.

As found[11], these N-benzyl derivatives can undergo an intermolecular transfer reaction in the presence of alkyl N-phenylcarbamate and a carboxylic acid having $pK < 4$, or sulfuric acid of greater than 75 wt. % to afford the corresponding mono-, di- and polymethylene polyphenyl carbamates.



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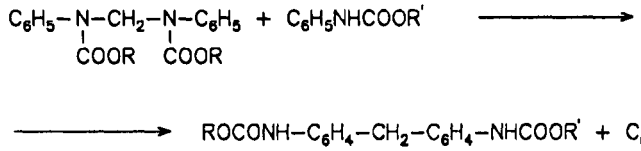

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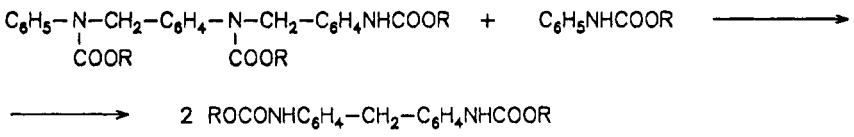

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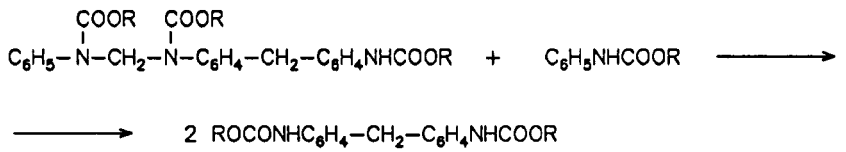

(11)

Concentrated Sulfuric Acid as Catalyst

The best yields of MDDC in two-step syntheses, where a rearrangement of N-benzyl derivatives to MPC, MDDC and PMPPC took place in the second step of the condensation could be obtained with concentrated (96 wt. %) sulfuric acid.

Better yields of condensation were observed at 60 – 70 °C than at 80 – 100 °C. This is due to the fact that higher temperatures and longer reaction times promote rearrangements of N-benzyl derivatives and facilitate also hydrolyses and oxidations ($H_2SO_4 \rightarrow H_2O + SO_2 + 1/2\ O_2$).

The calculated molar ratio of MPC/HCHO for a 100% reaction course is 2 : 1, but all patents[12] stressed a great excess of MPC in reactions with concentrated sulfuric acid, i.e. the HCHO to MPC ratio substantially lower than 0.5 thereby ensuring the maximum content of the 4,4'-isomer in the product (Table III and Fig. 2*a*).

A great excess of formaldehyde is, on the other hand unfavourable because it leads to PMPPC of lower quality. Very long reaction times lower the content of MDDC in favour of polycondensates. The condensation product thus obtained is smeary and not crystalline; as a consequence, it is impossible to separate sulfuric acid from the condensation product with water, nor separation with aqueous methanol, recommended

TABLE II

Effect of the catalyst and the ratio of the catalyst/nitrobenzene (m_c/m_{NB}) on the catalytic carbonylation of nitrobenzene with conversion of nitrobenzene (C_{NB}) and selectivity for MPC (S_{MPC}) and aniline (S_{AN})

Co-catalyst	m_c/m_{NB}	C_{NB}, %	S_{MPC}, %	S_{AN}, %
CH_3ONa	0.7	100	84.6	10.7
CH_3ONa	1	100	86.4	6.8
CH_3OK	0.7	100	85.1	10.6
CH_3OK	1	98.3	89.0	2.6
NaOH + CaO	0.5 + 1.0	97.3	86.7	9.1
NaOH	1.5	99.9	82.3	14.7
KOH + $(MgOH)_2$	0.5 + 1.5	97.9	86.9	8.9
CH_3COONa	5	34.0	74.5	15.1
CH_3COONa	10	99.5	74.3	15.5
CH_3COONa + CH_3ONa	5 + 3.85	100	74.7	15.9

TABLE III

Condensation products of methyl N-phenylcarbamate and formaldehyde at an initial (T_d) and second reaction (T_r) temperatures as determined by RP-HPLC

No.	Catalyst	Molar ratio		Solvent	T_d °C	T_r °C	Time min		Content, %			Yield, %	
		MPC/Cat	MPC/HCHO						MPC	DPU[c]	MDDC	MDDC	Comment
1[a]	96% H_2SO_4	2.08	4.7	hexane	69.5	69.5	50	80	–	–	–	–	
2	96% H_2SO_4	2.08	4.7	heptane		97.5		20	8.4	0.1	87.8	61.2	Fig. 2*a*
				hexane	69.5	69.5	50	80	23.1	0.4	50.3	56.9	–
3[a]	96% H_2SO_4	2.08	4.7	hexane	69.5	69.5	20	75	–	–	–	–	
				heptane		97.5		20	28.0	0.4	65.4	53.4	–
4	43% H_2SO_4	0.025	0.71	–	82	82	45	55	3.3	0.06	73.3	67.5	Fig. 2*b*
5	43% H_2SO_4	0.025	0.73	–	82	82	45	55	3.5	0.6	59.5	56.0	Fig. 3*a*
6	18% HCl	0.018	1	–	100	100	15	15	1.8	0.6	76.1	58.6	Fig. 3*b*
7	18% HCl + 25% H_2SO_4	0.019	1	–	100	100	15	15	3.0	0.7	87.4	65.6	Fig. 4*a*
8	18% HCl + 25% H_2SO_4	0.019	1	–	100	100	15	60	3.3	0.4	72.7	56.4	–
9[b]	Bentonite								80.8	0.8	16.6	72.2	Fig. 4*b*

[a] A two-step condensation process; [b] for details see ref.[28]; [c] diphenylurea.

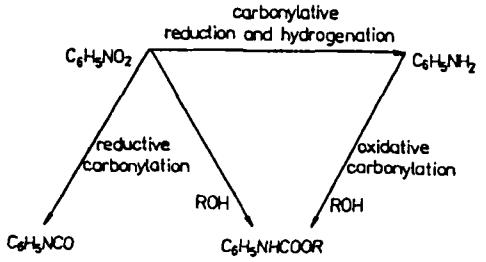

FIG. 1

Progressive methods for the synthesis of phenyl isocyanates and "blocked" phenyl isocyanates i.e. alkyl N-phenylcarbamates

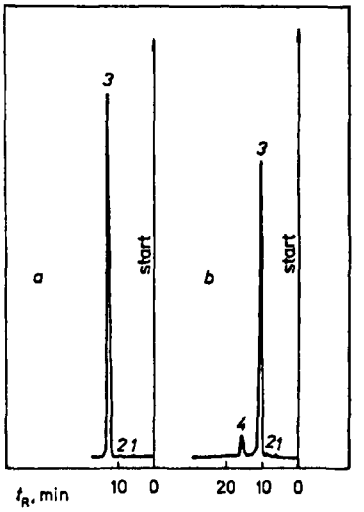

FIG. 2

Chromatograms of condensation products of MPC *a* 96 wt. % and *b* 43 wt. % sulfuric acids. *1* Methyl N-phenylcarbamate; *2* diphenylurea; *3* dimethyl 4,4'-diphenylmethane dicarbamate; *4* unidentified compound

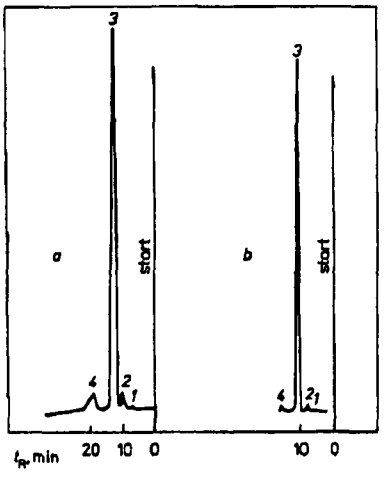

FIG. 3

Chromatograms of condensation products of MPC (carbonylation product of nitrobenzene) using *a* 43 wt. % sulfuric acid and *b* 18 wt. % hydrochloric acid. *1* MPC; 2 DPU; *3* dimethyl 4,4'-MDDC; *4* unidentified compound

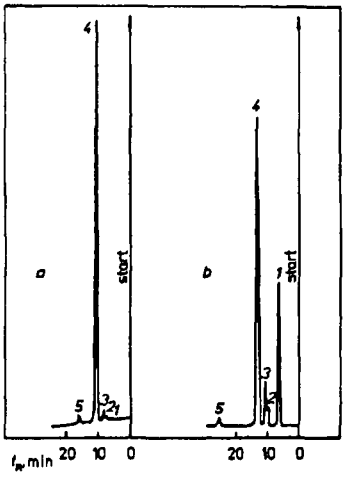

FIG. 4

Chromatograms of condensation products of MPC using *a* 18 wt. % HCl + 25 wt. % H_2SO_4 and *b* bentonite. *1* MPC; *2* nitrobenzene; *3* DPU; *4* dimethyl 4,4'-MDDC; *5* unidentified compound

in ref.[37] proved successful. We found the solubility of MPC and MDDC in methanol at 24 °C to be 81.3 and 0.65 wt. %, respectively. Basing on this finding, we elaborated an effective separation procedure for MPC, MDDC and other components with methanol.

Dilute Sulfuric Acid as Catalyst

Dilute (43 wt. %) sulfuric acid in a volume ratio to the organic phase greater than 15:1, and formaldehyde (concentration less than 0.5 mol l^{-1}) were used according to paper[36]. Dilute sulfuric acid was added to formaldehyde in order the acidity H_0 to be less than −1. Dilute sulfuric was found to be a good catalyst (Table III and Figs 2*b*, 3*a*) and it is noteworthy that this concentration of acid in a great volume excess at a low formaldehyde concentration afforded better yields than concentrated sulfuric acid in lesser amount. The required reaction time is relatively short.

Dilute Hydrochloric Acid and its Mixture with Dilute Sulfuric Acid as Catalysts

Excellent yields (89 wt. %) of MDDC can be obtained according to ref.[17] with dilute (18 wt. %) hydrochloric acid and a little worse ones (72 wt. %) with 25% H_2SO_4. The amount of acid has to dissolve all the MPC at 100 °C. This procedure was checked in experiments using 18% HCl (Table III and Fig. 3*b*) and 25% H_2SO_4, but yield of MDDC reported in ref.[17] could not be reached. Not even white product could be obtained under these conditions; its colour was more or less pinky. A white product was obtained by lowering the temperature to 90 °C. It is useful to lower the molar ratio HCHO/MPC to 0.5 – 1.0 instead of 1.5. It is also advantageous according to ref.[36] to add a part of the catalyst acid to formaldehyde prior to reaction in order to dilute the reagent and to depolymerize its polymeric forms.

A little higher yields were achieved when using a mixture of hydrochloric and sulfuric acids (Table III and Fig. 4*a*), or the recycled acid instead of a new one. Experiments 7 and 8 are comparable. Extension of the reaction time for getting the reaction through from 20 to 60 min lowered the yields of MDDC.

Bentonite as Catalyst

Like or better yields than with dilute hydrochloric acid or with its mixture with sulfuric acid afforded bentonite as catalyst[28] (Table III and Fig. 4*b*). Nevertheless, this process requires a long reaction time (10 – 20 h), a great excess of MPC, higher temperature and a more energy-demanding separation than with acid as catalyst.

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