Experimental

All operations were performed under dry argon and in absolute solvents. ^{31}P, ^{29}Si, and ^{13}C NMR spectra were recorded using a FT-80 A device (Varian) in C_6H_6 using 85 % H_3PO_4 and tetramethylsilane as external standards. ^1H NMR spectra were registered using an AM-360 instrument (Bruker) in the same solvent.

1-*tert*-Butyl-2,4-bis(*tert*-butylamino)-4-methyl-1,2λ^3,4-azaphosphasiletidine (2a). A solution of dichlorophosphine **1a** (11.5 g, 0.05 mol) in pentane (100 mL) was added for 0.5 h to a solution of *tert*-butylamine (29.26 g, 0.4 mol) in 400 mL of abs. pentane cooled to 0 °C. The mixture was stirred for 1 h, then the temperature was raised to ~20 °C, the precipitate was separated by centrifugation, the solvent was removed by distillation, and the residue was fractionated *in vacuo* to afford 7.57 g of compound **2a** (50 % yield); b.p. 75—77 °C (0.01 Torr), n_D^{20} 1.4750. Found (%): C, 55.23; H, 11.15. $C_{14}H_{34}N_3PSi$. Calculated (%): C, 55.40; H, 11.29. ^{31}P NMR, δ: 76.56 (*cis*-form); 65.69 (*trans*-form). ^{29}Si NMR, δ: −9.07 (d, $^2J_{Si-P} = 3.0$ Hz, *cis*-form); −17.3 (d, $^2J_{Si-P} = 2.0$ Hz, *trans*-form). ^{13}C NMR, δ: 6.49 (d, $^3J_{P-C} = 1.7$ Hz, MeSi, *cis*-form,); 3.58 (s, $^3J_{P-C} < 1$ Hz, MeSi, *trans*-form); 24.08 (d, $^1J_{P-C} = 14.0$ Hz, $SiCH_2P$, *cis*-form); 24.98 ($^1J_{P-C} = 16.1$ Hz, $SiCH_2P$, *trans*-form).

1-*tert*-Butyl-2-*tert*-butylamino-4-dimethyl-1,2λ^3,4-azaphosphasiletidine (2b) was prepared similarly to **2a**. The yield of **2b** was 42 %; b.p. 85—90 °C (0.02 Torr), n_D^{20} 1.4646. Found (%): C, 54.10; H, 11.06. $C_{11}H_{27}N_2PSi$. Calculated (%): C, 53.62; H, 11.05. ^{31}P NMR, δ: 92.96. ^{29}Si NMR, δ: 14.85 (d, $^2J_{Si-P} =$ 2.1 Hz). ^1H NMR, δ: 0.35 (s, 3 H, MeSi); 0.44 (s, 3 H, MeSi); 0.53 (dd, $^2J_{P-H^\alpha} = 3.8$, $^2J_{H^\alpha-H^\beta} = 14.7$, 1 H^α, CH_2); 1.34 (s, 9 H Bu^t); 1.35 (s, 9 H, Bu^t); 1.58 (dd, $^2J_{P-H^\beta} = 23.9$ Hz, $^2J_{H^\alpha-H^\beta} = 14.7$ Hz, 1 H^β, CH_2); 1.98 (d, $^2J_{P-H}$, = 6.6 Hz, 1 H, NH). ^{13}C NMR δ: 5.21 (s, MeSi); 8.20 (d, $^3J_{P-C} = 1.7$ Hz, MeSi,); 19.54 (d, $^1J_{P-C} = 12.9$ Hz, $SiCH_2P$,); 32.5—33.2 (m, Me_3C); 50.1—51.0 (m, NC).

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Alkylation of 4-methoxyphenol with styrene in the presence of alumoxane compounds

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The catalytic properties of alumoxane compounds in the alkylation of 4-methoxyphenol with styrene were studied. Structures and yields of alkylation products depend on the amount of catalyst, the phenol: olefin ratio, and the reaction time. Phenoxyalumoxanes are effective *ortho*-directing catalysts with respect to the hydroxy group. Under optimum conditions, 2-(α-methylbenzyl)-4-methoxyphenol and 2,5-di-(α-methylbenzyl)-4-methoxyphenol were obtained in 94 % and 84—86 % yields, respectively.

Key words: 4-methoxyphenol, alkylation with styrene; alumoxanes; catalysts.

Metal phenoxides, *e.g.*, aluminum phenoxide, known as *ortho*-directing catalysts, have scarcely been studied in the alkylation of dihydroxybenzenes and their ethers. The sudies on the alkylation of catechol and resorcinol with isobutylene, styrene, and cyclohexene in the presence of titanium catecholate and aluminum phenoxide are exceptions.[1—3] It is noteworthly that the composition of the catalyst changes in the course of aluminum

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phenoxide-catalyzed alkylation of dihydroxybenzenes due to exchange of the phenoxide group.[3]

$$\mathrm{Al(OPh_3) + HOC_6H_4OMe \rightarrow Al(OPh)_2OC_6H_4OMe + PhOH}$$

As a result, the corresponding alkylphenols are formed,[4] which is a very undesirable side reaction.

When monomethyl ethers are alkylated, the number of isomeric alkylation products is higher than in the case of dihydroxybenzenes or their dimethyl ethers. Therefore selective catalysts are needed to prevent the accumulation of impurities. Previously we established[5] that aluminum tris-(4-methoxyphenoxide) did not afford phenol derivatives in the reaction mixture. Unfortunately, just as in the case of $\mathrm{Al(OPh)_3}$, it could not be used repeatedly. Thus the search for effective and technologically acceptable regioselective catalysts remained an open problem.

It had been stated that phenoxyalumoxanes, which are formed from aluminum phenoxide in the following reaction,

$$\mathrm{(PhO)_2AlOH + (PhO)_3Al \rightarrow (PhO)_2Al{-}O{-}Al(OPh)_2 + PhOH}$$

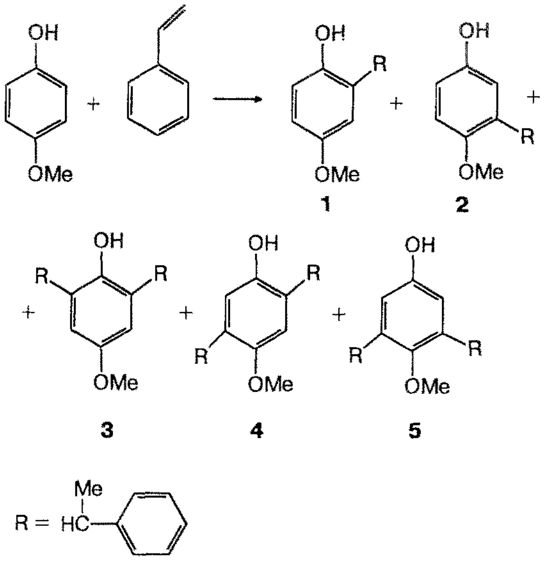
have no catalytic activity.[6]

However, phenoxyalumoxanes proved to be effective in the alkylation of phenol with isobutylene, styrene, and indene.[7,8] Alumoxane compounds can also be used for the preparation of the corresponding aryloxyalumoxanes which exhibit the properties of homogeneous and heterogenous catalysts.

In this work the catalytic activity of some novel oligomeric (4-methoxyphenoxy)alumoxanes of different molecular mass were studied in the alkylation of 4-methoxyphenol (4-MP). Oligomeric (4-methoxyphenoxy)alumoxanes were obtained using the reaction of alkylalumoxanes with 4-MP at 60—90 °C.

In contrast to the case of hydroquinone, the alkylation of 4-MP can give rise to five products differing in the position of substituents in the aromatic ring (Scheme 1).

Scheme 1

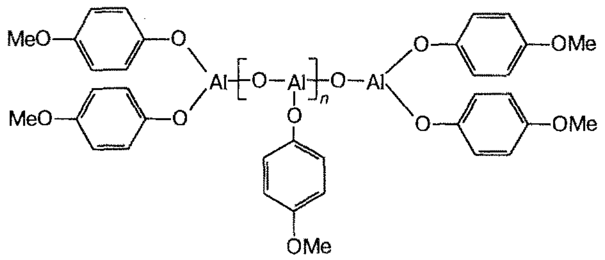


The formation of ethers and trisubstituted 4-MP (not shown in Scheme 1) is also possible. Experimental data concerning the alkylation of 4-MP in the presence of oligomeric phenoxyalumoxanes are presented in Table 1. Rates of alkylation were rather high and total conversion of styrene at 140 °C was normally completed in 15—30 min. The compositions of the resulting product mixtures were determined by GLC, and by IR, and ^{1}H NMR spectroscopy. Phenoxyalumoxanes proved to be effective *ortho*-directing catalysts with respect to the hydroxy group, so the major reaction products were 2-(α-methylbenzyl)-4-methoxyphenol and 2,6-di-(α-methylbenzyl)-4-methoxyphenol (**1** and **3**, respectively).

Varying the molar ratios of the reactants does not change the sum of **1** and **3** (*ca.* 93—98 % yield); however, selective formation of **1** (in 94 % yield) and **3** (in 86 % yield) can be achieved.

Increasing the styrene content in the reaction mixture results in higher yields of di-(α-methylbenzyl)-4-methoxyphenols **4** and **5**, and also of trisubstituted methoxyphenols. The content of 3-(α-methylbenzyl)-4-methoxyphenol **2** decreases as the yields of **4** and **5** increase. The yield of **4** increased as the styrene: 4-MP

Table 1. Isomeric composition of the products of mono- and dialkylation of 4-methoxyphenol with styrene in the presence of poly-(4-methoxyphenoxy)alumoxanes*



n	4-MP: styrene (molar ratio)	Total yields of alkylphenols** (mass. %)	Alkylphenols (mass. %)				
			1	**2**	**3**	**4**	**5**
0	4 : 1	98.5	92.6	1.1	5.5	0.8	—
25		98.7	94.1	1.0	4.3	0.6	—
4		98.6	78.6	0.4	17.7	3.3	—
9	2 : 1	98.3	79.3	0.5	17.3	2.9	—
25			80.2	0.4	16.5	2.9	—
2		98.3	75.4	0.3	22.5	1.1	—
9	1 : 1	98.2	73.8	0.2	22.7	1.3	—
25		98.1	73.0	0.2	25.1	1.3	—
4		98.0	9.2	0.1	86.0	4.2	0.3
9	1 : 2	97.5	8.9	0.1	86.8	3.8	0.3
25		97.7	9.5	0.1	86.4	3.4	0.5

* At 140 °C, 0.5 mass. % of Al. ** For 100 % conversion of styrene.

molar ratio increased, whereas the formation of **5** was observed only when a twofold excess of styrene was used. The content of these isomers increased to 13 % and 5 % respectively, when the temperature was increased to 180 °C. Lowering the reaction temperature to 90 °C resulted in a decrease in the conversion of styrene and the number of isomeric products, and in an increase in the content of ethers in the alkylate mixture.

We established that the alkylation of phenol with styrene in the presence of alumoxane catalysts is accompanied by alkylation and polymerization of styrene. Oligoalkylphenols with molecular mass *ca.* 7600—9300 were obtained, but their total content did not exceeded 1—3 mass. % in the alkylate mixture (*cf.* ref. 9).

The optimum quantity of catalyst is 0.5 mass. % of Al in relation to both reactants. Lowering the Al content to 0.1 mass. % resulted in drastic prolongation of the total conversion time (up to 5 h) and in formation of di- and oligomers of styrene. Increasing the concentration of the catalyst up to 1 mass. % diminished the yields of **1** and **3** and increased the yields of **2**, **4**, and **5**.

4-Methoxyphenoxyalumoxanes of different molecular mass were used as catalysts. Other conditions being equal, the number of Al atoms in the alumoxanes does not affect the isomeric composition of the alkylate mixture or the activity of the catalysts (see Table 1).

These data show that the "polymeric effect" is not important for the *ortho*-directing properties of alumoxane catalysts or the regioselectivity of electrophilic substitution in the benzene ring of 4-MP .[10] Phenoxyalumoxanes with 25 or more aluminum atoms are heterogenic catalytic systems and are not soluble in the alkylate. Alumoxanes having fewer than 25 aluminum atoms are soluble in the alkylate during the process of alkylation. Apparently, not only 4-MP, but 4-methoxyphenyl ligands in alumoxanes are also alkylated.

The alkylation of *p*-cresol in the presence of aluminum *p*-methylphenoxide gave 2-methylbenzyl-4-methylphenol in a maximum yield of 76.3 %, while the total yield of mono- and disubstituted *p*-cresols did not exceed 86.8 %,[11] and the total conversion of styrene was achieved in 3.5 h. Therefore, the catalytic activity and *ortho*-directing effect of alumoxane catalysts are more pronounced.

The experimental evidence shows that unsubstituted and substituted phenoxyalumoxanes are effective catalysts in the alkylation of 4-MP. Their use makes it possible selectively obtain the *ortho*-monosubstituted and *ortho*-disubstituted derivatives of 4-MP (up to 94 mass. % and 86 mass. % respectively). The total yield of *ortho*-substituted methoxyphenols is 96—98 %.

Experimental

Analyses and monitoring of the alkylation reactions were carried out by GLC with a Tsvet-530 chromatograph equipped with FID and a column (1.8 m × 1 mm) with 5 % OV-17 on Celite-545 (80—100 mesh). Helium was used as the carrier gas. The temperature programming was as follows: initial temperature 100 °C, temperature increase at 15 °C/min up to 305 °C; injector and detector temperatures were 330 °C.

^{1}H NMR spectra were registered on a Bruker MSL-300 spectrometer (300 MHz) for 10 % solutions in DMSO (with tetramethylsilane as the internal standard). Electron impact mass spectra (70 eV) of individual compounds were obtained with a GC-MS Kratos MS 25 RF instrument. IR spectra were recorded with a Bruker 113v Fourier transform spectrometer.

Preparation of the catalyst. A solution of tetraisobutylalumoxane (0.01 mol in 50 mL of toluene) was added to a solution of 4-MP (1.0 mol) in 150 mL of toluene with stirring at 40 °C. The mixture was agitated for 60 min at 90 °C until the evolution of isobutane ceased, diluted with *n*-heptane, and cooled to *ca.* 20 °C. The precipitate of tetra(4-methoxyphenoxy)alumoxane (OMPA-2) was collected by filtation, washed with dry heptane to remove the traces of 4-MP, and dried. OMPA-2 was obtained in 93 % yield. Found (%): C, 58.80; H, 5.15; Al, 9.42. $C_{28}H_{28}O_9Al_2$. Calculated (%): C, 59.79; H, 5.60; Al, 9.59.

Oligomeric 4-methoxy phenoxyalumoxanes (OMPA-4, 9, 27) were synthesized by a similar procedure. All of the reactions were carried out under special purity grade argon. All reagents were dried and distilled.

Alkylation of 4-methoxyphenol with styrene. The alkylation of 4-MP (freshly distilled, m.p. 55—57 °C, b.p. 243 °C, moisture content 50 ppm) with styrene was carried out under various conditions (molar ratio of reagents, structure and quantity of catalysts, reaction temperature, and reaction time).

When the reaction was completed, the alkylate mixture was worked up with toluene and washed with dilute HCl (5—10 %) to decompose the catalyst. The organic layer was separated, and the aqueous layer was extracted with toluene. Combined organic extracts were washed with water to the neutral reaction. The solvent and the excess 4-MP were evaporated, and the alkylate mixture was worked up with methanol to destroy oligoalkylphenols. Then the alkylate was distilled under reduced pressure (3—4 Torr).

2-(α-Methylbenzyl)-4-methoxyphenol (1) was obtained by crystallization of the fraction with b.p. 180—200 °C (6 Torr) from hexane. After repeated crystallization chromatographically pure **1** was obtained, m.p. 62 °C (from hexane), b.p. 180—185 °C (6 Torr). Found (%): C, 79.71; H, 6.80; OH, 7.30. $C_{15}H_{16}O_2$. Calculated (%): C, 78.95; H, 7.02; OH, 7.46. IR, ν/cm^{-1}: 705, 740 (Ph); 1050, 1280, 1455, 2830, 2890, 2895 (MeO); 1370, 2870, 2965 (Me); 2860, 2930 (CH_2); 800, 865 (1,2,4-substituted benzene ring); 1440, 1490, 1510, 1600, 3010, 3030, 3080 (aromatic rings); 3400, 3550 (sh, OH). ^{1}H NMR, δ: 1.5 (d, J = 6.9 Hz, 3 H, CH_3); 4.46 (q, J = 6.9 Hz, 1 H, CH); 6.67 (d, J = 2.7 Hz, 1 H, H-3); 6.59 (dd, J = 9.0 Hz, 2.7 Hz, 1 H, H-5); 6.73 (d, J = 9.0 Hz, 1 H, H-6); 8.94 (c, 1 H, OH); 3.62 (s, 3 H, MeO); 7—7.5 (m, 5 H, Ph). MS, m/z ($I_{\rm rel}$ (%)): 39 (31), 51 (43), 63 (18), 65 (10), 77 (44), 78 (24), 79 (21), 91 (35), 103 (20), 105 (20), 115 (23), 135 (22), 150 (55), 151 (17), 152 (19), 153 (18), 169 (10), 181 (14), 197 (10), 198 (12), 213 (100), 214 (14), 228 $[M]^+$ (98), 229 (14).

2,6-Di-(α-methylbenzyl)-4-methoxyphenol (3) was obtained from the fraction with b.p. 200—230 °C (4—5 Torr) by column chromatography on silica gel (Chemapol 40/100), benzene—hexane (2 : 1) as the eluent. The course of separation was monitored by GLC and TLC (Silufol UV-254). M.p. 71 °C (hexane), b.p. 220—230 °C (4—5 Torr). Found (%): C, 83.50; H, 7.15; OH, 5.00. $C_{23}H_{24}O_2$. Calculated (%): C, 83.13; H, 7.24; OH, 5.12. IR, ν/cm^{-1}: 705, 740 (Ph); 1060, 1210, 1230, 2830, 2890, 2945 (MeO); 1370, 2870, 2965 (Me); 2860, 2930 (CH_2); 1440, 1490, 1510, 1600, 3010, 3030, 3080 (aromatic rings); 3440, 3550 (sh, OH); 870 (1,2,3,5-substituted aromatic ring). ^{1}H NMR, δ: 1.40—1.42 (3 H, Me); 4.3—4.35 (1 H, CH); 6.4 (s, 1 H, H-3); 7.0 (s, 1 H, H-5); 8.0 (1 H, OH); 3.75 (s, 3 H, OMe); 7.05—7.4 (5 H, Ph). MS, *m/z* ($I_{\rm rel}$ (%)): 39 (17), 50 (10), 51 (18), 63 (8), 65 (8), 77 (22), 78 (29), 105 (85), 115 (18), 128 (5), 129 (4), 141 (4), 152 (7), 153 (6), 165 (12), 181 (4), 197 (3), 213 (12), 227 (4), 239 (5), 255 (5), 301 (2), 317 (39), 332 [M]$^+$ (100), 333 (27).

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