References and Notes

(1) J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 3332 (1970).

(2) Although Pincock and Yates state in the Results and Discussion section of their paper (ref 1) that only *trans*-dibromide is formed, the Experimental Section indicates that a mixture of *trans*- and *cis*-1,2-dibromide (72:28%) is formed when bromine in acetic acid is added to 1-hexyne in acetic acid. Therefore, we reinvestigated the bromination of 1-hexyne in acetic acid and found that *cis* dibromide is formed in concentrated solutions (13:87% cis to trans at a mole fraction of 0.8 in 1-hexyne), but that only *trans*-dibromide is formed in dilute solutions. We interpret these data as suggesting that *cis*-dibromide is a product of a molecule-induced radical reaction at higher concentrations, whereas ionic addition occurs in dilute solution.

(3) G. A. Olah and T. R. Hochswender, Jr., *J. Am. Chem. Soc.*, **96**, 3574 (1974).

(4) W. Puterbaugh and M. Newman, *J. Am. Chem. Soc.*, **79**, 3469 (1957).

(5) V. L. Heasley, C. L. Frye, G. E. Heasley, K. A. Martin, D. A. Redfield, and P. S. Wilday, *Tetrahedron Lett.*, **18**, 1573 (1970).

(6) The formation and stability of five-membered cyclic halonium ions in the mass spectrometer is well established. See H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds", Holden-Day, San Francisco, Calif., 1964, chapter 7.

(7) We found analogous isotope cluster patterns for the 1,2-dichloro- and 1,2-dibromohexanes.

(8) The ^{13}C chemical shifts for *trans*-dibromoethylene and *trans*-dichloroethylene are 109 and 119.4 ppm, respectively. See G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, p 64.

(9) P. B. D. De La Mare and S. Galandauer, *J. Chem. Soc.*, 36 (1958), obtained a Markownikoff to anti-Markownikoff ratio of 54:46 in the addition of BrCl to 1-propene in the polar solvent water.

(10) Two alkynes which apparently involve open vinyl cations give both *trans*- and *cis*-dibromides: phenylacetylene[1] and cyclopropylacetylene (D. F. Shellhamer and M. L. Oakes, *J. Org. Chem.*, in press).

(11) G. J. Schmid, A. Modro, F. Lenz, D. G. Garratt, and K. Yates, *J. Org. Chem.*, **41**, 2331 (1976).

(12) A mixture of the methoxy bromides (**3a,b**) was prepared unambiguously by addition of *N*-bromosuccinimide to 1-hexene in methanol. The structures of **3a,b** have been established previously.[4,5]

Heterogeneous Catalysis by Solid Superacids. 4.[1] Methylation of Phenols with Methyl Alcohol and the Rearrangement of Anisole and Methylanisoles over a Perfluorinated Resinsulfonic Acid (Nafion-H) Catalyst

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Anisole and methylanisoles are rearranged when passed in the gas phase over highly acidic solid perfluorinated resinsulfonic acid (Nafion-H) catalyst at 205 °C and atmospheric pressure. A mixture of anisole, mono- and dimethylanisoles, phenol, cresols, and xylenols was obtained. Methyl alcohol and phenol (for cresols) reacted under the same conditions to give a mixture of O- and C-methylated products. The latter reaction was shown to proceed via fast initial O-methylation of the phenol followed by an intermolecular rearrangement of the aryl methyl ether to methylphenols. Rearrangement of anisole and methylation of phenol gave *o*- and *p*-cresol. Methylanisoles or a mixture of cresol and methyl alcohol yielded mixtures of mono- and dimethylated ring products. When the directing effects of the methyl, methoxyl, or hydroxyl groups oppose each other, as is the case with *o*- and *p*-methylanisoles or cresols, 6–14% of products methylated meta to the methoxyl or hydroxyl group was obtained. Isomerization and ring transmethylation were negligible under the experimental conditions. Nafion-H was also compared to other solid catalysts. Its lack of selectivity toward ortho methylation is attributed to the absence of basic sites on the catalyst.

Alkylation of phenols by alcohols is well known.[3] Gas-phase methylation of phenol by methyl alcohol was reported by Ipatieff as early as 1925.[4] Liquid phase, acid catalyzed methylation gave ortho and para substitution with low selectivity. Meta alkylation was reported in some cases,[5] but forcing conditions were required and the meta isomer was obtained via secondary isomerization. Lately, solid catalysts of the mixed oxides type containing basic sites, or acidic and basic sites, were found to catalyze efficiently the methylation of phenols with methyl alcohol with high selectivity for ortho methylation.

Recently we reported the use of highly acidic perfluorinated resin sulfonic acid catalysts, such as Nafion-H,[6] for the alkylation of benzene and alkylbenzenes.[7] In continuation of our studies we felt it of particular interest to study the methylation of phenols with methyl alcohol using mild reaction conditions (ca. 200 °C and atmospheric pressure) and to compare the activity of Nafion-H with other solid catalysts. The behavior of anisoles and methylanisoles was also studied under the same conditions.

Experimental Section

Materials. Methyl alcohol, phenols, and anisoles used were of highest commercially available purity, higher than 99%. Dimethylanisoles and xylenols used for comparison in identifying products in the GLC analyses were also commercially available. The activation of the Nafion-H catalyst was as mentioned.[7]

Experimental Procedure. The catalytic flow reactor and the general procedures used were described previously.[8] All the reactions were carried out at 205 °C in a N_2 flow of 5 mL/min, using 2 g of the catalyst. Phenols, anisoles, or their mixtures with methyl alcohol (1:1 molar ratio) were introduced at a liquid rate of 0.02 mL/min. The contact time of the reagents over the catalyst under these conditions is 6–7 s.

Analysis. Product compositions were determined by gas liquid chromatography using a Perkin-Elmer Model 226 gas chromatograph equipped with a flame ionization detector. A capillary column of 150 ft × 0.01 in. coated with *m*-bis(*m*-phenoxyphenoxy)benzene + Apiezon L was used to separate the products. Anisoles were separated as such. Phenols were first silylated by hexamethyldisilazane or trimethylchlorosilane and identified as the trimethylsilyl ethers. Some of the dimethylanisole peaks overlapped with those of aryl trimethylsilyl ethers. Therefore, each fraction was analyzed twice. One portion was dissolved in ether and extracted with aqueous NaOH and the ethereal solution was analyzed for anisoles. Another portion was silylated and analyzed for phenols and anisoles. In cases where peak overlap occurred, corrections were made on the basis of the known composition of the anisoles. *m*- and *p*-methylanisole were not separated under these conditions. They were, however, separated by using a 20 ft × 0.125 in. column packed with 15% *p*-azoxyanisole on Chromosorb W at 125 °C (a liquid crystal column[9]), using a Perkin-Elmer Model 900 gas chromatograph. Peak areas were measured by an electronic integrator, using corrections for differences in detector sensitivities. The accuracy of the determination of the product com-

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Table I. Products from Rearrangement of Anisole and Methylanisoles over Nafion-H Catalyst

		% product composition						
starting reactant	registry no.	starting material	anisole[a]	methyl-anisoles[a]	dimethyl-anisoles	phenol	cresols	xylenols
anisole	100-66-3	44.4		9.3	1.8	30.3	9.5	4.7
o-methylanisole	578-58-5	39.2	0.2	0.2	7.8	0.3	33.9	18.4
m-methylanisole	100-84-5	28.9	0.1	tr	10.1	0.2	37.5	23.2
p-methylanisole	104-93-8	35.1	3.4	1.1	8.3	4.6	34.7	12.8

[a] Excluding starting material

Table II. Methylation of Phenol, Cresols, and Anisole with Methyl Alcohol over Nafion-H Catalyst

	% product composition						
	unreacted starting material	anisole[a]	methyl-anisoles	dimethyl-anisoles	phenol[a]	cresols[a]	xylenols
phenol	37.3	37.2	9.7	1.0		10.4	4.4
anisole	58.6		13.9	3.0	18.1	4.7	1.7
o-cresol	51.4	0.1	23.4	4.7	0.4	0.6	19.4
m-cresol	48.1	tr	26.0	5.8	0.2	1.0	18.9
p-cresol	39.2	3.3	23.4	6.4	8.4	4.6	14.8

[a] Excluding starting material.

Table III. Composition of Methylanisoles and Cresols Obtained in the Nafion-H Catalyzed Transformation Reactions

starting reactant(s)	% methylanisoles			% cresols		
	ortho	meta	para	ortho	meta	para
anisole	45	1	54	58	1	41
phenol + methanol	54	tr	46	61	6	33
anisole + methanol	48	1	51	45	2	53

positions is considered, based on comparison with mixtures of known composition, ±0.5%.

Results

When anisole, or any of the isomeric methylanisoles, was passed over Nafion-H in the gas phase at 205 °C and atmospheric pressure (in N_2 atmosphere) mixtures of phenols and ring-methylated anisoles were obtained. About 60–70% of the starting materials were converted giving anisole, methylanisoles, dimethylanisoles, phenol, cresols, and xylenols. The product compositions obtained (in mole percent) are given in Table I. The relative amounts of methylanisoles and cresols obtained in the rearrangement of anisole are given in Table III. The isomeric compositions of obtained dimethylanisoles and xylenols are listed in Table IV. Equimolar mixtures of phenol, or an isomeric cresol with methyl alcohol, were passed over Nafion-H catalyst using the same experimental conditions. Both O- and C-methylation occurred giving anisoles and higher ring methylated phenols and anisoles. Similar results were obtained from the reaction of anisole and methyl alcohol. The amount of products obtained, the relative amounts of methylanisoles and cresols, as well as the isomeric compositions of dimethylanisoles and xylenols are given in Tables II, III, and IV, respectively. Usually about 40–50% of the starting phenol was methylated. Methyl alcohol was hardly detected in the products.

When neat methyl alcohol was passed over Nafion-H catalyst at 190 °C with a contact time of 4 s, the liquid product obtained contained 19% methyl alcohol and 81% water (by ^1H NMR), while in a subsequent cold trap at −78 °C dimethyl ether was condensed in the corresponding amount. The gaseous effluent contained only the carrier N_2 gas. Dehydration of methyl alcohol to form dimethyl ether thus competes with the methylation process. Indeed, small amounts of dissolved dimethyl ether could always be detected in the products obtained from the phenol–methyl alcohol reaction mixtures.

We also studied the activity of the catalyst as a consequence of onstream time. Figure 1 shows the product composition obtained as a function of onstream time in the reaction of anisole with methyl alcohol. After 3 h the catalytic activity was stabilized and did not change between 3 to 6 h of reaction time.

Table IV. Isomeric Dimethylanisoles and Xylenols Formed in Transmethylation and Methylation Reactions

starting reactant(s)	% dimethylanisoles					% xylenols				
	2,3[a]	2,4[b]	2,5[c]	2,6[d]	3,4[e]	2,3[f]	2,4[g]	2,5[h]	2,6[i]	3,4[j]
anisole	6	76	6	6	6	4	41	2	51	2
o-methylanisole	10	76	4	10		6	44	5	45	
m-methylanisole	24		34		42	28		42		30
p-methylanisole		87			13		94			6
phenol + methanol		100					55		45	
anisole + methanol	7	83	3	tr	7	12	64	12	6	6
o-cresol + methanol	7	70	7	16		14	43	2	41	
m-cresol + methanol	25		30		45	34		41		25
p-cresol + methanol		89			11		96			4

[a] Registry no. 2944-49-2, [b] Registry no. 6738-23-4. [c] Registry no. 1706-11-2. [d] Registry no. 1004-66-6. [e] Registry no. 4685-47-6. [f] Registry no. 526-75-0. [g] Registry no. 105-67-9. [h] Registry no. 95-87-4. [i] Registry no. 576-26-1. [j] Registry no. 95-65-8.

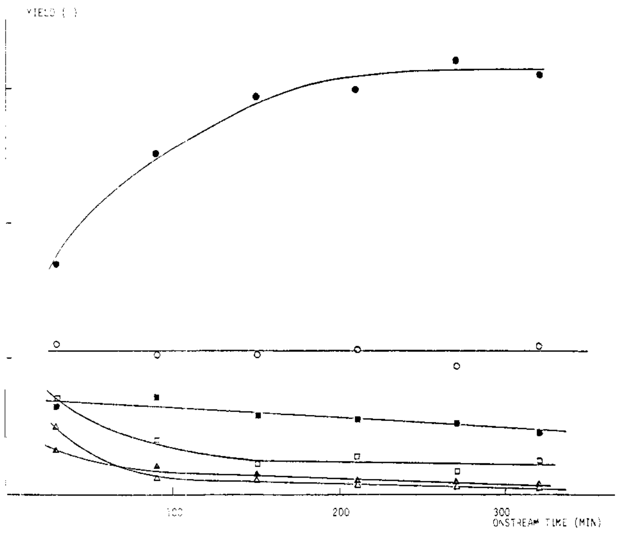


Figure 1. Reaction of anisole with methyl alcohol over Nafion-H. Yields vs. onstream time: (●) anisole; (■) methylanisoles; (▲) dimethylanisoles; (○) phenol; (□) cresols; (△) xylenols.

Discussion

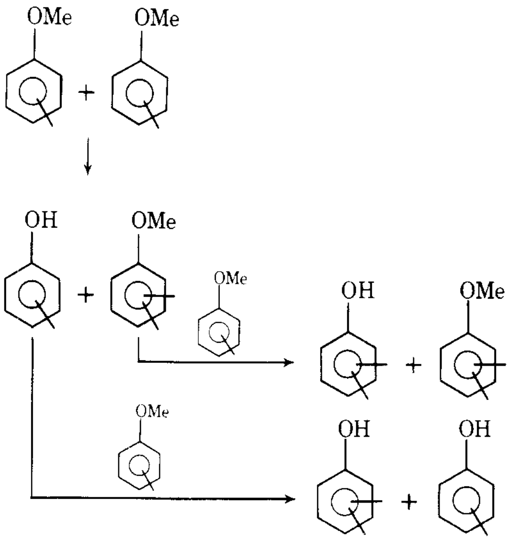
As seen from the results in Tables I and II, under the experimental conditions Nafion-H readily catalyzes both the rearrangement of anisoles and the methylation of phenols with methyl alcohol. Anisoles rearranged to an extent of 60–70% in the flow system. Phenol was methylated in 65% yield and cresols in 40–50% yield. The consumption of methyl alcohol was somewhat higher.

Methylation of phenols with methyl alcohol in the gas phase over solid catalysts is well known. Reports in the literature (including the patent literature) are numerous and thus only representative ones can be cited. Recently the selective ortho methylation of phenols was reported. Catalysts such as Al_2O_3,[10] TiO_2,[11] $ZnO{\cdot}Fe_2O_3$,[12] ZnO·MO (M = Cu, Ba, Ca, Co, Mn, Mg, Ni),[13] MgO alone,[14] or mixed with oxides of Mn,[14] Cu,[15] Sn,[15] Bi,[15] Pb,[15] or Cr,[15] as well many other oxides showed good to excellent selectivity toward ortho methylation. Temperatures employed were in the range of 250–400 °C and were typically around 350 °C. However, it is questionable whether acid catalysis is involved in these cases.[12a] Rearrangement of anisole in the gas phase over alumina[16] and zeolite catalyst[17] was also reported.

C- vs. O-Methylation. The intermediacy of anisole in the ring methylation of phenols is a question of still unresolved controversy. It was reported[18] that alkoxybenzenes are intermediates in the alkylation of phenols over alumina. Other authors,[10a] however, reported that over the same catalyst O- and C-alkylation are parallel reactions and suggested different mechanisms for each. Kotanigawa[12a] found anisole and its mixtures with methyl alcohol to be unreactive over $ZnO{\cdot}Fe_2O_3$ catalyst, thus excluding anisole as a possible C-alkylation intermediate. Using Nafion-H as the catalyst the situation is more complicated. Methylation of phenols always gives also significant amounts of the appropriate anisole. In the reaction of phenol and methyl alcohol 48% anisole and isomeric methylanisoles were obtained. Cresols and methyl alcohol gave ca. 30% anisoles. Further, anisole and methylanisoles were found to rearrange when passed over Nafion-H (Table I).

We suggest that under the experimental conditions initial O-methylation forming aryl methyl ether takes place followed by intermolecular O → C methyl transfer leading to ring methylated products. It is significant to point out that when anisole and methyl alcohol were passed over Nafion-H, only 5% of the methyl alcohol methylated any aromatic compound. With phenol 79% of the methyl alcohol was consumed in methylation and with cresols 40–55%. Thus, competition from the transmethylation by anisole minimized alkylation by methyl alcohol. The small amount of methyl alcohol used can be due to secondary O-methylation of the phenols formed and maybe to some direct C-methylation.

Scheme I



If O-methylation occurs first, the reaction of phenols (such as *m*-cresol) and methyl alcohol should give similar product composition (excluding unreacted starting material) as would be obtained from the intermolecular rearrangement of the appropriate anisole (i.e., *m*-methylanisole). In order to test this assumption we should consider, first, the suggested reaction paths. Transmethylation from anisoles is depicted in Scheme I. In the first step one molecule of methylanisole transmethylates another molecule of methylanisole giving cresol and dimethylanisole. The formed cresol can be further methylated by a second molecule of the starting anisole (present in large excess) to give the related xylenol and cresol. The dimethylanisole obtained in the first step can also methylate another molecule of the starting material to give xylenol and dimethylanisole. The other possibility, i.e., methylation of the dimethylanisole by methylanisole, is less likely as the former has better methylating ability. We assume only intermolecular transfer of O-methyl groups, as cresols were found hardly to isomerize or transfer ring methyl groups (vide infra) and the amount of ring isomerization of methylanisoles is also negligible (Table I). Further, in preceding studies it was shown that methyl migration in phenyl alkyl oxonium ions is an exclusively intermolecular process.[19]

The reaction of cresol and methyl alcohol is schematically depicted in Scheme II. The first step is the fast formation of methylanisole, which then methyl transfers. The relative high amount of the appropriate methylanisole (no isomerization has appeared under the experimental conditions) present shows that methyl transfer is slower than its formation in the O-methylation by methyl alcohol. Phenols formed by the transmethylation can be further O-methylated by methyl alcohol to give anisoles, which subsequently can continue the transmethylation process. The extent of the second transmethylation is limited due to the short contact time of the feed over the catalyst. In fact, the observed conversions of methyl alcohol were always higher than the conversion of the starting phenol, in accord with the suggested reaction path.

If the reaction mechanisms are those outlined in Schemes I and II, and the assumption is correct that O-methylation by methyl alcohol is faster than the subsequent O → C transmethylation, then the combined fraction of xylenols and dimethylanisoles should be obtained in comparable yield and should have similar composition whether we start with a methylanisole (e.g., *o*-methylanisole) or a mixture of methyl alcohol and the appropriate cresol (*o*-cresol). One cannot, however, compare the composition of the dimethylanisoles or xylenols, as secondary O-methylation is possible only in the presence of methyl alcohol (the lack of C → O transmethylation is shown by the absence of any detectable anisoles when a neat cresol was passed over Nafion-H catalyst). We consequently calculated the combined isomeric compositions of xylenols and dimethylanisoles. The results obtained, shown in Table V, support our assumption. *o*-Methylanisole gave 26% of dimethylated ring products, while *o*-cresol and methyl alcohol gave these products in 24% yield. The isomeric compositions are also very similar. Similar results were obtained for the meta and para methyl compounds too (Table V).

Dimethyl ether, which was formed in the dehydration of methyl alcohol over Nafion-H, is also a possible methylating agent. It was observed that dimethyl ether methylates benzene over Nafion-H[20] and methylates phenol over alumina.[21] We, however, did not establish whether dimethyl ether is involved in the present reaction as a reactant.

Isomerization and Transmethylation. Alkylbenzenes are known to isomerize and disproportionate (transalkylate) by acid catalysis.[22] We have shown that Nafion-H catalyzes the isomerization and transalkylation of methyl,[1] ethyl, propyl, and isopropylbenzenes.[8] We expected a higher degree of isomerization and transmethylation from methylanisoles and methylphenols due to their high reactivity in electrophilic aromatic substitution. Methylbenzenes show higher reactivity both for electrophilic substitution and methyl transformations when the number of the methyl groups increases. However, this is not the case with the studied methylanisoles and phenols. Under the present experimental conditions ring methyl groups remain inert. Neither methyl transfer nor isomerization occurs to any significant extent. When *o*- and *m*-methylanisoles were reacted over Nafion-H, or when *o*- or *m*-cresol were methylated with methyl alcohol over the same catalyst, ring methyl isomerization was limited to the extent of 0.5% or less. Disproportionation was also minimal, as seen from the minute amounts of anisole and phenol formed. *p*-Cresol and *p*-methylanisole were an exception. They showed 3–4% isomerization and 8–10% disproportionation (combined yield of phenol and anisole). Ethylphenols showed similar behavior. *p*-Ethylphenol disproportionated in the gas phase over an aluminum fluoride–alumina catalyst twice as much as the other isomers.[23] Under reducing conditions (Ni on alumina catalyst, H_2 atmosphere) para-alkylphenols disproportionated almost exclusively rather than hydrodealkylated, in contrast with other isomers.[24] Enhancement of disproportionation of the para isomer was also reported for xylenes.[1,25]

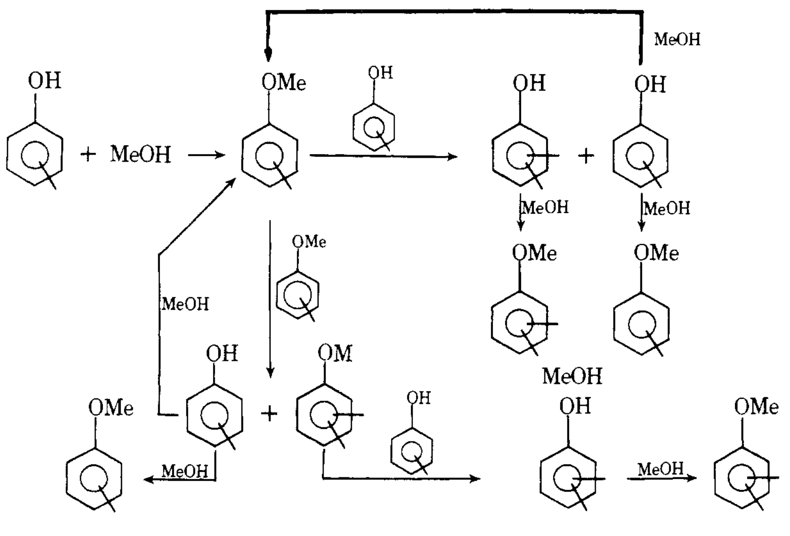
Table V. Isomer Composition of Ring Dimethylated Products Obtained in Methylation Reactions

reactants	% ring dimethylated products composition 2,3	2,4	2,5	2,6	3,4
o-methylanisole	8	53	5	34	
o-cresol + methanol	12	50	2	36	
m-methylanisole	26		40		34
m-cresol + methanol	32		38		30
p-methylanisole		91			9
p-cresol + methanol		94			6

We did not check the possibility of methyl transfer from dimethylanisoles and xylenols. It was shown[26] in gas-phase reactions that the migratory ability of the ethyl group in ethylphenols decreased by the introduction of a methyl group into the ring. Thus, we do not anticipate dimethylanisoles and xylenols to show a higher tendency toward methyl transfer than is the case with cresols and methylanisoles. In addition, the dimethylated species obtained were always structurally related to the monomethyl precursors, indicating that methylation is the sole process to take place. When dimethylanisoles were isomerized over silica–alumina,[27] 3,5-xylenol was always formed in sizable amounts. With excess of the stronger $AlCl_3$–HCl catalyst 3,5-xylenol was the major product (>90%) and probably the only isomer formed (if reaction was carried out to completion).[28] Both 3,5-xylenol and 3,5-dimethylanisole were totally absent in the products of our experiments, showing that isomerization does not take place.

Isomeric Dimethylanisoles and Xylenols. Cresols or methylanisoles have two different functional groups, i.e., methyl and hydroxyl (methoxyl), which exert activating and directing effects on the aromatic ring. As already mentioned[10–15] many solid acid catalysts direct the alkylation selectively ortho to the hydroxyl group, regardless of other substituents. *o*-Cresol and 2,6-xylenol were obtained from phenol and methyl alcohol. Ortho substitution was also found to predominate in the methylation of cresol. Thus, *p*-cresol and methyl alcohol gave over alumina 2,4-xylenol and 2,4,6-trimethylphenol[29] and over MgO 2,4,6-trimethylphenol.[30] *m*-Cresol and methyl alcohol gave 2,3,6-trimethylphenol over MgO[30] or PBO–MgO[15] while *o*-cresol gave 2,6-xylenol

Scheme II



over alumina,[10c] MgO,[30] or PbO–MnO_2.[15] Nafion-H, on the other hand, did not show any special tendency toward ortho methylation and the isomer distributions reflect kinetic control, i.e., the activation of ring positions for methylation.

Rearrangement of anisole or methylation of phenol by methyl alcohol showed (Table III) that methylation occurred at the ortho and para positions to the same extent (calculated for the sum of cresols and methylanisoles). The para position is thus preferred by a factor of 2. Meta methylated products comprised only 1% of this fraction. The observed regioselectivity thus is para > ortho ≫ meta.

A different reactivity pattern is observed when the starting material is a cresol or a methylanisole. The methyl and the hydroxyl (or methoxyl) group can either augment each others directing effect (for the *m*-methyl compounds) or oppose it (for the ortho and para isomers).

Starting with a *m*-methyl compound three out of the four available positions are activated toward methylation. The 5 position being meta to both hydroxyl and methyl groups is not activated, and, indeed, 3,5-xylenol (or dimethylanisole) was not observed as product. Methylation of the 2, 4, or 6 position leading to the 2,3-, 3,4-, or 2,5-dimethyl products occurs almost to the same extent (Tables IV and V).

When the directing effects oppose each other, the effect of the methyl group is expected to be minor in comparison with that of a hydroxyl or methoxyl group, in view of the large difference of the σ^+ values of these substituents and the high ρ values characteristic of electrophilic aromatic substitution.[31] However, we found that with Nafion-H catalysis in the gas phase, the directing effects of the methyl groups are small, but not negligible. Starting with *p*-cresol or *p*-methylanisole we obtained 6–9% of the "abnormal" 3,4-dimethyl product. Four xylenols and four dimethylanisoles were obtained from *o*-methylanisole or *o*-cresol, respectively (Table IV). The composition of the isomeric dimethylanisoles is different from that of the isomeric xylenols. The reason may be the sluggishness of the ortho methylation of 2,6-xylenol by methyl alcohol due to the obvious steric hinderance by the two methyl groups in the 2 and 6 positions. When the xylenol and dimethylanisole fractions are combined (Table V) one can see that methylation directed by hydroxyl and methoxyl groups (2,4 and 2,6 isomers) comprises 86% of the dimethylated products, while the directing effect of the methyl group (2,3 and 2,5 isomers) accounts for 14% of the products. From these results it seems that hydroxyl (or methoxyl) groups are 10–15 times more effective in directing the intermolecular O → C methyl transfer than a *p*-ethyl group and only 6 times more so than an *o*-methyl group. These ratios of the competing directing effects are surprisingly low, as usually no substitution directed by methyl group while being opposed by that of a hydroxyl group was found. An exception is the reported acetylation of 2,4-xylenol which gave 9% of the "abnormal" 5-acetyl-2,4-dimethylphenol, but it probably involved 2,4-dimethylphenyl acetate as an intermediate which can account for this result.[32] But, in this case two methyl groups give a combined directing effect against the hydroxyl.

A possible reason for the diminished directing effect of the hydroxyl and methoxyl groups is the partial protonation (or strong protosolvation) of the oxygen atoms by the acidic sites of Nafion-H. This will weaken the ortho–para directing effect and will permit methylation at positions meta to the hydroxyl or methoxyl groups when these positions are activated by methyl groups. Phenols and anisoles were found to be ring protonated by superacids in the liquid phase,[33] rather than O-protonated. With somewhat weaker acids and at low temperatures, however, oxygen protonation also takes place, with both C- and O-protonated species being observed simultaneously.

Conclusions

Products obtained in the Nafion-H catalyzed methylation of phenols with methyl alcohol or from the intermolecular rearrangement of anisoles are derived from substitution of all the activated positions. These results are quite different from those obtained with a wide range of solid catalysts which show high selectivity for ortho methylation. Kotanigawa studied the mechanism of phenol methylation over ZnO–Fe_2O_3.[12a] He found that phenol is dissociated upon adsorbtion on the catalyst to give the phenoxide anion. Methyl alcohol is then adsorbed onto the proton to form an adsorbed methyl cation. This intermediate dictates the location of the methylating agent close to the ortho position explaining the selectivity in the reaction. Similar intermediates were suggested for the specific ortho alkylation in homogeneous solution catalyzed by aluminum phenoxide.[34] Such a mechanism raises the question whether this reaction is catalyzed by basic sites[12a] or some sort of dual acid–base catalysis. Kotanigawa found[12b] that methylation of phenol by methyl alcohol over ZnO–Fe_2O_3 is not the major reaction path. About 80% of the methyl alcohol decomposed, giving H_2, CH_4, CO, and CO_2 as products. Similar reactions were obtained by substituting ZnO with other metal oxides.[13] The primary reaction is the dehydrogenation of methyl alcohol to give hydrogen and CO. Alkylation with higher alcohols over ZnO–Fe_2O_3 was also accompanied by dehydrogenation to give aldehydes or ketones.[35] The reaction of 2-propanol was studied over a zeolite catalyst.[36] By selective poisoning, dehydration was found to be acid catalyzed, while dehydrogenation was base catalyzed. Thus, it seems that selective ortho alkylation is connected with the basicity of the catalyst, which is absent in the case of Nafion-H. We checked the reaction of methyl alcohol over Nafion-H for possible dehydrogenation. Only water and dimethyl ether were formed. We were unable to detect any CO in the gaseous affluent. Higher alcohols were also found to only dehydrate, when passed over Nafion-H.[7]

Acknowledgment. Support of our work by the National Science Foundation and the University of Southern California is gratefully acknowledged.

Registry No.—Nafion-H, 63937-00-8; phenol, 108-95-2; *o*-cresol, 95-48-7; *m*-cresol, 108-39-4; *p*-cresol, 106-44-5; methyl alcohol, 67-56-1.

References and Notes

(1) Part 3: G. A. Olah, J. Kaspi and J. Bukala, *J. Org. Chem.*, **42,** 4187 (1977).

(2) Postdoctoral Research Associate 1975–1977. Research was carried out in part at the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio.

(3) A. Schriesheim in "Friedel Crafts and Related Reactions", Vol. II, Part 1, G. A. Olah, Ed., Interscience, New York, N.Y., 1964, Chapter 18.

(4) (a) V. N. Ipatieff, N. Orloff, and G. Razuvaeff, *Bull. Soc. Chim. Fr.*, **37,** 1576 (1925); (b) V. N. Ipatieff, N. Orloff, and A. Petrov, *Ber.*, **60,** 1006 (1927).

(5) (a) M. Inoue and S. Enomoto, *Chem. Pharm. Bull.*, **19,** 2518 (1971); **20,** 232 (1972); (b) J. F. Olim, U. S. Patent 3 014 079 (1961); *Chem. Abstr.*, **57,** 12385 (1962).

(6) Nafion is a registered trademark of the DuPont Co. whom we thank for samples of the potassium salt of Nafion 501.

(7) The active H form was generated from the commercial potassium salt by treatment with nitric acid, washing with water, and drying at 105 °C.

(8) G. A. Olah, J. Kaspi and J. Bukala, *J. Org. Chem.*, **42,** 4191 (1977).

(9) M. J. S. Dewar and J. P. Schroeder, *J. Am. Chem. Soc.*, **86**, 5235 (1964); *J. Org. Chem.*, **30,** 3485 (1965).

(10) (a) S. V. Kannan and C. N. Pillai, *Indian J. Chem.*, **8,** 1144 (1970); (b) Y. Ogata, K. Sakanishi, and H. Hosoi, *Kogyo Kagaku Zasshi*, **72,** 1102 (1969); *Chem. Abstr.*, **71,** 80842 (1969); (c) H. L. Schlichting, A. D. Barbopoulos, and W. H. Prahl, U.S. Patent 3 426 358 (1969); (d) J. Jonas, Czech. Patent 132 353 (1967); *Chem. Abstr.* **73,** 35039 (1970); *Chem. Abstr.*, **71,** 12809 (1969); (e) Y. V. Churkin, L. A. Rusanova, and R. M. Masagutov, Tr., Nauchno-Issled. *Inst. Neftekhim. Proizvod.*, 13 (2) (1970); *Chem. Abstr.* **74,** 76120 (1971).

(11) J. A. Sharp and R. E. Dean, British Patent 1 125 087 (1968) *Chem. Abstr.*, **70,** 37452 (1969).

(12) (a) T. Kotanigawa, *Bull. Chem. Soc. Jpn.* **47,** 950 (1974); (b) *ibid.*, **47,** 2466 (1974); (c) T. Wada, Japan Kokai 75 76 033 (1975); *Chem. Abstr.*, **83,** 178557 (1975).

(13) T. Kotanigawa, M. Yamamoto, K. Shimokawa, and Y. Yoshida, *Bull. Chem.*

Soc. Jpn. **44,** 1961 (1971).

(14) Y. Ichikawa, Y. Yamanaka, and O. Kobayashi, Japan Kokai 73 99129 (1973); *Chem. Abstr.*, **80,** 95477 (1974); Japan Kokai 73 96529 (1973); *Chem. Abstr.*, **80,** 95481 (1974); Japan Kokai 73 99128 (1973); *Chem. Abstr.*, **80,** 95486 (1974).

(15) W. Funakoshi, T. Urasaki, I. Oka, and T. Shima, Japan Kokai 73 97825 (1973); *Chem. Abstr.*, 80, 59675 (1974); Japan Kokai 74 07235 (1974); *Chem. Abstr.*, **80,** 120534 (1974); Japan Kokai 74 13128 (1974); *Chem. Abstr.*, **80,** 120532 (1974); Japan Kokai 74 14432 (1974); *Chem. Abstr.*, **80,** 120527 (1974); Japan Kokai 74 18834 (1974); *Chem. Abstr.*, **81,** 3586 (1974).

(16) V. N. Vinogradova and G. D. Kharlampovich, *Izv. Vyssh, Uchebn. Zaved., Khim. Khim. Tekhnol.*, **18,** 71 (1975); *Chem. Abstr.*, **82,** 124966 (1975).

(17) (a) S. Kawakami and S. Fujii, *Kogyo Kagaku Zasshi,* **73,** 2180 (1970); *Chem. Abstr.,* **74,** 80220 (1971); (b) S. Kawakami, S. Takanashi, and S. Fujii, *Kogyo Kagaku Zasshi,* **74,** 899 (1971); *Chem. Abstr.*, **75,** 48168 (1971).

(18) Reference 6 in ref 12a.

(19) G. A. Olah and E. G. Melby, *J. Am. Chem. Soc.*, **95,** 4971 (1973).

(20) J. Kaspi and G. A. Olah, unpublished results.

(21) P. Mueting and J. Zimmerman, German Offen. 2 237 591 (1974); *Chem. Abstr.*, **80,** 133026 (1974).

(22) D. A. McCaulay in "Friedel Crafts and Related Reactions", Vol. II, Part 1, G. A. Olah, Ed., Interscience, New York, N.Y. 1964, Chapter 24.

(23) P. Schneider, M. Kraus, and V. Bazant, *Collect. Czech. Chem. Commun.*, **26,** 1636 (1961).

(24) L. Beranek, M. Kraus, and V. Bazant, *Collect. Czech. Chem. Commun.*, **29,** 239 (1964).

(25) (a) M. A. Lanewala and A. P. Bolton, *J. Org. Chem.*, **34,** 3107 (1969); (b) R. H. Allen and L. D. Yats, *J. Am. Chem. Soc.*, **81,** 5289 (1959).

(26) M. Kraus and V. Bazant, *Collect. Czech. Chem. Commun.*, **28,** 1,877 (1963).

(27) M. B. Nevworth, British Patent 748 269 (1956); *Chem. Abstr.*, **51,** 471 (1957).

(28) L. A. Fury, Jr., and D. E. Pearson, *J. Org. Chem.*, **30,** 2301 (1965).

(29) Y. V. Churkin, A. G. Lebekhov, and R. M. Masagutov, *Neftekhimiya,* **12,** 87 (1972); *Chem. Abstr.*, **77,** 61432 (1972).

(30) General Electric, Netherlands Appl. 6 506 830 (1965); *Chem. Abstr.*, **65,** 2173 (1966).

(31) D. A. R. Happer and J. Vaughan in "The Chemistry of the OH Group", Part 1, S. Patai, Ed., Interscience, London, 1971, Chapter 8.

(32) N. M. Cullinane and B. F. R. Edwards, *J. Appl. Chem.*, **9,** 133 (1959).

(33) G. A. Olah and Y. K. Mo, *J. Org. Chem.*, **38,** 353 (1973), and references given therein.

(34) A. J. Kolka, J. P. Napolitano, A. H. Filbey, and G. G. Ecke, *J. Org. Chem.*, **22,** 642 (1957).

(35) T. Kotanigawa and K. Shimokawa, *Bull. Chem. Soc. Jpn.*, **47,** 1535 (1974).

(36) T. Yashima, H. Suzuki, and N. Hara, *J. Catal.*, **33,** 486 (1974).

Heterogeneous Catalysis by Solid Superacids. 5.[1] Methylation of Benzene and Methylbenzenes with Methyl Alcohol over a Perfluorinated Resinsulfonic Acid (Nafion-H) Catalyst

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Nafion-H,[4] a perfluorinated resinsulfonic acid, catalyzes the gas-phase methylation of benzene and methylbenzenes with methyl alcohol under relatively mild experimental conditions (185 °C and atmospheric pressure). Reactions are clean, and water formed as byproduct does not deactivate the catalyst. Dimethyl ether is also formed in the competitive dehydration of methyl alcohol when the extent of methylation is low. Generally, low substrate selectivity is observed, indicating that a highly energetic methylating species is participating in the reaction. Dimethyl ether was also found to be an effective methylating agent, but weaker than methyl alcohol. The catalytic activity was found to drop quickly with onstream time when using dimethyl ether, probably due to esterification of the acidic sites. The catalytic activity can be, however, regenerated by steam treatment of the catalyst. Mechanistic aspects of the reactions are also discussed.

Nafion-H,[4] a perfluorinated resinsulfonic acid, activated in its H form, was found to be an efficient alkylating catalyst for heterogeneous gas-phase reactions.[5] Ethene and propene alkylate benzene to give ethylbenzene and cumene, respectively. Alkylations with ethyl and isopropyl alcohol are also catalyzed by Nafion-H. The observations that propylation of benzene with *n*-propyl alcohol gave only cumene as the alkylation product and that the alcohols dehydrate to the corresponding alkenes almost quantitatively when passed over Nafion-H raise the question whether the alcohols are merely precursors to the corresponding alkenes (or their protonated form, i.e., the corresponding carbenium ions). In the case of methylations with methyl alcohol no alkene formation is possible, and under the experimental conditions carbene formation is improbable. The high energy of the methyl cation makes its formation in the reactions also questionable.

In recent work[1] we found that gas-phase methylation of phenol and cresols with methyl alcohol over Nafion-H catalyst proceeds readily. The reaction involves fast initial O-methylation of the phenol followed by intermolecular rearrangement to ring-methylated phenols. In continuation of our work, we would like to report that the methylation of less activated aromatic hydrocarbons, such as benzene and methylbenzenes, also takes place with methyl alcohol in the gas phase over Nafion-H as catalyst.

Experimental Section

The catalytic reactor and the experimental procedures were previously described.[5c] Dry nitrogen was passed at the rate of 5 mL/min. The liquid feed rate was 0.02 mL/min. Contact time of the catalyst with the gaseous feed was 5–7 s. The temperature was kept at 185 ± 2 °C, except when temperature effects were studied. All compounds used were of commercially available high purity, generally higher than 99.5%. Products were analyzed by gas liquid chromatography using a Perkin-Elmer Model 226 gas chromatograph, equipped with a flame ionization detector. Separation was obtained with a 150 ft × 0.01 in. capillary column coated with *m*-bis(*m*-phenoxyphenoxy)benzene + Apiezon L. Peak areas were measured with an electronic integrator and were corrected for differences in detector sensitivity. The accuracy of the determination of the product compositions is considered, based on comparison with mixtures of known composition, as ±0.5%.

Results

Benzene, toluene, and the three isomeric xylenes were methylated with methyl alcohol over Nafion-H catalyst. Polymethylation hardly occurred in the case of reaction of benzene and toluene. The increased reactivity of xylenes and trimethylbenzenes toward methylation is reflected in the

$$\mathrm{ArH} + \mathrm{CH_3OH} \xrightarrow[185\ ^\circ\mathrm{C}]{\text{Nafion-H}} \mathrm{ArCH_3} + \mathrm{H_2O}$$