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Alkylation of Phenol by 1-Dodecene and 1-Decanol. A Literature Correction

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A recent literature report that 1-dodecene reacts with phenol in the presence of sulfated zirconium oxide (superacid), or 1-dodecanol with phenol in the precsence of H-Mordenite (zeolite), to afford mostly para-substituted alkylphenols has been shown to be incorrect. The product with zirconium is a mixture of ortho/para isomers (≈50—65/50—35), and not the exclusive para isomer as reported. The major product in the case of zeolite catalysis is the *o*-alkylphenol, with a high degree of end attachment, and not the predominantly claimed para isomers. The selectivity obtained with H-Mordenite during alkylation of phenol differs from the alkylation of alkylbenzenes and anisole, and is best explained on the basis of a surface catalysis phenomenon.

The literature reports numerous alkylations of phenol under a variety of catalysts and conditions.[1–4] Because alkylphenols are important in a wide range of commercial products, most data are taken from patents which often do not provide experimental details and usually lack detailed structural information. Even in the recent literature, the main concern is on catalyst development with emphasis on catalyst activity and stability for fixed-bed operations rather than selectivity.[5,6] Thus, there is limited information on the isomer distribution and the position of attachment of the alkyl side chain to the phenolic moiety in alkylphenols. Structural information on alkylphenols was sought by us to establish some of their structure-property-performance relationships as lubricating oil additives. In the area of anionic detergents, for example, both the *o*- and *p*-alkylphenols are acceptable products as long as the position of phenol attachment is near the end of the alkyl chain to provide biodegradability.[7] In the area of antioxidants, however, alkylphenols substituted in the ortho position are superior to those of para-substitution because of the greater influence of the free para position.[8,9] Alkylphenols based on propylene or isobutylene oligomers give a high proportion of the preferred para isomers for the manufacture of metallic detergents, but in all cases using linear olefins a mixture of isomers is obtained.[10] The boiling points of the isomers are generally too close to permit their separation by distillation.

We were delighted to find two recent reports in which 1-dodecene[5] and 1-dodecanol[11] were used to alkylate phenol selectively at the para position, employing sulfated zirconium oxide[5] and H-Mordenite[11] catalysts, respectively. Unfortunately, the products in both cases were completely misidentified. Our data show that a mixture of the ortho and para isomers was formed with zirconium.[5] With zeolite catalyst, the major product was shown to be the ortho isomer (>90%), with a high degree of end attachment, and not the para isomer as reported.[11]

Results and Discussion

When phenol and 1-dodecene were stirred at 135 °C in the presence of sulfated zirconium oxide (ZrO_2:H_2SO_4, 4%),[5] a 98% olefin conversion was obtained in 1 h. A large excess of phenol relative to olefin (9.6/1 mol ratio) was used to prevent formation of dialkylated products and serve as the solvent. Zirconium catalyst was chosen because it is a superacid having a high Hammett acidity value ($-H_0=16$)[12] compared to commonly used Amberlyst-15 ($-H_0=2.2$)[13] or Nafion-H ($-H_0=11$ to 13).[13] It seemed reasonable that para alkylation could be obtained from 1-dodecene in this case due to the likelihood of extensive isomerization.

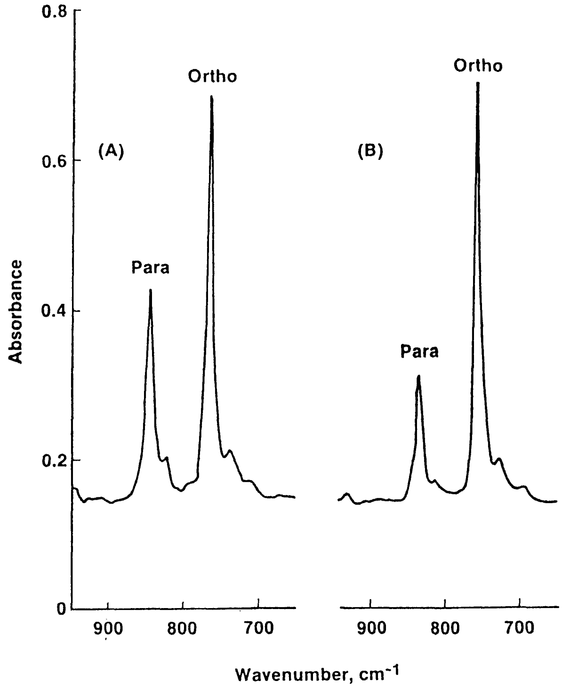
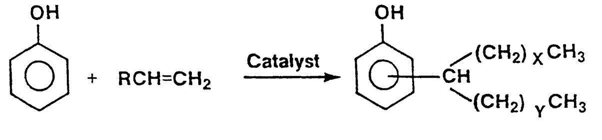


Fig. 1. IR spectra of products from alkylation of phenol with 1-dodecene: (A) 135 °C, ZrO_2:H_2SO_4; (B) 180 °C, H-Mordenite.



Ortho , Para I -V

Analysis of the product by infrared (Fig. 1) showed ortho and para substitution at 750 and 825 cm^{-1}, respectively. This result was confirmed by a combination of glc (Fig. 2) and mass spectral (Table 1) and ^{1}H NMR (Fig. 3) analyses. Clearly, the product was not the exclusive *p*-dodecylphenol reported.[5] Repeating the alkylation with zirconium catalyst at reflux (180 °C) gave the same isomers as above, but the catalyst started to lose activity. Analysis of the 180 °C product by infrared gave an ortho/para ratio of ca. 50/50 compared to ca. 65/35 ratio at 135 °C. For practical purposes, the isomer distribution obtained with zirconium oxide at 135 °C was no different than that observed using conventional catalyst such as Amberlyst-15.

The large pore zeolites (REX and HY) have been used for alkylation of phenol with 1-decanol, 1-decene, and 1-hexadecene by stirring at 180—210 °C, but with little selectivity (ortho/para, 50—68/50—32).[14] A reference was found in which zeolites having pore dimensions between 6—7 Å, including H-Mordenite, dealuminated H-Mordenite, and ZSM-12, were used for alkylation of phenol with reasonable selectivity for the para isomer.[11] This report was not unexpected since alkylation of toluene or ethylbenzene by C_{10} to C_{14} olefins over H-Mordenite gave over 80% of the corresponding *p*-dialkylbenzenes.[15] A similar result was obtained for ethylbenzene alkylation with ethanol using ZSM-5 zeolite.[16]

When 1-dodecene and phenol were stirred at reflux (180 °C) in the presence of ZSM-12 or H-Mordenite, the catalysts varied in activity and selectivity. When the activity was low, only low conversions were obtained and the product often contained alkyl phenyl ether by-products (to ca. 40%). In some runs, ether formation was supressed by increasing catalyst concentration. In all cases, however, ortho isomers predominated. In the present study H-Mordenite (Si/Al, 50/1 mol ratio) was used as representative of the above group of zeolites. Thus, on a screening scale (10 g), 1-dodecene reacted with phenol at 180 °C to give a 96% olefin conversion in 3.5 h. The product was mostly

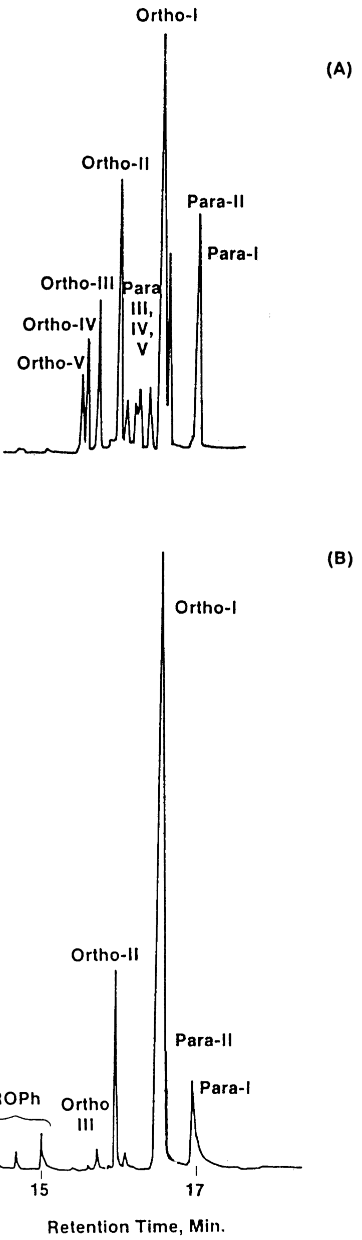


Fig. 2. GLC chromatograms of products from alkylation of phenol with 1-dodecene: (A) 135 °C, $ZrO_2:H_2SO_4$; (B) 180 °C, H-Mordenite.

Table 1. Product Composition from Alkylation of Phenol by 1-Dodecene/%

Isomer[a]	x=	y=	GC/MS	m/z	(rel intensity)	$ZrO_2:H_2SO_4$ GLC	$ZrO_2:H_2SO_4$ NMR[b]	H-Mordenite GLC	H-Mordenite NMR[b]
Ortho-V	4	5	262	(1)	M^+, 191 (6) $(M-C_5)^+$, 177 (6) $(M-C_6)^+$, 107 (100)	4	14	tr	3
Ortho-IV	3	6	262	(2)	M^+, 205 (6) $(M-C_4)^+$, 163 (8) $(M-C_7)^+$, 107 (100)	5		tr	
Ortho-III	2	7	262	(2)	M^+, 219 (5) $(M-C_3)^+$, 149 (7) $(M-C_8)^+$, 107 (100)	7		tr	
Ortho-II	1	8	262	(4)	M^+, 233 (7) $(M-C_2)^+$, 135 (33) $(M-C_9)^+$, 107 (100)	16	15	8	7
Para-V	4	5	262	(1)	M^+, 191 (7) $(M-C_5)^+$, 177 (7) $(M-C_6)^+$, 107 (100)	2	10	0	0
Para-IV	3	6	262	(1)	M^+, 205 (5) $(M-C_4)^+$, 163 (12) $(M-C_7)^+$, 107 (100)	3		0	
Para-III	2	7	262	(1)	M^+, 219 (5) $(M-C_3)^+$, 149 (16) $(M-C_8)^+$, 107 (100)	4		0	
Ortho-I	0	9	262	(5)	M^+, 247 (1) $(M-C_1)^+$, 121 (100) $(M-C_{10})^+$	35	32	89	88
Para-II	1	8	262	(3)	M^+, 233 (10) $(M-C_2)^+$, 135 (60) $(M-C_9)^+$, 107 (100)	10	11	tr	0
Para-I	0	9	262	(2)	M^+, 247 (1) $(M-C_1)^+$, 121 (100) $(M-C_{10})^+$	14	18	3	2

a) In order of emergence off the capillary column. b) Integration of ArCH region.

dodecylphenol (98%), ortho/para ratio ca. 95/5, along with dodecyl phenyl ethers (2%) (Table 1). Analysis of this product by infrared supported the ortho structure (Fig. 1B), although IR cannot be used for quantification purposes without standards for samples containing a high ortho content.[14)] The most diagnostic feature in the NMR spectrum of *s*-alkylphenols is the methine proton at δ=3.0 (ortho) and δ=2.5 (para), respectively.[17,18)] By use of high field NMR (300 MHz), the methine region was expanded to give a more detailed composition of isomers (Fig. 3). The methine proton in ortho and para-I, for example, appears as a well resolved sextet at δ=3.04 and 2.58, respectively. The same proton in ortho and para-II appeared at δ=2.83 and 2.33, respectively. The methine proton in structures III, IV, and V overlapped and appeared in the spectrum centered at δ=2.93 (ortho) and 2.42 (para), respectively.

The *s*-dodecylphenols were also identified by mass spectrometry (GC/MS). All isomers showed weak parent ions at *m*/*z* 262, and peak ions for the loss of alkyl groups at the point of branching. Except for the methyl-branched isomer I, which showed a base ion peak at *m*/*z* 121, all of the remaining *s*-dodecylphenols gave base ion peaks at *m*/*z* 107.

Alkylation on a preparative scale (500 g) at 175—185 °C, required isolation, reactivation, and recycling of the catalyst to achieve 86% olefin conversion and 90% ortho isomer selectivity in 12 h.

Continuous flow experiments were carried out in a micro reactor under conditions indicated in Table 2, using either 1-decene or 1-decanol as the alkylating reagent. Although optimum reaction conditions were not determined, from the data obtained it is very clear that the dominant alkylation product is the *o*-alkylphenol, and not the reported para isomer.[11)] Alkylations with olefin in a batch procedure gave a higher ortho/para ratio than in a continuous mode (95/5 vs. 82/18), a reflection of using different temperatures.[14)] Comparison of 225 and 260 °C products using 1-decanol as the alkylating agent (Table 2) showed that higher temperature was more efficient in alkylating phenol with dialkyl ethers. Higher temperature, however, had little effect on alcohol dehydration and alkyl phenyl ether formation. The use of alcohols in a continuous mode differed from the use of olefins in that a small amount of normal substitution product was formed, and the alkylation was accompanied by severe alcohol

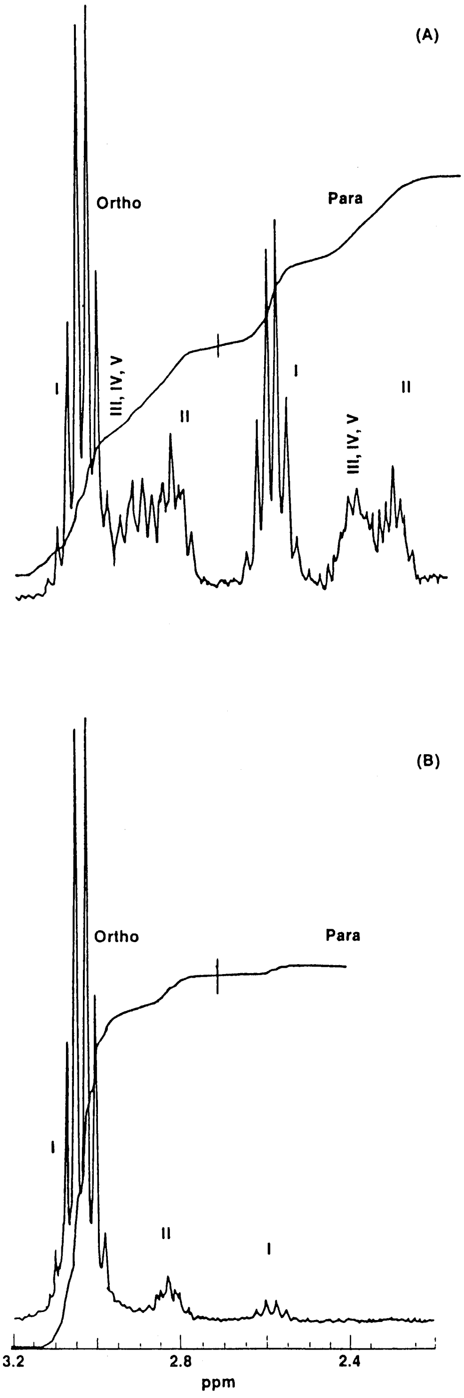


Fig. 3. ^{1}H NMR spectra (300 MHz, ArCH region) of products from alkylation of phenol with 1-dodecene: (A) 135 °C, ZrO_2: H_2SO_4; (B) 180 °C, H-Mordenite.

Table 2. Alkylation of Phenol in a Micro Flow Reactor at 20 atm[a)], LHSV≈5, H-Mordenite, Si/Al≈50/1 mol ratio, Phenol/Alkylating Reagent: 2/1 mol ratio

Alkylating reagent	Temp	Conversion	Product distribution/mol%			
	°C	% (per pass)	Alkylphenols	Olefins	Alkylphenyl ethers	Dialkyl ethers
1-Decanol	225	15	21	39	8	32
1-Decanol	260	77	41	41	5	13
1-Decene	225	18	84	—	16	0

a) 1 atm=1.01325×10^5 Pa.

Table 3. Alkylation of Phenol in a Micro Flow Reactor at 20 atm[a], LHSV≈5, H-Mordenite, Si/Al≈50/1 mol ratio, Phenol/Alkylating Reagent: 2/1 mol ratio

Alkylating agent	Temp/°C	Decylphenol isomers/%								Ortho/Para ratio
		Ortho				Para				
		1-Decyl	1-Methylnonyl	1-Ethyloctyl	1-Propylheptyl	1-Decyl	1-Methylnonyl	1-Ethyloctyl	1-Propylheptyl	
1-Decanol	225	13.6	42.9	6.6	—	3.1	26.3	7.5	—	63/37
1-Decanol	260	6.5	48.7	6.9	—	0.6	28.5	8.8	—	62/38
1-Decene	225	—	73.1	7.0	1.6	—	14.0	3.4	0.9	82/18

a) 1 atm=1.01325×10^5 Pa.

dehydration and condensation to give olefins and dialkyl ether by-products. The use of decanol gave twice as much para isomers than obtained with decene, but the dominant isomers were still ortho (Table 3). From a limited study it is further apparent that olefins give much cleaner products than the alcohols and are generally preferred since they are less expensive than the alcohols.

The reaction of anisole with 1-dodecene at reflux (155 °C) over H-Mordenite for 6 h gave ca. 10% olefin conversion to a product which was largely *p*-(2-methylundecyl)anisole (80%).

Conclusion

In conclusion, we confirm the results of a recent patent that the phenol alkylation product consists of end-attached isomers, but the major product is not the reported para-I structure. Our data are overwhelmingly in support of the ortho-I structure. More recent literature, unfortunately, continues to propagate this erroneous assignment.[19,23] It is further apparent that the alkylation of phenol does not follow the course well-established for the corresponding alkylation of toluene, ethylbenzene, or even anisole which give mostly the para isomers. These results suggest that H-Mordenite perhaps does not belong to the class of shape selective zeolites, and that alkylation of phenol in this case may involve complex formation between reacting components on the surface.[20,21]

Sulfated zirconium oxide catalyst, in spite of its high acidity, offered no advantage in isomer composition of product over conventional acid catalysts.

Experimental

Catalysts. The synthesis of sulfated zirconium oxide has been previously described.[5,12] The distribution of acid sites by IR, after treatment with pyridine, gave values of 0.04 mequiv g^{-1} (Brønsted) and 0.06 mequiv g^{-1} (Lewis), respectively. All zeolites were calcined in air prior to use at 550 °C for 1—2 h. The dealuminated H-Mordenite (Si/Al, 50/1 mol ratio) was prepared from commercial H-Mordenite (Si/Al, 15/1 mol ratio) by steaming at 550 °C for 6 h, followed by leaching with 0.6 M HCl at reflux ($M=mol\ dm^{-3}$), and calcination.[22] This catalyst had a pour volume of 0.106 compared to initial volume 0.074 ml g^{-1} (C_6H_{12} absorption), a sodium content of 3.6 ppm, and 94% crystallinity by X-ray. Acidity by IR gave values of 0.05 mequiv g^{-1} (Brønsted) and 0.07 mequiv g^{-1} (Lewis), respectively.

Analyses. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer in CS_2 solvent. Nuclear magnetic resonance (NMR) spectra were recorded as solution in $CDCl_3$ on a Nicolet (300 MHz) spectrometer. The chemical shifts are in δ units (ppm) relative to Me_4Si. GC/MS data were obtained on a Finnigan 4510 system with an electron impact source at 70 eV. Chromatographic analyses were performed on a Hewlett-Packard 5880A (FID) chromatograph, using a 25-m methylsilicone column (SPB-1, fused silica capillary) programmed from 50 to 300 °C at 8 deg min^{-1}.

General Alkylation Procedure. A 100-ml, three-necked, round-bottomed flask, fitted with a Dean-Stark trap, a stirrer, a condenser connected to a dry nitrogen source, and a thermometer, was charged with phenol (10.6 g, 11.3 mmol), 1-dodecene (1.96 g, 1.17 mmol) and zirconium catalyst (0.46 g). The mixture was heated at ca. 135 °C for 2 h, following the course of reaction by GLC. The mixture was filtered, and the filtrate was stripped under reduced pressure to give 2.6 g (85%) of amber colored oil for analysis.

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