acetate–petroleum ether). The first fractions eluted gave 150 mg of white solid, which was recrystallized from ether to give 100 mg of **18b**, mp 123–124 °C: IR 1695, 1640, 1602, 1590 cm^{-1}; UV max 270 nm; ^1H NMR δ 1.71 (d, 3, J = 6.9 Hz, 7-CH_3), 1.95 (s, 6, 3- and 5-CH_3), 6.46 (q, 1, J = 6.9 Hz, 7-H), 7.44 (m, 7), 8.01 (m, 2); ^{13}C NMR 14.1 (q), 15.3 (q), 21.0 (q), 58.6 (d), 127.8–128.9 (5 lines) 133.0 (d), 135.6 (s), 135.8 (s), 136.4 (s), 143.3 (s), 144.2 (s), 160.5 (s), 196.8 (s); *m/e* calcd for $C_{21}H_{20}N_2O_2$ 332.1524, found 332.152.

Further elution of the column with 100% ethyl acetate and finally ethanol gave 125 mg of very insoluble material and 210 mg of soluble material which was recrystallized to give 45 mg of colorless crystals, mp 241–243 °C, which was not further investigated.

4-Benzamido-5-phenyl-2,4,6-trimethyl-3-aza-2,5-cyclohexadienone (25). A solution of 310 mg (0.93 mmol) of bicyclic ketone 15 (mp 126–127 °C) in 7 mL of $CHCl_3$–MeOH–Et_3N (5:10:0.4) was heated for 3.7 h at 50 °C. TLC showed nearly complete disappearance of starting material and formation of a single, less polar product. Solvent was removed in vacuo, and the residue was evaporated twice with CCl_4 and then crystallized from ether to give 245 mg of yellow solid. Recrystallization from methylene chloride–petroleum ether gave 210 mg of large greenish yellow crystals, mp 157–158 °C, and a second crop of 30 mg, mp 155–156 °C (75% yield): IR (KBr) 3320 (NH), 1675, 1655, 1640 cm^{-1}; ^1H NMR δ 1.68 (s, 6), 2.38 (s, 3), 6.80 (br, 1), 7.1–7.9 (m, 10); ^{13}C NMR 12.3 (q), 20.1 (q), 28.6 (q), 70.2 (s), 127–128 (aryl), 131.8 (d), 132.2 (s), 134.1 (s), 136.8 (s), 162.4 (s), 163.5 (s), 167.4 (s), 176.9 (s); *m/e* calcd for $C_{21}H_{20}N_2O_2$ 332.153, found 332.154.

Acknowledgment. We thank Dr. Karl Blom for the mass spectral measurements and Rebecca Durney for assistance with the crystallography.

Registry No. (*E*)-3 (R′ = $CH_2CH(CH_3)_2$), 96213-69-3; **5**, 96213-61-5; **10**, 96213-62-6; **11**, 96213-63-7; **12**, 96213-64-8; **13**, 19971-06-3; 14, 1706-26-9; **15a**, 5109-45-5; **15b**, 96213-65-9; **18a**, 96213-66-0; **18b**, 96213-67-1; **19a**, 10137-20-9; **25**, 96213-68-2.

Supplementary Material Available: Tables of mass spectral data for diazepinones **11–14** and crystallographic data and tables of atomic coordinates, bond lengths, and bond angles for compounds **15** and **25** (17 pages). Ordering information is given on any current masthead page.

Regioselective Para Chlorination of Activated Aromatic Compounds

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A series of 2-alkylphenols were chlorinated with chlorine, sulfuryl chloride, and sulfuryl chloride catalyzed with a divalent sulfur compound and a metal halide. The latter chlorinating system is the most regioselective for both para chlorination and for the degree of chlorination, i.e., monochlorination. The selectivity is also demonstrated for 2-halophenols, 3-substituted phenols, and aromatic ethers. The reactive intermediate is proposed to be $[R_2SCl^+][MCl_4^-]$ which explains the selectivity to the para isomer due to the bulkiness of the chlorinating agent. The observed differences in isomer distribution with the studied phenols are explained by the degree of hydrogen bonding of the phenol as seen in the IR and NMR as well as the differences in reactivity.

It has long been the desire of organic chemists to control isomer distributions in electrophilic aromatic substitution reactions. Techniques used in the chlorination of activated aromatic compounds such as phenols include reagents,[2] solvents,[3] catalysts,[4] concentrations,[5] and temperature.[6] Previous work in this laboratory on the chlorination of phenols has demonstrated techniques to enhance ortho chlorination.[7] For example, the chlorine chlorination of a 5% solution of phenol in refluxing carbon tetrachloride yields a maximum of 68% 2-chlorophenol. After this work our attention turned to methods to enhance para chlorination. A preliminary paper[8] has reported the regioselective para chlorination of 2-methylphenol using sulfuryl chloride catalyzed by diphenyl sulfide and aluminum chloride.

It is the purpose of this work to report the generality of the regioselective para-chlorinating system by reporting data on various substituted phenols and aromatic ethers and to compare these results with data generated when chlorine and sulfuryl chloride are used. Chlorine is a strong electrophile and reacts rapidly with neat aromatic compounds. Sulfuryl chloride[9] is a relatively weak electrophile[10] and monochlorinates activated compounds slowly at room temperature. A metal halide catalyst with sulfuryl chloride does not significantly increase the rate of reaction but does improve selectivity to the *p*-chloro isomer.[11]

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Table I. Chlorination of Phenol with Chlorine and Sulfuryl Chloride Using Various Catalysts

				weight %						
chlorinating agent	cat.	temp, °C	time, h	1	2	3	4	5	6	para/ortho
Cl_2	none	50	2.1	14.2	28.9	46.1	0.8	10.0	0.0	1.6
Cl_2	Ph_2S, $AlCl_3$	35	1.5	14.3	18.4	58.6	0.5	7.7	0.5	3.2
SO_2Cl_2	none	25	22	8.7	16.9	73.3	0.0	1.0	0.0	4.3
SO_2Cl_2	$AlCl_3$	25	24	4.7	14.5	80.0	0.0	0.8	0.0	5.5
SO_2Cl_2	Ph_2S	35	2	2.2	15.2	81.1	0.0	1.5	0.0	5.3
SO_2Cl_2	Ph_2S, $AlCl_3$	25	1	1.7	8.5	89.5	0.0	0.2	0.0	10.5

Table II. Chlorination of 2-Alkylphenols

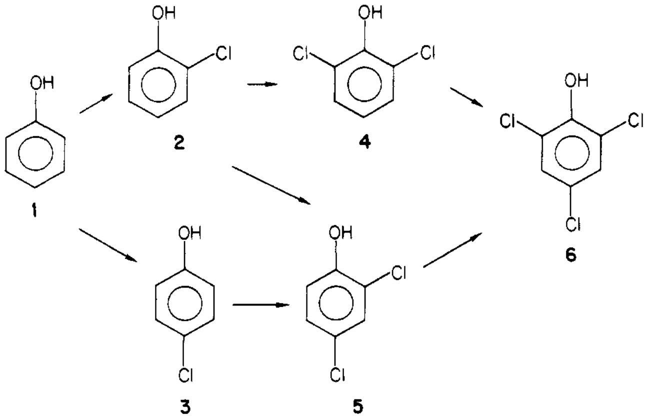
	chlorine		sulfuryl chloride		catalyzed sulfuryl chloride	
reactant	max yield[a] of para isomer	para/ortho	max yield[a] of para isomer	para/ortho	max yield[a] of para isomer	para/ortho
phenol	49	1.6	75	4.3	89	10.5
2-methylphenol	57	2.4	83	6.2	94	19
2-ethylphenol	54	2.0	84	7.6	92	16
2-*n*-propylphenol	53	1.7	82	6.6	92	15
2-isopropylphenol	47	1.4	69	2.8	89	13
2-*sec*-butylphenol	44	1.2	78	4.5	91	14
2-*tert*-butylphenol	35	0.88	69	2.8	80	4.6
2-cyclopentylphenol	40	1.6	70	3.8	80	6.7
2-cyclohexylphenol	39	1.3	64	2.1	83	6.6

[a] Weight percent.

Sulfuryl chloride chlorination of phenols catalyzed with a divalent sulfur compound and a metal halide is fast, regioselective for para chlorination, and specific for monochlorination.

Results

The characteristics of neat chlorinations are typified by the reaction of chlorine with phenol. The products are shown below:



There is difficulty in isolating the above products in a high degree of purity due to similar boiling and melting points of the pure components. For example, the boiling points of **1** and **2** are 175 and 182 °C, respectively, while those of **3**, **4**, and **5** are 220, 219, and 210 °C, respectively.[12]

The chlorination of phenol with chlorine is fast and can be run essentially as fast as the heat of reaction can be removed. Data taken at 50 °C and a chlorine addition rate of ca. 0.5 mol of Cl_2/mol of phenol/h show that the relative rates of mono- and dichlorination are similar so that dichloro- and even some trichlorophenol appear very early in the reaction profile. The maximum yield of 4-chlorophenol is 49%. The maximum yield is defined as the highest weight percent of the 4-chlorophenol observed from the reaction profile. Maximum yields are seldom the same as isolated yields due to losses during isolation. The para/ortho ratio remains relatively constant at 1.6 until dichlorination exceeds 20%. At this point the ratio decreases due to change in the polarity of the reaction mixture and the relative rates of chlorination of **2** and **3**.

Table I shows data from the chlorination of phenol with the various chlorinating agents and catalysts. The para/ortho ratio is increased from 1.6 to 3.2 when a cocatalyst system of diphenyl sulfide and aluminum chloride is used in the chlorine chlorination of phenol. Considerable dichlorophenol is formed, however, making isolation of 4-chlorophenol difficult. When sulfuryl chloride is used as the chlorinating agent the reaction is slow, the para/ortho ratio is improved over chlorine chlorinations, and very little dichlorophenol forms. The use of aluminum chloride as a catalyst improves the para selectivity but does not significantly increase the rate of reaction. The use of diphenyl sulfide as a catalyst increases the rate of reaction but para selectivity is not improved. By use of a catalytic combination of diphenyl sulfide and aluminum chloride and rate of reaction is increased, the highest para/ortho ratio, 10.5, is observed, and the reaction is very selective to monochlorination; i.e., the 2- and 4-chlorophenol products sum to 98.0%.

The data for the chlorination of a series of 2-alkylphenols with chlorine, sulfuryl chloride, and catalyzed sulfuryl chloride are shown in Table II. These data confirm that the selectivity for para chlorination improves from chlorine to sulfuryl chloride to catalyzed sulfuryl chloride. In the catalyzed sulfuryl chloride chlorinations, GLC yields of 4-chloro-2-alkylphenol range from 80% to 94% compared to 35–57% with chlorine and 64–84% with sulfuryl chloride. In general, as the size of the 2-alkyl group increases the para selectivity decreases; i.e., phenol and 2-methylphenol give the highest para/ortho ratios while *tert*-butylphenol gives the lowest. The observed order for decreasing para/ortho ratio of the 2-alkyl substituent is H > CH_3 > C_2H_5 > *n*-C_3H_7 > *sec*-C_4H_9 > c-C_5H_9 > *i*-C_3H_7 > c-C_6H_{11} > *t*-C_4H_9.

A series of 2-halophenols, 3-substituted phenols, and aromatic ethers were chlorinated with the catalyzed sulfuryl chloride system. The results are shown in Table III. For the series of 2-halophenols the para/ortho ratio decreases as F > Cl > Br > I. Chlorination of 2-iodophenol

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(11) Sullivan, J. D. U.S. Patent 2 277 002, 1957.

(12) 1982/1983 Aldrich Handbook.

Table III. Catalyzed Sulfuryl Chloride Chlorination of Some Activated Aromatic Compounds

reactant	max yield[a] of para isomer	para/ortho
3-methylphenol	83	7.5
2-fluorophenol	97	45
2-chlorophenol	94	22
3-chlorophenol	82	6
2,5-dichlorophenol	94	41
2-bromophenol	94	22
2-iodophenol	62	15
anisole	87	8.1
2-methylanisole	95	26
phenyl ether	66	10

[a] Weight percent.

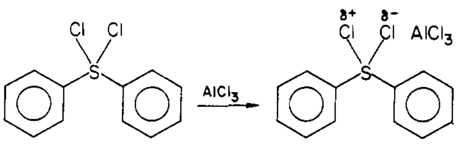
results in considerable byproduct formation including mono- and dichlorophenols. In the case of 2,5-dichlorophenol, chlorination is not favored ortho between the meta-positioned chloro and hydroxyl groups. 3-Methyl- and 3-chlorophenols produce good yields of the 4-chloro isomer. There are also high yields of the para isomer when anisole, 2-methylanisole, and phenyl ether are chlorinated. Under these catalytic conditions, nonaromatic products are not formed as has been reported for the neat chlorine chlorination of anisole[13] and phenyl ether.[14]

When the catalyzed sulfuryl chloride system was used to chlorinate less active aromatic compounds such as chlorobenzene, toluene, and isopropylbenzene, the para/ortho ratios were identical with those obtained with a catalyzed chlorine system.[15]

Discussion

Chlorine is a very reactive and small chlorinating agent. Thus it would be expected to give the lowest para/ortho ratios and considerable dichlorination even when less than 1 equiv of chlorine is used. Sulfuryl chloride is a relatively weak electrophile[10] as well as being bulkier than chlorine. Thus, it produces higher para/ortho ratios with little dichlorination at 1 equiv of sulfuryl chloride.

When diphenyl sulfide and a Friedel–Crafts catalyst are used with sulfuryl chloride, the reaction is fast and regioselective to para chlorination, and very little dichlorination is observed with 1 equiv of sulfuryl chloride. This is proposed to proceed by sulfuryl chloride reacting with diphenyl sulfide to form diphenylsulfur dichloride (7), which complexes with aluminum chloride to form the active chlorinating agent 8. The reaction is fast because the sulfuryl chloride reacts rapidly with diphenyl sulfide to form 8, which reacts rapidly with the phenol. The reaction is para regioselective and little dichlorination is formed because 8 is bulky and prefers attack at the more accessable para position. Analysis of the final reaction mixture reveals that diphenyl sulfide is essentially recovered unreacted with a small amount of 4-chlorophenyl phenyl sulfide. Other divalent sulfur compounds and metal halides have been observed to be active catalysts.[16]



7 8

Diphenyl sulfide is known to form compounds with the halogens, iodine,[17] bromine,[18] chlorine,[19] and fluorine.[20] The product of this reaction, the diphenylsulfur dihalides, have been used as the standard method for preparing sulfoxides. Sulfuryl chloride has also been used in place of chlorine in the preparation of sulfoxides.[21] There are other examples of reactions of sulfur compounds where chlorine and sulfuryl chloride give similar products.[22]

When phenol is chlorinated with chlorine and diphenyl sulfide and aluminum chloride are used as catalysts, the para/ortho ratio is increased over chlorine but much less than with the catalyzed sulfuryl chloride system. This is due to only part of the reaction pathway going through 8 with most of the chlorination occurring directly between phenol and chlorine.

When chlorobenzene, toluene, ethylbenzene, and isopropylbenzene are chlorinated in the presence of diphenyl sulfide and aluminum chloride, identical para/ortho ratios are obtained with either sulfuryl chloride or chlorine. This indicates that sulfuryl chloride decomposes to chlorine, which is the chlorinating agent in these less activated systems.

The second major point that needs to be explained from Tables II and III is the observed para/ortho ratio trends with various substituents in the 2-position. For both the 2-alkyl- and 2-halophenols it is observed that as the size of the substituent becomes larger the para/ortho ratio decreases. The most possible explanation to account for these trends is hydrogen bonding. Hydrogen bonding differences between various phenols can be seen in the infrared and proton NMR spectra.[23-25] 2-Alkylphenols are known to be planar[26] and to have no intramolecular hydrogen bonding.[27] In comparing the IR spectra of a 1.0 N CCl_4 solution of the phenols, it is qualatatively observed as one goes from phenol to 2-*tert*-butylphenol that the amount of free OH increases with a corresponding decrease in polymeric hydrogen bonding. The relative shifts of the OH in the NMR also shows that dilution has a relatively large effect on phenol but very little on *tert*-butylphenol. Thus, it appears that hydrogen bonding plays a major role in explaining the observed para/ortho ratio. That is, there is considerable polymeric hydrogen bonding in the phenols with small alkyl groups and this association effectively sterically hinders attack at the *ortho* position. With large

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alkyl groups such as *tert*-butylphenol there is primarily free OH, and therefore the *ortho* position is more susceptable to electrophilic attack.

These differences in hydrogen bonding may be responsible for the observed differences in reactivity noted between 2-*tert*-butylphenol and 2-methylphenol. When equimolar quantities of the above two phenols were reacted with the catalyzed sulfuryl chloride system it was observed that 2-*tert*-butylphenol reacted 2.0 times faster than 2-methylphenol.

It is difficult to adequately explain the observed trends in the 2-halophenols because intramolecular hydrogen bonding must be taken into consideration.[23,24] The trend in the strength of the intramolecular hydrogen bonding of a 2-halophenol in the liquid phase is Cl > Br > I ≈ F.[23] However, there has been considerable discussion regarding the position of F in this series.[28] In table III it is observed that the para/ortho reaction decreases as F > Cl > Br > I.

Experimental Section

The phenols and aromatic ethers used in these experiments were obtained from Aldrich, Eastman Organic Chemicals, or prepared in our laboratory. Generally, these compounds were distilled prior to use. Satisfactory analysis were done using GLC, NMR, and IR. Chlorine gs (99.5%) was obtained from Matheson Corp. Sulfuryl chloride was practical grade from Eastman and was generally distilled prior to use.

The chlorinated aromatic products were analyzed by GLC. Standard mixtures were prepared from pure isomers and were used to determine response factors for the thermal conductivity unit. The pure isomers were separated from the reaction mixtures by distillation, crystallization, and chromatographic separation. 6-Chloro 2-substituted phenols were prepared by chlorinating to the extinction of the 2-substituted phenol in carbon tetrachloride[7] and separated by distillation. The 4-chloro 2-substituted phenols from the catalyzed sulfuryl chloride chlorinations were first distilled and then crystallized. The 4,6-dichloro 2-substituted phenols were prepared by chlorinating with 2 mol of sulfuryl chloride per mol of substituted phenol in the presence of catalytic amounts of diphenyl sulfide. After distillation the product was recrystallized. All chlorination samples were distilled and found to contain less the 2% nondistillable residue. The final products were also analyzed by NMR and in some cases GLC/MS.

Chlorination with Chlorine. Chlorine was bubbled into the well-agitated neat phenol (1.0 mol). The liberated HCl was absorbed in a water scrubber. All the chlorinations should be done in a well-ventilated hood. The initial temperature was slightly above the melting point of the phenol but was rapidly decreased to 15–20 °C after chlorination began. Chlorine addition rate was ca. 0.5 mol of Cl_2/mol of phenol/h. Samples were taken periodically. Phenol, 2-methylphenol, and 2-cyclohexylphenol were chlorinated at 50, 35, and 40 °C, respectively.

Chlorination with Sulfuryl Chloride. Sulfuryl chloride (10% molar excess) was added to the phenol (1.0 mol) in an agitated glass reactor. The solution was allowed to react at 25 °C for 24 h. Samples taken periodically determined that the reaction was essentially complete after 24 h. Samples were thoroughly degassed under vacuum before analysis.

Catalyzed Chlorination with Sulfuryl Chloride. The catalyst system, diphenyl sulfide, and either aluminum chloride or ferric chloride were dissolved in the phenol (1.0 mol) slightly above the melting point. Catalyst concentrations were ≤1 g of each catalyst per mol of phenol. To the phenolic solution was added sulfuryl chloride in ca. 2 h. The temperature was decreased to 15–20 °C soon after the chlorination began. It was necessary with some of the phenols to heat the reaction mixture near the end of the chlorination to keep the product liquid. These reactions could be run as fast as the heat could be removed. The products were thoroughly degassed prior to analysis.

Registry No. **1**, 108-95-2; **2**, 95-57-8; **3**, 106-48-9; **4**, 87-65-0; **5**, 120-83-2; **6**, 88-06-2; 2-$CH_3C_6H_4OH$, 95-48-7; 2-Cl-6-$CH_3C_6H_3OH$, 87-64-9; 4-Cl-2-$CH_3C_6H_3OH$, 1570-64-5; 2,4-Cl_2-6-$CH_3C_6H_2OH$, 1570-65-6; 2-$C_2H_5C_6H_4OH$, 90-00-6; 2-Cl-6-$C_2H_5C_6H_3OH$, 24539-93-3; 4-Cl-2-$C_2H_5C_6H_3OH$, 18979-90-3; 2,4-Cl_2-6-$C_2H_5C_6H_2OH$, 24539-94-4; 2-*n*-$C_3H_7C_6H_4OH$, 644-35-9; 2-Cl-6-*n*-$C_3H_7C_6H_3OH$, 57883-01-9; 4-Cl-2-*n*-$C_3H_7C_6H_3OH$, 18979-91-4; 2,4-Cl_2-6-*n*-$C_3H_7C_6H_2OH$, 91399-12-1; 2-*i*-$C_3H_7C_6H_4OH$, 88-69-7; 2-Cl-6-*i*-$C_3H_7C_6H_3OH$, 57883-02-0; 4-Cl-2-*i*-$C_3H_7C_6H_3OH$, 54461-05-1; 2,4-Cl_2-6-*i*-$C_3H_7C_6H_2OH$, 96293-23-1; 2-*sec*-$C_4H_9C_6H_4OH$, 89-72-5; 2-Cl-6-*sec*-$C_4H_9C_6H_3OH$, 57883-03-1; 4-Cl-2-*sec*-$C_4H_9C_6H_3OH$, 52184-12-0; 2,4-Cl_2-6-*sec*-$C_4H_9C_6H_2OH$, 96293-24-2; 2-*t*-$C_4H_9C_6H_4OH$, 88-18-6; 2-Cl-6-*t*-$C_4H_9C_6H_3OH$, 4237-37-0; 4-Cl-2-*t*-$C_4H_9C_6H_3OH$, 13395-85-2; 2,4-Cl_2-6-*t*-$C_4H_9C_6H_2OH$, 13395-86-3; 2-*c*-$C_5H_9C_6H_4OH$, 1518-84-9; 2-Cl-6-c-$C_5H_9C_6H_3OH$, 65565-61-9; 4-Cl-2-c-$C_5H_9C_6H_3OH$, 13347-42-7; 2,4-Cl_2-6-c-$C_5H_9C_6H_2OH$, 96293-25-3; 2-c-$C_6H_{11}C_6H_4OH$, 119-42-6; 2-Cl-6-c-$C_6H_{11}C_6H_3OH$, 57883-04-2; 4-Cl-2-c-$C_6H_{11}C_6H_3OH$, 13081-17-9; 2,4-Cl_2-6-c-$C_6H_{11}C_6H_3OH$, 39206-07-0; 3-$CH_3C_6H_4OH$, 108-39-4; 2-Cl-5-$CH_3C_6H_3OH$, 615-74-7; 4-Cl-3-$CH_3C_6H_3OH$, 59-50-7; 2,4-Cl_2-5-$CH_3C_6H_2OH$, 1124-07-8; 2-FC_6H_4OH, 367-12-4; 2-Cl-6-FC_6H_3OH, 2040-90-6; 4-Cl-2-FC_6H_3OH, 348-62-9; 2,4-Cl_2-6-FC_6H_2OH, 344-21-8; 3-ClC_6H_4OH, 108-43-0; 3,4-$Cl_2C_6H_3OH$, 95-77-2; 2,4,5-$Cl_3C_6H_2OH$, 15950-66-0; 2,5-$Cl_2C_6H_3OH$, 583-78-8; 2,3,6-$Cl_3C_6H_2OH$, 933-75-5; 2,3,4,6-Cl_4C_6HOH, 58-90-2; 2-BrC_6H_4OH, 95-56-7; 2-Cl-6-BrC_6H_3OH, 2040-88-2; 4-Cl-2-BrC_6H_3OH, 695-96-5; 2-IC_6H_4OH, 533-58-4; 2-Cl-6-IC_6H_3OH, 28177-52-8; 4-Cl-2-IC_6H_3OH, 71643-66-8; 2,4-Cl_2-6-IC_6H_2OH, 2040-83-7; $PhOCH_3$, 100-66-3; 2-$ClC_6H_4OCH_3$, 766-51-8; 4-$ClC_6H_4OCH_3$, 623-12-1; 2,4-$Cl_2C_6H_3OCH_3$, 553-82-2; 2-$CH_3C_6H_4OCH_3$, 578-58-5; 2-Cl-6-$CH_3C_6H_3OCH_3$, 3438-15-1; 4-Cl-2-$CH_3C_6H_3OCH_3$, 3260-85-3; Ph_2O, 101-84-8; $PhOC_6H_4$-2-Cl, 2689-07-8; $PhOC_6H_4$-4-Cl, 7005-72-3; $PhOC_6H_3$-2,4-Cl_2, 51892-26-3; 2-$ClC_6H_4OC_6H_4$-4-Cl, 6903-65-7; 4-$ClC_6H_4OC_6H_4$-4-Cl, 2444-89-5; Cl_2, 7782-50-5; SO_2Cl_2, 7791-25-5; Ph_2S, 139-66-2; $AlCl_3$, 7446-70-0.

Supplementary Material Available: Table IV, GLC data for the chlorination of phenol with chlorine, Figure 1, reaction profile of the same data, Table V, detailed GLC data of the chlorination of the substituted phenols and aromatic ethers with chlorine, sulfuryl chloride, and catalyzed chloride, and detailed GLC conditions (5 pages). Ordering information is given on any current masthead page.

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[28] Canadell, E.; Catalan, J.; Fernandex Alonso, J. I. *Adv. Mol. Relax. Interact. Processes* **1978**, *12* (4), 265. Dale, A. J.; Granstad, J. *Spectrochim. Acta, Part A* **1972**, *28* (4), 639. Kobayaski, T.; Hirota, M. *Chem. Lett.* **1972**, *10*, 1975.