Table I

Chemical Shifts[a,b] of Alkylphenols

Compd.	R_1	R_2	δ_1	Δ_1	δ_2	Δ_2
Ia	H	H	1.2	0.15	1.2	0.15
Ib	H	CH_3	1.49 ± 0.01	0.26 ± 0.01	1.13 ± 0.01	0.11 ± 0.01
Ic	H	C_6H_5	3.2	0.35	1.3	. . .
Id	H	$C(CH_3)_3$	1.7	0.28	1.3	0.13
Ie	CH_3	CH_3	1.8	0.75	1.2	0.10
IIa	H	$C(CH_3)_2OH$	1.8	0.01	. . .	. . .
IIb	CH_3	CH_3	. . .	0[c]	. . .	. . .

[a] δ_i is the chemical shift in p.p.m. from internal TMS of proton (i) for the *para* isomer. [b] Δ_i is the value of δ_i (*ortho*) − δ_i (*para*). [c] The *para* isomer used here for reference was Ie.

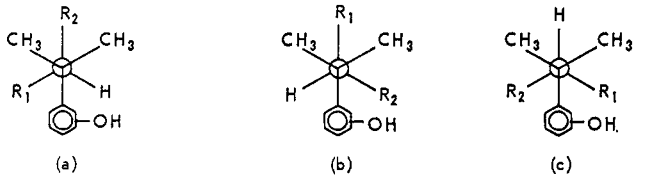


Figure 1.—Conformations of compound I about bond a.

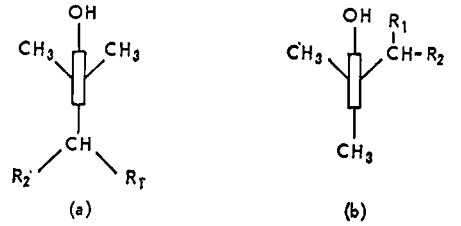
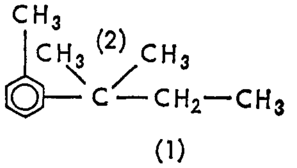


Figure 2.—Conformations of compound I about bond b.

increases with increasing steric crowding owing to increasing conformational preference.

Typical conformations of compound I obtained by rotation about bond b are shown in Figure 2. If these conformations are equally populated in the *ortho* isomer then only the local shielding effects of the hydroxyl group can be responsible for the observed shifts since the ring current is almost certainly the same for the *ortho* and *para* isomers. If the conformations are not equally populated, however, the *effect* of the ring current will be different in the two isomers due to differences in the position of the hydrogen with respect to the plane of the benzene ring.[5]

An attempt was made to determine the relative magnitude of the two effects by measuring the spectrum of compound III, for which the steric situation is similar,[4] but any electric field effect of the OH group will be absent. The *ortho–para* shift for protons (1) of III was found to be 0.18 ± 0.01 p.p.m., *i.e.*, about 70% of that found for the corresponding phenol Ib. The shift of protons (2) was 0.13 ± 0.01, nearly identical with Δ_2 of series I.



III

These observations indicate that an electric field effect of the hydroxyl group as well as ring current effects of the phenyl group (and thus preferred conformations about bond b) are involved.

Although more work is clearly required to elucidate the exact nature of the shifts, the work is presented here for those who may be interested in further investigation.

Experimental

Most of the n.m.r. spectra were recorded at room temperature with a Varian Associates high-resolution spectrometer (V-4300) at 40 Mc.p.s. The chemical shifts were measured in 50% carbon tetrachloride solution relative to tetramethylsilane as internal standard. For the temperature-dependent studies, a Varian A60 spectrometer was used.

Alkylphenols.—These compounds were prepared by the aluminum phenoxide catalyzed alkylation of phenol with the appropriate olefin according to the procedure of Dewhirst and Rust.[2] The only unreported compound is 2-(2-hydroxyphenyl)-2,4,4-trimethylpentane (*ortho*-Id), b.p. 130° (10 mm.), m.p. 40–42°.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.5; H, 10.8. Found: C, 81.4; H, 10.7.

2-(2-Tolyl)-2-methylbutane (IIIa).—The *para* isomer has already been reported.[6] The *ortho* isomer was prepared by adding 1.7 moles of *t*-amyl chloride to 1.7 moles of *o*-tolylmagnesium bromide in ether. The mixture was hydrolyzed with dilute hydrochloric acid, washed with water, and dried. The isoamylene and ether were distilled off, and the residue was refluxed with sodium in amyl alcohol to remove halogen impurities. The mixture was distilled to give 3 g. (1.1%) of product, b.p. 120–121° (50 mm.), $n^{25}D$ 1.5032.

The infrared spectrum of this material showed strong bands at 728 and 758 cm.$^{-1}$, characteristic of an *ortho* disubstituted benzene, and a doublet at 1358 and 1373 cm.$^{-1}$, characteristic of a *gem*-dimethyl group.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.8; H, 11.2; mol. wt., 162. Found: C, 88.2; H, 11.0; mol. wt., 158.

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(6) M. J. Schlatter and R. D. Clark, *J. Am. Chem. Soc.* **75**, 361 (1953).

The *ortho–para* Ratio in Electrophilic Aromatic Substitution. Evidence for a Linear Coordination Effect in Nitration of Anisole[1]

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The literature contains a goodly number of reports dealing with the cyclic or quasi-ring coordination effect[2]

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(1) From the Ph.D. Thesis (1965) of J. J. H., presented at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964.

(2) For a review, see ref. 1.

in electrophilic aromatic substitution. Recently, evidence was found which pointed to the existence of another type which has been designated the linear coordination effect.[3] The reactions involved were alkylation and mercuration of chlorobenzene and anisole. This report provides additional support for the operation of this novel orientation factor from studies involving aromatic nitration.

The *ortho–para* ratios for nitration of toluene, chlorobenzene, and anisole with mixed acid, acetyl nitrate, and nitronium tetrafluoroborate[4,5] are summarized in Table I. Our detailed data for the reactions of nitronium tetrafluoroborate with anisole and toluene are presented in Tables II and III. The toluene results confirm the previous findings.[6]

TABLE I

NITRATION OF AROMATICS

R in C_6H_5R	$RC_6H_4NO_2$, *ortho–para* from HNO_3–H_2SO_4	$CH_3CO_2NO_2$	$NO_2^+BF_4^-$
CH_3	1.6–1.9[a,b]	1.4–1.9[c–e]	1.8–2.1[f–i]
Cl	0.5[j]	0.4[k]	0.3[l]
OCH_3	0.5[m]	2.3[n]	2.2

[a] W. W. Jones and M. Russell, *J. Chem. Soc.*, 921 (1947). [b] P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution—Nitration and Halogenation," Academic Press Inc., New York, N. Y., 1959, p. 50. [c] L. M. Stock, *J. Org. Chem.*, **26**, 4120 (1961). [d] C. K. Ingold, A. Lapworth, E. Rothstein, and D. Ward, *J. Chem. Soc.*, 1959 (1931). [e] H. Cohn, E. D. Hughes, M. H. Jones, and M. G. Peeling, *Nature*, **169**, 291 (1952). [f] See ref. 6. [g] W. S. Tolgyesi, *Can. J. Chem.*, **43**, 343 (1965). [h] C. D. Ritchie and H. Win, *J. Org. Chem.*, **29**, 3093 (1964). [i] See Experimental. [j] H. H. Bieber and W. F. Schurig, *Ind. Eng. Chem.*, **49**, 832 (1957). [k] M. L. Bird and C. K. Ingold, *J. Chem. Soc.*, 918 (1938). [l] G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Am. Chem. Soc.*, **83**, 4581 (1961). [m] P. H. Griffiths, W. A. Walkey, and H. B. Watson, *J. Chem. Soc.*, 631 (1934). [n] R. O. C. Norman and G. K. Radda, *ibid.* 3030 (1961).

TABLE II

NITRATION OF ANISOLE WITH NITRONIUM TETRAFLUOROBORATE

	$CH_3OC_6H_4NO_2$, %			
Time,[a] min.	*ortho*	*meta*	*para*	*ortho/para*
8	69	<2	31	2.2
10	69	<2	31	2.2
15[b]	68	<2	32	2.1

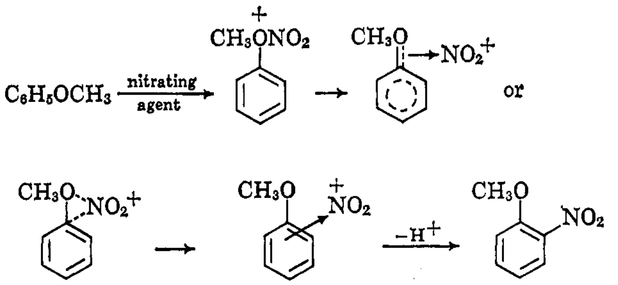
[a] Total reaction time including 5 min. addition time. [b] Yield, 92% (based on $NO_2^+BF_4^-$).

TABLE III

NITRATION OF TOLUENE WITH NITRONIUM TETRAFLUOROBORATE

	$CH_3C_6H_4NO_2$, %			
Time, min.	*ortho*	*meta*	*para*	*ortho/para*
10	64	4	32	2.0
15	64	3	33	1.9

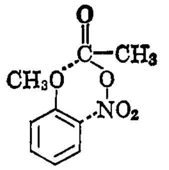
With toluene and chlorobenzene there is little change in the *ortho–para* ratio with variation in the nitrating species. In contrast, the ratio from anisole can be drastically altered by appropriate choice of the reagent. We conclude that the high *ortho–para* ratios (greater than statistical) for nitration of anisole by acetyl nitrate and nitronium tetrafluoroborate result from a linear coordination mechanism.[3] After initial complexing of the attacking electrophile with the side chain, migration to the nucleus could conceivably take place by means of the delocalized electron cloud or by a bridging mechanism. Since entrance to the nucleus would occur nearest the *ortho* position, this site should then be most susceptible to substitution. Reaction would also be proceeding by direct nuclear attack.



Our proposal is similar to those advanced for the nitramine and aralkyl ether rearrangements.[7] In addition, there is a resemblance to base-catalyzed intramolecular 1,3- and 1,5-proton transfers.[8]

The hypothesis is strengthened by the insufficiency of the other operative factors in completely rationalizing the results. Since similar *ortho–para* ratios were obtained from toluene, as well as chlorobenzene, in the three systems, steric and activity effects cannot serve as satisfactory interpretations. The close correspondence in activity is further illustrated by the $k_{\text{toluene}}/k_{\text{benzene}}$ reactivity ratios (mixed acid[9] 18 and acetyl nitrate[10] 23). Nitration studies of Olah, Kuhn, and Flood[6] with nitronium tetrafluoroborate indicated a relative reactivity of 1.7. Subsequently, values of 25–30 were obtained under somewhat different conditions.[11] The interpretation[11] of Tolgyesi's results has been recently questioned.[12] In any event the isomer distribution remained essentially unchanged in all cases.[6,11-13]

Halvarson and Melander[14] invoked a cyclic coordination mechanism to explain the high *ortho–para* ratio from the anisole–acetyl nitrate reaction. The inherent weaknesses of this conjecture have been pointed out.[14] Furthermore, it is very unlikely that the cyclic pathway is operative in the case of nitronium tetrafluoroborate.



As noted previously,[3] the nature of both the donor and acceptor plays an important role in determining whether complexing at the side chain, followed by intramolecular rearrangement, will occur. Presumably, anisole occupies a unique position in the present series

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(3) P. Kovacic and J. J. Hiller, Jr., *J. Org. Chem.*, **30**, 1581 (1965).

(4) G. Olah and S. Kuhn, *Chem. Ind.* (London), 98 (1956).

(5) G. Olah, S. Kuhn, and A. Mlinko, *J. Chem. Soc.*, 4257 (1956).

(6) G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Am. Chem. Soc.*, **83**, 4571 (1961).

(7) M. J. S. Dewar in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 5.

(8) D. J. Cram, F. Willey, H. P. Fischer, and D. A. Scott, *J. Am. Chem. Soc.*, **86**, 5370 (1964).

(9) Calculated from the data of W. W. Jones and M. Russell [*J. Chem. Soc.*, 921 (1947)] according to the method of H. C. Brown and C. R. Smoot [*J. Am. Chem. Soc.*, **78**, 6255 (1956)].

(10) See Table I, footnote *d*.

(11) See Table I, footnote *g*.

(12) G. A. Olah and N. A. Overchuk, unpublished work.

(13) See Table I, footnote *h*.

(14) K. Halvarson and L. Melander, *Arkiv Kemi*, **11**, 77 (1957).

because of the increased facility for side-chain coordination. The specificity associated with the nitrating agent presents a more difficult problem. Perhaps solvent effects play an important role. In any case the differences are not surprising since analogous situations exist. Norman and Radda[15] remarked on the dissimilar *ortho–para* ratios obtained from the reactions of methyl phenethyl ether with mixed acid and nitric acid–acetic anhydride. To explain the high *ortho–para* ratio with nitric acid–acetic anhydride, the authors proposed an S$_\text{N}$2 displacement followed by cyclic coordination.

Experimental

Nitration of Anisole with Nitronium Tetrafluoroborate.—Nitronium tetrafluoroborate was prepared from fuming nitric acid–hydrogen fluoride–boron trifluoride–nitromethane according to the method of Kuhn and Olah.[16]

A solution of nitronium tetrafluoroborate (0.05 mole) in tetramethylene sulfone (100 g.) was added during 5 min. to a stirred solution of anisole (0.5 mole) in tetramethylene sulfone (30 g.) at 21–24°. The reaction was terminated after the desired time span by dilution with water (300 ml.). The organic layer was diluted with ether (250 ml.), washed with water, and dried over calcium chloride. After evaporation of the ether, analysis was performed by gas chromatography on an Apiezon L (14% w./w.) column (12 ft., 200°, He flow rate of 80 cc./min.). In one reaction the amount of nonvolatile product, determined by distillation, was found to be 4% of the total product. The orientation data are recorded in Table II.

Nitration of Toluene with Nitronium Tetrafluoroborate.[6,11-13]—Nitration of toluene, as well as product analysis, was carried out under the same conditions as employed for anisole. The results are summarized in Table III.

Acknowledgment.—We are grateful to the National Science Foundation for support of this work.

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[15] R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 3030 (1961).

[16] S. J. Kuhn and G. A. Olah, *J. Am. Chem. Soc.*, **83**, 4564 (1961).

Some Electrochemical Oxidations in Anhydrous Acetic Acid

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In a recent publication,[1] Ross, Finkelstein, and Petersen suggested that aromatic hydrocarbons are anodically oxidized in anhydrous acetic acid, forming radical cations. Their argument is based primarily upon the analysis of the products of electrolysis in anhydrous acetic acid–potassium acetate solutions containing various added hydrocarbons, although they also reported that the discharge potential was lowered when naphthalene was added to a solution of potassium acetate in acetic acid. We have reported[2] direct evidence for the anodic oxidation of aromatic hydrocarbons in anhydrous acetic acid solutions, obtained by the measurement of anode potentials in the presence and in the absence of aromatic substrates. Under our conditions, naphthalene and anthracene were oxidized at potentials which were about 0.5 and 0.8 v. less anodic, respectively, than those required for the oxidation of acetic acid. Benzene did not oxidize under our conditions. We wish now to report the extension of our work to other classes of substrates.

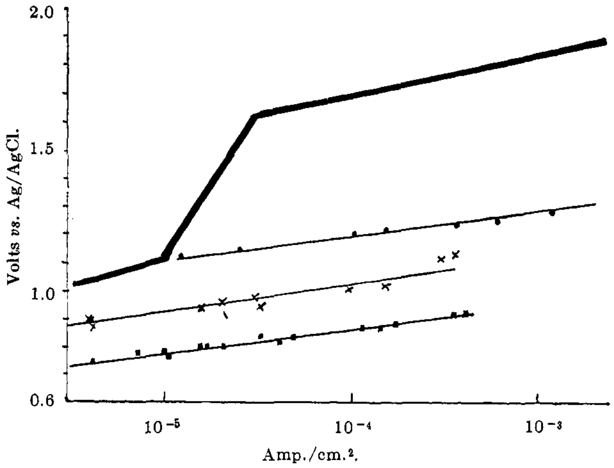

Figure 1.—Anode potential *vs.* current density (semilog scale): ●, naphthalene; ×, α-naphthyl acetate; and ■, anthracene.

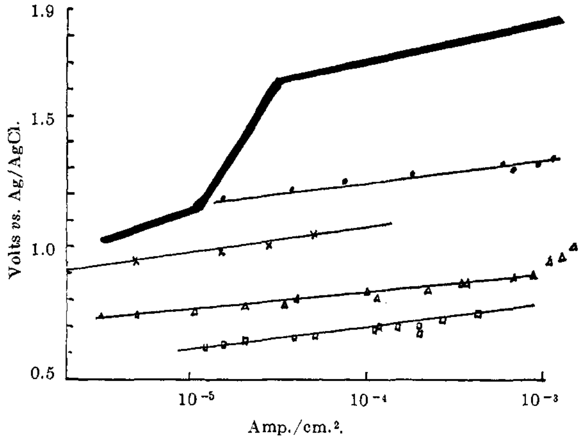

Figure 2.—Anode potential *vs.* current density (semilog scale): ●, phenyl methyl ether; ×, acetanilide; △, α-naphthyl methyl ether; and □, aniline.

Experimental

The apparatus and general procedure were those of the previous work.[2] Liquids were purified by distillation. Solids were recrystallized, when necessary, until the melting points agreed with those reported in the literature. The substrates were α-naphthyl methyl ether, phenyl methyl ether, α-naphthoquinone, α-naphthyl acetate, acetanilide, aniline, and mesitylene. The current densities ranged from 10^{-6} to 5 × 10^{-3} amp./cm.^{2}. Stationary state electrode potentials were measured against a Ag/AgCl(s) reference. The anode was a 1-cm.^{2} piece of platinized titanium. As reported previously,[2] the results using the titanium-based platinum surface were in good agreement with those obtained using pure platinum. To avoid evolution of hydrogen, the cathode was a large Ag/AgCl(s) electrode. No attempts were made at product analysis. For any particular run, the data were reproducible within 25 mv., but repeat runs in fresh solution sometimes gave results that varied by as much as 60 mv. All solutions contained KOAc.

Results

Figures 1 and 2 show the variation of anode potential with current density, on semilog paper. (The previously published results with anthracene and naphthal-

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[1] S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Am. Chem. Soc.*, **86**, 4139 (1964).

[2] M. Leung, J. Herz, and H. W. Salzberg, *J. Org. Chem.*, **30**, 310 (1965).