reaction was carried out under a static nitrogen atmosphere using an ice water cooled reflux condenser protected by a drying tube. Thus, the dealkylation products were not removed from the rest of the reaction mixture, which was worked up in the usual way by careful addition of cold water. Further experimental details and results are given in Table III.

Procedure B. The reactions were carried out in a three-neck flask equipped with a magnetic stirrer, an addition funnel, and an ice water cooled condenser protected by a drying tube. The reactants were stirred at the temperatures and for the times specified in Table III, and then the reaction mixtures were quenched by the dropwise addition of ice-cold water. The organic layer was separated, the aqueous layer was extracted with two portions of ether which were combined with the organic layer, and the organic layer was then washed with 5% $NaHCO_3$ solution and two portions of water. The organic solution was dried over anhydrous Na_2SO_4 and weighed. A known weight of cyclohexane was added to serve as an internal standard, and a 5-mL aliquot of the mixture was taken for GLC analysis of the dealkylation products. The remainder of the reaction mixture was distilled, first at atmospheric pressure and then under reduced pressure. The fractions collected between 62 and 90 °C (2 mm) were analyzed by GLC, with the results presented in Table VI for four representative experiments.

The reactions in which HF–SbF_5 was used were carried out essetially according to procedure B. Details of experimental conditions and results are given in Table V.

Alkylation–Dealkylation with Bromohexanes as Starting Materials. These reactions were carried out as in procedure B except that the hexylbenzenes were produced in situ by reaction of 2- or 3-bromohexane with benzene under the conditions given in Table IV, with the results presented there. The rearrangement and cyclialkylation products were analyzed and found to be essentially the same as those formed from hexylbenzenes as starting materials (Table VI).

Registry No.—PhR (R = Me), 108-88-3; PhR (R = Et), 100-41-4; PhR (R = *n*-Pr), 103-65-1; PhR (R = *i*-Pr), 98-82-8; PhR (R = *sec*-Bu), 135-98-8; PhR (R - *i*-Bu), 538-93-2; PhR (R = *n*-Bu), 104-51-8; PhR (R = 2-Pe), 2719-52-0; PhR (R = 3-Pe), 1196-58-3; PhR (R = 2-methyl-1-butyl), 3968-85-2; 2-phenylhexane, 6031-02-3; 3-phenylhexane, 4468-42-2; 3-methyl-2-phenylpentane, 66418-14-2; 2-methylpentane, 107-83-5; 3-methylpentane, 96-14-0; *n*-hexane, 110-54-3; 2-bromohexane, 3377-86-4; 3-bromohexane, 3377-87-5; 2,2-dimethylbutane, 75-83-2; 2,3-dimethylbutane, 79-29-8; 2-methyl-1 phenylpentane, 39916-61-5; 1-ethyl-3-methylindan, 66418-15-3; 1,1,3-trimethylindene, 2177-45-9; 1,3-dimethyltetralin, 5195-37-9; 1,4-dimethyltetralin, 4175-54-6; 1,3-dimethylnaphthalene, 575-41-7; 1,4-dimethylnaphthalene, 571-58-4; 1-methyl-2-phenylcyclohexane, 17733-68-5; 1-methyl-4-phenylcyclohexane, 1603-60-7.

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Kinetics of the Reactions of Weakly Basic Amines with Activated Aromatic Substrates. Reaction of Imidazole and Aniline with 1-Fluoro-2,4-dinitrobenzene

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The reactions named in the title were studied in water solution at different pH and buffer concentrations to search for the possibility of base catalysis in the addition step of nucleophilic aromatic substitution. The reaction of imidazole is independent of buffer and pH below pH 10.9 with a mean second-order rate constant of (1.09 ∓ 0.05) 10^{-3} M^{-1} s^{-1}. At higher pH the second-order rate constant increases linearly with hydroxide ion concentration. The rate acceleration was ascribed to the reaction of imidazole anion, the second-order rate constant of which is calculated as 0.195 M^{-1} s^{-1}. The reaction of aniline is independent of pH and buffer concentration below pH 10.56. At higher pH and higher ionic strength the reaction is slightly dependent on the phosphate trianion concentration, but this dependence changes with the compensating electrolyte used, and is attributed to a specific salt effect.

The study of reactions of amine nucleophiles has been of great importance in firmly establishing the multistep nature of the mechanism of aromatic nucleophilic substitution.[1]

The reactions of amines with compounds bearing poor leaving groups, such as methoxide ion, are base catalyzed with change in the rate-determining step at high base concentration,[2,3] whereas with substrates with good leaving groups such as chloride ion in protic solvents, base catalysis is not observed.[4]

The body of experimental results is consistent with the mechanism depicted in Scheme I, where k_3^B and k_{-3}^B are the rate constant for the proton transfer reactions, k_4 is the rate constant for the leaving group expulsion from **2**, and k_2 is the rate constant for the spontaneous or solvent-catalyzed elimination of HX from **1**.

Base catalysis is observed when the conversion of **1** to products is slower than the k_{-1} step. In such cases two different situations have been shown to occur.[5] In the first, $k_4 \gg k_{-3}^B(BH)$ so that deprotonation of **1** is rate limiting in the base-catalyzed pathway. This situation is recognized by the

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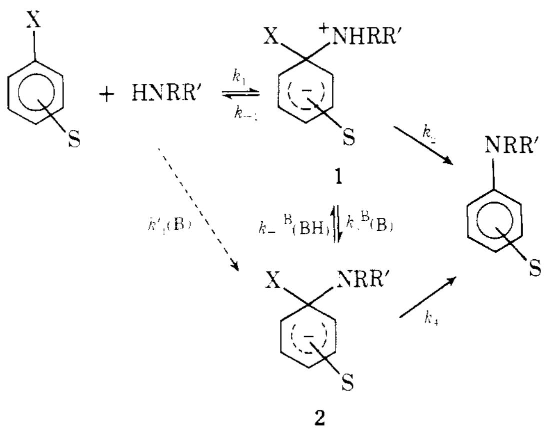
Table I. Reaction of 1-Fluoro-2,4-dinitrobenzene with Imidazole at 25 °C[a]

5 [Imidazole]$_{free}$, M	pH	Buffer, M	Yield, %	$k_\psi \times 10^4$, s^{-1}	$k_A \times 10^3$, M^{-1} s^{-1}
0.200	6.95	0.400[b]	100	2.34	1.17
0.301	7.43	0.401[b]	100	3.34	1.11
0.132	7.43	0.176[b]	100	1.46	1.11
0.0364	7.43	0.0486[b]	100	0.417	1.14
0.208	8.17	0.220[b]	100	2.31	1.11
0.145	8.15	0.154[b]	100	1.61[c]	1.11
0.083	8.15	0.088[b]	100	0.97	1.17
0.0207	8.15	0.022[b]	100	0.246	1.19
0.103	9.05	0.010[d]	92.7	1.15	1.03
0.101	9.05	0.033[d]	92.2	1.18	1.08
0.100	9.05	0.066[d]	92.8	1.13	1.05
0.101	9.05	0.100[d]	91.9	1.11	1.01
0.100	10.08	0.100[d]	85.8	1.26	1.08
0.101	10.08	0.075[d]	86.0	1.26	1.07
0.100	10.08	0.050[d]	86.0	1.17	1.01
0.098	10.08	0.025[d]	86.8	1.18	1.04
0.101	10.92	0.050[e]	48.1	2.63	1.25
0.099	10.92	0.035[e]	50.4	2.43	1.24
0.100	10.92	0.020[e]	53.3	2.30	1.23
0.101	10.92	0.005[e]	57.8	2.20	1.26

[a] $[S_0] = 8\text{–}9 \times 10^{-5}$ M, $\mu = 0.2$ M NaCl. [b] Im/ImH. [c] Mean value of two determination. [d] Borax. [e] Bicarbonate.

Scheme I

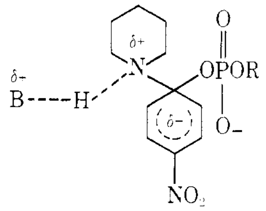


observation of *general* base catalysis.[6] In the second situation, $k_4 \ll k_{-3}^B(BH)$, so that leaving group departure (k_4) is rate limiting. In this case one observes *specific* base catalysis.[5]

An interesting question is whether base catalysis could be observed when the product-forming steps are much faster than the k_{-1} step. Such an observation would imply that the addition step is subject to base catalysis. Mild accelerations by hydroxide ion in reactions where the product-forming steps are believed to be much faster than the k_{-1} step have in fact been observed and interpreted in terms of base catalysis of the addition step, though without mechanistic rationalization.[8,9]

Base-catalyzed addition of the amine could in principle be possible through a concerted mechanism, k_1' (dashed line) in Scheme I. A fairly widely accepted premise is that the primary reason for the existence of concerted general acid–base catalysis is that it avoids highly unstable intermediates and the high energy transition states leading to them.[10] Applied to nucleophilic aromatic substitution it means that if the zwitterionic intermediate 1 were too unstable, a mechanism like the dashed line in Scheme I could become the lowest energy path. Other things being equal, the energy of 1 relative to starting material will increase as the activation of the aromatic substrate decreases and as the amine nucleophile becomes less basic. Therefore the absence of base catalysis in the addition step of nucleophilic aromatic substitution may be due to the fact that the commonly studied amines are fairly basic (pK_a > 8). With less basic amines like aniline the catalysts used were too weak.[11]

A case where 1 might be unstable enough to make a concerted mechanism possible is the catalysis by hydroxide ion in the reactions of piperidine with 4-nitrophenyl phosphate dianion[8] and methyl-4-nitrophenyl phosphate monoanion,[9] under conditions where k_1 is the rate-determining step. The transition state for such a concerted mechanism is shown in **3.** On the other hand, catalysis by the amine is not expected to occur by this mechanism, because the pK difference between 1 and the amine is small;[12] the same would be true for other base catalysts which are substantially weaker bases than hydroxide ion.[13]



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Concerted catalysis with weaker bases might become feasible if a more weakly basic amine nucleophile is used. Thus we undertook the investigation of the reaction of aniline (pK_a = 4.6) and imidazole (pK_a = 7) with 1-fluoro-2,4-dinitrobenzene under experimental conditions where we expected to find base catalysis of the k_1 step. We chose 1-fluoro-2,4-dinitrobenzene as a substrate because its reactivity is in a convenient range for rate measurements, and fluoride ion is a good enough leaving group in protic solvents so as to guarantee that the k_1 step is rate determining.

Results and Discussion

Imidazole. The reaction of imidazole with 1-fluoro-2,4-dinitrobenzene was studied in water solution between pH 6.95 and 10.90 at four buffer concentrations at each pH studied (Table I). The reaction is independent of the buffer concentration under all our reaction conditions, but it is slightly dependent on the hydroxide ion concentration at high pH (Tables I and II). Hydrolysis of the product is a complication at high pH, which becomes even more important at high buffer concentration since it is general base catalyzed.[14] This com-

Table II. Reaction of 1-Fluoro-2,4-dinitrobenzene with Aniline and Imidazole as a Function of Hydroxide Ion Concentration

$[HO^-] \times 10^3$, M	Yield, %	$k_\psi \times 10^4$, s^{-1}	$k_A \times 10^2$, $M^{-1} s^{-1}$	k_{OH}, $M^{-1} s^{-1}$
	A. Reactions with Aniline[a]			
	100	24.8	5.64	
0.5	100	24.7	5.61	
1.0	97.3	24.7	5.46	
4.0	84.4	29.3	5.63	0.112
7.0	71.4	34.6	5.61	0.141
10.0	63.2	40.3	5.79	0.149
16.0	53.2	48.5	5.86	0.142
20.0	47.6	54.2	5.86	0.142
	B. Reactions with Imidazole[b]			
1.06	67.9	3.47	0.118	0.105
1.50	60.8	4.06	0.123	0.106
2.12	54.8	4.78	0.131	0.102
2.50	50.8	5.38	0.136	0.105
3.18	45.4	6.38	0.144	0.109

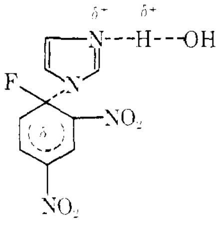
[a] Ionic strength 1.5 M, NaCl as compensating electrolyte. Solvent: dioxane–water 1:10 v/v. $[S_0] = 1.9 \times 10^{-5}$ M, $[\text{aniline}]_0 = 0.044$ M. [b] Ionic strength 0.2 M, NaCl as compensating electrolyte. Solvent: dioxane 2% in water. $[S_0]$, 7.39 10^{-5} M, $[\text{imidazole}]_0 = 0.2$ M.

Table III. Reactions of Aniline with 1-Fluoro-2,4-dinitrobenzene in Dioxane–Water at 25 °C[a]

pH	Buffer	Yield, %	$k_\psi \times 10^4$, s^{-1}	$k_A \times 10^2$, $M^{-1} s^{-1}$
9.378	Borax[b]	100	8.81	4.00[c]
10.248	Borax[b]	100	9.07	4.12[c]
10.925	Bicarbonate[d]	96.8	17.9	3.94
11.654[e]	Phosphate[f]	78.4	22.8	4.06
10.565	Bicarbonate[g]	99.2	26.8	6.04

[a] $[S_0] = 1.9\text{–}2.1 \times 10^{-5}$ M; ionic strength 0.2 M, with NaCl as compensating electrolyte unless otherwise stated; $[\text{aniline}]_0 = 0.044$ M. [b] Total buffer concentration: 0.01–0.1 M, four determinations. [c] $[\text{aniline}]_0 = 0.022$ M. [d] Total buffer concentration 0.005–0.035 M, four determinations. [e] This pH value may be erroneous in about 0.05 pH units. [f] Total buffer concentration 0.005–0.02 M. [g] Total buffer concentration 0.02–0.25 M, ionic strength 1.5 M with NaCl as compensating electrolyte.

plication prevented us from doing determinations at higher buffer concentrations which would be desirable to detect weak base catalysis. The rate enhancement by hydroxide ion can be interpreted as specific base catalysis with imidazole anion acting as nucleophile or concerted base catalysis with the hydroxide ion acting as general base catalyst with a transition state like **4**.

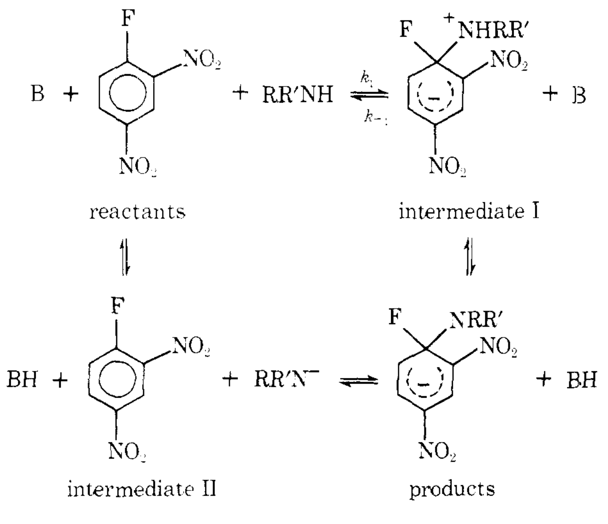


4

A transition state like **4** was suggested for the displacement of a strong base in an amide by imidazole.[15]

Free energy contour maps have become an increasingly popular tool for visualizing and discussing the mechanism of base-catalyzed reactions.[10,16] Applied to our reaction, the four corners of the contour map can be represented by Scheme II.

Scheme II



The standard free energy for reactant → intermediate II, when B = hydroxide ion and RR′NH = imidazole, can be calculated as 0.27 kcal/mol from the relationship $\Delta G = -RT \ln K_{\text{Im}}/K_w$, where K_{Im} is the acid dissociation constant of imidazole equal to 6.31×10^{-15}.[17] This is certainly a very low value and the secuence reactant → intermediate II → product must be the preferred reaction pathway. Regardless of the energy of intermediate I, the energy of intermediate II seems to be low enough to prevent concerted catalysis, thus hydroxide ion will probably act as specific base catalyst even with a less activated substrate, whereas with a less activated substrate and a weaker base concerted catalysis might become possible. To have intermediate I with energy close to that of intermediate II, which is a requirement for concerted base catalysis,[10] k_{-1} in Scheme II would have to be 1.7×10^{-3} s^{-1}; this is a totally unrealistic value as can be seen from the following considerations.

The reversion of the initially formed zwitterionic intermediate from compounds of the type 1-X-2,4-dinitrobenzene with a secondary amine of p$K \sim 11$ was estimated to be in the order of 10^7–10^8 s^{-1}.[12] Although we might expect protonated imidazole, where the positive charge is divided between the two nitrogens, to be a poorer leaving group than an ordinary amine with a full positive charge on nitrogen,[18] it is very unlikely that this effect would amount to a factor of 10^{10}–10^{11}. We conclude that the catalysis by hydroxide ion must be due to the reaction of imidazole anion.

A plot of the second-order rate constant k_A as a function of the hydroxide ion concentration (not shown) is linear with slope 0.123 M^{-2} s^{-1} and intercept of 1.05×10^{-3} M^{-1} s^{-1}. From the slope of this plot the second-order rate constant for the reaction of imidazole anion with 1-fluoro-2,4-dinitrobenzene is calculated as 0.195 M^{-1} s^{-1}. The value of the intercept represents the reaction of neutral imidazole and is in good agreement with the value of the rate constant determined directly at low pH.

Incidentally our measurements furnished rate coefficients for the reaction of hydroxide ion with 1-fluoro-2,4-dinitrobenzene (Table II). The average value of k_{OH}, among the experiments in water and 10% dioxane–water, is 0.105 and 0.143 M^{-1} s^{-1}, respectively, in good agreement with literature values.[19]

Aniline. The reaction of 1-fluoro-2,4-dinitrobenzene with aniline was studied in a wider range of pH and buffer concentration, but the reactions were carried out in dioxane/water 1:10 v/v as solvent because the product 2,4-dinitrophenylphenylamine is quite insoluble in pure water. In a first set of experiments at low buffer concentration and ionic strength of 0.2 M, the reaction is independent of pH and buffer concentration (Table III). The reaction is slightly faster than in water[20] in agreement with the general finding that reactions

Table IV. Reaction of Aniline with 1-Fluoro-2,4-dinitrobenzene as a Function of Phosphate Concentration[a]

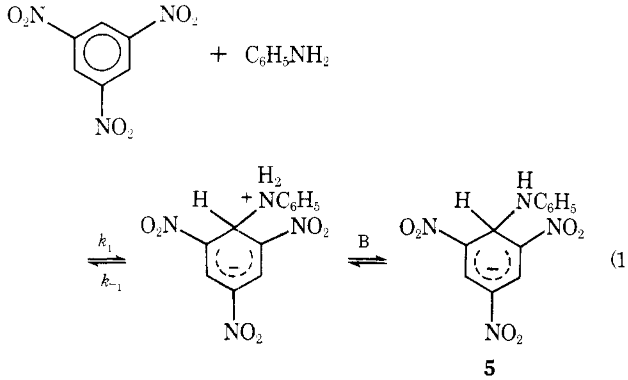
[Buffer], M	$[PO_4^{3-}]$,[b] M	Yield, %	$k_\psi \times 10^4$, s^{-1}	$k_A \times 10^2$, $M^{-1} s^{-1}$
A. Sodium Chloride as Compensating Electrolyte				
0.25	0.158	62.5	49.4	7.02
0.16	0.094	80.6	36.5	6.69
0.07	0.034	77.2	32.0	5.61
0.02	0.0062	88.1	26.9	5.39
B. Sodium Nitrate as Compensating Electrolyte				
0.25	0.158	69.3	33.3	5.25
0.16	0.094	80.6	28.4	5.21
0.07	0.034	91.0	23.1	4.78
0.02	0.0062	93.2	21.3	4.51
0.25	0.187	35.5	70.0	5.65
0.16	0.112	49.2	43.3	4.84
0.07	0.041	68.2	30.1	4.66
0.02	0.0076	90.4	23.3	4.79

[a] $[S_0] = 1.9\text{–}2.1 \times 10^{-5}$ M, $[\text{aniline}]_0 = 0.044$ M, ionic strength 1.5 M, buffer = Na_2HPO_4/Na_3PO_4. [b] The phosphate trianion concentration was calculated from the stoichiometric concentration of PO_4^{3-} and HPO_4^{2-} and dissociation constant of HPO_4^{2-} in water (pK_a = 12.32, J. N. Buttler, "Ionic Equilibrium, A Mathematical Approach", Addison-Wesley, Reading, Mass., 1964, p 209).

of amines with neutral aromatic substrates are faster in dioxane/water than in water.[21]

At high ionic strength (μ = 1.5) and high pH there is a slight dependence of the rate constant on the phosphate trianion concentration (Table IV). The effect of several electrolytes on the reaction of 1-fluoro-2,4-dinitrobenzene with aniline was studied by Bunton et al.[20] and they found that the highest effect on the reaction is caused by anions of low charge density like sulfate, which at μ = 1 M increase the rate as much as 70%. We found that the rate increase is about 20% with a 23-fold variation in the concentration of phosphate trianion using sodium chloride as compensating electrolyte, whereas with sodium nitrate the rate increases about 10% under otherwise equal conditions. The different slope of the plot (not shown) of k_A vs. phosphate trianion concentration indicates that the effect found should be ascribed to specific salt effect rather than to base catalysis.[22] The lack of catalysis by hydroxide ion supports this interpretation (Table IIB).

If we analyze Scheme II for B = HO^- and RR′NH = aniline, we find that the standard free energy for reactant → intermediate II is ca. 18 kcal/mol based on pK_a = 27.3 for aniline.[23] In order to stimate ΔG for the reaction reactant → intermediate I we can estimate k_{-1} as follows. According to Buncel et al.[24] k_{-1} for eq 1 is $>10^7$ s^{-1} in dimethyl sulfoxide and it is expected to be higher in water.[25]



(1)

5

Less activation in the 2,4-dinitrofluorobenzene ring as compared with trinitrobenzene will further increase k_{-1}, thus k_{-1} in Scheme II (RR′NH = aniline) may well be close to diffusion controlled, $10^9\text{–}10^{10}$ s^{-1}. From the relationship $K_1 = k_1/k_{-1}$ with $k_1 = 5.62 \times 10^{-2}$ $M^{-1} s^{-1}$ (Table IIA), we calculated that the standard free energy for the reaction reactant → intermediate I should be in the order of 14–15 kcal/mol, 3–4 kcal/mol lower than the energy of intermediate II. This difference seems to be enough to make the sequence reactant → intermediate I → products the preferred reaction pathway.[26]

The stepwise formation of σ complex anion **5** from 1,3,5-trinitrobenzene and aniline was demonstrated in the reaction catalyzed by methoxide anion.[27] Concerted catalysis by 1,4-diazabicyclo[2.2.2]octane (Dabco) in the same reaction was disfavored by the authors although on different grounds.[24]

The fact that general base catalysis of the addition step of nucleophilic aromatic substitution could not be demonstrated in the two reactions reported in this paper does not prove that a mechanism like that represented for the dashed line in Scheme I cannot take place.

Since a concerted pathway is less favorable from an entropy point of view than the stepwise pathway, the concerted reaction will only become significant if the intermediates are of much higher energy than reactants and products. In the reactions reported in this study the energy of the intermediates is apparently not high enough.

Experimental Section

Materials. Imidazole was sublimated at 55 °C (5 Torr) and used within 2 weeks. 1-Fluoro-2,4-dinitrobenzene (Aldrich) was redistilled, bp 121–122 °C (3 Torr). Aniline was twice distilled from KOH and Zn dust and was stored at 0 °C under N_2 in the dark. Dioxane was purified by the method of Fieser[28] and was stored over $LiAlH_4$ from which it was distilled as needed. The solvent dioxane–water 1:10 was made up from 10 mL of *p*-dioxane in 100 mL of solution. Bidistilled water was used throughout.

2,4-Dinitrophenylimidazole and 2,4-dinitrophenylphenylamine from previous work were recrystallized.[29] Reagent grade sodium hydrogen phosphate, sodium bicarbonate, borax, sodium nitrate, and sodium chloride were used without further purification. UV spectra were recorded in a Cary 14 spectrophotometer and the change in optical density during a kinetic run was measured in a Shymadzu spectrophotometer. pH measurements were carried out in a Seybold digital pH meter at 25 °C. The electrode did not work properly at pH higher than 11 thus this pH determination may be erroneous in ∓0.05 pH units.

Kinetic Procedures. Rate constants were determined by following the appearance of the amminolysis or hydrolysis product at 25 ∓ 0.1 °C. 2,4-Dinitrophenylimidazole does not have an absorption maximum at any wavelength useful for determinations, thus the rate was followed by measuring the change in optical density at 310 nm where the difference between the extinction coefficients of substrate and product is highest. In runs were substantial amounts of 2,4-dinitrophenol were formed, it was found convenient to measure the appearance of this product at 400 nm.

In runs reported in Table II, the hydrolysis of the product introduces a consecutive reaction which under the conditions of the experiment is very slow; thus we corrected the infinity absorption by extrapolation.

The yield was calculated from the infinity absorption at 400 nm and the known extinction coefficient of 2,4-dinitrophenol since 2,4-dinitrophenylimidazole does not absorbe at this wavelength. In the reactions of aniline the yield was determined by measuring the optical density of the infinity solution made acidic with 1 M H_2SO_4 in 50% ethanol-water corrected for the small contribution by the 2,4-dinitrophenol.

Runs were set up so that the nucleophile was always in large excess over the substrate, thus pseudo-first-order kinetics were assured for all reactions taking place. In all cases good pseudo-first-order kinetic plots were obtained over 80–90% reaction.

Rate coefficients are symbolyzed and were computed as follows: k_ψ is the pseudo-first-order coefficient for the disappearance of the substrate as determined from the slope of the plot of ln $(A_\infty - A)$ vs. time; k_A is the second-order coefficient for the formation of the aminolysis product and equals k_ψ(fractional yield of aminolysis)/(amine);

k_{OH} is the second-order coefficient for the formation of 2,4-dinitrophenol and equals k_ψ(fractional yield of 2,4-dinitrophenol)/(HO^-).

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Registry No.—1-Fluoro-2,4-dinitrobenzene, 7-34-8; imidazole, 288-32-4; aniline, 62-53-3; 2,4-dinitrophenylimidazole, 14545-01-8; 2,4-dinitrophenol, 51-28-5.

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Some Unusual Oxidation Products of 2,6-Di-*tert*-butyl-4-methylphenol[1]

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The potassium permanganate oxidation of 2,6-di-*tert*-butyl-4-methylphenol (1), adsorbed on a stationary Celite phase, gives several interesting monomeric products in low yields. These products were identified primarily by ^{13}C and ^1H NMR. The products of oxidation of 1 with performic acid and also with oxygen in alkaline ethanol are related and their structures and NMR spectral features are also discussed.

We have been interested in devising a method for oxidizing coal while simultaneously removing the aqueous base-soluble oxidation products from further reaction with the oxidizing agent. In batch processes the fragments cannot be protected from contact with fresh oxidizing agent. Because some coals are, at least partly, phenolic substances,[2,3] we believe that the oxidation fragments derived from the coals in ordinary batch processes may undergo coupling reactions typical of phenols.[4,5] The idea that phenol coupling reactions can lead to erroneous conclusions concerning the structure of coal was expressed earlier by Yohe.[6] Such coupling reactions lead to highly substituted aromatic molecules which ultimately may be broken down to mellitic acid and benzene pentacarboxylic acid, not accurately reflecting the lower degree of aromatic substitution in untreated coal. In our experiments[7] with coal, no mellitic acid could be isolated. Reactions other than coupling, e.g., hydroxylations, ketonizations, and rearrangements, can also occur under strongly basic conditions and a representative product distribution should reflect these reactions. Any interpretation of coal structure, based on oxidation studies, must take into account these chemical transformations. In consideration of these remarks, in part, we undertook a comparative study of the oxidation of 4-methyl-2,6-di-*tert*-butylphenol[7] (1) (BHT) by our method and by the batch method. The purpose of this paper is to describe the structures of some of the neutral, ether-soluble compounds isolated from these reactions.

The batch oxidation procedure of 1 using permanganate initially gives coupled or dimeric products which with an excess of oxidizing agent are converted to acids and carbon dioxide. Our procedure gives mostly acids, some of which we could not identify, and a small yield of neutral monomeric oxidation products. In attempting to independently synthesize some of these compounds, we prepared intermediates by oxidizing 1 with performic acid as well as with oxygen in the presence of alcoholic potassium hydroxide. Structures of the minor products of these reactions are described also.

Our procedure for oxidizing coal[7] consists of grinding it to a fine powder in an inert atmosphere and mixing it intimately with Celite. The mixture is then placed in a chromatographic column, and a solution of potassium permanganate is percolated by gravity feed through the contents of the column. The effluent, which contains the oxidation products, is collected for analysis of its contents. Using this procedure, oxidation takes place in a narrow, well-defined zone. The oxidizing agent is exhausted in that zone and the soluble products which are formed are eluted through the column away from exposure to more oxidizing agent.

Experimental Section

General. 2,6-Di-*tert*-butyl-4-methylphenol was purchased from Aldrich Chemical Co. It was better than 99% pure as determined by GC analysis. It was used as received. Melting points were determined on a Koffler hot bench. IR spectra were determined in CCl_4 solution on a Beckmann IR-8 infrared spectrometer. Carbon–hydrogen analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

NMR spectra were recorded on a Varian XL-100-15 NMR spectrometer. Chemical shifts of the ^1H NMR spectra were measured