Table III. Values of ΔG_t° (from MeOH, kcal/mol) at 298 K for Me_4N^+ and Cl^- [a]

solvent	π^*	α	β	ΔG_t° (Me_4N^+)	ΔG_t° (Cl^-)
acetone	0.68	0.10	0.48	−2.5	9.9
acetonitrile	0.76	0.22	0.31	−1.4	6.1
tert-butyl alcohol	0.40	0.66	1.01	1.9	7.0
2-propanol	0.47	0.77	0.95	0.5	2.6
methanol	0.60	0.98	0.62	0.0	0.0

[a] From ref 21, 39, and: Abraham, M. H.; Danil de Namor, A. F. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 955; *Ibid.* **1978**, *74*, 2101; Kolthoff, I. M.; Chantooni, M. K. *J. Phys. Chem.* **1979**, *83*, 473; *Anal. Chem.* **1979**, *51*, 133.

shown that the term in Cl^- is dominant, suggesting that anion (nucleophilic) solvation is important. For the 11 aliphatic aprotic and hydroxylic solvents for which Parker et al.[50] list available data (based on the Ph_4As^+/Ph_4B^- assumption), we find the regression equation to be eq 6,

$$\Delta G_t^\circ(\mathrm{Tr}) = 0.03 + 0.53\Delta G_t^\circ(\mathrm{Cl}^-) + 0.21\Delta G_t^\circ(\mathrm{K}^+)\ \mathrm{kJ/mol} \quad (6)$$

with $r = 0.991$; this represents a good correlation, only slightly poorer than the π^*/α correlation, for which $r = 0.995$ for 15 similar solvents.

For the *tert*-butyl bromide reaction, again using the data of Parker and co-workers, we find eq 7, with $r = 0.990$ for

$$\Delta G_t^\circ(\mathrm{Tr}) = 0.73 + 0.37\Delta G_t^\circ(\mathrm{Br}^-) + 0.18\Delta G_t^\circ(\mathrm{K}^+)\ \mathrm{kJ/mol} \quad (7)$$

7 solvents (c.f. $r = 0.995$ for the π^*/α correlation over 15 solvents). Again, electrophilic solvation seems more important than nucleophilic solvation, although it is by no means clear how good a model is K^+ for the positive pole in the transition state.

In further support of these conclusions, if the free energies of the ions Me_4N^+ and Cl^- are examined in some moderately dipolar solvents (Table III), it is clear that hydroxylic solvents stabilize Cl^- through electrophilic solvation but do not stabilize Me_4N^+ through nucleophilic solvation [the $\Delta G_t^\circ(Me_4N^+)$ terms becoming more exogenic with increasing solvent dipolarity, but not with increasing solvent HBA basicity]. But if the free ion Me_4N^+ is not nucleophilically solvated, neither will be the Me_4N^+ moiety in the $Me_4N^+Cl^-$ ion pair. Since this ion pair has been shown to be a very good model for the *tert*-butyl chloride transition state,[18,20-22] by implication the latter will also not be nucleophilically solvated by the hydroxylic solvents but will (c.f. Cl^-) be subject to electrophilic solvation.

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Registry No. *t*-BuCl, 507-20-0; *t*-BuBr, 507-19-7; *t*-BuI, 558-17-8.

Nitrations and Oxidations with Inorganic Nitrate Salts in Trifluoroacetic Anhydride

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Metal nitrates in trifluoroacetic anhydride nitrate many aromatic compounds in high yields at room temperature, including polymers with aromatic groups. However, this system oxidizes phenols to quinoid products.

Inorganic nitrate salts have been used in the presence of strong mineral acids to nitrate organic compounds. Numerous examples of their use may be found primarily in the patent literature. Olah has recently reviewed the field of organic nitration reactions employing a variety of inorganic nitrate salts as nitrating agents.[1] Menke has shown that transition-metal nitrate salts, particularly copper nitrate, in acetic anhydride can be used to nitrate certain reactive, aromatic compounds such as phenol.[2] The yields appear to vary widely, and alkali and alkaline earth metal nitrates gave either very poor yields or did not react at all. Trifluoroacetic anhydride[3] (TFAA) and trifluoroacetic acid[4] (TFA) have also been used to a limited extent with nitric acid and form very effective nitrating agents. However, the use of nitrate salts in TFAA has not been investigated as a nitrating agent.

During the course of studies involving transition-metal-catalyzed oxidations of aromatic compounds, it was found that ammonium nitrate and TFAA react with aromatic substrates at 25 °C to produce aromatic nitro compounds in very good yields. Later it was found that it is possible to use any inorganic nitrate salt in TFAA.[5,6] It was decided to pursue this investigation further to determine the optimum reaction conditions and to broaden the scope of this reaction.

Results and Discussion

The general reaction shown in eq 1 may be written to describe the nitration of organic compounds with inorganic nitrate salts in TFAA.

$$\mathrm{ArH} + \mathrm{MNO_3} + (\mathrm{CF_3CO})_2\mathrm{O} \rightarrow \mathrm{ArNO_2} + \mathrm{CF_3CO_2M} + \mathrm{CF_3CO_2H} \quad (1)$$

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(1) G. A. Olah, *Aldrichimica Acta*, **12**(3), 43 (1979).
(2) J. B. Menke, *Recl. Trav. Chem. Pays-Bas*, **44**, 141 (1925).
(3) J. M. Tedder, *Chem. Rev.*, **55**, 287 (1955).
(4) E. J. Bourne, M. Stacey, J. C. Tatlow, and J. M. Tedder, *J. Chem. Soc.*, 1695 (1952).
(5) J. V. Crivello, U.S. Patent 3634520, Jan 11, 1972.
(6) J. V. Crivello, U.S. Patent 3715323, Feb 6, 1973.

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Table I. Nitration of Benzene with Various Acids and Anhydrides[a]

anhydride	% yield of nitrobenzene	acid	% yield of nitrobenzene
$(CF_3CO)_2O$	95	CF_3COOH	69
$(CCl_3CO)_2O$	66	CCl_3COOH	0
$(Cl_2CHCO)_2O$	29	$Cl_2CHCOOH$	0
$(ClCH_2CO)_2O$	0	$ClCH_2COOH$	0
$(CH_3CO)_2O$	0	CH_3COOH	0

[a] 0.01 mol of NH_4NO_3, 70 mL of $CHCl_3$, 5 mL of benzene, and 0.35 mol of acid or anhydride at 25 °C for 2 h.

The rate of the above reaction has been found to be dependent on the solubility of the inorganic nitrate salt in the reaction medium employed. For example, when benzene is nitrated with a mixture of NH_4NO_3 and TFAA at 25 °C in chloroform for 1 h, when a homogeneous solution was formed, the yield of nitrobenzene was 95%. The yield was not increased further when the reaction time was extended to 8 h. Ammonium nitrate has moderate solubility in many organic solvents, and for this reason, it was used in most of these experiments. The reaction is slightly exothermic, but the boiling point of TFAA prevents the temperature from rising above 40 °C. Usually the organic products remain in solution while the byproduct, an inorganic salt of TFA, precipitates and may be removed by filtration.

A brief study was undertaken to determine whether other anhydrides and acids may be substituted for TFAA. The data from these experiments are collected in Table I.

Under the conditions of these reactions, two anhydrides, trichloroacetic anhydride and dichloroacetic anhydride, were useful for the nitration of benzene. There is, however, a marked decrease in the yield of nitrobenzene as one goes from the anhydride of the strongest acid, TFA, to the anhydride of the comparatively weak acid, acetic acid. The reaction of ammonium nitrate with these anhydrides appears to bear a close resemblance to the well-known nitrating agent "acetyl nitrate". Acetyl nitrate may be generated in situ from the reaction of acetic anhydride with nitric acid (eq 2). Presumably heterolytic dissociation of

$$(CH_3CO)_2O + HNO_3 \rightarrow CH_3C(O)ONO_2 + CH_3COOH \tag{2}$$

the oxygen–nitrogen bond gives rise to the nitronium ion which is the true nitrating agent (eq 3). The reaction of

$$CH_3C(O)ONO_2 \rightleftharpoons CH_3C(O)O^- + NO_2^+ \tag{3}$$

TFAA, trichloroacetic anhydride, and dichloroacetic anhydride with metal salts may also generate similar mixed anhydrides which are reactive nitrating agents. With TFAA, trifluoroacetyl nitrate would be formed (eq 4).

$$(CF_3CO)_2O + MNO_3 \rightleftharpoons CF_3C(O)ONO_2 + CF_3C(O)OM$$
$$CF_3C(O)ONO_2 \rightleftharpoons CF_3COO^- + NO_2^+ \tag{4}$$

Attempts to isolate trifluoroacetyl nitrate by distillation led to extensive decomposition. Acetyl nitrate is known to give high ratios of ortho-nitrated products.[7] Similar trends in orientation are seen in the product distributions obtained in TFAA–NH_4NO_3 nitrations. However, in contrast to the rather limited range of substrates which can be nitrated by using acetyl nitrate, trifluoroacetyl nitrate prepared by the present method is a much more efficient and versatile nitrating agent.

Table II. Nitration of Benzene with Various Salts at 25 °C[a]

salt	reaction time, h	yield,[b] %
NH_4NO_3	2	99
$NaNO_3$	15	67
KNO_3	24	98
$Cu(NO_3)_2\cdot 3H_2O$	5	98
$AgNO_3$	15	86
$Pb(NO_3)_2$	15	46
$Cd(NO_3)_2\cdot 4H_2O$	24	93
$Cr(NO_3)_3\cdot 9H_2O$	24	92

[a] 5 mL of benzene, 0.01 mol of nitrate, 0.35 mol of TFAA, and 10 mL of $CHCl_3$. [b] Yield based on nitrate salt.

Since the relative acid strengths of both nitric acid and TFA are of the same order of magnitude,[8] it is not surprising that NH_4NO_3–TFA is an effective nitrating agent for benzene. The following sequence of reactions (eq 5) appear to be involved.

$$CF_3COOH + NH_4NO_3 \rightleftharpoons CF_3COONH_4 + HNO_3 \tag{5a}$$
$$HNO_3 + C_6H_6 \rightleftharpoons C_6H_5NO_2 + H_2O \tag{5b}$$

Since the generation of the nitronium ion is dependent only on a source of nitrate and is independent of the metal cation, it is possible to use any metal nitrate salt in these reactions. Accordingly, a variety of metal nitrate salts were employed for the nitration of benzene, and the results are recorded in Table II.

In general, these reactions proceeded satisfactorily, giving good to excellent yields of products. Both sodium and lead nitrates give poorer yields of nitrobenzene because of their insolubility in the reaction medium. Even after 15 h, these salts had not completely dissolved. When hydrated metal salts were used, as for example $Cu(NO_3)_2\cdot 3H_2O$, the amount of TFAA was increased correspondingly to keep the medium anhydrous. Although in no case were the resulting metal trifluoroacetates purified, it appears that this reaction is also a convenient synthesis for these compounds.

Chloroform has been the solvent most often employed in these reactions; however, a number of other solvents have also been employed. Nitrations have been successfully carried out in hexane, cyclohexane, nitromethane, acetonitrile, chloroform, methylene chloride, and nitrobenzene.

Nitrations carried out in polar solvents such as nitromethane and acetonitrile proceed at a much faster rate than in solvents of lower dielectric constant because of the greater solubility of inorganic salts in these solvents.

In Table III are shown a number of aromatic compounds which have been nitrated with inorganic salts and TFAA to demonstrate the scope of this reaction. Nitration by this procedure is successful with many aromatic and heteroaromatic compounds. Reactivity in deactivated substrates lies between nitrobenzene which is not reactive under these conditions and benzoic acid which nitrates quantitatively in the meta position. The substitution patterns, i.e., ortho > para ≫ meta, are similar to those obtained in nitrations with acetyl nitrate and are generally ascribed to association of the directing group on the ring with the nitronium ion which favors attack at the ortho position rather than the para position which is the site of highest electron density. Compounds such as aniline, which contain a reactive amino group, undergo trifluoro-

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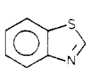
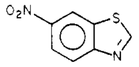
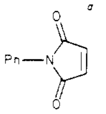
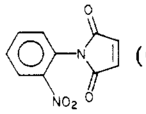
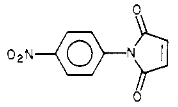
(7) M. J. S. Dewar, T. Mole, D. S. Urch, and E. W. T. Warford, *J. Chem. Soc.*, 3576 (1956).

(8) O. Redlich and G. C. Hood, *Discuss. Faraday Soc.*, *24*, 87 (1957).

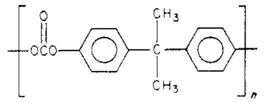
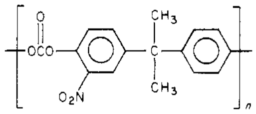
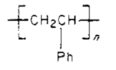
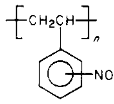
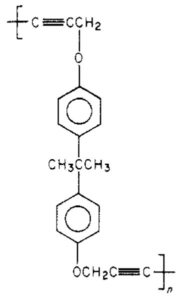
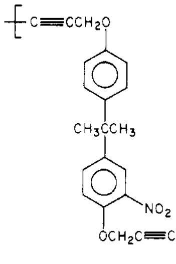
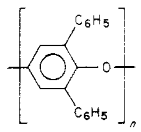
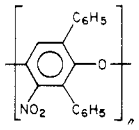
(9) J. V. Crivello, *Synth. Commun.* 3(1), 9 (1973).

Table III. Nitration of Aromatic Compounds at 25 °C

substrate	reaction time, h	products (% yield)
C_6H_6[a]	2	$C_6H_5NO_2$ (95)
$C_6H_5CH_3$[b]	2	o-$NO_2C_6H_4CH_3$ (53), m-$NO_2C_6H_4CH_3$ (>1), p-$NO_2C_6H_4CH_3$ (35)
C_6H_5Cl[b]	2	o-$NO_2C_6H_4Cl$ (20), p-$NO_2C_6H_4Cl$ (80)
C_6H_5COOH[a]	2	m-$NO_2C_6H_4COOH$ (98)
$C_6H_5NH_2$[a]	0.5	o-$NO_2C_6H_4NHC(O)CF_3$ (87)
$C_6H_5NO_2$[c]	2	no reaction
 [b]	2	 (63)
 [a]	2	 (62),  (37)
$C_6H_5OCH_3$[a]	2	o-$NO_2C_6H_4OCH_3$ (55), p-$NO_2C_6H_4OCH_3$ (22)
$C_6H_5OCH_2C{\equiv}CH$[a]	2	o-$NO_2C_6H_4OCH_2C{\equiv}CH$ (48), p-$NO_2C_6H_4$-$OCH_2C{\equiv}CH$ (16)
$C_{10}H_8$[a]	4	1-$NO_2C_{10}H_7$ (88), 2-$NO_2C_{10}H_7$ (trace)
$C_6H_5C_6H_5$[b]	2	o-$NO_2C_6H_4C_6H_5$ (63), p-$NO_2C_6H_4C_6H_5$ (26), $NO_2C_6H_4C_6H_4NO_2$ (mxr ~3)
$C_6H_5OC_6H_5$[d]	3	o-$NO_2C_6H_4OC_6H_4NO_2$-o (52), o-$NO_2C_6H_4$-$OC_6H_4NO_2$-p (13), p-$NO_2C_6H_4OC_6H_4NO_2$-p (18)
$(C_6H_5)_3P$[a]	2	$(C_6H_5)_3PO$
C_6H_6[e]	2	$C_6H_5NO_2$ (86)

[a] 0.01 mol of substrate and NH_4NO_3, 0.035 mol of TFAA, and 10 mL of $CHCl_3$. [b] Same as *a* but without $CHCl_3$. [c] 0.01 mol of substrate, 0.02 mol of NH_4NO_3, and 0.07 mol of TFA. [d] Same as *c* but with 10 mL of $CHCl_3$. [e] 0.01 mol of substrate and $NaNO_2$, 0.35 mol of TFAA, and 10 mL of $CHCl_3$.

Table IV. Nitration of Polymers with NH_4NO_3-TFAA at 25 °C

polymer	$[\eta]_0$[a]	reaction time, h	product	$[\eta]$[b]
	0.56	15		0.29
	0.19	15		0.18
	0.92	4		0.86
	1.1	15		0.95

[a] $[\eta]_0$ intrinsic viscosity (g/dL) in DMF before nitration. [b] $[\eta]$ intrinsic viscosity (g/dL) in DMF after nitration.

acetylation prior to nitration. Substrates containing acid-sensitive acetylenic groups such as phenyl propargyl ether are smoothly converted to their nitro compounds under the mild conditions of this reaction. Since this method introduces only one nitro group per aromatic ring and because the stoichiometry can be easily controlled, it is possible to introduce preferentially either one or two nitro groups into compounds such as biphenyl and diphenyl ether. The reaction of benzene with $NaNO_2$–TFAA is an example of nitrosation/oxidation. During the reaction, a transient green color was observed which is indicative of the presence of nitrosobenzene. This color rapidly faded as the reaction proceeded and was replaced by the pale yellow color of nitrobenzene.

The nitration of polymeric substrates by conventional nitration methods presents two major problems: inhomogeneous nitration due to solubility difficulties and degradation of polymer molecular weight due to cleavage of sensitive bonds. In contrast, polymers containing aromatic groups in their backbones undergo smooth homo-

Table V. Oxidation of Substituted Phenols with NH_4OH-TFAA at 25 °C

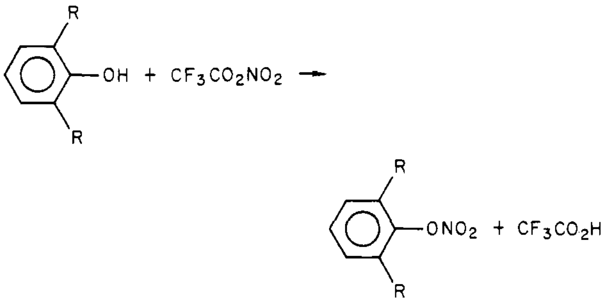
phenol	solvent	product (% yield)	mp, °C	ref
2,6-di-*tert*-butylphenol	$CHCl_3$	3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (83)	241	12
2,6-dimethoxyphenol	CH_3COOH	3,3′,5,5′-tetramethoxydiphenoquinone (41)	284-285	13
2,6-dimethylphenol	CH_3COOH	3,3′,5,5′-tetramethyldiphenoquinone (45)	184-185	14
2,6-diphenylphenol	CH_3COOH	3,3′,5,5′-tetraphenyldiphenoquinone (1)	290 dec	15
		2,6-diphenyl-1,4-benzoquinone (87)	129-132	16
tetrachlorohydroquinone	$CHCl_3$	tetrachloro-1,4-benzoquinone (98)	290	17
pentachlorophenol	$CHCl_2$	tetrachloro-1,2-benzoquinone (80)	122-126	18
		tetrachloro-1,4-benzoquinone (8.5)	290	

geneous nitration at room temperature by NH_4NO_3–TFAA mixtures in a nonreactive solvent for the polymer. These reactions are summarized in Table IV. Only in the case of the very hydrolytically sensitive polycarbonate was there evidence of slight molecular weight reduction in these polymers as indicated by intrinsic viscosity measurements. In each case, only one nitro group per repeating unit was introduced as determined by infrared and NMR spectroscopy.

With certain substrates, oxidation rather than nitration is observed as the major reaction. For example, mixtures of TFAA and NH_4NO_3 oxidizes cycloheptatriene to the tropylium salt[9] and triphenylphosphine to triphenylphosphene oxide. Similarly, when phenols are treated with inorganic salts in TFAA, nitrated compounds are not obtained as the major products; instead, quinoid compounds resulting from carbon–oxygen coupling and carbon–carbon coupling are produced.[10] The type of quinoid product obtained is determined by the presence and character of the group or groups substituted on the aromatic ring in positions ortho and para to the hydroxyl group.[11] Table V shows the results of the oxidation of several substituted phenolic substrates.

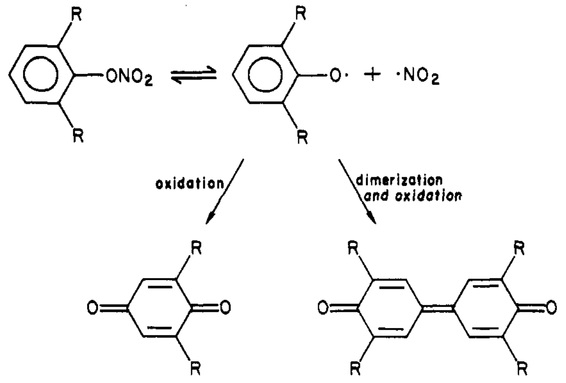
Phenols having two or more open ortho or para positions give mixtures of products. Phenol itself is readily oxidized with ammonium nitrate in TFAA to give a variety of products among which have been identified 1,2- and 1,4-benzoquinone. The tendency toward carbon–carbon coupling is enhanced when the positions on the aromatic nucleus immediately adjacent to the hydroxyl group are occupied by bulky alkyl or alkoxy substituents. For example, the oxidation of 2,6-di-*tert*-butylphenol gives exclusively 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone. Electron-withdrawing substituents such as phenyl in the 2- and 6-positions favor the formation of the 1,4-benzoquinone.

The formation of products in the above cases can be explained by proposing the initial formation of a phenyl nitrate ester (eq 6). Since aromatic nitrate esters are



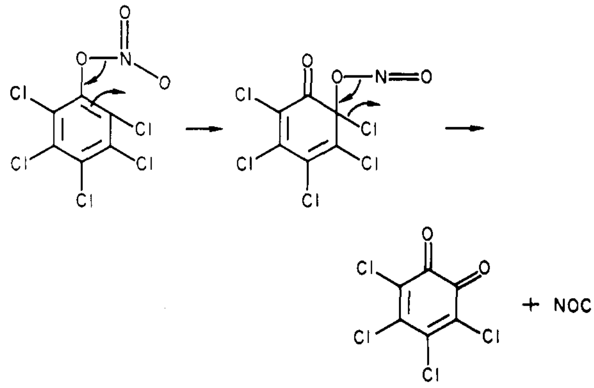
(6)

Scheme I



unstable, they undergo rapid homolytic cleavage to generate as one fragment, the phenoxy radical (see Scheme I). Depending on the nature of R, the phenoxy radical can be either oxidized to the 1,4-benzoquinone or undergo dimerization and further oxidization to the diphenoquinone.

Treatment of pentachlorophenol with NH_4NO_3–TFAA in CH_2Cl_2 results in the predominant formation of tetrachloro-1,2-benzoquinone by oxidative dechlorination. The formation of this product can be viewed as proceeding from the intermediate phenyl nitrate ester by the process shown in eq 7.



(7)

The high yield of tetrachloro-1,2-benzoquinone obtained in this reaction makes this a convenient preparative route for its synthesis.

Experimental Section

Starting Materials. All inorganic reagents were used as purchased from their suppliers. Organic substrates, solvents, acids, and anhydrides were assayed for purity by GLC and purified where necessary by conventional techniques.

General Procedure for the Nitration of Aromatic Compounds. Into a 50-mL, single-necked, round-bottomed flask equipped with a magnetic stirrer, reflux condenser, and drying tube were placed 0.01 mol of the aromatic substrate, 0.01 mol of the inorganic nitrate salt, and 5 mL (0.035 mol) of TFAA. In those cases in which the inorganic salt was hydrated or when no other solvent was present, 10 mL of TFAA was used. Next, 10 mL of the appropriate solvent was added, and the reaction was allowed

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(10) J. V. Crivello, U.S. Patent 3678081, July 18, 1973.

(11) W. I. Taylor and A. R. Battersby, Eds., "Oxidative Coupling of Phenols", Marcel Dekker, New York, 1967.

(12) S. J. Metro, *J. Am. Chem. Soc.*, 77, 2901 (1955).

(13) C. G. Haynes, A. H. Turner, and W. A. Waters, *J. Chem. Soc.*, 2823 (1956).

(14) R. G. R. Bacon and A. R. Izzat, *J. Chem. Soc.*, 791 (1966).

(15) J. Plesek, *Chem. Listy*, 50, 246 (1956).

(16) H. Finkbeiner and A. M. Toothaker, *J. Org. Chem.*, 33, 4347 (1968).

to proceed with stirring at room temperature. Reaction times were of the order of 1–5 h, and the reaction was complete when all the inorganic salt had dissolved.

The reaction mixture was poured into 50 mL of water and extracted three times with 15-mL portions of chloroform. Products were isolated by trapping from GLC and characterized by comparing their infrared, NMR, and mass spectra with those from authentic samples of the compounds.

General Procedure for the Nitration of Benzene with Acids and Anhydrides Other Than TFA and TFAA. By the same procedure as described above, 5 mL of benzene was nitrated with 0.01 mol (0.80 g) of ammonium nitrate in 70 mL of $CHCl_3$. In these cases, TFAA was replaced by 0.35 mol of the appropriate acid or anhydride. Reactions were carried out at 25 °C for 2 h, and the products were analyzed by GLC.

General Procedure for the Nitration of Polymers. Into a 100-mL resin flask equipped with a reflux condenser, magnetic stirrer, and drying tube were placed 0.02 mol (based on segmer molecular weight) of the polymer, 0.02 mol of NH_4NO_3, 70 mL of chloroform, and 10 mL of TFAA. In most cases, the reaction mixture was stirred at room temperature for 15 h, although the salt had dissolved within 3 h. During this time, the polymer solution took on a yellow or orange color. The polymers were precipitated into either *n*-hexane or methanol, washed with water, and dried at 60 °C in vacuo.

General Procedure for the Oxidation of Phenols. To a 100-mL single-neck flask equipped with a magnetic stirrer, reflux condenser, and drying tube were placed 0.01 mol of the phenol, 0.02 mol of NH_4NO_3, 0.05 mol of TFAA, and 50 mL of the indicated solvent. Reaction occurred spontaneously, and the reaction temperature was controlled by placing the flask in a water bath at 25 °C. The reaction was complete within 2–5 h when the inorganic salt had dissolved. In all cases the product was insoluble in the medium and was recovered by filtration. After the quinone was washed with a small amount of the reaction solvent, it was dried for 15 h in a vacuum oven.

Oxidation of Pentachlorophenol. Into a 500-mL reaction vessel equipped with a stirrer, thermometer, reflux condenser, and drying tube were placed 26.6 g (0.01 mol) of pentachlorophenol, 8 g (0.1 mol) of NH_4NO_3, and 300 mL of methylene chloride. To this mixture was added 20 mL (0.13 mol) of TFAA, and the reaction mixture was stirred in a water bath for 4 h at 25–30 °C. The reaction mixture was filtered to remove impure tetrachloro-1,4-benzoquinone, and the solvent was removed from the filtrate by means of a rotary evaporator. The solid which remained was dissolved in hot cyclohexane, filtered, and allowed to crystallize to give 19.74 g (80% yield) of tetrachloro-1,2-benzoquinone, mp 122–126 °C (lit.[18] mp 121–127 °C). Anal. Calcd for $C_6Cl_4O_2$: C, 29.27; Cl, 57.24; O, 13.49. Found: C, 29.16; Cl, 57.55; O, 13.29. Further workup of the impure tetrachloro-1,4-benzoquinone gave an 8.5% yield of pure quinone, mp 290 °C (lit.[17] mp 290 °C).

Registry No. $(CF_3CO)_2O$, 407-25-0; $(CCl_3CO)_2O$, 4124-31-6; $(Cl_2CHCO)_2O$, 4124-30-5; CF_3COOH, 76-05-1; NH_4NO_3, 6484-52-2; $NaNO_3$, 7631-99-4; KNO_3, 7757-79-1; $Cu(NO_3)_2$, 3251-23-8; $AgNO_3$, 7761-88-8; $Pb(NO_3)_2$, 10099-74-8; $Cd(NO_3)_2$, 10325-94-7; $Cr(NO_3)_3$, 13548-38-4; $NaNO_2$, 7632-00-0; C_6H_6, 71-43-2; $C_6H_5CH_3$, 108-88-3; C_6H_5Cl, 108-90-7; C_6H_5COOH, 65-85-0; $C_6H_5NH_2$, 62-53-3; benzothiazole, 95-16-9; 1-phenyl-1*H*-pyrrole-2,5-dione, 941-69-5; $C_6H_5OCH_3$, 100-66-3; $C_6H_5OCH_2C\equiv CH$, 13610-02-1; C_8H_{10}, 91-20-3; $C_6H_5C_6H_5$, 92-52-4; $C_6H_5OC_6H_5$, 101-84-8; $(C_6H_5)_3P$, 603-35-0; poly[oxycarbonyloxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene], 24936-68-3; ethyenylbenzene homopolymer, 9003-53-6; poly[oxy-2,4-hexadiyne-1,6-diyloxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene], 41227-07-0; poly(oxy[1,1′:3,1″-terphenyl]-2′,5′-diyl), 24938-68-9; 2,6-di-*tert*-butylphenol, 128-39-2; 2,6-dimethoxyphenol, 91-10-1; 2,6-dimethylphenol, 576-26-1; 2,6-diphenylphenol, 2432-11-3; tetrachlorohydroquinone, 87-87-6; pentachlorophenol, 87-86-5; $C_6H_5NO_2$, 98-95-3; *o*-$NO_2C_6H_4CH_3$, 88-72-2; *m*-$NO_2C_6H_4CH_3$, 99-08-1; *p*-$NO_2C_6H_4CH_3$, 99-99-0; *o*-$NO_2C_6H_4Cl$, 88-73-3; *p*-$NO_2C_6H_4Cl$, 100-00-5; *m*-$NO_2C_6H_4COOH$, 121-92-6; *o*-$NO_2C_6H_4NHC(O)CF_3$, 2727-72-2; 6-nitrobenzothiazole, 2942-06-5; 1-(2-nitrophenyl)-1*H*-pyrrole-2,5-dione, 52274-95-0; 1-(4-nitrophenyl)-1*H*-pyrrole-2,5-dione, 4338-06-1; *o*-$NO_2C_6H_4OCH_3$, 91-23-6; *p*-$NO_2C_6H_4OCH_3$, 100-17-4; *o*-$NO_2C_6H_4OCH_2C\equiv CH$, 13350-09-9; *p*-$NO_2C_6H_4OCH_2C\equiv CH$, 17061-85-7; 1-$NO_2C_{10}H_7$, 86-57-7; 2-$NO_2C_{10}H_7$, 581-89-5; *o*-$NO_2C_6H_4C_6H_5$, 86-00-0; *p*-$NO_2C_6H_4C_6H_5$, 92-93-3; *o*-$NO_2C_6H_4C_6H_4NO_2$-*o*, 2436-96-6; *o*-$NO_2C_6H_4C_6H_4NO_2$-*p*, 606-81-5; *p*-$NO_2C_6H_4C_6H_4NO_2$-*p*, 1528-74-1; *o*-$NO_2C_6H_4OC_6H_4NO_2$-*o*, 2217-65-4; *o*-$NO_2C_6H_4OC_6H_4NO_2$-*p*, 5950-83-4; *p*-$NO_2C_6H_4OC_6H_4NO_2$-*p*, 101-63-3; $(C_6H_5)_3PO$, 791-28-6; carbonic acid, polymer with 4,4′-(1-methylethylidene)bis[phenol], 25037-45-0; 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone, 2455-14-3; 3,3′,5,5′-tetramethoxydiphenoquinone, 493-74-3; 3,3′,5,5′-tetramethyldiphenoquinone, 4906-22-3; 3,3′,5,5′-tetraphenyldiphenoquinone, 3550-01-4; 2,6-diphenyl-1,4-benzoquinone, 2887-97-0; tetrachloro-1,4-benzoquinone, 118-75-2; tetrachloro-1,2-benzoquinone, 2435-53-2.

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(17) E. Clar and M. Zander, *J. Chem. Soc.*, 4616 (1957).

(18) W. H. Chang, *J. Org. Chem.*, 27, 2921 (1962).

Nucleophilic Substitutions on 1,2-Dihydro-2,2-disubstituted-3-oxo-3*H*-indole-1-oxyl Radicals. Direct Acyloxylation and Methoxylation

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1,2-Dihydro-3-oxo-3*H*-indole-1-oxyl (1) undergoes direct acyloxylation and methoxylation on the indole ring when treated with lead(IV) in the presence of acyl anions or methanol. The reaction has been interpreted by assuming the intermediate formation of an oxoammonium salt.

On the basis of their structure, nitroxide radicals can be divided into two main groups:[1] (i) stable nitroxides, with the unpaired electron localized on the N-O· group, i.e., 2,2,6,6-tetramethylpiperidine-1-oxyl or 2,2,5,5-pyrrolidine-1-oxyl, and (ii) relatively stable nitroxides with the unpaired electron delocalized in the molecule through the conjugated π system, i.e., alkyl aryl or diaryl nitroxides. The well-studied chemical behavior of the two different groups (e.g., reduction to hydroxylamines,[2] oxidation to

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(1) (a) A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals", Academic Press, London, New York, 1968, p 180; (b) J. F. W. Keana, *Chem. Rev.*, 78, 37 (1978).

(2) C. Berti, L. Greci, and M. Poloni, *J. Chem. Soc.*, *Perkin Trans. 2*, 710 (1980).

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