CF_3COOH (0.4 M) was warmed for 8 h at 65 °C. The solution was made basic with 10% NaOH, extracted with ether, and analyzed by GLC. The results are reported in Tables I–VIII.

h. Benzylation by Toluene and Perkadox. A toluene solution (20 mL) of heteroaromatic base (0.2 M), perkadox (0.05 M), and CF_3COOH (0.4 M) was heated for 3 h at 70 °C. The solution was washed with 10% NaOH and analyzed by GLC. The results are reported in Tables IV–VI.

i. Isopropylation of Pyridine by *i*-PrI and Diazonium Salt in Me_2SO. A solution of 1.6 mmol of *p*-chlorobenzenediazonium tetrafluoroborate in 3 mL of Me_2SO was added dropwise with stirring over a period of 30 min to a mixture of 35 mmol of heteroaromatic base, 7 mmol of CF_3COOH, 4 mmol of *i*-PrI, 0.5 mmol of Cu powder, and 0.05 mmol of $Cu(OAc)_2$ in 10 mL of Me_2SO at 40 °C. The solution was diluted with 30 mL of water, made basic with 10% NaOH, extracted with EtOAc, and analyzed by GLC. The results are reported in Table I.

All the reaction products have been identified by comparison with authentic samples previously obtained by similar procedures.[6]

Relative Rates. The relative rates shown in Tables IV, VI, and VII were determined by the competitive method, using pairs of heteroaromatic bases according to the procedures reported in the tables and analyzing the reaction products by GLC.

Isotope Effect. The isotope effects shown in Table VIII were determined by the competitive method, using equimolecular amounts of pyridine and deuteriated pyridine according to the procedures reported in the table. The α- and γ-isomers (as mixtures of deuteriated and nondeuteriated derivatives) were isolated by silica gel chromatography (eluent hexane–EtAc, 7:3) and analyzed by mass spectrometry, checking the reliability of the method starting from the known mixtures of the pure isomers obtained from pyridine and deuteriated pyridine.

Acknowledgment. This work was supported by "Progetto Finalizzato Chimica Fine e Secondaria", CNR, Roma, Italy.

Registry No. 2-THF·, 19426-60-9; Ph·, 2396-01-2; Me·, 2229-07-4; *n*-Pr·, 2143-61-5; *i*-Pr·, 2025-55-0; *n*-Bu·, 2492-36-6; *t*-Bu·, 1605-73-8; $PhCH_2$·, 2154-56-5; D_2, 7782-39-0; pyridine conjugate acid, 16969-45-2; quinaldine conjugate acid, 41229-56-5; lepidine conjugate acid, 41229-57-6; 3-cyanopyridine conjugate acid, 53760-43-3; 4-cyanopyridine conjugate acid, 37449-63-1; 1,4-dioxan-2-yl, 4598-47-4.

Carbanions: Electron Transfer vs. Proton Capture. 8. Use of Sterically Protected Aromatic Nitro Compounds as Base-Resistant, One-Electron Oxidants

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The behavior of two sterically protected nitroarenes, 2,4,6-tri-*tert*-butylnitrobenzene and 1,1,4,4,5,5,8,8-octamethyl-1,2,3,4,5,6,7,8-octahydro-9-nitroanthracene, was studied in the presence of strong bases. These compounds are resistant to the oxygen-base-promoted reactions observed with nitrobenzene, but they retain the capacity to oxidize carbon bases such as 9-methoxyfluorenide and triphenylmethide ions. Alkyllithium compounds are converted to alkyl radicals but phenyllithium does not react. Unexpectedly, the radical anions formed when these nitro compounds serve as oxidants undergo slow denitration to the corresponding aryl radicals.

Nitroarenes are useful as oxidants in strongly basic media[1,2] because they combine resistance to base and nucleophile attack with ease of one-electron reduction. For nitroarenes unsubstituted in the 2- or 6-positions, strong bases can remove a proton ($A_{xh}D_H$)[3] to produce a nitro-stabilized phenyl anion. Minimal conditions for this reaction to occur with nitrobenzene are potassium *tert*-butoxide in *tert*-butyl alcohol at 50 °C,[4] suggesting a pK_a in the high twenties.[5] While this reaction is usually reversible and nondestructive, a more serious complication arises when the hydrogen-bonding stabilization of *tert*-butyl alcohol is removed. In tetrahydrofuran (THF), potassium *tert*-butoxide at 25 °C, nucleophilic attack at a ring carbon is followed by proton removal to produce a dianion finally giving alkoxy-substituted nitroarene and 2 equiv of radical anion ($A_N + A_{xh}D_H + 2T$).[3,6]

It seemed reasonable that replacement of ring hydrogens, particularly those ortho and para to the nitro group, with nonacidic, bulky alkyl groups would increase the resistance of nitroarenes to attack by bases and nucleophiles. Of course such substituents, when positioned ortho to the nitro group, interfere with the radical-anion stabilizing coplanarity of the $NO_2^{\bullet-}$ group and the aromatic ring. The reduction potential of 2,4,6-tri-*tert*-butylnitrobenzene is $E_{1/2} = -1.50$ V vs. SCE in acetonitrile[7] as compared to nitrobenzene, $E_{1/2} = -1.15$ V[8] under the same conditions.

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(1) For a review, see: Guthrie, R. D. In "Comprehensive Carbanion Chemistry", Buncel, E.; Durst, T. Eds.; Elsevier: Amsterdam, 1980, pp 197–269.

(2) Preceding papers in this series are: (a) Guthrie, R. D.; Hrovat, D. A; Prahl, F. G.; Swan, J. *J. Org. Chem.* **1981**, *46*, 498–501. (b) Guthrie, R. D.; Cho, N. S. *J. Am. Chem. Soc.* **1979**, *101*, 4698–4705.

(3) "A" and "D" indicate associative and dissociative processes respectively. "T" indicates electron transfer. "A" and "D" symbols are subscripted in various ways to indicate the apportionment of electrons. "A_N" thus indicates bond formation between a core atom (for a substitution reaction this is the atom at which substitution takes place) and a nucleophile. "D_H" represents bond breaking between a proton and a core atom. "A_{xh}" is bond formation between a proton and a generalized base (x). Lower case subscripts indicate that no core atom is involved in the bond being made or broken. "+" Signs indicate a new (nonconcerted) reaction step ($S_N2 = A_ND_N$, $S_N1 = D_N + A_N$). Commission on Physical Organic Chemistry, IUPAC, Pure and Applied Chemistry, in press. A primitive version of this system was published earlier: Guthrie, R. D. *J. Org. Chem.* **1975**, *40*, 402–407.

(4) Guthrie, R. D.; Wesley, D. P. *J. Am. Chem. Soc.* **1970**, *92*, 4057–4062.

(5) This is a localized anion so the pK_a should be greater in polar, nonhydroxylic medium.

(6) Guthrie, R. D.; Nutter, D. E. *J. Am. Chem. Soc.* **1982**, *104*, 7478–7482.

(7) Geske, D. H.; Ragle, J. L.; Bambenek, M. A.; Blach, A. L. *J. Am. Chem. Soc.* **1964**, *86*, 987–1002.

(8) Maki, A. H.; Geske, D. H. *J. Chem. Phys.* **1960**, *33*, 825–832; *J. Am. Chem. Soc.* **1961**, *83*, 1852–1860.

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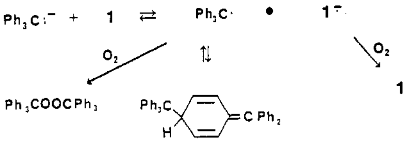
Scheme I

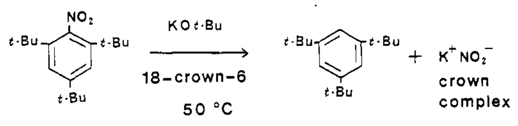


Nevertheless, it might be expected that such compounds could still be effective carbanion oxidants if the deficit in reduction potential was counterbalanced by the increased carbanion concentrations accessible in the presence of stronger bases. Moreover, more difficultly accessible carbanions (from weaker carbon acids) would normally be more readily oxidized.[9] We decided to explore the relative importance of these factors for two available alkylated nitroarenes.

Results and Discussion

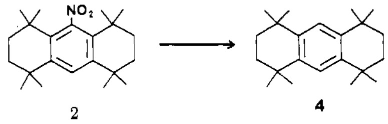
As expected, 2,4,6-tri-*tert*-butylnitrobenzene (1) and 1,1,4,4,5,5,8,8-octamethyl-1,2,3,4,5,6,7,8-octahydro-9-nitroanthracene (2) are stable in potassium *tert*-butoxide/THF (48 h at 50 °C with 0.35 M base) and in a number of other highly basic, nucleophilic media such as potassium *tert*-butoxide in hexamethylphosphoric triamide (HMPA) or dipropylsulfoxide (Pr_2SO),[10] sodium bis(trimethylsilyl)amide in THF, or even phenyllithium in THF.[11]

When 1 or 2 was treated with a solution of potassium *tert*-butoxide in THF containing 18-crown-6 ether,[12] a precipitate of the crown ether complex of potassium nitrite was observed. Workup gave the hydro-de-nitration[13] products 3 and 4 from 1 and 2, respectively, as shown in eq 1 and 2. To the best of our knowledge, this is a new reaction of nitroarenes. When 1 equiv of triphenylmethane was included in the reaction mixture described above, the yield of 3 and 4 increased, suggesting that electron transfer from the potassium salt of triphenylmethyl carbanion promotes hydro-de-nitration. The nature of the electron donor when 18-crown-6 and potassium *tert*-butoxide react with 1 and 2 in the absence of triphenylmethane was not determined, but products of crown ether decomposition were detected by NMR.



(1)

1 3

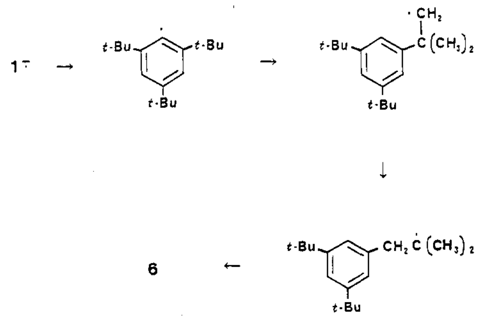


(2)

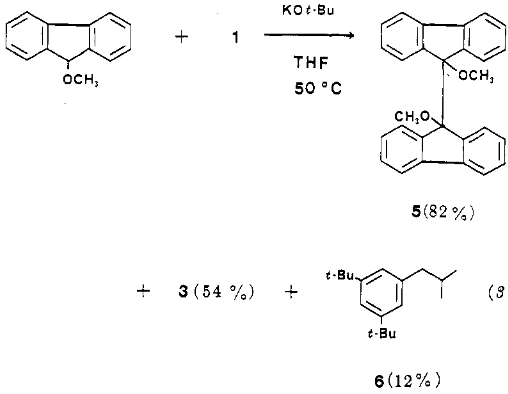
2 4

More direct evidence for electron transfer from triphenylmethide ion was obtained by treating (triphenylmethyl)lithium with 1 in THF. The red solution immediately changed to orange-red and displayed the characteristic ESR triplet for $1^{\bullet-}$. The lithium salt of $1^{\bullet-}$ did not undergo hydro-de-nitration to any significant extent over a period of several hours at 25 °C. Addition of 1 equiv of O_2 eliminated the ESR signals from $1^{\bullet-}$. After a few minutes, the spectrum of triphenylmethyl radical appeared. This suggests the sequence shown in Scheme I. (Triphenylmethyl)lithium is oxidized to triphenylmethyl radical which dimerizes.[14] The amount of triphenylmethyl radical in equilibrium with its dimer is known to be about 2%, and its spectrum is therefore overwhelmed by the intense spectrum of $1^{\bullet-}$. When the solution is mixed with O_2, $1^{\bullet-}$ is destroyed immediately as is the small amount of undimerized radical. On standing, the O_2 remaining in solution is consumed by triphenylmethyl radical generated from its dimer, and the spectrum of triphenylmethyl radical appears. Shaking the reaction vessel again removes the radical but its spectrum slowly reappears.

Scheme II



To more firmly establish the connection between radical anion generation and the hydro-de-nitration transformation, a carbanion undergoing previously characterized nitroarene-promoted oxidation was selected for study. Treatment of 9-methoxyfluorene[15] with 1 or 2 in 0.24 M potassium *tert*-butoxide in THF at 50 °C for 48 h caused both 1 and 2 to undergo extensive hydro-de-nitration. The dimer of 9-methoxyfluorenyl radical (5) was formed in 82% yield with 1 and 78% yield with 2. In the case of 1, 3 was produced in 54% yield but 12% of 3,5-di-*tert*-butyl-1-isobutylbenzene (6) was also isolated as shown in eq 3.



(3)

The presence of 6 constitutes evidence for the intermediacy of 2,4,6-tri-*tert*-butylphenyl radical through the sequence of Scheme II. This radical has been generated through the reaction of trimethyltin radicals[16] with 2,4,6-tri-*tert*-butylbromobenzene and, at the temperature of our experiments is known to follow the rearrangement sequence of Scheme II.[16c]

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[9] Bordwell, F. G.; Clemens, A. H. *J. Org. Chem.* **1982**, *17*, 2510–2516.

[10] Dimethyl sulfoxide was not a suitable solvent due to low solubility of 1 and 2.

[11] Compounds 1 and 2 were destroyed by lithium diisopropylamide in THF. The products were not identified.

[12] 1,4,7,10,13,16-Hexaoxacyclooctadecane.

[13] We employ the convention for naming substitution transformations recommended by the IUPAC Commission on Physical Organic Chemistry, *Pure and Applied Chemistry*, in press.

[14] For a summary and leading references, see: March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley, New York, 1985; pp 164–165.

[15] Guthrie, R. D.; Pendygraft, G. W.; Young, A. T. *J. Am. Chem. Soc.* **1976**, *98*, 5877–5883.

[16] (a) Brunton, G.; Gray, J. A.; Griller, D.; Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1978**, *100*, 4197–4200. (b) Brunton, G.; Griller, D.; Barclay, L. R. C.; Ingold, K. U. *Ibid.* **1976**, *98*, 6803–6811. (c) Maillard, B.; Ingold, K. U. *Ibid.* **1976**, *98*, 1224–1226.

When **2** was employed as oxidant with 9-methoxyfluorene under the same conditions, the results were similar with **5** being formed in 78% yield along with 79% of **4**. No rearrangement was observed with **2**.

Finally, the interaction of **1** and **2** with alkyllithium compounds was studied. It was found that the nitro compounds reacted instantaneously with methyllithium, butyllithium, or octyllithium in THF or DME to produce a solution of the lithium salts of $1^{\bullet-}$ or $2^{\bullet-}$. Radical ion production was essentially quantitative, and the procedure proved to be a convenient method for preparation of stable solutions of $1^{\bullet-}$ (at 25 °C), useful for the preparation of radical anions from other nitroarenes.[17] Interestingly, THF solutions of the lithium salts of $1^{\bullet-}$ and $2^{\bullet-}$ did not undergo the hydro-de-nitration reaction even at 50 °C for 48 h. Quenching of the radical anion ($1^{\bullet-}$) solution with oxygen-free water gave only **1** and 2,4,6-tri-*tert*-butylaniline in the amounts anticipated. In the case of reaction with octyllithium, both **1** and **2** produced hexadecane in approximately 50% of the theoretical amount. Use of excess octyllithium did not change this result. It is assumed that the other products were octane and octene but no attempt was made to separate these volatile products from solvent.

The rapidity of the oxidation–coupling sequence was demonstrated by adding butyllithium and octyllithium solutions simultaneously but separately to a vigorously stirred THF solution of **1**. No dodecane was observed. When the two alkyllithium solutions were mixed prior to injection into the reaction solution, dodecane was the major nonvolatile product.

Aside from coupling reactions, no success was encountered in attempts to trap the alkyl radicals presumed to be produced in these reactions. Both naphthalene[18] and triphenylmethide ion[19] had previously been observed to react with methyl radicals; however, the expected products from reaction with these reagents were not observed when the reagents were mixed with **1** prior to addition of methyllithium. We believe that an explanation lies in the fact that the previous methyl radical trapping procedures were used under conditions where methyl radicals were generated in relatively slow processes and thus were present at very low concentrations. Self-coupling of simple radicals is extremely fast, $k = 10^9–10^{10}\ \mathrm{M^{-1}\ s^{-1}}$.[20] Thus, even when both **1** and methyllithium are added dropwise from opposite sides of a stirred reaction vessel containing a high concentration of trapping agent, it can be safely predicted that the relatively high concentration of methyl radical extant during the lifetimes of the vast majority of radicals will dictate essentially exclusive formation of radical–radical combination products. In the case where (triphenylmethyl)lithium was present, a small amount of 1,1,1-triphenylethane was detected, but this is the expected product of coupling between triphenylmethyl radical and methyl radical.[21] No tolyldiphenylmethane, expected[19] from methyl radical and triphenylmethide ion, could be detected.

Summary and Conclusions

Compounds **1** and **2** are resistant to reaction with basic and nucleophilic reagents except when electron transfer is possible. Alkoxide ions, even under conditions of minimal solvational stabilization, and phenyllithium do not react. Easily oxidized carbanions and alkyllithium compounds give electron transfer. We anticipate that **1** and **2** will be useful for diverting base- and nucleophile-promoted reactions into radical pathways by trapping easily oxidized intermediates. The potassium salts of nitroarene radical anions $1^{\bullet-}$ and $2^{\bullet-}$ undergo unprecedented conversion to aryl radicals.

Experimental Section

Solvents and Reagents. Tetrahydrofuran (THF) was purified by distillation from sodium benzophenone ketyl. Hexamethylphosphoric triamide (HMPA) was distilled from calcium hydride at 0.3 torr. Dipropyl sulfoxide (Pr_2SO) was generously donated by Phillips 66 Petroleum Co. and was purified by distillation at 0.3 torr. Potassium *tert*-butoxide was purified by vacuum sublimation and transferred in a nitrogen atmosphere glove box. Butyllithium and methyllithium were commercial products (Aldrich). Octyllithium and phenyllithium were prepared by standard procedures.[22] 2,4,6-Tri-*tert*-butylnitrobenzene (**1**) was used as obtained from Aldrich Chemical Co. In some batches, a small amount of 1,3,5-tri-*tert*-butylbenzene (**3**) was present. 18-Crown-6[12] was used as obtained from Aldrich Chemical Co. Preparation and purification of 9-methoxyfluorene was described earlier.[15] All other solvents and reagents were reagent-grade commercial products.

Preparation of 1,1,4,4,5,5,8,8-Octamethyl-1,2,3,4,5,6,7,8-octahydro-9-nitroanthracene (2). The required arene was prepared directly from benzene employing a modification of the procedure of Barclay[23] which, in his case, started with 1,4-di-*tert*-butylbenzene. Freshly distilled benzene (24.7 mL, 0.29 mol) in 100 mL of CH_2Cl_2 was cooled to −10 °C and anhydrous $AlCl_3$ (38.7 g, 0.143 mol) was added. *tert*-Butyl chloride (217 mL, 2.0 mol) was added to the stirred mixture over 50 min at −5 to −10 °C. The reaction mixture was stirred for an additional 2 h at −10 °C during which time reaction progress was monitored by gas chromatography on a 17 ft × 1/4 in column of SF-96 on Chromosorb W. 1,3,5-Tri-*tert*-butylbenzene (**3**) was observed to form and then disappear, and **4** appeared. When the peak corresponding to **3** decreased to a few percent of the total peak area and the relative peak area for **4** no longer increased (ca. 3 h total reaction time including addition period), the entire mixture was added to 2 L of crushed ice and extracted with 1.5 L of CH_2Cl_2. Washing with 1 L water, drying over Na_2SO_4, and evaporation of CH_2Cl_2 gave 13.8 g of white crystals, mp 203–207 °C. Recrystallization from ether–ethanol gave 8.5 g (61%) of **4**, mp 210–212 °C. This material was used for nitration as several additional recrystallizations were required to raise the melting point to 223–224 °C [lit.[23a] mp 218.5–219 °C].

Nitration was carried out as described by Barclay[23a] to give **2** in 51% yield, mp 259–262 °C. Several recrystallizations from CH_2Cl_2–ethanol gave crystals mp 263.5–265 °C [lit.[23a] 266.5–267 °C]. This material contained less than 1% of GC observable impurities. The major impurity in initially isolated **2** was **4**.

Treatment of 1 and 2 with Strong Bases. Samples of **1** and **2** (0.20 to 0.26 mmol) were treated separately with 1.5 mL of 0.5 M potassium *tert*-butoxide in HMPA, Pr_2SO, or THF. Additional samples of **1** and **2** (0.20 mmol) were treated with 2 mL of 0.27 M $(Me_3Si)_2NNa$ in THF. All solutions were prepared under oxygen-free argon and heated at 50 °C in an evacuated ampule for 24 h. In all cases, **1** and **2** were recovered in at least 92% of their original amounts (by NMR and GC after workup as described for reactions with 9-substituted fluorenes, below).

Reaction of (Triphenylmethyl)lithium with 1 in THF. When a 0.2 M solution of triphenylmethane in THF was treated with 1 equiv of a 1.5 M solution of butyllithium in ether, the intense red color of triphenylmethide ion was immediately produced. Addition of 1 equiv of 0.20 M **1** removed the red color

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[22] Jones, R. G.; Gilman, H. In *Organic Reactions*; R. Adams et. al., Eds.; Wiley: New York, 1951, vol. VI, Ch. 7, pp 352–356.

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leaving an orange-red hue typical of $1^{\bullet-}$. When this experiment was carried out in a reaction vessel attached to a length of 3-mm pyrex tubing for insertion in the probe of a Varian E-109 ESR Spectrometer, an intense spectrum characteristic of $1^{\bullet-}$ was observed (a^N = 19.1 G). Addition of a volume of air estimated to contain one molar equivalent of oxygen and mixing removed the spectral lines of $1^{\bullet-}$ leaving a weak residual spectrum of triphenylmethyl radical identical with the literature spectrum.[24] Shaking the entire reaction solution with air and refilling the tube section decreased the intensity of the triphenylmethyl radical spectrum. The signal then gradually returned to its initial intensity. When (triphenylmethyl)lithium was treated with **1** followed by excess methyllithium, 1,1,1-triphenylethane was formed in low yield (5–10%). No (4-methylphenyl)diphenylmethane could be detected (<1%).

Attempted Reaction of (Triphenylmethyl)lithium with 1 in Polar Solvent and Attempted Trapping of Methyl Radicals. When a 0.2 M solution of triphenylmethane in Pr_2SO or HMPA was treated with 1 equiv of methyllithium, the characteristic deep red colored solution of triphenylmethide ion was formed as for reactions in THF. In these solvents, however, addition of **1** did not noticeably change the color. After addition of **1**, the solutions did show the ESR spectrum of $1^{\bullet-}$ (a^N = 18.9 G in Pr_2SO, a^N = 18.6 G in HMPA), but, in HMPA the ESR spectral intensity for $1^{\bullet-}$ was relatively weak and increased by a factor of more than 50 upon addition of an equivalent of methyllithium. In Pr_2SO, the signals from $1^{\bullet-}$ were stronger, and the increase in spectral intensity produced by addition of excess methyllithium was relatively small (2–3 times). Solutions of (triphenylmethyl)lithium which had been treated with **1** followed by an equivalent of methyllithium contained traces of 1,1,1-triphenylethane (0.5–2%) when Pr_2SO was the solvent but no detectable amount of this product was observed in HMPA (<0.1%). In neither solvent was it possible to observe any (4-methylphenyl)diphenylmethane (<0.1%).

Procedure for Reaction of 9-Methoxyfluorene with 1 or 2 in the Presence of Potassium *tert*-Butoxide in THF. The nitro compound (0.20 mmol), the carbon acid (0.20 mmol), and an internal hydrocarbon standard (usually eicosane) were placed in an argon filled ampule. THF (1.0 mL) and 2.0 mL of 0.35 M potassium *tert*-butoxide in THF were added, the mixture was vacuum degassed, and the ampule was sealed under vacuum. When the reaction period was complete, the contents of the ampule were added to a mixture of 50 mL of water and 50 mL of CH_2Cl_2. The CH_2Cl_2 layer was washed with three 50-mL portions of water and dried over Na_2SO_4. Vacuum evaporation of the CH_2Cl_2 gave a product mixture for NMR and GC analysis. Products soluble in pentane were collected from the gas chromatograph and identified by comparison with authentic materials. 9,9′-Dimethoxy-9,9′-bifluorene (**5**) was largely insoluble in pentane and was separated by filtration. The yields of these products are indicated in eq 3. Preparation of authentic **6** is described below.

Synthesis of 3,5-Di-*tert*-butyl-1-isobutylbenzene (6) Method A. 1,3,5-Tri-*tert*-butylbenzene (**3**) (212 mg, 1.20 mmol) and 0.15 mL of di-*tert*-butyl peroxide were sealed in an evacuated ampule and heated at 150 °C for 19 h. GC collection gave **6** in 15% yield: ^1H NMR (200 mHz, $CDCl_3$) δ 7.45 (s, 1 H), 6.98 (s, 2 H), 2.44 (d, 2 H), 1.86 (m, 1 H), 1.3 (s, 18 H), 0.88 (d, 6 H); MS, *m/e* 246, 231.

Method B. The procedure used by Baas[25] for *tert*-butylation of toluene was applied to isobutylbenzene. This gave **6** having spectral properties described above.

Hydro-de-nitration of 1 and 2 with Potassium *tert*-Butoxide in the Presence of 18-Crown-6. Compound **1** (57.6 mg, 0.198 mmol) and 18-crown-6 (233 mg, 0.295 mmol) were sealed in an evacuated ampule with 2.0 mL of 0.35 M potassium *tert*-butoxide in THF and kept at 50 °C for 24 h. A precipitate was separated by decantation and washed with THF. ^1H NMR (90 MHz, $CDCl_3$) δ 3.65 (s); IR (KBr) 2880 (m), 1470 (m), 1350 (s), 1280 (s), 1250 (m), 1100 (b), 970 (s), and 840 (s) cm^{-1}. These spectral properties were identical with those of a product obtained by boiling potassium nitrite with 1 equiv of 18-crown-6 in THF.

The reaction solution was added to a mixture of 50 mL of CH_2Cl_2 and 50 mL of water. The CH_2Cl_2 layer was washed with three 50-mL portions of 17% aqueous KCl and dried over Na_2SO_4 and the CH_2Cl_2 evaporated. GC and NMR of the reaction products showed a 30% conversion of **1** to **3** (hydro-de-nitration) with 70% unreacted **1**. Minor peaks in the NMR spectrum suggested the presence of material containing the structural unit, $CH_2{=}CH{-}O$: ^1H (90 MHz, $CDCl_3$) δ 6.47 (d of d, 1 H, *J* = 7 Hz and 15 Hz), 4.18 (d of m, 1 H, *J* = 15 Hz), 3.98 (d of m, 1 H, *J* = 7 Hz), 3.65 (m, ca. 10 H). When **1** was replaced with **2**, **4** replaced **3** in the product mixture.

The reactions described were carried out under identical conditions in the presence of triphenylmethane (48.9 mg, 0.200 mmol). This resulted, for each nitroarene, in an increase to 70% yield of hydro-de-nitration products (**3** and **4**). NMR spectra of the product mixtures showed that a minimum of 50% of the triphenylmethane had been converted to products lacking the methine hydrogen. With the exception of a small amount of triphenylmethanol, we were unable to isolate these products, despite earlier experience with the expected products of triphenylmethide oxidation.[26]

In the absence of 18-crown-6, no reaction was detected between **1** or **2** and potassium *tert*-butoxide in THF regardless of whether triphenylmethane was present. Curiously, if **1** is exposed to sunlight and then treated with potassium *tert*-butoxide in THF, hydro-de-nitration is observed at 50 °C in the absence of 18-crown-6.

It was also found that 18-crown-6 promoted hydro-de-nitration of **1** and **2** in HMPA and Pr_2SO. For example, when **1** (58.1 mg, 0.200 mmol) was treated with 1.5 mL of 0.47 M potassium *tert*-butoxide in HMPA for 24 h at 50 °C followed by the workup described above, less than 1% of **3** was observed. When the same procedure was carried out adding 18-crown-6 (242 mg, 0.307 mmol), **3** was produced in 85% yield.

Reaction of Alkyllithium Compounds with 1 and 2. Addition of 1 equiv of a solution of methyllithium in diethyl ether or butyllithium in hexane to **1** or **2** in THF resulted in immediate formation of an orange solution of $1^{\bullet-}$ (a_N = 19.1 G) or $2^{\bullet-}$ (a_N = 18.9 G). The reactions are quantitative in that addition of a second equivalent of alkyllithium did not increase the intensity of the ESR signal. The signals were of constant intensity for several hours at 25 °C and exposure to molecular oxygen regenerated **1** or **2** essentially quantitatively. If the solution of $1^{\bullet-}$ was treated with oxygen-free water, approximately $^1/_6$ equiv of 2,4,5-tri-*tert*-butylaniline was produced (GC) and no other detectable products. If the addition of methyllithium to **1** was carried out slowly and the $1^{\bullet-}$ then destroyed with O_2 or water, a residual ESR spectrum of methyl 2,4,6-tri-*tert*-butylphenyl methyl nitroxide[27] was observed but the amount of this material was small. At temperatures above 25 °C with excess alkyllithium, other reactions were observed as indicated below.

When **1** (116 mg, 0.40 mmol) was treated with excess methyllithium (0.78 mL of 1.5 M solution in diethyl ether, 1.17 mmol) and the mixture heated in an evacuated tube for 48 h at 50 °C, quenching with water followed by the previously described workup and analysis gave **3**, 4%; tri-*tert*-butylaniline, 15%; and 2-methyl-4,6-di-*tert*-butylaniline, 25%. The latter compound was isolated by GC: ^1H NMR (200 mHz, $CDCl_3$) δ 7.16 (s, 1 H), 6.98 (s, 1 H), 3.71 (br s, 2 H), 2.17 (s, 3 H), 1.43 (s, 9 H), 1.27 (s, 9 H); MS, *m/e* 219. This product has been isolated earlier from the reaction of **1** with methylmagnesium iodide but only the methyl group chemical shift (δ = 2.12) was reported.[28]

When **1** (58.8 mg, 0.202 mmol) and eicosane (53.9 mg, 0.191 mmol—internal standard) were allowed to dissolve in 2.0 mL THF and treated with 0.23 mL of 0.88 M octyllithium in diethyl ether at 25 °C under argon, workup as described above using nitrogen-bubbled solvents gave 111.4 mg of products which contained

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hexadecane in 60% yield based on GC comparison with standard mixtures of eicosane and hexadecane. The same procedure using **2** gave 47% hexadecane. Neither heating at 50 °C nor use of 3 equiv of octyllithium significantly changed the amount of hexadecane produced in these experiments.

Treatment of a stirred solution of **1** (231.2 mg, 0.797 mmol) and eicosane (73.8 mg, 0.262 mmol) in 3.0 mL of THF in a septum-protected, 3-necked flask under argon with butyllithium (0.25 mL of 1.6 M solution in hexane, 0.40 mmol) and octyllithium (0.48 mL of 0.83 M solution in diethyl ether, 0.40 mmol), added simultaneously from opposite necks of the reaction flask over 20 min and workup after 30 min, gave hexadecane in 40% yield. Dodecane was essentially absent (<0.5%). No attempt was made to separate octane from the solvent. When a similar experiment was carried out using identical amounts of ocytllithium and butyllithium solutions which were premixed then added to the solution of **1**, 0.11 mmol of hexadecane and 0.13 mmol of dodecane were produced.

Phenyllithium (0.2 mL of 1.0 M solution in hexane, 0.2 mmol) was added to **1** (57.8 mg, 0.199 mmol) in 1.0 mL of THF and the mixture sealed in an evacuated ampule and heated at 50 °C for 48 h. The usual workup returned 53.3 mg of **1** with no GC- or NMR-detectable impurities (<2% biphenyl). Parallel results were obtained using **2**.

Effect of the Leaving Group in the Hydrolysis of *N*-Acylimidazoles. The Hydroxide Ion, Water, and General Base Catalyzed Hydrolysis of *N*-Acyl-4(5)-nitroimidazoles

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The second-order rate constants k_{OH} for hydroxide ion catalyzed hydrolysis of *N*-acylimidazoles substituted in the imidazole group show only a moderate dependence on the pK_a of the leaving group ($\beta_{lg} = -0.28$), which indicates that there is little C–N bond breaking in the transition state. In this reaction the transition state must resemble the reactants. A plot of log k_{OH} vs. σ_p, the Hammett substituent constant ($\sigma_p = 0.778$ with NO_2), for hydrolysis of a series of *N*-(3,3-dimethylbutyryl)-4(5)-substituted-imidazoles, is linear ($r = 0.99$) with a slope of 1.9. The pK_a of the conjugate acid of *N*-acylbenzimidazoles is ~2 in contrast with a value of ~4 with corresponding *N*-acylimidazoles. The apparent hydronium ion catalyzed hydrolysis reactions of *N*-acylbenzimidazoles are accordingly ~100-fold slower than the corresponding reactions of analogous *N*-acylimidazoles, and the pH-independent reactions of the *N*-acylbenzimidazoles are 5–10-fold slower. The most likely mechanism for the pH-independent hydrolysis of the *N*-acylbenzimidazoles is concerted nucleophilic attack and protonation of the leaving group by water. The rates of hydrolysis of *N*-acyl-4(5)-nitroimidazoles are pH-independent from pH 6 to at least pH 1, and the reactions are considerably faster than those of the corresponding unsubstituted *N*-acylimidazoles. Thus, the reactions of the nitro derivatives are water reactions in which the ease of nucleophilic attack is of greater importance than protonation of the leaving group. General base catalysis by buffer bases occurs in the hydrolysis of *N*-(3,3-dimethylbutyryl)-4(5)-nitroimidazole, and the Brønsted β coefficient is 0.5 for the reactions of oxygen anions. The strict general base catalysis by acetate ion is in contrast with the apparent general acid catalysis in acetate buffers in the hydrolysis of *N*-acetylimidazole. The second-order rate constant for imidazole-catalyzed release of 4-nitroimidazole shows a large positive deviation from the Brønsted plot. That imidazole acts as a nucleophile was demonstrated by kinetically and spectrally identifying an intermediate, *N*-(3,3-dimethylbutyryl)imidazole, which hydrolyzes slowly.

The hydrolysis reactions of *N*-acylimidazoles have been actively studied[2-13] in view of the likely role of histidine in biological acyl group transfer reactions. Hydroxide ion and hydronium ion catalysis has been observed in these reactions, and a pH-independent reaction occurs near pH 6–7. The hydrolysis reactions are subject to general acid–general base catalysis. In addition, neighboring carboxyl[14] and acetamido[15] group participation occurs in suitable derivatives. Thus, most of the important pathways encountered in hydrolytic reactions[2] are exemplified in the reactions of *N*-acylimidazoles.

Hydrolysis reactions that are independent of pH have also been detected in the hydrolysis of acyl activated esters[16-18] and esters having a leaving group of low pK_a.[2,19,20] There is kinetic ambiguity in these reactions and in the similar reactions of *N*-acylimidazoles in that they could involve water catalysis, attack of OH^- on a protonated species, or other mechanistic possibilities. Likewise, there can be kinetically equivalent possibilities in general acid–base catalysis. For example, the apparent general acid catalysis by acetic acid in the hydrolysis of *N*-acetylimidazole[4] could reflect a reaction of acetic acid and neutral

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