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Deoxygenation of Arene 1,4-Endoxides with Low-Valent Metals

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Low-valent forms of iron, tungsten, and titanium, produced by treatment of the metal chlorides with butyllithium at −78 °C, are useful deoxygenation catalysts for the conversion of 1,4-endoxides to the corresponding arenes in a single step. In some instances, particularly with highly substituted endoxides, other reactions may interefere. For example, with methyl substituents at C2 and C3 and with reduced iron, reduction of the C2–C3 double bond and a 1,3 hydrogen shift occur. Also, hindered aromatic methoxyls may be replaced by hydrogen. Use of this deoxygenation method to prepare 1,4,5,8,9,10-hexamethylanthracene, a compound with multiple peri interactions, is described.

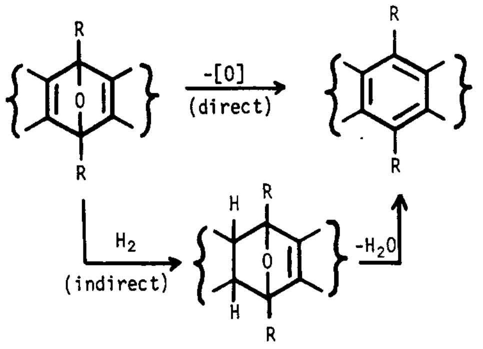
Arene 1,4-endoxides can function as useful synthetic precursors to arenes. They are easily prepared through cycloaddition to furans[1] or benzo[*c*]furans,[2] and the oxygen bridge can be removed by a variety of methods. Previous methods for removing the oxygen have some limitations, however, and we describe here new methods for achieving this goal by using reduced metals.

In general, two routes, which may be characterized as direct or indirect, have been used to deoxygenated endoxides (see Scheme I). Zinc and acetic acid,[3,4] heat,[4] and lithium naphthalenide[5] have been used in the direct process. Each has its drawbacks, however. Acid-sensitive compounds may rearrange, the thermal method is not general, and in the third method equivalent amounts of lithium naphthalenide are required, which may make separating the desired product from substantial quantities of naphthalene tedious. Use of acid (usually hydrogen chloride in methanol) sometimes results in aromatization without removal of the oxygen; for example, naphthalene endoxides can be converted to naphthols or their derivatives.[6] Although this conversion can be useful, it also can be complex when other substituents are present.[7]

Indirect methods involve hydrogenation followed by dehydration. Reagents for the latter step include acid,[6,8-10] bromotriphenylphosphonium bromide,[9] and a variety of modern ether-cleaving reagents.[10,11] Aside from requiring two steps and being inapplicable to dibenzo endoxides, the acid-catalyzed dehydration sometimes does not work well.

During recent years, many new methods have been developed for converting epoxides to alkenes.[12] Among the more successful of these methods, especially where stereochemistry is unimportant, are low-valent forms of iron,[13] tungsten,[14,15] and titanium.[16] We decided to examine the utility of these reagents in the deoxygenation of arene 1,4-endoxides.[17]

Scheme I



Results and Discussion

We have found that low-valent forms of iron, tungsten, and titanium, produced by treatment of the metal chloride at low temperature with butyllithium, can be effective in removing the oxygen from 1,4-endoxides to produce arenes. Some examples are shown in Table I.

The usual method for carrying out the deoxygenations involved addition of *n*-butyllithium (in hexane) to a slurry of the metal halide ($FeCl_3$, WCl_6, or $TiCl_3$) in THF or ether at −78 °C. After 1 h, the mixture was allowed to warm to room temperature, the substrate was added, and the mixture was stirred for the time shown Table I. In some cases, the substrate was added prior to warming of the reaction mixture. This generally made little differenc in the results. Reactions could be followed by thin-layer chromatography. Workup involved filtration through neutral alumina to remove the reduced metals, solvent removal, and chromatography.

The examples in Table I illustrate that the method can be used effectively to aromatize 1,4-endoxides. Although the particular metal used sometimes matters little (entry

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(11) $FeCl_3$–silica gel, P_2S_5–CS_2, Cl_2CHOCH_3–NaI, and $(CH_3)_3SiCl$–NaI.

(12) Harrison, I. T.; Harrison, S. "Compendium of Organic Synthetic Methods"; Wiley-Interscience: New York, 1971; Vol. 1, pp 502–504; 1974, Vol. 2, pp 200–201; Hedgedus, L. S., Wade, L., Eds.; 1977, Vol. 3, pp 317–319.

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(16) McMurry, J. E.; Fleming, M. P. *J. Org. Chem.* **1975**, *40*, 2555. McMurry, J. E.; Silvestri, M. G.; Fleming, M. P.; Hoz, T.; Grayston, M. W. *Ibid.* **1978**, *43*, 3249.

(17) Naphthalene 1,4-endoxide has been deoxygenated with iron pentacarbonyl: Lombardo, L.; Wege, D.; Wilkinson, S. P. *Aust. J. Chem.* **1974**, *27*, 143.

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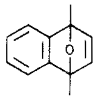
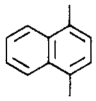
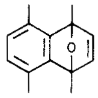
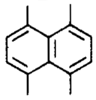
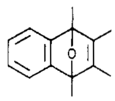
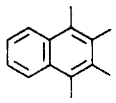
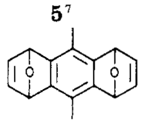
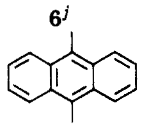
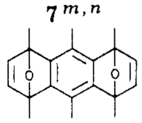
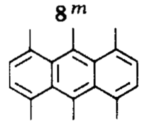
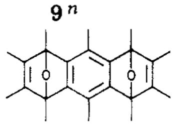
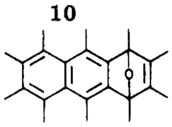
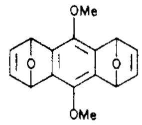
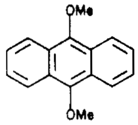
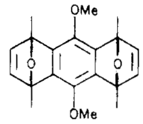
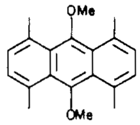
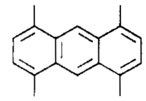
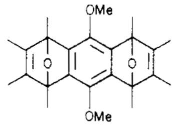
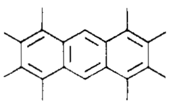
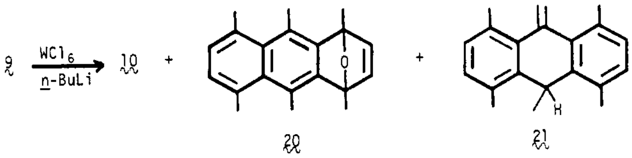
Table I. Deoxygenation of 1,4-Endoxides with Low-Valent Metals[a]

entry	substrate	molar ratio[b]	time, h[c]	product	yield, %[d]
1	 **1**[e]	1:3:12	6	 **2**[f]	81 (88,[g] 81[h])
2	 **3**[i]	1:3:12	6	 **4**[i]	63
3	 **5**[7]	1:3:12	5	 **6**[j]	(89[k]) [55[k,l]]
4	 **7**[m,n]	1:6:24	10	 **8**[m]	56
5	 **9**[n]	1:6:24	9	 **10**	40 (16[o]) [79[p]]
6	 **11**[n]	1:6:24	10	 **12**	[50[q]]
7	 **13**[n,r]	1:3:12	6	 **14**[s]	20,[t] (89[u])
8	 **15**[n]	1:6:24	24	 **16**	(47[v])
9	**15**	1:6:24	18	 **17**[w]	60 [54[x]]
10	 **18**[n]	1:6:24	90	 **19**[j]	61

[a] See the Experimental Section for typical reaction procedures. The reaction medium is THF unless otherwise specified. [b] Substrate/metal halide/*n*-BuLi. [c] This is the reaction time after addition of the substrate to the reduced metal. [d] Yields are for FeCl$_3$, (WCl$_6$), and [TiCl$_3$], are for isolated pure product, and are not optimized. [e] For preparation, see ref 8, first entry. [f] Riemschneider, R.; Nolde, K.; Henning, K. *Monatsh. Chem.* **1973**, *104*, 987. [g] The molar ratio with WCl$_6$ was 1:2:12. [h] The molar ratio (WCl$_6$) was 1:1:3. [i] Sy, A.; Hart, H. *J. Org. Chem.* **1979**, *44*, 7. [j] Krysin, A. P.; Bodoev, N. V.; Koptyug, V. A. *Zh. Org. Khim.* **1977**, *13*, 1290; *Zh. Org. Khim.* (*Engl. Transl.*) **1977**, *13*, 1183. [k] For results with low-valent iron, see text. [l] Reaction time 11 h, ether solvent; 28% of unchanged **5** was recovered. [m] Wittig, G.; Härle, H. *Justus Liebigs Ann. Chem.* **1959**, *623*, 17. [n] Prepared via a bis(aryne) equivalent; see: Hart, H.; Lai, C.-Y.; Nwokogu, G.; Shamouilian, S.; Teuerstein, A.; Zlotogorski, C. *J. Am. Chem. Soc.* **1980**, *102*, 6649. [o] For other products, see Results and Discussion. [p] Molar ratio of 1:6:24, ether solvent, reaction time 9 h. [q] The solvent was ether; 40% of unreacted **11** was recovered. Longer reaction times removed both oxygens but also resulted in isomerization[17] and reduction of the central ring. [r] Cragg, G. M. L.; Giles, R. G. F.; Roos, G. H. P. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1339. [s] Meyer, K. H. *Justus Liebigs Ann. Chem.* **1911**, *379*, 37. [t] At a molar ratio of 1:6:24 and with a 48-h reaction time the product was anthraquinone (55%); in a separate experiment it was shown that the reagent converts **14** to anthraquinone. [u] Molar ratio of 1:2:7, reaction time 10 h. [v] The product resulting from removal of only one endoxide bridge was also formed (47%). [w] Caspar, M. L.; Stothers, J. B.; Wilson, N. K. *Can. J. Chem.* **1975**, *53*, 1958. [x] Same molar ratio, 42-h reaction time.

1) it sometimes makes an appreciable difference in the results (entries 3, 5, 8, 9; also vide infra). Thus **10** was best prepared from **9** by using reduced titanium; iron gave the same product cleanly but in lower yield, whereas with tungsten, two other products (**20** and **21**) were also formed.

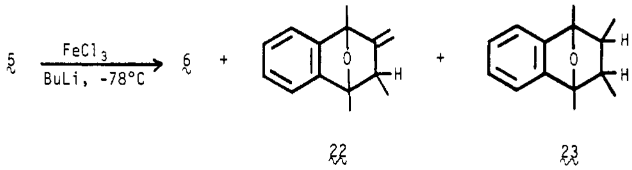


With a substrate/WCl_6/n-BuLi ratio of 1:2:6 and 3 h reaction time the major product was **20** (46%), together with **10** (16%) and small amounts of **21**. With a molar ratio 1:3:9 and 48 h reaction time the main product was **21** (49%). Compound **20** is readily susceptible to acid-catalyzed rearrangement to **21**.[18]

Tungsten was also more effective than iron in converting **13** to **14** (entry 7). Attempts to increase the yield of **14** by using longer reaction times with iron gave instead the oxidation product anthraquinone.

Methoxyls constrained by peri interactions may be removed by these reagents. Although **15** could be converted to **16** with reduced tungsten (entry 8), use of iron or titanium led instead to **17** (entry 9). Similarly, **18** was converted to **19** by iron (entry 10). A separate experiment showed that reduced titanium removed the methoxyl groups from **16** to give **17**.

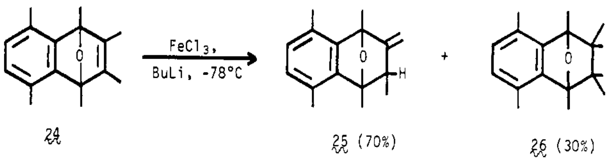
Two reactions other than deoxygenation were encountered when low-valent iron was used with certain polymethyl-substituted 1,4-endoxides. Although **5** could be converted to **6** in good yield with tungsten or titanium (entry 3), iron reacted differently. For example, **5** (substrate/$FeCl_3$/n-BuLi molar ratio 1:3:12, reaction time 1 h at −78 °C) gave only 7% of the desired **6**. The major product resulted from a 1,3 hydrogen migration (**22**, 59%),

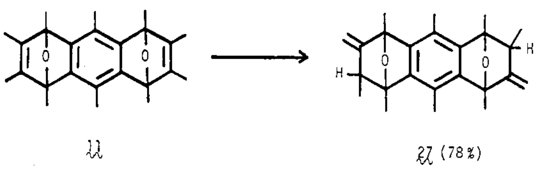


and some reduction to **23** also occurred (7%). Catalytic hydrogenation of either **5** or **22** gave **23**, thus interrelating their structures. Only one stereoisomer of **22** and **23** appeared to be formed, probably with the hydrogens exo.

Analogous allylic rearrangements were observed with **24** and **27**. No deoxygenation product was observed. With **25** and **26** only one stereoisomer was observed. Compound **11** (one isomer, probably anti) gave a single product which appeared to have the methylene groups located as shown in structure **27**. Products of this type were not formed with titanium (entry 6). Catalytic hydrogenation of either **11** or **27** gave the same saturated product.

Of the substrates listed in Table I, the aromatization of only the first four entries has been previously described. Compounds **1** and **5** were aromatized (but not deoxygenated) with methanol and hydrogen chloride. 2-Methoxy-1,4-dimethylnaphthalene and a dinaphthylmethane were obtained from **1** whereas **5** gave a side-chain-oxygenated product [1-(methoxymethyl)-2,3,4-trimethylnaphthalene].[7] Our method gives the corresponding hydrocarbon instead. Literature procedures for converting **3** to **4** and **7** to **8** involve two steps, hydrogenation and dehydration, whereas the method we described here involves only one step.





In summary, low-valent iron, tungsten, and titanium can be used to deoxygenate 1,4-endoxides to arenes in a single step. For a particular case, the general procedures described here can be used as a starting point for developing an optimum method.

Experimental Section

General Procedures. ^1H NMR spectra were measured at 60 MHz (Varian T-60) or 180 MHz (Bruker) with $(CH_3)_4Si$ as an internal standard. Chemical shifts are reported in parts per million (δ). ^{13}C NMR spectra were measured on a Varian CFT-20 spectrometer. UV spectra were obtained with a Unicam SP-800 spectrometer, and mass spectra were measured at 70 eV by using a Finnigan 4000 with the INCOS data system, operated by Mr. Ernest Oliver. Melting points are uncorrected. Alumina for chromatography was Brockmann activity II grade. Microanalyses were performed by Spang Microanalytical Laboratory.

Typical Deoxygenation Procedures. (a) Ferric Chloride. 1,4,5,8-Tetramethylnaphthalene (4). To 25 mL of anhydrous THF under argon and cooled to −78 °C was added 0.98 g (6.0 mmol) of sublimed $FeCl_3$. n-Butyllithium (12 mL, 2 M in hexane) was added, and the mixture was stirred for 2 h. A solution of **3** (0.43 g, 2.0 mmol) in 10 mL of anhydrous THF was added (syringe), and the mixture was allowed to warm with stirring to room temperature (6 h). The THF was removed on a rotary evaporator, the black residue was shaken with ether (100 mL), and the mixture was filtered. The ether extract was washed with water, dried (Na_2SO_4), and concentrated, and the residue was chromatographed on alumina (neutral) by using chloroform as eluent. The product was recrystallized from chloroform to give 0.25 g (63%) of pure **4** as thin needles, mp 129–131 °C (lit. 131–132 °C, Table I, footnote *i*).

(b) Tungsten Chloride. 1,2,3,4-Tetramethylnaphthalene (6). To a suspension of 2.45 g (6.2 mmol) of tungsten hexachloride in 25 mL of anhydrous THF under argon at −78 °C was added 10 mL of 2.4 M n-butyllithium in hexane. The mixture was stirred for 1 h and then warmed to room temperature (1 h). A solution of **5** (0.405 g, 2.0 mmol) in 10 mL of THF was added over 10 min, and the mixture was stirred for 5 h. The solvent was removed by rotary evaporator, and the residue was extracted with ether (100 mL). The blue ether solution was washed with dilute aqueous alkali until colorless and then with water and dried (Na_2SO_4). The ether solution was concentrated until crystals of **6** deposited when the mixture was cooled, and the product was collected as long white needles: 0.34 g (89%); mp 106–107 °C (lit.[19] mp 106.5–107.5 °C).

(c) Titanium Chloride. 1,4,5,8,9,10-Hexamethylanthracene (10). To a stirred suspension of 1.3 g (8.4 mmol) of titanium trichloride in 25 mL of anhydrous ether under argon at −78 °C was added dropwise over 10 min 16 mL of n-butyllithium (2 M in hexane). After 1 h at −78 °C the mixture was warmed to room temperature (1 h), a suspension of **9** (0.42 g, 1.4 mmol) in 50 mL of ether was added (20 min), and the mixture was stirred for 9 h. The reaction mixture was filtered through alumina (neutral), and the ether solution was concentrated to give 0.29 g (79%) of **10** which was recrystallized from hexane: mp 196–198 °C; NMR

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(18) For a similar case, see: Hart, H.; Ruge, B. *Tetrahedron Lett.* **1977**, 3143.

(19) Hewett, C. L. *J. Chem. Soc.* **1940**, 293.

(CCl_4) δ 2.70 (s, 12 H), 2.83 (s, 6 H), 6.87 (s, 4 H); mass spectrum, *m/e* (relative intensity) 262 (100), 247 (88), 232 (19); UV (heptane) λ_{max} 425 nm (log ε 3.71), 404 (3.73), 276 (4.76), 224 (3.9). Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.71; H, 8.39.

Decamethyl-1,4-dihydroanthracene 1,4-Endoxide (12). To a suspension of titanium trichloride (1.26 g, 8.2 mmol) in 25 mL of anhydrous ether at −78 °C under argon was added (5 min) 16 mL of 2 M *n*-butyllithium in hexane. The mixture was stirred for 1 h and then warmed to room temperature in 1 h. A suspension of **11** (0.48 g, 1.4 mmol) in 75 mL of ether was added, and the mixture was stirred for 10 h. Filtration through alumina (neutral), removal of the solvent by rotary evaporator, and trituration with hexane left 0.19 g of a white residue shown (NMR) to be unreacted **11**. The hexane extract gave a yellow tinted solid on concentration to dryness. Recrystallization from hexane gave **12**: 0.23 g (50%); mp 148–150 °C; ^1H NMR (CCl_4) δ 1.63 (s, 6 H), 1.84 (s, 6 H), 2.27 (s, 6 H), 2.42 (s, 6 H), 2.45 (s, 6 H); mass spectrum, *m/e* (relative intensity) 334 (11), 291 (100), 276 (11), 261 (11).

9,10-Dimethoxy-1,4,5,8-tetramethylanthracene (16). A suspension of tungsten hexachloride (1.37 g, 3.5 mmol) in 25 mL anhydrous THF at −78 °C under argon was treated with 6 mL of *n*-butyllithium (2.4 M in hexane), stirred for 1 h, and then warmed to room temperature in 1 h. A solution of **15** (0.16 g, 0.5 mmol) in 5 mL of THF was added, and the mixture was stirred for 24 h. After rotary evaporation of the solvent, the residue was extracted with ether, and the ether extract was washed successively with 40% aqueous sodium hydroxide and water and dried (Na_2SO_4). Removal of the solvent left a yellow oil (0.149 g) which was chromatographed on neutral alumina eluted with hexane to give **16**: 0.069 g (47%); mp 153–155 °C (hexane); ^1H NMR ($CDCl_3$) δ 2.80 (s, 12 H), 3.45 (s, 6 H), 6.88 (s, 4 H); mass spectrum, *m/e* (relative intensity) 294 (31), 279 (100), 263 (9), 147 (35). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.52; H, 7.70. Further elution with chloroform gave 0.072 g (47%) of a second product, 9,10-dimethoxy-1,4,5,8-tetramethyl-1,4-dihydroanthracene 1,4-endoxide: mp 125–127 °C (chloroform); ^1H NMR ($CDCl_3$) δ 2.05 (s, 6 H), 2.70 (s, 6 H), 3.53 (s, 6 H), 6.63 (s, 2 H), 6.92 (s, 2 H); mass spectrum, *m/e* (relative intensity) 310 (31), 267 (100), 237 (22), 165 (20).

Demethoxylation of 16. To a suspension of titanium trichloride (0.50 g, 3.2 mmol) in 10 mL of anhydrous THF at −78 °C under argon was added 7 mL of *n*-butyllithium (1.9 M in hexane). The mixture was stirred 1 h at −78 °C and warmed to room temperature (2 h), and a solution of **16** (0.10 g, 0.30 mmol) in 75 mL of THF was added. After 16 h the mixture was filtered over neutral alumina and the solvent separated. The residue was chromatographed on alumina (hexane eluent) to give 0.07 g (93%) of **17** which was recrystallized from 1:1 chloroform/heptane: thin, shiny, pale yellow plates; mp 220–222 °C (lit. mp 221–221.5 °C, Table I, footnote *w*).

1,2,3,4,5,6,7,8-Octamethylanthracene (19). To a slurry of 1.96 g (12.1 mmol) of anhydrous sublimed ferric chloride in 50 mL of anhydrous THF at −78 °C under argon was added 32 mL of *n*-butyllithium (1.6 M in hexane). The mixture was stirred at −78 °C for 2 h, and 0.66 g (1.73 mmol) of **18** suspended in 100 mL of THF was added. The mixture stirred for 90 h as it slowly warmed to room temperature. The reaction was followed by TLC (alumina, hexane) until the fluorescence of **19** reached a maximum. The mixture was filtered through neutral alumina, the alumina was washed several times with THF, and the combined filtrates were evaporated to dryness, leaving a yellow solid. Repeated trituration with hexane to remove oily products left 0.31 g (62%) of **19**, whose ^1H NMR spectrum matched the reported spectrum (Table I, footnote *j*).

Deoxygenation of 9 with Tungsten. A suspension of tungsten hexachloride (1.60 g, 4 mmol) in 25 mL of anhydrous THF at −78 °C under argon was stirred with 5.6 mL of *n*-butyllithium (2.2 M in hexane) for 10 min and then warmed to room temperature. A solution of **9** (0.55 g, 1.9 mmol) in 50 mL of THF was added, and the mixture was stirred for 3 h. Evaporation of the solvent left a dark residue which was extracted with ether. The ether layers were washed with aqueous alkali and water and dried (Na_2SO_4). The dark yellow solid left after solvent removal was chromatographed over neutral alumina with hexane as eluent to give 0.08 g (16%) of a mixture of **10** and **21** (in about a 1:4 ratio by NMR). Further elution with THF gave **20** (0.24 g, 46%) as a white solid: mp 155–157 °C; ^1H NMR (CCl_4) δ 1.92 (s, 6 H), 2.52 (s, 6 H), 2.63 (s, 6 H), 6.47 (s, 2 H), 6.77 (s, 2 H); mass spectrum, *m/e* (relative intensity) 278 (10), 252 (22), 236 (20), 235 (100), 220 (21), 205 (12).

By using the same amount of **9** but 6 mmol of tungsten hexachloride, 18 mmol of *n*-butyllithium, and a reaction time of 48 h, the major product was **21**: 0.24 g (49%); mp 159–161 °C; ^1H NMR (CCl_4) δ 1.27 (d, 3 H, *J* = 7 Hz), 2.33 (s, 6 H), 2.47 (s, 6 H), 4.23 (q, 1 H, *J* = 7 Hz), 5.43 (s, 2 H), 6.70 (s, 4 H); mass spectrum, *m/e* (relative intensity) 262 (23), 247 (100), 230 (5), 215 (9), 202 (6).

Deoxygenation of 5 with Iron. To a slurry of 0.90 g (5.6 mmol) of anhydrous sublimed ferric chloride in 25 mL of anhydrous ether at −78 °C under argon was added 10 mL of *n*-butyllithium (2.3 M in hexane). After 2 h, a solution of **5** (0.38 g, 2.0 mmol) in 10 mL of ether was added, and stirring was continued for 1 h. The cold reaction mixture was filtered (suction), and the filtrate was washed with water and dried (Na_2SO_4). Removal of the solvent left 0.28 g of an oil whose NMR spectrum showed the presence of **6**, **22**, and **23** in a ratio of 1:8:1. Column chromatography on neutral alumina eluted with 1:9 hexane/chloroform gave **6**, mp 106–107 °C (lit. mp 106.5–107.5 °C, Table I, footnote *j*). A pure sample of **22** was obtained by gas chromatography (SE-30 on Chromosorb W, 200 °C): ^1H NMR (CCl_4) δ 0.61 (d, 3 H, *J* = 7 Hz), 1.63 (s, 3 H), 1.70 (s, 3 H), 2.50 (m, 1 H), 4.47 (d, 2 H, *J* = 2.3 Hz), 4.77 (d, 2 H, *J* = 2.3 Hz), 6.88 (br s, 4 H); mass spectrum, *m/e* (relative intensity) 200 (23), 185 (10), 157 (72), 146 (100), 129 (23), 115 (36), 103 (16).

Hydrogenation of 5 and 22. A solution of **5** (0.35 g, 18 mmol) in 50 mL of absolute ethanol was hydrogenated at 70 psi of H_2 for 6 h at room temperature over 0.3 g of 10% palladium on charcoal. The catalyst was removed by filtration, the solvent was removed, and the residue was purified by chromatography on alumina (hexane and then chloroform) to give 0.34 g (96%) of **23** as an oil: ^1H NMR ($CDCl_3$) δ 0.32 (d, 6 H, *J* = 7 Hz), 1.57 (s, 6 H), 2.07 (m, 2 H), 6.87 (br s, 4 H); mass spectrum, *m/e* (relative intensity) 146 (100), 131 (38), 115 (17); with chemical ionization *m/e* 203 [$(M + 1)^+$]. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.01; H, 9.07.

The NMR spectrum of **23** obtained by deoxygenation of **5** with iron (vide supra) was identical with that obtained from hydrogenation of **5**.

Hydrogenation of a 1:1 mixture of **5** and **22** (obtained in a deoxygenation of **5**) gave **23** in 93% yield.

Treatment of 24 with Low-Valent Iron. To 25 mL of anhydrous ether at −78 °C under argon was added 1.44 g (8.9 mmol) of anhydrous sublimed ferric chloride, followed by 16 mL of *n*-butyllithium (2.2 M in hexane). After 2 h, a solution of **24**[20] (0.44 g, 2.0 mmol) in 20 mL of ether was added, and the mixture was stirred at −78 °C for 4 h. The cold mixture was filtered (suction), and the filtrate was washed with water, dried (Na_2SO_4), and evaporated. The viscous oil (0.44 g) solidified after several hours. The ^1H NMR spectrum showed this material to be a 7:3 mixture of **25** and **26**. Pure **25** was obtained by gas chromatography (10% SE-30 on Chromosorb W, 210 °C): mp 55–57 °C; ^1H NMR (CCl_4) δ 0.66 (d, 3 H, *J* = 7 Hz), 1.76 (s, 3 H), 1.77 (s, 3 H), 2.27–2.28 (m, 6 H), 2.43–2.49 (m, 1 H), 4.53 (d, 1 H, *J* = 2.3 Hz), 4.89 (d, 1 H, *J* = 2.3 Hz), 6.67 (s, 2 H); mass spectrum, *m/e* (relative intensity) 228 (32), 185 (42), 174 (100).

Hydrogenation of 24 and 25. A solution of **24** (0.21 g, 0.9 mmol) in 50 mL of absolute ethanol was hydrogenated at atmospheric pressure and room temperature with 0.3 g of 10% palladium on charcoal as catalyst. Filtration of the catalyst and evaporation of the solvent gave an oil which was chromatographed over neutral alumina (3:7 hexane/chloroform) to give 0.21 g (99%) of **26**: mp 45–47 °C; ^1H NMR (CCl_4) δ 0.43 (d, 6 H, *J* = 7 Hz), 1.72 (s, 6 H), 2.06–2.18 (m, 2 H), 2.27 (s, 6 H), 6.57 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 8.93, 16.62, 17.18, 42.38, 85.72, 126.31, 126.81, 141.71; mass spectrum, *m/e* (relative intensity) 174 (100), 159 (9); with chemical ionization *m/e* 231 [$(M + 1)^+$]. Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.26; H, 9.55.

Similar hydrogenation of **25** gave a quantitative yield of **26**. Also, **26** obtained from deoxygenation of **24** with low-valent iron

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[20] Prepared as described for **5** in the second reference of footnote 7 but with 3,6-dimethylbenzenediazonium carboxylate hydrochloride.

(vide supra) had the same NMR spectrum as the hydrogenation product.

Treatment of 11 with Low-Valent Iron. To 25 mL of anhydrous THF at −78 °C under argon was added 0.93 g (5.7 mmol) of anhydrous sublimed ferric chloride, followed by 10 mL of *n*-butyllithium (2.1 M in hexane). After the mixture was stirred for 2 h, a solution of 11 (0.32 g, 0.9 mmol) in 25 mL of THF was added (15 min), and the mixture was stirred at −78 °C for 4 h. Filtration and evaporation of the solvent left a residue which was taken up in methylene chloride, washed with water, and dried (Na_2SO_4). The yellow solid (0.33 g) left after solvent removal was chromatographed on neutral alumina, hexane removed a yellow impurity, and further elution with 9:1 methylene chloride/hexane gave 0.25 g (78%) of **27**: mp 233–235 °C (ethanol); ^1H NMR ($CDCl_3$) δ 0.72 (d, 6 H, J = 7 Hz), 1.86 (s, 6 H), 1.89 (s, 6 H), 2.33 (s, 6 H), 2.56 (m, 2 H); mass spectrum, *m/e* (relative intensity) 350 (63), 306 (48), 296 (77), 253 (100).

Hydrogenation of 11 and 27. A single isomer of 11 (0.33 g, 0.9 mmol) in 40 mL of absolute ethanol was hydrogenated at atmospheric pressure and room temperature overnight over 0.3 g of 10% palladium on carbon. Removal of the catalyst and solvent gave 0.31 g (93%) of 1,2,3,4,5,6,7,8,9,10-decamethyl-1,2,3,4,5,6,7,8-octahydroanthracene 1,4;5,8-diendoxide: mp 251–252 °C (ethanol); ^1H NMR (CCl_4) δ 0.43 (d, 12 H, J = 7 Hz), 1.67 (s, 12 H), 1.8–2.3 (m, 4 H), 2.20 (s, 6 H); mass spectrum, *m/e* (relative intensity) 298 (31), 242 (100), 122 (17); with chemical ionization *m/e* 355 [(M + 1)$^+$]. Anal. Calcd for $C_{24}H_{34}O_2$: C, 81.31; H, 9.67. Found: C, 81.45; H, 9.61.

Similar hydrogenation of **27** gave the same product (melting point, NMR) in 98% yield.

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Registry No. **1**, 4705-93-5; **2**, 571-58-4; **3**, 68185-75-1; **4**, 2717-39-7; **5**, 68437-68-3; **6**, 3031-15-0; **7**, 76466-54-1; **8**, 781-43-1; **9**, 76497-63-7; **10**, 75670-42-7; **11**, 76466-55-2; **12**, 76466-56-3; **13**, 57188-23-5; **14**, 2395-97-3; **15**, 76466-57-4; **16**, 76466-58-5; **17**, 2960-97-6; **18**, 76497-64-8; **19**, 64094-28-6; **20**, 76466-59-6; **21**, 76466-60-9; **22**, 76479-87-3; **23**, 76466-61-0; **24**, 76466-62-1; **25**, 76479-88-4; **26**, 76466-63-2; **27**, 76498-71-0; 9,10-dimethoxy-1,4,5,8-tetramethyl-1,4-dihydroanthracene-1,4-endoxide, 76466-64-3; 1,2,3,4,5,6,7,8,9,10-decamethyl-1,2,3,4,5,6,7,8-octahydroanthracene-1,4:5,8-diendoxide, 76466-65-4; $FeCl_3$, 7705-08-0; WCl_6, 13283-01-7; $TiCl_3$, 7705-07-9.

Rates and Mechanism for Oxidation of Paraquat and Diquat Radical Cations by Several Peroxides

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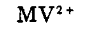
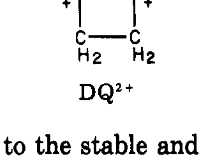
The rates of oxidation of the free radicals $MV^{+}\cdot$ and $DQ^{+}\cdot$ derived from herbicides Paraquat (MV^{2+}) and Diquat (DQ^{2+}) by hydrogen peroxide, peroxodiphosphate species, and peroxodisulfate have been investigated. Where consistent data were obtainable, the reactions are first order each in peroxide and radical. Results for H_2O_2 and $MV^{+}\cdot$ are $k = 2.0\ M^{-1}\ s^{-1}$ at 25 °C, $\Delta H^{*} = 92$ kJ mol^{-1}, and $\Delta S^{*} = 73$ J mol^{-1} K^{-1}; similar results were found with H_2O_2 and $DQ^{+}\cdot$. Although hydroxyl radicals are likely intermediates, the predicted inhibition when methanol is present did not materialize; a mechanistic rationalization is presented. The rates with peroxodiphosphate were pH dependent and could be interpreted as different contributions from $H_2P_2O_8^{2-}$, $HP_2O_8^{3-}$, and $P_2O_8^{4-}$ in the same order as found for peroxodiphosphate and unstable radicals. The rate with $S_2O_8^{2-}$ is fastest, but complications prevented the evaluation of a rate constant.

Methylviologen dichloride (1,1′-dimethyl-4,4′-bipyridylium chloride) and 6,7-dihydrodipyrido[1,2-*a*:1′,2′-*c*]pyrazinium dibromide are marketed as herbicides under the names of Paraquat and Diquat. Both compounds in water as the dications (here symbolized MV^{2+} and DQ^{2+},



MV^{2+}



DQ^{2+}

respectively) are readily reduced to the stable and persistent radicals $MV^{+}\cdot$ and $DQ^{+}\cdot$ by chemical, electrochemical, and photochemical means.[1] The herbicidal activity appears to be associated with the formation of these stable radicals and with the reduction potentials of the dications as they can substitute for a normal electron acceptor in the photosynthetic pathway.[2] The radicals are air sensitive and can be reoxidized by oxygen.[3] For plant death, both oxygen and light are required;[4] the oxygen intermediates $O_2^{-}\cdot$ and/or H_2O_2 have been considered to be the active lethal agents.[2,5]

Paraquat and Diquat are also potent mammalian poisons. The mechanism of mammalian toxicity may be related to herbicidal activity but cannot depend on photochemical activation.[6]

Methylviologen has also been used as an oxygen meter; a solution of the radical cation, buffered at pH 6.5 and prepared by photoreduction of MV^{2+} by using proflavine and EDTA,[7] is reported to react quantitatively with oxygen according to the stoichiometry of eq 1. The system can

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