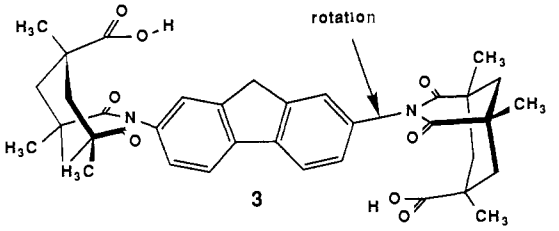


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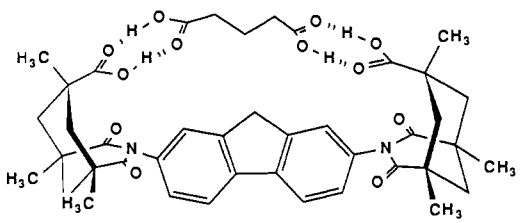

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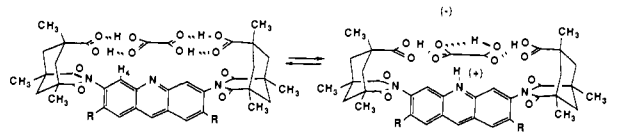
conformations can provide specific stabilization of the substrates by involving both carboxyls of the receptor in hydrogen bonding so that rotation is stopped. For the acridines, some protonation also occurs; this is accommodated in the tautomeric structures **5a** ⇄ **5b** proposed for these complexes. Similar structures can



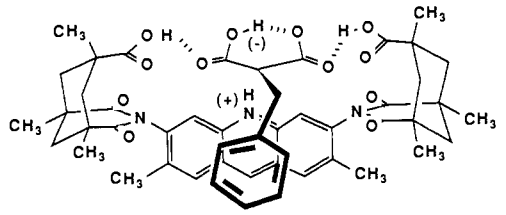
5a 5b

be envisioned for the complexes of malonate, maleate, and other anions that can be chelated between the convergent carboxyls.

Second, intermolecular NOE experiments[11] revealed an 18% enhancement of the $^{13}C$ oxalate signal when $H_4$ of the receptor **1b** was irradiated in the 1:1 complex. These establish a propinquity between these nuclei that is consistent with the proposed structures **5**.

Finally, a highly specific means of stabilization can be observed with substrates bearing suitably placed aromatic functions. These are *stacking interactions* between the pendant aryl and the large $\pi$ surface presented by **1**. For example, benzylmalonic acid forms complexes with **1a** or **1b** in which large upfield shiftsd of the phenyl protons are observed in the NMR.[12] In addition, homonuclear intermolecular NOE was observed between the ortho protons of the substrate and those lining the cleft of **1**. These are similar to those observed in phenylalanine[9] and heterocyclic diamines[6] when these substrates are in contact with **1** in organic solvents.

The structural details of these complexes must await crystallographic analysis, but the facts are in accord with structure **6** for the benzylmalonic acid complex. In the meantime, we note



6

that the reversal of acidities resulting from the specific stabilization of conjugate bases has also been observed by Kimura[13] in the chemistry of carboxylic acids in contact with macrocyclic polyamines.

**Acknowledgment.** We are grateful to the National Science Foundation and the National Institutes of Health for support of this research.

(11) The program described by Cativiela and Sanchez-Ferrando (Cativiela, C.; Sanchez-Ferrando, F. *Magn. Reson. Chem.* **1985**, 1072-1075) was used on an IBM 300-MHz instrument; 90% enriched $^{13}C$ oxalic acid was dissolved in $CDCl_3$ using the receptor **1b** and selective irradiation of $H_4$ led to the difference spectra for the $^{13}C$ resonance of the bound oxalate at 162.84 ppm.

(12) Chemical shifts ($CDCl_3$) observed for the phenyl group of **6** were 6.85, t (para); 7.02, t (meta); and 7.25 ppm, d (ortho). The difference NOE experiment was similar to that recently described: Pirkle, W. H.; Pochapsky, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 5627-5628. Nehaus, D. *J. Magn. Reson.* **1983**, *53*, 109-114. A 5% enhancement of the $H_4$ signal was observed.

(13) Kimura, E.; Sakonaka, A. *J. Am. Chem. Soc.* **1982**, *104*, 4984-4985. For other studies of selective binding of carboxylic acids, see: Breslow, R.; Rajagopalan, R.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2905-2907. Kimura, E.; Sakonaka, A.; Yatsunami, T.; Kodama, M. *Ibid.* **1981**, *103*, 3041-3045. Hosseini, M. W.; Lehn, J. M. *Ibid.* **1982**, *104*, 3525-3527.

## Synthesis and X-ray Crystal Structure Analysis of a $\eta^4$-1-Phosphabutadiene Tetracarbonyltungsten Complex

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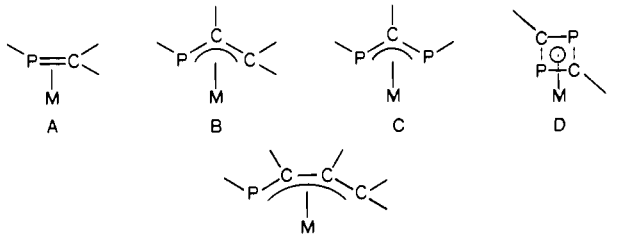
*Received December 2, 1986*

The formal replacement of a carbon by a phosphorus unit in the skeleton of each known type of alkene and cyclic or acyclic polyalkene $\pi$-complex ($\eta^2$-$\eta^8$) suggests a wide range of interesting new structures. Until recently, these new structures were either unknown or very poorly investigated. However, during the last 4 years, it has become increasingly evident that such a formal replacement is possible in almost every conceivable case.[2] For example, $\eta^2$-phosphaalkene (A),[3] $\eta^3$-phosphaallyl ($B^4$ and $C^5$), and $\eta^4$-diphosphacyclobutadiene (D)[6] complexes have all been described recently. At the moment, the most obvious gap in this series concerns the open $\eta^4$-phosphabutadiene structure (E). We wish to report here on the first known complexes of this type. Our



A B C D



E

(1) (a) Ecole Polytechnique. (b) Institut Le Bel.

(2) This topic has been reviewed very recently: Mathey, F. *Nouv. J. Chim.*, in press.

(3) (a) van der Knaap, Th. A.; Jenneskens, L. W.; Meeuwissen, H. J.; Bickelhaupt, F. *J. Organomet. Chem.* **1983**, *254*, C33. (b) Cowley, A. H.; Jones, R. A.; Stewart, C. A.; Stuart, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 3737. (c) Cowley, A. H.; Jones, R. A.; Lasch, J. G.; Norman, N. C.; Stewart, C. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Zhang, H.-M. *J. Am. Chem. Soc.* **1984**, *106*, 7015. (d) Al-Resayes, S. I.; Klein, S. I.; Kroto, H. W.; Meidine, M. F.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 930. (e) Werner, H.; Paul, W.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 626. (f) Appel, R.; Casser, C.; Knoch, F. *J. Organomet. Chem.* **1985**, *293*, 213. (g) Deschamps, B.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1985**, 1010.

(4) Mercier, F.; Fischer, J.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 357.

(5) Appel, R.; Schuhn, W.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 420.

(6) Hitchcock, P. B.; Maah, M. J.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1986**, 737. Binger, P.; Milczarek, R.; Mynott, R.; Regitz, M.; Rösch, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 644.

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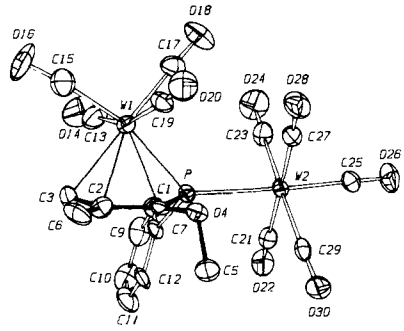
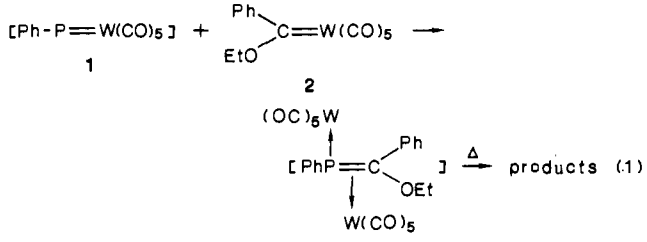
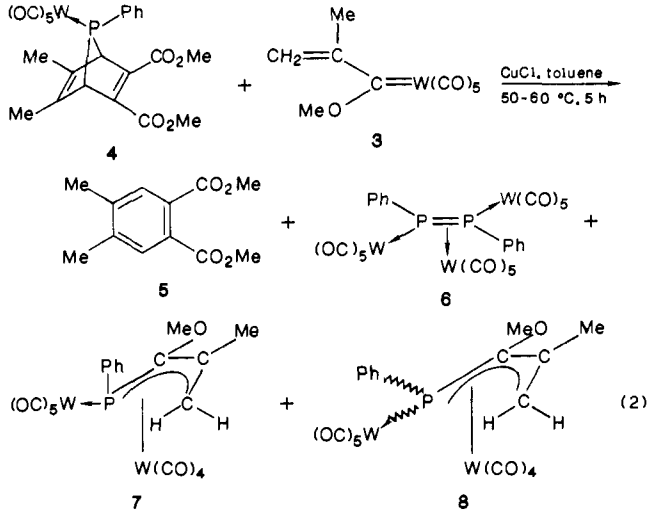



**Figure 1.** ORTEP drawing of one molecule of **7**. Vibrational ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted. Principal bond distances (Å): W1-P 2.551 (2); W1-Cl 2.327 (7); W1-C2 2.334 (8); W1-C3 2.366 (8); P-W2 2.512 (2); P-C1 1.783 (8); P-C7 1.826 (8); C1-C2 1.44 (2); C2-C3 1.41 (1); C1-O4 1.387 (9); C2-C6 1.51 (1). Selected bond angles (deg): W1-P-C1 62.0 (2); W1-P-C7 112.3 (3); W1-P-W2 128.86 (8); C1-P-C7 110.9 (4); C1-P-W2 121.9 (3); C7-P-W2 111.7 (3); P-C1-C2 124.7 (6); P-C1-O4 116.9 (5); C2-C1-O4 117.8 (7); C1-C2-C3 118.0 (7); C1-C2-C6 120.5 (8); C3-C2-C6 121.3 (8); P-W1-C1 42.6 (2); P-W1-C2 71.6 (2); P-W1-C3 79.1 (2); C1-W1-C2 36.0 (3); C1-W1-C3 62.9 (3); C2-W1-C3 35.0 (4).

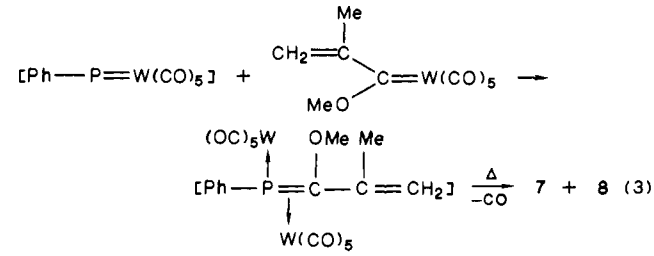
approach was based on the phosphinidene-carbene coupling previously described by us[7] (eq 1).




We decided to replace the phenylethoxycarbene complex **2** by the vinylmethoxycarbene complex **3** in this kind of scheme. Accordingly, the precursor of **1** (**4**)[9] was reacted with an equimolecular amount of carbene complex **3** in the presence of CuCl "which promotes the thermal decomposition of **4**" at ca. 50 °C[10] (eq 2).




The four main products thus obtained were separated by two careful chromatographies on florisil at −10 °C with pentane/$CH_2Cl_2$ (9/1 then 10/1). Complex **6** results from the spontaneous dimerization of **1**.[11] The two isomeric complexes **7**[12] and **8**[13] result from the expected coupling (eq 3). Only **7** was fully characterized.




From a synthetic standpoint, the reaction described in this paper provides a new route for the preparation of a wide range of unhindered 1-phosphabutadienes stabilized by π-complexation. Only a limited number of uncomplexed phospha- and diphosphabutadienes are presently known[14] and all of them are heavily substituted by bulky groups for kinetic stabilization. From a spectroscopic standpoint, two peculiar features of **7** and **8** deserve some comments. In both cases, the phosphorus atom appears to be coupled only with the σ-bonded tungsten. The absence of coupling with the π-bonded tungsten has been already noted in a $\eta^2$-phosphaalkene-$W(CO)_5$ complex[3g] and in a $\eta^5$-phosphacyclopentadienyl-$W(CO)_3I$ complex.[15] This seems to be a general feature of all π-bonded phosphorus-transition-metal complexes. Indeed, similar π-complexes with platinum also show abnormally low $^1J$(Pt-P) couplings when compared to "normal" σ-complexes.[16] In the $^{13}C$ spectra of **7** and **8**, all the CO's of the $W(CO)_4$ moiety appear equivalent, suggesting fast CO exchange on the NMR time scale. Such is not the case in a $\eta^4$-1,4-diphenylbutadiene $W(CO)_4$ complex which shows three different CO resonances at room temperature.[17] The role of phosphorus on favoring this CO exchange in **7** and **8** is not yet understood. From a structural standpoint[18] (Figure 1), the most noteworthy feature of **7** is the planarity of the phosphabutadiene unit (deviations are P, 0.000

(7) Hoa Tran Huy, N.; Mathey, F. *Organometallics* **1987**, *6*, 207.
(8) Dötz, K. H.; Kuhn, W.; Ackermann, K. *Z. Naturforsch., B* **1983**, *38B*, 1351.
(9) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1982**, 667.
(10) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.
(11) Marinetti, A.; Charrier, C.; Mathey, F.; Fischer, J. *Oganometallics* **1985**, *4*, 2134.
(12) **7**: major isomer, $R_f \sim 0.15$ with pentane/$CH_2Cl_2$ 10/1; red crystals, mp ~102 °C; $^{31}P$ NMR ($CH_2Cl_2$) δ −47.8 (reference, external 85% $H_3PO_4$, δ + ve for downfield shifts), $^1J(^{31}P-^{183}W)$ = 244 Hz ($W(CO)_5$); $^{13}C$ NMR ($CDCl_3$) δ 20.72 (s, Me), 51.07 (s, $CH_2$), 65.85 (s, OMe), 109.11 (d, $^2J$(C-P) = 4.9 Hz, *C*Me), 197.05 [d, $^2J$(C-P) = 6.1 Hz, cis CO ($W(CO)_5$)], 205.13 (s, $W(CO)_4$); $^1H$ NMR ($CDCl_3$) δ 0.68 (*A*MX, $^2J$(A-M) = 2 Hz, $CH_2$ endo), 2.69 (s, Me), 3.19 (A*M*X, $CH_2$ exo), 4.19 (s, OMe); IR ($CH_2Cl_2$) ν (CO) ~2080 w, 2060 m, 2010 m, 1977 m, 1955 shoulder, 1933 vs; mass spectrum (EI, 70 eV, $^{184}W$), *m/z* 812 (M, 16%), 560 (M − 9CO, 96%), 514 (560 − Me − OMe, 100%). Anal. Calcd for $C_{20}H_{13}O_{10}PW_2$: C, 29.56; H, 1.60; O, 19.71; P, 3.82; W, 45.30. Found: C, 29.81; H, 1.66; O, 19.22; P, 3.77; W, 45.43.
(13) **8**: minor isomer, $R_f \sim 0.26$ with pentane/$CH_2Cl_2$ 10/1; red crystals, mp 75-78 °C; $^{31}P$ NMR ($CDCl_3$) δ −85.8 ppm, $^1J(^{31}P-^{183}W)$ = 219.7 Hz ($W(CO)_5$); $^{13}C$ NMR ($CDCl_3$) δ 19.87 (s, Me), 49.00 (d, $^3J$(C-P) = 13 Hz, $CH_2$), 64.48 (s, OMe), 101.32 (d, $^2J$(C-P) 19 Hz, *C*Me), 197.38 [d, $^2J$(C-P) = 6 Hz, cis CO ($W(CO)_5$)], 205.47 (s, $W(CO)_4$); $^1H$ NMR ($CDCl_3$) δ 1.44 (*A*MX, $^2J$(A-M) = 2.1, $^4J$(A-X) = 2.4 Hz, $CH_2$ endo), 2.62 (s, Me), 3.27 (A*M*X, $^4J$(M-X) = 5.1 Hz, $CH_2$ exo), 3.67 (s, OMe); IR ($CH_2Cl_2$) ν(CO) ~2080 w, 2062 m, 2018 m, 1970 shoulder, 1945 vs.; mass spectrum (EI, 70 eV, $^{184}W$), *m/z* 812 (M, 27%), 560 (M − 9CO, 100%); correct C, H elemental analysis.
(14) See, for example: Neilson, R. H. "X International Conference on Phosphorus Chemistry"; lecture B12, Bonn, 1986. Appel, R.; Fölling, P.; Schuhn, W.; Knoch, F. *Tetrahedron Lett.* **1986**, *27*, 1661 and references cited herein.
(15) Holand, S.; Mathey, F.; Fisher, J. *Polyhedron* **1986**, *5*, 1413.
(16) See, for example: Kroto, H. W.; Klein, S. I.;Meidine, M. F.; Nixon, J. F.; Harris, R. K.; Packer, K. J.; Reams, P. *J. Organomet. Chem.* **1985**, *280*, 281.
(17) Özkar, S.; Peynircioglu, N. B. *Inorg. Chim. Acta* **1986**, *119*, 127.
(18) Appropriate crystals of **7** were obtained by slow recrystallization in pentane/$CH_2Cl_2$ (2/1). $C_{20}H_{13}O_{10}PW_2$: MW = 811.99; monoclinic, $P2_1/c$, $a$ = 9.207 (3) Å, $b$ = 15.523 (4) Å, $c$ = 17.137 (5) Å, $\beta$ = 103.40 (2)°, $V$ = 2382.5 Å$^3$, $Z$ = 4, $d_c$ = 2.264 g cm$^{-3}$, Mo Kα radiation, $t$ = −100 °C; red crystals (0.30 × 0.40 × 0.12 mm approximately); experimental absorption corrections; 5875 independent ±*hkl* reflections measured on a Philips PW1100/16 using the $\theta/2\theta$ flying step-scan mode; 4181 with $I > 3\sigma(I)$, $R_F$ = 0.029, $R_wF$ = 0.041, GOF = 1.35 with $p$ = 0.08 in $\sigma^2(F) = \sigma^2_{counts} + (pI)^2$. Refinements were conducted by using full-matrix least squares, anisotropic factors for all nonhydrogen atoms, and isotropic factors for the hydrogens ($B_H = 1.3B_{eqv}(c)$) which were introduced by their computed coordinates (C-H = 0.95 Å). All computations were done using the ENRAF NONIUS SPD/PDP package.

(2); C1 0.009 (8); C2, -0.013 (9); C3, 0.007 (10) Å); W2 is out of this plane by -0.108 Å. W1 is above this plane and the three W1-C*i* bond lengths are not significantly different from each other with a mean value of 2.342 (5) Å. The W1-P bond length of 2.550 (2) Å is somewhat longer than 2.512 (2) Å, the W2-P bond length which is in the range of those found elsewhere. The C7-C12 phenyl ring lies on the opposite side of the $PC_3$ plane with respect to the $W1(CO)_4$ group and its mean plane makes a dihedral angle of 106.6 (2)° with the $PC_3$ mean plane. The $PC_3$ system seems to be fully delocalized: the two C—C bond lengths are nearly equal (respectively 1.442 (11) and 1.414 (11) Å for the central and terminal bonds) and the P-C bond is short (1.783 (8) Å vs. 1.84 Å for a single P-C bond length, compare with the structure of a $\eta^5$-phosphacyclopentadienyl-$W(CO)_3I$ complex[15]).

We are currently starting to develop the chemistry of these new $\eta^4$-phosphabutadiene complexes.

**Supplementary Material Available:** Table I, positional parameters and their estimated standard deviations for all non-hydrogen atoms; Table II, $U_{ij}$ with their estimated standard deviations; Table III, positional parameters for the hydrogen atoms; Table IV, bond distances with their estimated standard deviations; and Table V, bond angles with their estimated standard deviations (8 pages); Table VI, observed and calculated structure factor amplitudes (×10) for all observed reflections (17 pages). Ordering information is given on any current masthead page.

## Dramatic Solvent and Stereoelectronic Effects in a Biomimetic Oxidation: 9,10-Dialkylanthracenes

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*Received January 27, 1987*

7,12-Dimethylbenz[*a*]anthracene (DMBA) and other alkylated aromatics undergo ring oxygenation in the presence of rat-liver microsomes containing the ubiquitous cytochrome $P_{450}$ to yield a dihydroepoxy diol.[1] The water-soluble fraction from the same tissue, i.e., cytosol, yields not ring oxygenation but methyl hydroxylation (see Figure 1).[2] This diversity has been interpreted in terms of a dichotomy between direct ring oxygenation in the former case and one-electron oxidation to a radical cation in the latter. Because of their high acidity, such radical cations undergo rapid deprotonation leading ultimately to formation of hydroxymethyl products.[3] Thus the absence of such products during oxidation of DMBA by cytochrome $P_{450}$ is difficult to reconcile with the known propensity of this enzyme to form radical cations of higher potential hydrocarbons.[4] We now report results on the oxidation of the title compounds which suggest that this dichotomy is the result of a solvent effect.

Our curiosity was stimulated by the divergent biochemistry of the structurally analogous yet noncarcinogenic 7,12-diethylbenz[*a*]anthracene and 6-ethylbenzo[*a*]pyrene.[5] These possible

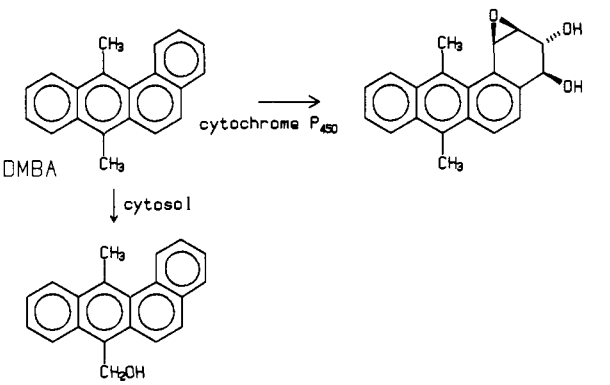


**Figure 1.** Ring vs. side-chain oxidation in DMBA oxidation.

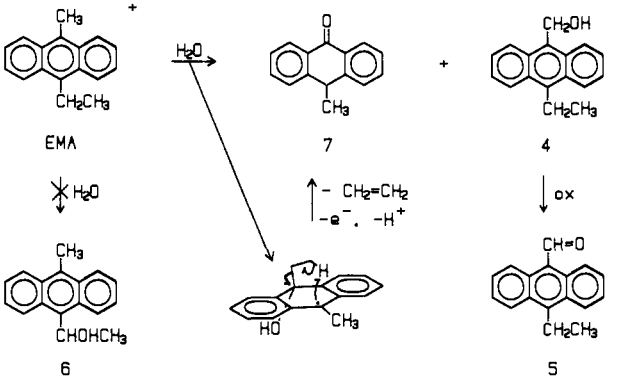


**Figure 2.** Oxidation of EMA.

**Table I.** Effect of $[H_2O]$ on Oxidation of 9-Ethyl-10-methylanthracene[a]

| | % yield[b] | | |
|---|---|---|---|
| $[H_2O]$, M | 4 | 5 | 7 |
| 2.78 | 11.1 | 4.0 | 76.5 |
| 5.56 | 24.9 | 5.7 | 62.9 |
| 8.33 | 37.1 | 7.0 | 50.2 |
| 11.1 | 46.2 | 8.4 | 40.6 |
| rat-liver microsomes[c,d] | | | |
| 1 h | 3.2 | | 83.4 |
| 20 h | 4.1 | | 77.3 |
| rat-liver cytosol[c] | | | |
| 20 h | 85.7 | | 8.9 |

[a] Reaction in 20 mL of $H_2O$-MeCN with 3.00 mM 9-ethyl-10-methylanthracene (EMA) and 4.5 mM tris(phenanthroline)tris(hexafluorophosphate)iron at 25 °C for 30 min was followed by ether precipitation of iron salts. [b] Yields based upon recovered starting material. [c] Solutions of dialkylanthracene in 20% aqueous dimethylformamide were incubated at room temperature (ca. 25 °C). [d] Anthraquinone was also formed in yields of 6.5% (1 h) and 10.7% (20 h). No oxidation was observed with denatured enzyme.

"changes in metabolism"[5] might have their origin in a stereoelectronic effect inhibiting facile deprotonation of the ethyl group of the radical cation, which is maintained perpendicular to the aromatic plane by the presence of significant peri interactions.[6] Thus use of a substrate, 9-ethyl-10-methylanthracene, which incorporated both features, should allow us to quantitatively assess the importance of such a stereoelectronic effect by determining the relative ratio of hydroxymethyl- to 1-hydroxyethyl-substituted anthracenes upon one-electron oxidation.

Treatment of a 3 mM solution of 9,10-dimethylanthracene (DMA), 9-ethyl-10-methylanthracene (EMA), and 9,10-diethylanthracene (DEA) with tris(phenanthroline)tris(hexafluorophosphate)iron in 10:90 water acetonitrile[7] under argon

(1) (a) Lee, H.; Harvey, R. G. *J. Org. Chem.* **1986**, *51*, 3502. (b) For a general review, see: Dipple, A.; Moschel, R. C.; Bigger, C. A. H. *Chemical Carcinogenesis*, 2nd ed.; Searle, C. E., Ed.; ACS Monograph 182, American Chemical Society: Washington, DC, 1984; Vol. 1, pp 41-163.

(2) (a) Flesher, J. W.; Myers, S. R. *Cancer Lett.* **1985**, *26*, 83. See also: (b) Boyland, E.; Sims, P. *Biochem. J.* **1965**, *95*, 780. (c) Dipple, A.; Lawley, P. D.; Brookes, P. *Eur. J. Cancer* **1968**, *4*, 493. (d) Cavalieri, E.; Sinha, D.; Rogan, E. *Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects*; Battelle Memorial Institute Fourth International Symposium, Battelle Press: Columbus, OH, 1980; p 214.

(3) (a) Minisci, F.; Citterio, A.; Giordano, C. *Acc. Chem. Res.* **1983**, *16*, 27. (b) Walling, C.; Zhao, C.; El-Taliawi, G. M. *J. Org. Chem.* **1983**, *48*, 4910. (c) Walling, C.; Camainoi, D. M. *J. Am. Chem. Soc.* **1975**, *97*, 1603. (d) Walling, C.; Camaioni, D. M.; Kim, S. S. *J. Am. Chem. Soc.* **1978**, *100*, 4814. (e) Camaioni, D. M.; Franz, J. A. *J. Org. Chem.* **1984**, *49*, 1607. (f) Camaioni, D. M.; Alnajjar, M. S. *J. Org. Chem.* **1985**, *50*, 4456. (g) Dearduff, L. A.; Alnajjar, M. S.; Camaioni, D. M. *J. Org. Chem.* **1986**, *51*, 3686.

(4) Guengerich, F. P.; MacDonald, T. L. *Acc. Chem. Res.* **1984**, *17*, 9.

(5) Sullivan, P. D.; Ocasio, I. J.; Chen, X.; Bannoura, F. *J. Am. Chem. Soc.* **1986**, *108*, 257.

(6) Greene, D. H. *Prog. Phys. Org. Chem.* **1967**, *4*, 135-211.

0002-7863/87/1509-3477$01.50/0 