wavelength with increasing pressure for an analogous band in bis(dimethylglyoximato)nickel(II).

When $Ni(dpg)_2I$ is stirred in chloroform at 25°, one obtains a solution which has an absorption spectrum (240–700 mμ) which is simply a superposition of those of $Ni(dpg)_2$ and I_2. There is no spectroscopic evidence for the presence of another species in solution.

An interesting feature common to the four compounds is a prominent epr absorption which disappears when the halogen is driven out. For powdered samples this consists of a double peak, about 20 gauss wide, with the stronger component at lower field. Studies of oriented single crystals of $Ni(dpg)_2I$ show that the doubling arises from magnetic anisotropy. Table I lists $g_{\parallel}$ and $g_{\perp}$ (23°), corresponding to parallel and perpendicular orientations of the c axes with the magnetic field. We note that the epr spectrum changes more with a change in metal than with a change in halogen. Qualitative observations show that the signal strengths increase with decreasing temperature.

A Gouy bulk magnetic susceptibility measurement for $Ni(dpg)_2I$ gives an uncorrected molar susceptibility of -216×10^{-6} cgs unit at 28°. This diamagnetic susceptibility is in approximate agreement with the results of Simek.[1]

$Ni(dpg)_2I$ is an electrical semiconductor. Its specific conductivity increases with increasing temperature and exceeds that of $Ni(dpg)_2$ by a factor of at least 10^5 at room temperature.

We conclude that the four $M(dpg)_2X$ compounds contain halogen molecules surrounded by and interacting with phenyl groups in a $M(dpg)_2$ host. The characteristic but poorly understood epr spectra apparently result from this charge-transfer interaction. We suspect that these compounds are related to the weakly paramagnetic, semiconducting complexes of iodine with polycyclic aromatic hydrocarbons,[7] but a detailed study of the temperature dependence of the spin concentration will be needed to decide this.

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One Electron Transfer Oxidation of 7,12-Dimethylbenz[*a*]anthracene, a Model for the Metabolic Activation of Carcinogenic Hydrocarbons[1]

Sir:

In spite of a wealth of significant work concerned with the problem of relating the carcinogenicity of certain polycyclic aromatic hydrocarbons to their molecular structure,[2–5] there remains today great uncertainty regarding the basic question of whether it is the hydrocarbon itself or some metabolite produced *in vivo* that is the primary trigger for biological activity. Metabolites of several of the hydrocarbons, mostly phenolic or quinoid in nature, have been isolated, but these have proved to be either inactive or less active than the parent hydrocarbons.[6] We wish to describe a chemical model system capable of converting the potent 7,12-dimethylbenz[*a*]anthracene (DMBA) into biologically more active products.

Polycyclic hydrocarbons possess low ionization potentials and readily form radical cations under oxidizing conditions.[7,8] One electron transfer oxidants should therefore produce such species[9] as reactive intermediates; these could become stabilized either by addition of a nucleophile or loss of a proton, followed by dimerization[10] of the resulting radical or further oxidation of the latter to a cation and subsequent reaction with a medium constituent. The potential biochemical significance of such processes derives from the fact that one electron transfer agents such as manganese dioxide, ferricyanide, and Ce^{IV} have been shown to effect oxidative coupling reactions of phenols *via* radical intermediates[11] to produce from appropriate precursors a wide variety of natural products by pathways paralleling those occurring in plant cells.[12]

We have therefore investigated the action of the above reagents on DMBA, with the results summarized in Table I. With MnO_2[13] 25–35% conversion was achieved in 4 days, whereas almost complete utilization of DMBA within 24 hr was observed with $Fe^{III}Fe^{III}(CN)_6$[14] and $(NH_4)_2Ce^{IV}(NO_3)_6$. $K_3Fe^{III}(CN)_6$ yielded the same products but at a much slower rate. $FeCl_3$ showed no reaction. Fractionation of the MnO_2-oxidation products by preparative tlc on silica gel furnished in addition to DMBA five compounds, identified as DMBA-7,12-peroxide (I),[15] 7,12-benz[*a*]anthraquinone (II), 12-methyl-12-hydroxybenz[*a*]anthrone (III), 7-methyl-12-formyl-BA (IV), and 7-formyl-12-methyl-BA (V).[16] 7-Methyl-12-hydroxymethyl-BA (VI)[17] and 7-methyl-7-hydroxybenz[*a*] anthrone (VII) were isolated in addition to I, II, and III by tlc of the mixture derived by oxidation with $(NH_4)_2Ce^{IV}(NO_3)_6$. I, II, V, and VI were identified by melting point, infrared, nmr, and glpc com-

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Table I. Gas Chromatographic Analysis[a] of the Oxidation Products of DMBA with MnO_2, $(NH_4)_2Ce^{IV}(NO_3)_6$, and $Fe^{III}Fe^{III}(CN)_6$[c]

Product	MnO_2,[b] %[d]	$(NH_4)_2Ce^{IV}(NO_3)_6$,[c] %	$Fe^{III}Fe^{III}(CN)_6$,[c] %
I	25	1.5	10
Peak 2[e]	10	6	20
II	14	33	15
VII	8	23	16
III	13	28	22
IV	22	2.5	9
V	8	4.5	5
VI	0	~3	3

[a] Gas-liquid partition chromatography was performed on an F & M Model 400 instrument fitted with a 6-ft 2% SE 30 on Diatoport S column at a He flow rate of 65 cc/min. [b] Four days at 25° under He in benzene in the dark; no reaction took place in chloroform or acetone. [c] 2 equiv in acetone–water, 3:1, at 25° in the dark for 24 hr. [d] Based on converted material only. [e] Unidentified peak.

parison with authentic samples. III,[17a] IV, and VII[17a] had not been reported before. III had mp 139–140°; λ_{max}^{KBr} 3.00, 6.06, 6.25, 13.09, 13.33, 14.13 μ; nmr[18] three-proton singlet at τ 8.09 (7-CH_3), one-proton singlet at 6.94 (OH) (broad), one-proton multiplet at 0.67 (1-CH);[19] *m/e* 274.09992 (M^+), M − 15 (base peak), M − 15 − 28, M − 15 − 28 − 29; IV,[20] mp 127–128°; λ_{max}^{KBr} 6.02, sh 6.04, 12.17, 12.39, 12.58, 13.22, 13.43, and 14.63 μ; nmr[21] three-proton singlet at τ 6.97 (7-CH_3), one-proton multiplet at 0.67 (1-CH),[19] one-proton singlet at −0.36 (12-CH); *m/e* 270.10368 (M^+), M − 1 (base peak), M − 15, M − 29, M − 29 − 15; and VII had mp 127–128°; λ_{max}^{KBr} 3.0, 6.10, 6.28, 13.30, 14.12, and 14.80 μ; nmr three-proton singlet at τ 8.40 (7-CH_3), one-proton singlet at 7.03 (OH), one-proton multiplet at 0.57 (1-CH);[19] *m/e* 274.09939 (M^+), M − 15 (base peak). Compounds I–V were stable toward MnO_2, indicating that none of the products is an intermediate for any of the others. As expected, VI and its 7-hydroxy isomer were readily oxidized by MnO_2 to IV and V, respectively. The similarity in product composition for the three oxidants suggests parallel mechanisms for all of them. As a common precursor we postulate the radical cation of DMBA, from which all the products may be accounted for by primary attack by solvent at positions 7 and 12 and at the methyl carbons. Such preference is in line with the high unpaired spin densities at these sites indicated by the esr spectra of anthracene and 9,10-dimethylanthracene.[22]

I, II, IV, and V were kindly assayed by Drs. S. B. Weiss and W. Moohr in their elegant *E. coli* phage system,[23] which these authors have shown to be inhibited by hydrocarbons in proportion to their carcinogenicity. I and II were found to be inactive, whereas IV and V had twice and ten times the activity of DMBA, respectively.[24] 7-Formyl-12-ethyl-BA (VII)[25] was ten times more active than DMBA and 9-formyl-10-methylanthracene[25] was inactive. V and VII are the most active substances in this system encountered to date.

We suggest as a serious possibility that metabolism of DMBA to IV and/or V may represent the first step in the sequence of events leading to the observed biological activity of the hydrocarbon. It has been shown conclusively that benz[*a*]anthracenes carrying both electron-donating and electron-withdrawing substituents can be potent carcinogens.[3] This finding is difficult to translate into consistent structure–activity relationships for this group of substances. If one assumes, however, that the activity of DMBA is dependent on the metabolic conversion of a methyl into a formyl group, a more rational picture would emerge requiring the presence of an electron-withdrawing group in the molecule. Finally, we wish to point out the utility of this model system in exploring the potential metabolism of other carcinogenic hydrocarbons.[26]

(17a) NOTE ADDED IN PROOF. III and VII were identical with samples isolated from the reaction of II with 1 equiv of CH_3MgI.

(18) Nmr spectra in $CDCl_3$ on a Varian A-60 instrument.

(19) This proton is sufficiently deshielded by the oxygen function at C-12 to be separated from the remainder of the aromatic protons.

(20) IV was identical with an authentic sample prepared by a different procedure by Dr. J. Pataki. We wish to thank Dr. Pataki for gifts of this and other samples for comparison purposes.

(21) All the peaks in this spectrum are shifted downfield by 10 cps on dilution from 0.2 to 0.02 *M*, indicating intermolecular interactions. Similar shifts of 10 and 3.5 cps, respectively, were observed with 7-formyl-12-methylbenz[*a*]anthracene, τ 6.73 (12-CH_3), −1.3 (7-CH); and DMBA, τ 6.99 (7-CH_3), 6.71 (12-CH_3).

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(24) I and II are known to be noncarcinogens. V has been reported to be carcinogenic (*cf.* ref 6, p 123).

(25) Kindly supplied by Dr. J. Pataki.

(26) 3,4-Benzopyrene and 3-methylcholanthrene are readily oxidized by $Fe^{III}Fe^{III}(CN)_6$. The nature of the products is being investigated.

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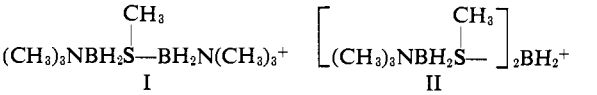
Bis- and Trisborane Monovalent Cations

Sir:

We wish to report new types of borane cations (I and II) containing sulfur bridges, the first examples of bis- and trisborane cations. Whereas trimethylamine-



(methyl trimethylamineboryl sulfide)boron(1+) (I) has very good thermal and hydrolytic stability, bis(methyl trimethylamineboryl sulfide)boron(1+) (II) hydrolyzes in water at a moderate rate. Both can be isolated and handled in air as their crystalline hexafluorophosphate salts.

The infrared spectra of I and II are closely related, having strong, symmetrical doublet BH absorption characteristic of borane cations of soft bases such as phosphines and arsines.[1] The ^1H nmr spectrum of I as the PF_6^- salt in CH_2Cl_2 shows two singlets at 2.31 and 2.78 ppm (downfield from tetramethylsilane) in a ratio of 1:6, assigned to S–CH_3 and N–CH_3 protons, respectively. The spectrum of II has two singlets at 2.20 and 2.72 ppm in a ratio of 1:3. Thus the nmr spectra support structures with free rotation as written.

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