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).

(22) J. R. Bolton, H. Carrington, and A. D. McLachlan, *Mol. Phys.*, **5**, 31 (1962).

(23) W. T. Hsu, W. Moohr, and S. B. Weiss, *Proc. Natl. Acad. Sci. U. S.*, **53**, 517 (1965); W. T. Hsu, W. Moohr, A. Y. M. Tsai, and S. B. Weiss, *ibid.*, **54**, 1475 (1966).

(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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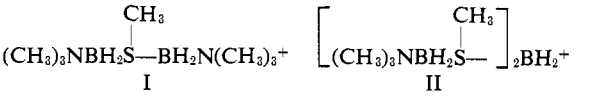
Bis- and Trisborane Monovalent Cations

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.

(1) N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964).

Hydrolysis in the presence of platinum black confirmed the compositions.

Anal. Calcd for $[(CH_3)_3NBH_2]_2SCH_3^+PF_6^-$ (mmoles/mg $\times 10^2$): H_2, 1.21; CH_3SH, 0.302; $(CH_3)_3N$, 0.596. Found: H_2, 1.19; CH_3SH, 0.304; $(CH_3)_3N$, 0.540.[2] Calcd for $[(CH_3)_3NBH_2SCH_3]_2BH_2^+PF_6^-$ (mmoles/mg $\times 10^2$): H_2, 1.51; CH_3SH, 0.505; $(CH_3)_3N$, 0.505. Found: H_2, 1.48; CH_3SH, 0.499; $(CH_3)_3N$, 0.443.[2]

Contrary to other experience[3] that -SR groups are easily displaced in boranes, the bridging thiomethyl group of I is quite inert. Neither trimethylamine nor pyridine, nor pyridine in refluxing methylene chloride, react. A high degree of stability was also observed for I toward both hot acid and hot base. As the PF_6^- salt it appears to be indefinitely stable in air. For the most part such stability must result from the steric protection of the sulfur atom by the two $BH_2N(CH_3)_3$ groups which are homomorphs[4] of neopentyl. The cation II which has less steric protection of bridging sulfur atoms is not nearly as stable to degradative attack.

The strong S–B dative bonds in both I and II are in sharp contrast to weak, easily displaced bonds in other simple borane complexes such as $(CH_3)_2S$–BH_3[5] or $[(CH_3)_2S]_2BH_2^+$.[1] It seems proper, therefore, to describe the $(CH_3)_3N$–$BH_2\cdot$ group as very strongly electron releasing in comparison to H· or even $\cdot CH_3$. This inductive effect has been suggested earlier,[5,6] but its magnitude has been overlooked. For example, trimethylamine methylthioborane, $(CH_3)_3NBH_2SCH_3$, has been shown by this work to be a strong base, stronger than methyl sulfide, and perhaps even as strong as alkylphosphines. A study of the effects of the $(CH_3)_3NBH_2$ group has therefore been initiated.

The new cations were prepared by a modification[7] of Douglass's reaction.[8] Trimethylamine methylthioborane was prepared from methanethiol, diborane, and trimethylamine in ether by a method not essentially different from literature directions.[5] A solution of this adduct in chloroform was added to a chloroform solution of $(CH_3)_3NBH_2I$, followed by evaporation and conversion of the iodide salt to the hexafluorophosphate salt.

Anal. Calcd for $[(CH_3)_3NBH_2]_2SCH_3^+PF_6^-$: C, 25.0; H, 7.4; N, 8.4. Found: C, 24.5, 25.0; H, 7.1, 7.4; N, 8.2, 9.6.

Similarly, the trisborane cation II was prepared from the new borane adduct III of trimethylamine methylthioborane. This adduct, a white solid soluble in chloroform, has a proton nmr spectrum showing S–CH_3 and N–CH_3 singlets at 2.00 and 2.72 ppm, respectively (downfield from tetramethylsilane in methylene chloride solution), in a 1:3 ratio.[9] A solution of III in chloroform was treated with 0.5 mole of iodine at room temperature. After hydrogen release was terminated, a solution of trimethylamine methylthioborane was added. The mixture was evaporated and the residue dissolved in water. The cation II was isolated as the hexafluorophosphate salt which recrystallized from methylene chloride as colorless plates.

$$\begin{array}{c} CH_3 \\ | \\ (CH_3)_3NBH_2S{-}BH_3 \end{array}$$
III

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(2) Quantitative recovery of trimethylamine from the aqueous hydrolysates was difficult because of its good solubility.

(3) V. D. Scheludyakov, T. A. Shchegoleva, and B. M. Mikhailov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **4**, 632 (1964).

(4) H. C. Brown, G. K. Barbaras, H. L. Berneis, W. H. Bonner, R. B. Johannesen, M. Grayson, and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 1 (1953).

(5) A. B. Burg and R. I. Wagner, *ibid.*, **76**, 3307 (1954).

(6) N. E. Miller, *ibid.*, **88**, 4284 (1966).

(7) G. E. Ryschkewitsch, *ibid.*, **89**, 3145 (1967).

(8) J. E. Douglass, *ibid.*, **86**, 5431 (1964).

(9) No trimethylamine borane was detected in the ^1H nmr spectrum (resonance at -2.61 ppm in methylene chloride) or the infrared spectrum. This spectral evidence, along with the invariance of the adduct's infrared spectrum on recrystallization, supports the assigned structure and eliminates the possibility that the adduct is a mixture of trimethylamine borane and methylthioborane polymer.

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The Relative Importance of Inductive and Steric Effects in Producing Secondary Hydrogen Isotope Effects on Triphenyl Cation Formation[1]

Sir:

There is good reason to believe that secondary hydrogen isotope effects are principally vibrational in origin; such isotope effects are now understood to be the result of force constant changes between initial and transition (final) states.[2] Less, however, is known about the factors responsible for these force constant changes, and quite recently the suggestion was made that they may be wholly steric in origin.[3] We wish to present evidence which demonstrates that steric effects make at best only a minor contribution to secondary hydrogen isotope effects on the ionization of triphenylcarbinol to the triphenyl cation.

$$Ph_3COH + H^+ \underset{}{\overset{K}{\rightleftharpoons}} Ph_3C^+ + H_2O \qquad (1)$$

We have used a spectroscopic method to measure the position of equilibrium of the reaction represented by eq 1 for normal and variously deuterated substrates. By operating in a single acidic medium of fixed composition at low per cent conversion of carbinol to cation where ratios of equilibrium constants, K_H/K_D, are approximately equal to ratios of molar absorbances of the respective cations, we were able to determine isotope effects with a precision of $\pm 0.3\%$. This is sufficient to establish with confidence the magnitude of even the smallest isotope effect we encountered. The data for seven deuterated substrates (Table I) show

(1) Based upon a thesis submitted by R. J. Preto to the Illinois Institute of Technology, June 1967, in partial fulfillment of the requirements for the Ph.D. degree; this research was supported by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-1025 to the Illinois Institute of Technology.

(2) M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 225 (1964); *J. Chem. Phys.*, **45**, 2618 (1966); E. R. Thornton, *Ann. Rev. Phys. Chem.*, **17**, 349 (1966); J. C. Evans and G. Y.-S. Lo, *J. Am. Chem. Soc.*, **88**, 2118 (1966).

(3) H. C. Brown, M. E. Azzaro, J. G. Koelling, and G. J. MacDonald, *ibid.*, **88**, 2520 (1966).