Hydrolysis in the presence of platinum black confirmed the compositions.

Anal. Calcd for $[(CH_3)_3NBH_2]_2SCH_3{}^+PF_6{}^-$ (mmoles/mg × 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 × 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]

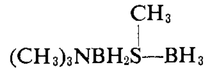
Contrary to other experience[3] that –SR groups are easily displaced in boranes, the bridging thiomethyl group of I is quite inert. Neither trimethylamine nor pyridine, nor pyridine in refluxing methylene chloride, react. A high degree of stability was also observed for I toward both hot acid and hot 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 $H\cdot$ 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.



$$(CH_3)_3NBH_2\overset{CH_3}{\overset{|}{S}}—BH_3$$

III

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.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation and a grant from the Research Fund of the University of South Dakota.

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

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(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.

(10) National Defense Education Act Fellow.

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Received July 24, 1967

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.

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

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 ±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

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(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).

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that the effect of successive isotopic substitution at *ortho*, *meta*, or *para* positions is cumulative. Least-squares analysis gives a set of individual position isotope effects per deuterium atom, $(K_D/K_H)_{ortho} = 1.0133 \pm 0.0004$, $(K_D/K_H)_{meta} = 1.0133 \pm 0.0007$, and $(K_D/K_H)_{para} = 1.0082 \pm 0.004$, which fit the data within the experimental uncertainty (Table I, columns 3 and 4).

Table I. Isotope Effects on the Equilibrium Formation of Triphenyl Cation from Triphenylcarbinol[a]

Substrate[b]	K_D/K_H Obsd[c]	Calcd	Obsd − calcd
Triphenyl-2,2′,2′′-d_3-methanol	1.0443 ± 0.0030	1.0403	+0.0040
Triphenyl-3,3′,3′′-d_3-methanol	1.0458 ± 0.0027	1.0404	−0.0054
Triphenyl-4,4′,4′′-d_3-methanol	1.0222 ± 0.0030	1.0250	−0.0028
Triphenyl-2,2′,2′′,-6,6′,6′′-d_6-methanol	1.0784 ± 0.0027	1.0822	−0.0038
Triphenyl-3,3′,3′′,-5,5′,5′′-d_6-methanol	1.0800 ± 0.0019	1.0824	−0.0024
Triphenyl-2,2′,2′′,-4,4′,4′′-6,6′,6′′-d_9-methanol	1.1094 ± 0.0014	1.1093	+0.0001
Triphenyl-d_{15}-methanol	1.2014 ± 0.0016	1.2007	+0.0007

[a] At 25° in a solvent consisting of four parts by volume of 50% aqueous H_2SO_4 and one part of glacial acetic acid. [b] Deuterium content at labeled position, 97–99%. [c] Error estimates are standard deviations of mean values; measurements were performed at least in triplicate.

These isotope effects are all inverse: ring deuteration at any position increases the extent of ionization of triphenylcarbinol. This is the same as the direction of isotope effects found in other cases where positive charge is generated next to a benzene ring[4] and is opposite to the direction of isotope effects found in situations where negative charge is produced at a similar position.[4b,5] It seems likely, therefore, that charge (inductive effect) plays an important role in the origin of these isotope effects. A steric explanation, on the other hand, is inconsistent with the direction and relative magnitude of these isotope effects. Since the present reaction is a process in which a tetrahedral substrate is converted to a trigonal carbonium ion, it should proceed with relief of steric strain[6] provided principally by nonbonded interactions between *ortho* ring hydrogens. This relief of steric repulsion should lower the *ortho* C–H force constant, loosening this bond and producing an isotope effect in the normal direction ($K_H/K_D > 1$). There should, of course, be no isotope effect at the *meta* and *para* positions. The observed isotope effect at the *ortho* position, however, is inverse, and the *meta* and *para* effects are not unity.

Thus, steric effects cannot be the major cause of the presently observed isotope effects; the explanation must lie in an inductive tightening of *ortho*, *meta*, and *para* C–H bonds. Nevertheless, a case can be made for a *minor* steric contribution to the isotope effect at the *ortho* position. In the solvolysis of benzhydryl chlorides,[4b,c] a system closely analogous to the present reaction, isotope effects of 1.9 ± 0.1, 1.5 ± 0.1, and 1.0 ± 0.1% per deuterium atom were found for isotopic substitution at *ortho*, *meta*, and *para* positions, respectively. When account is taken of the fact that the electron demand of this reaction ($\rho = -4.0$)[7a] is slightly greater than that of triphenylcarbinol ionization ($\rho = -3.5$),[7b] these *meta* and *para* isotope effects agree remarkedly well with those measured here: *meta*, $(1.33 \pm 0.07)\% \times {}^{4.0}/_{3.5} = 1.52 \pm 0.08\%$; *para*, $(0.82 \pm 0.04)\% \times {}^{4.0}/_{3.5} = 0.94 \pm 0.05\%$. On this basis, however, the present *ortho* isotope effect is too small: $(1.33 \pm 0.04)\% \times {}^{4.0}/_{3.5} = 1.52 \pm 0.05\%$. This suggests that an additional effect is operative in the present reaction which is absent from the solvolysis case, and, since triphenylcarbinol is a much more crowded molecule than benzhydryl chloride, it is reasonable that this added effect be steric. This possible steric lowering of the *ortho* isotope effect, however, amounts only to one-fifth of the expected *ortho* inductive isotope effect, and this shows that steric isotope effects in this system are decidedly of secondary importance.

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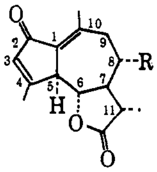
Received September 5, 1967

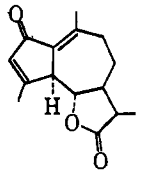
The Synthesis and Stereochemistry of Desacetoxymatricarin and Achillin

Sir:

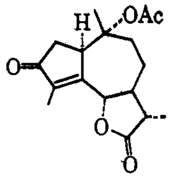
We wish to report syntheses of desacetoxymatricarin[1–4] (Ia) and achillin[1,5] (II) that establish the absolute stereochemistry of the compounds and provide ready access to the 2-ketoguianolides. The stereochemistry of matricarin[1,6] (Ic),[7] jacquenilin,[8] and ar-



Ia, R = H
b, R = OH
c, R = CH_3CO_2



II



III

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