Table II. Quenching of 1' with Acetic Acid

Dithio-carba-mate	Solvent HMPT–THF (w/w)	Reaction time (min)	Yield (%)	Product ratio (%) 3	1
1a	0:1	5	99	0	100
1a	1:2	10	98	65	35
1a	1:1	10	97.5	98	2
1b	0:1	5	99	0	100
1b	1:2	17	93	75	25
1b	1:1	60	96	100	0

solution, seems to be characteristic of this rearrangement, whose end point can be indicated by disappearance of the color. When the reaction was stopped by quenching with acetic acid or methyl iodide before disappearance of the color, a mixture of 1 and 3 or 2 and 4 was obtained, the ratio depending on the reaction time and solvent ratio. As seen in Tables I and II, an increase of HMPT–THF ratio leads to the acceleration of the rearrangement. The reaction, conducted in 1:3 HMPT–THF solution for 1a, required 30 min for 100% completion, whereas the reaction in 1:1 solution completed in only 10 min. Tables I and II also show that the rearrangement rate is much faster for 1a than for 1b; 1 hr was necessary for 100% completion of the 1,2-shift of 1b even in 1:1 HMPT–THF solution. Further studies on the mechanism and extension of the 1,2-rearrangement are underway.

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Correlations between Carbon-13 and Boron-11 Chemical Shifts. IV. Carbenium Ions and Their Trigonal Boron Analogs[1]

Sir:

Many of the recent advances in the study of carbocations have been achieved by the discovery of Olah and coworkers[2] of methods to prepare stable carbocations in solution and the application of NMR spectroscopy to study them. Of the NMR methods, ^{13}C techniques are especially powerful in that the positively charged carbon nuclei can be directly observed.[3] In this communication, we present the results of a

Table I. Carbon-13 and Boron-11 Chemical Shifts for Some Carbenium Ions and Their Trigonal Boron Analogs

No.	Carbenium Ion	$^{13}C^a$	Boron compd	$^{11}B^b$
1	$C(OH)_3^+$	28.0[c]	$B(OH)_3$	-18.8[i]
2	$CH_3C(OH)_2^+$	-1.6[c]	$CH_3B(OH)_2$	-31.9[j]
3	$(CH_3)_2COH^+$	-55.7[c]	$(CH_3)_2BOH$	-54.6[j]
4	$(CH_3)_3C^+$	-135.4[c]	$(CH_3)_3B$	-86.0[k]
5	$(CH_3)_2CCl^+$	-120.0[d]	$(CH_3)_2BCl$	-77.2[l]
6	$(CH_3)_2CBr^+$	-126.0[d]	$(CH_3)_2BBr$	-78.8[l]
7	$(CH_3)_2CF^+$	-89.1[d,e]	$(CH_3)_2BF$	-59.0[l]
8	$(C_6H_5)_2CCl^+$	-75.8[f]	$(C_6H_5)_2BCl$	-61.0[l]
9	$C_6H_5C(OH)_2^+$	12.0[g]	$C_6H_5B(OH)_2$	-28.4[m]
10	$(C_6H_5)_3C^+$	-18.1[c]	$(C_6H_5)_3B$	-60.2[n]
11	$c\text{-}C_3H_5C(CH_3)_2^+$	-86.8[c]	$c\text{-}C_3H_5B(CH_3)_2$	-81.6[o]
12	$(CH_3)_2CH^+$	-125.0[h]	$(CH_3)_2BH$	-73.5[p]
13	$(CH_3)_2CC_2H_5^+$	-139.2[c]	$(CH_3)_2BC_2H_5$	-85.1[p]
14	$(C_2H_5)_2CCH_3^+$	-139.4[c]	$(C_2H_5)_2BCH_3$	-85.5[p]
15	$(C_6H_5)_2COH^+$	-15.4[h]	$(C_6H_5)_2BOH$	-42.5[p]

[a] Chemical shifts (for carbenium ion centers) are in parts per million from $^{13}CS_2$. Positive sign indicates shielding from the reference. [b] In parts per million from $BF_3\cdot(C_2H_5)_2O$. Positive sign indicates shielding from the reference. [c] Reference 3a. [d] G. A. Olah, Y. K. Mo, and Y. Halpern, J. Am. Chem. Soc., 94, 3551 (1972). [e] G. A. Olah, Y. K. Mo, and Y. Halpern, ibid., 96, 1642 (1974). Correction of shift for $(CH_3)_2CF^+$, reported as -142.7 in footnote d due to a computational error made using the endor method. [f] This work; from $(C_6H_5)_2CCl^+SbF_6^-$ in CH_2Cl_2. [g] G. A. Olah and A. M. White, J. Am. Chem. Soc., 89, 7072 (1967). [h] G. A. Olah, P. W. Westerman, and J. Nishimura, ibid., 96, 3548 (1974). [i] T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, J. Phys. Chem., 63, 1533 (1959). [j] J. E. DeMoor and G. P. Van der Kelen, J. Organomet. Chem., 6, 235 (1966). [k] H. Nöth and H. Vahrenkamp, Chem. Ber., 99, 1049 (1966). [l] H. Nöth and H. Vahrenkamp, J. Organomet. Chem., 11, 399 (1968). [m] M. J. S. Dewar and R. Jones, J. Am. Chem. Soc., 89, 2408 (1967). [n] H. Landesman and R. E. Williams, ibid., 83, 2663 (1961). [o] A. H. Cowley and T. A. Furtsch, ibid., 91, 39 (1969). [p] Calculated by pairwise additivity parameters as described in text.

correlation of ^{13}C chemical shifts in carbenium ion[4] centers with ^{11}B shifts in the isoelectronic trigonal boron analogs. Such a correlation should have considerable implications for the study and interpretation of chemical shifts in these species.

Table I contains chemical shift data for some carbenium ions and their isoelectronic boron analogs. All chemical shifts are experimentally observed values except for the ^{11}B shifts for entries 12–15. These values were calculated from pairwise additivity parameters which have been found to closely reproduce experimentally observed ^{11}B shifts.[5,6] Figure 1 shows a plot of the ^{13}C shifts of the carbenium ion centers vs. the ^{11}B shifts of the analogous boron compounds. With the exception of the triphenyl and cyclopropyldimethyl analogs, a linear relationship exists. With the first nine entries in Table I, represented by solid circles in Figure 1, a least-squares analysis yields the equation[7]

$$\delta^{11}B = 0.384\delta^{13}C - 31.6$$

The correlation coefficient is 0.987 and the standard deviation of ^{11}B shifts calculated from ^{13}C values is 2.7 ppm (in shift) out of range of ^{11}B values of 67 ppm. Of considerable interest is the fact that the slope is very close to that observed (0.40) in the linear correlation of ^{13}C and ^{11}B chemical shift data between tetracoordinate boron and carbon compounds.[1a]

The correlation was extended by inclusion of ^{11}B shifts (entries 12–15 in Table I) calculated from pairwise additivity parameters for species whose shifts have not yet been measured or do not exist under ordinary conditions. The rule of pairwise additivity, shown by Malinowski[5] to closely reproduce observed ^{11}B shifts in some mixed boron trihalides, was applied to some 73 observed ^{11}B shifts in trigonal
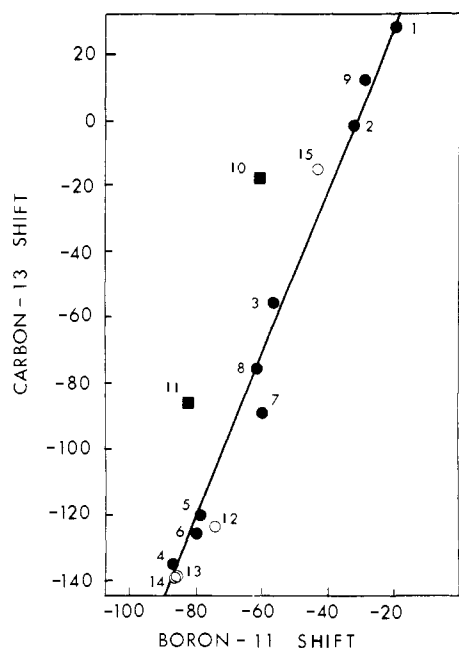
Figure 1. A plot of ^{13}C shifts in carbenium ions vs. ^{11}B shifts in the analogous trigonal boron compounds. ^{13}C shifts are in parts per million from CS_2 and ^{11}B shifts are in parts per million from $BF_3 \cdot Et_2O$. Positive sign indicates shielding from the reference. Numbers refer to entries in Table I. The line represents the least-square fit for entries 1–9 (solid circles). Open circles represent points whose ^{11}B shifts were calculated using pairwise additivity parameters. Squares represent the two entries not included in the least-squares analysis.

Table II. Comparison between Observed ^{13}C Chemical Shifts and Values Calculated by Pairwise Additivity

Ion	Obsd[a]	Calcd
$(C_6H_5)_2COH^+$	-15.4[b]	-15.9
$C_6H_5C(OH)_2^+$	$+12.0$[c]	$+12.5$
$C(OH)_3^+$	$+28.0$[d]	$+27.8$
$(CH_3)_3C^+$	-135.4[c]	-135.2
$(CH_3)_2COH^+$	-55.7[c]	-55.8
$CH_3C(OH)_2^+$	-1.6[c]	-1.5
$(C_6H_5)_2CCH_3^+$	-35.5[b]	-35.0
$C_6H_5C(CH_3)_2^+$	-60.6[b]	-61.1

[a] Chemical shifts are in parts per million from $^{13}CS_2$. Positive sign indicates shielding from the reference. [b] Reference h, Table I. [c] Reference g, Table I.

boron compounds.[6] The standard deviation between observed and calculated values was 1.3 ppm in shift out of a range of ^{11}B values of 94 ppm. Some typical pairwise interaction parameters $(\eta_{i,j})$ obtained in this study were (ppm from $BF_3 \cdot Et_2O$): $\eta_{Me,Me}$ (-28.7), $\eta_{Et,Et}$ (-29.1), $\eta_{Me,Et}$ (-28.2), η_{NMe_2,NMe_2} (-10.1), $\eta_{OH,OH}$ (-6.3), and $\eta_{Me,H}$ (-22.2).[8] Using these parameters, shifts for entries 12–15 were calculated, e.g.

$$\delta_{Me_2BH} = \eta_{Me,Me} + 2\eta_{Me,H} = -73.5 \text{ ppm}$$

Interestingly, almost identical values for the shifts of Me_2BEt and $MeBEt_2$ are obtained, and this unusual substituent effect has been noted by Olah and White[3a] in the carbenium ion analogs. Inclusion of entries 12–15 in the least-squares analysis yields the equation

$$\delta^{11}B = 0.368\delta^{13}C - 32.1$$

with a standard deviation of 3.1 ppm in shift (correlation coefficient 0.982).

Concerning entry 11, Olah and Pittman,[9] on the basis of low temperature ^1H NMR studies, showed that the cyclopropane ring does not rotate in c-PrCMe$_2^+$ (up to $-30°$) and proposed that this ion exists in the "bisected" form. In contrast, the optical and ^1H NMR studies of Cowley and Furtsch[10] on c-PrBMe$_3$ were consistent with a freely rotating cyclopropyl group at temperatures as low as $-100°$. Figure 1 shows that the carbenium ion center for c-PrCMe$_2^+$ is shielded by some 43 ppm more than would be predicted from the ^{11}B shift of its analog and is consistent with the apparent lack of conjugation in the boron species relative to the carbenium ion as found above.

Concerning entry 10, it is now well established that both triarylboranes and carbenium ions have a propeller conformation in the ground state due to steric crowding in the ortho positions.[11] However, ^{11}B shifts for Ph$_3$B and a series

of diphenyl- and phenyl-substituted trigonal boranes all obey the rule of pairwise additivity.[6] In contrast, Ph$_3$C$^+$, does not. Table II, listing observed and calculated shifts for some carbenium ions, shows that these species closely obey the pairwise additivity rule (standard deviation 0.368 ppm in chemical shift). Inclusion of Ph$_3$C$^+$ in the treatment increases the standard deviation to 4.2 ppm. Interestingly, the value calculated for Ph$_3$C$^+$ $(-57$ ppm) using the $\eta_{Ph,Ph}$ value (-19.0) obtained by the pairwise additivity treatment of the shifts in Table II is much closer to that predicted from the ^{11}B shift of Ph$_3$B. Recently, Djerassi et al.,[12] on the basis of absorption and magnetic circular dichroism spectroscopic studies of Ph$_3$C$^+$, have concluded that the propeller-shaped structure of this ion is very sensitive to the nature of the counterion. The deviations for Ph$_3$C$^+$ noted above may, in part, reflect a significant counterion or solvent effect on the ^{13}C shift for this species. Further studies to better define this correlation are underway.[13]

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