nation with the electrochemically determined[14] equilibrium quotient K_5 (= k_5/k_{-5} = 1.9×10^{-3}) yields k_6 = 7.4×10^{-3} sec^{-1}, in satisfactory agreement with the value of 9.2×10^{-3} sec^{-1} derived from direct measurements of the rate of decomposition of $[n\text{-}C_3H_7Co(DH)_2(H_2O)]^+$ as described above.

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(13) These measurements encompassed the initial concentration ranges 2×10^{-2} to 8×10^{-3} *M* CoR, 3.7×10^{-5} to 7.5×10^{-4} *M* $IrCl_6^{2-}$, and 0 to 3.1×10^{-3} *M* $IrCl_6^{3-}$, all at 25° and 1 *M* $HClO_4$.
(14) $\log K_5 = [E_{1/2}(IrCl_6^{3-}) - E_{1/2}(CoR)]/0.059$.
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A New 1,2-Rearrangement of Carbon from Sulfur to Carbon in Allyl and Benzyl Dithiocarbamates

Sir:

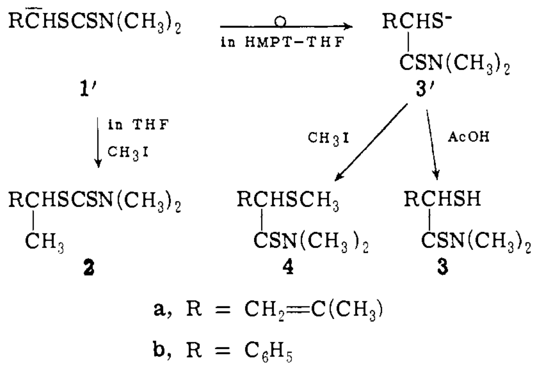
A 1,2-rearrangement of an ether to its isomeric alcohol which can occur upon metalation with excess organolithium reagent is well known as the Wittig rearrangement.[1,2] Here migration of carbon from sulfur to a negatively charged carbon occurs. However, rearrangement of this type has not been reported for sulfur analogs, except for the case in which silicon is the migrating atom.[3,4] In general, metalation of the rather acidic proton flanked by sulfur in sulfides,[5] sulfoxides,[6] and sulfones[7] produces stable carbanions which do not rearrange.

We now report the first example of a Wittig type rearrangement, where migration of carbon from sulfur to an α-carbanion occurs.[8] β-Methallyl and benzyl *N,N*-dimethyldithiocarbamates (**1a** and **1b**) are quite readily metalated with a slight excess of lithium diisopropylamide in tetrahydrofuran(THF) at −60°. Treatment of the resulting carbanions (**1′**) with methyl iodide affords α-methyl-β-methallyl and α-methylbenzyl *N,N*-dimethyldithiocarbamates (**2a** and **2b**) in an excellent yield.[9] However, the reaction, when conducted in the presence of hexamethylphosphoric triamide (HMPT), takes a wholly different course to give *N,N*-dimethyl-2-methylthio-3-methylbut-3-enethioamide (**4a**) and phenylthioacetamide (**4b**) in a practically quantitative yield.

Table I. Reaction of 1 with CH_3I

Dithio-carbamate	Solvent HMPT–THF (w/w)	Reaction time (min)	Yield (%)	Product ratio (%) 4	2
1a	0:1	5	98	0	100
1a	1:5	10	84.8	50	50
1a	1:3	30	96.2	100	0
1a	1:2	10	87.2	86	14
1a	1:1	10	82	97.3	2.7
1b	0:1	5	99	0	100
1b	1:2	7	93	53	47
1b	1:1	60	96	100	0

In a typical experiment, 14 mmol of **1** was introduced at −60° to 15 mmol of lithium diisopropylamide in a mixture of 10 ml of *n*-hexane and 25 ml of HMPT–THF (1:3 (w/w)) during 5 min. A deep violet color developed at once. The solution was stirred at −60°, until the violet color disappeared. The resulting orange solution was quenched with methyl iodide or acetic acid, becoming pale yellow. Quenching with acetic acid yielded *N,N*-dimethyl-2-mercapto-3-methylbut-3-enethioamide (**3a**) or phenylthioacetamide (**3b**), a new class of compounds. After washing with water, evaporation of the solvent gave products **3** or **4** in a practically quantitative yield.



Elemental analysis and mass spectra showed that **3** and **4** are isomeric with **1** and **2**, respectively. Structures **2**, **3**, and **4** were assigned by spectral studies: **2b**,[10] mp 42–43°; NMR ($CDCl_3$) δ 1.79 (t, *J* = 6.8 Hz, CH_3), 3.30 and 3.42 (s, broad, $(CH_3)_2N$), 5.26 (q, *J* = 6.8 Hz, CH), and 7.20–7.54 ppm (m, C_6H_5); ir (Nujol) 1140 cm ($\nu_{C=S}$); *m/e* 225 (M^+), 105 ($M^+ - SCSN(CH_3)_2$); **3a**, oil which solidified in a refrigerator and gradually decomposed on standing at room temperature, NMR ($CDCl_3$) δ 1.92 (s, $CH_3C=$), 2.95 (d, *J* = 7.6 Hz, SH), 3.40 and 3.56 (s, $(CH_3)_2N-$), 4.83 (d, *J* = 7.6 Hz, CH), 5.02 and 5.16 (m, $CH_2=$); ir (Nujol) 2540 (ν_{SH}), 1140 cm ($\nu_{C=S}$); *m/e* 175 (M^+), 142 ($M^+ - SH$); **3b**, mp 104–105°, which gradually decomposed on standing at room temperature; NMR ($CDCl_3$) δ 3.17 (d, *J* = 7.0 Hz, SH), 3.24 and 3.53 (s, $(CH_3)_2N-$), 5.54 (d, *J* = 7.0 Hz, CH), 7.30 ppm (m, C_6H_5); ir (Nujol) 2540 (ν_{SH}), 1140 cm ($\nu_{C=S}$); *m/e* 221 (M^+), 178 ($M^+ - SH$); **4a**, mp 66–67°; NMR ($CDCl_3$) δ 1.84 (s, $CH_3C=$), 2.07 (s, CH_3S), 3.38 and 3.49 (s, $(CH_3)_2N-$), 4.60 (s, CH), 5.00 and 5.08 ppm (m, $CH_2=$); ir (Nujol) 1140, 1112 cm ($\nu_{C=S}$); *m/e* 189 (M^+), 142 ($M^+ - SCH_3$); **4b**, mp 104–105°; NMR ($CDCl_3$) δ 2.08 (s, CH_3S), 3.21 and 4.46 (s, $(CH_3)_2N-$), 5.21 (s, CH), 7.20 −7.65 ppm (m, C_6H_5); ir (Nujol) 1140, 1112 cm ($\nu_{C=S}$); *m/e* 225 (M^+), 173 ($M^+ - SCH_3$).

The reaction conditions and yield are summarized in Tables I and II. A deep violet color, which develops upon metalation of **1** with organolithium reagent in HMPT–THF

Table II. Quenching of 1′ with Acetic Acid

Dithiocarbamate	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 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. 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.

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