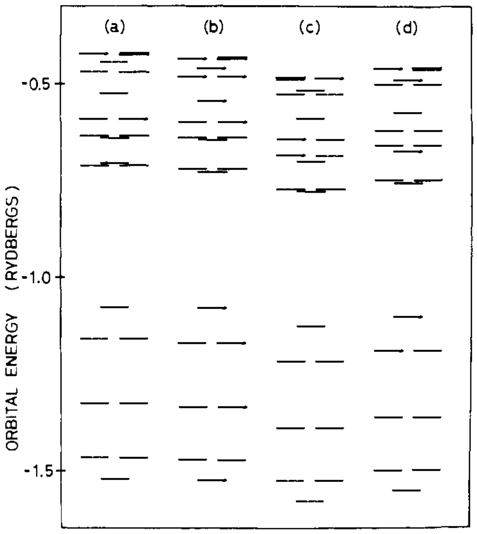

Figure 2. SCF-Xα-SW orbital eigenvalues (Rydbergs) for S_8 using various basis sets (l_{max} on S, l_{max} on outer sphere); (a) (1,2); (b) (2,2); (c) (2,4); (d) (3,3).

a discussion). Further work is required to assess the importance of each of these factors; however the degree of agreement between Figures 1b and 1c discussed below indicates that, for the qualitative purposes with which we are concerned, the comparison is valid.

For the purpose of discussion we will divide the plane into three regions (i) the core region, near the sulfur nuclei, (ii) the region further removed from the nuclei perpendicular to the S–S line, and (iii) the bond region along the S–S line.

For region i the experimental results are "notoriously unreliable" [3a] and, since we have used the frozen core approximation in our calculations, this region will not be discussed in detail. The hatched areas on Figures 1a and 1b correspond to regions of large valence electron deformation density and yield a rough indication of the extent of the core area.

Region ii is also rather easily dealt with. Experimentally one finds "lone-pair" lobes with a maximum density difference of ~0.5 e Å^{-3} which is precisely what we have found in our calculations for all basis sets considered. There is relatively little effect of the higher partial waves for this region. The agreement is very good and therefore promotes optimism as to the accuracy of the Xα wave functions.

Region iii, along the S–S line, is more complicated. Here Coppens et al.[5] found a complicated double maximum distribution with a remarkably small electron surplus at the midpoint of the bond. The minimum basis set calculation, Figure 1a, is completely unsatisfactory for this region, almost all of the S–S line having a negative deformation density. A similar lack, or underestimate, of electron density gain in the bonding region for other molecules has previously been noted[3,11] if small basis sets are used in the approximate Hartree–Fock or the discrete variational-Xα method. For example the CO molecule shows a negative deformation density throughout the bonding region if a minimum basis set of Slater orbitals is used in a Hartree–Fock-type calculation.[11]

In the present case the bond region can be systematically improved by adding further partial waves to the basis set, first d waves (not shown) and then both d and f waves (Figure 1b). The large negative area of Figure 1a shrinks and by the time one has f waves it is reduced to a number of small regions along the border of the muffin-tin sphere which surrounds the atom. It is clear that at this stage the negative regions are unphysical but are rather a result of slight discontinuities in the wave functions which would disappear if calculations were performed with an even larger set of partial waves. For the calculations including f waves the deformation density is now positive for most of the interatomic region although it is still much smaller than the experimental values.

Overall the qualitative features of the change in electron density upon formation of the S_8 molecule from eight sulfur atoms are reasonably well accounted for in the extended basis set calculation. Partial waves of high angular momentum quantum number are necessary in order to account for the details of the deformation density. Spectroscopic results, i.e., the positions of the orbital eigenvalues, are much less sensitive to the changes in basis set as shown in Figure 2. Clearly the same overall pattern of energy levels is obtained for all of the sets of partial waves considered, typical energy level shifts being of the order of at most a few tenths of an electron volt. The spectroscopic results for S_8 will be discussed elsewhere.[12]

In conclusion the electron density distribution for S_8 as calculated by the SCF-Xα-SW method with an extended basis set is found to be remarkably accurate, especially in light of the approximations (muffin-tin potential, truncated partial wave expansion etc.) made in the method.

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A Novel Class of Alkylating Reagent, RCu·BF$_3$. Substitution of Allyl Halides with Complete Allylic Rearrangement

Sir:

Substitution of allylic substrates with (or without) complete allylic rearrangement is still a challenge for chemists.[1] We now wish to report that the substitution with complete allylic rearrangement is achieved by using a new alkylating reagent, RCu·BF$_3$ (eq 1). To our knowledge, this is the first example

Table I. Reaction of Cinnamyl Halides with Various CH_3Cu-borane Complexes[a]

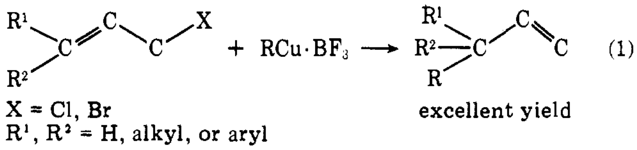
Entry	Reagent	$PhCH{=}CHCH_2X$, X	Products, %[b] $PhCH(CH_3)CH{=}CH_2$	Products, %[b] $PhCH{=}CHC_2H_5$	Yield, %[b] (isold)
1	$(CH_3)_2CuLi$	Br	30	70	97
2	CH_3Cu	Cl	74	26	95
3	$CH_3Cu{\cdot}B(C_2H_5)_3$	Cl	87	13	92
4	$CH_3Cu{\cdot}B(n\text{-}C_4H_9)_3$	Cl	89	11	95
5	$CH_3Cu{\cdot}B(n\text{-}C_4H_9)_3$	Br	90	10	95
6	$CH_3Cu{\cdot}B(OCH_3)_3$	Cl	79	21	96
7	$CH_3Cu{\cdot}BF_3$	Cl	89	11	97
8	$CH_3Cu{\cdot}BF_3$[c]	Cl	>99.5	<0.5	(90)

[a] CH_3Cu-borane complexes were prepared by addition of the borane derivatives to CH_3Cu at −70 °C in ether, except where otherwise indicated. All reactions were performed on 1-mmol scales with the same procedure as described in the text. Isolation was carried out on a 10-mmol scale. [b] By GLPC analysis. [c] THF was used as the solvent.

Table II. Reaction of Allyl Halides with $RCu{\cdot}BF_3$[a]

$RCu{\cdot}BF_3$, R	Solvent	Allyl Halide	Product[b]	γ-Alkylation, %[c]	Yield, %[c] (isold)
CH_3	Ether	$PhCH{=}CHCH_2Br$	$PhCH(CH_3)CH{=}CH_2$	90	95
CH_3	THF	$PhCH{=}CHCH_2Br$	$PhCH(CH_3)CH{=}CH_2$	>99	(90)
n-C_4H_9	Ether	$PhCH{=}CHCH_2Cl$	$PhCH(n\text{-}C_4H_9)CH{=}CH_2$	91	97
n-C_4H_9	THF	$PhCH{=}CHCH_2Cl$	$PhCH(n\text{-}C_4H_9)CH{=}CH_2$	>99	(94)
n-C_4H_9	Ether	$CH_3CH{=}CHCH_2Cl$	$CH_3CH(n\text{-}C_4H_9)CH{=}CH_2$	94	94
n-C_4H_9	THF	$CH_3CH{=}CHCH_2Cl$	$CH_3CH(n\text{-}C_4H_9)CH{=}CH_2$	>98	90 (80)
CH_3	Ether	$(CH_3)_2C{=}CHCH_2Br$	$(CH_3)_3CCH{=}CH_2$	94	92
CH_3	THF	$(CH_3)_2C{=}CHCH_2Br$	$(CH_3)_3CCH{=}CH_2$	95	82
n-C_4H_9	Ether	$(CH_3)_2C{=}CHCH_2Br$	$(CH_3)_2(n\text{-}C_4H_9)CCH{=}CH_2$	90	93 (80)
n-C_4H_9	Ether	$CH_2{=}CHCH(Cl)CH_3$	$n\text{-}C_4H_9CH_2CH{=}CHCH_3$	96	90 (80)

[a] See footnotes to Table I. [b] Satisfactory NMR, IR, and elemental analysis data were obtained for all new compounds. [c] By GLPC.



of exclusive γ-alkylation of γ-substituted allylic substrates.[2]

Previously we reported that the alkenylcopper generated from the reaction of the dialkenylchloroborane with 3 molar equiv of methylcopper reacted with cinnamyl bromide to give an 86:14 mixture of $RCHPhCH{=}CH_2$ and $RCH_2CH{=}CHPh$ (R = alkenyl).[3] The isomer ratio was higher than that expected from the reaction of normal alkylcoppers with cinnamyl bromide.[4] It appeared that this may be due to the complex formation between RCu (R = alkenyl) and the borane.[5] Accordingly, we examined the reaction of various CH_3Cu-borane complexes with cinnamyl halides.

As is apparent from Table I, CH_3Cu-trialkylborane complexes attack the γ position more predominantly than free CH_3Cu (entries 3-5 vs. 2). The exclusive attack at the γ position can be realized with $CH_3Cu{\cdot}BF_3$ in THF (entry 8). Therefore, we explored the scope of this novel alkylating reagent and the results are summarized in Table II.

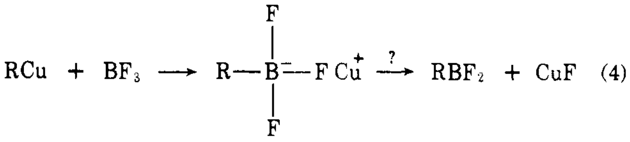
It is clear that the new alkylating reagent regioselectively attacks the γ position irrespective of the structure of allyl halides. Butylation of crotyl chloride and its isomer, 3-chloro-1-butene, produced 3-methyl-1-heptene and 2-octene, respectively (eq 2 and 3). This suggests that the butylation reactions do not involve a common intermediate such as an allyl radical.

$$CH_3CH{=}CHCH_2Cl \xrightarrow{n\text{-}C_4H_9Cu\cdot BF_3} CH_3(n\text{-}C_4H_9)CHCH{=}CH_2 \quad (2)$$

$$CH_2{=}CHCH(Cl)CH_3 \xrightarrow{n\text{-}C_4H_9Cu\cdot BF_3} n\text{-}C_4H_9CH_2CH{=}CHCH_3 \quad (3)$$

The following procedure for the synthesis of 3-phenyl-1-heptene is representative. In a 200-mL flask, equipped with a magnetic stirrer and maintained under N_2, were placed 1.9 g (10 mmol) of CuI and 20 mL of dry THF. n-Butyllithium in hexane (1.3 M, 10 mmol) was added at −30 °C, and the resulting mixture was stirred at this temperature for 5 min. The mixture was then cooled to −70 °C, and $BF_3{\cdot}OEt_2$ (47%, 1.3 mL, 10 mmol) was added. After the mixture was stirred for a few minutes, cinnamyl chloride (1.53 g, 10 mmol) was added, and the mixture was allowed to warm slowly to room temperature with stirring. The product was filtered through the column of alumina using petroleum ether. The olefin thus obtained in an essentially pure form was distilled under reduced pressure: 1.64 g, 94%, bp 65-66 °C (5 mmHg).

It is well known that lithium, sodium, and magnesium borates are formed from the reaction of alkyllithium, -sodium, and -magnesium with trialkylboranes.[6] The similar ate complexes of copper are presumably produced from the reaction between alkylcoppers and trialkylboranes.[5] Therefore, it is favorable to depict the new reagent as an ate complex, $RB^-F_3Cu^+$, instead of $RCu{\cdot}BF_3$ (eq 4). The reactive species



$$RCu + BF_3 \longrightarrow R{-}\overset{F}{\underset{F}{\overset{|}{\underset{|}{B^-}}}}{-}F\,\overset{+}{Cu} \xrightarrow{?} RBF_2 + CuF \quad (4)$$

in the present alkylation reactions is probably this ate complex. It seems that the ate complex, unlike the corresponding $RB^-Cl_3Cu^+$, is considerably stable and does not give RBF_2 easily.[7] Actually, when a mixture of n-C_4H_9Cu and BF_3 was quenched at −70 °C and oxidized with H_2O_2-NaOH, considerable amount of n-C_4H_9OH was obtained. If the origin of this n-C_4H_9-B bond is n-$C_4H_9BF_2$, allyl halides can not be alkylated. Irrespective of the precise mechanism of the present regioselective γ-alkylation,[8] the new reagent offers promising possibilities for organic synthesis. Further aspects of this new reagent are under active investigation in our laboratories.

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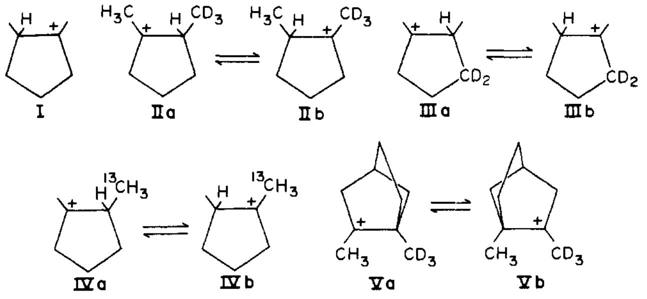
Isotopic Perturbation of Degeneracy. Carbon-13 Nuclear Magnetic Resonance Spectra of Dimethylcyclopentyl and Dimethylnorbornyl Cations

Sir:

We have reported isotope induced splittings and shifts in the ^1H NMR spectra of dimethylisopropyl[1] and dimethyl-*tert*-butyl[2] carbonium ions (undergoing rapid 1,2-hydride and 1,2-methide shifts) where deuterium on the methyl groups perturbs the degenerate equilibria. The observed splitting or shift, δ, depends on the equilibrium isotope effect, K, and the difference, Δ, between chemical shifts averaged by the rearrangement. We now report using the large chemical shifts in ^{13}C NMR to greatly increase sensitivity.



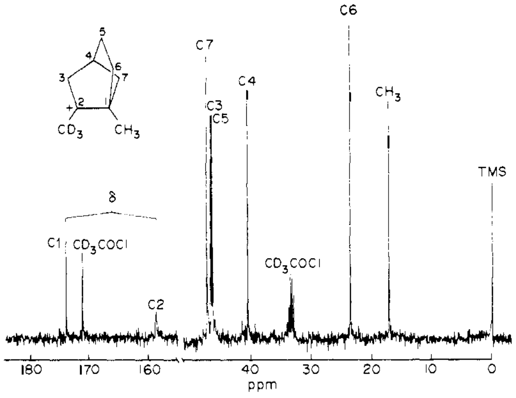


Figure 1. 67.9-MHz ^{13}C NMR spectrum of V at −71 °C.

Labeled dimethylcyclopentyl (I–IV) and dimethylnorbornyl (V) cations were prepared, using standard techniques.[3] Methyl deuteration in II lifts the chemical shift degeneracy of the carbonium and methine carbons, averaged by the rapid 1,2-hydride shift. Two peaks are observed, split symmetrically about the averaged resonance of the protio compound, separated by δ. The chemical shifts are weighted averages of isomer fractions, giving

$$\delta = [(\delta_1 A + \delta_2 B) - (\delta_2 A + \delta_1 B)]/(A + B)$$

where δ_2 and δ_1 are shifts of the carbonium and methine carbons, and A and B are concentrations of IIa and IIb. Substituting $K = B/A$ and $\Delta = \delta_2 - \delta_1$, yields

$$K = (\Delta + \delta)/(\Delta - \delta)$$

If the reaction is fast, Δ cannot be determined directly. It was estimated for I–IV from the ^{13}C NMR spectrum of a mixture of I and the methylcyclopentyl cation, by doubling the separation between the cationic carbon peak in the static molecule and the averaged carbons in I, that $\Delta = 261 \pm 2$ ppm. An analogous procedure yielded $\Delta = 202$ ppm for V.[4,5] σ-Delocalization[6,7] might reduce this value.

Table I summarizes ^{13}C NMR[8] results for II–V (Figure 1). The *direction* of isotope effects in II and III was determined from proton spectra.[1,4] In V, C–D coupling broadens and hence identifies C_2. The charge prefers to be away from deuterium in these cases.

At sufficiently low temperatures, ln K should vary linearly with $1/T$,[9] and analysis yields enthalpy and entropy differences. Data from II (Figure 2) are typical. We obtain for II, $\Delta H = 60 \pm 1$ cal/mol and $\Delta S = 0.012 + 0.001$ cal/deg per D; for III, $\Delta H = 137 \pm 4$ cal/mol and $\Delta S = 0.05 \pm 0.01$ cal/deg per D; for IV, $\Delta H = 1.2 \pm 0.7$ cal/mol and $\Delta S = 0.002 \pm 0.002$ cal/deg; for V, $\Delta H = 20 \pm 1$ cal/mol and $\Delta S = 0.002 \pm 0.002$ cal/deg per D. Positive ΔS means that the isotope effect extrapolated to $1/T = 0$ is *opposite* from that at low temperature. Reported error limits are standard deviations.

Case IV demonstrates the sensitivity of this method. The

Table I. Isotope Splittings

Compd	T, °C	δ^a	Compd	T, °C	δ^a	Compd	T, °C	δ^a
II^b	−142	81.8	II	−56	48.2	IV	−65	0.10
	−136	77.5		−45	45.4	V^c	−127	20.5
	−126	73.0	III^b	−130	105.3		−121	20.2
	−117	68.4		−126	102.4		−119	19.1
	−110	65.0		−122	98.4		−108	18.8
	−102	62.0		−109	91.0		−89	16.4
	−95	59.4		−101	86.6		−71	14.9
	−90	57.5		−91	81.6		−60	13.8
	−81	55.7	IV^b	−125	0.25		−40	12.6
	−70	51.8		−90	0.15		−21	11.9

[a] In parts per million. [b] $\Delta = 261 \pm 2$ ppm. [c] $\Delta = 202$ ppm.