yield.[11]

The chemistry of this molybdenum system mimics that observed in the oxo reaction very closely. The only major difference appears to be the difficulty of converting $[CpMo(CO)_3]_2$ into **1** by reaction with H_2; this prevents closure of the catalytic cycle. Even the formation of ketones from cobalt acyls and olefins has been observed when only small amounts of hydride are present.[12] Concerning the mechanism of the molybdenum reactions reported here, a radical pathway is ruled out, except as a minor component in the benzyl system. An alternative consistent with our data is illustrated in Scheme III. This postulates initial isomerization of **2** to metal acyl **A**, followed by rapid entry of metal hydride into the unsaturated acyl coordination sphere and reductive elimination of aldehyde.[13] The overall similarity of the molybdenum and cobalt systems reinforces the recent conclusions of others[4] that the aldehyde-forming step in the oxo process also involves reaction between a cobalt hydride and cobalt acyl. In the presence of large amounts of ethylene and reduced concentrations of $CpMo(CO)_3H$, alkene traps the initially formed acyl, and the reaction is diverted to form ketone by the alternate route shown in Scheme III. In summary, there now exists good evidence for the accessibility of *three* mechanistic routes in metal hydride–metal alkyl reactions: (a) acyl formation, coordination of metal hydride to unsaturated acyl, and reductive elimination to aldehyde (this work); (b) acyl formation, reaction of acyl with hydride, and reductive elimination to *alkane*;[6] and (c) M–C bond homolysis to give an organic radical, followed by hydrogen atom transfer from metal hydride to the radical.[7]

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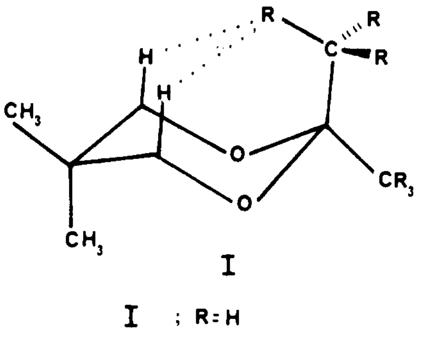
Intrinsic Steric Deuterium Isotope Effects on Proton and Carbon-13 Chemical Shifts

Sir:

Deuterium isotope effects on the NMR chemical shifts of ^1H and ^{13}C in organic molecules are well known.[1] It is useful to distinguish two extreme types of chemical-shift isotope effects: (a) an "equilibrium" chemical-shift isotope effect[2] which involves changes in the populations of two (or more) equilibrating species (double-minimum energy surface), and (b) an "intrinsic" chemical-shift isotope effect which involves a single species (single-minimum energy surface).[3] The intrinsic effects are largest when the deuteron is bonded directly to the observed nucleus, and they generally decrease to virtually zero when the nuclei are separated by more than three bonds.[4] Long-range chemical-shift isotope effects can easily occur in equilibrating systems.[2] In contrast, long-range *intrinsic* isotope effects would be expected only in conjugated (resonance stabilized) anions or cations or in molecules where the deuteron is close in space to the observed nucleus. Although a rough correlation of the intrinsic chemical shift isotope effect with internuclear distance has been noted[5] in two-bond systems for the first-row elements (i.e., in the group XHD vs. XH_2), it is not known whether such a correlation is applicable to compounds where the deuteron and the observed nucleus are separated by several bonds.

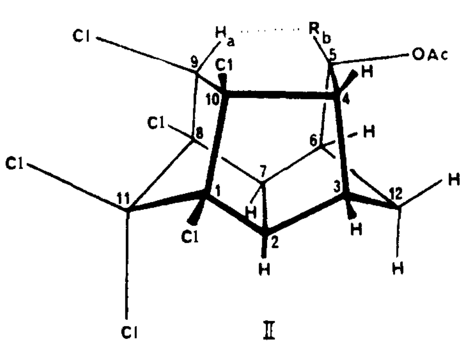
We now report the first examples of intrinsic isotope effects on the proton chemical shifts in compounds where the deuteron(s) and the observed proton(s) are separated by five bonds, but where the nuclei are close together in space. The compounds studied are the 1,3-dioxanes, I and I-d_6,[6] and the half-cage acetates, II and II-d.[7] Although I is not a rigid molecule, I and I-d_6 each exist as equal mixtures of two rapidly interconverting chair conformers having exactly the same energies, and isotope effects observed in this system cannot be attributed to population changes. Compound II has a rigid skeleton and is therefore a single species.



I

I ; R:H
I-d_6 ; R:D

The 348-MHz ^1H NMR spectrum of an equal mixture of the 1,3-dioxanes I and I-d_6 exhibits two resolved lines for the methylene protons, which are located about 3.35 ppm from Me_4Si. These signals are separated by 0.90 Hz (2.6 ± 0.07 ppb)[8] (Figure 1), and the splitting is the same at −20 as at +32 °C.[9] The low-field signal corresponds to the methylene protons



II ; R=H

II-d ; R=D

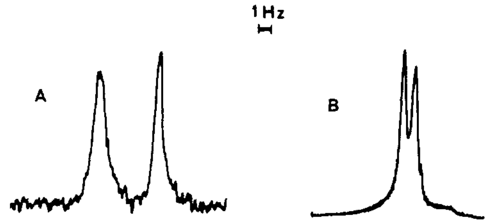


Figure 1. Partial 348-MHz ^{1}H NMR spectra of the half-cage acetate mixture, II/II-d, and the 1,3-dioxane mixture, I/I-d_6: (A) signals of H_a in the II/II-d mixture (the sharper and upfield signal belongs to II-d); (B) methylene signals in the I/I-d_6 mixture.

of pure I, whereas the upfield one corresponds to that of pure I-d_6. Because of rapid ring inversion, the observed splitting in the CH_2 protons is the average of the splittings for the axial and equatorial protons in that group. Since the intrinsic isotope effect for the equatorial proton is expected to be negligible, that of the axial proton must be twice the observed splitting, i.e., 5.2 ppb.

A 3:2 mixture of the half-cage acetates II and II-d shows two signals for H_a, 4.8 Hz apart at 348 MHz (13.7 ± 0.1 ppb), as shown in Figure 1. This remarkably large deuterium chemical-shift isotope effect, which occurs in a molecule where the H and D are separated by five bonds, is of comparable magnitude to the isotope effects in CHD groups,[5] where the H and D nuclei are separated by only two bonds. The $H_a \cdots H_b$ distance in the half-cage acetate II is estimated to be 1.60 ± 0.05 Å based on ^{1}H and ^{13}C T_1 measurements,[10] and 1.65 Å based on force-field calculations.[11] Thus, the H···D distance in II-d is even shorter than that (1.78 Å) in a CHD group, and thus the large isotope shift in II-d is not unreasonable. In I-d_6, the estimated H···D distance is ~2.0 Å[12] and this is consistent with the rather small isotope shift of 5.2 ppb.

Chemical-shift isotope effects originate from changes in vibrational and rotational frequencies of a molecule.[1,13,14] With large molecules the rotational contribution should be negligible. Various treatments of the vibrational contributions have been used to investigate the nature of the deuterium chemical-shift isotope effects.[5,15,16] A simple electrostatic model has been proposed to explain the istotope effects in CHD groups, but this requires placing a relatively large positive charge on the hydrogen.[15] Other workers have considered diamagnetic shielding contributions which arise from changes in bond hybridization upon isotopic substitution.[5,16] These calculations have been used mainly to show that certain contributions are of the right order of magnitude to explain the isotope shifts; however, they do not reproduce quantitatively the observed shifts.

Both I and II have strong van der Waals intramolecular repulsions on the protons of interest. Although the chemical shifts changes arising from such intramolecular[17] and intermolecular[18] effects have been extensively studied, the effect of isotopic substitution has apparently not been investigated previously, either theoretically or experimentally. Strong steric repulsions are known to lead to large downfield shifts of protons.[17] Since the repulsion in the H···D system should be less than that in the corresponding H···H system because of the lower vibrational amplitude (i.e., smaller effective size) of deuterium, the downfield shift should be less in the H···D than in the H···H system, in agreement with the experimental findings. The isotope effects observed in systems such as I-d_6 and II-d, where the pertinent H and D atoms have appreciable mutual van der Waals repulsive interactions, may be termed steric isotope effects.

It appears that observable deuterium isotope effects on proton chemical shifts occur whenever the H···D distance is distinctly less than the sum of the two van der Waals radii (2.4 Å), irrespective of the number of bonds separating the two nuclei. Additionally, deuterium chemical-shift isotope effects are also observable in certain molecules such as $HC \equiv CD$[16] and $PhCD{=}CH_2$,[19] where the distances are >2.4 Å and where there are no direct H···D steric interactions. These effects presumably take place because of changes in bond hybridization upon isotopic substitution, as mentioned earlier.[5,16] Nevertheless, it is possible that steric chemical-shift isotope effects that occur in rigid molecules may be of some use for the estimation of H···D distances, especially if these atoms are separated by five or more bonds. The relative orientation of the CH and CD groups might be expected to influence the isotope effect, and thus might complicate any distance estimation, but we currently have no data bearing on this point.

The 50-MHz ^{13}C NMR spectra of I/I-d_6 and II/II-d mixtures were also investigated. The methylene carbons in the I/I-d_6 mixture and C_9 in the II/II-d mixture did not show any splitting nor any broadening of their resonance signals. Thus, the deuterium isotope effects on the shifts of these sterically compressed carbons are <4 ppb, which is rather surprising since the deuteriums are involved in γ-shielding effects[20,21] on these carbons. Grant and Cheney have postulated that the shielding effect (~3–8 ppm) which is observed in such a situation arises from steric compression between the two CH groups.[20] Since the CD group is effectively smaller than the CH group, this compression should change slightly upon isotopic substitution, but apparently the isotope effect arising from this mechanism is not large enough to be observed.[20] Thus, intrinsic deuterium isotope effects on the chemical shifts of δ or more remote carbons should be negligible.[22]

The isotope effects on the carbons in α, β, and γ positions to the deuterium in II-d have the expected magnitudes[23] and show that some of the assignments in the recently reported ^{13}C NMR spectrum of II should be interchanged.[24]

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(8) Since the magnitudes of most isotope chemical shifts are a fraction of 1 ppm, it is convenient to express these shifts and their errors in parts per billion (ppb), where 1000 ppb = 1 ppm.
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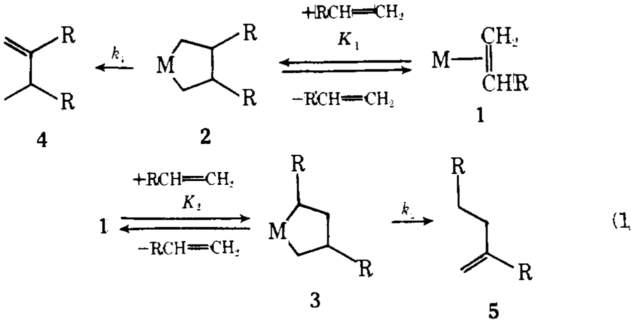
Metallacyclopentane to Metallacyclobutane Ring Contraction

Sir:

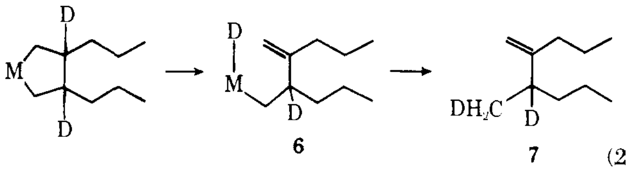
We recently reported that $(\eta^5\text{-}C_5H_5)Cl_2\overline{TaCH_2CH\text{-}MeCHMeCH_2}$ is the crucial intermediate in the catalytic dimerization of propylene to largely 2,3-dimethyl-1-butene (93%).[1] Unfortunately, this catalyst system becomes inactive after ~20 turnovers, possible because $Ta(\eta^5\text{-}C_5H_5)Cl_2$(propylene), which almost certainly must be formed at some point, is apparently unstable at 25 °C.[2] In contrast, we find that the corresponding $\eta^5\text{-}C_5Me_5$ catalyst system is indefinitely active for dimerizing monosubstituted α olefins[3] (in the absence of air and water), probably because the $Ta(\eta^5\text{-}C_5Me_5)Cl_2(RCH{=}CH_2)$ complexes are comparatively stable and isolable.[2] This communication is concerned with the mechanism of this olefin dimerization reaction.

Table I shows the results of four dimerization reactions.[4,5] Two types of products are formed. The "tail-to-tail" (tt) dimer (**4**, eq 1, $M = (\eta^5\text{-}C_5Me_5)Cl_2Ta$) must come from the trans-β,β'-substituted metallacycle (**2**),[2] while the "head-to-tail" (ht) dimer (**5**) most likely comes from an α,β'-substituted metallacycle (**3**) (stereochemistry unknown). So far, we have observed only **2** spectroscopically (under conditions where dimerization is negligible), even in the last case where only **5** is formed.[8] The drastic change in the ratio of **4** to **5** can be ascribed to marked changes in k_1 and k_2 (and/or K_1 and K_2) under catalytic conditions as R becomes larger (see later).[6]



(1)

We chose to study the mechanism of catalytic dimerization using 1-pentene-*2-d* (≥99% d_1). The tt dimer was formed more slowly than that made with unlabeled 1-pentene ($k_H/k_D = 3.3$



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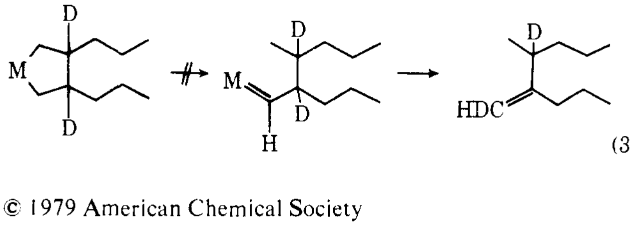

(3)

0002-7863/79/1501-5451$01.00/0