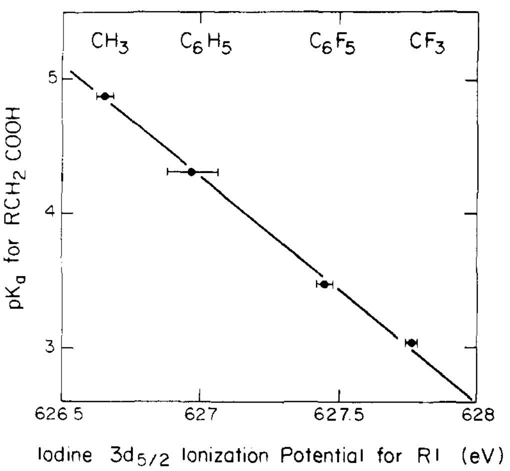

Figure 1. Correlation of pK_a for RCH_2COOH with $3d_{5/2}$ ionization potential of iodine in RI.

responding acids RCH_2COOH.[5] It is likely that both the relative core ionization potentials and the relative acidities for these compounds are, for the most part, due to the ground state charge distribution rather than to relaxation effects in the final species. If this is the case, we will expect to find a positive correlation between acid strength and core ionization potential.

The correlation is shown in Figure 1, where we have plotted pK for the acid against the core ionization potential for the appropriate iodide. We see that the points all fall on a straight line with negative slope, implying, as expected, that acidity increases with core-electron ionization potential.

From the slope of the line in Figure 1, together with the relationship between free energy and pK, we can calculate the change in free energy of ionization for a change in core ionization potential. If the site from which the proton is ionized in the acid were the same as the location of the iodine in the iodide, the expected value of this quantity would be -1. The actual value is -0.1, reflecting the fact that the carboxyl group is distant from the R group and the effect of changing R is, therefore, diminished.

Martin and Shirley have pointed out that two factors play important roles in determining the ease with which charge (core electron or proton) can be added to or removed from an isolated molecule. These are the initial-state charge distribution and the redistribution of the valence electrons caused by removal or addition of a charge. For solvated molecules we must consider also redistribution of the solvent electrons, or solvent polarization.

If the initial state charge distribution is favorable for electron removal, it is also favorable for proton attachment but unfavorable for proton removal. If such ground state properties are the major factor in determining the ease with which charge can be added or removed, we will expect positive correlation between core-electron ionization potentials and proton affinities and positive[6] correlation with acid strength (or negative correlation with pK_a). An example of this situation is the series of molecules described above, where the R groups differ from one another quite markedly in their inductive effects. Here we see the expected correlation between the core ionization potentials and acidity.

The rearrangement of valence electrons on removal or addition of charge of either sign leads to a lowering of the energy of the final species. The more polarizable the molecule, the greater will be this relaxation energy and the easier it will be to change the charge in either direction. If these final state properties are the most important factors in determining the ease of charge addition or removal, we will expect the acidity to decrease with increasing core ionization potential. An example of such a situation is the molecules ROH in which R is successively larger alkyl groups. Martin and Shirley have, as noted above, found that gas-phase acidity does decrease with increasing core ionization potential.

A second example of the importance of relaxation effects is found in a comparison of core ionization potentials in the series of molecules RI (R = alkyl groups of increasing size) with the aqueous acidities of the corresponding acids RCH_2COOH. Internal relaxation after ionization is greatest for the largest alkyl groups with the result that the 3d ionization potential in *tert*-butyl iodide is less by 0.63 eV than it is in methyl iodide.[7] The acidities, however, vary by less than 0.1 pK unit over the series of compounds. As has been pointed out by Brauman and Blair and by Martin and Shirley for the alcohols, there is a counteracting change in solvent polarization. Making the anion larger simply replaces one polarizable medium (the solvent) with another (the R group). If the polarizability per unit volume is the same for both media, the acidity will be nearly independent of the size of the anion, as is observed. The core-electron binding energies, however, being measured in the absence of a polarizable medium, will depend on the size of the R group, as is observed.

Acknowledgment. This work was supported by the U.S. Atomic Energy Commission.

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Received October 8, 1974

Hydrogenation of Arenes with Discrete Coordination Catalysts. III.[1] Synthesis and Nuclear Magnetic Resonance Spectrum of *all-cis*-Cyclohexane-d_6

Sir:

We wish to report the first synthesis of pure[2] *all-cis*-cyclohexane-d_6 by the catalytic hydrogenation of C_6D_6 with the new[1,3,4] soluble catalyst, η^3-$C_3H_5Co[P(OCH_3)_3]_3$. The stereoselectivity of this catalyst is decisively established by this result. Accordingly, a simple procedure is now in hand for synthesis of stereospecifically labeled cyclohexane-d_x derivatives as well as[1] polyalkylcyclohexanes. We also note that these experimental studies, in addition to competitive hydrogenation studies[1] of benzene, cyclohexadiene, and cyclohexene, clearly define certain stereochemical and qualitative features about the intimate mechanism through which the catalytic hydrogenation proceeds.

Catalytic hydrogenation of polyalkylarenes with η^3-$C_3H_5Co[P(OCH_3)_3]_3$ invariably led to polyalkylcyclohexanes with all-cis stereochemistry.[3] These observations suggested the possibility that hydrogenation of C_6D_6 with the cobalt catalyst might selectively yield the all-cis stereo-

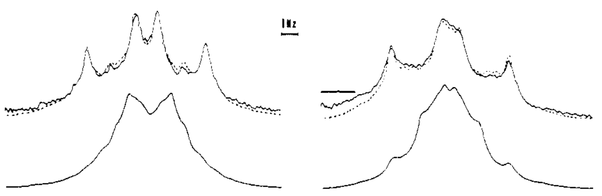


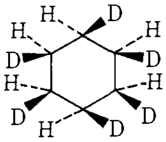
Figure 1. Top (solid line), experimental Fourier transform ^{1}H $\{$D$\}$ NMR spectrum of I at −100° (the region indicated by the asterisk is affected by a nearby spinning side-band of the cyclopentane peak); top (dotted line), calculated and convoluted[7] ^{1}H $\{$D$\}$ spectrum for *all-cis*-cyclohexane-d_6 (II); bottom: calculated and convoluted ^{1}H $\{$D$\}$ spectrum of III.

isomer. As reported earlier,[3] the only compositional isomer we detect in this hydrogenation is $C_6D_6H_6$[5] (I). The ^{1}H NMR spectrum of I, with deuterons decoupled, is a single line at room temperature, in agreement with a structure of the type $(CHD)_6$, and shows that CH_2 groups are not present to a significant extent.[6] Much more information can be obtained at low temperatures under conditions that ring inversion is slow on the NMR time scale. Figure 1 shows the Fourier transform ^{1}H$\{$D$\}$ spectrum of I in a CS_2 solution,[7] and a theoretical spectrum calculated for *all-cis*-cyclohexane-*1,2,3,4,5,6*-d_6 (II) with $\nu_{a,e}$ = 120.0 and $^3J_{ae}$ = 3.62, $^4J_{ec}$ = 1.90 and $^4J_{aa}$ = −0.30, and $^5J_{ae}$ = 0 Hz.[8] These parameters agree with chemical shifts and coupling constants found in other partially deuterated cyclohexanes at low temperatures,[8] with the exception of $^4J_{aa}$, which has not been determined before. A poor fit of the axial proton band shape occurs if $^4J_{aa}$ is zero or positive and a negative value is expected.[9] The agreement between the observed and calculated spectra is very good.

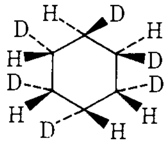
We have also calculated the spectrum (Figure 1) of *cis,cis,trans,cis,trans*-cyclohexane-*1,2,3,4,5,6*-d_6 (III) with the parameters given above and $^3J_{ee}$ = 3.0, $^3J_{aa}$ = 13.2, and $^4J_{ae}$ = $^5J_{aa}$ = 0 Hz.[8] If the hydrogenation proceeds through addition of pairs of hydrogen atoms in a cis-1,2 fashion with the formation of free $C_6D_6H_2$ and $C_6D_6H_4$ as intermediates, 25% of II and 75% of III should be produced, provided that secondary isotopes effects are negligible as is likely. Comparisons of the observed spectrum with sums of the spectra of II and III in various proportions show that the fits of the calculated to the observed spectra become progressively worse as the amount of III increases and that there must be less than 10% (and probably less than 5%) of III in the reduction product. The purity of the C_6D_6 reagent was 99.6 ± 0.1%; accordingly, there should be ~2.4% cyclohexane-d_5 in our product. Because the resonances of this compound are rather well spread out, this $C_6D_5H_7$ impurity has very little effect upon the simulated spectrum.

The pervasive facial hydrogen addition to arenes in the η^3-$C_3H_5Co[P(OCH_3)_3]_3$ system demands that certain stereochemical and qualitative features be accommodated in any viable outline of the intimate mechanism of the hydrogenation reaction. First and foremost, the arene once bound to the cobalt[10] must rarely leave until the sixth hydrogen atom is transferred. Secondly, a relatively fixed orientation of the ring must be maintained through the sequential hydrogen addition.[11,12] The ring must remain largely in a plane perpendicular to the C_6 centroid-cobalt axis. We defer speculation about the detailed geometric and electronic character of the intermediates until our synthesis of intermediates or models thereof is completed, but a reaction sequence previously presented by us[1] demands this stereochemical feature.

This unique reaction for stereospecific deuterium labeling of cyclohexane derivatives should be extendable to polynuclear aromatic hydrocarbons. In fact, naphthalene is hydrogenated in the presence of this cobalt catalyst to decalin. Careful GC-MS analysis of the product decalin against standard *cis*- and *trans*-decalin showed evidence only for the presence of the cis isomer. Clearly the gross stereochemical feature of the reaction with mononuclear arenes is established. Extensions to other polynuclear arenes are being made.



II



III

Acknowledgments. This research was supported at Cornell University by National Science Foundation, Grant No. GP-39306X, and by the Materials Science Center, Cornell University, and at UCLA by the National Science Foundation, Grant No. GP-36504X.

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(7) A small amount of cyclopentane was included in the sample to provide a line shape for convolution of theoretical spectra. The cyclopentane line had half-, quarter-, and eighth-height widths at −100° of 0.56, 1.5, and 2.5 Hz, respectively. An extra Lorentzian broadening of 0.17 Hz was also used in the calculations to take into account the finite rate of ring inversion in I and the fact that the decoupling was not quite complete.

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(10) More precisely, once the first hydrogen atom is transferred to the arene.

(11) At least to the point that the fifth hydrogen atom is transferred to the ring.

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Geminal and Vicinal ^{13}C–^{13}C Coupling Constants of 85% ^{13}C-Enriched Amino Acids

Sir:

During the last few years, the carbon-carbon coupling constants have been widely investigated,[1-10] most of the couplings observed being the single bonded $^1J_{C-C}$ type. This kind of coupling can reflect the hybridization state of the bonding orbitals and the electronegativity of the substituents of a molecule. Some recent studies[6,7] have shown that the geminal, $^2J_{C-C}$, and vicinal, $^3J_{C-C}$, exist. In general