Our approach generates cyclotetradecenone (III), which we succeeded in obtaining in 70% yield as a 1:1 $\alpha,\beta:\beta,\gamma$ mixture[2] from the C_{12} ketone by hot aqueous hydrochloric acid hydrolysis of the known reaction product II[3] of 1-pyrrolidinocyclododecene with ethyl propiolate. Treatment of the enone mixture with triethylsilane in refluxing glyme containing a catalytic amount of chloroplatinic acid afforded 1-triethylsiloxycyclotetradecene (III)[4] (92%; ν_{max} 1675^{-1} (C=C); NMR δ 4.42 quintet, J = 7.0 Hz, 1 H; 2.0, b s, 4 H). Addition of dichlorocarbene (sodium trichloroacetate (2 equiv) in refluxing glyme–tetrachloroethylene (1:4) for 18 hr, followed by aqueous 1 N hydrochloric acid–tetrahydrofuran (1 hr, room temperature), gave 2-chloro-2-cyclopentadecenone (V) in 66% yield (ν_{max} 1700, 1625 cm^{-1}; NMR δ 6.83, t, J = 7.0 Hz, 1 H; 2.60, m, 4 H). Conjugate addition of dimethylcopper lithium in ether ($-10°$, 30 min), followed by saturated ammonium chloride workup and subsequent chromium(II) perchlorate reduction of the resulting α-chloro ketone in dimethyl formamide[5] yielded d,l-muscone (VI) as a light yellow oil (89%) which was identical with an authentic sample[6] in spectral and analytical characteristics. The overall yield of d,l-muscone from cyclododecanone is about 36%.
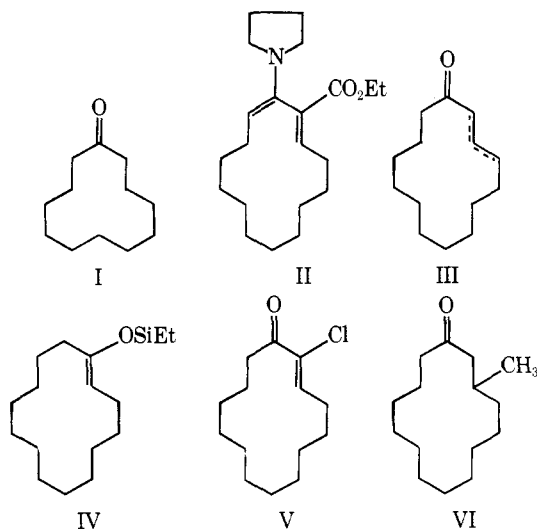
This synthesis demonstrates that, as we anticipated, rapid equilibration of an $\alpha,\beta-\beta,\gamma$ mixture of unsaturated ketones takes place under the platinum-catalyzed silylation conditions,[7] thus allowing the clean formation of IV from III. Further, the dichlorocyclopropanation of enol silyl ethers (which can often be prepared regiospecifically), followed by hydrolysis, offers an efficient alternative to current methods[8] for the transformation of ketones into specifically homologated α-chloroenones. It should be noted that cyclopentadecenone derivatives are known to be equilibrated to mixtures rich in the β,γ isomer.[9] Thus, the α-chloro substituent helps to stabilize the unsaturated C_{15} ketone in the α,β-enone configuration required for conjugate addition. The compatibility of the α-chloroenone system with alkyl copper reagents is due to the fact that the chlorine becomes a relatively unreactive vinyl chloride in the enolate resulting from 1,4-addition.[10]

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Correlation between Acidities of Carboxylic Acids and Core Ionization Potentials

Sir:

It has recently been shown by Martin and Shirley[1] and by Davis and Rabalais[2] that there is a strong correlation between core-electron binding energies and proton affinities. For a series of alcohols, Martin and Shirley have found that the change in oxygen 1s binding energy from one alcohol to the next in the series is nearly identical with the change in proton affinity. The reason for this remarkable result is that the removal of an electron from the oxygen is electrically equivalent to the addition of a proton at the same site.

Martin and Shirley also suggested that there should be a correlation between the oxygen 1s ionization potentials and the gas-phase acidities of these compounds and noted that the results obtained by Brauman and Blair[3,4] on a series of alcohols are in accord with their expectation. No quantitative comparison was possible since only relative acidities were measured by Brauman and Blair. The acidities for alcohols in aqueous phase are the reverse of what they are in the gas phase because of solvent effects. The aqueous-phase acidities of the alcohols do not, therefore, correlate in the expected way with the core-electron ionization potentials.

If, however, we direct our attention to substances in which the relative aqueous-phase acidity is largely determined by the charge distribution in the original molecule (i.e., by inductive effects) rather than by either solvent or internal polarization effects, we may expect to find acid strength increasing with increasing core-electron binding energy. An electrostatic potential from which it is relatively difficult to remove an electron is one from which it is relatively easy to remove a proton.

In the course of some research unrelated to this problem, we have measured the ionizatiion potentials for iodine 3d electrons in the compounds RI (R = CH_3, CF_3, C_6H_5, and C_6F_5). We compare these here with the acidities of the cor-
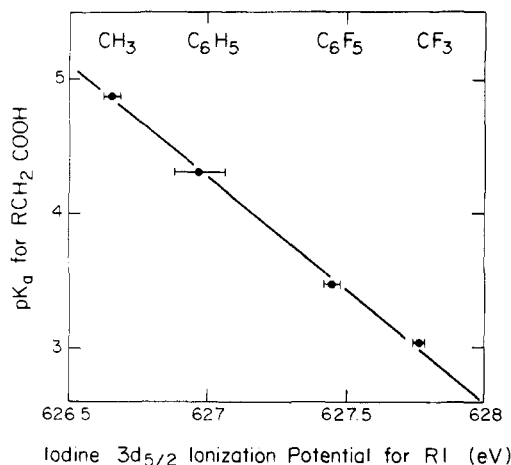
Figure 1. Correlation of pK_a for RCH_2COOH with $3d_{5/2}$ ionization potential of iodine in RI.

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 ioniza-

tion 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 gasphase 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.

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(5) We choose the series RCH_2COOH rather than RCOOH in order to minimize resonance effects that might stabilize the anion but not affect the core-ionization potential.
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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-