in 79% yield after chromatography (silica gel plate).

Saponification of **13** (NaOH in CH_3OH/H_2O) at 0 °C followed by acidification (Amberlite IR-120 resin) and concentration gave a mixture of **2** (80%) and aromatic product. Recrystallization from ethyl acetate gave pure, crystalline (±)-**2** (23%). Comparison of the spectral data (IR, UV, ^1H NMR)[13] of (±)-**2** with those reported for **2** isolated from *A. Aerogenes*[2] established their structural identity.

We have confirmed the instability of **2** described by Gibson and co-workers.[2] It is interesting to note that dimethyl ester **13** slowly undergoes Claisen rearrangement on standing in $CDCl_3$ solution at 0 °C to afford the dimethyl ester of **5**. Attempts to prepare the disodium salt of **5**, which has not been isolated from natural sources, are under investigation in our laboratory.

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(12) **13**: IR (neat) 3475, 1715, 1620, 1590 cm^{-1}; ^1H NMR (CDCl$_3$, 250 MHz) δ 7.09 (dd, 1 H, J = 4.8, 1.6 Hz), 6.27 (m, 2 H), 5.56 (d, 1 H, J = 2.8 Hz), 4.96 (d, 1 H, J = 2.8 Hz), 4.88 (m, 2 H), 3.83 (s, 6 H), 3.31 (br s, 1 H); ^{13}C NMR (CDCl$_3$, 67.9 MHz) δ 167.0 (s), 163.4 (s), 149.2 (s), 132.2 (d), 129.3 (d), 125.0 (d), 97.4 (t), 76.4 (d), 66.3 (d), 52.2 (q), 51.8 (q), the signal for C_1 is not observed perhaps due to overlap with other absorption in the region of 130 ppm.

(13) (±)-**2**: mp 116–117 °C; IR (KBr) 3400, 1695, 1625, 1585 cm^{-1}; UV (H$_2$O), 280 nm (ε 12 200); ^1H NMR (9:1 acetone-d_6/CD$_3$CO$_2$D, 250 MHz) δ 10.1 (br s), 7.11 (1 H, dd, J = 5.4, 1.2 Hz), 6.37 (1 H, dd, J = 9.7, 5.4 Hz), 6.32 (1 H, dm, J = 9.7 Hz), 5.44 (1 H, d, J = 2.4 Hz), 4.96 (1 H, d, J = 2.4 Hz), 4.74 (2 H, m).

When Is Allylic Resonance Unimportant?

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Electron delocalization (resonance) has important consequences for both the structure and stability of the allyl radical.[1] EPR spectroscopy indicates that the allyl radical possesses C_{2v} symmetry[2] and that the barrier to rotation of one methylene group out of conjugation is greater than 15 kcal/mol.[3] When π-electron correlation is included in the wave function for the radical, ab initio calculations are successful in reproducing both the C_{2v} geometry of, and substantial barrier to, rotation in allyl.[4]

Given these experimental and theoretical indications of the importance of resonance in allyl, we were surprised to discover in our calculations on the lowest π state of the isoelectronic formyloxyl radical that there was little preference for a C_{2v} geometry over one with unequal C–O bond lengths.[5] In this communication we present a simple explanation of the apparently small amount of resonance stabilization in the lowest π state of formyloxyl. This explanation can be used to predict with generality the types of molecules containing three electrons in three p–π orbitals in which allylic resonance will be relatively unimportant.

Formyloxyl differs from allyl in that the two terminal heavy atoms are much more electronegative than the central atom. Consequently, in formyloxyl the nonbonding π MO ($1a_2$), which is confined to these two atoms, is separated from the bonding π MO ($1b_1$) by a smaller energy gap than in allyl. The $1a_2$–$1b_1$ orbital energy difference, calculated with the 3-21G basis set,[6]

is 0.052 hartree in formyloxyl, which is less than half of the 0.124 hartree computed with the same basis set for allyl.

Because of the relatively low energy of the $1b_1 \rightarrow 1a_2$ excitation in formyloxyl, the excited $^2B_1$ π configuration, $1b_1 1a_2^2$, in this radical is separated from the lowest π configuration, $1b_1^2 1a_2$ ($^2A_2$), by a relatively small energy gap. These two configurations can be mixed by a b_2 distortion that shortens the bond to one terminal heavy atom and lengthens the bond to the other. The mixing between $^2B_1$ and $^2A_2$ lowers the energy required for this type of distortion in the ground state. The closer in energy that these two configurations are, the greater the effect that their mixing will have on facilitating asymmetric bond length distortion from C_{2v} symmetry.[7] Therefore, the propensity of formyloxyl for undergoing distortion from C_{2v} symmetry may be attributed to the existence of a low-lying $^2B_1$ configuration in this radical.

A decrease in the importance of allylic resonance is also anticipated when the central atom is more electronegative than the heavy atoms at the termini. This expectation is based on the fact that another excited $^2B_1$ configuration, $1b_1^2 2b_1$, differs from the lowest configuration by the excitation $1a_2 \rightarrow 2b_1$. Consequently, a small energy for this excitation will facilitate mixing between these two configurations on a b_2-type distortion. Since $2b_1$ has density on the central atom, where $1a_2$ has a node, the energy difference between these two MO's will be reduced when the central atom is more electronegative than the two terminal heavy atoms.

In order to test the prediction that substitution of the central carbon in allyl by a more electronegative element would also lead to a decrease in the importance of allylic resonance, we have carried out calculations on $O(CH_2)_2^+$, a radical that is isoelectronic with allyl. A previous theoretical study by Radom and co-workers led to the intriguing result that $O(CH_2)_2^+$ prefers a geometry with one methylene group twisted out of conjugation.[8] The apparent preference for this geometry over a planar one, in which the radical might have been stabilized by allylic resonance, was not commented upon.

The optimal C_{2v} structure for $O(CH_2)_2^+$ was found by MC-SCF calculations[9] with the 3-21G basis set. Evaluation of the Hessian matrix at this geometry[10] showed one negative eigenvalue, corresponding to asymmetric stretching of the C–O bonds. Thus, at this level of theory the C_{2v} structure represents the transition state for interconversion of two mirror image structures with unequal bond lengths. Optimization of one of these two structures gave an MC-SCF energy of -115.7370 hartrees, which is lower than that of the optimal C_{2v} structure, although by only 0.4 kcal/mol. The surface for the planar molecule is sufficiently flat that higher quality calculations could find a C_{2v} geometry to be the energy minimum instead of a transition state. Nevertheless, the flatness of the surface indicates that allylic resonance in the planar radical is relatively unimportant.

A geometry with one methylene group twisted out of a conjugation was also optimized, by using an MC-SCF wave function that correlated two of the four electrons that occupy orbitals of a'' (π) symmetry. The resulting structure is similar to those obtained by Radom et al.[8] However, unlike Radom and co-workers, we find this structure to be 1.9 kcal/mol above the energy of the lower of the two planar structures. Higher quality calculations would be necessary in order to predict unequivocally the equilibrium geometry of $O(CH_2)_2^+$, but it appears that methylene group rotation from planarity in this allylic radical costs little, if any, energy. This situation contrasts with that in allyl, where resonance stabilization of the planar radical results in a barrier to methylene group rotation of more than 15 kcal/mol.

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(10) Optimal geometries will be published in our full paper.

In summary, we have shown that in allylic radicals differences in electronegativity between the central atom and the terminal heavy atoms can greatly reduce the importance of allylic resonance. The same electronegativity differences might also be expected to reduce the importance of resonance in allylic systems containing even numbers of π electrons, for instance in neutral $O(CH_2)_2$. However, as will be discussed in our full paper, electron repulsion effects cause allylic resonance to remain important in $O(CH_2)_2$ and related diradicals.

Registry No. $O(CH_2)_2$, 56971-75-6; $O(CH_2)_2^+$, 74427-28-4.

Practical Method for α-Alkenyl Ketone Synthesis Based on a Facile Reductive Rearrangement of Alkynyl Halohydrins

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The importance of methodology for α-alkenyl ketone (**1a**) and carbinol (**1b**) synthesis is amply documented in reports of their intermediacy in many synthetically significant transformations, particularly ring-expansion reactions,[2] and their occurrence in biologically active compounds such as the prostaglandins and cytotoxic terpenes.[3] Access to these systems has commonly involved reactions of metallo alkenes with electrophiles such as epoxides,[4] α-halo ketones,[5] or the more recently introduced enolonium ion equivalents[6] (Scheme I). Vinyl cation equivalents, the polarity complement of the nucleophilic metallo alkene, have also found service in this area.[7] Herein, we describe an approach to α-alkenyl ketones and carbinols from alkynes and halo ketones that involves a novel rearrangement and, in general, offers several advantages over existing methodology. This process affords a more cost-effective solution, which is based on readily available (frequently bulk) substrates and reagents, can be conducted on a large or small scale, and allows both for considerable variation in alkene substitution and for control of alkene geometry. The method additionally provides a practical route to hitherto difficult to prepare α-alkadienyl ketones[8] and consequently a convenient route to large-ring compounds based on recently introduced macroexpansion methodology,[9] as evidenced below by its application in a strategically novel total synthesis of muscone (**12**).

Central to the success of this method is the finding that readily available alkynyl chlorohydrins under aluminum hydride reduction conditions[10] suffer an unusually facile rearrangement[11] to provide

Scheme I
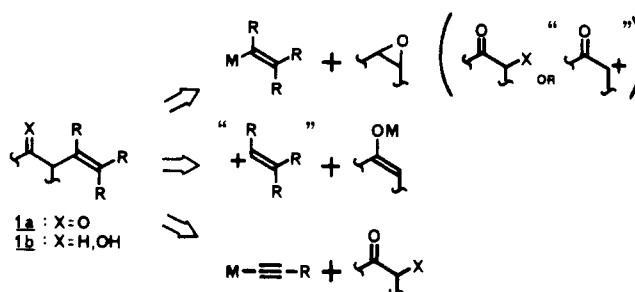
Scheme II
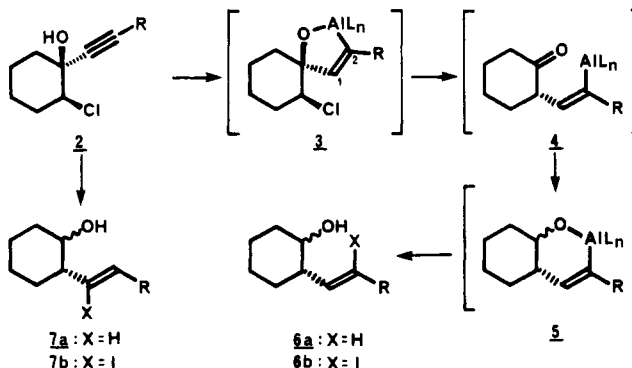
alkenyl carbinols directly. Thus, treatment of cis-1-propynyl-2-chlorocyclohexanol (**2**, R = Me; Scheme II) with excess lithium aluminum hydride and sodium methoxide[10d] for 2 h at ambient temperature provided 2-*E*-propenylcyclohexanol (**6a**, R = Me)[12] as a 3:1 mixture of epimers in 97% yield as determined by GC analysis (72% yield after isolation). Of the possible mechanistic itineraries for this reaction it would appear that alkyne reduction precedes rearrangement, since the magnesium salt of **2** (R = Me) does not readily rearrange, even at 67 °C.[13] Equally important, exposure of the initial product expected from such an alkynyl migration, 2-propynylcyclohexanone, to the above noted conditions resulted only in carbonyl reduction, to provide 2-propynylcyclohexanol. For the alternative sequence, initial reduction would lead to an intermediate of the type **3**, whose formation can be inferred from the isolation (81% yield) of 2-(2-iodo-1-propenyl)cyclohexanol (**6b**, R = Me) when the reaction was quenched with iodine. However, attempts to detect **3** or its unrearranged derivatives in reactions run to partial conversion or under hydride-deficient conditions gave only starting material and rearranged reduced product, suggesting that the formation of **3** is rate determining. Even at temperatures as low as −20 °C, reduction rearrangement occurred. In contrast, the magnesium alkoxide of 1-vinyl-2-chlorocyclohexanol must be heated to temperatures in excess of 50 °C in order to induce its rearrangement.[5] It would appear, therefore, that this efficient and unusually facile process proceeds with initial hydroalumination. Subsequent propenyl migration is presumably facilitated by alanate stabilization of the electron-deficient center that develops at C2 during migration, involving initial π-electron participation (Scheme II).

In connection with the more synthetic features of this process, several points are noteworthy. First, the alkynyl halohydrins used in this method are readily prepared in high yield from either commercially available or readily prepared halocarbonyls and alkynes.[11b] As documented in extensive studies on nucleophilic

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(12) All new compounds gave satisfactory NMR, IR, and mass spectral and exact mass or combustion analyses.

(13) See also ref 11b.