bl Coulomb integrals are nearly angle independent and bl pair overlap repulsion favors small angles.

The sum of valence shell Coulomb repulsions mimics the HF potential curve accurately for H_2O but does not even show a minimum for H_2S. Similarly, the constraint energy for relaxing all valence overlap constraints mimics the HF potential curve well for H_2O but poorly for H_2S. One must be careful of the interpretation of this because the orthogonality relaxation causes all eight valence electrons to collapse into one s-like orbital. The total exchange energy over LHF orbitals has a small (compared to the HF energy curve) maximum near the equilibrium angle for both molecules. However, in H_2S, it is the inner shell terms that create this maximum. We conclude that some of the assumptions of VSEPR theory are borne out by our calculations, but many are not. A simple explanation of the equilibrium bond angles in H_2O and H_2S in terms of the physical interactions in the molecule remains to be given.

The present results do not contradict the notion that the bonds in these molecules are formed primarily of p orbitals[9] rather than tetrahedral hybrids. Perhaps the problem is best studied from this viewpoint.[10] The situation is complicated by the presence of bent bonds that do not appreciably follow the nuclei during bending.[11]

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Influence of Substituents upon Ionization Potential. Dependence of the π-Ionization Energy on the Orientation of an Allylic Hydroxyl or Methoxyl Substituent

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Abstract: The dependence of the π-ionization energy of some allylic alcohols and ethers of rigid geometry was investigated by photoelectron spectroscopy. The π bond was found to be most stabilized (hardest to ionize) when the allylic C–O bond is coplanar with the π system, and becomes progressively less stabilized (relative to the parent olefin with no substituent) as the allylic C–O bond is perpendicular to the π bond. This observed dependence of π-IP on orientation is consistent with (a) a hyperconjugative σ*–π stabilization of the olefin when the adjacent σ* bond is coplanar; (b) a reinforcing inductive stabilization of the olefin which is independent of orientation; and (c) an opposing through-bond destabilization of the π bond when the allylic C–O bond is orthogonal to the olefin. An evaluation of some of the available literature data in the light of the present observations is presented.

I. Introduction

The mechanisms by which substituents remote from each other interact and thereby alter their respective properties merits continued experimental and theoretical investigation. Substituent effects are commonly considered in terms of inductive[1] and conjugative[2] components with the former depending largely on the differences in electronegativity of the interacting groups as well as their separation, and the latter depending upon the mutual interaction of orbitals of like symmetry. Usually the two operate simultaneously to reinforce or oppose each other, thereby introducing uncertainty into quantifying one or the other effect.

Recently our attention was drawn to a series of theoretical studies by Pople et al.[3] who have considered the interaction of two electronegative groups bridged by a methylene unit. According to the bond separation energies as defined for eq 1,[3] when both X and Y are "heavy groups" such as CH_3, NH_2, OR, or F, the calculated energy of the left is lower than that
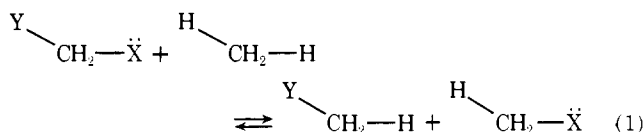
of the right side of eq 1, corresponding to a stabilization of the larger molecule. The findings were interpreted[3] as arising from a π-type donation from X and a σ (σ*) acceptance by the polarized C–Y bond as in **1** which requires a coplanarity of the
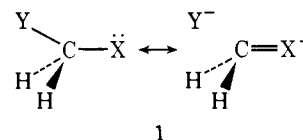
two orbitals for maximal effect. According to these calculations, there is a reduced gross population in the donor (Ẍ) orbital, and an increased π-overlap population between X and

**Table I.** Vertical Ionization Energies and Assignments for Compounds 8–11

compd	vertical ionization energies, eV[a,b]		
	$n_{\ddot{O}R}$	π	$\Delta IP(\pi)^{d}$
X = H (8a)		9.05[c]	0.0
X = OH (8b)	9.95	9.21	0.16
X = OCH₃ (8c)	9.44	9.17	0.12
X = OH (9b)	9.65		
X = OCH₃ (9c)	9.17		
X = H (10a)		8.92	0.0
X = OH (10b)	9.58	9.35	0.43
X = OCH₃ (10c)	9.00[e]	9.34	0.42
X = OH (11b)	9.41		
X = OCH₃ (11c)	9.10		

[a] Values are the average of three or more runs and have a precision of ±0.02 eV. [b] Calibrated against argon as an internal standard. [c] This work. A value of 9.05 eV was also reported by P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Horming, *Helv. Chim. Acta*, **52**, 1745 (1969). [d] $\Delta IP(\pi) = IP(\pi) - IP(\pi, parent)$. [e] See ref 9b.

C. Additionally one expects that the energy of the π-donor orbital ($n_{\ddot{X}}$) should be lowered if such hyperconjugation is present, and its relative energy should depend upon the orientation of the C–Y bond.

Some time ago during a study of some dialkyl peroxides by photoelectron spectroscopy (PES) we noted that the π bond in ascaridole (2) had an unusually high ionization energy (IP).[4]

2   3   4   5
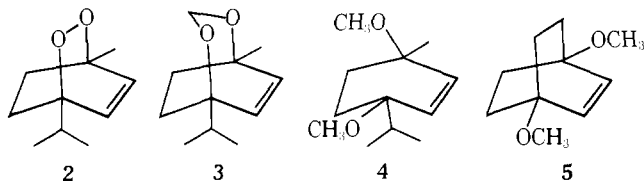
Subsequently we prepared a series of similarly substituted bisallylic compounds (3–5) with different orientations of the bis oxygens relative to the π bond, and assigned the π IPs by comparison with the saturated counterparts.[5] The results seemed to indicate an invariance of the π IP to the orientation of the bisallylic C–O bonds.

In view of the apparent discrepancy between the experimental[5] and theoretical results,[3] we have undertaken a further study into the question of the dependence of π IPs on the orientation of an allylic electronegative substituent. Our model compounds contain an olefin π donor ($\ddot{X}$ in eq 1) and one allylic substituent (OR) which may be oriented orthogonal to (6) or coplanar with (7) the π system. A single allylic substituent

6   7
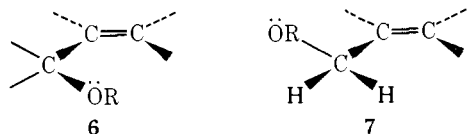
simplifies the PE spectrum[6] and allows an unambiguous assignment of the ionizations.

The following reveals the findings of this study, concerning the conformationally rigid molecules 8–13, and compares them with other examples from the literature.

II. Results

The vertical IPs and assignments for compounds 8–11 are presented in Table I. The saturated analogues were prepared to assist in assignment of the predominantly nonbonded[7] oxygen orbital ($n_{\ddot{O}R}$) in the absence of the π bond. The interpretation of the data (vide infra) requires the unambiguous assignment of the ionizations which were made as follows. For bicyclooctene (8a) the π bond appears at 9.05 eV,[8] while the saturated alcohol 9b exhibits $n_{\ddot{O}H}$ at 9.65 eV. Previous expe-

Table II. Vertical Ionization Energies and Assignments for 1-Substituted 5-*tert*-Butylmethylidenecyclohexanes 12 and 13

compd	ionization energies, eV[a]		
	$n_{\ddot{O}R}$	π	$\Delta IP(\pi)^{b}$
X = H (12a)		9.09 (ν^{+} = 0.18)	
X = OH (12b)	10.15[c]	9.18	0.09
X = OCH₃ (12c)	9.55	8.97	−0.12
X = OH (13b)	9.97[c]	9.37	0.28
X = OCH₃ (13c)	9.54	9.30	0.21

[a] Values are the average of at least three runs and have a precision of ±0.02 eV unless otherwise noted. Calibrated against argon. [b] $\Delta IP(\pi) = IP(\pi) - IP(\pi, 12a)$. [c] Tentatively assigned; appears as well-defined shoulder on the edge of the σ envelope. Precision of ±0.05 eV.
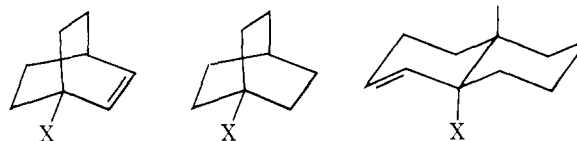
8a, X = H   9b,c   10a–c
b, X = OH
c, X = OCH₃
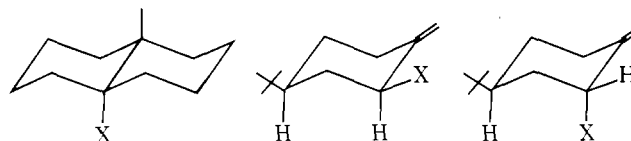
11b,c   12a–c   13b,c

rience with olefins possessing electronegative substituents illustrates that the IP of each group is increased in the presence of the other.[9a,10] Thus in bicyclo[2.2.2]oct-2-en-1-ol (8b) the π bond appears at 9.21 eV, 0.16 eV higher than in 8a, while the $n_{\ddot{O}H}$ ionization is at 9.95 eV. Substitution of a methyl group for H generally lowers the IP of $n_{\ddot{O}R}$ by between 0.6 and 0.4 eV depending on the system, and sharpens the band considerably.[9b] Thus in ether 8c, $n_{\ddot{O}CH_3}$ appears at 9.44 eV as the second band; the remaining IP of 9.17 eV arises from the π bond.

In the case of the 3-octalin (10a) the π IP of 8.92 eV is without question. For the trans-substituted octalins (10b,c) the $n_{\ddot{O}R}$ ionization is assigned on the basis of which band moves markedly on substitution of CH₃ for H. Here it becomes clear that $n_{\ddot{O}R}$ and π ionizations change their relative positions, but the π bond appears at 9.35 ± 0.01 eV in both alcohol 10b and ether 10c.[9b] Comparison of the saturated analogues (11b,c) also verifies the assignment, although the CH₃-substitution shift of $n_{\ddot{O}R}$ is not as drastic as for the other cases.

Data for the stereochemically anchored[12] 1-substituted 5-*tert*-butyl-2-methylidenecyclohexanes (12 and 13) are presented in Table II, and their spectra presented in Figures 1–3. In this system, assignments are relatively straightforward, and in each case the π band has the lowest IP. For ether 12c (Figure 3) the second band at 9.55 eV is much sharper than the first and hence is assigned to $n_{\ddot{O}CH_3}$. For its isomer 13c, the π and $n_{\ddot{O}CH_3}$ bands are overlapped and by analogy with 12c the higher one is assigned to $n_{\ddot{O}CH_3}$, leaving the π IP at 9.30 eV.

III. Discussion

The effect of an electronegative allylic substituent on the IP of a π bond has been determined in a few studies,[10a,c,d,13] although only one systematic orientation study has been reported.[13] In the latter, the effect of an equatorial or axial 2-Cl on the IP of the carbonyl π bond in cyclohexanone was monitored and a stabilizing hyperconjugative interaction between π C=O and the axial C–Cl bond (which was said to be absent
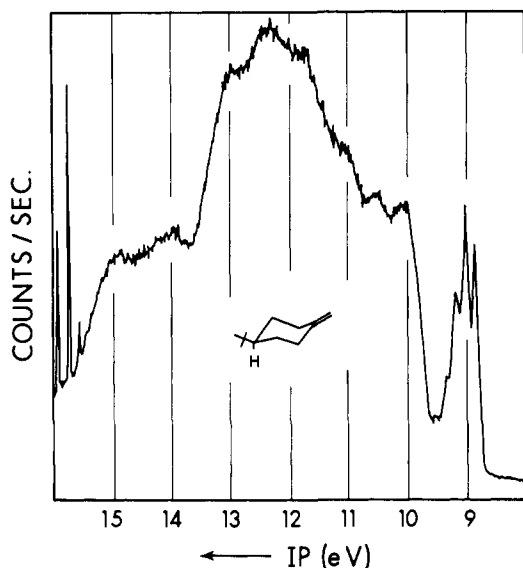
Figure 1. The PE spectrum of 4-*tert*-butylmethylidenecyclohexane (**12a**) using Ar as an internal calibrant.

in the equatorial isomer) was postulated.[14] Invariably unless destabilizing conjugative effects dominate[10e,16] such substituents of any orientation stabilize the π bond thereby increasing its IP.

The data of Table I indicate that a larger stabilization of the π bond by the substituent is observed when the allylic C–ÖR bond is coplanar with the π system. Within the framework of Koopmans' theorem,[17] the olefin in octalins **10b,c** is stabilized by 0.43 and 0.42 eV relative to the parent **10a**. Correspondingly, when the same substituent is perpendicular to the π bond as in **8b** and **8c** a net stabilization of only 0.16 and 0.12 (respectively) relative to parent **8a** is observed. The data are suggestive of a variance of π IP with the orientation of the allylic C–ÖR bond. It may, however, be argued that the octalins, because of their greater mass, may be more polarizable than the bicyclo[2.2.2]octene nucleus, and therefore respond more drastically to the presence of the substituent. In order to test the above possibility, a rigid system of geometric isomers which differ only in the orientation of the allylic substituent was investigated. The data (Table II) for the 1-substituted 5-*tert*-butylmethylidenecyclohexanes (**12** and **13**) show that in the trans isomers (**13b,c**)[18] the π bond is stabilized by 0.28 and 0.21 eV, respectively, relative to the parent (**12a**) while in the cis isomers[18] the stabilization is only 0.09 eV for **12b** and a net *destabilization* of 0.12 eV is seen in ether **12c** (vide infra). Apparently, regardless of the system, a rotational variance of π IP is observed. At least three explanations are consistent with the above observations and will be considered in turn.

(a) The theoretical concept of σ (σ^*) hyperconjugative stabilization of n or π symmetry orbitals was invoked to explain the lowering of the total energy of heavy molecules as in eq 1.[3] If important, an additional consequence of this mechanism should be an energy lowering of the n or π donor which (assuming the validity of Koopmans' theorem[17]) should be amenable to PE analysis. A simplified perturbation diagram showing the interaction of the π bond with the symmetry correct C–X σ or σ^* orbitals is displayed in Figure 4. Clearly the data (vide supra) could be used to support the existence of the π–σ^* hyperconjugative stabilization[3] in the absence of other effects, since in these systems it is observed that the π bond is always more stabilized when the adjacent C–X bond is coplanar.

(b) While the above analysis may be correct since it is consistent with the data, it is incomplete as it stands since other possible interactions which may be operative are ignored.
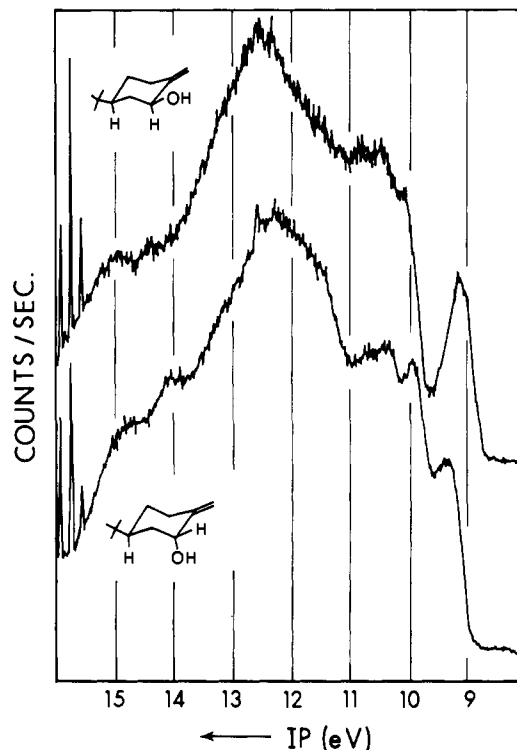

Figure 2. The PE spectrum of *cis*- and *trans*-5-*tert*-butyl-2-methylidenecyclohexanol (**12b** and **13b**) using Ar as an internal calibrant.
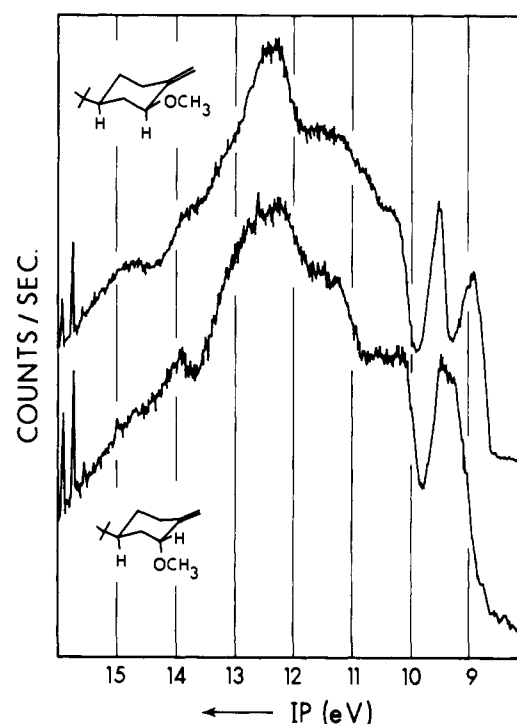

Figure 3. The PE spectra of *cis*- and *trans*-2-methoxy-4-*tert*-butyl-methylidenecyclohexane (**12c** and **13c**) using Ar as an internal calibrant.

Equation 2[19] outlines more completely the possible substituent effects on the π bond:

$$E_\pi = E_{\pi,\text{ref}} - \delta A_\pi + \beta_{\pi,\text{C-X}} + \beta_{\beta,\ddot{X}} \qquad (2)$$

$E_{\pi,\text{ref}}$ is the reference π energy for the appropriate parent olefin, $-\delta A_\pi$ is the inductive raising of the π-bond IP by the substituent X, $\beta_{\pi,\text{C-X}}$ is the net change in the π IP introduced by both stabilizing and destabilizing hyperconjugative inter-
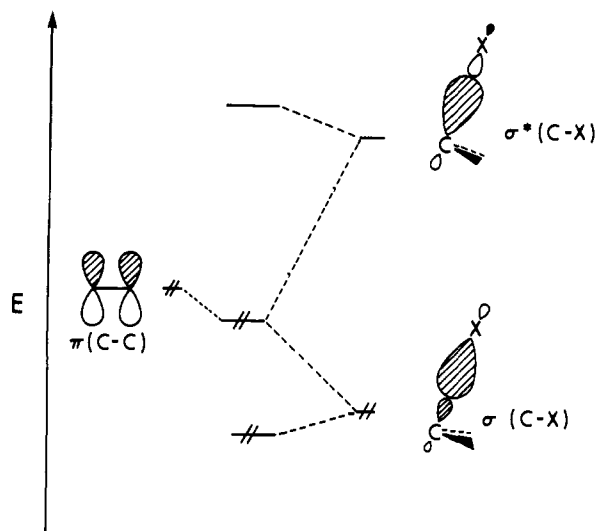
Figure 4. A partial energy diagram showing the interaction of a C–C π bond with adjacent C–X σ and σ^* orbitals leading to a net stabilization of the predominantly π bond.

actions, and $\beta_{\pi,\ddot{x}}$ is the change in the π IP introduced by homoconjugative interactions either through space or through bond.[2a]

The inductive effect (δA_π) is reasonably assumed to be independent of the orientation of the C–X bond as long as its relative connectivity remains constant. The net hyperconjugative stabilization (Figure 4) which reinforces the inductive effect can be switched off by reorientating the C–X bond from a coplanar to orthogonal orientation. Additionally, however, through-bond conjugation as elaborated by Hoffmann[2a] is particularly effective in coupling the π bond and $n_{\dot{O}R}$ but is expected to require their mutual interaction with a pseudo-π orbital located on the adjoining carbon as in **14**. Clearly this

14
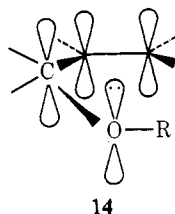
is most effective when the C–ÖR bond and σ system of the olefin are coplanar, and may lead to a destabilization of the π bond by virtue of its interaction with low-lying adjacent filled orbitals.[2a] Hence in cases where we deactivate the stabilizing σ^*–π conjugation, we may activate a destabilizing homoconjugative mechanism (which cannot be evaluated independently), leading to the observed result. Nevertheless this second rationalization is still consistent with the ideas of Pople,[3] although it is difficult to assess the σ^*–π stabilization quantitatively.

(c) On the other hand, a third possible explanation consistent with the data and eq 2 can be envisioned. In this case, however, the importance of the stabilizing σ^*–π conjugation is negligible $(\beta_{\pi,C-X} = 0)$, and only the inductive (δA_π) and homoconjugative effects $(\beta_{\pi,\ddot{x}})$ come into play, the former in all orientations of the C–X bond, and the latter only in circumstances where the allylic C–X bond is perpendicular to the π system (coplanar with the olefinic σ system) (**14**). Some evidence which supports the possibility can be derived from Table II. For the *cis*-methoxymethylidenecyclohexane (**12c**), the π ionization appears at 8.97 eV, *lower* than the parent (**12a**) perhaps as a result of the homoconjugative effect (**14**), outweighing the inductive effect of the OCH3. In the trans isomer

(**13c**), however, such homoconjugation is turned off, and the inductive effect dominates, stabilizing the π bond.

Whichever one or combination of the above explanations proves correct, it is clear from these examples that there is a rotational variance of the π IP when the allylic substituent is ÖR. One might expect similar observations with other electronegative allylic substituents in order of increasing electronegativity, but the available literature data are sparse. Some isolated examples, however, serve to illustrate the point and may suggest further investigation.

IV. Additional Literature Data

A. Allylamines. While nitrogen is less electronegative than oxygen, still some σ^*–π effect might be observed with different orientations. Compounds **15** and **16** have the allylic N–C bond


15[20]	**16**[20]
π 9.36 eV	π 9.33 eV
n_N 8.35 eV	n_N 8.64 eV
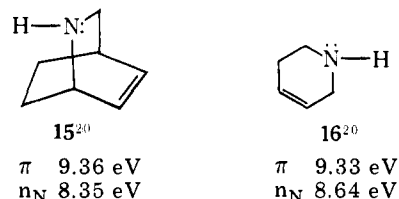
coplanar and orthogonal to[21] the π bond, respectively. The π IP for **15** is 0.31 eV greater than that in bicyclooctene (**8a**)[8] while that of **16** is 0.21 eV larger than its counterpart in cyclohexene.[22] While the experimental errors in the reported IPs may bring the differences closer together, the values as given appear to suggest a rotational variance of π IP.[23] Of course other explanations such as a preferred through-space interaction in **15** (but absent in **16**) cannot be excluded.

B. Allylic Oxygen. Compounds **17** and **18** possibly represent

17	**18**
π 9.44 eV[16]	π 9.14 eV[16]
n 9.83 eV	n 10.59 eV
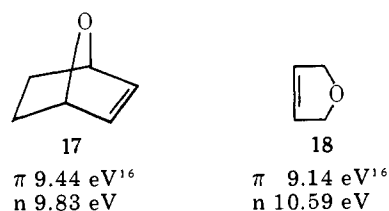
an interesting addition to the hyperconjugative stabilization $(\sigma^*$–$\pi)$ argument. Relative to norbornene (π IP 8.97 eV),[8] the π IP of **17** is stabilized by 0.47 eV, while that in **18** is about the same as cyclopentene (9.18 eV).[22] The authors concluded[16] that the latter occurred from a 1,3-conjugative interaction between π and 0 in **18** which was absent in **17**.[24] These unsaturated ethers too exhibit such a rotational variance of IP as could be accommodated by any or all of the explanations (vide supra).

For allyl alcohol (**19**) gas-phase microwave data[25] indicate that the gauche conformation (**19a**) is preferred over the cis

19a	**19b**
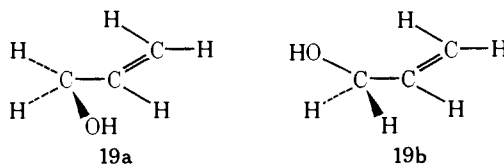
conformation (**19b**). The former holds the C–O σ bond nearly coplanar with the π system,[26] and the PE data[27] for allyl alcohol indicates that the π IP (10.22 eV)[27] is 0.34 eV greater than that in the parent propene.[10c] This rather large stabilization of the π IP is consistent with that found for the rigid coplanar alcohols (**10b**, 0.43 eV, and **13b**,[18] 0.28 eV) from Tables I and II; unfortunately no comparison orthogonal primary allylic alcohols are available.

C. Allyl Halides (F, Cl, Br).[10c] Relative to propene (π 9.88

eV)[10c] allyl fluoride, chloride, and bromide show π IPs at 10.56, 10.34, and 10.18 eV, respectively,[10c] with the largest stabilization found for the most electronegative F. The result is consistent with an inductive stabilization (F > Cl > Br), but is also consistent with a hyperconjugative stabilization of π with the C–X bond[28,29] if it is coplanar. Conformationally rigid allyl halides have not been investigated presumably owing to synthetic difficulties.

V. Conclusions

The above study has shown a definite variance of π IP with the orientation of an allylic alcohol or ether in rigid systems. Whether this is a general phenomenon for all electronegative elements remains to be seen, although some of the available literature data suggest that this might be so. The largest stabilization occurs when the allylic substituent is coplanar with the π system; stabilization decreases as the allylic C–O bond approaches perpendicularity. The observations are consistent with a hyperconjugative $\sigma^*-\pi$ stabilization[3] which requires coplanarity of the interacting orbitals for maximum effect. Alternative explanations involving an inductive stabilization of the π orbital coupled with a homoconjugative through-bond destabilization when the allylic C–O bond is orthogonal to the π bond are also consistent, and the data do not allow a distinction of the mechanisms. A possible probe for this would involve the use of electronegative substituents ($-CF_3$, $-N^+R_3$) which would not allow the through-bond mechanism, although for reasons of synthetic difficulty the CF_3 substituent is inappropriate, and the quaternary ammonium salts would be too involatile for gas-phase work.

On the positive side, however, the present findings may be used to infer the orientation of an allylic C–O bond in cases where the molecule could adopt one of several conformations in the gas phase. Our findings in this context will be reported separately.

Experimental Section

Photoelectron spectra were measured using a MacPherson Model 36 ESCA spectrometer and were calibrated against argon. Spectral data reported are the average of at least three runs and the precision is 0.02 eV or better unless noted otherwise (Table II). Routine IR and NMR spectra were run on a Perkin-Elmer 421 grating infrared spectrophotometer or Nicolet 7199 FT-IR machine, and on a Varian Associates A-60 NMR spectrometer or HA-100 spectrometer, respectively. All melting points and boiling points are uncorrected.

Bicyclooctene (8a) was prepared as described by Garbisch et al.[30]

1-Methoxybicyclooctene (8c) was prepared according to the following sequence, utilizing a general procedure of Birch[31] for the Diels-Alder addition of maleic anhydride to 2,5-dihydroanisole.[32]

1-Methoxybicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic Acid Anhydride. To 11 g (0.1 mol) of 2,5-dihydroanisole[32] in 100 mL of ether was added in one portion 9.8 g (0.1 mol) of maleic anhydride. The yellow solution was stirred at room temperature for 3 days and filtered to give 12.9 g (62%) of colorless solid: mp 87–89 °C; NMR (CDCl₃) δ 6.31 (m, 2 H), 3.48 (s, 3 H), 3.33–3.09 (m, 3 H), 1.64 (m, 4 H); IR (CHCl₃) 1830, 1775 cm⁻¹.

1-Methoxybicyclo[2.2.2]octane-2,3-dicarboxylic Anhydride. Hydrogenation of the unsaturated anhydride (4.16 g, 0.02 mol) over 0.1 g of PtO₂ in 75 mL of THF consumed 450 mL of H₂ and yielded, after filtration, removal of solvent, and recrystallization from ether, 4.0 g (95%) of needles: mp 99–102 °C; NMR (CDCl₃) δ 3.31 (br s, 5 H), 2.20 (br s, 1 H), 2.11–1.44 (m, 8 H); IR (CHCl₃) 1867, 1780, 1450 cm⁻¹.

1-Methoxybicyclo[2.2.2]octane-2,3-dicarboxylic Acid. The following procedure was adapted from that of Alfaro et al.[33] A solution of 50 mL of acetone, 40 mL of water, and 6.2 g (0.03 mol) of anhydride (prepared as above) was refluxed overnight (crystals formed) and then cooled to 0 °C and filtered to give 6.5 g of white crystals: mp 183.5–185 °C (–CO₂); NMR (Me₂SO-d_6) δ 11.87 (br s, 2 H, exchanges with D₂), 3.12 (s, 3 H), 1.17–2.5 (m, 8 H), 3.35–2.68 (m, 3 H).

1-Methoxybicyclo[2.2.2]oct-2-ene (8c). The above diacid (17.6 g, 0.077 mol) in 75 mL of CH₃CN and 25 mL of pyridine was treated with 37.65 g of freshly recrystallized Pb(OAc)₄ (acetic acid) according to the procedure of Grob et al.,[34] to yield after final workup 5.7 g (54%) of **8c**: bp 55 °C (9 mm); NMR (CDCl₃) δ 6.42–6.11 (m, 2 H), 3.34 (s, 3 H), 2.47 (br s, 1 H), 1.80–1.13 (m, 8 H); IR (CHCl₃) 1445, 1338, 1105, 1080 cm⁻¹. Exact mass. Calcd for C₇H₁₀O (M⁺ − C₂H₄): 110.0731. Found: 110.0729. Anal. Calcd for C₉H₁₄O: C, 78.21; H, 10.21. Found: C, 78.14; H, 10.21.

1-Methoxybicyclo[2.2.2]octane (9c). Hydrogenation of olefin **8c** (3 g, 0.022 mol) in 30 mL of THF with 0.1 g of Pt₂O yielded after filtration and vacuum distillation 2.5 g (83%) of ether **9c**: bp 62 °C (9 mm); NMR (CDCl₃) δ 3.18 (s, 3 H), 1.67 (s, 12 H), 1.58 (br s, 1 H); IR (CHCl₃), 1447, 1338, 1313, 1105, 1080 cm⁻¹.

Bicyclo[2.2.2]oct-2-en-1-ol (8b). A demethylation procedure of Jung and Lyster[35] successfully yielded **8b** from ether **8c**. To 1.38 g (0.01 mol) of **8c** treated with 4 mL of dry CHCl₃ and 0.5 mL (0.006 mol) of pyridine in a 25-mL oven-dried flask under nitrogen was added 3.5 mL (0.024 mol) of (CH₃)₃SiI[35] via dried syringes. The mixture was allowed to stand at 60 °C for 4 days and then cooled to 25 °C; 2 mL of dry CH₃OH was added and then the volatiles were removed under vacuum. Addition of dry ether to the residue followed by filtration of the pyridinium iodide and evaporation of the filtrate yielded a crude residue which was chromatographed over 38 g of silica gel with dry ether. Final yield based upon recovered ether was 0.73 g of **8b** (75%): mp 143–148 °C (hexane) (lit. mp 155–156 °C);[36] NMR (CDCl₃) δ 6.3–6.04 (m, 2 H), 2.52 (br s, 1 H), 2.15 (s, 1 H, exchanges with D₂O), 1.80–1.30 (m, 8 H); IR (CHCl₃) 3250, 2950, 1610, 1450, 1330, 1140, 1115, 1090, 689 cm⁻¹.

Bicyclo[2.2.2]octan-1-ol (9b). Demethylation[35] of 1.45 g (0.01 mol) of the ether **9c** following the same procedure was above for the unsaturated ether **8c** yielded after workup[35] 0.92 g (80% based on recovered **9c**) of alcohol **9b**, mp 214–215 °C (lit. mp 213–215 °C).[36]

10-Methyl-*trans*-3-octalin (10a).[37] Lithium–ammonia reduction (0.3 g of Li, 0.043 mol) with 125 ml of liquid NH₃ at −78 °C of 1 g (0.006 mol) of 10-methyl-4-octal-3-one (prepared by the methodology of ref 38) in 15 mL of dry THF[39] produced the corresponding lithium enolate which after evaporation of *all* residual ammonia under N₂ at room temperature was treated with 7.0 g (0.041 mol) of *N,N,N′,N′*-tetramethyldiamidophosphochloridate[40] and 2.5 mL of tetramethylethylenediamine in 10 mL of dry THF over a 6-min period. After stirring overnight, the reaction mixture was worked up by the addition of 3 mL of saturated NH₄Cl solution followed by 40 mL of H₂O. Extraction of this mixture with 3 × 50 mL of CH₂Cl₂ and drying of the combined organic phases over MgSO₄, after filtration and solvent removal, a crude residue which was reduced[37] as follows. Lithium metal (0.40 g, 0.058 mol) was added over a 20-min period to 60 mL of dry ethylamine at −78 °C. After stirring at −78 °C for 45 min, this solution was treated dropwise (30 min) with a solution of 1.2 g of the crude phosphorus ester (prepared as above) and 2 mL (0.021 mol) of *tert*-butyl alcohol. The final mixture was stirred for 2 h, warmed to room temperature, and then decomposed by the addition of 2 mL of saturated NH₄Cl solution, followed by 35 mL of H₂O. Extraction of the aqueous phase with 3 × 50 mL of CH₂Cl₂ which were then combined, dried over MgSO₄, filtered, and evaporated under aspirator pressure yielded 0.8 g (88% crude yield) of 10-methyl-*trans*-3-octalin (**10a**). Preparative GC (15 ft × ³⁄₈ in., 20% DEGS on Chromosorb WAW-DMCS) followed by microdistillation, bath temperature 100 °C (3 mm), yielded pure **10a**: NMR (CDCl₃) δ 0.81 (s, 3 H), 5.4 (m, 2 H); IR (neat) 3012, 2923, 2845, 1450, 1275 cm⁻¹. Exact mass. Calcd for C₁₁H₁₈: 150.1409. Found: 150.1410.

5α-Hydroxy-10β-methyl-3-octalin (10b). A mixture of **10b** and its cis isomer, 5β-hydroxy-10β-methyl-3-octalin, was prepared as described.[41] They were separated by preparative TLC (silica gel (1 mm), pentane–ether, 4:1). Exact mass. Calcd for C₁₁H₁₈O: 166.1358. Found: 166.1364. NMR (CDCl₃) δ 0.96 (s, 3 H); IR (neat) 3480, 1640 cm⁻¹.

5α-Hydroxy-10β-methyldecalin (11b).[41,42] Hydrogenation of olefin **10b** (50 mg, 0.0003 mol) in 30 mL of dry ether containing 4 drops of triethylamine over 250 mg of 5% Pd/C in a Paar hydrogenator at 50 lb pressure for 24 h, followed by filtration through a column (0.5 × 3.5 in.) of silica gel (28–200 mesh) and removal of solvent under aspirator pressure, gave a yellow oil. Microdistillation, bath temperature 85 °C (3 mm), gave 37 mg (73%) of a clear oil (**11b**): NMR (CDCl₃) δ 1.03 (s, 3 H); IR (neat) 3480, 2860, 1451 cm⁻¹. Exact mass. Calcd

for $C_{11}H_{18}$ ($M^+ - H_2O$): 150.1409. Found: 150.1412.

5α-Methoxy-10β-methyl-3-octalin (10c). Methylation[43] of the trans allylic alcohol (**10b**) plus its cis isomer using 1.0 g (0.009 mol) of mixture, 1.0 g (0.007 mol) of CH_3I, and 0.3 g (0.012 mol) of NaH in 25 mL of dry DME gave after workup 0.95 g (88%) of a crude residue which contained both cis and trans allylic ethers. Preparative GC (16 ft × ⅜ in., 10% polyphenyl ether on Chromosorb WAW-DMCS (80–100 mesh)) gave as a minor component the desired **10c** which was microdistilled, bath temperature 85 °C (6 mm), to give a clear liquid: NMR ($CDCl_3$) δ 0.92 (s, 3 H), 3.10 (s, 3 H); IR (neat) 2920, 1645, 1458, 1078 cm^{-1}. Exact mass. Calcd for $C_{12}H_{20}O$: 180.1515. Found: 180.1511.

5α-Methoxy-10β-methyldecalin (11c). Hydrogenation[41] of 40 mg (0.022 mol) of **10c** in 45 mL of dry ether containing 4 drops of triethylamine, over 600 mg of 5% Pd/C at 52 psi for 20 h yielded, after filtration through a small column of silica gel and evaporation under aspirator pressure, a brownish residue. Sublimation (80–90 °C (8 mm)) gave 38 mg (95%) of white solid, mp 58–60 °C, identified as ether **11c**: NMR ($CDCl_3$) δ 1.02 (s, 3 H), 3.05 (s, 3 H); IR (neat) 1470, 1457, 1443, 1431, 1378, 1213, 1191, 1180, 1114 cm^{-1}. Exact mass. Calcd for $C_{12}H_{22}O$: 182.1672. Found: 182.1669.

1-Methylidene-4-*tert*-butylcyclohexane (12a).[44] This was prepared by the method of Cross and Whitham,[44] in 62% crude yield. Preparative GC (15 ft × ⅜ in., 20% DEGS on Chromosorb WAW-DMCS (80–100 mesh)) followed by microdistillation, bath temperature 75 °C (12 mm), gave **12a**: lit. bp 78–80 °C (18 mm);[44] NMR ($CDCl_3$) δ 0.85 (s, 9 H), 4.57(m, 2 H); IR (neat) 2944, 1650, 1365, 886 cm^{-1}. Exact mass. Calcd for $C_{11}H_2O$: 152.1566. Found: 152.1571.

2-Methylidene-*trans*-5-*tert*-butylcyclohexanol (13b). Following the reported procedure[44] **12a** was hydroxylated in 26% crude yield to give **13b**. Purification by preparative GC (15 ft × ⅜ in., 20% DEGS on Chromosorb WAW-DMCS (80–100 mesh)) followed by sublimation (120 °C (8 mm)) gave a waxy, white solid: mp 35–37 °C (lit. mp ca. 25 °C);[44] NMR ($CDCl_3$) δ 0.86 (s, 9 H), 4.33 (t, 1 H), 4.75 (m, 2 H); IR (neat) 3366, 3070, 1656, 1365, 1084, 1041, 1015, 980, 900 cm^{-1}. Exact mass. Calcd for $C_{11}H_{20}O$: 168.1515. Found: 168.1513.

1-Methoxy-2-methylidene-*trans*-5-*tert*-butylcyclohexane (13c). Methylation[43] of alcohol **13b** gave after workup 0.5 g (83% crude yield) of a yellow oil. Preparative GC (15 ft × ⅜ in., 20% DEGS on Chromosorb WAW-DMCS (80–100 mesh)) followed by microdistillation, bath temperature 70 °C (12 mm), gave pure **13c**: NMR ($CDCl_3$) δ 0.85 (s, 9 H), 3.18 (s, 3 H), 3.70 (t, 1 H), 4.80 (m, 2 H); IR (neat) 1365, 1261, 1107, 1090, 1078, 962, 901, 855 cm^{-1}. Exact mass. Calcd for $C_{12}H_{22}O$: 182.1672. Found: 182.1664.

2-Methylidene-*cis*-5-*tert*-butylcyclohexanol (12b).[45] Preparation[45] of **12b** in 32% crude yield yielded an oil which was microdistilled, bath temperature 75 °C (0.5 mm), and proved to be a mixture of **12b** and its trans isomer **13b**. Preparative GC (15 ft × ⅜ in., 20% DEGS on Chromosorb WAW-DMCS) gave a major component which was microdistilled (70 °C (0.5 mm)) to yield a clear liquid which solidified on standing: mp 44–44.5 °C (lit. mp ca. 20 °C);[45] NMR ($CDCl_3$) δ 0.87 (s, 9 H), 4.83 (m, 2 H); IR (neat) 3605, 3013, 2960, 2867, 1653, 1367, 1055, 1069, 1088, 898 cm^{-1}. Exact mass. Calcd for $C_{11}H_{20}O$: 168.1515. Found: 168.1516.

1-Methoxy-2-methylidene-*cis*-5-*tert*-butylcyclohexane (12c). Methylation[43] of 2.0 g (0.012 mol) of **12b** gave a crude yield of 97% of **12c**. Preparative GC under the same conditions used for **13c** followed by microdistillation, bath temperature 77 °C (8 mm), gave pure **12c**: NMR ($CDCl_3$) δ 0.86 (s, 9 H), 3.45 (s, 3 H), 4.80 (m, 2 H); IR (neat) 2954, 1367, 1138, 1116, 1084, 897 cm^{-1}. Exact mass. Calcd for $C_{12}H_{22}O$: 182.1672. Found: 182.1668.

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Genesis of a Supported-Metal Catalyst.
Aggregation of Polymer-Bound Rhodium Clusters

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Abstract: Poly(styrene–divinylbenzene) functionalized with PPh_2 groups was allowed to react with a solution of $Rh_6(CO)_{16}$ in benzene at 25 °C. The product was a polymer containing small Rh clusters, which after reaction with CO exhibited carbonyl spectra like that of $Rh_6(CO)_{13}(PPh_3)_3$. The polymer was an active, stable catalyst for the hydrogenation of ethylene and cyclohexene at 1 atm and 80 °C. When traces of oxygen were present in the reactants flowing over the catalyst, the phosphine groups were oxidized and the Rh agglomerated, slowly forming a supported-metal catalyst having Rh entities about 20 Å in diameter. The metal entities of various sizes were distinguished by kinetics of the olefin hydrogenation reactions, by their carbonyl infrared spectra, and by electron microscopy.

Introduction

Catalysts used in many processes are small metal particles stably dispersed on a support like silica or alumina. Preparation of a supported-metal catalyst involves (1) impregnation of the support with a solution of a metal salt or ion exchange of a metal, (2) calcination, and (3) reduction (e.g., with hydrogen) leading to migration and agglomeration of metal on the support and formation of an array of particles of varying sizes and structures, typically having hundreds or thousands of atoms and referred to as crystallites. The reduction and agglomeration processes are poorly understood, there being almost no experimental evidence of the metal entities smaller than about 15 Å, the ones large enough to be characterized by electron microscopy; surface titration with hydrogen determines the dispersion (the fraction of metal atoms accessible on a surface), but it is nearly unity for all crystallites smaller than 15 Å.[2]

Recent efforts to prepare small, well-defined metal entities supported on surfaces have taken advantage of metal-cluster compounds; for example Ichikawa[3] brought platinum and nickel carbonyl clusters into contact with silica and alumina, producing highly dispersed metal catalysts, but the cluster-surface interactions and the pyrolytic agglomeration processes remain uncharacterized. Collman et al.[4a] allowed $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ to react with poly(sytrene–divinylbenzene) resins functionalized with PPh_2 groups, and the ensuing ligand-exchange reactions produced attached rhodium clusters of undetermined structures. Oxidation with air led to loss of the carbonyl spectrum and yielded catalysts having activity for arene hydrogenation at 25 °C and 1 atm; similar catalytic behavior was exhibited by a commercial catalyst consisting of Rh crystallites (having an average dimension of about 20 Å) supported on alumina (Rh/Al_2O_3). Collman's and related results[4] provided a starting point into the research described here, since they indicated that chelation by the polymer matrix might allow stable bonding of small metal clusters to a solid support. The present study focused on the process of aggregation of the metal entities; the characterization of the metal

included infrared spectroscopy of carbonylated species, electron microscopy, and kinetics of catalytic hydrogenation reactions.

Results

Catalysts prepared by ligand exchange of $Rh_6(CO)_{16}$ with 7-μm thick membranes of poly(styrene–divinylbenzene) functionalized with PPh_2 groups gave infrared spectra like those reported previously,[4] the results being consistent with the hypothesis that small Rh clusters were attached to the phosphine groups of the polymer.[5] The golden-brown membrane samples could be reversibly carbonylated and decarbonylated in a flow reactor at 80 °C, and they were stable catalysts, experiencing tens of thousands of turnovers and maintaining unchanged activity for hydrogenation of cyclohexene or of ethylene for as long as 80 h of continuous operation, provided that they were exposed to only reactants (olefin + H_2), He, and/or CO.[5]

When the catalyst preparation procedure was modified so that a $Rh_6(CO)_{16}$–benzene solution was brought in contact with the functionalized polymer at 50 °C instead of the usual 25 °C, black spots of metallic Rh deposited on the glassware, and the resulting membranes were gray or black. Transmission electron microscopy showed that aggregated metal species were present in the polymer, having an average diameter of about 25–40 Å and consisting of several hundred atoms each. We infer that the aggregation was much slower at 25 °C, the usual temperature of preparation, since the usual membranes were golden-brown and had no metal crystallites observable by electron microscopy.

A group of catalysts (Table I) was used to determine kinetics of catalytic hydrogenation of cyclohexene, ethylene, and benzene vapors at 1 atm and about 80 °C. The observed reaction products were cyclohexane, ethane, and cyclohexane, respectively. Conversions were less than about 4%; they were shown experimentally to be differential, determining reaction rates directly. For each olefin, the rate data were well repre-

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