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Registry No. 1, 84131-33-9; **2**, 84131-34-0; **3**, 84131-35-1; **4**, 16736-13-3; **5**, 96633-25-9; **6**, 96633-23-7; **7**, 96633-26-0; **8**, 96633-27-1; **9**, 96633-28-2; **10**, 96633-29-3; **11**, 96633-30-6; **12**, 96633-31-7; **13**, 96633-32-8; **14**, 96633-34-0; **15**, 96633-52-2; **17**, 14618-89-4; **18**, 5650-07-7; **19**, 37471-46-8; **20**, 96633-36-2; **21**, 96633-37-3; **22**, 96633-35-1; **23**, 96633-42-0; **24**, 96633-41-9; **25**, 84131-36-2; **26**, 84131-38-4; **27a**, 96633-45-3; **27b**, 96633-46-4; **28**, 2430-99-1; **29**, 2001-28-7; **30**, 96633-38-4; **31**, 96633-40-8; **32**, 96633-43-1; **33**, 96633-44-2; **34**, 84131-37-3; **35**, 84131-39-5; **37**, 96633-48-6; **37** (1-carbomethoxy analogue), 96633-47-5; **38**, 96633-49-7; **39**, 96633-50-0; $(PhSe)_2$, 1666-13-3; Br_2, 7726-95-6; PhSeBr, 34837-55-3; $CH_3COCHPhCH(Tol)CH{=}C(CH_3)_2$, 96633-24-8; $TolCH_2COCH_3$, 2096-86-8; PhCHO, 100-52-7; $TsNHNH_2$, 1576-35-8; $TolCH{=}C(Ph)C(CH_3){=}NNHTs$, 96633-33-9; $(CH_3)_2C{=}CHMgBr$, 38614-36-7; $ClCO_2CH_3$, 79-22-1; mesityl oxide, 141-79-7; 3-phenyl-4-*p*-tolyl-5,5-dimethyl-2-cyclohexen-1-one, 96633-39-5; 3-*p*-tolyl-4-phenyl-5,5-dimethyl-2-cyclohexen-1-one, 96648-86-1.

Transmission of Electronic Substituent Effects in 4-Substituted Bicyclo[2.2.2]octyl Systems

William Adcock,*[†] Graeme Butt,[‡] Gaik B. Kok,[†] Stephen Marriott,[‡] and Ronald D. Topsom*[‡]

School of Physical Sciences, The Flinders University of South Australia, Bedford Park,
South Australia, 5042 Australia, and Department of Organic Chemistry, La Trobe University,
Bundoora, Victoria, 3083 Australia

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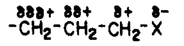
Carbon-13 substituent chemical shifts are reported for a series of 4-substituted bicyclo[2.2.2]octyl acetylenes, benzenes, cyanides, ethylenes, aldehydes, and esters. These shifts, for atoms contained in unsaturated probe linkages, are proportional to substituent field effects (σ_F). Unlike fluorine-19 chemical shifts in corresponding bicyclo[2.2.2]octyl fluorides, no definitive evidence is found for significant substituent electronegativity effects. This result is confirmed by ab initio molecular orbital calculations on bicyclo[2.2.2]octyl acetylenes and cyanides and some corresponding model systems. Unlike the corresponding aromatic side-chain derivatives, infrared intensity data for stretching absorptions of the unsaturated probes in the bicyclo[2.2.2]octyl compounds do not follow polar substituent effects.

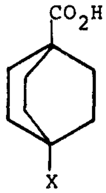
The three principal electronic interactions between a probe group and a relatively remote substituent are[1-4] the electronegativity (χ), field (F), and resonance (R) effects. The electronegativity effect[2,5] (also earlier referred to as a σ-inductive effect) originates in an electronegativity difference between a substituent (X) and the atom to which it is attached and is transmitted by successive, but diminishing, relay along chains of atoms as shown schematically.



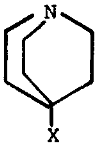
$$\overset{\delta\delta\delta+}{-CH_2}-\overset{\delta\delta+}{CH_2}-\overset{\delta+}{CH_2}-\overset{\delta-}{X}$$

The field effect involves the direct through-space transmission to the probe of the electrostatic dipole at the substituent. The weight of recent evidence suggests[1-3] that, compared to field effects, electronegativity effects are not significant after the first atom of attachment. Nevertheless, there are some results[6,7] suggesting that electronegativity, or related effects, are important in certain systems.

Suitable model compounds to study the relative importance of these two effects should be structurally rigid, to avoid problems arising from uncertain conformation, and capable of being synthesized with a reasonable range of substituents. Many earlier studies of electronic substituent effects involved meta- and para-substituted benzenes, which meet these criteria, but the concomitant presence of resonance and π-inductive[4] effects make analysis difficult. The "classic systems[1]" for such studies therefore have been 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids[8,9] (1) and 4-substituted quinuclidines[9,10] (2), although it has been suggested[11] that results in the latter case may not be completely insulated from through-bond and substituent-induced structural effects.



(1)



(2)

Such systems have been used[9] to define σ_F values.[12]

[†] The Flinders University of South Australia.

[‡] La Trobe University.

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(12) Previously known as σ_I—see ref 2.

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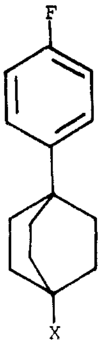
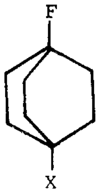
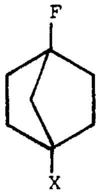
Gas-phase proton-transfer energies for system **1** have also been found[13] to be proportional to σ_F. Furthermore, fluorine-19 substituent chemical shifts (SCS) in 1-substituted (X)-4-(*p*-fluorophenyl)bicyclo[2.2.2]octanes (**3**), give an excellent measure of σ_F parameters.[14,15] By contrast, the fluorine-19 SCS in 4-substituted bicyclo[2.2.2]-oct-1-yl fluorides[15] (**4**) and in the corresponding bicyclo-[2.2.1]hept-1-yl fluorides[16] (**5**) seem dependent on both field and electronegativity effects. Most importantly, it was shown[15] that the latter influence is not transmitted by sucessive polarization of the bonds as indicated schematically above. The electronegativity dependence, which is of *opposite* sign in **4** and **5**, has been ascribed to "through-bond" and "through-space" electron delocalization mechanisms.[15,16]



(3)

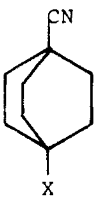


(4)

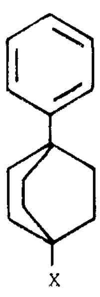


(5)

In a preliminary communication we reported carbon-13 SCS for the cyano carbon in the bicyclo[2.2.2]octyl cyanides (**6**),[17] and such shifts for the various aromatic carbons in the bicyclo[2.2.2]octylbenzenes have also been published (**7**).[14,18] In both **6** and **7**, the values are proportional to σ_F. This result in **6** contrasts with the only approximate relationship found for the cyano carbon in 2-substituted 1-cyanoethanes[19] and of the ethylenic carbon in 4-substituted 1-butenes,[20] presumably because of conformational lability. Related results include reactivities[21] of 3-substituted bicyclo[1.1.1]pentanecarboxylic acids, which apparently follow σ_F.

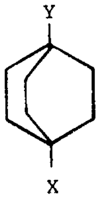


(6)



(7)

We report here results for 4-substituted bicyclo[2.2.2]-octanes (**8**), where Y is C≡CH, CN, CHO, CO_2R, Ph, $CH{=}CH_2$, $CH{=}CCl_2$, and $CH{=}CF_2$. These include carbon-13 SCS for carbon atoms in Y, together with infrared results for the acetylenes, esters, and cyanides. Theoretical calculations at the STO-3G ab initio molecular orbital level are reported for the acetylenes and cyanides. Most series include a wide range of substituents, X.



(8)

Results and Discussion

In Table I we list the carbon-13 SCS for the substituted bicyclo[2.2.2]octyl acetylenes, cyanides, and benzenes. Similar results for the aldehydes, esters, and ethylenes are given in Table II. Table III gives the infrared results for the acetylenes, esters, and cyanides, while Table IV reports the theoretical calculations for the acetylenes and cyanides. Table V gives proton SCS for the acetylenic proton and the Δ^1J_{CH} coupling constants at the same position in the bicyclo[2.2.2]octylacetylenes.

Carbon-13 SCS. The carbon-13 SCS of the α-carbon in the group Y are very similar for the acetylenes, benzenes, ethylenes, and dichloroethylenes and rather smaller for the esters, cyanides, and difluoroethylenes, where the β-atoms have significant electronegativity. This is shown in correlations according to eq 1. The σ_F values used were those

$$\mathrm{SCS} = \rho_F\sigma_F + c \qquad (1)$$

for the appropriate solvents taken from a recent compilation.[15,22] The resultant values of ρ_F, c, and the correlation coefficients are listed in Table VI. It can be seen that the ρ_F values in $CDCl_3$ for the α-carbons of the acetylenes, benzenes, ethylenes, and dichloroethylenes are in the range −4.6 to −5.7, while lower values are found for the cyanides (−3.9), esters, and difluoroethylenes (−3.4). The correlations are of reasonable precision with the exception of the esters and dihaloethylenes. It is interesting that the acetylenes, benzenes, and ethylenes have such similar ρ_F values since theoretical results[23] suggest that the triple bond in the acetylene is considerably less polarizable than the ethylenic or benzene systems. We return to this matter below. The reduced ρ_F value in the difluoroethylene compared to ethylene parallels results reported for the 4-substituted, β,β-difluorostyrenes compared to styrenes. The basis for these differences is not known.[24]

The correlations for SCS of the β-carbon atom in the bicyclo[2.2.2]octylacetylenes and -ethylenes and the para carbon atom in the benzenes are also listed in Table VI.

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[22] Results were also correlated against a set of σ_F values reported in: Reynolds, W. F.; Gomes, A.; Maron, A.; MacIntyre, D. W.; Tanin, A.; Hamer, G. K.; Peat, I. R. *Can. J. Chem.* **1983**, *61*, 2376. The correlations gave very similar parameters and correlation coefficients.

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Table I. ^{13}C Substituent Chemical Shifts for 4-Substituted Bicyclo[2.2.2]octyl Acetylenes, Cyanides, and Benzenes (Values are in ppm from parent, positive shifts are downfield)

	acetylenes		cyanides	benzenes[a]	
subst	C_α	C_β	C(CN)	C_1[b]	C_4
H	0.00[c] (0.00)[d]	0.00[c] (0.00)[d]	0.00[c]	0.00[c] (0.00)[d]	0.00[c] (0.00)[d]
Me	−0.24 (−0.26)	0.38 (0.37)	0.00	−0.39 (−0.40)	0.05 (0.03)
Ph	−0.66 (−0.42)	0.63 (0.51)	−0.24	−0.80 (−0.61)	0.25 (0.24)
NMe_2[e]	−1.00 (−0.58)	0.60 (0.39)		−1.24[e] (−1.03)[f]	0.19[e] (0.20)[f]
OMe	−1.69 (−1.17)	0.87 (0.65)	−0.97	−1.88 (−1.44)	0.33 (0.28)
CO_2Me	−1.46 (−1.04)	0.88 (0.66)	−0.94	−1.50 (−1.16)	0.39 (0.37)
COMe	−1.54 (−1.10)	0.96 (0.77)		−1.60 (−1.25)	0.43 (0.42)
CF_3	−2.14 (−1.82)	1.25 (1.08)		−2.10 (−1.88)	0.58 (0.62)
I	−2.01 (−1.52)	1.47 (1.26)	−1.19	−2.06 (−1.68)	0.57 (0.60)
Br	−2.56 (−2.03)	1.55 (1.31)	−1.75	−2.58 (−2.18)	0.59 (0.62)
Cl	−2.64 (−2.14)	1.51 (1.26)	−1.65	−2.68 (−2.30)	0.58 (0.60)
F	−2.72 (−2.17)	1.38 (1.11)	−1.76	−2.86 (−2.42)	0.55 (0.56)
CN	−2.94 (−2.34)	1.67 (1.35)	−2.04	−2.78 (−2.34)	0.77 (0.83)
NO_2	−3.64 (−2.95)	1.99 (1.67)		−3.64 (−3.13)	0.89 (0.93)

[a] The SCS values for $CDCl_3$ as solvent are carefully remeasured results of those reported in ref 14. These values are more accurate than those previously reported in this solvent. [b] C_1 is position of attachment. [c] In $CDCl_3$ solvent. [d] In CCl_4 solvent. [e] Reference 18. [f] SCS for NH_2.

Table II. ^{13}C Substituent Chemical Shifts of 4-Substituted Bicyclo[2.2.2]octyl Derivatives (Values are in ppm from parent, positive shifts are downfield)

			$CH{=}CH_2$		$CH{=}CCl_2$		$CH{=}CF_2$[a]	
subst	CHO[a]	CO_2Et	C_α	C_β	C_α	C_β	C_α	C_β
H	0.00[b] (0.00)[c]	0.00[b]	0.00[b] (0.00)[c]	0.00[b] (0.00)[c]	0.00[b] (0.00)[c]	0.00[b] (0.00)[c]	0.00[b]	0.00[b]
Me	0.13 (0.11)	−0.19	−0.29 (−0.31)	0.17 (0.03)	−0.34 (−0.36)	0.11 (0.11)	−0.46	−0.14
Ph	−0.38 (−0.14)		−0.76 (−0.55)	0.54 (0.29)	−0.69 (−0.54)	0.58 (0.47)	−0.62	−0.02
NMe_2	−0.79 (−0.41)				−1.12 (−0.68)	0.74 (0.41)		
OMe	−1.17 (−0.65)	−1.16	−1.82 (−1.35)	0.87 (0.46)	−1.71 (−1.33)	0.97 (0.70)	−1.56	−0.13
CO_2Me	−1.11 (−0.68)	−0.87					−1.07	−0.03
CF_3	−1.73 (−1.27)				−1.92 (−1.79)	1.45 (1.33)	−1.48	0.09
I	−1.60 (−0.95)				−1.82 (−1.50)	1.34 (1.17)		
Br	−2.01 (−1.19)		−2.45 (−1.97)	1.34 (1.00)	−2.42 (−2.04)	1.45 (1.25)	−1.69	−0.01
Cl	−2.09 (−1.19)	−1.04			−2.55 (−2.24)	1.49 (1.32)	−1.92	0.02
F	−2.03 (−1.40)	−1.77	−2.77 (−2.26)	1.37 (0.95)	−2.70 (−2.32)	1.52 (1.25)	−2.21	0.02
CN	−2.66 *d*	−2.23					−2.00	−0.24
NO_2	−2.95 (−2.06)						−2.53	0.14

[a] Compounds available from another study.[40] [b] In $CDCl_3$ solvent. [c] In CCl_4 solvent. [d] Insoluble in CCl_4.

Table III. Infrared Spectra of 4-Substituted Bicyclo[2.2.2]octyl Cyanides, Carboxylates, and Acetylenes (ν in cm^{-1}; A in L mol^{-1} cm^{-2})

	CN		CO_2Et		CCH	
	ν_{CN}	A_{CN}	ν_{CO}	A_{CO}	ν_{CC}	A_{CC}
H	2240.0	670	1725.3	11 831	2111.8	439
NMe_2					2109.0	317
Me	2239.0	655	1724.1	13 355		
OMe	2234.5	583	1728.5	13 870	2115.0	313
CO_2R	2242.0	241	1727.8	12 203	2111.4	332
COMe					2114.1	249
F	2235.0	408	1730.2	14 134	2111.9	236
Cl			1730.0	13 293		
Br					2115.0	350
CN	2246.5	214	1731.4	12 300		
NO_2					2117.6	214
Ph					2110.0	423

Once again, rather similar ρ_F values (2.7–3.2 in $CDCl_3$) are found for the acetylenes, ethylenes, and dichloroethylenes, but smaller values for the benzenes (1.3) with almost no change in SCS at the β-carbon of the difluoroethylenes, in which the fluorine atoms exert a considerable electronegative influence.

The most important result overall is that no evidence is found for any significant electronegativity effect of substituent X on the SCS, particularly for the α-carbon centers. Most of the correlations are of fair to good precision, and in the case of the β-carbon of the difluoroethylenes (8, Y is $CH{=}CF_2$), the SCS are very small. It should be noted that a multiple linear least-squares regression analysis of the data indicated no statistical dependence on electronegativity.[16] This contrasts markedly with the situation for the fluorine-19 SCS of 4-substituted bicyclo[2.2.2]octyl fluorides (4) and bicyclo[2.2.1]heptyl fluorides (5). It was earlier shown[15,16] that such shifts had opposite signs in the two series and that correlation with σ_F alone was very poor. The results were rationalized in terms of concurrent field and electronegativity contributions ("through-bond" and "through-space" electron delocalization mechanisms) with the latter of opposite sign in the two series.[16] In the case of the bicyclo[2.2.2]octyl system 4, it was pointed out that the "through-three-bond" effect, which is dominant, involves the coupling of the appropriate bond MOs (CF and CX) by the bridging ethano bond MOs.[15,16] Thus, in terms of this simple orbital interaction model, the lack of significant electronegativity effects at the α-carbon center in the current systems (8,

Table IV. Ab Initio Molecular Orbital Calculations (STO-3G) for 4-Substituted Bicyclooct-1-yl Acetylenes and Cyanides (q_π Values in 10^4 Electrons)

	acetylenes, Δq_π		cyanides, Δq_π
	C_α	C_β	C_α
Me	1 (1)[a]	-1 (-1)[a]	1 (2)[b]
H	0[c] (0)	0[d] (0)	0[e] (0)[d]
NH_2	-1 (-7)	1 (7)	0 (-5)
OMe	-12 (-23)	16 (23)	-11 (-19)
CHO	-13 (-13)	17 (13)	-12 (-10)
F	-19 (-34)	24 (34)	-16 (-27)
CN	-39 (-40)	48 (40)	-30 (-32)
NO_2	-52 (-59)	64 (59)	-42 (-47)

[a] Values in parentheses are HCCH, polarised by HX (see text). [b] Values in parentheses are HCN polarised by HX (see text). [c] Atomic population, 0.9841 electron. [d] Atomic population, 1.0267 electrons. [e] Atomic population, 0.9587 electron.

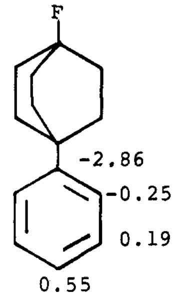
Table V. Proton Substituent Chemical Shifts and J_{CH} Coupling Constants in 4-Substituted Bicyclooctylacetylenes

X	^1H SCS[a]	$\Delta ^1J_{CH}$[b]
H	0.000	0.00
Me	0.020	0.00
Ph	0.069	0.24
NMe_2	0.019	0.36
OMe	0.035	0.47
CO_2Me	0.051	0.61
COMe	0.061	0.73
CF_3	0.093	1.10
I	0.072	1.34
Br	0.078	1.34
Cl	0.078	1.22
F	0.068	1.00
CN	0.102	1.71
NO_2	0.131	1.83

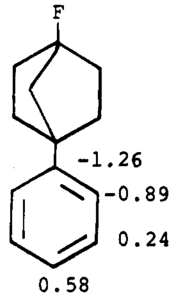
[a] Acetylenic proton ppm from parent in c-C_6D_{12}. Parent 1.772 ppm relative to Me_4Si. [b] Parent 246.58 Hz in CCl_4.

Y is C≡CH, C_6H_5, CH=CH_2, CH=CCl_2, CH=CF_2, CN, CHO, and COOEt) is understandable in terms of weak or negligible coupling of the appropriate bond MOs by the bridging ethano bonds. This may result from the coefficients and energies of the substrate–probe bonds ($\sigma_{C_{sp}3}$–$\sigma_{C_{sp}2}$ or $\sigma_{C_{sp}3}$–$\sigma_{C_{sp}}$) being unfavorably disposed for interaction.

It should be noted that the correlations in the various series, except for C4 in 7 and Cβ in 8 (where Y is CH=CH_2 and CH=CCl_2), are not so precise as to totally exclude the presence of substituent influences other than field effects. Of particular interest in this regard is the fact that the precision of fit for the correlation of the ^{13}C SCS of Cl in 7 has been shown previously,[14] and confirmed by others,[20] to be significantly improved by including a resonance parameter ($\sigma_R{}^0$) in the analysis (DSP method). Although it is possible to visualize π-resonance transmission through the bicyclo[2.2.2]octane skeleton,[25,26] it was suggested[14] that it is more likely that the additional substituent parameter simply provides statistical freedom to accommodate other ill-defined extraneous minor factors including electronegativity related phenomena (σ-electron delocalization effects). Any small influence by the latter factor is probably masked in this system, as well as the others with unsaturated carbon probes, by the relatively large electrostatic field contributions (σ_F effect), since the parameters characterizing polar field and electronegativity effects are not completely independent of one another. The likelihood of some contribution to the α-carbon SCS of system 8 (Y is an unsaturated carbon probe) by σ-electron delocalization is given credence by the carbon-13 SCS induced by a 4-substituted fluoro atom at the ring carbon atoms of phenylbicyclo[2.2.2]octane[14] and phenylbicyclo[2.2.1]heptane[16] (given in 9 and 10 in parts per million).



(9)



(10)

The overall π-polarization of the benzene ring, as measured at the meta and para carbon atom, would seem to be similar and is in accord with electric field expectations. However, the large differences at the ipso and ortho carbon atoms was not expected on this basis and, thus, suggest a different ratio of "through-bond" and "through-space" contributions for the two systems.[16] Differing shift/charge ratios may also be partly responsible. The remarkable similarity in the carbon-13 SCS between the α-carbon of the 4-substituted bicyclo[2.2.2]octylacetylenes (8, Y is C≡CH) and the ipso carbon of the 4-substituted bicyclo[2.2.2]octylbenzenes (7) ($\rho = 1.06$, $r = 0.992$) may reflect a combination of the lower polarizability of the triple bond[24] coupled with a different shift/charge ratio.

The significantly higher precision of fit of the correlations for the β-carbon atom in the bicyclo[2.2.2]octylethylenes (8, Y is CH=CH_2 *and* CH=CCl_2*) than that for* the correlation of the corresponding center in the acetylenes (8, Y is C≡CH) is surprising given that in the latter system the unsaturated probe and the substituent dipole are perfectly aligned along the major axis of the ring system. However, an examination of the ^{13}C SCS of the acetylene derivatives (Table I, β-carbon) reveals that the values for Me are much more *positive* than expected on the basis of its weak polar influence ($\sigma_F = 0$).[11,15,22] Moreover, the SCS for Me are invariant to the change in solvent. The origin of this anomaly is not clear but a weak π-transmission, which is conveyed more efficiently by the acetylenic linkage than the ethylene one, may be responsible.[11] Whatever the cause, it should be emphasized that it is a minor perturbation since the proton chemical shifts and the $^1J_{CH}$ values in the acetylenes (8, Y C≡CH) also show satisfactory correlations (Table VI) with the field parameter (σ_F).

It was earlier shown[11,14,27] that the carbon-13 SCS at the para carbon (C4) in system 7 provided an excellent measure of σ_F values. The present results allow the determination of some additional values as follows ($CDCl_3$): C≡CH, 0.28; CH=CH_2, 0.14; CH=CCl_2, 0.25; CH=CF_2, 0.23. Values in CCl_4 are almost identical.

Finally, the enhanced sensitivity of the carbon-13 SCS of the various carbon centers to the polar field in $CDCl_3$ vs. CCl_4 (see ρ_F values in Table VI) is also noteworthy. In particular, note that whereas the ρ_F values for the α-carbon of CH=CH_2 drops from -5.66 to -4.51, the corresponding drop for CH=O is much larger (-4.95 to -3.14). Hydrogen bonding is clearly implicated since $CDCl_3$ can act[28] as a

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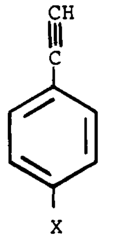
Table VI. Correlation of Results with σ_F According to Equation 1 (See Text)

data (Y)	ρ_F		c	n^a	r^b
		NMR SCS			
$\mathit{C}{\equiv}\mathrm{CH}$	($DCCl_3$)	−5.43	−0.06	13	0.974
	(CCl_4)	−4.16	−0.10	13	0.956
$\mathrm{C}{\equiv}\mathit{CH}$	($DCCl_3$)	2.72	0.23	13	0.980
	(CCl_4)	2.15	0.23	13	0.973
$\mathit{C}\mathrm{N}$	($DCCl_3$)	−3.94	0.15	11^c	0.956
Ph, Cl	($DCCl_3$)	−4.60	−0.38	23^d	0.951
	(CCl_4)	−4.05	−0.26	17^e	0.949
Ph, C4	($DCCl_3$)	1.33	0.01	13	0.996
	(CCl_4)	1.37	0.02	13	0.998
$\mathit{C}\mathrm{HO}$	($DCCl_3$)	−4.95	0.20	12	0.987
	(CCl_4)	−3.14	0.11	11	0.963
$\mathit{C}\mathrm{O_2Et}$	($DCCl_3$)	−3.34	−0.14	5	0.911
$\mathit{C}\mathrm{H{=}CH_2}$	($DCCl_3$)	−5.66	−0.16	5	0.969
	(CCl_4)	−4.51	−0.21	5	0.942
$\mathrm{CH{=}}\mathit{C}\mathrm{H_2}$	($DCCl_3$)	2.81	0.13	5	0.995
	(CCl_4)	2.34	−0.02	5	0.993
$\mathit{C}\mathrm{H{=}CCl_2}$	($DCCl_3$)	−5.34	−0.01	9	0.892
	(CCl_4)	−3.99	−0.26	9	0.906
$\mathrm{CH{=}}\mathit{C}\mathrm{Cl_2}$	($DCCl_3$)	3.17	0.12	9	0.991
	(CCl_4)	2.75	0.09	9	0.992
$\mathit{C}\mathrm{H{=}CF_2}$	($DCCl_3$)	−3.39	−0.28	13^f	0.935
$\mathrm{CH{=}}\mathit{C}\mathrm{F_2}$	($DCCl_3$)			13^f	*h*
$^1H(C{\equiv}CH)$	(c-C_6D_{12})	0.15	0.02	13^g	0.928
$\Delta^1J_{CH}(C{\equiv}CH)$	(CCl_4)	2.98	−0.08	13	0.986
		MO Calculations			
$\mathit{C}{\equiv}\mathrm{CH}$	Δq_π	−73.2	4.3	8	0.957
(isol)		−78.3	0.7	8	0.934
$\mathrm{C}{\equiv}\mathit{CH}$	Δq_π	90.0	−4.9	8	0.959
(isol)		78.3	−0.7	8	0.934
$\mathit{C}\mathrm{N}$	Δq_π	−58.6	3.2	8	0.960
(isol)		−63.3	1.0	8	0.931
		IR data			
ν_{CN}	(CN)				*h*
$\nu_{C{\equiv}C}$	($C{\equiv}CH$)				*h*
ν_{CO}	(CO_2R)	11.46	0.45	7	0.969
$A_{C{\equiv}C}$	($C{\equiv}CH$)				*h*
A_{CN}	(CN)				*h*
A_{CO}	(CO)				*h*

[a] No. of data points used in correlation. [b] Correlation coefficient. [c] SCS (ppm) for C≡CH (−0.87) and CHO (−1.14) included in basis set. [d] In addition to the substituents listed in Table I, the following SCS (ppm) of other substituents were included in the basis set: −4.01 ($C(CN)_3$), −1.81 (CHO), −1.80 ($NHCOCH_3$), −1.46 (NH_2), −2.10 (OH), −2.27 ($OCOCH_3$), −1.84 (CH_2CN), −3.00 ($CH(CN)_2$), −1.27 (CH_2Cl), −0.78 (CH_2OH), −1.57 (CHF_2). [e] SCS (ppm) of other substituents included in the basis set: −3.52 ($C(CN)_3$), −1.84 ($OCOCH_3$), −0.58 ($CH{=}CH_2$), −1.12 (C≡CH). [f] SCS (ppm) for C≡CH (−1.12 and −0.24), $C{\equiv}CSiMe_3$ (−0.88 and −0.08), and $C(CH_3)_3$ (−0.27 and −0.08) included in basis set. [g] Using σ_F values for c-C_6H_{12}. [h] No significant correlation ($r < 0.80$).

very strong hydrogen bond donor.

Comparison of Results in 4-Substituted Bicyclo[2.2.2]octylacetylenes and 4-Substituted Phenylacetylenes. In Table VII we compare the SCS for the α and β-carbon atoms for some 4-substituted bicyclo[2.2.2]octylacetylenes with those[29] for the corresponding 4-substituted phenylacetylenes (11).



(11)

The results were analyzed by the dual substituent parameter (DSP) method[30] which utilizes eq 2, where P_X is

$$P_X - P_O = \rho_F\sigma_F + \rho_R\bar{\sigma}_R \qquad (2)$$

the data for substituent X, P_O for substituent H, and $\bar{\sigma}_R$ can have the values σ_R^+, σ_R^-, σ_R^0, or σ_R^{BA}. The data for the phenyl acetylenes are already known to reflect field and resonance effects, particularly at the β-carbon. The SCS for this carbon atom is given by eq 3 with a goodness

$$\mathrm{SCS} = 5.10\sigma_F + 6.05\sigma_R^0 \qquad (3)$$

of fit (f) of 0.17. This is in close agreement with a similar analysis reported earlier.[29] The field component is considered to include both a direct through space polarization of the carbon–carbon triple bond and also indirect effects resulting from the polarization of the π-system of the benzene ring.

The corresponding equation for the β-carbon of the bicyclo[2.2.2]octylacetylenes is (4) with $f = 0.18$. The ρ_R

$$\mathrm{SCS} = 2.93\sigma_F - 0.44\sigma_R^0 \qquad (4)$$

term is not significant as expected; Table VI shows a correlation coefficient of 0.980 for a correlation of σ_F alone ($\rho_F = 2.72$).

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Table VII. ^{13}C Substituent Chemical Shifts in 4-Substituted Phenylacetylenes and Bicyclo[2.2.2]octylacetylenes

subst	phenylacetylenes[a]		bicyclo[2.2.2]octylacetylenes		Δ	
	C_α	C_β	C_α	C_β	C_α	C_β
NMe_2	1.00	-2.28	-1.00	0.60	2.00	-2.88
OMe	0.00	-1.39	-1.69	0.87	1.69	-2.26
F	-1.09	0.28	-2.72	1.38	1.63	-1.10
Cl	-1.16	0.97	-2.64	1.51	1.48	-0.54
Me	0.10	-0.70	-0.24	0.39	0.34	-1.09
H	0.00	0.00	0.00	0.00	0.00	0.00
CF_3	-1.44	2.43	-2.14	1.25	0.70	1.18
CN	-1.69	4.02	-2.94	1.67	1.25	2.35
NO_2	-1.93	4.68	-3.64	1.99	1.71	2.69

[a] From ref 29.

Allowing for the small difference in geometry between the two systems, it would seem that a very significant indirect field effect does occur in the phenylacetylenes via the benzene ring. This supports earlier arguments[29] which have not always[31] been accepted.

Theoretical Results. The ab initio molecular orbital calculations are reported in Table IV, and the correlations of the data by eq 1 are given in Table VI. The correlations of π-electron populations are of fair precision, again with no evidence for substituent electronegativity effects. Correlations with total electron populations are of less or poor precision, but it is the π-electron effects that are generally considered[24] to best mirror carbon-13 SCS. The lower ρ_F for the π values in the bicyclo[2.2.2]octyl cyanides compared to acetylenes is in accord with experimental carbon-13 shifts. The shift charge ratios are 670 and 740 ppm/electron, respectively. The value for the β-carbon in the acetylenes, however, is only 300. In the para-substituted styrenes, the shift charge ratios (calculations of π-densities also at STO-3G level) are 180 and 190 ppm/electron for the α-carbon and the β-carbon, respectively.[24,32]

Calculations are also reported for the electron populations in the triple bond of an acetylene molecule or the cyanide group in an isolated HCN molecule polarized by HX. Here, the $C\equiv CH$ or CN and X have the same geometry as in the 4-X-bicyclo[2.2.2]octylacetylenes and cyanides. Results for these isolated molecules are very similar to those for the corresponding bicyclooctanes. This suggests that through-bond effects are not significant in these systems.

Infrared Results. The correlations of the infrared results (Table III) with eq 1 are also given in Table VI. None of the series of intensities of the bicyclo[2.2.2]octyl acetylenes, cyanides, or esters show any relationship to σ_F and indeed the differences seem random and do not appear to be a function of electronegativity or of both field and electronegativity effects. A similar result has been observed in the intensity of the carbonyl stretching vibration of 4-substituted camphors[33] where the authors suggest that the intensity is almost insensitive to electronegativity and field effects. This is in contrast to examples[34] where such probes are directly attached to unsaturated systems. Here, the intensities are known to vary markedly with substitution. There are some earlier examples[35] of aliphatic systems where probe intensities are reported to follow σ_F. The basis for these different relationships remains to be determined.

The frequencies of ν_{CO} in the esters do correlate reasonably well with σ_F values (Table VI). Again, a corresponding correlation was found[33] for the carbonyl group in 4-substituted camphors. However, no significant correlations with σ_F were found for $\nu_{C\equiv C}$ in the acetylenes or ν_{CN} in the cyanides. An earlier review[36] revealed very few series of aliphatic compounds where substituent frequencies followed σ_F. Further work is clearly needed to determine when ν/σ_F correlations can be anticipated in aliphatic systems.

Conclusion

The carbon-13 SCS for a wide variety of unsaturated probe groups attached to position 1 of the bicyclo[2.2.2]octane molecule follow the field effect of 4-substituents with no evidence for any significant electronegativity effect. The SCS of the β-carbon in acetylenic or ethylenic probes or the 4-carbon in a phenyl probe in particular show good to excellent correlations with σ_F values, and the latter can be used to measure such values for additional substituents. Molecular orbital calculations show similar results for π-electron populations. By contrast, it would appear that infrared intensities of probe groups such as $C\equiv CH$, CO, and CN stretching vibrations do not follow substituent electronic effects in aliphatic molecules. The corresponding frequencies may follow field effects, but further work is necessary to ascertain for which probes and aliphatic molecules this occurs.

Experimental Section

Theoretical Calculations. All calculations were performed at the ab initio molecular orbital STO-3G level, using the Gaussian-80 program.[37] The calculations used standard bond lengths.[38] The energies for the bicyclo[2.2.2]octyl acetylenes and cyanides will be reported elsewhere.[39]

Synthesis of Compounds. The 4-substituted bicyclo[2.2.2]oct-1-yl derivatives (8, Y = $CH{=}CCl_2$ $C\equiv CH$, $CH{=}CH_2$, C_6H_5, $COOC_2H_5$, and $C\equiv N$) were prepared by known reactions. Details of the synthetic procedures and characterization data for the various dichloroethenes (8, Y = $CH{=}CCl_2$), acetylenes (8, Y = $C\equiv CH$), and ethylenes (8, Y = $CH{=}CH_2$), together with similar information for 4-(1-(trimethylsilyl)ethynyl)bicyclo[2.2.2]octane-1-carbonitrile, 1-(trimethylsilyl)-2-(4-acetylbicyclo[2.2.2]-

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oct-1-yl)ethyne, and 4-(dimethylamino)bicyclo[2.2.2]octane-1-carbaldehyde, are contained in supplementary pages following this article.

Acknowledgment. We thank Dr. A. N. Abeywickrema for his assistance in the synthesis of some of the cyanides and esters, and R.D.T. thanks the Australian Research Grants Scheme for financial help.

Registry No. 1 (X = Ph), 953-69-5; 4 ($X = C\equiv CH$), 96454-83-0; 4 (X = CHO), 78385-82-7; 4 ($X = CO_2Et$), 20277-39-8; 4 ($X = CH{=}CH_2$), 34300-61-3; 4 ($X = CH{=}CCl_2$), 96455-03-7; 4 ($X = CH{=}CF_2$), 94993-90-5; 6 (X = H), 25938-93-6; 6 (X = Me), 40636-39-3; 6 (X = Ph), 950-22-1; 6 (X = OMe), 82896-48-8; 6 ($X = CO_2Me$), 54202-05-0; 6 (X = I), 80745-57-9; 6 (X = Br), 82896-47-7; 6 (X = Cl), 699-59-2; 6 (X = F), 78385-80-5; 6 (X = CN), 41034-58-6; 6 ($X = C\equiv CSi(CH_3)_3$, 96455-04-8; 7 (X = H), 23062-62-6; 7 (X = Me), 23062-66-0; 7 (X = Ph), 23062-63-7; 7 ($X = NMe_2$), 64852-67-1; 7 (X = OMe), 6555-88-0; 7 ($X = CO_2Me$), 23062-52-4; 7 (X = COMe), 64872-47-5; 7 ($X = CF_3$), 96454-86-3; 7 (X = I), 55044-15-0; 7 (X = Br), 714-68-1; 7 (X = Cl), 33732-68-2; 7 ($X = NO_2$), 64852-68-2; 8 ($X = H, Y = C\equiv CH$), 96454-73-8; 8 ($X = Me, Y = C\equiv CH$), 96454-74-9; 8 ($X = Ph, Y = C\equiv CH$), 96454-75-0; 8 ($X = NMe_2, Y = C\equiv CH$), 96454-76-1; 8 ($X = OMe, Y = C\equiv CH$), 96454-77-2; 8 ($X = CO_2Me, Y = C\equiv CH$), 96481-32-2; 8 ($X = COMe, Y = C\equiv CH$), 96454-78-3; 8 ($X = CF_3, Y = C\equiv CH$), 96454-79-4; 8 ($X = I, Y = C\equiv CH$), 96454-80-7; 8 ($X = Br, Y = C\equiv CH$), 96454-81-8; 8 ($X = Cl, Y = C\equiv CH$), 96454-82-9; 8 ($X = CN, Y = C\equiv CH$), 96454-84-1; 8 ($X = NO_2, Y = C\equiv CH$), 96454-85-2; 8 (X = H, Y = CHO), 2064-05-3; 8 (X = Me, Y = CHO), 94994-30-6; 8 (X = Ph, Y = CHO), 94994-29-3; 8 ($X = NMe_2$, Y = CHO), 96454-87-4; 8 (X = OMe, Y = CHO), 94994-28-2; 8 ($X = CO_2Me$, Y = CHO), 94994-25-9; 8 ($X = CF_3$, Y = CHO), 94994-24-8; 8 (X = I, Y = CHO), 94994-09-9; 8 (X = Br, Y = CHO), 94994-27-1; 8 (X = Cl, Y = CHO), 94994-26-0; 8 (X = CN, Y = CHO), 94994-23-7; 8 ($X = NO_2$, Y = CHO), 94994-22-6; 8 ($X = H, Y = CO_2Et$), 31818-12-9; 8 ($X = Me, Y = CO_2Et$), 5971-03-9; 8 ($X = OMe, Y = CO_2Et$), 96454-88-5; 8 ($X = CO_2Me, Y = CO_2Et$), 96454-89-6; 8 ($X = Cl, Y = CO_2Et$), 96454-90-9; 8 ($X = CN, Y = CO_2Et$), 54829-94-6; 8 ($X = H, Y = CH{=}CH_2$), 96454-91-0; 8 ($X = Me, Y = CH{=}CH_2$), 96454-92-1; 8 ($X = Ph, Y = CH{=}CH_2$), 96454-93-2; 8 ($X = OMe, Y = CH{=}CH_2$), 96454-94-3; 8 ($X = Br, Y = CH{=}CH_2$), 96454-95-4; 8 ($X = H, Y = CH{=}CCl_2$), 96454-96-5; 8 ($X = Me, Y = CH{=}CCl_2$), 96454-97-6; 8 ($X = Ph, Y = CH{=}CCl_2$), 96454-98-7; 8 ($X = NMe_2, Y = CH{=}CCl_2$), 96454-99-8; 8 ($X = OMe, Y = CH{=}CCl_2$), 96455-00-4; 8 ($X = CF_3, Y = CH{=}CCl_2$), 96455-01-5; 8 ($X = I, Y = CH{=}CCl_2$), 94994-10-2; 8 ($X = Br, Y = CH{=}CCl_2$), 96481-33-3; 8 ($X = Cl, Y = CH{=}CCl_2$), 96455-02-6; 8 ($X = H, Y = CH{=}CF_2$), 94993-85-8; 8 ($X = Me, Y = CH{=}CF_2$), 94993-95-0; 8 ($X = Ph, Y = CH{=}CF_2$), 94993-94-9; 8 ($X = OMe, Y = CH{=}CF_2$), 94993-93-8; 8 ($X = CO_2Me, Y = CH{=}CF_2$), 94993-89-2; 8 ($X = CF_3, Y = CH{=}CF_2$), 94993-88-1; 8 ($X = Br, Y = CH{=}CF_2$), 94993-92-7; 8 ($X = Cl, Y = CH{=}CF_2$), 94993-91-6; 8 ($X = CN, Y = CH{=}CF_2$), 94993-87-0; 8 ($X = NO_2, Y = CH{=}CF_2$), 94993-86-9; 8 ($X = C\equiv CSi(CH_3)_3, Y = CH{=}NOH$), 96481-34-4; 8 ($X = C\equiv CSi(CH_3)_3, Y = COCH_3$), 96455-05-9; 8 ($X = NMe_2$, Y = I), 80745-60-4; 9, 22947-58-6; CH_3Cl, 74-87-3; C_6H_6, 71-43-2; 1-formylpiperidine, 2591-86-8.

Supplementary Material Available: General methods, instrumentation, and parameters for spectral measurements; details of the synthesis of 4-substituted bicyclo[2.2.2]oct-1-yl derivatives (8, $Y = CH{=}CCl_2$, $C\equiv CH$, $CH{=}CH_2$, C_6H_5, $COOC_2H_5$, and $C\equiv N$), 4-[1-(trimethylsilyl)ethynyl]bicyclo[2.2.2]octane-1-carbonitrile, 1-(trimethylsilyl)-2-(4-acetylbicyclo[2.2.2]oct-1-yl)-ethyne, and 4-(dimethylamino)bicyclo[2.2.2]octane-1-carbaldehyde, and physical properties, elemental analytical data, and ^1H and ^{13}C NMR parameters for the dichloroethenes (8, $Y = CH{=}CCl_2$), acetylenes (8, $Y = C\equiv CH$), and ethylenes (8, $Y = CH{=}CH_2$) (14 pages). Ordering information is given on any current masthead page.

Intramolecular C–H Insertions of Alkylidenecarbenes. 2. Stereochemistry and Isotope Effects

John C. Gilbert,* David H. Giamalva,[1] and Mark E. Baze

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

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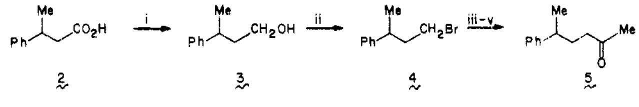
The stereochemistry of the intramolecular 1,5 carbon–hydrogen insertion reaction of alkylidenecarbenes to form cyclopentenes has been determined. The isotope effects for two intramolecular examples of insertion reactions of this class of carbenes have been measured, and the dependence upon temperature of one of them has been evaluated. It is concluded that the reaction path is devoid of long-lived intermediates and that its trajectory involves a nonlinear disposition of the carbenic carbon atom and the carbon–hydrogen bond into which insertion occurs.

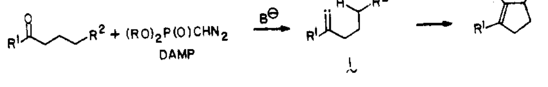
Introduction

The first paper in this series described our finding that cyclopentenes are formed by the base-promoted reaction between dialkyl ketones having γ-hydrogen atoms and dialkyl (diazomethyl)phosphonates (DAMP, eq 1).[2] The selectivity of this C–H insertion reaction, as measured by the relative reactivity of various types of C–H bonds, was found to be 1° < 2° aliphatic < 2° benzylic < 3°, and it was concluded that the process involved intermediacy of alkylidenecarbenes (1, eq 1).[3] The present contribution addresses additional details of the mechanism of this interesting reaction by describing the results of studies defining its stereospecificity and kinetic isotope effect.

Scheme I. Preparation of 5-Phenyl-2-hexanone (5)[a]



[a] i, LAH (91%); ii, PBr_3 (82%); iii, Mg; iv, MeCHO; v, H_2CrO_4 (81% for iii–v).



(1)

Results and Discussion

The chiral substrate selected for the study of the stereochemistry of the insertion process was the known[4] 5-

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[1] Giamalva, D. H. Ph.D. Dissertation, University of Texas, Austin, TX.

[2] Gilbert, J. C.; Giamalva, D. H.; Weerasooriya, U. *J. Org. Chem.* **1983**, *48*, 5251.

[3] Reviews: (a) Hartzler, H. D. In "Carbenes", Moss, R. A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975; Vol. 2, Chapter 2. (b) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383. Stang, P. J. *Acc. Chem. Res.* **1982**, *15*, 348.