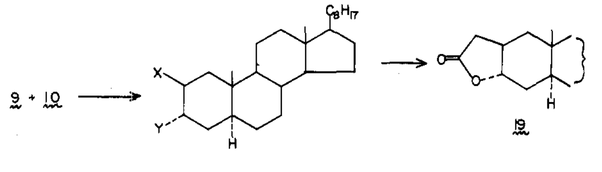
with methanolic KOH to give the known acid,[4] **14**, mp 114–116 °C which was converted to the known[4] boat lactone system **15**, mp 49–51 °C (lit.[4] 49.6 °C). No evidence for the formation of stereoisomers of **13** could be detected.

Reaction of **10** with 2,3-oxido-α-cholestane (**9**) under these conditions gave a 63% yield of **16**,[13] mp 92–93 °C, $[\alpha]$D ($CHCl_3$) +4.7°. The epoxide was recovered to the extent of 15%. The diaxial nature of **16** was confirmed through the NMR spectrum[17] of its derived acetate, **17**,[13a] mp 112–114 °C. Treatment of **17** with methanolic HCl gave the methyl ester **18**,[13,16] mp 163–164 °C, $[\alpha]$D ($CHCl_3$) +32.0°, in 85% yield. The latter was converted to the pentacyclic steroidal lactone **19**,[13a] mp 165–167 °C, $[\alpha]$D ($CHCl_3$) +31.7°, in 73% yield by the forcing conditions of Johnson[4] (tosyl acid–xylene, reflux).



16 X = C≡C-OEt; Y = OH
17 X = C≡C-OEt; Y = OAc
18 X = CH_2CO_2Me; Y = OH

It is thus seen that this method of cleavage occurs in a stereoelectronically specific trans-diaxial fashion. The efficacy and stereoelectronic specificity of the method are not seriously disrupted by a 1,3-diaxial interaction with an angular methyl group. Other applications of these aluminum bound synthetic equivalents of acetic acid carbanion are currently under investigation.

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Supplementary Material Available. Experimental procedures for these reactions (6 pages). Ordering information is given on any current masthead page.

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(13) The structure and homogeneity of this compound was established by (a) its ir, NMR, and mass spectra; (b) C and H combustion analysis was within 0.4% of theory.
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(15) Compound **11** is an artifact produced on chromatography of the labile ethynyl ether **6**.
(16) We have found that treatment of the *trans*-2-hydroxyethynyl ethers **12** and **16** with ostensibly anhydrous HCl–methanol gives cleanly the methyl esters. We are, at present, unable to define the mechanism of this transformation. It may involve the presence of adventitious water, leading to a mixing of methyl and ethyl esters followed by transesterification of the latter in favor of the former. Alternatively, it may be the consequence of protonation followed by demethylation giving rise to a ketone intermediate. The latter is then captured by the solvent, methanol, to give the observed methyl ester. In any case, it is a useful method for transforming ethoxyethynyl ethers, arising from the commercially available ethoxyacetylene, into methyl esters which tend to be more easily crystalline and more readily amenable to NMR analysis.
(17) The resonance of the methine proton at C_3 in compound **16** is obscured by overlap with the methylene protons of the ethoxy group. However, in the derived acetate **17** the resonance ($CDCl_3$) is seen as a multiplet centered at δ 5 ppm with a line width at half-height of 5 Hz, clearly indicative of an equatorial proton. The β stereochemistry of the X group in compounds **16–18** follows from inversion of the α stereochemistry of the epoxide.

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Carbon-13 Magnetic Resonance. Downfield Shifts Induced by $M(CH_3)_3$ (M = Si, Ge, Sn, Pb) at the γ Position and Antiperiplanar to the Carbon-13 Center

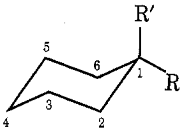
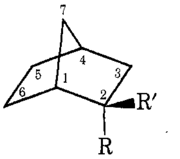
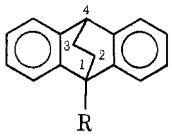
Summary: Carbon-13 NMR spectra of certain cycloalkyl derivatives of group 4B have been obtained, and the chemical shifts of γ carbons are discussed in terms of geometrical array and possible electronic interactions.

Sir: The γ effect (the usually *upfield* shift of a resonance for a carbon-13 nucleus gauche to another carbon or heteroatom at the γ position) is generally ascribed to steric compression which polarizes the C–H bonds causing shielding of the carbon nucleus.[1] When heteroatoms are incorporated, it was recognized[2–4] some years ago that significant upfield γ shifts may occur when such heteroatoms are anti to the carbon nucleus. More recently, Eliel and co-workers[5] established that a carbon nucleus anti to a second row heteroatom (N, O, F) in the γ positions generally resonates at higher field than when anti to methyl or methylene. The nature of this shielding mechanism is not established, but Eliel[5] favored interaction of free electron pairs (on N, O, F) with the C_α–C_β bond, resulting in a type of "conjugative" transfer of electron density to the C_γ region. On the other hand, Heumann and Kolshorn,[6] from their studies of 2-substituted bicyclo[3.3.1]nonan-9-ones, suggested that "electronically induced" anti γ effects were associated with back-lobe overlap, as originally outlined by Grutzner and Roberts.[2] Our studies of the ^{13}C spectra of geometrically well-defined cycloalkyl derivatives of group 4B elements have provided values for the γ effects of $M(CH_3)_3$ (M = Si, Ge, Sn, Pb) in gauche and antiperiplanar arrays. These data are particularly pertinent to the mechanism of the anti γ effect, but also make available a further assignment criterion for the spectra of the group 4B derived systems.

The chemical shift data for cyclohexyl[7] and certain norbornyltin compounds[8] are assembled in Table I, together with relevant information on the bicyclo[2.2.2]octyltin system.[9] The values in parentheses are the substituent chemical shifts and the γ effects are italicized. For the tin compounds, the γ effects are substantially downfield in anti arrangements (where steric compression cannot be important) and largest at C_6 in the *exo*-2-norbornyl compound (+3.9 ppm). Where steric compression is operative, e.g., in the axial conformer[7] of cyclohexyl trimethylstannane, the γ effect is upfield, perhaps as expected. The γ effect of $Sn(CH_3)_3$ attached to a bridgehead position (in the bicyclo[2.2.2]octyl system) is still significantly downfield (+2.4 ppm), in contrast to the observation[5] that the normally upfield anti γ effect of fluorine becomes downfield in such a situation.[10]

The equatorial cyclohexyl derivatives[11] of group 4B exhibit anti γ effects that are significantly downfield, i.e., from +0.8 ppm for $C(CH_3)_3$[4] to +3.06 ppm for $Pb(CH_3)_3$. It is instructive

Table I. Carbon-13 Chemical Shifts[a] of Some Group 4B Substituted Cycloalkyl Systems

Substituents	Carbon Number 1	2	3	4	5	6	7	Other
								
R^1 = H; R = H	27.0	27.0	27.0	27.0	27.0	27.0		
R^1 = H; R = $C(CH_3)_3$	48.9	28.2	27.8	27.2	27.8	28.2		32.7, 27.7
	(+21.9)	(+1.2)	*(+0.8)*	(+0.2)	*(+0.8)*	(+1.2)		
R^1 = H; R = $Si(CH_3)_3$[b]	26.39	27.49	28.25	27.14	28.25	27.49		−3.56
	(−0.61)	(+0.49)	*(+1.25)*	(+0.14)	*(+1.25)*	(+0.49)		
R^1 = H; R = $Ge(CH_3)_3$[c]	27.90	28.74	28.31	27.06	28.31	28.74		−4.50
	(+0.9)	(+1.74)	*(+1.31)*	(+0.06)	*(+1.31)*	(+1.74)		
R^1 = H; R = $Sn(CH_3)_3$	24.75	30.87	28.98	26.93	28.98	30.87		−11.92
	(−2.25)	(+3.87)	*(+1.98)*	(−0.07)	(+1.98)	(+3.87)		
R^1 = $Sn(CH_3)_3$; R = H	nl	nl	25.89	nl	25.89	nl		−9.18
			(−1.11)		*(−1.11)*			
R^1 = H; R = $Pb(CH_3)_3$	35.04	33.66	30.06	26.75	30.06	33.66		−5.31
	(+8.04)	(+6.66)	*(+3.06)*	(−0.25)	*(+3.06)*	(+6.66)		
R^1 $Pb(CH_3)_3$; R = H	38.72	32.19	25.88	26.75	25.88	32.19		−3.18
	(+11.72)	(+5.19)	*(−1.12)*	(−0.25)	*(−1.12)*	(+5.19)		
								
R^1 = H; R = H	36.8	30.1	30.1	36.8	30.1	30.1	38.7	
R^1 = $Sn(CH_3)_3$; R = H	40.3	27.6	37.6	34.9	29.5	34.0	38.6	−10.8
	(+3.5)	(−2.5)	(+7.5)	*(−1.9)*	(−0.6)	*(+3.9)*	*(−0.1)*	
R^1 = H; R = $Sn(CH_3)_3$	40.9	28.7	33.8	36.9	30.3	30.1	40.9	−10.2
	(+4.1)	(−1.4)	(−3.8)	*(+2.0)*	(+0.8)	*0*	*(+2.2)*	
								
R = H[d]	44.1	26.7	26.7	44.1				
R = $Sn(CH_3)_3$	43.0	30.7	29.1	44.8	*e*			
	(−1.1)	(+4.0)	*(+2.4)*	(+0.7)				

[a] For 10% solutions in $CDCl_3$ referenced to internal TMS. nl means not located. γ effects are italicized. [b] The assignments for $C_{2,6}$ and $C_{3,5}$ could be reversed, but this reversal does not alter any arguments. The listed values provide a more reasonable periodic response in the $C_{3,5}$ chemical shifts. [c] Confirmed by examination of the (2,6) deuterated analogue. [d] Arbitrary numbering system. [e] Reference 9.

to consider how this trend is accommodated by the possible mechanisms of the anti γ effect given the present understanding of the periodic properties of the elements in their compounds. The hyperconjugative mechanism suggested by Eliel[5] for atoms bearing free electron pairs could be applied to the lower members (i.e., Si downward) and would result in deshielding at C_γ, as observed. This would necessitate interaction of a vacant orbital, of π or pseudo-π symmetry on the central atom, and could conceivably be nd or C–M σ^* in nature.[12] The degree of hyperconjugative interaction would then be reciprocal function of the energy difference between this π orbital and the C–C bonding level, to a rough approximation. As the interaction between a vacant "π level" on Si and adjacent π systems is not large,[13] it is difficult to envisage significant interaction with a σ level. Even if it were, we would expect a greater effect for Si, as the evidence[13–15] is that π bonding is more efficient for this element, presumably owing to better energy and radial matching of the interacting orbitals.[16]

We are left to consider the original "back-lobe overlap" idea,[2] which is also favored by a planar "zig-zag" or "W" array. Larger downfield γ effects then are related to a number of factors, including electronegativity, regulating the nature of the C–M σ bond. This explanation is consistent with the much enhanced γ effect (+3.9 ppm) at C_6 in the *exo*-2-norbornyltin compounds apparently because the C_2–C_1–C_6 angle is smaller, promoting the back-lobe interaction. It is of importance to note that vicinal $^{117,119}Sn$–^{13}C coupling is maximized[8] for a dihedral angle of 180°, and back-lobe transmission is a strong possibility. Furthermore, the vicinal coupling to C_6 in *exo*-2-norbornyltrimethylstannane appears to be the largest measured for a $RSn(CH_3)_3$ system.[8] Eliel noted[5] that anti γ effects did not extend to third row elements (e.g., chlorine), whereas such (deshielding) effects become more pronounced as group 4B is descended. It is possible that different blends of factors are involved in the two situations, and further experimental and theoretical efforts are required. In the meantime, it is essential to note that, for some substituents, γ effects of possibly variable sign but comparable magnitude may be encountered, depending on geometrical factors.

Acknowledgments. This work was supported in part by the Australian Research Grants Committee.

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(10) We have noted also a positive (+0.94 ppm) anti γ effect of fluorine in the maleic anhydride adduct of 9-fluoroanthracene [W. Kitching, W. Adcock, T. C. Khor, and D. Doddrell, *J. Org. Chem.*, unpublished work].

(11) The data for the equatorial tin and lead compounds were obtained by direct observation of these conformers at low temperatures,[7] while the data for the silicon and germanium derivatives pertains to ambient (+35°) conditions. The populations of axial forms for these derivatives would be very small, with introduction of little error.

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(16) In relation to the mechanism (of the anti γ effect) favored by Eliel and coworkers,[5] CNDO/2 calculations suggest that the donation of the free-electrons on a heteroatom, in a σ-bonded framework, is preferentially to the β and not the γ position, the latter being positively charged [J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967)]. Some experimental results appear to support these calculations [S. A. Holmes and T. D. Thomas, *ibid.*, **97**, 2337 (1975)]. Unfortunately, many factors determine the C_β chemical shift, and the electronic component is therefore difficult to assess.

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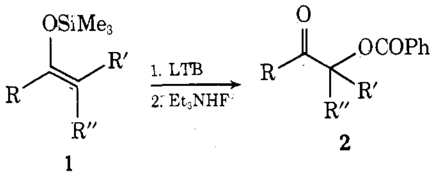
Lead Tetrabenzoate Oxidation of Trimethylsilyl Enol Ethers

Summary: A high yield, regiospecific procedure for the preparation of α-benzoyloxy carbonyl compounds is reported.

Sir: We wish to report that the reaction of trimethylsilyl enol ethers, **1**, with lead tetrabenzoate (LTB), followed by treatment with triethylammonium fluoride, affords α-benzoyloxy carbonyl compounds, **2**, in excellent yield (eq 1). Previous interest in the introduction of an acyloxy group adjacent to the carbonyl moiety has centered mainly upon the use of lead tetraacetate (LTA).[1] Enolizable ketones react with LTA in refluxing benzene to produce α-acetoxy ketones in moderate yield,[2] but the reaction is limited by the concurrent production of diacetates[2a] and rearrangement products.[3] The latter problem is a major deterrent in the use of LTA for the formation of α-acetoxy aldehydes[4] and no high yield method for the synthesis of these useful intermediates has as yet been reported.[5] Boron trifluoride has been employed to catalyze the LTA reaction with ketones,[6] and, in one instance, an enolate has been successfully trapped by LTA.[7] Other approaches have used the reactions of enamines with LTA[8] and thallium triacetate,[9] but both methods are of limited preparative value. The reaction of mercuric acetate with ketones also affords the corresponding acetoxy derivative, but the method lacks regiospecificity.[10] Electrochemical procedures for the introduction of acetoxy groups have also been investigated.[11] Recently, we have shown that **1** reacts with LTA to afford excellent yields of α-acetoxy ketones,[12,13] but this method when applied to the trimethylsilyl enol ethers of aldehydes results in the production of glycolic acid as well as acetic acid derivatives.[14]



(1)

Representative examples of the LTB method are shown in Table I. The individual entries serve to point out the advantages of the procedure. All of the yields shown in Table I are quite acceptable, and the yields obtained for the production of **2a–d** are comparable with those obtained via LTA treatment of **1a–d** to afford the corresponding α-acetoxy ketones.[12] The successful preparation of **2f**, **2g**, and **2h** indicates the generality of the method as applied to the synthesis of α-benzoyloxy aldehydes. NMR analyses of crude reaction mixtures evidenced that no rearrangement products (α-benzoyloxy ketones) were present.[15] The mildness of the procedure is exemplified by the isolation of **2l** and **2h**. Heating of **2h** resulted in the loss of benzoic acid and formation of cinnamaldehyde. Pyrolysis of **2** is currently being studied as an entry into regiospecifically generated α,β-unsaturated carbonyl systems. That the method provides a regiospecific synthesis of **2** from ketones, via **1**, is noted by the production of **2j**,[16] **2k**,[17] **2l**, and **2m**. The selectivity of LTB for the enol double bond in **1m** to form **2m** is in line with the reactivity of this linkage toward ozone[13d] and the Simmons–Smith reagent[18] in the presence of other unsaturation in **1**. Further, no evidence was obtained for the formation of cyclization products from **1m**, a reaction noted in the reaction of 1,5-pentadiene with LTA.[19]

The general mechanism for the formation of **2** from **1** appears to be analogous to that observed in the treatment of **1** with LTA, in which the initial step of the reaction is the production of a diacetate.[12] In the present case, **1** reacts with LTB to form the dibenzoate **3**.[20] Subsequent attack by fluoride ion[21] frees the α-benzoyloxy compound, **2** (Scheme I).

Scheme I