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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 Chem.*, unpublished work].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.
(12) See C. G. Pitt, *J. Organometal. Chem.*, **61**, 49 (1973).
(13) A π-bond order of 0.18 for an aryl silicon system has been calculated [M. D. Curtis and A. L. Allred, *J. Am. Chem. Soc.*, **87**, 2554 (1965)]. See also P. Bischof, M. J. S. Dewar, D. W. Goodman, and T. B. Jones, *J. Organometal. Chem.*, **82**, 88 (1974).
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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$_\beta$ chemical shift, and the electronic component is therefore difficult to assess.
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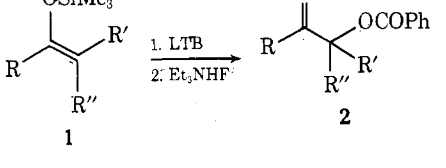
Lead Tetrabenzoate Oxidation of Trimethylsilyl Enol Ethers

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

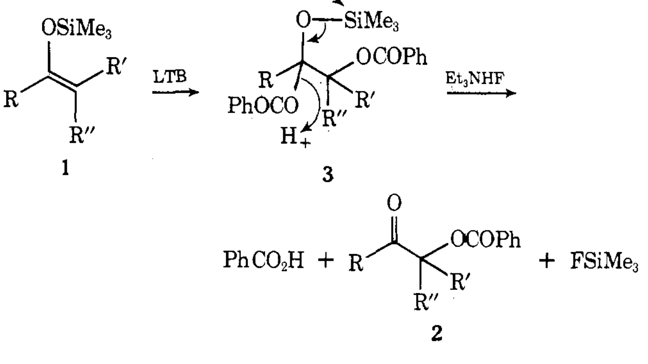
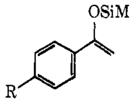
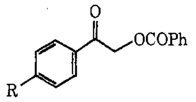
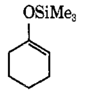
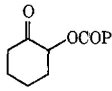
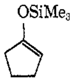
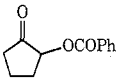
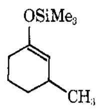
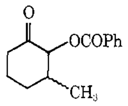
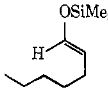
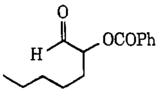
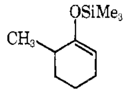
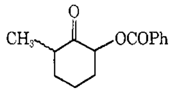
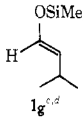
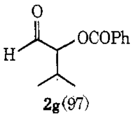
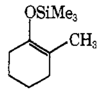
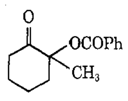
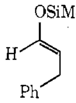
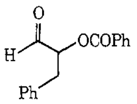
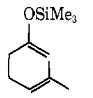
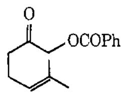


Table I. Oxidation of Trimethylsilyl Enol Ethers, 1, With Lead Tetrabenzoate

1^{a,b}	Isolated **2**^{a,b} (% yield)	**1**^{a,b}	Isolated **2**^{a,b} (% yield)
 **1a**,^{c} R = H **1b**,^{c} R = Cl **1c**,^{c} R = OCH$_3$ **1d**,^{c} R = F	 **2a**(99), R = H **2b**(96), R = Cl **2c**(90), R = OCH$_3$ **2d**(97), R = F	 **1i**^{c}	 **2i** (91)
 **1e**^{c}	 **2e** (77)	 **1j**^{e}	 **2j**^{f} (83)
 **1f**^{c,d}	 **2f** (90)	 **1k**^{c}	 **2k**^{g} (92)
 **1g**^{c,d}	 **2g**(97)	 **1l**^{c}	 **2l** (80)
 **1h**^{c,d}	 **2h** (87)	 **1m**^{c}	 **2m** (92)

^{a} All compounds have ir, NMR, and mass spectral properties consistent with the proposed structures. ^{b} All new compounds show C and H analyses within ±0.3% of theoretical. ^{c} Prepared by the method of H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, 34, 2324 (1969). ^{d} Mixture of *E* and *Z* isomers. ^{e} Prepared by the method of R. K. Beckman, Jr., *J. Am. Chem. Soc.*, 96, 6179 (1974). ^{f} Mixture containing 75% 1:1 mixture of *cis*-**2j** and *trans*-**2j** and 25% unidentified isomer; see ref 16. ^{g} Isolated as a 2:1 mixture of *trans*-**2k** and *cis*-**2k**; see ref 17.

The following is a typical experimental procedure. A solution of 2 mmol of LTB[22] in 30 ml of dry methylene chloride was cooled to 0 °C (ice bath) and treated with 2 mmol of **1i** (addition time ~30 sec). After 0.5 hr of stirring at room temperature, the resulting slurry was filtered to remove lead dibenzoate, and the solution thus obtained was treated with 6 mmol of triethylammonium fluoride.[21] The resulting solution was stirred at room temperature for 8 hr and then washed sequentially with 20 ml of 50% aqueous sodium carbonate solution, 20 ml of 1.5 N hydrochloric acid, and 20 ml of saturated sodium bicarbonate solution. After drying over anhydrous magnesium sulfate and filtration, solvent was removed in vacuo and the residue crystallized from ether to afford a 91% yield of **2i**, mp 86–87 °C (lit.[23] mp 85–86 °C).

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(13) For recent examples of methods devised for the introduction of hydroxy groups adjacent to the carbonyl function, see (a) G. M. Rubottom, M. A. Vazquez, and D. R. Pelegrina, *Tetrahedron Lett.*, 4319 (1974); (b) G. M. Rubottom and R. Marrero, *J. Org. Chem.*, **40**, 3783 (1975); (c) A. G. Brooke and D. M. MacRae, *J. Organometal. Chem*, **77**, C19 (1974); (d) R. D. Clark and C. H. Heathcock, *Tetrahedron Lett.*, 2027 (1974); (e) H. H. Wasserman and B. H. Lipshutz, *ibid.*, 1713 (1975), and ref 7 cited therein; (f) E. Vedejs, *J. Am. Chem. Soc.*, **96**, 5944 (1974).
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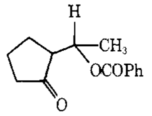
(15) Oxidation of the trimethylsilyl enol ether of phenylacetaldehyde with LTB afforded **2a**.
(16) NMR analysis of the distilled reaction product indicated the presence of a 1:1 mixture of *cis*-**2j** [δ 1.05 (d, 3, J = 7 Hz, CH$_3$), 5.45 (d, 1, J = 5 Hz, CHOCOPh)] and *trans*-**2j** [δ 1.18 (d, 3, J = 7 Hz, CH$_3$), 5.08 (d, 1, J = 11 Hz, CHOCOPh)] which accounted for 75% of the product. The presence of a third isomer was indicated by a methyl doublet at δ 1.08 coupled to a proton at ~5.4–5.5 (decoupling experiment). A tentative structure for this isomer is **i** which might arise from a small amount of rearrangement during oxidation.[3]



i

(17) *cis*-**2k**: mp 148.5–150 °C; ir (Nujol) 1710, 1725 (sh) cm^{-1}; NMR (CDCl$_3$/TMS) δ 1.08 (d, 3, J = 6 Hz, CH$_3$), 5.30 (m, 1, width at half-height ~20 Hz, CHOCOPh); mass spectrum (15eV) *m/e* (rel intensity) 232 (M$^+$, 51), 127 (18), 110 (9), 105 (100). *trans*-**2k**: mp 58.5–59.5 °C; ir (Nujol) 1719 cm^{-1}; NMR (CDCl$_3$/TMS) δ 1.17 (d, 3, J = 7 Hz, CH$_3$), 5.37 (m, 1, width at half-height ~14 Hz, CHOCOPh); mass spectrum (15eV) *m/e* (rel intensity) 232 (M$^+$, 35), 127 (23), 110 (8), 106 (10), 105 (100).
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(20) NMR analysis of the reaction mixture obtained from the treatment of **1b** with LTB, prior to fluoride treatment, showed the presence of dibenzoate **3b**: NMR (CDCl$_3$/TMS) δ 0.19 [s, 9, Si(CH$_3$)$_3$], 4.89 (AB d of d, J = 12 Hz, 2, CH$_2$OCOPh), 7.2–8.2 (m, 14, Ar H).
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