Reaction of Trimethylsilyloxy-1,3-dienes with Lead(IV) Benzoate

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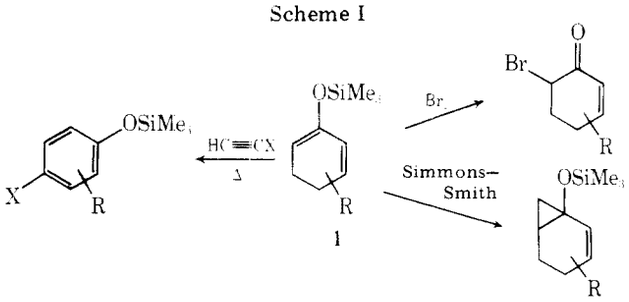
General methods for the synthesis of trimethylsilyloxy-1,3-dienes 1 are discussed. The reaction of 1 with lead(IV) benzoate (LTB), followed by treatment with fluoride ion, affords a variety of keto benzoates **4.** The structural features present in **1** determine the type of 4 which results. 1-Trimethylsilyloxy-1,3-cyclohexadienes **1d** and **1e** as well as alicyclic 2-trimethylsilyloxy-1,3-dienes **1f** and **1g** afford products arising from the 1,2 addition of benzoate to 1. A carbonium ion mechanism involving neighboring group participation by a benzoyloxy group accounts for the 3,4-addition products occurring from the LTB reaction with **1a–e.**

Substituted trimethylsilyloxy-1,3-cyclohexadienes, **1,** react regiospecifically at the 1,2 double bond with electrophiles such as bromine[1] and the Simmons–Smith reagent.[2] Further, the diene system in **1** has proven to be a suitable component for [4 + 2] cycloaddition reactions, again with high regiospecificity.[3] Scheme I summarizes these findings.

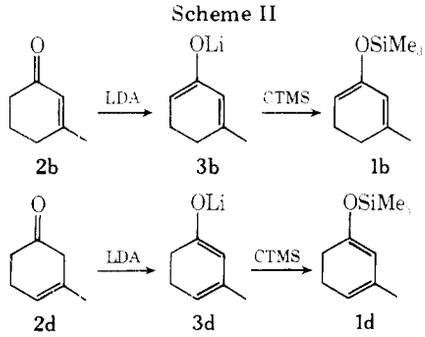
Scheme I



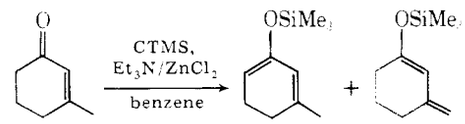
Since trimethylsilyl enol ethers react cleanly with lead(IV) benzoate to afford, upon workup, α-benzoyloxycarbonyl compounds,[4] a study was undertaken to extend this reaction with **1.** Previous to the current work, the lead(IV) carboxylate oxidation of conjugated dienes had been noted in but a few cases.[5]

In general, **1** was prepared by treatment of the appropriate ketone, **2,** with strong base (LDA), followed by quenching of the dienolate **3** with chlorotrimethylsilane (CTMS).[2a,6] Owing to the kinetic selectivity of the reactions employed, it was possible to obtain both 1- and 2-trimethylsilyloxy substitution of the 1,3-diene system. The use of β,γ-unsaturated **2** provides the former and α,β-unsaturated **2** affords the latter. This synthetic flexibility for the generation of **1** is outlined in Scheme II, and compounds **1** thus prepared are noted in Table I.

Scheme II



Production of **1** employing weak base proved to be a less general entry into the system. Standard methods for this mode of generation of **1** (CTMS/Et_3N/DMF[2a,6,7] or CTMS/Et_3N/$ZnCl_2$/benzene[3b]) afford inseparable mixtures of isomers when the enone **2** is substituted in the 3 position. Hence, the reaction of **2b** with CTMS/Et_3N in benzene, as shown in eq 1, results

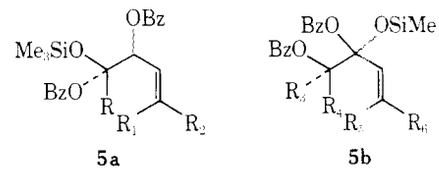


(1)

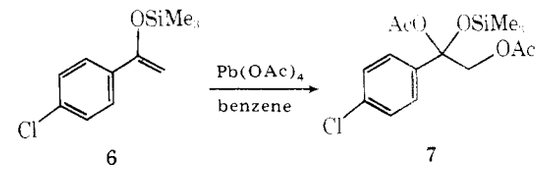
in a mixture containing both **1b** and **1h.**[2a,8] This method, however, has been used successfully in one instance to prepare the heteroannular silyloxy diene of testosterone,[2] in a specific manner. As noted in eq 1, no product of type **1d** was observed.[9] Indeed, if no 3 substitution is present, this procedure is the most convenient for the preparation of dienes of type **1a,** when large quantities are required. Compound **1g** was conveniently prepared via this route.

Mixing of **1** with an equimolar quantity of lead(IV) benzoate[10] (LTB) in methylene chloride resulted in the immediate precipitation of lead(II) benzoate. Filtration and subsequent treatment of the filtrate with triethylammonium fluoride[11] afforded the benzoates, **4,** as summarized in Table II.

The appearance of **4d–g** seems to be very much in line with literature analogy concerning the reaction of **1** with electrophiles.[1,2] Attempts to isolate intermediate dibenzoates of type **5,** by omission of the fluoride treatment, proved unsuccessful.



It had been anticipated that **5** would be present based on the known reaction of **6** with lead(IV) acetate to give **7** (eq 2).[4b]

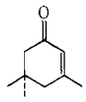
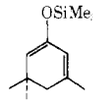
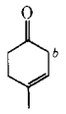
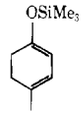
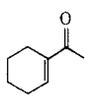
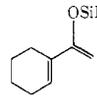
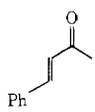
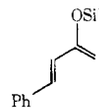


(2)

Previous attempts to isolate dibenzoates analogous to **7** from the reaction of **6** with LTB have established that the loss of trimethylsilyl benzoate is very facile,[4,12] so that failure to isolate **5** is not unexpected. Circumstantial evidence for the existence of **5** was obtained from the reaction of **1d** with LTB. In this case, the NMR spectrum of the reaction mixture, after anhydrous workup, revealed that only **4d** and trimethylsilyl benzoate were present.[13] Thus, it appears quite likely that intermediates of type **5** are involved in the production of **4d–g.**

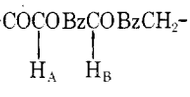
Identification of the structures for **4a** and **4a′** was forthcoming from a consideration of both NMR data and the

Table I. Physical Data for Alkyl Substituted Trimethylsilyloxy Dienes, 1[a,b]

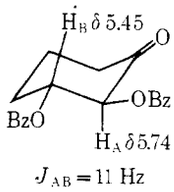
2[f]	1[g] (% yield of isolated 1)	Bp, °C (mm) [lit. bp, °C]	n^{25}D	IR (neat), cm^{-1}	NMR (CCl_4/ Me_4Si), δ	MS (15 eV), m/e (rel abundance); m*, metastable peak
 2a	 1a (80)	56–58 (6.0) [33–37 (0.01)[c]]	1.4590	1648, 1590	0.23 (s, 9 H) 2.12 (m, 4 H) 4.75 (m, 1, H) 5.70 (m, 2 H)	169 (15), 168 (M^+, 100), 167 (14), 153 (12), 75 (32), 73 (17); m* 166, 139
 2b	 1b (75)	51–53 (1.0)	1.4626	1660, 1610	0.14 (s, 9 H) 1.77 (s, 3 H) 1.9–2.2 (m, 4 H) 4.55 (m, 1 H) 5.35 (m, 1 H)	183 (17), 182 (M^+, 100), 181 (13), 167 (35), 73 (15); m* 153.5
 2c	 1c (81)	54–57 (1.5) [45–47 (0.05)[d]]	1.4509	1660, 1610	0.13 (s, 9 H) 1.97 (s, 6 H) 1.74 (s, 3 H) 1.89 (s, 2 H) 4.38 (broad s, 1 H) 5.34 (m, 1 H)	210 (M^+, 28), 196 (17), 195 (100), 179 (9); m* 164
 2d	 1d (77)	76–82 (10.0)	1.4630	1660, 1600	0.23 (s, 9 H) 1.67 (s, 3 H) 2.10 (broad s, 4 H) 4.91 (s, 1 H) 5.04 (broad s, 1 H)	183 (18), 182 (M^+, 181 (12), 167 (26), 165 (10), 73 (17); m* 180, 153.5, 136.5
 2e	 1e (77)	81–83 (9.7)	1.4633	1657, 1607	0.12 (s, 9 H) 1.70 (s, 3 H) 2.14 (m, 4 H) 4.88 (d, 1 H, J = 6 Hz) 5.40 (d, 1 H, J = 6 Hz)	183 (16), 182 (M^+, 100), 181 (12), 167 167 (30), 165 (8), 151 (7), 75 (7), 73 (22); m* 180, 153.5, 136.5
 2f	 1f (69)	85–89 (4.8) [111–115 (18)[e]]	1.4707	1640, 1590	0.18 (s, 9 H) 1.4–1.75 (m, 4 H) 1.9–2.3 (m, 4 H) 4.05 (s, 1 H) 4.22 (s, 1 H) 6.10 (m, 1 H)	197 (17), 196 (M^+ 100), 181 (88), 167 (27), 154 (32). 147 (20), 75 (24); m* 167, 121
 2g	 1g (80)	88.5–90.5 (0.25)	1.5480	1635, 1590	0.27 (s, 9 H) 4.35 (broad s, 2 H) 6.60 (AB, 2 H, J = 16 Hz) 7.06–7.46 (m, 5 H)	219 (21), 218 (M^+ 100), 217 (28), 203 (49), 127 (11), 103 (10), 75 (32), 73 (21); m* 216, 188.5

[a] Satisfactory analytical data (± 0.3/ for C and H) were reported for all new compounds listed in the table. [b] See Experimental Section for specific procedures. [c] Value cited in ref 2a. [d] Value cited in ref 1. [e] Value cited in ref 3d. [f] Registry no. are, respectively, 930-68-7, 1193-18-6, 78-59-1, 31883-98-4, 5259-65-4, 932-66-1, 1896-62-4. [g] Registry no. are, respectively, 54781-19-0, 54781-27-0, 54781-28-1, 61140-45-2, 61140-46-3, 57781-35-0, 61140-47-4.

chemical behavior of the two compounds. Decoupling experiments[14] indicated the presence of a

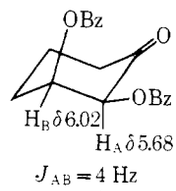


unit in both compounds. The chemical shift of H_B in **4a** compared to that of H_B in **4a'** (δ 5.45 vs. 6.02) is indicative of an axial H_B in the former and an equatorial H_B in the latter.[15] The observed coupling constants of J_{AB} = 11 Hz in **4a** and J_{AB} = 4 Hz in **4a'** lead to the conclusion that in **4a**, H_B and H_A are



J_{AB} = 11 Hz

4a



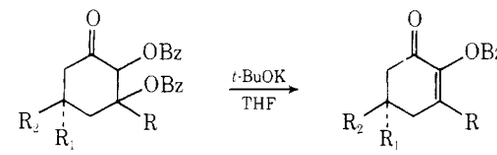
J_{AB} = 4 Hz

4a'

trans diaxial, while in **4a'**, H_B is equatorial and H_A is axial.[15] Therefore, structure **4a** is assigned to the trans dibenzoate and **4a'** to the cis dibenzoate.

Treatment of a 50:50 mixture of **4a** and **4a'** with potassium *tert*-butoxide in THF resulted in the production of **8a**, a known compound.[16] This result is consistent with the NMR data given above and the same procedure was also successful for transforming **4b** and **4c** into **8b** and **8c**, respectively (Scheme III). Although the formation of **8b** and **8c** serves to

Scheme III

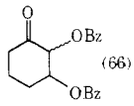
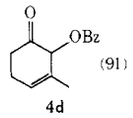
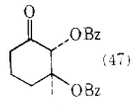
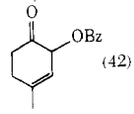
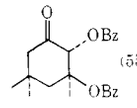
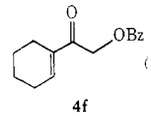
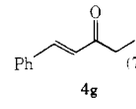


4a/**4a'**, R, R_1, R_2 = H
b, R = Me; R_1, R_2 = H
c, R, R_1, R_2 = Me

8a, R, R_1, R_2 = H (80%)
b, R = Me; R_1, R_2 = H (65%)
c, R, R_1, R_2 = Me (63%)

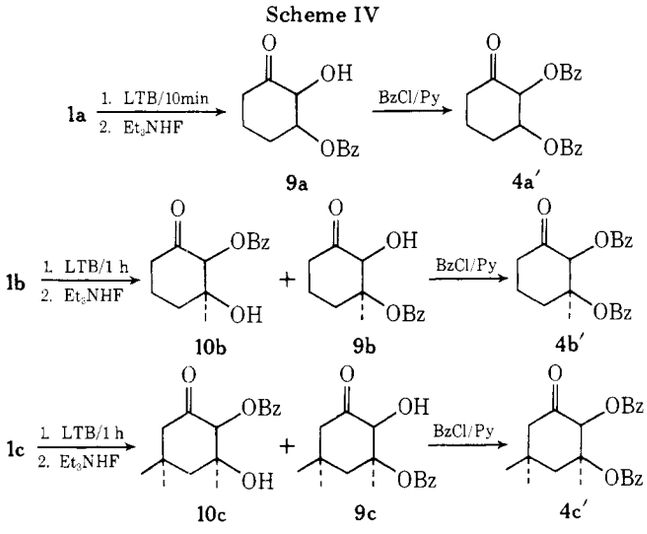
show the gross structural features of **4b** and **4c**, further evidence was deemed necessary to prove the trans stereochemistry indicated for these compounds (cf. Table II). This evidence was obtained from the reactions of **1a–c** with LTB using abbreviated reaction times. Whereas **4a** and **4a'** were produced

Table II. Reaction of 1 with Lead(IV) Benzoate Followed by Fluoride Treatment

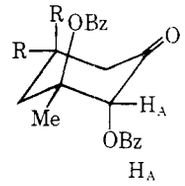
1	4 (% yield of isolated 4)	1	4 (% yield of isolated 4)
1a	 (66) 4a/4a′: trans/cis 50/50	1d	 (91) 4d
1b	 (47) 4b	1e	 (42) 4e
1c	 (55) 4c	1f	 (54) 4f
		1g	 (78) 4g

after ca. 2 h contact time with LTB, and **4b** and **4c** arose after ca. 20 h, contact time of ca. 10 min with **1a** and 1 h with **1b** and **1c** led to the results summarized in Scheme IV.

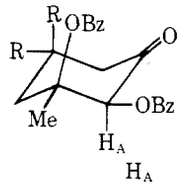
Scheme IV



The spectral properties of **9a**[14] are consistent with the proposed structure, and further proof of the cis stereochemistry in **9a** was obtained by transforming it into the previously characterized **4a′** via treatment with benzoyl chloride in pyridine. Analogous behavior by **1b** and **1c** led to the production of **9b** and **9c**, respectively, which, in turn, were transformed into the corresponding cis dibenzoates **4b′** and **4c′**. Comparison of the NMR spectra of **4b** and **4c** with those of **4b′** and **4c′** strengthens the proposed assignments. In each pair of isomers the proton designated H_A in the cis isomer



4b, R = H δ 6.06
c, R = Me δ 5.87

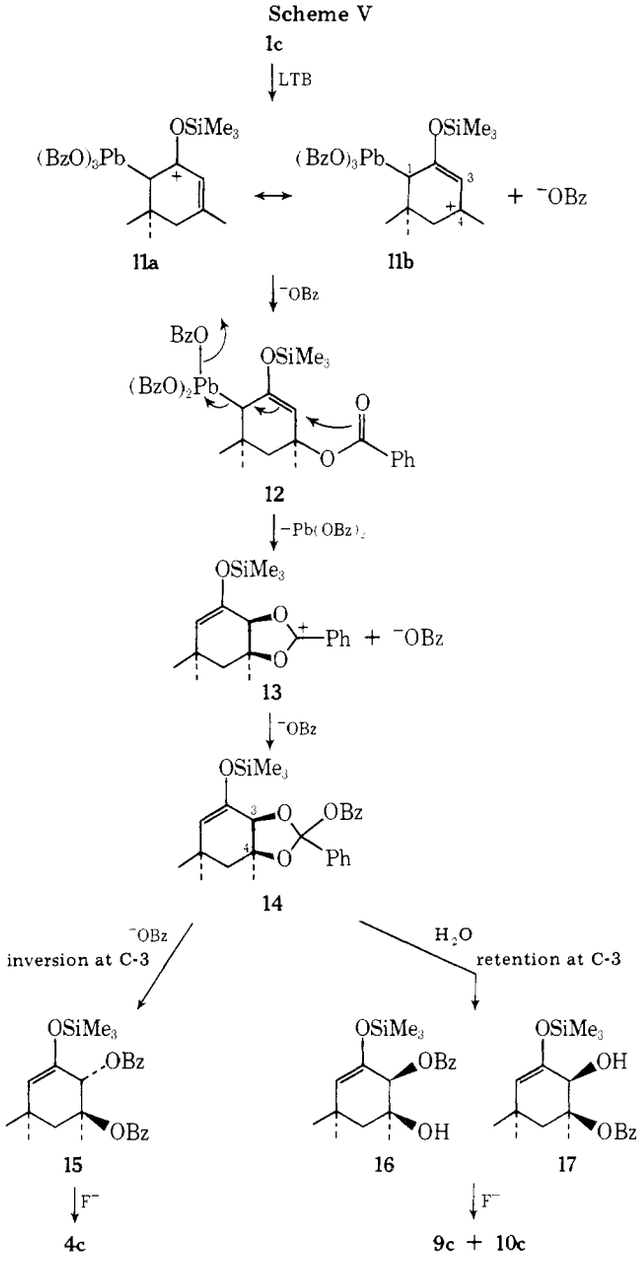


4b′, R = H δ 5.32
c′, R = Me δ 5.34

occurs at higher field, as would be expected for the structures as described.

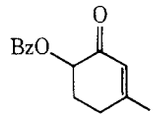
A mechanistic interpretation for the above findings is presented in Scheme V using, as an example, the transformations of **1c**.

Scheme V



Attack of LTB at the electron-rich 1,2 double bond of **1c** affords **11**, analogous to the normal behavior shown by 1 toward electrophiles. Trapping of **11** by benzoate addition at C-4 via either an intra- or intermolecular process gives **12**. Expulsion of lead(II) benzoate from **12** with neighboring group participation leads to **14** via the carbocation **13**. Prolonged time in the reaction medium (dry solvent) then affords **15** with inversion most likely occurring at the allylic center, C-3. Subsequent reaction of **15** with fluoride ion at silicon gives the trans dibenzoate **4c**. On the other hand, short reaction time prevents the inversion mechanism from functioning and **14** is intercepted by water,[17] thereby affording **16** and **17**. These, in turn, are transformed into **9c** and **10c** upon fluoride treatment. The proposed mechanism finds direct analogy from that postulated for the reaction of cyclopentadiene with LTB.[5a] It is of interest that the data presented in ref 5b do not pre-

clude 1,4-addition leading eventually to 3,4-substituted products as indicated in the present work. A small amount of **18** (ca. 5%) isolated from the reaction of **1b** with LTB implies



18

that, at least in this case, **11** can be channeled into a 1,2-addition product to a small extent. This compound could arise either from 1,2-addition or from 1,4-addition followed by loss of benzoic acid to afford **18**.[18]

Appearance of both **4a** and **4a'** from the reaction of **1a** with LTB may argue for decomposition of **14** via both an inversion process at C-3 to produce **4a** and a concerted six-center rearrangement with retention at C-3 leading to **4a'**. The latter process would be severely restricted in **14** generated from **1b** and **1c** owing to nonbonded interactions caused by the C-4 methyl substituent. In fact, no cis dibenzoates (i.e., **4b'** and **4c'**) were discovered in the reactions of **1b** and **1c** with LTB. The possibility of equilibration between **4a** and **4a'** was ruled out when pure **4a'** remained unchanged after treatment with Et_3NHF for 10 h.

Direct proof for the intermediacy of **15** and **16** was obtained by isolation of the two compounds. Treatment of **1c** with LTB for 20 h followed by aqueous workup gave **15**, which was quantitatively converted into **4c** upon treatment with Et_3NHF. Reaction of **1c** with LTB for 10 min followed by addition of methanol gave **16**. When **16** was treated with Et_3NHF, **10c** was obtained as the sole reaction product.

Experimental Section

General. Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Proton magnetic resonance (NMR) spectra were recorded at 60 MHz on a Varian Anaspect EM 360 spectrometer using tetramethylsilane as internal standard. Infrared spectra were obtained on a Perkin-Elmer 621 grating infrared spectrometer. Low-resolution mass spectral data was obtained with an Hitachi Perkin-Elmer RMU-6E instrument (15 eV) equipped with a direct inlet system. Elemental microanalyses were determined employing a Perkin-Elmer 240 Elemental Analyzer. Indices of refraction were measured on a Bausch and Lomb Abbe-type refractometer utilizing the D line of sodium at a temperature of 25 °C. For all column chromatography, silica gel Woelm 0.032–0.063 mm (ICN Pharmaceuticals GmbH & Co.) was used. TLC analyses utilized silica gel 7GF (Baker). The lead tetrabenzoate was prepared from commercial lead tetraacetate (90%, Alfa-Ventron) by the method of Hurd and Austin,[10] mp 186–187 °C dec. The triethylammonium fluoride was obtained as a white solid (very hygroscopic) by the procedure of Hunig.[11] Anhydrous magnesium sulfate was employed as drying agent.

Preparation of Trimethylsilyloxy Dienes 1a–f. The procedure employed was essentially the same as that outlined by Conia for the synthesis of **1a–c**.[2a] To 100 ml of tetrahydrofuran[19] (distilled from $LiAlH_4$) at −18 °C (ice/methanol) was added 5.0 g (49.4 mmol) of diisopropylamine followed by 20.6 ml of *n*-butyllithium (2.45 M in hexane, Alfa-Ventron). After 10 min, 45 mmol of enone **2** was added over 10 min. For the preparation of **1d, 1e,** and **1f** the enone was dissolved in ca. 10 ml of tetrahydrofuran and the reaction run at −78 °C. After 10 min, 12 ml (94 mmol) of chlorotrimethylsilane was added rapidly. The reaction mixture was warmed to room temperature and allowed to stir for 2 h and then diluted with 200 ml of pentane. Extraction with 150 ml of cold (ca. 5 °C) aqueous sodium bicarbonate, drying, filtration, and removal of solvent in vacuo gave crude **1a–f**. Distillation at reduced pressure afforded pure **1a–f**. The physical data for **1a–f** are presented in Table I.

***trans*-1-Phenyl-3-trimethylsilyloxybutadiene (1g).** The method of Danishefsky was applied.[3b] To a suspension of 0.20 g (1.5 mmol) of zinc chloride in 15 ml of triethylamine was added 7.3 g (50 mmol) of **2g** in 15 ml of dry benzene followed by 13 ml (100 mmol) of chlorotrimethylsilane. After stirring for 15 h at 40 °C, the reaction mixture was cooled and added to 100 ml of ether. Filtration and removal of solvent in vacuo gave crude **1g**. Distillation at reduced pressure afforded pure **1g**. The physical constants are listed in Table I.

3-Methyl-3-cyclohexen-1-one (2d). To 600 ml of ammonia (distilled from sodium) was added 250 ml of ether (distilled from $LiAlH_4$) containing 24.4 g (200 mmol) of *m*-methylanisole. Then 250 ml of *tert*-buttyl alcohol (distilled from calcium hydride) was added rapidly with stirring, and 7.0 g (1.0 mol) of lithium (in small pieces) was added in portions over 20 min. This mixture was allowed to stir under ammonia reflux for 2 h. The excess Li/NH_3 was then destroyed with solid ammonium chloride and the ammonia allowed to evaporate under an atmosphere of nitrogen (fume hood). Pentane (500 ml) was added and gentle heat was applied (water bath) to drive off any residual ammonia. The reaction mixture was then partitioned between an additional 300 ml of pentane and 500 ml of water. The pentane layer was then extracted with water until no change in volume of the water extract was noted. The pentane layer was dried and concentrated in vacuo. The crude enol ether was dissolved in 400 ml of methanol/water (3:1) containing 800 mg of oxalic acid dihydrate and allowed to stir for ca. 1 h. This mixture was diluted with 500 ml of water and extracted several times with methylene chloride. The methylene chloride extracts were combined and washed once with 100 ml of water, dried, filtered, and concentrated in vacuo. Distillation at reduced pressure gave 13.3 g (60%) of **2d**, bp 65.5–66.0 °C (13 mm) [lit.[20] bp 61–62 °C (14 mm)].

4-Methyl-3-cyclohexen-1-one (2e). The method cited for the preparation of **2d** was applied to *p*-methylanisole and afforded 14.3 g (65%) of pure **2e**, bp 68–70 °C (14 mm) [lit.[21] bp 74 °C (17 mm)].

Lead Tetrabenzoate Oxidations. General Procedure. To a solution of 1.52 g (2.2 mmol) of LTB in 40 ml of methylene chloride (stored over calcium chloride) cooled to −18 °C (ice/methanol) was added a solution of 2.0 mmol of trimethylsilyloxydiene 1 in 2 ml of methylene chloride (nitrogen atmosphere). After 5 min at −18 °C, the reaction mixture was stirred for 1 h at room temperature (deviations from the standard 1 h are noted in the specific instances below). The slurry was then filtered to remove lead dibenzoate and the filtrate treated with triethylammonium fluoride (725 mg, 6.0 mmol). After stirring under nitrogen for 2–8 h, the reaction mixture was diluted with 60 ml of methylene chloride and washed successively with 20 ml of 50% aqueous sodium carbonate, 20 ml of 1.5 M hydrochloric acid, and 20 ml of aqueous sodium bicarbonate. The organic solution was dried and filtered. Removal of solvent in vacuo yielded crude products which were purified by the specific methods noted below.

***trans*-2,3-Dibenzoyloxycyclohexanone (4a) and *cis*-2,3-Dibenzoyloxycyclohexanone (4a').** From 2.0 mmol of **1a** was obtained LTB reaction time) 443 mg (66%) of trans/cis **4a/4a'**. Separation was effected by fractional crystallization from ether/petroleum ether (bp 30–60 °C).

Compound 4a (32% isolated): mp 128–129 °C; IR (KBr) 1740, 1720, 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.5–2.8 (m, 6 H), 5.22–5.85 (complex m, 2 H, CH_BOBzCH_AOBz) (irradiation in the methylene region reduces the multiplet to an AB pattern, δ, 5.74, d (sharp) and 5.45 d (broad), J = 11 Hz), 7.2–8.2 (m, 10 H); mass spectrum *m/e* (rel abundance) 338 (M^+, <1), 310 (7), 216 (16), 122 (19), 106 (10), 105 (100).

Anal. Calcd for $C_{20}H_{18}O_5$: C, 71.00; H, 5.36. Found: C, 70.86; H, 5.33.

Compound 4a' (29% isolated): mp 130–131 °C; IR (KBr) 1745, 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.8–2.8 (m, 6 H), 5.68 (d, 1 H, J = 4 Hz), 6.02 (m, 1 H) (irradiation at ca. δ 6.02 collapses the δ 5.68 signal into a singlet, while irradiation in the methylene region collapses the δ 6.02 signal into a doublet, J = 4 Hz), 7.2–8.2 (m, 10 H); mass spectrum *m/e* (rel abundance) 338 (M^+, 3), 310 (12), 216 (12), 122 (16), 106 (10), 105 (100).

Anal. Calcd for $C_{20}H_{18}O_5$: C, 71.00; H, 5.36. Found: C, 71.26; H, 5.34.

Attempted Equilibration of 4a/4a'. A solution of 120 mg (0.36 mmol) of **4a'** in 25 ml of methylene chloride containing 0.25 g (2 mmol) of triethylammonium fluoride was stirred under nitrogen for 10 h. NMR analysis of the crude product after normal LTB reaction workup conditions revealed the presence of only **4a'**.

***trans*-2,3-Dibenzoyloxy-3-methylcyclohexanone (4b) and 6-Benzoyloxy-3-methyl-2-cyclohexen-1-one (18).** From 2.0 mmol of **1b** was obtained (20 h LTB reaction time), after column chromatography ($CHCl_3$), 218 mg (31%) of **4b** and 25 mg (5%) of **18**. With methylene chloride distilled form P_2O_5, 47% of **4b** was obtained.

Compound 4b: mp 117.5–118.0 °C; IR (KBr) 1740 (sh), 1720 (sh), 1702 cm^{-1}; NMR ($CDCl_3$) δ 1.73 (s, 3 H), 1.8–3.0 (m, 6 H), 6.06 (s, 1 H), 7.1–8.3 (m, 10 H); mass spectrum *m/e* (rel abundance) 252 (M^+, <1), 324 (7), 230 (65), 122 (13), 106 (10), 105 (100), 98 (11).

Anal. Calcd for $C_{21}H_{20}O_5$: C, 71.58; H, 5.72. Found: C, 71.76; H, 5.72.

Compound 18: mp 92–93 °C; IR (KBr) 1722, 1678, 1630 cm^{-1}; NMR ($CDCl_3$) δ 2.0 (s, 3 H), 2.2–2.6 (m, 4 H), 5.49 (d of d, 1 H, J = 7, 11 Hz), 5.93 (broad s, 1 H), 7.2–8.2 (m, 5 H); mass spectrum m/e (rel abundance) 230 (M^+, 6), , 125 (43), 109 (13), 108 (100), 105 (43), 97 (13), 82 (37).

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.85; H, 6.06.

***trans*-2,3-Dibenzoyloxy-3,5,5-trimethylcyclohexanone (4c).** From 2.0 mmol of **1c** was obtained (20 h reaction time), after column chromatography ($CHCl_3$), 417 mg (55%) of **4c,** as a colorless oil: IR (neat) 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.07 (s, 3 H), 1.10 (s, 3 H), 1.86 (s, 3 H), 2.47 (s, 2 H), 2.48 (d, 1 H, J = 14 Hz), 2.79 (d, 1 H, J = 14 Hz), 5.87 (s, 1 H), 7.2–8.2 (m, 10 H); mass spectrum m/e (rel abundance) 258 (27), 122 (16), 106 (10), 105 (100).

Anal. Calcd for $C_{23}H_{24}O_5$: C, 72.61; H, 6.36. Found: C, 72.90; H, 6.17.

2-Benzoyloxy-3-methyl-3-cyclohexen-1-one (4d). From 2.0 mmol of **1d** was obtained, after removal of solvent, 418 mg (91%) of essentially pure **4d** (NMR, TLC). Column chromatography ($CHCl_3$) afforded an analytical sample: IR (neat) 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.80 (s, 3 H), 2.35–2.73 (m, 4 H), 5.77 (broad s, 1 H), 5.90 (broad s, 1 H), 7.2–8.2 (m, 5 H); mass spectrum m/e (rel abundance) 230 (M^+, 6), 108 (12), 106 (10), 105 (100), metastable 47.

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.28; H, 6.11.

2-Benzoyloxy-4-methyl-3-cyclohexen-1-one (4e). From 2.0 mmol of **1e** was obtained 194 mg (42%) of **4e:** mp 68.5–69.5 °C (ether/petroleum ether); IR (KBr) 1725 cm^{-1}; NMR ($CDCl_3$) δ 1.81 (s, 3 H), 2.3–2.7 (m, 4 H), 5.50 (m, 1 H), 5.92 (m, 1 H), 7.2–8.2 (m, 5 H); mass spectrum m/e (rel abundance) 230 (M^+, 5), 122 (14), 108 (26), 106 (10), 105 (100).

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.87; H, 6.12.

1-Benzoyloxy-3,4-tetramethylene-3-buten-2-one (4f). From 2.0 mmol of **1f** was obtained 262 mg (54%) of **4f:** mp 97.5–98.5 °C (ether/petroleum ether); IR (KBr) 1720, 1675, 1630 cm^{-1}; NMR ($CDCl_3$) δ 1.5–1.8 (m, 4 H), 2.00–2.42 (m, 4 H), 5.27 (s, 2 H), 6.93 (m, 1 H), 7.2–8.2 (m, 5 H); mass spectrum m/e (rel abundance) 244 (M^+, 5), 122 (15), 110 (10), 109 (100), 105 (50), 81 (10), metastable 60.

Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.69; H, 6.54.

***trans*-1-Benzoyloxy-4-phenyl-3-buten-2-one (4g).** From 2.0 mmol of **1g** was obtained 413 mg (78%) of **4g:** mp 120–121 °C (ether); IR (KBr) 1725, 1700 cm^{-1}; NMR ($CDCl_3$) δ 5.17 (s, 2 H), 6.83 (d, 1 H, J = 16 Hz), 7.20 (d, 1 H, J = 16 Hz), 7.2–8.2 (m, 10 H); mass spectrum m/e (rel abundance) 266 (M^+, 9), 144 (28), 127 (10), 126 (100), 105 (48).

Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.58; H, 5.58.

***cis*-3-Benzoyloxy-2-hydroxycyclohexanone (9a).** From 2.0 mmol of **1a** was obtained (solvent not dried and LTB reaction time of 10 min) 70 mg (15%) of **9a,** by fractional crystallization (ether/petroleum ether): mp 120.5–121.5 °C; IR (KBr) 3480, 1710 cm^{-1} (broad); NMR ($CDCl_3$) δ 1.75–2.76 (m, 6 H), 3.79 (d, 1 H, J = 4 Hz, –OH), 4.38 (d of d, 1 H, J = 4, 4 Hz), 5.76 (m, 1 H), 7.2–8.2 (m, 5 H); mass spectrum m/e (rel abundance) 234 (M^+, 18), 206 (10), 122 (72), 112 (70), 106 (10), 105 (100), 83 (15), 82 (10).

Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.65; H, 5.98.

***cis*-2-Benzoyloxy-3-hydroxy-3-methylcyclohexanone (10b) and *cis*-3-Benzoyloxy-2-hydroxy-3-methylcyclohexanone (9b).** From 2.0 mmol of **1b** was obtained 70 mg (14%) of **10b** and 60 mg (12%) of **9b,** by fractional crystallization (ether/petroleum ether) from the crude reaction mixture.

Compound 10b: mp 147–148 °C; IR (KBr) 3510, 1730, 1700 cm^{-1}; NMR ($CDCl_3$) δ 1.38 (s, 3 H), 1.8–2.7 (m, ? H), 5.34 (s, 1 H), 7.2–8.2 (m, 5 H); mass spectrum m/e (rel abundance) 248 (M^+, 8), 126 (30), 106 (10), 105 (100).

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.60; H, 6.41.

Compound 9b: mp 112–113 °C; IR (KBr) 3460, 1720 (sh), 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.83 (s, 3 H), 1.6–3.2 (m, 6 H), 3.83 (d, 1 H, J = 12 Hz, –OH), 4.06 (d, 1 H, J = 12 Hz), 7.2–8.2 (m, 5 H); mass spectrum m/e (rel abundance) 248 (M^+, 11), 126 (78), 122 (36), 106 (10), 105 (100), 98 (13).

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.45; H, 6.51.

***cis*-2-Benzoyloxy-3-hydroxy-3,5,5-trimethylcyclohexanone (10c) and *cis*-3-Benzoyloxy-2-hydroxy-3,5,5-trimethylcyclohexanone (9c).** From 2.0 mmol of **1c** was obtained 100 mg (18%) of **10c** and 90 mg (16%) of **9c,** by fractional crystallization from the crude reaction mixture (ether/petroleum ether).

Compound 10c: mp 164.5–165.0 °C; IR (KBr), 3510, 1733, 1700 cm^{-1}; NMR ($CDCl_3$) δ 1.10 (s, 3 H), 1.07 (s, 3 H), 1.33 (s, 3 H), 1.93 (s, 2 H), 2.25 (d, 1 H, J = 14 Hz), 2.55 (d, 1 H, J = 14 Hz), 2.44 (s, 1 H, –OH), 5.33 (s, 1 H), 7.2–8.2 (m, 5 H); mass spectrum m/e (rel abundance) 276 (M^+, 11), 155 (9), 154 (69), 106 (10), 105 (100), metastable 86.5.

Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30. Found: C, 69.73; H, 7.47.

Compound 9c: mp 133–134 °C; IR (Kbr) 3460, 1725 (sh), 1715 cm^{-1}; NMR ($CDCl_3$) δ 0.90 (s, 3 H), 1.12 (s, 3 H), 1.85 (s, 3 H), 1.85 (d, 1 H, J = 16 Hz), 2.44 (s, 2 H), 3.06 (d, 1 H, J = 16 Hz), 3.82 (d, 1 H, J = 7 Hz, –OH), 4.10 (d, 1 H, J = 7 Hz), 7.2–8.2 (m, 5 H); mass spectrum m/e (rel abundance) 276 (M^+, 3), 155 (10), 154 (100), 139 (11).

Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, /.30. Found: C, 69.76; H, 7.49.

2-Benzoyloxy-2-cyclohexen-1-one (8a). To 200 ml of dry diethyl ether (containing 10% tetrahydrofuran) was added 300 mg (0.89 mmol) of **4a/4a′** followed by 200 mg (1.8 mmol) of potassium *tert*-butoxide. After refluxing overnight, under nitrogen, the reaction mixture was diluted with 100 ml of ether and washed with water (2 × 20 ml). After drying and removal of solvent in vacuo, crystallization from ether/hexane yielded 150 mg (80%) of **8a:** mp 89–90 °C (lit.[16] mp 86.5–87.0 °C); IR (KBr) 1728, 1683 cm^{-1}; NMR ($CDCl_3$) δ 1.8–2.8 (m, 6 H), 6.67 (t, 1 H, J = 4 Hz), 7.2–8.2 (m, 5 H); mass spectrum m/e (rel abundance) 216 (M^+, 12), 106 (10), 105 (100), metastable 51.

Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.60. Found: C, 72.47; H, 5.52.

2-Benzoyloxy-3-methyl-2-cyclohexen-1-one (8b). To 20 ml of dry tetrahydrofuran, through which dry nitrogen had been bubbled for ca. 30 min, was added 119 mg (0.34 mmol) of **4b** followed by 56 mg (0.50 mmol) of potassium *tert*-butoxide. After stirring under nitrogen for 1.5 h at room temperature, the reaction mixture was diluted with 100 ml of ether and washed with water (3 × 20 ml). The water washings were combined and extracted with 30 ml of ether. The ether extracts were combined, dried, and concentrated in vacuo affording 51 mg (65%) of **8b** as a colorless oil. Molecular distillation at 120 °C (0.2 mm) gave an analytical sample: IR (neat) 1733, 1680, 1650 cm^{-1} (sh); NMR ($CDCl_3$) δ 2.0–2.8 (m, 6 H), 1.93 (s, 3 H), 7.2–8.2 (m, 5 H); mass spectrum m/e (rel abundance) 230 (M^+, 62), 106 (10), 105 (100).

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.89; H, 6.37.

2-Benzoyloxy-3,5,5-trimethyl-2-cyclohexen-1-one (8c). To 20 ml of dry tetrahydrofuran, through which dry nitrogen had been bubbled for ca. 30 min, was added 183 mg (0.48 mmol) of **4c** followed by 112 mg (1.0 mmol) of potassium *tert*-butoxide. After 30 min of stirring at room temperature under nitrogen, the reaction mixture was diluted with 100 ml of ether and washed with water (3 × 20 ml). The water extracts were combined and extracted with 30 ml of ether. The ether extracts were combined, dried, filtered, and concentrated in vacuo. Crystallization of the crude product from ether/hexane afforded 78 mg (63%) of **8c:** mp 70.0–70.5 °C; IR (KBr) 1730, 1682, 1660 cm^{-1}; NMR)cdcl$_3$) δ 1.13 (s, 6 H), 1.86 (s, 3 H), 2.42 (s, 4 H), 7.4–8.3 (m, 5 H); mass spectrum m/e (rel abundance) 258 (M^+, 33), 106 (10), 105 (100).

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 74.66; H, 7.07.

Benzoylation of Alcohols 9a, 9b, and 9c. General Procedure. To 40–60 mg of alcohol was added 2 ml of pyridine and 40 mg of benzoyl chloride. After 30 h at room temperature, the reaction mixture was added to 15 ml of 10% hydrochloric acid. Extraction with ether (3 × 20 ml), washing with 15 ml of 1.5 N hydrochloric acid and 15 ml of aqueous sodium bicarbonate, drying, and removal of solvent in vacuo gave crude dibenzoate. Column chromatography or crystallization provided pure dibenzoate.

***cis*-2,3-Dibenzoyloxy-3-methylcyclohexanone (4b′).** From 45 mg (0.18 mmol) of **9b** was obtained, after column chromatography (hexane/ethyl acetate, 8:1), 51 mg (81%) of **4b′** as a colorless oil: IR (neat) 1720, 1710 cm^{-1} (sh); NMR ($CDCl_3$) δ 1.7–2.7 (m, 5 H), 1.85 (s, 3 H), 3.0–3.4 (m, 1 H), 5.32 (s, 1 H), 7.2–8.2 (m, 10 H); mass spectrum m/e (rel abundance) 352 (M^+, 1), 324 (8), 230 (55), 122 (15), 106 (10), 105 (100).

Anal. Calcd for $C_{21}H_{20}O_5$: C, 71.58; H, 5.72. Found: C, 71.65; H, 5.89.

***cis*-2,3-Dibenzoyloxycyclohexanone (4a′).** From 50 mg (0.21 mmol) of **9a** was obtained, after crystallization from ether, 42 mg (59%) of **4a′,** mp 130–131 °C. The **4a′** so produced was spectrally identical (IR, NMR) with the **4a′** obtained from LTB treatment of

1a, and further, no depression of melting point (mmp 130–131 °C) was noted upon admixture.

***cis*-2,3-Dibenzoyloxy-3,5,5-trimethylcyclohexanone (4c').** From 37.5 mg (0.136 mmol) of **9c** (50 mg of a 75:25 mixture of **9c** and **10c**) was obtained, after column chromatography ($CHCl_3$), 20 mg (53%) of **4c'**: mp 125–126 °C (ether/petroleum ether); IR (KBr) 1740, 1715 cm^{-1}; NMR ($CDCl_3$) δ 0.98 (s, 2 H), 1.15 (s, 3 H), 1.85 (s, 3 H), 1.95 (d, 1 H, J = 14 Hz), 2.33 (d, 1 H, j = 14 Hz), 2.62 (d, 1 H, J = 14 Hz), 3.22 (d, 1 H, J = 14 Hz), 5.34 (s, 1 H), 7.8–8.2 (m, 10 H); mass spectrum *m/e* (rel abundance) 380 (M^+, 2), 352 (10), 322 (12), 258 (55), 154 (22), 126 (10), 122 (10), 106 (10), 105 (100), metastables 175, 42.5.

Anal. Calcd for $C_{23}H_{24}O_5$: C, ?2.61; H, 6.36. Found: C, 72.61; H, 6.42.

***trans*-5,6-Dibenzoyloxy-3,3,5-trimethyl-1-trimethylsilyloxycyclohexene (15).** To 1.52 g (2.2 mmol) of LTB in 40 ml of dry methylene chloride (distilled from P_2O_5) was added 420 mg (2.0 mmol) of **1c** at room temperature. After 20 h of stirring under nitrogen, the reaction mixture was diluted with 50 ml of methylene chloride and washed with 50 ml of water and 50 ml of aqueous sodium bicarbonate. Drying and removal of solvent in vacuo gave crude **15**. Column chromatography (hexane/ethyl acetate, 7:1) gave 140 mg (15%) (hydrolysis noted upon chromatography) of analytically pure **15**: IR (neat) 1720, 1675 cm^{-1}; NMR ($CDCl_3$) δ 0.16 (s, 9 H), 1.07 (s, 3 H), 1.18 (s, 3 H), 1.72 (s, 3 H), 1.98 (d, 1 H, J = 14 Hz), 2.58 (d, 1 H, J = 14 Hz), 5.00 (s, 1 H), 5.91 (s, 1 H), 7.2–8.2 (m, 10 H); mass spectrum *m/e* (rel abundance) 330 (10), 315 (5), 235 (12), 234 (19), 219 (31), 211 (14), 137 (17), 136 (31), 110 (10), 109 (100), 105 (21), metastable 301.

Anal. Calcd for $C_{26}H_{32}O_5Si$: C, 68.99; H, 7.13. Found: C, 69.15; H, 7.22.

Hydrolysis of 15. To 120 mg (0.27 mmol) of **15** in 15 ml of methylene chloride was added 0.25 g (2 mmol) of triethylammonium fluoride. After 1 h at room temperature, the reaction mixture was diluted with 30 ml of methylene chloride, washed with 20 ml of aqueous sodium bicarbonate, dried, and concentrated in vacuo, affording 100 mg (99%) of **4c**, spectrally (IR, NMR) identical with that obtained via LTB treatment of **1c**.

***cis*-6-Benzoyloxy-5-hydroxy-3,3,5-trimethyl-1-trimethylsilyloxycyclohexene (16).** To 1.52 g (2.2 mmol) of LTB in 40 ml of methylene chloride was added 420 mg (2.0 mmol) of **1c** at −18 °C. After 10 min of stirring at room temperature under nitrogen, 2.5 ml of anhydrous methanol was added and the mixture allowed to stir overnight. The reaction mixture was then diluted with 50 ml of methylene chloride and washed with 50 ml of water followed by 50 ml of aqueous sodium bicarbonate. Drying and removal of solvent in vacuo gave crude **16** as a colorless oil. Column chromatography (hexane/ethyl acetate, 7:1) afforded 313 mg (45%) of pure **16**: IR (neat) 3500, 1720, 1665 cm^{-1}; NMR ($CDCl_3$) δ 0.10 (s, 9 H), 1.08 (s, 3 H), 1.22 (s, 3 H), 1.33 (s, 3 H), 1.53 (d, 1 H, J = 14 Hz), 1.90 (d, 1 H, J = 14 Hz), 2.22 (s, 1 H, –OH), 4.86 (s, 1 H), 5.43 (s, 1 H), 7.2–8.2 (m, 5 H); mass spectrum *m/e* (rel abundance) 348 (M^+, 5), 333 (7), 330 (41), 315 (40), 226 (14), 225 (22), 216 (38), 169 (100), 105 (74), metastables 301, 154, 147, 128, 35.

Anal. Calcd for $C_{19}H_{28}O_4Si$: C, 65.48; H, 8.10. Found: C, 65.53; H, 8.23.

Hydrolysis of 16. The same proceduce cited for the hydrolysis of **15** was applied to **16**, affording a 64% yield of pure **10c**. The **10c** so produced had a melting point of 164–165 °C which showed no depression upon admixture (mmp 164–165 °C) with **10c** produced from LTB treatment of **1c**. Further, the spectral properties (IR and NMR) of the **10c** produced by both methods were identical.

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Registry No.—**4a**, 61140-48-5; **4a'**, 61140-49-6; **4b**, 61140-50-9; **4b'**, 61140-51-0; **4c**, 61140-52-1; **4c'**, 61140-53-2; **4d**, 61140-54-3; **4e**, 61140-55-4; **4f**, 61140-56-5; **4g**, 61140-57-6; **8a**, 4884-82-6; **8b**, 61140-58-7; **8c**, 61140-59-8; **9a**, 61140-60-1; **9b**, 61140-61-2; **9c**, 61140-62-3; **10b**, 61140-63-4; **10c**, 61140-64-5; **15**, 61140-65-6; **16**, 61140-66-7; **18**, 61140-67-8; *m*-methylanisole, 100-84-5; *p*-methylanisole, 104-93-8; benzoyl chloride, 98-88-4; lead(IV) benzoate, 7717-48-8.

References and Notes

(1) L. Blanco, P. Amice, and J. M. Conia, *Synthesis*, 194 (1976).
(2) (a) C. Girard and J. M. Conia, *Tetrahedron Lett.*, 3327 (1974); (b) J. M. Conia and C. Girard, *ibid.*, 2767 (1973).
(3) (a) G. M. Rubottom and D. S. Krueger, *Tetrahedron Lett.*, in press; (b) S. Danishefsky and T. Kitahara, *J. Am. Chem. Soc.*, **95**, 7807 (1974); (c) M. E. Jung and C. A. McCombs, *Tetrahedron Lett.*, 2935 (1976); (d) C. Symmes, Jr., and L. D. Quinn, *J. Org. Chem.*, **41**, 238 (1976).
(4) (a) G. M. Rubottom, J. M. Gruber, and G. M. Mong, *J. Org. Chem.*, **41**, 1673 (1976); (b) G. M. Rubottom, J. M. Gruber, and K. Kincaid, *Synth. Commun.*, **6**, 59 (1976).
(5) (a) F. V. Brutcher, Jr., and F. J. Vara, *J. Am. Chem. Soc.*, **78**, 5695 (1956); (b) R. Criegee, *Justus Liebigs Ann. Chem.*, **481**, 263 (1930); (c) R. Criegee and H. Beuker, *ibid.*, **541**, 218 (1939).
(6) This method is an extention of the method developed by H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969).
(7) C. Girard, P. Amice, J. P. Barnier, and J. M. Conia, *Tetrahedron Lett.*, 3329 (1974).
(8) NMR analysis of distilled product.
(9) This phenomenon seems to be general; see ref 1, 3a, 3b, and 7.
(10) C. D. Hurd and P. R. Austin, *J. Am. Chem. Soc.*, **53**, 1543 (1931).
(11) S. Hunig and G. Wehner, *Synthesis*, 180 (1975).
(12) This reaction is analogous to the loss of acetic anhydride to afford α-acetoxy ketones when enol acetates are treated with lead(IV) acetate: (a) R. Criegee, *Angew. Chem.*, **70**, 173 (1958); (b) W. S. Johnson, B. Gastambide, and R. Pappo, *J. Am. Chem. Soc.*, **79**, 1991 (1957).
(13) Comparison of the spectra of pure **4d** and pure trimethylsilyl benzoate with that of the reaction mixture indicated that no other components were present.
(14) See Experimental Section.
(15) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry", Holden-Day, San Francisco, Calif., 1964, Chapter 3.
(16) F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, **31**, 351 (1966).
(17) The water present in trace amounts in the reaction solvent, as well as the water used in workup procedures, effects the transformation described.
(18) Products analogous to **17** have been observed when enones are treated with lead(IV) acetate (LTA); see (a) W. Oppolzer and K. K. Muhalanabis, *Tetrahedron Lett.*, 3411 (1975); (b) T. Sone, S. Terashima, and S. Yamada, *Synthesis*, 725 (1974); (c) Y. Fukuyama and T. Tokoroyama, *Tetrahedron Lett.*, 4869 (1973); (d) L. F. Fieser and M. A. Romero, *J. Am. Chem. Soc.*, **75**, 4716 (1953); (e) S. Seebeck and T. Reichstein, *Helv. Chim. Acta*, **27**, 948 (1944). This transformation apparently involves the intermediacy of enol derivatives of LTA; see (f) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, N.Y., 1967, p 537; (g) R. Criegee in "Oxidations in Organic Chemistry", Part A, K. B. Wiberg, Ed., Academic Press, New York, N.Y., 1965, p 277.
(19) Subsequent to the preparation of most of compounds **1**, it was discovered that DME affords **1** of higher purity upon distillation. Therefore, the use of this solvent is to be recommended.
(20) R. M. Acheson, *J. Chem. Soc.*, 4232 (1956).
(21) A. J. Birch, *J. Chem. Soc.*, 593 (1946).