aqueous HCl, extracted with ether, and then recrystallized from ether–CCl_4; the benzoic acid was shown to contain 0.61% excess ^{18}O, about half of that in phenyl benzoate.[37] These results show that one oxygen atom in $PhCO_2Ph$ is incorporated from $*O_2$ gas, half in each oxygen.

Attempted mass spectral analyses of unreacted benzil were all unsuccessful because of the small parent peak of benzil and difficulty in purification; chromatographic purification was not applicable since the oxygen exchange with water is very facile for the carbonyl oxygen in benzil.

Quantum Yield Determinations. Quantum yields were determined for the photolysis of 5 M benzil in benzene saturated with oxygen (3 mL of solution in a 1-cm Pyrex cell), irradiating at 366 nm with a Hitachi MPF-2A fluorescence spectrometer (Xe lamp). The irradiation was carried to less than 20% conversion, as determined by UV. The incident light intensity was determined by ferrioxalate actinometry.[39] The result was $\phi = 0.039$ as listed in Table IV (run 22).

For the other runs in Table IV, relative yields were determined by irradiating benzene solutions through a Pyrex filter with a Hanovia medium-pressure 450-W Hg lamp using a water cooled merry-go-round for 15 min at room temperature (10 cm distance from the lamp). The solutions were of 4-mL volume in 10-mL Pyrex test tubes fitted with serum caps and were saturated with O_2 or N_2 by flushing through syringe needles. The conversions of benzil were determined after 15 min irradiation. The results in Table IV are mostly means of two or three determinations.

Cross Experiments. To test the possible intermediacy of the benzoyl radical, cross experiments were undertaken between 0.01 M *p*-anisil and 0.01 M benzil under nitrogen. No cross product (*p*-methoxybenzil) was detected by repeated irradiations; the conversion of the benzil was as high as 33–81% and 0.5% of the cross product could easily have been detected.

A similar attempt failed to detect benzil or *p*-anisil from irradiation of a 0.01 M benzene solution of *p*-methoxybenzil under N_2 or O_2. In contrast to the results under O_2, attempted trapping of the benzoyl radical by CCl_4 failed to afford benzoyl chloride under N_2.

Acknowledgment. This work was supported by Public Health Grant No. GM-20080 and NSF Grant No. CHE77-21560.

Registry No. $Ph_2C{=}CMe_2$, 781-33-9; $Ph_2C{=}CH_2$, 530-48-3; $PhCH{=}CHCH_3$, 637-50-3; $Me_2C{=}CMe_2$, 563-79-1; β-methylstyrene, 637-50-3; norbornene, 498-66-8; benzil, 134-81-6; biacetyl, 431-03-8; 1,3-cyclohexadiene, 592-57-4; *trans*-stilbene, 103-30-0.

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[37] It was assumed that no exchange of oxygen between H_2O and phenyl benzoate occurs during the alkaline hydrolysis. This assumption is based on the fact that, although $*O$ exchange occurs in the hydrolysis of $PhCO_2R$ (R = Me or Et),[38] the exchange is only 10–20% of the hydrolysis and that for the present case of the phenyl ester (R = Ph), the exchange should be much slower because PhO^- is a much more effective departing group than MeO^- or EtO^-.

[38] Samuel, D.; Silver, B. L. *Adv. Phys. Org. Chem.* **1965**, *3*, 157.

[39] Calvert, J. G.; Pitts, J. N., Jr. "Photochemistry"; Wiley: New York, 1966, p 783.

Oxidation of Alkyl Trimethylsilyl Ketene Acetals with Lead(IV) Carboxylates

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Received March 3, 1982

Alkyl trimethylsilyl ketene acetals generated from either esters or lactones react with lead(IV) acetate (LTA) or lead(IV) benzoate (LTB) to afford useful yields of the corresponding α-carboyloxy esters and α-carboyloxy lactones. Yields of the reaction products are optimized by use of the appropriate solvent (methylene chloride or benzene) during oxidation. Alkyl groups such as methyl, ethyl, and *tert*-butyl are all compatible with the procedure, and lactones containing five-, six-, and seven-membered rings give good yields of oxidation products.

The direct oxygenation of ester enolates,[1] treatment of ester enolates with MoOPh ($MoO_5{\cdot}py{\cdot}HMPA$),[2] and the treatment of alkyl trimethylsilyl ketene acetals with *m*-chloroperbenzoic acid (MCPBA)[3] or singlet oxygen[4] have been used as methods for the placement of oxygen on the α-carbon adjacent to a carboxy unit. We have previously reported that enol silyl ethers react smoothly with lead(IV) carboxylates to afford the corresponding α-acetoxy[5] and α-benzoyloxy[6] carbonyl compounds in high yield. Although accounts in the literature concerned with the lead(IV) acetate (LTA) oxidation of esters do exist,[7] the inability of esters to enolize readily under the conditions normally used for LTA oxidation places a severe limitation on this method of α-position functionalization. This being the case, we felt that preformed ester enols or analogues of these species should react rapidly with lead(IV) carboxylates to afford α-carboyloxy esters. Further, it might also be possible to modify this approach to give a useful synthetic method for the preparation of α-carboyloxy lactones.

We report here that alkyl trimethylsilyl ketene acetals **1** or **2**, derived from esters and lactones, respectively, react with either LTA or lead(IV) benzoate (LTB). When the crude reaction product is treated with triethylammonium

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[1] See, for instance: Konen, D. A.; Silbert, L. S.; Pfeffer, P. E. *J. Org. Chem.* **1975**, *40*, 3253–3258.

[2] Vedejs, E.; Engler, D. A.; Telschow, J. E. *J. Org. Chem.* **1978**, *43*, 188–196.

[3] (a) Rubottom, G. M.; Marrero, R. *Synth. Commun.* **1981**, *11*, 505–511. (b) Rubottom, G. M.; Marrero, R. *J. Org. Chem.* **1975**, *40*, 3783–3784.

[4] (a) Wasserman, H. H.; Lipshutz, B. H.; Tremper, A. W.; Wu, J. S. *J. Org. Chem.* **1981**, *46*, 2991–2999. (b) Adam, W.; del Fierro, J.; Quiroz, F.; Yany, F. *J. Am. Chem. Soc.* **1980**, *102*, 2127–2128.

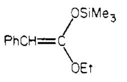
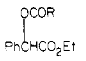
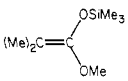
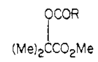
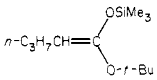
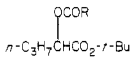
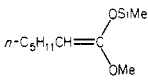
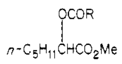
[5] (a) Rubottom, G. M.; Marrero, R.; Gruber, J. M. *Tetrahedron* **1983**, *39*, 861–865. (b) Rubottom, G. M.; Gruber, J. M.; Kincaid, K. *Synth. Commun.* **1976**, *6*, 59–62.

[6] (a) Rubottom, G. M.; Gruber, J. M. *J. Org. Chem.* **1977**, *42*, 1051–1056. (b) Rubottom, G. M.; Gruber, J. M.; Mong, G. M. *J. Org. Chem.* **1976**, *41*, 1673–1674. (c) See also: Asaoka, M.; Yanagida, N.; Takei, H. *Tetrahedron Lett.* **1980**, *21*, 4611–4614. Asaoka, M.; Yanagida, N.; Sugimura, N.; Takei, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1061–1064.

[7] See: Criegee, R. In "Oxidation in Organic Chemistry"; Wiberg, K. B., Ed; Academic Press: New York, 1965; Part A, pp 277–366.

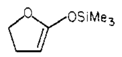
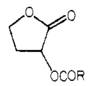
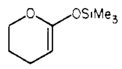
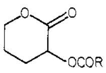
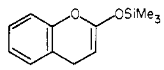
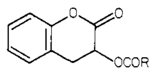
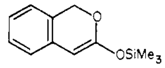
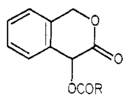
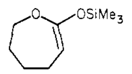
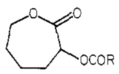
0022-3263/83/1948-4940$01.50/0

Table I. Lead(IV) Carboxylate Oxidation of Alkyl Trimethylsilyl Ketene Acetals 1

starting compd	3	% yield of isolated 3	
		R = Me[b,d]	R = Ph[c,d]
 **1a**[a]		75 (**3a**)	92 (**3b**)
 **1b**		81 (**3c**)	69 (**3d**)
 **1c**[a]		85 (**3e**)	
 **1d**[a]		92 (**3f**)	85 (**3g**)

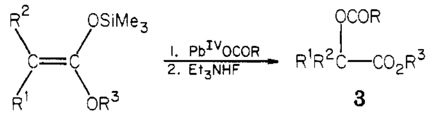
[a] *E/Z* mixture; see Experimental Section. [b] LTA as oxidant. [c] LTB as oxidant. [d] Methylene chloride used as solvent during oxidation.

Table II. Lead(IV) Carboxylate Oxidation of Alkyl Trimethylsilyl Ketene Acetals 2

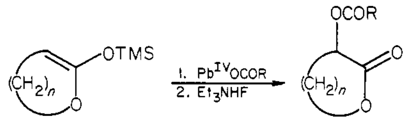
starting compd	4	% yield of isolated 4	
		R = Me[a]	R = Ph[b]
 **2a**		47[c] (**4a**)	31[c] (**4b**)
 **2b**		66[d] (**4c**)	50[c] (**4d**)
 **2c**		38[d,e] (**4e**)	57[d,e] (**4f**)
 **2d**		57[d] (**4g**)	52[c] (**4h**)
 **2e**		82[d] (**4i**)	78[d] (**4j**)

[a] LTA as oxidant. [b] LTB as oxidant. [c] Benzene used as solvent during oxidation. [d] Methylene chloride used as solvent during oxidation. [e] Coumarin isolated as a major by-product; see experimental.

fluoride, the corresponding α-carboyloxy esters **3** or α-carboyloxy lactones **4** are produced in good yields (eq 1 and 2).

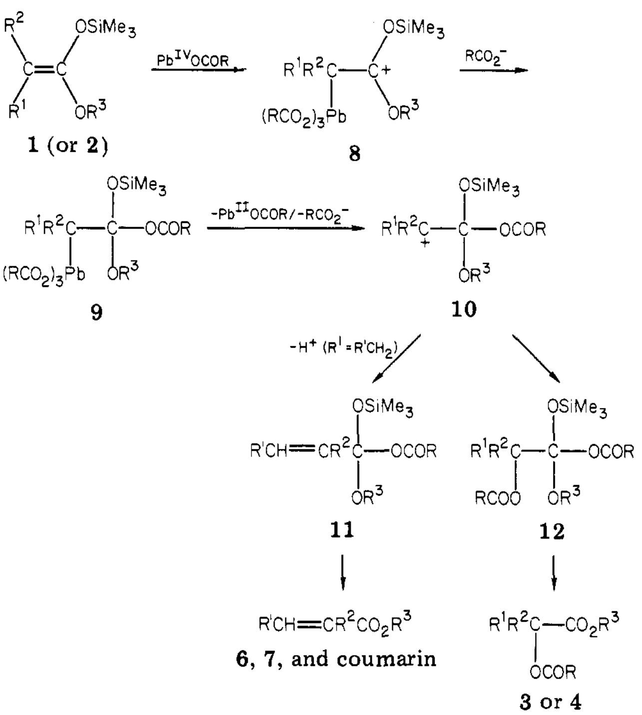


1 3 (1)

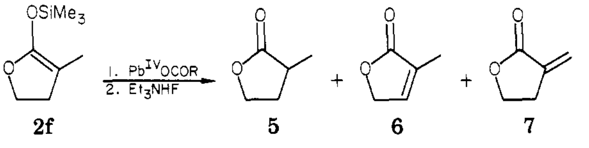


2 4 (2)

Scheme I



A number of examples of the transformation of **1** into **3** are noted in Table I. With both α-acetoxy esters and α-benzoyloxy esters, the yields generated by the current method are uniformly high. NMR analysis of the crude reaction products obtained from the LTB reactions with **1a,b,d** revealed only the corresponding α-benzoyloxy esters prior to final purification steps. Further, the use of methyl, ethyl, or *tert*-butyl in the alkoxy portion of **1** is compatible with the procedure. Table II affords examples of the method as applied to the transformation of **2** into **4**. The oxidation of **2** leads, in general, to acceptable yields of **4**; however, the proper choice of solvent is crucial in these cases. Thus, in the LTA oxidation of **2a** and the LTB oxidation of **2a,b,d**, it was found that benzene was superior to methylene chloride. The use of methylene chloride, employed exclusively in the oxidation of **1**, resulted in the formation of mixtures when applied to the oxidation of **2**. The mixtures contained, for the most part, the lactone corresponding to **2** and α,β-unsaturated lactones. In the oxidation of **2c**, coumarin was isolated as a major byproduct (42% with LTA; 31% with LTB) regardless of the solvent, and **2f** gave no α-carboyloxy lactone but rather mixtures of **5**–**7** (eq 3).[8] The conversion of **2** back to the starting lactone was also observed previously when methylene chloride was used as solvent in the MCPBA oxidation of **2**.[3a]



(3)

	5	6	7
LTA:	52%	37%	11%
LTB:	17%	58%	25%

A mechanistic picture consistent with the above results is outlined in Scheme I. Attack of Pb^{IV}OCOR on the alkyl trimethylsilyl ketene acetal **1** gives carbocation **8** which is trapped by carboxylate to produce **9**. This sequence finds analogy in the reaction of simple alkenes with LTA.[9] Loss

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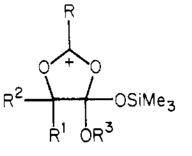
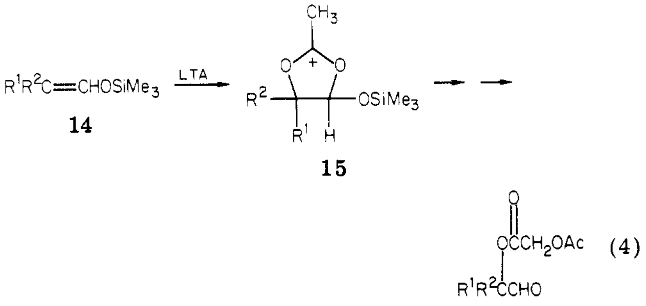
(8) See Experimental Section.

of lead(II) carboxylate from **9** results in the formation of a new carbocation, **10**. Deprotonation of **10**, in turn, affords **11**, the direct precursor of elimination products such as **6** and **7** (i.e., the oxidation of **2f**). The appearance of coumarin from the oxidation of **2c** can also be rationalized by this route, although, in the case of the LTA reaction, some coumarin resulted from the decomposition of the primary reaction product **4e**.[8] Trapping of **10** by carboxylate gives **12** which is then transformed into **3** or **4**.

The partitioning of **10** between **11** and **12** most probably reflects the ease of carboxylate transfer via dioxolenium ions such as **13**. Intermediates analogous to **13** were noted in the LTA oxidation of aldehyde enol silyl ethers **14** (eq 4).[5a] In these studies it was found that the intermediate **15** gave rise to products **16**. The reluctance of **2a** and **2f** toward dioxolenium ions accounts for the low yields of **4** production in the former case and to the formation of **6** and **7** in the oxidation of the latter. The same phenomenon has also been observed in the products of the LTA and LTB oxidations of the enol silyl ethers derived from medium-ring ketones. In these cases, the relative amounts of α-carboyloxy ketone and α,β-unsaturated ketone formed can be related to the intrinsic ring strain found in the medium-size ring and thus to the relative ability of each system to form dioxolenium ions.[10]

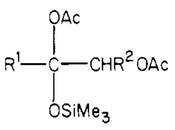


13



16

Evidence for the formation of intermediates such as **11** and **12** comes from our prior observation of the production of **17** from the oxidation of the appropriate enol silyl ethers.[5b,10b] The use of fluoride ion in the workup procedure in the current investigation simply makes sure that the desired esters will be the final products obtained. It is possible that thermal loss of RCO_2SiMe_3 is also occurring, but this point was not investigated.



17

In summary, the treatment of alkyl trimethylsilyl ketene acetals **1** and **2** with either LTA or LTB affords a high-yield method for the preparation of the corresponding α-carboyloxy esters **3** and α-carboyloxy lactones **4**. For the oxidation of **1** methylene chloride is generally the solvent of choice, while for **2** the use of benzene as solvent proves advantageous. We are continuing our studies on the use of enol silyl ethers in the development of new organic reactions.

Experimental Section

General Methods. Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. Proton nuclear magnetic resonance (NMR) spectra were recorded at 60 MHz on a Varian Anaspect EM 360 spectrometer with Me_4Si as an internal standard. Infrared (IR) spectra were obtained on a Perkin-Elmer 621 grating infrared spectrometer, and low-resolution mass spectra (MS) were obtained on a Hitachi Perkin-Elmer RMU 6E instrument at 15 eV. Elemental microanalyses were determined with a Perkin-Elmer Model 240 elemental analyzer. For column chromatography, Woelm silica gel (0.032–0.063 mm, ICN Pharmaceuticals GmbH & Co.) was used. For the oxidation reactions, commercial LTA (Alfa-Ventron) was dried by the azeotropic removal of acetic acid with benzene and was then used with no further purification. LTB (mp 186–187 °C dec) was prepared by the method of Hurd and Austin from commercial LTA.[11] Triethylammonium fluoride was obtained as a hygroscopic white solid by the procedure of Hünig.[12] Anhydrous magnesium sulfate was used as drying agent.

Synthesis of Alkyl Trimethylsilyl Ketene Acetals 1 and 2. General Procedure. The procedure described is a modification of the method presented by Ainsworth.[13] To 5.10 g (49.4 mmol) of diisopropylamine in 100 mL of dry THF ($LiAlH_4$) at −15 °C (ice/methanol) under an atmosphere of nitrogen was added 20.6 mL (49.0 mmol) of *n*-butyllithium (2.4 M in hexane). After the mixture was cooled to −78 °C (dry ice/ethanol), 45.4 mmol of neat ester or lactone was added slowly with stirring. When the addition was complete, the resulting mixture was stirred for an additional 10 min at which point 10 mL of Me_3SiCl was rapidly added to the mixture. Stirring was then continued for 3 h during which time the reaction vessel gradually warmed to room temperature. Solvent was then removed in vacuo by rotoevaporation, and then ca. 75 mL of pentane was added to the residue. Rapid filtration and removal of the solvent in vacuo yielded crude **1** or **2**. Short-path distillation at reduced pressure then gave pure **1** or **2**.

Alkyl Trimethylsilyl Ketene Acetals 1a–d. The physical properties for **1a** (85%), **1b** (83%), **1c** (75%), and **1d** (82%) are given in ref 3a.

5-Oxa-1-(trimethylsiloxy)cyclopentene (2a): 98%; bp 42–44 °C (10 mm); IR (neat) 1683 cm^{-1} [lit.[14] IR (neat) 1685 cm^{-1}]; NMR (CCl_4) δ 0.16 (s, 9 H), 2.51 (d of t, 2 H, $J = 2, 9$ Hz), 3.50 (t, 1 H, $J = 2$ Hz), 4.17 (t, 2 H, $J = 9$ Hz); MS, *m/z* (relative intensity) 158 (M^+, 100), 157 (31), 103 (40), 73 (59).

6-Oxa-1-(trimethylsiloxy)cyclohexene (2b): 60%; bp 62–65 °C (10 mm); IR (neat) 1688 cm^{-1}; NMR (CCl_4) δ 0.18 (s, 9 H), 1.50–2.26 (m, 4 H), 3.70 (t, 1 H, $J = 4$ Hz), 4.02 (t, 2 H, $J = 4.5$ Hz); MS, *m/z* (relative intensity) 172 (M^+, 100), 171 (24). Anal. Calcd for $C_8H_{16}O_2Si$: C, 55.77; H, 9.36. Found: C, 55.50; H, 9.47.

2-(Trimethylsiloxy)-4*H*-1-benzopyran (2c): 83%; bp 96–100 °C (1.3 mm); IR (neat) 1708 cm^{-1}; NMR (CCl_4) δ 0.23 (s, 9 H), 3.40 (d, 2 H, $J = 4$ Hz), 3.91 (t, 1 H, $J = 4$ Hz), 6.6–7.1 (m, 4 H); MS, *m/z* (relative intensity) 220 (M^+, 100), 219 (64). Anal. Calcd for $C_{12}H_{16}O_2Si$: C, 65.41; H, 7.32. Found: C, 65.57; H, 7.09.

3-(Trimethylsiloxy)-1*H*-2-benzopyran (2d): 64%; mp 35–35.5 °C; IR (Nujol) 1650 cm^{-1}; NMR (CCl_4) δ 0.28 (s, 9 H), 4.93 (s, 1 H), 5.08 (s, 2 H), 6.7–7.3 (m, 4 H); MS, *m/z* (relative intensity) 220 (M^+, 100), 219 (8). Anal. Calcd for $C_{12}H_{16}O_2Si$: C, 65.41; H, 7.32. Found: C, 65.48; H, 7.33.

7-Oxa-1-(trimethylsiloxy)cycloheptene (2e): 60%; bp 57–60 °C (2.5 mm); IR (neat) 1680 cm^{-1}; NMR (CCl_4) δ 0.16 (s, 9 H), 1.36–2.18 (m, 6 H), 3.90 (t, 2 H, $J = 5$ Hz), 3.92 (t, 1 H, $J = 5$ Hz); MS, *m/z* (relative intensity) 186 (M^+, 100). Anal. Calcd for

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[9] See: Moriarty, R. M. In "Selective Organic Transformations"; Thyagarajan, B. S., Ed.; Wiley-Interscience: New York, 1972; Vol. II, pp 183–237.

[10] (a) See: Rubottom, G. M.; Mott, R. C.; Juve, H. D., Jr. *J. Org. Chem.* 1981, *46*, 2717–2721. (b) Rubottom, G. M., unpublished results.

[11] Hurd, C. D.; Austin, P. R. *J. Am. Chem. Soc.* **1931**, *53*, 1543–1547.

[12] Hünig, S.; Wehner, G. *Synthesis* **1975**, 180–182.

[13] Ainsworth, C.; Chen, F.; Kuo, Y. N. *J. Organomet. Chem.* **1972**, *46*, 59–71.

[14] Rasmussen, J. K.; Hassner, A. *J. Org. Chem.* **1974**, *39*, 2558–2561.

$C_9H_{18}O_2Si$: C, 58.02; H, 9.74. Found: C, 58.03; H, 9.70.

2-Methyl-5-oxa-1-(trimethylsiloxy)cyclopentene (2f): 80%; bp 148–150 °C; IR (neat) 1678 cm^{-1}; NMR (CCl_4) δ 0.20 (s, 9 H), 1.50 (m, 3 H), 2.50 (br t, 2 H, J = 9 Hz), 4.15 (t, 2 H, J = 9 Hz); MS, m/z (relative intensity) 172 (M^+, 100), 171 (35). Anal. Calcd for $C_8H_{16}O_2Si$: C, 55.77; H, 9.36. Found: C, 55.93; H, 9.15.

LTA Oxidation of Alkyl Trimethylsilyl Ketene Acetals 1 and 2. General Procedure. To a solution of 0.98 g (2.2 mmol) of acetic acid free LTA in 30 mL of the appropriate solvent (methylene chloride or benzene) under 1 atm of nitrogen was added 2.0 mmol of **1** or **2**. During the addition the solution was cooled (ice/methanol bath) and the reaction mixture stirred. After the addition was complete, stirring was continued for 30 min at room temperature. The mixture was then filtered and the filtrate treated with 0.73 g (6.0 mmol) of triethylammonium fluoride. After 5–10 h of stirring at room temperature, the reaction mixture was diluted with an additional 50 mL of solvent (methylene chloride or benzene), and the organic portion was sequentially washed with 20 mL of 50% aqueous sodium bicarbonate, 20 mL of 1.5 N hydrochloric acid, and 20 mL of 50% aqueous sodium bicarbonate. The organic layer was dried, and, after filtration, the solvent was removed in vacuo to afford crude **3** or **4**, respectively. Purification of crude **3** or **4** by distillation, crystallization, column chromatography, or sublimation gave pure **3** or **4**.

Ethyl 2-acetoxy-2-phenylacetate (3a): 75%, oxidation of **1a** in methylene chloride; bp 75 °C (1 mm), molecular distillation; n^{21}_{D} 1.4920 (lit.[15] n^{25}_{D} 1.4888); IR (neat) 1740 cm^{-1} (br); NMR (CCl_4) δ 1.20 (t, 3 H, J = 6 Hz), 2.15 (s, 3 H), 3.13 (q, 2 H, J = 6 Hz), 5.72 (s, 1 H), 7.32 (s, 5 H); MS, m/z (relative intensity) 222 (M^+, 26), 184 (54), 176 (64), 149 (100), 107 (99).

Methyl 2-acetoxy-2-methylpropanoate (3c): 81%, oxidation of **1b** in methylene chloride; bp 75 °C (12 mm), molecular distillation, followed by preparative GLC (5% Se-30 on Anakrom ABS 110-120, 9 ft × 0.25 in.) at 110 °C [lit.[16] bp 76–77 °C (18 mm)]; IR (neat) 1730 cm^{-1} (br); NMR (CCl_4) δ 1.48 (s, 6 H), 1.98 s, 3 H), 3.64 (s, 3 H); MS, m/z (relative intensity) 160 (M^+, 1), 101 (100), 43 (48).

***tert*-Butyl 2-acetoxypentanoate (3e)**: 85%, oxidation of **1c** in methylene chloride; purified by column chromatography on silica gel with a solvent gradient of hexane-hexane/chloroform (5/1); both GLC and molecular distillation resulted in the decomposition of **3e**; IR (neat) 1746 cm^{-1}; NMR ($CDCl_3$) δ 0.60–2.10 (m, 7 H), 1.48 (s, 9 H), 2.11 (s, 3 H), 4.82 (t, 1 H, J = 6 Hz); MS, m/z (relative intensity) 143 (M^+ – 2-methylpropene, 23), 115 (36), 57 (100), 43 (67), metastable 92.4. Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 61.33; H, 9.61.

Methyl 2-acetoxyheptanoate (3f): 92%, oxidation of **1d** in methylene chloride; bp 75 °C (0.3 mm) molecular distillation; IR (neat) 1750 cm^{-1} (br); NMR (CCl_4) δ 0.68–2.05 (m, 11 H), 2.10 (s, 3 H), 3.65 (s, 3 H), 4.83 (d of d, 1 H, J = 6.5, 5 Hz); MS, m/z (relative intensity) 202 (M^+, <1), 143 (100), 43 (55). Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.42; H, 8.97. Found: C, 59.20; H, 9.22.

α-Acetoxy-γ-butyrolactone (4a): 47%, oxidation of **2a** in benzene; bp 50 °C (1 mm) molecular distillation; IR (neat) 1780 cm^{-1} (br), 1750 cm^{-1}; NMR (CCl_4) δ 1.78–2.89 (m, 2 H), 2.15 (s, 3 H), 4.04–4.51 (m, 2 H), 5.18–5.52 (m, 1 H); MS, m/z (relative intensity) 144 (M^+, 3), 43 (100). Anal. Calcd for $C_6H_8O_4$: C, 50.00; H, 5.59. Found: C, 50.15; H, 5.64.

α-Acetoxy-δ-valerolactone (4c): 66%, oxidation of **2b** in methylene chloride; mp 31.5–32 °C, purified by column chromatography on silica gel with a hexane–ether solvent gradient; IR (Nujol) 1775 cm^{-1} (br); NMR (CCl_4) δ 1.82–2.47 (m, 4 H), 2.16 (s, 3 H), 4.20–4.50 (m, 2 H), 5.08–5.47 (m, 1 H); MS, m/z (relative intensity) 158 (M^+, 3), 86 (52), 72 (62), 71 (66), 43 (100). Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 53.18; H, 6.41.

α-Acetoxydihydrocoumarin (4e) and Coumarin. NMR analysis of crude reaction product (oxidation of **2c** in methylene chloride) indicated a mixture of dihydrocoumarin (20%), **4e** (38%), and coumarin (42%). Crystallization with pentane gave pure coumarin, while repeated column chromatography on silica gel (hexane–ether solvent gradient) gave pure **4e**. During the separation a great deal of decomposition of **4e** into coumarin took place.

α-Acetoxydihydrocoumarin (4e): IR (neat) 1780, 1750 cm^{-1}; NMR (CCl_4) δ 2.17 (s, 3 H), 3.08–3.13 (overlapping d of d, 2 H, J = 9, 10 Hz), 5.25–5.60 (d of d, 1 H, J = 9, 10 Hz), 6.8–7.4 (m, 4 H); MS, m/z (relative intensity) 206 (M^+, 2), 148 (100), 146 (50). Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.08; H, 4.89. Found: C, 63.94; H, 4.92.

Coumarin: mp 67–68 °C (lit.[17] mp 67 °C).

α-Acetoxyisochromanone (4g): 57%, oxidation of **2d** in methylene chloride; mp 95–96 °C (sublimation); IR (Nujol) 1770, 1743 cm^{-1}; NMR ($CDCl_3$) δ 2.34 (s, 3 H), 5.31 (br s, 2 H), 6.05 (s, 1 H), 7.20–7.52 (m, 4 H); MS, m/z (relative intensity) 206 (M^+, 14), 164 (100). Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.08; H, 4.89. Found: C, 64.04; H, 5.09.

α-Acetoxy-ϵ-caprolactone (4i): 82%, oxidation of **2e** in methylene chloride; 66–67.5 °C (pentane); IR (neat) broad band with shoulders at 1762, 1736 cm^{-1}; NMR (CCl_4) δ 1.40–2.30 (m, 6 H), 2.06 (s, 3 H), 4.00–4.40 (m, 2 H), 4.89–5.38 (m, 1 H); MS, m/z (relative intensity) 142 (M^+, <1), 86 (66), 85 (81), 43 (100). Anal. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 7.02. Found: C, 56.01; H, 6.90.

LTA Oxidation of 2-Methyl-5-oxa-1-(trimethylsiloxy)-cyclopentene (2f). Oxidation of **2f** gave a quantitative yield of a mixture of α-methyl-γ-butyrolactone (**5**), α-methyl-Δ^{α}-butenolide (**6**), and α-methylene-γ-butyrolactone (**7**). GLC on a 12% SE-52 column at 122 °C revealed two peaks with relative retention times of 1.00 and 1.21. The relative areas of the two peaks were 52:48. The major peak was collected and identified as **5** by comparison of the GLC retention time and NMR spectrum with those of authentic **5** (Aldrich). Collection of the smaller peak and NMR analysis revealed a 77:33 mixture of **6**[18] and **7**.[19] The relative yields of **5**–**7** were therefore 52%, 37%, and 11%. Product ratios were similar when the oxidation of **2f** was carried out by using either methylene chloride or benzene as the solvent.

LTB Oxidation of Alkyl Trimethylsilyl Ketene Acetals 1 and 2. General Procedure. The procedure outlined above for the LTA oxidation of **1** and **2** was repeated by using LTB in conjunction with the appropriate solvent (either methylene chloride or benzene) to afford **3** and **4**.

Ethyl 2-(benzoyloxy)-2-phenylacetate (3b): 92%, oxidation of **1a** in methylene chloride; mp 26–28 °C (petroleum ether (bp 30–60 °C) after molecular distillation at 160 °C (0.25 mm)) [lit.[15] mp 29–30 °C].

Methyl 2-(benzoyloxy)-2-methylpropanoate (3d): 69%, oxidation of **1b** in methylene chloride; bp 100 °C (5.0 mm) molecular distillation; n^{23}_{D} 1.4952 (lit.[16] n^{20}_{D} 1.4992); IR (neat) 1748, 1718 cm^{-1}; NMR (CCl_4) δ 1.62 (s, 6 H), 3.64 (s, 3 H), 7.2–8.2 (m, 5 H); MS, m/z (relative intensity) 222 (M^+, 25), 163 (64), 105 (100).

Methyl 2-(benzoyloxy)heptanoate (3g): 85%, oxidation of **1d** in methylene chloride; bp 150 °C (0.05 mm) molecular distillation; IR (neat) 1758, 1725 cm^{-1}; NMR (CCl_4) δ 0.6–2.2 (m, 11 H), 3.73 (s, 3 H), 5.17 (t, 1 H, J = 5 Hz), 7.2–8.2 (m, 5 H); MS, m/z (relative intensity) 264 (M^+, 6), 105 (100). Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.12; H, 7.77.

α-(Benzoyloxy)-γ-butyrolactone (4b): 31%, oxidation of **2a** in benzene; mp 92–93 °C (sublimation after preparative TLC on silica gel using chloroform as eluent); IR (KBr) 1785, 1725 cm^{-1}; NMR (CCl_4) δ 2.1–3.1 (m 2 H), 4.20–4.60 (m, 2 H), 5.55 (t, 1 H, J = 5 Hz), 7.2–8.2 (m, 5 H); MS, m/z (relative intensity) 206 (M^+, 18), 105 (100) Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.08; H, 4.89. Found: C, 63.72; H, 5.17.

α-(Benzoyloxy)-δ-valerolactone (4d): 50%, oxidation of **2b** in benzene; mp 98–99 °C (ether–pentane after Kugelrohr distillation); IR (KBr) 1750, 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.95–2.50 (m, 4 H), 4.42 (br t, 2 H, J = 6 Hz), 5.40–5.78 (m, 1 H), 7.3–8.2 (m, 5 H); MS, m/z (relative intensity) 220 (M^+, 16), 105 (100).

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Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.44; H, 5.50. Found: C, 65.44; H, 5.37.

α-(Benzoyloxy)dihydrocoumarin (4f) and Coumarin. Oxidation of **2c** in methylene chloride; sequential crystallization of the crude reaction mixture with ether and then with ether–petroleum ether (bp 30–60 °C) afforded pure **4f** and coumarin.

α-(Benzoyloxy)dihydrocoumarin (4f): 57%; mp 143.5–144.5 °C (ether); IR (KBr) 1775, 1715 cm^{-1}; NMR ($CDCl_3$) δ 3.24–3.50 (overlapping d of d, 2 H, *J* = 9, 11 Hz), 5.62–5.99 (d of d, 1 H, *J* = 9, 11 Hz), 6.93–8.26 (m, 9 H); MS, *m/z* (relative intensity) 268 (M^+, 1), 146 (100), 105 (34). Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.42; H, 4.38.

Coumarin: 31%; mp 67–68 °C [ether–petroleum ether (bp 30–60 °C)]; IR, NMR, and MS characteristics are identical with those of the coumarin isolated from the reaction of **2c** with LTA (see above).

α-(Benzoyloxy)isochromanone (4h): 52%, oxidation of **2d** in benzene; 88–89 °C [crystallized from a glass after Kugelrohr distillation at 141–150 °C (0.2 mm)]; IR (neat) 1765, 1730 cm^{-1}; NMR ($CDCl_3$) δ 5.18–5.70 (AB d of d, 2 H, *J* = 14 Hz), 6.60 (s, 1 H), 7.18–8.41 (m, 9 H); MS, *m/z* (relative intensity) 268 (M^+, 4), 105 (100). Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.62; H, 4.72.

α-(Benzoyloxy)-ε-caprolactone (4j): 78%, oxidation of **2e** in methylene chloride; mp 125–126 °C (ether–chloroform); IR (KBr) 1740, 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.40–2.47 (m, 6 H), 4.02–4.60 (m, 2 H), 5.30–5.73 (m, 1 H), 7.20–8.23 (m, 5 H); MS, *m/z* (relative intensity) 234 (M^+, 13), 105 (100). Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.91; H, 5.82.

LTB Oxidation of 2f. Oxidation of **2f** gave a quantitative yield of a mixture of **5** (17%), **6** (58%), and **7** (25%). Product distribution was determined as described above for the LTA oxidation of **2f**. Similar results were obtained by using either methylene chloride or benzene as the solvent during the oxidation.

Acknowledgment. We thank the Research Council of the University of Idaho and acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Registry No. (*E*)-**1a**, 78935-57-6; (*Z*)-**1a**, 78935-61-2; **1b**, 31469-15-5; (*E*)-**1c**, 78935-58-7; (*Z*)-**1c**, 78935-62-3; (*E*)-**1d**, 78935-59-8; (*Z*)-**1d**, 78935-63-4; **2a**, 51425-66-2; **2b**, 71309-70-1; **2c**, 87532-03-4; **2d**, 87532-04-5; **2e**, 87532-05-6; **2f**, 87532-06-7; **3a**, 61624-15-5; **3b**, 73981-13-2; **3c**, 57865-37-9; **3d**, 87532-07-8; **3e**, 87532-08-9; **3f**, 56196-51-1; **3g**, 87532-09-0; **4a**, 19405-99-3; **4b**, 25600-23-1; **4c**, 87532-10-3; **4d**, 87532-11-4; **4e**, 87532-12-5; **4f**, 87532-13-6; **4g**, 87532-14-7; **4h**, 87532-15-8; **4i**, 87532-16-9; **4j**, 87532-17-0; **5**, 1679-47-6; **6**, 22122-36-7; **7**, 547-65-9; LTA, 546-67-8; LTB, 7717-48-8; coumarin, 91-64-5.

Thermolysis of 4-Methyl-4-phenylmalonyl Peroxide: A New Oxygen Dependent Chemiluminescent Reaction

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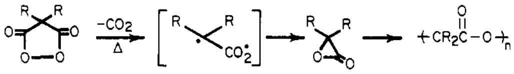
Received July 6, 1983

Thermolysis of 4-methyl-4-phenylmalonyl peroxide in acetonitrile is accelerated by electron donors, such as perylene. When both the perylene and oxygen are present in solution, the reaction gives acetophenone and a small amount of light. Investigation of the mechanism of light generation reveals that it involves formation and fragmentation of a tetraoxide. The chemically initiated electron-exchange luminescence mechanism appears to be responsible for light generation.

Extensive research over the past 50 years has revealed that nearly all of the known chemiluminescent reactions of organic compounds in solution involve the conversion of a peroxide linkage to a carbonyl group.[1] The molecular basis of this selectivity is tied strongly to the energy required to generate light. Only reactions capable of releasing at least 40 kcal/mol of energy can generate visible light, and few reactions other than peroxide fragmentations can satisfy this requirement.

Complementing the requirement of energy sufficiency is a mechanistic requirement for chemiluminescence. There must be a path that directs the potential energy stored in the peroxide toward formation of an electronically excited state of a product. Two such paths have been found to operate.[1] The first is a unimolecular reaction of a peroxide, typically proceeding through a biradical, to generate directly an excited product. The second is the sequence of reactions we have identified as chemically initiated electron-exchange luminescence (CIEEL).[2]

For reasons we have detailed previously,[3] malonyl peroxides possess several characteristics that may make them efficient sources of chemiluminescence by the CIEEL path. The thermal and photochemical properties of malonyl peroxides were first investigated by Adam and his coworkers,[4] who found that simple alkyl-substituted examples decarboxylate and then cyclize to α-lactones. The lactones typically are not isolable but go on to form polyesters. This sequence of reactions is illustrated in eq 1.



(1)

In order for malonyl peroxides to generate light efficiently by the CIEEL path, their reaction must be catalyzed by electron donation from an activator (ACT). Also, to satisfy the energy requirement, the biradical shown in eq 1 must be diverted away from formation of α-lactone toward a more exothermic path. Our recently reported study of the thermal chemistry of cyclopropyl-substituted malonyl peroxides showed that the first requirement is easily met. However, the cyclization of the biradical to the α-lactone is apparently faster than even the rearrangement of the cyclopropylcarbinyl radical to the allylcarbinyl radical.[5] Thus, easily detected but very inefficient

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