Photoaddition Reactions of Silyl Ketene Acetals with Aromatic Carbonyl Compounds: A New Procedure for β-Hydroxyester Synthesis†

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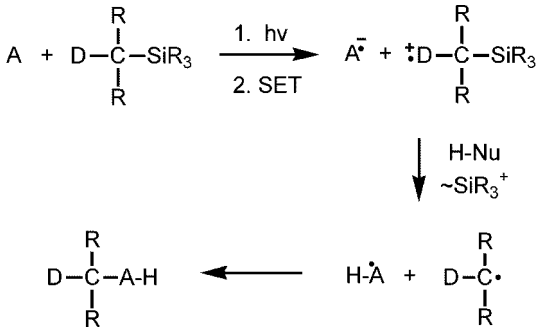
Photochemical reactions of aromatic carbonyl compounds with silyl ketene acetals have been explored. Irradiation of acetonitrile or benzene solutions containing aryl aldehydes or ketones in the presence of silyl ketene acetals is observed to promote formation of β-hydroxyester, 2,2-dioxyoxetane and 3,3-dioxyoxetane products. The ratios of these photoproducts, which arise by competitive single electron transfer (SET) and classical Paterno-Buchi mechanistic pathways, is found to be dependent on the degree of methyl-substitution on the vinyl moieties of the ketene acetals in a manner which reflects expected alkyl substituent effects on the oxidation potentials of these electron rich donors. An analysis of the product distribution arising by irradiation of a solution containing butyrophenone (**6**) and the silyl ketene acetal **9**, derived from methyl isobutyrate, provides an estimate of the rate constants for the competitive Norrish type II, SET and Paterno-Buchi processes occuring. Finally, sequences involving silyl ketene acetal-aryl aldehyde or ketone photoaddition followed by 2,2-dioxyoxetane hydrolysis represent useful procedures for Claisen-condensation type, β-hydroxyester synthesis.

Key Words : Photoaddition reaction, Silyl ketene acetals, Aromatic carbonyl compound, β-Hydroxyester, Single electron transfer photochemistry

Introduction

The operation of sequential single electron transfer (SET)-desilylation pathways in the photochemistry of acceptor/α-silyl electron donor systems is now well-documented.[1] Product formation in photochemical reactions which follow this mechanistic course is typically highly selective owing to the fact that transfer of a silyl group from an α-silyl cation radical intermediate to a silophile often occurs more rapidly than other possible α-heterolytic fragmentation modes such as base induced deprotonation.[2] Consequently, sequential SET-desilylation can serve as an efficient and regioselective pathway leading to carbon-centered radical generation and, eventually, to carbon-carbon bond formation (Scheme 1).[1-7] Examples of SET-promoted excited state processes in which intermediate cation radical desilylation serves as the driving force are found in the photochemistry of iminium salts,[3] cyanoarenes,[4] conjugated-cyclohexenones,[5] ortho-quinones[6] and phthalimides.[7]

Our interests in this area of photochemistry has encouraged a recent exploration probing the photochemical reactivity of aryl aldehyde and ketone/silyl ketene acetal systems. Consideration of the chemical and redox properties of excited states of aromatic carbonyl compounds and ground states of silyl ketene acetals suggests that these substrate

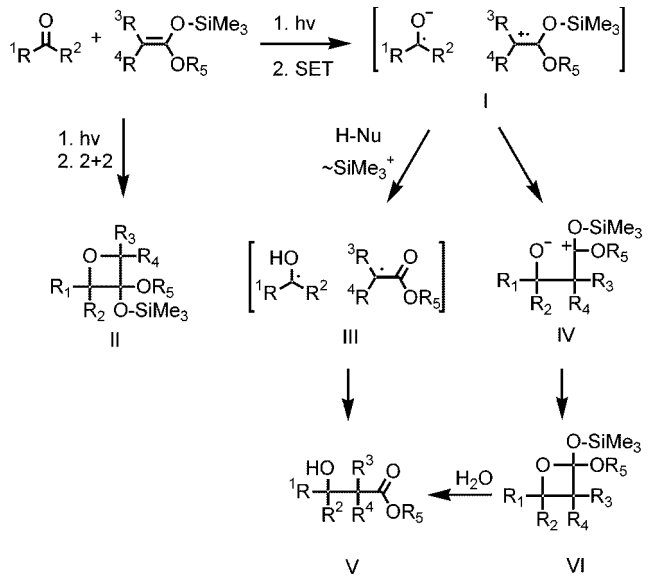


Scheme 1

combinations have the potential of participating in several types of photochemical reaction pathways. For, example, SET from the electron rich silyl ketene acetal donors to aryl aldehyde and ketone excited states should be thermodynamically favorable (see below) and, as a result, it might effectively compete with other excited state deactivation modes to generate ion radical intermediates **I** (Scheme 2). Collapse of these species to produce zwitterionic **IV** or radical **III** intermediates could serve to drive formation of the respective oxetane **VI** or β-hydroxyester **V** products. Alternatively, excited state reactivity of aryl aldehyde and ketone/silyl ketene acetal sytem might adhere to classical patterens in which case oxetanes **II** arising by Paterno-Buchi type cycloaddition[8] would be the major products.

The mechanistic questions posed above and their potential synthetic consequences have stimulated an exploration of the photoreactions occuring between a variety of aryl aldehydes

†The authors dedicate this paper to the memory of Professor Sang Chul Shim who has been a great organic photochemist and a prominent leader of the rapidly advancing Korean chemical community.



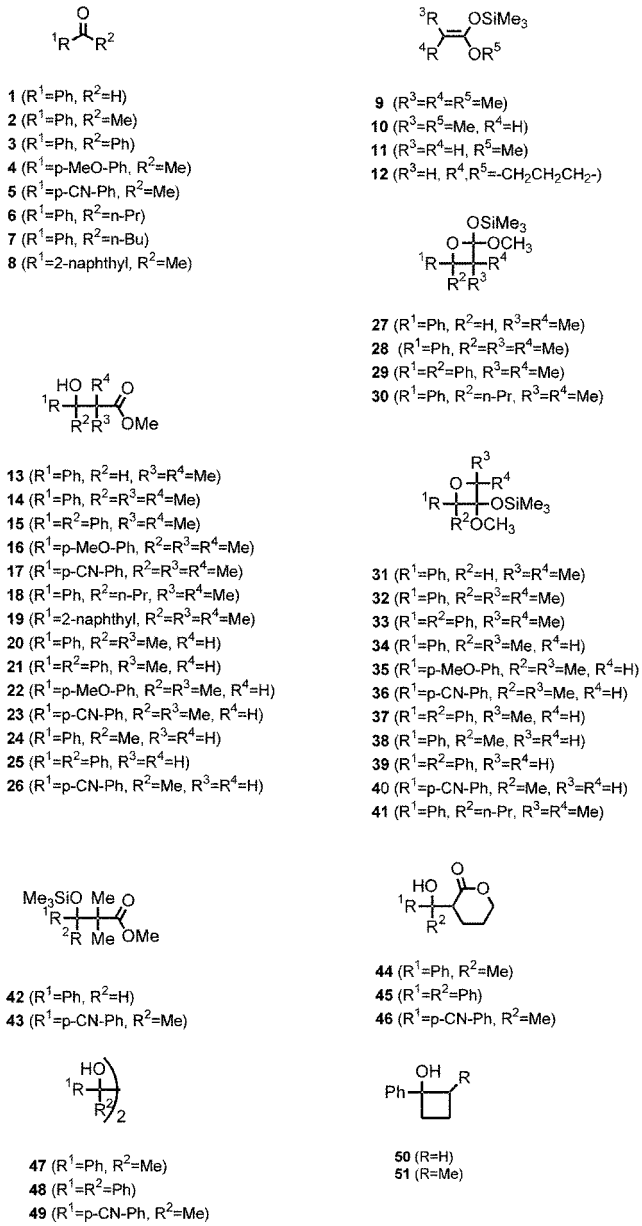
Scheme 2

and ketones **1-8** and silyl ketene acetals **9-12**. Below, we present the results of this study[9] which demonstrate that (1) aromatic carbonyl compounds and silyl ketene acetals[10] participate in two competing excited state reaction pathways involving SET-induced and classical oxetane formation, the relative efficiencies of which are dependent upon the nature of the silyl ketene acetal donors, (2) SET-induced oxetane formation competes with Norrish type II processes in the photochemistry of aryl ketones which possess γ-hydrogens, and (3) oxetanes arising by the SET route and containing silyl ortho ester functionality are readily transformed to β-hydroxyesters, thus, providing an efficient procedure for preparation of these Claisen-condensation type products.

Results

Photochemical reactions were performed by irradiation of CH_3CN or benzene solutions of the carbonyl compounds **1-8** (30-37 mM) and the silyl ketene acetals **9-12** (37-72 mM) by using Pyrex filtered-light (λ > 290 nm) for time periods resulting in 26-100% conversion of the carbonyl compounds. Product separation in each case was performed by silica gel chromatography. Irradiation times, solvents, products and yields for these processes are recorded in Table 1.

By viewing the data in Table 1, it can be seen that irradiation of the aromatic carbonyl compounds in solutions containing the silyl ketene acetals results in the predominant formation of three kinds of products including 3-aryl-3-hydroxyesters **V**, 2-methoxy-2-silyloxy-4-aryloxetanes **VI** and 2-aryl-3-methoxy-3-silyloxyoxetanes **II** (see Scheme 2). In addition, the aromatic ketones **2**, **3** and **5** produce the dimers **47**, **48** and **49** by photoreduction while carbonyl compounds **1** and **5** generate 3-aryl-3-silyloxyesters **42** and **43** as minor products. The ratios of the major products, **II**, **V** and **VI**, are observed to be dependent on the nature of the silyl ketene acetal substrates **9-12**. Specifically, this is seen in the effect of alkyl substitution in the silyl ketene acetal on the relative amounts of 2-aryl-3-methoxy-3-silyloxyoxetane **II** *vs.* 3-aryl-3-hydroxyesters **V** and 2-methoxy-2-silyloxy-4-aryloxetanes **VI** that are produced in these photochemical processes. Thus, formation of 3-aryl-3-hydroxy esters and their precursors, the 2-methoxy-2-silyloxy-4-aryloxetanes (see below), greatly predominates over that of the 2-aryl-3-



1 (R^1=Ph, R^2=H)
2 (R^1=Ph, R^2=Me)
3 (R^1=Ph, R^2=Ph)
4 (R^1=p-MeO-Ph, R^2=Me)
5 (R^1=p-CN-Ph, R^2=Me)
6 (R^1=Ph, R^2=n-Pr)
7 (R^1=Ph, R^2=n-Bu)
8 (R^1=2-naphthyl, R^2=Me)

9 (R^3=R^4=R^5=Me)
10 (R^3=R^5=Me, R^4=H)
11 (R^3=R^4=H, R^5=Me)
12 (R^3=H, R^4,R^5=-$CH_2CH_2CH_2$-)

13 (R^1=Ph, R^2=H, R^3=R^4=Me)
14 (R^1=Ph, R^2=R^3=R^4=Me)
15 (R^1=R^2=Ph, R^3=R^4=Me)
16 (R^1=p-MeO-Ph, R^2=R^3=R^4=Me)
17 (R^1=p-CN-Ph, R^2=R^3=R^4=Me)
18 (R^1=Ph, R^2=n-Pr, R^3=R^4=Me)
19 (R^1=2-naphthyl, R^2=R^3=R^4=Me)
20 (R^1=Ph, R^2=R^3=Me, R^4=H)
21 (R^1=R^2=Ph, R^3=Me, R^4=H)
22 (R^1=p-MeO-Ph, R^2=R^3=Me, R^4=H)
23 (R^1=p-CN-Ph, R^2=R^3=Me, R^4=H)
24 (R^1=Ph, R^2=Me, R^3=R^4=H)
25 (R^1=R^2=Ph, R^3=R^4=H)
26 (R^1=p-CN-Ph, R^2=Me, R^3=R^4=H)

27 (R^1=Ph, R^2=H, R^3=R^4=Me)
28 (R^1=Ph, R^2=R^3=R^4=Me)
29 (R^1=R^2=Ph, R^3=R^4=Me)
30 (R^1=Ph, R^2=n-Pr, R^3=R^4=Me)

31 (R^1=Ph, R^2=H, R^3=R^4=Me)
32 (R^1=Ph, R^2=R^3=R^4=Me)
33 (R^1=R^2=Ph, R^3=R^4=Me)
34 (R^1=Ph, R^2=R^3=Me, R^4=H)
35 (R^1=p-MeO-Ph, R^2=R^3=Me, R^4=H)
36 (R^1=p-CN-Ph, R^2=R^3=Me, R^4=H)
37 (R^1=R^2=Ph, R^3=Me, R^4=H)
38 (R^1=Ph, R^2=Me, R^3=R^4=H)
39 (R^1=R^2=Ph, R^3=R^4=H)
40 (R^1=p-CN-Ph, R^2=Me, R^3=R^4=H)
41 (R^1=Ph, R^2=n-Pr, R^3=R^4=Me)

42 (R^1=Ph, R^2=H)
43 (R^1=p-CN-Ph, R^2=Me)

44 (R^1=Ph, R^2=Me)
45 (R^1=R^2=Ph)
46 (R^1=p-CN-Ph, R^2=Me)

47 (R^1=Ph, R^2=Me)
48 (R^1=R^2=Ph)
49 (R^1=p-CN-Ph, R^2=Me)

50 (R=H)
51 (R=Me)

methoxy-3-silyloxyoxetanes in the photoreactions of the dimethyl-substituted ketene acetal **9**. In contrast, reactions of carbonyl compounds with the non-methyl substituted silyl ketene acetal **11** lead to the predominant production of 2-aryl-3-methoxy-3-silyloxyoxetanes (entries 19-23, 31) while photoreactions with mono-methyl ketene acetal **10** generate both 3-aryl-3-hydroxy esters and 2-aryl-3-methoxy-3-silyoxyoxetanes in roughly equal ratios (entries 12-18). Finally, the cyclic ketene acetal **12** produces Claisen-type products

44-46 exclusively.

It is interesting that the 2-methoxy-2-silyloxy-4-aryloxetane products **VI**, which contain labile ortho ester functions, are observed to undergo rapid hydrolysis to form the Claisen-condensation type β-hydroxyesters products **V**. As a result of this property, 2-methoxy-2-silyloxy-4-aryloxetanes are isolated as major products only in the reactions of carbonyl compounds **1-3** with only the dimethyl-substituted silyl ketene acetal **9**. In the other processes, only β-hydroxyesters are isolated and these derive from hydrolysis of the more labile 2,2-dioxyoxetanes during work-up and chromatographic separation.

Photoreactions of butyrophenone (**6**) with the dimethyl silyl ketene acetal **9** (68 mM) in CH_3CN and benzene (entries 27 and 28) produce the Norrish type II products acetophenone (**2**, 45% and 31%) and 1-phenylcyclobutanol (**50**, 4% and 6%) along with the adducts, 3-phenyl-3-propyl-3-hydroxyester (**18**), 2-methoxy-2-silyloxy-4-phenyl-4-propyloxetane (**30**) and 3-methoxy-3-siloxy-2-phenyl-2-propyloxetane (**41**). However, photoreactions of valerophenone (**7**) in the presence of **9** are dominated by products arising from Norrish type II pathways (**2** and **51**) and secondary photoreaction of **2** with **9** (*i.e.*, **14** and **32**).

Discussion

Two competing mechanistic pathways appear to be responsible for formation of the major 3-aryl-3-hydroxyester **V**, 2-methoxy-2-silyloxy-4-aryloxetane **VI** and 2-aryl-3-methoxy-3-silyloxyoxetane **II** (see Scheme 2) products produced in the photoreactions of aryl aldehydes and ketones with silyl ketene acetals. Excitation of the aromatic carbonyl 3-silyloxyoxetane **II** (see Scheme 2) products produced in the photoreactions of aryl aldehydes and ketones with silyl ketene acetals. Excitation of the aromatic carbonyl compounds in each case is followed by rapid intersystem crossing (k_{isc} = *ca.* 1×10^{10} s^{-1}) to produce the corresponding triplet excited states which have long lifetimes (0.15-12 ms).[11] Electron

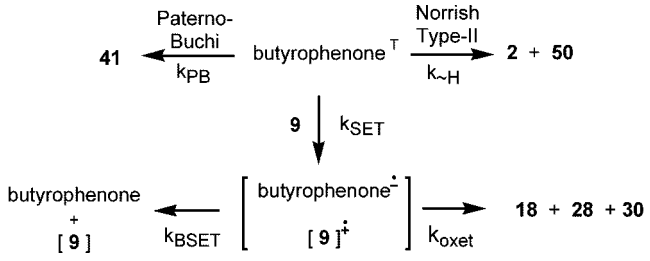
Table 1. Photoreactions of Aryl Ketones **1-8** and Silyl Ketene Acetals **9-12**[a]

Entry	Reactants	Solvent	Reaction time (h)	Conversion (%)	Products (% yield)[b]
1	**1+9**	CH_3CN	3	98	**13**(76), **30**(5)
2	**1+9**	Benzene	11	79	**13**(72), **31**(8), **27**(4), **42**(14)
3	**2+9**	CH_3CN	16	100	**28**(83), **32a**(5), **32b**(6), **47**(5)
4	**2+9**	Benzene	33	77	**28**(64), **32a**(11), **32b**(7), **47**(3)
5	**3+9**	CH_3CN	6	100	**15**(13), **29**(65), **48**(23)
6	**3+9**	Benzene	4	95	**15**(11), **29**(27), **33**(3), **48**(40)
7	**4+9**	CH_3CN	43	74	**16**(62)
8	**5+9**	CH_3CN	28	88	**17**(32), **43**(10), **49**(34)
9	**5+9**	Benzene	10	86	**17**(86), **43**(trace), **49**(5)
10	**5+9**	35% H_2O-CH_3CN	37	62	**17**(11), **43**(3), **49**(72)
11	**8+9**	CH_3CN	40	44	**19**(11)
12	**2+10**	CH_3CN	12	72	**20a**(19), **20b**(24), **34a**(8), **34b**(16), **47**(16)
13	**2+10**	Benzene	14	47	**20a**(15), **20b**(25), **34a**(21), **34b**(34)
14	**3+10**	CH_3CN	8	85	**21**(41), **37a**(12), **37b**(25), **48**(6)
15	**3+10**	Benzene	7	90	**21**(39), **37a**(12), **37b**(24), **48**(14)
16	**4+10**	CH_3CN	50	26	**22a**(17), **22b**(18), **35a**(26), **35b**(22)
17	**4+10**	Benzene	19	46	**22a**(24), **22b**(31), **35a**(18), **35b**(25)
18	**5+10**	Benzene	13.5	87	**23a**(17), **23b**(47), **36a**(8), **36b**(17), **49**(5)
19	**2+11**	CH_3CN	20	49	**24**(25), **38a**(16), **38b**(30)
20	**2+11**	Benzene	16	65	**24**(22), **38a**(21), **38b**(32)
21	**3+11**	Benzene	25	89	**25**(16), **39**(68), **48**(4)
22	**4+11**	Benzene	48	0	no reaction
23	**5+11**	Benzene	25	43	**26**(40), **40a**(14), **40b**(32), **49**(6)
24	**2+12**	CH_3CN	37	30	**44**(21)
25	**3+12**	CH_3CN	21	61	**45**(20), **48**(20)
26	**5+12**	Benzene	25	54	**46**(20), **49**(50)
27	**6+9**	CH_3CN	9	100	**2**(45), **18**(29), **30**(5), **28a**(3), **28b**(3), **41a**(3), **42b**(4), **50**(4)
28	**6+9**	Benzene	8	95	**2**(31), **18**(25), **30**(7), **28a**(2), **28b**(3), **41a**(11), **41b**(3), **50**(6)
29	**7+9**	CH_3CN	5.5	96	**2**(31), **14**(14), **32a**(1), **32b**(2), **51a**(7), **51b**(19)
30	**7+9**	Benzene	6.5	88	**2**(18), **14**(11), **32a**(8), **32b**(13), **51a**(13), **51b**(19)
31	**6+11**	CH_3CN	2	95	**2**(63), **50**(17), **38a**(3), **38b**(7)

[a]Concentrations of reactants, [ketone]/[acetal] are 36/72 (mM) for entryies1-23, 30/60 (mM) for entries 24-26, 34/68 (mM) for entries 27-28, 31, and 37/37 (mM) for entries 29-30. [b]Yields are based on consumed carbonyl compounds.

transfer from the dimethyl-substituted silyl ketene acetal **9** ($E_{1/2}(+)$ = +0.66 V)[12] to the triplet excited aryl aldehyde or ketone ($E^{T}_{1/2}(-)$ = -1.19 ~ -1.28 V)[11,13] is thermodynamically favorable (ΔG_{SET} = *ca.* -0.5 ~ -0.6 eV) and thus should occur rapidly[14] for the acetal concentrations in the range of 37-72 mM used in these processes. As depicted in Scheme 2 above, the SET-process results in production of the ion radical pair **I** which can partition to the β-hydroxyester **V** or 2,2-dioxyoxetanes **VI** adducts by respective desilylation and zwitterion forming C-C bonding pathways. Owing to the lability of the ortho-ester containing oxetanes **VI**, they undergo rapid hydrolytic conversion to the β-hydroxyesters **V** in all cases except those arising from the dimethyl-substituted ketene acetal **9**.

In competition with these routes, direct cycloaddition of the ketene acetals with the triplet carbonyl compounds occurs to generate classical Paterno-Buchi products,[8] 3,3-dioxyoxetanes **II**. The relative efficiencies of the SET and classical cycloaddition reactions should be governed by the oxidation potential of the silyl ketene acetal which, in turn, is a function of the degree of methyl substitution on the vinyl moiety. Thus, the predominant production of 2,2-dioxyoxetanes (from SET routes) in photoreactions with the dimethyl-substituted acetal **9** *versus* 3,3-dioxyoxetanes (from Paterno-Buchi routes) with the non-methyl-substututed analog **11** clearly reflects the controll offered by this property.



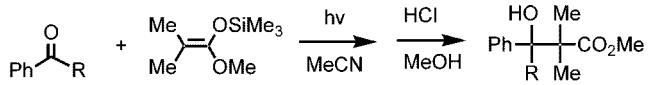
Scheme 3

Observations made in studies with butyrophenone (**6**) provide qualitative information about the kinetics of oxetane formation by the SET mechanistic pathway. The rate constant for butyrophenone triplet γ-hydrogen abstraction (leading to **2** and **50**) has been measured previously ($k_{\sim H} = 8 \times 10^6$ sec^{-1}).[15] As shown in Scheme 3, this process competes with classical Paterno-Buchi reaction to produce oxetane **41** ($k_{PB} \times$ [keten acetal]) and SET from the silyl ketene acetal **9** with a bimolecular rate that is controlled by k_{SET} (*ca.* 1×10^{10} M^{-1} s^{-1})[14] and the acetal concentration (6.8×10^{-2} M). The ion radical pair produced following SET then partitions to ground state starting materials by back electron transfer (k_{BSET} = *ca.* 1×10^{10} M^{-1}s^{-1}) or to oxetanes **28+30** and β-hydroxyester **18** by sequential C-C and C-O bond formation (k_{oxet}). The kinetic sequence depicted in Scheme 3 translates into the Norrish Type II to Paterno-Buchi and SET-oxetane photoreaction quantum efficiencies given in equations 1 and 2. Based upon these formulations, estimated rate constants given above and the product ratios, we estimate that in the reaction of ketene acetal **9** with triplet butyrophenone k_{PB} = *ca.* 2×10^7 M^{-1}s^{-1} and k_{oxet} = *ca.* 1×10^8 M^{-1}s^{-1}. Interestingly, SET is not a competitive route followed in the photoreaction of valerophenone (**7**) with ketene acetal **9**. The major reason for this lies in the rate for intramolecular H-atom abstraction in triplet valerophenone (1.3×10^8 sec^{-1})[15] which is much larger than diffusion controlled bimolecular SET in the concentration range (10^{-2} M) of **9** used in these experiments.

$$\frac{\phi_{\text{Norrish}}}{\phi_{\text{Paterno}-\text{Buchi}}} = \frac{k_{\sim H}}{k_{PB}[\mathbf{9}]} \quad (1)$$

$$\frac{\phi_{\text{Norrish}}}{\phi_{\text{SET}-\text{oxetane}}} = \left[\frac{k_{\sim H}}{k_{SET}[\mathbf{9}]}\right]\left[\frac{k_{BSET}}{k_{oxet}} + 1\right] \quad (2)$$

Finally, it is worth mentioning that photoreactions of aromatic carbonyl compounds with silyl ketene acetals in most cases serve as highly efficient procedures to prepare Claisen type β-hydroxyester products either by *in situ* or subsequent acid-catalyzed methanolysis of the initially formed 2,2-dioxyoxetanes. Examples which provide support for this conclusion are given in Scheme 4.



1 (R = H)
2 (R = Me)

9

13 (R = H)
14 (R = Me)

Scheme 4

Experimental Section

General Procedure. The chemical shifts of resonances in the ^{1}H-NMR (200 and 300 MHz) and ^{13}C-NMR (50 and 75 MHz) spectra were recorded on $CDCl_3$ solutions are reported in parts per million relative to Me_4Si as an internal standard. For compounds containing Me_3Si groups, $CHCl_3$ was used as an internal standard. ^{13}C-NMR resonances were assigned by use of the DEPT technique to determine the numbers of attached hydrogens. IR spectral bands are reported in cm^{-1}. Preparative photochemical reactions were conducted with an apparatus consisting of a 450W Hanovia medium pressure mercury vapor lamp surrounded by a Pyrex glass filter in a water-cooled quartz immersion well surrounded by the solution being irradiated. The photolysis solutions were purged with nitrogen before and during irradiations. The photolysates were concentrated under reduced pressure giving residues which were subjected to preparative TLC on 20×20 cm silica gel coated plates. Low and high resolution (HRMS) mass spectra were obtained by use of electron impact ionization unless otherwise noted. All starting materials used in the photoreactions derived from commercial sources. All new compounds described are isolated as oils in >90% purity (by NMR analysis) unless noted otherwise.

Irradiation of Benzaldehyde (1) and 1-Trimethylsilyloxy-1-methoxy-2,2-dimethylethylene (9). Acetonitrile. A

solution of benzaldehyde (**1**) (382 mg, 3.6 mmol) and ketene acetal **9** (1.26 g, 7.2 mmol) in 100 mL of acetonitrile was irradiated for 3 h (*ca.* 98% conversion of **1**). Work-up and chromatographic (1 : 8, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 556 mg (76%) of **13** and 45 mg (5%) of **31**. A solution of oxetane **31** (100 mg, 0.36 mmol) and trace of 5% HCl in 50 mL of methanol was stirred for 4h at 25 °C. Work-up and chromatographic (1 : 8, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 76 mg (76%) of **13**.

13: mp 65-67 °C; ^{1}H NMR 1.10 (s, 3H, C(CH_3)$_2$), 1.14 (s, 3H, C(CH_3)$_2$), 3.17 (s, 1H, OH), 3.71 (s, 3H, OCH_3), 4.89 (d, 1H, *J* = 3.7 Hz, C(OH)H), 7.27-7.37 (m, 5H, aromatic); ^{13}C NMR 19.0 (C(CH_3)$_2$), 22.9 (C(CH_3)$_2$), 47.7 (C(CH_3)$_2$), 52.0 (OCH_3), 78.6 (C(OH)H), 127.6 and 127.7, (CH, aromatic), 140.0 (C, aromatic), 178.1 (C=O); Ir (KBr), 3350-3520 (br, OH stretching), 1700 cm^{-1} (C=O streching); CIMS, m/z (rel. intensity) 209 (M^++1, 1), 191 (M^+-OH, 10), 149 (2), 132 (3), 107 (28), 102 (100), 77 (22); HRMS, m/z 209.1185 ($C_{12}H_{17}O_3$ requires 209.1178).

31: ^{1}H NMR -0.05 (s, 9H, $OSiMe_3$), 1.41 (s, 3H, C(CH_3)$_2$), 1.52 (s, 3H, C(CH_3)$_2$), 3.39 (s, 3H, OCH_3), 5.57 (s, 1H, C(Ph)H), 7.27-7.39 (m, 5H, aromatic); ^{13}C NMR 1.1 ($OSiMe_3$), 23.8 (C(CH_3)$_2$), 24.7 (C(CH_3)$_2$), 51.2 (OCH_3), 87.4 (C(CH_3)$_2$), 91.3 (C(Ph)H), 102.9 (C(OCH_3)OSiMe3), 127.3, 127.6 and 127.7 (CH, aromatic), 138.0 (C, aromatic); Ir (neat), 1250 cm^{-1} (C-O stretching); EIMS, m/z (rel. intensity) 280 (M^+, 0.1), 222 (13), 174 (100), 159 (22), 118 (94), 105 (98); HRMS, m/z 280.1491 ($C_{15}H_{24}O_3Si$ requires 280.1495).

Benzene. A solution of benzaldehyde (**1**) (382 mg, 3.6 mmol) and ketene acetal **9** (1.26 g, 7.2 mmol) in 100 mL of benzene was irradiated for 11 h (*ca.* 79% conversion of **1**). Work-up and chromatographic (1 : 8, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 424 mg (72%) of **13**, 55 mg (8%) of **31**, 28 mg (4%) of **27**, and 111 mg (14%) of **42**.

27: ^{1}H NMR 0.24 (s, 9H, $OSiMe_3$), 1.48 (s, 3H, C(CH_3)$_2$), 1.50 (s, 3H, C(CH_3)$_2$), 2.88 (s, 3H, OCH_3), 5.49 (s, 1H, C(Ph)H), 7.32-7.49 (s, 5H, aromatic).

42: ^{1}H NMR -0.04 (s, 9H, $OSiMe_3$), 0.99 (s, 3H, C(CH_3)$_2$), 1.13 (s, 3H, C(CH_3)$_2$), 3.68 (s, 3H, OCH_3), 4.97 (s, 1H, C(Ph)H), 7.27 (s, 5H, aromatic); ^{13}C NMR -0.1 ($OSiMe_3$), 19.1 (C(CH_3)$_2$), 21.7 (C(CH_3)$_2$), 49.0 (C(CH_3)$_2$), 51.6 (OCH_3), 79.1 (C(Ph)H), 127.4, 127.8 and 127.8 (CH, aromatic), 140.8 (C, aromatic), 177.3 (C=O); Ir(neat) 1810 (C=O stretching), 1250 cm^{-1} (C-O stretching); EIMS, m/z (rel. intensity) 279 (M^+, 19), 265 (4), 235 (1), 213 (2), 205 (3), 179 (100), 174 (23), 107 (46); HRMS, 279.1383 ($C_{15}H_{23}O_3Si$ requires 279.1417).

Irradiation of Acetophenone (2) and 1-Trimethylsilyloxy-1-methoxy-2,2-dimethylethylene (9). Acetonitrile. A solution of acetophenone (**2**) (430 mg, 3.6 mmol) and ketene acetal **9** (1.26 g, 7.2 mmol) in 100 mL of acetonitrile was irradiated for 32 h (*ca.* 100% conversion of **2**). Work-up and chromatographic (1 : 8, ethyl acetate : *n*-hexane, v/v) separation (see General) gave the diastereomeric oxetanes **32a** (55 mg, 5%) and **32b** (65 mg, 6%), 666 mg (83%) of **28**, and 22 mg (5%) of diol **47**. A solution of oxetane **32** (100 mg, 0.34 mmol) and trace of 5% HCl in 50 mL of methanol was stirred for 4h at 25 °C. Work-up and chromatographic (1 : 8, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 83 mg (83%) of **14**.

28: ^{1}H NMR 1.15 (s, 3H, C(CH_3)$_2$), 1.16 (s, 3H, C(CH_3)$_2$), 1.61 (s, 3H, C(CH_3)OH), 3.67 (s, 3H, OCH_3), 4.39 (s, 1H, OH), 7.23-7.47 (m, 5H, aromatic); ^{13}C NMR (acetone-d_6) 22.2 (C(CH_3)$_2$), 22.4 (C(CH_3)$_2$), 26.1 (C(OH)CH_3), 51.6 (C(CH_3)$_2$), 52.3 (OCH_3), 77.5 (C(OH)CH_3), 127.6, 128.0 and 128.1 (CH, aromatic), 146.2 (C, aromatic), 178.3 (C=O); Ir(neat), 3300-3600 (br, OH stretching), 1700 (C=O stretching), 1280 (C-O stretching); EIMS, m/z (rel.intensity) 222 (M^+, 1), 205 (M^+-OH, 15), 189 (4), 145 (3), 121 (100), 105 (16), 102 (66), 77 (8); HRMS, m/z 222.1260 ($C_{13}H_{18}O_3$ requires 222.1256).

32a: ^{1}H NMR -0.07 (s, 9H, $OSiMe_3$), 1.28 (s, 3H, C(CH_3)$_2$), 1.49 (s, 3H, C(CH_3)$_2$), 1.67 (s, 3H, C(CH_3)Ph), 3.44 (s, 3H, OCH_3), 7.25-7.40 (m, 5H, aromatic); ^{13}C NMR 1.1 ($OSiMe_3$), 24.9 (C(CH_3)$_2$), 25.9 (C(CH_3)$_2$), 26.7 (C(CH_3)Ph), 51.6 (OCH_3), 89.1 (C(CH_3)$_2$), 92.3 (C(CH_3)Ph), 103.0 (C(OCH_3)$OSiMe_3$), 125.7, 126.3 and 127.4 (CH, aromatic), 144.4 (C, aromatic); Ir (neat) 1250 (C-O stretching); CIMS, m/z (rel. intensity) 295 (M^++1, 2), 236 (10), 193 (8), 132 (43), 105 (43); HRMS, m/z 295.1715 ($C_{16}H_{27}O_3Si$ requires 295.1729).

32b: ^{1}H NMR 0.28 (s, 9H, $OSiMe_3$), 1.42 (s, 3H, C(CH_3)$_2$), 1.48 (s, 3H, C(CH_3)$_2$), 1.67 (s, 3H, C(CH_3)Ph), 2.89 (s, 3H, OCH_3), 7.21-7.51 (m, 5H, aromatic); ^{13}C NMR 1.6 ($OSiMe_3$), 24.3 (C(CH_3)$_2$), 26.5 (C(CH_3)$_2$), 26.6 (C(CH_3)Ph), 51.2 (OCH_3), 89.6 (C(CH_3)$_2$), 91.2 (C(CH_3)Ph), 103.2 (C(OCH_3)$OSiMe_3$), 126.2, 126.7 and 127.4 (CH, aromatic), 143.8 (C,aromatic); Ir(neat) 1260 (C-O stretching); CIMS, m/z (rel. intensity) 295 (M^++1, 1), 279 (2), 247 (2), 236 (11), 132 (52), 105 (10); HRMS, m/z 295.1704 ($C_{16}H_{27}O_3Si$ requires 295.1729).

Benzene. A solution of acetophenone (**2**) (430 mg, 3.6 mmol) and ketene acetal **9** (1.26 g, 7.2 mmol) in 100 mL of benzene was irradiated for 33 h, (*ca.* 77% conversion of **2**) Work-up and chromatographic (1 : 20, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 392 mg (64%) of **28**, 90 mg (11%) of **32a**, 57 mg (7%) of **32b** and 8 mg (3%) of diol **47**.

Irradiation of Benzophenone (3) and 1-Trimethylsilyloxy-1-methoxy-2,2-dimethylethylene (9). Acetonitrile. A solution of benzophenone (**2**) (656 mg, 3.6 mmol) and ketene acetal **9** (1.26 g, 7.2 mmol) in 100 mL of acetonitrile was irradiated for 6 h (*ca.* 100% conversion of **3**). Work-up and chromatographic (1 : 8, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 130 mg (13%) of **15**, 840 mg (65%) of **29** and 150 mg (23%) of benzopinacole **48**.

15: mp 37-38°C; ^{1}H NMR 1.35 (s, 6H, C(CH_3)$_2$), 3.74 (s, 3H, OCH_3), 5.08 (s, 1H, OH), 7.23-7.37 (m, 10H, aromatic); ^{13}C NMR 24.0 (C(CH_3)$_2$), 49.0 (C(CH_3)$_2$), 52.5 (OCH_3), 82.2 (COH), 126.9, 127.2 and 128.6 (CH, aromatic), 145.2 (C, aromatic), 180.3 (C=O); Ir (KBr) 3350-3550 (br, OH stretching), 1700 (C=O stretching), 1270 cm^{-1} (C-O stretching); EIMS, m/z (rel. intensity), 284 (M^+, 0.1), 267 (38), 183 (100), 105 (98), 77 (33); HRMS, m/z 284.1419 ($C_{18}H_{20}O_3$ requires 284.1412).

29: ^{1}H NMR 0.30 (s, 9H, $OSiMe_3$), 1.19 (s, 3H, C(CH_3)$_2$),

1.20 (s, 3H, C(CH_3)$_2$), 3.46 (s, 3H, OCH_3), 7.22-7.63 (m, 10H, aromatic); ^{13}C NMR 1.5 ($OSiMe_3$), 21.4 (C($\underline{C}H_3$)$_2$), 23.4 (C($\underline{C}H_3$)$_2$), 48.6 ($\underline{C}(CH_3)_2$), 53.6 (OCH_3), 86.1 ($\underline{C}(Ph)_2$), 115.0 ($\underline{C}(OCH_3)OSiMe_3$), 125.5, 125.7, 126.3, 126.3, 127.5 and 127.6 (CH, aromatic), 144. and 144.3 (C, aromatic); Ir(neat) 1260 cm^{-1} (C-O stretching); CIMS, m/z (rel. intensity), 357 (M^++1, 0.1), 341 (4), 325 (6), 281 (23), 255 (58), 208 (71), 183 (57), 105 (100), 77 (32); HRMS, m/z 357.1882 ($C_{21}H_{29}O_3Si$ requires 357.1886).

Benzene. A solution of benzophenone (**3**) (656 mg, 3.6 mmol) and ketene acetal **9** (1.26 g, 7.2 mmol) in 100 mL of benzene was irradiated for 4 h (*ca.* 95% conversion of **3**). Work-up and chromatographic (1 : 8, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 104 mg (11%) of **15**, 325 mg (27%) of **29**, 33 mg (3%) of **33** and 248 mg (40%) of benzopinacole **48**.

33: mp 100-102 °C; ^{1}H NMR 0.07 (s, 9H, $OSiMe_3$), 1.29 (s, 3H, C(CH_3)$_2$), 1.53 (s, 3H, C(CH_3)$_2$), 2.86 (s, 3H, OCH_3), 7.26-7.60 (m, 10H, aromatic); ^{13}C NMR 1.2 ($OSiMe_3$), 23.3 (C($\underline{C}H_3$)$_2$), 25.8 (C($\underline{C}H_3$)$_2$), 51.0 (OCH_3), 89.8 ($\underline{C}(CH_3)_2$), 93.8 ($\underline{C}(Ph)_2$), 104.5 ($\underline{C}(OCH_3)OSiMe_3$), 126.6, 126.9, 127.0, 127.3, 128.0 and 128.1 (CH, aromatic), 141.8 and 142.2 (C, aromatic); Ir(neat) 1250 cm^{-1} (C-O, stretching); EIMS, m/z (rel. intensity) 356 (M^+, 0.04), 288 (4), 256 (2), 194 (17), 182 (9), 176 (5), 174 (100), 166 (14); HRMS, m/z 356.1820 ($C_{21}H_{28}O_3Si$ requires 356.1808).

Irradiation of 4'-Methoxyacetophenone (4) and 1-Trimethylsilyloxy-1-methoxy-2,2-dimethylethylene (9). Acetonitrile. A solution of 4'-methoxyacetophenone (**4**) (540 mg, 3.6 mmol) and ketene acetal **9** (1.26 g, 7.2 mmol) in 100 mL of acetonitrile was irradiated for 43 h (*ca.* 74% conversion of **4**). Work-up and chromatographic ($CHCl_3$) separation (see General) gave 391 mg (62%) of **16**.

16: mp 82-84 °C; ^{1}H NMR 1.14 (s, 6H, C(CH_3)$_2$), 1.57 (s, 3H, C(OH)C$\underline{H}_3$), 3.68 (s, 3H, CO_2CH_3), 3.79 (s, 3H, PhOC$\underline{H}_3$), 6.84 (d, 2H, J = 9.0 Hz, aromatic), 7.36 (d, 2H, J = 9.0 Hz, aromatic); ^{13}C NMR 21.6 (C($\underline{C}H_3$)$_2$), 21.7 (C($\underline{C}H_3$)$_2$), 25.1 (C(OH)$\underline{C}H_3$), 50.4 ($\underline{C}(CH_3)_2$), 52.1 ($CO_2\underline{C}H_3$), 55.1 (PhO$\underline{C}H_3$), 76.8 ($\underline{C}(OH)CH_3$), 112.5 and 128.3 (CH, aromatic), 135.6 and 158.4 (C, aromatic), 179.0 (C=O); Ir (KBr) 3280-3500 (br, OH stretching), 1700 cm^{-1} (C=O stretching); EIMS, m/z (rel. intensity), 236 (M^+, 2), 235 (13), 219 (3), 175 (2), 151 (100), 135 (24), 92 (5); HRMS, m/z 236.1411 ($C_{14}H_{20}O_3$ requires 236.1413).

Irradiation of 4-Cyanoacetophenone (5) and 1-Trimethylsilyloxy-1-methoxy-2,2-dimethylethylene (9). Acetonitrile. A solution of 4-cyanoacetophenone (**5**) (520 mg, 3.6 mmol) and ketene acetal **9** (1.26 g, 7.2 mmol) in 100 mL of acetonitrile was irradiated for 28 h (*ca.* 88% conversion of **5**). Work-up and chromatographic (1 : 5, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 246 mg (32%) of **17**, 104 mg (10%) of **43** and 158 mg (34%) of **49**.

17: ^{1}H NMR 1.10 (s, 3H, C(CH_3)$_2$), 1.13 (s, 3H, C(CH_3)$_2$), 1.59 (s, 3H, C(OH)C$\underline{H}_3$), 3.68 (s, 3H, OCH_3), 4.52 (s, 1H, OH), 7.57 (s, 4H, aromatic); ^{13}C NMR (acetone-d_6) 22.1 (C($\underline{C}H_3$)$_2$), 22.4 (C($\underline{C}H_3$)$_2$), 25.9 (C(OH)$\underline{C}H_3$), 51.8 ($\underline{C}(CH_3)_2$), 52.5 (OCH_3), 77.7 ($\underline{C}(OH)CH_3$), 111.7 (CN), 119.8 and 152.2 (C, aromatic), 129.2 and 132.1 (CH, aromatic), 177.7 (C=O); Ir (neat), 3250-3600 (br, OH stretching), 2230 (CN stretching), 1720 cm^{-1} (C=O stretching); CIMS, m/z (rel. intensity) 248 (M^++1, 26), 230 (M^+-OH, 41), 146 (43), 130 (26), 102 (100); HRMS, m/z 248.1290 ($C_{14}H_{18}NO_3$ requires 248.1287).

43: ^{1}H NMR 0.06 (s, 9H, $OSiMe_3$), 1.06 (s, 3H, C(CH_3)$_2$), 1.13 (s, 3H, C(CH_3)$_2$), 1.78 (s, 3H, (C($OSiMe_3$)C$\underline{H}_3$), 3.54 (s, 3H, OCH_3), 7.43 (d, 2H, J = 8.4 Hz, aromatic), 7.59 (d, 2H, J = 8.4 Hz, aromatic); ^{13}C NMR 2.5 ($OSiMe_3$), 21.6 (C($\underline{C}H_3$)$_2$), 22.1 (C($\underline{C}H_3$)$_2$), 25.0 (C($OSiMe_3$)$\underline{C}H_3$), 51.9 ($\underline{C}(CH_3)_2$), 52.7 (OCH_3), 80.6 ($\underline{C}(OSiMe_3)CH_3$), 111.2 (CN), 119.4 and 151.5 (C, aromatic), 128.1 and 131.4 (CH, aromatic), 176.4 (C=O); Ir(neat) 2230 (CN stretching), 1730 cm^{-1} (C=O stretching); CIMS, m/z (rel. intensity), 320 (M^++1, 3), 304 (8), 291 (9), 218 (100), 89 (2), 73 (9); HRMS, m/z 320.1682 ($C_{17}H_{26}NO_3Si$ requires 320.1682).

49: mp 221-223 °C; ^{1}H NMR (DMSO-d_6) 1.23 (s, 3H, CH_3), 1.62 (s, 3H, CH_3), 5.37 (s, 1H, OH), 5.55 (s, 1H, OH), 7.24 (d, 2H, J = 8.0 Hz, aromatic), 7.51 (d, 2H, J = 8.0 Hz, aromatic), 7.67 (d, 2H, J = 8.0 Hz, aromatic), 7.74 (d, 2H, J = 8.0 Hz, aromatic); ^{13}C NMR (DMSO-d_6) 24.5 and 24.8 (C(OH)$\underline{C}H_3$), 76.9 and 77.2 ($\underline{C}(OH)CH_3$), 108.7 and 109.1 (CN), 128.1, 128.8, 130.3 and 130.7 (CH, aromatic), 152.2 and 152.6 (C, aromatic); Ir (KBr) 3200-3600 (br, OH stretching), 2230 cm^{-1} (CN stretching); CIMS, m/z (rel. intensity) 293 (M^++1, 3), 258 (6), 147 (100), 130 (50); HRMS, m/z 293.1281 ($C_{18}H_{17}N_2O_2$ requires 293.1290).

Benzene. A solution of 4-cyanoacetophenone (**5**) (520 mg, 3.6 mmol) and ketene acetal **9** (1.26 g, 7.2 mmol) in 100 mL of benzene was irradiated for 10 h (*ca.* 86% conversion of **5**). Work-up and chromatographic (1 : 15, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 652 mg (86%) of **17**, trace of **43** and 21 mg (5%) of **49**.

35%H_2O-Acetonitrile. A solution of 4-cyanoacetophenone (**5**) (520 mg, 3.6 mmol) and ketene acetal **9** (1.26 g, 7.2 mmol)) in a solution of 65 mL of acetonitrile and 35 mL of H_2O was irradiated for 37 h (*ca.* 62% conversion of **5**). Work-up and chromatographic (1 : 8, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 60 mg (11%) of **17**, 20 mg (3%) of **43** and 235 mg (72%) of **49**.

Irradiation of Butyrophenone (6) and 1-Trimethylsilyloxy-1-methoxy-2,2-dimethylethylene (9). Acetonitrile. A solution of butyrophenone (**6**) (500 mg, 3.4 mmol) and ketene acetal **9** (1.18 g, 6.8 mmol) in 100 mL of acetonitrile was irradiated for 9 h (*ca.* 100% conversion of **6**). Work-up and chromatographic (1 : 8, ethyl acetate : *n*-hexane, v/v) separation (see General) gave the diastreomeric oxetanes **28a** (30 mg, 3%) and **28b** (30 mg, 3%), **41a** (33 mg, 3%) and **41b** (45 mg, 4%), 184 mg (45%) of **2**, 20 mg (4%) of **50**, 247 mg (29%) of **18**, and 55 mg (5%) of **30**.

18: ^{1}H NMR 0.85 (t, 3H, J = 6.6 Hz, -$CH_2CH_2C\underline{H}_3$), 0.92-1.03 and 1.27-1.43 (m, 2H, -$CH_2C\underline{H}_2CH_3$), 1.11 (s, 3H, C(C$\underline{H}_3$)$_2$), 1.18 (s, 3H, C(C$\underline{H}_3$)$_2$), 1.49-1.65 and 2.14-2.28 (m, 2H, -$C\underline{H}_2CH_2CH_3$), 3.66 (s, 3H, CO_2CH_3), 4.32 (s, 1H, OH), 7.22-7.44 (m, 5H, aromatic); ^{13}C NMR 14.5 (-CH_2-$CH_2\underline{C}H_3$), 16.9 (-$CH_2\underline{C}H_2CH_3$), 21.4 (C($\underline{C}H_3$)$_2$), 21.8 (C($\underline{C}H_3$)$_2$), 38.1 (-$\underline{C}H_2CH_2CH_3$), 50.6 ($\underline{C}(CH_3)_2$), 52.0 ($CO_2\underline{C}H_3$), 79.6

(C(OH)$CH_2CH_2CH_3$), 126.6, 127.1 and 127.8 (CH, aromatic), 140.7 (C, aromatic), 179.2 (C=O); Ir (neat) 3600-3300 (br, OH streching), 1700 cm^{-1} (C=O streching); CIMS, m/z (rel. intensity) 251 (M^++1, 0.2), 235 (0.3), 233 (14), 207 (3), 176 (0.6), 150 (12), 149 (100); HRMS, m/z 251.1647 ($C_{15}H_{23}O_3$ requires 251.1647).

41a: ^{1}H NMR 0.29 (s, 9H, $OSiMe_3$), 0.84 (t, 3H, J = 6.4 Hz, -$CH_2CH_2CH_3$), 1.38 (s, 3H, C(CH_3)$_2$), 1.45 (s, 3H, C(CH_3)$_2$), 1.82-1.96 (m, 2H, -$CH_2CH_2CH_3$), 2.06-2.21 (m, 2H, -$CH_2CH_2CH_3$), 2.93 (s, 3H, OCH_3), 7.21-7.45 (m, 5H, aromatic); ^{13}C NMR 1.6 ($OSiMe_3$), 14.5 (-$CH_2CH_2CH_3$), 15.9 (-$CH_2CH_2CH_3$), 24.5 (C(CH_3)$_2$), 26.5 (C(CH_3)$_2$), 40.6 (-CH_2-CH_2CH_3), 51.3 (OCH_3), 89.6 (C(CH_3)$_2$), 93.8 (C(Ph)O-), 103.4 (C(OCH_3)$OSiMe_3$), 126.3, 126.6 and 127.3 (CH, aromatic), 141.9 (C, aromatic); Ir (neat) 1250 cm^{-1} (C-O streching); EIMS, m/z (rel. intensity) 322 (M^+, 0.3), 307 (0.5), 282 (1), 265 (2), 255 (1), 237 (2), 221 (27), 175 (16), 174 (100); HRMS, m/z 322.1972 ($C_{18}H_{30}O_3Si$ requires 322.1964).

41b: ^{1}H NMR -0.08 (s, 9H, $OSiMe_3$), 0.82 (t, 3H, J = 6.5 Hz, -$CH_2CH_2CH_3$), 1.26 (s, 3H, C(CH_3)$_2$), 1.47 (s, 3H, C(CH_3)$_2$), 1.82-1.95 (m, 2H, -$CH_2CH_2CH_3$), 2.12-2.28 (m, 2H, -$CH_2CH_2CH_3$), 3.43 (s, 3H, OCH_3), 7.21-7.32 (m, 5H, aromatic); ^{13}C NMR 1.2 ($OSiMe_3$), 14.6 (-$CH_2CH_2CH_3$), 16.1 (-$CH_2CH_2CH_3$), 25.0 (C(CH_3)$_2$), 26.1 (C(CH_3)$_2$), 40.2 (-$CH_2CH_2CH_3$), 51.9 (OCH_3), 89.1 (C(CH_3)$_2$), 95.2 (C(Ph)O-), 103.2 (C(OCH_3)$OSiMe_3$), 126.1, 126.1 and 127.2 (CH, aromatic), 142.7 (C, aromatic); Ir (neat) 1250 cm^{-1} (C-O streching); EIMS, m/z (rel. intensity) 322 (M^+, 0.3), 307 (1), 265 (1), 221 (13), 175 (16), 174 (100); HRMS, m/z 322.1953 ($C_{18}H_{30}O_3Si$ requires 322.1964).

30: ^{1}H NMR 0.29 (s, 9H, $OSiMe_3$), 0.73 (s, 3H, C(CH_3)$_2$), 0.81 (t, 3H, J = 7.0 Hz, -$CH_2CH_2CH_3$), 1.30 (s, 3H, C(CH_3)$_2$), 1.71-1.89 (m, 2H, -$CH_2CH_2CH_3$), 2.06-2.21 (m, 2H, -CH_2-CH_2CH_3), 3.33 (s, 3H, OCH_3), 7.21-7.32 (m, 5H, aromatic); ^{13}C NMR 1.3 ($OSiMe_3$), 14.3 (-$CH_2CH_2CH_3$), 16.7 (-CH_2CH_2-CH_3), 19.5 (C(CH_3)$_2$), 21.7 (C(CH_3)$_2$), 39.5 (-$CH_2CH_2CH_3$), 50.0 (OCH_3), 51.1 (C(CH_3)$_2$), 85.2 (C(Ph)O-), 115.6 (C(OCH_3)-$OSiMe_3$), 125.4, 126.1 and 127.6 (CH, aromatic), 143.0 (C, aromatic); Ir (neat) 1250 cm^{-1} (C-O streching).

Benzene. A solution of butyrophenone (**6**) (500 mg, 3.4 mmol) and ketene acetal **9** (1.18 g, 6.8 mmol) in 100 mL of benzene was irradiated for 8 h (*ca.* 95% conversion of **6**). Work-up and chromatographic (1 : 8, ethyl acetate : *n*-hexane, v/v) separation (see General) gave the diastreomeric oxetanes **28a** (20 mg, 2%) and **28b** (28 mg, 3%), **41a** (114 mg, 11%) and **41b** (30 mg, 3%), 120 mg (31%) of **2**, 30 mg (6%) of **50**, 200 mg (25%) of **18**, and 73 mg (7%) of **30**.

Irradiation of Valerophenone (7) and 1-Trimethylsilyloxy-1-methoxy-2,2-dimethylethylene (9). Acetonitrile. A solution of valerophenone (**7**) (600 mg, 3.7 mmol) and ketene acetal **9** (645 mg, 6.7 mmol) in 100 mL of acetonitrile was irradiated for 5.5 h, (*ca.* 96% conversion of **7**) Work-up and chromatographic (1 : 6, ethyl acetate : *n*-hexane) separation (see General) gave the diastreomeric oxetanes **32a** (12 mg, 1%) and **32b** (18 mg, 2%), **51a** (40 mg, 7%) and **51b** (147 mg, 19%), 132 mg (31%) of **2**, and 80 mg (14%) of **14**.

Benzene. A solution of valerophenone (**7**) (600 mg, 3.7 mmol) and ketene acetal **9** (645 mg, 6.7 mmol) in 100 mL of benzene was irradiated for 6.5 h (*ca.* 88% conversion of **7**). Work-up and chromatographic (1 : 6, ethyl acetate : *n*-hexane, v/v) separation (see General) gave the diastreomeric oxetanes **32a** (80 mg, 8%) and **32b** (124 mg, 13%), **51a** (70 mg, 13%) and **51b** (140 mg, 19%), 70 mg (18%) of **2**, and 58 mg (11%) of **14**.

Irradiation of 2'-Acetonaphthone (8) and 1-Trimethylsilyloxy-1-methoxy-2,2-dimethylethylene (9). Acetonitrile. A solution of 2'-acetonaphthone (**8**) (610 mg, 3.6 mmol) and ketene acetal **9** (1.26 g, 7.2 mmol) in 100 mL of acetonitrile was irradiated for 40 h (*ca.* 44% conversion of **8**). Work-up and chromatographic (1 : 1, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 48 mg (11%) of **19**.

19: ^{1}H NMR 1.21 (s, 3H, C(CH_3)$_2$), 1.22 (s, 3H, C(CH_3)$_2$), 1.73 (s, 3H, C(OH)CH_3), 3.70 (s, 3H, OCH_3), 4.57 (s, 1H, OH), 7.45-7.94 (m, 7H, aromatic); ^{13}C NMR 21.8 (C(CH_3)$_2$), 21.9 (C(CH_3)$_2$), 25.2 (C(OH)CH_3), 50.5 (OCH_3), 52.2 (C(CH_3)$_2$), 77.3 (C(OH)CH_3), 125.5, 125.8, 126.2, 126.6, 127.3 and 128.3 (CH, aromatic), 132.3, 132.6 and 140.9 (C, aromatic), 179.0 (C=O); Ir (neat) 3280-3600 (br, OH stretching), 1700 (C=O stretching), 1280 cm^{-1} (C-O stretching); EIMS, m/z (rel. intensity), 272 (M^+, 2), 255 (M^+-OH, 21), 171 (100), 155 (18), 127 (20), 102 (18); HRMS, m/z 272.1424 ($C_{17}H_{20}O_3$ requires 272.1412).

Irradiation of Acetophenone (2) and 1-(Methoxy)-1-(trimethylsilyloxy)propene (10). Acetonitrile. A solution of acetophenone (**2**) (430 mg, 3.6 mmol) and ketene acetal **10** (1.15 g, 7.2 mmol) in 100 mL of acetonitrile was irradiated for 12 h (*ca.* 72% conversion of **2**). Work-up and chromatographic (1 : 15, ethyl acetate : *n*-hexane, v/v) separation (see General) gave the diastreomeric photoproducts **20a** (102 mg, 19%) and **20b** (130 mg, 24%), diastreomeric oxetanes **34a** (60 mg, 8%) of and **34b** (115 mg, 16%), and 50 mg (8%) of diol **47**.

20a: mp 50-52 °C; ^{1}H NMR 0.96 (d, 3H, J = 7.2 Hz, CHCH_3), 1.56 (s, 3H, C(OH)CH_3), 2.85 (q, 1H, J = 7.2 Hz, CHCH_3), 3.76 (s, 3H, OCH_3), 3.82 (s, 1H, OH), 7.23-7.46 (m, 5H, aromatic); ^{13}C NMR 12.7 (CHCH_3), 29.9 (C(OH)CH_3), 49.3 (CHCH_3), 51.9 (OCH_3), 74.3 (C(OH)CH_3), 124.8, 126.7 and 129.1 (CH, aromatic), 145.0 (C, aromatic), 177.6 (C=O); Ir (KBr) 3300-3600 (br, OH stretching), 1710 (C=O stretching), 1200 cm^{-1} (C-O stretching); EIMS, m/z (rel. intensity) 208 (1), 159 (18), 121 (100), 105 (37), 77 (15); HRMS (EI), 208.1108 ($C_{12}H_{16}O_3$ requires 208.1099).

20b: ^{1}H NMR 1.32 (d, 3H, J = 7.0 Hz, CHCH_3), 1.46 (s, 3H, C(OH)CH_3), 3.03 (q, 1H, J = 7.0 Hz, CHCH_3), 3.46 (s, 3H, OCH_3), 4.03 (s, 1H, OH), 7.21-7.45 (m, 5H, aromatic); ^{13}C NMR 12.4 (CHCH_3), 26.6 (C(OH)CH_3), 48.5 (CHCH_3), 51.6 (OCH_3), 74.6 (C(OH)CH_3), 124.6, 126.7 and 128.1 (CH, aromatic), 147.5 (C, aromatic), 177.0 (C=O); Ir (neat) 3300-3600 (br, OH stretching), 1710 (C=O stretching), 1200 cm^{-1} (C-O stretching); EIMS, m/z (rel. intensity) 208 (0.3), 191 (2), 159 (6), 121 (100), 105 (23), 88 (11), 77 (14); HRMS (EI), 208.1100 ($C_{12}H_{16}O_3$ requires 208.1099).

34a: ^{1}H NMR 0.20 (s, 9H, $OSiMe_3$), 1.43 (d, 3H, J = 6.3 Hz, CHCH_3), 1.77 (s, 3H,C(Ph)CH_3), 2.58 (s, 3H, OCH_3),

4.87 (q, 1H, *J* = 6.3 Hz, C<u>H</u>CH$_3$), 7.27-7.59 (m, 5H, aromatic); ^{13}C NMR 1.1 (OSiMe$_3$), 15.4 (CH<u>C</u>H$_3$), 23.3 (C(Ph)<u>C</u>H$_3$), 49.4 (OCH$_3$), 84.6 (<u>C</u>HCH$_3$), 93.0 (<u>C</u>(Ph)CH$_3$), 101.2 (<u>C</u>(OCH$_3$)-OSiMe$_3$), 126.8, 127.2 and 127.6 (CH, aromatic), 142.1 (C, aromatic); Ir (neat) 1220 cm^{-1} (C-O stretching); EIMS, m/z (rel, intensity) 280 (0.8), 279 (3), 236 (12), 193 (100), 159 (85), 132 (29), 105 (19); HRMS (EI), 280.1485 ($C_{15}H_{24}O_3Si$ requires 280 1495).

34b: ^{1}H NMR -0.22 (s, 9H, OSiMe$_3$), 1.35 (d, 3H, *J* = 6.3 Hz, CHC<u>H</u>$_3$), 1.75 (s, 3H, C(Ph)C<u>H</u>$_3$), 3.31 (s, 3H, OCH$_3$), 4.91 (q, 1H, *J* = 6.3 Hz, C<u>H</u>CH$_3$), 7.21-7.48 (m, 5H, aromatic); ^{13}C NMR 1.1 (OSiMe$_3$), 16.7 (CH<u>C</u>H$_3$), 23.4 (C(Ph)<u>C</u>H$_3$), 51.1 (OCH$_3$), 82.3 (<u>C</u>HCH$_3$), 93.3 (<u>C</u>(Ph)CH$_3$), 103.1 (<u>C</u>(OCH$_3$)OSiMe$_3$), 126.8, 127.1 and 127.6 (CH, aromatic), 142.7 (C, aromatic); Ir(neat) 1220 cm^{-1} (C-O stretching); EIMS, m/z (rel. intensity) 280 (0.04), 237 (2), 221 (1), 193 (46), 160 (44), 105 (53), 73 (100); HRMS (EI), 280.1483 ($C_{15}H_{14}O_3Si$ requires 280.1495).

Benzene. A solution of acetophenone (**2**) (430 mg, 3.6 mmol) and ketene acetal **10** (1.15 g, 7.2 mmol) in 100 mL of benzene was irradiated for 14 h (*ca.* 47% conversion of **2**). Work-up and chromatographic (1 : 15, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 53 mg (15%) of **20a**, 88 mg (25%) of **20b**, 100 mg (21%) of **34a** and 160 mg (34%) of **34b**.

Irradiation of Benzophenone (3) and 1-(Methoxy)-1-(trimethylsilyloxy) propene (10). Acetonitrile. A solution of benzophenone (**3**) (656 mg, 3.6 mmol) and ketene acetal **10** (1.15 g, 7.2 mmol) in 100 mL of acetonitrile was irradiated for 8 h (*ca.* 85% conversion of **3**). Work-up and chromatographic (1 : 10, ethyl acetate : *n*-hexane, v/v) separation (see General) gave the diastreomeric oxetanes **37a** (122 mg, 12%) of and **37b** (260 mg ,25%), 340 mg (41%) of **21**, and 34 mg (6%) of **48**.

21: mp 128-130°C; ^{1}H NMR 1.23 (d, 3H, *J* = 7.2 Hz, CHCH$_3$), 3.63 (s, 3H, OCH$_3$), 3.74 (q,1H, *J* = 7.2 Hz, C<u>H</u>CH$_3$), 4.77 (s, 1H, OH), 7.16-7.64 (m, 10H, aromatic); ^{13}C NMR 12.9 (CH<u>C</u>H$_3$), 46.7 (CO$_2$<u>C</u>H$_3$), 51.9 (<u>C</u>HCH$_3$), 78.0 (<u>C</u>(Ph)$_2$OH), 125.2, 125.3, 126.5, 126.9, 128.1 and 128.3 (CH, aromatic), 144.0 and 147.5 (C, aromatic), 177.9 (C=O); Ir (neat), 3200-3600 (br, OH streching), 1710 cm^{-1} (C=O streching); EIMS, m/z (rel. intensity) 270 (M$^+$, 0.2), 239 (1), 183 (100), 165 (2), 105 (65), 77 (31); HRMS, m/z 270.1263 ($C_{17}H_{18}O_3$ requires 270.1256).

37a: ^{1}H NMR -0.06 (s, 9H, OSiMe$_3$), 1.43 (d, 3H, *J* = 6.2 Hz, CHC<u>H</u>$_3$), 3.08 (s, 3H, OCH$_3$), 4.92 (q, 1H, *J* = 6.2 Hz, C<u>H</u>CH$_3$), 7.20-7.65 (m, 10H, aromatic); ^{13}C NMR 1.2 (OSiMe$_3$), 16.7 (CH<u>C</u>H$_3$), 51.4 (OCH$_3$), 82.6 (<u>C</u>HCH$_3$), 95.8 (<u>C</u>(Ph)$_2$), 103.8 (<u>C</u>(OCH$_3$)OSiMe$_3$), 126.6, 127.0, 127.2, 127.3, 127.9 and 128.2 (CH, aromatic), 141.3 and 141.5 (C, aromatic); Ir (neat), 1250 cm^{-1} (C-O streching); CIMS, m/z (rel. intensity) 343 (6), 255 (53), 183 (33), 160 (98), 105 (100), 73 (94); HRMS(CI) 34.1734 ($C_{20}H_{27}O_3Si$ requires 343.1729).

37b: ^{1}H NMR 0.01 (s, 9H, OSiMe$_3$), 1.58 (d, 3H, *J* = 6.3 Hz, CHC<u>H</u>$_3$), 2.90 (s, 3H, OCH$_3$), 4.81 (q, 1H, *J* = 6.2 Hz, C<u>H</u>CH$_3$), 7.26-7.69 (m, 10H, aromatic); ^{13}C NMR 0.7 (OSiMe$_3$), 15.2 (CH<u>C</u>H$_3$), 49.7 (OCH$_3$), 84.5 (<u>C</u>HCH$_3$), 95.9 (<u>C</u>(Ph)$_2$), 101.8 (<u>C</u>(OCH$_3$)OSiMe$_3$), 126.7, 127.1, 127.2, 127.4, 127.6 and 127.9 (CH, aromatic), 140.8 and 141.2 (C, aromatic); Ir (neat), 1250 cm^{-1} (C-O strching); CIMS, m/z (rel. intensity) 343 (M$^+$+1, 1), 255 (3), 225 (3), 210 (20), 198 (19), 197 (100), 183 (45), 166 (42); HRMS, m/z 343.1725 ($C_{20}H_{27}O_3Si$ requires 343.1729).

Benzene. A solution of benzophenone (**3**) (656 mg, 3.6 mmol) and ketene acetal **10** (1.15 g, 7.2 mmol) in 100 mL of acetonitrile was irradiated for 7 h (*ca.* 90% conversion of **3**). Work-up and chromatographic (1 : 10, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 380 mg (39%) of **21**, 147 mg (12%) of **37a**, 294 mg (24%) of **37b** and 44 mg (14%) of **48**.

Irradiation of 4-Methoxyacetophenone (4) and 1-(Methoxy)-1-(trimethylsilyloxy) propene (10). Acetonitrile. A solution of 4-methoxyacetophenone (**4**) (540 mg, 3.6 mmol) and ketene acetal **10** (1.15 g, 7.2 mmol) in 100 mL of acetonitrile was irradiated for 50 h (*ca.* 26% conversion of **4**). Work-up and chromatographic (1 : 4, ethyl acetate : *n*-hexane) separation (see General) gave the diastreomeric photoproducts **22a** (38 mg, 17%) and **22b** (40 mg, 18%), diastreomeric oxetanes **35a** (70 mg, 26%) of and **35b** (60 mg, 22%).

22a: mp 45-47 °C; ^{1}H NMR 0.97 (d, 3H, *J* = 7.2 Hz, CHCH$_3$), 1.54 (s, 3H, C(OH)CH$_3$), 2.56 (s, 1H, OH), 2.81 (q, 1H, *J* = 7.2 Hz, C<u>H</u>CH$_3$), 3.75 (s, 3H, CO$_2$CH$_3$), 3.80 (s, 3H, Ph-OC<u>H</u>$_3$), 6.87 (d, 2H, *J* = 9.0 Hz, aromatic), 7.36 (d, 2H, *J* = 9.0 Hz, aromatic); ^{13}C NMR 12.7 (CH<u>C</u>H$_3$), 29.8 (C(OH)<u>C</u>H$_3$), 49.4 (CO$_2$<u>C</u>H$_3$), 51.8 (<u>C</u>HCH$_3$), 55.1 (Ph-O<u>C</u>H$_3$), 74.0 (<u>C</u>(OH)CH$_3$), 113.6 and 126.0 (CH, aromatic), 137.1 and 158.2 (C, aromatic), 177.6 (C=O); Ir (KBr) 3600-3200 (br, OH streching), 1700 cm^{-1} (C=O streching); EIMS, m/z (rel. intensity) 238 (M$^+$, 2), 221 (4), 161 (1), 152 (11), 151 (100), 135 (13); HRMS, m/z 238.1209 ($C_{13}H_{18}O_4$ requires 238.1205).

22b: ^{1}H NMR 1.30 (d, 3H, *J* = 7.2 Hz, CHC<u>H</u>$_3$), 1.44 (s, 3H, C(OH)C<u>H</u>$_3$), 2.99 (q, 1H, *J* = 7.2 Hz, C<u>H</u>CH$_3$), 3.49 (s, 3H, CO$_2$CH$_3$), 3.79 (s, 3H, Ph-OC<u>H</u>$_3$), 3.97 (s, 1H, OH), 6.85 (d, 2H, *J* = 9.0 Hz, aromatic), 7.34 (d, 2H, *J* = 9.0 Hz, aromatic); ^{13}C NMR 12.5 (CH<u>C</u>H$_3$), 26.6 (C(OH)<u>C</u>H$_3$), 48.7 (CO$_2$<u>C</u>H$_3$), 51.6 (<u>C</u>HCH$_3$), 55.1 (Ph-O<u>C</u>H$_3$), 74.4 (<u>C</u>(OH)CH$_3$), 113.4 and 125.8 (CH, aromatic), 139.6 and 158.3 (C, aromatic), 177.1 (C=O); Ir (neat), 3600-3200 (br, OH streching), 1710 cm^{-1} (C=O streching); EIMS, m/z (rel. intensity) 238 (M$^+$, 2), 221 (2), 161 (3), 160 (5), 159 (12), 151 (100), 149 (14); HRMS, m/z 238.1206 ($C_{13}H_{18}O_4$ requires 238.1205).

35a: ^{1}H NMR 0.19 (s, 9H, OSiMe$_3$), 1.42 (d, 3H, *J* = 6.8 Hz, CHC<u>H</u>$_3$), 1.74 (s, 3H, C(Ph-OCH$_3$)C<u>H</u>$_3$), 2.57 (s, 3H, C(OSiMe$_3$)OC<u>H</u>$_3$) 3.82 (s, 3H, Ph-OC<u>H</u>$_3$), 4.84 (q, 1H, *J* = 6.3 Hz, C<u>H</u>CH$_3$), 6.88 (d, 2H, *J* = 8.4 Hz, aromatic), 7.47 (d, 2H, *J* = 8.4 Hz, aromatic); ^{13}C NMR 1.1 (OSiMe$_3$), 15.3 (CH<u>C</u>H$_3$), 23.1 (C(Ph-OCH$_3$)<u>C</u>H$_3$), 49.3 (C(OSiMe$_3$)O<u>C</u>H$_3$), 55.1 (Ph-O<u>C</u>H$_3$), 84.3 (<u>C</u>HCH$_3$), 92.6 (<u>C</u>(Ph-OCH$_3$)CH$_3$), 101.2 (<u>C</u>(OSiMe$_3$)OCH$_3$), 112.9 and 128.1 (CH, aromatic), 134.2 and 158.9 (C, aromatic); Ir (neat) 1250 cm^{-1} (C-O

streching); CIMS, m/z (rel. intensity) 295 (M^++1, 1), 267 (10), 224 (11), 223 (60), 177 (3), 162 (29), 160 (100); HRMS, m/z 294.1656 ($C_{16}H_{26}O_3Si$ requires 294.1651).

35b: ^{1}H NMR -0.21 (s, 9H, $OSiMe_3$), 1.35 (d, 3H, J = 6.3 Hz, $CHCH_3$), 1.73 (s, 3H, C(Ph-OCH_3)C$\underline{H}_3$), 3.29 (s, 3H, C($OSiMe_3$)O$\underline{CH}_3$), 3.81 (s, 3H, Ph-O$\underline{CH}_3$), 4.89 (q, 1H, J = 6.2 Hz, C$\underline{H}CH_3$), 6.87 (d, 2H, J = 8.9 Hz, aromatic), 7.38 (d, 2H, J = 8.8 Hz, aromatic); ^{13}C NMR 1.1 ($OSiMe_3$), 16.5 (CH$\underline{C}H_3$), 23.1 (C(Ph-OCH_3)$\underline{C}H_3$), 51.0 (C($OSiMe_3$)O$\underline{C}H_3$), 55.2 (Ph-O$\underline{C}H_3$), 81.9 ($\underline{C}HCH_3$), 92.9 ($\underline{C}$(Ph-OCH_3)CH_3), 103.3 ($\underline{C}$($OSiMe_3$)OCH_3), 112.9 and 128.4 (CH, aromatic), 134.8 and 158.9 (C, aromatic); Ir (neat) 1250 cm^{-1} (C-O streching); CIMS, m/z (rel. intensity) 295 (M^++1, 1), 266 (16), 251 (3), 223 (16), 162 (29), 160 (100); HRMS, m/z 294.1659 ($C_{16}H_{26}O_3Si$ requires 294.1651).

Benzene. A solution of 4-methoxyacetophenone (**4**) (540 mg, 3.6 mmol) and ketene acetal **10** (1.15 g, 7.2 mmol) in 100 mL of benzene was irradiated for 19 h (*ca.* 46% conversion of **4**). Work-up and chromatographic (1 : 4, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 95 mg (24%) of **22a**, 122 mg (31%) of **22b**, 88 mg (18%) of **35a** and 120 mg (25%) of **35b**.

Irradiation of 4-Cyanoacetophenone (5) and 1-(Methoxy)-1-(trimethylsilyloxy) propene (10). Benzene. A solution of 4-cyanoacetophenone (**5**) (520 mg, 3.6 mmol) and ketene acetal **10** (1.15 g, 7.2 mmol) in 100 mL of benzene was irradiated for 13.5 h (*ca.* 87% conversion of **5**). Work-up and chromatographic (1 : 5, ethyl acetate : *n*-hexane, v/v) separation (see General) gave the diastreomeric photoproducts **23a** (124 mg, 17%) and **23b** (340 mg, 47%), diastreomeric oxetanes **36a** (78 mg, 8%) of and **36b** (160 mg, 17%), and 45 mg (5%) of diol **49**.

23a: mp 84-86 °C; ^{1}H NMR 0.92 (d, 3H, J = 7.1 Hz, $CHCH_3$), 1.54 (s, 3H, C(OH)C$\underline{H}_3$), 2.83 (q, 1H, J = 7.1 Hz, C$\underline{H}CH_3$), 3.77 (s, 3H, CO_2CH_3), 4.03 (s, 1H, OH), 7.52-7.66 (m, 4H, aromatic); ^{13}C NMR 12.6 (CH$\underline{C}H_3$), 29.5 (C(OH)$\underline{C}H_3$), 48.7 ($CO_2\underline{C}H_3$), 52.0 ($\underline{C}HCH_3$), 74.2 ($\underline{C}$(OH)CH_3), 110.6 (CN), 126.8 and 131.9 (CH, aromatic), 118.9 and 150.4 (C, aromatic) 177.1 (C=O); Ir (KBr), 3600-3200 (br, OH streching), 2230 (CN streching), 1710 cm^{-1} (C=O streching); CIMS, m/z (rel. intensity) 234 (M^++1, 4), 218 (8), 146 (49), 130 (46), 122 (8), 116 (4), 102 (17), 88 (100); HRMS, m/z 234.1136 ($C_{13}H_{16}NO_3$ requires 234.1130).

23b: mp 36-38°C, ^{1}H NMR 1.36 (d, 3H, J = 7.0 Hz, CHC$\underline{H}_3$), 1.44 (s, 3H, C(OH)C$\underline{H}_3$), 3.01 (q, 1H, J = 7.0 Hz, C$\underline{H}CH_3$), 3.47 (s, 3H, $CO_2C\underline{H}_3$), 4.19 (s, 1H, OH), 7.52-7.65 (m, 4H, aromatic); ^{13}C NMR 12.2 (CH$\underline{C}$H3), 26.5 (C(OH)-$\underline{C}H_3$), 47.9 ($CO_2\underline{C}H_3$), 51.7 ($\underline{C}HCH_3$), 74.5 ($\underline{C}$(OH)CH_3), 110.6 (CN), 125.5 and 131.9 (CH, aromatic), 118.6 and 153.0 (C, aromatic), 176.6 (C=O); Ir (KBr), 3600-3200 (br, OH streching), 2230 (CN streching), 1710 cm^{-1} (C=O streching); CIMS, m/z (rel. intensity) 234 (M^++1, 5), 216 (8), 146 (51), 130 (22), 102 (8), 88 (100), 57 (22); HRMS, m/z 234.1137 ($C_{13}H_{16}NO_3$ requires 234.1130).

36a: ^{1}H NMR 0.21 (s, 9H, $OSiMe_3$), 1.41 (d, 3H, J = 6.3 Hz, $CHCH_3$), 1.73 (s, 3H, C(Ph-CN)C$\underline{H}_3$), 2.63 (s, 3H, OCH_3), 4.88 (q, 1H, J = 6.3 Hz, C$\underline{H}CH_3$), 7.64 (s, 4H, aromatic); ^{13}C NMR 1.1 ($OSiMe_3$), 15.5 (CH$\underline{C}H_3$), 23.2 (C(Ph-CN)$\underline{C}H_3$), 49.6 (OCH_3), 85.2 ($\underline{C}HCH_3$), 92.7 ($\underline{C}$(Ph-CN)CH_3), 101.9 ($\underline{C}$($OSiMe_3$)OCH_3), 110.9 (CN), 127.4 and 131.4 (CH, aromatic), 147.8 (C,aromatic); Ir (neat) 2230 (CN streching); CIMS, m/z (rel. intensity) 306 (M^++1, 0.1), 290 (1), 261 (7), 248 (3), 218 (40), 186 (5), 105 (38), 89 (35), 73 (100); HRMS, m/z 306.1536 ($C_{16}H_{24}NO_3Si$ requires 306.1526)

36b: ^{1}H NMR -0.18 (s, 9H, $OSiMe_3$), 1.31 (d, 3H, J = 6.3 Hz, $CHCH_3$), 1.71 (s, 3H, C(Ph-CN)C$\underline{H}_3$), 3.34 (s, 3H, OCH_3), 4.92 (q, 1H, J = 6.3 Hz, C$\underline{H}CH_3$), 7.51-7.66 (m, 4H, aromatic); ^{13}C NMR 1.1 ($OSiMe_3$), 16.8 (CH$\underline{C}H_3$), 23.3 (C(Ph-CN)$\underline{C}H_3$), 51.3 (OCH_3), 82.8 ($\underline{C}HCH_3$), 93.0 ($\underline{C}$(Ph-CN)CH_3), 102.8 ($\underline{C}$($OSiMe_3$)OCH_3), 110.7 (CN), 127.2 and 131.3 (CH, aromatic) 148.5 (C,aromatic); Ir (neat) 2230 (CN streching); CIMS, m/z (rel. intensity) 306 (M^++1, 0.04), 290 (1), 261 (7), 248 (4), 218 (26), 160 (94), 105 (68), 73 (100); HRMS, m/z 306.1527 ($C_{16}H_{24}NO_3Si$ requires 306.1526).

Irradiation of Acetophenone (2) and 1-(Methoxy)-1-(trimethylsilyloxy)ethane (11). Acetonitrile. A solution of acetophenone (**2**) (430 mg, 3.6 mmol) and ketene acetal **11** (1.05 g, 7.2 mmol) in 100 mL of acetonitrile was irradiated for 20 h (*ca.* 49% conversion of **2**). Work-up and chromatographic (1 : 4, ethyl acetate : *n*-hexane, v/v) separation (see General) gave the diastreomeric oxetanes **38a** (75 mg, 16%) and **38b** (140 mg, 30%), and 86 mg (25%) of **24**.

24: ^{1}H NMR 1.56 (s, 3H, C(OH)CH_3), 2.81 (d, 1H, J = 16 Hz, CH_2), 3.01 (d, 1H, J = 16 Hz, CH_2), 3.61 (s, 3H, CO_2CH_3), 4.34 (s, 1H, OH), 7.24-7.48 (m, 5H, aromatic); ^{13}C NMR 30.5 (C(OH)$\underline{C}H_3$), 46.1 (CH_2), 51.6 ($CO_2\underline{C}H_3$), 72.6 ($\underline{C}$(OH)CH_3), 124.3, 126.8 and 128.5 (CH, aromatic), 146.8 (C, aromatic), 173.0 (C=O); Ir (neat) 3600-3200 (br, OH streching), 1720 cm^{-1} (C=O streching); EIMS, m/z (rel. intensity) 194 (M^+, 1), 179 (48), 177 (3), 167 (8), 149 (18), 145 (3), 121 (100), 105 (71); HRMS, m/z 194.0937 ($C_{11}H_{14}O_3$ requires 194.0943).

38a: ^{1}H NMR 0.22 (s, 9H, $OSiMe_3$), 1.77 (s, 3H, C(Ph)-C$\underline{H}_3$), 2.74 (s, 3H, OCH_3), 4.60 (d, 1H, J = 6.7 Hz, -OCH_2), 4.66 (d, 1H, J = 6.6 Hz, -OCH_2), 7.31-7.54 (m, 5H, aromatic); ^{13}C NMR 1.1 ($OSiMe_3$), 23.4 (C(Ph)$\underline{C}H_3$), 49.9 (OCH_3), 79.0 (OCH_2), 96.1 ($\underline{C}$(Ph)CH_3), 101.6 ($\underline{C}$($OSiMe_3$)OCH_3), 126.3, 127.2 and 127.7 (CH, aromatic), 141.9 (C, aromatic); Ir (neat) 1210 cm^{-1} (C-O streching); EIMS, m/z (rel. intensity) 266 (0.1). 236 (39), 207 (20), 191 (32), 146 (100), 89 (29); HRMS, 266.1337 ($C_{14}H_{22}O_3Si$ requires 266,1338).

38b: ^{1}H NMR -0.14 (s, 9H, $OSiMe_3$), 1.70 (s, 3H, C(Ph)-C$\underline{H}_3$), 3.37 (s, 3H, OCH_3), 4.49 (d, 1H, J = 6.8 Hz, -OCH_2), 4.63 (d, 1H, J = 6.9 Hz, -OCH_2), 7.22-7.38 (m, 5H, aromatic); ^{13}C NMR 0.0 ($OSiMe_3$), 23.6 (C(Ph)$\underline{C}H_3$), 49.8 (OCH_3), 75.7 (OCH_2), 96.7 ($\underline{C}$(Ph)CH_3), 100.1 ($\underline{C}$($OSiMe_3$)OCH_3), 125.0, 126.0 and 126.9 (CH, aromatic), 142.1 (C, aromatic); Ir (neat) 1220 cm^{-1} (C-O streching); EIMS, m/z (rel. intensity) 266 (M^+, 0.2), 251 (2), 236 (5), 219 (1), 207 (3), 193 (12), 151 (12), 146 (100); HRMS, 266.1337 ($C_{14}H_{22}O_3Si$ requires 266.1338).

Benzene. A solution of acetophenone (**2**) (430 mg, 3.6 mmol) and ketene acetal **11** (1.05 g, 7.2 mmol) in 100 mL of

benzene was irradiated for 16 h (*ca.* 65% conversion of **2**). Work-up and chromatographic (1 : 4, ethyl acetate : *n*-hexane, v/v) separation (see General) gave the diastreomeric oxetanes **38a** (130 mg, 21 %) and **38b** (200 mg, 32%), and 100 mg (22%) of **24**.

Irradiation of Benzophenone (3) and 1-(Methoxy)-1-(trimethylsilyloxy)ethane (11). Benzene. A solution of benzophenone (**3**) (656 mg, 3.6 mmol) and ketene acetal **11** (1.05 g, 7.2 mmol) in 100 mL of benzene was irradiated for 25 h (*ca.* 89% conversion of **3**). Work-up and chromatographic (1 : 10, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 131 mg (16%) of **25**, 710 mg (68%) of **39** and 23 mg (4%) of **48**.

25: ^{1}H NMR 3.30 (s, 2H, CH_2), 3.65 (s, 3H, CO_2CH_3), 5.06 (s, 1H, OH), 7.17-7.47 (m, 10H, aromatic); ^{13}C NMR 45.3 (CH_2), 51.9 ($CO_2\underline{C}H_3$), 83.0 ($\underline{C}(OH)Ph_2$), 125.6, 127.1, 127.2, 128.2 and 128.6 (CH, aromatic), 144.2 and 145.9 (C, aromatic), 173.2 (C=O); Ir (neat) 3600-3200 cm^{-1} (br, OH streching); EIMS, m/z (rel. intensity) 256 (M^+, 3), 239 (3), 184 (15), 183 (100), 148 (14), 105 (71), 77 (26); HRMS, m/z 256. 1100 ($C_{16}H_{16}O_3$ requires 256.1100).

39: ^{1}H NMR -0.05 (s, 9H, $OSiMe_3$), 2.97 (s, 3H, OCH_3), 4.61 (d, 1H, J = 6.8 Hz, OCH_2), 4.72 (d, 1H, J = 6.7 Hz, OCH_2), 7.26-7.58 (m, 10H, aromatic); ^{13}C NMR 0.7 ($OSiMe_3$), 50.0 (OCH_3), 78.8 (OCH_2), 98.9 ($\underline{C}(Ph)_2$), 101.7 ($\underline{C}(OSiMe_3)$-OCH_3), 126.8, 127.1 and 127.5 (CH, aromatic), 141.1 (C, aromatic); Ir (neat) 1200 cm^{-1} (C-O streching); EIMS, m/z (rel. intensity) 328 (M^+, 0.2), 313 (1), 269 (3), 255 (8), 193 (8), 164 (12), 147 (13), 146 (100); HRMS, m/z 328.1495 ($C_{19}H_{24}O_3Si$ requires 328.1495).

Irradiation of 4-Cyanoacetophenone (5) and 1-(Methoxy)-1-(trimethylsilyloxy) ethane (11). Benzene. A solution of 4-cyanoacetophenone (**5**) (520 mg, 3.6 mmol) and ketene acetal **11** (1.05 g, 7.2 mmol) in 100 mL of benzene was irradiated for 25 h (*ca.* 43% conversion of **5**). Work-up and chromatographic (1 : 5, ethyl acetate : *n*-hexane, v/v) separation (see General) gave the diastreomeric oxetanes **40a** (63 mg, 14%) and **40b** (144 mg, 32%), 136 mg (40%) of **26** and 14 mg (6%) of diol **49**.

26: ^{1}H NMR 1.53 (s, 3H, $C(OH)CH_3$), 2.82 (d, 1H, J = 16.0 Hz, CH_2), 2.98 (d, 1H, J = 16.0 Hz, CH_2), 3.62 (s, 3H, CO_2CH_3), 4.46 (s, 1H, OH), 7.54-7.66 (m, 4H, aromatic); ^{13}C NMR 30.3 ($C(OH)\underline{C}H_3$), 45.6 (CH_2), 51.9 ($CO_2\underline{C}H_3$), 72.5 ($\underline{C}(OH)CH_3$), 110.8 (CN), 125.4 and 132.1 (CH, aromatic), 118.7 and 152.2 (C, aromatic), 172.6 (C=O); Ir(neat) 3600-3200 (br, OH streching), 2230 (CN streching), 1730 cm^{-1} (C=O streching); CIMS, m/z (rel. intensity) 220 (M^++1, 12), 203 (50), 202 (13), 172 (10), 147 (11), 146 (100), 130 (83); HRMS, m/z 220.0975 ($C_{12}H_{14}NO_3$ requires 220.0974).

40a: ^{1}H NMR 0.22 (s, 9H, $OSiMe_3$), 1.72 (s, 3H, $C(Ph\text{-}CN)C\underline{H}_3$), 2.80 (s, 3H, OCH_3), 4.58 (d, 1H, J = 6.8 Hz, OCH_2), 4.64 (d, 1H, J = 6.9 Hz, OCH_2), 7.56-7.67 (m, 4H, aromatic); ^{13}C NMR 1.1 ($OSiMe_3$), 23.5 ($C(OH)\underline{C}H_3$), 50.1 (OCH_3), 78.9 (OCH_2), 95.8 ($\underline{C}(Ph\text{-}CN)CH_3$), 101.4 ($\underline{C}(OSiMe_3)$-$OCH_3$), 111.0 (CN), 126.9 and 131.5 (CH, aromatic), 119.0 and 147.6 (C, aromatic); Ir (neat) 2230 (CN streching), 1220 cm^{-1} (C-O streching); EIMS, m/z (rel. intensity) 291 (M^+, 0.1), 266 (0.3), 249 (2), 157 (28), 146 (88), 129 (28), 89 (66), 73 (100); HRMS, m/z 291.1289 ($C_{15}H_{21}NO_3$ requires 291.1291).

40b: ^{1}H NMR -0.12 (s, 9H, $OSiMe_3$), 1.67 (s, 3H, $C(Ph\text{-}CN)C\underline{H}_3$), 3.36 (s, 3H, OCH_3), 4.46 (d, 1H, J = 7.0 Hz, OCH_2), 4.61 (d, 1H, J = 7.0 Hz, OCH_2), 7.46-7.67 (m, 4H, aromatic); ^{13}C NMR 0.6 ($OSiMe_3$), 24.1 ($C(OH)\underline{C}H_3$), 50.4 (OCH_3), 78.5 (OCH_2), 96.9 ($\underline{C}(Ph\text{-}CN)CH_3$), 100.4 ($\underline{C}(OSiMe_3)$-$OCH_3$), 110.4 (CN), 126.3 and 131.4 (CH, aromatic),119.0 and 148.4 (C, aromatic); Ir (neat) 2230 (CN streching), 1220 cm^{-1} (C-O streching); EIMS, m/z (rel. intensity) 291 (M^+, 0.3), 266 (2), 247 (1), 232 (2), 224 (1), 216 (2), 206 (1), 159 (62), 130 (70), 102 (46), 69 (100); HRMS, m/z 291.1288 ($C_{15}H_{21}NO_3Si$ requires 291.1291).

Irradiation of Butyrophenone (6) and 1-(Methoxy)-1-(trimethylsilyloxy)ethane (11). Acetonitrile. A solution of butyrophenone (**6**) (500 mg, 3.4 mmol) and ketene acetal **11** (990 mg, 6.8 mmol) in 100 mL of acetonitrile was irradiated for 2 h (*ca.* 95% conversion of **6**). Work-up and chromatographic (1 : 18, ethyl acetate : *n*-hexane, v/v) separation (see General) gave the diastreomeric oxetanes **31a** (27 mg, 3%) and **31b** (60 mg, 7%), 244 mg (63%) of **2** and diol 80 mg (17%) of **50**.

Irradiation of Acetophenone (2) and 3,4-Dihydro-6-(trimethylsilyloxy)-2H-pyrane (12). Acetonitrile. A solution of acetophenone (**2**) (360 mg, 3.0 mmol) and ketene acetal **12** (1.03 g, 6.0 mmol) in 100 mL of acetonitrile was irradiated for 37 h (*ca.* 30% conversion of **2**). Work-up and chromatographic (1 : 4, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 42 mg (21%) of **44**.

44: ^{1}H NMR 1.64-1.74 (m, 2H, $CH_2C\underline{H}_2CH_2$), 1.78 (s, 3H, CH_3), 1.78-1.82 (m, 2H, $CHC\underline{H}_2$), 2.90 (t, 1H, J = 10.0 Hz, $C\underline{H}CH_2CH_2$-), 4.11-4.32 (m, 2H, CO_2CH_2-), 4.45 (s, 1H, OH), 7.26-7.46 (m, 5H, aromatic); ^{13}C NMR 21.0 ($CH_2\underline{C}H_2$-CH_2), 22.1 ($CH\underline{C}H_2$), 29.4 ($C(OH)\underline{C}H_3$), 49.3 ($\underline{C}HCH_2CH_2$-), 68.1 ($CO_2\underline{C}H_2$-), 74.5 ($\underline{C}(OH)CH_3$), 125.1, 126.8 and 128.2 (CH, aromatic), 144.8 (C, aromatic), 174.9 (C=O); Ir (neat) 3600-3000 (br, OH streching), 1720 cm^{-1} (C=O streching); EIMS, m/z (rel. intensity) 220 (M^+, 0.3), 205 (1), 146 (2), 131 (2), 121 (51), 120 (23), 115 (2), 106 (8), 104 (100), 77 (55); HRMS, m/z 220.1096 ($C_{13}H_{16}O_3$ requires 220.1099).

Irradiation of Benzophenone (3) and 3,4-Dihydro-6-(trimethylsilyloxy)-2H-pyrane (12). Acetonitrile. A solution of benzophenone (**3**) (547 mg, 3.0 mmol) and ketene acetal **12** (1.03 g, 6.0 mmol) in 100 mL of acetonitrile was irradiated for 21 h (*ca.* 61% conversion of **3**). Work-up and chromatographic (1 : 10, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 103 mg (20%) of **45** and 67 mg (20%) of **48**.

45: mp 150-152 °C; ^{1}H NMR 1.45-1.58 (m, 2H, $CH_2C\underline{H}_2$-CH_2), 1.81-1.97 (m, 2H, $CHC\underline{H}_2$), 3.62 (dd, 1H, J = 8.0 Hz and J = 12.0 Hz, CH), 4.38-4.50 (m, 2H, CO_2CH_2-), 4.52 (s, 1H, OH), 7.17-7.46 (m, 10H, aromatic); ^{13}C NMR 20.5 ($CH_2\underline{C}H_2CH_2$), 22.1 ($CH\underline{C}H_2$), 46.8 ($CO_2\underline{C}H_2$-), 67.8 ($\underline{C}H$-CH_2CH_2-), 77.8 ($\underline{C}(OH)Ph_2$), 125.7, 125.8, 126.7, 127.0, 128.1 and 128.2 (CH, aromatic), 144.0 and 146.7 (C,

aromatic), 175.2 (C=O); Ir (KBr) 3200-3600 (br, OH streching), 1710 cm^{-1} (C=O streching); EIMS, m/z (rel. intensity) 282 (M^+, 2), 265 (22), 205 (6), 185 (44), 183 (100), 165 (5), 105 (18), 104 (97); HRMS, m/z 282.1251 ($C_{18}H_{18}O_3$ requires 282.1256).

Irradiation of 4-Cyanoacetophenone (5) and 3,4-Dihydro-6-(trimethylsilyloxy)-2H-pyrane (12). Benzene. A solution of 4-cyanoacetophenone (**5**) (435 mg, 3.0 mmol) and ketene acetal **12** (1.03 g, 6.0 mmol) in 100 mL of benzene was irradiated for 25 h (*ca.* 54% conversion of **5**). Work-up and chromatographic (1 : 4, ether : *n*-hexane, v/v) separation (see General) gave 80 mg (20%)of **46** and 148 mg (50%) of **49**.

46: ^{1}H NMR 1.52-1.69 (m, 2H, $CH_2C\underline{H}_2CH_2$), 1.77 (s, 3H, $C(OH)C\underline{H}_3$), 1.80-1.88 (m, 2H, $CHC\underline{H}_2$), 2.89 (t, 1H, J = 9.5 Hz, $C\underline{H}CH_2CH_2$-), 4.21-4.28 (m, 2H, CO_2CH_2-), 4.40 (s, 1H, OH), 7.55 (d, 2H, J = 8.5 Hz, aromatic), 7.65 (d, 2H, J = 8.5 Hz, aromatic); ^{13}C NMR 20.7 ($CH_2\underline{C}H_2CH_2$), 21.9 ($CH\underline{C}H_2$), 29.3 ($C(OH)\underline{C}H_3$), 48.6 ($\underline{C}HCH_2CH_2$-), 68.0 ($CO_2\underline{C}H_2$-), 74.4 ($\underline{C}(OH)CH_3$), 110.9 (CN), 125.5 and 131.9 (CH, aromatic), 118.6 and 150.3 (C, aromatic), 176.6 (C=O); Ir (neat) 3600-3200 (br, OH streching), 2240 (CN streching), 1740 cm^{-1} (C=O streching); CIMS, m/z (rel. intensity) 246 (M^++1, 1), 231 (2), 230 (16), 186 (1), 146 (25), 130 (65), 116 (3), 103 (4), 102 (22), 100 (100); HRMS, m/z 246.1131 ($C_{14}H_{16}NO_3$ requires 246.1130).

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