

p-Benzoyltriphenylmethyl O¹⁸ peroxide (Ib): mp 161–162 °C; IR (KBr) 1657 (C=O), 966 and 756 cm⁻¹ (peroxide).

***m*-Benzoyltriphenylmethyl Peroxide (IIa).** A dry benzene solution (100 mL) containing 1 g of *m*-benzoyltriphenylmethyl chloride and 3 mL of mercury was shaken for 2–4 h. The resulting brown solution was separated, and a stream of oxygen was bubbled into this solution until it became colorless. The solvent was removed under reduced pressure, and the wet residue was then washed several times with acetone: yield (1.72 g, 76%): mp 161–162 °C; IR (KBr) 1658 (C=O), 976 and 758 cm⁻¹ (peroxide). Anal. Calcd for C₅₂H₃₈O₄: C, 85.93; H, 5.27. Found: C, 85.65; H, 5.62.

(*m*-Benzoylphenyl)decadeuteriodiphenylmethyl Peroxide (IIb). This peroxide was obtained in 81% yield from *m*-(benzoylphenyl)decadeuteriodiphenylmethyl chloride (vide supra): mp 161–162 °C; IR (KBr) 1658 (C=O), 978 and 760 cm⁻¹ (peroxide).

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Photochemical Reactions of Arenecarboxylic Acid Esters with Electron-Rich Alkenes: 2 + 2 Cycloaddition, Hydrogen Abstraction, and Cycloreversion

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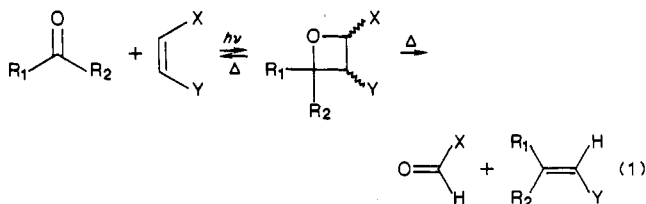
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The photochemical reaction of arenecarboxylic acid methyl esters and isopropyl esters with alkenes has been examined and found to afford three types of products: (a) 2-alkoxyoxetanes **3** via a direct 2 + 2 cycloaddition to the substrate alkenes; (b) β,γ -unsaturated ketones **5** via hydrogen abstraction by the carbonyl oxygen of the photoexcited ester from an allylic position of the substrate alkene; and (c) alkoxyalkenes **4**, which arise via 2 + 2 cycloreversion of the oxetanes **3**. The quantum yields for the formation of the various products generally fell in the range 0.005–0.03, approximately 1 order of magnitude less than those of aryl ketones and aldehydes undergoing similar reactions.

Introduction

The photochemical 2 + 2 cycloaddition of ketones and aldehydes to the carbon–carbon double bond of alkenes affording oxetanes is one of the earliest reported organic photochemical reactions.^{1,2} The reaction was long neglected, as the product oxetanes seemed to be of little interest or value. However, in the past ten years, this reaction, termed the Paterno–Buchi cycloaddition, has proven to be of considerable synthetic utility. Most of the oxetanes, thereby available, undergo a thermal retro 2 + 2 cleavage at relatively low temperatures. In some cases



this thermal 2 + 2 cycloreversion (Carbonyl–Olefin Metathesis, or COM) leads to unsaturated long-chain compounds that are otherwise accessible only with considerably more difficulty, especially in the case of bicyclic oxetanes derived from carbonyl compounds and cyclic alkenes.^{3a} Furthermore, aqueous acidic hydrolysis of certain oxetanes, particularly those derived by photochemical addition of carbonyl compounds to furans as olefinic substrates, can

provide a convenient and high-yield route to dihydroxy ketones and dihydroxy aldehydes of known relative stereochemistry at three or four contiguous asymmetric centers.^{3b}

Some time ago one of us reported in preliminary fashion that esters of benzoic acid underwent photochemical 2 + 2 cycloaddition to several electron-rich alkenes across the carbonyl group to afford 2-alkoxyoxetanes and their oxetane-derived retro 2 + 2 cleavage (COM) products.⁴ These were accompanied by smaller amounts of acyclic ketones formed by an initial hydrogen abstraction, followed by subsequent ground-state free-radical reactions.⁴ The details of the various photochemical processes and the results of subsequent studies of the photochemical, thermal, and hydrolytic behavior of the products are reported here.

Results and Discussion

Irradiation through Vycor of hexane solutions of methyl benzoate (or the ethyl or isopropyl esters as well) and excess 2,3-dimethyl-2-butene (**2a**), 2-methyl-2-butene (**2b**), 1,1-dimethyl-2,2-dimethoxyethene (**2c**), 1,2-dimethylcyclohexene (**2d**), and 1,1-diethoxyethene (**2e**) gave oxetane

(1) (a) Paterno, L.; Chieffi, G. *Gazz. Chim. Ital.* **1909**, *39*, 341–347. (b) Buchi, G.; Inman, C. G.; Lipinsky, E. S. *J. Am. Chem. Soc.* **1954**, *76*, 4327–4332.

(2) Arnold, D. R.; Hinman, V. Y.; Glick, A. H. *Adv. Photochem.* **1968**, *6*, 301–350.

(3) (a) Jones, G., II In *Organic Photochemistry*; Padwa, A., Ed.; Wiley: New York, 1981; Vol. 5. (b) Schreiber, S. W. *Science (Washington, D.C.)* **1985**, *227*, 858–863 and references therein.

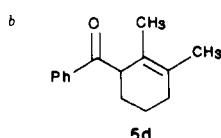
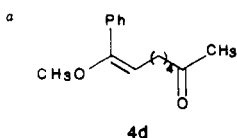
(4) Cantrell, T. S. *J. Chem. Soc., Chem. Commun.* **1973**, 468–469.

[†]National Institutes of Health.

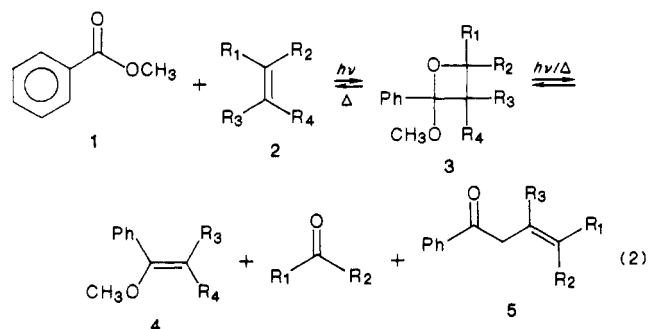
[‡]American University.

Table I. Photochemical Reactions of Methyl Benzoates with Alkenes 2

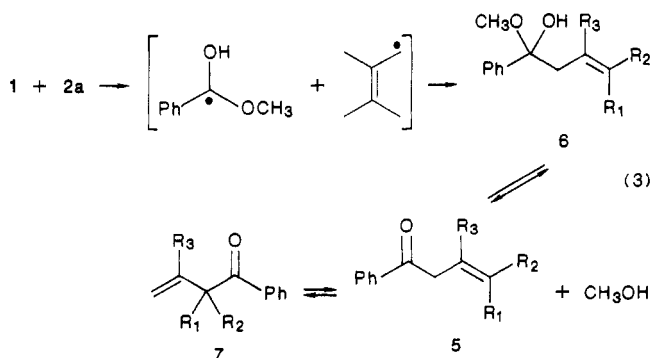
alkene	chemical yield			% quantum yield	
	3	4	5	3	5
2a: R ₁ = R ₂ = R ₃ = R ₄ = CH ₃	52	7	19	0.034	0.014
2b: R ₁ = H; R ₂ = R ₃ = R ₄ = CH ₃	33	10	34	0.020	0.017
2c: R ₁ = R ₂ = CH ₃ ; R ₃ = R ₄ = OCH ₃	40	-	11	0.05	~0.01
2d: R ₁ = R ₃ = CH ₃ ; R ₂ , R ₄ = (CH ₂) ₄	48	5 ^a	14 ^b	0.03	~0.01 ^b
2e: R ₁ = R ₂ = H; R ₃ = R ₄ = OC ₂ H ₅	29	-	-	~0.01	-
2f: R ₁ = R ₃ = H; R ₂ = R ₄ = OCH ₃	37	-	-	-	-



oxetanes **3a-e** as the major products, together with varying amounts of alkoxyalkenes **4** and ketones **5** (eq 2). The

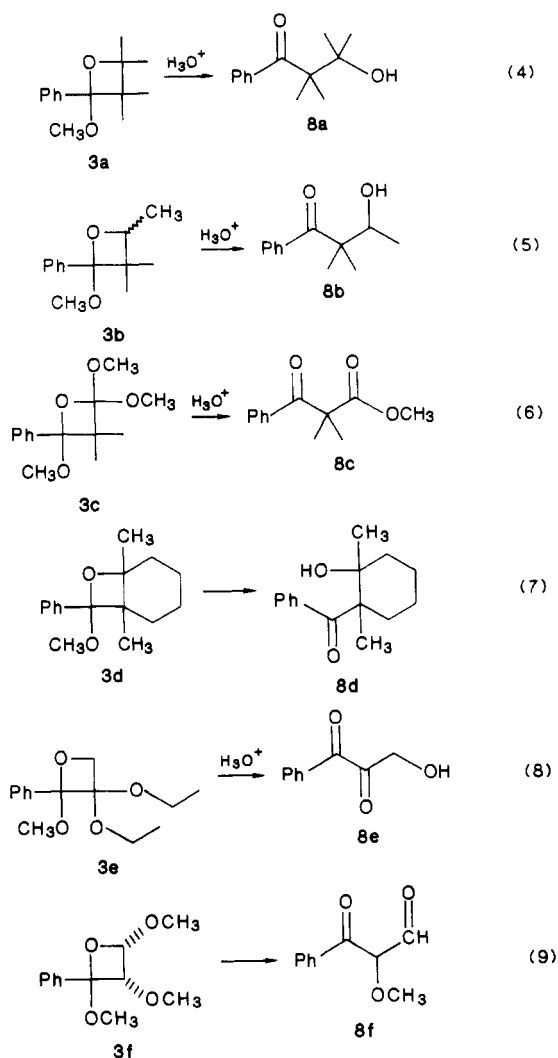


enol ethers **4** are the products of the alternate 2 + 2 process, a cycloreversion termed the Carbonyl-Olefin Metathesis (COM) by Jones.^{3a} The ketones **5** arise via initial hydrogen abstraction from an allylic position on the substrate alkene by the carbonyl oxygen of the photoexcited ester, as shown in eq 3. The two radicals produced combine to afford hemiketals **6**, which then rapidly lose methanol to yield ketones **5**. These β,γ -unsaturated ketones are themselves in a photochemical equilibrium with their isomers **7** via 1,3-acyl shifts.⁵



The chemical yields and quantum yields for oxetanes **3a-e**, together with the measurable data for COM products **4** and ketones **5**, are shown in Table I. The quantum yields are those at 2-5% conversion of ester; the chemical yields are those after 50-60% consumption of ester and

(5) Such 1,3-acyl shifts are quite common among β,γ -enones. For a comprehensive review, see: Houk, K. N. *Chem. Rev.* 1976, 76, 1-74.

Scheme I

are based on unrecovered ester. One noteworthy aspect of these data is that the quantum yields of the 2-alkoxyoxetanes **3** are lower by factors of 10-20 compared to those of several simple phenyl ketones and aldehydes, these commonly being 0.15-0.50.^{3a,6,7} This will be discussed later.

The structures of the oxetanes **3a-e** were assigned in most cases from their IR and ¹H NMR spectra. The orientations of the addends in the unsymmetrical compounds **3b**, **3c**, and **3e** were established by chemical degradation (Scheme I). The alkoxyoxetanes are mixed ketals and, as such, readily undergo hydrolysis in cold dilute aqueous acid to afford phenyl hydroxyalkyl ketones. Thus, oxetane **3a** from the symmetrical substrate **2a** gave 2,3-dimethyl-3-benzoyl-2-butanol (**8a**, eq 4). Spectral data were in accord with the assigned structure. Similar treatment of **3b** gave 3-methyl-3-benzoyl-2-butanol (**8b**, eq 5) as the major product, identical with an authentic sample. Oxetane **3c** is not simply a ketal but a mixed ortho ester, which underwent hydrolysis only after prolonged warming with dilute acid. The methyl α -benzoyliso-butyrate thus obtained was identical with authentic material.⁸ Hydrolysis of **3e** gave an unstable oil, whose data

(6) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin-Cummings: Menlo Park, CA, 1978; Chapter 11, pp 432-552.

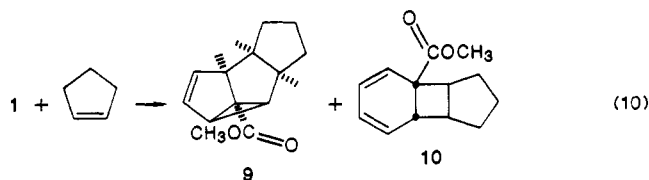
(7) Cowan, D. O.; Drisko, R. *Elements of Organic Photochemistry*; Plenum: New York, 1976; pp 181-194.

(8) McElvain, S. M.; Aldridge, C. L. *J. Am. Chem. Soc.* 1953, 75, 3987-3995.

indicated it to be 3-hydroxy-1-phenyl-1,2-propanedione (8e, eq 8).

The parent ion peaks of oxetanes 3 in the EI mass spectra were very weak when obtained at 50–70 eV, being only 0–0.5% of the intensity of the base peak. The base peak of these oxetanes 3 is consistent with the COM product, enol ether 4, i.e., an EI-induced 2 + 2 cycloreversion. However, the chemical ionization technique, with isobutane as the ionizing gas, gave prominent P + 1 ions, which greatly helped in characterizing the present oxetanes.

A matter of interest is whether the cycloaddition process leading to the oxetanes 3 is concerted. In some other photochemical cycloadditions, the retention or loss of geometric identity in reactions with substrates such as the 2-butenes and 1,2-dichloroethenes has been firm evidence supporting a concerted or stepwise pathway, respectively.^{3a,6,7} Those substrates were unsuitable for this question (i.e., concertedness) in the present study as they, and photoexcited benzoate esters, did not afford oxetanes. Instead, these alkenes, and others less electron rich than 2a–f, e.g., cyclopentene, did not add across the ester carbonyl group. They did, rather, add across the benzene ring of 1a in 1,2- and 1,3-manner to afford products of type 9 and 10 (eq 10). This parallels the photochemical behavior of both benzene itself and simple alkyl and alkoxybenzenes.⁹



This photochemical behavior of benzoate esters also parallels that of benzonitrile and simple alkylbenzonitriles, which we earlier found to react photochemically with electron-rich alkenes 2a–f across the C≡N triple bond to afford azetines and (mainly) their ring-opened isomers, 2-azabutadienes.¹⁰ In contrast, benzonitrile with more electron deficient alkenes underwent addition across the benzene ring in 1,2-fashion to produce 1-cyanobicyclo[4.2.0]octa-2,4-dienes (similar to 10, except cyano instead of carbomethoxy).^{11,12}

The only alkene existing as cis and trans isomers, and found here to undergo 2 + 2 cycloaddition to the carbonyl group of benzoate ester 1a, was 2f, cis-1,2-dimethoxyethene.¹³ The sole product obtained was oxetane 3f (37%), whose methyls are still cis. The observed retention of geometry suggests a concerted 2 + 2 process. This single finding supports the intermediacy of excited singlets in the formation of oxetanes. However, the NMR spectrum of the reaction mixture showed an additional minor methoxyl signal, which may be due to the corresponding trans isomer. This minor product did not survive GC separation.

(9) For a comprehensive review on benzene photochemistry, see: (a) Bryce-Smith, D.; Gilbert, A. *Tetrahedron* 1976, 32, 1309–1326. (b) Bryce-Smith, D.; Gilbert, A. *Tetrahedron* 1977, 33, 2459–2490.

(10) Cantrell, T. S. *J. Org. Chem.* 1977, 42, 4238–4245.

(11) Details of our results on the photochemical reactions of arene-carboxylic acid esters with electron-deficient alkenes will be reported separately: Cantrell, T.; Greenwood, W.; Allen, A., to be submitted.

(12) The 1,3-1,2-cycloaddition of photoexcited benzonitrile to cyclopentene was recently reported as a minor process competing with 2 + 2 cycloaddition and forming a product of type 9: Osseltson, E. M.; Corneliisse, J. *Tetrahedron Lett.* 1985, 26, 527–530.

(13) Prepared according to the procedure given by Schaap et al.: Schaap, A. P.; Thayer, A. L.; Kees, K. In *Organic Photochem. Syn.*; Srinivasan, R.; Roberts, T. D., Eds.; Wiley-Interscience: New York, 1976; Vol. 2, pp 49–51.

Table II. Thermolysis of Oxetanes^a

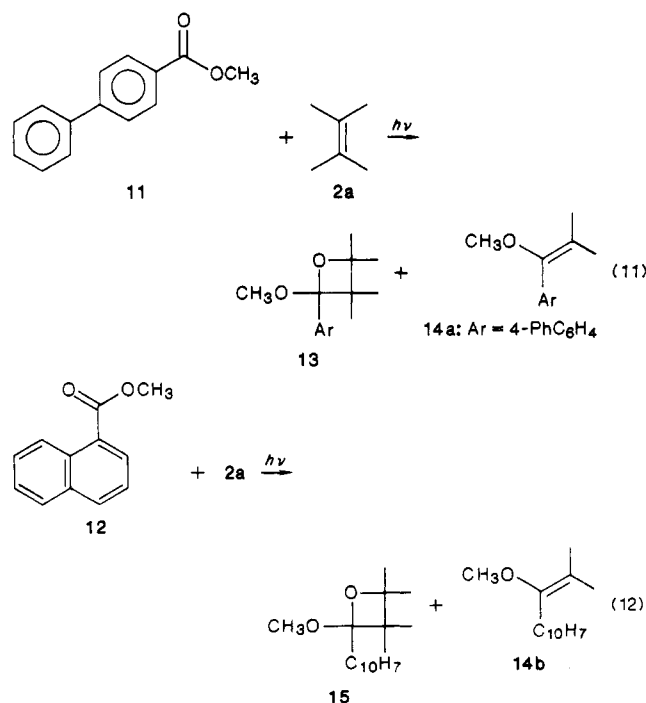
oxetane	1:3:4		
	250 °C	300 °C	350 °C
3a	22:61:17	40:31:29	91:4:5
3b	23:57:20	31:42:27	85:6:9
3d	10:79:11	30:60:–	–

^a Conditions: Flow pyrolysis through a quartz tube packed with 1/4-in. quartz helices at 0.5–5 mm of nitrogen pressure; contact time 2–10 s. Ratio of adduct benzoate ester:recovered oxetane:enol ethers—determined by NMR integration and/or GC.

The formation in the photochemical reaction mixtures described in the present study of the enol ethers 4 under nonpyrolytic conditions is evidently the result of a photochemical cycloreversion of the oxetanes 3. Indeed, reirradiation of isolated and purified 3a and 3d with Vycor-filtered light resulted in low conversions to the enol ethers 4a and 4d. The only chromophore in the oxetanes that can absorb the light used (220–300 nm) is the aromatic ring, i.e., monosubstituted phenyl. This 2 + 2 cycloreversion appears to be a case of intramolecular photosensitization in which the phenyl group, whose extinction coefficient at 254 nm would be ca. 300–500, absorbs a photon and subsequently transfers the excitation energy to the σ bond system of the oxetane ring, which then undergoes retro 2 + 2 fragmentation.

To test this hypothesis, the photochemical behavior of the arenecarboxylic acid esters methyl biphenyl-4-carboxylate (11) and methyl 2-naphthoate (12) was studied. These esters possess chromophores that absorb light of wavelengths 240–310 nm much more efficiently than do the toluene-type chromophores in the simple benzoate ester series 1. It seemed likely that the formation of enol ethers of type 4 by retro 2 + 2 cleavage might be a faster and more efficient process with 11 and 12.

In experimental practice, biphenyl derivative 11, when irradiated with excess 2,3-dimethyl-2-butene (2a), was consumed rather slowly. Oxetane 13 was isolated from the reaction mixture in 58% yield, along with 17% of the COM product, enol ether 14a (eq 11). The naphthoate ester 12



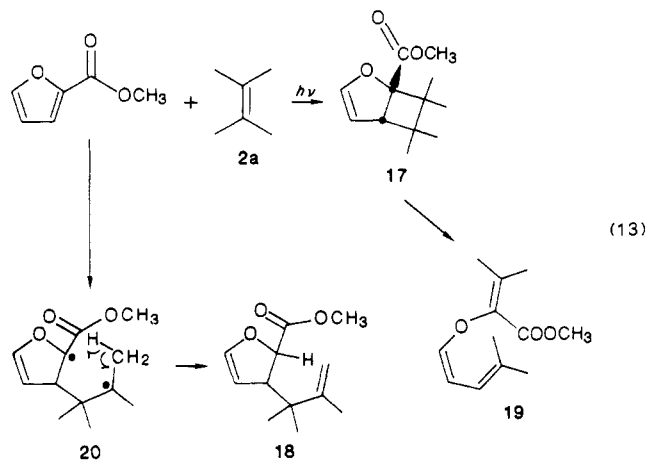
underwent a very slow conversion to oxetane 15. A 30% conversion of starting ester 12 after 15-h irradiation with

a Hanovia 450-W UV source was observed. The modest increase in the efficiency of the formation of the COM products (here, **14a** and **14b**) is thus inconclusive on the question of internal photosensitization.

Thermolyses. In connection with the question of thermal 2 + 2 cycloreversion of the oxetanes studied here, flash vacuum pyrolysis of **3a**, **3b**, and **3d** was studied. These experiments were performed at 0.1–5 mm of pressure in a horizontally mounted quartz tube on a 3–10-mmol scale.

The data in Table II show that the major thermal process is 2 + 2 cycloreversion to starting esters **1**, with the amount of those esters increasing at the higher temperatures. This supports our contention that the alkenes of type **4** arise by a photochemical cleavage of a benzyl bond.¹⁴

Finally, the photochemical reaction of methyl 2-furoate (**16**) with alkene **2a** was examined. Rather long irradiation times gave reaction mixtures from which were isolated the carbonyl 2 + 2 adduct, oxetane **17** (27%), the ring-opened dihydrofuran **18** (35%), and a small amount of the ester-enol ether **19** (6%). The most likely path leading to ester **18** is shown in eq 13, involving a 1,6-hydrogen atom transfer in a diradical intermediate **20**. Enol ether **19** is produced by 2 + 2 cycloreversion as in the cases of **4a–e**.



Conclusions

Several of the reactions described here provide convenient access to alkoxyoxetanes in clean processes proceeding in good chemical yields, if on a small scale. Thus, the conversion of methyl benzoate to products such as **3a** may have appreciable synthetic value. In view of the applications by Schreiber et al. to the synthesis of oxetanes derived from 2 + 2 cycloaddition of certain functionalized aldehydes to substituted furans,^{3b} we have been examining the photochemical reactions of aromatic esters with simple furans in our laboratory. The results obtained so far are described in the accompanying paper.¹⁵

Experimental Section

All reactions were conducted under an atmosphere of purified argon. NMR spectra were obtained on Varian EM-360, HR-220, and XL-300 instruments. Infrared spectra were obtained on a Beckman Acculab 4 instrument and mass spectra on a Perkin-Elmer Hitachi RMU-6E (EI) or a Finnegan 4500 instrument. GC separations were performed on a Varian A-90P instrument with either (A) 6 ft \times 1/4 in. SE-30, (B) 9 ft \times 3/8 in. SE-30, or (C) 10 ft \times 3/8 in. Carbowax 20-M columns.

(14) Cristol, S. *J. Org. Photochem.* 1985, 6.

(15) Cantrell, T. S.; Allen, A. C.; Ziffer, H. *J. Org. Chem.*, following paper in this issue.

General Procedure for Reactions of Arenecarboxylic Acid Esters with Alkenes. A solution of the alkyl arenecarboxylate **1** (usually 5–30 mmol) and the alkene (3–10-fold excess) in spectrograde pentane (120 mL) was irradiated through a Vycor, or in some cases a Corex, filter sleeve by using a Hanovia 450-W medium-pressure mercury arc lamp. The progress of the reactions was followed by IR spectroscopy and TLC. After the stated reaction time, the bulk of the solvent was recovered by rotary evaporation and the components of the reaction mixture were separated by a combination of fractional distillation and GC, or by spin chromatography (Chromatotron). Details of specific cases follow.

Methyl Benzoate and 2,3-Dimethyl-2-butene (2a). After irradiation of 4.0 g of **1a** (0.030 mol) and excess **2a** for 30 h, fractional distillation of the reaction mixture gave fractions A, B, and C. Fraction A, bp 35–42 °C (A) (0.5 mm), 2.0 g, was separated by GC on column A into recovered **1a** (1.5 g) and COM product **4a** (0.21 g, 7%), 1-phenyl-1-methoxy-2-methylpropene: ¹H NMR (CDCl₃) δ 7.3 (5 H, s, br), 3.43 (3 H, s), and 1.77 and 1.70 (3 H each, s); MS (EI), m/z 162 (P, 100). Anal. Calcd for C₁₄H₂₀O₂: C, 76.38; H, 9.13. Found: C, 76.25; H, 9.30. (B) 63 °C (0.5 mm), proved to be essentially pure oxetane **3a**; recrystallization from hexane at –20 °C gave colorless chunky prisms: mp 50–51 °C (2.0 g, 52%); IR (KBr) 1160 (m), 1096 (s), 1000 (s), and 971 (s) cm⁻¹; ¹H NMR (CDCl₃) δ 7.4 (5 H, m), 3.02 (3 H, s), 1.55, 1.29, 1.23, and 0.70 (all 3 H each, s); MS (EI), m/z 220 (P, 0.2), 189 (5), 162 (74), 161 (72), 105 (88), and 84 (100). Anal. C, H, okay. (C) Fraction C, bp 70–83 °C (0.05 mm), 0.54 g, was refracted to afford purer material, bp 71–74 °C (0.05 mm), 0.33 g, which was separated on GC column B; the faster moving peak (retention time 14.3 min, 170 °C) proved to be enone **7a**: ¹H NMR (CDCl₃) δ 7.8–7.7 (2 H, m), 7.4–7.2 (3 H, m), 5.06 (1 H, m), 4.92 (1 H, m), 1.75 (3 H, s, br), and 1.38 (6 H, s, br); MS (CI), m/z 188 (100) and 105 (83). Anal. Calcd: C, 82.94; H, 8.55. Found: C, 82.79; H, 8.40. 170 °C was enone **5a**: IR (film) 1682 cm⁻¹; ¹H NMR (CDCl₃) δ 7.9 (2 H, m), 7.3 (3 H, m), 3.22 (2 H, s, br), 1.84 (3 H, s, br), and 1.74 (6 H, s, br); MS (EI), m/z 188 (P, 21), 105 (100), and 77 (63). Anal. Calcd for C₁₃H₁₆O: C, 82.94; H, 8.55. Found: C, 83.16; H, 8.69.

Hydrolysis of Oxetane 3a. A sample of **3a** (0–0.80 g) was stirred with 80% aqueous THF containing 2 drops of concentrated HCl for 5 h at 25 °C. Dilution of the reaction mixture with water and extraction with ether, followed by washing of the ether extracts with NaHCO₃ and with water, drying (MgSO₄), and distillation, gave a colorless oil, bp 83–85 °C (0.3 mm), identified as 3-benzoyl-2,3-dimethyl-2-butanol (**8a**) on the basis of spectral data: IR (film) 3380 (m) and 1685 (s) cm⁻¹; NMR (CDCl₃) δ 7.5–7.2 (5 H, m), 1.43 (1 H, s, br, OH), 1.37 (6 H, s), and 1.32 (6 H, s); MS (EI), m/z 210 (P, 0.8), 192 (100), 105 (60). Anal. Calcd for C₁₃H₁₈O₂: C, 75.74; H, 8.78. Found: C, 75.64; H, 8.94.

Photochemical Reaction of Methyl Benzoate with 2-Methyl-2-butene (2b). A solution of methyl benzoate (5.0 g, 0.038 mol) and 2-methyl-2-butene, **2b** (15 g), in spectrograde pentane (115 mL) was irradiated through Vycor for 44 h. After evaporation of the solvent and unreacted alkene **2b**, the residue was fractionally distilled to yield (A) recovered ester **1a**, 1.9 g, bp 35–40 °C (0.2 mm), followed by (B) the mixture of oxetane geometric isomers **3b**, bp 50–53 °C (0.2 mm) (1.85 g, 36%): ¹H NMR (CDCl₃) δ 7.3 (5 H, m), 4.56 (1 H, q), 4.40 (1 H, q), 3.76 and 3.71 (3 H, s each), 1.60 and 1.62 (3 H, d), and 1.08 and 1.23 (6 H each, s); MS (CI), m/z 206 (P), 148 (32), and 105 (16). Anal. Calcd for C₁₃H₁₈O₂: C, 75.74; H, 8.78. Found: C, 75.52; H, 8.80. *E* and *Z* isomers of **5b**, R₁ = R₄ = H and R₂ = R₃ = CH₃: bp 77–80 °C (0.2 mm); IR 1685 cm⁻¹; ¹H NMR (CDCl₃) δ 7.8 (2 H, m), 7.3 (3 H, m), 5.94 (1 H, m), 5.80 (1 H, m), 3.30 (2 H, br), 1.85–1.72 (4 s, br, total 6 H); MS (CI), m/z 174 (P, 100). Anal. Calcd for C₁₂H₁₄O: C, 83.68; H, 8.19. Found: C, 83.50; H, 7.99.

Photochemical Reaction of Methyl Benzoate and 1,1-Dimethoxy-2,2-dimethylethene (Dimethylketene Dimethyl Acetal) (2c). A solution of ester **1a** (4.0 g, 0.03 mol) and acetal **2c** (15 g) in spectrograde hexane (110 mL) was irradiated through Vycor for 30 h. After recovery of the excess ketene acetal by distillation (35–45 °C (18 mm)), there were obtained fractions A and B. (A) Fraction A, bp 70–74 °C (0.5 mm), proved to be almost pure dimethyl tetramethylsuccinate: NMR (CDCl₃) δ 3.89 (6 H, m, s) and 1.47 (12 H, s); MS (EI), m/z 202 (P, 30) and 187

(100). (B) Fraction B: 3,3-dimethyl-2,2,4-trimethoxy-4-phenyloxetane (**3c**); bp 92–95 °C (0.08 mm); 1.7 g (40%, based on unrecovered **1a**); IR 1160, 1095, 1020 cm^{-1} ; NMR (CDCl_3) δ 7.4 (5 H, m), 3.44 (3 H, s), 3.35 (3 H, s), 3.12 (3 H, s), 1.32 and 0.78 (3 H each, s); MS (CI), m/z 252 (P, 54), 162 (100), and 90 (80). Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_4$: C, 66.67; H, 7.97. Found: C, 66.45; H, 7.79.

Hydrolysis of oxetane **3c**, by an identical procedure as described above for **3a**, led to **7c**, methyl α -benzoylisobutyrate, identical with an authentic sample prepared by the following method: (i) addition of methyl isobutyrate (4 g) to lithium diisopropylamide (LDA) in THF (–30 °C, 1.1 equiv) and stirring for 2 h; (ii) slow addition of benzoyl chloride (6 g) to the ester enolate at –30 °C, followed by warming of the reaction mixture to room temperature, followed by a further 12 h of stirring. Quenching of the reaction mixture with ice water, extraction into ether–pentane, and the usual workup gave 1.4 g of keto ester **7c** as a colorless liquid: bp 120–122 °C (0.1 mm); IR (film) 1735 and 1680 cm^{-1} ; NMR (CDCl_3) δ 7.8 (2 H, m), 7.3 (3 H, m), 3.73 (3 H, s), and 1.25 (6 H, s); MS (CI), m/z 206 (P).

Photochemical Reaction of Methyl Benzoate and 1,2-Dimethylcyclohexene (2d). A solution of methyl benzoate (1.36 g, 0.010 mol) and 1,2-dimethylcyclohexene (10 g, 0.004 mol, 10-fold excess) in spectro hexane (120 mL) was irradiated through Vycor under the usual conditions for 44 h and worked up in the aforementioned way. Fractionation gave, besides recovered ester **1a** (0.61 g), a product fraction, bp 93–120 °C (0.1 mm) (1.0 g); GC separation on column B at 170 °C afforded fractions A and B. (A) Fraction A: oxetane **3d**, (0.63 g, 49%); IR 1100 and 1055 cm^{-1} ; NMR (CDCl_3) δ 7.4–7.2 (5 H, m), 3.45 (3 H, s), 2.1–1.5 (8 H, m), 1.45 and 1.37 (3 H, each, s); MS (CI), m/z 230 (P). Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_2$: C, 78.07; H, 9.01. Found: C, 77.79; H, 8.89. Fraction B: (B) **4d**; IR (film) 1712 cm^{-1} ; NMR (CDCl_3) δ 7.3–7.1 (5 H, m), 5.3 (1 H, t, br), 3.46 (3 H, s), 2.18 (3 H, s), 2.4–1.2 (8 H, m); MS (CI), m/z 230 (P, 56), 145 (100). Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}$: C, 84.13; H, 8.50. Found: C, 83.98; H, 8.3.

Methyl Benzoate and 1,1-Diethoxyethene (2e). A solution of methyl benzoate (**1a**, 2.0 g, 0.012 mol) and 1,1-diethoxyethene, **2e** (10 g, 0.093 mol), in spectro hexane (100 mL) was irradiated through Vycor for 20 h, following which the solvent and excess ketene acetal were removed by rotary evaporation under reduced pressure. Fractional distillation of the residue gave, in addition to 1.0 g of recovered ester **1a**, oxetane **3e**, bp 80–84 °C (0.1 mm) (0.76 g, 29%); IR 1100–1120 (s, br), 10454 cm^{-1} (s); NMR (CDCl_3) δ 7.3 (5 H, m), 4.2 (2 H, AB, $J = 6$), 4.0–4.1 (4 H, 2 q, $J = 7$), 3.41 (3 H, s), and 1.2–1.3 (6 H, 2 t); MS (CI), m/z 252 (P) and 222 (100). Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_4$: C, 66.70; H, 8.01. Found: C, 65.29; H, 7.66 (low due to air oxidation).

Hydrolysis of 3e for 3 h at 25 °C in aqueous THF containing 2 drops of concentrated HCl, followed by the standard workup, gave an oil, which decomposed on attempted short-path distillation (0.05 mm, bath temperature 120 °C), but whose crude spectral data support its assignment as 1-phenyl-3-hydroxy-1,2-propanedione: IR 1710–1780 (s, v br), 3400 (v br), 1090 cm^{-1} (s); NMR (CDCl_3) δ 7.6–7.3 (5 H, m), 5.8 (2 H, s, br), and 3.2 (1 H, br); MS (CI), m/z 148 (P); MS (EI), m/z 105 (100).

Photochemical Reaction of Methyl Furan-2-carboxylate (16) with 2,3-Dimethyl-2-butene (2a). A solution of methyl 2-furoate, **16** (2.0 g, 0.01 mol), and 2,3-dimethyl-2-butene (20 g) in spectro hexane (100 mL) was irradiated through Vycor for 36 h. Workup in the usual way gave 0.3 g of recovered furoate ester and 1.05 g of a product mixture, bp 60–100 °C (0.2 mm). This fraction was separated by GC on column B at 170 °C. Peak A, retention time 16.6 min at 170 °C, was 2 + 2 cycloadduct **17**: IR 1736 cm^{-1} ; NMR (CDCl_3) δ 6.36 (2 d, $J = 3.5$, $J = 1.6$, H_5), 5.03 (2 d, $J = 3.5$, $J' = 0.7$, H_4), 3.31 (1 H, 2 d, $J = 1.6$, $J' = 0.7$, H_3), 3.74 (3 H, s, OCH_3), and 1.35, 1.29, 1.10, and 0.92 (3 H each, all s); MS (CI), m/z 210 (P); MS (EI), m/z 179 (100). Peak B was the Michael-type product **18**: IR 1730 cm^{-1} (s); NMR (CDCl_3) δ 6.52 (1 H, 2 d, br, $J = 5.2$, $J = 3.6$, $\text{OCH}=\text{CH}$), 5.19 (1 H, 2 d, br, $J = 5$, $\text{OCH}=\text{CH}$), 4.86 and 4.70 (1 H each, s, br, $\text{C}=\text{CH}_2$), 4.10 (1 H, d, br, OCHCOOCH_3), 3.66 (3 H, s, oCH_3), 1.72 (3 H, s, br), and 1.30 (3 H, d, $J = 7$); MS (CI), m/z 210 (P, 60) and 127 (100). Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_5$: C, 68.60; H, 8.66. Found: C,

68.48; H, 8.69. On application of the freshly distilled reaction mixture to a new 6 ft \times 1/4 in. Carbowax 20-M column, we obtained a small amount of a third component, to which we assign the COM structure **19**, methyl 3-methyl-2-(4-methyl-1,3-pentadien-1-yloxy)-2-butenate (6%): IR (film) 1726, 1210, 1140 cm^{-1} ; NMR (CDCl_3) δ 6.24 (1 H, d, br, $J = 3$, H_1), 6.05 (1 H, d, br, $J \sim 6$, H_3), 5.41 (1 H, 2 d, $J \sim 6$, $J' \sim 3$, H_2), 3.43 (3 H, s, OCH_3), 1.77 (6 H, s), 1.74 (3 H, s), and 1.64 (3 H, s); MS (CI), m/z 210 (P).

Photochemical Reaction of Methyl Benzoate (1a) with cis-1,2-Dimethoxyethene (2f). A solution of methyl benzoate (4.0 g) and (*Z*)-1,2-dimethoxyethene (ca. 90% pure)¹³ was irradiated through Vycor for 20 h. The dark yellow reaction mixture was evaporated and distilled to give 0.9 g of distillate, bp 60–66 °C (0.1 mm). Only one isomer was obtained by GC collection (column B, 150 °C): ^1H NMR (CDCl_3) δ 7.3 (5 H, s, br), 5.9 (1 H, d, $J = 7$), 4.6 (1 H, d), 3.3 and 3.17 (3 H each, s).

Photochemical Reaction of Methyl Biphenyl-4-carboxylate (11) with 2,3-Dimethyl-2-butene (2a). A solution of methyl biphenyl-4-carboxylate (**11**) (2.0 g, 0.025 mol) in spectro hexane (100 mL) was irradiated through Pyrex for 50 h. After evaporation of the solvent and excess alkene, the residue was taken up in 1:1 benzene–hexane and flash chromatographed on a 5 cm \times 2 cm column of 100–200-mesh silica. The eluate was concentrated to a syrup under reduced pressure. Dissolution of the syrup in 3:1 hexane–benzene was followed by crystallization at –20 °C. There was thus obtained oxetane **13** (0.96 g, 56% based on unrecovered ester **11**, which was retained on the silica column): mp 65–67 °C dec; IR (KBr) 1160, 1110, 1055 cm^{-1} ; ^1H NMR δ 7.6–7.1 (9 H, m), 3.69 (3 H, s), 1.50, 1.48, 1.36, and 1.22 (3 H each, s); MS (CI), m/z 284 (44), 226 (100). Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_2$: C, 81.07; H, 8.17. Found: C, 80.89; H, 8.00.

From the mother liquors of the above-described crystallization there was isolated by GC on column B COM product **14a**, 1-(4-biphenyl)-1-methoxy-2-methylpropene (17%): IR 1630 cm^{-1} ; ^1H NMR δ 7.8–7.2 (9 H, m), 3.70 (3 H, s) 1.72 and 1.64 (3 H each, s); MS (CI), m/z 226 (100).

Photochemical Reaction of Methyl 2-Naphthoate (12) and Tetramethylethene (2a). A solution of naphthoate ester **12** (2.0 g, 1.0 mmol) and 2,3-dimethyl-2-butene (15 g) in spectrograde hexane (120 mL) was irradiated through Vycor as previously described for 20 h. Evaporation of solvent and excess alkene gave a semisolid residue, which was flash chromatographed on a 15 \times 100 mm silica gel column, eluting with 0.5–6% ethyl acetate–hexane. Early fractions contained oxetane **15**, which was recrystallized from pentane at –20 °C to give pure material: mp 53–55 °C; ^1H NMR δ 7.9–7.6 (3 H, m), 7.3–7.0 (4 H, m), 3.81 (3 H, s), 3.23 (3 H, s), and 1.37, 1.29, 1.16 (3 H each, s); MS (CI), m/z 270 (P, 100), 222 (P – acetone). The mother liquors on short-path distillation gave enol ether **14b**: bp 80 °C (bath) (0.07 mm); ^1H NMR δ 7.9–7.3 (3 H, m), 3.23 (3 H, s, OCH_3), 1.85 and 1.74 (3 H each, s); MS (CI), m/z 222.

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