(13) W. Freytag and K. H. Ney, *J. Chromatogr.*, **41**, 473 (1969).
(14) M. Hamberg, *Chem. Phys. Lipids*, **6**, 152 (1971).
(15) Helmchen believes[8] that, in view of the distances involved, the C substituents do not interact with the A substituents.
(16) The consequences of conformational immobility have been recognized and demonstrated[11b,c] insofar as diastereomeric amides derived from some chiral cyclic acids and chiral cyclic amines separate better than those similarly derived from acyclic components.
(17) M. Hudlicky, "Chemistry of Organic Fluorine Compounds", Macmillan, New York, N.Y., 1961, p 304, and references cited therein.
(18) When the diastereomeric carbamates derived from (±)-1,1,1-trifluoro-3,3-dimethyl-2-butanol and (+)-1-(1-naphthyl)ethylamine are chromatographed, the diastereomer which has *tert*-butyl and α-naphthyl on the *same* face (erythroid) is *first* eluted. Since the van der Waals radius of *tert*-butyl is larger than trifluoromethyl (6.1 vs. 5.1 Å respectively), this elution order reflects that the greater "warding off" effect of the trifluoromethyl group is not simply steric in nature, but has other origins.
(19) C. S. Springer, Jr., S. R. Tahny, and M. Pickering, *J. Am. Chem. Soc.*, **95**, 6227 (1973).
(20) R. A. Bauman, *Tetrahedron Lett.*, 419 (1971).
(21) H. Kessler and M. Molter, *Angew. Chem., Int. Ed. Engl.*, **13**, 538 (1974).
(22) H. Kessler and M. Molter, *J. Am. Chem. Soc.*, **98**, 5969 (1976).
(23) Thiocarbamates with Ar = α-naphthyl and Ar = 9-anthryl were also synthesized. Although NMR and chromatographic properties appear to be analogous to those of the corresponding carbamates, the instability of these thiocarbamates did not permit thorough characterization.
(24) Diethyl ether, tetrahydrofuran, and methylene chloride as well as toluene may be used as solvents with essentially *no* diminishment in overall yield.
(25) Ethynyl carbamates were prepared by C. Boeder.

Solid Phase and Solution Photochemistry of Coumalate Esters

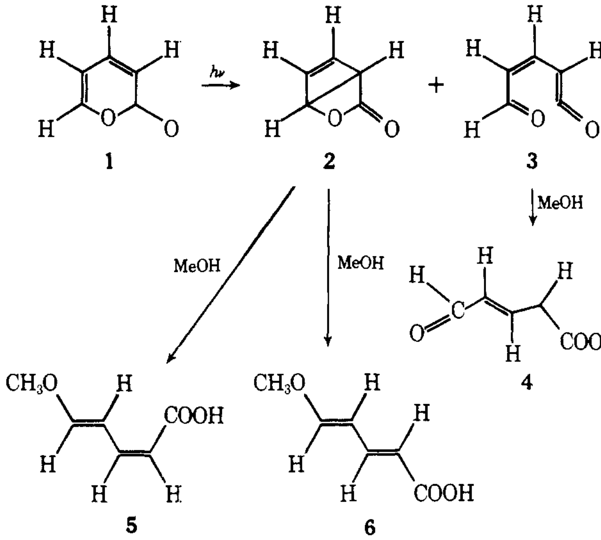
Hooshmand Javaheripour[†] and Douglas C. Neckers*

Department of Chemistry, Bowling Green State University, Bowling Green, Ohio 43403

Received August 12, 1976

Photochemical reactions of coumalic acid (**12**) and its methyl, isopropyl, and benzyl esters have been investigated in solution and in the solid phase. In solution the photochemistry has been carried out in hydroxylic and nonhydroxylic solvents as well as in ethyl bromide. In the solid phase, the reaction has been studied in a potassium bromide matrix and as a sandwich between quartz plates. A particularly interesting effect of KBr, suggested to be a heavy atom effect of the matrix, has been observed in the photochemical reactions of coumalate esters.

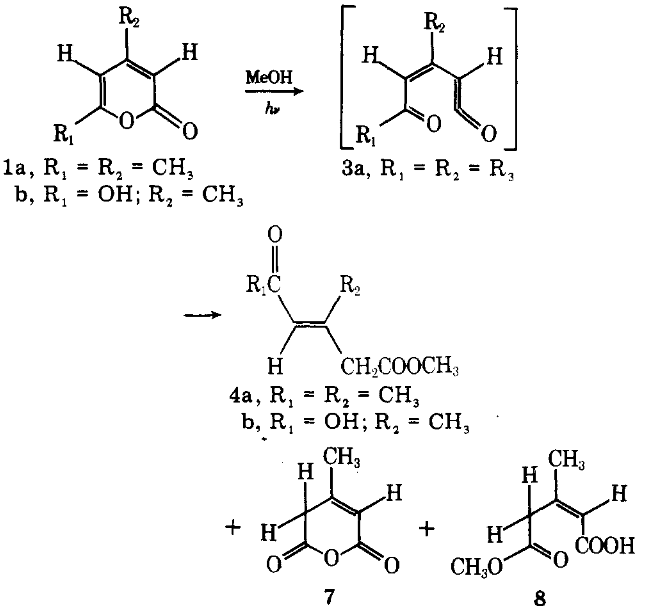
The photochemistry of α-pyrone (**1**) and its derivatives has been the subject of several studies and the systems have proven to be rich in variation.[1-10] In spite of their apparent complexity, however, all the observed unimolecular primary photoproducts arise from the critical intermediates bicyclic lactone **2** and ketene **3** (eq 1). Thus, irradiation of α-pyrone in ether at 300 nm produces only isolable **2** in quantitative yield[1-3] while in methanol under similar conditions, the three noncyclic products **4**, **5**, and **6** result. Compound **4** has been shown to derive from ketene **3**, whereas **5** and **6** are from the photolactone **2**.



(1)

Intermediate ketenes like **3** have been the subject of several studies. The current view is that, in the case of α-pyrone[2,3,9] and certain properly substituted ones,[5,6] such ketenes form, though in apparently analogous cases[8] ketenes seem not important. Thus irradiation of 4,6-dimethyl-2-pyrone (**1a**) in methanol produces **4a** through ketene **3a**[2], while 4-hydroxy-6-methyl-2-pyrone (**1b**), when irradiated in methanol, produces **4b** (in tautomeric form) in addition to anhydride **7**. The half-ester **8** which originates from lactone **2b**[6] is also formed, Scheme I. The analogous 4-methoxy-6-methyl-2-pyrone (**1c**), when irradiated in water at 300 nm, produces the half-esters **9a** and **10a** and the corresponding diacids **9b** and **10b**. Both these products are said to originate from lactone **2c**[5] (eq 2).

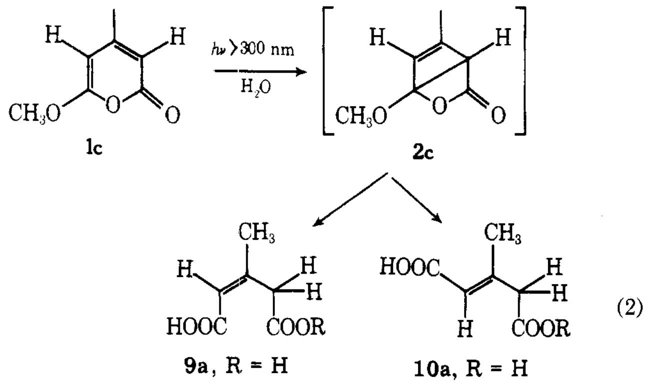
Scheme I



---

* Fellow of the Alfred P. Sloan Foundation, 1971–1976.

[†] Submitted in partial fulfillment of the requirements for the Ph.D. degree, University of Toledo, 1976. Deceased March 21, 1977.

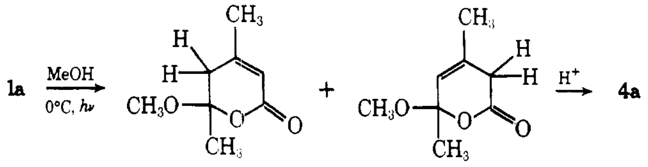

1c 2c

9a, R = H
b, R = CH_3

10a, R = H
b, R = CH_3

(2)

Chapman and McIntosh[8] disagree that ketene **3a** is formed from **1a** in methanol, claiming formation of two acid-sensitive isomeric lactones, **11** and **11a**. Addition of acidic methanol to **11** and **11a** produces **4a**.

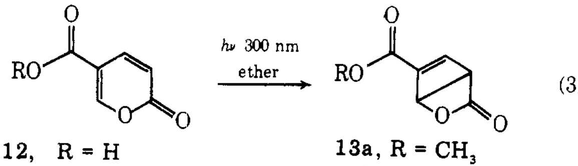

11 **11a**

Still another complication is the observation of dimerization reactions of α-pyrones which occurs from triplet states of α-pyrone derivatives. Thus cyclic adducts have been isolated both from direct and from sensitized reactions of α-pyrone,[4,11] in triplet state reactions.

In this paper we report on the photochemistry of coumalic acid (**12**) and its esters, both in solution and the solid phase. As part of a series of model studies, we were interested in the effect of carboxylate residues on the photoreactions of pyrone derivatives.

Results and Discussion

The photochemistry of coumalic acid and its ester derivatives has been studied in solution using hydroxylic and nonhydroxylic solvents, as well as heavy atom solvents, such as ethyl bromide. These reactions were also studied in the solid phase, with the coumalate either a suspension in a potassium bromide matrix or sandwiched between two quartz plates. The observed results were dependent on the physical state and the solvent as well as on the wavelength of irradiating light. For example, methyl coumalate (**12a**) in ether, when irradiated at 300 nm, produced 5-carbomethoxy-3-oxabicyclo[2.2.0]hex-5-en-2-one (**13a**) quantitatively (eq 3).


(3)

12, R = H
12a, R = CH_3
b, R = $(CH_3)_2CH$
c, R = $C_6H_5CH_2$

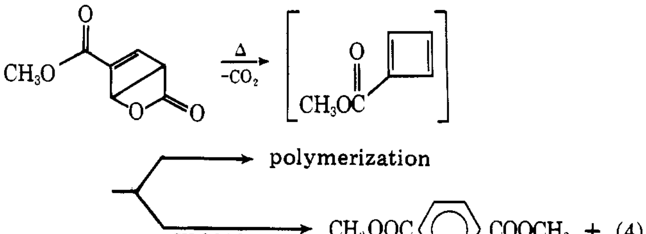
13a, R = CH_3
b, R = $(CH_3)_2CH$
c, R = $C_6H_5CH_2$

Lactone **13a** was stable when compared to the parent photo-α-pyrone **2** and could be stored indefinitely and even bulb to bulb distilled at 40 °C and 3 mm. During this distillation **3a** only partially (≈10%) reverted to methyl coumalate. Isopropyl coumalate (**12b**) behaved similarly as did benzyl coumalate (**12c**). In the latter case, however, some side chain photodecarboxylation also occurred.

The spectral properties of isolated photopyrones **13a–c** are shown in Table I.

The mass spectrum of **13a** revealed a base peak at *m/e* 110, formed by loss of CO_2 from the parent compound. Since the loss of CO_2 is more likely from the lactone group than the ester, the ion at *m/e* 110 is likely the cyclobutadiene methyl carboxylate ion or a ring-opened isomer. The comparable mass spectrum of methyl coumalate places the base peak at *m/e* 126. This same ion, in the mass spectrum of **13a**, is minor (10%) indicating that **13a** did not rearrange to methyl coumalate under the conditions where the mass spectrum was recorded.

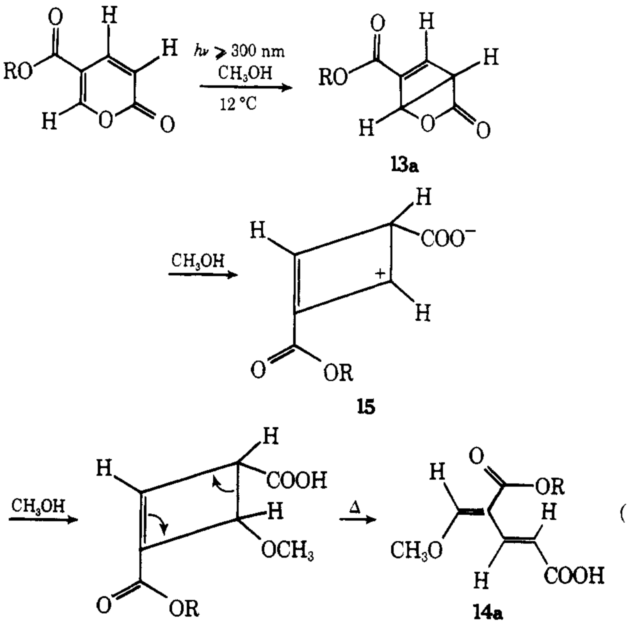
The loss of CO_2 from **13a** is also observed when it is heated in a melting point capillary tube or between KBr plates at 110 °C. The NMR spectrum of the thermal product from **13a** contains a strong and broad signal at 3.80 ppm indicating the presence of polymeric methyl ester protons. These likely arise from cyclobutadiene derivatives which, if formed, do not survive the experimental conditions and are polymerized in an unidentified manner (eq 4).



(4)

Several attempts were made to trap the theorized cyclobutadiene derivatives produced in the thermolysis of **13a** by carrying out the reaction in the presence of active dienophiles. Though dimethyl phthalate esters were discovered among the products, the results are still premature and further investigations are needed.

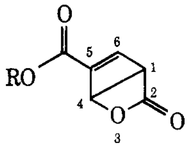
When methyl coumalate is irradiated in methanol, similar reactions occur. However, secondary thermal reactions cause complications and none of the primary photoproducts are stable in methanol at room temperature. Thus, **13a**, the ring closure product of methyl coumalate, isolated from photolysis in ether, adds methanol thermally to form the dienoic acid **14a** via secondary intermediates **15** and **16** (eq 5). In our hands


13a **15** **16** **14a**

(5)

14a, R = CH_3
b, R = $(CH_3)_2CH$

Table I. Spectral Properties of Photopyrones 13a–c

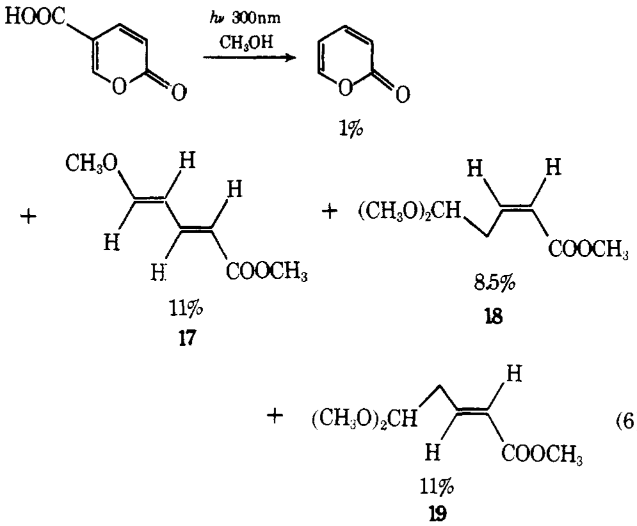


	Chemical shifts, ppm[a]				Coupling constants, Hz			IR, cm^{-1} [b]	
Compd	R	C_1	C_4	C_6	$J_{1,4}$	$J_{1,6}$	$J_{4,6}$	C=O lactone	C=O ester
13a	Methyl 3.90	5.63	4.58	7.41	2	4	1	1825	1725
13b	Isopropyl 1.29 5.13	5.58	4.52	7.35	2	4	1	1825	1722
13c	Benzyl 7.41 5.79	5.52	4.45	7.35	2	4	1	1823	1720

[a] In $CDCl_3$. [b] Thin film on KBr plates.

there was no evidence favoring formation of any intermediate but bicyclic lactone **13a** from methyl coumalate when irradiated in methanol. Thus we obtained no evidence for either the ketene or Chapman–McIntosh intermediates.

We did not study the photochemistry of coumalic acid in ether or benzene owing to solubility problems. However, in methanol its photochemistry, too, proved to be rich and varied. At 300 nm the major photoproduct from irradiation was a decarboxylation product, α-pyrone, the analogue of the thermal reaction by which α-pyrone is prepared.[12] Consequently, the products produced in methanol were those from photoreaction of α-pyrone except that the methanol solution of coumalic acid was acidic enough to produce acetals rather than aldehydes. The products isolated from irradiation of coumalic acid in methanol are shown in eq 6. We judge that ketene intermediates are involved in formation of **18** and **19** but have no definitive proof.

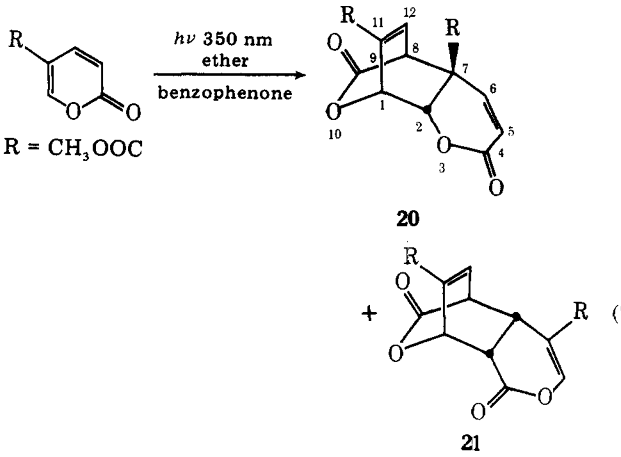


(6)

Potassium bromide matrix photochemistry is possible[13–15] owing to the excellent transparency of this medium. Thus irradiation of all the coumalates, pressed in KBr disks, produced markedly different results. When irradiated at 254 nm in KBr, the coumalate esters, as well as coumalic acid itself, lost CO_2. The infrared spectrum of methyl and benzyl coumalate before and at selected periods after irradiation demonstrated that both the ester and lactone carbonyls serve as the source of CO_2. Though ring closure to photolactones is not expected from coumalates at short irradiating wavelengths, it is surprising that ring closure could not be observed when coumalates were irradiated at longer wavelengths (300 and 350 nm) in a KBr matrix.

The rate of CO_2 loss from the various coumalate esters differed and was dependent on the attached alkyl or aryl group. Thus the loss of CO_2 from the side chain of benzyl coumalate, when irradiated in KBr at 254 nm, is faster than is the loss of CO_2 from the side chain of methyl coumalate. The same observation was made when a 300-nm light was used.

When irradiated at 350 nm in a KBr matrix, no CO_2 is produced from methyl coumalate; instead, [4 + 2] dimeric adducts **20** and **21** are formed. These dimers are the same as those isolated from benzophenone sensitized irradiation of methyl coumalate in ether or from irradiation in ethyl bromide, a known heavy atom solvent (eq 7). These dimers are triplet state products.

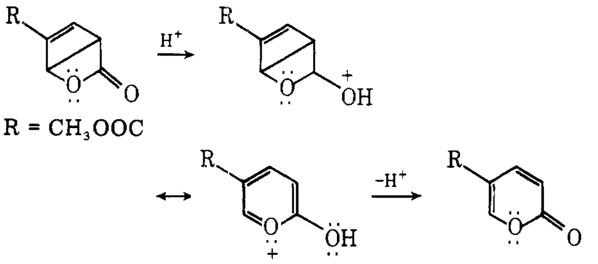


(7)

The source of CO_2 from methyl coumalate irradiation is not methyl coumalate itself, but is instead the dimers **20** and **21**. This can be shown by two studies. In the first, dimers **20** and **21**, prepared from benzophenone sensitized reaction of methyl coumalate in ether at 350 nm, are isolated and then pressed into KBr matrix and irradiated at 300 nm. CO_2 evolution can be demonstrated to be similar in rate to that obtained by the direct irradiation of methyl coumalate under identical conditions. In the second study, irradiation of methyl coumalate at 350 nm produces dimerization which can be demonstrated by the disappearance of the diene double bond stretching frequency at 1550 cm^{-1}. At 350 nm, however, almost no CO_2 is evolved. When irradiation is continued at 300 nm using the same pellet, CO_2 evolution begins though the dimerization continues at the same rate. Benzyl coumalate behaves similarly when irradiated at 350 nm as does isopropyl coumalate when irradiated in a KBr matrix under similar conditions.

The fact that, in KBr matrix, none of the photochemistry observed in solution is observed is curious, and at least two explanations are possible. The first is that, in a KBr matrix, the derivatives of the photopyrones are unstable and revert back to the starting material immediately after formation, thus escaping detection. The second is that the excited state multiplicity of the coumalates is different in solution than in a KBr matrix.

To examine the first of the above postulates a small amount of **13a** was sandwiched between two KBr plates and irradiated. The IR spectrum of the ester was recorded periodically for 120 min. During this period the carbonyl band at 1825 cm^{-1} slowly disappeared and the spectrum completely changed to that of methyl coumalate. A KBr matrix of **13a** gave similar results rapidly enough so that no photopyrone could be detected at all. We think that the slightly acidic condition of the plate causes isomerization of **13a** to **12a** (eq 8).



(8)

Examining the second postulate, heavy atom solvents have been shown to enhance forbidden $t_1 \leftarrow s_1$ intersystem crossing transitions.[16-23] The effects that can be observed spectroscopically are an increase in the extinction coefficient in the absorption spectra, an increase in the quantum yield of 0–0 band in the phosphorescence spectra, and a decrease in the lifetime of phosphorescence. External heavy atom effects[18-20,23] and internal heavy atom effects[16,23] have been investigated extensively with a number of photochemical processes in solution but the heavy atom effect of alkali halides in solid phase[25-29] has not been explored as extensively.

The UV spectra of coumalate esters in a KBr matrix are similar to the respective solution spectra (Figure 1), with the exception of a slight line broadening and an accompanying red shift of the peaks at 246 and 298 nm, to 251 and 305 nm, respectively. (Similar observations have been made by Pitts[26] and by Drickamar[15] in their studies involving anthracene.) Enhancements of the extinction coefficients of the 246- and 298-nm bands are to be expected if a heavy atom effect is effective, but these effects cannot be quantitatively assessed in a solid KBr matrix because of concomitant light scattering from the KBr surface. The latter is confirmed by the observation that the extinction coefficient of the band or at shorter wavelength (246 nm) is decreased more than that in the longer wavelength region (298 nm) (Figure 1). When the UV spectrum of methyl coumalate was recorded in a methanol solution containing KBr a small increase (7%) in the extinction coefficient was observed for the 298-nm peak.

Although the investigation of the UV spectra of coumalate esters and, in particular, methyl coumalate did not give sufficient evidence for an external heavy atom effect, the chemical evidence favoring a heavy atom effect is significant. Thus when methyl coumalate was irradiated in ethyl bromide (a heavy atom solvent), formation of the same [4 + 2] dimeric adducts as those observed in the benzophenone sensitized reaction of methyl coumalate in ether resulted. Even though the photolactones are not stable in a KBr matrix, the same distribution of dimeric products results in ethyl bromide solution, in ether with benzophenone sensitizer, or in a matrix of KBr. We think it compelling and suggest that methyl coumalate, irradiated in KBr matrix, may well be *the first conclusive example of the external heavy atom effect observed in solid KBr*.

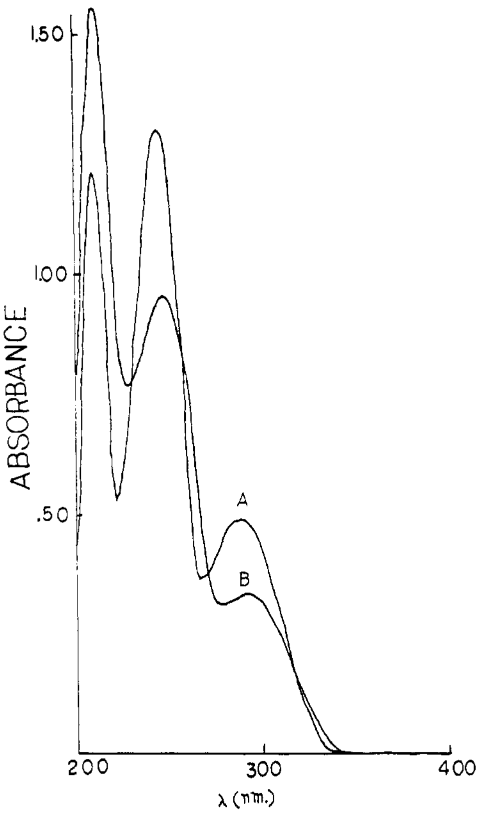


Figure 1. (A) UV spectrum of benzyl coumalate (1.32 × 10^{-4} M) in methanol, λ_{max} 288 nm (ϵ 3700) and 246 (9800). (B) UV spectrum of benzyl coumalate (1.32 × 10^{-3} M) in KBr matrix, λ_{max} 292 nm (ϵ 1800) and 247 (5250).

There are at least four pieces of evidence to support this statement. First, irradiation of methyl coumalate in crystalline form did not produce dimers. Second, irradiation of methyl coumalate sensitized with benzophenone produced dimers which are necessarily derived from its triplet states and these dimers were the same as those produced from irradiation of methyl coumalate in a KBr matrix. Third, irradiation of methyl coumalate in ethyl bromide, a known heavy atom solvent, produced the same dimers as those observed in the benzophenone sensitized reaction and those obtained from irradiation of methyl coumalate in a KBr matrix. Fourth, irradiation of methyl coumalate in ether produced a nondimeric product derived from a singlet excited state.

In conclusion, then, ether solutions of coumalate esters, when irradiated at 300 nm, produce corresponding ester derivatives of 3-oxabicyclo[2.2.0]hex-5-en-2-one. These products are derived from singlet excited states of coumalate esters. In contrast to their unsubstituted counterpart carboxylated photopyrones are stable at room temperature and can survive molecular distillation at reduced pressures. In hydroxylic solvents such as methanol, substituted photopyrones undergo thermal reactions to form the corresponding derivatives of 5-methoxy-2-*cis*-4-*trans*-pentadienoic acid. Coumalic acid itself, upon irradiation in methanol, behaved differently since it initially underwent photodecarboxylation to produce α-pyrone. Only the thermal chemistry was changed due to the acidic nature of the medium. Irradiation (300 nm) of coumalate esters, as well as coumalic acid, in a KBr matrix produces CO_2. In the case of coumalate esters, the CO_2 comes from [4 + 2] dimeric adducts of the type **20** and **21** rather than from the esters themselves. In the case of methyl coumalate, the same dimers **20** and **21** are formed whether irradiation is carried out in a KBr matrix, sensitized with benzophenone, or in a heavy atom solvent, such as ethyl bromide. Since irradiation of the crystalline coumalate esters does not produce dimers, the dimers in KBr matrix are produced from a triplet excited state of the coumalate, likely brought about by the heavy atom.

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were obtained using a Perkin-Elmer Model 337 or 621 infrared spectrophotometer and are obtained as KBr plates unless otherwise noted. The proton magnetic resonance spectra (NMR) were obtained by using either a Varian Model A-60 or T-60A instrument and are relative to Me_4Si internal standard. In reporting NMR data, the following abbreviations are used: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, q = quartet, quin = quintet, and m = multiplet. The mass spectra were obtained using a Varian MAT Model CH7 mass spectrometer. Analytical gas–liquid chromatography (GLC) was carried out using a Varian Aerograph 1200 (column 8 ft × 18 in. UCON LB 10% on Chromosorb 60/90). For preparative work a Varian Aerograph 1800 (column 8 ft × 16 in. UCON LB 10% on Chromosorb W) was utilized. When necessary samples were also analyzed by a high-pressure liquid chromatograph (HPLC) Analab equipped with Tracor 500 pump. The column was packed with Partisil 10/25, no. 1144761.

Photochemistry. All the irradiation experiments were performed by one of the methods 1–4. Modifications were made when needed.

Method 1. A standard photochemical quartz immersion apparatus (capacity 350 mL) and a 450-W Hanovia medium-pressure lamp was surrounded by a cylindrical glass filter and submerged in a constant temperature bath maintained at 12 °C. Samples to be irradiated were dissolved in 350 mL of the appropriate solvent, degassed under nitrogen for 15–20 min, and irradiated, with stirring, under a nitrogen atmosphere.

Method 2. A merry-go-round irradiation apparatus (ACE) was submerged in a constant temperature bath and kept at 12 °C. Solutions to be irradiated were kept in 13 × 100 mm Pyrex culture tubes (capacity 8 mL) with Teflon-lined screw caps. All solutions were degassed with nitrogen, placed in the submerged irradiation apparatus, and photolyzed with a 450-W Hanovia medium-pressure lamp.

Method 3. A commercial air-cooled Rayonet photochemical reactor (Southern New England Ultraviolet Inc.) was utilized with 16 standard lamps which would be changed for 254, 300, or 350 nm radiation. The entire apparatus could be placed in a refrigerator if lower temperatures than ambient temperature were desired. Samples were irradiated in the same manner as mentioned in method 2.

Method 4. Solid samples were irradiated in potassium bromide (KBr) matrices prepared in the following manner. Approximately 0.5 mg (this amount varied depending on the extinction coefficient of a sample) was mixed with about 500 mg of anhydrous KBr and made into KBr, a pellet, in the usual manner.

Coumalic acid was prepared in 72% yield from DL-malic acid according to the method developed by Wiley and Smith.[29] Several recrystallizations were needed to obtain colorless crystals, mp 209–211 °C (lit.[29] mp 206–209 °C). α-Pyrone was prepared by a slight modification of the procedures developed by Zimmerman and co-workers.[12] The crude α-pyrone was a pink, oily material which, after distillation, resulted in 75% yield of a colorless liquid, bp 39–40 °C (3 Torr) [lit.[12] 110 °C (26 Torr)]. Methyl coumalate was prepared by the modification of the method used by Caldwell and co-workers[30] and purified by several recrystallizations from ether containing Norite. The yield was 13.8 g (33%), mp 70–71 °C (lit.[30] mp 73–74 °C). Isopropyl coumalate was prepared in 55% yield according to a modified procedure,[30] mp 43.5–44.5 °C (lit.[30] 44 °C).

Preparation of Benzyl Coumalate from Coumaloyl Chloride. A solution of 25 mL of anhydrous ether containing benzyl alcohol (2.05 g, 0.019 mol) and *N,N*-dimethylaniline (3.50 mL, 0.03 mol) was placed in a 100-mL round-bottom flask which was equipped with reflux condenser, drying tube, magnetic stirrer, and addition funnel. The entire coumaloyl chloride prepared above was dissolved in 50 mL of ether, filtered, and added slowly (~45 min) through the addition funnel. The solution was then allowed to reflux for 10 h.

The reaction mixture was worked up as follows. The brown reaction mixture was poured into 50 mL of water and the ether layer which separated was washed three times with 10 mL of 10% sulfuric acid, once with 10 mL of saturated sodium bicarbonate, and finally with 15 mL of water. It was then dried over anhydrous magnesium sulfate and filtered and solvent was evaporated. The resultant yellow, crystalline benzyl coumalate (40%) was recrystallized from hot ether containing Norite, mp 90–92 °C (lit.[30] 92 °C).

Coumaloyl Chloride. A 25-mL round-bottom flask was set up with reflux condenser, drying tube, and magnetic stirrer. Coumalic acid (2.80 g, 0.02 mol) and thionyl chloride (10 mL, 0.137 mol) were placed in the flask and refluxed for 10 h. During this period all the coumalic acid dissolved. The excess thionyl chloride was vacuum distilled using a water aspirator. The remaining oily material crystallized in the refrigerator.

The coumaloyl chloride obtained this way was used in preparation of benzyl coumalate with no further purification: IR 1750 cm^{-1} (C=O stretch); NMR ($CDCl_3$) δ 6.50 (1 H, dd, $J_{3,4}$ = 10, $J_{3,6}$ = 1 Hz), 7.90 (1 H, dd, $J_{4,3}$ = 10, $J_{4,6}$ = 3 Hz), 8.80 (1 H, dd, $J_{4,6}$ = 3, $J_{3,6}$ = 1 Hz).

Irradiation of Coumalic Acid in Methanol. A solution of coumalic acid (400 mg in 80 mL of methanol) (3.58×10^{-2} M) was introduced into ten 8 × 13 mm borosilicate culture tubes and irradiated (method 2) for 24 h at $h\nu > 310$ nm. The original colorless solution changed to light yellow at the end of the irradiation period. The solutions were combined and concentrated to 20 mL using a rotary evaporator and extracted with 200 mL of pentane using a continuous extractor, and the pentane solution was evaporated to yield 144 mg (36.20% total conversion) of a light yellow oil. When analyzed by gas–liquid chromatography (6 ft × 0.125 in. UCON Hp 10% on Chromosorb P 60/90) the oil contained four major compounds with retention times of 1.60, 3.24, 6.40, and 4.4 min in ratio of 3.2:5.2:4:1, respectively. These compounds were separated by preparative GLC (8 ft × 0.25 in. UCON LB 10% on Chromosorb P 60/80) and were identified to be methyl 5-methoxy-2,4-*trans,trans*-pentadienoate (**17**), methyl 5,5-dimethoxy-*cis*-2-pentenoate (**18**), methyl 5,5-dimethoxy-*trans*-2,2-pentenoate (**19**), and methyl coumalate (**12a**).

The infrared spectrum of **17** contained absorption bands at 1735 (C=O stretch), 1700, 1278 (=$COCH_3$ symmetrical and asymmetrical stretch), 1238, 1175, 1167 (C–O–C symmetrical and asymmetrical stretch), and 975 cm^{-1} (for all trans C=C conjugated); UV λ_{max} (CH_3OH) 284 nm (ϵ 19 500); mass spectrum *m/e* (rel intensity) 142 (3), 111 (100), 96 (58), 68 (62), and 59 (92).

The infrared spectrum of **18** on KBr showed the following bands: 1720 (conjugated C=O stretch), 1625 (C=C stretch), 1719, 1710, 1120 (C–O–C stretch known as acetal bands), 1070 (C–O–C symmetrical stretch), and 820 cm^{-1} (C=CH out of plane bend); UV λ_{max} (CH_3OH) 218 nm (ϵ 5000). The mass spectrum indicated no parent peak but a base peak was at *m/e* 111. Other peaks *m/e* (rel intensity) 143 (10), 142 (26), 112 (10), 75 (55), and 68 (95); NMR ($CDCl_3$) δ 3.05 (2 H, d of t), 3.39 (6 H, s), 3.75 (3 H, s), 4.35 (1 H, t), and 6.10 (2 H, m).

Compound **19** had a similar IR to that of **18**. Of special interest is the band at 974 cm^{-1} present in **19** which is assigned to out of plane bending vibrations in trans-disubstituted olefins. This band is absent in compound **18**. Other absorption frequencies were at 1720 (conjugated C=O stretch), 1650 (C=C stretch), 1205, 1172, 1128 (C–O–C, stretch known as acetal bands), 1275 (C–O–C asymmetrical stretch), and 1070 cm^{-1} (C–O–C symmetrical stretch); UV λ_{max} (CH_3OH) 218 nm (ϵ 15 500). The mass spectrum had a small peak at *m/e* 173, a base peak at *m/e* 75, and other significant fragments *m/e* (rel intensity) 143 (10), 112 (3), 111 (42), and 59 (25), NMR ($CDCl_3$) δ 2.57 (2 H, dd, J = 6 Hz), 3.39 (6 H, s), 3.78 (3 H, s), 3.52 (1 H, t, J = 6 Hz), 5.97 (1 H, t, d, $J_{1,3}$ = 16, $J_{1,3}$ = 1 Hz), and ~7 (1 H, m).

Irradiation of Isopropyl Coumalate in Methanol. A solution of isopropyl coumalate (1.50 g, 8.29×10^{-3} mol) in 370 ml of methanol was irradiated (method 1) for 7.5 h at 310 nm and 5 °C. At the end of this period the solvent was evaporated on a rotary evaporator and a TLC (silica gel PF-254, eluted with ether) of the resultant yellow oil obtained. Three compounds with R_f values of 0.60, 0.40, and 0.23 were present. The compound with R_f 0.60 was isopropyl coumalate and the compound with R_f 0.40 was the corresponding photolactone **13b**. The compound with R_f 0.25 was isolated by preparative TLC to yield 30 mg of a yellow oil: NMR ($CDCl_3$) δ 1.30 (12 H, 3, J = 6 Hz), 4.12 (3 H, s), 5.23 (1 H, quint, J = 6 Hz), 6.22 (1 H, d, $J_{2,3}$ = 16 Hz), 7.00 (1 H, s), 7.30 (1 H, d, $J_{3,2}$ = 16 Hz), 9.00 (1 H, broad). The mass spectrum of this compound had a molecular ion at *m/e* 214 (63) and two equally intense base peaks *m/e* 155 and 126. Other peaks were at *m/e* 154 (78), 140 (88), 123 (60), 112 (90), and 84 (61). On the basis of the above spectral data, structure **14b** was assigned to this compound.

Methyl coumalate behaved similarly and produced **14a** in small yield.

Methanolysis of 5-Carbomethoxy-3-oxabicyclo[2.2.0]hex-5-en-2-one (13a). A solution containing methyl coumalate (400 mg,

2.6×10^{-3} mol) in 35 mL of ahydrous ether was irradiated (method 2) for a period of 68 h. Immediately after irradiation a small amount of this solution was dissolved in 3.00 mL of methanol (2.77×10^{-4} M) and the UV spectrum recorded at time intervals of 0, 25, 50, 75, and 470 min. The ether was then evaporated on a rotary evaporator and 5.0 mL of methanol added to the entire sample. The reaction mixture was allowed to stand overnight. The methanol was evaporated and the NMR spectrum of the resultant yellow oil determined in $CDCl_3$. Only 30% of the photopyrone had reacted with the methanol but 70% had thermolyzed to methyl coumalate. The spectrum, in addition to the signals of methyl coumalate, contained the following signals: δ 3.78 (3 H, s), 3.98 (3 H, s), 6.33 (1 H, dd, $J_{2,3} = 16$, $J_{2,5} = 1$ Hz), 7.18 (1 H, m), and 7.38 ppm (1 H, dd), $J_{3,2} = 16$, $J_{3,5} = 2$ Hz) consistent with structure assigned to 4-carbomethoxy-5-methoxy-2,4-(*E*,*E*)-pentadienoic acid (**14a**).

Irradiation of Methyl Coumalate in Diethyl Ether. Preparation of 5-Carbomethoxy-3-oxabicyclo[2.2.0]hex-5-en-2-one (13a). A solution of methyl coumalate (500 mg, 3.25×10^{-3} mol) in 40 mL of anhydrous ether was irradiated (method 2) for a period of 68 h. At the end of this period the solvent was removed (rotary evaporator) and the resultant light yellow oil (485 mg) was molecularly distilled at 40 °C (0.005 Torr). Analysis of this oil proved it to be 5-carbomethoxy-3-oxabicyclo[2.2.0]hex-5-en-2-one (**13a**): IR (KBr) 1745 and 1840 cm^{-1}; UV λ_{max} (ether) 246 nm (ϵ 6550), 270 (shoulder) (3800); NMR ($CDCl_3$) δ 3.90 (3 H, s), 4.58 (1 H, m), 5.63 (1 H, dd, $J_{1,4} = 2$, $J_{1,6} = 4$ Hz), and 7.41 (1 H, dd, $J_{4,6} = 1$, $J_{3,4} = 4.5$ Hz); mass spectrum of **13a** *m/e* (rel intensity) 154 (20), 110 (100), 93 (44), 82 (90), 53 (60), and 39 (90). Other coumalate esters gave similar results when irradiated under similar conditions.

Irradiation of Methyl Coumalate in Benzene. A solution of 100 mg (6.50×10^{-4} mol) of methyl coumalate in 80 mL of anhydrous benzene (0.081 M) was irradiated (method 2) for 40 h. The solvent was evaporated and the infrared spectrum (neat on KBr plates) recorded. It contained the typical photopyrone carbonyl absorption band at 1825 cm^{-1} in addition to the methyl coumalate band at 1740 cm^{-1}. The NMR taken in $CDCl_3$ revealed that over 90% of methyl coumalate had been converted to the photopyrone **13a**. A small amount (<10%) of dimeric products was also present but these were not investigated. The bicyclic lactone **13a** was redissolved in benzene and allowed to stand on a lab bench at room temperature for over 1 week. At the end of this period the infrared spectrum was taken again though no significant change in the intensity of 1825 and 1740 cm^{-1} was observed. Isopropyl and benzyl coumalate also behaved similarly when irradiated in benzene.

Irradiation of Methyl Coumalate in Ether Sensitized with Benzophenone. In two 8 × 13 mm culture tubes was placed 16 mL of an ether solution containing methyl coumalate (200 mg, 1.29×10^{-3} mol). Benzophenone (0.50 mL, 9.9×10^{-2} M) in ether was introduced. The tubes were placed in a Rayonet reactor and irradiated at 5 °C (method 3) at 350 nm for 10.5 h.

At the end of this period, the reaction mixture remained colorless, but a white solid material had formed on the wall of the reaction vessel. The solid material was isolated by suction filtration, and washed with acetone. A white material (26 mg) which decomposed at 188 °C was isolated. This compound was later identified to be a [4 + 2] dimer adduct of methyl coumalate (**20**).

The filtrate was then concentrated to 8 mL and cooled in an ice bath. Another white solid crystallized out of solution. This compound was also isolated and washed with cold ether to yield 26 mg of white solid material which decomposed at 153–155 °C. This compound upon further analysis proved to be another [4 + 2] dimeric adduct of methyl coumalate (**21**).

The infrared spectrum of adduct **20** showed absorptions at 1780 (C=O stretch, lactone), 1725 (=C–C=O stretch, ester), 1675 ($R_1R_2C{=}CR_3H$ stretch), 1265 [=C–C(=O)–O–C symmetrical stretch], and 770 cm^{-1} ($R_1R_2C{=}CR_3H$ bend); NMR (Me_2SO-d_6) δ 3.65 (1 H, m), 3.79 (6 H, s), 3.95 (1 H, m), 4.00 (1 H, dd, $J_{7,12} = 6$, $J_{7,8} = 2$ Hz), 5.95 (1 H, m), 7.50 (1 H, dd, $J_{8,12} = 6$, $J_{1,12} = 2$ Hz), and 7.78 (1 H, s), mass spectrum *m/e* (rel intensity) 252 (44), 221 (100), 193 (45), 126 (22), 97 (43), 95 (43), 85 (40), 83 (43), and 69 (51). Anal. Calcd for $C_{14}H_4O_8$: C, 64.54; H, 3.89. Found: C, 64.51; H, 4.00.

The infrared spectrum of adduct **21** consisted of the following bands: 1700 (C=O stretch, ester), 1725 (C=O stretch, lactone), 1645 (R_1R_2C–CR_2H stretch), 1245 [=C–C(=O)–O–C asymmetrical stretch], 1175 [=C–C(=O)–O–C symmetrical stretch] 755 cm^{-1} (=C–H bend); NMR (Me_2SO-d_6) δ 3.72 (3 H, s), 3.74 (3 H, s), 4.20 (1 H, d, $J_{8,12} = 6$ Hz), 5.40 (1 H, d, $J = 2$ Hz), 5.69 (1 H, m), 6.20 (1 H, d, $J_{5,6} = 10$ Hz), 7.00 (1 H, d, $J_{6,5} = 10$ Hz), and 7.50 (1 H, dd, $J_{8,12} = 6$, $J_{1,12} = 2$ Hz); mass spectrum *m/e* (rel intensity) 264 (12), 252 (24), 221 (100), 193 (30), 163 (22), 154 (20.2), 126 (39), 95 (30), 85 (20), and 83 (20). Anal. Calcd for $C_{14}H_4O_8$: C, 54.54; H, 3.89. Found: C, 53.95; H, 4.19.

Irradiation of Methyl Coumalate in Ethyl Bromide. In a Pyrex test tube containing 8 mL of ethyl bromide was placed methyl coumalate (100 mg, 1.29×10^{-3} mol). Irradiation (method 2) was carried out at 5 °C for a period of 20 h. At the end of this period the solvent was evaporated and the solid material remaining dissolved in Me_2SO-d_6 for NMR analysis. Almost no methyl coumalate was present and the spectrum was identical with that of a mixture of **20** and **21**.

Irradiation of KBr Matrix at 254 nm. Control Experiment. A sample of 500 mg of anhydrous potassium bromide was made into a KBr pellet (method 4) and irradiated in a Rayonet photochemical reactor at 254 nm. The irradiation was monitored (infrared) and spectra were taken after 0, 2, 3, 4, 7, and 14.5 h of irradiation. From the obtained spectra the absorbance of the CO_2 band at 2330 cm^{-1} was measured and shown to be negligible over the first 7 h and to have reached a reading of 0.03 absorbance units in a 14.5-h period.

A. Irradiation at 254 nm. A potassium bromide disk was prepared by pressing a mixture of methyl coumalate (0.44 mg, 3.24×10^{-6} mol) in 370 mg of KBr in the usual manner. The infrared spectrum was recorded and the pellet irradiated (method 4) at 254 nm. The infrared spectrum was recorded again after 15, 30, and 60 min of irradiation. From the recorded IR spectra the absorbance of 1721 (C=O stretch, lactone), 1750 (C=O stretch, ester), and 2330 cm^{-1} (CO_2) were measured. The results are shown in order of increasing time of irradiation: 1721 cm^{-1}, 1.18, 0.87, 0.76, and 0.64; 1750 cm^{-1}, 1.25, 0.90, 0.15, and 0.34; 2330 cm^{-1}, 0, 0.18, 0.23, and 0.36.

B. Irradiation at 300 nm. A KBr matrix containing methyl coumalate (0.27 mg, 1.75×10^{-6} mol) and 489 mg of potassium bromide was prepared. The infrared spectrum was recorded and the pellet was irradiated (method 4) at 300 nm and 5 °C. The IR spectrum was obtained again after 15, 30, and 60 min of irradiation. A visual change from transparent to translucent, and from colorless to a light yellow, was observed. The absorbance at 1721, 1750, and 2330 cm^{-1} bands are shown in the order recorded: 1721 cm^{-1}, 1.05, 0.78, 0.65, and 0.53; 1750 cm^{-1}, 1.35, 1.00, 0.90, and 0.74; 2330 cm^{-1}, 0, 0.07, 0.16, and 0.31.

C. Irradiation at 350 nm. Methyl coumalate (0.13 mg, 8.45×10^{-7} mol) was mixed with 496 mg of KBr and pressed into a disk. The infrared spectrum was recorded and the matrix was irradiated (method 4) at 350 nm and 5 °C. The infrared spectrum was recorded after 10, 20, 30, and 40 min of irradiation. When the irradiation was over the visual properties of the matrix had not changed much. The absorbances of 1721, 1750, and 2330 cm^{-1} were measured and corrected for baseline. The result is shown in order of increasing time of irradiation: 1721 cm^{-1}, 0.64, 0.59, 0.57, 0.53, and 0.49; 1750 cm^{-1}, 0.48, 0.45, 0.41, 0.38, and 0.34; 2330 cm^{-1}, 0.00, 0.00, 0.00, 0.00 and 0.005.

D. Irradiation at 250 nm Followed by Irradiation at 300 nm. A KBr matrix containing 0.30 mg (1.94×10^{-6} mol) of methyl coumalate and 498 mg (4.19×10^{-3} mol) of KBr was prepared and after the IR spectrum was recorded it was irradiated (method 4) at 350 nm for 40 min. During this period the irradiation was interrupted after 10, 20, 30, and 40 min to record the infrared spectrum. The matrix was then irradiated for an additional 40 min at 300 nm and the IR spectra were recorded in the same manner. The visual appearance of the matrix did not change during the initial 40 min of irradition but the change (to yellow and translucent) was appreciable during the latter 40 min. The absorbance of 1550 (C=C stretch) and 2330 cm^{-1} (CO_2) bands after correction for baseline are presented in the order of the increasing time of irradiation at 350 and 300 nm: $h\nu$ 350, 1550 cm^{-1}, 0.120, 0.165, 0.115, 0.105, 0.100, and 0.091; 2330 cm^{-1}, 0, 0.0, 0.005, 0.01, 0.010, and 0.012; $h\nu$ 300, 1550 cm^{-1}, 0.091, 0.080, 0.075, 0.067, and 0.060; 2330 cm^{-1}, 0.012, 0.078, 0.130, 0.20, and 0.260.

In a subsequent experiment 7.12 mg (4.62×10^{-5} mol) of methyl coumalate was mixed with 4.46 g of anhydrous potassium bromide and made into nine KBr disks. The KBr disks were irradiated (method 4) at 350 nm for 7.6 h. The temperature was kept at 5 °C during the illumination time. The pellets were then pulverized (Wig-L-Bug) and dissolved in 25-mL of water. The aqueous solution was extracted with three 5-mL portions of methylene chloride. The methylene chloride extracts were combined, dried over anhydrous calcium chloride, and filtered, and solvent was evaporated to yield 5.0 mg of a light yellow, viscous material (70% recovery). When analyzed by HPLC (10 ft × 0.25 in. silica gel, $CHCl_3$, 1 mL/min) it contained nine compounds among which dimeric adducts **20** and **21** were identified by HPLC.

Isopropyl coumalate as well as benzyl coumalate, though not reported, behaved similarly when irradiated in a KBr matrix; the latter produced a trace amount of benzaldehyde also.

Acknowledgment. The work reported has been supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We gratefully acknowledge the generosity of the donors of this fund.

Registry No.—**12**, 500-05-0; **12a**, 6018-41-3; **12b**, 61752-09-8; **12c**, 61752-10-1; **13a**, 61752-11-2; **13b**, 61752-12-3; **13c**, 61752-13-4; **14a**, 61752-14-5; **14b**, 61752-15-6; **17**, 61752-16-7; **18**, 61752-17-8; **19**, 61752-18-9; **20**, 61787-98-2; **21**, 61752-19-0; coumaloyl chloride, 23090-18-8.

References and Notes

(1) E. J. Corey and J. Streith, *J. Am. Chem. Soc.*, **86**, 950 (1964).
(2) P. DeMayo, *Adv. Org. Chem.*, **2**, 394 (1960).
(3) W. H. Pirkle and L. H. McKendary, *J. Am. Chem. Soc.*, **91**, 1179 (1969).
(4) W. H. Pirkle and L. H. McKendary, *Tetrahedron Lett.*, 5279 (1968).
(5) J. P. Guthrie, C. L. McIntosh, and P. DeMayo, *Can. J. Chem.*, **48**, 237 (1970).
(6) C. T. Bedford, J. M. Forrester, and T. Money, *Can. J. Chem.*, **48**, 2645 (1970).
(7) O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Am. Chem. Soc.*, **95**, 244 (1973).
(8) C. L. McIntosh and O. L. Chapman, *J. Am. Chem. Soc.*, **95**, 247 (1973).
(9) R. G. Pong and J. S. Shirk, *J. Am. Chem. Soc.*, **95**, 248 (1973).
(10) O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Am. Chem. Soc.*, **95**, 614 (1973).
(11) C. L. McIntosh, P. de Mayo, and R. W. Yu, "Photochemical Syntheses", R. Srinivason, Ed., Interscience, New York, N.Y., 1971, p 99.
(12) H. E. Zimmerman, G. L. Grunewald, and R. M. Paudler, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 101.
(13) A. W. Baker, *J. Phys. Chem.*, **61**, 450 (1957).
(14) J. K. S. Wan, R. N. McCormick, E. J. Baum, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **87**, 4409 (1965).
(15) S. Wiederhorn and H. G. Drickamer, *Phys. Chem. Solids*, **9**, 330 (1959).
(16) W. W. Schloman, Jr., and B. F. Plummer, *J. Am. Chem. Soc.*, **98**, 3254 (1976).
(17) D. O. Cowan and J. C. Kozia, *J. Am. Chem. Soc.*, **98**, 1001 (1976).
(18) D. O. Cowan and J. C. Kozia, *J. Am. Chem. Soc.*, **96**, 1229 (1974).
(19) D. O. Cowan and J. C. Kozia, *J. Am. Chem. Soc.*, **97**, 249 (1975).
(20) D. O. Cowan and J. C. Kozia, *J. Am. Chem. Soc.*, **97**, 3283 (1975).
(21) W. I. Ferree, B. F. Plummer, and W. W. Schloman, *J. Am. Chem. Soc.*, **96**, 7741 (1974).
(22) W. I. Ferre and B. F. Plummer, *J. Am. Chem. Soc.*, **95**, 6709 (1973).
(23) D. O. Cowan and R. C. E. Drisko, *J. Am. Chem. Soc.*, **92**, 6281 (1970), and references cited therein.
(24) G. O. Schenck, I. M. Hartmann, and W. Hartmann, *Chem. Ber.*, **100**, 3146 (1967).
(25) P. S. Song, Q. Chae, M. Fujita, and H. Baba, *J. Am. Chem. Soc.*, **98**, 819 (1976).
(26) J. N. Pitts, Jr., J. K. S. Wan, and E. A. Schuck, *J. Am. Chem. Soc.*, **86**, 3606 (1964).
(27) J. N. Pitts, Jr., E. A. Schuck, and J. K. S. Wan, *J. Am. Chem. Soc.*, **86**, 296 (1964).
(28) S. Siegel and H. S. Judeikis, *J. Chem. Phys.*, **42**, 3060 (1965).
(29) R. H. Wiley and N. R. Smith, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 201.
(30) W. T. Caldwell, F. T. Tyson, and L. Lauer, *J. Am. Chem. Soc.*, **66**, 1483 (1944).

Photochemistry of 3-Ethoxy-3-methylpent-4-en-2-one, an α-Alkoxy β,γ-Unsaturated Ketone

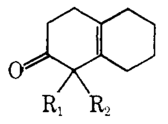
Kenneth G. Hancock* and Philip L. Wylie

Department of Chemistry, University of California at Davis, Davis, California 95616

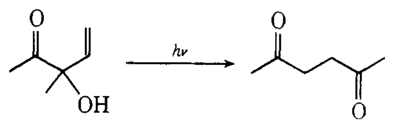
Received January 19, 1977

Irradiation of 3-ethoxy-3-methylpent-4-en-2-one gives (*E*)- and (*Z*)-5-ethoxyhex-4-en-2-one by 1,3-acyl shift; acetaldehyde, 3-methylpent-4-en-2-one, (*Z*)- and (*E*)-3-methylpent-3-en-2-one by Norrish type II cleavage; 2,3,4-trimethyl-2-vinyloxetan-3-ol (two isomers) by type II cyclization; and 3,4-dimethylhexane-2,5-dione (*dl*- and *meso*-) and 5-ethoxyhex-5-en-2-one by secondary reactions. Disappearance of 3-ethoxy-3-methylpent-4-en-2-one is neither sensitized by xanthone nor quenched by piperylene. The 1,3 shift is reversible. Mechanisms and relevance to other α-substituted β,γ-unsaturated ketones are discussed; isolation of γ-keto enol ethers from photolysis of α-ethoxy β,γ-unsaturated ketones provides circumstantial evidence that a γ-keto enol is the likely intermediate in photochemical conversion of α-hydroxy β,γ-unsaturated ketones to 1,4-diketones.

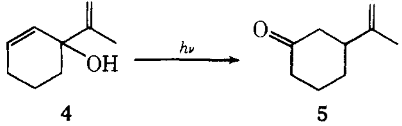
It has recently become apparent that α-substitution can cause dramatic alterations in the photochemical behavior of β,γ-unsaturated ketones.[1] For example, Engel et al.[2] have shown that α-methylation of **1a** enhances the likelihood of 1,3-shift (α-cleavage) at the expense of 1,2-shift products, although the multiplicity of the reactive excited state is uncertain.[3] Sasaki,[4] Carlson,[5] McMurry,[6] and we[7,8] have shown that α-hydroxylation introduces a synthetically useful modification to the usual reaction pattern of 1,3-acyl shifts. We previously reported the photochemistry of the two α-hydroxy β,γ-unsaturated ketones **2** and **4** which, on direct irradiation or with triplet sensitization, gave the 1,4-diketones **3** and **5**.[7,8] The rearrangements of **2** and **4** were suggested to involve a 1,3-acyl shift (probably via discrete acetyl and allyl radicals), followed by tautomerization of the resultant γ-keto enol. The (inefficient) sensitized 1,3-acyl shift of both **2** and **4**, though not unprecedented,[9] is highly unusual in β,γ-unsaturated ketone photochemistry.



1a, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = R_2 = CH_3$



2 **3**



4 **5**