Carbonyl Group Photochemistry via the Enol Form. Photoisomerization of 4-Substituted 3-Chromanones[1]

Albert Padwa,* Andrew Au, George A. Lee, and William Owens

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. *Received September 29, 1975*

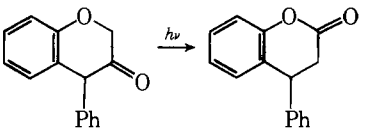
Abstract: The mechanism of the photochemical rearrangement of 4-phenyl-3-chromanone to 4-phenyldihydrocoumarin has been investigated. The rearrangement was shown to proceed via the small amount of enol present in tautomeric equilibrium with the keto form. Electronic excitation of the enol results in a photochemical ring opening to give an *o*-quinoneallide intermediate which undergoes a novel intramolecular Michael addition to form an *o*-hydroxyphenylcyclopropanone. This species is in tautomeric equilibrium with an oxabenzobicyclo[3.1.0]hexene. The oxabicyclohexene undergoes a subsequent ring opening to give the observed dihydrocoumarin. Evidence for the proposed sequence was obtained by studying the photochemistry of the closely related 3-acetoxy- and 3-methoxy-4-phenylchromene systems. The excited state behavior of 4-carbomethoxy-3-chromanone was also examined. In this case, the transient cyclopropanone was trapped with furan to give an oxabicyclo[3.2.1]octene derivative. The results obtained establish the significant role which the small amount of enol can play in carbonyl group photochemistry.

One of the most active areas of organic photochemistry has been the study of systems which possess a carbonyl group.[2-8] As a result of these studies, the photochemical transformations of organic molecules containing this functional group have been categorized into a number of primary photochemical processes.[6] Despite the fact that the photochemical behavior of the carbonyl group has received much scrutiny in the past decade, relatively little is known about the photochemistry of the small amount of enol tautomer which exists in equilibrium with the keto form. Outside of several examples of intermolecular photocycloaddition of conjugated enols,[9-14] the behavior of excited state enols has not been studied in any detail.[15] Of special significance and interest is the possibility of observing further photochemistry from the excited enol (or enolate) when the keto tautomer is the absorbing species. Recently, a number of widely scattered and isolated reports[16-21] have appeared which indicate that 1,3-tautomerization of certain ketones can occur upon electronic excitation. Whether this tautomerization can be viewed simply as an allowed [1,3]-sigmatropic shift is currently an unanswered problem. Usually, the enol and enolate anions formed from the excited state either emit phosphorescence or undergo reketonization.[15-21] It should be noted that the much larger extinction coefficients and bathochromically shifted absorption maxima of enols or enolates,[22] in comparison with their carbonyl progenitors, make them particularly strong competitors for absorption of the incident light. Significant concentrations of the enol tautomer of the original carbonyl compound may also be present in solution, particularly when polar solvents are employed. Consequently, it should be possible to selectively excite the keto and enol tautomers with light of different wavelength and observe different types of photochemistry from each form.

The small amount of enol present in tautomeric equilibrium with the keto form occasionally plays an important role in influencing the chemical reactivity of the carbonyl group in the ground state. An interesting example of this effect was reported by Gassman and co-workers.[23-25] These workers found that in rigid bicyclic systems, where participation of the π and nonbonding electrons of the carbonyl group is stereochemically prohibited from interacting with an incipient carbonium ion center, the enol content is the overriding factor in determining the rates and products of solvolysis. As part of our continuing studies dealing with carbonyl group photochemistry,[26] we became interested in determining whether the enol content can contribute in controlling the photochemical behavior of the carbonyl chromophore. The present paper describes the excited state behavior of some model compounds which allow an evaluation of this possibility.

Results and Discussion

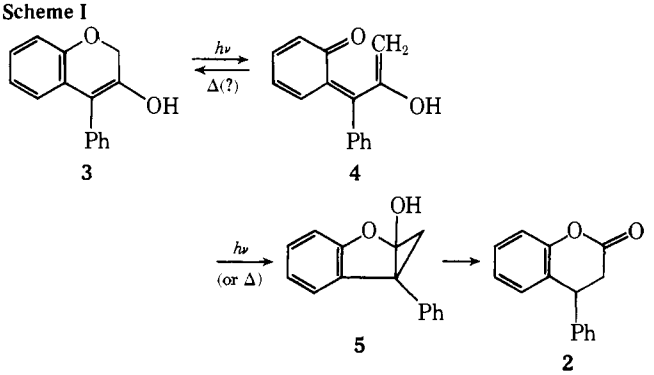
Photoisomerization of 4-Phenyl-3-chromanone to 4-Phenyldihydrocoumarin. A recent report dealing with the photoisomerization of 4-phenyl-3-chromanone (**1**) to 4-phenyldihydrocoumarin (**2**) led us to speculate that the small amount



1 **2**

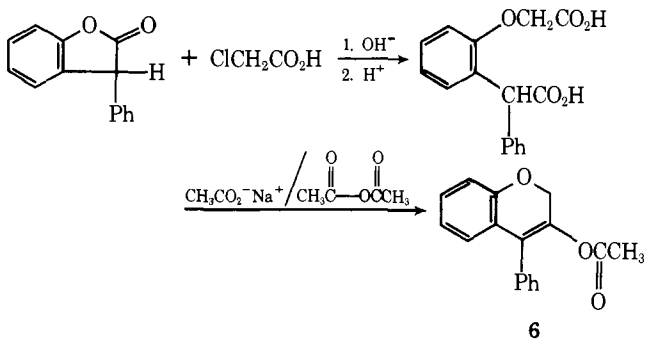
of enol tautomer **3** present in solution plays an important role in this unusual rearrangement.[27] The above transformation was initially rationalized in terms of a mechanism in which two critical steps involve intramolecular hydrogen abstraction through a five-membered transition state.[27] It seemed to us that a more viable explanation involved the prior enolization of chromanone **1** into its enol tautomer **3**, which undergoes photochemical ring opening to *o*-quinoneallide **4**.[28] Closure of **4** either by photochemical or thermal means[29] would give 1-hydroxy-5-phenyl-2-oxabenzobicyclo[3.1.0]hex-3-ene (**5**) which would be expected to ring open to the observed dihydrocoumarin (Scheme I).[30]

Scheme I



3 **4** **5** **2**

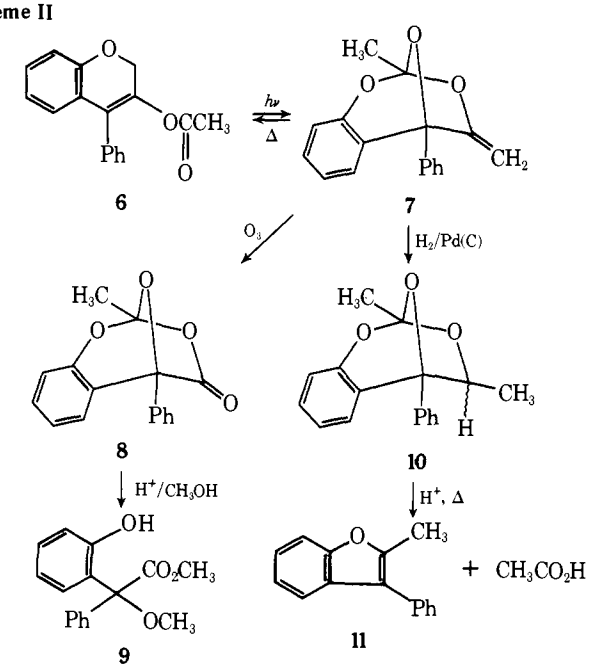
Since it was the 4-phenyl-3-hydroxychromene (**3**) tautomer of **1** which was suspected of giving rise to dihydrocoumarin **2**, we sought to permanently lock **1** into its enol form (i.e., **3**) and examine the behavior of the resulting system. This was accomplished by synthesizing the corresponding enol acetate **6**



6

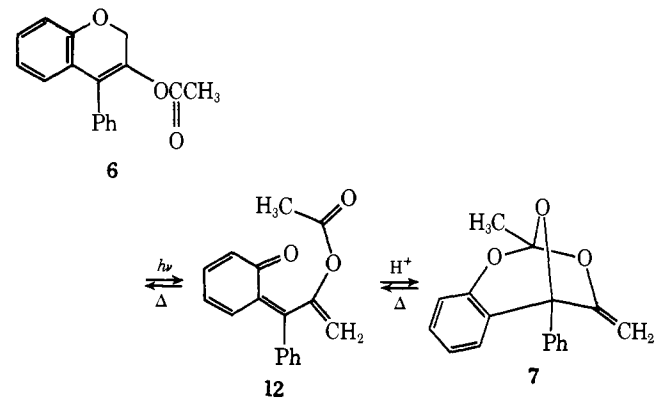
and studying its photochemical behavior. Irradiation of a methanolic solution (Fisher Scientific reagent grade) of **6** with Pyrex-filtered light gave a single compound (77%) whose structure was identified as 2-methyl-4,5-dihydro-4-methylene-5-phenyl-2,5-epoxy-1,3-benzodioxepin (**7**) on the basis of its spectroscopic and chemical properties [NMR τ 8.10 (s, 3 H), 5.86 (d, 1 H, J = 3.0 Mz), 5.55 (d, 1 H, J = 3.0 Hz), 2.1–3.2 (m, 9 H)]. On thermolysis, photoproduct **7** regenerated enol acetate **6.** Additional evidence for the assigned structure was obtained by ozonization of **7** to 2-methyl-4,5-dihydro-4-oxo-5-phenyl-2,5-epoxy-1,3-benzodioxepin (**8**) which was, in turn, converted to methyl 2-methoxy-2-(*o*-hydroxyphenyl)phenylacetate (**9**) on treatment with acidic methanol (Scheme II). Structure **7** was further supported by catalytic

Scheme II

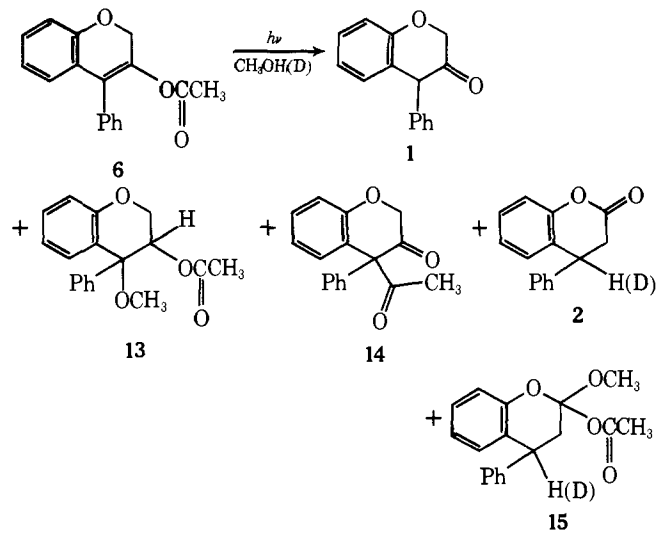


reduction to 2,4-dimethyl-4,5-dihydro-5-phenyl-2,5-epoxy-1,3-benzodioxepin (**10**). Treatment of **10** with *p*-toluenesulfonic acid gave 2-methyl-3-phenylbenzofuran (**11**) in excellent yield.

The formation of epoxybenzodioxepin **7** from the photolysis of enol acetate **6** is a rather unique process and can be explained in terms of an initial photochemical ring opening of the chromene ring to give an *o*-quinoneallide intermediate (**12**). This reactive species undergoes a subsequent acid-catalyzed cyclization to afford **7**. The thermal conversion of **7** → **6** can be rationalized as proceeding via intermediate **12.** Previous work in the literature has shown that *o*-quinoneallide intermediates are readily transformed to the thermodynamically more stable chromene form[28,31-33] thereby providing good analogy for the last step of the thermal isomerization of epoxybenzodioxepin **7.**



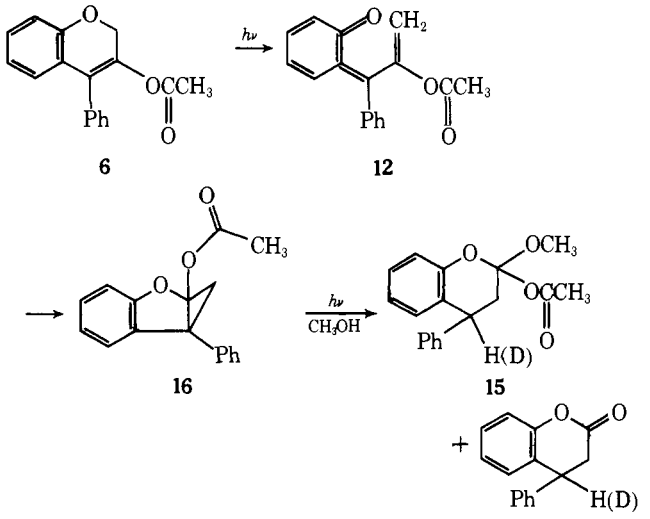
The irradiation of enol acetate **6** was also carried out in methanol which had been rigorously purified. *Under these conditions*, the photolysis of **6** produced a mixture of five compounds which could be readily separated by preparative vapor-phase chromatography. The three minor products obtained from the photolysis of **6** were identified as 4-phenyl-3-chromanone (**1**) (3%),[34] 3-acetoxy-4-methoxy-4-phenylchroman (**13**) (8%), and 4-acetyl-4-phenyl-3-chromanone (**14**) (10%) while the two major products were identified as 4-phenyldihydrocoumarin (**2**) (18%) and 2-acetoxy-2-methoxy-4-phenylchroman (**15**) (30%). The structures of **13, 14,**



and **15** are based on the following observations. The NMR spectrum of **14** consisted of two singlets at τ 8.02 (3 H) and 5.74 (2 H) in addition to the aromatic multiplet at τ 2.8 (9 H). Treatment of **14** with methanolic sodium methoxide afforded 4-phenyl-3-chromanone (**1**) in high yield. Structure **15** showed peaks at τ 7.50 (*s*, 3 H), 7.05 (2 H, d, J = 8.0 Hz), 6.48 (s, 3 H), 5.36 (1 H, t, J = 8.0 Hz), and 2.85 (m, 9 H) in the NMR spectrum and was readily converted to **2** when exposed to a slightly acidic aqueous solution. Structure **13** was assigned on the basis of its spectral properties: ir (CCl_4) 5.68 μ; *m/e* 298 (M^+); NMR (100 MHz) τ 7.45 (s, 3 H), 6.96 (2 H, dd, J = 8.0 Hz), 6.47 (s, 3 H), 5.08 (1 H, t, J = 8.0 Hz), and 2.8 (m, 9 H).

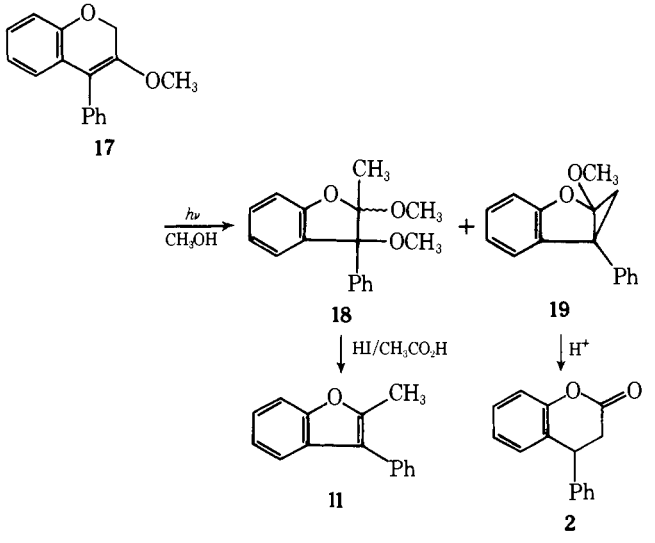
It is particularly interesting to note that no detectable quantities of epoxybenzodioxepin **7** were found in the crude photolysate when the solvent was rigorously purified or when small amounts of sodium bicarbonate were added to the solvent. This observation clearly establishes that the formation of **7** from **12** is an acid-catalyzed process. Control experiments showed that enol acetate **6** can be recovered unchanged from an acidic methanolic solution which had been allowed to stand in the dark for 24 h. The salient features of our data indicate that three distinct transformations occur on irradiation of **6.**

The two minor paths involve (1) a 1,3-acyl shift of enol acetate to give **14**[35] and (2) addition of methanol across the C–C double bond of **6.** Both of these paths are well documented in the literature.[35,36] The major photochemical route, which ultimately leads to the formation of **2** and **15,** can be readily understood on the basis of an oxabicyclohexene (**16**) intermediate. This transient species collapses to **2** and **15** on reaction with methanol. Examination of the reaction as a function of time demonstrated that dihydrocoumarin **2** was also derived, in part, from the hydrolysis of **15** on workup.

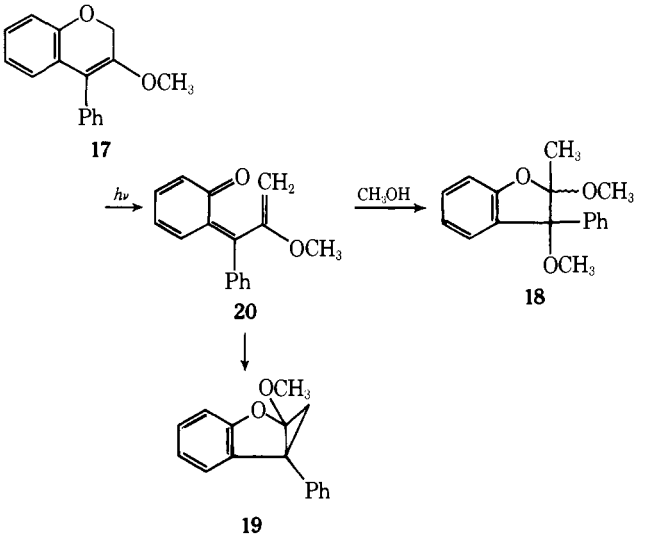


Additional evidence for the mechanism outlined in Scheme I was obtained by studying the photochemistry of **6** in deuteriomethanol. NMR analysis of products **2** and **15** obtained from the reaction clearly indicates that one atom of deuterium has been exclusively incorporated into the 4 position of both products. This is to be expected for an intermediate corresponding to **16** (or **5**). It should be pointed out that a similar result was obtained when chromanone **1** was irradiated in deuteriomethanol. In this case, dihydrocoumarin **2** contained one deuterium atom in the 4 position of the coumarin ring.

We have also examined the photobehavior of the related enol ether **17.** Unlike the complex photochemistry observed with **6,** in which a plethora of products is obtained, the photochemistry of **17** was relatively simple. Irradiation of **17** in methanol produced a mixture of two compounds, **18** and **19,**



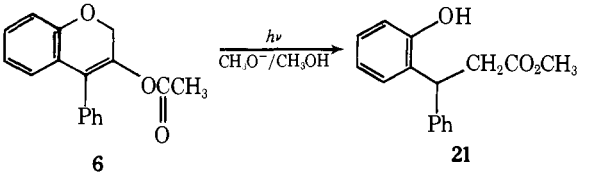
in nearly equal amounts. The two components were separated by fractional crystallization. Elemental analysis, the ultraviolet spectrum (methanol 285 and 278 nm (ϵ 2500 and 2900), and the NMR spectrum [100 MHz, τ 8.36 (s, 3 H), 7.00 (s, 3 H), 6.85 (s, 3 H), 2.5–3.2 (m, 9 H)] suggested 2,3-dimethoxy-2-methyl-3-phenyldihydrobenzofuran (**18**), mp 109–110 °C, as the structure of the more insoluble photoproduct. Chemical confirmation was obtained by treating **18** with hydriodic acid and isolating 2-methyl-3-phenylbenzofuran (**11**) in quantitative yield. Spectral and analytical data for **19** showed that



(a) it was isomeric with **17,** (b) it possessed a cyclopropane ring, and (c) its NMR spectrum consisted of a pair of doublets at τ 9.12 and 7.83 (J = 7.0 Hz), a methoxyl singlet at 6.60, and nine aromatic protons at τ 2.5–3.2. That the actual structure of **19** was 1-methoxy-5-phenyl-2-oxabenzobicyclo-[3.1.0]hexene was established by its ready conversion to 4-phenyldihydrocoumarin (**2**) on treatment with acid. Structure **19** was the only product formed when the irradiation of **17** was carried out in benzene.

The isolation of oxabenzobicyclohexene **19** from the irradiation of **17** provides strong support for the sequence of reactions outlined in Scheme I. With regard to the mechanism of formation of **18,** photochemical ring opening of **17** to *o*-quinoneallide **20** followed by 1,4 addition of methanol and cyclization nicely accommodates the formation of the observed product. Control experiments showed that **19** is not converted to **18** on further irradiation.

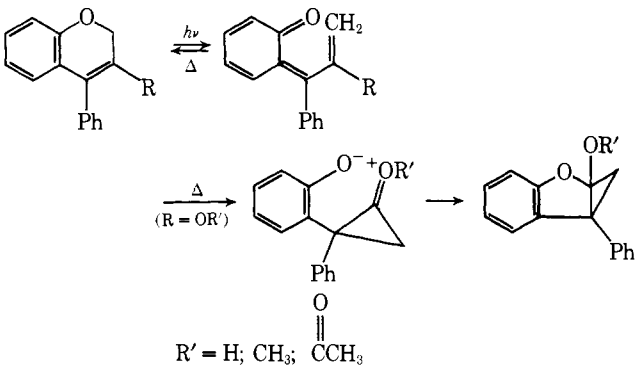
Based on the results obtained with enol acetate **6** and enol ether **17,** we propose that the photoisomerization of **1** → **2** proceeds via photoreaction of the enol (or enolate) tautomer of **1** (i.e., **3**). To test this conclusion, we have studied the photochemistry of the corresponding enolate anion. Addition of sodium methoxide to a methanolic solution of **1** caused a very rapid change in the absorption spectra with new maxima appearing at 314 and 239 nm. The extinction coefficients for these new maxima were on the order of 10^4. The sodium enolate of **1** could also be generated by addition of sodium methoxide to solutions of enol acetate **6.** When a thoroughly deareated methanolic solution of **6** (or **1**) was first treated with sodium methoxide and then irradiated with light of wavelength >300 nm, an extremely rapid and clean conversion to methyl 3-(2-hydroxyphenyl)-3-phenylpropionate (**21**) was observed.



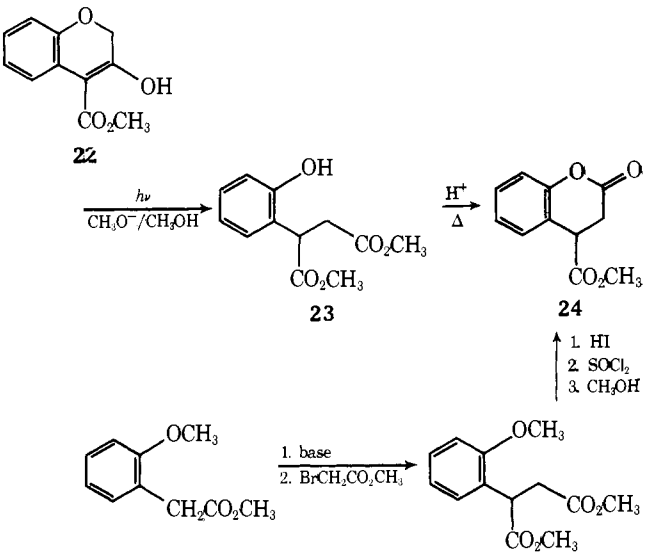
The identity of **21** was determined by its straightforward spectral characteristics as well as its facile conversion to **2** on heating. Structure **21** is not the primary photoproduct of the

reaction but rather is derived by attack of methoxide on dihydrocoumarin **2**. A control experiment clearly demonstrated that when trace amounts of sodium methoxide were added to a methanolic solution of **2**, ester **21** was formed in quantitative yield. In addition to being a cleaner reaction than that observed with either **1** or **6**, the base-catalyzed photolysis of **6** proceeded with a much higher quantum efficiency (i.e., $\Phi_{(6\rightarrow 2)}$base = 0.24; $\Phi_{(1\rightarrow 2)} = 0.007$; $\Phi_{(6\rightarrow 15)} = 0.001$). The difference in reaction efficiency must be related to the high concentration of the reactive enolate tautomer present in solution during the photolysis of **6** in basic methanol.

Photorearrangement in the 4-Carbomethoxy-3-chromanone System. As was pointed out elsewhere,[28] irradiation of 3-alkyl- or 3-aryl-2*H*-chromenes produces *o*-quinoneallide intermediates which do not undergo an intramolecular [4 + 2] photocycloaddition reaction,[37] but rather are attacked by methanol to give phenolic ethers. This observation indicates that the rearrangement of *o*-quinoneallides **4**, **12**, and **20** to oxabenzobicyclohexenes **5**, **16**, and **19** is not an excited-state reaction. The results show that only those 2*H*-chromenes which possess electron-donating substituents in the 3 position of the ring are capable of rearranging to the bicyclic intermediate. From a first approximation, it would appear as though the more electron donating the 3-substituent group is, the more facile is the rearrangement (i.e., $O^- \gg OCH_3 \sim OH > OCOCH_3$). This in turn suggests that the initially formed *o*-quinoneallide intermediate undergoes a novel intramolecular *thermal* Michael addition to form the oxabenzobicyclohexene. There is no reason to invoke a photo-Diels–Alder reaction[37] to account for the formation of the oxabicyclohexene intermediate in these systems.

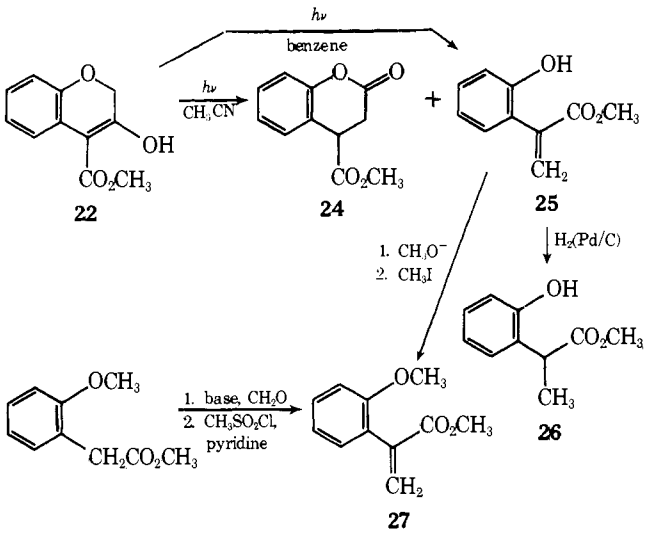


Evidence supporting the above hypothesis was obtained by studying the photochemical behavior of 4-carbomethoxy-3-chromanone (**22**). Using procedures similar to those described for the preparation of other chomanones,[38] 4-carbomethoxy-3-chromanone (**22**), mp 35–36 °C, was prepared in high yield. The NMR spectrum of **22** indicates that this β-ketoester exists predominantly (>98%) in the enol form [τ 5.98 (s, 3 H), 5.24 (s, 2 H), 2.0–3.1 (m, 4 H), and −3.0 (s, 1 H, exchanged with D_2O)]. When a thoroughly deaerated methanolic solution of **22** was treated with sodium methoxide and then irradiated with light of wavelength >300 nm,[39] an extremely rapid and clean conversion to methyl 3-(*o*-hydroxyphenyl)-3-carbomethoxypropanoate (**23**), mp 101–102 °C was observed. The identity of **23** was determined by its straightforward spectral characteristics as well as its facile conversion to 4-carbomethoxydihydrocoumarin (**24**), mp 79–80 °C, on heating in the presence of a trace of acid. The structure of dihydrocoumarin **24** was established by comparison with an independently synthesized sample as shown above. A control experiment showed that when trace amounts of sodium methoxide were added to a methanolic solution of dihydrocoumarin **24**, diester **23** was formed in quantitative yield. This observation suggests that structure **23** is not the primary photoproduct of the reaction



but rather is derived by attack of methoxide on **24**.

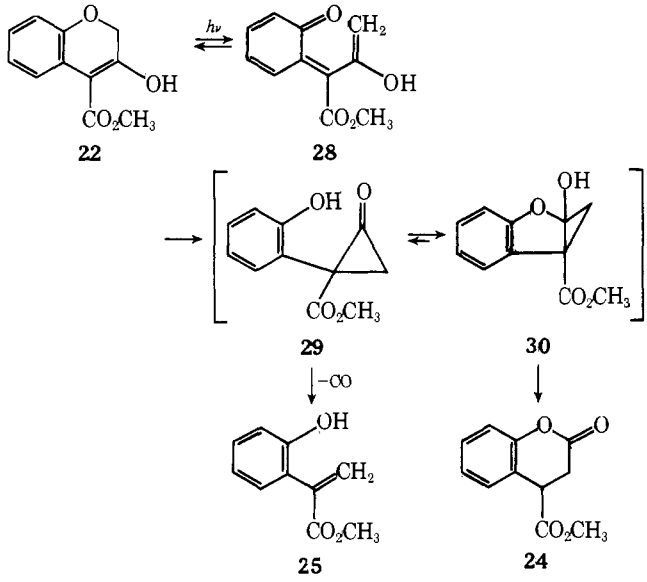
When the irradiation of **22** was carried out in acetonitrile for 14 h under a nitrogen atmosphere with Pyrex-filtered light, a 3:1 mixture of 4-carbomethoxydihydrocoumarin (**24**) and *o*-hydroxy-α-carbomethoxystyrene (**25**) was isolated. The two photoproducts could be easily separated by thick-layer chromatography. Elemental analysis, the ultraviolet spectrum, and the NMR spectrum suggested *o*-hydroxy-α-carbomethoxystyrene (**25**), mp 76–77 °C, as the structure of the minor photoproduct. Chemical confirmation was obtained by (a) catalytic reduction to methyl 2-(*o*-hydroxyphenyl)propionate (**26**) and (b) conversion to *o*-methoxy-α-carbomethoxystyrene (**27**), which was, in turn, independently synthesized. It is



especially interesting to note that when the irradiation of **22** was carried out in benzene, the only product detected was *o*-hydroxy-α-carbomethoxystyrene (**25**).[40]

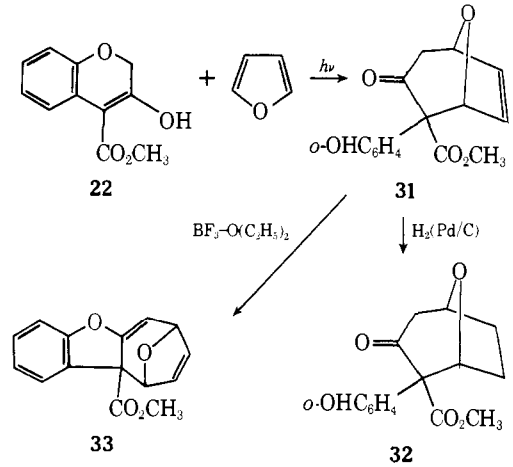
The formation of these products (see Scheme III) is readily explicable in terms of a photoinduced ring opening of chromanone **22** to an *o*-quinoneallide intermediate (i.e., **28**). Closure of **28** by thermal means gives 2-carbomethoxy-2-(*o*-hydroxyphenyl)cyclopropanone (**29**) as a transient intermediate. This species exists in tautomeric equilibrium with 1-hydroxy-5-carbomethoxy-2-oxabenzobicyclo[3.1.0]hex-3-ene (**30**). In polar solvents such as methanol or acetonitrile, the oxabicyclohexene (**30**) is rapidly opened to give the observed dihydrocoumarin (i.e., **24**).[30] Opening of the cyclopropanol ring would be expected to proceed at a much slower rate in benzene, however, since the developing charges are not sig-

Scheme III

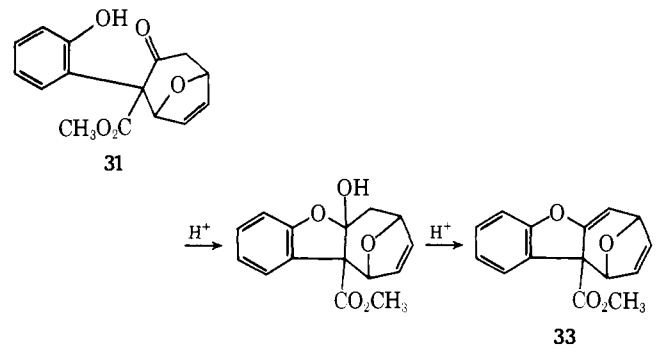


nificantly solvated in this medium. Consequently, the tautomeric mixture of **29** and **30** can exist for a sufficient period of time in benzene[41] to allow the system to extrude carbon monoxide. It is not clear whether the loss of carbon monoxide proceeds from an electronically excited state or from some high ground-state vibrational level of **29.** Cyclopropanones are known to extrude carbon monoxide on thermal[42-44] and photochemical[45] excitation providing reasonable analogy for both possibilities. Presumably the tautomeric equilibrium lies mainly in the direction of **30** since the high strain energy (*I* strain)[46] associated with the sp^2 center in tautomer **29** is released on going to **30.**

Supporting evidence for the above scheme was obtained by carrying out the irradiation of **22** in the presence of furan. Turro and co-workers had previously demonstrated that cyclopropanones undergo ready (3 + 4 → 7) cycloadditions with furan.[42,47] This type of cycloaddition has been suggested to proceed from a transient "bidentate 1,3-dipole".[42] When the irradiation of **22** was carried out in benzene in the presence of a large excess of furan, a new photoproduct was isolated (47%). On the basis of its spectroscopic and chemical properties, this material is assigned the structure of methyl 2-(*o*-hydroxyphenyl)-3-oxo-8-oxabicyclo[3.2.1]oct-6-ene-2-carboxylate (**31**), mp 66-69 °C. The NMR spectrum of **31** was very similar

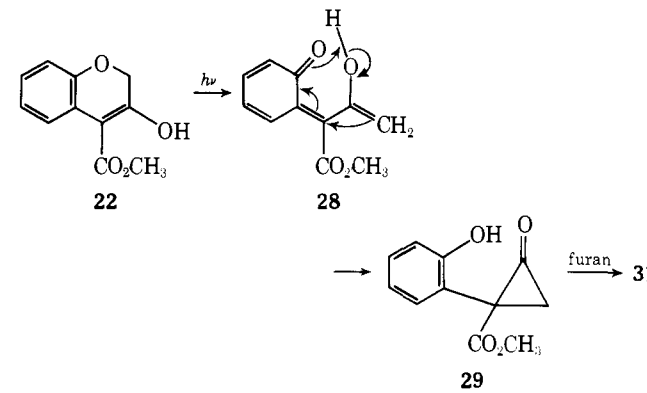


to related cycloadducts[47] and showed signals at τ 7.60 (2 H, d), 6.08 (s, 3 H), 5.02 (m, 1 H), 4.85 (d, 1 H, J = 2.0 Hz), 4.65 (dd, 1 H, J = 6.0 and 2.0 Hz), 3.82 (dd, 1 H, J = 6.0 and 2.0 Hz), 2.6-3.4 (m, 4 H). Addition of incremental amounts of $Eu(fod)_3$[48] to solutions of adduct **31** caused a downfield shift of the signal at τ 7.60 and its conversion into an AB quartet (J_{AB} = 14.5 Hz, low-field half split J = 4.5 Hz, high-field half split J = 1.2 Hz). Cycloadduct **31** was also characterized by catalytic hydrogenation to oxabicyclo[3.2.1]octane **32,** mp 113-114 °C. Treatment of cycloadduct **31** with acid at room temperature gave methyl 7,10-dihydro-7,10-epoxy-10a*H*-benzo[*b*]cyclohepta[*d*]furan-10a-carboxylate (**33**), mp 35-36



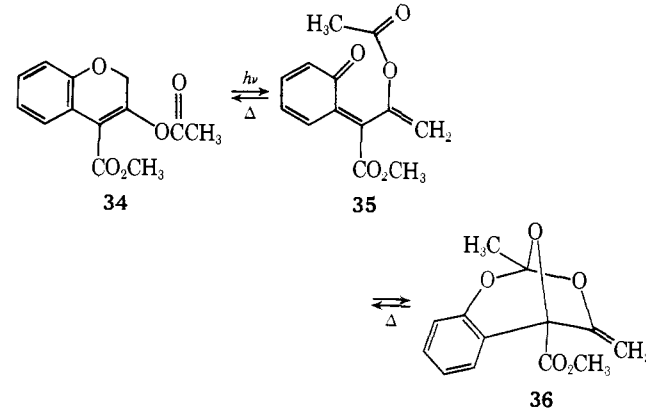
°C, in high yield. The structure of **33** was based on its spectral properties (see Experimental Section) and an elemental analysis which indicated the molecular formula $C_{15}H_{12}O_4$. The formation of **33** is envisaged to occur by protonation of the carbonyl oxygen, followed by addition of the neighboring phenol group and loss of water.

The isolation of cycloadduct **31** and the complete absence of **24** and **25** provide compelling evidence for the intermediacy of a cyclopropanone in the photolysis of **22.** In this case, the initially formed *o*-quinoneallide intermediate (**28**) undergoes



a novel homoconjugative intramolecular Michael addition to give cyclopropanone **29,** which is subsequently trapped by furan.

It is interesting to note that the closely related 3-acetoxy-4-carbomethoxychromene (**34**) followed a different path and gave 2-methyl-4,5-dihydro-4-methylene-5-carbomethoxy-2,5-epoxy-1,3-benzodioxepin (**36**) as the major photoproduct



(53%).[49] Supporting evidence for this structure was obtained by ozonization and catalytic reduction experiments as well as by regenerating chromene **34** on thermolysis. This reaction is identical with that previously encountered with chromene **6** and undoubtedly involves the intermediacy of *o*-quinoneallide **35.** The presence of the acetoxy group provides the *o*-quinoneallide intermediate with an alternate path from that encountered with chromene **22.**

In conclusion, we have shown that the photoisomerization of 4-phenyl-3-chromanone (**1**) to 4-phenyldihydrocoumarin (**2**) proceeds via the small amount of enol present in tautomeric equilibrium with the keto form. Electronic excitation of the enol tautomer results in a photochemical ring opening to give an *o*-quinoneallide intermediate. The subsequent products obtained from the *o*-quinoneallide depends on the substituent groups present and the particular solvent employed. These results establish the significant role which the small amount of enol can play in carbonyl group photochemistry. It is anticipated that carbonyl group photochemistry which proceeds via the enol form should be a general phenomenon in systems where the enol concentration is significant. The results obtained also indicate that the tautomeric forms of certain carbonyl derivatives undergo diverse and interesting photochemistry. We are continuing to examine wavelength and solvent effects in enol photochemistry and will report additional findings at a later date.

Experimental Section[50]

Irradiation of 3-Acetoxy-4-phenylchromene in Acidic Methanol. A solution containing 400 mg of 3-acetoxy-4-phenylchromene[51] (**6**) in 450 ml of Fisher Scientific reagent methanol was irradiated using a 550-W Hanovia lamp equipped with a Pyrex filter sleeve for 10.5 h. Removal of the solvent under reduced pressure gave a pale-yellow oil which was chromatographed on a thick-layer plate using a 10% ether–pentane mixture as the eluent. The major band contained 273 mg (77%) of a colorless oil whose structure was assigned as 2-methyl-4,5-dihydro-4-methylene-5-phenyl-2,5-epoxy-1,3-benzodioxepin (**7**) on the basis of the following spectral and chemical properties: ir (neat) 6.19, 6.28, 6.74, 6.84, 7.13, and 7.51 μ; uv (methanol) 283 and 276 nm (ϵ 1625 and 1785); NMR ($CDCl_3$) τ 8.10 (s, 3 H), 5.86 (d, 1 H, J = 3.0 Hz), 5.55 (d, 1 H, J = 3.0 Hz), 2.1–3.2 (m, 9 H); *m/e* 266 (M^+), 225, 224 (base), 207, 195, 165, and 152. The photoproduct could easily be reconverted to 3-acetoxy-4-phenylchromene (**6**) under a variety of conditions. Thus, a 35-mg sample of **7** in 10 ml of chloroform was stirred with 1 g of Brinkmann PF254 silica gel for 4 h. Filtration of the silica gel followed by removal of the solvent afforded a quantitative yield of **6.** Similarly, a 30-mg sample of **7** in 0.5 ml of chloroform was heated at 75 °C for 15 h. Removal of the solvent produced a quantitative yield of 3-acetoxy-4-phenylchromene (**6**).

Further support for the structure of photoproduct **7** was obtained from hydrogenation and ozonization experiments. A 50-mg sample of **7** in 25 ml of ethyl acetate was hydrogenated over platinum oxide for 20 min. Filtration of the catalyst followed by removal of the solvent gave a quantitative yield of 2,4-dimethyl-4,5-dihydro-5-phenyl-2,5-epoxy-1,3-benzodioxepin (**10**); ir (neat) 6.21, 6.31, 6.74, 6.88, 7.14, 7.25, 7.63, 7.83, and 8.56 μ; NMR ($CDCl_3$) τ 8.73 (d, 3 H, J = 7.0 Hz), 8.15 (s, 3 H), 5.28 (q, 1 H, J = 7.0 Hz), and 2.4–3.6 (m, 9 H). The above material (43 mg) was dissolved in 5 ml of chloroform which contained a trace of *p*-toluenesulfonic acid. The mixture was heated at 70 °C for 40 h, and then the solvent was removed under reduced pressure. The crude oil obtained was chromatographed on a thick-layer plate using a 10% ether–pentane mixture as the eluent to give 2-methyl-3-phenylbenzofuran (**11**) as the major product (90%). This material was identical with an authentic sample.[52]

A 85-mg sample of photoproduct **7** was dissolved in 200 ml of methylene chloride and cooled to −78 °C. Ozone was bubbled through the solution until the solution turned pale blue. The solution was allowed to stand at −78 °C for 20 min and then warmed to −20 °C. The excess ozone was removed with a nitrogen stream, and then dimethyl sulfide was added dropwise until a colorless solution resulted. This solution was washed with water, dried over sodium sulfate, and concentrated under reduced pressure to give 78 mg (92%) of a white solid, mp 82–84 °C, whose structure was assigned as 2-methyl-4,5-dihydro-4-oxo-5-phenyl-2,5-epoxy-1,3-benzodioxepin (**8**); ir (CCl_4) 5.51, 6.23, 7.10, 7.81, 8.69, 9.18, 9.35, 9.86, 10.65, 11.30, 12.12, 13.28 and 14.25 μ; NMR ($CDCl_3$) τ 7.97 (s, 3 H), 2.0–3.3 (m, 9 H); *m/e* 268 (M^+), 226, 210, 198 (base), 152, 105, and 77. A 70-mg sample of the ozonolysis product was stirred in 5 ml of methanol which was previously saturated with hydrogen chloride gas for 1.5 h. The solvent was removed under reduced pressure, and the crude residue was taken up in ether. The ethereal solution was washed with water and dried over sodium sulfate. Removal of the solvent left a pale-yellow oil which was recrystallized from hexane to give 58 mg (81%) of methyl 2-methoxy-2-(*o*-hydroxyphenyl)phenylacetate (**9**) as a white solid: mp 119–121 °C; ir (KBr) 2.97 and 5.74 μ; NMR ($CDCl_3$) τ 6.76 (s, 3 H), 6.21 (s, 3 H), 2.4–3.3 (m, 9 H), and 1.93 (s, 1 H, exchanged with D_2O).

Irradiation of 3-Acetoxy-4-phenylchromene in Purified Methanol. A solution containing 302 mg of 3-acetoxy-4-phenylchromene (**6**) in 170 ml of purified methanol was deaerated with argon and irradiated with a 450-W Hanovia mercury arc lamp equipped with a Corex filter sleeve. Aliquots were periodically removed and analyzed by vapor phase chromatography. A 10-ml aliquot was removed from the irradiated solution after 285 min, and a standardized solution was added for calibration. The mixture was concentrated in a stream of nitrogen and subsequently analyzed by GLC using a 6 ft × 0.25 in. copper column packed with 10% FS-1265 on Diatoport S (60/80 mesh) at 180 °C with a Hewlett-Packard Model 5750 gas chromatograph. The three minor products obtained from the photolysis of **6** were 4-phenyl-3-chromanone (**1,** 3%), 3-acetoxy-4-methoxy-4-phenylchroman (**13,** 8%), and 4-acetyl-4-phenyl-3-chromanone (**14,** 10%). Structure **13** was assigned on the basis of its spectral properties: ir (CCl_4) 5.68 μ; *m/e* 298 (M^+); NMR (100 MHz) τ 7.45 (s, 3 H), 6.96 (2 H, dd, J = 8.0 Hz), 6.47 (3 H, s), 5.08 (1 H, t, J = 8.0 Hz), and 2.80 (m, 9 H). The NMR spectrum of **14** consisted of two singlets at τ 8.02 (3 H) and 5.74 (2 H) in addition to the aromatic multiplet at δ 2.8 (9 H). A 8.2-mg sample of **14** was treated with 1 ml of a methanolic sodium methoxide solution (2%) for 3 h at room temperature. At the end of this time the solution was taken up in ether, washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 7.4 mg of 4-phenyl-3-chromanone (**1**).[51]

The two major components in the GLC chromatogram were identified as 4-phenyldihydrocoumarin (**2,** 18%) by comparison with an authentic sample[53] and 2-acetoxy-2-methoxy-4-phenylchroman (**15,** 30%): ir (CCl_4) 3.30, 5.73, 8.31, 9.02, 9.11, 10.93, and 14.34 μ; NMR ($CDCl_3$) τ 7.50 (s, 3 H), 7.05 (d, 2 H, J = 8.0 Hz), 6.48 (s, 3 H), 5.36 (t, 1 H, J = 8.0 Hz), and 2.85 (m, 9 H); *m/e* 298 (M^+), 253, 224 (base), 196, 195, 183, and 181. A 15.3-mg sample of **15** was dissolved in 3 ml of tetrahydrofuran which contained 0.5 ml of a 10% hydrochloric acid solution. The solution was allowed to stand at room temperature for 12 h. At the end of this time the mixture was taken up in ether and washed with a 5% sodium bicarbonate solution followed by water. The ethereal extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure to give 12.6 mg of a pale-yellow oil. Analysis of the oil by NMR and GLC showed it to be 4-phenyldihydrocoumarin (**2**). The irradiation of **6** (70 mg) was also carried out in deuteriomethanol (10 ml) using a quartz tube for 14 h. Removal of the solvent followed by preparative gas chromatographic isolation of the two major products showed that one atom of deuterium had been exclusively incorporated into the 4 position of both **2** and **15.** The NMR spectrum of **2** showed a two-proton singlet at τ 7.03 but was devoid of a signal for the tertiary proton at τ 5.80. Similarly, the NMR of **15** showed a singlet at τ 7.50 (3 H), a two-proton singlet at τ 7.05, a singlet at 6.48 (3 H), and a multiplet at τ 2.85 (9 H). The signal at τ 5.36 had completely disappeared.

Irradiation of 3-Acetoxy-4-phenylchromene in Methanol Containing Sodium Methoxide. In a typical experiment, 90 mg of 3-acetoxy-4-phenylchromene (**6**) was dissolved in 110 ml of purified methanol and irradiated through Pyrex with a 450-W Hanovia lamp. Prior to irradiating the sample, a small amount (ca. 5 mg) of sodium hydride was added to the solution. At the termination of the photolysis, 20 μl of glacial acetic acid was added to the reaction mixture. Removal of the solvent followed by GLC and NMR analysis indicated that better than 95% of methyl 3-(2-hydroxyphenyl)-3-phenylpropionate (**21**) had formed. A small amount (3%) of unrearranged 4-phenyl-3-chromanone was also present. The structure of **21** was verified by comparison with an authentic sample prepared by the procedure described below.

A solution containing 45 mg of 4-phenyldihydrocoumarin in 20 ml of methanol which contained a catalytic amount of sodium methoxide was stirred at room temperature for 15 min. The solution was then neutralized with a saturated aqueous ammonium chloride solution and extracted with ether. The ether layer was dried over magnesium sulfate and concentrated to a clear oil whose spectral properties were identical with the material obtained from the irradiation of enol acetate **6**: NMR ($CDCl_3$) τ 6.90 (d, 2 H, J = 8.0 Hz), 6.44 (s, 3 H), 5.13 (t, 1 H, J = 8.0 Hz), 3.60 (broad s, 1 H), 2.60–3.30 (m, 9 H); ir (neat) 2.95, 3.39, 5.82, 6.22; *m/e* 225, 207, 196, 181 (base), 165, 91, and 77. When a sample of ester **21** was heated in toluene it was quantitatively coverted to 4-phenyldihydrocoumarin (**2**).

Preparation of 3-Methoxy-4-phenylchromene. Into a dry 100-ml 3-necked flask flushed with argon was injected 6 ml of freshly distilled dimethoxyethane and 6 ml of a 1.7 M solution of methyllithium. The reaction vessel was cooled in an ice bath, and 2.0 g of 3-acetoxy-4-phenylchromene (**6**)[51] in 10 ml of dimethoxyethane was added dropwise. The resulting yellow solution was allowed to warm to room temperature and then 1.5 g of freshly distilled dimethyl sulfate was added. The solution was stirred for an additional 12 h at room temperature. At the end of this time water was added, and the mixture was extracted with ether. The ethereal extracts were washed with water, dried over magnesium sulfate, and concentrated to a pale oil which was recrystallized from 95% ethanol to give 950 mg (53%) of 3-methoxy-4-phenylchromene (**17**) as a white solid, mp 66–67 °C; ir (KBr) 6.10 μ; uv (methanol) 301 and 276 nm (ϵ 4830 and 6080); NMR ($CDCl_3$) τ 6.58 (s, 3 H), 5.24 (s, 2 H), 3.42–3.04 (m, 4 H), and 2.76 (s, 5 H). All attempts to obtain a proper analysis failed since this material was unstable when allowed to stand at room temperature for several days.

Irradiation of 3-Methoxy-4-phenylchromene. A 100-mg sample of 3-methoxy-4-phenylchromene (**17**) in 175 ml of methanol was irradiated for 12 h using a 550-W Hanovia lamp equipped with a Pyrex filter sleeve. Removal of the solvent left a pale-yellow oil which consisted of two components. The major component (41 mg, 36%) could be obtained in pure form by fractional crystallization of the photolysate from methanol. This material was identified as 2,3-dimethoxy-2-methyl-3-phenyldihydrobenzofuran (**18**), mp 109–110 °C, on the basis of its chemical and spectroscopic properties: ir (KBr) 6.18, 6.23, 6.79, 6.85, 7.24, 7.92, 9.25, 10.38, 11.39 and 13.30 μ; uv (methanol) 285 and 278 nm (ϵ 2500 and 2900); NMR ($CDCl_3$) τ 8.36 (s, 3 H), 7.00 (s, 3 H), 6.85 (s, 3 H), 2.5–3.2 (m, 9 H).

Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.68; H, 6.79.

A 50-mg sample of photoproduct **18** was dissolved in 5 ml of acetic acid which contained 1 ml of 57% hydriodic acid. The resulting solution was stirred at room temperature for 20 min and was then taken up in ether. The ethereal solution was washed with water, 5% sodium bicarbonate, 10% sodium thiosulfate, and then with water. The ethereal solution was dried over magnesium sulfate and concentrated under reduced pressure. The pale-yellow oil obtained (37 mg, 96%) was identified as 2-methyl-3-phenylbenzofuran (**11**) by comparison with an authentic sample.[52]

The minor component (32 mg, 32%) of the above photolysis mixture could be more easily obtained by carrying out the irradiation of **17** in benzene. A solution containing 60 mg of **17** in 190 ml of benzene was irradiated for 6 h using a 550-W Hanovia lamp equipped with a Pyrex filter. Removal of the solvent left a yellow oil which was chromatographed on a thick-layer plate using a 5% ether–pentane mixture as the eluent. The only component isolated (32 mg, 53%) was a colorless oil whose structure was assigned as 1-methoxy-5-phenyl-2-oxabenzobicyclo[3.1.0]hexene (**19**): ir (neat) 6.26, 6.65, 6.76, 6.88, 7.03, 7.34, 7.47, 7.81, 8.21, 8.72, 9.0, 9.45, and 9.76 μ; uv (methanol) 284 and 277 nm (ϵ 2200 and 2300); NMR ($CDCl_3$) τ 9.12 (d, 1 H, J = 7.0 Hz), 7.83 (d, 1 H, J = 7.0 Hz), 6.60 (s, 3 H), and 2.5–3.2 (m, 9 H); *m/e* 238 (M^+), 237, 223, 207, 178, 161 (base), and 77.

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.38; H, 5.95.

A solution containing 47 mg of oxabenzobicyclohexene **19** in 5 ml of acetic acid which contained 1 ml of a 57% hydriodic acid solution was heated at reflux for 45 min. The cooled solution was diluted with water and extracted with ether. The ethereal extracts were washed with water, 5% sodium bicarbonate, 10% sodium thiosulfate, water, and dried over magnesium sulfate. Removal of the solvent gave 40 mg (91%) of 4-phenyldihydrocoumarin (**2**), mp 83–84 °C, which was identified by comparison with an authentic sample.[51]

Preparation of 4-Carbomethoxy-3-chromanone. A mixture containing 10.0 g of *o*-hydroxyphenylacetic acid and 10.0 ml of thionyl chloride was refluxed for 30 min. The brown mixture was concentrated under reduced pressure and was then cooled to 0 °C. To the ice-cooled mixture was added 30 ml of methanol, and the resulting mixture was heated at reflux for 20 min. After cooling, the residue was dissolved in 300 ml of ether, washed twice with 10-ml portions of water and a saturated sodium chloride solution. The ethereal solution was dried over magnesium sulfate and then concentrated to give a brown solid. The solid was recrystallized from cyclohexane to give methyl *o*-hydroxyphenylacetate as a white crystalline solid: mp 68.5–70 °C (9.7 g, 90%); ir (KBr) 2.98, 5.82, 6.28, 6.90, 7.00, 7.40, 8.22 and 13.4 μ; NMR ($CDCl_3$, 100 MMz) τ 6.33 (s, 2 H), 6.24 (s, 3 H), and 3.2–2.7 (m, 4 H).

To a mixture of 9.7 g of methyl *o*-hydroxyphenylacetate and 0.2 g of tetra-*n*-butylammonium chloride in 25 ml of methylene chloride at 0 °C was carefully added 2.0 g of sodium hydroxide in small portions. After stirring at room temperature for 30 min, 10.0 g of methyl bromoacetate was added dropwise, and the solution was allowed to stand for 8 h at room temperature. At the end of this time the solution was washed with water and a saturated ammonium chloride solution, dried over magnesium sulfate, and concentrated to give a pink solid, mp 61–67 °C. The resulting solid was purified by distillation at 120 °C (0.01 mm) to give 9.8 g (71%) of methyl *o*-carbomethoxymethoxyphenylacetate: mp 68–69 °C; ir (KBr) 5.76, 6.27, 6.70, 7.0, 8.24, and 13.1 μ; NMR ($CDCl_3$, 100 MHz) τ 6.32 (s, 3 H), 6.25 (s, 3 H), 5.38 (s, 2 H), and 3.35–2.60 (m, 4 H).

Under a nitrogen atmosphere, 2.5 g of methyl *o*-carbomethoxymethoxyphenylacetate was heated at reflux with 300 mg of metallic sodium in 40 ml of anhydrous toluene. After cooling, the dark mixture was taken up in 100 ml of ether, washed with a saturated ammonium chloride solution, dried over magnesium sulfate, and concentrated under reduced pressure. The crude oil obtained was distilled at 93–94 °C (0.07 mm) to give 1.5 g (69%) of a crystalline solid, mp 34.5–36.5 °C. The spectral and analytical data obtained are compatible with 4-carbomethoxy-3-chromanone (**22**): ir (CCl_4) 3.0, 6.05, 6.2, 6.72, 6.95, 7.5, 8.18, 9.55, and 13.3 μ; uv (methanol) 293 (ϵ 4650) and 233 nm (ϵ 8800); NMR ($CDCl_3$, 100 MHz) τ 5.98 (s, 3 H), 5.24 (s, 2 H), 3.1–2.6 and 2.2–2.0 (m, 4 H), and −3.0 (s, 1 H, exchangeable); *m/e* 206 (M^+), 148, 120, 119, 91 (base), 78, 77, 63 and 44.

Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 63.92; H, 4.75.

Irradiation of 4-Carbomethoxy-3-chromanone in Methanol Containing Sodium Methoxide. A 200-mg sample of 4-carbomethoxy-3-chromanone (**22**) in 400 ml of methanol which contained 8 ml of a 0.2 N sodium methoxide solution was irradiated for 10 h using a 450-W Hanovia lamp equipped with a Pyrex filter. After the irradiation was completed, 2.0 g of ammonium chloride was added. The solution was filtered and concentrated under reduced pressure. The crude residue was chromatographed on a thick layer plate using a 15% acetone–cyclohexane mixture as the eluent. The major band contained 182 mg (80%) of a white solid, mp 101–102 °C, whose structure was assigned as methyl 3-(*o*-hydroxyphenyl)-3-carbomethoxypropanoate (**23**): ir (KBr) 3.0, 5.77, 5.85 μ; NMR ($CDCl_3$) τ 7.26 (dd, 1 H, J = 16.0 and 7.0 Hz), 6.68 (dd, 1 H, J = 16 and 9.0 Hz), 6.32 (s, 3 H), 6.28 (s, 3 H), 5.70 (dd, 1 H, J = 9.0 and 7.0 Hz), 2.6–3.3 (m, 4 H); *m/e* 206, 174, 146 (base), 133, 118, and 77.

Anal. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92. Found: C, 60.18; H, 5.86.

Further proof for the structure of **23** was obtained by its facile conversion to 4-carbomethoxydihydrocoumarin (**24**), mp 79–80 °C, on heating in the presence of a trace of acid. A 15-mg sample of **23** was dissolved in 5 ml of glacial acetic acid which contained two drops of water and 0.5 ml of concentrated sulfuric acid. The mixture was heated at 75 °C for 15 min. After cooling to room temperature, the mixture was diluted with ether, washed several times with water, followed by a saturated sodium bicarbonate solution. The ether extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The resulting residue was chromatographed on a preparative thick-layer plate using a 12% acetone–cyclohexane mixture as the eluent. The major band contained 8 mg (61%) of a white solid, mp 79–80 °C, whose structure was assigned as dihydrocoumarin **24**: ir (KBr) 5.70, 5.80 μ; NMR ($CDCl_3$) τ 7.18 (dd, 1 H, J = 17.0 and 6.0 Hz), 6.84 (dd, 1 H, J = 17.0 and 3.0 Hz), 6.28 (s, 3 H), 6.05 (dd, 1 H, J = 6.0 and 3.0 Hz), 3.0–3.6 (m, 4 H); *m/e* 206 (M^+), 174, 146 (base), 118, 103, 91, and 77.

Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 64.19; H, 4.79.

The structure of 4-carbomethoxydihydrocoumarin (**24**) was unambiguously established by comparison with an independently synthesized sample. To a mixture containing 0.4 g of isopropylcyclohexylamine and 1.3 ml of *n*-butyllithium (2.4 M, in hexane) in 20 ml of anhydrous ether at −78 °C was added 0.4 g of methyl *o*-methoxyphenylacetate in 2 ml of ether. After stirring for 1 h at −78 °C, 0.4 g of methyl bromoacetate was added, and the solution was allowed to warm to room temperature. The mixture was poured onto 15 ml of a 10% hydrochloric acid solution and was then extracted with ether. The ethereal extracts were washed with water, followed by a saturated sodium bicarbonate solution. The solution was dried over magnesium sulfate and then the solvent was removed under reduced pressure. Chromatographic separation of the crude oil by thick-layer chromatography (15% acetone–cyclohexane) gave two major bands. The first band (110 mg) was recovered starting material (27.5%). The second band contained 205 mg (37%) of a clear oil, which was identified as methyl α-carbomethoxy-*o*-methoxyphenylacetate on the basis of its spectral properties: ir (CCl_4) 5.72 μ; NMR ($CDCl_3$, 100 MHz) τ 6.8–7.6 (d of q, 2 H, J_{AB} = 5, J_{BC} = 9 Hz), 6.45 (s, 6 H), 6.30 (s, 3 H), 5.70 (d of d, 1 H, J_{AC} = 5, J_{BC} = 9 Hz), and 3.4–2.95 (m, 4 H).

A mixture containing 7 ml of 47–50% hydriodic acid, 7 ml of acetic anhydride, 0.5 g of amorphorous phosphorus, and 80 mg of the above diester was refluxed for 2 h. After cooling, the solution was filtered and ether was added. The ethereal extracts were washed several times with water, followed by a saturated sodium chloride solution and then dried and concentrated under reduced pressure. The light-brown oil obtained was assigned the structure of 4-carboxydihydrocoumarin. This material was used without further purification. The crude carboxylic acid was heated at reflux in the presence of 1 ml of thionyl chloride for 20 min. The excess thionyl chloride was removed under reduced pressure, and excess methanol was carefully added. After refluxing for 15 min, the excess methanol was removed under reduced pressure. The crude residue was subjected to thick-layer chromatography (15% acetone–cyclohexane), and two major bands were isolated. The faster moving band contained 15 mg of a solid which was identical in all respects with 4-carbomethoxydihydrocoumarin (**24**) derived from the acid-catalyzed cyclization of diester **23**. The second band contained 24 mg of a solid, mp 101–102 °C, which was identical with methyl 3-(*o*-hydroxyphenyl)-3-carbomethoxypropanoate (**23**) obtained from the irradiation of 4-carbomethoxy-3-chromanone (**22**).

Irradiation of 4-Carbomethoxy-3-chromanone in Acetonitrile. A solution containing 400 mg of 4-carbomethoxy-3-chromanone in 400 ml of acetonitrile was irradiated for 14 h under a nitrogen atmosphere using a 450-W Hanovia lamp equipped with a Pyrex filter. The solvent was removed under reduced pressure, and the crude oil was chromatographed on a thick-layer plate. Development of the plate with a 3% acetone–carbon tetrachloride mixture as the eluent resulted in the separation of three major bands. The first band contained 51 mg (12.8%) of starting material. The second band contained 56 mg (14%) of a crystalline solid, mp 79–80 °C, whose structure was assigned as 4-carbomethoxydihydrocoumarin (**24**) on the basis of its physical properties and by comparison with the authentic sample previously synthesized.

The third band isolated from the thick layer plate contained 21 mg (5.5%) of a white crystalline solid, mp 76–77 °C, whose structure was assigned as *o*-hydroxy-α-carbomethoxystyrene (**25**). This same material could be more easily obtained by carrying out the irradiation of **22** in benzene. A 250-mg sample of **22** in 400 ml of benzene was irradiated for 9 h using a 550-W Hanovia lamp equipped with a Pyrex filter. Removal of the solvent left a clear oil which was subjected to thick-layer chromatography. The only component isolated from the thick-layer plate (115 mg, 53%) was *o*-hydroxy-α-carbomethoxystyrene (**25**), mp 76–77 °C: ir (KBr) 2.97, 5.87, 6.25, and 13.20 μ; uv (methanol) 295 (ε 470), 263 (ε 4700), 252 (ε 6300), and 243 nm (ε 6500); NMR ($CDCl_3$) τ 6.28 (s, 3 H), 4.05 (d, 1 H, *J* = 1.2 Hz), 3.55 (d, 1 H, *J* = 1.2 Hz), 2.70–3.20 (m, 4 H), and 2.50 (s, 1 H, exchanged with D_2O).

Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66. Found: C, 67.76; H, 5.84.

Chemical confirmation of the structure of *o*-hydroxy-α-carbomethoxystyrene (**25**) was obtained by catalytic reduction to methyl 2-(*o*-hydroxyphenyl)propanoate (**26**) and conversion to *o*-methoxy-α-carbomethoxystyrene (**27**), which was, in turn, independently synthesized. A 43-mg sample of *o*-hydroxy-α-carbomethoxystyrene in 20 ml of methanol containing a catalytic amount of 5% palladium on charcoal was hydrogenated under 10 psig of hydrogen for 2 h. The catalyst was removed by filtration, and the filtrate was concentrated under reduced pressure. Separation of the crude oil by thick-layer chromatography (15% ether–cyclohexane) gave a major band (34 mg, 78%) whose spectral properties were perfectly compatible with methyl 2-(*o*-hydroxyphenyl)propanoate (**26**); ir (CCl_4) 3.00, 5.85, 6.25 μ; uv (methanol) 275 (ε 2520) and 215 nm (ε 6830); NMR ($CDCl_3$, 100 MHz) τ 8.50 (d, 3 H, *J* = 7.5 Hz), 6.30 (s, 3 H), 6.15 (q, 1 H, *J* = 7.5 Hz), 3.3–2.8 (m, 4 H), and 2.5 (s, 1 H, exchangeable). The structure of this material was further confirmed by an independent synthesis.

A mixture containing 0.45 g of purified isopropylcyclohexylamine and 1.5 ml of *n*-butyllithium (2.4 M) at −78 °C was stirred for 2 h in 20 ml of dried tetrahydrofuran under a nitrogen atmosphere. To this mixture was added 0.55 g of methyl *o*-methoxyphenylacetate in 2 ml of tetrahydrofuran. After stirring for an additional 2 h, 2 ml of methyl iodide was added, and the mixture was allowed to warm to room temperature. The solution was diluted with 100 ml of ether, washed with 20 ml of a 10% hydrochloric acid solution, 60 ml of water, followed by a saturated sodium bicarbonate solution. The solution was dried over magnesium sulfate and concentrated to give 0.75 g of an oil. Chromatography of this oil on a thick-layer plate afforded a major band which contained 180 mg (31%) of methyl 2-(*o*-methoxyphenyl)propanoate; ir (neat) 5.75, 6.25, 6.72, and 13.25 μ; NMR ($CDCl_3$, 100 MHz) τ 8.5 (d, 3 H, *J* = 7.0 Hz), 6.4 (s, 3 H), 6.22 (s, 3 H), 5.95 (q, 3 H, *J* = 7.0 Hz), and 3.3–2.7 (m, 4 H).

A 110-mg sample of the above methyl ester in 1 ml of acetic anhydride was added dropwise to a mixture which contained 5 ml of 47–50% hydriodic acid and 1.0 g of amorphous phosphorus. The mixture was then refluxed for 2 h, cooled, filtered, and diluted with 100 ml of ether. The ethereal solution was washed with water and saturated sodium bicarbonate, dried over magnesium sulfate, and concentrated under reduced pressure. Isolation of the product was accomplished by thick-layer chromatography using a 15% ether–cyclohexane mixture as the eluent. The major band contained 41 mg (49%) of an oil whose spectral properties are compatible with 3-methyl-2-benzofuranone: ir (CCl_4) 5.50, 6.18, 6.75, 9.7, and 11.35 μ; NMR ($CDCl_3$, 100 MHz) τ 8.35 (d, 3 H, *J* = 8 Hz), 6.18 (q, 1 H, *J* = 8 Hz), and 2.9–2.5 (m, 4 H).

A 21-mg sample of the above lactone was refluxed for 2 h with 20 ml of dried methanol containing a catalytic amount of metallic sodium. After cooling, the methanolic solution was diluted with 100 ml of ether, washed with saturated ammonium chloride, dried over magnesium sulfate, and concentrated to give a clear oil (21 mg, 83%). This material was identical in every respect with methyl 2-(*o*-hydroxyphenyl)propanoate (**26**) obtained from the catalytic hydrogenation of *o*-hydroxy-α-carbomethoxystyrene (**25**).

Preparation of *o*-Methoxy-α-carbomethoxystyrene. To a sodium methoxide solution prepared by dissolving 50 mg of sodium in 50 ml of methanol at 0 °C was added 85 mg of *o*-hydroxy-α-carbomethoxystyrene (**25**) in 1 ml of methanol. After stirring for 30 min, 0.5 ml of methyl iodide was added, and the resulting solution was stirred for an additional 3 h at room temperature. The mixture was then diluted with 100 ml of ether and was washed with a saturated ammonium chloride solution, dried over magnesium sulfate, and concentrated under reduced pressure. The crude reaction mixture was purified by thick-layer chromatography using a 10% acetone–cyclohexane mixture as the eluent. The major band contained 75 mg (85%) of *o*-methoxy-α-carbomethoxystyrene (**27**); ir (neat) 5.82, 6.3, 6.85, 7.05, and 13.3 μ; NMR ($CDCl_3$, 100 MHz) τ 6.29 (s, 3 H), 6.24 (s, 2 H), 4.31 (d, 1 H, *J* = 1 Hz), 3.78 (d, 1 H *J* = 1 Hz), and 3.24–2.64 (m, 4 H). This material was further verified by comparison with an authentic sample which was synthesized by the procedure outlined below.

To a mixture containing 5.2 ml of *n*-butyllithium (2.4 M) and 1.25 g of diisopropylamine in 20 ml of dried tetrahydrofuran at −78 °C was added 1.13 g of methyl *o*-methoxyphenylacetate in 2 ml of tetrahydrofuran. The solution was stirred at −78 °C for 1.5 h and was then allowed to warm up to −20 °C. A 1.0-g sample of formaldehyde was passed into the above solution using a stream of nitrogen gas. The solution was stirred for an additional 30 min and was then poured into 20 ml of dilute hydrochloric acid and extracted with ether. The extracts were washed with water and a sodium bicarbonate solution, dried, and concentrated to give 1.26 g of a clear oil. This material was used without further purification for the next step. A 150-mg sample of the above methyl *o*-methoxy-α-hydroxymethylphenylacetate in 5 ml of dried yridine at 0 °C was treated with 100 mg of meth-

anesulfonyl chloride. After stirring at 0 °C for 40 min, the mixture was heated at reflux for 1 h, cooled, then poured onto ice and extracted with ether. The extracts were washed with water, followed by a saturated sodium bicarbonate solution, then dried over magnesium sulfate and concentrated under reduced pressure. The crude material showed one major spot on a thin-layer plate. This component was isolated by thick-layer chromatography with 10% acetone–cyclohexane as the eluent (85 mg, 62%) and was identical in every respect with the *o*-methylation product of *o*-hydroxy-α-carbomethoxystyrene (**25**).

Irradiation of 4-Carbomethoxy-3-chromanone in the Presence of Furan. A mixture containing 400 mg of 4-carbomethoxy-3-chromanone (**22**) and 40 g of furan in 400 ml of benzene was irradiated for 15 h under a nitrogen atmosphere using a 450-W Hanovia lamp equipped with a Pyrex filter. The solvent was removed under reduced pressure, and the crude residue was purified by thick-layer chromatography. The major band obtained (250 mg, 47%) was identified as methyl 2-(*o*-hydroxyphenyl)-3-oxo-8-oxabicyclo[3.2.1]oct-6-ene-2-carboxylate (**31**), mp 66–69 °C. This material showed the following spectral properties: ir (CCl_4) 3.00, 5.80, 6.25, 6.80, 8.00, and 9.60 μ; NMR ($CDCl_3$, 100 MHz) τ 7.60 (d, 2 H), 6.08 (s, 3 H), 5.02 (m, 1 H), 4.85 (d, 1 H, J = 2.0 Hz), 4.65 (dd, 1 H, J = 6.0 and 2.0 Mz), 3.82 (dd, 1 H, J = 6.0 and 2.0 Hz), and 2.6–3.4 (m, 4 H). Addition of incremental amounts of $Eu(fod)_3$[48] to solutions of adduct **31** caused a downfield shift of the signal at τ 7.60 and its conversion into an AB quartet (J_{AB} = 14.5 Hz, low-field half split J = 4.5 Hz, high-field half split J = 1.2 Hz).

The structure of the trapped photoadduct **31** was further established by catalytic hydrogenation. A mixture containing 63 mg of photoadduct and a catalytic amount of 5% palladium on charcoal in 20 ml of methanol was hydrogenated at 10 psig hydrogen for 6 h. The catalyst was removed by filtration, and the filtrate was concentrated under reduced pressure. Chromatography of the crude mixture on a preparative thick-layer plate (15% acetone–cyclohexane) led to the isolation of the dihydro photoadduct (**32**) which amounted to 38 mg (59.8%): mp 113–114 °C; ir (KBr) 3.05, 5.83, 6.28, 6.85, 8.90, and 13.4 μ; NMR ($CDCl_3$, 100 MHz) τ 8.9–7.9 (m, 4 H), 7.65 (d, 2 H), 6.10 (s, 3 H), 5.40 (m, 2 H), and 3.3–2.7 (m, 4 H).

Anal. Calcd for $C_{15}H_{16}O_5$: C, 65.21; H, 5.84. Found: C, 65.14; H, 5.88.

Reaction of Methyl 2-(*o*-Hydroxyphenyl)-3-oxo-8-oxabicyclo[3.2.1]oct-6-ene-2-carboxylate with Boron Trifluoride. A 60-mg sample of photoadduct **31** in 20 ml of methylene chloride was treated with 1 ml of distilled boron trifluoride etherate. After stirring for 10 min, the light-brown mixture was washed with several portions of a saturated sodium bicarbonate solution and was then dried and concentrated under reduced pressure. The mixture was chromatographed on a thick-layer plate using a 15% acetone–cyclohexane mixture as the eluent. The major band contained 39 mg (65%) of methyl 7,10-dihydro-7,10-epoxy-10a*H*-benzo[*b*]cyclohepta[*d*]furan-10a-carboxylate (**33**) as an oil which solidified on standing. The solid was recrystallized from pentane to give a white crystalline solid: mp 35–36.5 °C; ir (CCl_4) 3.0, 5.80, 6.29 μ; uv (methanol) 383, 276, 260, and 220 nm (ε 5940, 7290, 8530, and 20 700); NMR ($CDCl_3$, 100 MHz) τ 6.01 (s, 3 H), 5.42 (s, 2 H), 3.60 (d, 1 H, J = 3.0 Hz), 3.80 (d, 1 H, J = 3.0 Hz), 2.0–2.8 (m, 5 H); *m/e* 256 (M^+, base), 224, 196, 168, 139, 114, and 84.

Anal. Calcd for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72. Found: C, 70.06; H, 4.88.

Preparation of 3-Acetoxy-4-carbomethoxychromene. A solution containing 150 mg of 4-carbomethoxy-3-chromanone, 15 drops of acetic anhydride, and a catalytic amount of perchloric acid was stirred overnight. The mixture was then diluted with ether, washed with a saturated sodium bicarbonate solution, dried over magnesium sulfate, and concentrated under reduced pressure to a crude oil. Recrystallization of this material from hexane gave a crystalline solid (100 mg, 56%), mp 72–73 °C, which was assigned as 3-acetoxy-4-carbomethoxychromene (**34**) on the basis of its spectral properties; ir (KBr) 5.66, 5.85, and 6.18 μ; uv (methanol) 305, 275, and 220 nm (ε 1980, 3280, and 8530); NMR ($CDCl_3$, 100 MHz) τ 7.82 (s, 3 H), 6.22 (s, 3 H), 5.38 (s, 2 H), and 3.4–2.7 (m, 4 H).

Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87. Found: C, 63.08; H, 4.91.

Irradiation of 3-Acetoxy-4-carbomethoxychromene in Methanol. A solution containing 250 mg of 3-acetoxy-4-carbomethoxychromene (**34**) in 450 ml of reagent grade methanol was irradiated under a nitrogen atmosphere using a 550-W Hanovia lamp equipped with a Pyrex filter for 55 h. Removal of the solvent under reduced pressure left a crude oil which was purified by thick-layer chromatography using a 15% acetone–cyclohexane mixture as the eluent. The major band contained a clear oil (132 mg, 53%), which was identified as 2-methyl-4,5-dihydro-4-methylene-5-carbomethoxy-2,5-epoxy-1,3-benzodioxepin (**36**) on the basis of its physical and chemical properties: ir (CCl_4) 5.68, 6.17, 6.27, 7.10, 8.62, and 11.0 μ; uv (methanol) 283 and 275 nm (ε 2740 and 2840); NMR ($CDCl_3$, 100 MHz) τ 8.04 (s, 3 H), 6.04 (s, 3 H), 5.68 (d, 1 H, J = 3 Hz), 5.46 (d, 1 H, J = 3 Hz), and 3.2–2.5 (M, 4 H); *m/e* 248 (M^+), 206, 174 (base), 118, and 43.

Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87. Found: C, 62.99; H, 5.19.

Further support for the structure of photoproduct **36** was obtained from hydrogenation and ozonization experiments. A 35-mg sample of **36** in 20 ml of ethyl acetate was hydrogenated over platinum oxide for 20 min. Removal of the catalyst followed by evaporation under reduced pressure gave a pale-yellow oil. The residue obtained was chromatographed on a thick-layer plate to give 31 mg (89%) of 2,4-dimethyl-4,5-dihydro-5-carbomethoxy-2,5-epoxy-1,3-benzodioxepin as a clear oil: ir (neat) 5.68, 6.15, and 6.27 μ; NMR ($CDCl_3$, 100 MHz) τ 8.84 (d, 3 H, J = 6 Hz); 8.16 (s, 3 H), 6.10 (s, 3 H), 5.45 (q, 1 H, J = 6 Hz), and 3.3–2.7 (m, 4 H); *m/e* 250 (M^+), 190, 176 (base), 134, 106, 91, 77, and 43.

Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.38; H, 5.87.

The structure of the photoadduct was further supported by an ozonization experiment. A stream of ozone was passed into a solution containing 40 mg of **36** in 30 ml of methylene chloride at −78 °C until a light-blue color appeared. After standing for 20 min, the temperature of the mixture was raised to −20 °C. A stream of nitrogen was passed through the solution to purge away the excess ozone. To this solution was added 0.5 ml of dimethyl sulfide. The mixture was then washed with water, followed by a saturated sodium chloride solution, then dried over magnesium sulfate and concentrated under reduced pressure to give a solid, mp 94–103 °C. The solid showed signals at 5.53 and 5.77 μ in the infrared (KBr) and was homogeneous as judged by NMR spectroscopy; ($CDCl_3$, 100 MHz) τ 8.0 (s, 3 H), 6.04 (s, 3 H), and 3.25–2.4 (m, 4 H). On the basis of the above data, the solid was assigned the structure of 2-methyl-4,5-dihydro-4-oxo-5-carbomethoxy-2,5-epoxy-1,3-benzodioxepin. This material was somewhat unstable on standing under laboratory conditions and decomposed on attempted purification.

The photoproduct was converted to 4-carbomethoxy-3-chromanone (**22**) under basic conditions. Thus, a 36-mg sample of **36** was dissolved in 10 ml of methanol which contained 15 mg of metallic sodium. The mixture was heated at reflux for 2 h. At the end of this time, the mixture was poured onto a saturated ammonium chloride solution and extracted with ether. The extracts were washed with water, followed by a saturated sodium chloride solution, then dried over magnesium sulfate and concentrated under reduced pressure. Purification of the crude residue by thick-layer chromatography gave a clear oil (29 mg, 100%), whose structure was established as 4-carbomethoxy-3-chromanone by comparison with an authentic sample.

The thermolysis of photoproduct **36** afforded 3-acetoxy-4-carbomethoxychromene (**34**) in quantitative yield, thus providing additional supporting data for the structure assignment. A 100-mg sample of **36** in 0.5 ml of deuteriochloroform was heated at 120 °C in a sealed NMR tube. Analysis of the mixture after 15 h showed that **36** was quantitatively converted to 3-acetoxy-4-carbomethoxychromene (**34**).

Quantum Yield Determinations. Quantitative measurements were made on a rotating assembly with a series of 2537- or 3130-Å lamps in a Rayonet reactor. Samples in 13-mm Pyrex or Quartz ampules were placed in holders on the assembly approximately 6 cm from the light source. All studies were made at room temperature. Samples were degassed to 10^{-4} mm in several freeze–pump–thaw cycles and then sealed. Cyclopentanone solutions were used as the chemical actinometer (a quantum yield of 0.38 was used).[54] After irradiation, the degree of reaction was determined by quantitative NMR or vapor phase chromatography. The conversions were run to 15% or less.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

References and Notes

(1) Photochemical Transformations of Small Ring Heterocyclic Compounds. 77. For part 76, see A. Padwa, *Angew. Chem., Int. Ed. Engl.*, **15**, 123 (1976).
(2) N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, New York, N.Y., 1965, Chapter 6.
(3) R. O. Kan, "Organic Photochemistry", McGraw-Hill, New York, N.Y., 1966.
(4) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966.
(5) D. C. Neckers, "Mechanistic Organic Photochemistry", Reinhold, New York, N.Y., 1967.
(6) J. N. Pitts, Jr., and J. Wan, "The Chemistry of the Carbonyl Group", S. Patai, Ed., Wiley, New York, N.Y., 1966, pp 823–916.
(7) P. J. Wagner and G. S. Hammond, *Adv. Photochem.*, **5**, 323 (1968).
(8) A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry", Wiley-Interscience, New York, N.Y., 1969, Chapter 3.
(9) P. de Mayo and H. Takeshita, *Can. J. Chem.*, **41**, 440 (1963).
(10) H. Nozaki, M. Kurita, T. Mori, and R. Noyori, *Tetrahedron*, **24**, 1821 (1968).
(11) G. Buchi, J. A. Carlson, J. F. Powell, Jr., and L. F. Tietze, *J. Am. Chem. Soc.*, **92**, 2165 (1970); **95**, 540 (1973).
(12) H. Takeshita and S. Tanno, *Bull. Chem. Soc. Jpn.*, **46**, 880 (1973).
(13) R. G. Hunt, C. J. Potter, S. T. Reid, and M. L. Roantree, *Tetrahedron Lett.*, 2327 (1975).
(14) B. D. Challand, H. Hikino, G. Kornis, G. Lange, and P. de Mayo, *J. Org. Chem.*, **34**, 794 (1969).
(15) For two notable exceptions, see E. E. van Tamelen, J. Schwartz, and J. I. Brauman, *J. Am. Chem. Soc.*, **92**, 5798 (1970); and A. Padwa, D. Dehm, T. Oine, and G. A. Lee, *ibid.*, **97**, 1837 (1975); A. Padwa and G. A. Lee, *ibid.*, **95**, 6147 (1973).
(16) J. Lemaire, *J. Phys. Chem.*, **71**, 2653 (1967).
(17) R. Bishop and N. K. Hamer, *J. Chem. Soc. C*, 1197 (1970).
(18) Y. Kanda, J. Stainislaus, and E. C. Lin, *J. Am. Chem. Soc.*, **91**, 5085 (1969).
(19) R. G. Zepp and P. J. Wagner, *J. Am. Chem. Soc.*, **92**, 7566 (1970).
(20) N. J. Turro and T. J. Lee, *J. Am. Chem. Soc.*, **92**, 7467 (1970).
(21) F. Bergmann and Y. Hirshberg, *J. Am. Chem. Soc.*, **65**, 1429 (1943).
(22) H. E. Zaugg and A. D. Schaefer, *J. Am. Chem. Soc.*, **86**, 5208 (1964).
(23) P. G. Gassman and J. M. Hornback, *Tetrahedron Lett.*, 1325 (1969); *J. Am. Chem. Soc.*, **91**, 5817 (1969).
(24) P. G. Gassmann and J. L. Marshall, *J. Am. Chem. Soc.*, **88**, 2599 (1966).
(25) P. G. Gassman, J. L. Marshall, and J. M. Hornback, *J. Am. Chem. Soc.*, **91**, 5811 (1969).
(26) For earlier reports on enol photochemistry, see A. Padwa and G. A. Lee, *J. Am. Chem. Soc.*, **96**, 1634 (1974); A. Padwa and A. Au, *ibid.*, **96**, 1633 (1974); **97**, 242 (1975).
(27) P. K. Grover and N. Anand, *Chem. Commun.*, 982 (1969).
(28) For related photochemical reactions, see A. Padwa, A. Au, G. A. Lee, and W. Owens, *J. Org. Chem.*, **40**, 1142 (1975).
(29) A number of reports have appeared in the literature which provide good analogy for this closure; see A. Padwa, A. Au, and W. Owens, *Chem. Commun.*, 675 (1974); M. Ikeda, S. Matsugashita, H. Ishibashi, and Y. Tamma, *ibid.*, 922 (1973); 433 (1974); 575 (1975).
(30) For ring opening reactions of cyclopropanols, see C. H. Depuy, *Acc. Chem. Res.*, **1**, 33 (1968).
(31) A. Padwa and G. Lee, *Chem. Commun.*, 795 (1972); 675 (1974).
(32) R. S. Becker and J. Michl, *J. Am. Chem. Soc.*, **88**, 5931 (1966).
(33) J. Kolc and R. S. Becker, *J. Phys. Chem.*, **71**, 4045 (1967).
(34) The small quantities of chromanone **1** obtained from the irradiation of **6** can be attributed to partial hydrolysis of **14** on workup.
(35) D. Bellus, *Adv. Photochem.*, **8**, 146 (1971).
(36) For a related case of photoaddition of methanol across a carbon–carbon double bond, see S. S. Hixson, *Tetrahedron Lett.*, 4211 (1971).
(37) A. Padwa, L. Brodsky, and S. Clough, *J. Am. Chem. Soc.*, **94**, 6767 (1972), and references cited therein.
(38) F. Baranton, G. Fontaine, and P. Maitte, *Bull. Soc. Chim. Fr.*, 4203 (1968).
(39) Irradiation of **22** in the presence of methanol afforded a rather complex mixture of photoproducts. The photoreaction was found to be remarkably clean, however, when a small amount of sodium methoxide was added to the methanolic solution. Control experiments showed that chromanone **22** was stable to these basic conditions in the dark.
(40) A control experiment clearly demonstrated that dihydrocoumarin **24** was stable to extended irradiation, both in benzene and acetonitrile.
(41) To date, all attempts to detect cyclopropanone **29** by infrared spectroscopy have failed. This may be due to the low concentration of this tautomer or to a ring opening reaction which occurs during our experimental manipulations.
(42) N. Turro, *Acc. Chem. Res.*, **2**, 25 (1969).
(43) J. E. Baldwin, *Can. J. Chem.*, **44**, 2051 (1966).
(44) J. K. Crandall and W. H. Machleder, *J. Am. Chem. Soc.*, **90**, 7347 (1968).
(45) N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *J. Am. Chem. Soc.*, **87**, 2613 (1965).
(46) H. C. Brown, R. S. Fletcher, and R. B. Johannser, *J. Am. Chem. Soc.*, **73**, 212 (1951); H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).
(47) N. J. Turro, S. S. Edelson, J. R. Williams, T. R. Darling, and W. B. Hammond, *J. Am. Chem. Soc.*, **91**, 2283 (1969); **90**, 1926 (1968).
(48) R. E. Rondeau and R. E. Sievers, *J. Am. Chem. Soc.*, **93**, 1522 (1971).
(49) We originally assigned 2-methylene-3-acetoxy-3-carbomethoxydihydrobenzofuran as the structure of the photoproduct.[26c] This structure has now been reassigned as **36**.
(50) All melting points are corrected and boiling points are uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 100 MHz using a Jeol MH-100 spectrometer.
(51) P. K. Grover and N. Anand, *Indian J. Chem.*, **7**, 196 (1969).
(52) G. Cardillo, R. Cricchio, and L. Merlini, *Tetrahedron*, **27**, 1875 (1971).
(53) J. D. Simpson and H. Stephen, *J. Chem. Soc.*, 1382 (1956).
(54) J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Am. Chem. Soc.*, **92**, 1318 (1970).

Thiocarbonyl Ylides. Photogeneration, Rearrangement, and Cycloaddition Reactions

Arthur G. Schultz* and Marvin B. DeTar

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14853.

Received November 11, 1975

Abstract: Naphthyl vinyl sulfides **8–13** undergo regiospecific photocyclization to thiocarbonyl ylides. These reactive intermediates rearrange to [2,1-*b*]dihydrothiophenes **14, 21, 22, 24, 25,** and **26,** and cycloadd to *N*-phenylmaleimide to give multicyclic adducts in high yield (e.g., **16a, 16b,** and **23**). Conversion of **8** to **21** has been shown to occur by conrotatory photocyclization of **8** to thiocarbonyl ylide **29** (stereochemistry determined by isolation and x-ray analysis of adduct **23**); subsequent suprafacial hydrogen migration in **29** gives highly strained trans-fused dihydrothiophene **21.**

We recently reported that 2-naphthyl vinyl sulfides undergo regiospecific photocyclization rearrangement to give dihydronaphtho[2,1-*b*]thiophenes in high yield.[1] Herein, we present additional information regarding this potentially general reaction and complete experimental details of our work.

Prior to this investigation, little was known about the photochemistry of α,β-unsaturated sulfides. Thiophenes were reported to undergo rearrangement, possibly via a photochemically induced valence shell expansion of the sulfur atom.[2] That valence bond isomers may be important in observed photorearrangements of thiophenes was suggested by the isolation of tetrakis(trifluoromethyl)cyclobutadiene episulfide from the vapor phase photolysis of tetrakis(trifluoromethyl)-thiophene.[3]

In 1969, Corey and Block reported that, on quartz-filtered irradiation, divinyl sulfide underwent polymerization; more interestingly, bis(β-phenylvinyl)sulfide (**1**) gave *trans*-2,3-diphenyl-5-thiabicyclo[2.1.0]pentane (**2**) in moderate yield and trace amounts of 2,3-dihydro-3,4-diphenylthiophene (**3**).[4] We felt a reasonable mechanism for this transformation was that **1** underwent photocyclization to thiocarbonyl ylide **4**,