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Involvement of Enol Tautomers in the Photoisomerization of 3-Substituted Isochromanones[1]

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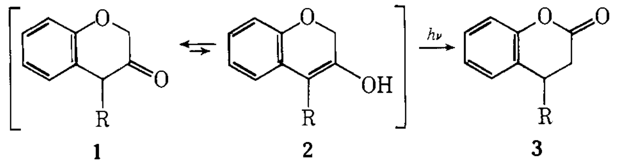
Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. Received December 8, 1975

Abstract: Irradiation of 3-carbomethoxyisochromanone (**4**) in methanol under an argon atmosphere produced a mixture of 1-hydroxy-3-carbomethoxyisochromene (**7**) and 2-hydroxy-2-carbomethoxyindanone (**6**) in high yield. A study of the product distribution as a function of time showed that indanone **6** was produced initially. On further irradiation **6** was quantitatively transformed into **7**. When the irradiation of **4** was carried out in the presence of oxygen, 3-hydroxy-3-carbomethoxyisochromanone was the major product formed. The photochemical rearrangement of **4** → **6** has been rationalized by a ring opening reaction of the excited enol tautomer followed by an internal aldol cyclization. The conversion of **6** → **7** involves a Norrish type I reaction followed by a 1,4-hydrogen transfer and subsequent cyclization. The excited-state behavior of the 3-phenylisochromanone system was also examined. In this case, the major photochemical path resulted in photoreduction and occurred from the n-π^* triplet state of the keto tautomer. In the presence of a triplet quencher, the photoreduction route was suppressed and the system reacted from the singlet state of the enol tautomer.

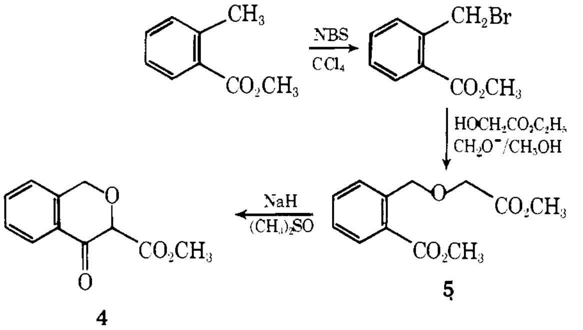
Introduction

Photoenolization of carbonyl compounds is a reaction of considerable importance and current interest.[2-19] The concept of internal photoactivated hydrogen transfer (photoenolization) was originally postulated to explain the apparent lack of bimolecular photoreduction of 2-alkyl-, 2-amino-, and 2-hydroxybenzophenones.[2-5] Yang[2-4] and other workers[5-8] have provided chemical and physical evidence which demonstrate that the photoenolization process is an intramolecular photochemical reaction analogous to the Norrish type II process.[20] Enols generated in this fashion have relatively long lifetimes[4,8] and can be trapped with dienophiles.[2,15] The remarkable stability of these enols is probably due principally to the absence of catalytic ionic contaminants which are generally present in nonphotochemical reactions. Recently, a number of widely scattered and isolated reports have appeared which indicate that 1,3-tautomerization of certain ketones can also occur upon electronic excitation.[21-26] In earlier reports from this laboratory,[27] evidence was presented which demonstrated that the enol content can be an overriding factor in determining the excited-state behavior of a carbonyl group. Particular attention was focused on relativly acidic ketones[28-32] and esters[27] and the question as to whether it is possible to observe photochemistry from an excited enol (or enolate) when the carbonyl tautomer is the absorbing species. As part of a program directed toward determining the scope and limitations of enol photochemistry, we studied the photorearrangement of 4-substituted-3-chromanones (**1**) to 4-substituted dihydrocoumarins (**3**) and found that the reaction involves the prior conversion of **1** into its enol tautomer **2**, which is subsequently converted to **3** on exposure to uv light.[27,33,34] In view of the fascinating rearrangement uncovered with this system, we thought it of considerable interest to determine if comparable photochemistry might occur with the closely related 3-substituted isochromanone system. In order to probe this possibility, the excited-state behavior of 3-carbomethoxyisochromanone (**4**) was examined.[32]



1 **2** **3**

Scheme I. Synthesis of 3-Carbomethoxyisochromanone (4)

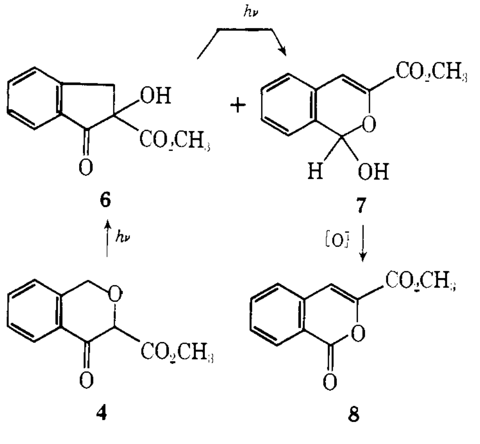


Results

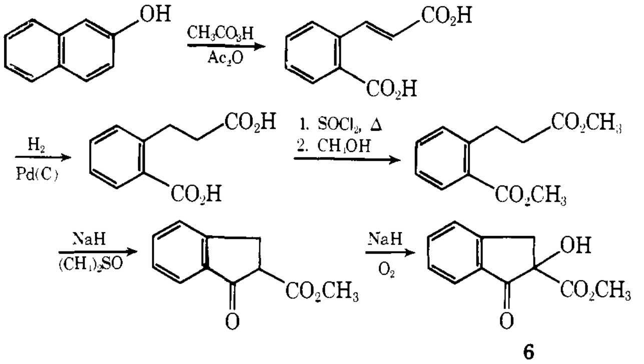
The synthesis of **4** began with methyl *o*-toluate. The sequence of reactions used is indicated in Scheme I.

The NMR spectrum of **4** in a carbon tetrachloride solution indicates the existence of an equilibrium between the keto (47%) and enol (53%) forms. The NMR spectrum showed signals at τ 6.25 (s, 3 H), 5.2 (s, 1 H), 4.7–5.25 (q, 2 H, J = 14.0 Hz), and 2.0–3.2 (m, 4 H) for the keto form. The enol tautomer contained signals at τ 6.18 (s, 3 H), 4.9 (s, 2 H), 2.0–3.2 (m, 4 H), and −0.2 (s, 1 H, exchanged with D_2O). As the polarity of the solvent increased, the concentration of the enol form also increased (i.e., acetone-d_6, enol/keto = 1.86). The uv spectrum of **4** in methanol showed absorption maxima at 342 (ϵ 4500) and 247 nm (ϵ 9250) suggesting that, even in a dilute solution, the concentration of the enol form is substantial. The n-π^* absorption associated with the keto tautomer of **4** should resemble acetophenone and consequently would be expected to have a very low extinction coefficient at 342 nm.

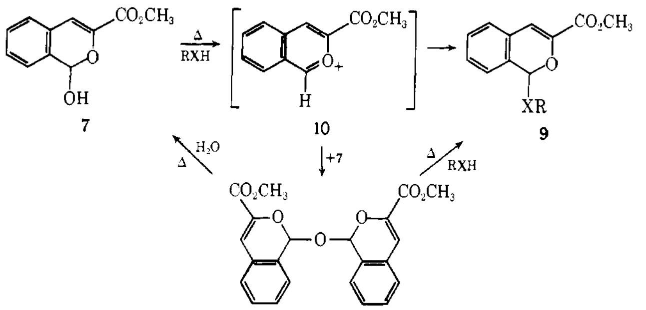
Irradiation of **4** in methanol at 25 °C for 8 h under an argon atmosphere with Pyrex-filtered light gave a 95% yield of a mixture of two compounds, **6** and **7**, in nearly equal amounts. The two components were separated by thick-layer chromatography. Spectroscopic analysis (see Experimental Section) suggested 1-hydroxy-3-carbomethoxyisochromene (**7**), mp 110–111 °C, as the structure of the slower moving component. Chemical confirmation was obtained by oxidation of **7** to 1-oxo-3-carbomethoxyisochromene (**8**) which was, in turn, independently synthesized.[35] Spectral and analytical data for **6**, mp 131–132 °C, showed that (a) it was isomeric with **7**, (b) it also possessed a hydroxyl function, and (c) its NMR consisted of a pair of doublets at τ 6.75 and 6,25 (J = 18.0 Hz), a methyl ester singlet at τ 6.28, an exchangeable proton at τ 6.02, and four aromatic protons at τ 2.1–2.7. That the actual structure of **6** was 2-hydroxy-2-carbomethoxyindanone was established from the independent synthesis outlined in Scheme II. This synthesis led to material identical with photoproduct **6**.



Scheme II. Synthesis of Photoproduct 6



Scheme III

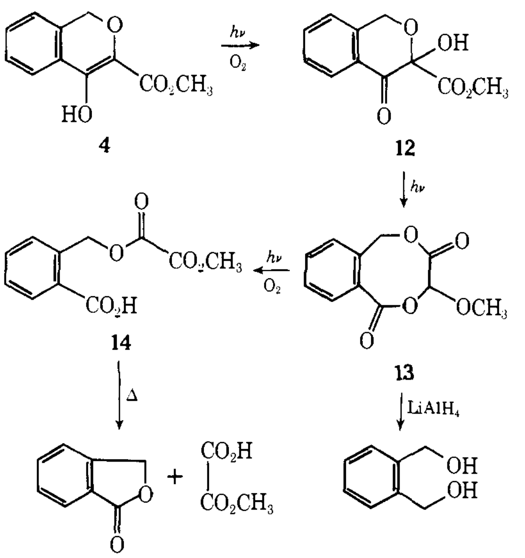


The ratio of **6**:**7** varied as a function of time. With short exposures, 2-hydroxy-2-carbomethoxyindanone (**6**) accounts for nearly all of the product produced. At longer exposures, owing to a secondary photoreaction of **6**, the amount of **7** increased. This was independently demonstrated by the quantitative conversion of **6** to **7** in methanol under comparable photolytic conditions. The quantum yield of formation of **6** on direct irradiation of **4** was found to be Φ = 0.32 and that for **7** from **6** was 0.08.

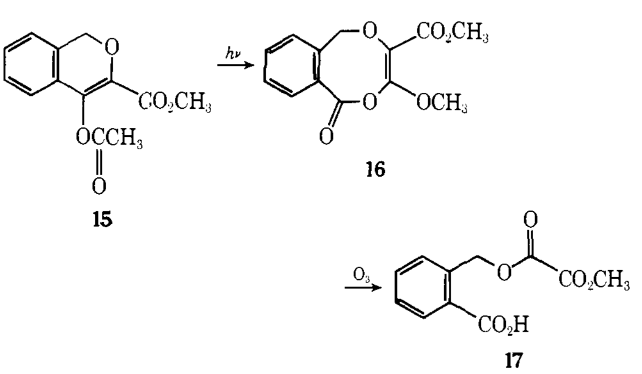
During our studies with isochromene **7** we found that this material reacted with a variety of nucleophilic reagents to give isochromene derivatives **9** with different substituents in the 1 position of the ring. This transformation can be rationalized in terms of intermediate **10**, which is formed by loss of hydroxide from **7**. In the absence of a nucleophilic reagent, isochromene **7** was converted to dimer **11** in high yield. This dimeric compound could be converted to the corresponding methoxy derivative on treatment with methanol (see Scheme III).

Another point meriting comment is that the photochemistry of **4** was found to depend on the reaction conditions. In the presence of oxygen it is initially converted to 3-carbomethoxy-3-hydroxyisochromanone (**12**) in high yield. Control experiments show that although isochromene **4** is converted to **12** in an aerated methanol solution in the dark, the dark reaction required a much longer period of time. On further irradiation **12** is converted to a mixture of lactone **13** and methyl 2-carboxybenzyl oxalate (**14**). Evidence for the above structures was derived from elemental analysis, spectral information, and degradation studies. Supporting evidence for the structure of **13** was obtained by its reduction to *o*-hydroxymethylbenzyl alcohol with lithium aluminum hydride.[36] Corroborative evidence for structure **14** was obtained by its thermal degradation to phthalide and monomethyl oxalate.

Since it was the 4-hydroxy-3-carbomethoxyisochromene tautomer of **4** which was suspected of giving rise to hydroxyindanone **6**, we sought to totally lock **4** into its enol form and examine the behavior of the resulting system. This was accomplished by synthesizing the corresponding enol acetate **15**

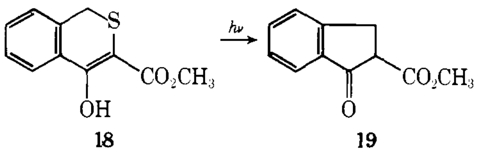


and studying its photochemical behavior. Irradiation of a benzene solution of **15** with Pyrex-filtered light gave a single compound whose structure was assigned as methyl 1,6-dihydro-4-methyl-6-oxo-2,5-benzodioxocin-3-carboxylate (**16**), mp 106–107 °C. The mass spectrum of **16** showed the molecular ion at *m/e* 248 and had an elemental analysis consistent with the empirical formula $C_{13}H_{12}O_5$. The infrared spectrum showed two different carbonyls at 5.68 and 5.81 μm. The NMR spectrum contained singlets at τ 7.61 (3 H), 6.18 (3 H), and 4.79 (2 H) in addition to the aromatic protons. Ozonolysis of **16** followed by an aqueous workup gave a 65% yield of methyl 2-carboxybenzyl oxalate (**17**).



The structure of **16** was unequivocally established by an x-ray single-crystal structure analysis. The structure was derived from Patterson and Fourier synthesis and refined by least squares to an *R* value of 0.0514 for all the data. The overall geometry of the molecule is shown in Figure 1.

We next turned our attention to the related isothiochromanone system in order to assess the generality of the photorearrangement. Irradiation of 3-carbomethoxyisothiochroman-4-one (**18**) in a basic methanol solution using a 550-W Hanovia mercury arc with a Pyrex filter gave 2-carbomethoxyindanone (**19**) in 96% yield. It is particularly interesting to note that isothiochromanone **18** exists predominantly (>95%) in the enol form as judged by NMR analysis.



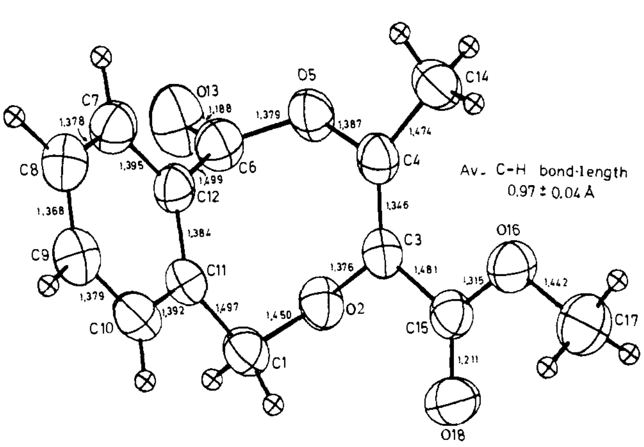
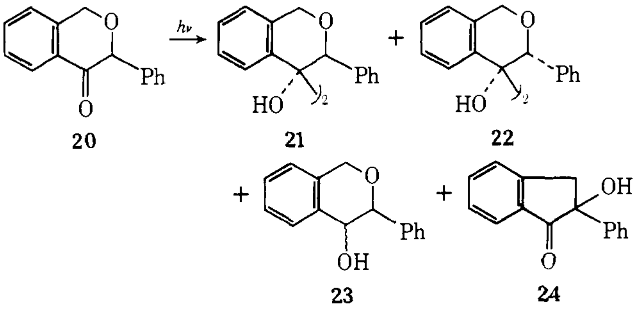


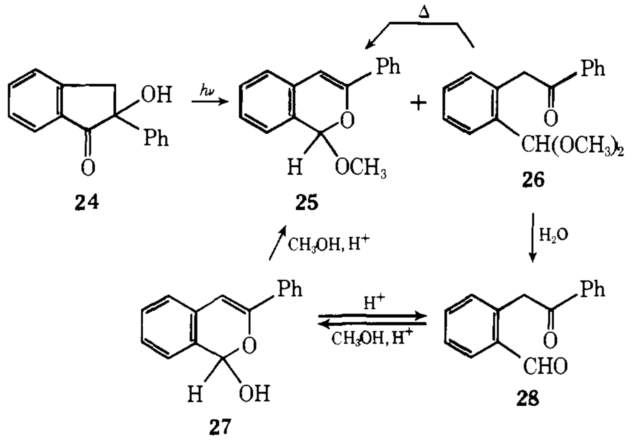
Figure 1. A general view of methyl 1,6-dihydro-4-methyl-6-oxo-2,5-benzodioxocin-3-carboxylate (**16**).

At this stage of our studies we considered another facet of the problem, namely an examination of the photochemistry of a 3-substituted isochromanone which possessed a negligible concentration of the reactive enol form. For this aspect of the study 3-phenylisochromanone (**20**) was selected. Using procedures similar to those described for the preparation of other isochromanones, 3-phenylisochromanone (**20**), mp 34–36 °C, was prepared in good yield.[37] The NMR spectrum of **20** in carbon tetrachloride indicates that only small quantities of the enol tautomer (i.e. ~1%) are present in solution. Photolysis of 3-phenylisochromanone (**20**) in 2-propanol produced a relatively complex reaction mixture. The product mixture was readily separated by thick-layer chromatography into four components. The two major products were identified as the epimeric pinacols **21** and **22**. Lead tetraacetate cleavage of these pinacols regenerated 3-phenylisochromanone, not only providing a structure proof, but also a method for assaying pinacol. Further evidence for the structure of **22** was obtained by its synthesis from 3-phenylisochromanone (**20**) by reductive dimerization with aluminum amalgam. The structure of the third component from the chromatography plate was assigned as the reduced alcohol **23** on the basis of its spectroscopic data and by comparison with an authentic sample prepared by the sodium borohydride reduction of 3-phenylisochromanone. The last component isolated from the thick-layer plate (13%) was identified as 2-hydroxy-2-phenylindanone (**24**). Conclusive evidence for structure **24** was obtained by comparison with an authentic sample prepared by treating 2-phenylindanone with molecular bromine followed by reaction with aqueous silver perchlorate.



During the course of our investigations we found that 2-hydroxy-2-phenylindanone (**24**) also exhibits some interesting photochemistry. Irradiation of **24** in methanol for 7 h gave a mixture of 1-methoxy-3-phenyl-1*H*-2-benzopyran (**25**) and α-benzoyl-*o*-tolualdehyde dimethylacetal (**26**). The yield of these two products was found to be markedly dependent on the reaction conditions and the work-up procedure used. When the crude photolysate was washed with aqueous acid and then chromatographed, two new compounds were obtained and identified as 1-hydroxy-3-phenyl-1*H*-2-benzopyran (**27**) and

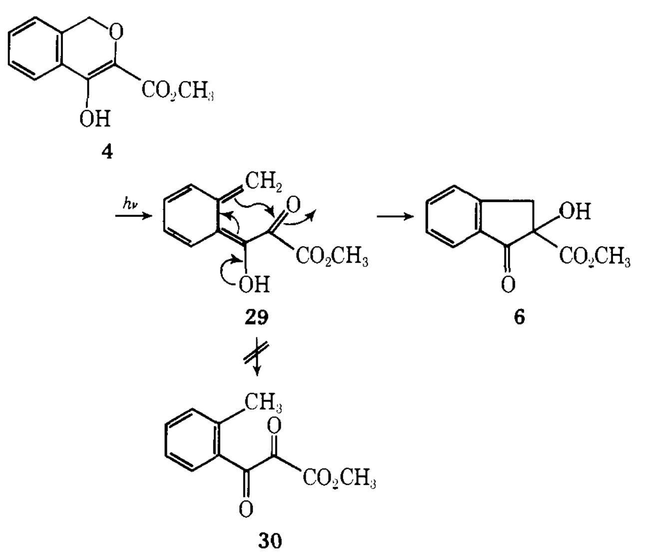
Scheme IV

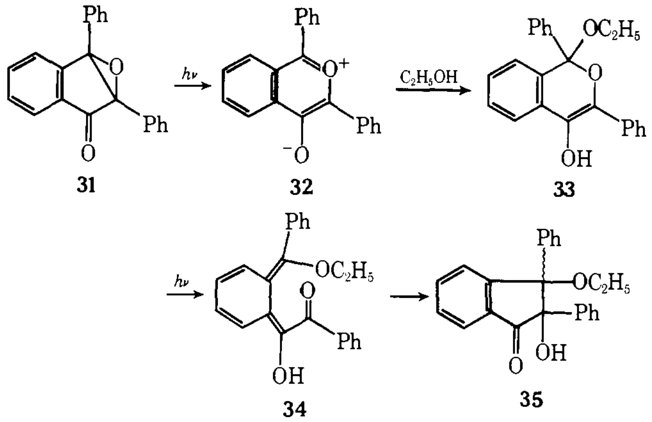


α-benzoyl-*o*-tolualdehyde (**28**). Purification of this mixture by thick-layer chromatography resulted in the isolation of only aldehyde **28**. Additional studies showed that (a) **27** rearranges to **28** on contact with silica gel, (b) **25** is formed from **28** in the presence of acidic methanol, and (c) **26** is converted to **25** and **28** on standing under atmospheric conditions in the dark. A summary of the results obtained is outlined in Scheme IV.

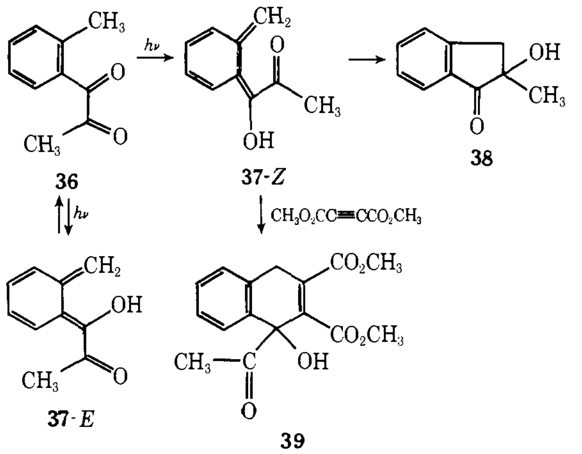
Discussion

The first point to be made is that the photochemical rearrangement of 3-carbomethoxyisochromanone (**4**) to 2-hydroxy-2-carbomethoxyindanone (**6**) proceeds through the enol tautomer of **4**. The reaction is initiated by a photochemical ring-cleavage reaction analogous to the well-known ring openings of pyrans, chromenes, isochromenes, and other related benzo-heterocyclic olefins.[38–44] The resulting intermediate (**29**) has the appropriate structural elements to undergo a rapid internal aldol condensation to give hydroxyindanone **6**. The rearrangement proceeds via the singlet excited state of **4**, since the reaction could not be sensitized (acetophenone) or quenched (piperylene). The formation of **6** from **4** is very similar to the reaction encountered on irradiation of benzopyrylium oxide **32** in ethanol.[45] Ullman and Henderson had previously reported that the irradiation of **32** produced 2,3-diphenyl-3-ethoxy-2-hydroxyindanone (**35**) as a mixture of stereoisomers.[45] This transformation was rationalized in terms of a transient enol intermediate (i.e., **33**) which undergoes photochemical ring opening followed by a subsequent internal aldol reaction.

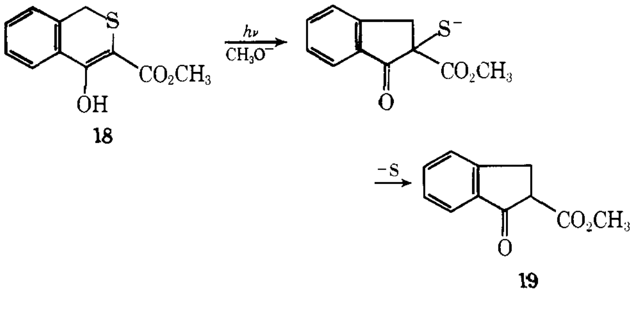




The cyclization of *o*-quinone methide **29** to **6** also finds excellent analogy in the known photocyclization of 1-(*o*-tolyl)-1,2-propanedione (**36**) to 2-hydroxy-2-methylindanone (**38**).[12,13,15] This transformation has been rationalized in terms of an initial photoenolization followed by a subsequent internal cyclization.[13,15] Enol **37**-*Z* was trapped by dimethylacetylene dicarboxylate and afforded cycloadduct **39**. The absence of deuterium incorporation into **38** or recovered **36** on irradiation of **36** in deuteriomethanol[12,13] was attributed to the formation of a mixture of stereoisomeric enols (i.e., **37**-*Z* and **37**-*E*).[13]



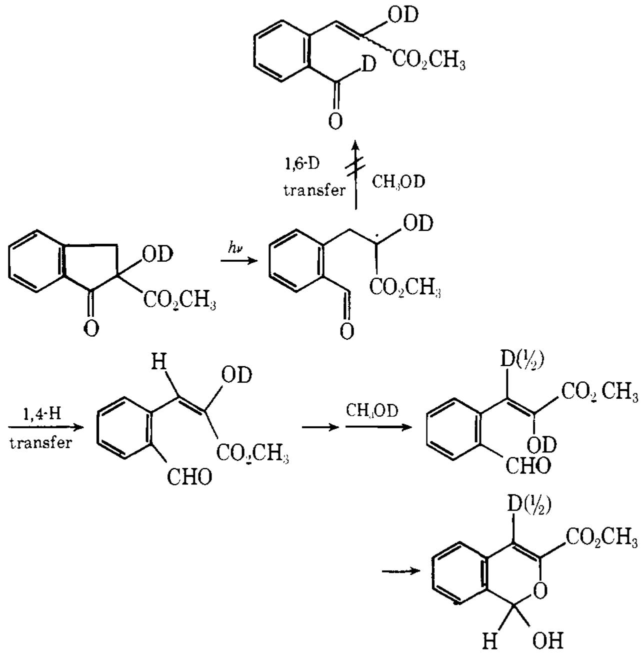
Enol **37**-*E* was suggested to revert very rapidly to **36** by an intramolecular 1,5-hydrogen shift, while **37**-*Z* cyclized to **38** by a fast concerted process requiring little atomic reorganization. The fact that we were unable to detect diketoester **30** from the irradiation of **4** is perfectly consistent with these observations. In this case, ring opening of the enol tautomer of **4** will produce a single stereoisomer (i.e., **29**) corresponding to **37**-*Z*. This stereoisomer would have to undergo isomerization about the enol double bond before it could be converted to **30**. Our inability to trap **29** with dimethylacetylene dicarboxylate could also be attributed to the rapid cyclization of **29**. The presence of an α-ketoester function should enhance the rate of internal cyclization and would account for the failure to trap a bimolecular cycloadduct, It should be pointed out that the photodesulfurization of isothiochromanone (**18**) to 2-carbomethoxyindanone (**19**) can also be explained by a similar



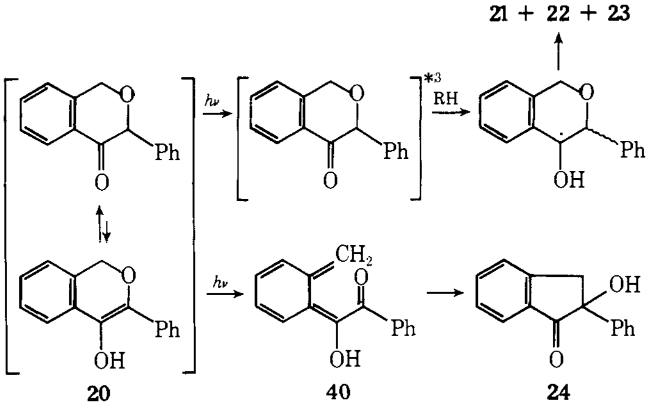
mechanism to that outlined with **4.** In this case, the initially formed intermediate readily loses sulfur to give **19.**

Our results also show that the fate of excited enol **4** depends on the reaction conditions. In the presence of oxygen **4** is trapped to give a transient hydroperoxide, which is subsequently converted to 3-carbomethoxy-3-hydroxyisochromanone (**12**). The formation of **12** can be attributed to the reaction of ground-state oxygen with the excited enol (or enolate) tautomer of **4.** Bordwell and others[46] have previously shown that related ketones undergo oxidative processes in the dark in the presence of base and oxygen. The facility with which the photooxidation occurs may be related to the studies of Förster[47] and Weller,[48] who demonstrated that phenols show enhanced acidity in the electronically excited state. A similar explanation with enols could explain the enhanced activity of **4** toward oxidation.[49] In the absence of oxygen, the excited enol (or enolate) rearranges to an *o*-quinone methide (i.e., **29**), which cyclizes to give the final product. The conversion of the initially formed hydroxyisochromanone **12** into lactone **13** can be explained by a 1,3 shift of the ketone carbonyl group.

Evidence concerning the mechanism of formation of isochromene **7** from **6** was obtained by carrying out the photolysis of **6** in dueteriomethanol. In this case, the final product was found to have incorporated 50% deuterium in the vinylic position. This observation is consistent with a mechanism involving an initial Norrish type I scission followed by a 1,4-hydrogen transfer from the benzylic carbon. In order to account for the distribution of deuterium in the final product, it is necessary to assume that the initially produced enol undergoes ketonization at a faster rate than it cyclizes. The lack of deuterium incorporation in the 1 position of the isochromene (**7**) eliminates the alternative 1,6-hydrogen atom transfer process. Control experiments demonstrated that isochromene **7** does not undergo deuterium exchange under the reaction conditions.



The nature of the products obtained from the photolysis of 3-phenylisochromanone (**20**) in 2-propanol suggests that the photochemistry of this system proceeds via two distinct paths. The major path involves hydrogen abstraction from the $n-\pi^*$ triplet state of the keto tautomer to give a ketyl radical. This radical can couple to form pinacols **21** and **22** or disproportionate to give carbinol **23** and starting ketone **20.** The photoreduction of related aromatic ketones in hydrogen-donor solvents is a well-documented photoreaction[50-54] and provides excellent precedent for the formation of photoproducts **21-23.**

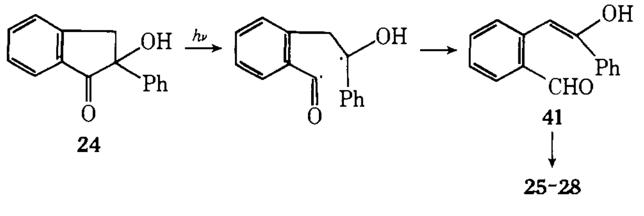


The reactive state generally responsible for the abstraction of hydrogen from an aryl ketone is an $n-\pi^*$ triplet state.[52] That this is also the case in this system was shown by carrying out the irradiation of **20** in the presence of a good triplet quencher (i.e., piperylene). Under these conditions, the yield of pinacols **21** and **22** and carbinol **23** was significantly diminished.

The minor photochemical path which ultimately leads to the formation of 2-hydroxy-2-phenylindanone (**24**) is best rationalized as proceeding via the enol tautomer of **20.** The electronically excited enol undergoes ring opening to give an *o*-quinoidal intermediate (**40**), which subsequently cyclizes to generate **24.** This route is identical with that previously suggested to rationalize the excited-state behavior of 3-carbomethoxyisochromanone (**4**). As was pointed out earlier, the photochemical reactions of 3-carbomethoxyisochromanone proceed via the singlet-excited state. This was also shown to be the case with the 3-phenylisochromanone system. Irradiation of **20** in the presence of excess *cis*-piperylene resulted in a substantial increase (300%) in the yield of 2-hydroxy-2-phenylindanone (**24**). The ability of *cis*-piperylene to quench the photoreduction of **20** but not affect the conversion of **20** → **24** provides convincing evidence for the involvement of a singlet state in the observed rearrangement.

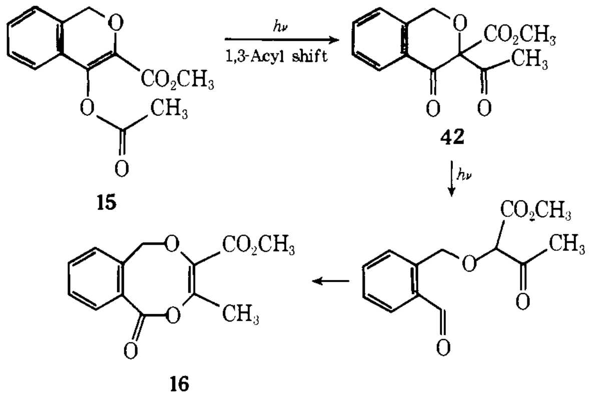
It is especially interesting to note that the photorearrangement of **20** → **24** occurs through the enol tautomer even though the tautomeric composition is heavily weighted in favor of the keto form (i.e., keto/enol > 98:2 by NMR analysis). This could be construed to mean that the absorption maximum of the enol possesses a much larger extinction coefficient than the corresponding keto form and consequently makes the enol a strong competitor for absorption of the incident light (Pyrex filtered). Another possibility is that photoenolization of **20** first occurs on irradiation. Ample precedence for the enolization of excited carbonyl compounds can be found in the literature[21-26] and provides reasonable analogy for the above suggestion.

The formation of the various products produced from **24** on further irradiation is envisaged to occur via an initial type I scission of **24** followed by a 1,4-hydrogen transfer to produce the enol tautomer of **28.** This reactive enol produces the observed products via a series of acid-catalyzed ground-state reactions. This sequence is analogous to the path previously suggested to account for the formation of 1-hydroxy-3-car-



bomethoxyisochromene (**7**) from 3-carbomethoxyisochromanone (**4**).

The last point to be made concerns the photorearrangement of enol acetate **15** to benzodioxocin **16**. We originally assumed that the photochemistry of **15** would serve as an appropriate model for the excited-state behavior of the enol form of **4**. Irradiation of **15** did not result in opening of the isochromene ring, however, but instead produced benzodioxocin **16**. This transformation may be envisioned as proceeding via an initial 1,3-acyl shift to produce diketoester **42** as a transient intermediate which undergoes a subsequent Norrish type I cleavage followed by recombination of the resulting diradical. Previous workers have found that enol acetates undergo 1,3-acyl shifts when subjected to uv irradiation,[55] thereby providing good analogy for the first step of the above transformation. The rearrangement of **15** → **16** apparently proceeds via the singlet state, since the reaction could not be sensitized (acetophenone) or quenched (piperylene). The quantum efficiency of the photorearrangement ($\Phi_{15\to16} = 0.003$) is significantly less than that obtained with the corresponding 3-carbomethoxyisochromanone system ($\Phi_{4\to6} = 0.32$). This is probably related to the fact that the *o*-quinoidal intermediate formed in these reactions can also undergo ring closure to regenerate starting material. With a hydroxyl substituent present in the 4 position of the isochromene ring, the transient *o*-quinoidal intermediate generated undergoes a rapid internal aldol condensation. When the 4 position of the isochromene ring is substituted with an acetate group, the initially formed *o*-quinoidal intermediate cannot undergo an internal aldol reaction and instead reverts back to starting material. Only on prolonged irradiation does the 1,3-acyl shift occur. Another possibility which can account for the lower quantum efficiency in the enol acetate system is that the formation of the final product (i.e., **16**) requires two photons of light. The absorption characteristics of intermediate **42** may be such that it cannot compete for the additional incident light. The net effect will be a substantial reduction in the quantum yield for product formation.



Conclusion

The photochemistry of 3-substituted isochromanones was found to be markedly influenced by the tautomeric composition of the ketone in solution. The triplet quenching effects which we have noted with **20** suggest that it may be possible to selectively suppress the photochemistry of the more predominant keto tautomer and be left with residual photochemistry from the enol form. Our results also indicate that enolic forms of certain carbonyl derivatives may yield diverse and interesting photochemistry. We are continuing to examine wavelength and solvent effects in these systems and will report additional findings later.

Experimental Section[56]

Preparation of 3-Carbomethoxyisochromanone. A 28-g sample of ethyl glycolate was added dropwise to a solution of sodium methoxide, prepared by dissolving 3.3 g of sodium in 55 ml of methanol. After the reaction has stirred for 4 h at −5 °C, the mixture was concentrated under reduced pressure to give a white solid. This solid was dissolved in 120 ml of anhydrous dimethyl sulfoxide. To this solution was added 33 g of methyl α-bromo-*o*-toluate in 20 ml of dimethyl sulfoxide. The mixture was stirred at 50 °C for 12 h, poured onto ice, and extracted with ether. The ethereal extracts were washed several times with water followed by a saturated sodium chloride solution, dried over magnesium sulfate, and concentrated under reduced pressure. The crude dark oil obtained was distilled at 136–138 °C (0.05 mm) to give 17.0 g (50%) of a clear liquid whose structure was assigned as methyl *o*-carbomethoxybenzyloxyacetate (**5**): ir (neat) 5.70 and 5.78 μm; NMR ($CDCl_3$, 100 MHz) τ 6.32 (s, 3 H), 6.18 (s, 3 H), 5.90 (s, 2 H), 5.12 (s, 2 H), and 2.0–3.1 (m, 4 H).

A sample of 2.0 g of sodium hydride (99%) was allowed to stir in 50 ml of anhydrous dimethyl sulfoxide for 1.5 h and then 8.0 g of the above methyl *o*-carbomethoxybenzyloxyacetate in 20 ml of dimethyl sulfoxide was added. After the reaction had stirred for 16 h at 50 °C, the mixture was cooled, acidified with dilute hydrochloric acid, poured onto ice, and extracted with ether. The extracts were washed several times with water followed by a saturated sodium chloride solution, dried over magnesium sulfate, and concentrated under reduced pressure to give a yellow liquid (5.2 g). This crude material was distilled at 132–133 °C (0.18 mm) to give 3.5 g (50%) of a yellow solid, mp 47–48 °C, identified as 3-carbomethoxyisochromanone[37] (**4**). Spectral data showed that this compound existed in both the keto and enol forms: ir (neat) 3.0, 5.70. 5.88, 6.02, and 6.22 μm; NMR ($CDCl_3$, 100 MHz) τ 6.25 (s, 3 H), 5.25 (s, 1 H), 4.7–5.2 (q, 2 H, *J* = 14 Hz), and 2.0–3.2 (m, 4 H) for the keto form and τ 6.18 (s, 3 H), 4.90 (s, 2 H), 2.0–3.2 (m, 4 H), and −0.2 (s, 1 H, exchangeable with D_2O) for the enol form; *m/e* 206 (M^+), 147, 118 (base), 105, 90, 77, 63, and 44; uv (methanol) 342 (ε 4500) and 247 nm (ε 9250).

Irradiation of 3-Carbomethoxyisochromanone. A solution containing 200 mg of 3-carbomethoxyisochromanone (**4**) in 60 ml of methanol was irradiated under an argon atmosphere for 8 h using a Rayonet reactor equipped with 3000-Å lamps. The solution was concentrated under reduced pressure and the crude solid obtained was shown to contain two components by thin-layer analysis. The crude solid was chromatographed on a thick-layer plate using a 20% ethyl acetate–methylene chloride mixture as the eluent. The fastest moving band contained 105 mg (52.5%) of a crystalline solid, mp 131–132 °C, which was assigned the structure of 2-hydroxy-2-carbomethoxyindanone (**6**) on the basis of its spectral properties and by comparison with an independently synthesized sample: ir (KBr) 2.90, 5.72, 5.82, 6.21, 6.85, 6.97, 8.00, 8.95, 10.5, and 13.36 μm; uv (methanol) 249 and 294 nm (ε 11 200 and 2300); NMR ($CDCl_3$, 100 MHz) τ 6.75 (d, 1 H, *J* = 18 Hz), 6.28 (s, 3 H), 6.25 (d, 1 H, *J* = 18.0 Hz), 6.02 (s, 1 H, exchangeable), and 2.1–2.7 (m, 4 H); *m/e* 206 (M^+), 147, 135, 118 (base), and 91.

Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 64.06; H, 4.92.

The slower moving band contained 80 mg (40%) of a white solid, mp 110–111 °C, whose structure is assigned as 1-hydroxy-3-carbomethoxyisochromene (**7**) on the basis of the following spectroscopic data: ir (KBr) 2.90, 5.84, 6.12, 7.05, 7.25, 7.70, 8.38, 9.62, 10.10, 10.96, 11.85, 12.55, and 13.15 μm; uv (methanol) 227, 233, and 296 nm (ε 8900, 7980, and 16 300); NMR ($CDCl_3$, 100 MHz) τ 6.15 (s, 3 H) 5.20 (br s, 1 H, exchangeable), 3.43 (s, 1 H, sharpened with D_2O addition), 2.90 (s, 1 H), and 2.65 (m, 4 H); *m/e* 206 (M^+), 147, 119, and 91 (base).

Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 63.65; H, 4.99.

Chemical confirmation of structure **7** was obtained by oxidation to 1-oxo-3-carbomethoxyisochromene (**8**), which was, in turn, independently synthesized. A solution containing 50 mg of **7** in 10 ml of anhydrous methylene chloride was added to a mixture containing 150 mg of chromium trioxide and 230 mg of pyridine in 15 ml of anhydrous methylene chloride. After the reaction had stirred for 30 min at room temperature, the solution was decanted into 50 ml of methylene chloride and washed with a 10% sodium hydroxide solution, water, and a saturated sodium chloride solution. The organic solution was dried over magnesium sulfate and concentrated under reduced pressure to give a white solid. Recrystallization of this solid from acetone–cyclohexane gave 27 mg (54%) of a white solid, mp 173–174 °C. This material was identified as 1-oxo-3-carbomethoxyisochromene (**7**) on the basis of its spectral properties and by comparison with an authentic sample:[57] ir (KBr) 5.80, 6.25, 6.50, and 7.7 μm; uv (methanol) 315 (ϵ 6370), 291 (13 500), 281 (1000), 251 (13 100), and 231 mm (21 900); NMR (CDCl$_3$, 100 MHz) τ 6.06 (s, 3 H) and 1.5–2.5 (m, 5 H).

Anal. Calcd for $C_{11}H_8O_4$: C, 64.70; H, 3.95. Found: C, 64.80; H, 4.34.

1-Oxo-3-carboxyisochromene was prepared in good yield according to the procedure of Johnston and co-workers,[58] mp 237–240 °C (lit. 242–244 °C).[58] A mixture containing 150 mg of 1-oxo-3-carboxyisochromene and 2 ml of thionyl chloride was heated at 140 °C for 2 h in a Carius tube. After cooling, the excess thionyl chloride was removed under reduced pressure. The residue was diluted with 10 ml of anhydrous methanol and the solution was refluxed for 5 min. The product obtained upon removal of excess methanol was a white solid (120 mg, 80%), mp 173–174 °C (lit. 173 °C),[57] whose spectral properties were identical with the compound obtained from the oxidation of 1-hydroxy-3-carbomethoxyisochromene (**7**).

Independent Synthesis of 2-Hydroxy-2-carbomethoxyindanone. The structure of the major photoproduct obtained from the photolysis of 3-carbomethoxyisochromanone (**4**) was unequivocally established by comparison with an authentic sample synthesized in the manner described below. A 2.0-g sample of *o*-carboxyhydrocinnamic acid, prepared according to the method of Page and Tarbell,[59] was added to 5 ml of thionyl chloride and the resulting mixture was heated at reflux for 30 min. The excess thionyl chloride was removed under reduced pressure. The residue was diluted with 20 ml of anhydrous methanol and the mixture was refluxed for 20 min. The white solid (mp >300 °C, 0.6 g) which initially formed was filtered and the filtrate was concentrated to give 1.4 g of an oil whose spectral properties are compatible with methyl *o*-carbomethoxyhydrocinnamate: ir (neat) 5.78, 6.20, 6.30, 6.95, 7.90, 8.80, 9.21, 13.20, and 14.0 μm; NMR (CDCl$_3$, 100 MHz) τ 7.35 (t, 2 H, J = 8 Hz), 6.75 (t, 2 H, J = 8 Hz), 6.40 (s, 3 H), 6.15 (s, 3 H), and 2.1–2.85 (m, 4 H).

A 0.8-g sample of methyl *o*-carbomethoxyhydrocinnamate in 10 ml of dimethyl sulfoxide was added to a mixture which contained 0.13 g of sodium hydride (99%) in 25 ml of dimethyl sulfoxide. The mixture was maintained at 50 °C for 12 h. After this time, the mixture was poured onto 100 g of crushed ice, acidified with 10% hydrochloric acid, and extracted with 300 ml of ether. The ethereal layer was washed with water, saturated sodium chloride solution, dried over magnesium sulfate, and concentrated under reduced pressure to give a brown oil (0.62 g). A 200-mg sample of this oil was chromatographed on a thick-layer plate using a 20% acetone–cyclohexane mixture as the eluent. The major band contained 120 mg of a clear liquid, whose spectral properties are consistent with 2-carbomethoxy-1-indanone: ir (neat) 5.80, 5.89, 6.25, 7.0, 8.30, 10.12, and 13.15 μm; NMR (CDCl$_3$, 100 MHz) τ 6.13 (s, 3 H), 6.20–6.80 (m, 3 H), and 2.2–2.7 (m, 4 H).

A stream of oxygen was passed through a solution which contained 120 mg of 2-carbomethoxy-1-indanone in 20 ml of methanol which also contained a few grains of sodium hydride (99%). After the reaction had stirred for 12 h at room temperature, 3 ml of a saturated ammonium chloride solution was added and the mixture was extracted with 100 ml of methylene chloride. The organic extracts were washed with a saturated sodium chloride solution, dried over magnesium sulfate, and concentrated under reduced pressure to give a clear oil. Isolation of the major reaction component was accomplished by thick-layer chromatography using a 20% ethyl acetate–methylene chloride mixture as the eluent. This band contained 40 mg of a white solid, mp 131–132 °C, whose spectral properties were identical in every detail with 2-hydroxy-2-carbomethoxyindanone (**6**) obtained from the photolysis of 3-carbomethoxyisochromanone (**4**).

Irradiation of 2-Hydroxy-2-carbomethoxyindanone. A solution containing 40 mg of 2-hydroxy-2-carbomethoxyindanone (**6**) in 20 ml of anhydrous methanol was irradiated under an argon atmosphere with a Rayonet reactor using 3000-Å lamps. The photoreaction was monitored as a function of time. The results obtained showed that as 2-hydroxy-2-carbomethoxyindanone (**6**) gradually disappeared, 1-hydroxy-3-carbomethoxyisochromene (**7**) was formed. After 24 h, hydroxyindanone **6** was completely converted into 1-hydroxy-3-carbomethoxyisochromene (**7**). The irradiation of hydroxyindanone **6** was also carried out in deuteriomethanol. Examination of the NMR spectrum of the solid obtained after 20 h of irradiation showed that 50% of the deuterium was incorporated into the C-4 position of 1-hydroxy-3-carbomethoxyisochromene (**7**). The singlet at τ 2.90 in **7** was also found to be diminished by 50%. A control experiment showed that isochromene **7** does not undergo deuterium exchange in the dark under similar reaction conditions.

Thermal Reactions of 1-Hydroxy-3-carbomethoxyisochromene. Isochromene **7** was found to react with a variety of alcohols, amines, and mercaptans to give isochromenes with different substituents in the 1 position of the ring. Thus, a solution containing 25 mg of 1-hydroxy-3-carbomethoxyisochromene (**7**) in 0.5 ml of chloroform was heated in a sealed tube in the presence of 2 drops of benzyl alcohol for 6 h. Removal of the excess chloroform and benzyl alcohol under reduced pressure gave a quantitative yield of a white crystalline solid whose structure was assigned as 1-benzyloxy-3-carbomethoxyisochromene (**9b**), mp 87–88 °C: ir (KBr) 5.80, 6.12, 8.22, 9.42, 10.1, 13.02, and 13.50 μm; uv (methanol) 307 (shoulder), 295, 234, and 227 nm (ϵ 8380, 11 350, 7280, and 8600); NMR (CDCl$_3$, 100 MHz) τ 6.13 (s, 3 H), 5.25 (s, 2 H), 3.97 (s, 1 H), 3.06 (s, 1 H), and 2.90 (m, 9 H); *m/e* 296 (M$^+$), 205, 118, 91 (base), and 65.

Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.82; H, 5.65.

A similar set of reactions was carried out with *tert*-butyl alcohol and methanol. The NMR spectrum of the *tert*-butyl ether displayed signals at τ 8.60 (s, 9 H), 6.15 (s, 3 H), 3.78 (s, 1 H), 2.90 (s, 1 H), and 2.4–2.80 (m, 4 H). Treatment of the *tert*-butyl ether in a sealed tube with 0.5 ml of methanol for 8 h at 130 °C gave 1-methoxy-3-carbomethoxyisochromene. This same material could also be prepared by heating **7** with methanol under similar thermal conditions: ir (CCl$_4$) 5.80, 6.10, 6.98, 7.21, 7.68, 8.30, 9.30, and 9.98 μm; uv (methanol) 225, 232, 294, and 307 (shoulder) nm (ϵ 7000, 6100, 10 600, and 7800); NMR (CDCl$_3$) τ 6.40 (s, 3 H), 6.08 (s, 3 H), 3.90 (s, 1 H), 2.82 (s, 1 H), and 2.2–2.8 (m, 4 H); *m/e* 220, 189 (base), 161, 118, 103, and 90. Both ethers were reconverted to hydroxychromene **7** on treatment with a 75% aqueous acetone solution.

Isochromene **7** was also converted to the corresponding 1-benzylthia ether. A solution containing 25 mg of 1-hydroxy-3-carbomethoxyisochromene in 0.5 ml of carbon tetrachloride was treated with 2 drops of benzyl mercaptan and the mixture was heated for 1.5 h at 130 °C in a sealed tube. Removal of the solvent followed by thick-layer chromatography using a 20% acetone–cyclohexane mixture as the eluent gave a white solid (22 mg, 64%), mp 84–85 °C, whose spectral properties are consistent with 1-benzylthia-3-carbomethoxyisochromene: ir (KBr) 5.80, 6.13, 6.98, 7.75, 8.29, 8.93, 9.15, 9.91, and 12.95 μm; uv (methanol) 311, 240, and 235 nm (ϵ 12 900, 20 650, and 25 100); NMR (CDCl$_3$, 100 MHz) τ 6.21 (s, 3 H), 5.95–6.95 (AB q, 2 H, J = 13.5 Hz), 3.65 (s, 1 H), and 2.4–3.3 (m, 10 H); *m/e* 312 (M$^+$), 189 (base), 157, 134, 102, and 91.

Anal. Calcd for $C_8H_{16}O_3S$: C, 69.23; H, 5.16; S, 10.28. Found: C, 68.93; H, 4.98; S, 10.73.

Treatment of **7** with *tert*-butylamine at 130 °C gave 1-*tert*-butylamino-3-carbomethoxyisochromene: NMR (CDCl$_3$) τ 8.60 (s, 9 H), 6.02 (s, 3 H), 3.72 (s, j H), 2.98 (s, 1 H), and 2.2–2.6 (m, 4 H).

Isochromene **7** could be converted to dimethyl 1,1′-oxybis-1*H*-2-benzopyran-3-carboxylate (**11**) on heating. Thus, a 50-mg sample of **7** in 0.5 ml of benzene was heated at 130 °C for 16 h. Removal of the solvent left a white solid which was purified by thick-layer chromatography. The solid obtained was identified as **11** on the basis of its physical and chemical properties: ir (CCl$_4$) 5.80, 6.10, 6.98, 7.68, 8.30, 9.11, 10.60, and 10.95 μm; NMR (CDCl$_3$) τ 6.03 (s, 3 H), 3.04 (s, 1 H), 2.85 (s, 1 H), and 2.2–2.8 (m, 4 H). A satisfactory elemental analysis could not be obtained due to the ready hydrolysis of the dimer back to isochromene **7**. Dimer **11** could also be readily converted to the corresponding methyl ether on treatment with methanol at 130 °C for 6 h.

Irradiation of 3-Carbomethoxyisochromanone in the Presence of Oxygen. A solution containing 120 mg of 3-carbomethoxyisochromanone (**4**) in 60 ml of methanol was irradiated in a Pyrex test tube under an oxygen atmosphere for 3.5 h using a Rayonet reactor equipped with 3000-Å lamps. Concentration of the solution under reduced pressure resulted in an oil which was shown to contain several components by thin-layer analysis. The crude oil was chromatographed on a thick-layer plate using a 75% methylene chloride–cyclohexane mixture as the eluent. The fastest moving band contained unreacted starting material. The second band was a white solid, mp 81–82 °C (13 mg, 12%), whose structure was assigned as 3-carbomethoxy-3-hydroxyisochromanone (**12**) on the basis of the following data: ir (neat) 2.91, 5.73, 5.88, 6.22, 6.94, 8.82, 9.35, 10.40, 12.52, and 13.60 μm; NMR (CDCl$_3$, 100 MHz) τ 6.06 (s, 3 H), 6.10 (d, 2

H, J = 15 Hz), 5.62 (d, 3 H, J = 15 Hz), and 1.90–2.90 (m, 4 H); *m/e* 223 (M^+), 163 (base), 119, 105, 91, and 77.

This same material could also be prepared by treating **7** with methanol in the presence of air in the dark. The dark reaction required 3 days for starting material to be totally consumed, while the photoreaction was complete in a matter of hours.

The third component isolated from the thick-layer plate contained 15 mg (13%) and was assigned the structure of lactone **13**, mp 108–109 °C, on the basis of the following data: ir (KBr) 5.69, 5.79, 6.90, 7.95, 8.70, 9.55, 12.70, and 13.45 μm; NMR ($CDCl_3$) τ 6.22 (s, 3 H), 4.75–5.15 (q, 2 H, J = 12 Hz), 4.50 (s, 1 H), and 2.0–2.7 (m, 4 H); *m/e* 213, 163 (base), 135, 119, 105, 95, and 77.

Anal. Calcd for $C_{11}H_{10}O_4$: C, 59.44; H, 4.54. Found: C, 59.16; H, 4.72.

The structure of this material was further supported by lithium aluminum hydride reduction to *o*-hydroxymethylbenzyl alcohol and by acid hydrolysis to phthalide.

The fourth component obtained from the photooxidation reaction was present in highest yield (65%) and was identified as methyl 2-carboxybenzyl oxalate (**14**), mp 132–133 °C: ir (KBr) 3.3–4.3 (br), 5.73, 5.93, 6.35, 7.09, 7.65, 8.25, 10.48, 12.40, and 13.55 μm; NMR ($CDCl_3$, 100 MHz) τ 6.12 (s, 3 H), 4.25 (s, 2 H), 1.8–2.8 (m, 4 H) and 0.4 (br s, 1 H, exchangeable with D_2O); *m/e* 134, 105 (base), 77, and 50.

Anal. Calcd for $C_{11}H_{10}O_5$: C, 55.46; H, 4.23. Found: C, 55.38; H, 4.35.

The presence of the carboxylic acid group in methyl 2-carboxybenzyl oxalate (**14**) was demonstrated by titrating a sample of this compound with standardized 0.0533 M aqueous sodium hydroxide solution to a methyl red end point. An average of 0.98 equiv of sodium hydroxide was required to neutralize one equiv of the acid. When methyl 2-carboxybenzyl oxalate (**14**) was injected onto a gas chromatographic column (0.25 in. × 6 ft 10% SE-30) maintained at 120 °C, two peaks were observed and were identified as methyl monooxalate and phthalide by comparison with authentic samples. Similar results were obtained when **14** was heated at 130 °C in deuteriochloroform for 32 h. In this case the products were identified by NMR analysis. A 14-mg sample of methyl 2-carboxybenzyl oxalate was also reduced with 10 mg of lithium aluminum hydride in 10 ml of ether. After the reaction had stirred at room temperature for 30 min, 10 drops of a 5% sodium hydroxide solution was added. Removal of the ether left a clear oil, which was identified as *o*-hydroxymethylbenzyl alcohol by comparison with an authentic sample.

The formation of compounds **13** and **14** were shown to be secondary photoproducts derived from further irradiation of 3-carbomethoxy-3-hydroxyisochromanone (**12**).

Preparation of 3-Carbomethoxy-4-acetoxyisochromene. A mixture containing 95 mg of 3-carbomethoxyisochromanone (**4**) and 20 mg of sodium acetate in 10 ml of acetic anhydride was refluxed under a nitrogen atmosphere for 4 h. At the end of this time the mixture was poured onto ice water and extracted with ether. The ethereal extracts were washed with a saturated sodium bicarbonate solution, dried, and concentrated under reduced pressure. The clear oil obtained solidified on standing, mp 63–65 °C, but was found to partially decompose on exposure to atmospheric conditions. The spectral data obtained indicated the solid to be 3-carbomethoxy-4-acetoxyisochromene (**15**): ir (CCl_4) 5.62 and 5.80 μm; uv (methanol) 313, 238, and 230 nm (ϵ 4800, 6750 and 7200); NMR ($CDCl_3$, 100 MHz) τ 7.60 (s, 3 H), 6.18 (s, 3 H), 4.42 (s, 2 H), and 2.5–3.1 (4 H); *m/e* 248 (M^+), 206, 174, 149, 118 (base), 105, 70, 77, and 44.

Irradiation of 3-Carbomethoxy-4-acetoxyisochromene. A solution containing 210 mg of 3-carbomethoxy-4-acetoxyisochromene (**15**) in 450 ml of benzene was irradiated under a nitrogen atmosphere for 48 h using a 450-W Hanovia lamp equipped with a Pyrex filter. The solvent was removed under reduced pressure and the residue was subjected to thick-layer chromatography. The major band amounted to 90 mg (46%) of a white solid, mp 97–101 °C. Further purification by recrystallization from ether-hexane afforded white crystals, mp 106–107 °C, whose structure was assigned as methyl 1,6-dihydro-4-methyl-6-oxo-2,5-benzodioxocin-3-carboxylate (**16**) on the basis of its physical and chemical properties: ir (CCl_4) 5.81 and 5.68 μm; uv (methanol) 238 nm (ϵ 7700); NMR ($CDCl_3$, 60 MHz) τ 7.61 (s, 3 H), 6.18 (s, 3 H), 4.79 (s, 2 H), 2.5–3.1 (m, 4 H); *m/e* 248, 206, 174, 118 (base), 90, and 43.

Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87. Found: C, 63.01; H, 4.87.

The structure of **16** was supported by an ozonization experiment. A stream of ozone was passed through a solution containing 50 mg of **16** in 30 ml of methylene chloride at −78 °C until a light blue color appeared. After 20 min, the temperature was raised to −20 °C and the solution purged with nitrogen. After the addition of 0.5 ml of dimethyl sulfide, the mixture was washed with water followed by a saturated sodium chloride solution, dried over magnesium sulfate, and concentrated under reduced pressure to leave 41 mg (75%) of methyl *o*-carboxybenzyl oxalate (**14**).

X-Ray Crystal Structure Analysis of Methyl 1,6-Dihydro-4-methyl-6-oxo-2,5-benzodioxocin-3-carboxylate (16). The molecular structure of methyl 1,6-dihydro-4-methyl-6-oxo-2,5-benzodioxocin-3-carboxylate (**16**) was unequivocally determined by an x-ray crystal structure analysis. Colorless prisms belonging to space group $P1$ were obtained from ether-hexane solutions. The following parameters were measured for these crystals: a = 8.881, b = 9.628, c = 7.747 Å; D_m = 1.386, D_c = 1.397 g/cm^3; Z = 2 molecules.

The intensity data were collected by the stationary counter-stationary crystal technique[60] on a General Electric XRD-6 diffractometer equipped with a single-crystal orienter. Balanced filters for CuK radiation were utilized for the measurement of peak intensities and backgrounds, Ni against Co. The measurement range was from 0 to 120° in 2θ, which gave 1751 independent reflections, of which 233 had intensities which were not significantly greater than their background counts; these were given zero weight through-out the computations. The intensities were corrected for absorption by applying a factor to correct for anisotropy of transmission of the x-ray beam. The other factors applied to convert the data to structure factor amplitudes, F's, were Lorentz polarization and $\alpha_1 - \alpha_2$ splitting corrections. The $|F\text{'s}|$ were put on an absolute scale by use of Wilson statistics[61] and then converted to their respective normalized structure factors, all having values of E greater than 1.6, determined using the Sayre equation,[62] which is the same as the Σ_2 formula of Hauptman and Karle.[63] A program written by Long was utilized for this purpose.[64] An E-Fourier map was calculated from the solution with the highest consistency index (0.69). The whole molecule was recognized from this map. The positional and thermal parameters were refined by least squares using a block-diagonal approximation to the thermal equations. After anisotropic temperature factors were introduced, the usual reliability index (R value) was found to be 0.149. The positions of the hydrogen atoms were found from a three-dimensional Fourier difference synthesis. These atoms were included in the final cycles of least squares and were refined to a final R value of 0.0514. The positional and thermal parameters obtained from the least-squares refinement are given in Tables I and II. (See paragraph at end of paper regarding supplementary material.) A view of the molecule along with the atomic labeling used is shown in Figure 1. There are no intermolecular contacts that suggest forces stronger than normal van der Waals are operative in the crystal.

Preparation of 3-Carbomethoxyisothiochroman-4-one. To a solution containing 10.6 g of methyl thioglycolate in 300 ml of methylene chloride was added 3.0 g of anhydrous sodium hydride at 25 °C. The solution was stirred at room temperature for 30 min and then 1.0 g of tetra-*n*-butylammonium chloride was added followed by 22.5 g of methyl α-bromo-*o*-toluate in 300 ml of methylene chloride. The mixture was stirred at room temperature for 17 h, poured onto ice, and extracted with ether. The ethereal extracts were washed several times with water, dried over magnesium sulfate, and then concentrated under reduced pressure. The crude oil obtained was distilled at 135–138 °C (0.1 mm) to give 18.4 g (74%) of methyl *o*-carbomethoxybenzylthioacetate as a clear liquid: ir (neat) 5.79 μm; NMR ($CDCl_3$) τ 6.93 (s, 2 H), 6.33 (s, 3 H), 6.14 (s, 3 H), 5.80 (s, 2 H), 2.0–3.0 (m, 5 H).

A 14.2-g sample of the above diester was dissolved in 750 ml of toluene and 1.5 g of metallic sodium was added. After the reaction had refluxed for 1.5 h, the mixture was cooled and 1 ml of methanol was added to destroy the excess sodium. The solution was then concentrated under reduced pressure and taken up in ether. The ethereal solution was washed with 10% hydrochloric acid, water dried over magnesium sulfate, and concentrated to give 10.8 g (87%) of 3-carbomethoxyisothiochroman-4-one (**18**) as a crystalline solid after recrystallization from ethanol, mp 87–88 °C: ir (KBr) 6.08, 6.22, 6.24, 6.45, and 7.00 μm; uv (methanol) 368 and 260 nm (ϵ 5400 and 10 300); NMR ($CDCl_3$) τ 6.28 (s, 2 H), 6.18 (s, 3 H), 2.20–3.0 (m, 5 H), and −2.20 (s, 1 H, exchanged with D_2O); *m/e* 164, 118 (base), and 90.

Anal. Calcd for $C_{11}H_{10}SO_3$: C, 59.44; H, 4.54; S, 14.42. Found: C, 59.32; H, 4.55; S, 14.48.

Irradiation of 3-Carbomethoxyisothiochromanone. A solution containing 200 mg of 3-carbomethoxyisothiochromanone (**18**) in 175 ml of methanol which contained 15 mg of sodium hydride was irradiated under an argon atmosphere for 3.5 h with a 550-W Hanovia mercury arc equipped with a Pyrex filter. At the end of this time, 1 ml of acetic acid was added to the photolysate and the solution was concentrated under reduced pressure. The residue was taken up in ether, washed with water, dried over magnesium sulfate, and concentrated to a yellow oil. Molecular distillation of this material (100 °C (0.03 mm)) afforded 165 mg (96%) of 2-carbomethoxyindanone (**19**), mp 56-58 °C. This material was identical in all respects with an independently synthesized sample.[65]

Preparation of 3-Phenylisochromanone. To a solution containing 33.2 g of methyl mandelate and 1.0 g of tetra-*n*-butylammonium chloride in 500 ml of methylene chloride was added 5.1 g of 99% sodium hydride followed by 46 g of methyl α-bromo-*o*-toluate. After the reaction has stirred for 3.5 h, the mixture was washed with several portions of water followed by a saturated ammonium chloride solution. The solution was dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude oil obtained was distilled at 180-182 °C (0.15 mm) to give 26.7 g (43%) of methyl *o*-carbomethoxybenzyloxy-α-phenylacetate:[37] ir (neat) 5.71, 5.80, 6.22, and 6.32 μm; NMR ($CDCl_3$, 100 MHz) τ 6.25 (s, 3 H), 6.15 (s, 3 H), 4.95 (d, 2 H, J = 1.5 Hz), and 1.9-2.8 (m, 5 H). A mixture containing anhydrous sodium methoxide (obtained by dissolving 2.5 g of sodium in 20 ml of methanol) and 26.7 g of the above diester in 200 ml of dry toluene was refluxed under a nitrogen atmosphere for 4 h. After cooling, the mixture was poured onto 50 ml of a 10% hydrochloric acid solution and extracted with ether. The ethereal extracts were washed with water and saturated sodium bicarbonate, dried over magnesium sulfate, and concentrated under reduced pressure. The crude oil obtained was distilled at 140-148 °C (0.15 mm) to give 11.0 g (58%) of a clear liquid whose structure was identified as 3-phenylisochromanone (**20**) on the basis of its spectral properties: ir (neat) 5.90 and 6.21 μm; uv (methanol) 290 (ϵ 2640) and 247 nm (ϵ 10 400); NMR ($CDCl_3$, 100 MHz) τ 4.95 (s, 2 H), 4.62 (s, 1 H) 1.6-3.0 (m, 9 H); *m/e* 224 (M^+), 134, 122, 118 (base), 105, 90, and 77. This clear oil solidified on standing, mp 34-36 °C, and was analyzed as its 2,4-dinitrophenylhydrazone, mp 244-245 °C.

Anal. Calcd for $C_{21}H_{15}N_4O_5$: C, 62.37; H, 3.99. Found: C, 62.12; H, 4.11.

Irradiation of 3-Phenylisochromanone in Isopropyl Alcohol. A solution containing 300 mg of 3-phenylisochromanone in 450 ml of isopropyl alcohol was irradiated for 20 h under a nitrogen atmosphere using a 450-W Hanovia lamp equipped with a Pyrex filter. Removal of solvent left an oil which was separated into five bands on preparative thick-layer chromatography. The five major components obtained were isolated and identified. The first band (33 mg, 12%), mp 173-174 °C, was assigned as pinacol **21** on the basis of its spectral properties and by chemical degradation with lead tetraacetate: ir (KBr), 2.96, 6.22, 9.45, 11.0, and 13.56 μm; NMR ($CDCl_3$, 100 MHz), τ 5.5 (AB q, 4 H, J = 16 Hz), 4.65 (s, 2 H, exchangeable with D_2O), 4.15 (s, 2 H), and 2.6-3.4 (m, 18 H).

Anal. Calcd for $C_{30}H_{26}O_4$: C, 79.98; H, 5.82. Found: C, 80.08; H, 5.92.

The second band (20 mg) isolated from the thick-layer plate was identified as unreacted starting material. The third band contained 48 mg (17%) of a white solid, mp 230-232 °C, whose structure was assigned as the epimeric pinacol **22** on the basis of its physical properties and by an independent synthesis: ir (KBr) 3.0, 6.25, 9.45, 11.0, and 13.2 μm; NMR ($CDCl_3$, 100 MHz) τ 5.58 (AB q, 4 H, J = 16 Hz), 5.30 (s, 2 H, exchangeable with D_2O), 4.20 (s, 2 H), and 2.4-3.3 (m, 18 H).

Anal. Calcd for $C_{30}H_{26}O_4$: C, 79.98; H, 5.82. Found: C, 79.67; H, 5.89.

The structures of the two pinacols were supported by cleavage with lead tetraacetate. A mixture containing 20 mg of pinacol **21** (or **22**) and 16 mg of lead tetraacetate was stirred in 10 ml of benzene at room temperature for 3 h. At the end of this time, the mixture was filtered and the filtrate was diluted with ether, washed with a saturated sodium bicarbonate solution, and dried over magnesium sulfate. Removal of the solvent left an oil whose spectral properties were identical in every detail with 3-phenylisochromanone (**20**).

The structure of pinacol **22** was further supported by comparison with an authentic sample. A mixture containing 200 mg of 3-phenylisochromanone, 300 mg of aluminum foil, and 200 mg of mercuric chloride in 5 ml of benzene and 6 ml of absolute ethanol was refluxed for 7 h. After cooling, the solution was poured onto 10 ml of a 10% hydrochloric acid solution and was then extracted with ether. The ethereal extracts were washed with a saturated sodium bicarbonate solution, dried over magnesium sulfate, and concentrated under reduced pressure to give a solid. The solid was purified by thick-layer chromatography and amounted to 110 mg (55%) of pinacol **22**, mp 173-174 °C. This material was identical in every detail with one of the pinacols obtained from the irradiation of 3-phenyl-4-chromanone in isopropyl alcohol.

The fourth band isolated from the thick-layer plate (56 mg, 25%) was assigned as 3-phenyl-4-hydroxyisochromane (**23**), mp 79-80 °C, on the basis of its spectral data and by an independent synthesis: ir 3.05 and 6.25 μm; NMR ($CDCl_3$, 100 MHz) τ 7.95 (s, 1 H, exchangeable with D_2O), 5.0-5.7 (m, 4 H), and 2.4-3.4 (m, 9 H). A 50-mg sample of 3-phenylisochromanone in 10 ml of 95% ethanol was treated with 20 mg of sodium borohydride. After standing for 12 h, the mixture was diluted with ether and washed with water and a saturated sodium chloride solution. The ether layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on a thick layer plate using a 20% acetone-cyclohexane mixture as the eluent. The major band contained 28 mg (55%) of 3-phenyl-4-hydroxyisochromane (**23**). This material was identical in every detail with the alcohol obtained from the photolysis of **20**.

The last band isolated from the photolysis of 3-phenylisochromanone was assigned as 2-hydroxy-2-phenylindanone (**24**) (38 mg, 13%), mp 127-128 °C. This material was also independently synthesized: ir (KBr) 2.90, 5.90, and 6.23 μm; uv (methanol) 285 (ϵ 1680) and 249 nm (ϵ 9730); NMR ($CDCl_3$, 100 MHz) τ 6.70 (s, 1 H, exchangeable with D_2O), 6.40 (s, 2 H), and 2.05-2.80 (m, 9 H).

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39. Found: C, 80.07; H, 5.65.

To a solution containing 200 mg of 2-phenylindanone[66] and 130 mg of triethylamine in 20 ml of chloroform was added a solution of bromine in chloroform until a red color persisted. After the reaction had stirred for 2 h, the mixture was concentrated under reduced pressure. The residue was taken up in 20 ml of acetone. To this solution was added 500 mg of silver perchlorate in 5 ml of water. After the reaction had stirred for 3 h, the precipitate was filtered and the filtrate was extracted with ether. The ethereal extracts were washed with water followed by a saturated sodium chloride solution and then dried over magnesium sulfate. Concentration of the solution left 156 mg (72%) of a white solid, mp 127-128 °C, whose spectral properties were identical with 2-hydroxy-2-phenylindanone (**24**) obtained from the irradiation of isochromanone **20**. A mixture melting point was undepressed at 126-127 °C.

Irradiation of 2-Hydroxy-2-phenylindanone in Methanol. A solution containing 300 mg of 2-hydroxy-2-phenylindanone (**24**) in 450 ml of methanol was irradiated for 7 h under a nitrogen atmosphere using a 550-W Hanovia lamp equipped with a Pyrex filter. Removal of the solvent left an oil which was shown to contain two major components by thin-layer and NMR analysis. Chromatography of the oil on a preparative thick-layer plate resulted in the separation of the two bands. The faster moving band contained 130 mg (43%) of an oil whose structure was assigned as 1-methoxy-3-phenyl-1*H*-2-benzopyran (**25**) on the basis of its chemical behavior and spectral properties: ir (CCl_4) 6.05, 6.20, 6.70, and 10.45 μm; NMR ($CDCl_3$, 100 MHz) τ 6.41 (s, 3 H), 3.92 (s, 1 H), 3.45 (s, 1 H), and 2.2-3.1 (m, 9 H).

The second band contained 95 mg (32%) and was identified as α-benzoyl-*o*-tolualdehyde dimethylacetal (**26**) on the basis of its chemical properties and spectral data: ir (CCl_4) 5.90 μm; NMR ($CDCl_3$, 100 MHz) τ 6.78 (s, 6 H), 5.58 (s, 2 H), 4.70 (s, 1 H), and 1.9-3.0 (m, 9 H).

In another irradiation experiment, 300 mg of 2-hydroxy-2-phenylindanone (**24**) was photolyzed in 90% methanol for 7 h. The reaction mixture was concentrated under reduced pressure and the NMR spectrum of the photolysate showed the presence of two compounds, which were assigned as 1-hydroxy-3-phenyl-1*H*-2-benzopyran (**27**) and α-benzoyl-*o*-tolualdehyde **28** in a ratio of 3:2. The NMR spectrum of **27** showed singlets at τ 3.8 (1 H) and 3.7 (1 H) in addition to the aromatic protons and a broad hydroxyl proton. Chromatography of the mixture by thick-layer chromatography have only the aldehyde tautomer (**28**) (195 mg, 65%), mp 87-88 °C; ir (KBr) 5.93 μm; NMR

(CDCl$_3$) τ 5.24 (s, 2 H), 1.7-3.0 (m, 9 H), and 0.2 (s, 1 H).

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39. Found: C, 80.21; H, 5.35.

Treatment of 40 mg of α-benzoyl-*o*-tolualdehyde with methanol at room temperature for 3 h in the presence of a trace of acid afforded a quantitative yield of 1-methoxy-3-phenyl-1*H*-2-benzopyran (**25**). When this compound was allowed to stand in the presence of methanol for an additional 5 h it was partially converted to α-benzoyl-*o*-tolualdehyde dimethylacetal. (**26**).

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).[67] 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. The authors also wish to thank Professor Eli Shefter and Ms. P. Sackman for assistance in the x-ray determination and Mr. William Owens for the results observed with the isothiochromanone system.

Supplementary Materials Available: The positional and thermal parameters obtained from the least-squares refinement (Tables I and II) (2 pages). Ordering information is given on any current masthead page.

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