the three stereoisomers. The results of this experiment are recorded in Table IV.

Photostationary State Compositions from Irradiations of 1tt with Various Triplet Sensitizers. Spectrograde cyclohexane solutions of *trans,trans*-bis(β-styryl)dimethylsilane (1.0×10^{-2} M) and the various triplet sensitizers (acetone, benzophenone, 1-acetonaphthone, and benzil), each 2.0×10^{-2} *M*, were placed individually in Pyrex test tubes and irradiated with Pyrex-filtered light until the photostationary states were obtained. Analyses of these solutions by gas chromatography yielded photostationary state isomer compositions tabulated in Table V.

Acknowledgment. Support of these studies by the Robert A. Welch Foundation is gratefully acknowledged. P.S.M. would like to thank the Environmental Quality Program at Texas A&M University for funds to purchase gas chromatographic equipment used in these studies.

Registry No.—**1tt**, 54366-27-7; **1ct**, 54366-28-8; **1cc**, 54366-29-9; **2**, 54366-30-2; **3**, 33105-34-9; *cis*-β-bromostyrene, 588-73-8; *trans*-β-bromostyrene, 588-72-7; dimethyldichlorosilane, 75-78-5; triphenylchlorosilane, 76-86-8.

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(1) The syntheses of highly substituted silacyclopropanes has recently been reported by R. L. Lambert and D. Seyferth, *J. Am. Chem. Soc.*, **94**, 9246 (1972).

(2) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).

(3) (a) The oxadi-π-methane rearrangement of β,γ-unsaturated ketones and aldehydes to cyclopropyl ketones and aldehydes was first discussed mechanistically by Swenton[3b] and related to the carbon analog by Givens;[3c] (b) J. S. Swenton, *J. Chem. Educ.*, **46**, 217 (1969); (c) R. S. Givens and W. F. Oettle, *Chem. Commun.*, 1164 (1969).

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(6) The initial results of this study, reported at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 26–31, 1973, Abstracts, No. ORGN-153, were found to be in error owing to impurities present in the starting materials which presumably changed the product ratios.

(7) R. A. Benkeser and R. A. Hickner, *J. Am. Chem. Soc.*, **80**, 5298 (1958).

(8) It is very likely that the potential vinylsilacyclopropanes expected in these reactions will not survive the reaction conditions but will either rearrange to silacyclopentenes[9a,9b] or react with the alcoholic solvent to yield methyl allylsilyl ethers.[5,9a]

(9) (a) Y. Nakadaira, S. Kanouchi, and H. Sakurai, *J. Am. Chem. Soc.*, **96**, 5621 (1974); (b) Y.-N. Tang, G. P. Gennaro, and Y. Y. Su, ibid., **94**, 4355 (1972).

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(13) G. W. Griffin et al., *Tetrahedron Lett.*, 2951 (1965).

(14) The evidence accumulated to date indicates that the di-π-methane reaction in the singlet excited manifold is most probably a concerted process.[15a,b] However, the effect of central[15c] and terminal[15d] carbon atom substitution indicates that stabilization of diradicaloids along the reaction coordinate is influential in determining the efficiency of the process.

(15) (a) P. S. Mariano and J. K. . Ko, *J. Am. Chem. Soc.*, **95**, 8670 (1973); (b) H. E. Zimmerman et al., ibid., **96**, 1459 (1974); (c) H. E. Zimmerman et al., ibid., **95**, 2155, 2157 (1973); (d) H. E. Zimmerman and A. A. Baum, ibid., **93**, 3646 (1971).

(16) P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, **86**, 1442 (1964).

(17) The lower limit of our detectability of **1tt** is ca. 0.1% and thus **1cc/1ct** ratios of less than 0.01 could not be measured.

(18) The relative integrated extinction coefficients of **1cc** and **1ct** were calculated from considerations of the relative absorption spectra of the two isomers along with the wavelength dependencies of the lamp output and Pyrex glass filter transmittance.

(19) The possibility does exist that the triplet excited state of **1tt** is responsible for π-bond isomerization in both the direct and sensitized irradiations. The quenching studies using 2,3-dimethyl-1,3-butadiene can be interpreted in terms of a direct irradiation singlet process or a fast unquenchable triplet process.

(20) The triplet energies of the three stereoisomers of **1** should all fall in the range of 62 kcal/mol, like that of styrene. Thus, triplet energy transfer from benzophenone (69 kcal/mol) to all three should be highly exothermic and should occur at the diffusion-controlled rates.[21] The constancy of the photostationary state isomer compositions when changing from acetone (76 kcal/mol) sensitization to benzophenone to 1-acetonaphthone (59 kcal/mol) sensitization indicates the correctness of the assumption that $k_{\mathrm{et,cc}} = k_{\mathrm{et,ct}}$ in the benzophenone-sensitized irradiation.[22]

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(22) G. S. Hammond et al., *J. Am. Chem. Soc.*, **86**, 3197 (1964).

Photochemical Ring-Opening Reactions of Substituted Chromenes and Isochromenes[1]

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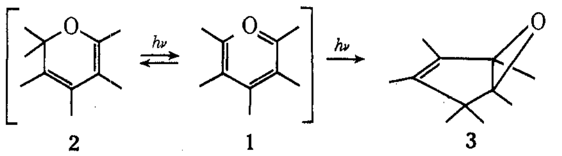
Irradiation of a number of substituted chromenes in methanol give products derived from an *o*-quinoneallide intermediate. The fate of the *o*-quinoneallide depends on the experimental conditions. The primary mode of reaction corresponds to 1,4 and 1,6 addition of methanol across the C–C double bonds of the *o*-quinoneallide intermediate. In nonreactive solvents, the *o*-quinoneallide undergoes a 1,7-sigmatropic hydrogen shift. Irradiation of several substituted isochromenes, on the other hand, give indene epoxides which produce ring-opened hydroxy ethers on further irradiation. The mechanism involves opening of the isochromene ring to give an *o*-quinoidal intermediate which undergoes a subsequent intramolecular [4 + 2] cycloaddition reaction. A similar path occurs with 4-phenylisothiochromene, except that in this case the initially formed indene episulfide loses sulfur on further irradiation to give a substituted indene.

Light-induced transformations of cyclic dienes have been the subject of recent intensive study.[2,3] Derivatives of 1,3-cyclohexadiene, for example, have been transformed into a vast array of photoproducts via ring-opening processes,[4–12] valence-bond tautomerization reactions,[13–15] bond-switching mechanisms,[16–22] and dimerization pathways.[23,24] Despite the fact that photochemical isomerizations of cyclic dienes have been well documented, investigation of suitable heterocyclic analogs in light-induced reactions has been somewhat limited.[25] With a desire to discover new photochemical pathways of appropriate heterocyclic dienes, we have examined the photochemical behavior of several substituted chromenes and isochromenes.[26] A number of investigators had previously observed that a ring–chain tautomerization could be established between substituted cis dienones **1** and 2*H*-pyrans **2**.[27–29] Transformations of this type are known to be responsible for the photochromism encountered on irradiation of 2*H*-chromenes[30,31] and *o*-vinylphenones.[32] Extended irradiation of the photoequilibrated dienone–pyran mixture might be expected to afford an oxabicyclo[3.1.0]hex-2-ene (**3**) as the ultimate photoproduct. This transformation would be



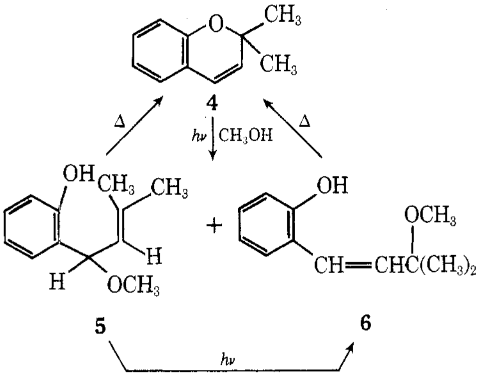
2 1 3

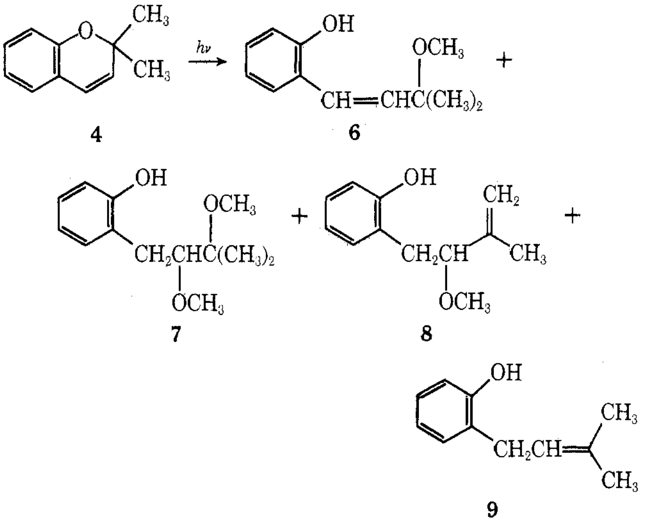
closely analogous to the photo-Diels–Alder reaction encountered with 1,3,5-hexatrienes.[33] Although rearrangements of this type have been reported for nitrogen analogs of cyclohexadienes,[34] no structurally related oxycyclic diene has been shown to undergo a photoreaction of this type.

The present paper describes the photochemical ring opening reaction of a number of substituted chromenes and isochromenes to give *o*-quinoidal intermediates. The fate of the *o*-quinoidal intermediate was found to depend on the nature of the substituent groups as well as the photolysis conditions. The primary mode of reaction of the intermediate generated from the 2*H*-chromene system involves 1,4 or 1,6 addition of alcohol across the reactive double bonds. In the isochromene system, however, the initially generated *o*-quinoidal intermediate undergoes a subsequent intramolecular [4 + 2] cycloaddition reaction to give an oxabenzobicyclo[3.1.0]hexene as the final photoproduct.

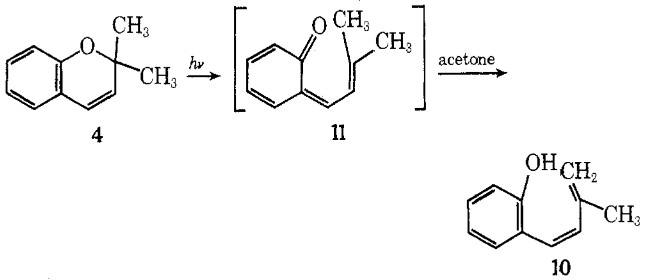
Results and Discussion

Irradiation of 2,2-dimethylchromene (4) in methanol through Pyrex using a 550-W Hanovia lamp gave two major products whose relative yields varied as a function of exposure duration. When a 0.018 *M* solution of 4 was irradiated for 5 hr, approximately 50% of starting material was consumed and the two products, isolated by preparative thick layer chromatography, were shown to be methanol adducts 5 and 6. The identification of the photoproducts was based on their characteristic spectral data (see Experimental Section). Both adducts were found to revert to starting material on standing in the dark. This thermal reversion is analogous to some recent reactions reported by Schmid and coworkers,[35] who found that the thermolysis of a number of (*o*-hydroxyaryl)-2-propen-1-ols produced 2*H*-chromenes by 1,4 elimination of water followed by thermal cyclization of the initially generated *o*-quinone methide intermediates. Further irradiation of the above solution for an additional 6 hr gave a mixture containing mainly 6 along with trace amounts of 5. This observation suggests that at least part of 6 is formed from a secondary photoisomerization of 5. When the irradiation of 2,2-dimethylchromene (4) was carried out in methanol using a Corex filter for 3 hr, a mixture of four products was obtained. In addition to adduct 6, 2,3-dimethoxy-2-methyl-4-(*o*-hydroxyphenyl)butane (7, 19%), 2-methyl-3-methoxy-4-(*o*-hydroxyphenyl)but-1-ene (8, 8%), and 2-methyl-4-(*o*-hydroxyphenyl)but-2-ene (9, 17%) were isolated from the crude photolysate. These products were identified by their characteristic spectral properties (see Experimental Section). Photoadduct 7 was shown to be a secondary product resulting from further irradiation of the ether 6. Interestingly, this compound corresponds to the anti-Markovnikov addition of methanol across the C–C double bond of 6. Hixson had previously reported on the anti-Markovnikov photochemical addition of methanol to acyclic aryl olefins.[36] His observations provide reasonable chemical analogy for the above addition. Methoxy ether 8 was shown to be a secondary product derived from an acid-catalyzed elimination of methanol from 7.



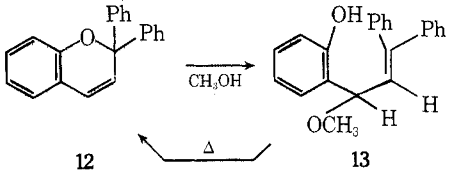


In contrast to the complex behavior encountered with the direct irradiation of 4, the acetone-sensitized photolysis gave 2-methyl-4-(*o*-hydroxyphenyl)-1,3-butadiene (10) as the exclusive photoproduct: NMR δ 1.86 (s, 3 H), 4.86 (m, 2 H), 5.30 (s, 1 H), and 6.4–7.2 (m, 6 H). Irradiation of 4 in benzene both with and without benzophenone sensitization likewise produced 10.



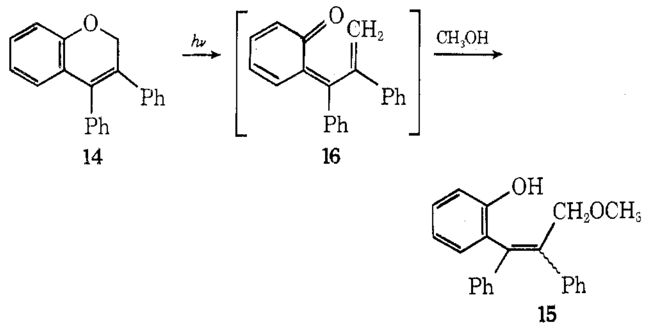
The observed results are best rationalized in terms of a photochemical ring opening of 4 to give an *o*-quinoneallide intermediate (11).[30] The fate of 11 depends on the experimental conditions. The primary mode of reaction (i.e., formation of 5 and 6) corresponds to 1,4 and 1,6 addition of methanol across the C–C double bonds of 11. Allyl phenol 9 is apparently formed by 1,4 photoreduction of 11 (Corex filter). Similar photoreductions of *o*-quinoneallide intermediates have been observed by Becker and Kolc[30] and provides reasonable chemical analogy. In nonreactive solvents such as acetone (or benzene), the primary reaction path corresponds to a 1,7-sigmatropic hydrogen shift.

We have also examined the photobehavior of the related 2,2-diphenylchromene system 12. Unlike the complex photochemistry observed with 4, in which a plethora of products is obtained, the photochemistry of 12 was relatively simple. Irradiation of 12 in methanol gave a single photoad-

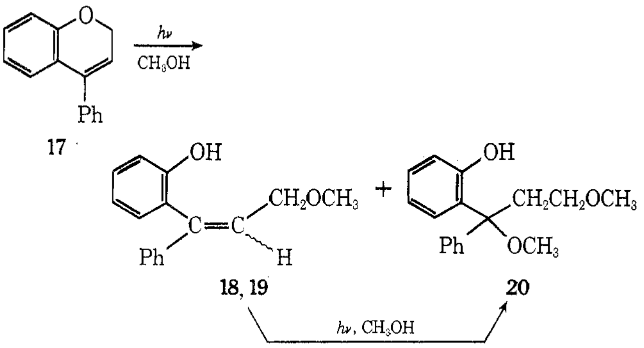


duct **13** which was unstable at room temperature and slowly reverted to starting material when left in the dark. The identity of **13** was established from its characteristic spectral properties (see Experimental Section). Irradiation of **12** in benzene (Pyrex) produced a deep red color which slowly disappeared upon sitting in the dark at room temperature. NMR analysis of the photolysate after removal of the solvent indicated that only starting chromene **12** was present. Attempts to trap the red-colored species with methanol in the dark failed. We can only suggest that thermal reversion of the labile *o*-quinoneallide intermediate is more rapid than 1,4 addition of methanol.

The photochemistry of the related 3,4-diphenylchromene (**14**) was also examined. Irradiation of **14** in methanol with Corex-filtered light gave a single photoadduct. Based on its spectral data, this compound has been identified as the 1,6-methanol adduct **15**. Here again, simple addition of methanol to the intermediate *o*-quinoneallide **16** best rationalizes the observed result.

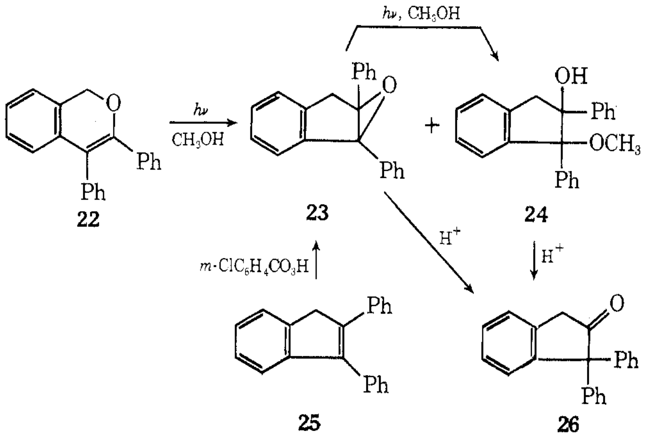


The photochemical ring opening reaction of 4-phenylchromene (**17**) was also studied. Irradiation of **17** in methanol with Corex-filtered light gave a mixture of three photoproducts. On the basis of their spectral properties (see Experimental Section) these compounds were identified as *cis*- and *trans*-1-phenyl-1-(*o*-hydroxyphenyl)-3-methoxy-1-propene (**18** and **19**) and 1-phenyl-1-(*o*-hydroxyphenyl)-1,3-dimethoxypropane (**20**). Photoadduct **20** was shown to be a secondary photoproduct derived from further irradiation of **18** or **19**. The products isolated in this case can also be accommodated in terms of 1,6 addition of methanol to the initially formed *o*-quinoneallide intermediate.

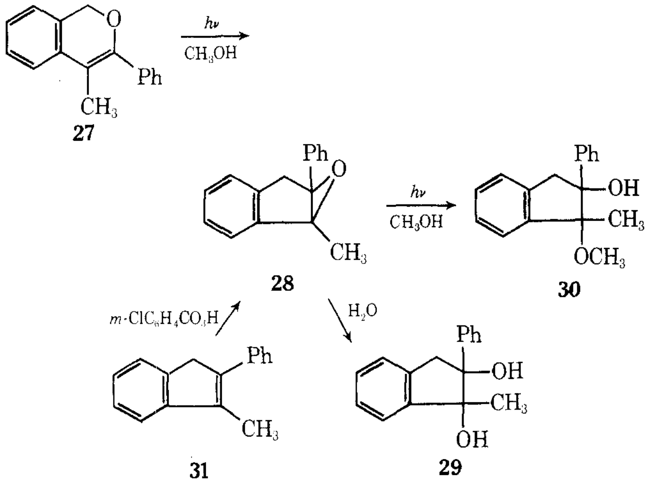


All of the aforementioned reactions of the 2*H*-chromene system conform to the same pattern. Electronic excitation results in a photochemical ring opening to give an *o*-quinoneallide intermediate. Our results, as well as those of other investigators,[30,37-40] indicate that the initially produced *o*-quinoneallide intermediates are rapidly attacked by alcoholic solvents. The distinction between 1,4- and 1,6-methanol addition may well represent a measure of the steric hindrance to attack at the 4 or 6 position of the *o*-quinoneallide intermediate. In no case was evidence found to suggest the involvement of an oxabicyclo[3.1.0]hexene intermediate. This set of affairs differs markedly with the results we have obtained with the corresponding isochromene system. Electronic excitation of this ring system was found to result in a smooth rearrangement giving indene epoxides as the major photoproducts.

Irradiation of 3,4-diphenylisochromene (**22**) in methanol through Pyrex using a 450-W Hanovia lamp gave two major products whose relative yields varied with the time of irradiation. When a 0.003 *M* solution of **22** was irradiated for 8 hr, ca. 50% of starting material was consumed and the two products, isolated by preparative thick layer chromatography, were shown to be 2,3-epoxy-2,3-diphenylindan (**23**), mp 89–90° (80%) and 2-hydroxy-3-methoxy-2,3-diphenylindan (**24**, 20%). The products were identified by their spectral data [NMR (**23**) τ 5.44 (broad s, 2 H) and 2.2–3.2 (m, 14 H); (**24**) τ 5.82 (s, 3 H), 5.35 (s, 2 H), 5.50 (s, 1 H, exchanged with D_2O), and 2.40–3.30 (m, 14 H)] and by comparison with authentic samples which were independently prepared by the peracid epoxidation of 2,3-diphenylindene (**25**). Treatment of **23** and/or **24** with a grain of *p*-toluenesulfonic acid in chloroform resulted in their quantitative rearrangement to 1,1-diphenyl-2-indanone (**26**). Irradiation of the solution for an additional 8 hr gave a mixture containing mainly **24** with traces of **23**, suggesting that **24** is formed in a secondary photoreaction of **23**. This was independently verified by irradiating a pure sample of **23** in methanol and obtaining a quantitative yield of the ring-opened product **24**. Although it is conceivable that the formation of **24** from **23** is an ionic reaction promoted by an acidic by-product formed adventitiously, this appears not to be the case. Photochemical oxidation of methanol to formic acid which then promotes an acid-catalyzed reaction has been reported in the literature[41] and merits consideration. This possibility, however, was eliminated by the finding that epoxide **23** is quantitatively converted into 1,1-diphenyl-2-indanone (**26**) on treatment with acidic methanol. The absence of **26** in the direct irradiation of **22** eliminates this ionic path. Also, the presence of sodium carbonate in the reaction mixture did not inhibit the formation of **24** from **23**. We conclude, therefore, that the ring-opening reaction of **23** is a photochemical process and not an acid-catalyzed reaction. There have been several cases reported in the literature where oxiranes have been noted to undergo photoaddition with protic solvents.[42-45] Tokumara and coworkers, for example, have reported that phenyloxirane undergoes photoaddition when 2-propanol, a substrate which is not readily oxidized to "acidic matter", is used as the solvent.[42] It would appear therefore, that epoxyindan **23** is another example of an epoxide which undergoes a bona fide photochemical ring-opening reaction.

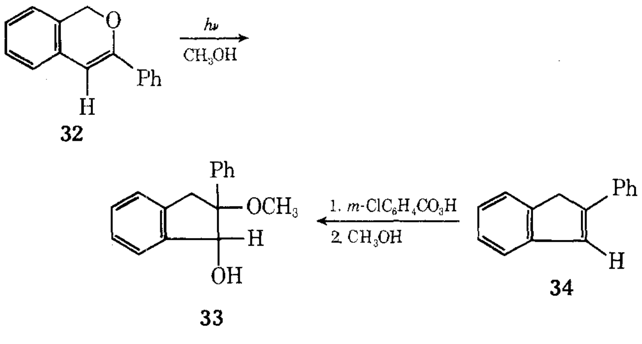


A similar set of reactions was observed with 3-phenyl-4-methylisochromene (**27**). Irradiation of **27** in methanol through Pyrex with a 450-W Hanovia lamp gave 2,3-epoxy-2-phenyl-3-methylindan (**28**) [NMR (CCl_4) δ 1.50 (s, 3 H), 3.40 (s, 2 H), and 6.9–7.7 (m, 9 H)] as the major photoproduct. Purification of epoxide **28** was not possible owing to the extreme ease with which it was converted into *trans*-2,3-dihydroxy-2-phenyl-3-methylindan (**29**). Further irradiation of **28** in methanol gave the ring-opened hydroxyalcohol **30** in high yield. All of these compounds were identified by comparison with authentic samples which were independently prepared by the epoxidation of 2-phenyl-3-methylindene (**31**).



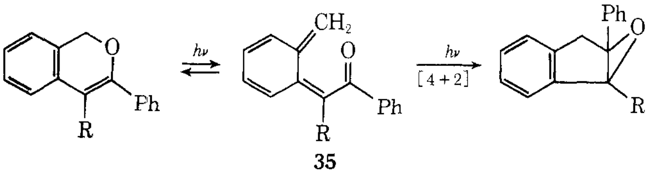
27 **28** **30** **31** **29**

The photochemical rearrangement of 3-phenylisochromene (**32**) was also examined. Irradiation of **32** in methanol for 20 hr with Pyrex-filtered light gave a single photoproduct, mp 103–105°. On the basis of its spectral data, this compound has been identified as *trans*-2-methoxy-3-hydroxy-2-phenylindan (**33**). This assignment was verified by comparison with an authentic sample prepared by treating the epoxide obtained from the peracid oxidation of 2-phenylindene (**34**) with methanol. In this case, the initially formed epoxide was converted to the ring-opened product **33** during the course of the irradiation.



32 **33** **34**

The formation of the indene epoxides is best explained by a photochemical ring opening of the isochromene ring to give an *o*-quinonoidal intermediate **35**, which can either revert to starting material or undergo a subsequent intramolecular [4 + 2] photocycloaddition reaction. The above reactions appear to proceed from the singlet state, since the photolyses could not be sensitized or quenched with standard triplet quenchers. The low quantum efficiences observed (i.e., $\Phi_{22} = 0.02$, $\Phi_{27} = 0.002$, $\Phi_{32} = 0.004$) are fully compatible with a two-photon process, in which the initially produced *o*-quinonoidal intermediate **35** partitions itself between starting material and product. It should be pointed out, however, that the low quantum efficiencies do not in any way require a two-photon process.

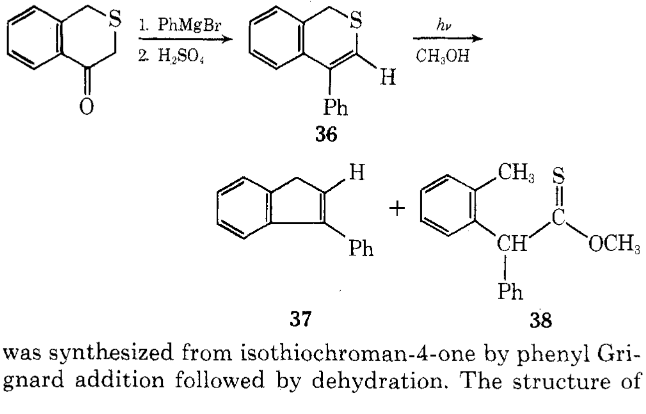


35

As was pointed out earlier, irradiation of the 2*H*-chromene ring produces an *o*-quinoneallide intermediate which does not undergo an intramolecular [4 + 2] cycloaddition, but rather is attacked by methanol to give a phenolic ether. Irradiation of the closely related isochromene system, on the other hand, results in the formation of an indene epoxide. The two systems behave similarly during the first phase of the photolysis. Both systems undergo an initial photochemical ring-opening reaction to produce an *o*-quinoidal intermediate. The difference in behavior of the two systems may be related to the difference in reactivity of the *o*-quinoidal intermediates. Michael addition of methanol to the labile *o*-quinoneallide obtained from the 2*H*-chromene system would be expected to occur quite readily. This facile conjugate addition destroys the necessary chromophore for the subsequent [4 + 2] photocycloaddition reaction. Attack by methanol on the *o*-quinoidal intermediate obtained from the isochromene system is not as rapid, and consequently this species is long enough lived to absorb another photon of light and undergo an intramolecular photocycloaddition reaction. An alternate explanation which could also rationalize the difference in the photochemical behavior of the two systems is based on conformational control of reactivity. The [4 + 2] photochemical cycloaddition in the hexatriene system has been shown to be derived from the s-trans,s-cis conformation.[3] It is perfectly possible to rationalize the difference between chromene and isochromene as being due to conformational preferences in the open, ketonic form.

Another point which is worthy of mention is a report by Griffin and coworkers on the photoisomerization of indene oxide into isochromene.[46] Although this transformation formally corresponds to the reverse reaction of that described above, the rearrangement has been proposed to proceed by a different path involving initial fission of the C–C bond of the oxirane ring followed by a hydrogen shift.[47] It should be kept in mind that the isochromene indene oxide photoreactions do not have the same two species in equilibrium and consequently microscopic reversibility would not be expected to apply.[48]

Although the photochemistry of 1,2-dihydronaphthalene[49,50] and its hetero analogs[34,51–54] has received some attention, relatively little is known about the photochemical behavior of heterocyclic systems isoelectronic with the isochromene ring. We therefore turned our attention to the related isothiochromene system in order to make a comparison with the photochemistry of the above isochromenes. In the present instance, the photochemical behavior of 4-phenylisothiochromene (**36**) was examined. This compound was synthesized from isothiochroman-4-one by phenyl Grignard addition followed by dehydration. The structure of

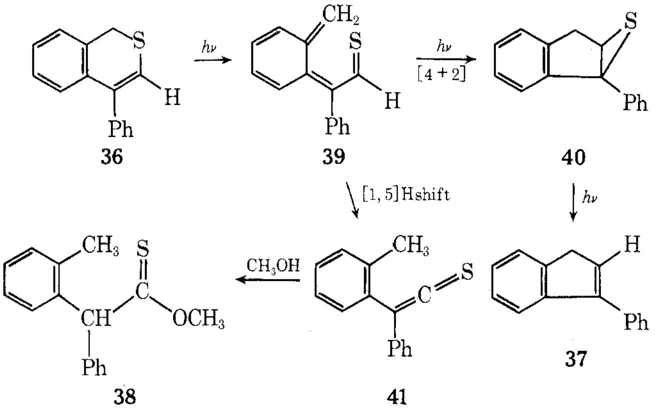


36 **37** **38**

36 was elucidated on the basis of the physical and chemical data: NMR ($CDCl_3$) δ 3.86 (s, 2 H), 6.50 (s, 1 H), and 6.9–7.4 (m, 9 H); uv 325 and 243 nm (ϵ 2800 and 7900).

Irradiation of **36** in dilute methanol solution using a 450-W Hanovia mercury arc with a Pyrex filter gave a mixture of two compounds. Preparative thick layer chromatography of the crude photolysate permitted the purification and isolation of the two components. The products were identified as 3-phenylindene (**37**) and methyl phenyl (*o*-tolyl)thionoacetate (**38**). In addition, a significant quantity of elemental sulfur was isolated from the thick layer plate. The major component, **37** (51%), was identified by comparison with an authentic sample.[55] The minor product (6%) was assigned structure **38** on the basis of its spectral data: ir (CCl_4) 8.14 and 8.40 μ (S=$COCH_3$);[56] NMR ($CDCl_3$) δ 2.22 (s, 3 H), 4.03 (s, 3 H), 5.64 (s, 1 H), and 6.9–7.4 (m, 9 H); MS *m/e* 256, 224, 181 (base), 169, 165, and 161.

The products formed by photolysis of **36** with Pyrex-filtered light are consistent with a photochemical ring opening of **36** to give an *o*-quinoidal intermediate (**39**). This transient species undergoes a subsequent [4 + 2] intramolecular photocycloaddition to give episulfide **40** which loses sulfur on further irradiation. The photochemical extrusion of sulfur from episulfides is a well-known photoreaction[57] and provides reasonable analogy for the final step. The formation of **38** from **36** probably proceeds via a [1,5] hydrogen transfer from **39** to give **41**, which is subsequently attacked by methanol.



The major photoreaction obtained with 4-phenylisothiochromene is quite similar to that encountered with the closely related isochromene system. These reactions may be visualized as being analogous to the photochemical transformation of 1,2-dihydronaphthalenes into benzobicyclo[3.1.0]hexenes.[49,50]

Experimental Section

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.

2,2-Dimethylchromene (4) was prepared in 66% yield by the method of Shriner and Sharp[58] as a clear oil: bp 64° (1.5 mm) [lit.[58] bp 79–80° (2.5 mm)]; NMR (CCl_4) δ 1.35 (s, 6 H), 5.38 (d, 1 H, J = 10 Hz), 6.13 (d, 1 H, J = 10 Hz), and 6.5–7.0 (m, 4 H); ir (neat) 3.33, 6.07, 6.20, 6.71, 6.85, 7.26, 7.83, 7.90, 8.20, 8.90, 9.68, 10.37, 12.90, 13.45, and 14.05 μ; uv (methanol) 308, 273, and 264 nm (ϵ 2650, 3100, and 3920).

2,2-Diphenylchromene (12) was prepared in 67% yield by the method of Cottam et al.[59] as a white solid: mp 92–93° (lit.[58] mp 93–94°); NMR (CCl_4) δ 6.11 (d, 1 H, J = 10.5 Hz), 6.66 (d, 1 H, J = 10.5 Hz), 6.80–7.7 (m, 14 H); ir (KBr) 3.23, 6.04, 6.17, 6.68 μ; uv (acetonitrile) 307, 275, 265, 260, 255, and 248 nm (ϵ 3000, 4790, 6150, 5960, 5410, and 4980); MS *m/e* 284 (M^+), 207 (base), 178, 91, and 77.

3,4-Diphenylchromene (14) was prepared by adding 4-phenyl-3-chromanone (0.86 g)[60] in 30 ml of ether to a Grignard reagent prepared from 0.624 g of bromobenzene and 0.1 g of magnesium turnings in 20 ml of ether. The mixture was heated at reflux for 3 hr and then decomposed with 20% aqueous ammonium chloride. The solution was extracted with ether and the ethereal extracts were dried over magnesium sulfate. Removal of the solvent left 1.09 g of a yellow oil which was immediately taken up in 20 ml of pyridine. Phosphorus oxychloride (3.0 ml) was added to the above solution, which was then allowed to reflux for 3 hr. The solution was cooled and the excess phosphorus oxychloride was decomposed by the addition of water. The mixture was extracted with ether, and the ether layer was washed with 10% aqueous hydrochloric acid, dried, and concentrated under reduced pressure to leave behind an oily residue. Chromatography of the oil on an alumina column with benzene as the eluent gave 3,4-diphenylchromene (**14**) as a crystalline solid: mp 133–134° (lit.[60] mp 134°); NMR (CCl_4) δ 5.12 (s, 2 H) and 6.8–7.5 (m, 14 H).

4-Phenylchromene (17) was prepared by adding an excess of lithium aluminum hydride to a solution containing 450 mg of 4-phenyl-3-chromanone[60] in 25 ml of anhydrous ether. The resulting gray suspension was stirred at room temperature for 6 hr. The excess lithium aluminum hydride was destroyed by the addition of 2 ml of water and the inorganic salts were removed by filtration. The ether layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The residue obtained was immediately dehydrated according to the procedure of Dauben and Boswell.[61] The above alcohol was dissolved in 15 ml of pyridine and the solution was cooled to 0°. To this cooled solution was added 5 ml of phosphorous oxychloride. The solution was allowed to warm to room temperature and was stirred for an additional 2 hr. At the end of this time, water was carefully added to the red solution. The solution was extracted with ether and the combined ether layers were washed with 10% aqueous hydrochloric acid, followed by water, and then dried over magnesium sulfate. Removal of the solvent left 360 mg of 4-phenylchromene as a clear oil: NMR (CCl_4) δ 4.68 (d, 2 H, J = 4.0 Hz), 5.58 (t, 1 H, J = 4.0 Hz), and 6.58–7.24 (m, 9 H).[35]

3,4-Diphenylisochromene (22). A 2.5-g sample of 3-phenylisochromanone was added at 0° to a Grignard solution prepared by treating 500 mg of magnesium turnings with 2.5 g of bromobenzene in 15 ml of anhydrous ether. The mixture was stirred at room temperature for 1 hr and was then heated at reflux for an additional 2 hr. After cooling, the mixture was poured onto 5 ml of concentrated sulfuric acid suspended on crushed ice. The mixture was then extracted with ether and the ethereal extracts were washed with water, followed by a sodium bicarbonate solution (10%), then dried over magnesium sulfate and concentrated under reduced pressure to an amber oil. The oil was dissolved in 10 ml of glacial acetic acid which contained 10 drops of water. To this mixture was added 1 ml of concentrated sulfuric acid. The dark brown mixture was kept at 75° for 10 min and was then poured onto ice and extracted with ether. The ethereal extracts were washed several times with water, followed by a saturated sodium chloride solution. The solution was dried over magnesium sulfate and concentrated under reduced pressure to give 3.2 g of a dark oil. The oil was chromatographed on 300 g of silica gel using 5% ether in cyclohexane as the eluent. Removal of the solvent left 1.48 g (45%) of 3,4-diphenylisochromene: mp 92–94°; ir (KBr) 6.22, 6.75, 8.07, 9.20, 10.65, 13.12, 14.22, and 14.46 μ; uv (methanol) 316 nm (ϵ 12,250) and 232 (12,900); NMR ($CDCl_3$) τ 4.78 (s, 2 H) and 2.2–3.4 (m, 14 H).

Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.50; H, 5.90.

3-Phenyl-4-methylisochromene (27). A solution containing 500 mg of 3-phenylisochromanone in 10 ml of anhydrous ether was added to a Grignard solution prepared by treating 270 mg of magnesium turnings with 1.6 g of methyl iodide in 40 ml of anhydrous ether. The mixture was allowed to stir at room temperature for 8 hr and the excess Grignard reagent was decomposed with 10% sulfuric acid. The mixture was extracted with ether and the organic layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a yellow oil which proved to be a mixture of isomeric alcohols: NMR ($CDCl_3$) δ 1.15 (s), 1.37 (s), 2.41, (s, OH), 4.50 (s), 4.90 (s), and 6.8–7.8 (m, 9 H); ir (neat) 2.90, 3.34, 6.68, 6.90, 7.30, 8.20 μ. The mixture of alcohols was subsequently dehydrated by stirring the mixture with 30 ml of 10% sulfuric acid in acetic acid for 2 min. Addition of water to the above solution followed by extraction with ether gave 250 mg

(50%) of 3-phenyl-4-methylisochromene, mp 84–85°, upon removal of the solvent. The structure of this material was assigned on the basis of its analytical and physical properties: ir (KBr) 6.15, 6.25, 6.75, 6.91, 7.30, 8.09, 8.28, 9.05, and 9.30 μ; NMR ($CDCl_3$) δ 2.13 (s, 3 H), 5.12 (s, 2 H), and 7.0–7.7 (m, 9 H); MS *m/e* 222 (M^+), 207, 193, 179 (base), 115, 105, 91, and 77; uv (methanol) 310 and 232 nm (ε 14,900 and 15,700).

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.39; H, 6.44.

3-Phenylisochromene (32). To a solution containing 400 mg of 3-phenylisochromanone in 20 ml of methanol was added 100 mg of sodium borohydride. After stirring at room temperature for 90 min, the methanol was removed under reduced pressure. Ether was then added to the residue and the organic phase was washed with water, then dried over magnesium sulfate and concentrated under reduced pressure to give 360 mg of a white solid (89%): mp 95–110°; NMR ($CDCl_3$) δ 2.0 (s, OH), 4.3–5.0 (m, 4 H), and 6.9–7.6 (m, 9 H); ir (KBr) 2.90, 6.72, 6.90, 7.32, 9.14, 9.42 μ. The impure alcohol was dehyrated without further purification using 450 mg of Burgess reagent[62] in refluxing benzene for 30 min. The mixture was diluted with ether, washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a crude solid which was recrystallized from 95% ethanol to give 280 mg (75%) of 3-phenylisochromene (**32**) as a white solid: mp 122–124°; NMR ($CDCl_3$) δ 5.17 (s, 2 H), 6.41 (s, 1 H), 6.8–7.8 (m, 9 H); ir (KBr) 6.18, 6.74, 6.90, 7.21, 7.84, 8.31, and 9.42 μ; uv (methanol) 323 and 235 nm (ε 14,700 and 14,600); MS *m/e* 208 (M^+), 181, 179 (base), 165, 152, 105, and 77.

Anal. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.28; H, 5.82.

Irradiation of 2,2-Dimethylchromene. A solution containing 442 mg of 2,2-dimethylchromene in 160 ml of methanol was irradiated under an argon atmosphere with a 450-W Hanovia lamp equipped with a Pyrex filter for 3 hr. Removal of the solvent under reduced pressure left a crude oil which was subjected to thick layer chromatography. In addition to recovered starting material (43%), two new compounds were obtained as clear oils. The major component (15%) was assigned as 4-methoxy-4-(2-hydroxyphenyl)-2-methylbut-2-ene (**5**): NMR (CCl_4) δ 1.64 (s, 6 H), 3.20 (s, 3 H), 4.87 (d, 1 H, *J* = 9.0 Hz), 5.24 (d, 1 H, *J* = 9.0 Hz), and 6.4–7.0 (m, 5 H). The minor component (7%) was assigned as 3-methoxy-3-methyl-1-(2-hydroxyphenyl)but-1-ene (**6**): NMR (CCl_4) δ 1.20 (s, 6 H), 3.10 (s, 3 H), 5.64 (d, 1 H, *J* = 13.0 Hz), 6.28 (d, 1 H, *J* = 13.0 Hz), 6.54–7.16 (m, 4 H), and 7.30 (s, 1 H); ir (CCl_4) 3.05, 3.38, 6.35, 6.73, 6.90, 7.28, 7.32, 7.80, 8.18, 8.70, 9.28, 9.48, 10.62, 11.20, 11.85, and 14.02 μ; MS *m/e* 178, 160, 145 (base), 115, 91, and 77. Continued irradiation of the reaction mixture gave **6** as the major photoproduct with only traces of **5**, suggesting that at least part of **6** is formed from the secondary photoisomerization of **5**. Both methanol adducts slowly reverted to starting material **4** when left in the dark. In contrast to the complex behavior obtained from the direct irradiation of 2,2-dimethylchromene, the xanthone-sensitized photolysis cleanly gave the terminal ether **6** in high yield. Irradiation of a solution containing 397 mg of 2,2-dimethylchromene and 202 mg of xanthone in 160 ml of methanol with a 450-W Hanovia lamp equipped with a Pyrex filter for 3 hr gave 360 mg of terminal ether **6** on removal of the solvent. A small amount (35 mg) of unreacted chromene was also present.

Irradiation of 2,2-dimethylchromene in neat acetone gave 3-methyl-1-(2-hydroxyphenyl)buta-1,3-diene (**10**) as the only photoproduct. A solution containing 410 mg of 2,2-dimethylchromene in 200 ml of acetone was irradiated with a 550-W Hanovia lamp equipped with a Pyrex filter for 2 hr. Removal of the solvent left a yellow oil which was chromatographed on a thick layer plate using methylene chloride as the eluent. In addition to unreacted starting material (206 mg) the only other product obtained was 80 mg of a clear oil whose structure is assigned as 3-methyl-1-(2-hydroxyphenyl)buta-1,3-diene (20%): NMR (CCl_4) δ 1.88 (s, 3 H), 4.90 (m, 2 H), 5.30 (broad s, 1 H), 6.44–7.30 (m, 6 H); MS *m/e* 161, 145 (base), 127, 115, 91, and 77.

Irradiation of 200 mg of **4** in 150 ml of methanol for 3 hr using a 450-W Hanovia lamp equipped with a Corex filter followed by removal of the solvent under reduced pressure gave a pale yellow residue. This material was subjected to thick layer chromatography and four products were obtained. The component present in the smallest quantity (4%) was identified as photoadduct **6** by comparison of its spectral properties with those of 3-methoxy-3-methyl-1-(2-hydroxyphenyl)but-1-ene (**6**). The major component isolated from the thick layer plate was identified as 2,3-dimethoxy-2-methyl-4-(*o*-hydroxyphenyl)butane (**7**, 19%): NMR ($CDCl_3$) δ 1.08 (s, 3 H), 1.21 (s, 3 H), 1.6–2.2 (m, 2 H), 3.11 (s, 3 H), 3.25 (s, 3 H), 4.40 (dd, 1 H, *J* = 7.3 and 3.3 Hz), 6.5–7.2 (m, 4 H), and 7.37 (s, 1 H). The next major fraction collected from the thick layer plate was identified as 2-methyl-4-(*o*-hydroxyphenyl)but-2-ene (**9**, 17%) on the basis of its NMR spectrum ($CDCl_3$): δ 1.69 (s, 6 H), 3.17 (d, 2 H, *J* = 8.0 Hz), 4.53 (s, 1 H), 5.12 (t, 1 H, *J* = 8.0 Hz), and 6.4–6.9 (m, 4 H). The remaining material isolated from the plate was identified as 2-methyl-3-methoxy-4-(*o*-hydroxyphenyl)but-1-ene (**8**, 8%): NMR ($CDCl_3$) δ 1.66 (s, 3 H), 2.30 (dd, 1 H, *J* = 15 and 8.0 Hz), 2.60 (dd, 1 H, *J* = 15 and 8.0 Hz), 3.33 (s, 3 H), 4.26 (t, 1 H, *J* = 8.0 Hz), 4.64 (d, 2 H), 6.5–7.2 (m, 4 H), and 7.20 (s, 1 H).

Irradiation of 2,2-Diphenylchromene in Methanol. A solution containing 228 mg of 2,2-diphenylchromene in 170 ml of methanol was irradiated under an argon atmosphere using a 450-W Hanovia lamp equipped with a Pyrex filter for 2 hr. Removal of the solvent left a yellow oil which was purified by thick layer chromatography. The major band contained 207 mg of a clear oil whose structure was assigned as 3-methoxy-3-(2-hydroxyphenyl)-1,1-diphenylpropene (**13**) on the basis of its characteristic spectra: ir (CCl_4) 2.97, 3.30, 6.32, 6.74, 6.94, 7.33, 8.10, 9.05, 9.40, 10.51, 10.69, 11.01, and 14.40 μ; NMR (CCl_4) δ 3.20 (s, 3 H), 4.72 (d, 1 H, *J* = 8.0 Hz), 6.12 (d, 1 H, *J* = 8.0 Hz), 6.4–7.4 (m, 14 H), and 7.64 (broad s, 1 H); MS *m/e* 316, 298, 296, 284, 207 (base), 178, 121, 119, 117, 83, and 77. When **13** (20 mg) was heated in methanol in the dark, the only product isolated was 2,2-diphenylchromene (**12**).

Irradiation of 3,4-Diphenylchromene in Methanol. A solution containing 50 mg of 3,4-diphenylchromene in 160 ml of methanol was irradiated under an argon atmoephere using a 450-W Hanovia lamp equipped with a Corex filter for 190 min. The solvent was removed under reduced pressure and the resulting oil was purified by thick layer chromatography. The major band contained 42 mg of a clear oil whose structure was assigned as 3-methoxy-1-(2-hydroxyphenyl)-1,2-diphenylpropene (**15**) on the basis of its characteristic spectra: ir (CCl_4) 3.25, 3.43, 6.25, 6.68, 8.36, 8.97, 9.08, 10.39, and 14.23 μ; NMR (CCl_4) δ 3.28 (s, 3 H), 4.67 (s, 2 H), 7.0–7.9 (m, 14 H), 8.90 (m, 1 H).

Irradiation of 4-Phenylchromene in Methanol. A solution containing 130 mg of 4-phenylchromene in 12 ml of methanol was irradiated in a quartz tube which had been purged with argon. Irradiation of the sample for 4 hr using a 450-W Hanovia lamp equipped with a Corex filter gave 185 mg of a crude residue. The thick oil obtained was subjected to thick layer chromatography using a cyclohexane–ether mixture as the eluent. The first band obtained (R_f 0.67) contained 64 mg of a clear oil whose structure was assigned as 1,3-dimethoxy-1-(2-hydroxyphenyl)-1-phenylpropane (**20**): ir (CCl_4) 3.0, 3.29, 3.40, 3.45, 6.19, 6.31, 6.73, 6.82, 6.91, 7.20, 7.71, 8.08, 8.50, 8.66, 8.96, 9.45, 10.29, 10.96 μ; NMR (CCl_4) δ 2.48 (t, 2 H, *J* = 7.0 Hz), 3.2 (m, 2 H), 3.14 (s, 3 H), 3.20 (s, 3 H), 6.58–7.12 (m, 9 H), and 7.92 (s, 1 H); MS *m/e* 240, 238, 209, 208, 207 (base), 181, 179, 178, 165, 152, and 131. The second band isolated from the thick layer plate (R_f 0.57) contained 43 mg of a clear oil whose spectral properties indicated it to be a 1:1 mixture of *cis*- and *trans*-3-methoxy-1-(2-hydroxyphenyl)-1-phenylpropene: NMR (CCl_4) δ 3.24 (s, 3 H), 3.76 (d, *J* = 7.0 Hz), 3.97 (d, *J* = 6.5 Hz), 5.29 (broad s, OH), 5.70 (s, OH), 5.94 (t, *J* = 6.5 Hz), 6.32 (t, *J* = 7.0 Hz), 6.6–7.4 (m, 9 H); MS *m/e* 240, 238, 224, 209, 208, 207 (base), 181, 178, 165, 152, 131, and 115. When the mixture of *cis*- and *trans*-3-methoxy-1-(2-hydroxyphenyl)-1-phenylpropene (**18** and **19**) was photolyzed in methanol for 3 hr, dimethoxypropane **20** was formed in quantitative yield.

Irradiation of 3,4-Diphenylisochromene in Methanol. A solution containing 80 mg of 3,4-diphenylisochromene in 120 ml of methanol under a nitrogen atmosphere was irradiated with a 450-W Hanovia lamp equipped with a Pyrex filter for 13 hr. Removal of the solvent left a crude residue which was separated into two major components by thick layer chromatography. The faster moving band contained 47 mg (59%) of a white solid, mp 89–90°, whose structure was assigned as 2,3-epoxy-2,3-diphenylindan (**23**) on the basis of its physical properties and by comparison with an authentic sample: ir (CCl_4) 6.92, 7.95, and 11.05 μ; NMR ($CDCl_3$) τ 5.44 (broad s, 2 H) and 3.2–2.20 (m, 14 H). An authentic sample of **23** was prepared by the peracid oxidation of 2,3-diphenylindene. A mixture containing 400 mg of 2,3-diphenylindene[63] (**25**) and 400 mg of *m*-chloroperbenzoic acid in 20 ml of methylene chloride was kept at −8° for 14 hr. At the end of this time a saturated sodium bicarbonate solution was added and the mixture was then extracted with ether. The extracts were dried over magnesium sulfate and concentrated under reduced pressure to give a crystalline solid. This material was purified by thick layer chromatography to give 205 mg (48%) of a white solid, mp 89–90°, whose physical properties were identical in every detail with those of the sample of 2,3-epoxy-2,3-diphenylindan isolated from the photolysis of 3,4-diphenylisochromene.

The slower moving component (25 mg, 27%) isolated from the thick layer plate was a clear oil whose structure was assigned as *trans*-2-hydroxy-3-methoxy-2,3-diphenylindan (**24**) on the basis of its physical and chemical properties: ir (CCl_4) 2.85, 6.91, 7.38, 7.95, 9.35, 9.80, 11.0, and 14.40 μ; uv (methanol) 287, 274, and 260 nm (ϵ 790, 650, and 725); NMR ($CDCl_3$) τ 5.82 (s, 3 H), 5.35 (s, 2 H), 5.50 (s, 1 H, exchanged with D_2O), and 3.3–2.40 (m, 14 H). Treatment of a 14-mg sample of *trans*-2-hydroxy-3-methoxy-2,3-diphenylindan in 0.5 ml of chloroform-*d* with a grain of *p*-toluenesulfonic acid for 9 hr resulted in the quantitative formation of 1,1-diphenylindanone (**26**): mp 120–121° (lit.[64] mp 120–121°); ir (CCl_4) 5.75, 6.22, 6.75, 6.98, 8.00, 8.44, 9.70, and 14.50 μ; uv (methanol) 305, 281, 273, and 268 nm (ϵ 675, 1420, 1440, and 1220); NMR ($CDCl_3$) τ 5.32 (s, 2 H) and 3.0–2.0 (m, 14 H).

Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.42; H, 5.66.

A similar reaction occurred when 2,3-epoxy-2,3-diphenylindan was treated with *p*-toluenesulfonic acid; however, when a 42-mg sample of 2,3-epoxy-2,3-diphenylindan was stirred with 4.0 g of silica gel in 20 ml of 5% ether–cyclohexane, the only product obtained was *trans*-2,3-dihydroxy-2,3-diphenylindan: ir (CCl_4) 2.80, 2.90, 6.22, 6.93, 9.50, 11.0, and 14.20 μ; uv (methanol) 305, 281, 273, and 268 nm (ϵ 6.75, 1420, 1440, and 1220); NMR ($CDCl_3$) τ 5.06–5.96 (AB quartet, 2 H, J = 17 Hz), 4.80 (s, 1 H, exchanged with D_2O), 4.30 (s, 1 H, exchanged with D_2O), and 2.40–3.40 (m, 14 H). Treatment of this diol with *p*-toluenesulfonic acid in chloroform-*d* gave a quantitative yield of 1,1-diphenyl-2-indanone (**26**).

2,3-Epoxy-2,3-diphenylindan (**23**, 15 mg) was quantitatively converted into *trans*-2-hydroxy-3-methoxy-2,3-diphenylindan by carrying out the irradiation in 6 ml of methanol for 15 hr. The conversion of epoxide **23** to **24** still proceeded when the irradiation was carried out in the presence of sodium bicarbonate.

Irradiation of 3-Phenyl-4-methylisochromene in Methanol. A solution containing 200 mg of 3-phenyl-4-methylisochromene (**27**) in 150 ml of methanol was irradiated under a nitrogen atmosphere with a 450-W Hanovia lamp equipped with a Pyrex filter for 23 hr. Removal of the solvent left a pale oil which was shown to contain 2,3-epoxy-2-phenyl-3-methylindan (**28**) as the major component by NMR analysis: NMR (CCl_4) δ 1.50 (s, 3 H), 3.40 (s, 2 H), and 6.9–7.7 (m, 9 H). Purification of the epoxide was not possible owing to the extreme ease with which it was converted into *trans*-2,3-hydroxy-2-phenyl-3-methylindan (**29**, 170 mg, 78%), mp 128–129°. The structure of epoxide **28** was verified by comparison with an authentic sample. A 200-mg sample of 2-phenyl-3-methylindene (**31**)[65] was dissolved in 5 ml of methylene chloride and cooled at 0°. To this solution was added 200 mg of *m*-chloroperbenzoic acid and the resulting solution was stirred at 0° for 25 min. The *m*-chlorobenzoic acid that had formed was filtered and the solvent was removed under reduced pressure to leave behind a pale oil whose NMR spectrum was identical with that obtained from the irradiation of 3-phenyl-4-methylisochromene (**27**). If the epoxidation reaction mixture was worked up by washing the methylene chloride layer with a dilute sodium bicarbonate solution the only product formed was *trans*-2,3-phenyl-3-methylindan: mp 128–129°; ir (KBr) 3.05, 6.25, 6.35, 6.70, 6.92, 7.35, 9.52 μ; NMR ($CDCl_3$) δ 3.12 (d, 1 H, J = 16.0 Hz), 3.65 (d, 1 H, J = 16.0 Hz), 3.94 (broad s, 2 H, exchanged with D_2O), and 7.2–7.64 (m, 9 H); MS *m/e* 222, 204, 195, 179 (base), 165, 115, and 77.

Irradiation of 100 mg of 3-phenyl-4-methylisochromene (**27**) in 150 ml of methanol with a 550-W Hanovia lamp for 32 hr did not give any significant quantities of epoxyindan **28** (<5%). Instead, the major product isolated from the thick layer plate was identified as *trans*-2-hydroxy-3-methoxy-2-phenyl-3-methylindan (**30**): NMR ($CDCl_3$) δ 1.06 (s, 3 H), 3.12 (s, 3 H), 3.38 (s, 2 H), 3.82 (broad s, 1 H, exchanged with D_2O), and 6.9–7.8 (m, 9 H).

Irradiation of 3-Phenylisochromene in Methanol. A solution containing 50 mg of 3-phenylisochromene (**32**) in 150 ml of methanol was irradiated under a nitrogen atmosphere with a 550-W Hanovia lamp equipped with a Pyrex filter for 20 hr. Removal of the solvent under reduced pressure left a yellow oil which was recrystallized from 95% ethanol to give 45 mg (87%) of a white solid, whose structure was assigned as *trans*-2-methoxy-3-hydroxy-2-phenylindan (**33**) on the basis of its physical properties and by comparison with an independently synthesized sample: mp 103–105°; ir (KBr) 6.18, 6.70, 6.89, 7.2, 7.91, 8.28, 9.41, 9.72, 10.32, 10.65, 10.89, 11.10, 11.48, 11.90, 12.30, 13.10, 13.32, 13.75, and 14.60 μ; NMR ($CDCl_3$) δ 3.10 (s, 3 H), 3.90 (broad s, 1 H), 4.93 (s, 2 H), and 6.8–7.8 (m, 9 H). An authentic sample of **33** was prepared by treating 200 mg of 2-phenylindene[66] (**34**) with 200 mg of *m*-chloroperbenzoic acid in 15 ml of methylene chloride at 0° for 12 hr. The organic layer was then washed with a 10% sodium bicarbonate solution followed by water. The methylene chloride solution was then dried over magnesium sulfate and the solvent was removed under reduced pressure to give 180 mg of a clear oil whose NMR spectrum indicated it to be 2,3-epoxy-2-phenylindan: NMR ($CDCl_3$) δ 3.42 (broad s, 2 H), 4.26 (s, 1 H), and 7.0–7.7 (m, 9 H). Conversion of this epoxide to methoxy alcohol **33** was achieved by dissolving the epoxide in methanol containing a trace of *p*-toluenesulfonic acid and allowing the solution to stir for 30 min. Removal of the solvent under reduced pressure gave a crystalline solid which was recrystallized from 95% ethanol to give methoxy alcohol **33**, mp 103–105°. This material was identical in every detail with the major product obtained from the irradiation of 3-phenylisochromene. A mixture melting point was undepressed at 103–105°.

4-Phenylisothiochromene (36) was prepared by adding 2.0 g of isothiochroman-4-one[67] in 10 ml of ether to a Grignard reagent prepared from 3.84 g of bromobenzene and 0.6 g of magnesium turnings in 30 ml of ether. The mixture was allowed to stir at room temperature for 2 hr and was then decomposed by pouring onto a 10% sulfuric acid solution on crushed ice. The ether layer was dried over magnesium sulfate and concentrated under reduced pressure to give 1.25 g of a yellow oil: ir (CCl_4) 2.90, 6.22, 6.70, 6.90, 7.84 μ; NMR (CCl_4) δ 2.7–4.2 (m, 5 H) and 6.8–7.5 (m, 9 H). The crude 4-phenylisothiochroman-4-ol was used without further purification. The oil was dissolved in 45 ml of glacial acetic acid which contained 5 ml of concentrated sulfuric acid and was allowed to stir at room temperature for 1 min. At the end of this time 70 ml of water was added and the aqueous solution was extracted with ether. The ethereal extracts were washed with 10% sodium bicarbonate followed by water. The organic phase was then dried over magnesium sulfate and the solvent was removed under reduced pressure to leave behind a yellow oil. This residue was purified by thick layer chromatography using a 5% ether–pentane mixture as the eluent. The major component amounted to 725 mg of a pale yellow oil whose structure was assigned as 4-phenylisothiochromene (**36**) on the basis of its physical properties: ir (CCl_4) 6.23, 6.72, 6.92, 7.08, and 10.96 μ; NMR (CCl_4) δ 3.86 (s, 2 H), 6.50 (s, 1 H), and 6.9–7.4 (m, 9 H); uv (methanol) 325 and 243 nm (ϵ 2800 and 7930); MS *m/e* 224, 223, 193, 155 (base), 122, 120, 118 (base), and 83.

Anal. Calcd for $C_{15}H_{12}S$: C, 80.31; H, 5.39; S, 14.29. Found: C, 80.03; H, 6.04; S, 14.06.

Irradiation of 4-Phenylisothiochromene in Methanol. A solution containing 189 mg of 4-phenylisothiochromene in 450 ml of methanol under a nitrogen atmosphere was irradiated with a 450-W Hanovia lamp equipped with a Pyrex filter for 1 hr. Removal of the solvent under reduced pressure gave a yellow oil which was subjected to thick layer chromatography using hexane as the eluent. The fastest moving band amounted to 16 mg of elemental sulfur, mp 118°. The second band contained 78 mg (51%) of a clear oil whose structure was assigned as 3-phenylindene (**37**): ir (CCl_4) 3.26, 6.34, 6.72, 6.86, 6.92, 7.20, and 10.25 μ; NMR ($CDCl_3$) δ 3.38 (d, 2 H, J = 2.0 Hz), 6.38 (t, 1 H, J = 2.0 Hz), and 7.0–7.6 (m, 9 H). This material was identical in every detail with an authentic sample of 3-phenylindene.[55] The third component isolated from the thick layer plate (12 mg) was starting material. The last band isolated from the thick layer plate contained 12 mg of a pale yellow oil (6%) whose structure was assigned as methyl phenyl (*o*-tolyl)thionoacetate (**38**) on the basis of its physical properties: ir (CCl_4) 3.22, 3.38, 6.20, 6.65, 6.85, 8.14, 8.40, 8.79, 9.90, 13.01, 13.40, 13.56, 13.90, and 14.38 μ; NMR ($CDCl_3$) δ 2.22 (s, 3 H), 4.03 (s, 3 H), 5.64 (s, 1 H), and 6.9–7.4 (m, 9 H); MS *m/e* 256, 224, 223, 181 (base), 169, 166, 165, and 161.

Quantum Yield Determinations. All quantitative measurements were made on a rotating assembly with a central light source (internal water-cooled mercury arc lamp, Hanovia Type L-450W). Samples in 13-mm Pyrex ampoules were placed in holders on the assembly approximately 6 cm from the immersion well. The light was filtered by circulation of 0.002 *M* potassium chromate in a 1% aqueous solution of potassium carbonate through the inner jacket to isolate the 3130-Å region of the medium-pressure mercury arc.[68] All studies were made at room temperature. Samples in 13-mm Pyrex test tubes were degassed to 5×10^{-3} mm in three freeze–thaw cycles and then sealed. Benzophenone–benzhydrol actinometry was used for quantum yield determinations.[69] After irradiation, the degree of reaction was determined by quantitative uv or vapor phase chromatography. The conversions in the irradiations were run to 15% or less. The mass balance in these runs were generally better than 95%.

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Registry No.—**4,** 2513-25-9; **5,** 36839-05-1; **6,** 36913-69-6; **7,** 36852-12-7; **8,** 36852-14-9; **9,** 1128-92-3; **10,** 36852-15-0; **12,** 4222-08-6; **13,** 36839-06-2; **14,** 5882-21-3; **15,** 54193-66-7; **17,** 51870-64-5; **18,** 54193-67-8; **19,** 54193-68-9; **20,** 54193-69-0; **22,** 54193-70-3; **23,** 54193-71-4; **24,** 54193-72-5; **26,** 54193-73-6; **27,** 54193-74-7; **28,** 54193-75-8; **29,** 54193-76-9; **30,** 54193-77-0; **31,** 10425-96-4; **32,** 29539-10-4; **33,** 54193-78-1; **34,** 4505-48-0; **36,** 54193-79-2; **37,** 1961-97-3; **38,** 54193-80-5; 4-phenyl-3-chromanone, 17698-43-0; bromobenzene, 108-86-1; 3-phenylisochromanone, 32521-36-1; methyl iodide, 74-88-4; *cis*-4-methyl-3-phenyl-4-isochromanol, 54193-81-6; *trans*-4-methyl-3-phenyl-4-isochromanol, 54193-82-7; 3-phenyl-4-isochromanol, 32727-55-2; *trans*-2,3-dihydroxy-2,3-diphenylindan, 54193-83-8; 2,3-epoxy-2-phenylindan, 54193-84-9; isothiochroman-4-one, 4426-76-0; 4-phenylisothiochroman-4-ol, 54193-85-0.

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