Photochemistry of the Chroman and 3-Chromanone Ring Systems. An Example of Tautomeric Control of Excited-State Chemistry[1]

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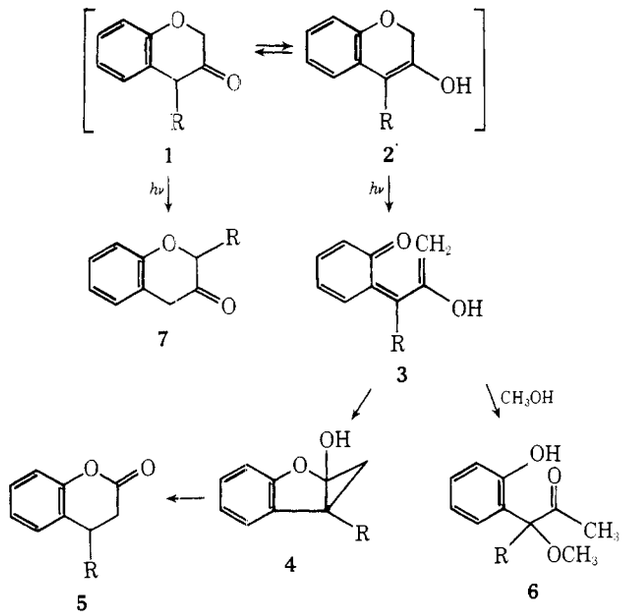
Photorearrangement reactions are described for 4-phenyl-3-chromanone (1) and 4,7-dimethyl-3-chromanone (10). Irradiation of these compounds in nonprotic solvents gives a 2-substituted 3-chromanone as the only photoproduct. The mechanism proposed involves β scission of the C–O bond and recoupling of the zwitterion through the aromatic ring to give a transient spirocyclohexadienone which gives the product by a [1,3]sigmatropic shift. Irradiation of the 3-chromanone system in methanol, however, proceeds via the small amount of enol present in tautomeric equilibrium with the keto form. The solvent effect noted can best be rationalized in terms of the enol content in each solvent. In alcoholic solvents there is a significant amount of the enol form present, which can be selectively excited with long wavelength light. In benzene or acetonitrile, insignificant quantities of the enol tautomer are present in solution and consequently the photoreaction is due to excitation of the keto form of the chromanone system. The excited-state behavior of the closely related chroman ring was also studied. The results obtained indicate that the reaction proceeds by homolytic cleavage of the C–O bond to give a diradical intermediate, which undergoes a subsequent fragmentation or internal hydrogen abstraction reaction.

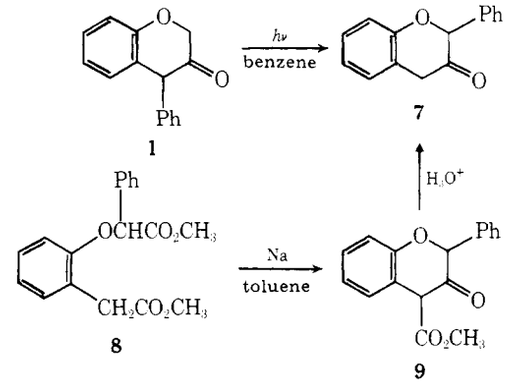
Previous papers from this laboratory have demonstrated the variety of transformations which ensue on electronic excitation of 4-substituted 3-chromanones.[2-5] The kinds of reactions which have been observed in alcoholic media have led to the suggestion that the photochemistry of this system involves the prior enolization of 1 into its enol tautomer (2) which subsequently undergoes photochemical ring opening to *o*-quinoneallide 3. The conversion of enol 2 to *o*-quinoneallide 3 is analogous to the well known ring openings of pyrans, chromenes, isochromenes, and other related benzoheterocyclic olefins.[6-14] The initially produced *o*-quinoneallide 3 was suggested to have two competitive pathways open to it. One path involves the ring closure of 3 to give a 1-hydroxy-5-substituted-2-oxabenzobicyclo[3.1.0]hex-3-ene (4) which is rapidly converted to a 4-substituted dihydrocoumarin (5). The other competing pathway consists of 1,4-addition of methanol across the C–C double bond of 3 to give a phenolic ketone.[5]



As part of our continuing studies dealing with carbonyl group photochemistry through the enol form, we became interested in determining whether the enol content can contribute in controlling the photochemical behavior of the carbonyl chromophore. This interest led us to examine the photochemistry of 1 in a nonprotic solvent where the concentration of the enol form (2) was negligible. In an earlier communication[4] we reported that the photochemistry of 4-phenyl-3-chromanone (1; R = Ph) could be completely diverted from dihydrocoumarin (5) formation to formation of a rearranged 3-chromanone (i.e., 7) when benzene was used as the solvent.[4] We now wish to report additional studies on the photochemistry of several 4-substituted 3-chromanones in nonprotic solvents which extend our previous observations and afford important information on the mechanism of this novel rearrangement. The present paper also describes the photochemical behavior of the closely related chroman system.

Results and Discussion

Irradiation of 4-phenyl-3-chromanone 1 (R = Ph) in benzene for 15 h resulted in the formation of a single photoproduct. This material was easily separable from the starting ketone which remained (15%) by preparative GLC. The photoproduct was an isomer of 1, having the same molecular weight (224) by mass spectral analysis. The assignment of 2-phenyl-3-chromanone (7; R = Ph) as the structure of the photoproduct was based on its spectroscopic properties (IR 5.80 μm; UV (methanol) 305 nm (ϵ 650); NMR ($CDCl_3$) τ 6.38 (s, 2 H), 4.80 (s, 1 H), 2.4–3.3 (m, 9 H)) and was further confirmed by comparison with an authentic sample prepared by treating 2-phenyl-4-carbomethoxy-3-chromanone (8) with aqueous acid. β-Keto ester 8 was synthesized, in turn, from a Dieckmann condensation of methyl α-phenyl(*o*-carbomethoxymethyl)phenoxyacetate (9) with sodium in refluxing toluene. Extended irradiation of 1 did not enhance the degree of conversion but only increased the amount of polymer formed. The possibility that the unreacted starting material present in the crude photolysate was derived by photoisom-



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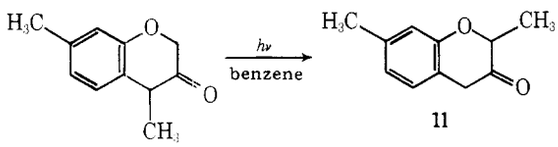
erization of the final photoproduct was eliminated by the finding that **7** did not give **1** on extended irradiation in benzene.

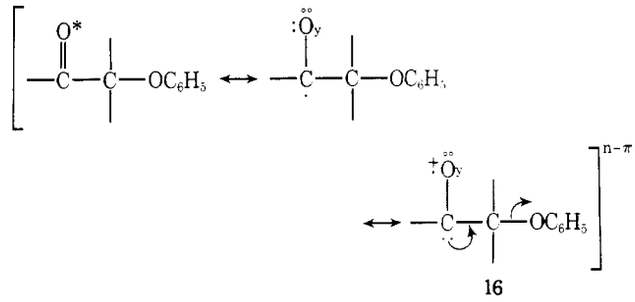
The photochemistry of the closely related 4,7-dimethyl-3-chromanone (**10**) system was also studied in order to assess the generality of the rearrangement. Photolysis of **10** in benzene resulted in the formation of a single photoproduct. The photoproduct, isolated by preparative GLC, was an isomeric ketone whose structure was assigned as 2,7-dimethyl-3-chromanone (**11**) on the basis of its spectral data (IR 5.78 μm; UV (methanol) 305 nm (ϵ 740); *m/e* 176 (M^+)). The NMR preperties of this compound ((($CDCl_3$), τ 8.54 (d, 2 H, J = 7.0 Hz), 7,70 (s, 3 H), 6.47 (s, 3 H), 5.73 (q, 1 H, J = 7.0 Hz), and 3.0–3.4 (m, 3 H)) were identical with those of an authentic sample of 2-methyl-3-chromanone except for the absence of the benzylic methyl group.



10 **11**

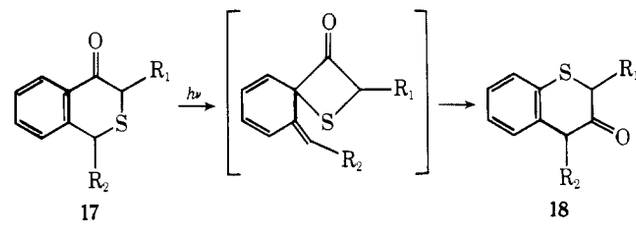
In the interest of understanding the mechanism of the rearrangement more fully, the photolytic behavior of 4-methyl-4-phenyl-3-chromanone (**12**) was also investigated. When a benzene solution of **12** was irradiated for 10 h in Pyrex with a 3130-Å source, a single product was formed. The spectral data obtained (see Experimental Section for details) indicate the product to be 3-methyl-3-phenyl-2,3-dihydrobenzofuran (**13**). This assignment was confirmed by an independent synthesis which is outlined in Scheme I.

The photochemical rearrangement of chromanones **1** and **10** in benzene can be rationalized according to the mechanism outlined in Scheme II. Initial n–π^* excitation followed by C–O bond cleavage and recoupling through the aromatic ring leads to spirocyclohexadienone **15**. This transient species can either revert back to starting material or proceed on to the final product by a [1,3]sigmatropic shift. The first step of the proposed mechanism is not unprecedented as related β-scission reactions of n–π^* excited ketones have appeared in the literature.[15–17] Zimmerman has explained these reactions by utilizing a simple atomic orbital resonance model for the excited carbonyl group.[18] In his description, the n–π^* excited state was suggested to have the dual capacity of ejecting a group in the α-position either as a radical or as an anion. A polar route for fragmentation of the C–O bond of **1** is particularly attractive, considering the relatively high electron density on the carbonyl carbon of the n–π^* excited ketone and the stability of the resulting phenoxide anion. In terms of resonance reasoning, canonical form **16** is quite important[18] (i.e., the

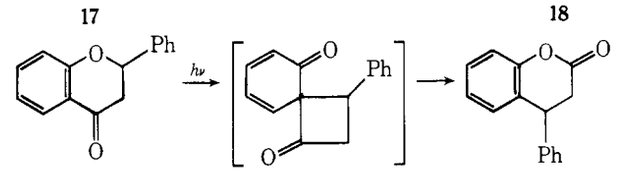


16

excited carbonyl is a good electron-donating group). This facile heterolysis is a manifestation of π^* assisted cleavage, of which there are a growing number of examples.[19–21] The conversion of **1** to **7** is also analogous to the light-induced rearrangements of isothiochroman-4-ones (**17**) to thiochroman-3-ones (**18**)[22–24] and flavone (**19**) to 4-phenyldihydrocoumarin (**20**)[25] where intermediates similar to **15** have been suggested. Related intermediates have also been postulated in abnormal Claisen rearrangements.[26–28]



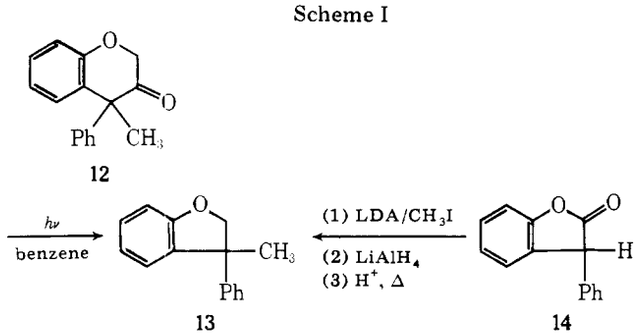
17 **18**



19 **20**

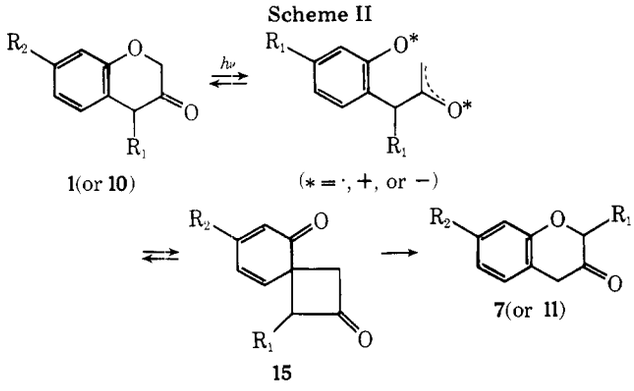
The transformations of chromanone **1** is especially interesting in view of the fact that the photolysis of this system is solvent dependent. As was pointed out in previous papers,[2–5] irradiation of **1** in a protic solvent such as methanol led to the formation of dihydrocoumarin **5**. A number of factors could account for this solvent perturbation, including the adjustment of ground- and excited-state energy levels, excited-state configurations and barriers, as well as the multiplicity of the electronically reactive state. We suggest, however, that the solvent effect noted can best be rationalized on the basis of the enol content present in each solvent. We have previously shown that the conversion of **1** to **5** proceeds via the small amount of enol present in tautomeric equilibrium with the keto form. In alcoholic solvents there is a significant (ca. 1–2%) amount of the enol form present in solution which can be selectively excited with long wavelength light. Electronic excitation of the enol tautomer results in a photochemical ring opening to give an *o*-quinoneallide intermediate (**3**) which is ultimately converted to dihydrocoumarin **5**. In benzene or acetonitrile, insignificant quantities of the enol tautomer are present in solution and consequently the photoreaction encountered in these solvents is due to excitation of the keto form of chromanone **1**. This conclusion was reached by ex-

Scheme I



12 **13** **14**

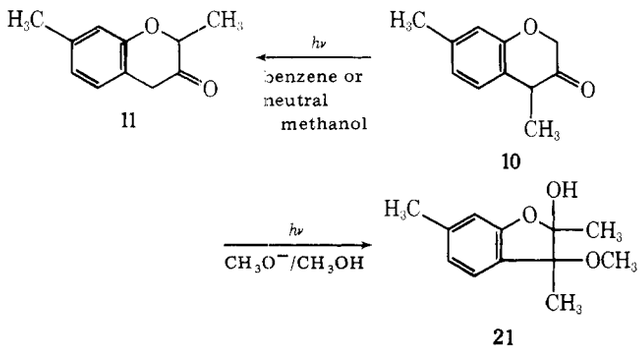
Scheme II



1(or **10**) **15**

amination of the UV spectrum of 1 in various solvents. This technique provides a convenient method of estimating the amount of the enol form present in solution. In acetonitrile, chromanone 1 shows three absorption bands with maxima at 298, 280, and 274 nm (ϵ 1500, 3000, and 3300) whereas in methanol solution a new long-wavelength absorption band at 314 nm is also present (ϵ 170). The possibility that the long wavelength absorption band in methanol was due to enol (or enolate) **2** was confirmed when trace amounts of base were added to spectral solutions. Under these conditions, a dramatic enhancement in the intensity of the 314-nm band occurred. Addition of a full equivalent of sodium methoxide to a methanolic solution of 1 resulted in the appearance of two new maxima at 314 and 239 nm. The extinction coefficients of these maxima were on the order of 10^4. Furthermore, the absorption spectrum of the corresponding methyl enol ether, which provides a reasonable model for the enol tautomer **2**, also showed a long wavelength maximum at 311 nm (ϵ 4800). Based on the above spectral data, we propose that in methanolic solutions approximately 1–2% of the enol (or enolate) exists in equilibrium with the keto form of 1. In benzene or acetonitrile solutions, however, concentrations of less than 0.1% of enol **2** exist in equilibrium with the keto tautomer. It is this difference in enol concentration which we believe is responsible for the dramatic solvent effect encountered with this system.

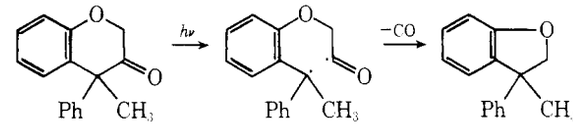
In contrast to 4-phenyl-3-chromanone (1), the photochemistry of the closely related 4,7-dimethyl-3-chromanone (**10**) system was not significantly altered upon changing the solvent from benzene to neutral methanol. Brief irradiation of **10** in methanol resulted in a moderate yield of chromanone **11**, whereas prolonged photolysis gave rise to a complex mixture of photoproducts. The absence of a dramatic solvent effect with this system is also understandable in terms of the enol content present in solution. With this system, the concentration of the enol form is significantly less than that present in the phenylchromanone system. In addition, the absorption characteristics of the enol derived from **10** would be expected to be hypsochromically shifted relative to the enol derived from the phenyl system. Thus, it will not be possible to selectively excite this tautomer as was the case with chromanone 1. It should be pointed out that when a basic methanolic solution of 10 was subjected to UV irradiation the only product obtained was 2-hydroxy-3-methoxy-2,3,6-trimethyl-2,3-dihydrobenzofuran (**21**).[5] The formation of **21** is



readily explicable in terms of a photoinduced ring opening of the enolate anion of **10** to give an *o*-quinoneallide intermediate which subsequently adds methanol across the C–C double bond. Under these conditions, the enolate anion derived from **10** absorbs almost all of the incident light whereas in neutral methanol the keto tautomer is the major light absorbing species.

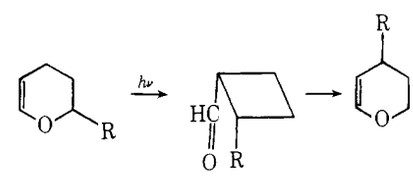
Several experiments were also carried out with the intent of identifying the excited state responsible for the rearrangement of 1 and **10**. The data obtained suggest that the above transformations (i.e., 1 → **7**) proceed from a n–π^* excited singlet state. As expected for a singlet reaction, we have found that the photochemical rearrangement of chromanones 1 and **10** were not quenched by piperylene or cyclohexadiene. When the triplet state was generated artificially by acetone sensitization, the rearrangement did not proceed. Quantum yields for product formation were determined in acetonitrile using cyclopentanone as the chemical actinometer.[29] The calculated values indicated the efficiency of the rearrangement to be about 0.02. The low efficiency of the rearrangement can be attributed, in part, to the fact that spirocyclohexadienone **15** can revert back to starting material in competition with rearrangement to the observed product. Alternatively, it is quite possible that the n–π^* singlet state undergoes a facile Norrish Type I cleavage to give a diradical which recombines to regenerate starting material. The two rationales are operationally indistinguishable with the present information, but both lead to the same conclusion that reorganization of the 4-substituted 3-chromanone system is an inefficient process. We thought that it might be possible to demonstrate the occurrence of the Norrish Type I cleavage with chromanones 1 and **10** by synthesizing optically pure starting material and demonstrating that it undergoes racemization prior to rearrangement. However, our attempts to prepare an optically active chromanone by conversion of the ketone to a pyrrolidine iminium *d*-camphor-10-sulfonate salt[30] failed, and consequently we abandoned this approach.

It should be pointed out that the formation of 3-methyl-3-phenyl-2,3-dihydrobenzofuran (**13**) from the irradiation of chromanone **12** does establish the credibility of the Norrish Type I cleavage with this ring system. The isolation of **13** from **12** is most simply viewed as proceeding via the loss of carbon

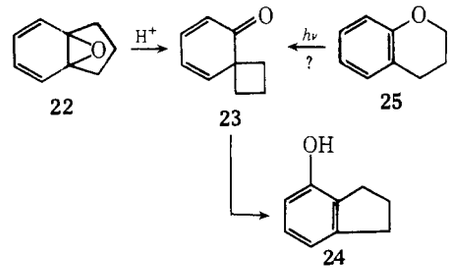


monoxide from an initially generated diradical. Similar decarbonylations of cyclic ketones have been reported in the literature[31–33] and provide reasonable chemical analogy for this reaction. Irradiation of **12** in benzene did not produce a rearranged chromanone, and it therefore seems that the incorporation of an additional methyl group in the 4-position of the chromanone ring facilitates the rate of Norrish Type I scission relative to C–O bond cleavage.

Srinivasan[34] had previously suggested that the photoisomerization of 3,4-dihydro-2*H*-pyrans to cyclobutane carboxaldehydes is a general process[35] which is analogous to the photochemical ring contraction that is known to occur with

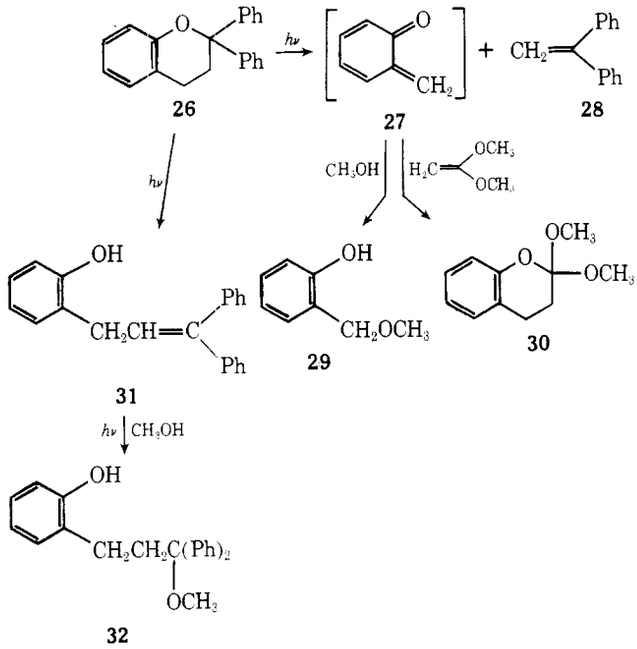


2,3-dihydrofurans[36,37] and furans.[36,38] The rearrangements that we have uncovered upon irradiation of 3-chromanones 1 and **10** in benzene may be viewed as specific examples of this general process. As part of a broader study dealing with enol ether photochemistry,[2–5] we thought it of considerable interest to determine whether a comparable rearrangement would occur with the related chroman system. In addition, a number of reports dealing with the aromatization of arene oxides (**22**) to 4-indanols (**24**) have shown that these reactions proceed via a spiroketone (**23**) intermediate.[39–42] These reports suggested that a related rearrangement might also occur upon irradiation



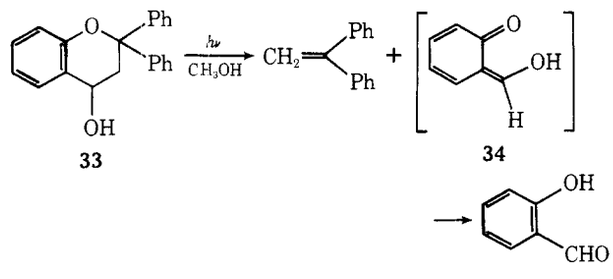
of the chroman ring (**25**). In order to test for this possibility, we investigated the photochemical behavior of several substituted chromans.

The first system we studied was 2,2-diphenylchroman (**26**). Irradiation of **26** in methanol through Corex using a 450-W Hanovia lamp gave a mixture of four products. On the basis of their spectral properties (see Experimental Section) these compounds were identified as 1,1-diphenylethylene (**28**), *o*-hydroxybenzyl methyl ether (**29**), 1,1-diphenyl-3-(*o*-hydroxyphenyl)-1-propene (**31**), and 1-methoxy-1,1-diphenyl-3-(*o*-hydroxyphenyl)propane (**32**). Photoproduct **32** was



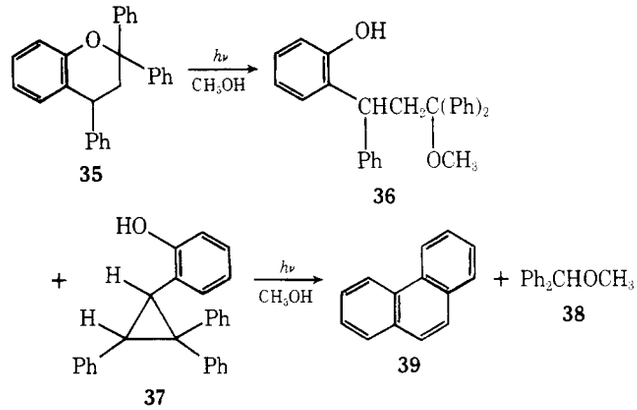
shown to be a secondary product resulting from further irradiation of **31**. No detectable quantities of a rearranged 4-indanol or chroman could be observed in the crude photolysate. The formation of **28** and **29** is readily explicable in terms of a photoinduced fragmentation of **26** to diphenylethylene and *o*-quinonemethide **27**. This transient species is rapidly trapped with methanol to give ether **29**. Additional support for the intermediacy of **27** comes from carrying out the irradiation of **26** in benzene in the presence of 1,1-dimethoxyethylene. Under these conditions, a high yield of chroman **30** could be isolated.[43]

The photochemical ring opening reaction of 2,2-diphenyl-4-chromanol (**33**) was also studied. Irradiation of **33** in

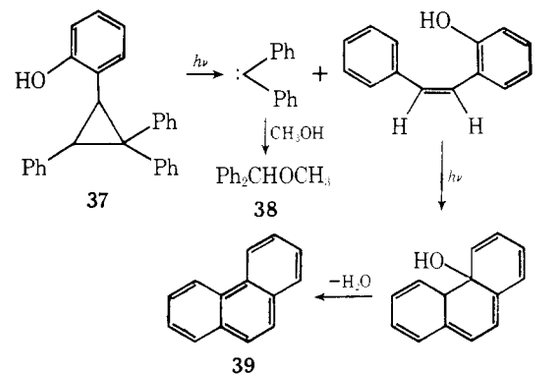


methanol produced a mixture of 1,1-diphenylethylene and salicylaldehyde. In this case, the initially produced *o*-quinonemethide **34** prefers to undergo a 1,5-sigmatropic hydrogen shift rather than reaction with the solvent.

The last system which was studied involved the photochemistry of 2,2,4-triphenylchroman (**35**). Irradiation of **35** in methanol with a 450-W Hanovia lamp through Corex led to the formation of four products (**36–39**) whose relative yields varied as a function of the reaction conditions. On prolonged irradiation the major products were benzhydryl methyl ether (**38**) and phenanthrene (**39**). With short exposure to UV light, the major photoproducts were identified as 3-(*o*-hydroxyphenyl)-3-phenyl-1-methoxy-1,1-diphenylpropane (**36**) and 3-(*o*-hydroxyphenyl)-1,1,2-triphenylcyclopropane (**37**). Structures **38** and **39** were shown to be secondary photo-



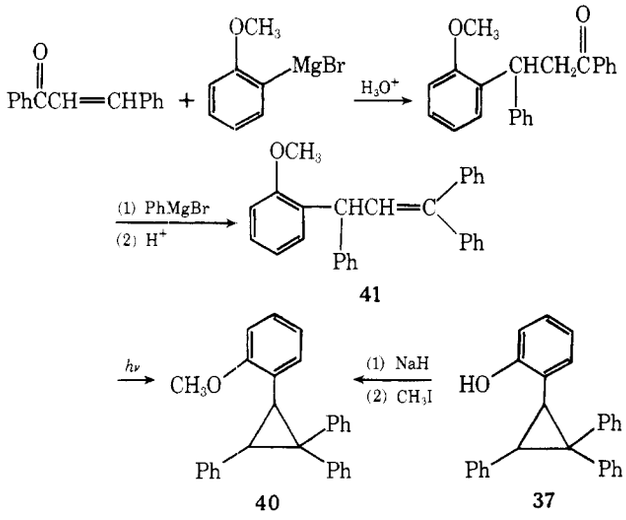
products resulting from the irradiation of cyclopropane **37**. This secondary photoreaction corresponds to a "Griffin type fragmentation".[44] The initially generated diphenylcarbene inserts into the O–H bond of methanol to give benzhydryl methyl ether **38**. The corresponding olefin produced from this [3 → 2 + 1] cycloelimination apparently undergoes a *cis*-stilbene–phenanthrene type cyclization[45] followed by loss of water to give phenanthrene (**39**).



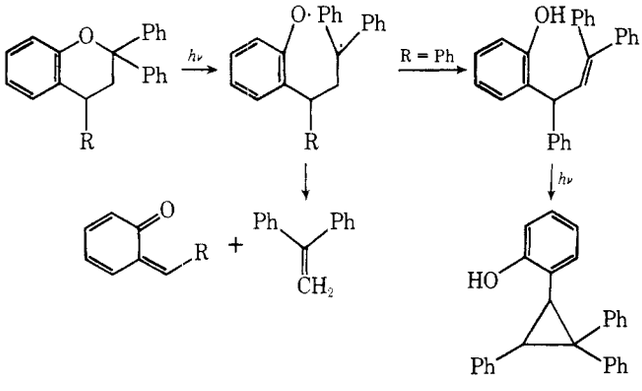
The identity of structure **37** was determined from its straightforward spectral properties (NMR (60 MHz) τ 6.32–6.40 (AB q, 2 H, J = 7.2 Hz), 4.95 (s, 1 H, exchanged with D_2O), 2.6–3.6 (m, 19 H)) as well as its conversion to the corresponding methyl ether **40**. The structure of **40** was established by comparison with an independently synthesized sample as shown in Scheme III. The key step in this independent synthesis involves a photochemical di-π-methane[46] rearrangement of **41** to **40**.

The photochemical cleavage reaction encountered upon irradiation of chromans **26** and **35** does not follow the same pattern as had been observed with the 3-chromanone system. Electronic excitation of the chromanone ring results in the formation of a spirocyclohexadienone whereas irradiation of chromans **26** and **35** produces a diradical intermediate which undergoes a subsequent cleavage or internal hydrogen ab-

Scheme III



straction. The initially produced olefin derived from internal hydrogen abstraction absorbs another photon of light and undergoes a di-π-methane reaction. The fact that we were able to independently synthesize **40** by a di-π-methane route clearly establishes the validity of this step. It should also be noted that Griffin and co-workers have previously shown that various substituted 3-arylpropenes undergo aryl migration on direct irradiation to yield cyclopropane products,[47,48] thereby providing excellent analogy for the above transformation.



Finally, the difference in photochemical reactivity between the chroman and chromanone systems should be briefly discussed. Possibly this difference is due to a polar route for C–O bond cleavage in the 3-chromanone system. This heterolysis is not unreasonable considering the relatively high electron density on the carbonyl carbon of the n–π^* excited ketone. In the chroman system, C–O bond cleavage proceeds via a homolytic fragmentation to give a diradical intermediate which prefers to undergo internal hydrogen abstraction or bond cleavage rather than recombination to a spirocyclohexadienone intermediate.

In conclusion, we have shown that the tautomeric forms of certain carbonyl derivatives undergo diverse and interesting photochemistry. Electronic excitation of the enol tautomer of the 3-chromanone system results in a photochemical ring opening to give an *o*-quinoneallide intermediate. In nonprotic solvents, insignificant quantities of the enol tautomer are present in solution and consequently the photoreaction is due to excitation of the keto form. We are continuing to examine wavelength and solvent effects in enol photochemistry and will report additional findings at a later date.

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 XL-100 and JEOL MH-100 spectrometer and at 60 MHz with a Varian T-60 spectrometer.

Irradiation of 4-Phenyl-3-chromanone (1) in Benzene. A solution containing 250 mg of 4-phenyl-3-chromanone[49] (**1**) in 80 mL of benzene was irradiated under an argon atmosphere using a Rayonet reactor equipped with 15 3000-Å lamps. After 15 h, the reaction mixture was concentrated under reduced pressure to leave a brown oil. This oil was found to decompose slowly at room temperature in the presence of air. The oil contained a band at 5.80 μm in its infrared spectrum. The NMR spectrum also indicated the presence of a new product along with 15% of unreacted starting material. All attempts to separate this mixture by distillation, sublimation, liquid and/or thick-layer chromatography were unsuccessful. Separation of the mixture was achieved, however, by gas chromatography using a 0.25 in. × 6-ft SF 1265 column at 200 °C. Under these conditions, 29.5 mg of a pale yellow liquid was obtained from 45 mg of the crude oil. This material was assigned the structure of 2-phenyl-3-chromanone (**7**) on the basis of its physical and chemical properties and by an independent synthesis: IR (CCl_4) 5.80 μm; UV (methanol) 305 nm (ϵ 650); NMR ($CDCl_3$, 100 MHz) τ 6.38 (s, 2 H), 4.8 (s, 1 H), and 2.4–3.3 (m, 9 H); *m/e* 224 (M^+), 210, 36, 181 (base), 152, 144, 91, 77, and 43.

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.81. Found: C, 80.24; H, 5.76.

extended irradiation of 4-phenyl-3-chromanone did not simplify the separation procedure but only increased the amount of polymer formed. It should be noted that 2-phenyl-3-chromanone (**7**) was thermally stable and did not give 4-phenyl-3-chromanone (**1**) when stirred overnight with silica gel in acetone.

Independent Synthesis of 2-Phenyl-3-chromanone (7). To a solution containing 0.84 g of methyl *o*-hydroxyacetate and 50 mg of tetra-*n*-butylammonium chloride in 50 mL of methylene chloride was added 150 mg of sodium hydride followed by 1.14 g of methyl α-bromophenylacetate. After stirring overnight, the mixture was washed with several portions of water, followed by a saturated ammonium chloride solution. The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude oil obtained was purified by thick-layer chromatography using 10% acetone–cyclohexane and then benzene as the eluents. The major band obtained (0.82 g, 52%) was identified as methyl α-phenyl(*o*-carbomethoxymethyl)phenoxyacetate (**9**): IR (neat) 5.70 and 5.75 μm; NMR τ 6.47 (s, 3 H), 6.39 (s, 3 H), 6.26 (AB q, 2 H, J = 16 Hz), 4.44 (s, 1 H), and 3.4–2.4 (m, 9 H).

A mixture containing 30 mg of metallic sodium and 80 mg of the above diester (**9**) in 30 mL of dry toluene was refluxed under a nitrogen atmosphere for 7 h. After cooling, the yellow mixture 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 and then dried over magnesium sulfate and concentrated under reduced pressure. The crude oil obtained was chromatographed on a thick-layer plate using a 10% acetone–cyclohexane mixture as the eluent. The major band contained 33 mg (57%) of 2-phenyl-4-carbomethoxy-3-chromanone (**8**): IR (neat) 5.76, 6,08, and 6.20; NMR (100 MHz, $CDCl_3$) 6.08 (s, 3 H), 4.30 (s, 1 H), 3.2–2.2 (m, 9 H), and −3.0 (s, 1 H, exchangeable); *m/e* 281, 224, 196, 135, 92, 77, and 44.

A sample of 106 mg of the above β-keto ester (**8**) was heated at reflux with a mixture containing 1 mL of concentrated sulfuric acid, 3 mL of water, and 5 mL of acetic acid for 7 h. After cooling, the solution was extracted with ether and the ether extracts were washed with a saturated sodium bicarbonate solution, dried over magnesium sulfate, and concentrated under reduced pressure to an oil. When this oil was chromatographed on a thick-layer plate using 7% acetone–cyclohexane as the eluent, 42 mg (49%) of the desired 2-phenyl-3-chromanone (**7**) was obtained. This material is identical in every respect with the compound obtained from the photolysis of 4-phenyl-3-chromanone (**1**) in benzene.

Irradiation of 4,7-Dimethylchroman-3-one (10) in Benzene. A solution containing 200 mg of 4,7-dimethylchroman-3-one[50] (**10**) in 150 mL of benzene was irradiated under an argon atmosphere using a 450-W Hanovia lamp equipped with a Corex filter sleeve. The photolysis was followed by gas chromatography using a 3-ft 10% Ucon on Chromosorb W column at 185 °C. After 35 min of irradiation, the gas chromatogram showed the presence of unreacted starting ketone (20%) and a major photoproduct (80%). Longer irradiation times resulted in decomposition of this material. Separation of the product

from starting material was achieved by preparative gas chromatography. The major component was assigned the structure of 2,7-dimethylchroman-3-one (11) on the basis of its spectral data and by comparison with a model system: IR (neat) 5.78 μm; NMR ($CDCl_3$, 60 MHz) τ 8.54 (d, 3 H, J = 7.0 Hz), 7.70 (s, 3 H), 6.47 (s, 2 H), 5.73 (q, 1 H, J = 7.0 Hz), and 3.4–3.0 (m, 3 H); UV (methanol) 305 and 227 nm (ε 740 and 2200); m/e 176 (M^+, base), 148, 133, 105, 91, 77, 51, and 44.

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 75.13; H, 6.84.

It should be noted that the NMR spectra of 2-methyl-3-chromanone and 2,7-dimethyl-3-chromanone (11) were superimposable except for the tolyl methyl and aromatic protons.

Preparation of 4-Methyl-4-phenyl-3-chromanone (12). A solution containing 6 mL of freshly distilled dimethoxyethane and 6 mL of a 1.7 M methyllithium solution was cooled to 0 °C and 2.0 g of 3-acetoxy-4-phenylchromene[49] in 10 mL of dimethoxyethane was added dropwise. The resulting yellow solution was allowed to warm to room temperature and was stirred for an additional 10 min at 25 °C. To this mixture was added 3.0 mL of iodomethane and the solution was allowed to stir at room temperature for 10 h. At the end of this time, water was added and the mixture was extracted with ether. The ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The oily solid that remained was sublimed at 40 °C (0.01 mm) to give 1.05 g (59%) of 4-methyl-4-phenyl-3-chromanone (12): mp 64–65 °C; IR (KBr) 5.78, 6.23, 6.32, 6.74, 8.11, 9.52, 13.13, and 14.33 μm; NMR ($CDCl_3$, 100 MHz) τ 8.20 (s, 3 H), 5.80–5.32 (AB q, 2 H, J_{AB} = 18.0 Hz), and 3.2–2.6 (m, 9 H); UV (methanol) 305 (shoulder) and 278 nm (ε 490 and 2070); m/e 238 (M^+), 210, 195 (base), 178, 167, 165, 115, 105, 91, and 77.

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.59; H, 5.93.

Irradiation of 4-Methyl-4-phenyl-3-chromanone (12) in Benzene. A 100-mg sample of 4-methyl-4-phenyl-3-chromanone (12) in 40 mL of benzene was distributed among five Pyrex test tubes which were then purged with argon for 5 min. The tubes were irradiated with 16 3000-Å low-pressure ultraviolet lamps using a Rayonet reactor. After 10.5 h, the solvent was removed under reduced pressure and the residual oil was purified by thick-layer chromatography using a 10% ether–pentane mixture as the eluent. The major component obtained contained 52 mg (59%) of 3-methyl-3-phenyl-2,3-dihydrobenzofuran (13) whose structure was assigned on the basis of its spectral data and by an independent synthesis: IR (neat) 6.24, 6.79, 8.13, 9.86, 10.21, 13.32, and 14.33 μm; NMR ($CDCl_3$, 60 MHz) τ 8.27 (s, 3 H), 5.68–5.34 (AB q, 2 H, J_{AB} = 9.0 Hz), and 3.2–2.6 (m, 9 H); m/e 210 (M^+), 195 (base), 167, 165, 152, 91, and 77.

Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.72; H, 6.74.

Independent Synthesis of 3-Methyl-3-phenyl-2,3-dihydrobenzofuran (13). A mixture containing 0.16 mL of diisopropylamine in 7 mL of dry tetrahydrofuran was cooled to 0 °C and 0.5 mL of a 2.1 M solution of n-butyllithium was added dropwise. After stirring for 15 min at 0 °C, 210 mg of 3-phenylbenzofuran-2-one[51] (14) in 5 mL of dry tetrahydrofuran was added dropwise over a 5-min interval. The resulting yellow solution was stirred for 15 min at 0 °C and then 200 mg of methyl iodide was added. The solution was allowed to warm to room temperature and then stirred at 25 °C for 2 h. The reaction mixture was diluted with ether and washed with water. The ethereal layer was dried over magnesium sulfate and concentrated under reduced pressure to give 206 mg (92%) of 3-methyl-3-phenyl-2-benzofuranone: IR (neat) 5.53, 6.18, 6.24, 6.85, 8.12, 9.67, 11.20, 13.26, and 14.37 μm; NMR ($CDCl_3$, 60 MHz) τ 8.18 (s, 3 H) and 2.9–2.6 (m, 9 H).

A 206-mg sample of 3-methyl-3-phenyl-2-benzofuranone in 5 mL of ether was added to a mixture of 34 mg of lithium aluminum hydride in 10 mL of anhydrous ether. The mixture was stirred for 25 min at room temperature and then 1 drop of water was added followed by 1 drop of a 15% sodium hydroxide solution and 3 additional drops of water. The precipitated salts were filtered, ether was added to the filtrate, and the ethereal solution was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 200 mg (95%) of 2-phenyl-2-(o-hydroxyphenyl)-1-propanol: mp 103–104 °C; IR (KBr) 3.00, 6.22, 6.33, 6.71, 6.92, 8.06, 9.73, 10.93, 11.88, 13.15, and 14.32 μm; NMR ($CDCl_3$, 60 MHz) τ 8.47 (s, 3 H), 6.29–5.68 (AB q, 2 H, J_{AB} = 11.0 Hz), 4.65 (s, 2 H, exchangeable with D_2O), and 3.4–2.6 (m, 9 H).

A mixture containing 100 mg of 2-phenyl-2-(o-hydroxyphenyl)-1-propanol and a grain of p-toluenesulfonic acid in 0.5 mL of deuteriochloroform was heated at 130 °C for 6 h. The NMR and IR spectra of the product were identical with those of 3-methyl-3-phenyl-2,3-dihydrobenzofuran (13) obtained from the irradiation of 4-methyl-4-phenyl-3-chromanone (12).

Irradiation of 2,2-Diphenylchroman (26) in Methanol. A solution containing 500 mg of 2,2-diphenylchroman[52] (26) in 450 mL of methanol was purged with argon and irradiated with a 450-W Hanovia lamp equipped with a Corex filter sleeve for 2 h. The solvent was removed under reduced pressure and the crude oil was subjected to thick-layer chromatography using a 10% ether–pentane mixture as the eluent. The top band contained 50 mg (18%) of 1,1-diphenylethylene (28): IR (neat) 6.22, 6.71, 6.93, 7.54, 9.71, 11.04, 12.89, and 14.35 μm; NMR ($CDCl_3$, 60 MHz) τ 4.57 (s, 1 H), and 2.70 (s, 5 H). This material was identified by comparison with an authentic sample. The middle band contained 88 mg of starting material. The bottom band contained 320 mg of an oil which proved to be a mixture of three phenols which could be separated further by extraction with a 10% sodium hydroxide solution. The base soluble component amounted to 60 mg (25%) and was identified as o-hydroxybenzylmethyl ether (29) on the basis of its spectral data and by comparison with an authentic sample: IR (neat) 3.04, 6.26, 6.73, 6.91, 8.04, 9.23, and 13.29 μm; NMR ($CDCl_3$, 60 MHz) τ 6.60 (s, 3 H), 5.40 (s, 2 H), 4.80 (s, 1 H, exchangeable with D_2O), and 3.4–2.6 (m, 4 H). The base insoluble fraction contained two components in a 3:1 ratio. The major component was identified as 1-methoxy-1,1-diphenyl-3-(o-hydroxyphenyl)propane (32): IR (neat) 3.03 μm; NMR ($CDCl_3$, 60 MHz) τ 7.6–7.4 (m, 4 H), 6.90 (s, 3 H), 4.69 (s, 1 H, exchangeable with D_2O), and 3.4–2.5 (m, 14 H). The minor component was identified as 1,1-diphenyl-3-(o-hydroxyphenyl)-1-propene (31): IR (neat) 2.90 μm; NMR ($CDCl_3$, 60 MHz) τ 6.60 (d, 2 H, J = 7.0 Hz), 5.30 (s, 1 H, exchangeable with D_2O), 3.83 (t, 1 H, J = 7 Hz), and 3.5–2.7 (m, 14 H).

The structure of the two insoluble phenols was established by the following chemical reactions. A 50-mg sample of 1-methoxy-1,1-diphenyl-3-(o-hydroxyphenyl)propane (32) was dissolved in 60 mL of methanol which was saturated with hydrogen chloride gas. The resulting solution was stirred at room temperature for 10 h and the methanol was removed under reduced pressure. Ether was added to the residual oil and the ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 37 mg (82%) of 2,2-diphenylchroman (26).

An authentic sample of phenol 31 was prepared from 2,2-diphenylchroman by treatment with acidic methanol. A solution containing 2.0 g of 2,2-diphenylchroman (26) in 75 mL of methanol was treated with 3 mL of concentrated hydrochloric acid. The resulting solution was heated at reflux for 6 h, cooled, and concentrated under reduced pressure. Ether was added and the ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The oil obtained proved to be a mixture containing 63% of unreacted 2,2-diphenylchroman and 37% of 1,1-diphenyl-3-(o-hydroxyphenyl)-1-propene (31). These two components were separated by dry column chromatography using a 10% ether–pentane mixture as the eluent to give 520 mg of 1,1-diphenyl-3-(o-hydroxyphenyl)-1-propene (31), which was identical with one of the insoluble phenols isolated from the irradiation of 2,2-diphenylchroman.

Irradiation of 2,2-Diphenylchroman (26) in Benzene Containing 1,1-Dimethoxyethylene. A solution containing 200 mg of 2,2-diphenylchroman (26) and 1.0 g of 1,1-dimethoxyethylene in 175 mL of benzene was purged with nitrogen and irradiated with a 450-W Hanovia lamp equipped with a Corex filter sleeve for 2 h. Removal of the solvent under reduced pressure gave a mixture of three components which were separated by thick-layer chromatography using a 10% ether–pentane solution as the eluent. The top band contained 65 mg (51%) of 1,1-diphenylethylene. The middle band contained 61 mg (45%) of 2,2-dimethoxychroman (30): IR (neat) 3.41, 6.30, 6.74, 6.95, 8.18, 9.13, 10.94, and 13.15 μm; NMR ($CDCl_3$, 60 MHz) τ 7.96 (t, 2 H, J = 7.0 Hz), 7.16 (t, 2 H, J = 7.0 Hz), 6.63 (s, 6 H), and 3.3–2.7 (m, 4 H). The bottom band contained 80 mg (40%) of 1,1-diphenyl-3-(o-hydroxyphenyl)-1-propene (31). The structure of 2,2-dimethoxychroman was verified by hydrolysis to dihydrocoumarin.

Irradiation of 2,2-Diphenyl-4-chromanol (33) in Methanol. A solution containing 100 mg of 2,2-diphenyl-4-chromanol[53] (33) in 170 mL of methanol was irradiated with a 450-W Hanovia lamp equipped with a Corex filter sleeve for 3 h. The solvent was removed under reduced pressure and the residial oil was subjected to thick-layer chromatography using a 10% acetone–hexane mixture as the eluent. The upper band contained 45 mg (75%) of 1,1-diphenylethylene (28), while the lower band contained 28 mg (70%) of salicylaldehyde which was identified by comparison with an authentic sample.

Preparation of 2,2,4-Triphenylchroman (35). To a solution containing 2.24 g of 4-phenyldihydrocourmarin[54] under nitrogen was added 11 mL of a 2.3 M ethereal solution of phenylmagnesium bro-

mide. The resulting solution was stirred at room temperature for 30 min followed by heating at reflux for 4 h. The ethereal solution was cooled, hydrolyzed using a 10% hydrochloric acid solution, washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 3.6 g (94%) of 3-(*o*-hydroxyphenyl-1,1-diphenyl-1-propanol: mp 109–110 °C; IR (KBr) 3.03, 6.32, 6.89, 8.19, 9.84, 13.06, and 14.24 μm; NMR (DCl_3, 60 MHz) τ 6.88 (d, 2 H, J = 5 Hz), 5.67 (t, 1 H, J = 5 Hz), and 3.6–2.6 (m, 19 H).

A solution containing 3.6 g of 3-(*o*-hydroxyphenyl-3-phenyl-1,1-diphenyl-1-propanol in 175 mL of benzene containing a catalytic amount of *p*-toluenesulfonic acid was heated at reflux for 1.3 h. The reaction mixture was cooled and the solvent was removed under reduced pressure to give an oil which was crystallized from 95% ethanol to give 2.7 g (75%) of 2,2,4-triphenylchroman (**35**): mp 158–160 °C (lit.[55] mp 162–163 °C); IR (KBr) 6.22, 6.32, 6.73, 6.91, 8.11, 9.83, 10.87, 12.70, 13.09, and 14.28 μm; NMR ($CDCl_3$, 60 MHz) τ 7.43 (d of d, 1 H, J_{AB} = 14 Hz, J_{BX} = 13 Hz), 6.90 (d of d, 1 H, J_{AB} = 14 Hz, J_{AX} = 5 Hz), 6.13 (d, of d, 1 H, J_{BX} = 13 Hz, J_{AX} = 5 Hz), and 3.4–2.4 (m, 19 H); UV (methanol) 284 and 277 nm (ε 2800 and 2800); *m/e* 362 (M^+), 284, 271, 268, 255, 181 (base), 167, 165, 152, 91, and 77.

Irradiation of 2,2,4-Triphenylchroman (35) in Methanol. A solution containing 300 mg of 2,2,4-triphenylchroman (**35**) in 475 mL of methanol was purged with nitrogen and irradiated with a 450-W Hanovia lamp equipped with a Corex filter sleeve for 1.75 h. The solvent was removed under reduced pressure and the resulting oil was purified by preparative thick-layer chromatography using a 10% acetone–hexane mixture as the eluent. After several elutions, four bands were obtained. The top two bands contained 60 mg (36%) of benzhydryl methyl ether (**38**) (identified by spectral data and comparison with an authentic sample prepared by the method of Rutherford)[56] and phenanthrene. The third band contained 24 mg of a material whose structure is assigned as 3-(*o*-hydroxyphenyl)-3-phenyl-1-methoxy-1,1-diphenylpropane (**36**) on the basis of its characteristic spectra: IR (CCl_4) 2.94, 6.23, 6.68, and 6.85 μm; NMR ($CDCl_3$, 60 MHz) τ 7.14 (s, 3 H), 6.81 (d, 2 H, J = 5 Hz), 5.75 (t, 1 H, J = 5 Hz), and 3.4–2.6 (m, 20 H). The bottom band contained 110 mg (37%) of 3-(*o*-hydroxyphenyl)-1,1,2-triphenylcyclopropane (**37**): mp 133–135 °C; IR (KBr) 2.83, 6.24, 6.70, 6.90, 7.56, 7.91, 8.30, 8.55, 9.12, 9.71, 13.35, and 14.31 μm; NMR ($CDCl_3$, 60 MHz) τ 6.40–6.32 (AB q, 2 H, J_{AB} = 7.2 Hz), 4.95 (s, 1 H, exchangeable with D_2O), and 3.6–2.6 (m, 19 H); UV (methanol) 283 (shoulder) and 277 nm (ε 3650 and 4000); *m/e* 362 (M^+), 284, 271, 268, 255, 195, 165, 121, 115, 105 (base), 91, and 77.

Anal. Calcd for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.53; H, 6.17.

Irradiation of cyclopropane **37** in methanol with Corex filtered light gave phenanthrene and benzhydryl methyl ether in good yield.

Independent Synthesis of 3-(*o*-Anisyl)-1,1,2-triphenylcyclopropane (40). The structure of **37** was further verified by conversion to the corresponding methyl ether which was, in turn, independently synthesized. To a stirred solution containing 180 mg of 3-(*o*-hydroxyphenyl)-1,1,3-triphenylcyclopropane (**37**) in 5 mL of methanol was added 20 mg of sodium hydride (99%) in 2 mL of methanol. The resulting solution was stirred under nitrogen for 30 min and then 1.0 mL of methyl iodide was added. After stirring at room temperature for 3 h, the reaction mixture was diluted with ether and washed with water. The ethereal layer was dried over magnesium sulfate and concentrated under reduced pressure to give 104 mg (55%) of 3-(*o*-anisyl)-1,1,2-triphenylcyclopropane (**40**): mp 111–112 °C; IR (KBr) 3.30, 6.22, 6.69, 8.06, 9.69, 12.90, and 14.37 μm; NMR ($CDCl_3$, 60 MHz) τ 6.60–6.27 (AB q, 2 H, J_{AB} = 7.0 Hz), 6.09 (s, 3 H), and 3.4–2.6 (m, 19 H); UV (methanol) 281 and 274 nm (ε 3100 and 3600); *m/e* 376 (M^+), 298, 285, 268 (base), 255, 239, 194, 191, 165, 91, and 77.

Anal. Calcd for $C_{28}H_{24}O$: C, 89.32; H, 6.43. Found: C, 89.35; H, 6.54.

This same material could be independently synthesized according to the procedure outlined below. To a Grignard solution prepared from 1.3 g of magnesium and 9.3 g of *o*-bromoanisole in 100 mL of ether was added 6.24 g of chalcone in 100 mL of ether. The resulting solution was stirred at room temperature for 1 h and then hydrolyzed using a 10% hydrochloric acid solution. The ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The oil obtained was crystallized from 95% ethanol to give 8.6 g (90%) of 3-(*o*-anisyl)-1,3-diphenyl-1-propanone: mp 117–118 °C; IR (KBr) 3.31, 5.90, 6.24, 6.69, 8.01, 9.70, 13.35, and 14.24 μm; NMR ($CDCl_3$, 60 MHz) τ 6.34 (d, 2 H, J = 8.0 Hz), 6.30 (s, 3 H), 4.85 (t, 1 H, J = 8.0 Hz), 3.3–2.6 (m, 12 H), and 2.3–2.0 (m, 2 H).

To a solution containing 3.6 g of 3-(*o*-anisyl)-1,3-diphenyl-1-propanone in 60 mL of ether was added 5 mL of a 2.5 M solution of phenylmagnesium bromide in ether. After stirring the resulting solution at room temperature for 1.5 h, 40 mL of a 10% hydrochloric acid solution was added. The ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 3.98 g (88%) of 3-(*o*-anisyl)-1,1,3-triphenyl-1-propanol: IR (neat) 2.83, 3.35, 6.24, 6.72, 8.04, 8.96, 9.68, 13.29, and 14.32 μm; NMR ($CDCl_3$, 60 MHz) τ 7.45 (s, 1 H, exchangeable with D_2O), 6.90 (d, 2 H, J = 7.0 Hz), 6.41 (s, 3 H), 5.46 (t, 1 H, J = 7.0 Hz), and 3.4–2.6 (m, 19 H).

A mixture containing 5 mL of concentrated sulfuric acid and 45 mL of glacial acetic acid was added to 3.98 g of 3-(*o*-anisyl)-1,1,3-triphenyl-1-propanol. The resulting solution was stirred at room temperature for 5 min and was then diluted with water and extracted with ether. The ethereal extracts were washed with a 5% sodium bicarbonate solution and water, dried over magnesium sulfate, and concentrated under reduced pressure. The crude oil obtained was purified by medium pressure column chromatography using a 3% acetone–hexane mixture as the eluent to give 2.9 g (76%) of 3-(*o*-anisyl)-1,1,3-triphenyl-1-propene (**1**): mp 88–90 °C; IR (KBr) 6.25, 6.72, 8.0, 9.71, 13.24, and 14.35 μm; NMR ($CDCl_3$, 60 MHz) τ 6.46 (s, 3 H), 4.86 (d, 1 H, J = 10 Hz), 3.46 (d, 1 H, J = 10 Hz), and 3.1–2.6 (m, 19 H); UV (methanol) 256 nm (ε 18 200); *m/e* 376 (M^+), 299, 285, 268 (base), 255, 191, 181, 165, 105, 91, and 77.

A solution containing 500 mg of 3-(*o*-anisyl)-1,1,3-triphenyl-1-propene (**41**) in 475 mL of methanol was irradiated for 1 h using a 450-W Hanovia lamp equipped with a Corex filter. The solvent was removed under reduced pressure and the resulting oil was purified by thick-layer chromatography using a 10% acetone–hexane mixture as the eluent. The oil obtained was crystallized from 95% ethanol to give 350 mg (70%) of 3-(*o*-anisyl)-1,1,2-triphenylcyclopropane (**40**) which was identical with that obtained from treating phenol **37** with methyl iodide.

Further irradiation of **40** in methanol with Corex-filtered light gave phenanthrene and benzhydryl methyl ether in high yield.

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Photochemical Reaction of 2,3-Dihydro-2,3-methano-1,4-naphthoquinone Derivatives. Three Different Types of Reaction

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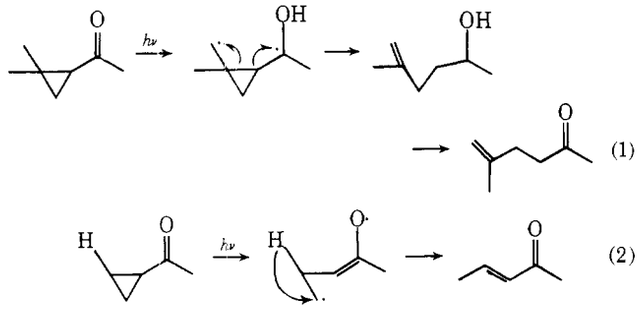
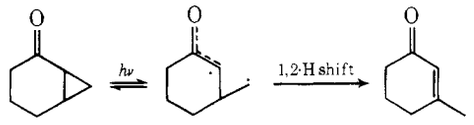
Photochemical reactions of 2,3-dihydro-2,3-methano-1,4-naphthoquinone derivatives in the presence or absence of a hydrogen donor were investigated. The modes of the photochemically induced reactions are dependent on the substituents on the cyclopropane ring, and the reactions can be classified as three different types: isomerization, hydrogen abstraction, and degradation.

The photochemistry of conjugated cyclopropyl ketones has been studied by W. G. Dauben et al. systematically.[1] Photoisomerization of the conjugated cyclopropyl ketones can occur via at least two different mechanistic sequences. The first is the well-known type II reaction (eq 1).[1] The second, found when the δ hydrogen is absent or its abstraction by the carbonyl oxygen atom is sterically impossible, is the cleavage of the bond of the cyclopropane ring adjacent to the carbonyl group. This reaction is accompanied with subsequent 1,2-hydrogen migration (eq 2).

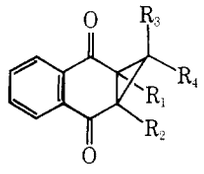


In the bicyclo[4.1.0]heptan-2-one series,[2] the two adjacent cyclopropyl bonds are in a different geometry with respect to the carbonyl group, and in these cases the C_1–C_7 bond cleaves to give cyclohexenones (eq 3). The irradiation of bicyclo[4.1.0]heptan-2-ones in 2-propanol gives cyclohexanones, resulting from the rupture of the outer bond.



(3)

In the present study, eight methanonaphthoquinones(**1a–h**) were prepared, and their photochemical behaviors were examined in both the presence and absence of xanthene, known as a highly reactive hydrogen donor.



1a	$R_1 = CH_3$; $R_2 = R_3 = R_4 = H$
b	$R_1 = R_2 = CH_3$; $R_3 = R_4 = H$
c	$R_1 = R_2 = R_3 = R_4 = H$
d	$R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
e	$R_1 = R_2 = COOEt$; $R_3 = R_4 = H$
f	$R_1 = CH_3$; $R_2 = R_3 = H$; $R_4 = Ph$
g	$R_1 = CH_3$; $R_2 = H$; $R_3 = R_4 = Ph$
h	$R_1 = CH_3$; $R_2 = H$; R_3,R_4 = fluorenyl

Results and Discussion

Photoisomerization of 2,3-Diethoxycarbonyl-2,3-dihydro-2,3-methano-1,4-naphthoquinone (1e). A solution of **1e** was irradiated under deaerated conditions in a Pyrex

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