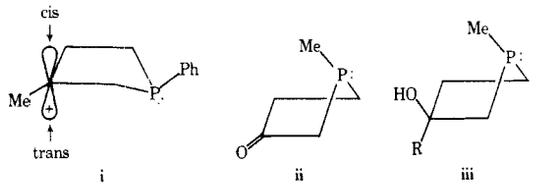
(1972); (b) W. G. Bentrude and H.-W. Tan, J. Am. Chem. Soc., 98, 1850 (1976).
(14) There is ample precedent for the deshielding effect by the P=O group, see, for example: K. L. Marsi and R. T. Clark, J. Am. Chem. Soc., 92, 3791 (1970).
(15) D. Z. Denney, G. Y. Chen, and D. B. Denney, J. Am. Chem. Soc., 91, 6838 (1969).
(16) (a) K. L. Marsi, F. B. Burns, and R. T. Clark, J. Org. Chem., 37, 238 (1972). (b) The only slight predominance of trans over cis isomers as well as no significant change in the ratio of cis/trans with change of alcohol suggested that contributions from structures such as I are important to the phospholanyl cation where no significant steric block to both faces of the phospholane ring is operative. This is in marked contrast with the previous observation[12] that the significantly higher content (>80%) of *cis*-alcohol **iii** was formed in the addition reaction of lithium aluminum hydride or Grignard reagents to 1-methyl-3-phospholanone **ii**, indicating contributions from structure **ii** to be important relative to the equatorially substituted form. Probably, nonbonded interaction in the phospholane ring system became much significant by the introduction of phenyl group on phosphorus atom.



i ii iii

(17) M. A. Weiner and G. Pasternack, J. Org. Chem., 32, 3707 (1967); 34, 1130 (1969).
(18) One might assign this absorption to the possible interaction of the lone pair on phosphorus with the phenyl ring since a similar single major band has been observed in the UV spectrum of triphenylphosphine; see H. H. Jaffé and M. Orchin "Theory and Applications of Ultraviolet Spectroscopy", Wiley, New York, N.Y., 1964, p 498. However, marked attenuation of this band in 2-methyl substituted phospholene is not consistent with this assignment.
(19) The interaction of the excited state of benzophenone with triphenylphosphine to give phosphine oxide and ylide has been reported; see L. D. Wescott, H. Sellers, and P. Poh, J. Chem. Soc., Chem. Commun., 586 (1970).
(20) Similar UV change upon addition of acid has been observed in 1-methylphosphole; see L. D. Quin, J. G. Bryson, and C. G. Moreland, J. Am. Chem. Soc., 91, 3307 (1969).
(21) L. D. Quin and D. A. Mathews, J. Org. Chem., 29, 835 (1964).
(22) W. B. McCormack, U.S. Patent 2663738 (1953); Chem. Abstr., 49, 7602f (1955).

Photochemical Rearrangements of 4,7-Dimethyl-3-chromanone and Related Compounds[1]

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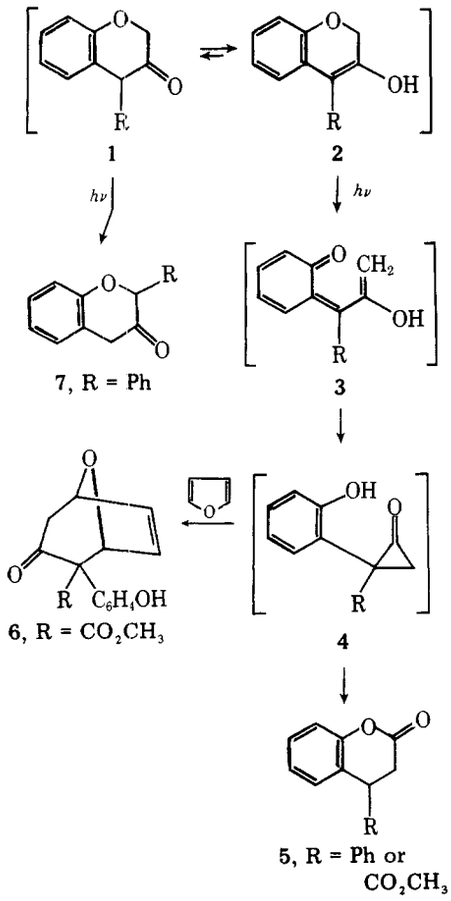
Photorearrangement reactions are described for 4,7-dimethyl-3-chromanone (**8**), 4,7-dimethyl-3-methoxychromene (**25**), and 1-phenyl-2-methoxy-3,4-dihydronaphthalene (**34**). Irradiation of **8** in basic methanol produces 2-hydroxy-3-methoxy-2,3,6-trimethyl-2,3-dihydrobenzofuran (**9**). The formation of **9** is readily explicable in terms of a photoinduced ring opening of the enol of **8** to give an *o*-quinoneallide intermediate (**17**) followed by 1,4-addition of methanol. Evidence for the proposed sequence was obtained by studying the photobehavior of the closely related 4,7-dimethyl-3-methoxychromene (**25**) system. Irradiation of **25** in methanol produced a mixture of 2,3-dimethoxy-3-(2-hydroxy-4-methylphenyl)-1-butene (**26**) and 2-methoxy-3-(2-hydroxy-4-methylphenyl)-1,3-butadiene (**27**). When the irradiation of **25** was carried out in benzene, a mixture of **27**, 2,6-dimethyl-2-methoxy-3-methylene-2,3-dihydrobenzofuran (**29**), and 1-methoxy-2-oxa-5,7-dimethylbenzobicyclo[3.1.0]hexene (**30**) was obtained. These products are most readily derived from an *o*-quinoneallide intermediate (**31**) formed by a photoinduced ring opening of the 3-chromene ring. The excited state behavior of the closely related 1-phenyl-2-methoxy-3,4-dihydronaphthalene (**34**) system was also studied and it was found to undergo a similar rearrangement.

In earlier reports from this laboratory,[2-4] evidence was presented which demonstrated that the enol content can be an overriding factor in determining the excited-state behavior of a carbonyl group. As part of our studies in this area, we investigated the photochemical rearrangement of several 4-substituted 3-chromanones (**1**) to 4-substituted dihydrocoumarins (**5**)[2,5] and found that the reaction involves the prior conversion of **1** into its enol tautomer **2**, which is subsequently converted to **5** on exposure to UV light in alcoholic solvents. When the irradiation was carried out in a nonpolar solvent, where the concentration of the enol form was negligible, photorearrangement from the keto tautomer occurred resulting in the formation of a rearranged 3-chromanone (i.e., **7**).[6] The unusual richness of the photochemistry of this system, which is a sensitive function of reaction conditions, including the choice of solvent, provides a useful probe for determination of reaction mechanism. The distribution of products and the ability to trap a cyclopropanone intermediate (i.e., **4**) with furan have permitted elucidation of the nature and sequence of intermediates involved in this photochemical system. We now wish to report that replacement of the 4-phenyl or carbomethoxy substituent with a methyl group markedly alters the outcome of the rearrangement. The present publication describes our findings with the 4,7-dimethyl-3-chromanone (**8**) system and delineates the significant role played by an *o*-quinoneallide intermediate in the overall photochemistry of this ring system.

Results and Discussion

4,7-Dimethyl-3-chromanone (**8**) was conveniently prepared by the series of reactions outlined in Scheme I. Its physical and spectroscopic properties are in excellent agreement with those previously reported by Still and Goldsmith.[7] The NMR spectrum of **8** in deuteriochloroform indicates that this system exists exclusively as the keto tautomer [60 MHz, τ 8.56 (d, 3 H, J = 7.0 Hz), 7.72 (s, 3 H), 6.52 (q, 1 H, J = 7.0 Hz), 5.67 (AB q, 2 H, J = 17.0 Hz), and 2.9–3.3 (m, 3 H)].

Irradiation of **8** in methanol resulted in a very slow and messy reaction; no characterizable products could be obtained. When a catalytic quantity of sodium methoxide was added to the solution, however, a very fast and clean reaction occurred upon irradiation. Under these conditions a high yield (75%) of 2-hydroxy-3-methoxy-2,3,6-trimethyl-2,3-dihydrobenzofuran (**9**) was obtained. The NMR spectrum of this compound showed that it consisted of a 79:21 equilibrium mixture of **9a** [(60 MHz, $CDCl_3$) τ 8.54 (s, 6 H), 7.68 (s, 3 H), 6.89 (s, 3 H), 4.85 (s, 1 H, exchanged with D_2O), and 2.8–3.5 (m, 3 H)] and 3-methoxy-3-(2-hydroxy-4-methylphenyl)-2-

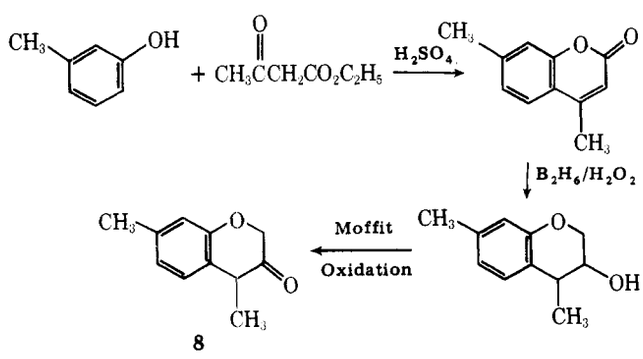


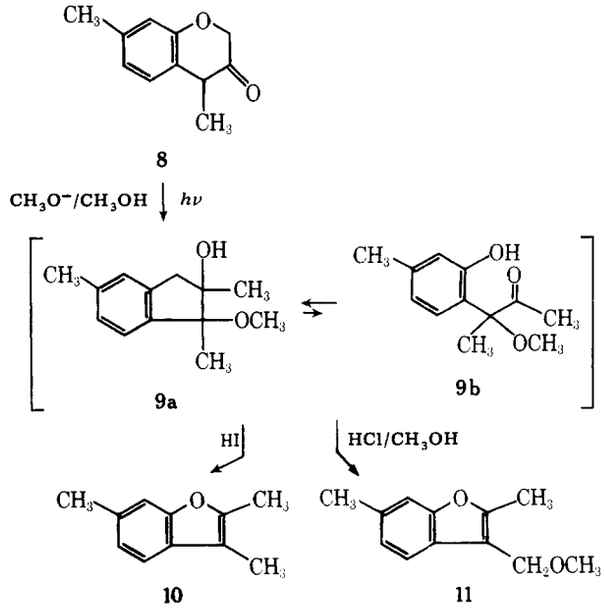
butanone (**9b**) [(60 MHz, $CDCl_3$) τ 8.31 (s, 3 H), 7.88 (s, 3 H), 7.72 (s, 3 H), 6.70 (s, 3 H), 2.8–3.5 (m, 3 H), and 1.94 (s, 1 H, exchanged with D_2O)]. Treatment of this equilibrium mixture with hydriodic acid resulted in the formation of 2,3,6-trimethylbenzofuran (**10**) in quantitative yield. Further evidence supporting the structure of the photoproduct was obtained by its ready conversion to 2,6-dimethyl-3-methoxybenzofuran (**11**) on treatment with acidic methanol.

A plausible mechanism for the formation of **11** from **9** is shown in Scheme II. Protonation of the ether oxygen will give carbonium ion **12** which subsequently loses a proton to produce allylic alcohol **13**, which, however, was not observed. Generation of the stable allylic cation **14** from **13** and reaction of this species with methanol readily rationalize the formation of **11**. As will be seen shortly, the closely related methyl ether derivative of alcohol **13** was also found to rapidly rearrange to **11** upon treatment with a trace of acid.

The formation of **9** from the irradiation of 3-chromanone **8** is readily explicable in terms of a photoinduced ring opening of enol **16** to give an *o*-quinoneallide intermediate **17** (see Scheme III). This transformation is analogous to the well-known ring openings of pyrans, chromenes, and other related

Scheme I

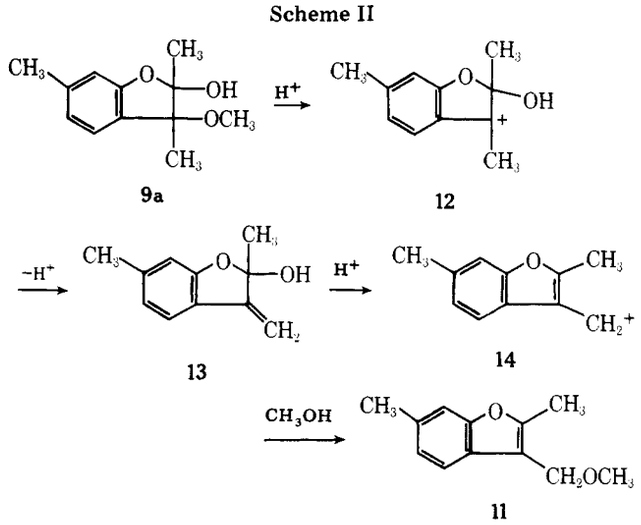




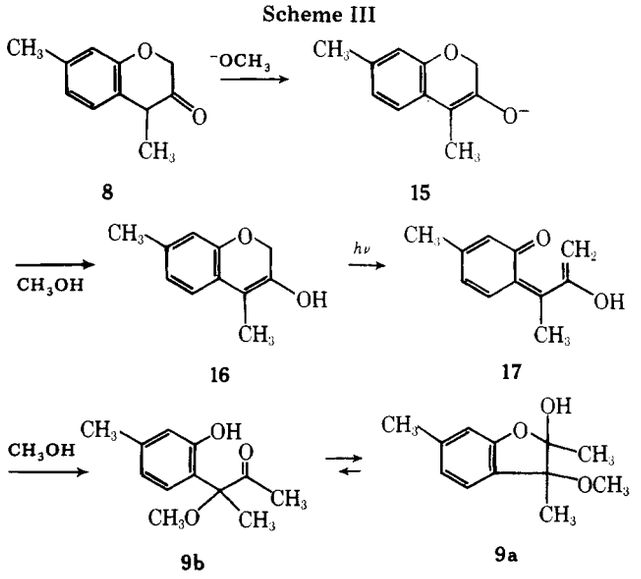
benzo-heterocyclic olefins.[8–15] Simple addition of methanol to *o*-quinoneallide **17** best rationalizes the formation of **9**.

Our present results are especially interesting in view of the fact that the irradiation of **8** does not afford any detectable quantities of a 4-substituted dihydrocoumarin (i.e., **5**, R = CH_3). As was pointed out in a previous report,[2] these hydroxyl

Scheme II

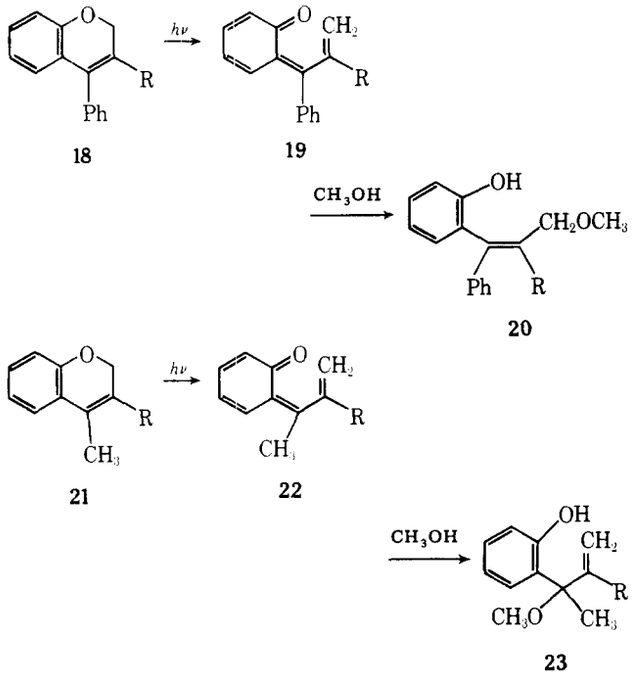


Scheme III



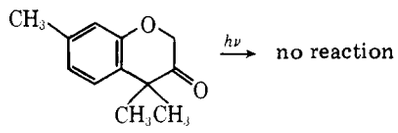
substituted o-quinoneallide intermediates (i.e., 3 or 17) have the appropriate structural elements to undergo an internal Michael addition to give a phenolic cyclopropanone (4) which is ultimately converted to a 4-substituted dihydrocoumarin (5). This type of transformation does indeed occur in the phenyl and carbomethoxy series.[2] The o-quinoneallide intermediate (17) generated from the irradiation of 8, however, prefers to undergo bimolecular addition of methanol across the C–C double bond. The diverse photobehavior of these substituted 3-chromanones may be related to the difference in reactivity of the o-quinoidal intermediates. Michael addition of methanol to the labile o-quinoneallide obtained from 8 would be expected to occur quite readily. This facile conjugate addition destroys the necessary chromophore for internal cyclization. Attack by methanol on the o-quinoidal intermediate containing a phenyl or carbomethoxy group on the β carbon is not as rapid, and consequently this species is long enough lived to undergo intramolecular cyclization to 5. The reactivity difference is presumably related to the fact that both the phenyl and carbomethoxy groups can conjugate with the o-quinonemethide portion of the transient o-quinoneallide intermediate. This added conjugation provides a stabilizing effect and moderates the bimolecular addition of nucleophiles at the β position of the unsaturated ketone.

Evidence supporting the above hypothesis is available from some earlier studies dealing with the photochemical ring opening reactions of substituted chromenes.[8,16] These studies showed that the photolysis of 4-phenylchromenes (18) in methanol resulted in the exclusive formation of a 1,6-methanol adduct (20). In contrast, the irradiation of 4-methyl substituted chromenes (21) in methanol gave rise to a 1,4 adduct (23) as the exclusive photoproduct. The difference in the mode of attack of methanol on the o-quinoidal intermediate formed from these chromenes (i.e., 19 or 22) can also be attributed to



a diminished propensity for bimolecular attack of methanol at the β position when a conjugating group is present on this carbon. The above data reinforce our contention that bimolecular conjugate addition of methanol is preferred over internal cyclization with o-quinoneallide 17. This difference in reactivity is presumably the factor which is responsible for the variation in the structures of the photoproducts obtained from these 4-substituted 3-chromanones.

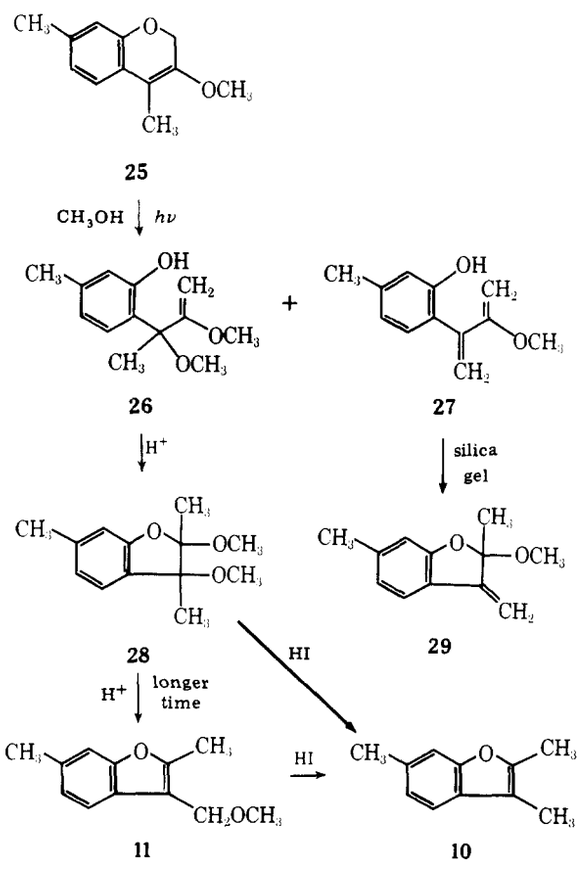
It is interesting to note that the irradiation of 8 in methanol is extremely complicated when the base was omitted. The effect of added base on the photochemistry of this system can best be rationalized in terms of the enol content present in solution. In pure methanol, insignificant amounts of the enol tautomer are present and consequently ring opening does not occur. The addition of sodium methoxide to a methanolic solution of 8 generates a sufficient quantity of the enol to allow the photochemical ring opening to proceed. Thus, the distribution of products obtained from the photolysis of the 3-chromanone system can be readily accounted for in terms of the small amount of enol (or enolate) present in tautomeric equilibrium with the keto form. Electronic excitation of the enol (or enolate) tautomer results in a photochemical ring opening to give an o-quinoneallide intermediate. The subsequent products obtained from the o-quinoneallide depend on the substituent groups present and the particular solvent employed. If the enol tautomer is unavailable, photochemical ring opening of the 3-chromanone system does not occur. For example, we note that 4,4,7-trimethyl-3-chromanone (24) fails to react even under lengthy photolytic conditions.



24

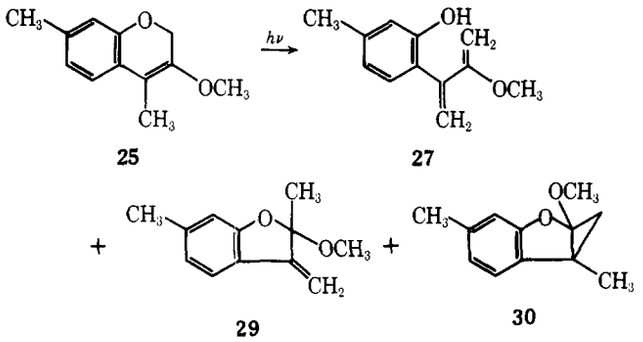
Since it was the 3-hydroxychromene tautomer of 8 which was suspected of giving rise to photoproduct 9, we sought to permanently lock 8 into its enol form and examine the behavior of the resulting system. This was accomplished by synthesizing the corresponding enol ether 25 and studying its photochemical behavior. Irradiation of 25 in methanol produced a mixture of two compounds, 26 and 27, in a 4:1 ratio. The structure of the major product (26) was established from its spectroscopic and chemical data (see Experimental Section). Chemical confirmation of structure 26 was obtained by

Scheme IV



treating it with acidic methanol and isolating 2,3,6-trimethyl-2,3-dimethoxy-2,3-dihydrobenzofuran (**28**) in quantitative yield. Prolonged treatment of **28** with acid produced benzofuran **11**. Both **11** and **28** gave 2,3,6-trimethylbenzofuran (**10**) when treated with hydriodic acid. The minor component (**27**) obtained from the photolysis of **25** rearranged on contact with silica gel to give 2,6-dimethyl-2-methoxy-3-methylene-2,3-dihydrobenzofuran (**29**). This material could be converted to **11** on treatment with a trace of acid. A summary of the results obtained is outlined in Scheme IV.

When the irradiation of enol ether **25** was carried out in benzene, the reaction followed a slightly different course. In this case a mixture of **27**, **29**, and 1-methoxy-2-oxa-5,7-dimethylbenzobicyclo[3.1.0]hexene (**30**) was isolated. The NMR spectrum of **30** showed doublets at τ 9.45 (1 H, J = 6.0 Hz) and



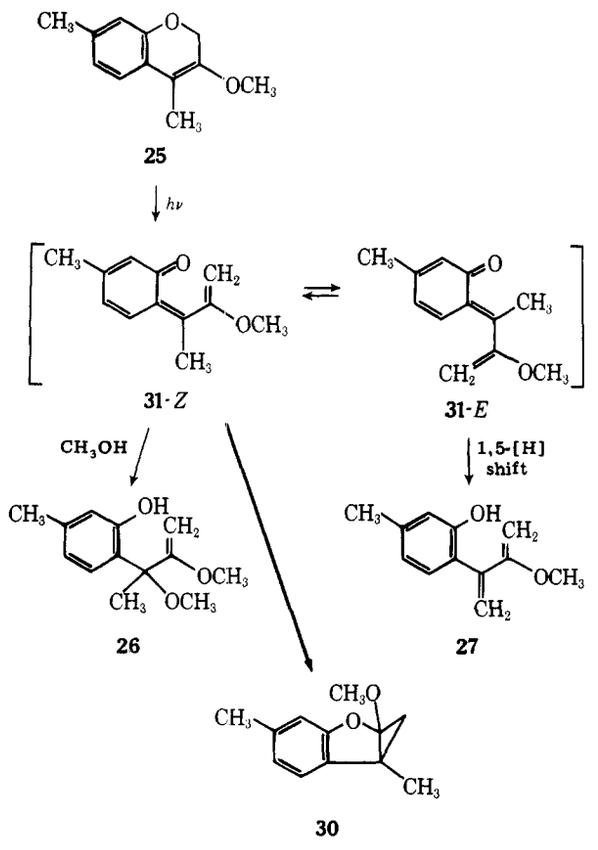
25 **27**

29 **30**

8.81 (1 H, J = 6.0 Hz) for the two cyclopropyl hydrogens and also contained three methyl singlets at τ 8.54, 7.72, and 6.48 in addition to the aromatic multiplet at τ 2.6–3.4.

We believe that all of the photochemical rearrangement products of **25** (i.e., **26**, **27**, **29**, and **30**) are derived from *o*-quinoneallide **31** as shown in Scheme V. The fate of **31** depends on the experimental conditions. The major product obtained in methanol corresponds to 1,4-addition of the solvent across the C–C double bond of **31**. The formation of **27**, on the other hand, involves a 1,5-sigmatropic hydrogen shift from the neighboring methyl group. In order for this transformation to proceed, the initially produced *o*-quinoneallide (**31**-*Z*) would have to undergo isomerization about the central double bond (i.e., formation of **31**-*E*) before it could be converted to **27**. This cis–trans isomerization could occur by a subsequent absorption of a photon of light. Alternatively, the photochemical ring opening of **25** could lead directly to an excited *o*-quinoneallide capable of subsequent geometrical isomerization to **31**-*E*. This latter possibility involves a direct conversion of an electronically excited state of the reactant (**25**) to an electronically excited state of the product (**31**-*Z*) followed by crossing to the ground state (**31**-*E*). Support for this viewpoint can be found in some work by Ullman and Huffman.[17,18] These authors found that the geometry of the photoenol produced in the photoenolization reaction of *o*-methylbenzophenone[19–21] is opposite that required for internal abstraction of a methyl hydrogen by the carbonyl group.[17] This observation was rationalized in terms of the formation of an excited enol which subsequently decayed to give a geometrically rearranged isomer. At this stage of our studies we do not have sufficient information to distinguish between the above two possibilities. Finally, the isolation of oxabenzobicyclohexene **30** from **25** in the benzene run is perfectly understandable since this solvent is incapable of undergoing conjugate addition to the *o*-quinoneallide intermediate and thus the system is sufficiently long enough lived to undergo cyclization by either thermal or photochemical means.[22]

Scheme V



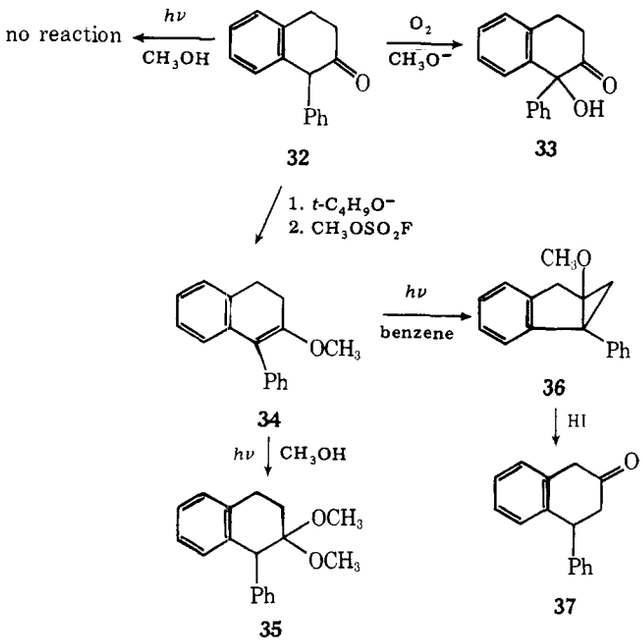
As part of our inquiries dealing with the photochemistry of carbonyl compounds through the enol form, we also decided to investigate the excited state behavior of the closely related 1-phenyl-2-tetralone (**32**) system. The procedure of Zaugg and co-workers[23] was followed for the preparation of this system. In contrast to the 4-phenyl-3-chromanone system,[2] this ketone was found to be inert toward a variety of photolytic conditions. When basic methanolic solutions were employed, the only reaction observed was the oxidation of **32** by trace amounts of oxygen present in solution. This oxidation, however, was subsequently shown to be a ground state reaction and can be attributed to the reaction of the enolate anion with ground state oxygen to give an α-hydroperoxy ketone which is subsequently reduced to **33**. Bordwell and others[24] have shown that related ketones undergo oxidative processes in the dark in the presence of base and oxygen via a similar path.

Although **32** was photochemically unreactive, the corresponding enol ether **34** did undergo smooth photochemistry. Irradiation of **34** in methanol produced 1-phenyl-2,2-dimethoxy-1,2,3,4-tetrahydronaphthalene (**35**) in high yield. A control experiment demonstrated that **34** was recovered unchanged from an acidic methanol solution which had been allowed to stand in the dark for 12 h. Thus, the formation of **35** involves a photochemical addition of methanol across the C–C double bond of starting material (Scheme VI). There have been several cases reported in the literature where olefins have been noted to undergo photoaddition with protic solvents.[25–29] It would appear, therefore, that **34** is another example of a system which undergoes a bona fide photochemical addition of methanol across the C–C double bond.

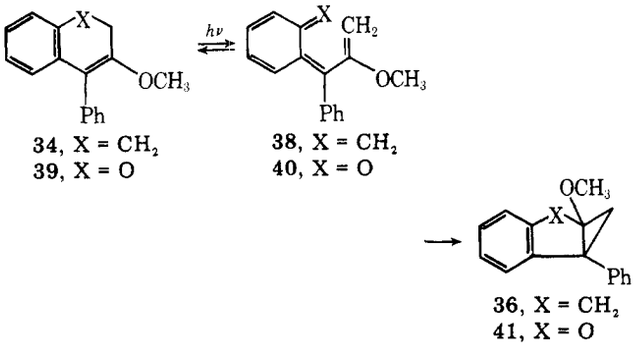
When the irradiation of **34** was carried out in benzene, the photoreaction followed an entirely different course. With this solvent system, a reaction analogous to that previously encountered with the 3-chromanone system occurred. Thus, the only product isolated upon direct irradiation of **34** in benzene was 1-methoxy-5-phenyl-3,4-benzobicyclo[3.1.0]-hexane (**36**). This material was readily converted to 4-phenyl-2-tetralone (**37**) on treatment with hydriodic acid.

The above results underscore the controlling effect of the oxygen atom on the photochemical behavior of these systems.

Scheme VI



Photolysis of **32** furnished none of the 2-tetralone (**37**) corresponding to dihydrocoumarin **5** but led instead to an overall oxidation (i.e., **33**). Similarly, irradiation of enol ether **34** does not produce a product derived from a ring-opened intermediate (i.e., **38**) when the irradiation is carried out in methanol. A possible explanation for the difference in the reactivity of this system relative to the chromene case (**39**) is that the initial ring-opened intermediate (**38**) derived from **34** may be converted back to starting material before it has a chance to react



further. This is probably related to the fact that **38** is incapable of undergoing a rapid thermal intramolecular Michael addition as was observed in the corresponding 3-chromanone system.[2] Bimolecular attack by methanol on **38** will also be a slow process. Thus the only path available to this system involves the addition of methanol to the excited state of **34** and formation of ketal **35**. In benzene, this competing mode of reaction cannot occur and the small amount of **38** present in steady state concentration eventually absorbs another photon of light and cyclizes to **36**. In support of this hypothesis, we note that the quantum yield for formation of **36** ($\Phi_{34\rightarrow 36}$ = 0.005) is much smaller than the value obtained in the 3-chromene system ($\Phi_{39\rightarrow 41}$ = 0.18).

In summary, the photolysis of 4-substituted 3-chromanones and their corresponding enol ether derivatives gives rise to a wide array of photoproducts. We have established plausible mechanisms for the observed rearrangements and have accounted for the role of solvent and substituent groups on the photobehavior of this ring system.

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 and at 60 MHz with a Varian T-60 spectrometer.

Preparation of 4,7-Dimethylchroman-3-one (8). 4,7-Dimethylcoumarin was prepared by a modification of the procedure described by Fries and Klostermann.[30] To a mixture containing 150 g of *m*-cresol and 130 g of ethyl acetoacetate at 0 °C was added 300 mL of concentrated sulfuric acid. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirred at 25 °C for 4 days. The deep red solution was poured onto ice and water was added until a white solid had formed. This material was collected and recrystallized from 95% ethanol to give 130 g (74%) of 4,7-dimethylcoumarin: mp 128–130 °C; IR (KBr) 5.82 μ; NMR ($CDCl_3$, 60 MHz) τ 7.41 (s, 6 H), 3.86 (s, 1 H), and 3.1–2.5 (m, 3 H).

A modification of the procedure described by Still and Goldsmith[7] was used to prepare 4,7-dimethylchroman-3-ol from 4,7-dimethylcoumarin. Diborane gas was generated by the dropwise addition of 50 g of boron trifluoride etherate to a solution of 11.5 g of sodium borohydride in 50 mL of diglyme. A nitrogen stream was used to transfer the diborane from the generating flask to the reaction vessel. The reaction vessel consisted of a gas drying tower with a fine frit, containing 30 g of 4,7-dimethylcoumarin in 300 mL of dry tetrahydrofuran. The entire system was thoroughly flushed with nitrogen and the reaction vessel was heated to 40 °C where it was maintained throughout the addition. When the gas flow was constant, the nitrogen stream was removed. The addition of diborane was complete after 3.5 h and the solution was transferred to a 1-L flask and allowed to stand at room temperature overnight. To this solution was added 160 mL of a 3 M sodium hydroxide solution followed by the cautious addition of 160 mL of a 30% hydrogen peroxide solution. The resulting mixture was stirred at room temperature for 6 h, acidified with a 10% hydrochloric acid solution, and extracted three times with ether. The ethereal extracts were washed with a 5% sodium hydroxide solution and water, and dried over magnesium sulfate. Concentration of the ether solution left a yellow oil which was distilled under reduced pressure to give 14 g (46%) of 4,7-dimethylchroman-3-ol: bp 128–132 °C (0.5 mm); mp 58–60 °C; IR (neat) 2.96 μ; NMR ($CDCl_3$, 60 MHz) τ 8.80 (d, 3 H, J = 7.0 Hz), 7.79 (s, 3 H), 7.26 (m, 1 H), 6.90 (s, 1 H, exchangeable with D_2O), 6.33 (m, 1 H), 6.03 (m, 2 H), and 3.4–2.9 (m, 3 H).

To an 8.0-g sample of 4,7-dimethylchroman-3-ol in 64 mL of anhydrous dimethyl sulfoxide was added 27.8 g of dicyclohexylcarbodiimide dissolved in 64 mL of anhydrous benzene. To this mixture was added 3.8 g of monophenyl phosphate in 10 mL of dry dimethyl sulfoxide. After the solution was stirred at room temperature for 2.5 h, 100 mL of ethyl acetate was added followed by the cautious addition of 100 mL of methanol containing 12.15 g of oxalic acid. The mixture was stirred for an additional 30 min and was then filtered. Benzene was added to the filtrate and the solution was washed several times with water, followed by a 5% sodium bicarbonate solution, dried over magnesium sulfate and concentrated under reduced pressure. The resulting oil was chromatographed on a silica gel column using a 20% ether–hexane mixture as the eluent. The oil obtained was distilled to give 6.4 g (81%) of 4,7-dimethylchroman-3-one (**8**): bp 65–67 °C (0.06 mm); IR (neat) 5.75, 6.12, 6.30, 6.65, 7.89, 9.48, and 12.26 μ; NMR ($CDCl_3$, 60 MHz) τ 8.56 (d, 3 H, J = 7.0 Hz), 7.72 (s, 3 H), 6.52 (q, 1 H, J = 7.0 Hz), 5.67 (AB q, 2 H, J_{AB} = 17 Hz), and 3.3–2.9 (m, 3 H); UV (methanol) 302 (shoulder) and 276 nm (ε 490 and 2100); m/e 176 (M^+), 161, 145, 133 (base), 105, 91, and 77.

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.76; H, 6.92.

Irradiation of 4,7-Dimethyl-3-chromanone in Methanol Containing Sodium Methoxide. A solution containing 300 mg of 4,7-dimethyl-3-chromanone (**8**) in 190 mL of methanol was purged with argon for 1 h and then a catalytic amount of sodium hydride (99%) was added. The resulting solution was irradiated with a 550-W Hanovia lamp equipped with a Pyrex filter for 10 min. The photolysate was neutralized using 1 g of ammonium chloride and the solution was concentrated under reduced pressure. Ether was added and the ethereal solution was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The oil obtained was purified by thick layer chromatography using a 10% acetone–hexane mixture as the eluent. The only band isolated contained 265 mg (75%) of an equilihrium mixture of 2-hydroxy-3-methoxy-2,3,6-trimethyldihydrobenzofuran (**9a**, 79%) and 3-methoxy-3-(2-hydroxy-4-methylphenyl)-2-butanone (**9b**, 21%). Major tautomer: IR (neat) 2.90 μ; NMR ($CDCl_3$, 60 MHz) τ 8.54 (s, 6 H), 7.68 (s, 3 H), 6.89 (s, 3 H), 4.85

(s, 1 H, exchangeable with D_2O), and 3.5–2.8 (m, 3 H); UV (methanol) 281 nm (ε 2500). Minor treatment: IR (neat) 5.81 μ; NMR ($CDCl_3$, 60 MHz) τ 8.31 (s, 3 H), 7.88 (s, 3 H), 7.72 (s, 3 H), 6.70 (s, 3 H), 3.5–2.8 (m, 3 H), and 1.94 (s, 1 H, exchangeable with D_2O).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.34; H, 7.82.

The structure of this tautomeric mixture was further verified by the chemical degradation studies outlined below. A 200-mg sample of 2-hydroxy-3-methoxy-2,3,6-trimethyldihydrobenzofuran (**9a**) was dissolved in 20 mL of methanol which contained 2 drops of concentrated hydrochloric acid. The resulting solution was stirred at room temperature for 4 h and was then concentrated under reduced pressure. Ether was added to the residue and the ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The resulting oil was purified by thick layer chromatography using a 10% acetone–hexane solution as the eluent to give 172 mg (94%) of 2,6-dimethyl-3-methoxymethylbenzofuran (**11**) as a colorless oil: IR (neat) 3.43, 6.12, 6.70, 7.85, 9.15, and 12.30 μ; NMR ($CDCl_3$, 60 MHz) τ 7.63 (s, 6 H), 6.72 (s, 3 H), 5.56 (s, 2 H), and 3.3–2.6 (m, 3 H); UV (methanol) 288 and 282 nm (ε 2925 and 3000).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.73; H, 7.46.

A solution containing 500 mg of 2-hydroxy-3-methoxy-2,3,6-trimethyldihydrobenzofuran (**9a**) in 15 mL of acetic acid containing 2 mL of 57% hydriodic acid was stirred at room temperature for 20 min. The reaction mixture was diluted with water and extracted with ether. The ethereal layer was washed with a saturated sodium bicarbonate solution, a 10% sodium thiosulfate solution, and water, and then dried over magnesium sulfate. The oil obtained after the removal of the solvent under reduced pressure was purified by thick layer chromatography using a 10% acetone–hexane mixture as the eluent. The major component isolated contained 340 mg (89%) of 2,3,6-trimethylbenzofuran (**10**): IR (neat) 3.43, 6.10, 6.71, 7.85, 11.64, and 12.39 μ; NMR ($CDCl_3$, 60 MHz) τ 7.92 (s, 3 H), 7.69 (s, 3 H), 7.60 (s, 3 H), and 3.2–2.7 (m, 3 H); UV (methanol) 291 and 283 nm (ε 2565 and 2815).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.52; H, 7.49.

Preparation and Irradiation of 4,4,7-Trimethyl-3-chromanone (24). A solution containing 1.6 mL of diisopropylamine in 75 mL of freshly distilled tetrahydrofuran was cooled to 0 °C and treated with 4.2 mL of a 2.4 M solution of *n*-butyllithium. The resulting solution was stirred at 0 °C for 20 min and 1.76 g of 4,7-dimethyl-3-chromanone (**8**) in 20 mL of tetrahydrofuran was added. After this solution was stirred at 0 °C for 30 min, 5 mL of methyl iodide was added. The solution was allowed to warm to room temperature and stirred at 25 °C for 12 h. The reaction mixture was diluted with ether, washed with a 10% hydrochloric acid solution and water, dried over magnesium sulfate, and concentrated under reduced pressure. The residual oil obtained was distilled to give 1.2 g (63%) of 4,4,7-trimethyl-3-chromanone (**24**): bp 80 °C (0.06 mm); IR (neat) 5.78, 6.77, 7.96, 8.58, 9.47, and 12.28 μ; NMR ($CDCl_3$, 60 MHz) τ 8.58 (s, 6 H), 7.72 (s, 3 H), 5.58 (s, 2 H), and 3.4–2.8 (m, 3 H); UV (methanol) 278 nm (ε 2020); *m/e* 190 (M^+), 175, 161, 147 (base), 133, 119, 91, and 77.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.70; H, 7.28.

Irradiation of 4,4,7-trimethyl-3-chromanone (**24**) under a variety of conditions led to the slow decomposition of the starting material but failed to produce any characterizable products.

Preparation of 4,7-Dimethyl-3-methoxychromene (25). A solution containing 2.8 g of potassium *tert*-butoxide in 50 mL of hexamethylphosphoramide in a thoroughly dry 100-mL round-bottom flask under nitrogen was cooled to 0 °C. To this solution was added 1.76 g of 4,7-dimethyl-3-chromanone (**8**) in 5 mL of hexamethylphosphoramide. After the resulting solution was stirred at 0 °C for 5 min, 2 mL of methyl fluorosulfonate was added and the reaction mixture was stirred for an additional 5 min at 0 °C. Ether was added and the ethereal solution was washed with several portions of water, dried over magnesium sulfate, and concentrated under reduced pressure. The crude oil obtained was purified by liquid–liquid chromatography[31] followed by distillation at 80 °C (0.03 mm) to give 1.1 g (58%) of 4,7-dimethyl-3-methoxychromene (**25**): IR (neat) 3.42, 6.20, 6.30, 6.68, 8.19, 8.83, 9.52, and 12.38 μ; NMR ($CDCl_3$, 60 MHz) τ 8.12 (t, 3 H, J = 1.5 Hz), 7.78 (s, 3 H), 6.43 (s, 3 H), 5.34 (q, 2 H, J = 1.5 Hz), and 3.5–3.0 (m, 3 H); UV (methanol) 302 and 272 nm (ε 4150 and 4900); *m/e* 190 (M^+), 175, 161, 147, (base), 105, 91, and 77.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75,81; H, 7.64.

Irradiation of 4,7-Dimethyl-3-methoxychromene in Methanol. A solution containing 200 mg of 4,7-dimethyl-3-methoxychromene (**25**) in 175 mL of methanol was irradiated with a 550-W Hanovia lamp equipped with a Pyrex filter for 1 h. Removal of the solvent under reduced pressure followed by purification of the residual oil by thick layer chromatography using a 10% acetone–hexane mixture as the eluent gave 185 mg (79%) of 2,3-dimethoxy-3-(4-methyl-2-hydroxyphenyl)-1-butene (**26**): IR (neat) 3.03, 3.43, 6.13, 6.34, 6.91, 8.75, 10.47, and 12.38 μ; NMR ($CDCl_3$, 60 MHz) τ 8.33 (s, 3 H), 7.78 (s, 3 H), 6.79 (s, 3 H), 6.52 (s, 3 H), 5.87 (d, 1 H, $J \approx 3.0$ Hz), 5.68 (d, 1 H, J = 3.0 Hz), 3.5–3.1 (m, 3 H), and 1.77 (s, 1 H, exchangeable with D_2O); UV (methanol) 281 (shoulder) and 276 nm (ε 2620 and 2690); *m/e* 222 (M^+), 207, 190, 175, 159 (base), 147, 133, 115, 105, 91, and 77. In addition to the signals described above, the crude photolysate contained peaks at 7.75 (s), 6.41 (s), 5.6–6.0 (m), 4.89 (m), 4.18 (m), 3.1–3.5 (m, 3 H), and 1.68 (s, 1 H, exchanged with D_2O) which were assigned to 2-methoxy-3-(2-hydroxy-4-methylphenyl)-1,3-butadiene (**27**). This material was unstable on silica gel giving rise to 2,6-dimethyl-2-methoxy-3-methylene-2,3-dihydrobenzofuran (**29**): IR (neat) 3.40, 6.15, 6.25, 6.67, 7.81, 8.86, 10.58, 11.65, and 12.31 μ; NMR ($CDCl_3$, 60 MHz) τ 8.42 (s, 3 H), 7.66 (s, 3 H), 6.87 (s, 3 H), 4.92 (s, 1 H), 4.44 (s, 1 H), and 3.4–2.6 (m, 3 H).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.92; H, 7.58.

The structure of **26** was further verified by treatment with acidic methanol. A solution containing 50 mg of 2,3-dimethoxy-3-(2-hydroxy-4-methylphenyl)-1-butene (**26**) in 15 mL of methanol containing 3 drops of concentrated hydrochloric acid was stirred at room temperature for 30 min. The solution was concentrated under reduced pressure and diluted with ether. The ethereal solution was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 45 mg (90%) of an oil which was identified as 2,3,6-trimethyl-2,3-dimethoxy-2,3-dihydrobenzofuran (**28**): IR (neat) 3.38, 6.14, 6.24, 6.67, 7.25, 8.89, 10.56, 11.49, 12.44, and 13.08 μ; NMR ($CDCl_3$, 60 MHz) τ 8.52 (s, 3 H), 8.42 (s, 3 H), 7.65 (s, 3 H), 7.02 (s, 3 H), 6.68 (s, 3 H), and 3.4–2.8 (m, 3 H); UV (methanol) 285 and 279 nm (ε 2570 and 2780); *m/e* 222 (M^+), 207, 190, 175, 159 (base), 133, 91, and 77.

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.42; H, 8.25.

If the above reaction was repeated by extending the reaction time to 5 h, no detectable quantity of 2,3,6-trimethyl-2,3-dimethoxy-2,3-dihydrobenzofuran (**28**) was obtained. The only product isolated was identified as 2,6-dimethyl-3-methoxymethylbenzofuran (**11**).

The structure of **28** was further verified by treatment with hydriodic acid. A 45-mg sample of 2,3,6-trimethyl-2,3-dimethoxy-2,3-dihydrobenzofuran (**28**) was dissolved in a mixture containing 4 mL of glacial acetic acid and 1 mL of 57% hydriodic acid. After stirring the resulting solution at room temperature for 20 min, the reaction mixture was diluted with water and extracted with ether. The ethereal extracts were washed with a saturated sodium bicarbonate solution followed by a 10% sodium thiosulfate solution and water. The organic phase was dried over magnesium sulfate and concentrated under reduced pressure. The residual oil obtained was chromatographed on a thick layer plate using a 10% acetone–hexane mixture as the eluent to give 23 mg (71%) of 2,3,6-trimethylbenzofuran (**10**).

Irradiation of 3-Methoxy-4,7-dimethylchromene in Benzene. A solution containing 200 mg of 3-methoxy-4,7-dimethylchromene (**25**) in 175 mL of benzene was purged with argon and irradiated with a 550-W Hanovia lamp equipped with a Pyrex filter for 3 h. The solvent was removed under reduced pressure leaving an oil which was purified by thick layer chromatography using a 10% acetone–hexane mixture as the eluent. The major band isolated contained 100 mg of 2,6-dimethyl-2-methoxy-3-methylene-2,3-dihydrobenzofuran (**29**), while the minor band contained 35 mg of an oil whose structure was assigned as 1-methoxy-2-oxa-5,7-dimethylbenzobicyclo[3.1.0]hexene (**30**) on the basis of its NMR spectrum: NMR ($CDCl_3$, 60 MHz) τ 9.45 (d, 1 H, J = 6.0 Hz), 8.81 (d, 1 H, J = 6.0 Hz), 8.45 (s, 3 H), 7.72 (s, 3 H), 6.48 (s, 3 H), and 3.4–2.6 (m, 3 H). The NMR spectrum of the crude photolysate also contained peaks at 7.75 (s), 6.41 (s), 6.0–5.6 (m), 4.89 (m), and 4.18 ppm (m) which are assigned to 2-methoxy-3-(2-hydroxy-4-methylphenyl)-1,3-butadiene (**27**). If the NMR sample was allowed to stand at room temperature for 2 weeks or stirred with silica gel for 3 h, the peaks due to 2-methoxy-3-(2-hydroxy-4-methylphenyl)-1,3-butadiene (**27**) disappeared and those peaks assigned to 2,6-dimethyl-2-methoxy-3-methylene-2,3-dihydrobenzofuran (**29**) were enhanced. When a solution of **29** was treated with acidic methanol it rearranged to give 2,6-dimethyl-3-methoxymethylbenzofuran (**11**) in 90% yield.

Preparation of 1-Phenyl-2-tetralone (32). The procedure of Weiss[32] was followed for the preparation of 1-phenyl-3,4-dihydronaphthalene: bp 135–140 °C (2 mm); IR (neat) 3.44, 6.28, 6.72, 6.95, 12.08, 12.93, 13.53, and 14.31 μ; NMR ($CDCl_3$, 60 MHz) τ 7.90–7.00

(m, 4 H), 4.02 (t, 1 H, J = 4.0 Hz), and 3.1–2.6 (m, 9 H).

A solution containing 24 g of the above 1-phenyl-3,4-dihydronaphthalene in 200 mL of chloroform was cooled to −10 °C and 25.6 g of *m*-chloroperbenzoic acid (85%) in 485 mL of chloroform was added dropwise over a period of 3.5 h. The solution was stirred at −10 °C for an additional 2 h and was then washed with a 2 M sodium hydroxide solution followed by water. The organic layer was dried over sodium sulfate and concentrated under reduced pressure to give 19.5 g (76%) of 1-phenyl-1,3-epoxy-3,4-dihydronaphthalene: mp 94–97 °C; IR (KBr) 3.54, 6.23, 6.92, 7.66, 8.65, 10.45, 11.06, 12.35, 12.78, 13.17, and 14.22 μ; NMR ($CDCl_3$, 60 MHz) τ 8.5–6.4 (m, 5 H) and 3.2–2.4 (m, 9 H).

A 19.0-g sample of 1-phenyl-1,2-epoxy-3,4-dihydronaphthalene was refluxed with 200 mL of 30% sulfuric acid solution for 3.5 h. The reaction mixture was cooled and extracted with ether. The ethereal extracts were washed with a saturated sodium bicarbonate solution and water, dried over magnesium sulfate, and concentrated under reduced pressure. The residual oil obtained was distilled to give 14 g (74%) of 1-phenyl-2-tetralone (**32**): bp 110–112 °C (0.05 mm) [lit.[23] bp 141–142 °C (0.5 mm)]; IR (neat) 5.80, 6.25, 6.71, 6.91, 8.72, 13.40, and 14.31 μ; NMR ($CDCl_3$, 60 MHz) τ 7.64–7.33 (m, 2 H), 7.14–6.87 (m, 2 H), 5.34 (s, 1 H), and 3.26–2.64 (m, 9 H); UV (methanol) 290 (shoulder), 272, 266, and 259 nm (ε 570, 850, 910, and 900).

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.32; H, 6.29.

Preparation of 1-Phenyl-2-methoxy-3,4-dihydronaphthalene (34). To a solution containing 2.8 g of potassium *tert*-butoxide in 50 mL of hexamethylphosphoramide at 0 °C was added 1.92 g of 1-phenyl-2-tetralone (**32**) in 5 mL of hexamethylphosphoramide. The resulting solution was stirred at 0 °C for 5 min and 2 mL of methyl fluorosulfonate was added. After this solution was stirred at 0 °C for 5 min, ether was added and the ethereal layer was removed, washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The solid obtained was recrystallized from 95% ethanol to give 1.2 g (59%) of 1-phenyl-2-methoxy-3,4-dihydronaphthalene (**34**): mp 81–82 °C; IR (KBr) 6.14, 6.76, 7.35, 7.99, 9.52, 13.12, 13.68, and 14.16 μ; NMR ($CDCl_3$, 60 MHz) τ 7.68–6.87 (m, 4 H), 6.53 (s, 3 H), and 3.45–2.52 (m, 9 H); UV (methanol) 276 nm (ε 10 800); *m/e* 236 (M^+, base), 221, 193, 178, 115, 91, and 77.

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.26; H, 6.83.

Irradiation of 1-Phenyl-2-methoxy-3,4-dihydronaphthalene in Methanol. A solution containing 200 mg of 1-phenyl-2-methoxy-3,4-dihydronaphthalene (**34**) in 160 mL of methanol was irradiated with a 550-W Hanovia lamp equipped with a Pyrex filter sleeve for 3.5 h. The solvent was removed under reduced pressure and the residual oil was purified by thick layer chromatography using a 10% acetone–hexane mixture to give 160 mg (70%) of 1-phenyl-2,2-dimethoxy-1,2,3,4-tetrahydronaphthalene (**35**): IR (neat) 3.38, 6.24, 6.67, 6.88, 8.90, 9.04, 9.45, 11.15, 13.46, and 14.27 μ; NMR ($CDCl_3$, 100 MHz) τ 8.02 (t, 2 H, J = 8 Hz), 7.03 (t, 2 H, J = 8 Hz), 6.81 (s, 6 H), 5.64 (s, 1 H), and 3.2–2.6 (m, 9 H); UV (methanol) 272 and 263 nm (ε 440 and 650); *m/e* 236 (base), 221, 205, 191, 178, 105, 91, and 77.

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.38; H, 7.46.

This same material was formed when the irradiation of **34** was carried out in the presence of 1 g of sodium bicarbonate in 150 mL of methanol. A control experiment showed that 1-phenyl-2-methoxy-3,4-dihydronaphthalene (**34**) was stable in the dark in the presence of methanol which contained formic acid.

The structure of **35** was further verified by hydrolysis to 1-phenyl-2-tetralone. A solution containing 100 mg of 1-phenyl-2,2-dimethoxy-1,2,3,4-tetrahydronaphthalene (**35**) in 25 mL of methanol was thoroughly deaerated with argon. To this solution was added 5 mL of a 10% hydrochloric acid solution and the resulting solution was stirred at room temperature for 2 h. The reaction mixture was diluted with ether, washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 70 mg (84%) of 1-phenyl-2-tetralone (**32**).

Irradiation of 1-Phenyl-2-methoxy-3,4-dihydronaphthalene in Benzene. A solution containing 150 mg of 1-phenyl-2-methoxy-3,4-dihydronaphthalene (**34**) in 160 mL of benzene was irradiated using a 550-W Hanovia lamp equipped with a Pyrex filter sleeve for 20 h. The solvent was removed under reduced pressure and the residual oil was subjected to thick layer chromatography using a 10% acetone–hexane mixture as the eluent. The only band isolated contained 87 mg (58%) of 1-methoxy-5-phenyl-3,4-benzobicyclo[3.1.0]hexene (**36**): IR (neat) 3.43, 6.27, 7.94, 8.71, 9.46, 10.97, 12.31, 13.12, and 14.30 μ; NMR ($CDCl_3$, 60 MHz) τ 9.19 (d, 1 H, J = 5.0 Hz), 7.98 (d, 1 H, J = 5.0 Hz), 6.73 (s, 3 H), 6.22 (s, 2 H), and 3.1–2.5 (m, 9 H); *m/e* 236 (M^+), 205 (base), 178, 159, 115, 91, and 77.

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.34; H, 6.81.

The structure of the photoproduct was further verified by chemical degradation to 4-phenyl-2-tetralone. To a solution containing 80 mg of 1-methoxy-5-phenyl-3,4-benzobicyclo[3.1.0]hexene (**36**) in 3 mL of glacial acetic acid was added 0.5 mL of hydriodic acid (57%). The resulting solution was heated at reflux for 35 min. The reaction mixture was cooled, diluted with water, and extracted with ether. The ethereal layer was washed with a saturated sodium bicarbonate solution, a 10% sodium thiosulfate solution, and water. After drying over magnesium sulfate, the ethereal solution was concentrated under reduced pressure to give 37 mg (49%) of 4-phenyl-2-tetralone (**37**): IR (neat) 5.81, 6.22, 6.70, 6.90, 8.11, 13.32, and 14.31 μ; NMR ($CDCl_3$, 60 MHz) τ 7.20 (d, 2 H, J = 6 Hz), 6.46 (s, 2 H), 5.64 (t, 1 H, J = 6 Hz), and 3.2–2.6 (m, 9 H). This material was identical in every respect with an authentic sample prepared by the method of Fine and Stern.[33]

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