A Study of Photoaddition Reactions of Chromone

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Abstract: Photoaddition reactions of chromone with different olefins and an acetylene have been carried out and the products identified. Photostability studies have shown that all of the 1:1 adducts are primary photoproducts. Competition experiments indicate that excited chromone is electrophilic in its reaction with extramolecular multiple bonds. Phosphorescence emission data indicates that the n $\rightarrow \pi^*$ triplet state of chromone is involved in these reactions. This is supported by additional chemical evidence. The photoaddition reaction of chromone with 1,1-dimethoxyethylene indicates that orientational specificity can operate in these reactions. The mechanism of these reactions is probably best described as an electrophilic attack by C_α of the n $\rightarrow \pi^*$ chromone triplet on the olefin to give a 1,4-diradical intermediate which closes to a cyclobutane. Products derived from initial hydrogen abstraction from the olefin by the carbonyl oxygen of excited chromone are also obtained.

Many examples of addition reactions of photochemically excited molecules to extramolecular multiple bonds have been reported in the literature.[1] Previously we have shown that coumarin undergoes sensitized photoaddition reactions to olefins.[2] It was then decided to examine the photochemistry of chromone. Since the ground-state chemistry of the two compounds is in many cases different, it was reasonable to assume that their excited-state reactions might also differ. Recently we have found that chromone undergoes unsensitized photoaddition reactions to olefins and acetylenes.[3] The reactions of chromone with tetramethylethylene, cyclopentene, butyne-2, and 1,1-dimethoxyethylene have been carried out.

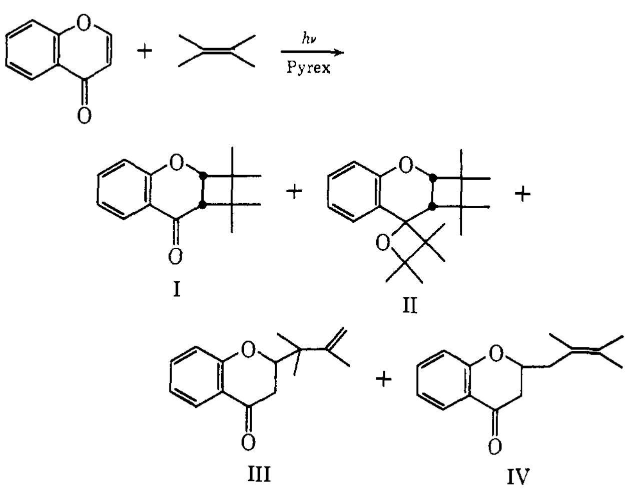
Additional photochemical studies have been made on these systems in an attempt to characterize the excited state of chromone and elucidate the mechanism of the reactions. The origin and photostability of the various products is described. Results of competition experiments and factors controlling product orientation are discussed. The absorption and emission spectra of chromone have been examined and an attempt has been made to correlate this data with the photoaddition reactions.

Results

A. Product and Photostability Studies. All compounds were irradiated through Pyrex glass with a 450-W mercury arc lamp.

Irradiation of a solution of chromone, tetramethylethylene, and dioxane produced four photoadducts which were isolated and identified as I-IV.[4] This reaction was examined in the presence and absence of benzophenone sensitizer. In both reactions the same number of adducts were obtained in the same ratio.

The nmr spectrum of adduct I contains two cyclobutane hydrogens at τ 6.95 and 5.30, each as a doublet (J = 9 cps). The nmr spectrum of II shows the two cyclobutane hydrogens at τ 6.42 and 5.83, each as a doublet (J = 9 cps). Based on the nmr spectra and other chemical data, it is believed that the rings are fused *cis* in adducts I and II. The large coupling constant (J = 9 cps) obtained for the cyclobutane hydrogens requires that they have a *cis* orientation[2] and the value is in agreement with that found for *cis* hydrogens in a similar system.[5] In addition these adducts can be chromatographed and separated unchanged on neutral alumina, conditions which Corey[1b] has shown will isomerize a *trans* 6–4 ring junction to the *cis*. No evidence was obtained for the *trans* form of I.



Using gas–liquid partition chromatography to follow the course of this reaction, it was seen that initially I was the only major product and that II, III, and IV were present in smaller amounts. However, at the end of the reaction the ratio of I to the other products had decreased. Therefore it was decided to examine the photostability of the products involved. Irradiation of I under reaction conditions produced II as the only major product. A trace of III was detected by glpc; however, the amount was far too small to account for the yield of III formed in the initial reaction. Adduct II was shown to be photostable by a similar experiment. Adducts III and IV were individually irradiated under the reaction conditions. It was shown that on pro-

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[1] (a) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2454 (1962); (b) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *ibid.*, **86**, 5570 (1964); (c) P. E. Eaton, *Tetrahedron Letters*, 3695 (1964); (d) D. Valentine, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 5202 (1964).

[2] J. W. Hanifin and E. Cohen, *Tetrahedron Letters*, 1419 (1966).

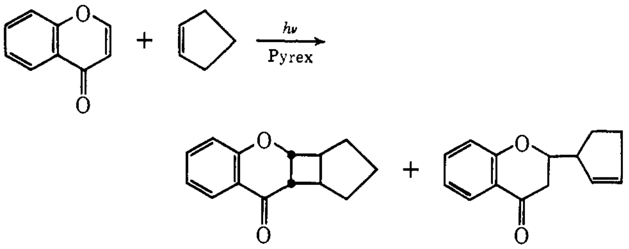
[3] J. W. Hanifin and E. Cohen, *ibid.*, 5421 (1966).

[4] The initial publication[3] describing this reaction does not list adduct IV as a reaction product. Since then IV has been successfully isolated and characterized.

[5] G. M. Blackburn and R. J. H. Davis, *Chem. Commun.*, 215 (1965).

longed irradiation neither adduct was photostable; however, neither one produced any of the other three photoadducts. These experiments indicate that III and IV are primary photoadducts.

To continue the scope of this reaction, the photoaddition of chromone with cyclopentene was investigated. Irradiation of a solution of chromone and cyclopentene yielded one major (V) and one minor (VI) product.

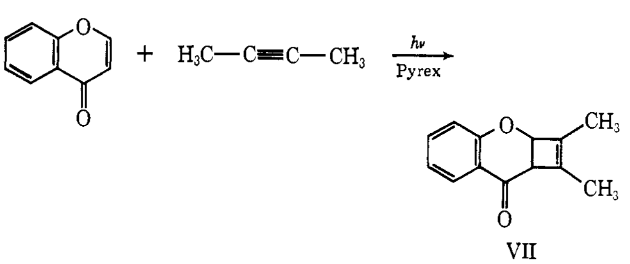


V VI

The stereochemistry of adduct V was again assigned on the basis of its nmr spectrum and chemical data. The compound can be chromatographed without change on neutral alumina indicating *cis* fusion at the 6–4 ring junction.[1b] The nmr spectrum shows the hydrogen α to the ether oxygen coupled to two hydrogens ($J = 8$ cps and $J = 3.5$ cps). Since it is known that this hydrogen is coupled to one *cis* hydrogen α to the carbonyl and this coupling is of the order 8–11 cps,[2,5] then the coupling to the other ring hydrogen, $J = 3.5$ cps, is presumably with a *trans* hydrogen.

Once again the photostability of the major product was investigated. It was shown that no amount of VI is formed by irradiation of V under the reaction conditions. Therefore, VI is a primary photoadduct.

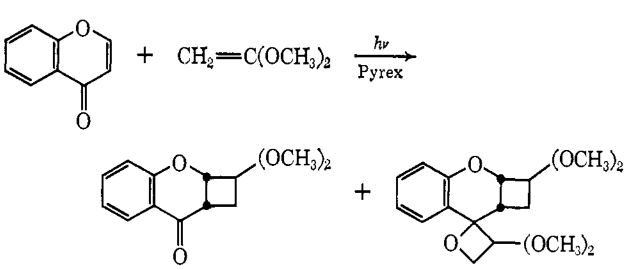
Photoaddition reactions of chromone were also carried out with an acetylene. Irradiation of a solution of chromone, butyne-2, and dioxane gave VII as the only photoproduct. Subsequent photochemical reactions of VII were not investigated.



VII

To further characterize the excited state of chromone, the photochemical reaction of chromone and 1,1-dimethoxyethylene was investigated. It was felt that the orientation of the product might be indicative of the charge distribution of chromone in the excited state.

Irradiation of a solution of chromone and 1,1-dimethoxyethylene gave two photoadducts which were isolated and identified as major and minor products VIII and IX. Further experiments have shown that IX is a secondary photolysis product arising from VIII.



VIII IX

The orientation of adduct VIII is readily deduced from its nmr spectrum. It shows that the hydrogen α to the ether oxygen is split only into a doublet. This eliminates the adduct with the opposite orientation since this hydrogen would then be coupled to three hydrogens. From the magnitude of the coupling constant, $J = 9$ cps, it is believed that the rings are fused *cis*.[2,5]

B. Competition Experiments to Determine Relative Rates of Reaction. In order to determine relative rates of addition of excited chromone with various olefins and acetylenes, competition experiments were carried out. In each case chromone was irradiated in the presence of cyclopentene and 1 molar equiv of another olefin or acetylene. The yields of products from these reactions were determined by gas–liquid partition chromatography and the ratio of primary products from the olefin or acetylene to those from cyclopentene was taken as a measure of relative rates.[6] The results of these experiments are given in Table I. The data suggest that excited chromone is electrophilic in its reaction with multiple bonds.

Table I. Competition between Various Olefins (Acetylenes) and Cyclopentene for Excited Chromone

Olefin (acetylene)	Obsd ratio of products	Rel rate factor[a]
1,1-Dimethoxyethylene	1.83	3.66
Cyclopentene		1.00
Tetramethylethylene	0.78	0.78
Butyne-2	0.06	0.06

[a] Factors of 2 were applied to observed ratios in the case of cyclopentene, tetramethylethylene, and butyne-2 in which there are two modes of addition which lead to the same product. This correction was also used by Corey[1b] in the competition experiments involving excited 2-cyclohexenone.

Emission and Absorption Spectra. In order to try to identify the excited state of chromone which is involved in these photoaddition reactions, the emission and absorption spectra were examined. In 2-methyltetrahydrofuran (2-MTHF) at 77°K, chromone shows a strong blue-violet phosphorescence with vibrational bands at 381, 392, 407, 419, 435, 447, and 465 mμ (see Figure 1). No fluorescence was observed. The lifetime of the triplet was determined to be 38 msec, which is in good agreement with that reported for n–π^* triplets.[7-9] The 0–0 band at 381 mμ corresponds to a triplet

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(6) Corey[1b] has conducted similar competition experiments with excited 2-cyclohexenone.

(7) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 46.

(8) The mean phosphorescence lifetime was the same at each of the vibrational bands.

(9) The spacing between successive vibrational bands is too small to correspond to the ground-state carbonyl stretching frequency. The spacing between the 0–0 and 0–1 bands is 740 cm^{-1} which may correspond to some ring deformation modes of the type reported for naphthalene.[10] It can be pointed out, however, that the spacing between alternate bands does correspond to the carbonyl stretching frequency. For instance, the spacing between the 0–0 and 0–2 bands is 1677 cm^{-1}. This may or may not be fortuitous.

(10) T. G. Pavlopoulos, *Mol. Phys.*, **14**, 87 (1968), and references therein.

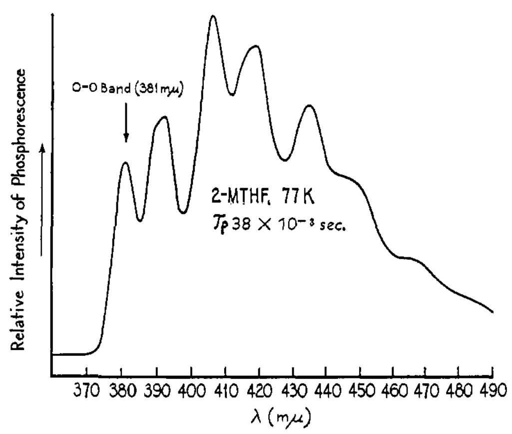


Figure 1. Phosphorescence emission spectrum of chromone.

energy of 75.1 kcal/mol. The phosphorescence emission spectrum was also examined in 3-methylpentane (3-MP) at a concentration of 10^{-4} *M* chromone and found to be essentially the same.

The absorption spectrum of chromone was examined in both solvents. In 3-MP the 0–0 band for the n,π^* (singlet–singlet) absorption is at 360 mμ (ϵ ~25). In 2-MTHF the 0–0 band is shifted to approximately 355 mμ which corresponds to an S_1 (n,π^*) of 80.5 kcal/mol. The blue shift observed on changing to a more polar solvent as well as the small extinction coefficient is characteristic of n,π^* absorption.[7] In 2-MTHF, the difference between S_1 and T_1 is therefore about 5 kcal/mol. The lowest π,π^* absorption maximum is at 301 mμ in 3-MP and 302.5 mμ (94.5 kcal/mol) in 2-MTHF.

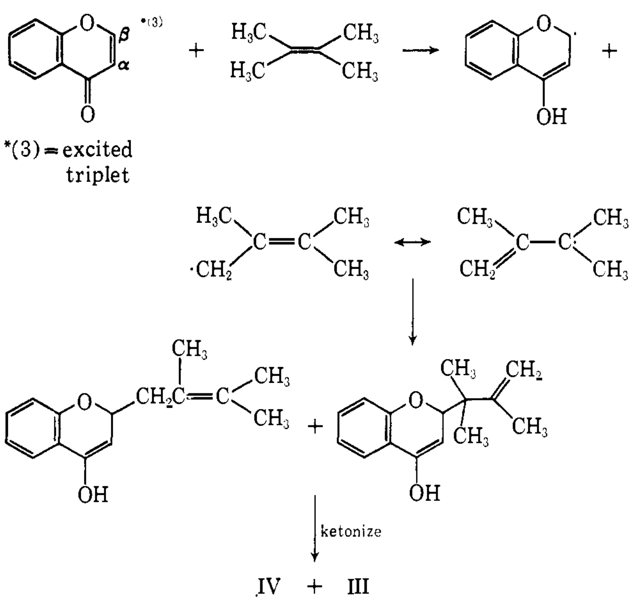
Discussion

The phosphorescence emission data indicates that the excited state of chromone which is most likely involved in these photoaddition reactions is the n–π^* triplet. The fact that only phosphorescence and no fluorescence emission is observed is consistent with the idea that intersystem crossing from the n–π^* singlet to the triplet should be rapid when the singlet–triplet energy gap is small.[11] As was previously pointed out from the spectral data, the singlet–triplet energy gap for chromone in 2-MTHF is only about 5 kcal/mol.[12]

Futher evidence for the triplet state being involved in these reactions comes from the attempted sensitization of the chromone–tetramethylethylene photoaddition. When this reaction was carried out in the presence of benzophenone sensitizer, the same products were obtained in the same ratio. The fact that the sensitizer has no effect on the reaction indicates that in the unsensitized reaction excited chromone singlet rapidly undergoes intersystem crossing to the triplet which then reacts with ground-state olefin. In this respect photoaddition reactions of chromone differ from those of coumarin where a sensitizer is required to produce the coumarin triplet which then reacts with olefin.[2,13]

Previously it was stated that irradiation of chromone in tetramethylethylene yielded four photoadducts (I–IV). Photostability studies established that adducts III and IV were indeed primary photoproducts. The most reasonable mechanism to account for the formation of III and IV is shown in Scheme I. It involves initial abstraction of a methyl hydrogen from the olefin by the carbonyl oxygen of the excited chromone triplet.

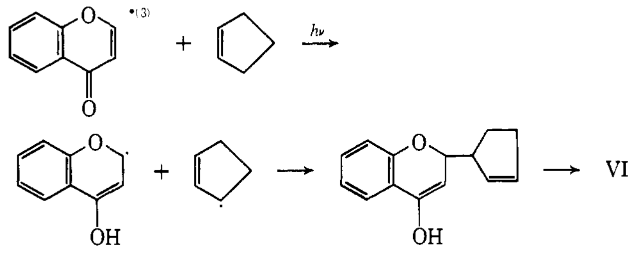
Scheme I



*(3) = excited triplet

The formation of IV is of particular significance because it can only be produced by an intial hydrogen abstraction. In addition, these results are in good agreement with the postulate that it is the n–π^* triplet of chromone which is involved in these reactions since the n–π^* triplet state is known to be a good hydrogen abstractor.[15,16]

Similarily, the formation of minor amounts of VI in the photoaddition reaction of chromone with cyclopentene is best accounted for by this type of mechanism.



In the case of the photoaddition reaction of chromone with 1,1-dimethoxyethylene only one of the possible

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[11] Reference 7, p 59.

[12] We have indicated that chromone undergoes intersystem crossing from its lowest n,π^* singlet directly to the lowest n,π^* triplet. An alternate possibility for the intersystem crossing could involve going from the lowest n,π^* singlet to an intermediate π,π^* triplet followed by internal conversion to the lowest n,π^* triplet. At this time no choice can be made between these two possibilities.

[13] For coumarin the singlet–triplet energy gap is reported to be about 20 kcal/mol.[14] This large energy gap is possibly one of the factors responsible for coumarin's less efficient or slower rate of intersystem crossing.

[14] G. S. Hammond, C. A. Stout, and A. A. Lamola, *J. Am. Chem. Soc.*, **86**, 3103 (1964).

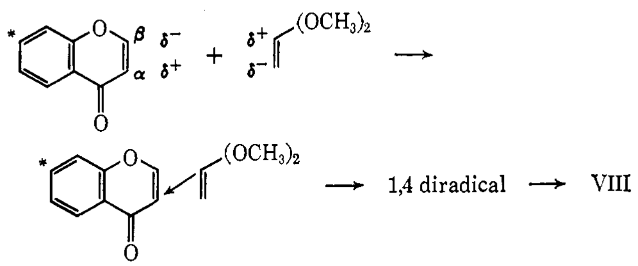
[15] P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 93 (1968).

[16] The phosphorescence of coumarin has been examined and the lifetime of the triplet determined to be 0.43 sec at several of the vibrational bands, with the 0–0 band being located at 460 mμ. This lifetime is in agreement with that reported for π,π^* triplets. Since the π,π^* triplet state is known to be a poor hydrogen abstractor,[17] this explains why no products of this nature were found in the photoaddition reactions of coumarin with olefins.[2]

[17] Reference 7, p 153.

position–isomeric structures is formed. This indicates that orientational specificity is involved in this reaction. It has been proposed by Corey[1b] that the photoaddition reactions of 2-cyclohexenones with substituted olefins may involve initial formation of a π complex between the excited state of one molecule and the ground state of another. The factor which controls the orientation of the product is the geometry of this intermediate π complex. The initial reason for suggesting a π complex was that the orientation of the product did not correspond to the stability of the intermediate 1,4 diradical involved. An intermediate π complex, however, would explain the orientation.

If such a π complex between the excited state of chromone and the ground state of 1,1-dimethoxyethylene is considered to intervene, then it is clear from the structure of VIII that the orientation of the π complex must be X. Further it is suggested that in the excited state of chromone C_α is positive relative to C_β.

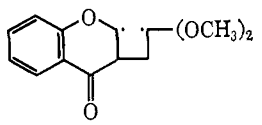


X

π complex

However, in these reactions involving excited chromone, the experimental evidence does not necessarily demand the intermediacy of this π complex because the orientation of the product (VIII) can be related to the stability of an intermediate 1,4 diradical. In attempting to decide whether a π complex is involved, an important fact is whether the initial carbon–carbon bond formation is with C_α or C_β of chromone. If the C_α of chromone initially bonds to the olefin to give a 1,4 diradical, then VIII can be considered as arising from the most stable diradical (XIa), and the necessary intermediacy of the π complex can be questioned. If, however, initial bond formation involves the C_β of chromone, then the orientation of VIII cannot be explained by the stability of the intermediate diradical, since the least stable diradical (XIIa) is involved. In this case the orientation of VIII might be explained by the intervention of a π complex.

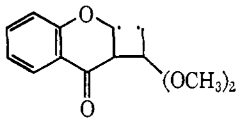
If α Attack



XIa

(most stable)

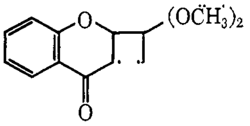
or



XIb

(least stable)

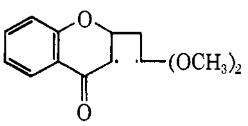
If β Attack



XIIa

(least stable)

or



XIIb

(most stable)

Our experimental evidence indicates that the initial carbon–carbon bond formation is with C_α of chromone. The results of the competition experiments characterize the excited chromone triplet as an electrophilic species since it prefers to react with an olefin with an electron-rich double bond. The orientation of VIII indicates that C_α is positive relative to C_β in the excited state since in the product C_α is bonded to the carbon of the olefin which is most nucleophilic. Therefore it is most reasonable to conclude that initial carbon–carbon bond formation is with C_α. In this case the most stable 1,4 diradical XIa would be expected to be produced. Since the product (VIII) can then be considered as proceeding from the most stable diradical intermediate, we can make no decision about the intermediacy of a π complex.

The question as to whether a π complex between the excited state of chromone and the ground state of olefin is involved in these reactions is still being investigated. Further phosphorescence studies have been conducted employing as a solvent the olefin used in the photoaddition reaction. While the results are somewhat inconclusive, no evidence for emission from such a π complex has been obtained. It should be emphasized, however, that although we have not yet found evidence for such a π complex, we certainly have not disproved its existence.

The possibility that these reactions might involve a donor-acceptor complex between ground-state chromone and olefin has also been investigated. Absorption studies were carried out on chromone dissolved in 1,1-dimethoxyethylene. No evidence for such a donor–acceptor complex was obtained. The absorption spectrum of chromone in 1,1-dimethoxyethylene was the same as in 2-MTHF.

In conclusion, the mechanism of cyclobutane formation is probably best described as an electrophilic attack by C_α of the n-π^* chromone triplet on the most nucleophilic carbon atom of the olefin to give a 1,4-diradical intermediate such as XIa. This is followed by formation of the cyclobutane ring. Depending upon the olefin used, one may also obtain products derived from initial hydrogen abstraction as a competing reaction.

Experimental Section

Procedure for Photoaddition Reactions. Two different techniques were used to carry out these irradiations depending upon the size of the reaction. In one case the immersion apparatus supplied by the Hanovia Lamp Division of Englehard Industries was used. This consisted of an irradiation vessel fitted with a water-cooled quartz immersion well, magnetic stirring bar, and a side arm connected to a mercury seal. A freshly prepared solution of the reactants to be irradiated was added to the vessel and then the solution was flushed with nitrogen for several minutes. Generally the irradiation vessel was immersed in a larger beaker of water for additional cooling. The solution was irradiated with a 450-W, medium-pressure mercury arc, type no. 679A-10. A cylindrical Pyrex glass filter was placed inside the lamp well. The alternate procedure used was to prepare a fresh solution of the reactants in a Pyrex test tube. The test tube was flushed with nitrogen, sealed, and then taped onto the outside of the quartz immersion well. The entire unit was then immersed in a large beaker of water for cooling.

The course of the reaction was followed by removing samples from the irradiation vessel and examining them by gas–liquid partition chromatography. The F & M Model 720 gas chromatograph fitted with a 6-ft 5% silicon rubber Se-30 column or a 6-ft 20% Apiezon 720L column was used for the analysis.

Spectra. Nmr spectra were determined on a Varian A-60 spectrometer using tetramethylsilane as an internal standard. Infrared spectra were determined on a Perkin-Elmer Infracord spectrophotometer. Ultraviolet spectra were measured on a Cary Model 11 MS spectrophotometer. Mass spectra were determined on a AEI MS9 mass spectrometer. Melting points were determined in a capillary tube in a Mel-Temp apparatus and are uncorrected.

Emission spectra were measured with a photoelectric luminescence spectrometer consisting of a converted Perkin-Elmer 12C detection monochromator,[18] an EMI 9558Q photomultiplier tube, and the appropriate recording electronics. Phosphorescence is separated from fluorescence by means of a mechanical chopper. Excitation is supplied by a 1000-W Xe arc fitted to an excitation monochromator. Samples were excited at 303 mμ. A front surface detection system ($\sim$30°) was employed.

Materials. Chromone was prepared by the method of Schönberg and Sina[19] with the exception that sodium was replaced by sodium hydride in the preparation. Benzophenone from Eastman Organic Chemicals was used without further purification. Dioxane from Matheson Coleman and Bell was purified by distillation from the sodium ketyl of benzophenone and stored frozen under nitrogen. Tetramethylethylene from Columbia Organic Chemicals Co., cyclopentene from Aldrich Chemical Co., and butyne-2 from Farchan Research Laboratories were used without additional purification.

1,1-Dimethoxyethylene was prepared by adding 280 g (1.66 mol) of bromoacetaldehyde dimethyl acetal to a solution of 51 g (2.22 mol) of sodium spheres in 1 kg of anhydrous pinacol. The reaction mixture was heated under reflux for 20 min and then distilled using a Vigreux column. A crude fraction was collected, bp 88–93°, which was then redistilled using a spinning-band column, bp 88–91° (lit.[20] 89–91°).

Photoaddition of Tetramethylethylene to Chromone. A solution of 3.1 g (0.021 mol) of chromone, 25 ml (0.211 mol) of tetramethylethylene, and 5 ml (0.059 mol) of dioxane was prepared in a Pyrex test tube. Nitrogen gas was bubbled through the test tube for several minutes, and then the tube was sealed. The test tube was then taped to the outside of the quartz immersion well. The solution was irradiated for 72 hr with the 450-W mercury lamp. The volatile material was removed on the rotating evaporator and the residue examined by gas chromatography. The 6-ft 5% silicon rubber Se-30 column was used for the analysis. By this technique the presence of four chromone–tetramethylethylene photoadducts as well as starting chromone was demonstrated. The relative ratio of peak heights of the four adducts was I:II:III:IV = 13.0:5.5:2.6:2.0.

Adduct I. A separation of the major adduct I was accomplished by chromatography of the reaction mixture on Fluorsil followed by chromatography on neutral alumina. Chromatography of the reaction mixture on Fluorsil gave adduct II pure and a mixture containing adducts I, III, and IV. The desired adduct I was then isolated pure by chromatography on neutral alumina. It was crystallized from methanol–water to give a white crystalline solid, mp 37–38°. It was later demonstrated that adduct I could be isolated pure by chromatography of the reaction mixture on neutral alumina alone. The infrared spectrum of the product showed strong carbonyl absorption at 5.97 μ as well as strong absorption at 6.23, 6.85, 7.56, and 9.40 μ. The nmr spectrum contained four methyl groups at τ 8.80, 8.85, 8.97, and 8.97 (singlets), two cyclobutane hydrogens at 6.95 and 5.30 (doublets) (J = 9 cps), two aromatic hydrogens at 3.05 (multiplet), one aromatic hydrogen at 2.58 (multiplet), and one aromatic hydrogen at 2.13 (multiplet). The uv spectrum of this material showed λ_{max}^{MeOH} 217 (20,300), 257 (7800), and 331 mμ (ϵ 2800).

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.2; H, 7.9. Found: C, 78.3; H, 7.8.

Adduct II. A separation of adduct II was obtained by chromatography of the reaction mixture on Fluorsil. It was crystallized from methanol–water to yield a white crystalline solid, mp 89–90°. It was also later shown that this adduct II could be obtained pure by chromatography on neutral alumina. The infrared spectrum of this product showed the characteristic prominent broad band at 9.98 μ which has been assigned to the asymmetrical ring stretching vibration involving carbon–oxygen bonds.[21] The nmr spectrum contained eight methyl groups at τ 8.50, 8.65, 8.77, 8.85, 8.87, 9.25, 9.32, 9.58 (singlets), two cyclobutane hydrogens at 6.42 and 5.83 (doublets) (J = 9 cps), three aromatic hydrogens at 3.03 (multiplet), and one aromatic hydrogen at 2.33 (multiplet).

Anal. Calcd for $C_{21}H_{30}O_2$: C, 80.2; H, 9.6. Found: C, 79.9; H, 9.4.

Adduct III. The minor photoadduct III was isolated in better than 90% purity by chromatography of the reaction mixture on Fluorsil followed by molecular distillation. Chromatography of the reaction mixture on Fluorsil initially gave a number of fractions which consisted mainly of adduct III with small amounts of I present. These fractions were rechromatographed on Fluorsil to give adduct III (90% pure). This material could not be obtained crystalline and an initial nmr spectrum indicated the presence of some hydrocarbon impurity. The compound was further purified by vacumn distillation at 90–95° (0.3 mm). The infrared spectrum of the adduct showed strong carbonyl absorption at 5.93 μ as well as strong absorption at 6.21, 6.83, 7.65, and 11.1 μ. The nmr spectrum contained two methyl groups at τ 8.80 and 8.73 (singlets), another vinyl methyl at 8.23 (multiplet), two methylene ring hydrogens at 7.45 (doublet, J = 6 cps) and 7.42 (doublet, J = 9 cps), one tertiary ring hydrogen at 5.65 (four-line pattern), two vinyl hydrogens at 5.08 (multiplet), two aromatic hydrogens at 2.95 (multiplet), one aromatic hydrogen at 2.58 (multiplet), and one aromatic hydrogen at 2.12 (multiplet). The uv spectrum of this material showed λ_{max}^{MeOH} 214 (19,500), 251 (6400), and 320 mμ (ϵ 2300). The mass spectrum of the compound showed a molecular ion at m/e 230, and fragment ions at m/e 147 and 83.

Adduct IV. A separation of the minor chromone–tetramethylethylene photoadduct IV was accomplished by chromatography of the reaction mixture on Fluorsil. Approximately 3.0 g of the reaction mixture was chromatographed over Fluorsil, using hexane–benzene mixtures for elution. By gas chromatography, using the 6-ft 5% silicon rubber Se-30 column at 200°, it was determined that a few of the chromatography fractions were rich in the desired minor product. These fractions were combined and rechromatographed over Fluorsil using the same solvent system. By gas chromatography it was shown that one of the new fractions contained adduct IV, 95% pure. Attempts to obtain IV crystalline were not successful. The infrared spectrum of the adduct showed strong carbonyl absorption at 5.93 μ as well as strong absorption at 6.22, 6.83, 7.56, and 7.66 μ. The nmr spectrum showed nine methyl hydrogens at τ 8.33 (singlet), two methylene hydrogens at 7.45 (broad doublet, J = 6 cps), two methylene ring hydrogens at 7.35 (doublet, J = 6 cps) and 7.38 (doublet, J = 8 cps), one tertiary ring hydrogen at 5.5 (multiplet), two aromatic hydrogens at 3.0 (multiplet), one aromatic hydrogen at 2.6 (multiplet), and one aromatic hydrogen at 2.2 (multiplet). The uv spectrum of the product showed λ_{max}^{MeOH} 214 (21,700), 251 (7300), and 320 mμ (ϵ 2800). The mass spectrum of the compound showed a molecular ion at m/e 230, and fragment ions at m/e 147 and 83.

Chromone–Tetramethylethylene Photoaddition Reaction in the Presence of a Triplet-State Sensitizer. A solution of 0.62 g (0.004 mol) of chromone, 5 ml (0.042 mol) of tetramethylethylene, 0.20 g (0.01 mol) of benzophenone, and 1 ml (0.012 mol) of dioxane was prepared in a Pyrex test tube. Nitrogen gas was bubbled through the solution and then the test tube sealed. The test tube was then irradiated for 72 hr. At the end of this period the reaction mixture was examined by gas chromatography using the 6-ft 5% silicon rubber Se-30 column at 200°. By this technique the presence of the four chromone–tetramethylethylene photoadducts was demonstrated which were in the same ratio as the reaction conducted in the absence of benzophenone.

Photoaddition of Cyclopentene to Chromone. A solution of 6.0 g (0.040 mol) of chromone and 100 g (1.47 mol) of cyclopentene was prepared and added to the irradiation vessel. Nitrogen gas was bubbled through the solution for several minutes and then the solution irradiated for 48 hr. At the end of that period the volatile solvent was removed on the rotating evaporator. The residue was then examined by gas chromatography. By this method it was shown that there was one major and one minor product formed and that no starting chromone remained. Initially the 6-ft 5% silicon rubber Se-30 column at 200° was used for the analysis; however, it was later shown that the 6-ft 20% Apiezon 720L column at 250° gave a better separation of the two products. During the photolysis samples of the reaction mixture were removed and examined by gas chromatography. It was shown that as the reaction proceeded the ratio of major to minor product decreased.

Adduct V. A separation of the major adduct V was obtained by absorption chromatography of the reaction mixture on neutral

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alumina. The major adduct V was recrystallized from hexane at $-60°$ to yield a white crystalline solid, mp 50–51°. The infrared spectrum of the material showed strong carbonyl absorption at 5.98 μ as well as absorption at 6.22, 6.84, and 7.55 μ. The nmr spectrum contained six methylene hydrogens at τ 8.25 (multiplet), three cyclobutane hydrogens at 7.00 (multiplet), one cyclobutane hydrogen at 5.37 (four-line pattern) (J = 8 cps; J' = 3.5 cps), two aromatic hydrogens at 3.03 (multiplet), one aromatic hydrogen at 2.58 (multiplet), and one aromatic hydrogen at 2.13 (multiplet). The uv spectrum of this material showed $\lambda_{\max}^{\mathrm{MeOH}}$ 216 (20,200), 255 (7500), and 330 mμ (ϵ 2800).

Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.5; H, 6.6. Found: C, 78.8; H, 6.8.

Adduct VI. The minor photoadduct VI was isolated in better than 95% purity by chromatography of the reaction mixture on Fluorsil. Initial chromatography of 3.0 g of the reaction mixture on Fluorsil gave a number of fractions which consisted mainly of the minor adduct VI. These fractions were rechromatographed on Fluorsil to give adduct VI (95% pure). Attempts to crystallize adduct VI were not successful. The infrared spectrum of the material showed strong carbonyl absorption at 5.93 μ as well as absorption at 6.21, 6.84, and 7.65 μ. The nmr spectrum contained two methylene ring hydrogens at τ 8.08 (multiplet), two methylene ring hydrogens at 7.67 (multiplet), two methylene ring hydrogens at 7.35 (doublet, J = 7 cps) and 7.32 (doublet, J = 8 cps), one tertiary ring hydrogen at 6.88 (multiplet), one tertiary ring hydrogen at 5.70 (multiplet), two vinyl hydrogens at 4.10 (multiplet), two aromatic hydrogens at 3.00 (multiplet), one aromatic hydrogen at 2.58 (multiplet), and one aromatic hydrogen at 2.13 (multiplet). The uv spectrum of this material showed $\lambda_{\max}^{\mathrm{MeOH}}$ 214 (22,000), 252 (7200), and 321 mμ (ϵ 2800).

Photoaddition of Butyne-2 to Chromone. A solution of 9.0 g (0.061 mol) of chromone, 75 ml (0.972 mol) of butyne-2, and 15 ml (0.177 mol) of dioxane was prepared in a large Pyrex test tube. Nitrogen gas was passed through this solution for about 2 min and then the test tube put into a Dry Ice–acetone bath. The solution solidified in the Pyrex tube and the tube was sealed with a torch. The test tube was then taped to the outside of the quartz immersion well. The test tube was irradiated for 90 hr. The butyne-2 was evaporated off under nitrogen and the residue examined by gas chromatography. By this technique it was shown that there was only one chromone–butyne-2 adduct (VII) and unreacted chromone. A separation of the product was obtained by absorption chromatography of the reaction mixture on Fluorsil. The course of the absorption chromatography as well as the purity of the product could be determined by gas chromatography. The product was recrystallized from hexane at $-60°$ to give a white crystalline solid, mp 77–78°. The infrared spectrum of this material showed strong carbonyl absorption at 5.98 μ as well as strong absorption at 6.21, 6.86, and 7.61 μ. The nmr spectrum contained two methyl groups at τ 8.37 (single line), one cyclobutane hydrogen at 6.33 (doublet, J = 2.5 cps), one cyclobutane hydrogen at 4.83 (doublet, J = 2.5 cps), two aromatic hydrogens at 2.92 (multiplet), one aromatic hydrogen at 2.50 (multiplet), and one aromatic hydrogen at 2.20 (multiplet). The uv spectrum of this material showed $\lambda_{\max}^{\mathrm{MeOH}}$ 216 (18,800), 254 (7800), and 322 mμ (ϵ 3000).

Anal. Calcd for $C_{13}H_{12}O_2$: C, 78.0; H, 6.0. Found: C, 77.5; H, 6.2.

Photoaddition of 1,1-Dimethoxyethylene to Chromone. In a small Pyrex test tube was placed 1.0 g (0.007 mol) of chromone and 12.0 g (0.136 mol) of 1,1-dimethoxyethylene. Nitrogen gas was bubbled through this clear solution for several minutes and then the test tube sealed. The test tube was taped to the outside of the quartz immersion well and irradiated with the 450-W mercury arc lamp for 80 hr. At the end of this time the solution was deep brown in color. The course of the irradiation was followed by removing samples of the reaction mixture at various time intervals and examining them by gas–liquid partition chromatography. By this technique the presence of a major and minor product as well as starting material was demonstrated. The 6-ft 5% silicon rubber Se-30 column was used to monitor the reaction. At the end of the 80 hr of irradiation, some starting chromone still remained unreacted.

Adduct VIII. A separation of the two products from chromone was accomplished by absorption chromatography on Fluorsil. Adduct VIII was then isolated pure by fractional crystallization. The mixture containing both products was dissolved in hot hexane. On cooling to 0°, VIII crystallized from solution as a white crystalline solid, mp 111–112°. The infrared spectrum of the material showed strong carbonyl absorption at 5.96 μ as well as strong absorption at 6.22, 6.87, and 7.55 μ. The nmr spectrum of the product contained one cyclobutane hydrogen at τ 7.72 (four-line pattern), one cyclobutane hydrogen at 7.42 (four-line pattern), one cyclobutane hydrogen at 6.78 (multiplet), one cyclobutane hydrogen at 5.00 (doublet, J = 9 cps), two aromatic hydrogens at 3.05 (multiplet), one aromatic hydrogen at 2.67 (multiplet), one aromatic hydrogen at 2.16 (multiplet), one methoxy methyl group at 6.88 (singlet), and one methoxy methyl group at 6.70 (singlet).

Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.6; H, 6.0. Found: C, 66.9; H, 6.0.

Adduct IX. The hexane filtrate from the above crystallization was then examined by gas–liquid partition chromatography. It was shown to be a mixture consisting largely of the minor photoproduct with some of the other product present. A separation of the minor product was accomplished by absorption chromatography of the mixture on neutral alumina. The minor product comes off the column as a crystalline white solid, mp 88–89°. The infrared spectrum of the material showed the characteristic prominent broad band at 10.2 μ that has been assigned to the asymmetrical ring stretching vibration involving the carbon–oxygen bonds. The nmr spectrum[22] of the product contained one cyclobutane hydrogen at τ 8.50 (four-line pattern), one cyclobutane hydrogen at 7.72 (eight lines), one methoxy methyl group at 7.23 (singlet), three methoxy methyl groups at 6.80 (singlet), one cyclobutane hydrogen at 6.43 (four-line pattern), two methylene hydrogens at 5.50 (singlet), one cyclobutane hydrogen at 5.35 (four-line pattern), three aromatic hydrogens at 2.92 (multiplet), and one aromatic hydrogen at 2.37 (multiplet). The mass spectrum of the compound showed a molecular ion at m/e 322.

Anal. Calcd for $C_{17}H_{22}O_6$: C, 63.3; H, 6.9. Found: C, 63.8; H, 7.1.

Irradiation of the Chromone–Tetramethylethylene Adduct I. A solution of 0.10 g (0.0004 mol) of adduct I, 2 ml (0.017 mol) of tetramethylethylene, and 0.5 ml (0.006 mol) of dioxane was prepared in a Pyrex test tube. The test tube was flushed with nitrogen, sealed, and taped to the outside of the 450-W mercury arc immersion well. The test tube was irradiated for 6 hr. At the end of this time it was removed and the contents examined by gas chromatography. A 6-ft 5% Se-30 silicon rubber column at 200° was used. It was shown that adduct I yields II as the only major product. A trace amount of III was also indicated. The ratio of II:III = 8.7:0.4. No amount of IV was formed.

A procedure similar to the above was employed to carry out the photostability studies on the other photoadducts.

Competition Experiments. **1.** A solution of 0.50 g (0.0034 mol) of chromone, 2.40 g (0.027 mol) of 1,1-dimethoxyethylene, 1.84 g (0.027 mol) of cyclopentene, and 1.0 ml of dioxane was prepared in a Pyrex test tube. The test tube was flushed with nitrogen, sealed, and taped to the outside of the quartz immersion well. The solution was then irradiated for 5 hr. The reaction mixture was analyzed by gas–liquid partition chromatography using the 6-ft 5% silicon rubber Se-30 column. By this technique it was shown that the ratio of moles of cyclopentene adducts:moles of 1,1-dimethoxyethylene adduct was 1.0:1.83.

2. A solution of 0.50 g (0.0034 mol) of chromone, 3.08 g (0.057 mol) of butyne-2, 3.85 g (0.057 mol) of cyclopentene, and 1 ml of dioxane was prepared in a Pyrex test tube. The test tube was irradiated and the reaction mixture analyzed as described above. It was shown that the ratio of moles of cyclopentene adduct:moles of butyne-2 adduct was 1.0:0.06.

3. A solution of 0.50 g (0.0034 mol) of chromone, 4.8 g (0.057 mol) of tetramethylethylene, 3.85 g (0.057 mol) of cyclopentene, and 1 ml of dioxane was prepared in a Pyrex test tube. The test tube was irradiated and the reaction mixture analyzed as described above. It was shown that the ratio of moles of cyclopentene adducts:moles of tetramethylethylene adducts was 1.0:0.78.

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[22] For an analysis of the nmr spectra of adducts VIII and IX see: J. W. Hanifin and G. O. Morton, *Tetrahedron Letters*, 2307 (1967).