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PHOTOADDITION REACTIONS OF CHROMONE

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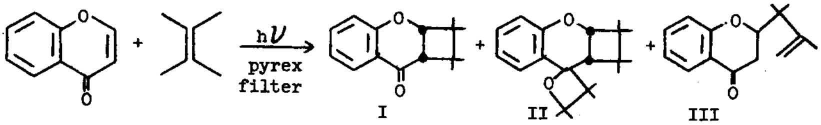
The literature contains several examples of addition reactions of photochemically excited molecules to unactivated multiple bonds (1). Recently we have shown that coumarin undergoes sensitized photoaddition reactions to extramolecular double bonds (2). The reactions of coumarin with tetramethylethylene, cyclopentene, and ketene diethyl acetal were described. In these reactions the sensitizer was essential. The mechanism of these photoaddition reactions could be summarized as attack of excited coumarin triplets on the ground state of the olefin.

We would now like to report the unsensitized photoaddition reaction of chromone to extramolecular multiple bonds. The reactions of chromone with tetramethylethylene, cyclopentene, 2-butyne, and ketene dimethyl acetal have been conducted.

A solution of chromone (.021 mole), tetramethylethylene (.211 mole) and dioxane (.059 mole) was irradiated through pyrex glass with a 500-watt mercury arc lamp. Three chromone-tetramethylethylene adducts, I, II and III, were isolated and identified from this reaction.

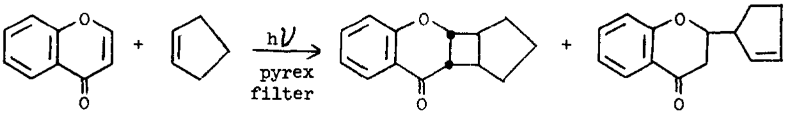


The infrared spectrum of adduct I, m.p. 38°, contained strong carbonyl absorption at 5.97μ. The n.m.r. spectrum showed four methyl groups at 8.80, 8.85, 8.97, and 8.97τ (singlets), two cyclobutane hydrogens at 6.95 and 5.30τ, each as a doublet (J=9 c.p.s.), and the four aromatic hydrogens. The infrared spectrum of adduct II, m.p. 90°, which contained no carbonyl absorption, showed the characteristic band at 10.0μ which has been assigned to the asymmetrical ring stretching vibration involving carbon-oxygen bonds(3). The n.m.r. spectrum of adduct II contained eight methyl groups at 8.50, 8.65, 8.77, 8.85, 8.87, 9.25, 9.32, and 9.58τ (singlets) and two cyclobutane hydrogens at 6.42 and 5.83τ, each as a doublet (J=9 c.p.s.). Based on the n.m.r. 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 c.p.s.) 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 (4). In addition these adducts can be chromatographed and separated pure on neutral alumina, conditions which Corey (1b) has shown will isomerize a trans 6-4 ring junction to the cis.

Adduct III, b.p. 90-5°/.3 mm was obtained as a minor product. It showed strong carbonyl absorption at 5.93μ as well as strong absorption at 11.1μ (=CH_2). Significant in the n.m.r. spectrum of this adduct were two methyl groups at 8.80 and 8.73τ (singlets), a vinyl methyl group at 8.23τ (multiplet), two vinyl hydrogens at 5.08τ (multiplet), two methylene ring hydrogens at 7.45 and 7.42τ, each as a doublet with J=6 c.p.s. and J'=9 c.p.s. respectively, and one tertiary hydrogen at 5.65τ (four line pattern), coupled to the two methylene hydrogens.

This photoaddition reaction of chromone and tetramethylethylene was examined in the presence and absence of benzophenone sensitizer. In both reactions the same number of chromone-tetramethylethylene adducts were obtained in the same ratio. The benzophenone appeared to have no effect on the reaction. Hence, it appears that attack of an excited chromone triplet on ground state olefin is involved in the reaction.

Mercury arc irradiation of a solution of chromone (.040 mole) and cyclopentene (1.47 mole) through pyrex glass yielded one major (IV) and one minor (V) photoadduct.

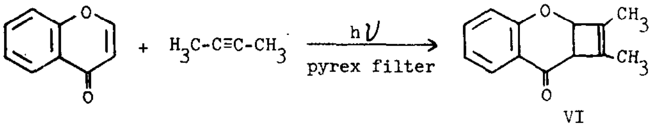


IV V

The infrared spectrum of adduct IV, m.p. 51°, showed strong carbonyl absorption at 5.98μ. The n.m.r. spectrum contained six methylene hydrogens at 8.25τ (multiplet), three cyclobutane hydrogens at 7.00τ (multiplet) and one cyclobutane hydrogen at 5.37τ (four line pattern). The stereochemistry has again been assigned from the n.m.r. spectrum and chemical data. The product can be chromatographed without change on neutral alumina, conditions which isomerize a <u>trans</u> 6-4 ring junction to the <u>cis</u> (1b). Secondly, the n.m.r. spectrum shows the hydrogen alpha to the ether oxygen (5.37τ) coupled to two hydrogens ($J \doteq 8$ c.p.s. and $J=3.5$ c.p.s.). Since it is known that this hydrogen is coupled to one <u>cis</u> hydrogen alpha to the carbonyl and this coupling is of the order 8-11 c.p.s. (2)(4), then the coupling to the other ring hydrogen, $J=3.5$ c.p.s., is presumably with a <u>trans</u> hydrogen.

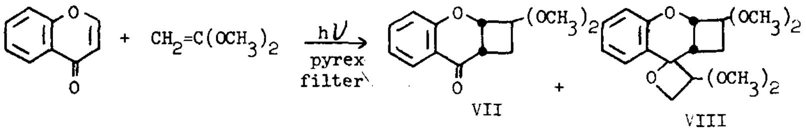
The infrared spectrum of the minor adduct V showed strong carbonyl absorption at 5.93μ. Its n.m.r. spectrum contained two groups of methylene ring hydrogens at 8.08 and 7.67τ (multiplets), one tertiary ring hydrogen at 6.88τ (multiplet), two vinyl hydrogens at 4.10τ (multiplet), two methylene ring hydrogens at 7.35 and 7.32τ, each as a doublet with coupling constants $J=7$ c.p.s. and $J \doteq 8$ c.p.s. respectively, and one tertiary ring hydrogen at 5.70τ (quartet).

Having shown that chromone will undergo reaction with olefins, photoadditions with other multiple bonds were attempted. A solution of chromone (.061 mole), 2-butyne (.972 mole) and dioxane (.177 mole) was irradiated through pyrex glass with the 500 watt mercury arc lamp. The chromone-butyne-2 adduct VI, m.p. 78°, was the only product obtained by this procedure.



The infrared spectra of adduct VI shows strong carbonyl absorption at 5.98μ. The n.m.r. spectrum contained two methyl groups at 8.37τ (single line), two cyclobutane hydrogens at 6.33 and 4.83τ, each as a doublet (J=2.5 c.p.s.) and the four aromatic hydrogens.

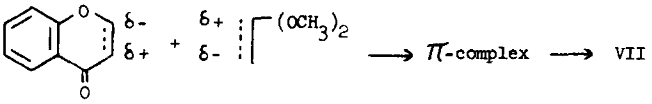
In an attempt to further characterize the excited state of chromone, the irradiation of chromone was conducted in the presence of an activated olefin. A solution of chromone (.007 mole) and ketene dimethyl acetal (.136 mole) was irradiated through pyrex glass with a 500-watt mercury arc lamp. Two chromone-ketene dimethyl acetal adducts, VII and VIII, were isolated and identified as the major and minor reaction products.



The infrared spectrum of adduct VII, m.p. 112°, showed strong carbonyl absorption at 5.96μ. The n.m.r. spectrum contained cyclobutane hydrogens at 7.72τ (four line pattern), 7.42τ (four line pattern), 6.78τ (multiplet), and 5.00τ (doublet, J=9 c.p.s.), as well as two methoxy methyl groups at 6.88 and 6.70τ (singlets). The orientation of this adduct is readily obtainable from the n.m.r. spectrum. It shows that the hydrogen alpha to the ether oxygen is split only into a doublet. This eliminates the adduct with the opposite orientation since this hydrogen would be coupled to three hydrogens. From the magnitude of the coupling constant it is believed that the rings are fused <u>cis</u> (2)(4).

The infrared spectrum of adduct VIII, m.p. 89°, which contained no carbonyl absorption, showed the characteristic band 10.2μ which has been assigned to the asymmetrical ring stretching vibration involving the carbon-oxygen bonds(3). Of note in the n.m.r. spectrum* of this adduct are three methoxy methyl groups at 6.80τ (single line), one methoxy methyl group at 7.23τ (singlet) and two methylene hydrogens at 5.50τ (singlet). The chemical shift of the two oxetane ring hydrogens is consistent with the structure proposed (3).

The mechanism for these photoaddition reactions may involve initial formation of a π-complex between the excited state of one molecule and the ground state of another (1b). The factor which controls the orientation of the product is the geometry of this intermediate π-complex. If such a π-complex is considered to intervene in the chromone-ketene dimethyl acetal reaction, it is quite clear from the orientation of adduct VII that C_α of chromone is quite positive relative to $C\beta$ in the excited state.



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* All n.m.r. spectra were taken by Mr. W. Fulmor and group on a Varian A-60 Spectrophotometer.

References

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