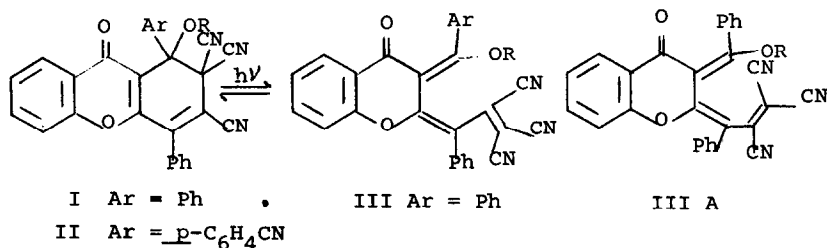


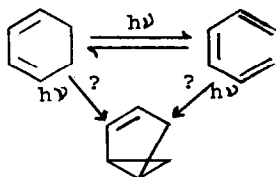
THE IDENTITY OF PHOTOCHEMICAL INTERMEDIATES IN  
CYCLOHEXADIENE VALENCE TAUTOMERIZATIONS. REARRANGEMENTS  
TO BICYCLO  $\overline{3}, 1, \overline{0}$  HEXENES

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(Received 12 December 1966)

In the previous paper<sup>2</sup> a new class of photochromic compounds  
I (R = H or COCH<sub>3</sub>) was described, and the photochemically produced  
colored modifications were shown to have structures III (R = H or COCH<sub>3</sub>).  
The reactions are analogous to a number of previously reported revers-  
ible cyclohexadiene-hexatriene photoisomerizations.<sup>3</sup> In several of



these examples bicyclo  $\overline{3}, 1, \overline{0}$  hexenes were formed<sup>4,5</sup>. Evidence pre-  
sented in two of these examples has been interpreted as support for a  
one step photochemical reaction of the trienes to give the bicyclic  
compounds<sup>5</sup>. While it has previously been assumed that this mechanism  
generally occurs<sup>3a</sup>, the possibility that a suitably substituted cyclo-  
hexadiene might rearrange directly to a bicyclo  $\overline{3}, 1, \overline{0}$  hexene cannot  
be excluded. Since the absorption maxima of the tautomers I and III are  
well separated<sup>2</sup>, these compounds seemed useful for further examination  
of this question.

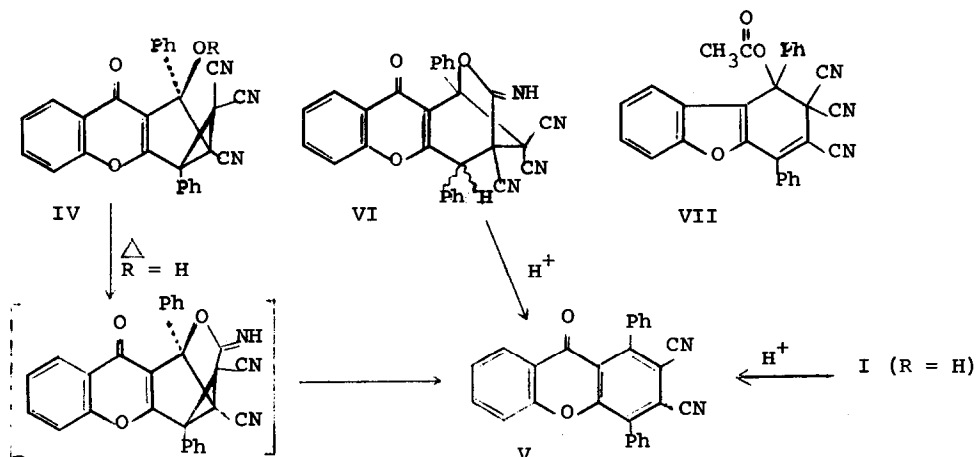


Irradiation of solutions of I (R = H) in ethyl acetate with 3100-4000 Å light initially gave the deep red III (R = H) which rapidly reached a stationary state concentration due to its rapid thermal return to I (R = H).<sup>2</sup> On long irradiation the red color gradually disappeared, and a photochemically inert alcohol IV (R = H), m.p. 196-198° (dec.),  $\lambda_{\text{max.}}^{\text{mull}}$  2.90 $\mu$  was isolated in 84% yield. When solutions of I (R = COCH<sub>3</sub>) were similarly irradiated, the relatively stable red III (R = COCH<sub>3</sub>)<sup>2</sup> could be isolated (35%) together with a 49% yield of a colorless acetate IV (R = COCH<sub>3</sub>), m.p. 217-220° (dec.),  $\lambda_{\text{max.}}^{\text{mull}}$  572 $\mu$ .

The relationship between these two new products IV (R = H and COCH<sub>3</sub>) was established by treatment of IV (R = H) with acetic anhydride-sulfuric acid to give IV (R = COCH<sub>3</sub>). Both products displayed spectra typical of an unconjugated chromone nucleus<sup>6</sup> together with unconjugated nitrile absorption at 4.45 $\mu$ . Since the mass spectra of both products displayed prominent peaks corresponding to C<sub>6</sub>H<sub>5</sub>CO<sup>+</sup> while the analogous photo-product derived from II (R = H)<sup>7</sup> gave instead a prominent NCC<sub>6</sub>H<sub>4</sub>CO<sup>+</sup> fragment, the ArCOH grouping is intact in the photo-products. On heating IV (R = H) in boiling xylene for five hours, there was isolated the xanthone V, m.p. 337-339°  $\lambda_{\text{C}\equiv\text{N}}$  4.48 $\mu$ . The structure of V was shown by its empirical formula (determined by mass spectrometry) and by its synthesis from either I (R = H) or VI<sup>2</sup> with sulfuric acid in acetonitrile.

The structural assignment IV for the photoproducts accounts in the simple manner shown for the formation of V, and is in good accord with the other data. Although an alternative formulation of IV which differs only in the direction of the chromone ring fusion is permitted by the data, the direction of fusion shown seems most likely based on analogy with the earlier work<sup>4,5</sup>.

In order to establish the immediate photochemical precursor(s) of IV, it seemed important to establish whether the reaction I → III might involve a transient intermediate which might lead to IV. For this purpose



1:1:1-methylcyclohexane-3-methylpentane-toluene glasses containing I were irradiated (3100-4000 Å) at 77°K. While I ( $R = COCH_3$ ) was photochemically inert at this temperature, glasses containing I ( $R = H$ ) turned blue. The blue species could be bleached by irradiation of the glass with visible light, while on warming the glass above its melting point, the blue color was replaced by red. On refreezing the red melt, a red glass was obtained which was no longer sensitive to visible light and was indistinguishable from glasses formed by cooling solutions of III ( $R = H$ ) prepared at room temperature. Apparently, therefore, there is an intermediate in the formation of III ( $R = H$ ) which thermally rearranges to III ( $R = H$ ) and is photochemically sensitive. This new photosensitive species might be either a frozen conformation of III ( $R = H$ ) or a cis-trans isomer made extremely labile by virtue of the special reactivity of the enol group. Since similar low temperature behavior has been observed among photochromic analogs of I (e. g. VII)<sup>7</sup> that lack a hydroxy group, the first-formed blue species may be a conformational isomer of III ( $R = H$ ) such as IIIA ( $R=H$ ). The different photochemical behavior of the two species might then be due to increased bond order of the C=C-C=C single bond in the excited states which effectively freezes the ground state conformation.<sup>8</sup>

These observations require that not only I and III, but also the

blue intermediate be considered as possible photochemical precursors of the cyclopropanes IV. Since III (R = H), the blue intermediate, and any intermediate in the formation of III (R = COCH<sub>3</sub>) are thermally unstable, their photostationary concentrations during formation of IV will depend on the light intensity. Thus if any one of these species were an immediate photochemical precursor of IV, the effective quantum yield for formation of IV should also depend on the light intensity. However, a three fold variation of the intensity of a 3650 Å source failed to cause a change in the quantum yields for formation of either IV (R = H or COCH<sub>3</sub>). Therefore, neither III (R = H) nor intermediates in the formation of III (R = H or COCH<sub>3</sub>) are photochemical precursors of IV. Similarly III (R = COCH<sub>3</sub>) cannot be an intermediate in the formation of IV (R = COCH<sub>3</sub>). Thus on irradiation of III (R = COCH<sub>3</sub>) with light not absorbed by I (R = COCH<sub>3</sub>) (*viz.*; > 4350 Å), the latter compound was formed slowly though nearly quantitatively with no formation of IV (R = COCH<sub>3</sub>), while with 3650 Å light IV (R = COCH<sub>3</sub>) was formed, but only at a low rate consistent with the reaction sequence III → I → IV (R = COCH<sub>3</sub>). Accordingly we conclude that the cyclohexadienes I (R = H and COCH<sub>3</sub>) are photochemically transformed to the cyclopropanes IV (R = H and COCH<sub>3</sub>) without the intermediacy of the hexatrienes III.

In the light of this conclusion there remain in doubt the identities of the immediate photochemical precursors of some of the simpler bicyclo [3, 1, 0] hexenes, since most of these have not been established by rigorous arguments<sup>3a,5b</sup>.

#### References

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8. For a related phenomenon see R. S. H. Liu, N. J. Turro and G. S. Hammond, ibid., 87, 3406 (1965).