Photochromic 1,2-Dihydro-9-xanthenones. An Example of Reversible Cyclohexadiene–Hexatriene Valence Isomerizations

K. R. HUFFMAN, M. LOY, W. A. HENDERSON, JR., AND E. F. ULLMAN[1]

Chemical Department, Central Research Division, American Cyanamid Company, Stamford, Connecticut 06904

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1,2-Dihydro-1,4-diphenyl-1-hydroxy-2,2,3-tricyano-9-xanthenone (**5**), synthesized by reaction of 3-benzoyl-2-benzylchromone with tetracyanoethylene, is converted by ultraviolet irradiation in high quantum yield into a red isomer (**7**) which thermally reverts back to **5** in the dark. This behavior is shown to be the result of a cyclohexadiene–hexatriene type of equilibrium. Upon prolonged irradiation, **5** is converted irreversibly in high yield into a bicyclo[3.1.0]hexene isomer (**10**) which is shown to arise directly from **5** and not from the hexatriene tautomer. The preparation and properties of several analogs of **5** is also described.

Photochemical ring opening of 1,3-cyclohexadienes to 1,3,5-hexatrienes is a well-known process encompassing a wide variety of both simple and complex organic molecules.[2] In certain cases a spontaneous thermal reversion of the triene to the cyclic diene has been observed.[3] In principle, therefore, appropriate substitution of the basic cyclohexadiene moiety could result in a photochromic system[4] in which a colorless cyclic diene could be reversibly transformed into a colored, highly conjugated triene. This paper describes the preparation and properties of the first examples of such a system, namely, some highly substituted 1,2-dihydro-9-xanthenones.[5]

Results

The first photochromic 1,2-dihydroxanthenone was encountered during an investigation of the photochromism of 3-benzoyl-2-benzylchromone (**1**) and related compounds.[6] In an effort to obtain confirmatory evidence for the assignment of the enol structure **2** as the colored species formed upon irradiation of **1**, a sample of **1** was photolyzed in the presence of an equivalent of tetracyanoethylene (TCNE) so as to trap **2** as a Diels–Alder adduct. This resulted in a good yield of a 1:1 adduct which was assigned structure **4**. The presence of infrared bands at 3.10 and 5.75 μ were in agreement with the C═NH group in a cyclic imidate, while the ultraviolet (uv) spectrum and other bands in the infrared (ir) spectrum were typical of a chromone ring system.[7] The nuclear magnetic resonance (nmr) spectrum of **4** in hexadeuterioacetone showed two singlets of unequal intensity at τ 4.13 and 4.33 with a total ratio to the aromatic protons of 1:14. This result suggested that **4** was in fact a mixture of isomers epimeric at C-4.

Evidently, **4** had been formed by thermal cyclization of the expected initial adduct **3**. The latter could be isolated by a rapid fractional crystallization of the crude reaction product using cold solvent. Compound **3** also displayed absorption spectra typical of a chromone and was thermally unstable. Upon standing in ethanol it was isomerized to **4**, but upon refluxing in ethanol it was converted into a mixture of **4** and a new photochromic product, resulting from loss of hydrogen cyanide. The spectral data obtained for the photochromic substance [$\lambda_{\max}^{\text{mull}}$ 2.90 (OH), 4.50 (weak, conjugated —C≡N), and 6.08 μ (C═O); $\lambda_{\max}^{C_6H_{12}}$ 266 mμ (ϵ 19,000), 273 (21,000), and 312 (14,500); no aliphatic protons in the nmr spectrum] allowed the tentative assignment of the dihydroxanthenone structure **5**.

Chemical confirmation of structure **5** was provided by its preparation by three additional routes. First, treatment of the imidate **4** with triethylamine gave an intensely purple solution from which **5** was obtained after acidification. The most convenient preparation of **5** involved formation of the anion of **1** by treatment of **1** with sodium hydride in tetrahydrofuran, followed by reaction with tetracyanoethylene and acidification. This resulted in a direct conversion of **1** into **5** in 84% yield. Finally, a poor yield of **5** was also obtained by a two-step procedure which involved bromination of **1** to give **6**, followed by reaction with the dianion of tetracyanoethane. The above transformations are outlined in Scheme I.

Dilute solutions ($\sim 10^{-4}$ to 10^{-3} *M*) of **5** in nonbasic solvents, such as benzene, cyclohexane, chloroform, or methylene chloride, were colorless to faintly pink at room temperature.[8] Upon irradiation with uv light or direct sunlight for several seconds these solutions became intensely red ($\lambda_{\max}^{C_6H_6}$ 532 mμ) and then faded rapidly by first-order kinetics in the dark; $k_{C_6H_6}^{25°} = 0.088$ sec^{-1}. The photochromic behavior of **5** was not affected by the presence of oxygen, nor was the fading rate of the red form increased by irradiation with visible light.

Thermochromic behavior of **5** was also observed. Thus, colorless solutions of **5** in diphenyl ether or acetic acid became moderately red when heated to approximately 100° and faded to colorless upon subsequent cooling.

Solutions of **5** in wet or weakly basic solvents, such as methanol (containing $\sim$0.1% water), dimethylformamide (DMF), or dimethyl sulfoxide (DMSO), were

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[1] Synvar Research Institute, Palo Alto, Calif.

[2] For a review, see W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964).

[3] H. Prinzbach, H. Hagemann, J. H. Hartenstein, and R. Kitzing, *Chem. Ber.*, **98**, 2201 (1965); (b) H. Prinzbach and E. Druckrey, *Tetrahedron Lett.*, 2959 (1965).

[4] For a recent review of photochromism, see E. Fischer, *Fortschr. Chem. Forsch.*, **7**, 605 (1967).

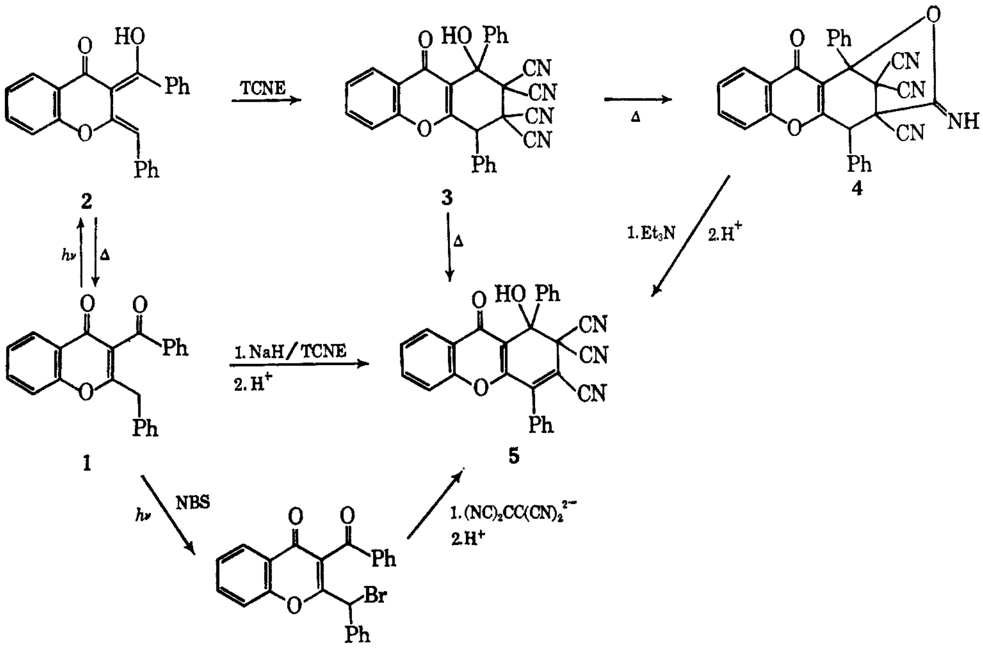
[5] Preliminary accounts of a part of this work have been published: (a) K. R. Huffman, M. Loy, W. A. Henderson, Jr., and E. F. Ullman, *Tetrahedron Lett.*, 931 (1967); (b) E. F. Ullman, W. A. Henderson, Jr., and K. R. Huffman, *ibid.*, 935 (1967).

[6] K. R. Huffman, M. Loy, and E. F. Ullman, *J. Amer. Chem. Soc.*, **87**, 5417 (1965); **88**, 601 (1966).

[7] W. A. Henderson, Jr., and E. F. Ullman, *ibid.*, **87**, 5424 (1965).

[8] (a) A variation in color intensity was frequently observed in identically prepared solutions. This was found to be due to the presence of varying amounts of water in the solvents, which led to partial ionization of the colored modification (*vide infra*). Little or no color was observed in dry hydrocarbons or chlorinated hydrocarbons. It should also be pointed out that the use of base-washed glassware is to be avoided if colorless solutions of **5** are desired. (b) E. M. Arnett in "Progress in Physical Organic Chemistry," Vol. 1, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed.. Interscience Publishers, Inc., New York, N. Y., 1963, p 223.

Scheme I



intensely colored even in the dark [$\lambda_{max}^{CH_3OH}$ 489 mμ (ϵ 12,000)] and were unaffected by brief irradiation with either uv or visible light. The red-orange solution obtained by dissolution of **5** in dimethyl sulfoxide was unchanged by the addition of hydrochloric acid or dilute alkali and showed intense nitrile bands at 4.55 and 4.65 μ. By contrast, the spectrum of colorless solutions of **5** in chloroform showed only a very weak band at 4.50 μ and was otherwise similar to the spectrum obtained in a mull. The visible and uv absorption of **5** in methanol, as in DMSO, was unchanged by addition of dilute alkali, but addition of dilute mineral acid or trifluoroacetic acid decolorized the methanol solutions and restored the uv spectrum and photochromic behavior manifest by solutions of **5** in hydrocarbon solvents. These observations implied that the colored modification was a sufficiently strong acid to be completely ionized in DMSO (pK_a = 0)[8b] and that the ionized form had strong charge delocalization into the nitrile groups.

The most plausible structure for this colored, highly acidic tautomer of **5** is the ring-opened triene **7** (Scheme II) or a geometrical isomer thereof. Further chemical transformations of **5** provided confirmatory evidence for this structure assignment. Thus, acetylation of **5** with acetic anhydride in the presence of sulfuric acid afforded the pale yellow acetate **8** in 95% yield. The spectra of **8** [λ_{max}^{mull} 4.50 and 5.72 μ, and chromone bands;[7] $\lambda_{max}^{C_6H_{12}}$ 264 mμ sh (ϵ 16,000), 272 (19,000), and 304 (14,500)] were very similar to those of **5** and suggested that no skeletal rearrangement had occurred. Unlike **5**, the acetate **8** was not affected by DMSO or DMF, but uv irradiation of its solutions produced a purple color ($\lambda_{max}^{C_6H_6}$ 530 mμ) which faded very slowly in the dark; $k_{C_6H_6}^{25°}$ = 6.2 × 10^{-6} sec^{-1}. Preparative-scale photolysis of **8** resulted in isolation of two photoisomers, one colorless and one highly colored. The latter compound was the triene **9**, obtained as dark purple crystals: mp 172–175°; λ_{max}^{mull} 4.54 (conjugated C≡N), 5.61 (enol acetate), and 6.00 μ (ketone C═O); $\lambda_{max}^{CH_2Cl_2}$ 255 mμ (ϵ 28,500) and 540 (27,000). The presence of a single methyl peak in the nmr spectrum of **9**, coupled with first-order kinetics of the thermal fading of **9** to **8** over many half-lives, suggests that **9** was formed as one pure geometrical isomer. Dissolution of **9** in wet methanol yielded a solution of the ionized **7**, which was characterized spectroscopically and by removal of the solvent to give **5**.

From qualitative studies of the photochromism of **5** it was evident that an irreversible photochemical side reaction was occurring since there was eventual loss of the photochromic properties of the solutions after prolonged irradiation. A preparative-scale photolysis of **5**, carried to the point of disappearance of the red color of **7**, resulted in the formation of a colorless photoisomer, isolated in 84% yield. The spectral properties of this product [λ_{max}^{mull} 2.90 (OH), 4.45 (unconjugated C≡N), and 6.05 μ (C═O); $\lambda_{max}^{C_6H_{12}}$ 236 mμ (ϵ 23,500), 270 sh (6800), 295 (7000), and 303 (6600)] indicated the presence of an intact chromone moiety which no longer was in conjugation with a double bond as was the case in **5**. These data, together with the absence of conjugated nitrile absorption, required that a new carbocyclic ring had been formed. Structure **10** was tentatively assigned to the photoisomer on the basis of these considerations and by analogy to known photochemical rearrangements of 1,3-cyclohexadienes to bicyclo[3.1.0]hexenes.[2,3,9] The mass spectrum of **10** confirmed the molecular formula, and in addition showed a major PhCO$^+$ fragment in agreement with the presence of an intact PhCOH grouping.[10] Although chemical degradation of **10** to recognizable fragments was not successful, it was found that **10** was converted into the aromatic xanthenone **12** simply by refluxing in xylene solution.

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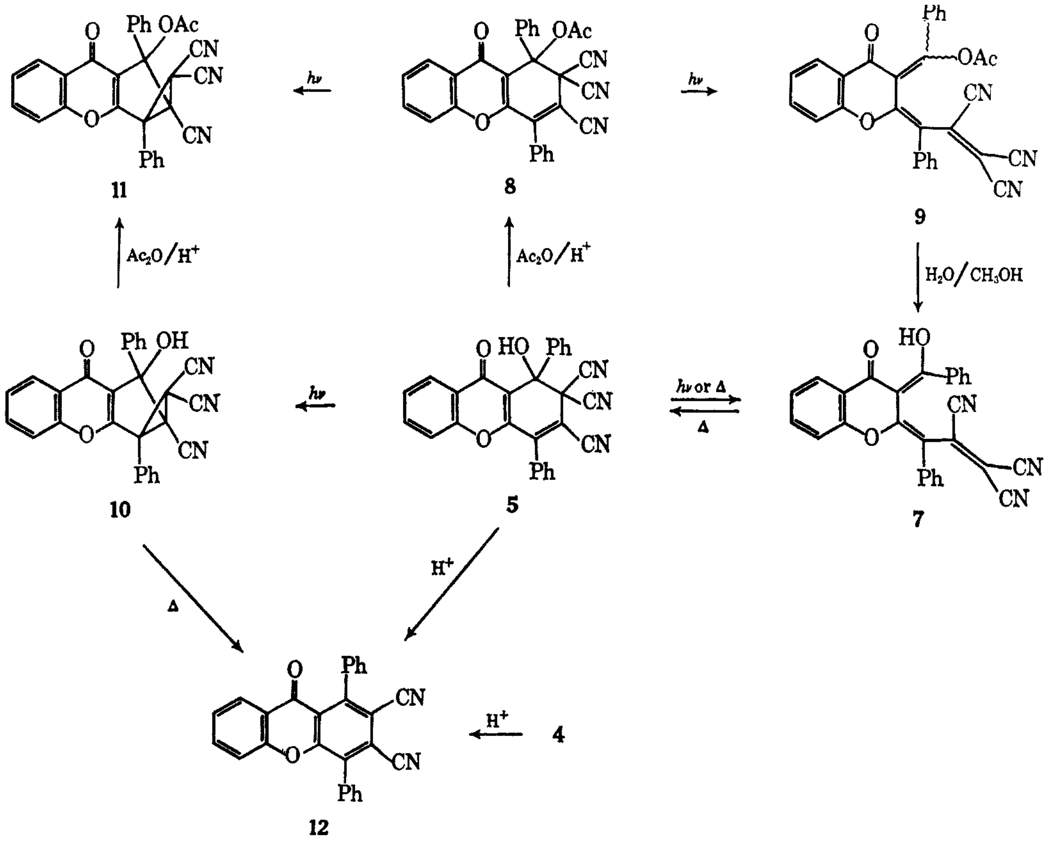
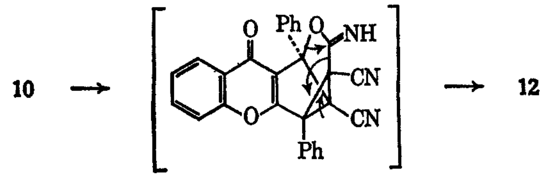
(9) (a) G. R. Evanega, W. Bergmann, and J. English, *J. Org. Chem.*, **27**, 13 (1962); (b) R. C. Cookson and D. W. Jones, *J. Chem. Soc.*, 1881 (1965). (c) K. J. Crowley, *Tetrahedron Lett.*, 2863 (1965); (d) J. Meinwald, A. Eckell, and K. L. Erickson, *J. Amer. Chem. Soc.*, **87**, 3532 (1965); (e) J. Meinwald and P. H. Mazzocchi, *ibid.*, **88**, 2850 (1966).

(10) The mass spectrum of the 1-(*p*-cyanophenyl) analog showed the expected *p*-cyanobenzoyl fragment.

SCHEME II



The structure of 12 was supported by its synthesis from both 4 and 5 by treatment of these compounds with sulfuric acid in acetonitrile. The thermal conversion of 10 into the xanthenone 12 can be rationalized by assuming initial isomerization to the bridged intermediate 13, followed by concerted or stepwise bond reorganization, and loss of HNCO. This would imply a *cis* relationship between the three-membered ring and the hydroxyl group in 10.



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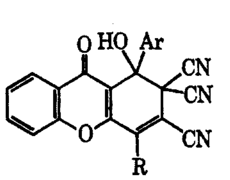
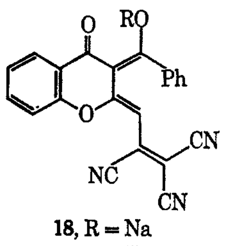
While structure 10 is not uniquely accommodated by these data,[11] analogy with the photochemistry of other 1,3-cyclohexadienes[2] and the multistep processes necessary to rationalize an alternative product[11] provide convincing arguments in favor of the assigned structure. The fact that the photoisomer of 5 was obtained in high yield with the formation of no isolable side products makes it unlikely that it resulted from several sequential photochemical reactions.

The colorless product from the aforementioned photolysis of the acetoxydihydroxanthenone 8 was readily identified as 11 by the close similarity of its spectral properties to those of 10 [λ_{max}^{mull} 4.45, 5.72, and 6.08 μ; $\lambda_{max}^{C_6H_{12}}$ 236 mμ (ϵ 25,000), 272 sh (6500), 295 (7400), and 305 (7000)] and by its preparation in high yield by acetylation of 10. The parallel nature of the photochemical reaction of 5 and 8 was thus established.

Several analogs of 5 were prepared by condensation of the appropriate 3-aroyl-2-alkylchromones with tetracyanoethylene in the presence of sodium hydride. In addition to the chromones available from our earlier work,[6] 3-benzoyl-2-ethylchromone[12] was prepared and used in the synthesis of 17. The dihydroxanthenones 14–17 were all photochromic at room temperature in hydrocarbon or chlorinated hydrocarbon solvents with the formation of red to purple colors, depending on the nature of the solvent and the concentration.[13]



14, Ar = *p*-CNPh; R = Ph
15, Ar = *p*-NO$_2$Ph; R = Ph
16, Ar = Ph; R = *p*-CH$_3$OPh
17, Ar = Ph; R = CH$_3$



18, R = Na
19, R = H

Alkaline condensation of tetracyanoethylene with 3-benzoyl-2-methylchromone followed by the usual acidification procedure (dilute hydrochloric acid) led to an

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[11] A structure analogous to 10 in which the direction of chromone ring fusion is reversed would also account for the data.

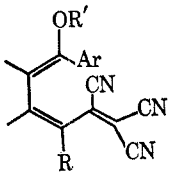
[12] Unlike the photochemically unreactive 3-benzoyl-2-methylchromone, the 2-ethyl analog was found to photoenolize in solution at room temperature. This may reflect the easier abstraction of secondary as opposed to primary hydrogen. See also the discussion in ref 6.

[13] Earlier it was found[6] that 3-(*p*-nitrobenzoyl)-2-benzylchromone, the precursor of 15, was unique among the 3-aroyl-2-(arylmethyl)chromones studied in that it failed to undergo the photoenolization reaction, apparently because of the intervention of a low lying unreactive excited state involving the nitro group. In the derived xanthenone 15, however, the nitro group did not inhibit the photochromic behavior.

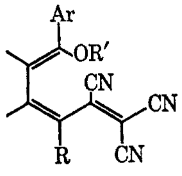
orange crystalline solid [$\lambda_{max}^{CH_3OH}$ 490 mμ (ϵ 52,000)], which was identified as the hydrated sodium salt of the triene anion, **18**. Treatment of this material with hydrochloric acid in acetic acid converted it into the enolic triene **19**, which was isolated as red needles: mp 227–230° dec; λ_{max}^{mull} 4.52, 6.20, and 6.28 μ; $\lambda_{max}^{CH_2Cl_2}$ 500 mμ (ϵ 40,000). The uv and visible spectra of **19** in methanol were identical with those of **18** in methanol, indicative of complete ionization of **19** in that solvent. Efforts to cyclize **19** to the dihydroxanthenone, either photochemically or thermally, were unsuccessful. This altered position of equilibrium for this compound is probably steric in origin (see following discussion).

Stereochemistry of the Colored Forms

The possible existence of four geometrically isomeric colored forms (A–D) makes it difficult to assign unambiguous stereochemical configurations to the colored species. Since models suggest that coplanarity of the double bonds of the hexatriene system cannot be attained in any of these isomers when R ≠ H, it may be inferred that the relief of steric interactions provides part of the driving force for thermal return to the unstrained cyclic forms. This conclusion is supported by the thermal stability of **19**, a compound which apparently exists in one of the unstrained geometries C or D which are ill-disposed for cyclization. The significantly higher extinction coefficients for the visible maximum of **18** in methanol (ϵ 52,000) compared with that of the anion of **7** in alkaline methanol (ϵ 12,000) and for **19** compared with that of **9** in methylene chloride (ϵ 40,000 and 27,000, respectively) are in agreement with this interpretation.[14]



A



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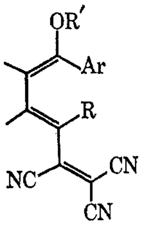
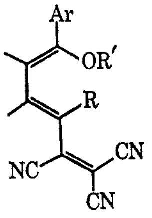


C



D

In an effort to further elucidate these stereochemical problems, the possible existence of colored intermediates in the photochemical generation of the trienes was examined by some qualitative photochemical experiments at low temperature in rigid media. Ultraviolet irradiation of the dihydroxanthenones **5**, **14**, **16**, and **17** in a hydrocarbon glass, composed of approximately equivalent volumes of toluene, methylcyclohexane, and isopentane, at −196° was found to produce weak blue or green colors which in each case were different from those obtained at room temperature in fluid solution (Table I). Upon warming these glasses, color changes, accompanied by increases in color intensity, occurred somewhat above the melting point of the glass and the resultant colors corresponded to those obtained by irradiation at 25°. Subsequent recooling gave colors that were identical with those obtained by cooling solutions which had been irradiated at room temperature. Unlike the normal colors, the colors obtained by uv irradiation of the low temperature glasses could be bleached by irradiation with visible light. These results imply the existence of a thermally and photochemically labile intermediate (blue form) in the photochemical generation of the colored trienes.

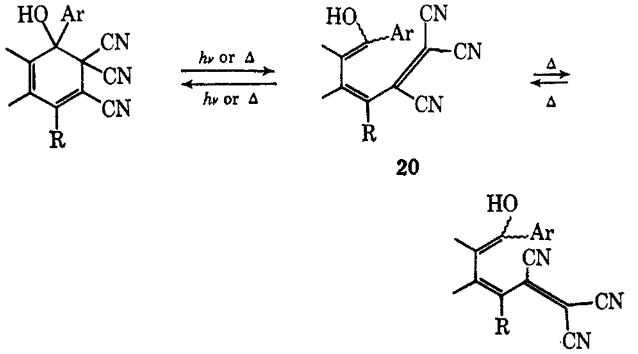
TABLE I

PHOTOCHROMIC BEHAVIOR OF DIHYDROXANTHENONES

Compd	$\lambda_{max}^{C_6H_6}$[a], mμ	Photochromism[b] at −196°	$\phi\epsilon$[c]
5	532 (red)	Blue	25,000,[d] 26,000[e]
14	536 (reddish purple)	Blue	...[f]
16	554 (purple)	Green	22,500[e]
17	503 (red)	Blue	...[f]
8	530 (reddish purple)	...[g]	620[h] (ϕ = 0.029)

[a] Maximum of colored species at 25°. [b] Color observed upon irradiation at −196° in 1:1:1 toluene–methylcyclohexane–isopentane. [c] Efficiency of the color-forming reaction in benzene. [d] Method I (see Experimental Section). [e] Method II. [f] Unable to measure accurately owing to excessively fast rate of the thermal bleaching reaction. [g] Not photochromic at −196°. [h] Measured directly.

We believe that the observed blue forms correspond to the "all-*cis*" conformation **20**, which is likely to be the initial product of the ring opening of the diene system. The high lability of this species at very low temperatures strongly suggests that a conformational change rather than a *cis–trans* isomerization is responsible for the color shifts. Thus, the species formed at room temperature is assigned configuration **21**.[15] The



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21

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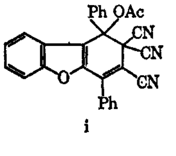
[14] In general, an increase in steric hindrance to coplanarity in conjugated systems causes a decrease in the ϵ values of the π,π^* absorption bands. See, for example, M. J. S. Dewar in "Steric Effects in Conjugated Systems," G. W. Gray, Ed., Academic Press Inc., New York, N. Y., 1958, p 46.

[15] Although these observations might also be interpreted by invoking the intermediacy of a prototropic isomer involving the highly acidic enolic hydroxyl group, the completely parallel behavior of the acetate i militates against this interpretation: information to be published.



i

all-*cis* conformer **20** is presumably also an intermediate in the thermal recyclization process. This implies the existence of a rapid equilibrium between **20** and **21** which lies heavily on the side of the latter. The failure of the red solutions to undergo bleaching by visible light, while the blue glasses are bleached, may mean that the excited state of **21** does not survive long enough to undergo a conformational change to an excited state of **20**, and, conversely, that the excited state of **20** must cyclize more rapidly than it undergoes conformational isomerization to **21**. These conclusions are in accord with the expected increase in the bond order of the conformationally important single bond in the excited states of **20** and **21**.[16]

As noted in Table I, the acetoxydihydroxanthenone **8** was not photosensitive in the low temperature glass, and even at higher temperatures in fluid solution the colored species **9** was produced at a considerably slower rate than was **7**. However, the close similarity of the visible maxima of the corresponding trienes **9** and **7** (530 and 532 mμ, respectively, in benzene) suggests that the tricyanovinyl group may have the same orientation in the two compounds. Presumably the intermediate all-*cis* acetate is also present in small amounts. Although it cannot be detected directly, its presence is consistent with the observation that the very slow thermal fading rate of the acetoxytriene **9** was accelerated by a factor of 4 upon irradiation with very intense visible light.

The orientation of the hydroxymethine group of the enolic trienes is probably that which permits hydrogen bonding with the chromone carbonyl as in structures A and C. This interpretation is supported by the ability of **7** to chelate certain metal ions. For example, addition of aluminum nitrate to a red solution prepared by dissolving **5** in methanol (λ_{max} 489 mμ) gave a purple chelate (λ_{max} 527 mμ). Similar treatment of colored solutions of related compounds not bearing a carbonyl group (*cf.* footnote 15, structure i) effected no change, an indication that the carbonyl group was in fact involved in the complexing reaction. Thus, the triene isomers of the alcohol **5**, and its analogs **14**, **15**, **16**, and **17**, which are formed in fluid solution, probably correspond to isomer A (R′ = H), while the stable triene **19** may correspond to configuration C.

Quantum Yields of the Photochromic Process

A direct determination of the quantum yields for the conversion of the hydroxydihydroxanthenones to the enolic trienes (*e.g.*, **5** → **7**) was not possible owing to the inability to measure directly the extinction coefficients of the transient colored species. We have therefore chosen the term $\phi\epsilon_b$ as a measure of the efficiency of the color-forming reaction. This term is defined by eq 1,

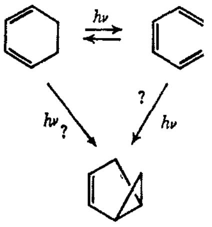
$$\phi\epsilon_b = 1/I_a[dD_b/dt]_0 \qquad (1)$$

where $(dD_b/dt]_0$ is the initial rate of decrease of the optical density D_b at the visible absorption maximum of the colored species b at the instant that a photostationary equilibrium between b and the colorless isomer a is interrupted by turning off the light source; I_a is the intensity of incident light absorbed by a at the photostationary state; ϕ is the quantum yield for the conversion of a into b; and ϵ_b is the extinction coefficient of b at the visible absorption maximum. Although a direct determination of the initial fading rate $[dD_b/dt]_0$ could be determined by two simple techniques (see Experimental) a direct measure of I_a was hampered by the competitive absorption of light by b. This error could be minimized, however, by measuring photostationary equilibria having very low percentages of b. In the case of the acetate **8**, the fading rate of the colored modification was so slow that ϕ and ϵ_b could be independently determined.

The results of these determinations are given in Table I. Although the data are inadequate to estimate accurate quantum yields for the hydroxy derivatives, it is of interest to note that the quantum yields for ring opening of these compounds must be much greater than for the corresponding reaction of the acetate **8**. Thus, if one assumes that the extinction coefficient of the hydroxytriene **7** is no more than half again as large as that of the closely related acetoxytriene **9** ($\epsilon_{C_6H_6}$ 21,200), ϕ_{5-7} must be >0.80, which contrasts to the directly measured value of ϕ_{8-9} of 0.029.

Mechanistic Results and Discussion

The identity of the intermediates in the above-described photoisomerization reactions is of some interest. Although related photoisomerizations of cyclohexadienes to linear hexatrienes with concomitant formation of bicyclo[3.1.0]hexenes have been frequently observed,[2,3,9,17] the structures of the immediate photochemical precursors to the bicyclic compounds remain a matter of some uncertainty.[5b,17a,c] The origin of this uncertainty lies in the usual existence of facile thermal and/or photochemical interconversion of the trienes and cyclohexadienes which prevent direct observation of the individual photochemistry of each isomer. The very large differences in absorption spectra of the present cyclohexadiene and hexatriene isomers and the ease of isolation of both acetate isomers **8** and **9** afforded a good opportunity to examine this question. Thus, upon following spectroscopically the appearance of the colored hexatriene acetate **9** during the irradiation of the cyclic acetate **8**, the color intensity was found to increase relatively rapidly ($\phi_{3650}^{C_6H_6} = 0.029$), until a maximum of 46% of the starting **8** had been converted into **9**. Continued irradiation led to a gradual disappearance of **9**: $\phi_{3650}^{C_6H_6} \sim 6 \times 10^{-4}$. Since the only detectable component of the reaction mixture other than the triene **9** was the bicyclic product **11**, the data require that **11** be formed from the cyclohexadiene **8** in a quantum yield of about 0.029(0.54/0.46) =



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[16] *Cf.* R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406 (1965).

[17] (a) J. Meinwald and P. H. Mazzocchi, *ibid.*, **89**, 1755 (1967); (b) W. G. Dauben and P. Baumann, *Tetrahedron Lett.*, 565 (1961); (c) W. G. Dauben and J. H. Smith, *J. Org. Chem.*, **32**, 3244 (1967).

0.034, and a maximum of only about 2% ($6 \times 10^{-4}/0.034$) of the bicyclohexene derivative **11** could, therefore, have arisen by direct photochemical rearrangement of the triene **9**. This conclusion is further supported by an experiment in which the pure triene **9** was irradiated with visible light (>435 mμ) which was not absorbed by either of the other isomers. As noted above, these conditions led to a modest light-induced acceleration of the slow thermal reversion to the cyclohexadiene **8** and no detectable amount of bicyclohexene **11** was formed.

Although a similar direct determination of the origin of the hydroxybicyclohexene **10** was precluded by the rapid thermal recyclization of the hydroxytriene **7**, it was possible to demonstrate indirectly that **7** was not a major photochemical precursor of **10**. Thus, on irradiation (3650-Å light) of solutions of the hydroxycyclohexadiene **5** that are sufficiently concentrated to absorb all the light, the photostationary concentration of the colored **7** at low light intensities is expected to be nearly proportional to the light intensity. The fraction of light absorbed by **7** and the effective quantum efficiency of formation of **10** should then be proportional to the light intensity provided that **7** is the immediate photochemical precursor of **10**. However, a threefold variation of the light intensity was found to cause no variation in the quantum yield of **10**, and thus the triene **7** cannot be a photochemical intermediate.

Although these experiments provide very strong evidence that the cyclohexadiene derivatives **5** and **8** rather than the trienes **7** and **9** are the immediate photochemical precursors of the bicyclohexenes **10** and **11**, a possible alternative must be considered. If on absorption of light the cyclohexadienes could undergo intersystem crossing to their triplets while the hexatrienes could not, then a mechanism can be envisaged in which absorption of light by the cyclohexadienes produces rearrangement of the hexatrienes to bicyclohexanes by a sensitization process. In order to test this alternative the effects of sensitizers and quenchers were examined. On irradiation of solutions of the cyclohexadiene acetate **8** with thioxanthone ($E_T = 65$ kcal) added in concentrations sufficient to absorb essentially all the light, the colored hexatriene **9** increased in concentration much as in the unsensitized process ($\phi^{C_6H_6} = 0.049$) and a maximum conversion into **9** of 40% was obtained. Continued irradiation of this solution or irradiation of solutions of the pure hexatriene **9** with this sensitizer led to only a slow disappearance of **9** ($\phi = 1 \times 10^{-3}$). A similar result was also obtained with β-acetonaphthone ($E_T = 59$ kcal). Sensitization of **9** cannot, therefore, be an important process in the formation of the bicyclohexene **11**. Moreover, any energy-transfer processes involving the cyclohexadiene acetate **8** appear very unlikely, since attempts to quench the color-forming process by oxygen, piperylene (neat), or di-*t*-butyl nitroxide (0.1 *M*) were all unsuccessful.

A similar study of the hydroxycyclohexadiene **5** was rendered more difficult by the rapid recyclization reaction. Thus only a qualitative observation was made that thioxanthone can sensitize formation of the colored species **7**, and no reliable information concerning the effect of quenchers could be obtained. However, the above-described observation, *i.e.*, that the quantum yield of formation of the bicyclohexene **10** does not vary with light intensity, effectively eliminated the possibility that **10** can be formed by sensitization of the hexatriene **7** since the efficiency of energy transfer to **7** would be expected to vary appreciably with the concentration of **7** particularly at the low photostationary concentrations ($10^{-5} - 10^{-6}$ *M*) attained in these experiments.

The above data require that (1) the cyclohexadienes are capable of rearranging to both the hexatrienes and the bicyclohexenes by way of their triplet states, but that direct absorption of light does not necessarily lead to intersystem crossing prior to the isomerizations; and (2) the hexatrienes undergo only very inefficient photochemical reaction whether or not they are sensitized and there is no evidence that any products other than the cyclohexadienes are produced. The latter conclusion stands in apparent contrast with previous work in simpler systems where it has been reported that 1,3,5-hexatrienes may rearrange directly to bicyclo[3.1.0]hexenes[3a,9c,17b] or assumed that the hexatrienes are intermediates in the conversion of 1,3-cyclohexadienes into the bicyclohexenes.[9c-e] However, these earlier studies have not excluded the possibility of competing direct photochemical rearrangement of the isomeric cyclohexadienes, and the primary difference in behavior of the present compounds may lie in the lack of photochemical reactivity of the present trienes.

Although generalizations based on the present results are hazardous, there are a number of previous observations which suggest that direct photochemical rearrangement of cyclohexadienes to bicyclo[3.1.0]hexenes may be a common process. For example, related 1-methylene-2,4-cyclohexadiene rearrangements have been reported in which formation of the hexatriene isomer is geometrically forbidden,[18] and a variety of both cyclic and acyclic olefins have recently been reported to undergo formally analogous rearrangements to cyclopropanes.[19] The observed rearrangements of cyclohexadienes to bicyclo[3.1.0]hexenes may well be only special examples of this more general olefin rearrangement.[20] However, on photochemical excitation of a given cyclohexadiene, this process must compete with hexatriene formation, and subtle factors will probably control the product ratio. Moreover, since the formation of the bicyclohexenes from the hexatrienes is also a competitive process, it too is likely to be sensitive to rather subtle variables. Hence, the immediate photochemical precursors of the bicyclohexenes in a given reaction are not likely to be easily predictable.

Experimental Section

Melting points are corrected. The nmr spectra were determined in deuteriochloroform solutions and the ir spectra were run in mineral oil suspensions, unless otherwise specified.

Light Sources.—All of the qualitative photochromic studies were performed in Pyrex tubes containing $10^{-4} - 10^{-2}$ *M* solu-

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(18) (a) D. H. R. Barton and A. S. Kende, *J. Chem. Soc.*, 688 (1958); (b) D. H. R. Barton, R. Bernasconi, and J. Klein, *ibid.*, 511 (1960).

(19) (a) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Amer. Chem. Soc.*, **87**, 1410 (1965); (b) G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965); (c) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 2882 (1966); (d) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); (e) D. Kumari and S. K. Mukerjee, *Tetrahedron Lett.*, 4169 (1967); (f) M. Pomerantz and G. W. Gruber, *J. Amer. Chem. Soc.*, **89**, 6798, 6799 (1967).

(20) A similar interpretation of a related rearrangement of 1,4-cyclohexadienes has recently been proposed: W. Reusch and D. W. Frey, *Tetrahedron Lett.*, 5193 (1967).

tions of the dihydroxanthenones which were irradiated with a 1000-W General Electric B-H6 high pressure mercury arc equipped with a Corning No. 9863 nickel oxide filter. The effective wavelength of irradiation was thus approximately 300–370 mμ. The light sources for the quantitative studies and for the preparative-scale experiments are described separately under the appropriate heading.

Visible light was obtained from a 500-W Argus No. 540 slide projector fitted with a Corning No. 3387 filter transmitting >435 mμ.

Rate and Quantum Yield Measurements.—Two experimental techniques were used to measure the quantum yield of formation of the colored isomers. **Method I** involved irradiation of a solution of the photochromic compound with a calibrated[21] source of 365-mμ light from a 100-W Hanovia No. 30620 mercury lamp equipped with Corning No. 5860 and 7380 filters. After a period of irradiation sufficient to reach a photostationary concentration of the colored form (generally about 30 sec) the rate of decay of the color produced was measured with a Cary Model 15 spectrophotometer on the 0–0.1 optical density scale. Extrapolation to the instant of removal of the sample from the exciting light gave the value of $[\mathrm{d}D_b/\mathrm{d}t]_0$ required in eq 1. In **method II** a solution of the photochromic compound was irradiated with 365-mμ light from a General Electric A-H6 high pressure mercury arc equipped with a water prism monochromator. Through the use of a mechanical chopper the spectrum was simultaneously recorded by a modified Beckman DU spectrophotometer connected to a Texas Instruments recorder having a 0.4-sec rise time.[22] The photostationary optical density of the colored form could then be monitored directly and the rate of fading was readily followed simply by interrrupting the activating light beam.

Photoaddition of Tetracyanoethylene to 3-Benzoyl-2-benzylchromone (1).—A solution of 1.13 g (0.0033 mol) of 3-benzoyl-2-benzylchromone[6] and 0.45 g (0.0035 mol) of tetracyanoethylene in 40 ml of ethyl acetate was stirred in a water-cooled quartz vessel under nitrogen for 24 hr while irradiating with the B-H6 lamp equipped with a Corning No. 9863 filter transmitting approximately 250–370 mμ. The solution was evaporated to dryness *in vacuo*, with the temperature kept below 30°. The adduct **4** crystallized slowly from an ether solution of the residue. Three crops of tan crystals were obtained during a 2-day period, in a total yield of 1.15 g (74%), with a melting point varying from 213–215° dec to 216–218° dec. Recrystallization from methylene chloride–petroleum ether raised the melting point to 219–221° dec.

Anal. Calcd for $C_{29}H_{16}N_4O_3$: C, 74.35; H, 3.44; N, 11.96. Found: C, 74.29; H, 3.77; N, 12.11.

The uv spectrum of **4** showed $\lambda_{\max}^{\mathrm{CH_3OH}}$ 253 mμ sh (ε12,300), 298 (6300), and 305 (6100).

In another experiment, a mixture of the above product and the more soluble initial photoadduct, **1,4-diphenyl-1-hydroxy-1,2,3,4-tetrahydro-2,2,3,3-tetracyano-9-xanthenone** (**3**), was obtained by fractional crystallization from cold ethanol. The latter had mp 144–146° dec; $\lambda_{\max}^{\mathrm{mull}}$ 2.8 (OH) and 6.05 μ (C═O).

Anal. Calcd for $C_{29}H_{16}N_4O_3 \cdot C_2H_6O$ (ethanol solvate): C, 72.36; H, 4.31; N, 10.89. Found: C, 72.17; H, 4.11; N, 11.18.

1,2-Dihydro-1,4-diphenyl-1-hydroxy-2,2,3-tricyano-9-xanthenone (**5**). A.—A suspension of 250 mg of photoadduct **4** in 50 ml of benzene was treated with 250 mg of triethylamine and refluxed under nitrogen for 2 hr. When the resulting deep purple solution was shaken with 25 ml of 5 *N* hydrochloric acid, the color faded. The organic layer was then separated and diluted with petroleum ether to precipitate a tan solid, mp 190–192° dec. Recrystallization from ether–petroleum ether gave light brown crystals of **5**, mp 196–198° dec.

Anal. Calcd for $C_{28}H_{15}N_3O_3$: C, 76.18; H, 3.43; N, 9.52. Found: C, 76.04; H, 3.60; N, 9.49.

B.—An ethanolic solution of 0.50 g of the crude photoadduct **3** was refluxed for 1 hr and filtered to remove some of compound **4**. The deep red filtrate was evaporated to give a dark gum which crystallized upon addition of a little ether. Recrystallization from benzene–hexane afforded the dihydroxanthenone **5**, mp 196–197.5° dec.

C.—A suspension of 0.75 g (0.015 mol) of 50% sodium hydride (dispersion in mineral oil) in 25 ml of dry tetrahydrofuran was stirred under nitrogen during dropwise addition of a solution of 3.4 g (0.010 mol) of 3-benzoyl-2-benzylchromone[6] in 25 ml of tetrahydrofuran. The resulting deep red solution was refluxed for 5 min, then cooled to room temperature, and treated dropwise with 1.3 g of tetracyanoethylene (0.010 mol) in 10 ml of tetrahydrofuran. The color changed to deep purple at this point.

After 1.5-hr reflux under nitrogen, a few drops of ethanol were added to decompose any excess sodium hydride and the solution was stirred for 10 min and then evaporated *in vacuo*. The residual purple gum was dissolved in 150 ml of ice water, a little sodium chloride was added, and the aqueous solution was extracted once with ether to remove the mineral oil. Acidification of the chilled solution with 6 *N* hydrochloric acid caused a dark oil to separate. The mixture was extracted four times with chloroform and the combined extracts were dried over magnesium sulfate and evaporated *in vacuo* to give a black solid. Trituration of this material with an ether–petroleum ether mixture gave 3.7 g (84%) of **5** as a brown solid, mp 191–194° dec. Two recrystallizations from methylene chloride–petroleum ether afforded tan crystals, mp 197–198.5° dec.

D.—A suspension of 50 mg of 50% sodium hydride in 5 ml of dry tetrahydrofuran was stirred in an ice bath while a solution of 50 mg of tetracyanoethane[23] in 5 ml of tetrahydrofuran was added. After 10 min a solution of 140 mg of 3-benzoyl-2-(α-bromobenzyl)chromone (**6**) was added and the mixture was stirred at 25° for 2 hr and then at reflux for 1 hr. The purple solution was evaporated to dryness and the residue was dissolved in 50% aqueous acetic acid, treated with a few drops of 6 *N* hydrochloric acid, and diluted further with water. The reddish solid was filtered off, washed with water, and recrystallized twice from methylene chloride–petroleum ether to give faintly red crystals of **5**, mp 190–193° dec. The yield was 15 mg (10%). The product was spectrally identical with that described above.

3-Benzoyl-2-(α-bromobenzyl)chromone (6).—A mixture of 0.34 g of 3-benzoyl-2-benzylchromone (0.0010 mol) and 0.18 g of N-bromosuccinimide (0.0010 mol) in 15 ml of carbon tetrachloride was refluxed for 4 hr in a Pyrex glass flask, while irradiating with a 100-W Hanovia medium pressure uv lamp. The resulting mixture was filtered and evaporated to give a yellow oil which was crystallized from ether–petroleum ether. The yield of **6** was 0.31 g (71%), mp 121.5–124.5°. Recrystallization from ethanol afforded pale yellow crystals, mp 122–124°.

Anal. Calcd for $C_{23}H_{15}BrO_3$: C, 65.86; H, 3.60; Br, 19.05. Found: C, 65.89; H, 3.42; Br, 19.29.

The nmr spectrum showed the tertiary proton as a singlet at τ 4.07, in addition to the aromatic protons at 1.8–2.7.

1-Acetoxy-1,2-dihydro-1,4-diphenyl-2,2,3-tricyano-9-xanthenone (8).—A solution of 1.0 g of **5** in 40 ml of acetic anhydride was treated with 3 drops of concentrated sulfuric acid. After 1.5 hr, the solution was poured into ice water and the mixture was stirred until crystallization was complete. Recrystallization from benzene gave 1.04 g (95%) of tan crystals, mp 204–207° dec. Successive recrystallizations from benzene–hexane and methanol afforded pale yellow crystals, mp 208–210° dec.

Anal. Calcd for $C_{30}H_{17}N_3O_4$: C, 74.53; H, 3.54; N, 8.69. Found: C, 74.61; H, 3.68; N, 8.44.

Photolysis of 1,2-Dihydro-1,4-diphenyl-1-hydroxy-2,2,3-tricyano-9-xanthenone (5).—A solution of 1.10 g of **5** in 100 ml of ethyl acetate in a Pyrex glass flask was irradiated in an air-cooled Rayonet photochemical reactor equipped with sixteen 1.5-W tubes having peak emission at 3500 Å. After 3 hr, the solvent was evaporated and the residue was crystallized from ether–petroleum ether to give 0.92 g (84%) of **10**, as tan crystals, mp 193–196° dec. Further recrystallization gave nearly colorless crystals, mp 196–198° dec.

Anal. Calcd for $C_{28}H_{15}N_3O_3$: C, 76.18; H, 3.43; N, 9.52; mol wt, 441. Found: C, 76.33; H, 3.65; N, 9.78; *m/e* 441.

Acetylation of 10.—A solution of 200 mg of **10** in 5 ml of acetic anhydride was treated with 1 drop of concentrated sulfuric acid. After standing for 1.5 hr, the solution was poured into ice water, from which the acetate crystallized after prolonged stirring. The yield of **11** was 210 mg (95%), mp 213–217° dec. Recrystallization from acetonitrile–water gave colorless crystals, mp 217–220° dec.

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[21] Actinometric measurements were performed according to the method of C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, [A] **235**, 518 (1956).

[22] The instrumentation was designed and constructed by Mr. J. Koren of the Research Service Department, to whom we are indebted.

[23] W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Amer. Chem. Soc.*, **80**, 2783 (1958).

Anal. Calcd for $C_{30}H_{17}N_3O_4$: C, 74.53; H, 3.54; N, 8.69; mol wt, 483. Found: C, 74.57; H, 3.61; N, 8.74; *m/e* 483.

Photolysis of 1-Acetoxy-1,2-dihydro-1,4-diphenyl-2,2,3-tricyano-9-xanthenone (**8**).—A solution of 150 mg of **8** in 10 ml of benzene in a Vycor flask was irradiated for 6 hr with the B-H6 lamp using a Corning No. 9863 filter. The resulting purple solution was diluted with 20 ml of hexane and concentrated on the steam bath until crystallization began. The mixture was chilled and filtered to give 25 mg of **9** as intensely purple crystals, mp 172–175°.

Anal. Calcd for $C_{30}H_{17}N_3O_4$: C, 74.53; H, 3.54; N, 8.69. Found: C, 74.55; H, 3.71; N, 8.68.

The mother liquor from above was concentrated further and allowed to stand overnight. The resulting solid was recrystallized from benzene–hexane to give 25 mg of colorless crystals, mp 215–220° dec. Spectral comparison established the identity of this product with **11**, described above.

From further experiments involving chromatography of the reaction mixture, yields of up to 35% **9** and 49% **11** were isolated. No other products were found.

2,3-Dicyano-1,4-diphenyl-9-xanthenone (**12**). **A.**—A solution of 100 mg of **10** in 5 ml of *o*-xylene was refluxed under nitrogen for 5 hr. The resulting tan solid was filtered and washed with ether to give 26 mg (29%) of crude **12**, mp >280°. It was purified by trituration with boiling ethanol, followed by recrystallization from a methylene chloride–benzene–hexane mixture, to give golden yellow crystals, mp 337–339°, λ_{max}^{mull} 4.49 and 5.96 μ.

Anal. Calcd for $C_{27}H_{14}N_2O_2$: C, 81.40; H, 3.54; N, 7.03; mol wt, 398. Found: C, 81.98; H, 3.90; N, 7.39; *m/e* 398.

B.—A solution of 120 mg of the imidate **4** in 10 ml of acetonitrile was treated with 5 drops of concentrated sulfuric acid and refluxed for 1 hr. About 1 ml of water was added and refluxing was continued for another 2 hr. The cooled mixture was filtered and the yellow solid was washed with water giving 18 mg (18%) of **12**, identical with the material obtained by method A.

C.—The above procedure (B), when applied to compound **5**, afforded a mixture of **12** and recovered **5**.

Preparation of Analogs of 5. General.—The 1,2-dihydro-1-hydroxy-2,2,3-tricyano-9-xanthenones **14–17** were prepared by condensation of the appropriate 3-aroyl-2-alkylchromone[6] with tetracyanoethylene in the presence of sodium hydride, as in the preparation of **5** by method C. All of these products were purified by recrystallization from methylene chloride–petroleum ether.

1-(*p*-Cyanophenyl)-1,2-dihydro-1-hydroxy-4-phenyl-2,2,3-tricyano-9-xanthenone (**14**).—Yellow crystals of **14**, mp 235–237° dec, were obtained in 71% yield: $\lambda_{max}^{CH_2Cl_2}$ 268 mμ sh (ϵ 16,500), 276 (18,500), and 322 (13,000).

Anal. Calcd for $C_{29}H_{14}N_4O_3$: C, 74.67; H, 3.02; N, 12.01. Found: C, 74.43; H, 3.22; N, 12.11.

1,2-Dihydro-1-hydroxy-1-(*p*-nitrophenyl)-4-phenyl-2,2,3-tricyano-9-xanthenone (**15**).—Pale orange crystals of **15**, mp >275°, were obtained in 20% yield: $\lambda_{max}^{CH_2Cl_2}$ 274 mμ (ϵ 19,000) and 320 (13,500).

Anal. Calcd for $C_{28}H_{14}N_4O_5$: C, 69.13; H, 2.90; N, 11.52. Found: C, 69.19; H, 3.20; N, 12.03.

1,2-Dihydro-1-hydroxy-4-(*p*-methoxyphenyl)-1-phenyl-2,2,3-tricyano-9-xanthenone (**16**).—Golden yellow crystals of **16**, mp 205–207° dec, were obtained in 72% yield: $\lambda_{max}^{C_6H_{12}}$ 268 mμ (ϵ 23,500), 308 (14,500), and 354 (10,500).

Anal. Calcd for $C_{29}H_{17}N_3O_4$: C, 73.88; H, 3.63; N, 8.91. Found: C, 73.88; H, 3.40; N, 9.10.

1,2-Dihydro-1-hydroxy-4-methyl-1-phenyl-2,2,3-tricyano-9-xanthenone (**17**).—Tan crystals of **17**, mp 222–227° dec, were obtained in 55% yield: $\lambda_{max}^{CH_2Cl_2}$ 266 mμ (ϵ 16,400), 274 (18,900), and 312 (14,400).

Anal. Calcd for $C_{23}H_{13}N_3O_3$: C, 72.81; H, 3.45; N, 11.08. Found: C, 73.06; H, 3.70; N, 11.39.

3-Benzoyl-2-ethylchromone[12] was prepared according to the general method in ref 6 in 79% yield: mp 86–88° from hexane; $\lambda_{max}^{CH_3OH}$ 223 mμ (ϵ 27,500), 250 (25,000), 294 (9400), and 302 (8500).

Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.70; H, 5.16.

Condensation of 3-Benzoyl-2-methylchromone with Tetracyanoethylene.—A suspension of 0.20 g of sodium hydride (50% dispersion in mineral oil) in 10 ml of dry tetrahydrofuran was stirred under nitrogen while a solution of 0.53 g (0.0020 mol) of 3-benzoyl-2-methylchromone[24] in 10 ml of tetrahydrofuran was added dropwise. The resulting deep red mixture was refluxed for 5 min, then cooled, and treated with 0.26 g (0.0020 mol) of tetracyanoethylene. The dark solution was refluxed with stirring for 2.5 hr and evaporated to dryness. The purple residue was taken up in water and washed once with ether to remove the mineral oil and unreacted starting materials. Addition of dilute hydrochloric acid to the aqueous solution precipitated 0.70 g of a red solid, mp 230–235° dec. Two recrystallizations from methanol–benzene afforded orange crystals of the hydrated salt **18**: mp 265–267° dec; $\lambda_{max}^{CH_3OH}$ 253 mμ (ϵ 23,500), 326 (6400), and 490 (52,000); λ_{max}^{mull} 2.90, 4.55, 6.10, 6.20, 6.28, and 6.58 μ. The nmr spectrum in DMSO-d_6 showed the aromatic protons at τ 2.1–2.5, the olefinic singlet at 4.35, and water at 6.65, in the correct ratios.

Anal. Calcd for $C_{22}H_{10}N_3O_3Na \cdot 2H_2O$: C, 62.41; H, 3.33; N, 9.92. Found: C, 62.07; H, 3.44; N, 10.43.

The above sodium salt (100 mg) was dissolved in 5 ml of acetic acid and treated with 6 *N* hydrochloric acid until no more solid came out. The red crystals were filtered and washed with water: mp 225–227° dec. Two recrystallizations from benzene–hexane yielded intensely red needles of **19**, mp 227–230° dec, which gave a greenish black color with ethanolic $FeCl_3$: λ_{max}^{mull} 4.52, 6.20, 6.28 and 6.58 μ; $\lambda_{max}^{CH_2Cl_2}$ 270 mμ (ϵ 22,000), 305 (12,000), and 500 (40,000). The uv and visible spectrum in methanol was identical with those of **18**.

Anal. Calcd for $C_{22}H_{11}N_3O_3$: C, 72.33; H, 3.04; N, 11.50. Found: C, 72.63; H, 3.08; N, 11.72.

Registry No.—**3**, 13564-63-1; **4**, 14724-82-4; **5**, 13562-55-5; **6**, 13562-54-4; **8**, 15725-91-4; **9**, 16396-67-1; **10**, 16282-38-5; **11**, 16282-39-6; **12**, 16282-40-9; **14**, 13562-58-8; **15**, 13562-57-7; **16**, 13562-56-6; **17**, 17003-38-2; **18**, 17021-88-4; **19**, 17003-40-6; 3-benzoyl-2-ethylchromone, 17003-39-3.

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