New Photochromic Cyclohexadienes

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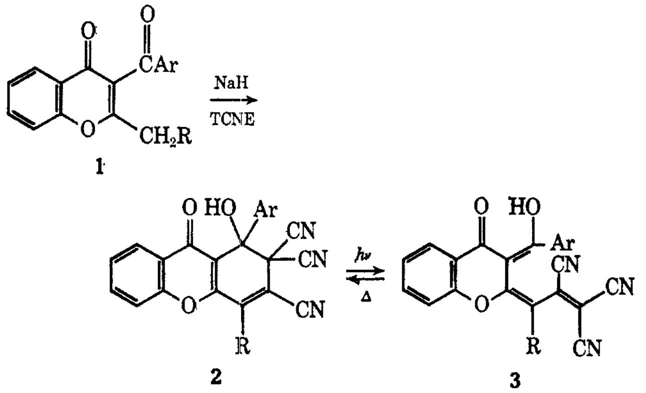
The effect of structural modification on the behavior of highly substituted cyclohexadienes has been studied. The new photochromic compounds, prepared by condensation of *vic*-alkylaroyl heterocycles with tetracyanoethylene and related olefins, include 2,2-dicyano-1,2-dihydro-9-xanthenones, 2-cyano-1,2-dihydro-9-xanthenone-2,3-dicarboximides, 1,2- and 3,4-dihydrotricyanodibenzofurans, and a 1,2-dihydro-2,2,3-tricyano-9-acridone. In addition the synthesis of some new 4-alkyl-3-benzoylcoumarins and 4-alkyl-3-benzoylcarbostyrils has provided further examples of photochromic *vic*-alkylaroyl heterocycles. The color forming efficiencies and thermal fading rates of several of the photochromic cyclohexadienes are reported and their photochemical behavior at −196° in rigid media is described.

The synthesis of several highly substituted 1,2-dihydro-9-xanthenones (2) has recently been described[2] and the dramatic photochromic behavior of these compounds has been characterized as a reversible cyclohexadiene–hexatriene valence isomerization process (2 $\rightleftarrows$ 3).



a, R = Ar = Ph

The most convenient preparation of compounds of structure 2 was found to be the base-promoted condensation of 3-aroyl-2-alkylchromones (1) with tetracyanoethylene. This reaction presumably proceeds *via* an addition–elimination mechanism[3] involving addition of the anion of the chromone to the olefin, followed by loss of cyanide and subsequent ionization to give the anion of the product. Upon acidification, the cyclic photochromic material (2) is obtained.

In principle, it appeared that electronegatively substituted olefins other than tetracyanoethylene should undergo similar reactions with 1, provided that a reasonably good leaving group was present. Moreover, one could envision a series of analogous compounds derived from various *vic*-alkylaroyl heterocycles other than chromones. If the cyclohexadiene moiety of 2 were the only feature necessary for the photosensitivity of the system, modifications such as these could provide a series of photochromic compounds encompassing a wide range of properties. The present investigation was designed to determine the scope of the reaction and to study the effect of structural modifications on factors such as position and intensity of the visible maxima of the colored forms, efficiency of the photochemical ring opening, return rates, and photochemical stability.

1,2-Dihydro-9-xanthenones.—The reaction of the 3-aroyl-2-alkylchromones **1a–e** with methoxymethylene malononitrile or ethoxymethylenemalononitrile was found to proceed in the manner analogous to that previously seen with tetracyanoethylene.[2] The resulting 2,2-dicyano-1,2-dihydro-9-xanthenones, 4 (Table I), were characterized by ultraviolet (Table II) and infrared spectra. These compounds were all photochromic at room temperature in nonbasic solvents, but their behavior differed significantly from the corresponding 2,2,3-tricyano analogs.[2]

The effect of the presence or absence of the 3-cyano group can best be illustrated by comparison of the two diphenyl derivatives **2a** and **4a**. Brief ultraviolet irradiation of dilute benzene solutions of **2a** led to intensely red solutions (λ^*_{max} 532 mμ), which faded to colorless within a few seconds in the dark.[2] When freshly prepared solutions of **4a** were treated in the same manner, an intense yellow-orange color (λ^*_{max} 420 mμ) was produced, which by analogy must be the ring-opened tautomer **5a** (or a geometrical isomer). The latter solutions faded in the dark over a period of several hours, but did not return completely to the original colorless state. On brief heating and subsequent cooling of solutions of **4a** similar color changes were observed, and the color intensities ultimately attained were equal to those resulting from fading of the same solutions after photochemical activation.

These results indicate that the colored form **5a** is present in equilibrium with **4a**. However, unlike the tricyano compounds, which are nearly colorless in nonpolar solvents at room temperature, the **4a** $\rightleftarrows$ **5a** equilibrium is displaced sufficiently toward **5a** to impart considerable color to the solutions (Chart I). This difference in the two groups of compounds is probably steric in nature. Thus in the colored forms of the dicyano compounds (**5**), it is clear that there is much less hindrance to planarity of the hexatriene system than in the tricyano compounds. This is manifest in the higher intensity visible absorption maxima of the dicyano compounds in alcoholic solution (**5a**, ϵ 39,000; **3a**, ϵ 12,000),[2b] where they apparently exist largely in the ionized form of the trienes (see ref 2b and Table II).

In other respects the behavior of the dicyano compounds 4 was similar to that previously observed for 2. Reaction of **4a** and **4d** with acetic anhydride gave the acetates **6a** and **6d** (Table III). Solutions of these acetates did not become colored on heating or standing, but, like the tricyanoacetate **8**, they became intensely colored upon irradiation and the colored solutions faded at a minimal rate at room temperature in the dark.

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[1] To whom all correspondence should be addressed.

[2] (a) K. R. Huffman, M. Loy, W. A. Henderson, Jr., and E. F. Ullman, *Tetrahedron Lett.*, 931 (1967); (b) K. R. Huffman, M. Loy, W. A. Henderson, Jr., and E. F. Ullman, *J. Org. Chem.*, **33**, 3469 (1968).

[3] See S. Patai and Z. Rappoport in "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964, pp 526 ff.

TABLE I

PRODUCTS FROM THE CONDENSATION OF *vic*-ALKYLAROYL HETEROCYCLES WITH ELECTRONEGATIVELY SUBSTITUTED OLEFINS

Compd	Reaction time, hr	Yield, %	Mp, dec, °C	Formula	Calcd, %			Found, %		
					C	H	N	C	H	N
4a	4[a]	49	175.5–177	$C_{27}H_{16}N_2O_3$	77.87	3.87	6.73	77.61	3.69	6.83
4b	6[b]	46	166.5–169.5	$C_{28}H_{18}N_2O_4$	75.32	4.06	6.28	75.15	4.13	6.06
4c	6[b]	30	159–162	$C_{28}H_{18}N_2O_4 \cdot H_2O$	72.40	4.34	6.03	72.35	4.24	6.05
4d	5.5[b]	35	190.5–193.5	$C_{22}H_{14}N_2O_3$	74.56	3.98	7.91	74.52	3.89	7.95
4e	6[b]	19	190.5–192.5	$C_{23}H_{16}N_2O_4$	71.87	4.20	7.29	71.52	4.35	7.38
12	2.5[a]	47	232–234	$C_{28}H_{16}N_2O_5 \cdot H_2O$	70.29	3.79	5.86	70.17	3.48	5.81
18	1.5[a]	20	>210	$C_{29}H_{18}N_4O_2 \cdot CH_2Cl_2$	66.80	3.73	10.39	66.23	3.91	10.44
21	1[a]	57	187.5–188.5	$C_{27}H_{15}N_3O_2$	78.44	3.66	10.16	78.41	3.69	10.21
36	3[a]	33	>180	$C_{29}H_{18}N_4O_2$	76.64	3.99	12.33	76.81	4.22	12.23

[a] In tetrahydrofuran. [b] In benzene.

TABLE II

SPECTRAL DATA FOR CYCLOHEXADIENE COMPOUNDS

Compd	$\lambda_{max}^{CH_2Cl_2}$, mμ (log ε)[a]	$\lambda_{max}^{CH_3OH}$, mμ (log ε)[b]	$\lambda*_{max}^{C_6H_6}$, mμ
4a	260 (4.27), 308 (3.98)[d]	309 (4.10), 453 (4.59)	420
4b	264 (4.40), 309 (4.09), 323 sh, (4.06)[d]	312 (4.16), 465 (4.60)	431
4c	260 (4.32), 307 (4.00)[d]	301 (4.24), 464 (4.54)	435
4d	259 (4.17), 265 (4.20), 306 (3.98)[d]	309 (3.99), 461 (4.47)	408
4e	256 (4.22), 264 (4.22), 300 (4.09)[d]	296 (4.20), 461 (4.41)	417
6a	257 (4.29), 304 (4.00)	*e*	452, 474, 506
6d	256 (4.27), 262 (4.28), 296 (4.00), 320 sh (3.81)	*e*	457
12	273 (4.17), 321 (4.06)	308 (4.05), 492 (3.88)	549
15	275 (4.08), 323 (4.03)	*e*	550
16	269 (4.22), 320 (4.11)	304 sh (4.06), 492 (3.97)	550
18	250 sh (4.27), 276 (4.30), 288 (4.32), 336 (4.08), 420 (3.63)	245 (4.60), 345 (4.24), 424 (3.96)	*f*
21	244 (4.20), 367 (4.30)	255 sh (4.30), 298 (4.11), 316 sh (4.06), 372 (4.00), 482 (4.06)	*f*
22	234 sh (4.17), 254 sh (4.04), 324 sh (4.06), 366 (4.27), 380 sh (4.19)[g]	*e*	553
25	251 (4.40), 295 (3.88), 344 (3.74)	329 (4.26), 369 sh (4.10), 485 (3.62)	*f*
26	255 (4.56), 296 (4.06), 340 sh (3.87)	*e*	637
36	237 (4.53), 263 (4.25), 296 (3.84), 345 (3.93), 410 sh (3.59)	230 sh (4.64), 282 sh (4.08), 359 (4.24), 445 sh (3.65)	*f*

[a] In Baker & Adamson reagent grade methylene chloride. [b] In methanol containing 0.1% water. [c] Visible maxima of the colored forms obtained by ultraviolet irradiation at 15–25°. Values are approximate only, as most of the bands were broad and somewhat flat. [d] The spectra of **4a–e** in methylene chloride were run on freshly prepared solutions so as to minimize thermal conversion into the colored modification. [e] No solvatochromism. [f] Not photochromic at room temperature. [g] In cyclohexane.

TABLE III

ACETOXYDIHYDROXANTHENONES AND -DIHYDRODIBENZOFURANS

Compd	Yield, %	Mp, dec, °C	Formula	Calcd, %			Found, %		
				C	H	N	C	H	N
6a	68	184–185[a]	$C_{29}H_{18}N_2O_4$	75.97	3.96	6.11	75.83	4.04	6.27
6d	70	191.5–192[a]	$C_{24}H_{16}N_2O_4$	72.72	4.07	7.07	72.77	4.17	7.02
15	90	221–222[b]	$C_{30}H_{18}N_2O_6 \cdot 0.5H_2O$	70.45	3.74	5.48	70.79	3.74	5.61
22	97	225.5–226.5[b]	$C_{29}H_{17}N_3O_3$	76.47	3.76	9.23	76.36	3.84	9.02
26	90	230–231[b]	$C_{29}H_{17}N_3O_3$	76.47	3.76	9.23	76.19	3.73	8.94

[a] Recrystallized from ethanol. [b] Recrystallized from methylene chloride–petroleum ether (bp 30–60°).

Upon preparative scale photolysis of **6d**, an isomeric compound was obtained as a stable, intensely purple crystalline solid. The structure **7d** was assigned to this product by analogy with the photochemical conversion of **8** into **9**.[2] The infrared spectrum of **7d** showed the expected maxima at 4.54, 5.67, and 6.00 μ, corresponding respectively to nitrile, enol ester, and chromone carbonyl absorptions.

Photochemical bleaching of **5** or **7** appeared to be negligible as previously found in the tricyano series. However, the smooth photochemical conversion of the tricyano compound **2a** into a bicyclo[3.1.0]hexene derivative (**10**)[2b,4] apparently was not duplicated in the dicyano series. Thus, a 100-mg sample of **4a** in benzene required 40-hr irradiation with ultraviolet light from a high-pressure mercury arc before the photochromic activity was completely destroyed and no pure photodecomposition products could be isolated from the resulting mixture. By contrast, photolysis of **2a** under the same conditions resulted in a >80% isolated yield of photoisomer **10** after 2 hr, with complete loss of photochromic activity of the solution. This difference in

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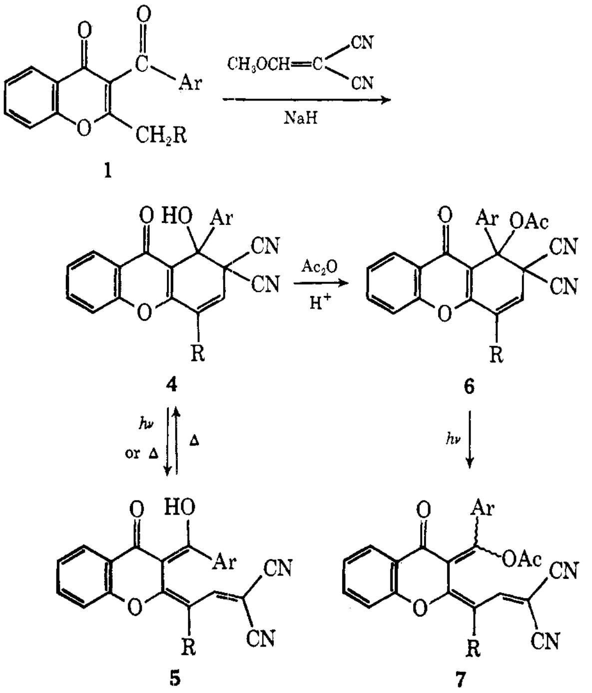
(4) E. F. Ullman, W. A. Henderson, Jr., and K. R. Huffman, *Tetrahedron Lett.*, 935 (1967).

TABLE IV
PHOTOCHEMICAL DATA

Compd	Photochromism[a]		k^{-1}, sec^{-1} [b]	$\Phi\epsilon$[c]
	−196°	+20°		
2a	Blue	Red	8.8×10^{-2}	25,000[f] 26,000[g]
4a	Red-orange	Orange	1.7×10^{-3}	12,000[f] 11,000[g]
4b	Red	Orange	1.4×10^{-3}	15,000[g]
4d	Yellow	Yellow	4.2×10^{-4}	11,000[g]
6a	*d*	Red-orange	$<1 \times 10^{-7}$	8,900[f]
6d	*d*	Red-orange	$<1 \times 10^{-7}$	9,300[f] (ϕ = 0.54)
8	*d*	Purple	6.2×10^{-6}	620[f] (ϕ = 0.029)
22	Blue-green	Purple	*e*	*e*
26	Green	Blue	2.7×10^{-1}	16,000[g]

[a] Color observed upon irradiation of compounds in a solvent of approximately equal volumes of toluene–methylcyclohexane–isopentane. [b] First-order rate of thermal bleaching reaction in benzene at 25° measured as described in ref 2b. [c] Quantum yield of color formation times extinction coefficient of visible maximum in benzene. See ref 2 b for description of methods. [d] Photochromic in liquid solutions only. [e] Fading rate too fast to measure. [f] Method I.[2b] [g] Method II.[2b]

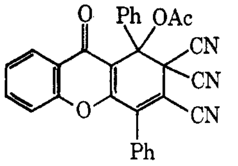
CHART I



a, R = Ph; Ar = Ph
b, R = p-CH$_3$OPh; Ar = Ph
c, R = Ph; Ar = p-CH$_3$OPh
d, R = CH$_3$; Ar = Ph
e, R = CH$_3$; Ar = p-CH$_3$OPh

reactivity is not surprising, as it had been previously demonstrated[2a,4] that the formation of **10** proceeds directly from light absorption by **2a**. Since the efficient photochemical process **4a** → **5a** (see Table IV) coupled with the relatively slow thermal process **5a** → **4a** results in a low photostationary concentration of **4a**, other efficient photochemical reactions of this isomer would be unlikely.

Condensation of 3-benzoyl-2-benzylchromone (**1a**) with 2-chloro-3-cyanomaleimide resulted in formation of the dihydroxanthenone **12**, which also exhibited photochromism at room temperature, giving deep purple solutions ($\lambda^{*C_6H_6}_{\max}$ 549 mμ). The purple color (**13**) faded within a few hours in the dark and was not noticeably destroyed by irradiation with visible light. Both the photochemical ring opening and the thermal recyclization reactions were considerably slower than the corresponding reactions of **2a**. Otherwise, the behavior of **2a** and **12** was similar (Chart II)



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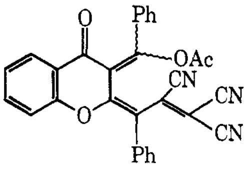

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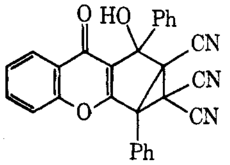

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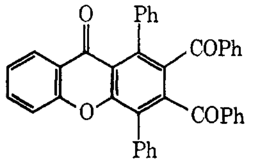

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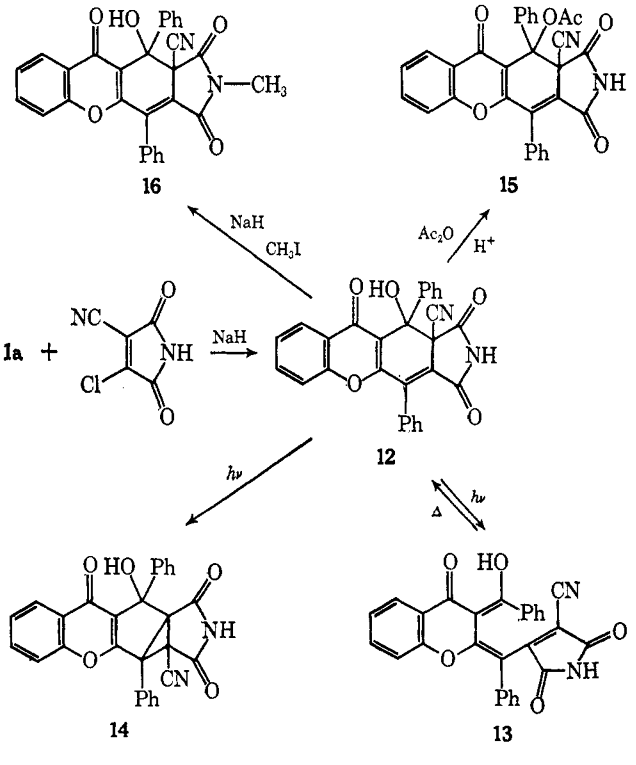
CHART II



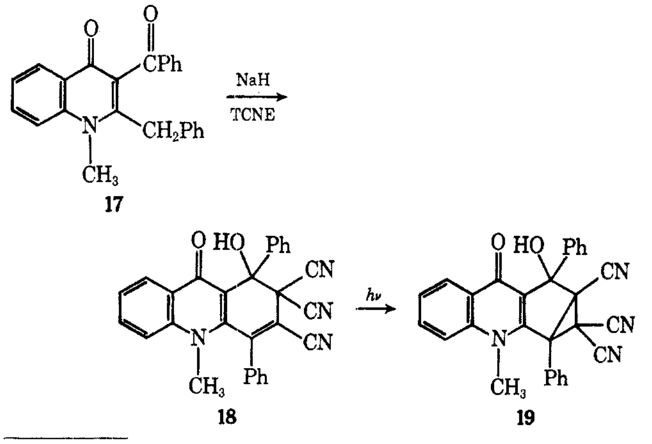
Prolonged irradiation of **12** converted it irreversibly into a photoisomer which was assigned structure **14** on the basis of spectral data (Experimental Section) and analogy with the photoisomerization of **2a**.

Acetylation of **12** afforded the O-acetate **15** which became permanently colored ($\lambda^{*C_6H_6}_{max}$ 550 mμ) upon irradiation. Compound **12** was also transformed into the N-methyl derivative **16**, by conversion into the dianion with sodium hydride, followed by treatment with methyl iodide. Like **12**, the N-methyl analog **16** was photochromic, but generation of the colored form appeared to be much less efficient.

Several other electronegatively substituted olefins, analogous to tetracyanoethylene or methoxymethylenemalononitrile, were prepared by literature methods and subjected to reaction with **1a** according to the usual procedure. Compounds such as 4-(tricyanovinyl)-N,N-dimethylaniline,[5] diethyl ethoxymethylenemalonate, and 1,1-dicyano-2,2-dimethoxyethylene[6] failed to condense with **1a** under these conditions. The reaction of **1a** with 2,3-dicyano-1,4-naphthoquinone[7] produced a small amount of uncharacterized, nonphotochromic material.

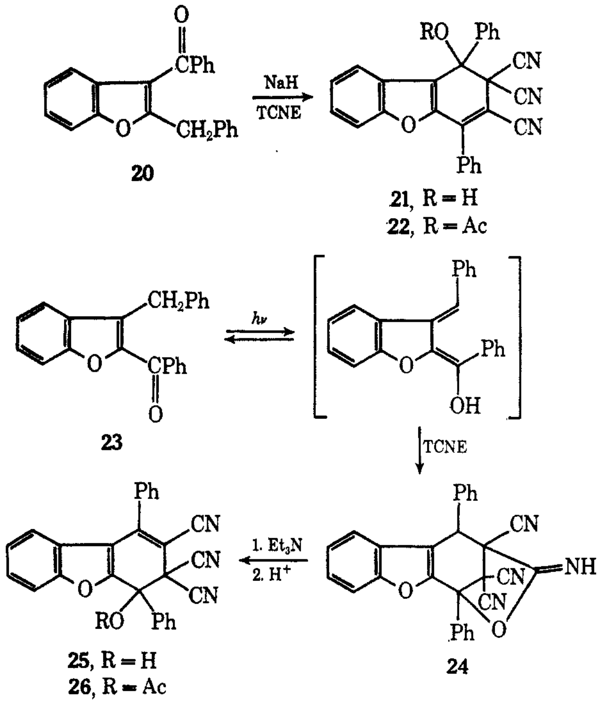
On the other hand, the condensation of **1a** with chlorotribenzoylethylene,[8] a compound with a better leaving group than most of the above examples, proceeded smoothly to give a good yield of crystalline product. However, this material proved to be the nonphotochromic aromatized xanthenone **11**, derived from formal loss of the elements of benzoic acid from the desired product.

1,2-Dihydro-9-acridones.—As an example of an analog containing a nitrogen atom in place of the heterooxygen of **2**, the 1,2-dihydro-9-acidone compound **18** was prepared from the quinolone **17**[9] and tetracyanoethylene. The yellow **18** was not photochromic at room temperature, but, at temperatures below −50° in methylene chloride, it became intensely purple in ultraviolet light and faded rapidly upon warming. Prolonged irradiation gave irreversibly formation of a photoisomer which is believed to be **19** based on spectral data (Experimental Section) and analogy. Attempted acetylation of the hydroxyl group in **18** gave dark tarry material.



Dihydrodibenzofurans.—In order to assess the effect of the presence or absence of the carbonyl group upon the behavior of these systems, the synthesis of dihydrodibenzofuran derivatives was investigated. Condensation of tetracyanoethylene with 3-benzoyl-2-benzylbenzofuran (**20**)[9] proceeded normally to give the required **21** (Chart III). The corresponding reaction with the isomeric 2-benzoyl-3-benzylbenzofuran (**23**)[9] failed, but the desired product (**25**) was eventually obtained by the photochemical addition method,[2] followed by treatment of the adduct **24** with base.

CHART III



The hydroxydihydrobenzofurans **21** and **25** did not exhibit photochromism at room temperature, although their pronounced solvatochromism, as had been observed previously with **2** and **4**, demonstrated that thermal ring opening was occurring in polar solvents. Photochemical ring opening was demonstrated by irradiation of **21** and **25** at −196° in glassy hydrocarbon mixtures. Under these conditions the thermal bleaching reaction was inhibited and ultraviolet irradiation produced colored glasses, which upon warming faded rapidly. The fact that **21** and **25** are not photochromic at room temperature is thus presumably due entirely to the fast return rate and not to any lack of photosensitivity.

Acetylation of the hydroxy compounds **21** and **25** readily gave the corresponding acetates, **22** and **26**. Both of the latter compounds were photochromic at 20° in benzene. The pale yellow 1,2-dihydro compound **22** gave a purple solution ($\lambda^{C_6H_6}_{max}$ 553 mμ) upon ultraviolet irradiation, while the isomeric colorless 3,4-dihydro compound **26** gave a blue solution ($\lambda^{C_6H_6}_{max}$ 637 mμ). The colored solutions faded rapidly in the dark; both had decolorized after several seconds at 20°.

The relatively fast fading rates of the colored modifications of the acetates **22** and **26** contrasts markedly with that of the analogous dihydroxanthenone acetate **8**,[2] which upon irradiation gives the isolable colored

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[5] B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Amer. Chem. Soc.*, **80**, 2806 (1958).

[6] W. J. Middleton and V. A. Engelhardt, *ibid.*, **80**, 2788 (1958).

[7] K. Wallenfels, G. Bachmann, D. Hofmann, and R. Kern, *Tetrahedron*, **21**, 2239 (1965).

[8] H. Kleinfeller and H. Trommsdorff, *Chem. Ber.*, **71**, 2448 (1938).

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

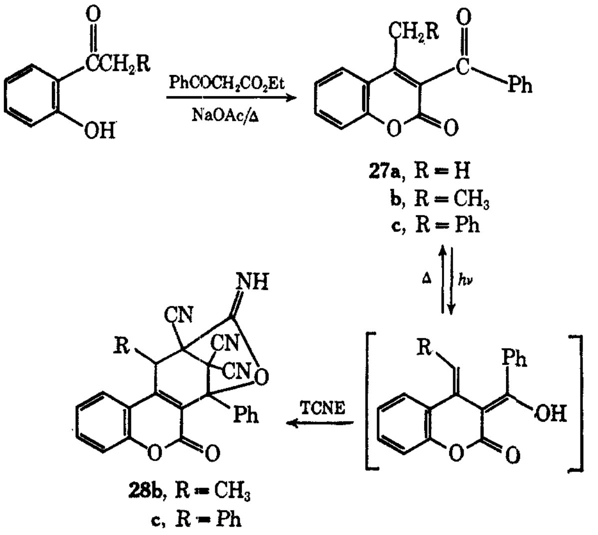
species **9**. Moreover the fading rates of the colored forms of **22** and **26** were found to be substantially accelerated by irradiation with visible light, an effect which also was not observed in the dihydroxanthenone series. Compounds **22** and **26** also seemed to be considerably more stable to prolonged irradiation than tricyanodihydroxanthenones. Although a gradual loss of photochromic activity and formation of permanent color did occur, the frequently observed efficient isomerization to bicyclohexene isomers (*e.g.*, **10**) was not found in the dihydrodibenzofuran series.

3-Benzoyl-4-alkylcoumarins and Their Reactions with Tetracyanoethylene.—A proposed synthesis of dihydrobenzocoumarin analogs of **2** required the preparation of 3-benzoyl-4-alkylcoumarins (**27**). Although 3-benzoyl-4-methylcoumarin (**27a**) has been reportedly obtained in low yield from the thermal condensation of σ-hydroxyacetophenone with ethyl benzoylacetate,[10] several attempts by us to obtain compounds **27a–c** by this method were unrewarding. Subsequently it was found that addition of a catalytic amount of sodium acetate to the reaction mixture resulted in moderate yields of the desired products.

The photochemistry of the 3-benzoyl-4-alkylcoumarins (**27**) was not studied in detail. Based upon qualitative observations, however, their behavior was similar to that of the isomeric 3-benzoyl-2-alkylchromones (**1**).[9] Thus, the 4-ethyl- and 4-benzyl-3-benzoylcoumarins (**27b** and **c**) underwent photoenolization, as evidenced by color formation and trapping experiments, while the 4-methyl derivative **27a** did not. The pale reddish solutions, formed by irradiation of **27b** and **27c** in hydrocarbon solvents at 25°, faded in a matter of seconds, as opposed to several hours for the corresponding chromones.

Attempted condensation of **27b** and **27c** with tetracyanoethylene, according to the usual technique, employing sodium hydride, was unsuccessful. The difficulty appeared to lie in our inability to generate the coumarin anions. Although irradiation of **27b** and **27c** in the presence of tetracyanoethylene afforded the expected Diels–Alder adducts of the photoenols, in the form of the cyclic imidates **28b** and **28c** (Chart IV), treatment of these adducts with triethylamine according to the method employed previously in the chromone and benzofuran series did not give the desired dihydrobenzocoumarins. The structures of the products of these reactions were not determined.

CHART IV

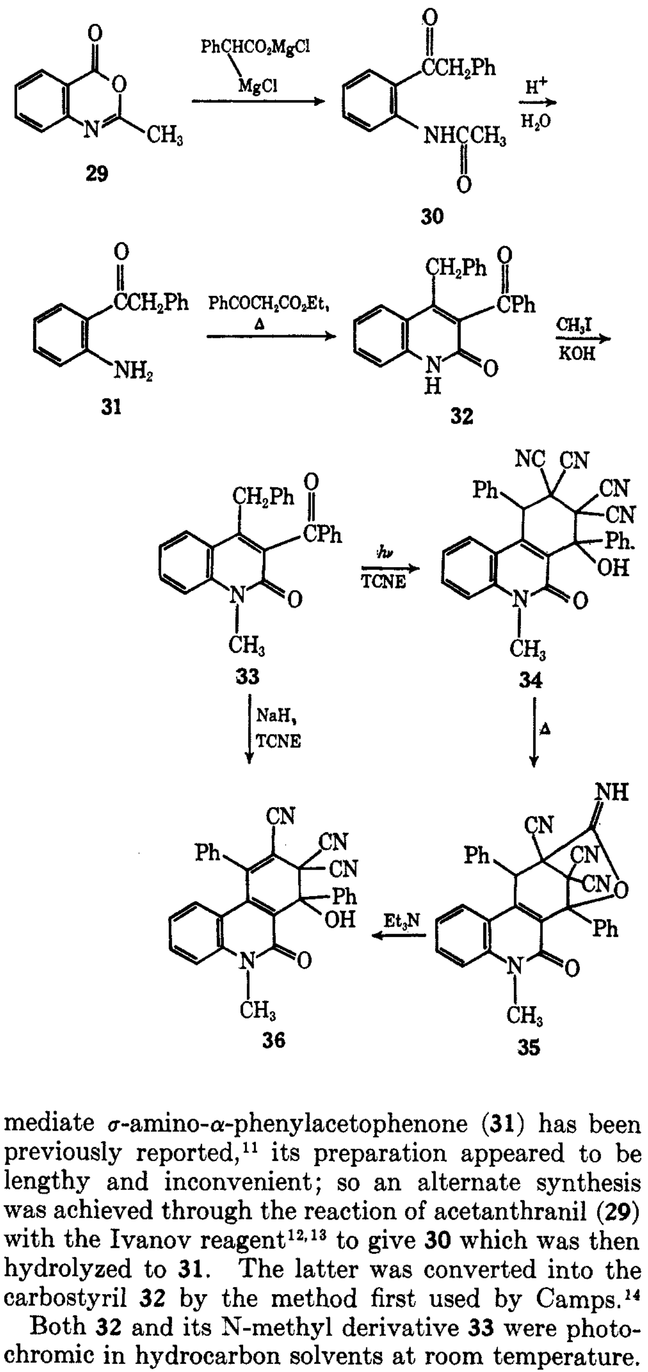


27a, R = H
b, R = CH₃
c, R = Ph

28b, R = CH₃
c, R = Ph

7,8-Dihydro-6-phenanthridinones.—The preparation of 3-benzoyl-4-benzyl-1-methylcarbostyril (**33**) and its reaction with tetracyanoethylene were also investigated (Chart V). Although the required intermediate σ-amino-α-phenylacetophenone (**31**) has been previously reported,[11] its preparation appeared to be lengthy and inconvenient; so an alternate synthesis was achieved through the reaction of acetanthranil (**29**) with the Ivanov reagent[12,13] to give **30** which was then hydrolyzed to **31**. The latter was converted into the carbostyril **32** by the method first used by Camps.[14]

CHART V



29 **30** **31** **32** **33** **34** **35** **36**

Both **32** and its N-methyl derivative **33** were photochromic in hydrocarbon solvents at room temperature. The pale yellow-orange photoenols produced on irradiation faded within a few seconds after removal from the

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(10) D. Molho and J. Brun, *Bull. Soc. Chim. Fr.*, [5] **29**, 1741 (1962).

(11) D. W. Ockenden and K. Schofield, *J. Chem. Soc.*, 3440 (1953).

(12) An analogous reaction of **29** with benzylmagnesium chloride was previously found to give no isolable amounts of **30**.[13]

(13) W. C. Lothrop and P. A. Goodwin, *J. Amer. Chem. Soc.*, **65**, 363 (1943).

(14) R. Camps, *Arch. Pharm.*, **240**, 135 (1902).

light. By contrast, in the isomeric 3-benzoyl-2-benzyl-4-quinolone series,[9] the N-methyl derivative (**17**) gave an intensely red photoenol which required several hours for complete fading at 25°, while the corresponding nonmethylated 4-quinolone was not photochromic at all.

Condensation of **33** with tetracyanoethylene, using sodium hydride as the base, gave a yellow product believed to be the desired **36** on the basis of analytical and spectral data. The same product was obtained *via* the photoadducts **34** and **35** which were formed by trapping of the photoenol of **33** with tetracyanoethylene. Unexpectedly, the dihydrophenanthridinone **36** was not photochromic when irradiated in a variety of solvents at temperatures from 25 to −196°, although some photochemical reaction did occur as evidenced by changes in the ultraviolet spectrum. Like its isomer **18**, compound **36** exhibited only a weak solvatochromism (Table II).

Inasmuch as **18** was photochromic only in fluid solutions at low temperature (<−50°) and not in low temperature glasses, a slight increase in the return rate of **36** over that of **18** might explain the lack of observable photochromism in **36**. Within the present series of cyano-substituted cyclohexadienes **36** is the only example which was not photochromic under any set of conditions.

Photochromic Behavior.—The results of quantitative determinations of the efficiencies of the color forming reactions and the rates of the thermal fading processes are presented in Table IV. Omitted from the table are compounds which were photochromic only at low temperatures (**18**, **21**, and **25**) and the imide derivatives **12**, **15**, and **16**, which were not studied in detail. The tricyanodihydroxanthenones **2a** and **8** are included for the purpose of comparison. Table IV also gives qualitative results of irradiation of these compounds in glassy hydrocarbon mixtures at −196°.

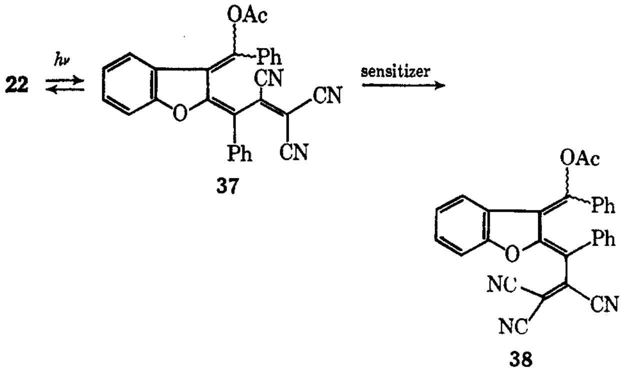
Significantly slower thermal fading rates were found in the dicyanodihydroxanthenone series compared with the corresponding tricyano derivatives. Comparison of molecular models of **3** and **5** shows that the extra cyano group present in **3** contributes greatly to the steric repulsions in this system and provides a greater driving force for cyclization to the unstrained colorless forms.

The reasons for the substantial increase in the thermal fading rates upon passing from the tricyanodihydroxanthenones to the tricyanodihydrodibenzofurans are less obvious. Since a large rate difference is observed not only between the hydroxy compounds of each class but also between the acetates (compare **2a** with **21** and **25**; **8** with **22** and **26**), it is doubtful if the hydrogen bonding available in the hydroxytriene **3a** is the primary cause of its increased stability relative to the colored modifications of **21** and **25**. Rather it appears that the rapid fading of the dihydrodibenzofuran derivatives may be related to the size of the heteroring which controls the angle between the two exocyclic double bonds in the colored forms and thus can affect the stereochemical interactions in the system. The greater bond angle between the exocyclic double bonds of the colored forms of the dihydrodibenzofurans, compared with the dihydroxanthenones, results in less steric crowding in the former and thereby facilitates conversion into the all-*cis* conformation required for both thermal and photochemical cyclization.

The results obtained upon low-temperature irradiation of the cyclohexadienes were generally similar to those observed previously in the tricyanodihydroxanthenone series.[2b,4] Thus irradiation of the hydroxydicyano derivatives **4** at −196° afforded colored glasses containing labile triene intermediates which were converted into the more stable triene forms **5** upon warming and which were readily bleached, while cold, upon irradiation with visible light. The colored species (**5**) obtained at room temperature did not readily photobleach. As discussed previously[2b] the low-temperature intermediates are believed to correspond to an all-*cis* conformation observable only in rigid media under conditions not allowing conversion into alternative lower energy conformations. Since the acetates **6** and the dihydroacridone **18** were photosensitive only in fluid solution, the related intermediates could not be observed in these instances.

The acetoxydihydrodibenzofurans **22** and **26** also afforded low temperature intermediates absorbing at longer wavelengths than the room temperature colored forms. In these cases both the colored species obtained at −196° and those formed by irradiation near room temperature were rapidly photobleached with visible light. However, if the colored solutions resulting from the room temperature irradiation were subsequently frozen at −196°, they were no longer sensitive to visible irradiation. Quite probably the photosensitive species are all-*cis* trienes (at −196°) or have all-*cis* conformations in equilibrium (at 20°) whereas the light-insensitive species resulting from cooling of the colored solutions are non-all-*cis* conformations (*e.g.*, **37**) which can not change in the frozen rigid medium.

Interestingly, **22**, which has no carbonyl group, behaved differently with sensitizers than the carbonyl-containing dihydroxanthenone derivatives **2a** and **8**. While the latter compounds both became colored during irradiation with benzophenone or thioxanthone in benzene, the benzofuran **22** remained colorless. If an amount of sensitizer was used that was insufficient to absorb all the light, then solutions of **22** very gradually turned blue. However, this color differed from the color produced upon direct irradiation, not only in hue but also in its greater thermal and light stability compared with the "normal" color. This result is most readily interpreted by assuming that the original color-forming process occurs solely by light absorbed directly by **22**, and that the initially formed "normal" colored modification **37** undergoes a photosensitized reaction to give the geometrical isomer **38**. The latter might then



owe its higher thermal and photochemical stability to its inability to undergo cyclization to **22** without prior *cis–trans* isomerization.

Experimental Section

All preparative photochemical reactions were performed in quartz or Vycor vessels using a 1000-W General Electric B-H6 high-pressure mercury arc equipped with a Corning No. 9863 nickel oxide filter, transmitting approximately 240–400-mμ light. The qualitative photochromic tests were performed in Pyrex glass tubes using the same lamp and filter combination. Visible light was obtained from a 500-W Argus No. 540 slide projector fitted with a Corning No. 3387 filter transmitting at >430 mμ. The rate and quantum yield measurements were carried out as described previously.[2b]

2-Benzyl-3-(*p*-methoxybenzoyl)chromone (1c) was prepared in 32% yield by the reaction of *o*-hydroxy-*p*′-methoxydibenzoylmethane[15] with phenylacetic anhydride, according to the general procedure of ref 9. It was obtained as colorless crystals, mp 143–144.5°, from ethanol.

Anal. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 77.95; H, 4.87.

2-Ethyl-3-(*p*-methoxybenzoyl)chromone (1e).—A similar reaction using propionic anhydride afforded a 64% yield of **1e** as colorless crystals, mp 100–101°, from hexane.

Anal. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.70; H, 5.25.

3-Benzoyl-4-methylcoumarin (27a).—A mixture of 6.8 g of σ-hydroxyacetophenone (0.05 mol), 9.6 g of ethyl benzoylacetate (0.05 mol), and 100 mg of sodium acetate was heated at 210–220° under nitrogen for 2.5 hr. The cooled reaction mixture was treated with 100 ml of 5% aqueous sodium hydroxide and extracted three times with a 2:1 ether–methylene chloride mixture. The dried extracts were evaporated and the oily residue was crystallized from ether–petroleum ether to give 4.35 g (33%) of tan crystals, mp 139–140.5°. Two recrystallizations from ethanol afforded colorless crystals, mp 140.5–141.5° (lit.[10] mp 143°).

3-Benzoyl-4-ethylcoumarin (27b).—The above procedure was repeated using σ-hydroxypropiophenone. The coumarin **27b** was obtained in 28% yield, mp 108.5–112.5°. Two recrystallizations from ethanol gave colorless prisms, mp 113–114°.

Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.54; H, 5.20.

3-Benzoyl-4-benzylcoumarin (27c).—The above procedure was applied to a mixture of 1.87 g of σ-hydroxy-α-phenylacetophenone,[16,17] 1.70 g of ethyl benzoylacetate, and 50 mg of sodium acetate. The yield of **27c** was 0.91 g (30%), mp 122.5–126.5°. After recrystallization from ethanol, the analytical sample had mp 127.5–128.5°.

Anal. Calcd for $C_{23}H_{16}O_3$: C, 81.16; H, 4.74. Found: C, 81.01; H, 4.97.

2′-(Phenylacetyl)acetanilide (30).—The Ivanov reagent was prepared by dropwise addition of a solution of 17.5 g of phenylacetic acid (0.13 mol) in 135 ml of benzene to a stirred solution of isopropylmagnesium chloride (from 7.0 g of magnesium and 24.5 g of isopropyl chloride) in 200 ml of ether.[18] The mixture was stirred overnight and then 18.9 g (0.117 mol) of 2-methyl-3,1-benzoxazin-4-one[19] (**29**) was added as a solid in portions. The reaction mixture was refluxed with stirring for 6 hr and treated with ice and concentrated hydrochloric acid. The organic layer was separated, washed with 5% sodium bicarbonate, dried, and evaporated. Recrystallization of the resulting solid from petroleum ether gave 8.4 g (28%) of **30** as a white solid, mp 98–100° (lit.[11] mp 97–98°).

σ-Amino-α-phenylacetophenone (31).—The above N-acetyl compound was hydrolyzed according to the literature procedure[11] to give a 95% yield of **31**, mp 101–103°. The reported[11] mp is 103–104°.

3-Benzoyl-4-benzylcarbostyril (32).—A mixture of 1.0 g of σ-amino-α-phenylacetophenone and 0.92 g of ethyl benzoylacetate was heated at 175° for 45 min under nitrogen. The resulting solid was washed with ether and recrystallized from ethanol to give 1.24 g (77%) of **32**, mp 262–265°. A second recrystallization from methanol afforded colorless plates, mp 263.5–265.5°.

Anal. Calcd for $C_{23}H_{17}NO_2$: C, 81.39; H, 5.05; N, 4.13. Found: C, 81.17; H, 4.80; N, 4.08.

3-Benzoyl-4-benzyl-1-methylcarbostyril (33).—To a solution of 10.9 g (0.19 mol) of potassium hydroxide in 350 ml of methanol was added 6.6 g (0.019 mol) of 3-benzoyl-4-benzylcarbostyril and 27.6 g (0.19 mol) of methyl iodide. The mixture was refluxed for 6 hr and evaporated to dryness. The residue was washed with water and crystallized from ethanol to give 5.4 g (78%) of colorless crystals of **33**, mp 176.5–179°. One further recrystallization raised the melting point to 178–179°.

Anal. Calcd for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42; N, 3.96. Found: C, 81.47; H, 5.34; N, 4.01.

Preparation of 1,2-Dihydroxanthenones and Related Compounds. General Procedure.—The following general procedure is illustrative of the preparation of compounds **4a–e**, **12**, **18**, **21**, and **36**. Analytical and melting point data are listed in Table I, along with yields and reaction times.

To a stirred suspension of 1.0 g (0.020 mol) of sodium hydride (50% dispersion in mineral oil) in 25 ml of dry tetrahydrofuran under nitrogen was added dropwise a solution of 0.015 mol of the *vic*-alkylaroyl heterocycle in the minimum amount of dry tetrahydrofuran. The mixture became deeply colored as hydrogen was evolved and the anion formed. After the addition was complete the mixture was refluxed with stirring for 10 min, then cooled to 25° and treated dropwise with a solution of 0.016 mol of the olefin component (tetracyanoethylene, methoxymethylenemalononitrile,[20] or 2-chloro-3-cyanomaleimide[21]) in tetrahydrofuran. The resulting mixture was stirred at reflux for 1–6 hr and evaporated to dryness *in vacuo*. The residual gum or solid was taken up in ice water and washed twice with ether or methylene chloride to remove the mineral oil and any unreacted starting materials. The aqueous solution was then acidified and extracted several times with methylene chloride. The combined extracts were dried and evaporated to give a gum or solid which was crystallized by trituration with an appropriate solvent and then purified by recrystallization from methylene chloride–petroleum ether.

2,3-Dibenzoyl-1,4-diphenyl-9-xanthenone (11).—Condensation of 0.34 g of 3-benzoyl-2-benzylchromone (**1a**) with chlorotribenzoylethylene[8] according to the above procedure afforded a water-insoluble orange solid which was triturated with boiling ethanol to give 0.33 g of **11**, mp 232–234°. A second crop of 0.12 g, mp 219–224°, was obtained by addition of water to the filtrate. The total yield of unrecrystallized material was 0.45 g (80%). Two recrystallizations from ethanol gave pale yellow crystals, mp 233–234°.

Anal. Calcd for $C_{39}H_{24}O_4$: C, 84.16; H, 4.35. Found: C, 83.90; H, 4.26.

Photoaddition of Tetracyanoethylene to 2-Benzoyl-3-benzylbenzofuran.—A stirred solution of 0.31 g of 2-benzoyl-3-benzylbenzofuran (**23**) and 0.13 g of tetracyanoethylene in 15 ml of ethyl acetate contained in a water-jacketed quartz vessel under nitrogen was irradiated with 240–400-mμ light from the B-H6 lamp. After 7 hr the solution was evaporated and the residue was crystallized from ether–petroleum ether to give 0.34 g (77%) of the photoadduct **24**, mp 176–180° dec. Three recrystallizations from methylene chloride–petroleum ether afforded pale yellow crystals: mp 190–192° dec; λ_{max}^{mull} 3.04 (N—H), 5.85 μ (C=N).

Anal. Calcd for $C_{28}H_{16}N_4O_2$: C, 76.36; H, 3.66; N, 12.72. Found: C, 75.83; H, 3.67; N, 12.77.

Photoaddition of Tetracyanoethylene to 3-Benzoyl-4-ethylcoumarin (27b).—The adduct **28b** was obtained in 20% yield as colorless crystals, mp >220° dec, from ethanol, after 18 hr irradiation according to the above procedure. It showed λ_{max}^{mull} 3.04, 5.78, and 5.81 μ.

Anal. Calcd for $C_{24}H_{14}N_4O_3$: C, 70.93; H, 3.47; N, 13.79. Found: C, 70.74; H, 3.37; N, 13.61.

Photoadduct of Tetracyanoethylene and 3-Benzoyl-4-benzylcoumarin.—Irradiation of **27c** and tetracyanoethylene in ethyl acetate for 18 hr afforded a mixture of products from which **28c** was separated by fractional crystallization from ethanol. Recrystallization from acetonitrile afforded a 15% yield of solvated **28c**: mp >275° dec; λ_{max}^{mull} 3.0, 5.67, and 5.82 μ.

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Anal. Calcd for $C_{29}H_{16}N_4O_3 \cdot CH_3CN$: C, 73.08; H, 3.76; N, 13.74. Found: C, 73.09; H, 3.79; N, 13.42.

Photoaddition of Tetracyanoethylene to 3-Benzoyl-4-benzyl-1-methylcarbostyril.—A solution of 707 mg of **33** and 256 mg of tetracyanoethylene in 60 ml of ethyl acetate was irradiated for 16 hr as above. The solvent was removed and the residue was crystallized from ether. **7,10-Diphenyl-7-hydroxy-5-methyl-8,8,-9,9-tetracyano-7,8,9,10-tetrahydro-6-phenanthridinone** (**34**) was obtained as a gray solid: 157 mg (16%); mp 202.5–204° dec; λ_{max}^{mull} 3.10, 6.12 μ.

Anal. Calcd for $C_{30}H_{19}N_5O_2$: C, 74.83; H, 3.98; N, 14.55. Found: C, 74.53; H, 4.32; N, 14.20.

The above adduct, when recrystallized from boiling ethanol, was converted into the cyclic imidate **35**: mp 238–240° dec; λ_{max}^{mull} 3.05, 5.80, 6.08 μ.

Anal. Calcd for $C_{30}H_{19}N_5O_2$: C, 74.83; H, 3.98; N, 14.55. Found: C, 74.54; H, 4.25; N, 14.64.

By reaction with triethylamine in tetrahydrofuran at 25° for 2 days compound **35** was converted into **7,8-dihydro-7,10-diphenyl-7-hydroxy-5-methyl-6-phenanthridinone** (**36**) which was identical with the sample prepared by direct condensation of **33** with tetracyanoethylene (Tables I and II, and earlier procedure).

3,4-Dihydro-1,4-diphenyl-4-hydroxy-2,3,3-tricyanodibenzofuran (**25**).—A solution of 0.27 g of the imidate **24** in 10 ml of tetrahydrofuran was treated with a few drops of triethylamine and allowed to stand overnight. The resulting purple gum was partitioned between ether and 5 *N* hydrochloric acid, which caused the color to fade. The ether layer was separated and combined with ethereal extracts of the aqueous layer. The dried extracts were evaporated and the resulting solid was recrystallized twice from ether–petroleum ether (bp 30–60°) to give 0.18 g (60%) of **25** as colorless crystals, mp 108.5–110.5° dec.

Anal. Calcd for $C_{27}H_{15}N_3O_2 . C_4H_{10}O$ (ether solvate): C, 76.37; H, 5.17; N, 8.62. Found: C, 76.31; H, 4.96; N, 8.59.

Acetylation of Hydroxydihydroxanthenones and Hydroxydihydrodibenzofurans.—The following general procedure was used in the preparation of compounds **6a**, **6d**, **15**, **22** and **26**. Yields, melting points, and analytical data are given in Table III.

A solution of 1 g of the hydroxy compound in the minimum amount of acetic anhydride was treated with 3 drops of concentrated sulfuric acid and kept at room temperature for 1–2 hr. The solution was then poured into ice water and the resulting mixture was stirred until crystallization of the product was complete. The product was filtered, washed with water, and recrystallized from ethanol or methylene chloride–petroleum ether.

Photolysis of 1-Acetoxy-2,2-dicyano-1,2-dihydro-4-methyl-1-phenyl-9-xanthenone.—A solution of 30 mg of **6d** in 20 ml of benzene in a Vycor flask was irradiated for 4 hr with the B-H6 lamp using a Corning No. 9863 filter. The resulting red solution was evaporated and the product was recrystallized from benzene–heptane giving the triene **7d** as purple-black crystals: mp 181–183°; λ_{max}^{mull} 4.54, 5.67, and 6.00 μ; $\lambda_{max}^{CH_2Cl_2}$ 251 (4.34), 295 sh (4.04), 372 sh (4.04), and 463 mμ (log ϵ 4.34).

Anal. Calcd for $C_{24}H_{16}N_2O_4$: C, 72.72; H, 4.07. Found: C, 72.77; H, 4.17.

2-Cyano-1,2-dihydro-1,4-diphenyl-1-hydroxy-9-xanthenone-2,3-(N-methyldicarboximide) (**16**).—A solution of 0.48 g of **12** in 25 ml of dry tetrahydrofuran was added dropwise with stirring to a suspension of 0.20 g of 50% sodium hydride (4.0 equiv) in 5 ml of tetrahydrofuran. The purple mixture was refluxed with stirring for 10 min giving an intensely blue solution. A 20-fold excess, 2.8 g of methyl iodide was added and refluxing was continued for 1.5 hr while the color gradually reverted to the original purple. The cooled solution was treated with wet tetrahydrofuran to decompose the excess sodium hydride and then evaporated to dryness. An aqueous solution of the residue was washed with methylene chloride and then acidified with dilute hydrochloric acid. The dark oil was extracted from the aqueous mixture with several portions of methylene chloride and crystallized from methylene chloride–petroleum ether. The product **16** was obtained as tan crystals: mp 177–180° dec; 0.26 g (46%); λ_{max}^{mull} 3.08, 4.45, 5.63, 5.85, 6.08, and 6.17 μ.

Anal. Calcd for $C_{29}H_{18}N_2O_5 \cdot CH_2Cl_2$: C, 64.41; H, 3.60; N, 5.01. Found: C, 64.26; H, 3.50; N, 5.17.

Photolysis of 2-Cyano-1,2-dihydro-1,4-diphenyl-1-hydroxy-9-xanthenone-2,3-dicarboximide.—A solution of 150 mg of **12** in 40 ml of methylene chloride in a Vycor flask was flushed with nitrogen, stoppered, and stirred for 14 hr while irradiating with the B-H6 lamp equipped with a Corning No. 9863 filter. The solution was concentrated and diluted with petroleum ether yielding 75 mg (50%) of tan crystals of **14**, mp 231.5–232.5° dec. Two recrystallizations from ethanol–water gave material of mp 237–239° dec; λ_{max}^{mull} 2.94, 3.60, 4.42, 5.61, 5.81, 6.10, and 6.21 μ; $\lambda_{max}^{CH_2Cl_2}$ 242 (4.40), 272 sh (3.93), and 300 mμ (log ϵ 3.93).

Anal. Calcd for $C_{28}H_{16}N_2O_5$: C, 73.04; H, 3.50; N, 6.08. Found: C, 72.75; H, 3.49; N, 5.92.

Photolysis of 1,2-Dihydro-1,4-diphenyl-1-hydroxy-10-methyl-2,2,3-tricyano-9-acridone.—A solution of 100 mg of **18** in methylene chloride was irradiated for 6 hr under the conditions described in the preceding example. The photoisomer **19** was obtained as tan crystals: mp 238–240° dec; λ_{max}^{mull} 2.95, 4.45, 6.20, and 6.30 μ; $\lambda_{max}^{CH_2Cl_2}$ 249 (4.35), 283 (3.57), 298 (3.52), 330 (3.99), and 343 mμ (log ϵ 4.02).

Anal. Calcd for $C_{29}H_{18}N_4O_2 \cdot 0.5H_2O$: C, 75.15; H, 4.13; N, 12.09. Found: C, 75.22; H, 4.07; N, 11.92.

Registry No.—**1c**, 19981-84-1; **1e**, 19981-85-2; **2a**, 13562-55-5; **4a**, 13562-62-4; **4b**, 19981-88-5; **4c**, 19981-89-6; **4d**, 19981-90-9; **4e**, 19981-91-0; **6a**, 13562-64-6; **6d**, 19981-93-2; **7d**, 19987-95-2; **8**, 15725-91-4; **11**, 19987-74-7; **12**, 19987-75-8; **14**, 19987-76-9; **15**, 19987-77-0; **16**, 19987-78-1; **18**, 13562-59-9; **19**, 20013-30-3; **21**, 13562-60-2; **22**, 13562-63-5; **24**, 14724-83-5; **25**, 13620-51-4; **26**, 13620-52-5; **27b**, 19988-00-2; **27c**, 19988-01-3; **28b**, 19988-02-4; **28c**, 19988-03-5; **30**, 19988-04-6; **32**, 19988-05-7; **33**, 19988-06-8; **34**, 19988-07-9; **35**, 19988-08-0; **36**, 19988-09-1.