

REVERSIBLE CYCLOHEXADIENE-HEXATRIENE VALENCE ISOMERIZATIONS.
A NEW CLASS OF PHOTOCHROMIC COMPOUNDS.

K. R. Huffman, M. Loy, Wm. A. Henderson, Jr. and Edwin F. Ullman¹
Central Research Division, American Cyanamid Company
Stamford, Connecticut

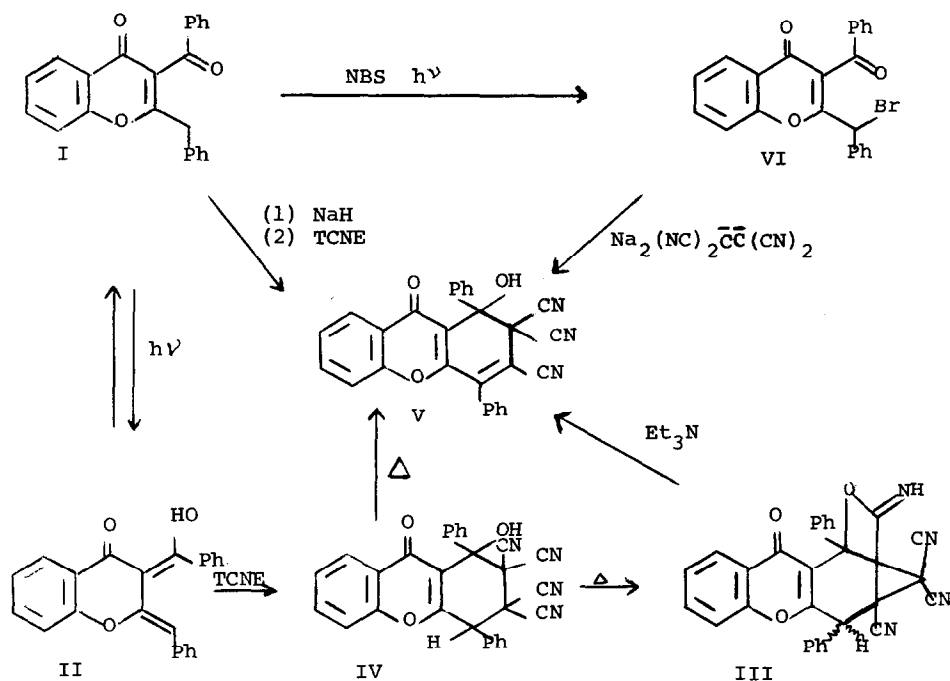
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It has previously been shown that irradiation of 3-benzoyl-2-benzylchromone (I) in solution produced a transient orange color². This colored species was identified as the enol II. In an attempt to trap II with tetracyanoethylene (TCNE) a compound was obtained that displayed dramatic photochromic properties. We report here evidence pertaining to the identity of this compound and its colored modification.

Irradiation (2400-4000Å) of an ethyl acetate solution of the chromone I containing TCNE gave two 1:1-adducts III and IV. Adduct III, m.p. 219-221^o (dec.), had infrared absorption at 3.10 and 5.75 μ which was consistent with the C=NH grouping in a cyclic imidate, together with absorption maxima typical of the chromone nucleus³ at $\lambda_{\text{max.}}^{\text{mull}}$ 6.03, 6.35, 7.15 and 10.32 μ and $\lambda_{\text{max.}}^{\text{CH}_3\text{OH}}$ 253 (sh) mμ (ε 12,300), 298 (6300), 305 (6100). The n.m.r. spectrum (CD₃COCD₃) showed signals at τ 1.95-2.60 (14 Ar-H) and unequal intensity singlets at τ 4.13 and τ 4.33 (total area ≈ 0.9 H) which suggested that the substance was a mixture of two epimers bearing single isolated hydrogens. The second adduct IV, m.p. 144-146^o (dec.), isolated as an 1:1-ethanol solvate, likewise displayed typical chromone absorption³.

This compound decomposed readily and was difficult to purify. On standing in alcohol it was converted to III, and in boiling alcohol there was obtained III and a new photochromic product V, m.p. 197-198.5^o (dec.), resulting from loss of hydrogen cyanide.

Convincing evidence for structures III-V was obtained by the preparation of V by three additional routes. First, refluxing the imidate III with triethylamine in benzene followed by acidification gave V. Second, the chromone I was converted directly to V (84% yield) by treatment with



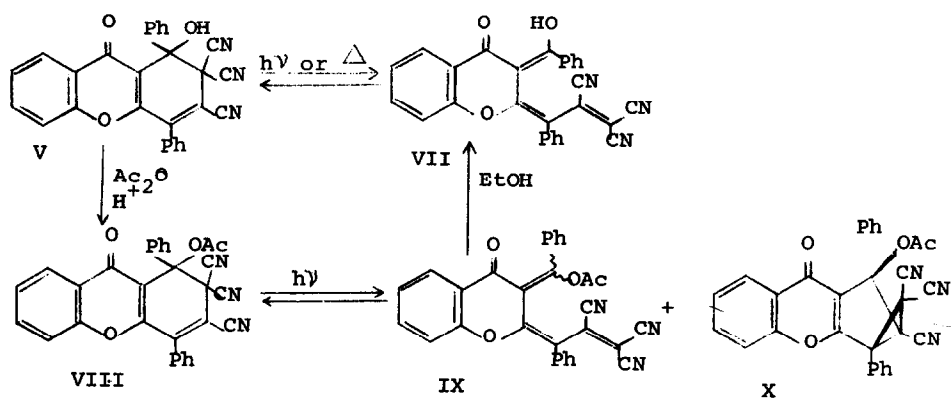
sodium hydride in tetrahydrofuran followed by addition of TCNE. Third, N-bromosuccinimide (NBS) treatment of the chromone I gave VI, m.p. 121-123°, which combined with the disodium salt of tetracyanoethane to give V. The photochromic product derived from each of these preparations was identical to the V obtained on heating the adduct IV. The compound V gave n.m.r. signals corresponding only to aromatic hydrogens, and absorption maxima were observed at $\lambda_{\text{max}}^{\text{mull}}$ 2.98 μ (OH), 4.50 μ (weak; conjugated C=N) and 6.08, 6.39, 7.12 and 10.55 μ (chromone peaks),³ and $\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$ 266 m μ (ϵ 19,000), 273 (21,000) and 312 (14,500).

Solutions of V in dry non-basic solvents such as benzene, chloroform or acetic acid were colorless to faintly red at room temperature and were thermochromic. At elevated temperatures the color became more intense and on cooling, the original color was restored. These solutions became bright red on irradiation for a few seconds with $<4000\text{\AA}$ light or sunlight.

The color became very intense in benzene (λ_{\max} . 532 m μ) and rapidly faded by first order kinetics in the dark, $k^{25^\circ} = 0.088 \text{ sec.}^{-1}$. In more polar solvents the rate was even higher. Solutions of V in wet solvents or basic solvents, such as alcohols, dimethylsulfoxide (DMSO) or dimethylformamide (DMF), were colored orange to red even in the dark ($\lambda_{\max}^{\text{CH}_3\text{OH}}$ 489 m μ , ϵ 12,000, unaffected by addition of dilute alkali). Except in the more basic solvents, DMSO and DMF ($\text{p}K_a$'s near 0),⁴ the colors were destroyed by the addition of strong acids and the typical ultraviolet spectrum and photochromic behavior of V was restored. Thus, the red species must be in thermal equilibrium with V and be a very strong acid ($\text{p}K_a < 0$) which remains colored on ionization. The only reasonable structure for such a highly acidic colored tautomer of V is the triene VII, a structure which was supported by strong conjugated nitrile absorption of the anion at 4.55 and 4.65 μ in DMSO solutions of V.

Treatment of V with acetic anhydride-sulfuric acid at 25 $^\circ$ for 30 minutes gave an acetate VIII, m.p. 208-210 $^\circ$ (dec.), $\lambda_{\max}^{\text{mull}}$ 4.50, 5.72 μ and chromone peaks,³ $\lambda_{\max}^{\text{C}_6\text{H}_{12}}$ 264 (sh) m μ (ϵ 16,000), 272 (19,000) and 304 (14,500). Solutions of VIII, like V, became red on ultraviolet irradiation. The color was produced only 2.3% as efficiently as from V, but since it faded only slowly in the dark, $k_{\text{C}_6\text{H}_6}^{25^\circ} = 6.2 \times 10^{-6} \text{ sec.}^{-1}$ the reaction could be carried to completion. There was obtained a 35% yield of an almost black isomer IX, [m.p. 172-175 $^\circ$, $\lambda_{\max}^{\text{mull}}$ 4.54 μ (C=C-C \equiv N), 5.61 μ (C=C-O-C=O) and 6.00 μ (C=O); $\lambda_{\max}^{\text{CH}_2\text{Cl}_2}$ 255 m μ (ϵ 28,500) and 540 (27,000)], together with a colorless product believed to have structure X.⁵ The assigned structure for IX was further supported by the reformation of VIII on thermal fading of IX and by the rapid hydrolysis of IX in alcohol to give, after acidification, the cyclic alcohol V.

The orientation given for the tricyanovinyl group in the colored acetate IX is required to permit the observed thermal recyclization. On the other hand, the orientation of the acetoxy group remains indeterminate. Apparently, only one of the two possible configurations is represented in the photochemical reaction mixture, since satisfactory first order kinetics of



fading were obtained and only a single methyl peak was observable in the n.m.r. As regards the stereochemistry of the colored alcohol VII, the possibility of prototropic shifts affords routes for equilibration among the various geometric isomers and no stereochemistry can be assigned with certainty. However, the similarity of the positions of the long wave length visible maxima in VII and IX ($\lambda_{\text{max}}^{\text{C}_6\text{H}_6}$ 532 and 530m μ , respectively) suggests that the tricyanovinyl group may have the same orientation in both compounds.

The existence of intermediates in the photochemical formation of VII and IX and the identity of side products and their photochemical precursors are considered in the following communication.⁵

References

1. To whom inquiries should be addressed. Present address: Synvar Research Institute, 3221 Porter Drive, Palo Alto, California.
2. K. R. Huffman, M. Loy and E. F. Ullman, *J. Am. Chem. Soc.*, **87**, 5417 (1965).
3. W. A. Henderson, Jr. and E. F. Ullman, *ibid.*, **87**, 5424 (1965)
4. (a) C. A. Streuli, *Anal. Chem.*, **30**, 997 (1958)
(b) R. Huisgen and H. Bräde, *Ber.*, **90**, 1432 (1957)
5. E. F. Ullman, W.A. Henderson, Jr. and K. R. Huffman, *Tetrahedron Letters*, 935 (1967).