# Photocyclisation of 2,6-Dichlorocinnamates to 5-Chlorocoumarin

By Rina Arad-Yellin, Bernard S. Green,* and Karol A. Muszkat*

(*Department of Structural Chemistry, The Weizmann Institute of Science, Rehovot, Israel*)

*Summary* 2,6-Dichlorocinnamic acid and its esters undergo photocyclization to yield 5-chlorocoumarin; the present evidence favours a mechanism involving the singlet excited state of the *cis*-isomer and an unstable *ortho*-quinomethylketen (**4**) as the precursor.

Cinnamic acid derivatives undergo photodimerization,[1] photocycloaddition,[2] and *cis* $\rightleftharpoons$ *trans* photoisomerization.[3] In solution, photoisomerization is generally the sole reaction observed.[3] Thus, irradiation of methyl 2,4-dichloro-*trans*-cinnamate results in a *cis* $\rightleftharpoons$ *trans* photoequilibrium and no further change.

We report a novel photoreaction observed on irradiating methyl 2,6-dichloro-*trans*-cinnamate (**1**), which photoisomerizes to the *cis*-isomer (**2**) which then undergoes photocycloelimination to yield 5-chlorocoumarin (**3**).† On irradiation (**3**) yields a photodimer, m.p. 260—262 °C. A different dimer of (**3**), m.p. 213–214 °C, is formed by irradiation in the solid state.

The formation of (**3**) also occurs on irradiating solutions of 2,6-dichlorocinnamic acid or other esters (see below). In each case reaction proceeds with the apparent elimination of the elements of R-Cl. Methyl 2-chloro-6-methoxycinnamate and the free acid‡ also photocyclize yielding

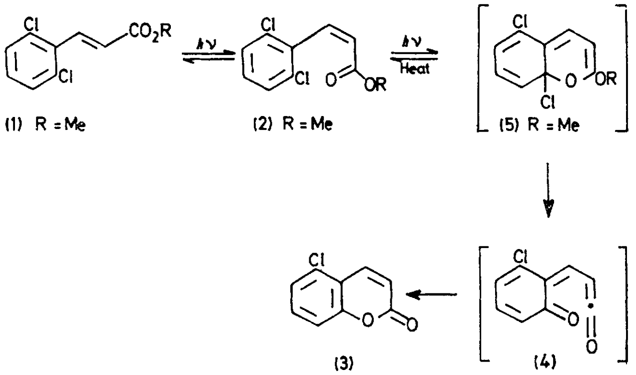
---

† This derivative, m.p. 94—95 °C, has not been thus far reported. This and other compounds were identified by $^1$H n.m.r., and mass spectroscopy, and elemental analysis.

‡ Prepared from 5-chlorocoumarin by basic ring opening of the lactone and methylation with $Me_2SO_4$.

5-methoxycoumarin,[4] m.p. 84·5 °C, but no (**3**). Since methyl 2,6-dimethoxycinnamate and ethyl 2,4,6-trimethylcinnamate only display *cis–trans* photoisomerization the photocyclization apparently requires two *ortho* substituents, at least one of which is a chlorine (other halogen derivatives have not yet been studied).

Triplet photosensitization of (**2**) does not lead to (**4**) and the presence of oxygen does not hinder the photocyclization. Thus we suggest that this reaction proceeds *via* the singlet excited state.



In order to elucidate the pathway of this unusual process we looked for intermediates. Upon irradiation of (**2**) at −190 °C a new, red species was formed with structured absorption extending to 640 nm (Figure). The same spectra were observed on irradiating solutions of other 2,6-dichlorocinnamic acid esters (R = Et, $\text{Pr}^i$, Ph, $\text{Bu}^t$, and n-octyl). When this thermally unstable species was warmed to *ca.* −170 °C its spectrum was replaced by that of (**3**) (in dilute solution the chemical yield approaches 100%). The i.r. spectrum of this intermediate [at −190 °C in neat (**2**)] revealed new bands at 2300, 1600, and 1615 $\text{cm}^{-1}$, which are characteristic of ketens[5,6] and disappeared on warming to −170 °C. We propose the *ortho*-quinomethylketen structure (**4**) for the red intermediate which, on electrocyclic ring closure, yields the product (**3**); such reactions are well known in related systems[6] and the u.v. and i.r. spectral properties are as expected for structure (**4**)[5,7] The formation of (**4**) was also observed in methylcyclohexane–isohexane (2:1), in methylcyclohexane–methylcyclopentane (1:1) and in 2-methyltetrahydrofuran glasses. Photochemical opening of the coumarin, (**3**) → (**4**), does not take place under the conditions of the reaction nor on extensive irradiation at wavelengths which led to ring opening in other unsaturated lactones.[8] The formation of the intermediate (**4**) requires the transfer of an oxygen atom to a position formerly occupied by a chlorine atom and we suggest a pathway involving an electrocyclic ring closure of the *cis*-cinnamate (**2**) to (**5**). The leaving chlorine in (**5**) is attached to a tertiary carbon and is α to oxygen, and is thus highly reactive. Elimination of chlorine and electronic reorganization with the subsequent loss of Me leads to (**4**)[9]. In the case of 2,6-dichlorocinnamic acid the formation of HCl was established.

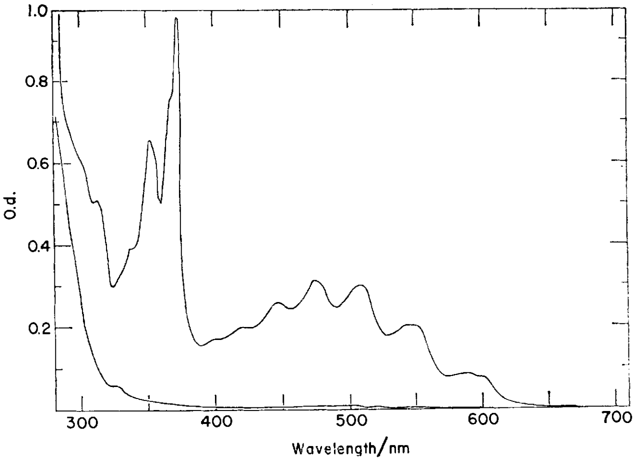


FIGURE. Absorption spectrum of (**4**) (upper curve) following u.v. irradiation of (**2**) ($3{\cdot}5 \times 10^{-1}$ M). Solution in methylcyclohexane–isohexane (2:1) irradiated at − 190 °C with light from a 100 W Hg arc filtered through a $NiSO_4$–$CuSO_4$ solution. Lower curve is spectrum before irradiation.

Efficient photocycloelimination may be restricted to 2,6-disubstituted cinnamates because of rapid reversal from (**5**) to (**2**) in other ring-substituted cinnamates and in those examples where the leaving group is not chlorine.

(*Received*, 13*th October* 1975; *Com.* 1165.)

---

[1] G. M. J. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647.

[2] O. L. Chapman, R. D. Lura, R. M. Owens, E. D. Plank, S. C. Shim, D. R. Arnold, and L. B. Gillis, *Canad. J. Chem.*, 1972, **50**, 1984; J. Rennert, S. Soloway, I. Waltcher, and B. Leong, *J. Amer. Chem. Soc.*, 1972, **92**, 7242.

[3] B. K. Vaidya, *Proc. Roy. Soc.* 1930, *A*, **129**, 299; H. G. Curme, C. C. Natale, and D. J. Kelley, *J. Phys. Chem.*, 1967, **71**, 767.

[4] H. A. Shah and R. C. Shah, *J. Chem. Soc.*, 1938, 1832; H. Bohme, *Ber.*, 1939, **72**, 2130.

[5] O. L. Chapman and J. D. Lassila, *J. Amer. Chem. Soc.*, 1968, **90**, 2449.

[6] O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Amer. Chem. Soc.*, 1973, **95**, 244.

[7] L. Edwards, J. Kolc, and R. S. Becker, *Photochem. Photobiol.*, 1971, **13**, 423.

[8] C. L. McIntosh, and O. L. Chapman, *J. Amer. Chem. Soc.*, 1973, **95**, 247 and references therein.

[9] For related photo-eliminations see A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 1945, 551; G. R. Lenz, *Tetrahedron Letters*, 1973, 1963; E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc. (C)*, 1970, 163.