Photochromism: Nature of the Coloured Form of 1,2-Dihydroquinolines

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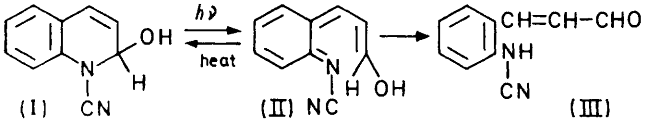
1-Cyano-1.2-dihydro-2-hydroxyquinolines when subjected to low-temperature rigid-matrix photochemistry and then warmed give rise principally to *N*-cyano-*o*-aminocinnamaldehyde. This result verifies the fact that the core molecular structure of the photocoloured forms of the 1.2-dihydroquinolines previously suggested is correct.

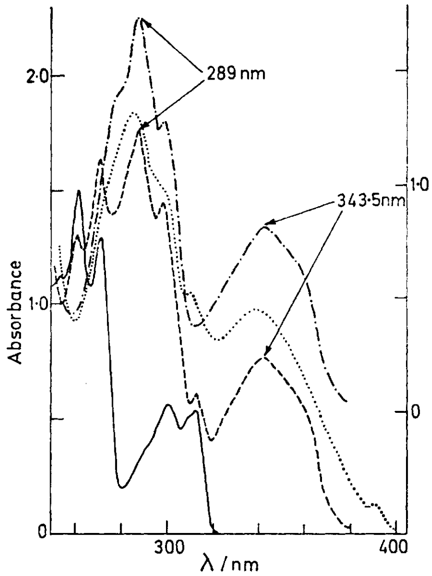
THE 1,2-dihydroquinolines investigated previously exhibited photocolouration upon irradiation by u.v. light in rigid matrix at -196 °C (and some at higher temperatures as well).[1] While investigating the photochromism of the 1,2-dihydroquinolines,[1] we noticed considerably different behaviour for a compound with a hydroxy-group at C-2, namely *N*-cyano-2-hydroxy-1,2-dihydroquinoline (I). In general, when the coloured forms were warmed to room temperature and then recooled to -196 °C, the original spectrum of the dihydroquinolines was largely restored.[1] However, this was not the case for compound (I).



Irradiation of compound (I) in EPA (ether–isopentane–alcohol 5 : 5 : 2) at -196 °C gives a blue photocoloured product with a broad, low-intensity band in the visible part of the spectrum (500—700 nm). The compound when warmed to room temperature became colourless and when recooled to -196 °C, the solution displays a completely different spectrum from that of the original dihydroquinoline. New peaks arise at 343·5 and 289 nm and a broad, low-intensity band exists between *ca.* 390 and 460 nm. The Figure shows the u.v. portion (to *ca.* 400 nm) of the spectrum of each of the foregoing cases.

If we suppose that the structure of the coloured form of the 1,2-dihydroquinolines is analogous to that of the chromens[2] and thiochromens[3] (as we have already suggested[1]), then the transformation (I) ⟶ (II) occurs during irradiation at -196 °C. The coloured form (II) is an enol which by tautomerization and aromatization of the ring could form *N*-cyano-*o*-aminocinnamaldehyde (III).

We prepared *N*-cyano-*o*-aminocinnamaldehyde as described previously[4] and took its absorption spectrum at -196 °C (Figure). The visible region, which is not shown, exhibits the same broad, low-intensity band between 390 and 460 nm as the product obtained when compound (I) was irradiated, warmed, and recooled to -196 °C. Comparison of the spectra proves that compound (III) is identical to authentic *N*-cyano-*o*-aminocinnamaldehyde. Therefore, the enol (II) is indeed formed by the irradiation of compound (I). Furthermore, compound (II) must represent the general core molecular structure of the coloured forms of the 1,2-dihydroquinolines as originally suggested.[1] For the specific case of the enol (II), warming results in predominant compound transformation to the aldehyde (III) and only a little reversion to compound (I). 1,2-Dihydroquinolines without a hydroxy-group at C-2 do not exhibit this phenomenon. It is also worth mentioning that irradiation of compound (I) in ether at room temperature (22 °C) does not result in the formation of the aldehyde (III).



1-Cyano-2-hydroxy-1,2-dihydroquinoline in EPA at 77 K (——); after irradiation with 1 kW Hg–Xe source and a Corning glass filter CS 7-54 (maximum transmission at *ca.* 325 nm) for 30 min. at 77 K (· · · ·); the irradiated sample after warming to room temperature and recooling to 77 K (– – – –); authentic *N*-cyano-*o*-aminocinnamaldehyde in EPA at 77 K (— · — · —). The scale on the right hand side refers to the last compound while that on the left refers to all others

Thus, we have elucidated the structure of the irreversible product formed by the irradiation of the dihydroquinoline (I) with subsequent warming and corroborated the general molecular structure suggested for the coloured form of the 1,2-dihydroquinolines (a 1,2 ring-scission product).[1]

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