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MECHANISTIC ASPECTS OF PHOTOCHEMISTRY OF ETHYL 2-CYANO-1,2-DIHYDROQUINOLINE-1-CARBOXYLATES (REISSERT COMPOUNDS)

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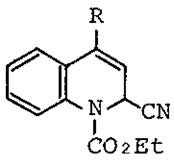
The previously proposed azahexatrienes are shown not to be intermediates of the photochemical transformation of ethyl 2-cyano-1,2-dihydroquinoline-1-carboxylates to cycloprop[b]indoles, allenic compounds and/or ethanol adducts.

In a series of papers, we have shown that irradiation of ethyl 2-cyano-1,2-dihydroquinoline-1-carboxylates (Reissert compounds) (1) produces cycloprop[b]indole (2),[1] allenic compounds (3),[2] and/or ethanol adduct (5)[2] depending upon the position of the substituents and the solvent used. These transformation reactions have been interpreted in terms of the intermediacy of azahexatrienes (6) with very little supporting evidence. The present mechanistic study, however, has revealed that these reactions actually do not involve (6) as intermediates.



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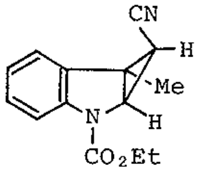
1b, R=H



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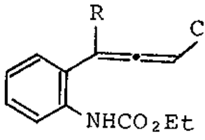

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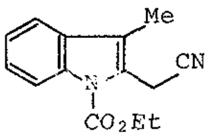

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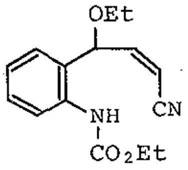

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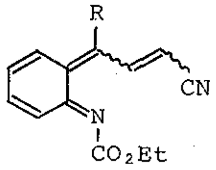


6a, R=Me
6b, R=H

The compound (1a) was irradiated under a variety of conditions in a u.v. cell (10×10 mm) (3.0×10^{-4} M solution) and the reaction was followed by u.v. spectroscopy (Table). The reaction course of (1a) seems to depend strongly upon the temperature. Thus, when irradiations were performed at 20° (runs 1, 2, and 5), cycloprop[b]indole (2) was obtained as the sole product. Irradiation at lower temperature (runs 3, 4, and 6) increased in the amount of the allene (3a) which underwent isomerization to the indole (4) by warming to room temperature. It is noteworthy that no color change of the solution (photochromism[2,3]) was observed in these experiments. Irradiation in EPA (ether-isopentane-alcohol 5:5:2) at -196°, however, produced a yellow solution,[4] u.v. spectrum,of which indicated the formation of the triene (6a)[5] and (3a). Warming up the photolysate to room temperature (the yellow color disappeared) gave the starting material (1a) and the indole (4) in a ratio of 1:2.8, but no cycloprop[b]indole (2). These experiments, together with the fact that u.v. spectral run at intervals during the reaction under the same conditions used for run 1 showed the presence of isosbestic points at 216, 238, 255, 284, and 288 nm, suggest that the triene (6a) does not play a role in the formation of (2) from (1a).

That the triene is also not a precursor of the allene (3) became evident by the photochemical behavior of (1b), which is known to afford exclusively allene (3b) by irradiation in ether at 0°.[2] The red colored triene (6b)[4] [contaminated with allene (3b)] built up by irradiation of (1b) in ether at -74° was reconverted to (1b) by warming up to room temperature and transformed to an unidentified product other than (3b) or cycloprop-[b]indole by irradiation of light of 420 nm. The u.v. spectra recorded at intervals during the irradiation at 0° again showed isosbestic points at 222, 238, 264, and 287 nm.

Irradiation of (1b) in ethanol using a glass filter (λ>310 nm) is known to give the ethanol adduct (5) exclusively.[2] The fact that irradiation of (1b) at -74° for 2 hr[6] produced a deep-red solution of (6b) which, upon warming up to room temperature, did not give (5) but only the starting material, suggests that (6b) is not a presursor of (5).

Table

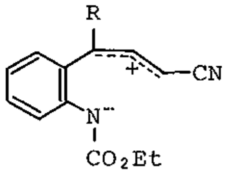
					Products[a]	
Run	Light nm	Time min	Temp. °C	Solvent	at reaction temp.	after warming-up to room temp.
1	313	20	15	EtOH	(2)	(2)
2	253.7	20	15	EtOH	(2)	(2)
3	313	30	-74	EtOH	(2)+(3a)	(2)+(4) (1.7:1)[b]
4	313	25	-100	EtOH	(2)+(3a)	(2)+(4) (1.1:1)[b]
5	313	20	15	EPA	(2)	(2)
6	313	30	-74	EPA	(2)+(3a)	(2)+(4) (1.3:1)[b]

[a] Products were assigned by using their characteristic u.v. absorption bands[1,2]: 317 nm for (1a), 281 and 288 nm for (2), 294 nm for (4), and 252 nm for (3a).

[b] Product ratio was determined by u.v. spectroscopy.

All of these observations are not consistent with a two-step mechanism involving azahexatriene (6) as a common intermediate. This is in sharp contrast to the photoisomerization of 1,2-dihydronaphthalenes to benzobicyclo[3.1.0]hexanes, which is believed to involve hexatriene intermediates which undergo photochemical cyclization.[7]

Sensitization data using benzophenone and benzhydrol in *tert*-butanol[8] suggest that the reaction (1a) → (2) proceeds *via* the excited singlet state of (1a). Although a concerted mechanism for the formation of (2) or a stepwise mechanism involving a dipolar structure (7) may be considered, a difinitive comment on the mechanism of the transformation could be premature at this stage. Further mechanistic investigations of this and related photochemical reactions[9] are highly desirable.



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4 It should be noted that (1a) and (1b) gave low-temperature products with different chromophores which may reflect the different stereochemistry.

5 The triene was identified by the u.v. spectrum which showed a broad band between 340 and 500 nm.[3]

6 Further irradiation (4 hr) gave the same result.

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