Tetrahedron Letters,Vol.26,No.48,pp 5859-5862,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

AN UNUSUAL PHOTOCHEMICAL REARRANGEMENT; MECHANISTIC AND EXPLORATORY ORGANIC PHOTOCHEMISTRY[1]

Howard E. Zimmerman* and Roger W. Binkley[2]
Chemistry Department, University of Wisconsin,
Madison, Wisconsin 53706

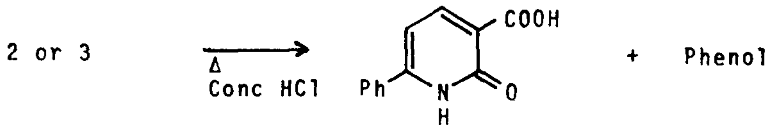
Summary: An unusual rearrangement of 1-benzoyl-2,2-dicyano-3-phenylcyclopropane is described and compared with the photochemistry of 1-benzoyl-2-phenylcyclopropane. Evidence is advanced for facile fission of the three-ring bond bearing benzoyl and cyano substituents.

trans-1-Benzoyl-2,2-dicyano-3-phenylcyclopropane (1a) was synthesized by the reaction of bromomalononitrile with benzalacetophenone in ethanol with a collidine catalyst at 0 °C. This compound, mp 135-137 °C, had an nmr AB quartet (ν_a 3.96, ν_b 4.04 δ) with J_{ab} = 7.8 Hz charactistic of trans hydrogens.

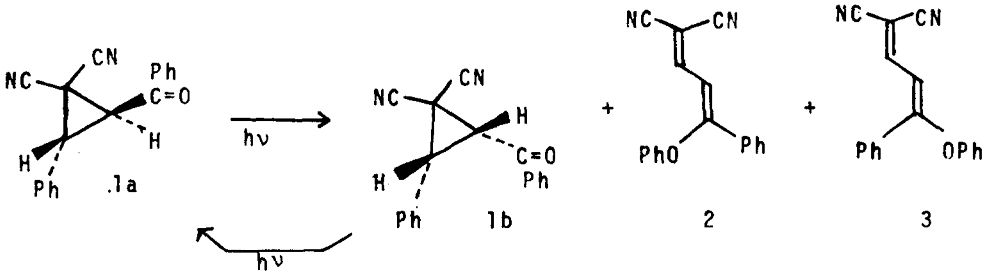
Irradiation in the region 310 - 370 nm produced three isomeric products -- 1b, 2 and 3. Isomer 1b, mp 169-170 °C, proved to be the cis stereoisomer of reactant (J_{ab} 10.8 Hz, ν_a 3.78, ν_b 3.94 δ). Furthermore, this stereoisomerization was reversible, as shown by isolation of 1a from photolysis of 1b.

The second and third photoproducts -- 2, mp 95.5-96.5 °C, and 3, mp 138-139 °C -- were yellow solids. Both lacked carbonyl absorption in the infrared but showed intense uv absorption (246 nm (ϵ 9,710) and 348 (ϵ 30,100) for 2 and quite similar absorption for 3). The nmr spectra revealed two vinyl hydrogens. Degradation with with hydrochloric acid led each of the two isomers to phenol and 1,2-dihydro-2-oxo-6-phenylnicotinic acid[3] as outlined in Equation 1. The spectral and degradative evidence led to identification of photo-isomers 2 and 3 as cis- and trans-1,1-dicyano-4-phenoxy-4-phenylbuta-1,3-diene. Hence the photochemistry may be depicted as in Equation 2. The stereochemistry is tentative and based on kinetic preference of isomer 2 (vide infra).

The counterpart photochemistry of the stereoisomeric 1-benzoyl-2-phenylcyclopropanes, 4a and 4b, was of interest. Cis-trans isomerization has previously been reported[4] and observed in this study; additionally, on prolonged irradiation the known *trans*-1,4-



(1)



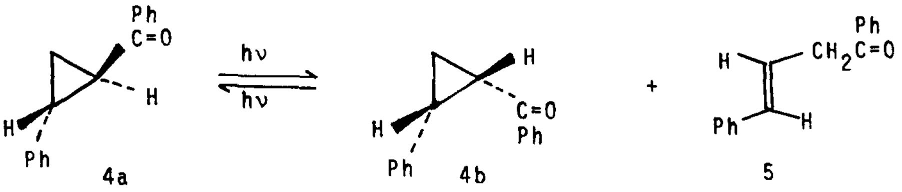
(2)

diphenyl-1-keto-3-butene[5] 5 was formed. This photochemistry is included in Equation 3.

In order to determine the reaction multiplicity, sensitization and quenching runs were carried out. Acetophenone sensitization effected the stereoisomerization of the *trans*- and *cis*-1-benzoyl-2-phenylcyclopropanes 4a and 4b and naphthalene totally quenched the reaction under conditions where it did not absorb light.

Similarly, acetophenone sensitization of *cis*- and *trans*-1-benzoyl-2,2-dicyano-3-phenylcyclopropanes 1a and 1b led to interconversion of these stereoisomers and also their conversion to the rearrangement products, *cis*- and *trans*-1,1-dicyano-4-phenoxy-4-phenylbuta-1,3-dienes 2 and 3. While napthalene quenching of the reaction of the trans dicyanocyclopropane 1a was successful, quenching of the reactions of the cis isomer 1b was not.

We can interpret the reactions as proceeding via the triplets. However, in the case of cis dicyanocyclopropane 1b, the reaction appears to be more rapid than the rate of quenching, even using 1.5 M naphthalene.

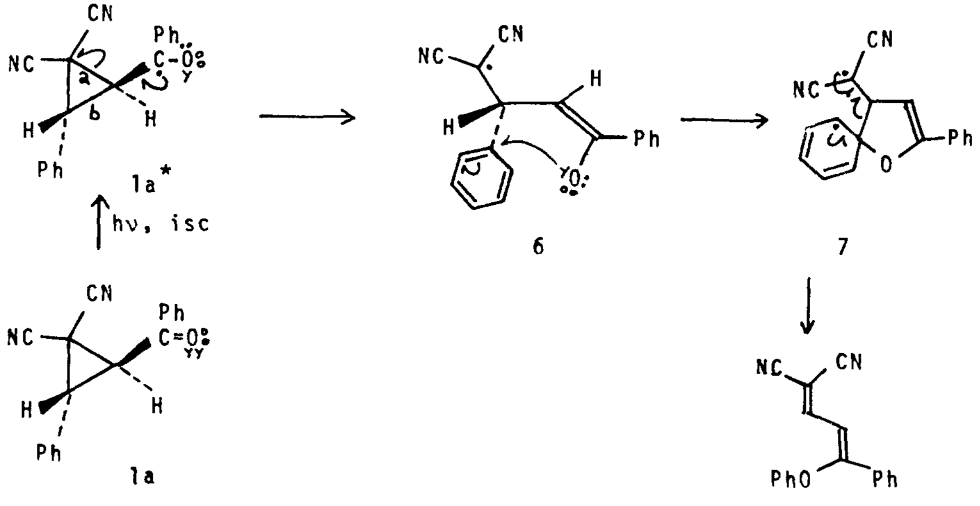

4a 4b 5 (3)

There remains the matter of the mechanism of the stereoisomerizations and the unusual rearrangement to the phenoxydienes 2 and 3. This is outlined in Scheme 1. The three-ring opening of n-π^* excited states has precedent[6] and is readily understood on the basis of the odd-electron density at the cyclopropylcarbinyl carbon.

The rearrangement to the phenoxydienes 2 and 3 seems most likely to proceed via the triplet diradical 6 by attack of the oxygen p_y orbital on C-1 of the migrating phenyl group. While one might consider a mechanism in which the same p_y orbital of the initial excited state bonded to the migrating phenyl simultaneous with three-ring fission, this would require reaction of the cis isomer of the cyclopropane. Some evidence against this is that even in 10% conversion runs with trans-cyclopropane reactant (i.e. 1a), the buildup of phenoxydienes 2 and 3 was occurring despite the low concentrations of cis-cyclopropane 1b formed.

One intriguing facet of these observations is that while, a priori, the benzoyl phenyl cyclopropane 4 might also have undergone the unusual phenyl migration reaction -- it did not. Our interpretation is that fission of bond a to give diradical 6 provides a pathway for migration of the phenyl group. In contrast, the photochemistry of the benzoyl phenyl cyclopropane 4 must therefore undergo fission only of its bond b. Thus, we can deduce an enhancement of bond fission by the cyano groups as in agreement with the n-π^* diradical mechanism postulated but not a dipolar one polarized towards oxygen.

SCHEME 1



Acknowledgements. This publication has been submitted in honor of the 65th birthday of Harry H. Wasserman. It was the privilege of the first author to have been Prof. Wasserman's first student when HEZ began undergraduate research at Yale in 1948. Support of this research by the National Science Foundation and by the National Institutes of Health is recognized with appreciation.

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(Received in USA 24 May 1985)