Di-π-Methane Photochemistry and Arylcyclopropane Synthesis

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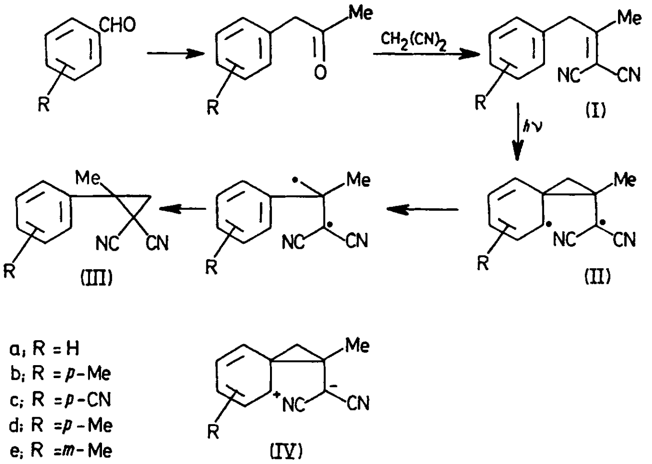
Summary 1,1-Dicyano-2-methyl-3-arylpropenes rearrange into 1-aryl-1-methyl-2,2-dicyanocyclopropanes on irradiation with 253·7 nm light; the chemical and quantum yields are sensitive to phenyl substitution.

THE photochemical rearrangements of 3-arylpropenes pose intriguing questions on mechanism and also present useful synthetic routes to a range of arylcyclopropanes. Zimmerman,[1] in his analysis of the di-π-methane rearrangement has considered the stability of the cyclopropyl dicarbinyl diradical species (*e.g.* II) as being crucial to the efficiency of the reaction and to its regiospecificity.

Assuming that 3-phenylpropenes may undergo a di-π-methane photochemical rearrangement, we reasoned that cyano-substituents at the terminus of the double bond should stabilise the intermediate (II) and thus facilitate the rearrangement. A series of 1,1-dicyano-2-methyl-3-arylpropenes (I) was synthesised and their solutions irradiated with a mercury resonance lamp (253·7 nm). The expected 1-aryl-1-methyl-2,2-dicyanocyclopropanes were formed in all cases (Scheme). Although the chemical yields from (Ia)—(Ic) were very high, for (Id) and (Ie), containing an electron-donating substituent, low quantum yields and loss of product by secondary processes resulted in lower chemical yields. The quantum yields were not affected by oxygen, perhaps indicating a singlet-state reaction.



The yields (based on g.l.c. analysis) for dioxan solutions were (IIIa) = 64%; (IIIb) = 45%; (IIIc) = 82%; (IIId), and (IIIe) = 15%.

The trend in the efficiency of the reaction with change in aromatic substituent is the opposite of that expected if a charge separated species such as (IV) were important on route from the initial excited state to the final product. For example, the quantum yield of formation of (IIIc) from (Ic), ϕ(IIIc) in dioxan or cyclohexane is approximately two orders of magnitude greater than ϕ(IIId), the quantum yield of formation of (IIId). This point is also borne out by the solvent effects. Thus, ϕ(IIIa) (cyclohexane) = *ca.* 5ϕ (IVa) (acetonitrile).

Recently, other studies have been carried out on substitution effects in the di-π-methane and related photochemical reactions.[2]

None of the compounds (I) studied, showed any detectable fluorescence ($\phi_f < 10^{-3}$) indicating much increased rate constants for the non-radiative processes, including chemical reaction, as compared to 1-phenylbut-2-ene [ϕ_f(soln.) = 0·08].[3]

Substitution and solvent effects in this study support the suggestion that in the di-π-methane rearrangement the cyclopropyldicarbinyl diradical species (II) is important, either as an intermediate or, if the reaction is concerted, as being a good description of a crucial point on the potential energy surface for the reaction.

The effect of the terminal cyano-substituents on the efficiency of the reaction is nicely illustrated by a comparison of the reactivities of (I) and 1-phenylbut-2-ene. The latter compound on irradiation in solution yields none of the methylphenylcyclopropane.[4]

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