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A Novel [2+4] Photocyclization Reaction between Quinone and Allene

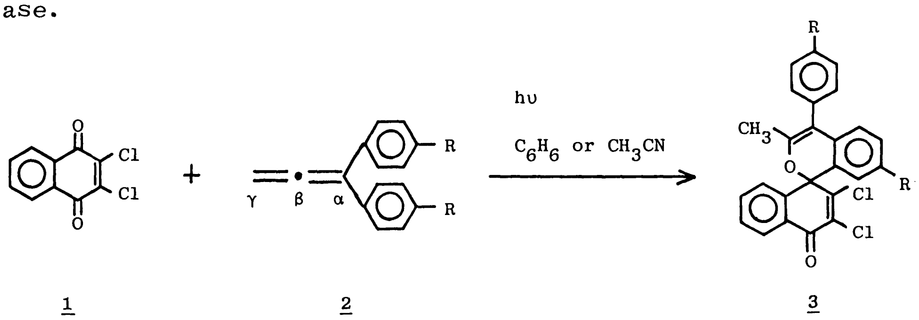
Kazuhiro MARUYAMA* and Hiroshi IMAHORI

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606

1,1-Diphenylallene underwent a [2+4] photocycloaddition reaction with the carbonyl group of 2,3-dichloro-1,4-naphthoquinone to produce a novel spiro compound.

Recently, much attention has been focussed in the area of electron-transfer photochemistry.[1)] Mariano and Johnson have reported the photoreactions between allene and iminium salt as well as the photoreactions between allene and cyano aromatics in polar solvent.[2,3)] Photochemical reactions of quinones with allenes have been studied by several groups,[4)] but they have paid no attention to electron-transfer processes. We now wish to report the new photochemical reactions of quinones with 1,1-diphenylallenes.

Irradiation of a benzene or an acetonitrile solution (25 ml) containing 2,3-dichloro-1,4-naphthoquinone (1, 1 mmol) and 1,1-diphenylallene (2b, 2 mmol) through a Pyrex filter with high pressure mercury lamp for 3 h under argon afforded 5,6-benzo-2-cyclohexene-2,3-dichloro-4-onespiro-3',4'-benzo-5'-ene-6'-methyl-5'-phenylpyran 3b as the sole photoproduct in 89% or 33% yield, respectively. The novel heterocyclic structure of 3b was assigned from spectroscopic data and elemental analysis, and confirmed by X-ray crystallography of the analogous product 3c. Interestingly, two aromatic moieties of spiro compounds 3 are perpendicular to each other. In a similar manner, spiro compounds 3 were obtained from the corresponding allene derivatives 2, except in the case of 2d. (Table 1) In our previous studies, it was shown that the photochemical reactions of halogeno-1,4-naphthoquinones with 1,1-diphenylethylenes resulted in the substitution product via ion radical pair composed of quinone anion radical and 1,1-diphenylethylene cation radical.[5)] Surprisingly, the reaction course was greatly altered; that is, substitution reaction of the halogen atom by ethylenic group in the latter case but the formal [2+4] cycloaddition reaction for carbonyl group of quinone in the present case.



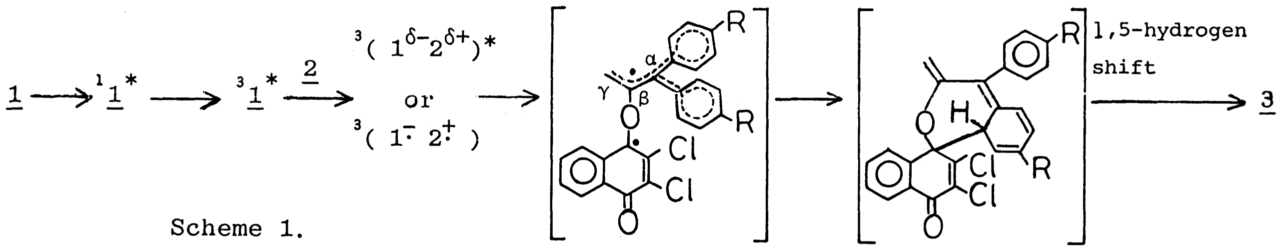
1 2 3

Table 1. Photochemical Reactions of Quinone 1 with 1,1-Diphenylallenes 2

Allene	Solvent	Conversion/%	Yield/%[a]
2a: R = F	C_6H_6	53	3a: 25
2b: R = H	C_6H_6	19	3b: 89
2b: R = H	CH_3CN	30	3b: 33
2c: R = CH_3	C_6H_6	40	3c: 85
2d: R = OCH_3	C_6H_6	34	3d: 0

a) Isolated yield based on a starting quinone consumed.

Although the reason has to be clarified in future, we are intending to propose the following mechanism shown in Scheme 1.[6] The reactions involve an exciplex or ion radical pair resulting in the formation of spiro compounds via biradical intermediates including a 1,5-hydrogen shift.[7]



Scheme 1.

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References

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6) The free energy changes(ΔG) for an electron transfer from 1,1-diphenylallene to the excited triplet quinone were estimated to be negative. Probably, both quantity of positive charge or free spin density and steric bulkiness around the reaction center C_β will be the controlling factors of the reaction course.

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