CHEMISTRY LETTERS, pp. 475-478, 1986.

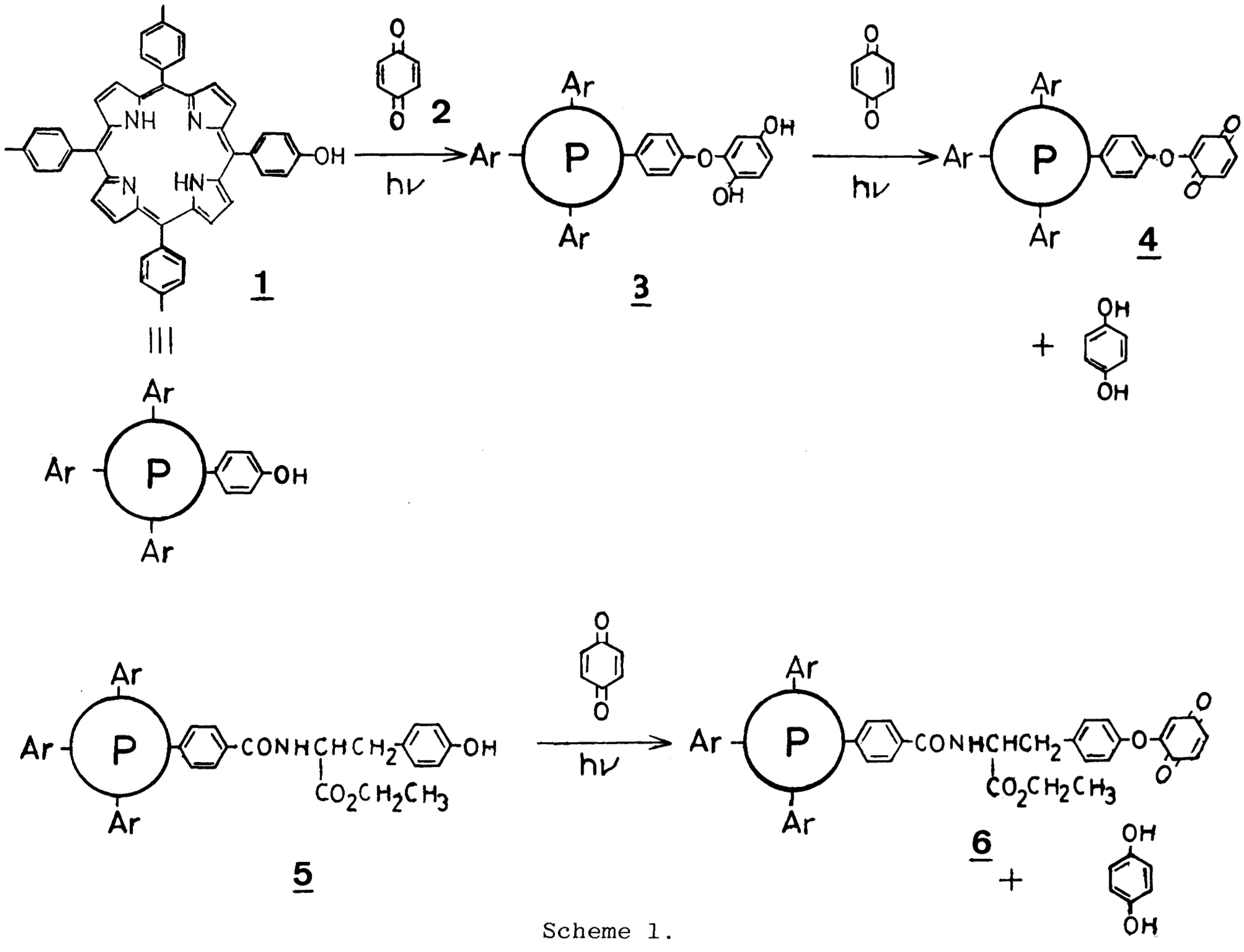
PHOTO-INDUCED CROSS-COUPLING REACTION BETWEEN PORPHYRIN AND QUINONE

Kazuhiro MARUYAMA,* Hiroyuki FURUTA, and Atsuhiro OSUKA
Department of Chemistry, Faculty of Science, Kyoto University,
Kyoto 606

A novel type of photo-induced cross-coupling reaction was developed in the photoreaction of "phenolic porphyrin" with quinone in benzene solution. Radical coupling mechanism was suggested by means of CIDNP technique.

Photo-induced electron transfer reactions of porphyrin have attracted considerable interest as simple models for the photosynthesis of natural plants. Among suitable candidates of electron acceptor, quinone has been widely used in the photo-induced charge separation studies under a variety of conditions (fluid,[1)] micelle,[2)] vesicle,[3)] etc.). However, there have been hardly observed permanent chemical changes in these photoreactions, because of rapid reverse electron transfer between porphyrin and quinones. In the previous paper we have noted the essential role of proton in the efficient charge separation between photo-excited porphyrin and quinone in non-polar media, by means of CIDNP technique.[4)] On the basis of the CIDNP results, we have now developed a novel type of photo-induced cross-coupling reaction of porphyrin and quinones by using "phenolic porphyrin", which contains phenol group in its own. By subsequent proton transfer from the phenol group, intervening radical ion pair, consisting of porphyrin cation radical and quinone anion radical, was transformed into stable neutral radical pair and eventually underwent in-cage cross-coupling reaction.

First, illumination of 5-(4-hydroxyphenyl)-10,15,20,-tris(p-tolyl)porphyrin (1) (2 mM) in C_6H_6-CH_3CN (50:1) in the presence of 1,4-benzoquinone (2) (≈10 mM) with light of wavelength longer than 590 nm under argon atmosphere produced a single porphyrin product 4 with concurrent formation of hydroquinone. No other product except the unreacted starting materials 1 and 2, was detected by TLC and 400 MHz ^{1}HNMR analysis. Benzoquinone end in 4 appears at δ 6.87 (d, J=10.3 Hz), 6.79 (dd, J=10.3 and 2.2 Hz), 6.22 (d, J=2.2 Hz) in its 400 MHz ^{1}HNMR spectrum ($CDCl_3$). Benzoquinone adduct 4 was quantitatively reduced to hydroquinone adduct 3 ($Na_2S_2O_4$, 10 min at 25 °C). Hydroquinone end in 3 appears at δ 6.87 (d, J=8.9 Hz), 6.63 (d, J=2.8 Hz), 6.43 (dd, J=8.9 and 2.8 Hz). Fluorescence property of 4 was characteristic of the quinone-linked porphyrin in that the relative fluorescence quantum yield of 4 was much less (0.02) than that of TPP (0.13).[5)] Under similar conditions, illumination of tyrosine-linked porphyrin 5 in the presence of 2 resulted in the predominant formation of coupling product 6 (ϕ=0.01).



Scheme 1.

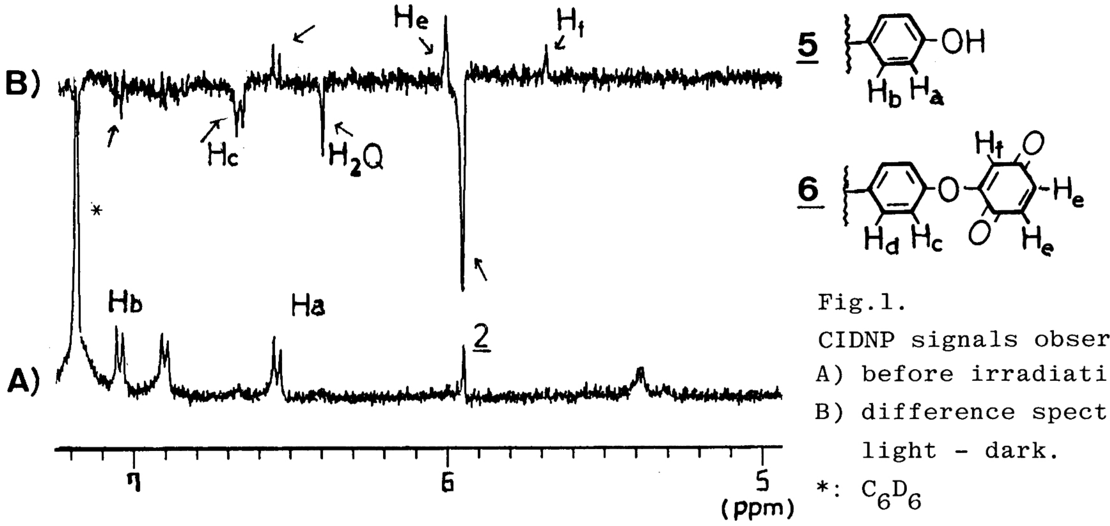


Fig.1.
CIDNP signals observed.
A) before irradiation.
B) difference spectrum; light - dark.
*: C_6D_6

When hydroquinone adduct 3 was illuminated in the presence of benzoquinone in deaerated benzene solution, compound 3 was found to convert immediately into benzoquinone adduct 4 with concurrent formation of hydroquinone. This result strongly suggests hydroquinone adduct 3 was the primary adduct, which could readily be oxidized to quinone adduct 4 by further illumination in the presence of excess benzoquinone (Scheme 1). Quantum Yield (Φ) for the formation of the quinone adduct was dependent upon the quinone concentration. With increasing the quinone concentration (1×10^{-2} M → 1×10^{-1} M), Φ decreased markedly (0.01 → 0.001). The higher values of Φ at the low concentration of quinone suggest that these photo-coupling reaction takes place via porphyrin triplet state. This is because, on the basis of the fluorescence quenching experiment, much of porphyrin singlet is quenched at high concentration of quinone.

To clarify the mechanistic details, we have investigated these photo-coupling reactions by CIDNP technique. When a benzene-d_6 solution of I (1×10^{-4} M) was illuminated in the presence of 2 (5×10^{-3} M), CIDNP signal due to 2 was observed as a weak emission.[6)] More distinct CIDNP signals were observed in the photoreaction of 5 with 2 (Fig.1). Polarized signals due to coupling product 6, as well as starting materials, whose assignments are indicated by the arrows, are detected clearly. Phenoxyl hydrogens in the tyrosine moiety in compound 5 and 6 showed similar polarization patterns ; emission for ortho-H and absorption for meta-H, which are characteristic of neutral phenoxy radical.[7)] CIDNP effects due to coupling product 6 clearly indicate the photo-induced coupling of quinone to "phenolic porphyrin" takes place via triplet neutral radical pair.8) Quenching of porphyrin triplet by 2 probably results in triplet radical ion pair, where phenol group will behave as proton donor and electron donor giving rise to the phenoxyl radical and semiquinone radical.

Today, much attention is focused on quinone-linked porphyrins as a model of the primary events in photosynthesis.9) It should be stressed here that this photo-coupling reaction is very useful for the synthesis of quinone-linked porphyrin compounds since it needs no quinone protection and only requires a simple one-pot photochemical procedure.

References

1) A.Harriman, G.Porter, and N.Searle, J. Chem. Soc., Faraday Trans.2, 75, 1515 (1979).

2) M.Grätzel, J. Chem. Soc., Faraday Discuss. 70, 359 (1980).

3) Y.Fang and G.Tollin, Photochem. Photobiol., 39, 685 (1984).

4) K.Maruyama and H.Furuta, Chem. Lett., preceding paper.

5) A.Harriman, J. Chem. Soc., Faraday Trans.1, 76, 1978 (1980).

6) By using 2,5- and 2,6-dichlorobenzoquinone as electron acceptors, we have observed opposite polarization of quinone ring-H's, that is, emission signal for 2,5-dichlorobenzoquinone and absorption for 2,6-dichlorobenzoquinone. This opposite polarization of the quinones is reasonably explained by the formation of neutral semiquinone radical. Ref.4.

7) K.A.Muszkat and M.Weinstein, Z. Phys. Chem. N.F., 101, 105 (1976).

8) For ortho-H of phenoxyl group in 6, $\Delta g < 0$, $a_H < 0$, $\mu > 0$, $\varepsilon > 0$, $\Gamma_{ne} > 0$, see R.Kaptein, J. Chem. Soc., Chem. Commun. 1971, 732. Thus, in-cage recombination of geminate radical pair will lead to the formation of 6. The polarized absorption due to ortho-hydrogen of phenol group in 5 and the polarized emission for the quinone-H appear to be derived from out-of-cage processes.

9) I.Tabushi, N.Koga, and M.Yanagita, Tetrahedron Lett., 1979, 257; J.Dalton and L.R.Milgram, J. Chem. Soc., Chem. Commun. 1979, 609; A.D.Jordan, B.A.Leland, G.G.Geller, J.H.Hopfield, and P.B.Dervan, J. Am. Chem. Soc., 106, 6090 (1984), and references cited therein.

(Received January 6, 1986)