CHEMISTRY LETTERS, pp. 843-844, 1983. © The Chemical Society of Japan 1983

REACTION MECHANISM OF ONE-POT SYNTHESIS OF POLYCYCLIC QUINONES
—— DIRECT EVIDENCE OF PHOTO-INDUCED ELECTRON TRANSFER PROCESS

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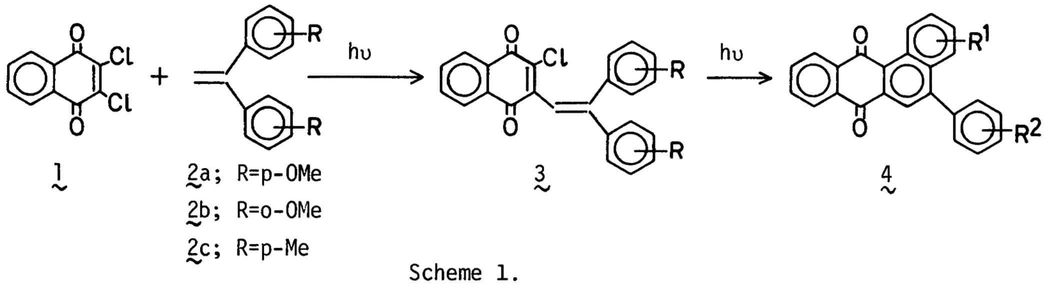
Photo-induced cyclocondensation of 2,3-disubstituted 1,4-naphthoquinone (substituents; halogen atom or methoxy group) with 1,1-diarylethylene provides us a powerful one-pot synthetic method of polycyclic quinones. Involvement of electron transfer process in the photochemical reaction was evidenced unambiguously by means of CIDNP technique.

Photochemical reaction of 2,3-dichloro-1,4-naphthoquinone with 1,1-diarylethylene affords substituted benz[a]anthracene-7,12-dione by two step reaction (Scheme 1).[1)] On the basis of several experimental results,[2)] involvement of photo-induced electron transfer process has been suggested by us during the course of the reaction to lead the intermediate 3. However, trials to detect the direct evidence of intervention of quinone anion radical and/or 1,1-diarylethylene cation radical in the reaction have ended in vain so far.[3)]

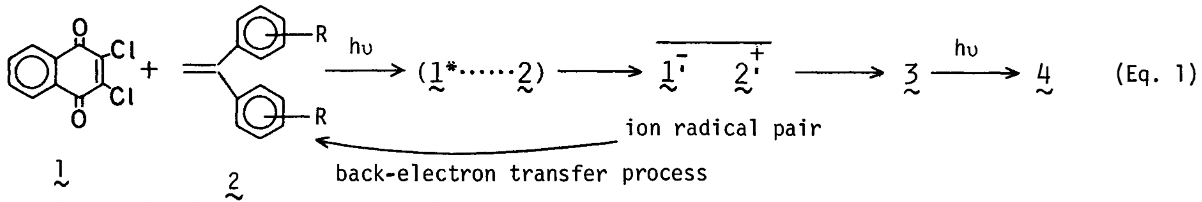


Scheme 1.

By means of CIDNP technique, we obtained here the first direct evidence of the formation of 1,1-diarylethylene cation radical[5)] in the photochemical reaction.

When an acetonitrile-d_3 solution[6)] of 2,3-dichloro-1,4-naphthoquinone (1) and 1,1-bis(p-methoxyphenyl)ethylene (2a), as a typical example, was irradiated (>370 nm) under argon atmosphere, the strong ^{1}H-CIDNP signals were observed in the methylene-H, the aromatic ring-H, and the methoxy-H of 1,1-bis(p-methoxyphenyl)ethylene (2a). As shown in Fig.1, the methylene-H and the ring-H_a showed enhanced absorption, whereas the methoxy-H and the ring-H_b enhanced emission. Upon irradiation of 1 in the presence of 2a in a CD_3OD solution, the similar CIDNP signals were detected. The CIDNP signals were also observed similarly when 1 was subjected to irradiation in the presence of 1,1-bis(o-methoxyphenyl)ethylene (2b) or 1,1-bis(p-tolyl)ethylene (2c) in CD_3CN and/or CD_3OD.[6)]

These CIDNP signals clearly indicate the photo-induced electron transfer from 1,1-diarylethylene (2) to quinone (1) to generate the ion radical pair; $\overline{1^{\cdot -}\ 2^{\cdot +}}$, which, in turn, regenerates 1,1-diarylethylene (2) and quinone (1) via back-electron transfer process. By analyzing the polarization pattern on the basis of Kaptein's rule,[7)] the ion radical pair; $\overline{1^{\cdot -}\ 2^{\cdot +}}$, is suggested to have the triplet multiplicity.[8)]



Thus, the involvement of photo-induced electron transfer process in the photochemical reaction of 2,3-dichloro-1,4-naphthoquinone (**1**) with 1,1-diarylethylene (**2**) was clearly confirmed (Eq.1).[10]

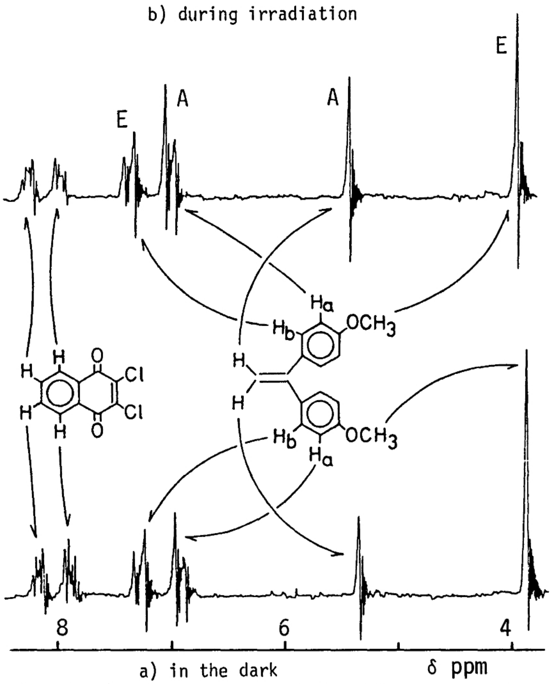


Fig. 1. a) NMR spectrum of freshly prepared CD_3CN solution of 2,3-dichloro-1,4-naphthoquinone (**1**) and 1,1-diarylethylene (**2**a). b) CIDNP signals observed upon irradiation of quinone **1** in the presence of **2**a with a high pressure Hg arc lamp at ambient temperature.

References

1) K.Maruyama, T.Otsuki, and K.Mitsui, Bull.Chem.Soc.Jpn., 49, 3361 (1976). K.Maruyama, T.Otsuki, and K.Mitsui, J.Org.Chem., 45, 1425 (1980).

2) a) Observation of charge transfer spectra. b) Dependency of the yield and the relative rate of formation of the intermediate **3** on the solvent polarity. c) Dependency of the product distributions on substituent of both quinone (**1**) and 1,1-diarylethylene (**2**). Cf. K.Maruyama, S.Tai, and T.Otsuki, Symposium on Photochemistry 1982. Presentation IA210 (Abstract p.77) (Kanazawa, Japan, 1982.10).

3) 1,1-Diphenylethylene cation radical formed by electron transfer in the presence of methanol is reported to react with methanol to give 2-methoxy-1,1-diphenylethane.[4] However, no methanol adduct such as 2-methoxy-1,1-diphenylethane was detected in our reaction system. This result strongly indicates that the in-cage electron transfer process is involved in the photochemical reaction of **1** with **2**.

4) R.A.Neunteufel and D.R.Arnold, J.Am.Chem.Soc., 95, 4080 (1973).

5) Upon irradiation, ^{1}H-NMR signals of the ring protons of quinone **1** showed broadening.

6) During the CIDNP measurement, a detectable consumption of **1** or production of **3** was not observed. However, a longer irradiation (5 min) gave **3** and **4** in reasonable yields.

7) R.Kaptein, J.Chem.Soc., Chem.Commun., 1971, 732.

8) The g-value of 1,1-diarylethylene cation radical is assumed to be smaller than that of quinone anion radical. The sign of hfcc of 1,1-diarylethylene (**2**) was estimated on the basis of its Hückel molecular orbital calculation.[9]

9) E.Heilbronner and H.Bock, "The HMO Model and its Application, 3, Tables of Hückel Molecular Orbitals", (English translation by W.Martin and A.J.Rackstraw) John Wiley & Sons, London/New York/Sydney/Toronto, 1976, p.117.

10) Other experimental results which support the conclusion will be described in detail elsewhere.

(Received March 19, 1983)