Novel Photoinduced Self-substitution of 2,5-Dichloro-1,4-benzoquinone

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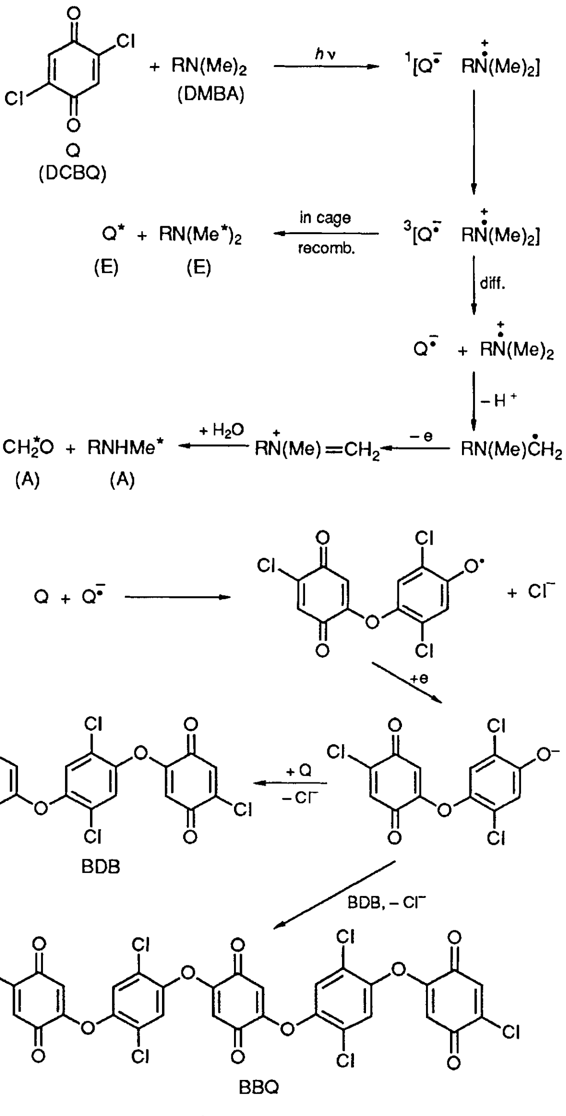
2,5-Dichloro-1,4-benzoquinone (DCBQ) undergoes self-substitution to 1,4-bis(4-chloro-3,6-dioxocyclohexa-1,4-dienyloxy)-2,5-dichlorobenzene (BDB) and 2,5-bis[4-(4-chloro-3,6-dioxocyclohexa-1,4-dienyloxy)-2,5-dichlorophenoxy]benzoquinone (BBQ) in the presence of *N,N*-dimethyl-*tert*-butylamine (DMBA) or *N,N*-dimethyl-4-phenylbicyclo[2.2.2]octan-1-ylamine (DMPA) in sunlight; photo-CIDNP[†] studies show that the reaction is initiated by photoinduced electron transfer between DCBQ and the amine with the triplet radical ion pair as the intermediate.

The nucleophilic substitution of quinones and their chloroderivatives by aliphatic amines has been extensively studied.[1] Mono- and/or di-substituted alkylamino-, dialkylamino- or dialkylaminovinyl-quinones were formed from primary, secondary and dialkylethylamines respectively.[2-4] Hindered tertiary amines such as triisopropylamine and *N*-methylpiperidine were reported[3,4] to show no such reaction with quinones other than the formation of the quinone radical anion. We report here a novel self-substitution of 2,5-dichloro-1,4-benzoquinone (DCBQ) which was initiated by photoinduced electron transfer between the quinone and the hindered amines, *i.e.* *N,N*-dimethyl-*tert*-butylamine (DMBA) or *N,N*-dimethyl-4-phenylbicyclo[2.2.2]octan-1-ylamine (DMPA).

When equimolar (0.1 mol dm^{-3}) DCBQ and DMBA were mixed in dry acetonitrile and allowed to stand in sunlight yellow crystals gradually precipitated; the reaction was complete in 24 h. Irradiation with a Hg–Xe lamp accelerated the reaction bringing about completion within 0.5 h. The main reaction products were isolated by silica gel column chromatography giving 1,4-bis(1-chloro-3,6-dioxocyclohexa-1,4-dienyloxy)-2,5-dichlorobenzene (BDB) in 38% yield and 2,5-bis[4-(4-chloro-3,6-dioxocyclohexa-1,4-dienyloxy)-2,5-dichlorophenoxy]benzoquinone (BBQ) in 35% yield. The prime photoproduct 4-(4-chloro-3,6-dioxocyclohexa-1,4-dienyloxy)-2,5-dichlorophenol was observed using mass spectroscopy, but the yield was too low to be isolated from the other products. Reaction of DCBQ and DMPA gave the same products in similar yields. However, treatment of DCBQ with other amines such as trimethylamine, tripropylamine and triphenylamine did not produce any BDB or BBQ as shown by TLC.

In order to elucidate the reaction mechanism a photo-CIDNP study was performed at 80.131 MHz on a Bruker AC-80 NMR spectrometer equipped with a photo-CIDNP probe. The spectrometer was operated in the routine KINETICS mode. Sample solutions, deaerated by bubbling with argon, were irradiated *in situ* with the full spectrum of a SQX 1000 W high pressure Hg–Xe lamp. The main features of the NMR spectrum obtained under irradiation are a strong emission at δ 2.23, enhanced absorptions at δ 2.76 and *ca.* 4.50 and a broad enhanced absorption at δ 9.55. Another feature was the disappearance of the *N*-methyl signal of DMBA at δ 2.14. Careful examination of the CIDNP spectra obtained at different times from the beginning of irradiation showed that the *N*-methyl peak changed to emission and moved downfield gradually to δ 2.23 during the irradiation. This can be explained by the formation of the hydrochloride of the amine, which would cause a down-field shift. Enhanced absorption at δ 2.76 is assigned to the hydrochloride of the demethylated DMBA (RNHMe·HCl). Enhanced peaks at δ 9.55 and *ca.* 4.50 are assigned to formaldehyde and its hydrate. The broadening of the formaldehyde peak is due to the fast equilibrium of $CH_2O + H_2O \leftrightharpoons HOCH_2OH$ as pointed out previously.[5]

On the basis of these observations it is suggested that the reaction is initiated by photoinduced electron transfer between DCBQ and the amine with the triplet radical ion pair as the reaction precursor (Scheme 1). The polarization phases predicted by Kaptein's rule[6] are indicated in the parentheses which are in agreement with our experimental observation except that the polarization of the parent quinone is not obvious. The obscurity of this polarization may be caused by degenerate electron exchange between the quinone radical anion and its parent quinone. We noted a broadening effect (DCBQ, δ 7.22) in the solution of DCBQ and DMBA in the dark. It has been pointed out that if the concentration of the radical ion is sufficiently high and its life-time sufficiently long



Scheme 1

[†] CIDNP = Chemically induced dynamic nuclear polarization.

to permit spin lattice relaxation, then line broadening and not polarization would be observed. In fact the concentration of the DCBQ radical anion was so high that it was detectable by EPR. The intermediacy of the amine radical cation is shown by the formation of formaldehyde and the demethylated amine RNHMe which are typical fragmentation products of aminium radical cation[8] as illustrated in Scheme 1. It seems that the occurrence of self-substitution of the quinone is caused by the steric hindrance and rigid geometry of DMBA or DMPA that make the general hydrogen abstraction and amine substitution reaction unfavourable. The extension of this reaction to other substrates is in progress.

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