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Photoinduced Reactions of Chloranil with Aromatic Imines

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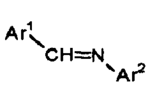
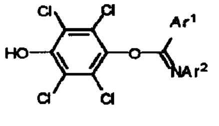
Abstract: Photoinduced reactions of chloranil with Schiff bases($Ar^1CH{=}NAr^2$) **1-7** gave the corresponding 4-hydroxy-2,3,5,6-tetrachlorophenyl arylbenzenecarboximidates **8-14** respectively in good yields *via* an electron transfer mechanism.

Photoinduced reactions of halogenoquinones with electron donors as alkenes[1-4], heterocycles[5], aromatic hydrocarbons[6] and amines[7] are of current research interest. The halogen substitution often cause a change in the quinone reactive excited state and always increases them electron acceptor ability, which leads to a more frequent involvement of single electron transfer (SET) processes. As a result, then reactions of haloquinones often give quite different and more varied results comparing with the parent benzoquinone (BQ) and naphthoquinone (NQ) in reaction modes and mechanisms. For instance, while photoreactions of BQ with alkenes always take place at BQ's carbonyl group to give spirooxetane products, reflecting a normal $n\pi^*$ reactivity[1,8], photoinduced cycloaddition of chloranil (CA) with alkenes can occur selectively on the C=O or the C=C double bond of CA. It has been shown that terminal and 1,1-disubstituted alkenes of high oxidation potential afford cyclobutane products with CA, in accord with the $\pi\pi^*$ triplet state of the latter[4,9]. When the alkenes are good electron donors, the reaction site is driven to the carbonyl group of CA by the involvement of an SET process[8,14] to give spirooxetane products selectively.

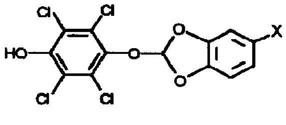
With the aim of discovering further reaction modes of CA-electron donor photoreactions, and also since we have noticed that although Schiff bases have rather low ionization potentials (~8 eV)[10] and should be good electron donors, photoinduced SET reactions with these imines as electron donors have rarely been studied[11], we have investigated the photoinduced reactions of CA with Schiff bases **1-7**.



1-7



8-14



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Photolysis of CA (0.05 mol dm^{-3}) with benzylideneaniline **1** (0.08 mol dm^{-3}) in benzene with light of $\lambda > 400nm$ for 6.5h led to 100% conversion of CA and give a single product **8** in 94% yield. Photoinduced reactions of CA with Schiff bases **2-7** under same conditions similarly give products **9-14** respectively in moderate to high yields[12] (table 1).

Since photoinduced reactions of CA with alkenes are characterized by the formation of 2+2 cycloaddition products as it has been shown that styrene derivatives gave cyclobutanes and stilbene derivatives gave spirooxetanes[4] in good yields with $^3CA^*$, it is interesting to note that irradiation of CA with **7** which has both C=C and C=N bonds afforded products **14** exclusively in 84% yield with no 2+2 cycloaddition products being detected . It is also found that, although photoinduced reactions of CA with 1,3-benzodioxole derivatives usually gave triaryl orthoformate products (**15**) in high yield[13], similar irradiation of CA with **2** yielded product **9**, leaving the methylenedioxy group untouched.

Table 1. Photoinduced Reactions of CA with Schiff Bases $Ar^1CH{=}NAr^2$ **1-7**

Imine (Ar^1 , Ar^2)	Solvent	E^{ox}(V, SCE)	ΔG_{ET}(Kcal mol^{-1})^a	Irrad. time/h	Conversion (%)	Product & Yield (%)
1 (Ph, Ph)	C_6H_6	1.68	-1.8	6.5	100	**8** (94)
2 (3,4,-(CH_2O_2)C_6H_3, Ph)	C_6H_6	1.44	-7.4	11	100	**9** (56)
3 (4-Fph, 4-ClPh)	C_6H_6	1.70	1.4	5.5	100	**10** (99)
4 (2,4-Cl_2Ph, Ph)	C_6H_6	1.75	-0.2	5	100	**11** (95)
5 (4-CH_3Ph, Ph)	C_6H_6	1.67	-2.1	6.5	100	**12**(91)
6 (4-ClPh, Ph)	C_6H_6	1.72	0.9	5	100	**13** (95)
6	CH_3CN	1.72	-11.1	7.5	87	**13** (81)
7 (PhCH=CH, Ph)	C_6H_6	1.58	-4.2	7	100	**14** (84)

[a] Calculated by Weller equations: in benzene, $\Delta G_{ET}=23.06[E^{ox}-E^{red}-E_T+0.38]$kcal/mol; in acetonitrile, $\Delta G_{ET}=23.06[E^{ox}-E^{red}-E_T-0.06]$kcal/mol. E_T is the triplet energy of CA (2.12 eV) and E^{red} is the reduction potential of CA (-0.02V,SCE).

Oxidation potentials of **1-7** were measured in acetonitrile with tetrabutylammonium perchlorate as supporting electrolyte *vs.* SCE electrode. The oxidations are irreversible for all the imines investigated. The peak potentials and the free energy change (ΔG_{ET}) for SET between $^3CA^*$ and the imines as estimated by Weller equations[14] are in table 1. Since all the ΔG_{ET}s are negative, the involvement of SET process between $^3CA^*$ and the imines is strongly implied.

Schiff bases **1-7** form charge transfer complex (CTC) with CA in solution. When the donor is added in large excess to a solution of CA in chloroform, a new broad absorption band occurs in the long wavelength region >367nm where the forbidden $\pi\pi^*$ transition of CA is located. Formation constants (K_{CT}) and ε^{CT}_{max} for CTC of CA with **1,2,4-7** have been calculated from UV spectroscopic measurements of these CA-imines systems by Benesi-Hildebrand[15a] and related treatments[15b]. The results are in Table 2. By comparing the ε values of CA and CTC in the region >400nm and the relative concentration of CA monomer and the CTC formed, it is estimated that, in the preparative irradiation of CA(0.05 mol dm^{-3}) with **1**(0.08 mol dm^{-3}), CA monomer absorbs ~70% of the incident light and the CTC absorption is ~30%. The excitation of CTC also resulted in SET from the donor to CA and the formation of contact ion radical pairs of singlet multiplicity[6].

Preliminary results from photo-CIDNP studies support the SET mechanism The ^1H NMR spectra of (CA-**5**) system in CD_3CN in the dark (A) and during irradiation (B) are shown in Fig 1. The characteristic feature is that the methine proton absorption at δ 8.6 in **5** becomes an emission (E) during irradiation. Considering that [16] (1) the initial ion radical pair has a triplet precursor (μ=+) and the polarized **5** is formed by in cage back electron transfer (ε=+); (2) the nitrogen centered $5^{\ddagger}$ should have a smaller g value than $CA^{-\cdot}$ (2.0062) (Δg=-) and (3) the methine proton has a positive hyperfine coupling constant with the unpaired electron in the localized linear imine cation radical[17], the negative polarization (E) for the methine proton is compatible with the SET mechanism with ion radical pair formation. Irradiation of CA with **5** in C_6D_6, on the other hand, did not lead to any significant polarization of the methine and the aromatic protons in the imine, in accord with the fact that electron transfer interaction between $^3CA^*$ and the imines in a nonpolar solvent as benzene resulted in the formation of polar exciplex or CIP without SSIP or formation of free ions.

Table 2. Formation Constants and Molar Absorptivities of CTC between CA and the Imines[a,b]

Imine	λ(nm)	K_{CT} (M^{-1})	$10^{-2}\varepsilon_{CT}$ ($M^{-1}cm^{-1}$)	S[c]
1	454	0.64	11.2	0.17-0.31
2	500	0.59	7.7	0.17-0.33
4	440	0.28	16.8	0.11-0.19
5	463	0.62	13.3	0.16-0.28
6	448	0.45	14.3	0.13-0.22
7	485	0.66	17.8	0.18-0.32

[a] in $CHCl_3$. [b] Linear regression coefficient r≥0.998.
[c] Saturation factor in the measurements.
($S=K_{CT}[donor]/1+K_{CT}[donor]^{15c}$).

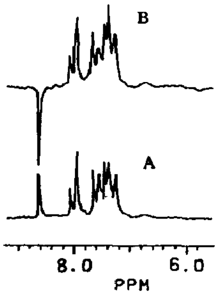

Fig. 1. ^1H NMR of CA(0.02M) and **5**(0.02M) in CD_3CN.

The mechanistic detail following the initial electron transfer between $^3CA^*$ and the imine needs to be further investigated. By analogy with amine SET photochemistry, where deprotonation from the C_α-H bond of a tertiary amine cation radical to produced the α-aminoalkyl radical is a well established process[18], an obvious possibility in these CA-imine reactions is that, hydrogen atom transfer in exciplex, or proton transfer in CIP (in benzene) or in SSIP (in acetonitrile) leads to the formation of a semiquinone-imidoyl radical pair, which on collapse gives the product.

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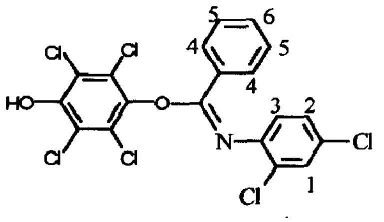
12. Selected spectral data of products: **9**: M.p. 187-188°C. *V*max/cm^{-1} 1663, 1590, 1540,1500, 1483, 1438, 1394, 1330, 1285, 1260, 1190, 1100, 1070, 1035, 890, 770, 710. δ_H (ppm) (500 MHz, DMSO-d_6) 6.08(2H, s, CH_2), 6.63-7.23(8H, m, ArH), 11.12(1H, s, OH). m/z 469(M^+, 0.1), 434(M^+-Cl, 0.3), 246(38.8), 224(base). Found: C,51.20; H, 2 31, N, 2.94 Calcd. for $C_{20}H_{11}Cl_4NO_4$: C, 50.96, H, 2.34; N, 2.97. **11**: M.p 229-230°C *V*max/cm^{-1} 1670, 1582, 1442, 1390, 1330, 1290, 1242, 1180. 1116, 1100. 1045, 910, 885, 864, 762, 712, 692. δ_H(ppm) (500 MHz , DMSO-d_6) 6.66(2H, d, J_{45}=7.50Hz, H_4), 6.96(1H, t, J_{56}=7.50Hz, H_6), 7.16(2H, t, J_{45}=J_{56}=7.50Hz, H_5), 7.55(2H., d, J_{23}=8.25Hz), 7.69(1H,s, H_1) δ_C(ppm) (125 MHz, DMSO-d_6) 154.32, 149.33, 144.97, 138 75, 136.16, 132.05, 131.86, 129 47, 128.85, 127.81, 126.38, 124.25, 120.81, 120.71. m/z 493(M^+, <0.1), 458(0.3), 422(0.3) 248(base) 173(5 8). Found. C, 45 90; H, 1.80; N, 2.80 Cacd. for $C_{19}H_9Cl_6NO_2$. C,45 97; H, 1.82; N, 2.82 **14** M.p. 194-195°C. *V*max/cm^{-1} 1652, 1616, 1588, 1546, 1483, 1448, 1391, 1335, 1258, 1209, 1075, 1033, 977, 948, 899, 822, 759, 716, 688. δ_H(ppm) (500 MHz, $CDCl_3$) 6.45(1H, d, J=15 0 Hz, CH=), 6.66-7.43(10H, m, ArH), 7.78(1H, d, J=15 0 Hz,CH=), 15.78(1H, s, OH). m/z 451(M^+, 0.2), 416(M^+-Cl, 4.6), 246(35.3), 206(base). Found: C,56.06, H, 3 01 Calcd for $C_{21}H_{13}Cl_4NO_2$: C,55.66; H, 2.89.



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