Dehydrosilylation *versus* α-Coupling in the Electron-transfer of Enol Silyl Ethers to Quinones. Strong Solvent Effect on Photogenerated Ion Pairs

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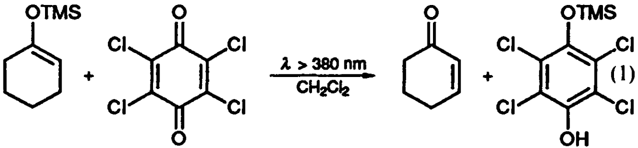
Time-resolved (picosecond) spectroscopy identifies the critical role of solvent polarity in modulating the ion-pair dynamics of the reactive intermediate [$CTE^{\bullet+}$, $CA^{\bullet-}$] from the photoinduced electron transfer of cyclohexanone enol trimethylsilyl ether (CTE) and chloranil (CA) to yield selectively the dehydrosilylated enone **1** in dichloromethane but the oxidative adduct **2** in acetonitrile.

Reactivity of ketones and aldehydes at the α-carbon centres is considerably enhanced by their ready conversion into enol derivatives, particularly enol silyl ethers.[1] Such a derivatization effectively converts an electron-poor carbonyl functionality into an electron-rich donor, as illustrated in Fig. 1 by the appearance of the diagnostic intermolecular charge-transfer spectrum of the electron donor–acceptor (EDA) complex with an electron acceptor such as chloranil (CA). We now report how the latter can be exploited in the novel photochemical activation of silyl enol ethers.

When an equimolar solution of cyclohexanone enol trimethylsilyl ether[2] (CTE) and chloranil in dichloromethane was continuously irradiated with visible (λ > 380 nm) light, the yellow colour was gradually bleached—accompanied by the corresponding diminution of the resolved charge-transfer band (Fig. 1), as well as the simultaneous decrease in the more intense π–π* band of chloranil at λ_{max} = 375 nm and ε_{max} = 300 dm^3 mol^{-1} cm^{-1}.[3] The combined ^1H NMR, GC–MS and HPLC analysis of the photolysate revealed the presence of cyclohexenone[4] **1** in high yields. The direct transfer of the trimethylsilyl (TMS) group upon dehydrosilylation[5] according to eqn. (1) was indicated by the formation of tetrachlorohydroquinone solely as the mono-trimethylsilyl ether.[6]



1 (80%)

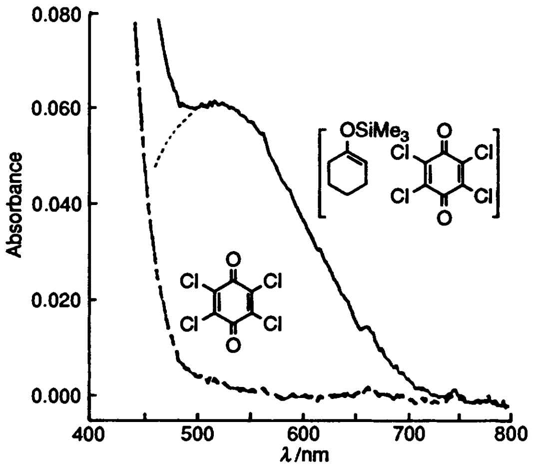
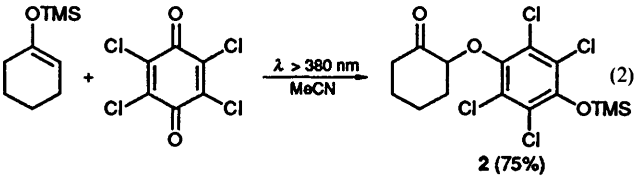


Fig. 1 Typical charge-transfer spectrum (——) of the electron donor–acceptor (EDA) complex of an enol silyl ether (CTE) with chloranil, in comparison with the tail absorption spectrum of chloranil alone (— · — ·) in dichloromethane

Typical Procedure.—A solution of the silyl enol ether (CTE; 0.036 g, 0.20 mmol) and chloranil (0.052 g, 0.21 mmol) in 10 cm^3 of dichloromethane was irradiated at ambient temperature with the focussed output from a 500 W Hg lamp passed through a 380 nm sharp cut-off filter (Corning 3-75) and a water filter to remove UV and IR components, respectively. After 45 min, the photolysate was concentrated *in vacuo* to yield 0.016 g (80%) cyclohex-2-enone (^1H NMR, IR) together with small amounts of the adduct **2**.

Although similar results were obtained in benzene solutions, the equivalent experiment carried out in the more polar acetonitrile yielded little enone **1**; instead the major product was the oxidative adduct **2** (^1H NMR, GC–MS), eqn. (2), which was



2 (75%)

isolated by column chromatography and identified by spectral comparison with the desilylated DDQ analogue.[7] Structural confirmation of the adduct was achieved (see the ORTEP diagram in Fig. 2) following the successful growth and X-ray crystallography[8] of the single crystal from the homologous 2-methylcyclohexanone TMS enol ether.

In order to establish the origin of the dramatic solvent effect on the oxidative photochemistry of silyl enol ethers, as expressed in eqns. (1) and (2), we examined the phototransients immediately following the application of a 30 ps (fwhm) laser pulse. Thus when a CA solution in dichloromethane was excited at λ_{exc} = 355 nm (corresponding to the third harmonic of the Nd^{3+} : YAG laser), the spectrum of chloranil triplet ^3CA with λ_{max} = 510 nm and ε_{max} = 7300 dm^3 mol^{-1} cm^{-1} [9] was apparent within the risetime of the laser pulse,[10] as illustrated in Fig. 3

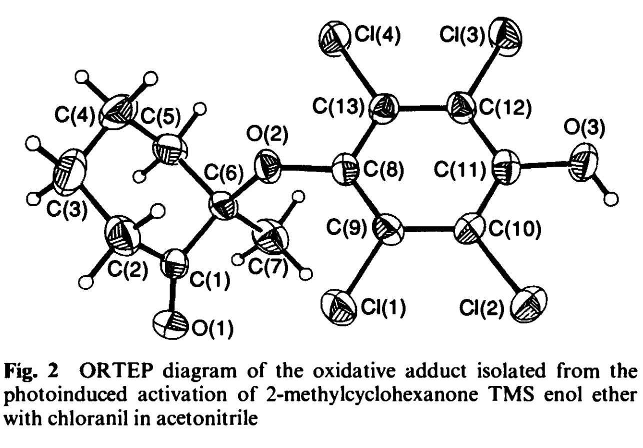


Fig. 2 ORTEP diagram of the oxidative adduct isolated from the photoinduced activation of 2-methylcyclohexanone TMS enol ether with chloranil in acetonitrile

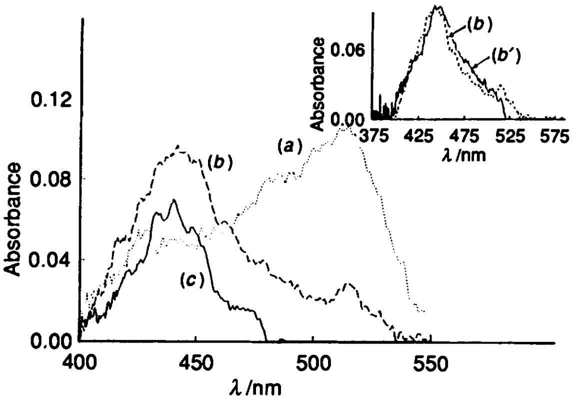


Fig. 3 Time-resolved absorption spectra recorded at (*a*) 50 ps, (*b*) 1.0 ns and (*c*) 3.0 ns following the application of a 30 ps laser pulse at λ_{exc} = 355 nm to 8.0 mmol dm^{-3} chloranil and 0.05 mol dm^{-3} CTE in dichloromethane. The inset compares quantitatively the 1.0 ns spectrum (*b*) (above) with that (*b*′) generated in acetonitrile under the same conditions.

by the transient spectrum (*a*). The quenching of ^{3}CA in the presence of the silyl enol ether CTE is shown in Fig. 3 by the (almost) complete disappearance of ^{3}CA, and its replacement by spectrum (*b*) of chloranil anion radical (CA$^{\bullet-}$ with λ_{max} = 450 nm and ε_{max} = 9700 dm^3 mol^{-1} cm^{-1})[11] in the timespan of less than 1.0 ns following the laser pulse. Such a ready reductive conversion of ^{3}CA by added donor (CTE) relates to earlier photophysical studies of the π–π* excitation of benzoquinones to result in the efficient formation of the quinone triplets, which are quenched (k_q) by (aromatic) donors to yield the triplet ion radical pair with nearly unit efficiency.[12] As applied to the chloranil-sensitized oxidation of CTE, the photophysical process is given in Scheme 1.

$$\mathrm{CA} \xrightarrow[\text{(isc)}]{h\nu} {}^3\mathrm{CA} \qquad (3)$$

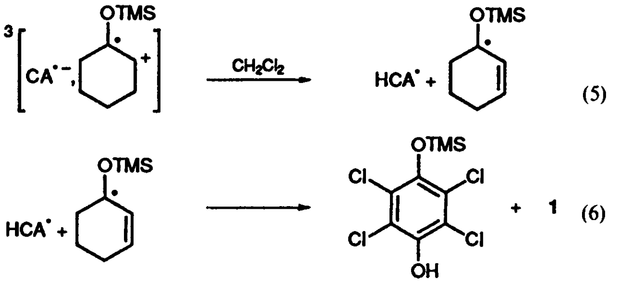
$$^3\mathrm{CA} + \mathrm{CTE} \xrightarrow{k_q} {}^3[\mathrm{CA}^{\bullet-}, \mathrm{CTE}^{\bullet+}] \qquad (4)$$

Scheme 1

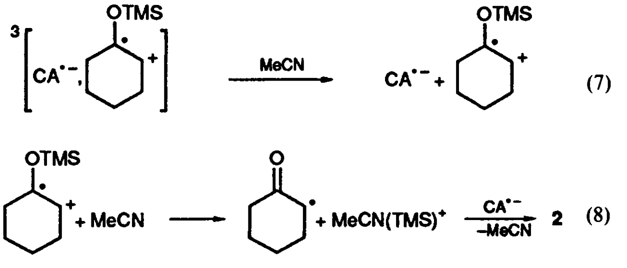
The same basic process outlined in Scheme 1 also applies to the excitation of the CA–CTE pair in the polar medium, as indicated in the inset of Fig. 3 by superimposable spectra of CA$^{\bullet-}$ obtained in both acetonitrile and dichloromethane. Therefore, the photochemical divergence that is delineated by eqns. (1) and (2) must occur subsequent to the formation of the ion radical pair in eqn. (4). Indeed, the anion radical CA$^{\bullet-}$ is a *transient species* in dichloromethane, and spectrum (*c*) (Fig. 3) recorded at 3.0 ns after the laser pulse corresponds to that of the radical HCA$^\bullet$ with λ_{max} = 435 nm and ε_{max} = 7700 dm^3 mol^{-3} cm^{-1}.[13] Since the radical HCA$^\bullet$ is the protonated form of CA$^{\bullet-}$, we propose that it derives from the transfer of an allylic proton of the labile cation-radical[14] moiety CTE$^{\bullet+}$, Scheme 2.†

TMS transfer within the radical pair in eqn. (6) represents the most direct formulation for the ultimate production of the enone **1** according to the stoichiometry in eqn. (1). Such a (dark) process is undoubtedly complex since spectrum (*c*) (Fig. 3) of the semiquinone radical HCA$^\bullet$ decays (to the spectral baseline) over several microseconds.

In marked contrast with the fleeting behaviour of CA$^{\bullet-}$ in dichloromethane, the anion radical CA$^{\bullet-}$ is *long lived* in acetonitrile as indicated by the persistence of spectrum (*b*′) over the course of several hundreds of microseconds in this polar medium. Such a time-span is sufficient for the diffusive separation of the ion radical pair [eqn. (7)]—especially to allow TMS transfer from the labile CTE$^{\bullet+}$ moiety to acetonitrile.[15] The resulting α-ketoalkyl radical[16] is then free to undergo homolytic coupling to form the adduct **2**, Scheme 3.



Scheme 2



Scheme 3

The striking changeover from enone **1** to adduct **2** derives from the strong solvent modulation of ion-pair dynamics,[17] particularly as exemplified in eqn. (5) (Scheme 2) and eqn. (7) (Scheme 3). We hope to establish the generality of this remarkable solvent effect in the photoactivation of other enol donors‡ with quinones and generally to exploit such ion-pair behaviour in effecting the selective photochemical transformation of organic functional groups.

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† The lifetime for CA$^{\bullet-}$ of τ < 3 ns indicates that the radical pair is formed in eqn. (5) *via* proton transfer within the triplet ion pair followed by diffusive separation.

‡ For example, a third photochemical process leading to the aromatization of CTE to phenyl ethers has also been identified under certain conditions.

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