Photoinduced Electron Transfer by Charge-transfer and Singlet-sensitized Activation. Facile Retro-pinacol *via* Fragmentation of Cation Radicals

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Direct comparison of the efficiency of photoinduced electron transfer by charge-transfer activation of electron donor–acceptor (EDA) complexes and diffusional quenching of excited singlet acceptors is allowed by a series of silylated pinacols derived from the *p*-methoxytoluene donor.

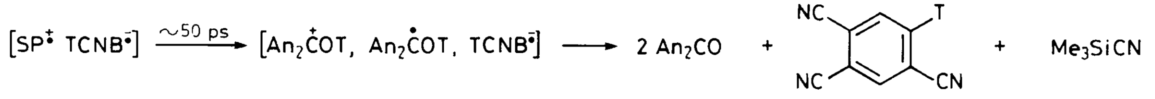
Chemical activation of otherwise unreactive donors (D) by electron transfer occurs upon the specific irradiation of the charge-transfer band ($h\nu_{CT}$) of the electron donor–acceptor (EDA) precursor complex with an acceptor (A),[1] *i.e.* Scheme 1.

Unfortunately the utilization of this conceptually simple photoinduced electron transfer is limited by an efficient back electron transfer (k_2).[2] The latter is a general problem in photoredox processes that can be resolved by the deliberate design of labile intermediates (either $D^{+\bullet}$ or $A^{-\bullet}$), especially those with differing lifetimes.[3] We now report the use of pinacolic donors derived from the *p*-methoxytoluene chromophore, in which the efficiency of the charge-transfer process

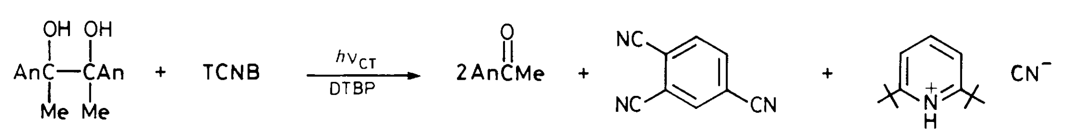
$$D + A \overset{K}{\rightleftharpoons} [D,A] \qquad (1)$$

$$[D,A] \underset{k_2}{\overset{h\nu_{CT}}{\rightleftharpoons}} [D^{+\bullet}, A^{-\bullet}] \xrightarrow{k_1} \text{Products} \qquad (2)$$

Scheme 1



(3)



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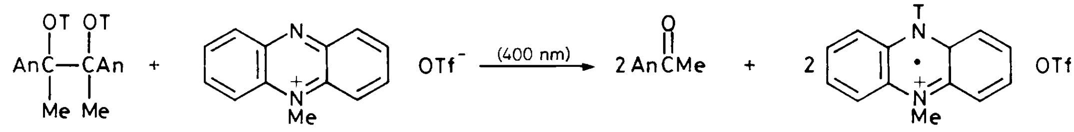

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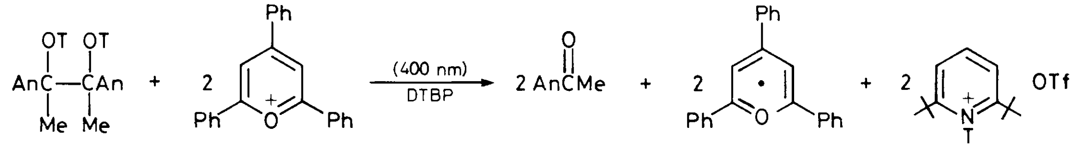

(7)

Table 1. Charge-transfer and singlet-sensitized photochemistry of pinacolic donors.[a]

SP Donor[b]	Acceptor[c]	λ_{exc}[d]/nm	ϕ	Products[e]
$(An_2COT)_2$	TCNB	400	0.23	$An_2CO(2)$, TCTB(1), TCN
$(AnCMeOT)_2$	TCNB	400	0.11	AnCOMe(2), TCTB(1), TCN
$(AnCMeOT)_2$	TCNB	313	0.45	AnCOMe(2), TCTB(1), TCN
$(AnCHOT)_2$	TCNB	400	0.01	AnCHO(2), TCTB(1), TCN
$(AnCHOT)_2$	TCNB	313	0.13	AnCHO(2), TCTB(1), TCN
$(AnCMeOT)_2$	P	400	0.38	AnCOMe(2), TP^+ OTf^-(2)
$(AnCMeOT)_2$	MA[f]	>400		AnCOMe(2), $[MA]_2$(1),[g]
$(AnCMeOT)_2$	TPP[f]	>400		AnCOMe(2), TPP·(2),[g]

[a] In dichloromethane containing ~0.05 M SP and 0.025 M acceptor at 25 °C. [b] An = p-$MeOC_6H_4$ and T = Me_3Si. [c] TCNB = 1,2,4,5-tetracyanobenzene, P = *N*-methylphenazinium, MA = *N*-methylacridinium, TPP = 2,4,6-triphenylpyrylium as triflates. [d] With Ealing interference filters ±5 nm (fwhm), except >400 indicates Corning sharp cut-off filter. [e] Numbers in parentheses are moles per mole SP consumed. TCTB = 2,4,5-tricyano-trimethylsilylbenzene, TCN = trimethylsilylcyanide (not quantified). [f] With 2 equiv. DTBP. [g] Mixture (2 equiv.) of *N*-trimethylsilyl-2,6-di-t-butylpyridinium triflate and hexamethyldisiloxane.

(equation 2) is found to rival that induced more conventionally by singlet sensitizers such as the cyanoarenes.[4,5] For example, tetracyanobenzene (TCNB) and the silylated pinacols (SP) in Table 1 form a series of coloured 1 : 1 EDA complexes that are all closely related to that derived from TCNB and the parent donor p-methoxytoluene with $K = 0.2\ mol^{-1}\ dm^3$ in dichloromethane (Figure 1B).[6] As such the irradiation with monochromatic light (λ_{exc} 400 nm) of the yellow–orange solutions involves specifically the charge-transfer excitation of only the EDA complex to the pertinent ion pair $[SP^{+\cdot}, TCNB^{-\cdot}]$.[7,8] The facile fragmentation[5,6] of $SP^{+\cdot}$ as well as the recently described silyl transfer[9] to $TCNB^{-\cdot}$ account for all the products in Table 1 (with An = p-$MeOC_6H_4$ and T = Me_3Si). Thus the measured quantum yields (ϕ) for charge-transfer photochemistry in column 4 lead to lifetimes (τ) of $SP^{+\cdot}$ when the estimated first-order rate constant k_2 ~$10^{11}\ s^{-1}$ is used to evaluate the back electron transfer.[10] In particular, the lifetime of ~50 ps for $(An_2COT)_2^{+\cdot}$ is sufficient to ensure unimolecular fragmentation within the caged ion pair (see equation 2), followed by intracage silyl transfer in accord with the observed stoicheiometry in Table 1, *e.g.* see equation (3).

Charge-transfer photochemistry of the corresponding diols with TCNB results in the retro-pinacol analogous to equation (3), but it occurs competitively with the acid-catalysed

$$TCNB \overset{h\nu_A}{\rightleftharpoons} TCNB^* \overset{SP}{\rightleftharpoons} [SP^{+\cdot}, TCNB^{-\cdot}] \xrightarrow{k_1} Products \qquad (5)$$

Scheme 2

formation of the corresponding pinacolone.[11] Although the complications from the latter are minimized by added bases such as 2,6-di-t-butylpyridine (DTBP), *e.g.* see equation (4), the silylated derivatives in Table 1 represent the donors chosen to unambiguously establish the retro-pinacol process.

The clean spectral separation of the uncomplexed TCNB ($\lambda_{max.}$ 320 nm) in Figure 1A also allows the separate evaluation of the efficiency of pinacolic cleavage *via* the diffusional quenching of the locally excited acceptor, *i.e.* Scheme 2. The latter ($h\nu_A$) is achieved with a narrow bandpass interference filter (λ_{exc} 313 ± 5 nm) for the specific excitation of only TCNB without ambiguities arising from either the CT absorption (Figure 1B) or from the uncomplexed SP (Figure 1A). The results in Table 1 show the products and stoicheiometry to be identical with those obtained by CT photochemistry; and the high quantum yields achieved with TCNB in column 4 accord with previous studies of photosensitization by singlet cyanonaphthalenes.[5] Indeed the enhanced efficiencies for the photoinduced retropinacol by singlet

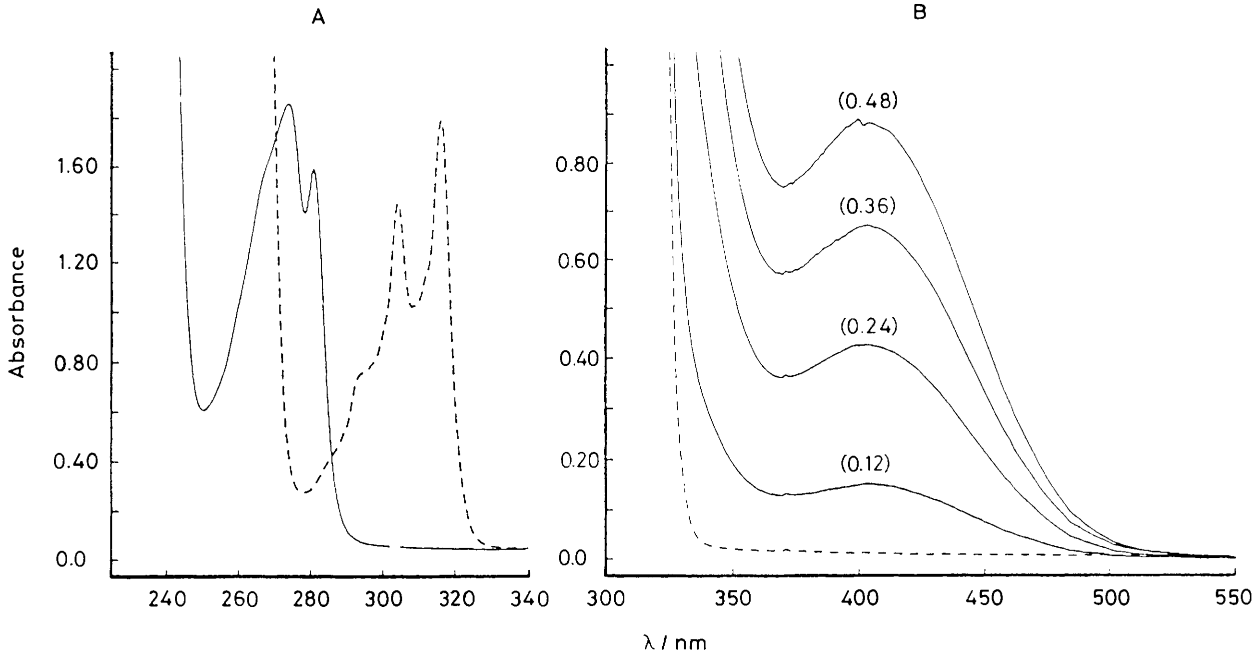

Figure 1. Absorption spectra of (A) 1.0 mM [AnC(OT)Me]$_2$ (——), 5.6 mM TCNB (- - - - -) alone, and (B) 0.01 M TCNB with various amounts of *p*-methoxytoluene (M as indicated) in dichloromethane.

excitation (ϕ_{sens}) and CT activation (ϕ_{CT}) both relate to highly transient ion-radical pairs [$SP^{+\cdot}$, $TCNB^{-\cdot}$], whether they arise *via* electron transfer as a result of diffusional quenching or direct CT excitation of the EDA complex, as described in Schemes 2 and 1, respectively.† In order to emphasize that such photoefficiencies derive from the labile donor moiety ($SP^{+\cdot}$), we also report the equivalent retro-pinacol with the structurally diverse phenazinium acceptor (P)[12] that proceeds with equal efficacy according to the stoicheiometry in equation (6).

The analogous photoinduced retro-pinacol is also effected with *N*-methylacridinium (MA)[13] and 2,4,6-triphenylpyrylium (TPP)[14] acceptors, but they require the addition of 2 equiv. of DTBP to quench the formation of the pinacolone, *e.g.* equation (7).

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† The difference in the photoefficiencies ϕ_{sens} and ϕ_{CT} will be elaborated in a forthcoming publication.