Photoinduced Electron Transfer in Pinacol Cleavage with Quinones *via* Highly Labile Cation Radicals. Direct Comparison of Charge-Transfer Excitation and Photosensitization

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Benzopinacol and related diphenylethane-like donors (D) form electron donor–acceptor (EDA) complexes with chloranil and similar benzoquinones (A), in which the deliberate irradiation of the charge-transfer absorption band ($h\nu_{CT}$) leads to oxidative cleavage (retropinacol) *via* electron transfer. Photosensitization by excitation of the π–π^* band of chloranil and diffusive quenching also effects the C–C bond cleavage of the same donors. The photoefficiencies of both photochemical processes are quantitatively compared with respect to the lifetimes of the pinacol cation radicals ($D^{+\bullet}$), as determined by the competition from back electron transfer and diffusion. These photoinduced processes are considered in the context of electron-transfer for an equivalent thermal reaction which occurs in the dark with high-potential quinones and electron-rich pinacols.

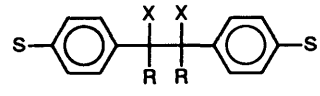
Electron-transfer oxidation of a neutral organic donor (D) by various oxidants or electron acceptors (A) produces a cation radical ($D^{+\bullet}$)[1] that can subsequently lead to a rich menu of organic transformations readily exploitable for organic synthesis.[2] Amongst the different procedures for effecting the initial electron-transfer step,[3-5] the photochemical method is particularly effective when it involves the prior actinic activation of the electron acceptor ($h\nu_A$), followed by the diffusive quenching with the organic donor,[6] eqn. (1), or the reverse sequence

$$A \xrightarrow{h\nu_A} A^* \underset{k_{et}}{\overset{D}{\rightleftharpoons}} [D^{+\bullet}, A^{-\bullet}] \xrightarrow{k_1} \text{Products} \qquad (1)$$

involving the prior activation of the organic donor ($h\nu_D$) and quenching with the acceptor. Photochemical electron transfer can also be effected by the specific irradiation of the charge-transfer absorption band ($h\nu_{CT}$) of the intramolecular electron donor–acceptor (EDA) complex formed in a pre-equilibrium step,[7,8] eqn. (2). The excitation of the charge-transfer (CT)

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

complex is the more direct method for the photoactivation of electron-transfer oxidation. Thus the absorbed energy ($h\nu_{CT}$) in eqn. (2) is directly applied to the conversion of the precursor EDA complex into the ion pair [$D^{+\bullet}$, $A^{-\bullet}$] by a vertical (Franck–Condon) process—with minimal ambiguity about the diffusional aspects[6] of electron transfer that are inherent in the sensitization process in eqn. (1). Unfortunately, the utilization of this conceptually simple photoinduced electron transfer is limited by an efficient back electron transfer (k_{et}).[9,10] The latter is a general problem in photoredox processes, including the more conventional sensitization methods,[11] that we believe will be resolved by the design of a variety of labile intermediates, either $A^{-\bullet}$[12] or $D^{+\bullet}$[12,13] with differing lifetimes. Such structural variations in the redox ion pairs could allow their passage to products (k_1) to compete effectively with back electron transfer (k_{et}) and thus serve as tunable gates for charge-transfer photochemistry. In order to evaluate the comparative effectiveness of such a CT process, we drew on the earlier studies of labile cation radicals ($D^{+\bullet}$) formed as intermediates during the photo-sensitized cleavage of aryl pinacols and their ethers (D) with either 1,4-dicyanonaphthalene[14,15] or 1,4-dicyanobenzene[16] acting as the singlet sensitizer A in eqn. (1). Since



Cpd.	S	R	X	Cpd.	S	R	X
1a	MeO	H	OH	**4**	H	Me	OT
1	MeO	H	OT	**5**	Br	Me	OT
2a	MeO	Me	OH	**6**	MeO	H	H
2	MeO	Me	OT	**7**	MeO	Me	Me
3a	MeO	An	OH	**8**	$(MeO)_2$	Me	OT
3	MeO	An	OT				

Chart 1

tetrachlorobenzoquinone (chloranil) can serve both as a sensitizer and an electron acceptor for arene activation,[17] we now report the comparative study of pinacol cleavage by *charge-transfer activation* of chloranil complexes according to eqn. (2) with that effected by chloranil *photosensitization* according to eqn. (1). In order to cover the spectrum of donor effects, we considered the aryl pinacols (Chart 1) derived from the reductive couplings of benzaldehyde, acetophenone and benzophenone, as well as their bis-trimethylsilyl ethers (**1**, **2** and **3**, respectively), with each containing the *p*-methoxyphenyl (An) chromophore [note: T = trimethylsilyl].[18]

Chart 1 also includes the graded series of related pinacols chosen to represent variations in (*i*) the donor strengths or oxidation potentials (E°_{ox}) with ring substitution (S) and (*ii*) the cation-radical lifetimes with bridge substitution (R and X). The parent hydrocarbon donors bibenzyl (**6**) and bicumene (**7**) are included together with the 3,3′,4,4′-tetramethoxy analogue (**8**), which was next to the strongest donor examined in this study. The variation in the acceptor strengths is represented in the quinone structures shown in Chart 2 with different reduction potentials (E°_{red})[19] to encompass a span of almost 13 kcal mol^{-1} in the change of the driving force for electron transfer.

Results

I. *The Formation and Charge-transfer Spectra of Quinone EDA Complexes with Aromatic (Pinacol) Donors.*—When chloranil was added to 4-methoxytoluene, the dichloromethane solution immediately turned bright orange. The quantitative

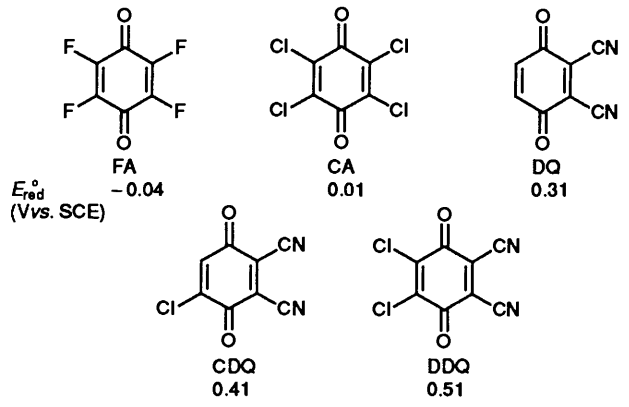


Chart 2

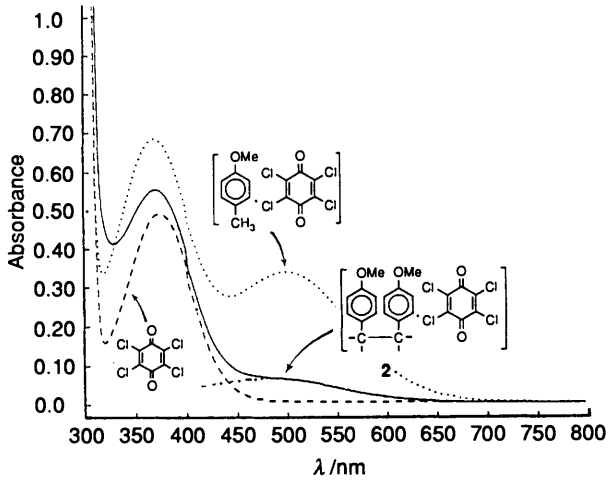
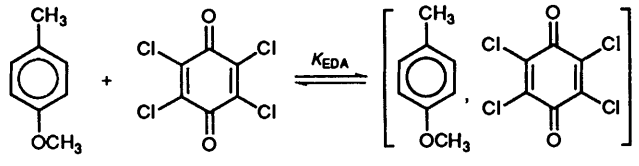


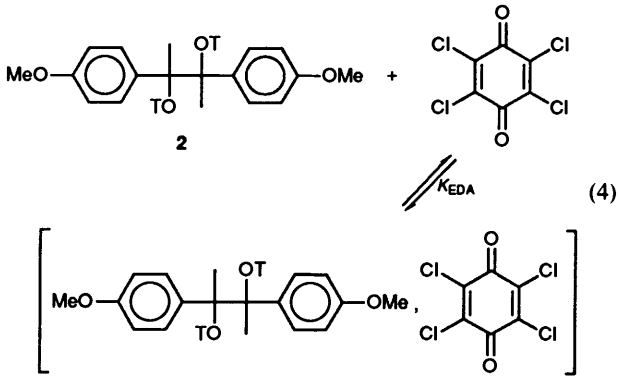
Fig. 1 The absorption spectrum of 0.002 mol dm^{-3} chloranil (- - - -) and its charge-transfer spectrum with 0.4 mol dm^{-3} 4-methoxytoluene (· · · ·) and with 0.2 mol dm^{-3} anisyl (TMS)pinacol **2** (——) in dichloromethane



(3)

effect of such a dramatic colour change is presented in Fig. 1 by the appearance in the electronic (UV–VIS) spectrum of a new absorption band with λ_{max} = 500 nm. The latter as a broad, unresolved envelope is a typical spectroscopic feature for charge-transfer excitation of the intermolecular (1 : 1) electron donor–acceptor (EDA) complex,[20,21] eqn. (3). The spectrophotometric determination of the formation constant of the EDA complex in eqn. (1) according to the Benesi–Hildebrand procedure[22] indicated a value K_{EDA} = 0.32 dm^3 mol^{-1} (ε_{CT} = 1500 dm^3 mol^{-1} cm^{-1}) in dichloromethane. Such a limited magnitude of the formation constant identified a weak EDA complex of chloranil and methoxytoluene, according to Mulliken's terminology.[23,24]

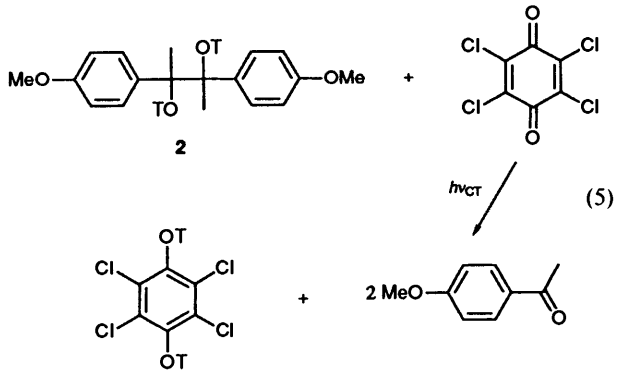
In order to utilize the charge-transfer character of the new (low energy) absorption band, we examined the 4-methoxyphenyl (anisyl) chromophore in the form of the various dimeric (pinacol) structures in Chart 1 for the systematic study of structural effects. For example, Fig. 1 includes a direct comparison of the absorption spectrum of the chloranil complex of methoxytoluene with that of the structurally related dimeric (pinacol) donor **2**—showing the charge-transfer band with λ_{CT} = 486 nm to be essentially unshifted (albeit with significantly reduced absorbance), *i.e.*, eqn. (4) where T = trimethylsilyl. Most importantly, the charge-transfer band was subject



(4)

to the characteristic spectral red shift with increasing donor strength[20,21] of ring-substituted pinacols (as trimethylsilyl ethers) in the order: **4** < **5** < **2** < **8**, as a result of 4-bromo, hydrogen, 4-methoxy and 3,4-dimethoxy substitution, respectively, in Fig. 2(*a*). Likewise, the new absorption band suffered a gradual blue shift with decreasing strength of the quinone acceptor (see Chart 2) in the order DDQ > CDQ > DQ, as illustrated in Fig. 2(*b*). The absorption maxima of the charge-transfer bands are listed as λ_{CT} in Table 1 for the various quinone complexes with representative pinacols, together with those of the parent (monomeric) donors. The trends in λ_{CT} with the changes in quinone acceptors and aromatic donors thus lead to the unambiguous identification of the new spectral bands to the charge-transfer excitation[25] of the electron donor–acceptor complexes.

II. *Charge-transfer Photochemistry of Chloranil EDA Complexes with Anisyl (Pinacol) Donors.*—The bright orange solution of chloranil and the pinacol TMS ether **2** (from 4-methoxyacetophenone)[26] persisted unchanged for prolonged periods at 23 °C, if carefully protected from exposure to adventitious (room) light. However, deliberate irradiation of the solution with filtered light (λ_{exc} > 500 nm), corresponding to low-energy tail absorption of the charge-transfer band, led to a gradual bleaching. The latter was accompanied by the corresponding diminution of the charge-transfer band with λ_{CT} = 486 nm, as well as the simultaneous decrease in the more intense π–π* band of chloranil at λ_{max} = 375 nm[27] in Fig. 1. The ^{1}H NMR and GC–MS analysis of the photolysate indicated the presence of the retropinacol (redox) product 4-methoxyacetophenone according to the stoichiometry in eqn. (5), as detailed in the Experimental section. The direct transfer of both trimethylsilyl (T) groups upon the C–C bond cleavage of the pinacol donor was indicated by the formation of tetra-



(5)

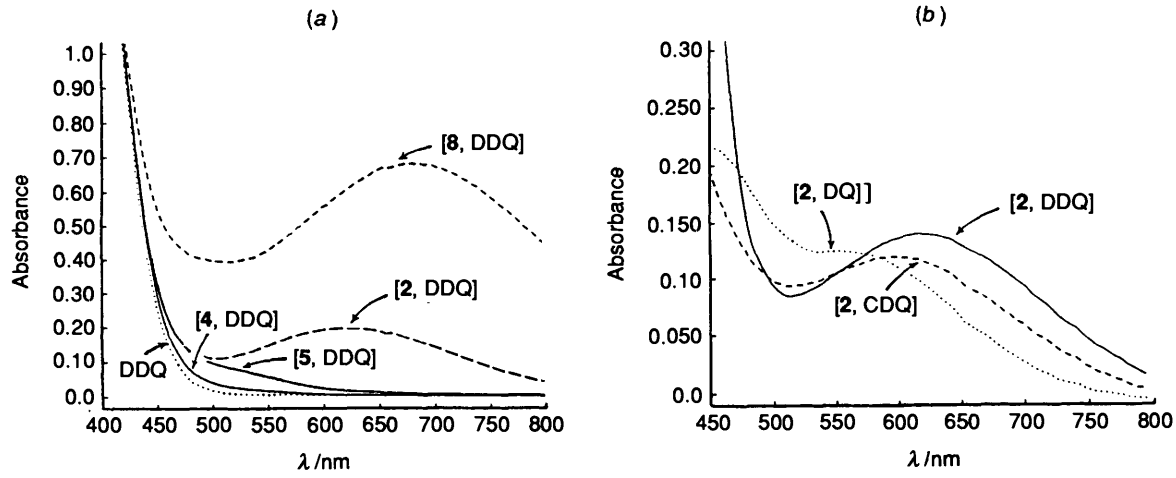
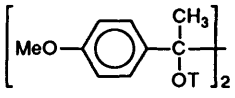
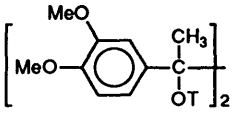
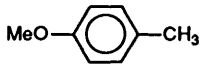
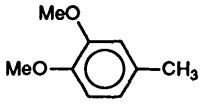
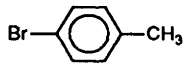
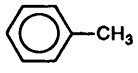


Fig. 2 Charge-transfer absorption bands of (*a*) DDQ complexes with the (ring-substituted) pinacolic donors in Chart 1, and (*b*) anisyl TMS(pinacol) **2** with the quinones in Chart 2

Table 1 Charge-transfer absorption spectra of quinone EDA complexes with aromatic (pinacol) donors[a]

Donor	E^{o}_{ox}/ V *vs.* SCE	Substituted 1,4-benzoquinones[b] FA	CA	DQ	CDQ	DDQ
	—	468 (2.66)	486 (2.56)	568 (2.19)	598 (2.08)	624 (1.99)
	—	514 (2.42)	530 (2.34)	618 (2.01)	662 (1.88)	684 (1.82)
	1.67	472 (2.63)	498 (2.50)	570 (2.18)	610 (2.04)	628 (1.98)
	1.34	524 (2.37)	570 (2.18)	658 (1.89)	694 (1.79)	720 (1.73)
	2.60	—	—	444 (2.80)	468 (2.66)	496 (2.51)
	2.36	—	—	—	440 (2.82)	470 (2.64)

[a] In dichloromethane solution at 23 °C. [b] FA = fluoranil, CA = chloranil, DQ = 2,3-dicyanobenzoquinone, CDQ = 5-chloro-2,3-dicyanobenzoquinone, DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone. λ_{CT} in nm (in parentheses, λ_{CT}^{-1}/eV).

chlorohydroquinone solely as the bis-trimethylsilyl ether.[28] Thus the treatment of the parent pinacol **2a** with chloranil under identical photochemical conditions led to quantitative yields of tetrachlorohydroquinone by essentially the same (redox) stoichiometry, *i.e.*, eqn. (6). Since the oxidative bond cleavages in eqns. (5) and (6) resulted directly from the specific activation of the EDA complex, the actinic process is referred to hereafter as *charge-transfer retropinacol.*

The analogous pinacols **1a** and **3a** derived from the reductive coupling of anisaldehyde and 4,4′-dimethoxybenzophenone, respectively, together with their bis-trimethylsilyl ethers **1** and **3**,[26,29] were also exposed to chloranil. Though all these brightly coloured solutions persisted unchanged in the dark, their exposure to light with λ_{exc} > 500 nm uniformly led to extensive C–C bond cleavage of the pinacol donors (Table 2) according to

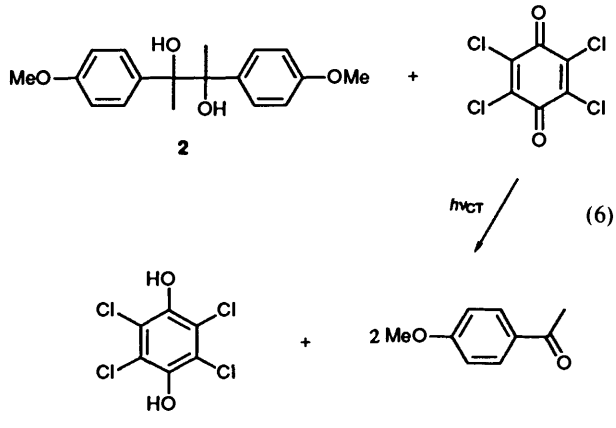
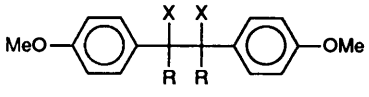


Table 2 Charge-transfer photochemistry of anisyl (pinacol) donors with chloroanil[a]

No.	R	X	t/h[b]	Conv. (%)[c]	Product (mmol) Carbonyl[d]	Hydroquin.[e]	Rec.[f] (mmol)	MB[g] (%)
1	H	OT	24	75	AnCHO (0.061)	T_2Q (0.030)	0.072	97
2	Me	OT	16	30	$AnCOCH_3$ (0.15)	T_2Q (0.075)	0.025	97
3	An	OT	12	70	An_2CO (0.14)	T_2Q (0.069)	0.028	98
1a	H	OH	16	50	AnCHO (0.063)	H_2Q (0.027)	0.068	99
2a	Me	OH	20	30	$AnCOCH_3$ (0.10)	H_2Q (0.045)	0.044	96
3a	An	OH	15	65	An_2CO (0.14)	H_2Q (0.060)	0.029	96
6	H	H	60	0	—	—	—	—
7	Me	Me	60	< 5	$AnC(CH_3)CH_2$ (< 0.05)	—	~0.09	—
8[h]	Me	OT	60	< 5	$ArCOCH_3$[h] (< 0.05)	—	~0.09	—

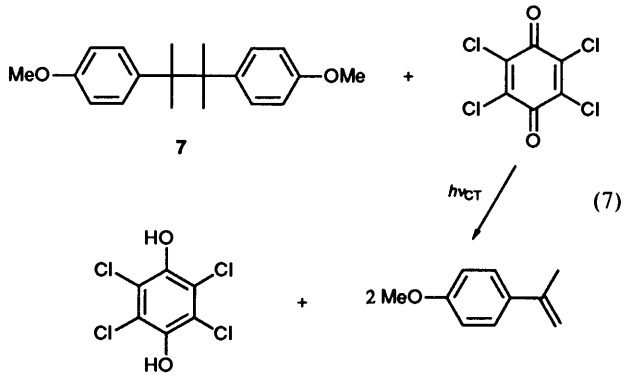
[a] In dichloromethane (5 cm^3) solution containing 0.10 mmol chloranil and 0.10 mmol anisyl (pinacol) donor at 23 °C. [b] Of irradiation with λ_{exc} > 500 nm. [c] Conversion based on recovered donor. [d] From C–C cleavage. [e] Reduced chloranil as H_2Q = tetrachlorohydroquinone or T_2Q = bis-trimethylsilyl ether. [f] Recovered donor. [g] Mass balance of products and recovered donor. [h] 3,4-Dimethoxy analogue of **2**.

Table 3 Quantum yields for the charge-transfer retropinacol of anisyl donors with chloranil[a]



No.	R	X	Φ[b]
1	H	OT	0.03
2	Me	OT	0.12
3	An	OT	0.18
1a	H	OH	0.01
2a	Me	OH	0.15
3a	An	OH	0.22
6	H	H	0
7	Me	Me	< 0.001

[a] From 0.04 mol dm^{-3} anisyl donor and 0.02 mol dm^{-3} chloranil in dichloromethane at 23 °C by irradiation at λ_{exc} = 505 ± 5 nm. [b] Based on chloranil disappearance by UV measurements at 375 nm and/or GC analysis at 5–10% conversions.



the stoichiometries in eqns. (5) and (6). The conversions listed in Table 2 (column 5) qualitatively measured the beneficial effects of substitution on the bridge carbons to favour pinacol cleavage, but the photo-reactivity of the alcohol was not distinguished from that of the trimethylsilyl derivative. However, substitution on the ring by an additional methoxy group, as in the 3,4-dimethoxy derivative **8**, led to inefficient charge-transfer retropinacol, as indicated by the small amounts of 3,4-dimethoxyacetophenone obtained only upon the prolonged exposure of the chloranil complex to λ_{exc} > 500 nm. It is also noteworthy that the presence of hydroxy or trimethylsiloxy substituents on the bridge carbons was necessary for efficient charge-transfer photochemistry since the corresponding bibenzyl and bicumene analogues **6** and **7** were singularly inert. Thus the exposure of 4,4′-dimethoxybicumene and chloranil in dichloromethane to actinic radiation with λ_{exc} > 500 nm led to small amounts of 4-methoxy-α-methylstyrene only after prolonged periods (> 12 h) with the (presumed) stoichiometry in eqn. (7). Moreover, no photoreaction was detected when 4,4′-dimethoxybibenzyl was treated with chloranil under the same conditions.

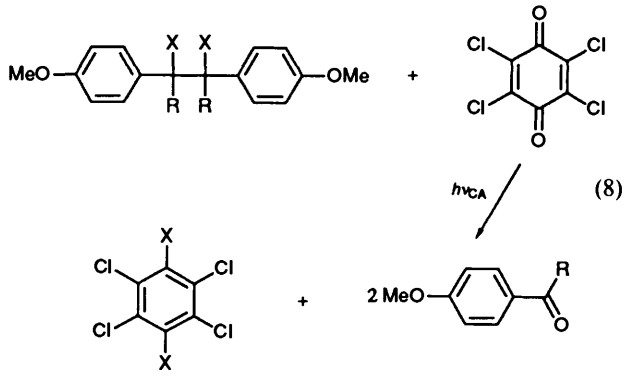
III. *Photo-efficiency of the C–C Bond Cleavages of Anisyl (Pinacol) Donors in Chloranil EDA Complexes.*—In order quantitatively to assess the charge-transfer retropinacol of the anisyl donors in Table 2, the EDA complexes were uniformly irradiated with monochromatic light at λ_{exc} = 505 nm by the use of a narrow-band (± 5 nm) interference filter. The light intensity was measured with the aid of the Reineckate actinometer,[30] and the photochemical conversion was established by spectrophotometric analysis of chloranil and/or quantitative gas chromatographic analysis of the carbonyl products (see the Experimental section). The results in Table 3 confirm the qualitative trend inferred from the photochemical conversions (*vide supra*), and the measured quantum yields establish the strong influence of the bridge substitution in the order: X = OTMS (or OH) ≫ CH_3 (or An) > H. Thus, the anisyl donors must clearly incorporate the pinacol functionality (or its bis-TMS ether) in order to achieve a modicum of photo-efficiency from the charge-transfer activation of chloranil EDA complexes.

IV. *The Quantitative Effects of Quinone Structure on Charge-transfer Retropinacol.*—In order to establish the quantitative role of the quinone acceptor, the charge-transfer retropinacol of the family of structurally related pinacols derived from ring-substituted acetophenones with 3,4-dimethoxy, 4-methoxy, 4-bromo and 4-hydrogen groups (as the bis-trimethylsilyl ether derivatives **8**, **2**, **5** and **4** respectively, in Chart 1), was treated serially with the graded series of quinones—fluoranil (FA), chloroanil (CA), dicyanoquinone (DQ), chlorodicyanoquinone (CDQ) and dichlorodicyanoquinone (DDQ). The charge-transfer excitation of each pinacol/quinone pair, listed in Table 4 was effected with monochromatic light (λ_{exc}) carefully chosen to optimize the CT absorbance of the EDA complex [the selection of the appropriate narrow-band (± 5 nm) interference filter is included in Table 4]. In all cases, the photo-induced C–C bond cleavage was quantitatively evaluated by GC–MS analysis for the ring-substituted acetophenone in the photolysate, and the photoefficiency determined with the aid of Reineckate actinometry.[30] The quantum yields in Table 4 show

a wide spectrum of values that are uniquely dependent on the particular pinacol/quinone combination—being the smallest ($\Phi \sim 0$) with the (strongest donor)/(weakest acceptor) pair, namely, [**8**, FA] and the largest ($\Phi = 0.57$) with the (weakest donor)/(strongest acceptor) pair, namely, [**5**, DDQ].

The effect of the excitation energy (λ_{exc}) on the charge-transfer photoefficiency was evaluated with the 4-methoxy and 3,4-dimethoxy pinacols **2** and **8**, respectively, since the charge-transfer absorption band with DDQ was well-resolved in each case; and it could be excited at various points on the absorption envelope without any complication arising from the local-band excitation of the quinone chromophore. The results in Table 5 show that the total energy span (column 5) was sufficient to demonstrate that the variation in the quantum yields in Table 4 related directly to the CT photoefficiency of each pinacol/quinone pair and not to the particular choice of λ_{exc}. The latter suggests λ_{exc} did not strongly affect the C–C bond vibrations in the CT excited state[8c]—symptomatic of the aromatic chromophore [and not the TMS(pinacol) functionality] as the critical component in the photoactivation of pinacol/quinone complexes.[31]

V. *Photo-sensitized Cleavage of Anisyl (Pinacol) Donors with Quinones.*—The π–π* bands of various *p*-benzoquinones typically lie in the spectral region about 330–380 nm,[27] which is generally well separated from the charge-transfer absorption band of the corresponding EDA complex with anisyl donors such as those included in Fig. 1. This unique spectral feature allowed the quinone-photosensitized reactions of anisyl pinacols to be examined in parallel with the charge-transfer process described in the foregoing sections. Typically, an equimolar mixture of chloranil and the appropriate pinacol donor was irradiated in dichloromethane solution with monochromatic light at $\lambda_{exc} = 405$ nm [with the aid of a narrow-band (± 5 nm) interference filter] to correspond closely to the π–π* band of chloranil with $\lambda_{max} = 375$ nm.[19] Alternatively, a broad-band light source with $380 < \lambda_{exc} < 480$ nm (see the Experimental section) was used for the preparative product studies described in Table 6.[32] For example, the irradiation of 0.02 mol dm^{-3} chloranil and 0.02 mol dm^{-3} pinacol TMS ether **2** (or the parent pinacol **2a**) under these conditions led to the bleaching of the yellow solution within 45 min—coincident with the disappearance of the π–π* band of chloranil. The subsequent ^{1}H NMR and GC–MS analyses of the photolysate indicated the presence of 4-methoxyacetophenone and tetrachlorohydroquinone with the same 1:2 stoichiometry observed in eqns. (5) and (6) for charge-transfer retropinacol. Since similar treatment of the pinacols derived from benzaldehyde and 4,4′-dimethoxybenzophenone (and the corresponding trimethylsilyl ethers **1** and **3**, respectively) also led to the same cleavage process (Table 6), it is hereafter generically referred to as *photosensitized retropinacol*, eqn. (8), where R = H, Me and An and X = OT or OH, and the

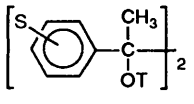


excitation energy was limited by the π–π* band of chloranil with $h\nu_{CA} \sim 2.6$ eV.

Chloranil photosensitization of 4,4′-dimethoxybicumene, as described in Table 6 (last entry), effected the extensive scission of the C–C bond to afford essentially quantitative yields of α-methylstyrene and tetrachlorohydroquinone, eqn. (9).

Extensive reduction of chloranil also accompanied its photosensitized reaction with 4,4′-dimethoxybibenzyl, but no cleav-

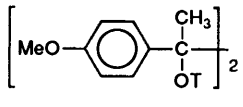
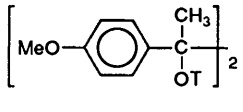
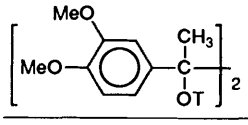
Table 4 Quantitative effects of quinone structure on charge-transfer retropinacol[a]



		Substituted 1,4-benzoquinones				
No.	Substituent	FA	CA	DQ	CDQ	DDQ
8	2,4-Dimethoxy	0	< 0.001	0.09[b]	0.14[b]	0.19[b]
2	4-Methoxy	0.10	0.12	0.25[b]	0.33[b]	0.37[b]
4	None	0.15[c]	—	0.32[d]	—	0.44[e]
5	4-Bromo	0.25[f]	—	0.38	—	0.57[e]

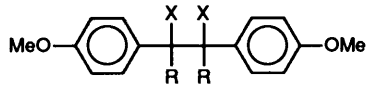
[a] As in Table 3 and Chart 2, except as noted otherwise. λ_{exc} [b] 580. [c] 440. [d] 560. [e] 540. [f] 460 nm (fwhm = 5 nm). Quantum yields ± 0.04.

Table 5 Effect of excitation energy on the photoefficiency on charge-transfer retropinacol[a]

TMS pinacol	Quinone	λ_{exc}/nm	Φ	ΔE/kcal mol^{-1}
	FA	460	0.11 ± 0.01	
		500	0.10 ± 0.01	
		540	0.10 ± 0.01	
		580	0.09 ± 0.01	10.4
	DDQ	500	0.42 ± 0.04	
		520	0.39 ± 0.04	
		540	0.40 ± 0.04	
		580	0.37 ± 0.04	
		600	0.36 ± 0.04	
		620	0.33 ± 0.04	9.0
	DDQ	540	0.22 ± 0.02	
		580	0.19 ± 0.02	
		620	0.20 ± 0.02	5.5

[a] As in Table 3, except as noted otherwise. [b] Total span of λ_{exc}.

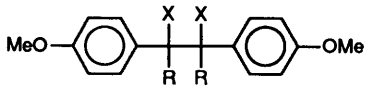
Table 6 Photosensitized cleavage of anisyl (pinacol) donors with chloroanil[a]



No.	R	X	(mmol)	Product (mmol) Conv.[b] (%)	Carbonyl[c]	Hydroquin.[d]	Rec.[e] (mmol)	MB[f] (%)
1	H	OT	(0.030)	55	AnCHO (0.036)	T_2Q (0.017)	0.011	97
2	Me	OT	(0.032)	57	$AnCOCH_3$ (0.036)	T_2Q (0.018)	0.014	100
3	An	OT	(0.040)	75	An_2CO (0.062)	T_2Q (0.030)	0.009	100
1a	H	OH	(0.038)	54	$AnCOCH_3$ (0.042)	H_2Q (0.021)	0.018	>100
2a	Me	OH	(0.039)	45	AnCHO (0.042)	H_2Q (0.017)	0.019	100
3a	An	OH	(0.040)	53	An_2CO (0.045)	H_2Q (0.022)	0.017	99
6	H	H	(0.050)	50	AnCH=CHAn (0.017)	H_2Q (0.025)	0.026	86
7	Me	Me	(0.050)	50	$AnC(CH_3)CH_2$ (0.045)	H_2Q (0.025)	0.025	95

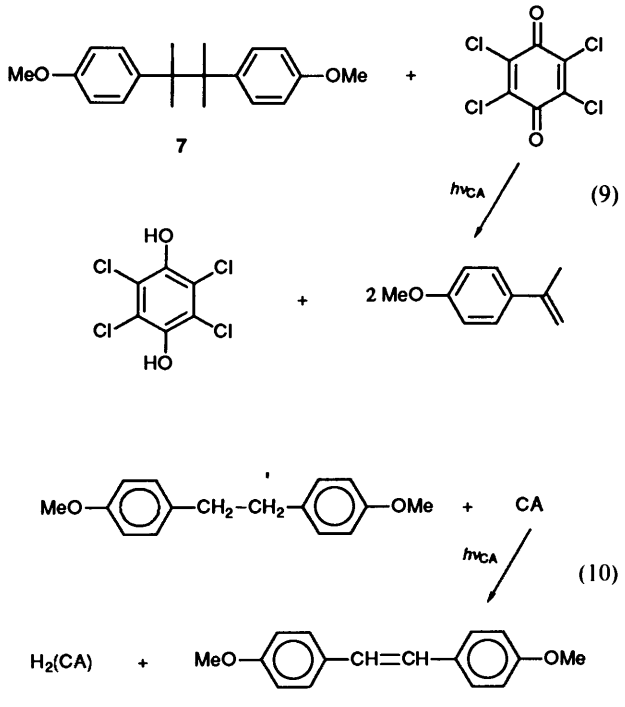
[a] In dichloromethane (5 cm^3) solution containing pinacol donor (specified) and an equimolar amount of chloranil with $380 < \lambda_{exc} < 480$ nm at 23 °C. [b] Conversion based on recovered donor. [c] From C–C cleavage. [d] Reduced chloranil as H_2Q = tetrachlorohydroquinone or T_2Q = bis-trimethylsilyl ether. [e] Recovered donor. [f] Mass balance of products and recovered donor.

Table 7 Quantum yields for the photosensitized cleavage of anisyl donors with chloranil[a]



No.	R	X	Φ[b]
1	H	OT	0.81
2	Me	OT	0.75
3	An	OT	0.87
1a	H	OH	0.84
2a	Me	OH	0.63
3a	An	OH	0.84
6	H	H	0.01
7	Me	Me	0.25

[a] As in Table 3 but with $\lambda_{exc} = 405 \pm 5$ nm. [b] Based on chloranil disappearance by absorbance decrease at 375 nm and/or GC analysis at 5–10% conversions.



age product(s) was found upon careful analysis of the photolysate—only 4,4'-dimethoxystilbene in high yields (entry 7), eqn. (10).

VI. *Quantum Yields for Chloranil Photosensitization of Anisyl (Pinacol) Cleavage.*—In order quantitatively to assess the photosensitized cleavage of the anisyl pinacols in Table 6, chloranil was specifically excited with monochromatic light at $\lambda_{exc} = 405 \pm 5$ nm (*vide supra*). The photochemical conversion was based on Reineckate actinometry and the spectrophotometric analysis of chloranil ($\lambda_{max} = 375$ nm and $\varepsilon_{max} = 220$ dm^3 mol^{-1} cm^{-1} in dichloromethane). The results in Table 7 show that the quantum yields of the photosensitized reactions all approached unity, and they were singularly invariant with the structure of the anisyl pinacol—in marked contrast with the trends in Φ measured for the corresponding charge-transfer process in Table 3. Moreover, even the hydrocarbon donors **6** and **7** (which were essentially inert in the charge-transfer process) underwent photo-oxidations according to eqns. (9) and (10) with reasonable efficiencies, as listed in Table 7 (entries 7 and 8).

VII. *Time-resolved Spectroscopy of the Reactive Intermediates in Charge-transfer Activation of the Quinone EDA Complexes.*—The reactive intermediates in the charge-transfer activation of the quinone EDA complexes pertinent to the C–C bond cleavage of anisyl (pinacol) donors were examined by time-resolved (picosecond) spectroscopy.[33] Owing to its photopersistence (*vide supra*), the EDA complex of chloranil (CA) with methoxytoluene ($AnCH_3$) in dichloromethane was initially selected for irradiation with the 532 nm pulse (representing the second harmonic) from a Quantel YG402 mode-locked Nd^{3+}:YAG laser. This excitation wavelength corresponded to the absorption maximum of the charge-transfer band of the [$AnCH_3$, CA] complex (see Fig. 1); and most importantly, the use of the 532 nm laser pulse precluded the possibility of the adventitious excitation of either the free (uncomplexed) chloranil or the anisyl donor.

Fig. 3(*a*) shows the growth of the spectral transient, attendant upon the application of the 30 ps (fwhm) laser pulse. It represents the composite spectrum of the chloranil anion radical ($CA^{-\bullet}$ with $\lambda_{max} = 450$ nm) and the methoxytoluene cation radical ($AnCH_3^{+\bullet}$ with $\lambda_{max} = 440$ nm) based on the comparison with the individual spectra of these species, as reported in the literature.[34–36] The temporal evolution of the transient spectrum monitored at $\lambda_{mon} = 452$ nm is illustrated in Fig.

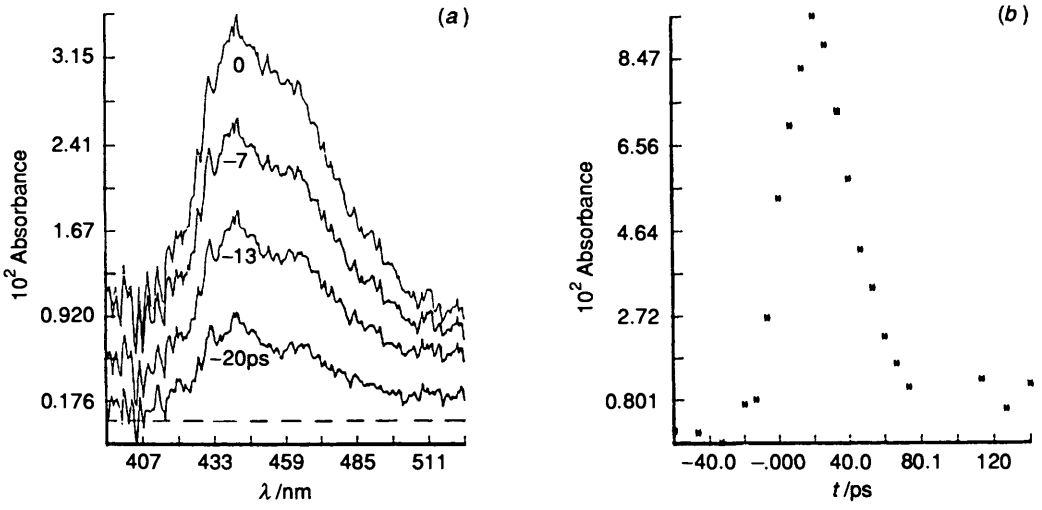


Fig. 3 (*a*) Time-resolved picosecond spectra following the application of the 30 ps laser pulse at λ_{exc} = 532 nm to a solution of 0.02 mol dm^{-3} chloranil and 0.4 mol dm^{-3} methoxytoluene in dichloromethane. (*b*) Temporal evolution of the spectral transient monitored at λ_{mon} = 452 nm.

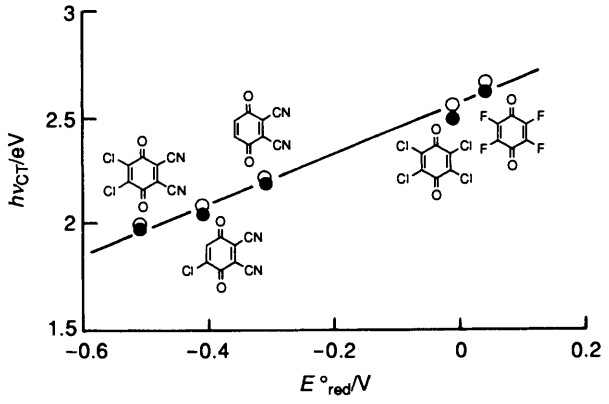
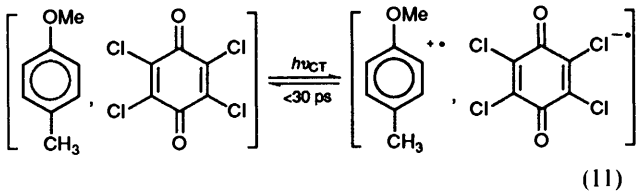


Fig. 4 Comparison of the Mulliken correlation of the charge-transfer absorption bands of 4-methoxytoluene (●) and anisyl (TMS)pinacol **2** (○) with various quinones (as indicated) in dichloromethane solution

3(*b*)—showing the decay of the transient to more or less mirror its growth. Thus Figs. 3(*a*) and 3(*b*) together show that the charge-transfer activation ($h\nu_{CT}$) of the chloranil EDA complex to the ion-pair state [$AnCH_3^{+\bullet}$, $CA^{-\bullet}$] is rapidly followed by its annihilation by back electron transfer, all within the 30 ps width of the laser pulse,[37] [eqn. (11)].



(11)

The extension of the time-resolved (picosecond) spectroscopic studies to the anisyl (pinacol) donors was unfortunately discouraged by the low absorbance of the corresponding EDA complex (see Fig. 1) to produce only a weak transient. Nonetheless, we judge from the similarity of the charge-transfer absorptions ($h\nu_{CT}$) that an analogous ion pair was generated during the irradiation of the chloranil EDA complexes with the anisyl (pinacol) donors listed in Table 2.

VIII. *Thermal Cleavage of Pinacol Donors with Quinones.*—All the anisyl (pinacol) donors in Chart 1 coexisted with the high potential quinone DDQ at room temperature for prolonged periods if the mixtures were protected from light, with the single exception of the tetraanisyl analogue **3**. Thus the bright blue–green solution of the DDQ complex with tetraanisyl TMS (pinacol) in dichloromethane spontaneously bleached (in the dark) within a short period after mixing. Concentration of the pale solution *in vacuo*, followed by ^1H NMR analysis, revealed the presence of 4,4′-dimethoxybenzophenone and the bis-trimethylsilyl ether of 2,3-dichloro-5,6-dicyanohydroquinone as the only products, eqn. (12).

$$An_2C(OT)\text{–}C(OT)An_2 + 2\,DDQ \xrightarrow[dark]{23\,°C} 2\,An_2CO + T_2(DDQ) \quad (12)$$

The same C–C cleavage also occurred when the tetraanisyl (TMS) pinacol **3** was exposed to either 5-chloro-2,3-dicyanobenzoquinone (CDQ) or 2,3-dicyanobenzoquinone (DQ), but the charge-transfer colours were discharged over successively prolonged periods. Contrastingly, the EDA complexes of **3** with the low potential quinones chloranil and fluoranil under the same conditions were unchanged at room temperature (in the dark), as visually judged by the persistent colours.

Discussion

The use of the anisyl (An = 4-methoxyphenyl) chromophore is particularly well suited to the direct comparison of charge-transfer activation and photosensitization of aromatic donors with substituted benzoquinones. Thus the absorption spectra in Fig. 1 show the typical pair of well-resolved bands (with maxima at 375 and 490 nm) that correspond to (*a*) the local excitation of the chloranil acceptor[27] and (*b*) the direct excitation of the chloranil EDA complex with 4-methoxytoluene ($AnCH_3$) or its dinuclear counterpart (represented here as [AnCMeOT]$_2$ **2**). The charge-transfer character of the latter is underscored by the related aryl pinacols (and their trimethylsilyl ethers) listed in Chart 1 that form variously coloured EDA complexes upon mixing with the different substituted benzoquinones in Chart 2. Most importantly, Fig. 4 shows the absorption bands ($h\nu_{CT}$) associated with the two series of EDA complexes (from the donors $AnCH_3$ and **2**) to vary linearly with the electrochemical reduction potentials of the different quinones, in accord with the expectations of Mulliken's theory of charge transfer.[23,24] Furthermore, the direct comparison of the transition energies $h\nu_{CT}$ of the mono- and di-nuclear aromatic donors in Table 1 reveals the aromatic moiety in the pinacols to be the donor site, primarily responsible for the charge-transfer interaction with quinones. As such, we take the substituted-

Table 8 Fragmentation lifetimes of cation radicals derived from anisyl donors[a]

No.	Anisyl donor	$\tau_{CT}/10^{10}$ s
3	$[An_2COT]_2$	0.67
3a	$[An_2COH]_2$	0.89
2	$[AnCMeOT]_2$	1.8
2a	$[AnCMeOH]_2$	1.4
1	$[AnCHOT]_2$	8.1
1a	$[AnCHOH]_2$	25
7	$[AnCMe_2]_2$	>200

[a] As described in the text.

toluene donors in Table 1 as reasonable models for their dinuclear (pinacol) counterparts—particularly insofar as the trends in either the ionization potential (E_i) or the oxidation potential (E°_{ox}) are to be evaluated.

Charge-transfer Activation of Quinone EDA Complexes in Pinacol Cleavages.—The activation of the quinone EDA complexes of the pinacols and their bis-trimethylsilyl ethers *via* the deliberate irradiation of the charge-transfer absorption bands (Table 1) results in C–C bond scissions according to eqns. (5) and (6) (Table 2). The time-resolved picosecond spectra in Fig. 3 correspond to Mulliken's generalized formulation of charge transfer within the (precursor) EDA complex to the ion pair state,[20] Scheme 1, where D and A are the generic represent-

$$D + A \overset{K_{EDA}}{\rightleftharpoons} [D, A] \quad (13)$$

$$[D, A] \overset{h\nu_{CT}}{\underset{k_{et}}{\rightleftharpoons}} [D^{+\bullet}, A^{-\bullet}] \xrightarrow{k_1} \quad (14)$$

Scheme 1

ations of the pinacols and quinones in Charts 1 and 2, respectively, and $h\nu_{CT}$ represents the charge-transfer excitation of the weak EDA complex [compare eqn. (4)]. According to Scheme 1, the initially formed ion pair undergoes back electron transfer (k_{et}) in competition with different types of (first-order) follow-up processes (k_1). This mechanistic formulation derives experimental support from various photophysical and photochemical studies of different EDA complexes by time-resolved spectroscopy, as reported earlier.[5,8,9] From the model study in Fig. 3, we thus formulate the charge-transfer excitation of the chloranil EDA complex with anisyl pinacol as eqn. (15).

$$[\text{AnC–CAn, CA}] \overset{h\nu_{CT}}{\underset{k_{et}}{\rightleftharpoons}} [\text{AnC–CAn}^{+\bullet}, \text{CA}^{-\bullet}] \quad (15)$$

For the pinacolic donors, direct deactivation of the ion pair in eqn. (15) by back electron transfer must compete with the facile rupture of the C–C bond,[15,38] which, in the case of the benzopinacol cation radical, has been shown to fragment (k_f) to the benzhydryl cation and the ketyl radical,[14] eqn. (16).

$$\text{Ph}_2\text{C(OH)–CPh}_2^{+\bullet} \xrightarrow{k_f} \text{Ph}_2\overset{+}{\text{C}}\text{–OH} + \text{Ph}_2\dot{\text{C}}\text{–OH} \quad (16)$$

Both fragments in eqn. (16) are subsequently converted into benzophenone by proton transfer and oxidation/proton transfer, respectively.[16] As applied to the anisyl pinacols in this study, the chloranil anion radical co-generated in eqn. (15) can serve as the base for proton transfer, as well as the electron acceptor in the ketyl oxidation to form tetrachlorohydroquinone [eqn. (5)]. Analogously for the trimethylsilyl ethers in Chart 1, the transfer of the trimethylsilyl group from the cation to chloranil anion radical is expected to be facile, and it accounts for the formation of tetrachlorohydroquinone bis-trimethylsilyl ether $T_2(CA)$ in Table 2, (Scheme 2).

$$[\text{AnC(OT)–CAn(OT)}^{+\bullet}, \text{CA}^{-\bullet}] \xrightarrow{k_1} \text{AnC(OT)}^{+} + \text{AnC}^{\bullet}\text{(OT)} + \text{CA}^{-\bullet} \quad (17)$$

$$\text{AnC(OT)}^{+} + \text{CA}^{-\bullet} \longrightarrow \text{AnC(=O)} + \text{T(CA)}^{\bullet} \quad (18)$$

$$\text{AnC}^{\bullet}\text{(OT)} + \text{T(CA)}^{\bullet} \longrightarrow \text{AnC(=O)} + \text{T}_2\text{(CA)} \quad (19)$$

Scheme 2

If so, the absence of isomerization of the (recovered) pinacol indicates that the fragmentation of the cation radical in eqn. (17) is irreversible during the charge-transfer (retropinacol) process. However, the precise sequence of rapid follow-up steps (Scheme 2) is somewhat uncertain, since the trimethylsilyl group is also known to be highly labile in the cation radical[39,40] (Scheme 3).

$$[\text{AnC(OT)–CAn(OT)}^{+\bullet}, \text{CA}^{-\bullet}] \xrightarrow{k_1} \text{AnC}^{\bullet}\text{–CAn(OT)} + \text{T(CA)}^{\bullet} \quad (20)$$

$$\text{AnC}^{\bullet}\text{–CAn(OT)} \longrightarrow \text{AnC(=O)} + \text{AnC}^{\bullet}\text{(OT)} \quad (21)$$

$$\text{AnC}^{\bullet}\text{(OT)} + \text{T(CA)}^{\bullet} \longrightarrow \text{AnC(=O)} + \text{T}_2\text{(CA)} \quad (22)$$

Scheme 3

The extent to which k_1 is limited by the transfer of the trimethylsilyl group in eqn. (2), will be reflected in the quantum yield for charge-transfer retropinacol.[41] The latter is expected to follow the base strength of the quinone anion radical which decreases in the order: $FA^{-\bullet} \geqslant CA^{-\bullet} > CDQ^{-\bullet} > DDQ^{-\bullet}$.[42] Since the quantum yields in Table 4 consistently follow the opposite trend, the mechanistic formulation in Scheme 3 is unlikely to describe the follow-up process in charge-transfer retropinacol. Despite this minor ambiguity, the follow-up steps in Scheme 2 (or 3) are sufficiently rapid to drive charge-transfer retropinacol according to eqns. (5) and (6), and for purposes of further discussion will be treated by an operational (first-order) rate constant (k_1) for fragmentation. As such, the photoefficiency of charge-transfer retropinacol according to eqn. (15) and Scheme 2 (or 3) is determined by the magnitude of k_1 relative to the rate constant for back electron transfer (k_{et}). The quantitative relationship, as experimentally determined by the quantum yields in Table 3, is given[43] as eqn. (23).

$$\Phi = k_1/(k_1 + k_{et}) \quad (23)$$

Owing to our inability directly to measure the rates of back electron-transfer by time-resolved spectroscopy (*vide supra*), we initially select a single value of $k_{et} = 4 \times 10^{10}\ s^{-1}$ based on the kinetic results in Fig. 3. The resulting trend in the fragmentation rates evaluated in this way are reciprocally listed as the lifetime τ_{CT} in Table 8 to represent semiquantitative measures of cation-radical stabilities. Indeed, the value of τ_{CT} for $[AnCHOH]_2^{+\bullet}$, which is almost 30 times longer than that of $[An_2COH]_2^{+\bullet}$, accords with the expected difference in the energetics of secondary/tertiary benzylic scissions.[44] The importance of the pinacolic centres is indicated by $\tau_{CT} > 20\,000$ ps for the bicumene cation radical $\mathbf{7}^{+\bullet}$, which is at least a hundred times longer lived[45] than that of the analogous $\mathbf{2}^{+\bullet}$ or $\mathbf{2a}^{+\bullet}$. Furthermore, the absence of CT photochemistry from the bibenzyl

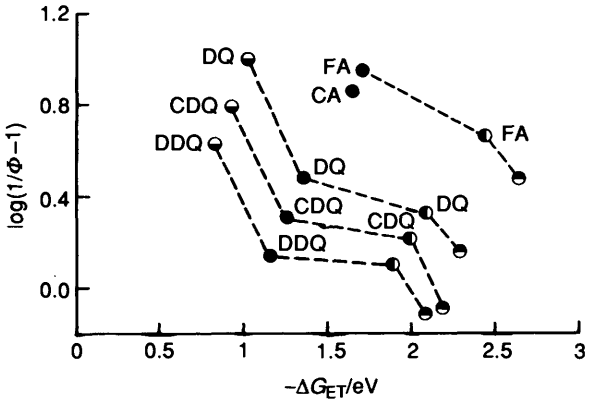


Fig. 5 Relative rates of back electron transfer (k_{et}) and fragmentation (k_f) for charge-transfer ion pairs from 3,4-dimethoxytoluene (◒), 4-methoxytoluene (●), toluene (◐) and 4-bromotoluene (◓) with the quinones in Chart 2 according to eqn. (24), as a function of the driving force ($-\Delta G_{ET}$) for back electron transfer

analogue indicates that the scission of $\mathbf{6}^{+\bullet}$ is too slow effectively to compete with back electron transfer.

As revealing as the qualitative trends in τ_{CT} may be, an alternative (more rigorous) approach is desirable to evaluate the relative stabilities of pinacolic donors. In particular, the competition between back electron transfer and fragmentation can be directly evaluated from the quantum yields by rearranging eqn. (23) to eqn. (24).

$$k_{et}/k_1 = (1 - \Phi)/\Phi \qquad (24)$$

Let us now consider the aryl pinacols **8**, **2**, **4** and **5**, which differ only in the ring substituents. For such a series of donors, the driving force ($-\Delta G_{et}$) for back electron transfer[5,6] can be uniformly evaluated from the redox potentials E°_{ox} and E°_{red} for the substituted toluenes and the quinones listed in Table 1 and Chart 2, respectively. Such values of $-\Delta G_{et}$ for the four series of toluene/quinone pairs in Table 1, when plotted against the values of log ($1/\Phi - 1$) from Table 4, yield the set of more or less parallel curves in Fig. 5. According to eqn. (24), the consistent downward trends in the slopes with increasing driving force largely reflect the rates of back electron transfer (k_{et}) which lie in the Marcus inverted region, as generally found in other CT ion pairs.[46,50] Thus for a given quinone, the fragmentation rates (k_1) of the pinacols effectively increase to keep up with k_{et}, *i.e.*, substituents decrease the relative stabilities of aryl pinacol cation radicals qualitatively in the order: 2,4-dimethoxy < 4-methoxy < H (unsubstituted) < 4-bromo. Indeed, the same trend has been reported for the analogous bicumene cation radicals—those bearing electron-releasing substituents being more prone to fragment relative to those with electron-withdrawing substituents.[45] The values of $-\Delta G_{et}$ can also be used to evaluate k_{et} from the electron-transfer data previously reported for a somewhat related series of charge-transfer complexes of alkylbenzenes with dicyano-and tetracyano-anthracenes.[48a] Based on these values of k_{et} and eqn. (23), the relative rates of fragmentation of the cation radicals of the 2,4-dimethoxy-, 4-methoxy-, H-(unsubstituted) and 4-bromo-substituted pinacols **8**, **2**, **4** and **5** are k_1 (relative) ~ 5000, 70, 1.0 and 0.2. The particularly fast fragmentation rates for cation radicals of the dimethoxy- and methoxy-substituted aryl pinacols can be accounted for by the enhanced stabilization of the cleavage products, particularly the cationic benzhydryl moiety [see eqn. (16)].[50] The same mechanistic conclusion can be reached from the lifetimes (τ_{CT}) of the cation radicals from the various anisyl donors in Table 8.

Photosensitization of Pinacol Cleavage with Quinones.—The clean spectral separation of the chloranil absorption (λ_{max} = 375 nm) from the charge-transfer absorption allows the separate evaluation of the efficiency of pinacolic cleavage *via* the diffusional quenching of the locally excited chloranil. Thus earlier photophysical studies established the direct excitation of the π–π^* band of benzoquinones to result in the efficient formation of the quinone triplet, which is quenched (k_q) by the aromatic donor to yield the triplet ion pair with nearly unit efficiency.[17,36,51] As applied to the chloranil-sensitized cleavage of anisyl pinacols, the photophysical process is as shown in Scheme 4.

$$CA \xrightarrow{\lambda_{exc} \sim 350\ nm} {}^3CA \qquad (25)$$

$$^3CA + AnC(OT)-CAn(OT) \underset{k_i}{\overset{k_q}{\rightleftharpoons}} {}^3[CA^{-\bullet}, AnC(OT)-CAn^{+\bullet}(OT)] \qquad (26)$$

$$^3[CA^{-\bullet}, AnC(OT)-CAn^{+\bullet}(OT)] \xrightarrow{k_{diff}} CA^{-\bullet} + AnC(OT)-CAn^{+\bullet}(OT) \qquad (27)$$

Scheme 4

According to Scheme 4, the rate of back electron transfer within the triplet ion pair in eqn. (26) is limited by the rate constant k_i for spin inversion (that is of the order of the electron spin–lattice relaxation time of 10^{-7} s or more).[52,53] As a result, back electron transfer generally follows diffusive separation (k_{diff}) and the second-order recombination of the free ions (with one-quarter efficiency).[36,54] On these sub-microsecond timescales, the short-lived pinacolic cation radicals can suffer extensive (first-and second-order) decomposition, *i.e.* eqns. (28)–(30)

$$AnC(OT)-CAn^{+\bullet}(OT) \xrightarrow{k_f} AnC^{+}-OT + AnC^{\bullet}-OT \qquad (28)$$

$$AnC^{+}-OT + CA^{-\bullet} \longrightarrow AnC{=}O + T(CA)^{\bullet} \qquad (29)$$

$$AnC^{\bullet}-OT + T(CA)^{\bullet} \longrightarrow AnC{=}O + T_2(CA) \qquad (30)$$

and/or

$$AnC(OT)-CAn^{+\bullet}(OT) + CA^{-\bullet} \xrightarrow[[-T(CA)^{\bullet}]]{k_2} AnC(O^{\bullet})-CAn(OT), \textit{etc.} \qquad (31)$$

as judged by the lifetimes in Table 8. That back electron transfer is not a governing factor, is indeed seen by the quantum yields in Table 8 that are close to unity, and essentially invariant for all the anisyl pinacols.

In the case of the bicumene derivative **7**, the somewhat reduced quantum yield of $\Phi = 0.25$ for the formation of the α-methylstyrene in eqn. (9) indicates that the fragmentation of the cation radical occurs with $k_f \sim 10^7\ s^{-1}$,[55] eqns. (32)–(34).

$$AnC(Me)(Me)-CAn^{+\bullet}(Me)(Me) \xrightarrow{k_f} AnC^{+}(Me)(Me) + AnC^{\bullet}(Me)(Me) \qquad (32)$$

$$AnC^{+}(Me)(Me) + CA^{-\bullet} \longrightarrow AnC(=CH_2)(CH_3) + H(CA)^{\bullet} \qquad (33)$$

$$AnC^{\cdot}(Me)_2 + H(CA)^{\cdot} \longrightarrow AnC(CH_2)(CH_3) + H_2(CA) \quad (34)$$

Photosensitization of the bibenzyl donor **6** by chloranil leads to the stilbene in eqn. (10) with a quantum yield $\Phi = 0.01$. Since the C–C bond cleavage of $\mathbf{6}^{+\cdot}$ is slow,[44] it is not surprising that the long lifetime allowed by Scheme 4 results in an alternative deprotonation (k_H) process, eqns. (35) and (36), at a rate that is typical for (cationic) benzylic centres.[56]

$$AnCH_2CH_2An^{+\cdot} + CA^{-\cdot} \xrightarrow{k_H} AnCHCH_2An + H(CA)^{\cdot} \quad (35)$$

$$AnCHCH_2An + H(CA)^{\cdot} \longrightarrow AnCH{=}CHAn + H_2(CA) \quad (36)$$

Comments on the Thermal Cleavage of Pinacols with Quinones.—The majority of quinone EDA complexes of anisyl (pinacol) donors examined in this study persist for prolonged periods, provided the solutions are protected from light, even adventitious room light. However, in some instances, the quinone/pinacol complexes react spontaneously in the dark. For example, the characteristically broad charge-transfer band is fleeting when the quinone is the high-potential dichlorodicyanoquinone DDQ and the pinacol is the tetraanisyl derivative **3**—the blue-green colour disappearing in less than 15 min after the solutions are mixed [see eqn. (12)]. We infer from the successively slower reactions of **3** with the chlorodicyano- and dicyano-quinones CDQ and DQ, respectively, that the decreased reduction potentials of these quinones (see Chart 2) are relevant, especially since the charge-transfer colours with chloranil and fluoranil are persistent. Moreover, the retropinacol process in eqn. (12) obtains in the dark only with **3**, which is the most electron-rich pinacol in Chart 1 from the spectral shifts of the CT bands in Table 1. In other words, the dark reactions derive from EDA complexes that clearly involve the most electron-rich donors and electron-poor acceptors, as judged by their oxidation and reduction potentials. Thus the inspection of Table 1 and Chart 2 reveals that the driving force for electron transfer, when evaluated as $-\Delta G_{et} = F(E^{\circ}_{ox} + E^{\circ}_{red})$, is the largest for DDQ then CDQ and DQ, especially when these acceptors are paired with the tetraanisyl pinacol **3** (or **3a**). As such, we propose the dark (thermal) process to arise *via* essentially the same multistep mechanism as that proposed in eqn. (15) and Scheme 2 for charge-transfer retropinacol—the difference arising from an initial *adiabatic* electron-transfer, eqn. (37), that is thermally allowed when the driving force $-\Delta G_{et}$ is sufficient to surmount the barrier that is otherwise overcome by charge-transfer activation in eqn. (15).

$$\begin{matrix} | & | \\ An_2C-CAn_2 \\ | & | \end{matrix} + DDQ \xrightarrow{k_T} \begin{matrix} | & | \\ An_2C-CAn_2^{+\cdot} \\ | & | \end{matrix} + DDQ^{-\cdot} \quad (37)$$

Summary and Conclusions

The photoinduced cleavage of benzopinacol and related diphenylethane donors (D) with various quinones (A) can be effected by two complementary processes involving (*a*) the *charge-transfer activation* ($h\nu_{CT}$) of the precursor [D,A] complex, and (*b*) *photosensitization via* the local excitation ($h\nu_A$) of the quinone acceptor followed by diffusional quenching with donor. Photoactivation in both cases results in electron transfer to generate the cation radical ($D^{+\cdot}$), in which the lability to C–C bond cleavage determines the photo-efficiency of the retropinacol process.

In charge-transfer activation, back electron transfer from the ion pair $[D^{+\cdot}, A^{-\cdot}]$ provides the competition for delimiting the quantum yields to only the most labile pinacol cation radicals with the estimated lifetimes in Table 8. In chloranil photosensitization, back electron transfer from the triplet ion pair $^3[D^{+\cdot}, A^{-\cdot}]$ is essentially precluded. As a result, the relatively long lifetimes of $D^{+\cdot}$ following diffusive separation, leads to quantum yields in Table 7 that approach unity for the retropinacol process. Thus, even bicumene which is (essentially) inert in charge-transfer activation, is subject to oxidative fragmentation *via* photosensitization with reasonable quantum yields.

Photoinduced cleavages of benzopinacols and diphenylethanes *via* charge-transfer activation and photosensitization have their thermal counterpart, in which the high-potential quinones DDQ, CDQ, *etc.*, oxidatively cleave the most electron-rich pinacols in the dark. In such cases, the driving force ($E^{\circ}_{ox} + E^{\circ}_{red}$) is sufficient to allow (adiabatic) electron transfer in eqn. (37). The latter is thus reminiscent of the diffusional quenching of the locally excited quinone in eqn. (26) (Scheme 4). Such mechanistic conclusions provide a relevant link to the unifying theme from the photochemical and thermal activations of electron transfer in various other organic processes.[57]

Experimental

Materials.—Tetrachloro-*p*-benzoquinone (chloranil, Aldrich) was sublimed *in vacuo* and recrystallized from benzene. 2,3-Dichloro-5,6-*p*-benzoquinone (DDQ, Aldrich) was recrystallized from a mixture of benzene and chloroform. Tetrafluoro-*p*-benzoquinone (fluoranil) was obtained from tetrafluorohydroquinone (Aldrich) by oxidation with ceric ammonium nitrate (Fisher).[58] 2,3-Dicyano-*p*-benzoquinone (DQ) prepared from the N_2O_4 oxidation of 2,3-dicyanohydroquinone (Aldrich),[59] was recrystallized from a 3:1 mixture of benzene and chloroform. DQ was converted into 5-chloro-2,3-dicyanohydroquinone by HCl addition in chloroform; the product was oxidized with N_2O_4 to 5-chloro-2,3-dicyano-*p*-benzoquinone (CDQ) which was recrystallized from a 3:1 vol/vol mixture of benzene and chloroform. Bis(trimethylsilyl)tetrachlorohydroquinone (T_2Q) was prepared from chloranil, hydrazine and hexamethyldisilazane (Aldrich) in toluene according to Kricheldorf and Kociel.[28] $\delta(CD_3COCD_3)$ 0.33 (s, 18 H).[60]

1,2-*Bis*(4-*methoxyphenyl*)-1,2-*bis*(*trimethylsiloxy*)*ethane* **1** was prepared from *p*-anisaldehyde (Aldrich) by reductive coupling with magnesium in the presence of chlorotrimethylsilane (Aldrich) in hexamethylphosphoric triamide as described by Chan and Vinokur.[26] Yield 40%, m.p. 94–95 °C (single isomer).

2,3-*Bis*(4-*methoxyphenyl*)-2,3-*bis*(*trimethylsiloxy*)*butane* **2** was prepared from 4-methoxyacetophenone (Aldrich) by a similar procedure. Yield: 45%; m.p. 130 °C (single isomer).

2,3-*Bis*(3,4-*dimethoxyphenyl*)-2,3-*bis*(*trimethylsiloxy*)*butane* **8** was prepared from 3,4-dimethoxyacetophenone by the Chan and Vinokur procedure.[26] Yield: 40%, m.p. 130 °C (single isomer).

1,1,2,2-*Tetrakis*(4-*methoxyphenyl*)-1,2-(*trimethylsiloxy*)-*ethane* **3** was prepared from the photoreduction of 4,4-dimethoxybenzophenone (Aldrich) with bis(trimethylsilyl)mercury in benzene as described by Neumann and coworkers.[29] Yield 30%, m.p. 117–118 °C.

1,2-*Diphenyl*-1,2-*bis*(*trimethylsiloxy*)*butane* **4** was obtained *via* the ultrasonically promoted reductive coupling of acetophenone (Aldrich) with zinc dust in the presence of chlorotrimethylsilane in THF, according to Boudjouk and coworkers.[61] Yield 75%. The mixture of isomers was resolved into the (±)- and *meso*-components by fractional crystallization. *meso*: δ-($CDCl_3$) 7.65–7.20 (m, 10 H), 1.40 (s, 2 CH_3), −0.13 (s, 2 $SiMe_3$); (±): δ 7.10–6.80 (m, 10 H), 1.78 (s, 2 CH_3), 0.06 (s, 2 $SiMe_3$).

2,3-*Bis*(4-*bromophenyl*)-2,3-*bis*(*trimethylsiloxy*)*butane* **5** was prepared from 4-bromoacetophenone (Aldrich) and zinc as described above.[61] Yield 40% as a mixture of (±)- and *meso*-isomers (not separated).

1,2-*Bis*(4-*methoxyphenyl*)*ethane*-1,2-*diol* **1a** was prepared from the initial condensation of anisaldehyde with potassium cyanide,[62] followed by the reduction of anisoin with lithium aluminium hydride.[63] Yield 50%, m.p. 168 °C.

2,3-*Bis*(4-*methoxyphenyl*)*butane*-2,3-*diol* **2a** was prepared *via* the reductive coupling of 4-methoxyacetophenone.[64] Yield 45% as a mixture of (±)-and *meso*-isomers. (±): δ($CDCl_3$) 7.15 (m, 4 H), 6.76 (m, 4 H), 3.80 (s, 2 OMe), 2.20 (s, 2 OH), 1.55 (s, 2 CH_3); *meso*: δ 7.36–6.81 (m, 8 H), 3.80 (s, 2 OMe), 2.53 (s, 2 OH), 1.46 (s, 2 CH_3).

1,1,2,2-*Tetrakis*(4-*methoxyphenyl*)*ethane*-1,2-*diol* **3a** was prepared from the photo-coupling of 4,4-dimethoxybenzophenone in isopropyl alcohol.[63] Yield 35%, m.p. 182 °C.

1,2-*Bis*(4-*methoxyphenyl*)*ethane* **6** was prepared from 4-methoxybenzyl alcohol by conversion into 4-methoxybenzyl chloride with thionyl chloride,[65] followed by reductive coupling with magnesium in ether.[44a] Yield 40%, m.p. 125 °C.

2,3-*Bis*(4-*methoxyphenyl*)*butane* **7** was prepared from 4-methoxyacetophenone by Grignard addition of methylmagnesium iodide, followed by the coupling of the alcohol with McMurray's reagent (titanium trichloride–lithium aluminium hydride).[66] Yield: 25%; m.p. 182–3 °C.

Dichloromethane (Mallinckrodt, reagent) was repeatedly stirred with fresh aliquots of conc. sulfuric acid until the acid layer remained colourless. It was then washed successively with water, and aqueous sodium hydrogen carbonate, and dried over anhydrous calcium chloride. It was initially distilled from phosphorus pentaoxide, and then redistilled from calcium hydride and stored in a Schlenk flask under an atmosphere of argon.

Instrumentation.—Electronic absorption spectra were recorded on a Hewlett–Packard 8450-A diode-array spectrometer with 2 nm resolution. Infrared spectra were obtained on a Nicolet 10 DX FT-IR spectrometer with 2 cm resolution by using KBr disks from solid samples or a NaCl cell. ^{1}H NMR spectra were measured in [^{2}H]chloroform or [$^2H_6$]acetone on either a JEOL FX90Q or a General Electric QE 300 FT spectrometer with Me_4Si as the internal standard. Gas chromatographic analyses were performed on a Hewlett–Packard 5890 gas chromatograph with 12.5 m cross-linked dimethylsilicone capillary column. GC–MS measurements were carried out on a Hewlett–Packard 5890A chromatograph interfaced to an HP 5970 mass spectrometer (70 eV, *EI*). Melting points determined on a MEL-TEMP are uncorrected. Elemental analyses were performed by Atlantic Microlab, Norcross, GA 30091.

Steady-state photochemical experiments utilized a focused beam from either a 500 W Osram (HBO-212) high pressure Hg lamp or an Osram 450 W xenon lamp. The beam was passed through an IR (water) filter, coupled to the appropriate sharp cut-off or interference filter and then onto a fused quartz 1 cm cell immersed in a water bath (transparent Pyrex Dewar).

The time-resolved (picosecond) spectroscopic studies were carried out with a laser-flash system that utilized the 532 nm (second harmonic) and 355 nm (third harmonic) 30 ps pulses from a Quantel YG-402 mode-locked Nd^{3+}:YAG laser as the excitation sources for the charge-transfer and photosensitization processes, respectively. The excitation beam was focused onto the sample contained in an argon-flushed 1 cm fused quartz fluorimeter cell as described previously.[43]

Spectrophotometric Determination of the Formation Constant of Quinone EDA Complexes.—The formation constant of the chloranil EDA complex with 4-methoxytoluene in eqn. (3) was measured by the spectrophotometric method of Benesi and Hildebrand.[22] In a typical experiment, a 1.0 cm^3 aliquot of a standard stock solution of chloranil (5 mmol dm^{-3}) in dichloromethane was treated serially with 400, 800, 1200, 1600 and 3200 equiv. of 4-methoxytoluene, and the mixture diluted to 5.0 cm^3 with additional dichloromethane. The absorbance A_{CT} at the maximum of the charge-transfer band at λ_{CT} = 498 nm was measured for each solution. The plot of [CA]/A_{CT} *versus* [$AnCH_3$]$^{-1}$ was linear, to evaluate (K_{EDA} ε_{CT})$^{-1}$ from the slope and ε_{CT}^{-1} from the intercept. The estimated errors in K_{EDA} = 0.32 dm^3 mol^{-1} and ε_{CT} = 1500 dm^3 mol^{-1} cm^{-1} were ±8%, as judged by the saturation fraction of 0.11–0.5 at the values of [CA] and [$AnCH_3$] employed in this study.[67]

Charge-transfer Activation of Quinone EDA Complexes with Anisyl(Pinacol) Donors.—In a typical experiment, a solution of 0.02 mol dm^{-3} chloranil and 0.02 mol dm^{-3} anisyl (pinacol) donor in 5 cm^3 of dichloromethane was irradiated with the focused beam from a 500 W Hg lamp passed through a 500 nm (Pyrex) sharp cut-off filter. When the orange solution was bleached (~ 1 h), the photolysate was evaporated *in vacuo* and the solvent replaced with [$^2H_6$]acetone. Either nitroethane or pentamethylbenzyl chloride was added as an internal standard for ^{1}H NMR analysis. For example, (TMS)pinacol **2** yielded a mixture of 4-methoxyacetophenone [δ 3.87 (methoxy) and 2.50 (methyl)] and 1,4-bis(trimethylsiloxy)tetrachlorobenzene [δ 0.33 (trimethylsiloxy)] in a 2:1 molar ratio. The same results were obtained by GC–MS analysis by quantitative comparison with authentic samples (*vide supra*). The photoinduced cleavages of the parent pinacol **2a**, as well as the analogues **1**, **1a**, **3** and **3a** proceeded in a similar manner. No photoreaction resulted from the treatment of the bicumene and bibenzyl analogues **6** and **7** under the same conditions, GC analysis of the photolysates indicating no consumption of the starting materials.

Charge-transfer activation of pinacol **8** with DDQ at λ_{exc} > 580 nm for 10 h led to the partial bleaching of the intense green (λ_{exc} = 688 nm) solution. Analysis of the photolysate indicated the presence of 3,4-dimethoxyacetophenone [δ 0.41 (methyl)] and 2,3-dichloro-5,6-dicyano-1,4-bis(trimethylsiloxy)]benzene-[δ 0.41 (trimethylsiloxy)], both in 30% yields. Treatment of the same pinacol with 2,3-dicyanobenzoquinone with λ_{exc} > 580 nm yielded the same dimethoxyacetophenone, together with 2,3-dicyano-1,4-bis(trimethylsiloxy)benzene [δ 0.28 (trimethylsiloxy)].

Owing to the successful isolation of the (±)- and *meso*-isomers of (TMS)pinacol **4** (*vide supra*), the reversibility in charge-transfer retropinacol was examined as follows. A yellow solution of 0.028 mol dm^{-3} *meso* isomer I of **4** and 0.14 mol dm^{-3} DDQ in 5.5 cm^3 of dichloromethane was irradiated in a 10 cm cell at λ_{exc} > 580 nm. Careful examination of the (almost colourless) photolysate (after standard work-up) by ^{1}H NMR spectroscopy indicated no isomerization of the residual of I, as judged by its diagnostic singlet resonance at δ – 0.13. The detection limit of the (±)-isomer II was established as < 1% by the observation of its characteristic singlet resonance at δ 0.06, when this amount was deliberately added to the photolysate. However, the equivalent experiment carried out with the (±)-isomer II of **4** and DDQ (by irradiation at λ_{exc} > 400 nm) indicated the absence of isomer I in the photolysate.

Quinone Photosensitization of(Anisyl) Pinacol Cleavage.—In a typical experiment, a solution of 7 × 10^{-3} mol dm^{-3} chloranil and an equimolar amount of the (anisyl) pinacol donor in 5 cm^3 of dichloromethane was irradiated with a focused beam from a 500 W Hg lamp that was passed through a tandem filter (consisting of a 380 nm sharp cut-off filter coupled to a broad-

band filter with a transmission between 320 and 480 nm) to effect a 100 nm window between 380 and 480 nm. After roughly an hour, the photolysate was evaporated *in vacuo* and analysed as described above. The photochemical products obtained from the pinacols and their trimethylsilyl ethers in Chart 1 were the same as those obtained *via* charge-transfer activation. The chloranil-sensitized activation of 2,3-di(4-methoxyphenyl)-2,3-dimethylbutane 7 afforded 2-(4-methoxyphenyl)propene, by the comparison of its ^{1}H NMR spectrum and GC–MS behaviour with that of an authentic sample (Aldrich), together with tetrachlorohydroquinone. The photochemical conversion of 1,2-di(4-methoxyphenyl)ethane under the same conditions led to 4,4′-dimethoxystilbene (Aldrich) as the sole product derived from the donor.

The Determination of Quantum Yields for the Photoactivation of Anisyl (Pinacol) Donors with Quinones.—All quantum yields were determined with a standard photochemical set-up consisting of a 450 W xenon lamp, equipped with an infrared (water) filter and an appropriately chosen narrow-band (±5 nm) interference filter (Ditric Optics). The light intensity was measured with an aqueous solution (10 cm^3) of Reineckate salt[30,68] in which a 1.0 cm^3 aliquot served as a dark control. The remainder was placed in either a 6 cm^3 cuvette with 10 cm pathlength or a 3 cm^3 cuvette with a 1 cm pathlength that was generally irradiated for 8–12 min. A 1.0 cm^3 aliquot of the irradiated solution (and the dark control) were diluted to 10 cm^3 with an aqueous 0.1 mol dm^{-3} ferric nitrate containing 0.5 mol dm^{-3} perchloric acid. After 45 min, the absorbance difference was measured at 450 nm, and the light flux (determined as einsteins min^{-1}) was found to be invariant (±5%) over the course of several hours.

The charge-transfer retropinacol was typically carried out with a solution of chloranil (0.2 mmol) and anisyl (pinacol) donor (0.4 mmol) in 10 cm^3 of dichloromethane. A 1.0 cm^3 aliquot was removed from the dark control, and the remainder used to fill the quartz cuvette to capacity. Irradiation at λ_{exc} = 505 nm was generally carried out to 5–10% conversion. Removal of a 1.0 cm^3 aliquot of photolysate (and dark control) was followed by dilution with 5.0 cm^3 dichloromethane. The change in chloranil absorbance at λ_{max} = 375 nm (ε = 220 dm^3 mol^{-1} cm^{-1}) was used to indicate the course of CT retropinacol. In selected cases, GC–MS analysis verified the validity of this measurement. The quantum yields in Table 3 were averages of triplicate runs and were reproducible to within ±10%. The photoefficiencies of the charge-transfer retropinacol with other quinones were carried out with the same procedure, summarized as follows. For the fluoranil acceptor, (λ_{max} = 330 nm and ε_{max} = 380 dm^3 mol^{-1} cm^{-1}) the excitation light was λ_{exc} = 440 nm. For the 2,3-dicyanobenzoquinone acceptor (λ_{max} = 440 nm and ε_{max} = 30 dm^3 mol^{-1} cm^{-1}), the 560 nm filter was used for λ_{exc}. For 2,3-dichloro-4,5-dicyanobenzoquinone (λ_{max} = 390 nm and ε_{max} = 890 dm^3 mol^{-1} cm^{-1}), the irradiation was carried out with λ_{exc} = 540 nm. For 5-chloro-2,3-dicyanobenzoquinone (λ_{max} = 350 nm and ε_{max} = 400 dm^3 mol^{-1} cm^{-1}), the 580 nm filter was used for λ_{exc}.

The quinone photosensitized cleavage of pinacol was typically carried out with 0.1 mmol of chloranil and 0.2 mmol of donor in 5 cm^3 of dichloromethane by irradiation at λ_{exc} = 405 nm. After 5–10% conversion, a 1.0 cm^3 aliquot was diluted with 5 cm^3 of dichloromethane, and the decrease in chloranil absorbance measured at 375 nm (ε = 220 dm^3 mol^{-1} cm^{-1}). The photoproducts (carbonyl compound and tetrachlorohydroquinone) were quantitatively analysed by GC–MS to confirm the chloranil conversion. Values of the quantum yields in Table 7 were measured in triplicate and were reproducible to within ±10%.

Thermal Cleavage of Tetraanisyl Pinacol Donors with High Potential Quinones.—The addition of the bis-trimethylsilyl ether of the tetraanisyl pinacol **3** (0.10 mmol) to a solution of 0.10 mmol DDQ in 3 cm^3 of dichloromethane resulted in a bright blue–green solution, which spontaneously decolourized upon standing in the dark. Evaporation of the solvent *in vacuo* was followed by the addition of [$^2H_6$]acetone, and ^{1}H NMR analysis indicated the complete conversion into 4,4′-dimethoxybenzophenone [δ 7.75 (m), 7.04 (m) and 3.89 (s)] by comparison with an authentic sample, together with the bis-trimethylsilyl ether of 2,3-dichloro-4,5-dicyanohydroquinone [δ 0.41 (s)]. A similar treatment of **3** with 2,3-dicyanobenzoquinone afforded a green solution which upon standing in the dark for 5 h yielded 4,4′-dimethoxybenzophenone (40%) and the bis-trimethylsilyl ether of 2,3-dicyanobenzoquinone [δ 0.28 (s)].

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