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ELECTRO-ORGANIC REACTIONS. PART 32. ELECTROGENERATED BASES FROM QUINONEMETHIDES

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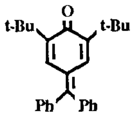
Abstract: The radical-anion of fuchsone (1), and the dianions of related quinonemethides, are generated at low cathodic potentials and act as bases in high yielding Wittig reactions; the phenolic product may be oxidatively reconverted into quinonemethide.

Organic dianions and radical-anions, generated cathodically from *probases*, have been successfully used as bases.[1] For *in situ* generation of anionic bases the relevant reduction potentials of the probase must be lower than those of the other reactants and products. Steric hindrance at the basic centre is also an advantage as it reduces nucleophilicity. Where the probase is expensive or difficult to prepare, convenient regeneration from the protonated form is desirable; this has been achieved in some cases by chemical or electrochemical oxidations[2,3].

We demonstrate herein that the radical-anion of the quinonemethide (1) and the dianions of (2) and (3), have useful basic properties; the hydrogenated products, the corresponding phenols, are conveniently re-oxidised to quinonemethide. The radical-anions are formed at modest potentials yet function as useful oxygen-anion bases in aprotic solvent.



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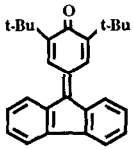

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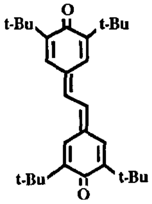

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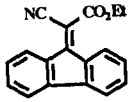

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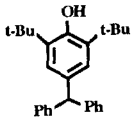

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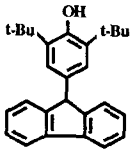

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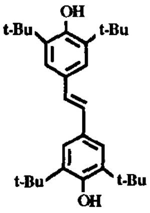


(7)

Results and Discussion. Cyclic voltammetric experiments gave for fuchsone (**1**) two reduction peaks; the first is reversible and the second irreversible. The quinonemethides (**2**) and (**3**) each give two reversible reduction peaks. In the presence of molar equivalents of benzyltriphenylphosphonium bromide the second wave for (**2**) becomes irreversible and the first wave for (**1**) becomes quasi-reversible in that the anodic peak current is slightly decreased. The relevant peak potentials are given in Table 1 together, for comparison, with those for one example, (**4**), of the fluoren-9-ylidine probases[4].

Table 1. Quinonemethide reduction: cyclic voltammetric data[a]

Entry	Quinonemethide	$-E_{p,c}(1)$	$-E_{p,a}(1)$	$-E_{p,c}(2)$	$-E_{p,a}(2)$
1	(1)	0.98	0.91	1.50	-
2	(2)	0.39	0.32	0.91	0.85
3	(3)	0.22	0.15	0.49	0.43
4	(4)[b]	0.27	0.20	0.87	0.76

Footnote: (a) Hg bead cathode, DMF-Bu_4NClO_4 (0.1M), 0.5 Vs^{-1}, substrate *ca.* 1-2 mM reference Ag/AgI(s); (b) fluorenylidene derivative, 1.06 Vs^{-1}

Preparative-scale electrolyses are described in Table 2. Stilbene formation by Wittig or Wittig-Horner reaction was used as the test reaction; consequently the cell contents for *in situ* electrolysis included probase, benzaldehyde, and either benzyltriphenylphosphoniumbromide ($PhCH_2\overset{+}{P}Ph_3Br^-$) or diethyl benzylphosphonate ($PhCH_2PO(OEt)_2$).

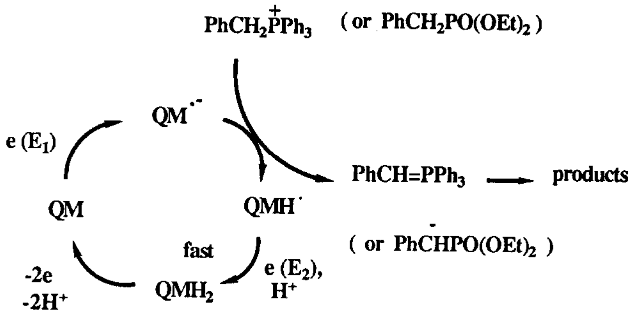
The major conclusion is that fuchsone (**1**) is a convenient probase and that its radical-anion, generated at -1.0V (*vs.* Ag/AgI(s)), effectively deprotonates both the phosphonium salt and the phosphonate. It is therefore a stronger base than the dianion[5] of (**4**) which does not effect a Wittig reaction between PhCHO and PhCH PO(OEt), a point demonstrated quantitatively by kinetic experiments (*vide infra*). The dianion of (2) works but is less effective. The radical-anion of (**3**) is not usefully basic, the corresponding dianion is.

The phenols (**5**)-(**7**) are the other major product of reaction and they may be recovered in high yield. Separate anodic oxidation of (**5**) gives efficient recovery of the probase (**1**) (Table 2, entry 2). This oxidation may also be achieved in the anode compartment of a cell whilst the cathodic compartment is in use for base generation. In one experiment (Table 2, entry 4) the phenol was re-oxidised to quinonemethide during prolonged work-up in air. The cycle shown in the Scheme, depicted only for the radical-anion case, is therefore established.

Table 2. Preparative-scale electrolyses[a]

	Reactants	E_{red}[b]	Major products[c]
1.	[(**1**), PhCHO, $PhCH_2\overset{+}{P}Ph_3$][d]	-1.00	PhCH=CHPh, 99% (*trans:cis*=1.9); (**5**), 90%
2.	(**5**)[e], $CaCO_3$	+1.90	(**1**), 72%; (**5**), 28%
3.	**cathode** [(**1**), PhCHO, $PhCH_2\overset{+}{P}Ph_3$][f]	-1.35	PhCH=CHPh, 90% (*trans:cis*=2.3); (**5**), 90%;
	anode [(**5**), $CaCO_3$][g]		(**1**), 58%; (**5**), 19%; others[h], 22%
4.	**cathode** [(**1**), PhCHO, $PhCH_2PO(OEt)_2$][i]	-1.10	PhCH=CHPh, 100% (*trans:cis*=9); (**5**), 32%; (**1**)[j], 56%
	anode [(**5**), $CaCO_3$]		(**1**), 60%; (**5**), 40%; others[k] traces
5.	[(**2**), PhCHO, $PhCH_2\overset{+}{P}Ph_3$][d]	-1.00	PhCH=CHPh, 48%; (*trans:cis*=1); (**6**), 95%
6.	[(**3**), PhCHO, $PhCH_2\overset{+}{P}Ph_3$][ℓ]	-0.70	PhCH=CHPh, 84% (*trans:cis*=1.3); (**7**), (**3**)[m]

Footnotes: (a) Divided cell, Al_2O_3 dried DMF-Bu_4NClO_4 (0.1M), N_2 atmosphere *ca.* 2 $F mol^{-1}$; solvent pre-electrolysed. (b) V *vs* Ag/AgI(s); (c) products from catholyte isolated chromatographically: from anolyte by ^1H n.m.r. analysis; (d) equimolar amounts, *ca.* 0.1 mmol; (e) Pt foil electrodes, 0.054 mmol (**5**); (f) Pt foil electrodes: scale, (**1**) 0.102 mmol, PhCHO 0.126 mmol, $PhCH_2\overset{+}{P}Ph_3Br^-$ 0.142 mmol; (g) (**5**) 0.094 mmol; (h) benzophenone, 15%: 2,6-di-t-butylbenzo-1,4-quinone; (i) Hg pool cathode, Pt foil anode; cathode reactants *ca.* 0.21 mmol, anode reactant, 0.054 mmol; (j) recovered after chromatography in air; (k) benzophenone, 2,6-di-t-butylbenzo-1,4-quinone; (ℓ) Hg pool cathode: (**3**), $PhCH_2\overset{+}{P}Ph_3Br^-$, 0.05 mmol, PhCHO 0.117 mmol; (m) not isolated.



QM = quinonemethide; $E_2 < E_1$

SCHEME

The kinetic basicity of the radical-anion of (**1**) has been compared with that of the dianion of (**4**) by measurement of rates of protonation in the presence of a 20-fold excess of dimethylmalonate. Pseudo first-order rate coefficients were determined by double potential step chronoamperometry using a modification of established methods[6].

The second-order rate coefficients so measured, in DMF at 25°C, are for $(\mathbf{1})^{\bullet-}$, $k = (1.38 \pm 0.14) \times 10^{4}\ \ell\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$), and for $(\mathbf{4})^{2-}$, $k = (7.24 \pm 0.63) \times 10^{2}\ \ell\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$ i.e. $(\mathbf{1})^{\bullet-}$ deprotonates dimethylmalonate about 19 times faster than does $(\mathbf{4})^{2-}$. Although formed at modest potentials $(\mathbf{1})^{\bullet-}$ is a relatively strong base. The effective base could be $(\mathbf{1})^{2-}$; $(\mathbf{1})^{2-}$ is strongly basic, possibly abstracting a proton from the Bu_4N^+ cation which would explain the irreversibility of the second wave. The dianion would be formed in low concentration, at the first reduction potential, by the rapid disproportionation:

$$2(\mathbf{1})^{\bullet-} \overset{K_d}{\rightleftharpoons} (\mathbf{1}) + (\mathbf{1})^{2-}$$

K_d may be calculated as *ca.* 10^{-11} from $[E_{p,c}(2)-E_{p,c}(1)]$; the uncertainly in this value arises from the irreversibility of the second reduction wave. The stationary state concentration of $(\mathbf{1})^{2-}$ is very low, but its intermediacy on the long time scale of preparative electrolyses cannot be ruled out at this stage.

Key experimental conditions are given as footnotes to Table 2. The preparation of the quinonemethides and characterisation of the phenolic products, together with details of further aspects of their electrochemistry, are fully described elsewhere[7].

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