

Homogeneous Rate Constants for Coupling between Electrochemically Generated Aromatic Anion Radicals and Alkyl Radicals

Steen U. Pedersen^a and Torben Lund^b

^aDepartment of Organic Chemistry, University of Aarhus, DK-8000 Århus C, Denmark and ^bInstitute of Lifescience and Chemistry, University of Roskilde, DK-4000 Roskilde, Denmark

Pedersen, S. U. and Lund, T., 1991. Homogeneous Rate Constants for Coupling between Electrochemically Generated Aromatic Anion Radicals and Alkyl Radicals. – Acta Chem. Scand. 45: 397–402.

Rate constants have been measured for the coupling between hexenyl radicals and 2,2-dimethylhexenyl radicals and electrogenerated anion radicals of anthracene, 9,10-diphenylanthracene, benzophenone and quinoxaline. The rate constant for all four reactions in *N,N*-dimethylformamide is $\log k_2 = 9.1(5)$, which is in accordance with previous results in 1,2-dimethoxyethane for naphthalene and benzophenone anion radicals and 1-hexenyl radicals. The data indicate that the redox potential of the aromatic anion radical has only a minor influence on the rate of coupling with alkyl radicals. The rate constants for anion radicals of 9,10-diphenylanthracene and benzophenone were somewhat lower, $6(1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, which for 9,10-diphenylanthracene might be caused by steric hindrance by the two phenyl groups. The conclusion is that the coupling reaction between aromatic anion radicals and alkyl radicals has all the characteristics of a radical–radical coupling.

In connection with recent attempts to estimate reversible redox potentials of alkyl and benzyl radicals from measured reduction potentials,^{1,2} it was desirable to determine rate constants for the coupling between different kinds of aromatic anion radicals and alkyl radicals. Only a few data on coupling rates between aromatic anion radicals and alkyl radicals have been reported. Garst *et al.* have obtained rate constants for the coupling reactions of naphthalene and benzophenone anion radicals with the 1-hexenyl radical.³ They found that 1-hexenyl radical couples with sodium naphthalene with a rate constant $k_2 = 2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in 1,2-dimethoxyethane (DME)^{3a,4} and with lithium diphenylketyl with $k_2 = 3.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in tetrahydrofuran (THF).^{3a,4} To our knowledge no other such coupling rates have been reported. We therefore decided to extend the available anion radical–radical coupling data in order to gain knowledge on some of the parameters influencing such rates.

Radical cyclization probes have been used in many investigations either to 'prove' involvement of radicals or as 'clocks' to measure reaction times for very fast reactions involving radicals.⁵ The 5-hexenyl radical, the rate of rearrangement of which has recently been recalibrated, is now regarded as a standard 'clock' in radical chemistry.⁶ Methyl substituted 6-halo-1-hexenes are available as faster 'clocks'.⁷ We have also used cyclopropylcarbiny radical as a radical probe but this system also isomerizes rapidly as an anion or cation. Newcomb recently discussed the use of radical cyclization probes emphasising the possibility of a radical chain isomerization sequence where the rate-deter-

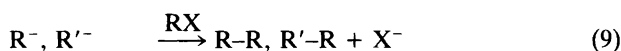
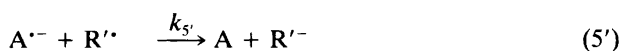
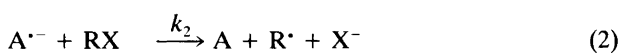
mining step is the halogen transfer from the alkyl halide (probe) to a radical.⁸ For probes with iodide this reaction sequence presents a very serious problem because the halogen transfer reaction is faster than most radical termination reactions. However, the termination step ($\text{A}^{\cdot-} + \text{R}^{\cdot} \xrightarrow{k} \text{AR}^-$) for even iodides will be around 100 times faster than the chain isomerization sequence emphasized by Newcomb. For bromides the chain isomerization sequence is at least 1000 times less important than for iodides.

Here we have measured the rate constant k_2 for coupling between electrochemically generated anion radicals of anthracene (**1**), 9,10-diphenylanthracene (**2**) and quinoxaline (**4**) in *N,N*-dimethylformamide (DMF) with the 2,2-dimethyl-1-hexenyl radical formed by dissociative electron transfer to 6-bromo-5,5-dimethyl-1-hexene (**6**). Benzophenone (**3**) and **4** were reacted with 6-bromo-1-hexene (**5**) and finally **4** was reacted with (bromomethyl)cyclopropane (**7**).

We were interested in reacting **1** and **2** with **5** but the initial electron transfer reaction is too fast so homogeneous reaction conditions can not be obtained. These radical clocks should elucidate the influence of the potential differences between aromatic anion radicals and radical clocks and the influence of steric hindrance on the rate constant for coupling between aromatic anion radicals and alkyl radicals.

The mechanism of the reaction between aromatic anion radical and alkyl halides is well established.⁹ The mechanism is shown in Scheme 1, where RX is a radical probe. The aromatic anion radical, $\text{A}^{\cdot-}$ is generated either chemically or electrochemically and transfers the electron to the

radical probe, RX. This latter undergoes dissociation concerted with the electron transfer (ET) to give the radical R[•] and the halide anion, X⁻, eqn. (2).¹⁰ Numerous investigations have focused on the measurements of k_2 .¹¹ The generated radical, R[•], can undergo a number of possible reactions. R[•] can isomerize to R'[•] in a fast reaction [eqn. (3)], (e.g. 1-hexenyl radical → cyclopentylmethyl radical,⁶ $k_3 = 2.35 \times 10^5 \text{ s}^{-1}$), and the two radicals R[•] and R'[•] can couple with an anion radical [(eqn. (4) and eqn. (4)'), respectively] or be reduced by the anion radical [(eqn. (5) and eqn. (5)'), respectively].



Scheme 1. Mechanism of the reaction between aromatic anion radicals (A^{•-}) and a radical probe (RX).

The competition between coupling (4) and indirect reduction (5) of the alkyl radical has recently been discussed with regard to the possibility of measuring the reduction and standard potential for various alkyl radicals.^{1,2} The competition parameter $q = k_5/(k_4 + k_5)$ is easily measured by linear sweep voltammetry.¹² The generated anions can either be protonated, [eqns. (6) and (7)] or react in a substitution reaction with the alkyl halide to form polyalkylated products [eqns. (8) and (9)]. However, the percentages of dialkylated products were always less than 10%. The dissociative electron transfer from AR⁻ to RX can generally be excluded because the oxidation potential of the former is approximately 1 V less cathodic than the

standard potential of A^{•-}. The sum ($k_4 + k_5$) relative to k_3 can be obtained from a product analysis of the reaction mixture. It is implicitly assumed in the following that $k_4' = k_4$. This assumption can be justified when both radicals R'[•] and R[•] are primary radicals and no serious steric hindrance is introduced into their β -positions during isomerization.

By measuring the ratio between RH and R'H, Garst *et al.*^{3a,4} determined that the sum ($k_4 + k_5$) is $4.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the reaction between the naphthalene anion radical (8) and the 1-hexenyl radical. The amount of coupling products (ARH + AR'H) was found to be the same as the total amount of reduced products (RH + R'H) which indicates that $k_4 = k_5$. This observation makes the product identification very easy because only the relative amount of RH and R'H has to be determined after each experiment, but the accuracy of k_4 will depend on the exact ratio between k_4 and k_5 . It was thus found that $k_4 = 2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, a number which has been widely accepted as a plausible rate constant for this fast radical-anion radical coupling without charge repulsion. This rate of Garst's has, however, been measured between the alkyl radical and a sodium-ion-paired anion radical in DME and the result might not be the same in DMF where ion-pairing is of less importance.

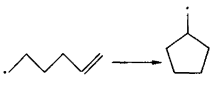
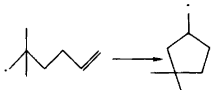

A new method for the indirect measurement of standard potentials for alkyl radicals has recently been published.^{1,2} Here k_4 was assumed to be equal to $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for all reactions between aromatic anion radicals and alkyl radicals. It is likely that the coupling reaction between two radicals without charge repulsion will be fast, probably near the diffusion limit and it is equally likely that differences in standard potentials between the two reactants will be less important than steric hindrance. It is however of interest to know which parameters influence the rate of coupling and to determine the importance of the parameters. It is particularly interesting to examine the influence of the standard potential of the electron donor on k_4 because we have postulated this dependency to be negligible in connection with the determination of reduction potentials of alkyl radicals.^{1,2}

All the alkyl radicals studied here are primary alkyl radicals for which it has been shown that the reduction potential is about -2.20 V vs. SCE and the reorganization energy for the electron transfer reaction (5) is about 30 kcal mol⁻¹.² This means that the second ET reaction, eqn. (5), for all the reactions studied here will be negligible, and the ratio k_4/k_5 can alone be calculated from the product ratio between AR'H and ARH. It should be noted that compared with the method of Garst we do not need the assumption that $k_4 = k_5$, but on the other hand the product identification is more tedious in this study because cyclized and non-cyclized coupling products have to be identified.

Results and discussion

The rate constants for the radical isomerization of the three clocks 5-7 used are given in Table 1. The isomerization reaction for 5 and 6 is the cyclization of the hexenyl radical

Table 1. The radical clocks employed, their isomerization reactions and the rate constant of the isomerizations.

RX	$R^{\cdot} \xrightarrow{k_3} R'^{\cdot}$	k_3/s^{-1} [Ref]
6-Bromo-1-hexene (5)		2.35×10^5 [6]
6-Bromo-5,5-dimethyl-1-hexene (6)		3.6×10^6 [7]
(Bromomethyl)cyclopropane (7)		1.3×10^8 [5]

to form the cyclopentylmethyl radical. For 7 the isomerization is the ring-opening of the cyclopropylmethyl radical to form the butenyl radical.

The Table 2 the measured rate constants k_2 for the reaction between the anion radicals of 1–4 and 5–7 are given. As expected for an ET reaction, the rate constant increases when the standard potential of the mediator becomes more negative. The fastest reaction measured is between 1 and 6 where the rate constant is measured to be $13.1 \text{ M}^{-1} \text{ s}^{-1}$. The time for complete mixing (1–2 s) is, however, much lower than the relevant half-life of $A^{\cdot-}$ (22.7 s for $[A^{\cdot-}]_0 = 1.5 \text{ mM}$ and $[RX]_0 = 2.09 \text{ mM}$). This means that almost all the coupling product is formed under homogeneous conditions and the reactions can be described by the usual coupled homogeneous differential equations.

The differential equations describing reactions (2)–(4) in Scheme 1 were solved numerically by the program Bego¹³ where the concentrations of all six reactants could be followed in arbitrary time steps. The ratio of final concentrations of the coupling products AR'H and ARH could thus be calculated for different experimental parameters $[A^{\cdot-}]_0$, $[RX]_0$, k_2 , k_3 and k_4 .

The range of the measurable rate constant for the coupling reaction, k_4 , is primarily determined by the rate of isomerization of the radical probe, k_3 , and by the detection

limits of the coupling products. Accurate determination of the product ratio $[AR'H]/[ARH]$ can be made in the range 0.05–20. This means that with the applied radical probes the range of measurable k_4 is from 2×10^7 to $2 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$. These limits are obtained from Bego when the appropriate limits in the experimental parameters are used. As the diffusion-limited rate constant, k_{dif} , is about $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, depending on the size of the reactants and the viscosity of the solvent,¹⁴ even diffusion-controlled coupling of the aromatic anion radical and the alkyl radical can be obtained by this method.

In Table 3 the percentage of isomerized coupling product is given for different concentrations of anion radical ($1^{\cdot-}$ – $4^{\cdot-}$) and radical probe (5–7). k_4 was determined iteratively employing Bego by using the experimental parameters and varying k_4 until the ratio $[AR'H]/[ARH]$ was equal to that found experimentally by gas chromatography (GLC). The calculated values of k_4 are included in Table 3.

Our results are shown in Table 4 together with the data previously reported by Garst for naphthalene (8) and benzophenone anion radicals (3) and 5 in DME. For the pure aromatic hydrocarbons (1, 2 and 8) the rate constant is almost equal whereas the two aromatics with heteroatoms deviate most from an average. The deviation is, however, less than a factor of 10 between the fastest and the slowest [$\log k_4 = 9.1(5)$]. It seems that k_4 is somewhat larger for 1 and 4 than for 2 and 3 which might be due to steric hindrance in 2 caused by the two phenyl groups, but, on the other hand, a similar value is found for diphenylketyl (3) and 5, and it is unlikely that there is any serious steric hindrance in the reaction with diphenylketyl. It was also observed that k_4 is insensitive to differences in the redox potential of the reactants. The difference in redox potential between 1 and 4 is more than 300 mV and the difference in k_4 is less than a factor of three. The same difference for a fast ET reaction like eqn. (5) would be a factor of approximately 1000 depending on the specific reorganization energy (30 kcal mol^{-1}) and the exact location of the donor's standard potential on the Marcus curve.

The findings in this study can be summarized in four points: (a) the rate of coupling between aromatic anion radicals and alkyl radicals is very high, almost at the diffusion limit, which means that the activation barrier ap-

Table 2. The rate constant k_2 for the electron transfer between aromatic anion radicals and radical clocks in 0.1 M TBABF₄ measured by the potentiostatic method.¹⁶

RX	A	$-E_A^{\cdot-}/V^a$	$k_2/\text{M}^{-1} \text{ s}^{-1}$
6-Bromo-1-hexene	Quinoxaline (4)	1.60	7.2
6-Bromo-5,5-dimethyl-1-hexene	Quinoxaline (4)	1.60	0.10
(Bromomethyl)cyclopropane	Quinoxaline (4)	1.60	6.0
6-Bromo-1-hexene	Benzophenone (3)	1.72	<50
6-Bromo-5,5-dimethyl-1-hexene	9,10-Diphenylanthracene (2)	1.78	4.1
6-Bromo-5,5-dimethyl-1-hexene	Anthracene (1)	1.89	13.1

^aMeasured against SCE.

Table 3. $[AR^{\cdot H}]/[ARH]$ found for different concentrations (mM) of $1^{\cdot-}-4^{\cdot-}$ and radical clocks; 5–7 in DMF/0.1 M TBABF₄. $T = 25^{\circ}C$.

A	$[A^{\cdot-}]_0/mM$	RX	$[RX]_0/mM$	$k_2/M^{-1} s^{-1}$	k_3/s^{-1}	$[AR^{\cdot H}]/[ARH]$	$k_4/M^{-1} s^{-1}$
4	6.0	6	18.7	0.10	3.6×10^6	0.32	3.5×10^9
4	5.7	6	15.9	0.10	3.6×10^6	0.59	3.0×10^9
4	3.0	6	19.4	0.10	3.6×10^6	0.82	4.0×10^9
4	8.0 ^a	5	82.0	7.2	2.3×10^5	<0.05	$>4 \times 10^9$
4	8.0 ^a	7	82.0	6.0	1.3×10^8	>20	$<4 \times 10^9$
3	1.2	5	2.52	<50	2.3×10^5	1.01	4.8×10^8
2	6.3	6	17.5	4.1	3.6×10^6	2.35	5.5×10^8
2	4.6	6	37.4	4.1	3.6×10^6	2.55	6.8×10^8
2	3.3	6	16.4	4.1	3.6×10^6	2.97	8.0×10^8
1	1.0	6	2.09	13.1	3.6×10^6	6.75	1.1×10^9
1	1.2	6	2.09	13.1	3.6×10^6	3.53	1.8×10^9
1	1.5	6	2.09	13.1	3.6×10^6	4.60	1.1×10^9

proaches zero; (b) the rate is insensitive to differences in redox potentials between the two reactants; (c) k_4 seems to be influenced by steric hindrance although this point needs further study, and finally (d) k_4 seems to be insensitive to the polarity of the solvent. These four observations are, however, common in radical chemistry.¹⁵ We therefore conclude that the aromatic anion radical behaves like a radical when it couples with an alkyl radical.

It was assumed in Refs. 1 and 2 that k_4 was equal to $1 \times 10^9 M^{-1} s^{-1}$ for all reactions between aromatic anion radicals and alkyl radicals. The present study has shown that this is true to within a factor of 2–3 for reasonably unhindered reactants. Small jumps in k_4 will show up in the q plots $[k_5/(k_5 + k_4)]$ versus E_A° as discontinuities. E° is, however, never obtained from a single measurement, but is determined from reactions of one alkyl radical with a number of aromatic anion radicals, and there will thus be some averaging in the determination of E° . If however for some reason all k_4 in one q -plot are off by a factor of two the maximum error in E° will be 75 mV, which is still acceptable in this kind of measurement.

Table 4. The rate constants of coupling between different anion radicals of aromatic compounds and alkyl radicals at 25 °C.

A	$-E_A^{\circ}/V^a$	RX	Solvent	$k_4/10^9 M^{-1} s^{-1}$
Naphthalene (8)	-2.46	5 ^b	DME	2.4 ^b
Anthracene (1)	-1.89	6	DMF	1.4(3)
9,10-Diphenylanthracene (2)	-1.78	6	DMF	0.7(1)
Benzophenone (3)	-1.72	5	DMF	0.5
Benzophenone (3)	-1.72	5 ^b	DME	0.36 ^b
Quinoxaline (4)	-1.60	6	DMF	3.5(4)

^aMeasured against SCE. ^bMeasured in Ref. 3.

Experimental

Materials. The mediators were the same as those used previously. The supporting electrolyte, Bu₄NBF₄, and the solvent, *N,N*-dimethylformamide, were purified by standard procedures.¹⁶

Compound 6 was synthesized according to Ashby *et al.*¹⁷ Compounds 5 and 7 and 4-bromo-1-butene (9) are commercially available (Aldrich) and were used as received. Bromomethylcyclopentane (10) was synthesized according to Noller.¹⁸

Equipment. Instrumentation and data treatment procedures have been described in detail elsewhere.¹⁶ The electrolyte solution was dried by being passed through a column containing activated alumina just before the experiments. A 10 μm platinum microdisc electrode and a rotating glassy carbon disc electrode were used in the potentiostatic method.¹⁹

GLC analysis was performed with a Hewlett Packard 5890A gas liquid chromatograph equipped with a 25 m OV-101 capillary column or an HP1 12 m capillary column, flow 1–2 ml min⁻¹, detector temp. 250 °C in 5 min to 270 °C rate 8 °C min⁻¹. Mass spectra were recorded with a Hewlett Packard MSD 5771A instrument.

Procedures. Potentiostatic method. The method has been described previously.¹⁹ All the experiments were carried out in DMF/0.1 M Bu₄NBF₄ at room temperature (25 °C). The determination of k_2 for 1 and 6 was made with a rotating glassy carbon disc electrode rotating at 3000 min⁻¹. For all the other measurements a 10 μm platinum microdisc electrode was used.

Preparative method. An H-cell with a 25 ml cathodic compartment was filled with DMF/0.1 M n-Bu₄NBF₄. 2–10 mmol of the aromatic compound were added. A steady-

state voltammogram was recorded at 20 mV s⁻¹. This voltammogram was S-shaped with a plateau instead of the peak and the forward and backward trace were coincident. The basis ($i_{b,b}$) and plateau ($i_{b,p}$) currents were measured. The aromatic compound was then reduced to the stable anion radical at a platinum foil electrode until the theoretical amount of charge had passed. Again a steady-state voltammogram was recorded and the current at the basis ($i_{a,b}$) and at the plateau ($i_{a,p}$) was measured. The actual concentration for aromatic anion radical was calculated from eqn. (10). The radical probe was then added to the stirred solution of aromatic anion radical and the strong colour of the latter gradually disappeared. When the solution became colourless two drops of acetic acid were added to protonate the electrogenerated bases.

$$[A^{\cdot-}] = [A] \cdot \frac{i_{a,b} - i_{b,b}}{i_{b,p} - i_{b,b}} \quad (10)$$

To the catholyte were then added 30 ml of water, after which it was extracted three times with 30 ml of diethyl ether. The ether solution was washed three times with 50 ml of water and dried overnight with molecular sieves (4 Å). Finally the solvent was evaporated and the sample analysed by GLC or GLC-MS.

Identification of coupling products. The GLC peaks corresponding to the cyclized coupling products AR'H and the non-cyclized coupling products ARH were identified in the following way.

The AR'H peaks obtained from the reactions of benzophenone (3) and quinoxaline (4) with 6-bromo-1-hexene (5) were identified by reaction 3 and 4 with the cyclized alkyl halide 10. In a similar way, the AR'H peaks from the reaction of 4 with (bromomethyl)cyclopropane (7) were identified by reacting 4 with the alkyl halide 9.

For the radical probe 6-bromo-5,5-dimethyl-1-hexene (6), the cyclized alkyl halide was not available. The AR'H products were instead identified by performing a preparative electrolysis in the presence of 6 at low current density (< 2 mA cm⁻¹) with rapid stirring. In this way a low steady-state concentration of anion radical was obtained resulting in a high ratio (> 10–20) of AR'H to ARH which was confirmed by ¹H NMR spectroscopy and GLC. A high yield of uncyclized coupling products ARH was obtained by generating a high anion radical concentration in the cathodic compartment of the electrolysis cell (10–20 mM) followed by the addition of the radical probe 6. Analysis of the product mixture by ¹H NMR spectroscopy and GLC, showed typically a two- to four-fold excess of ARH relative to AR'H. In all cases the retention times of the AR'H coupling products were longer than those of the ARH products, when positional isomers were compared.

Spectroscopic data are shown below for the main products in each of the following preparative electrolyses.

Reaction between 5 and benzophenone anion radicals 3⁻. Benzophenone (10.8 mg) in 25 ml DMF/0.1 M TBABF₄ was reduced at -1.4 V vs. Ag/AgI. After 5.7 C, 10.3 mg 5 in 0.5 ml DMF were added. The main products were identified by GLC-MS: 2-cyclopentyl-1,1-diphenylethanol: MS (m/z , %): 266 (0.6), 265 (1.2), 248 (1), 195 (6.2), 184 (12), 183 (100), 165 (2), 105 (59), 77 (21), 51 (2), 41 (3). 1,1-diphenyl-6-hepten-1-ol: MS (m/z , %): 248 (0.7), 184 (13), 183 (100), 165 (2), 152 (8), 105 (43), 91 (2), 77 (15), 51 (2), 41 (2).

Reduction of anthracene 1 and 6 at low current densities. Anthracene (50 mg) and 100 mg 6 were reduced in DMF/0.1 M TBABF₄ at -1.4 V vs. Ag/AgI with a current density of less than 2 mA cm⁻². The main product isolated was 9-(4,4-dimethylcyclopentylmethyl)-9,10-dihydroanthracene ¹H NMR (CDCl₃): δ 1.03 (s, 6 H), 1.2–1.7 (m, 7 H), 1.8–2.0 (q, 2 H), 3.84 (d, H₁₀, ²J_{10,10'} = 18.0 Hz), 3.95 (t, H₉, ³J = 7.3 Hz), 4.18 (d, H_{10'}, ²J_{10',10} = 18.0 Hz), 7.2–7.6 (m, 8 H). MS (m/z , %): 290 (0.7), 191 (0.9), 180 (20), 179 (100), 178 (50), 177 (3.7), 176 (4.5), 152 (2.4), 151 (1.4), 115 (0.7) 69 (1.1), 55 (2.8), 41 (4.1).

Reaction between 6 and high concentrations of anthracene anion radicals 1⁻. Anthracene (75 mg) in 30 ml DMF/0.1 M TBABF₄ was reduced at -1.5 V vs. Ag/AgI. After 50 C, 6 (100 mg) was added. The main product isolated was 9-(2,2-dimethyl-5-hexenyl)-9,10-dihydroanthracene, ¹H NMR (CDCl₃): δ 0.90 (s, 6 H), 1.3–1.47 (m, 2 H), 1.62 (d, 2 H, ³J = 5.9), 1.75–1.95 (m, 2 H), 3.80 (d, H₁₀, ²J = 17.58 Hz), 4.10 (t, H 9, ³J = 5.9 Hz), 4.16 (d, H_{10'}, ²J = 17.8 Hz), 4.82–5.0 (m, 2 H), 5.6–5.83 (m, 1 H), 7.2–7.6 (m, 8 H). MS (m/z , %): 290 (4.2), 191 (0.9), 180 (23.5), 179 (100), 178 (53), 177 (4.8), 152 (3.5), 115 (1.2), 55 (2.9), 41 (4.0).

Reduction of quinoxaline 4 and 6 at low current densities. Quinoxaline (50 mg) and 6 (100 mg) were reduced in 25 ml DMF/0.1 M TBABF₄ at -1.2 V vs. Ag/AgI at current densities less than 2 mA cm⁻². The main product isolated was 2-(4,4-dimethylcyclopentylmethyl)quinoxaline, ¹H NMR (CDCl₃): δ 1.02 (s, 6 H), 1.2–1.7 (7 H), 3.01 (d, 2 H, ³J = 7.6 Hz), 7.6–7.8 (m, 2 H), 7.95–8.1 (m, 2 H), 8.72 (s, 1 H). MS (m/z , %): 240 (6.5), 225 (1.8), 183 (6.2), 169 (12.0), 145 (25.2), 144 (100), 117 (6.6), 102 (8.8), 7.6 (6.7), 55 (6.6), 41 (9.0).

Reaction of 6 with quinoxaline anion radicals 4⁻ at high concentration. Quinoxaline (100 mg) was reduced in 25 ml 0.1 M TBABF₄/DMF at -1.4 V vs. Ag/AgI. After 122 C, 6 (74 mg) was added. The main product isolated was 2-(2,2-dimethyl-5-hexenyl)quinoxaline, ¹H NMR (CDCl₃): δ 0.97 (s, 6 H), 1.4 (t, 2 H), 2.1–2.25 (m, 2 H), 2.90 (s, 2 H), 4.9–5.05 (m, 2 H), 5.7–5.9 (m, 1 H), 7.67–7.9 (m, 2 H), 8.0–8.2 (m, 2 H), 8.67 (s, 1 H). MS (m/z , %): 240 (7.8), 225 (7.9), 185 (8.2), 171 (11.0), 145 (18.4), 144 (100), 143 (8.4), 117 (6.5), 102 (11.0), 55 (12.3), 41 (9.2).

Reduction of 9,10-diphenylanthracene 2 and 6 at low current densities. 9,10-Diphenylanthracene (33 mg) and **6** (74 mg) in 25 ml DMF/0.1 M TBABF₄ were reduced at -1.32 V vs. Ag/AgI with a current density of less than 0.1 mA cm⁻². GLC revealed five coupling products arising from the five possible coupling positions in 9,10-diphenylanthracene (positions 1, 2, 12, 13 and 14). The mass spectra of the AR'H coupling products were characterized by relative high ($M^+ = 442$) molecular ion. The mass spectrum of the major isomer showed MS (m/z , %): 443 (13), 442 (38), 332 (42), 331 (100), 330 (12), 254 (11), 253 (22), 252 (16), 69 (2.3), 55 (4.2), 41 (3.6).

Reduction of 9,10-diphenylanthracene 2 and 6 at moderate anion radical concentration. Diphenylanthracene (35.9 mg) was reduced at -1.50 V vs. Ag/AgI in 20.5 DMF/0.1 M TBABF₄. After the consumption of 10 C, **6** (63 mg) was added. Ten coupling products were detected by GLC, five peaks identified as AR'H products and five as ARH products. The mass spectrum of the major ARH product showed MS (m/z , %): 443 (0.09), 442 (0.19), 332 (34), 331 (100), 330 (90), 315 (4.1), 254 (13), 253 (19), 252 (14), 69 (1.6), 55 (1.8).

References

- Fuhlendorff, R., Occhialini, D., Pedersen, S. U. and Lund, H. *Acta Chem. Scand.* **43** (1989) 803.
- Occhialini, D., Pedersen, S. U. and Lund, H. *Acta Chem. Scand.* **44** (1990) 715.
- (a) Garst, J. F. and Barton, F. E. *Tetrahedron Lett.* (1969) 587; (b) Garst, J. F. and Smith, C. D. *J. Am. Chem. Soc.* **98** (1976) 1520; (c) Garst, J. F. *Acc. Chem. Res.* **4** (1971) 400; (d) Garst, J. F. In: Kochi, J. K., Ed., *Free Radicals*, Wiley 1972, Vol. 1, p. 520.
- The data of Garst *et al.* are referred to the isomerization rate of the 1-hexenyl radical. This value was originally $1.0 \times 10^5 \text{ s}^{-1}$ but was later recalibrated to $2.35 \times 10^5 \text{ s}^{-1}$ (Ref. 6).
- (a) Griller, D. and Ingold, K. U. *Acc. Chem. Res.* **13** (1980) 317; (b) Maillard, B., Forrest, D. and Ingold, K. U. *J. Am. Chem. Soc.* **98** (1976) 7024.
- Chatgililoglu, C., Ingold, K. U. and Scaiano, J. C. *J. Am. Chem. Soc.* **103** (1981) 7739.
- Beckwith, A. L. J., Easton, C. J., Lawrence, T. and Seralis, A. K. *Aust. J. Chem.* **36** (1983) 545.
- Newcomb, M. *Acta Chem. Scand., Ser. B* **44** (1990) 299.
- Simonet, J., Michel, M.-A. and Lund, H. *Acta Chem. Scand., Ser. B* **29** (1975) 489; Lund, H., Michel, M.-A. and Simonet, J. *Ibid.* **28** (1974) 900; Lund, H. and Kristensen, L. H. *Ibid.* **33** (1979) 495, 735; Savéant, J.-M. and Su, K. B. *J. Electroanal. Chem.* **196** (1985) 1; Nadjo, L., Savéant, J.-M. and Su, K. B. *Ibid.* **196** (1985) 23; Andriex, C. P., Gallardo, I., Savéant, J.-M. and Su, K. B. *J. Am. Chem. Soc.* **108** (1986) 638; Savéant, J.-M. *Bull. Soc. Chim. Fr.* (1988) 225; Lexa, D., Savéant, J.-M., Su, K. B. and Wang, D. L. *J. Am. Chem. Soc.* **110** (1988) 7617.
- Savéant, J.-M. *J. Am. Chem. Soc.* **109** (1987) 6788.
- Lund, T. and Lund, H. *Acta Chem. Scand., Ser. B* **41** (1987) 93; Lund, T. and Lund, H. *Ibid.* **40** (1986) 470; Daasbjerg, K., Pedersen, S. U. and Lund, H. *Ibid.* **43** (1989) 876.
- Pedersen, S. U. *Acta Chem. Scand., Ser. A* **41** (1987) 391; Nadjo, L., Savéant, J.-M. and Su, K. B. *J. Electroanal. Chem.* **196** (1985) 23.
- The program Bego was developed by C. Libak Pedersen, Department of Chemistry of Aarhus. The program integrates differential equations by the the Gears method which is part of a program package, Episode, from Argonne Nat. Laboratory.
- Ingold, K. U. In: Kochi, J. K., Ed., *Free Radicals*, Wiley, New York 1973, Vol. I, p. 39.
- Lowry, T. H. and Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, Harper & Row, New York 1981, 2nd ed.
- Pedersen, S. U. and Svensmark, B. *Acta Chem. Scand., Ser. A* **40** (1986) 607.
- Ashby, E. C., DePriest, R. N., Goel, A. B., Wenderoth, B. and Pham, T. N. *J. Org. Chem.* **49** (1984) 3545.
- Noller, C. R. and Adams, R. *J. Am. Chem. Soc.* **48** (1926) 1080.
- Pedersen, S. U. and Daasbjerg, K. *Acta Chem. Scand.* **43** (1989) 301.

Received August 24, 1990.