Indirect Electrochemical Reduction of Some Benzyl Chlorides
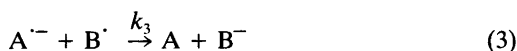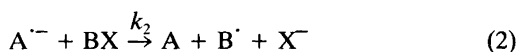
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Lund, T. and Lund, H., 1987. Indirect Electrochemical Reduction of Some Benzyl Chlorides. – Acta Chem. Scand., Ser. B 41: 93–102.

The indirect electrochemical reduction of benzyl chloride, p-methoxybenzyl chloride, 1-chloro-1-phenylethane and 2-chloro-2-phenylbutane has been investigated by cyclic voltammetry and preparative electrolysis. Electrogenerated anion radicals and an anion, 1,4-dihydro-4-methoxycarbonyl-1-methylpyridine anion (1^-), have been used as mediators. The rates of the electron transfer between the mediators and the benzyl halides have been measured by cyclic voltammetry, and it is concluded that the rate-determining step in the reaction of 1^- with 2-chloro-2-phenylbutane and possibly also 1-chloro-1-phenylethane is the transfer of a single electron. The mechanism of the reaction between benzyl chloride and some anion radicals apparently involves no coupling between the anion radical and benzyl radical; the isolated coupling products are presumably formed by reaction between benzyl anion and the mediator. The benzyl anion may act both as a strong electrogenerated base and as a nucleophile.

The indirect electrochemical reduction of benzyl chloride (2) by anthracene has been described previously, and it was concluded from cyclic voltammetric (CV) data that the reaction is mainly catalytic; furthermore, no coupling products were isolated in the reaction between anthracene anion radical and benzyl or aryl halides.[1,2] The reactions of benzyl and aryl halides were suggested to follow the scheme of eqns. (1)–(3), whereas

$$A + e^- \rightleftharpoons A^{\cdot-} \qquad (1)$$

$$A^{\cdot-} + BX \xrightarrow{k_2} A + B^{\cdot} + X^- \qquad (2)$$

$$A^{\cdot-} + B^{\cdot} \xrightarrow{k_3} A + B^- \qquad (3)$$

aliphatic halides also reacted to a certain degree according to eqn. (4).[3]

$$A^{\cdot-} + B^{\cdot} \xrightarrow{k_4} AB^- \qquad (4)$$

Several factors might be responsible for the lack of coupling of benzyl and aryl halides, e.g.

rapid hydrogen atom abstraction from the medium by the B radical [eqn. (5)] or a relatively

$$B^{\cdot} + HS \rightarrow HB + S^{\cdot} \qquad (5)$$

positive reduction potential of the benzyl radicals compared to those of the anion radicals employed. Both of these possibilities may be valid for aryl halides, but the former seems unlikely for benzyl halides since the C–H bond in toluene is relatively weak.

This investigation was undertaken to throw light on similarities and differences between the indirect reduction of some benzyl chlorides and aliphatic halides by aromatic anion radicals with respect to product distribution, reaction mechanism, and rate of electron transfer. Benzyl chloride (2), 4-methoxybenzyl chloride (3), 1-chloro-1-phenylethane (4) and 2-chloro-2-phenylbutane (5) were investigated; besides being a benzylic chloride, 5 is a tertiary halide and it has been found that tertiary halides are especially inclined to couple with anion radicals.[4,5]

It has been shown[4,5] that the anion of 1,4-dihydro-4-methoxycarbonyl-1-methylpyridine (1^-) reacts with sterically hindered aliphatic ha-
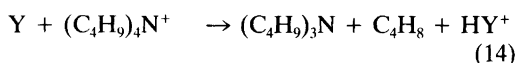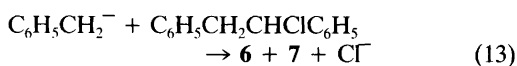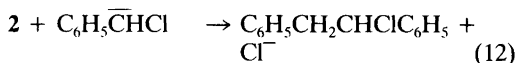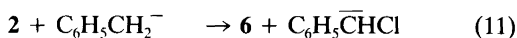
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R—〈○〉—C—Cl
with R', R'' substituents

2 R = R' = R'' = H
3 R = OCH$_3$, R' = R'' = H
4 R = R' = H, R'' = CH$_3$
5 R = H, R' = CH$_3$,
   R'' = C$_2$H$_5$

$$C_6H_5CH_2^- + H_2O \rightarrow 6 + OH^- \quad (6)$$

$$2 + OH^- \rightarrow C_6H_5CH_2OH + Cl^- \quad (7)$$

$$Y + C_6H_5CH_2OH \rightarrow C_6H_5CH_2O^- + HY^+ \quad (8)$$

$$2 + C_6H_5CH_2O^- \rightarrow 8 + Cl^- \quad (9)$$

$$2 + C_6H_5CH_2^- \rightarrow 9 + Cl^- \quad (10)$$

$$2 + C_6H_5CH_2^- \rightarrow 6 + C_6H_5\overline{C}HCl \quad (11)$$

$$2 + C_6H_5\overline{C}HCl \rightarrow C_6H_5CH_2CHClC_6H_5 + Cl^- \quad (12)$$

$$C_6H_5CH_2^- + C_6H_5CH_2CHClC_6H_5 \rightarrow 6 + 7 + Cl^- \quad (13)$$

$$Y + (C_4H_9)_4N^+ \rightarrow (C_4H_9)_3N + C_4H_8 + HY^+ \quad (14)$$
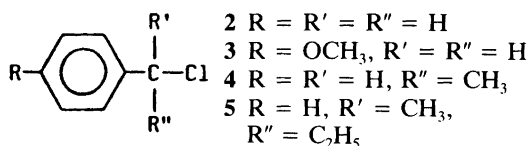
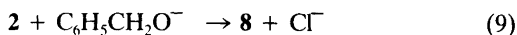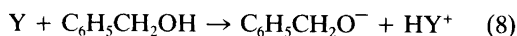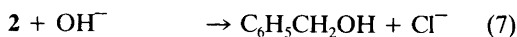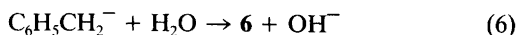lides in a nucleophilic substitution with the transfer of a single electron as the rate-determining step. The reaction between 1$^-$ and 4 and 5 has been included to investigate whether sterically hindered benzyl chlorides behave similarly.

Results and discussion

Preparative experiments. The indirect reduction of 2 by the anthracene anion radical in nominally dry DMF/TBABF$_4$ involved an electron consumption of 1 F mol^{-1} and gave toluene (6) in ~50 % yield. Besides 6 and a few per cent of unreacted 2, stilbene (7), dibenzyl ether (8), a small amount of bibenzyl (9) and some tributylamine were found (Table 1). Most of the anthracene (10) was recovered unchanged (87–100 %).

The formation of these products and the electron consumption $n = 1$ F mol^{-1} can be rationalized by eqns. (6)–(14), the benzyl anion (11) being formed via reactions (1), (2) and (3). Here, Y is any strong base (OH$^-$, 11, etc.).

In some of these reactions, 11 reacts as a nucleophile and in some as a base; the pK$_A$ of 6 in cyclohexylamine[6] and in DMSO[7] has been estimated as 41–42, which makes 11 a much stronger base than 10$^{\cdot-}$. In this way the relatively weak electrogenerated base (EGB) 10$^{\cdot-}$ forms a strong (and rather cheap) EGB 11. Further experiments are necessary to evaluate the synthetic possibil-

ities of creating a strong base in this way. However, in the case of 11 it cannot be used as base toward acids weaker than 2, since reactions (11), (12) and (13) will otherwise predominate.
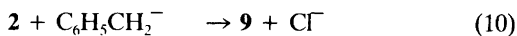
A reaction sequence analogous to (11), (12) and (13) has been reported previously for the electrochemical reduction of benzhydryl chloride.[8]

Addition of phenol to the catholyte changes the product pattern, since phenol becomes the dominant proton donor: No 7, 8, 9 or tributylamine are detected. It is noteworthy that 10$^{\cdot-}$ transfers an electron so much faster to 2 than it is protonated by phenol that the reaction is still catalytic. Since the phenolate ion reacts with 2 to

Table 1. Indirect electrochemical reduction of benzyl chloride by anthracene anion radical under different conditions. Yields and electron consumption n (F mol^{-1}) are based on the benzyl chloride consumed.

n	1.00	1.50	1.15	0.94
Supporting electrolyte	TBABF$_4$	TMABF$_4$	TMABF$_4$	TBABF$_4$
Proton donor (equiv. added)	–	–	Phenol (0.7)	H$_2$O (2.1)
Products/%				
Toluene	52	78	56	47
Bibenzyl	2	~0	~0	~0
Dibenzyl ether	27	7.5	~0	57
Stilbene	12.5	~0	~0	~0
Benzyl phenyl ether	0	0	43	0

Table 2. Indirect electrochemical reduction of benzyl chloride in DMF/TBABF$_4$ using anion radicals of benzophenone (**13**), diacetylbenzene (**16**), perylene (**20**), quinoxaline (**19**) and azobenzene (**21**). Yields and electron consumption n (F mol^{-1}) are based on the benzyl chloride consumed.

| Anion radicals	13·⁻	16·⁻	20·⁻	19·⁻	21·⁻
n	1.00	0.78	1.13	1.01	1.21
Products/%					
Mediator recovered[a]	38	~0	[b]	55	20
Toluene	44	26	49	35	18
Dibenzyl ether	26	~0	8.5		
Bibenzyl	~0	~0	~0	~0	~0
Stilbene	~0	~0	4	~0	~0
Coupling products	**14**(4.5), **15**(8)	**17**(27), **18**(17)	[c]	[c]	**22**(49)
Coupling products[a]	**14**(17), **15**(39)	**17**(62), **18**(38)	[c]	[c]	**22**(80)

[a] Calculated on basis of added mediator. [b] Not analysed. [c] Not analysed, several products.

give benzyl phenyl ether, $n = 1$ F mol^{-1} is still obtained.

A higher electron consumption ($n \sim 1.5$ F mol^{-1}) is observed when tetramethylammonium tetrafluoroborate (TMABF$_4$) is used as supporting electrolyte. This means that **11** is partly protonated by some compound, the conjugate base of which either does not react rapidly with **2** or is rapidly reprotonated by an acid whose base does not react rapidly with **2**. Hydroxide (or methoxide) ions possibly react with TMABF$_4$ in an S$_N$2 reaction forming methanol (or dimethyl ether) and trimethylamine, or **11** (or another base) abstracts a proton from TMA$^+$ with formation of an ylid.[9]

The benzyl anion may also react as a nucleophile, e.g. as in reactions (10) and (12). Furthermore, when anthracene is reduced in DMF/TBABF$_4$ in the presence of **2** and cyclohexanone, some 1-benzylcyclohexanol (**12**) is formed [eqn.

(15)], presumably in a nucleophilic addition of **11** to the ketone. Besides some **12**, 2-benzylcyclohexanone is also formed by reaction of **2** with cyclohexanone enolate ion; cyclohexanone is thus also functioning as proton donor. **6** is still a major product, but no stilbene or dibenzyl ether were detected. Further experiments are necessary to investigate the synthetic possibilities of such nucleophilic additions.

$$C_6H_5CH_2^- + C_6H_{10}O \xrightarrow{[H^+]}$$

$$C_6H_{10}(OH)CH_2C_6H_5 \qquad (15)$$

$$\mathbf{12}$$
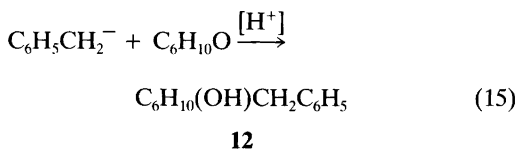
When benzophenone (**13**) is used as mediator in an indirect reduction of **2**, **6** is a major product; besides that, benzyl 1,1,2-triphenylethyl ether (**14**) and 1,1,2-triphenylethene (**15**) are formed.
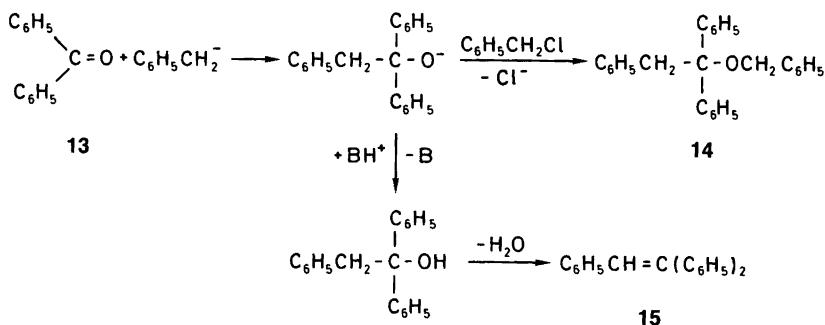
Scheme 1.

No products were found in which a phenyl group of **13** was benzylated (Table 2).

The benzylated products **14** and **15** may, in principle, be formed by several routes. The benzylation could be the result of a coupling between benzophenone anion radical and benzyl radical [eqn. (4)], in which case one would also expect some benzylation of a phenyl group of **13**, analogous to the reaction between **13**$^{\cdot-}$ and t-BuCl.[10] The electron transfer from **13**$^{\cdot-}$ to **2** and, especially, to the benzyl radical are very fast reactions, as indicated by CV, and nucleophilic substitution of **13**$^{\cdot-}$ or the carbanion of benzhydrol on **2** therefore seems unlikely. Addition of a small amount of water (~0.1 %) does not influence the electron transfer significantly (CV), but the formation of **14** and **15** is suppressed. **11** is protonated by water to **6**, so it may be suggested that **14** and **15** are formed via a nucleophilic addition of **11** to benzophenone, followed either by a normal S_N2 reaction with **2** to give **14** or by elimination of water to give **15** (Scheme 1).

p-Diacetylbenzene (**16**), when used as mediator in the indirect reduction of **2**, gives a product distribution similar to **13**. Besides **6**, 2-(4-acetylphenyl)-1-phenyl-2-propanol (**17**) and some 2-(4-acetylphenyl)-2-benzyloxy-1-phenyl-propane (**18**) were found. Using arguments similar to those put forward for **13**, it is proposed that the products **17** and **18** are formed by nucleophilic addition of **11** to **16**.

Anion radicals of quinoxaline (**19**) and perylene (**20**) react readily with **2**; several products were detected by TLC, but they were not separated and identified.

Indirect reduction of **2** using azobenzene (**21**) as mediator gives, besides some **6**, a good yield of 1-benzyl-1,2-diphenylhydrazine (**22**). Again, at least three reaction routes could lead to **22**, viz. coupling between **21**$^{\cdot-}$ and benzyl radical, nucleophilic attack of hydrazobenzene anion on **2**, and nucleophilic attack of **11** on **21**. CV indicates that $k_3 \gg k_4$, and in accordance with this, an anodic peak in CV at −0.3 V (Ag/AgI), assumed to be caused by reoxidation of **11**, is seen at sweep rates and at concentrations of **2** at which the anodic peak of **21**$^{\cdot-}$ has disappeared due to a fast chemical reaction between **21**$^{\cdot-}$ and **2**. However, at sweep rates lower than 100 mV s^{-1}, the anodic peak at −0.3 V disappears, showing that the peak is not due to a stable anion of a proton donor. On reduction of diphenylmethyl chloride[8]

a similar anodic peak was observed and was attributed to the diphenylmethyl anion. The fact that **11** reacts with cyclohexanone to give **12** indicates a reasonable lifetime for **11** under experimental conditions similar to those employed in the CV-experiment; so although **11** is a strong base, it is not (being an sp^2-hybridized species) protonated extremely fast.

By analogy with the coupling of **2** with **13** and **16**, the formation of **22** is proposed to proceed via a nucleophilic attack of **11** on **21**. Nucleophilic addition of an anion to an unpolarized double bond is usually not favoured, but it has been reported that benzhydryl anion[11] and the anion of 2,4,6-trimethylpyridine[12] add to **21** in THF at −78 °C in high yield. Furthermore, phenylpotassium,[13] phenylcalcium iodide[13] and phenyllithium[14] react with **21** with formation of 1,1,2-triphenylhydrazine. Grignard reagents, however, generally react with **21** with reduction.

The benzyl anion would be expected to be comparable in nucleophilicity with benzhydryl anion, so a probable reaction route seems to be that proposed above. The addition cannot proceed as a transfer of a single electron from **11** to **21**, since CV indicates a fast reduction of benzyl radical by **21**$^{\cdot-}$; the reduction potential of benzyl radical should then lie between the observed oxidation potential of **11**, which is probably shifted somewhat in the positive direction due to follow-up reactions, and the redox potential of **21**. The reaction might thus be formulated as a classical two-electron nucleophilic addition or as a shift of a single electron concerted with a radical combination. Coupling of a benzyl radical with an anion radical might be expected if an anion radical with a suitable redox potential was available.

The anion **1**$^{-}$, prepared by two one-electron reductions of 4-methoxycarbonyl-1-methylpyridinium iodide (**1**$^{+}$), has been shown to be a good electron donor and nucleophile;[4,5,15] it reacts with **2** giving 4-benzyl-1,4-dihydro-4-methoxycarbonyl-1-methylpyridine (**23a**) in high yield. No other products were detected in the ^{1}H NMR spectrum of the crude product.

Indirect reduction of 2-chloro-2-phenylbutane (**5**) by anthracene anion radical gave no coupling products and apparently only catalytic reduction of **5**.

Reaction between **1**$^{-}$ and 1-chloro-1-phenyl-ethane proceeded according to Scheme 2, the substitution product **23b** being isolated in good
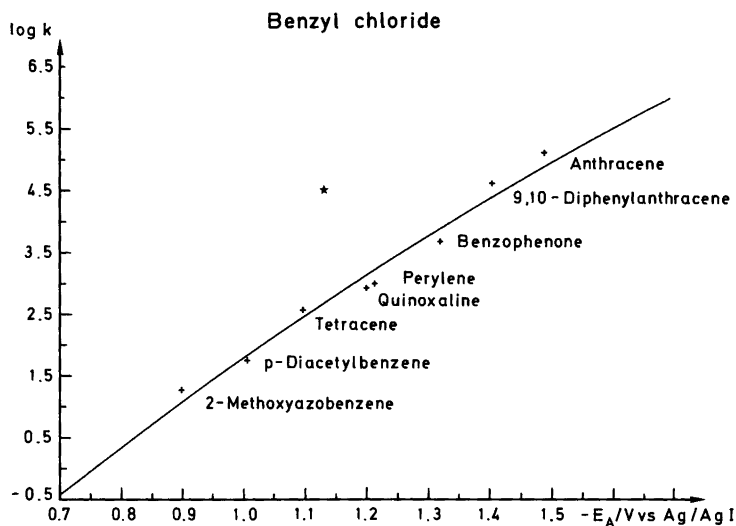
Fig. 1. Rate of electron transfer, k_{SET}, from some electrochemically generated anion radicals (+) to benzyl chloride (2) and rate of reaction between 1⁻ (*) and 2 in DMF/TBABF₄ (0.1 M).
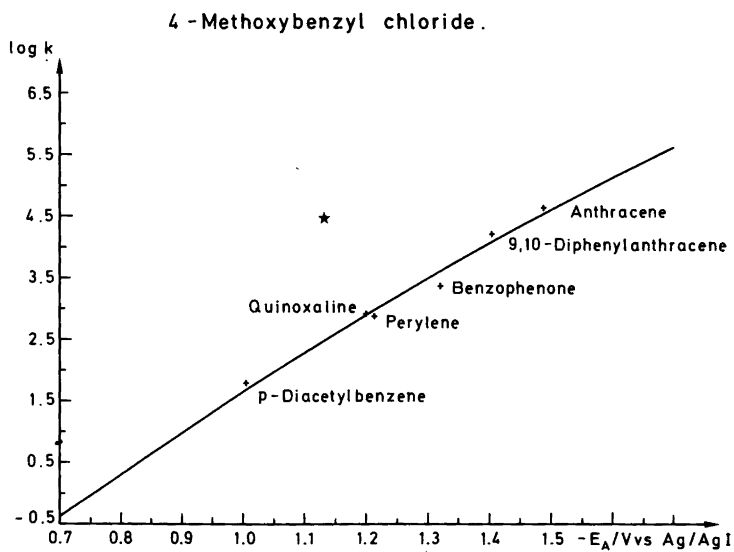
Fig. 2. Rate of electron transfer, k_{SET}, from some electrochemically generated anion radicals (+) to p-methoxybenzyl chloride (3) and rate of reaction between 1⁻ (*) and 3 in DMF/TBABF₄ (0.1 M).

Fig. 3. Rate of electron transfer, k_{SET}, from some electrochemically generated anion radicals (+) to 1-chloro-1-phenylethane (**4**) and rate of reaction between **1**⁻ (*) and **4** in DMF/TBABF₄ (0.1 M).
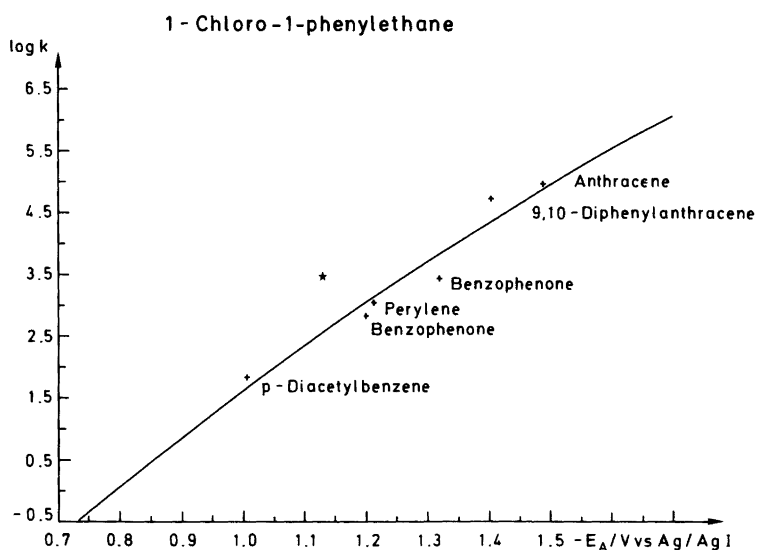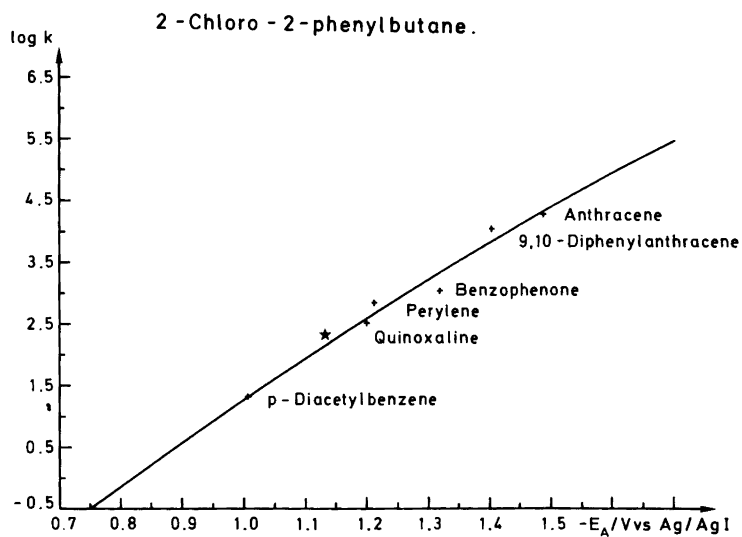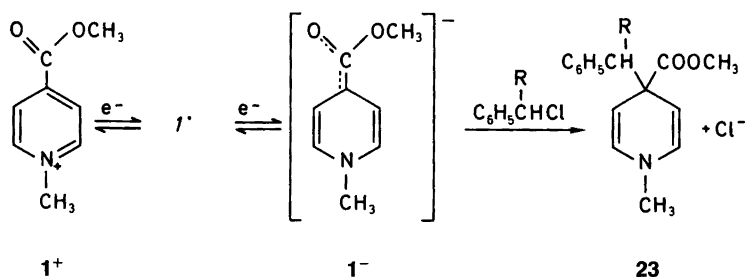

Fig. 4. Rate of electron transfer, k_{SET}, from some electrochemically generated anion radicals (+) to 2-chloro-2-phenylbutane (**5**) and rate of reaction between **1**⁻ (*) and **5** in DMF/TBABF₄ (0.1 M).

Scheme 2.   1⁺   1⁻   23   a R = H
                                                                              b R = CH₃

yield (~85%). The reaction between 1^- and 2-chloro-2-phenylbutane probably also followed Scheme 2, but in our hands the product was too unstable to permit isolation.

Cyclic voltammetry. CV indicates a catalytic reduction of **2** by the anion radicals; it has been established[16] that $k_3 > 10\,k_4$ for the anion radicals of anthracene and perylene. This means that the rate constant k_2 can be obtained using kinetic equations for a purely catalytic reduction without the complications of the coupling reaction. The rate constants are obtained by CV from the influence of the concentration of BX on the cathodic and anodic peaks of the mediator, by comparing the experimental curves with simulated data.[16]

The rate constants k_2 (k_{SET}) for electron transfer from an anion radical to **2, 3, 4** and **5** are given

Table 3. Rate constants (k_{SET}) and activation energies for electron transfer from electrochemically generated anion radicals (A) to some benzyl halides (BX) in DMF/0.1 MTBABF₄ measured by cyclic voltammetry.

BX	A	$-E_A$/V	k_{SET}/M^{-1} s^{-1}	log k_{SET}	ΔG^+/kcal mol^{-1}
2	2-Methoxyazobenzene	0.898	18.7	1.27	13.27
2	p-Diacetylbenzene	1.006	56	1.75	12.62
2	Tetracene	1.097	356	2.56	11.51
2	Quinoxaline	1.200	826	2.92	11.02
2	Perylene	1.213	961	2.98	10.94
2	Benzophenone	1.320	4694	3.67	10.00
2	9,10-Diphenylanthracene	1.404	40500	4.61	8.72
2	Anthracene	1.488	127000	5.10	8.05
3	p-Diacetylbenzene	1.006	62	1.79	12.56
3	Quinoxaline	1.200	800	2.90	11.05
3	Perylene	1.213	754	2.88	11.08
3	Benzophenone	1.320	2364	3.37	10.41
3	9,10-Diphenylanthracene	1.404	16400	4.21	9.26
3	Anthracene	1.488	42300	4.63	8.69
4	p-Diacetylbenzene	1.006	69	1.84	12.49
4	Quinoxaline	1.200	685	2.84	11.13
4	Perylene	1.213	1110	3.05	10.84
4	Benzophenone	1.32	2780	3.44	10.31
4	9,10-Diphenylanthracene	1.404	51600	4.71	8.58
4	Anthracene	1.488	90500	4.96	8.24
5	p-Diacetylbenzene	1.006	20.5	1.31	13.22
5	Quinoxaline	1.200	317	2.50	11.59
5	Perylene	1.213	682	2.83	11.14
5	Benzophenone	1.320	1081	3.03	10.87
5	9,10-Diphenylanthracene	1.404	10900	4.04	9.49
5	Anthracene	1.488	18000	4.26	9.19

Table 4. Rate of reaction (k) of the anion of 1,4-dihydro-4-methoxycarbonyl-1-methylpyridine (1^-) with some benzyl chlorides (BX) in DMF/0.1 M TBABF$_4$, and the expected k_{SET} for such reactions.

BX	k/M^{-1} s^{-1}	k_{SET}/M^{-1} s^{-1}	k/k_{SET}
2	31000	469	66
3	27500	295	93
4	2980	367	8.2
5	218	171	1.3

in Table 3, and curves for log k_{SET} vs $E°$ of the mediators for **2, 3, 4** and **5** are shown in Figs. 1, 2, 3 and 4. In Table 4, the rate constants k are given for the reaction of 1^- with **2, 3, 4** and **5**, and the results are included in Figs. 1, 2, 3 and 4, signified by a star.

From Table 3 it may be seen that $k_2 = 1.27 \times 10^5$ M^{-1} s^{-1} for the transfer of an electron from anthracene anion radical to benzyl chloride. The rate constant for the protonation of $10^{·-}$ by phenol is about 5×10^3 M^{-1} s^{-1}.[17,18] Under preparative conditions the concentrations of **2** and phenol are nearly equal, so that the values of the rate constants explain nicely the fact that $10^{·-}$ reacts with **2** rather than being protonated by phenol.

The anion 1^- reacts with **2** and **4** with coupling to give **23a** and **23b**, respectively, and the rate constants are calculated assuming $k_4 \gg k_3$. The rate constants expected for an electron transfer from an anion radical with the same redox potential as 1^- to the benzyl halide are also included in Table 4. The expected rate constant k_{SET} is calculated in a manner similar to that in Ref. 5. From the curves in Figs. 1–4 and the redox potential $E°_{1^·/1^-}$ for $1^·$ the rate constant can be found as the ordinate corresponding to the $E°_{1^·/1^-}$ value. Besides the curves shown, the data in Table 3 also provide a possibility of extracting the bond and solvent-reorganization energies and, in principle, the redox potentials for the benzyl halides using the Marcus eqn. (16). The redox potentials for **2, 3, 4** and **5** scatter around -0.35 V (Ag/AgI), but the number of data in Table 3 is too small to justify discussion of the trend of the potentials. The λ values for eqn. (2) calculated for **2, 3, 4** and **5** are 73, 87, 82 and 66 kcal mol^{-1}, respectively; these values are close to those obtained for the aliphatic halides.[5]

$$\Delta G^\ddagger = \frac{\lambda}{4}\left(1 + \frac{F(E_A - E_{BX})}{\lambda}\right)^2 \qquad (16)$$

The results in Table 4 show that 1^- reacts with **2** and **3** 50–100 times faster and with **4**, 8 times faster than expected for an electron transfer, whereas the reaction between 1^- and **5** proceeds at a rate equal to the expected rate for SET.

Conclusion

A comparison of the data [4,5] for the reaction between aromatic anion radicals and aliphatic halides with the results described here for benzylic halides shows that benzylic halides are reduced catalytically to the benzyl anion with no detectable coupling ($k_3 \gg k_4$), whereas aliphatic halides couple with aromatic anion radicals in moderate to high yields, with tertiary halides giving the highest degree ($k_3 \ll k_4$) of coupling and primary somewhat lower. More data are needed in order to decide which of the possible explanations for the observed differences is most likely.

The catalytic reduction of benzyl halides produces the benzyl anion; in this way a strong electrogenerated base is produced via the weakly basic anion radical. Besides reacting as a strong base, the benzyl anion may act as a nucleophile and add to suitable systems.

The reaction between the anion of 1,4-dihydro-4-methoxycarbonyl-1-methylpyridine (1^-) and sterically hindered aliphatic halides was interpreted as showing that the rate-determining step in this nucleophilic substitution is the transfer of a single electron.[4,5] The results for the reaction of 1^- with benzyl chlorides are similar to those for 1^- with alkyl halides; the sterically hindered **5** reacts with 1^- with $k/k_{SET} \sim 1$, and the sterically slightly less hindered **4** with $k/k_{SET} \sim 8$. Compound **4** is a borderline case, but even here the nucleophilic substitution of 1^- on **4** may be considered to have a transition state (TS) very close to a pure "outer-sphere electron transfer" TS. It was previously assumed that a ratio of k/k_{SET} of between $^1/_5$ and 5 indicated electron transfer as the rate-determining step, because the assumption that λ for 1^- and all the anion radicals employed was the same introduced an uncertainty in k_{SET}; the uncertainty in the measurements of k is also a factor, although less significant.

The α-unsubstituted benzyl chlorides react faster (50–100 times) than expected for SET, and an explanation similar to that proposed for alkyl halides[5] is suggested, in which a weak bond formation (1–3 kcal) is found in the TS; the TS is proposed to lie somewhere between the TS of an S_N2 reaction and the TS of a pure electron transfer reaction, although much closer to the latter than to the former.

Benzyl chlorides thus react with the anion 1^- in a manner similar to aliphatic halides, whereas their reaction with aromatic anion radicals differs from that of aliphatic halides.

Experimental

Materials. 2-Chloro-2-phenylbutane was obtained from 2-phenyl-2-butanol (acetophenone + C_2H_5MgBr) by treatment with hydrogen chloride in dichloromethane in the presence of calcium chloride. 1-Chloro-1-phenylethane was prepared similarly from 1-phenylethanol, b.p.$_{16}$ 79–79.5 °C. 4-Methoxybenzyl chloride was prepared from the alcohol using thionyl chloride. The compound should be stored at low temperature since it poly-

Table 6. Retention times for some compounds under the conditions used (see Experimental).

Compound	R_t	
	Column 1	Column 2
Toluene (6)	3.64	
Benzyl chloride (2)	15.46	
Naphthalene	20.99	3.62
Bibenzyl (9)	29.48	10.82
Dibenzyl ether (8)	33.96	13.64
Stilbene (7)	36.22	14.91
Anthracene (5)	41.33	
Benzophenone (12)		13.01
1,1,2-Triphenylethene (13)		23.53
		33.5
Benzhydrol		14.30
Diacetylbenzene (15)		8.84
17		23.17
Perylene		34.25

merizes on standing at ambient temperature. The other chemicals used were the same as in Ref. 5.

The *instrumentation* and *procedures* have been described previously.[5] To illustrate the procedure for, and uncertainties in, the determination of the rate constants the measured data used for the calculation of a single rate constant are presented in Table 5.

Preparative experiments. The indirect reduction of benzyl chloride by anthracene anion radical is described as an example; other reductions were performed similarly: Anthracene (155 mg) was reduced in 60 ml of deaerated DMF/0.1 M $TBABF_4$ at a mercury cathode at −1.5 V (Ag/AgI, 0.1 m I$^-$) in the presence of 0.50 ml of benzyl chloride. The catholyte had been purified by passing through a column of active alumina. The reduction was complete after consumption of 420 C, and naphthalene (252 mg) was added to the catholyte as internal standard for GLC. The catholyte was diluted with water (125 ml) and extracted with diethyl ether (100 ml), which was washed with water (100 ml). A sample of the ether phase was used for GLC and GLC–MS analysis. The rest of the ether solution was evaporated *in vacuo* and the residue was separated on a column of silica and the compounds isolated; in some cases, however, the products were identified only by GLC–MS and by their retention time

Table 5. Measured data used in the calculation of the rate constant k for the electron transfer from pyrene anion radical to benzyl chloride: C_A and C_{BX}, concentration of pyrene and benzyl chloride, respectively, v scan rate, I_a and I_c, the anodic and cathodic peak currents. From these data $k = 961 \pm 80$ $M^{-1} s^{-1}$ is obtained.

C_A/mM	C_{BX}/C_A	v_{SCAN}/Vs^{-1}	I_a/I_c	k/M^{-1} s^{-1}
1.96	2.0	0.75	0.167	1067
–	–	1.00	0.223	1075
–	–	1.00	0.216	1115
–	–	1.50	0.321	1016
1.90	5.0	1.50	0.122	944
–	–	2.00	0.182	929
–	–	2.49	0.236	924
–	–	3.00	0.278	911
1.87	10.0	2.49	0.084	884
–	–	3.50	0.152	902
–	–	4.99	0.236	901
–	–	7.48	0.325	894
1.85	20.0	7.48	0.161	929
–	–	4.99	0.082	853
–	–	9.98	0.218	966
–	–	14.97	0.291	1065

in GLC. For GLC, the following conditions were used: GLC 1, column cyanopropyl (15 m), 4 min at 50 °C to 200 °C/5 °C min^{-1}, injection temp. 250 °C, detector temp. 200 °C, flow 2 ml min^{-1}. GLC 2, column 10 % UCW-98 ($^1/_2$ m), 2 min at 100 °C to 200 °C/5 °C min^{-1}, injection temp. 200 °C, detector temp. 250 °C, flow 30 ml min^{-1}. The retention times are given in Table 6.

Isolated new products: Benzyl 1,1,2-triphenylethyl ether (14); ¹H NMR (CDCl₃): δ 3.75 (2H, s), 4.40 (2H, s), 6.7–6.8 (1H, m), 7.0–7.2 (2H, m), 7.25–7.31 (17H, m). MS [IP 70 eV; *m/e* (% rel. int.)]: 273 (24), 257 (3), 165 (9), 105 (10), 92 (10), 91 (100).

2-(4-Acetylphenyl)-1-phenyl-2-propanol (17); ¹H NMR (CDCl₃): δ 1.57 (3H, s), 1.92 (1H, s), 2.58 (3H, s), 3.01 (1H, d, *J* 13.50 Hz), 3.11 (1H, d, *J* 13.50 Hz), 6.8–7.3 (5H, m), 7.47 (2H, d, *J* 8.4 Hz), 7.90 (2H, d, *J* 8.4 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 255 (19), 237 (7), 164 (22), 163 (100), 121 (11), 120 (9), 105 (4), 92 (20), 91 (40), 43 (65).

4-Benzyl-1,4-dihydro-4-methoxycarbonyl-1-methylpyridine (22a); ¹H NMR (CDCl₃): δ 2.80 (3H, s), 2.91 (2H, s), 3.61 (3H, s), 4.52 (2H, d, *J* 7.6 Hz), 5.83 (2H, d, *J* 7.6 Hz), 6.9–7.4 (5H, m).

1,4-Dihydro-4-methoxycarbonyl-1-methyl-4-(1-phenylethyl)pyridine (23b). ¹H NMR (CDCl₃): δ 1.29 (3H, d, *J* 6.4 Hz), 2.80 (3H, s), 4.23 (1H, q, *J* 6.4 Hz), 3.53 (3H, s), 4.35–4.70 (2H, m), 5.80–6.02 (2H, m), 7.28–7.42 (5H, m).

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