Competitive Electron Transfer and S_N2 Reactions of Aromatic Radical Anions with Alkyl Halides and Methanesulfonates

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Dedicated to Professor Lennart Eberson on the occasion of his 65th birthday

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The competition between electron transfer and S_N2 processes in the reaction between a number of radical anions of aromatic compounds such as anthracene, pyrene, (E)-stilbene, m-tolunitrile and p-tolunitrile and different substrates such as the methyl, ethyl, butyl, 2-butyl, neopentyl and 1-adamantyl halides as well as methyl, ethyl, butyl and 2-butyl methanesulfonates has been investigated in N,N-dimethylformamide. By using the reaction of the radical anions with the appropriate alkyldimethylsulfonium iodide or trialkylsulfonium iodide as model for an electron transfer process the reaction mechanism could be characterized by electrochemical means in many of the cases listed. The presence of an S_N2 component is found to be related not only to the steric requirements at the substrate but also to the magnitude of the driving force for the electron transfer process. In general, the higher the standard potential of the aromatic compound is or the poorer the substrate is as electron acceptor, the more important the S_N2 mechanism becomes. An analysis of the substitution products obtained in the reaction between anthracene radical anion and the different substrates shows a considerable rise in the yield of the 9-alkyl-9,10-dihydroanthracene isomer as the magnitude of the S_N2 component increases.

The ability of aromatic radical anions $(A^{\cdot -})$ to act as electron donors as well as nucleophiles in the reaction with alkyl halides (RX) is an interesting feature both from an experimental[1–15] and theoretical[16–21] point of view. In general, aromatic radical anions are considered to be strong and efficient electron donors, although a nucleophilic behaviour has been suggested in a few cases such as for instance with the radical anion of 9-fluorenone.[2] Only a limited number of papers have actually reported a competition between electron transfer (ET) and S_N2 but in certain intermolecular reactions involving simple alkyl halides[4,5,10,11] and within intramolecular systems[12–14] incorporating both a radical anion site and a halogen atom such a situation has actually been achieved. The methodologies for detecting an S_N2 component have normally consisted in a direct optical detection of the intermediates involved,[12–14] kinetic measurements[7–10] or by employing optically active alkyl halides.[4–6]

These methods are, however, somewhat restrictive as

concerns the choice of substrate and recently we have reported another approach[11] which takes advantage of the fact that the competition between the ET and S_N2 mechanism in the reaction between a given radical anion and a series of alkyl halides RX is influenced by the nature of the halogen atom X. Based on an investigation of the development in the product distribution in the reaction between anthracene radical anion and the series of the three methyl halides (X = I, Br and Cl), the S_N2 component was found to constitute as much as 25, 77 and 97%, respectively, of the two reaction paths.[11] This result showed that a strong electron donor in terms of an aromatic delocalized radical anion actually may act as a nucleophile in an intermolecular reaction with an alkyl halide.
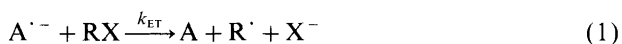
In this paper we have extended the previous investigation to include aromatic radical anions of pyrene, (E)-stilbene, m-tolunitrile and p-tolunitrile in order to elucidate among other things the importance of the electron donor ability on the reaction mechanism. The substrates chosen were the methyl, ethyl, butyl, 2-butyl, neopentyl and 1-adamantyl chlorides, bromides and iodides as well

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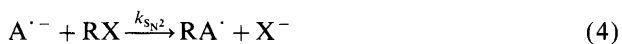* To whom correspondence should be addressed.

as the methyl, ethyl, butyl and 2-butyl methanesulfonates and the trimethylsulfonium, triethylsulfonium, ethyl-dimethylsulfonium, butyldimethylsulfonium and 2-butyl-dimethylsulfonium iodides characterized by having different electron acceptor abilities and steric requirements. The alkyl fluorides were not considered in this study since their reactions were too slow to allow reliable measurements to be carried out. The main reason for including the reactions of the sulfonium salts is based on their ability to function as models for pure electron transfer processes.[11] All experiments have been carried out in N,N-dimethylformamide (DMF).

The mechanism of the ET and $S_N 2$ processes generally accepted in the reaction between aromatic radical anions and alkyl halides can be described as shown in the scheme given below [eqns. (1)–(6)].[1–3,22–25]
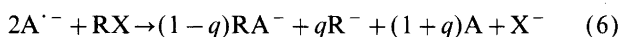
ET:

$$A^{\cdot -} + RX \xrightarrow{k_{ET}} A + R^{\cdot} + X^- \qquad (1)$$

$$A^{\cdot -} + R^{\cdot} \xrightarrow{k_2} RA^- \qquad (2)$$

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

$S_N 2$:

$$A^{\cdot -} + RX \xrightarrow{k_{S_N 2}} RA^{\cdot} + X^- \qquad (4)$$

$$A^{\cdot -} + RA^{\cdot} \xrightarrow{k_5} A + RA^- \qquad (5)$$

Total (ET + $S_N 2$):

$$2A^{\cdot -} + RX \rightarrow (1-q)RA^- + qR^- + (1+q)A + X^- \qquad (6)$$

The rate-determining step (1) of the ET reaction consists of an electron transfer concerted with a cleavage of the carbon–halogen bond in the alkyl halide. The alkyl radical $R^{\cdot}$ thus generated in this first step may either couple with or be further reduced by the radical anion in the fast follow-up reactions (2) or (3) to the carbanions RA^- or R^-. The rate-determining step (4) in the competing $S_N 2$ mechanism is characterized by a bonding between the radical anion and the central carbon atom in RX resulting in the coupled radical $RA^{\cdot}$. This radical could in principle couple with another molecule of $A^{\cdot -}$ in line with reaction (2) but due to the conjugated nature of $RA^{\cdot}$ the reduction process (5) is expected to be facilitated and dominant. Note that the carbanion thus generated is the same as the one obtained in the reaction sequence (1) and (2) in the ET mechanism when all stereochemical aspects are disregarded. Both R^- and RA^- will be alkylated or protonated in follow-up processes to the final products RR, RH, R_2A and RAH.

The overall reaction (6) can be expressed conveniently by introducing a parameter $q = [R^-]/([RA^-] + [R^-])$ that may range from zero to one. At the same time, the magnitude and the development in q for the reaction between a given radical anion and a series of alkyl halides

may be used to characterize the outcome of the reaction and ultimately the reaction mechanism. In general, a q-value dependent on the nature of the halogen atom X would be consistent with the presence of an $S_N 2$ component, whereas a constant value would be suggestive of a pure electron transfer mechanism. In practice, q may be determined directly through a yield determination of the products formed in the overall reaction (6) or indirectly by an electrochemical technique based on the use of a rotating disk electrode.[11,26] In many instances, the latter technique is attractive owing to its simplicity, and since the agreement with the yield determination was found to be excellent in the previous paper[11] this method was the one employed mainly herein. The distribution of substitution products (originating from RA^-) obtained in the case of anthracene as mediator, however, was analysed and used in a characterization of these specific reactions. Both approaches, the electrochemical method and the product study, and the results obtained will be presented in the following.

Results and discussion

Electrochemical method. The use of the electrochemical method is based on two important assumptions that determine its range of applicability. The first one, which is rather crucial and limits the choice of $A^{\cdot -}$ in the reaction with a given substrate, is related to the fact that a distinction between the $S_N 2$ and the ET mechanism will be possible only if the reduction process (3) is in play and competitive with the fast radical anion–radical coupling (2) in the ET scheme. Because the latter process proceeds by a rate constant in the order of $10^9 \ M^{-1} s^{-1}$, the value of k_3 has in reality to be close to the diffusion-controlled limit. In general, such a situation can be accomplished if the standard potential of the aromatic compound, E_A°, is of about the same magnitude as the reduction potential of the radical.[22–25] Since alkyl radicals, having reduction potentials in the range from -2.1 to -1.6 V vs. SCE, are rather difficult to reduce, this leaves us with radical anions of aromatic compounds having standard potentials lower than about -1.8 V vs. SCE.[22–25] The radical anions of anthracene ($E_A^\circ = -1.890$ V vs. SCE), pyrene ($E_A^\circ = -2.018$ V vs. SCE), (E)-stilbene ($E_A^\circ = -2.136$ V vs. SCE), m-tolunitrile ($E_A^\circ = -2.264$ V vs. SCE) and p-tolunitrile ($E_A^\circ = -2.337$ V vs. SCE) have been selected,[24] since they also possess a sufficient high stability to be generated electrochemically in a millimolar concentration range.

The second assumption is not as restrictive as the first one but states that a proper estimation of the $S_N 2$ component for a given substrate can be obtained only if a comparison with a pure ET reaction is possible. We use the alkyldimethylsulfonium iodide or trialkylsulfonium iodide as model substrates. This is based on the observation made earlier as well as in the present study (see later) that the substitution products formed in the reaction between anthracene radical anion and

tert-butyldimethylsulfonium iodide,[11] ethyldimethylsulfonium iodide, butyldimethylsulfonium iodide or 2-butyldimethylsulfonium iodide have been alkylated with the larger alkyl group and not with the sterically less hindered methyl group. Such a result is certainly not in line with the feature of an S_N2 process but closely related, on the other hand, to the order of alkyl radical stabilization and the presence of an ET mechanism.

The results obtained by the electrochemical method are presented in Tables 1–4 and will be discussed on the basis of the substrate. It should also be noted that we attempted to include the alkyl methanesulfonates as substrates in the investigation but that the reproducibility of the q measurements was found to be too low.

Methyl halides. In Table 1 the q-values measured for the reactions between the radical anions of anthracene, pyrene, (E)-stilbene, m-tolunitrile and p-tolunitrile and the substrates trimethylsulfonium iodide, methyl iodide, methyl bromide and methyl chloride are given. Note that the radical anions are listed as a function of their standard potential, E_A°, with p-tolunitrile radical anion being the better electron donor and that the results tabulated for anthracene radical anion originate from Ref. 11.

Without doubt the most interesting feature of the results given in Table 1 is that q for a given radical anion is dependent on the nature of the leaving group with the smallest values obtained for methyl chloride and the highest ones for methyl iodide or trimethylsulfonium iodide. As already pointed out such a development may be interpreted in terms of a competition between an electron transfer and S_N2 mechanism and the fact that the highest q-values and thus the highest degree of ET are found in the reactions involving trimethylsulfonium iodide is at the same time an underlining of its usefulness as a model substrate. The increase observed in q as a function of $-E_A^\circ$ in this case is simply a reflection of the development in the competition ratio of reactions (2) and (3) in the ET mechanism in terms of an increase in the rate of the latter process.

If the scheme [eqns. (1)–(6)] is assumed to represent an adequate description of the two reaction mechanisms, the q-value obtained for each methyl halide may easily be referenced to the value obtained for trimethylsulfonium iodide in a calculation of the magnitude of the S_N2 component with respect to the total process. The

percentage of S_N2 is simply given by the expression $(1 - q/q_{ET}) \times 100\%$, where q_{ET} denotes the value obtained for the expected ET process involving the sulfonium salt. The results are displayed in Table 2 and in Fig. 1 in which the percentage of S_N2 is plotted against the standard potential of the aromatic compound. Even though the uncertainty on the calculations of especially small S_N2 components is high and the slightly negative values obtained for methyl iodide of course have no physical significance, it should be recalled that the need of including optically active compounds to characterize the reaction mechanism is avoided by the method presented. From a synthetic point of view optical activity would be impossible or at least very difficult to introduce for the most simple alkyl halides.

The most significant observations appearing in Fig. 1 can be summarised as follows. In most cases a competition between ET and S_N2 exists ranging from a totally dominant S_N2 component in the reaction between anthracene radical anion and methyl chloride to a rate-determining ET step in the reactions between the radical anions of pyrene, (E)-stilbene, m-tolunitrile or p-tolu-
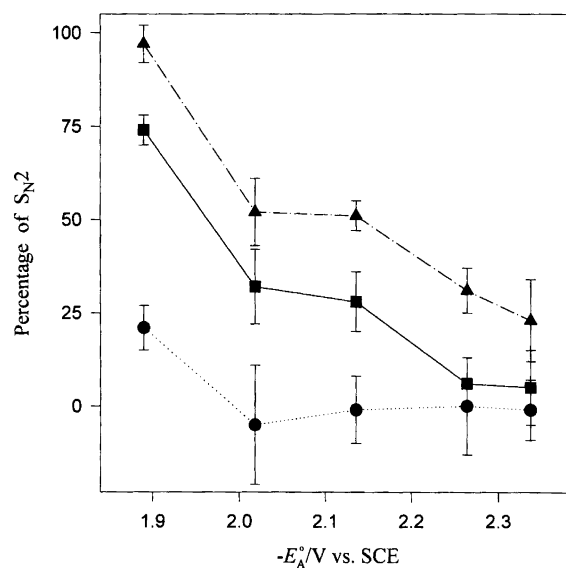

Fig. 1. Plot of the percentage of S_N2 against the standard potential, E_A°, of the aromatic compounds anthracene, pyrene, (E)-stilbene, m-tolunitrile and p-tolunitrile in the reactions involving methyl iodide (●), methyl bromide (■) and methyl chloride (▲).

Table 1. q-Values measured by use of the rotating disk electrode for the reaction between radical anions of different aromatic compounds and the methyl halides in 0.1 M TBABF$_4$/DMF at 20 °C.

RX \ A	Anthracene[a]	Pyrene[b]	(E)-Stilbene[c]	m-Tolunitrile[d]	p-Tolunitrile[e]
Trimethylsulfonium iodide	0.61(3)[f]	0.77(11)	0.85(7)	0.90(6)	1.02(7)
Methyl iodide	0.48(3)[f]	0.81(5)	0.86(4)	0.90(10)	1.03(4)
Methyl bromide	0.16(2)[f]	0.52(1)	0.61(5)	0.85(2)	0.97(8)
Methyl chloride	0.02(3)[f]	0.37(4)	0.42(1)	0.62(4)	0.79(10)

[a]$E_A^\circ = -1.890$ V vs. SCE. [b]$E_A^\circ = -2.018$ V vs. SCE. [c]$E_A^\circ = -2.136$ V vs. SCE. [d]$E_A^\circ = -2.264$ V vs. SCE. [e]$E_A^\circ = -2.337$ V vs. SCE. [f]From the results obtained in Ref. 11.

Table 2. The percentage of S_N2, calculated as $(1-q/q_{ET}) \times 100\%$, in the reaction between radical anions of different aromatic compounds and the methyl halides in 0.1 M $TBABF_4$/DMF at 20 °C.

RX \ A	Anthracene	Pyrene	(E)-Stilbene	m-Tolunitrile	p-Tolunitrile
Methyl iodide	21(6)	−5(16)	−1(10)	0(13)	−1(8)
Methyl bromide	74(4)	32(10)	28(8)	6(7)	5(10)
Methyl chloride	97(5)	52(9)	51(4)	31(6)	23(11)

Table 3. q-Values measured by use of the rotating disk electrode for the reaction between radical anions of different aromatic compounds and the ethyl, butyl, 2-butyl and neopentyl halides in 0.1 M $TBABF_4$/DMF at 20 °C.

RX \ A	Anthracene	Pyrene	(E)-Stilbene	m-Tolunitrile	p-Tolunitrile
Triethylsulfonium iodide[a]	0.07(5)	0.15(3)	0.47(4)	0.66(3)	0.87(6)
Ethyl iodide	0.00(5)	0.11(2)	0.41(3)	0.63(6)	0.85(6)
Ethyl bromide	−0.01(2)	0.06(2)	0.31(3)	0.49(5)	0.76(6)
Ethyl chloride	0.00(3)	0.06(1)	0.26(2)	0.39(4)	0.67(5)
Butyldimethylsulfonium iodide	0.10(5)	0.18(4)	0.75(4)	0.82(7)	0.97(5)
Butyl iodide	0.04(1)	0.15(2)	0.55(5)	0.63(6)	0.92(5)
Butyl bromide	0.01(5)	0.10(4)	0.40(3)	0.58(3)	0.72(9)
Butyl chloride	0.00(3)	0.09(1)	0.36(4)	0.51(5)	0.69(7)
2-Butyldimethylsulfonium iodide	0.09(4)	0.17(4)	0.13(2)	0.34(4)	0.62(4)
2-Butyl iodide	0.07(2)	0.14(2)	0.20(2)	0.43(4)	0.69(6)
2-Butyl bromide	0.07(2)	0.19(3)	0.09(4)	0.28(2)	0.61(6)
2-Butyl chloride	0.06(2)	0.06(2)	0.07(2)	0.27(3)	0.55(5)
Neopentyl iodide	0.08(1)	0.21(4)	0.68(9)	0.73(4)	0.85(8)
Neopentyl bromide	0.07(3)	0.24(3)	0.71(3)	0.75(7)	0.82(5)
Neopentyl chloride	0.07(3)	0.22(5)	0.72(2)	0.71(3)	0.86(7)

[a]The same results are obtained for ethyldimethylsulfonium iodide.

nitrile and methyl iodide. In general, the S_N2 percentage increases in the leaving group order $(CH_3)_2S$, I^-, Br^- and Cl^- with respect to the substrate. This trend is closely related to its electron accepting abilities as illustrated qualitatively by the magnitude of the peak potentials of reduction, E^p_{red}, obtained in linear sweep voltammetry. The values of E^p_{red} found at a gold electrode and a scan rate of 0.1 V s^{-1} are −1.78, −1.99, −2.32 and −2.85 V vs. SCE for trimethylsulfonium iodide, methyl iodide, methyl bromide and methyl chloride, respectively; in the latter case E^p_{red} was affected by the appearance of the background reduction. In fact, one would expect the transition state to occur later as the electron acceptor becomes poorer, with a diminished distance between the radical anion and the electron acceptor as a consequence. Ultimately, such a situation should favour the bonding interaction in the transition state and thus the S_N2 mechanism overall in agreement with the actual development observed in the results reported herein. Recent and more elaborated theoretical considerations[19-21] of possible reaction pathways involving the formyl radical anion and the different methyl halides do in fact sustain this simple description, but it is also worth to note the experimental case reported elsewhere[5] of an alkyl fluoride being an exception to the 'normal' order of acceptors. As regards the electron donor the percentage of S_N2, in general, increases as a function of the standard potential of the aromatic com-

pound going from the radical anion of p-tolunitrile to anthracene. This trend is closely related to the one found above for the substrates and indicates the influence of the electron donor ability on the position of the transition state, i.e. the transition state occurs later for a poorer donor in favour of the S_N2 mechanism.

Ethyl and butyl halides. The present study has been carried further on to include the ethyl and butyl halides. The q-values are presented in Table 3 and again the results obtained for the corresponding sulfonium salts could be used as references in a calculation of the S_N2 percentages from the expression $(1-q/q_{ET}) \times 100\%$ as shown in Table 4. Some of the q-values for butyl chloride[23] and ethyl bromide[24] have been measured previously

Table 4. The percentage of S_N2, calculated as $(1-q/q_{ET}) \times 100\%$, in the reaction between radical anions of different aromatic compounds and the ethyl and butyl halides in 0.1 M $TBABF_4$/DMF at 20 °C.

RX \ A	(E)-Stilbene	m-Tolunitrile	p-Tolunitrile
Ethyl iodide	13(10)	5(10)	2(10)
Ethyl bromide	34(9)	26(8)	13(9)
Ethyl chloride	45(6)	41(7)	23(8)
Butyl iodide	27(8)	23(10)	5(7)
Butyl bromide	47(5)	29(7)	26(10)
Butyl chloride	52(6)	38(8)	29(8)

by linear sweep voltammetry and they are in accordance with the findings in the present study.

First of all, it should be noted that an estimation of the S_N2 component was not possible for the radical anions of pyrene and anthracene, the reactions of which had q-values close to zero in all cases. This behaviour is a reflection of the fact that the reduction potentials of primary alkyl radicals are smaller compared to the one of the methyl radical[24] by about 450 mV, and in such a situation with reaction (3) out of play a distinction between the two mechanisms cannot simply be achieved by the electrochemical method. However, for each of the three mediators left, the results follow, by and large, the same trend as in the case of the methyl halides with the highest q-values obtained for the best electron acceptors, the ethyl and butyl iodides. Actually, the behaviour of ethyl iodide can hardly be discerned from the one of triethylsulfonium iodide pointing to a clear dominance of the ET mechanism in this case. With respect to the two poorest electron acceptors, ethyl and butyl chloride, the S_N2 character ranges from about 50% in the reaction with the radical anion of (E)-stilbene down to close to 20% with the better electron donor, p-tolunitrile radical anion. These percentages are of the same magnitude as for the sterically less hindered methyl chloride and they could thus be suspected to be slightly overestimated. We will return to this point later, and conclude for now that the trend in the results is consistent with the previous finding in the case of the methyl halides, i.e. an increase in the importance of the S_N2 component as the driving force of the reaction is lowered.

2-Butyl and neopentyl halides. If the sterically more hindered alkyl halides such as the 2-butyl and the neopentyl halides are incorporated in the study, the most significant observation is related to the much smaller dependency of q on the nature of X as shown in Table 3. Especially for the reactions involving the neopentyl halides, the q-values are essentially constant pointing to the presence of the expected ET mechanism for such sterically hindered systems.[6] In this situation, the inclusion of the corresponding sulfonium salt is thus not necessary in order to characterize the reaction mechanism. With respect to the reactions involving the 2-butyl halides, the tendency in the results (Table 3) shows a small decrease of q in the order X = I, Br and Cl, which would indicate the presence of a small S_N2 component. However, at the same time it was observed that the reactions with 2-butyldimethylsulfonium iodide gave values generally smaller than the ones for 2-butyl iodide and comparable to the values obtained for 2-butyl bromide and chloride. This could be suggestive of some mechanistic complications with the secondary butyl systems in terms of side reactions, and therefore the results obtained have not been quantified into a mechanistic description. In such a situation stereochemical experiments and product studies that exhibit a much higher sensitivity towards the detection of small S_N2 components are clearly to be preferred.

For instance, in the reactions between anthracene radical anion and the optically active 2-octyl iodide, bromide and chloride, the percentage of S_N2 has been estimated to 5, 8 and 11%, respectively.[5] Note also that in a previous investigation of the reaction between quinoxaline radical anion and optically active 2-butyl bromide no S_N2 component could actually be detected despite the relatively poorer electron donor ability of this radical anion ($E_A^\circ = -1.590$ V vs. SCE).[6] This result may be an illustration of the influence of the specific structural and electronic features of the reactants on the competition ratio.

Product study. The picture emerging from the above electrochemical experiments shows a substantial S_N2 component in the reactions involving methyl, ethyl and butyl bromides and chlorides while an ET mechanism is dominating for the alkyl iodides and sterically more hindered alkyl bromides and chlorides. In order to confirm the consistency of this interpretation by other means our attention was turned to a product study on the substitution products. Even though the substitution products R_2A and RAH (originating from a reaction between RA$^-$ and RX or H$^+$) obtained in the ET and the S_N2 reaction formally are the same, the competition between the two mechanisms might still be reflected in the distribution of different constitutional isomers as observed in the previous investigation concerning the series of methyl halides.[11] The radical anion of interest, in this context, is first of all the one of anthracene due to the possibility of alkylation in the 1, 2 and 9 positions.

The products obtained in a number of reactions with the ethyl, butyl, 2-butyl, neopentyl and 1-adamantyl halides as well as methyl, ethyl, butyl and 2-butyl methanesulfonates were analysed and identified by recording ^1H NMR and GC-MS spectra of the crude reaction mixtures. The trimethylsulfonium, triethylsulfonium, ethyldimethylsulfonium, butyldimethylsulfonium and 2-butyldimethylsulfonium iodides were also included in the study in order to serve as model compounds. In all cases, the major products consisted of 9-alkyl-9,10-dihydroanthracene, 2-alkyl-1,2-dihydroanthracene and 1-alkyl-1,2-dihydroanthracene accompanied by varying amounts of 9,10-dialkyl-9,10-dihydroanthracene in the reactions with the sterically less hindered substrates, i.e. the ethyl, butyl and 2-butyl bromides and iodides. The 9,10-dialkylated product that originates from an S_N2 reaction between RA$^-$ and RX was the only one detected of its kind and its formation was as expected found to be favoured by a high substrate concentration and a change of X from Br to I. In the reaction with the alkyl methanesulfonates no formation of alcohols that would point to cleavage of the O–S bond instead of the C–O bond could be detected. Note also that the stability of the radical anions of alkyl methanesulfonates is expected to be so high[27,28] that the cleavage process in this case will not be concerted with the electron transfer in reaction (1).

The distribution of the coupling products obtained in the reactions investigated is presented in Table 5 and discussed on the basis of the substrate.

Methyl halides and methanesulfonate. As described in detail in the previous investigation[11] the ratio of substitution in the 9 and 2 position of anthracene varies in the order 0.7:1, 1.4:1, 7.0:1 and 50:1 going from trimethylsulfonium iodide, methyl iodide, methyl bromide to methyl chloride. The product distribution thus seems to be closely related to the development in q in terms of an increase in the amount of substitution in the 9 position as the S_N2 component becomes more important, and on this basis the product distribution could be converted into a description of the reaction mechanism for the three methyl halides. Thus, the S_N2 reaction is found to constitute 29, 79 and 97% for X = I, Br and Cl, respectively, of the total process in excellent agreement with the percentages that have been obtained (and shown in Table 2) by the electrochemical method.[11]

In the reaction between anthracene radical anion and methyl methanesulfonate, 9-methyl-9,10-dihydroanthracene is the only substitution product detected pointing to the presence of a pure S_N2 mechanism in this case. This result could not be confirmed by the q method owing to experimental limitations, but it seems to be consistent with the overall picture presented in this paper and with other literature results.[5,27] Methyl methanesulfonate is probably about as bad an electron acceptor as methyl chloride in DMF as deduced from the linear sweep voltammetric behaviour; the reduction peaks of both compounds are close to the background reduction ($E^p_{red} \approx -2.85$ V vs. SCE at a scan rate of 0.1 V s^{-1}).

Ethyl and butyl halides and methanesulfonates. For the reactions involving these substrates, the trend in the product distribution follows the one observed in the case of the methyl halides, although less pronounced, with a variation in the ratios of substitution in the 9, 2 and 1 positions ranging from for instance 2.4:1:0.2 to 17.2:1:0.6 going from triethylsulfonium iodide to ethyl methanesulfonate. It is also worth noting that the product distribution is completely independent of whether triethylsulfonium iodide or ethyldimethylsulfonium iodide is used as substrate. In the latter case as well as in the cases of butyldimethylsulfonium and 2-butyldimethylsulfonium iodide no methyl substituted product could be detected at all. Such a result is as noted previously

Table 5. The coupling product distribution obtained in the 9, 2 and 1 positions (abbreviated as pos.) of anthracene in the reaction between anthracene radical anion and different substrates in 0.1 M TBABF$_4$/DMF at 20 °C.

RX	Pos. 9[a]	Pos. 2	Pos. 1	$n_9/(n_1 + n_2)$[b]
Trimethylsulfonium iodide[c]	0.7	1	[d]	0.7
Methyl iodide[c]	1.4	1	[d]	1.4
Methyl bromide[c]	7.0	1	[d]	7.0
Methyl chloride[c]	50	1	[d]	50
Methyl methanesulfonate[e]				>100
Triethylsulfonium iodide[f]	2.4	1	0.2	2.0
Ethyl iodide	3.8	1	0.6	2.4
Ethyl bromide	4.3	1	0.5	2.9
Ethyl chloride	7.9	1	0.6	4.9
Ethyl methanesulfonate	17.2	1	0.6	10.8
Butyldimethylsulfonium iodide	2.0	1	0.4	1.4
Butyl iodide	2.7	1	0.3	2.1
Butyl bromide	3.6	1	0.4	2.6
Butyl chloride	5.7	1	0.7	3.4
Butyl methanesulfonate	13.3	1	0.8	7.4
2-Butyldimethylsulfonium iodide	3.6	1	0.5	2.4
2-Butyl iodide	3.6	1	0.4	2.6
2-Butyl bromide	3.2	1	0.4	2.3
2-Butyl chloride	3.3	1	0.6	2.1
2-Butyl methanesulfonate	4.4	1	0.5	2.9
Neopentyl iodide	3.4	1	0.4	2.4
Neopentyl bromide	4.2	1	0.5	2.8
Neopentyl chloride	4.5	1	0.7	2.6
1-Adamantyl iodide	4.2	1	0.3	3.2
1-Adamantyl bromide	4.3	1	0.5	2.9
1-Adamantyl chloride	4.2	1	0.5	2.8

[a]The total amount of substitution in the 9 position is given as the sum of the amount (i.e. the number of moles) of 9-alkyl-9,10-dihydroanthracene and 9,10-dialkyl-9,10-dihydroanthracene. The amount of substitution in the 2 position is settled to one. [b]This term denotes the amount of 9-substitution divided by the total amount of 1- and 2-substitution. [c]From Ref. 11. [d]This isomer could be detected only in small amounts. [e]The only product detectable is 9-methyl-9,10-dihydroanthracene. [f]The same result is obtained for ethyldimethylsulfonium iodide.

certainly not in line with the feature of an S_N2 process but in accordance with the characteristics of an ET reaction and the higher stability of primary and secondary alkyl radicals as compared to the methyl radical.

If the product distribution obtained for the sulfonium salts therefore is the one to be expected for an ET reaction and the S_N2 reaction further is assumed to result solely in substitution in the 9 position, the product ratios (i.e. the amount of 9-substitution divided by the total amount of 1- and 2-substitution) calculated in the last column of Table 5 can be resolved into a determination of the competition ratio of the two mechanisms in each case. In this manner, a relatively small S_N2 component in the order of 12 and 23%, respectively, may be estimated to be present in the reaction between anthracene radical anion and ethyl iodide or bromide, whereas a somewhat higher component is observed when ethyl chloride (ca. 49%), and in particular ethyl methanesulfonate (ca. 75%), are used as substrates. The corresponding numbers for the butyl halides are of the same magnitude (23, 33, 45 and 71%, respectively). The suggestion made elsewhere[15] that the reaction between anthracene radical anion and butyl bromide is a pure electron transfer is thus not borned out by the present investigation.

A straightforward comparison of the above results with the ones obtained by the q measurements is not directly available as in the case of the methyl halides due to the inapplicability of the latter method to the mediator anthracene. Broadly speaking, however, the tendency in the results with an increase of the S_N2 component in the leaving group order R_2S, I^-, Br^-, Cl^- and $CH_3SO_3^-$ is in line with the electrochemical results. Yet, some minor discrepancies may be present on a more detailed level of description considering for instance that the S_N2 mechanism in the reaction of ethyl bromide and chloride with the better electron donor, (E)-stilbene radical anion, has been estimated in Table 4 to constitute 34% and 45%, respectively. These numbers are, in fact, of the same magnitude as the ones obtained for the radical anion of anthracene in the product study and this could point to the presence of a slight overestimation of the S_N2 component by the electrochemical method, as noted previously for the ethyl and butyl halides.

2-Butyl halides and methanesulfonate. No appreciable variation in the ratio of the constitutional isomers can be detected as the leaving group is changed in the series of the 2-butyl systems. This feature points to the presence of a dominating ET mechanism and at the same time it indicates that the q-values obtained for 2-butyl iodide in Table 3 as suspected are somewhat hampered presumably due to side reactions. The trend in the results does suggest, however, that the S_N2 reaction if present for any of the systems will be most pronounced for 2-butyl methanesulfonate (and in that case constitute about 13%). In a previous study of optically active 2-octyl methanesulfonate the S_N2 component has been measured to 25%.[5] It should also be emphasized that a small S_N2

component in the order of 10% as observed in the reaction between anthracene radical anion and the optically active 2-octyl halides[5] will not be within the detection limit of the product analysis method.

Neopentyl and 1-adamantyl halides. As concerns the expected ET reactions between anthracene radical anion and the sterically hindered neopentyl and 1-adamantyl halides, the product distribution is indeed as shown in Table 5 relatively independent of the nature of the leaving group. Note that neopentyl methanesulfonate has been reported to be unreactive towards the radical anion of anthracene.[27]

A final point to note about the results obtained in the product study is that the product distribution obtained in the ET reactions with anthracene radical anion depends very much on the nature of the alkyl radical. For instance, the ratios given in the last column in Table 5 increase from 0.7 in the coupling process (2) with the methyl radical to about three for the corresponding reaction with the 1-adamantyl radical. Clearly, a reliable prediction of the product distribution can not be based solely on the spin density distribution in the radical anion of anthracene (being highest in the 9 position)[29] and the steric conditions of the coupling process but must rely in each specific case on a calculation of the exact nature of the orbital interactions.

Conclusions

In summary, it may be concluded that the reaction between aromatic radical anions and alkyl halides and methanesulfonates can proceed by a competition between an ET and an S_N2 mechanism under the right circumstances. Even though aromatic radical anions normally are considered to be very strong electron donors, the S_N2 reaction can come into play if the substrate is not too sterically hindered (as is the case for the methyl, ethyl and butyl halides and methanesulfonates) and the driving force of the electron transfer reaction is low. The transition from an ET to an S_N2 mechanism is influenced by the exact electronic and steric features of the reactants involved but in general the importance of the S_N2 component increases as a function of E_A° for the aromatic compound and in the leaving group order $(CH_3)_2S$, I^-, Br^-, Cl^- and $CH_3SO_3^-$ with respect to the substrate. The rate-determining step in the reaction with the sulfonium salts can be considered as a pure electron transfer in the cases investigated. In a current project, the influence of temperature on the competition ratio of the two mechanisms is studied in order to gain further insight in the structure of the transition states.[7–9,16–21]

The above results have been obtained through an investigation and detection of the changes in the product distribution as the leaving group was changed, thereby avoiding the need of employing optically active compounds to characterize the reaction mechanism. It should be emphasized, though, that the two methods used, the electrochemical technique and the study of substitution

products, are not well suited for a detection of a small S_N2 component since they are associated with a relatively high uncertainty and may be rather sensitive to the presence of side reactions.

Finally we would like to draw the attention to the possible influence of this investigation on the standard potentials of alkyl radicals determined previously in our group.[22-25] This parameter has been extracted in a procedure taking advantage of the competition between reactions (2) and (3), and it would to some extent be hampered by the presence of a competing S_N2 mechanism. The consequence might be an underestimation of the potentials published for the methyl and primary alkyl radicals by about 100 mV. Also rate constants k_{ET} published previously[30] for assumed ET reactions with the primary alkyl halides should be corrected for a contribution from k_{S_N2}. Such a correction, however, would not affect any of the conclusions presented.

Experimental

Materials. Anthracene, pyrene, (E)-stilbene, m-tolunitrile, p-tolunitrile, trimethylsulfonium iodide, triethylsulfonium iodide, most of the alkyl halides and alkyl methanesulfonates were obtained commercially. 1-Adamantyl iodide[31] and 2-butyl methanesulfonate[32] were prepared according to the references given. Ethyldimethylsulfonium iodide, butyldimethylsulfonium iodide and 2-butyldimethylsulfonium iodide were prepared by mixing the appropriate sulfide with methyl iodide while keeping the temperature below 20 °C.[33,34] The precipitated product was recrystallised from ethanol. m-Tolunitrile and most alkyl halides were distilled prior to use. The supporting electrolyte, tetrabutylammonium tetrafluoroborate ($TBABF_4$) and the solvent, N,N-dimethylformamide (DMF), were purified using standard procedures. Before each experiment the electrolyte solution was dried by passage through a column of activated alumina.

Apparatus. The H-cell employed in all the electrochemical experiments for measuring q was home-made, and the cathodic compartment was equipped with a rotating disk electrode, a reference electrode consisting of a silver wire in 0.1 M tetrabutylammonium iodide/DMF, a platinum net and an inlet and outlet used for purging with argon. A carbon rod was positioned in the anodic compartment. The rotating disk electrode system (Metrohm 628-10, glassy carbon electrode with $\Phi=3$ mm) was obtained commercially. The signals from a home-built potentiostat were recorded using a Nicolet 4094/4570 digital oscilloscope. The equipment was controlled by means of a PC. The preparative reductions were carried out with a 200 W home-built three-electrode potentiostat in a H-cell using the platinum net as cathode, the reference electrode described above and the carbon rod as anode. The GC and GC-MS analysis was performed with a Hewlett-Packard 5890 gas chromatograph on a HP-1 column

combined with a VG Masslab mass spectrometer: injector temperature 250 °C; 40 °C for 5 min to 230 °C at 15 °C min^{-1}. Preparative HPLC (Waters 991, photodiode array detector) was carried out on an RP-18 column, length 25 cm and internal diameter 16 mm with 100% methanol as the eluent, flow 5 ml min^{-1} and detection wavelength 267 nm. The ^{1}H NMR spectra were recorded with a Varian Gemini 200 or 300 MHz spectrometer.

Procedure.

Electrochemical method. The method for determining q by the rotating disk electrode technique has been described elsewhere,[11,26] and only a short description will be given here. Basically, the method takes advantage of the steady-state properties of the rotating disk electrode which may be used to record the changes in the reduction current of A, Δi_A, and oxidation current of $A^{\cdot-}$, $\Delta i_{A^{\cdot-}}$ due to the reaction of $A^{\cdot-}$ with RX. From the reaction stoichiometry of the overall reaction (6), it follows that the relationship between q and the changes in the concentrations of A and $A^{\cdot-}$, ΔC_A and $\Delta C_{A^{\cdot-}}$, is given by eqn. (7).

$$\frac{1+q}{2} = \frac{\Delta C_A}{\Delta C_{A^{\cdot-}}} \tag{7}$$

Using then the relationship between Δi and ΔC given by the Levich equation,[35] the parameter q can be calculated as shown in eqn. (8).

$$q = 2\left(\frac{D_A}{D_{A^{\cdot-}}}\right)^{-2/3}\left(\frac{\Delta i_A}{\Delta i_{A^{\cdot-}}}\right) - 1 \tag{8}$$

In practice, the measurements of q were carried out by outgassing with argon a 40 ml 0.1 M $TBABF_4$/DMF solution containing the aromatic compound (8–10 mM) in the cathodic compartment. A check was made to see if the oxygen wave had disappeared in cyclic voltammetry, using the rotating disk electrode as working electrode and the platinum net as counter-electrode, before a preparative reduction of the aromatic compound was commenced at a constant potential ($E = E_A^\circ$) at the platinum net; a carbon rod in the anodic chamber served as counter-electrode. The reduction was stopped when about 0.4 F mol^{-1} had passed and 3–4 mM of the aromatic radical anion had been produced.

If the stability of the radical anion was high as deduced from steady-state voltammograms recorded by means of the rotating disk electrode, addition of the substrate followed. The liquid alkyl halides were normally added to the cell directly but it was also noted that a five- to ten-fold dilution with deaerated DMF prior to addition had no influence on the measurements. The alkyl methanesulfonates could not be used in this part of the study because they caused in most cases severe distortions of the steady-state voltammograms, thus preventing a reliable determination of q. The gaseous methyl chloride was added in terms of a saturated DMF solution and the sulfonium salts were dissolved in DMF prior to

addition. The concentration of the sulfonium salts and alkyl iodides was always kept below half the value of the radical anion concentration in order to be sure to deplete all substrate in reaction (6) and thus avoid a contribution of its direct reduction to the steady-state curves.

When the reaction had finished the current changes Δi_A and $\Delta i_{A^{\cdot -}}$ were measured from the steady-state diagrams recorded before and after addition of the substrate and the q-value was calculated from eqn. (8) settling $(D_A/D_{A^{\cdot -}})^{2/3}$ at 1.14, 1.07, 1.04, 1.08 and 1.13 for anthracene, pyrene, (E)-stilbene, m-tolunitrile and p-tolunitrile, respectively. The latter values were obtained by applying eqn. (8) to the fully catalytic reaction ($q = 1$) between the aromatic radical anion in question and iodine. For each alkyl halide and radical anion the q-measurements were carried out at least four times. Neither the concentration of the substrate or the radical anion in a range from 2 to 10 mM, nor the rate of addition of the substrate to the solution had any system-atic influence on the q-values obtained. The latter point is rather important in respect to the possible involvement of side reactions in the fast reactions with the alkyl iodides and sulfonium salts. The presence of processes such as hydrogen abstraction or dimerization due to inhomogenity of the reaction solution does thus not seem to be important at all. It should also be noted that nucleophilic reactions between RX and RA^-, R^- or HA^- (HA^- may be formed during the preparative electrolysis through a protonation of the radical anion followed by a further reduction) will not affect the determination of q by the rotating disk electrode method. An S_N2 reaction involving the dianion A^{2-} generated in a disproportionation reaction of $A^{\cdot -}$ is also unlikely from an energetic point of view as discussed elsewhere.[5]

Product study. The preparative reductions were carried out at a platinum net at a constant potential in a H-cell with 40 ml deaerated 0.1 M $TBABF_4/DMF$ in the cath-odic chamber. The initial concentration of anthracene was normally about 10 mM and the substrate was kept at a two- to five-fold excess. In the case of the alkyl iodides and the sulfonium salts the electrode potential was fixed at a potential corresponding to the foot of the reduction wave (ca. -1.8 V vs. SCE) in order to minim-ize as much as possible a direct reduction of the substrates. When the electrolysis was completed (corres-ponding to a charge consumption of about 2 F per mol anthracene) and all anthracene had been consumed, water was added to the catholyte and the products were extracted twice with diethyl ether. The combined ether phases were subsequently washed three times with water in order to remove any residual DMF and dried over magnesium sulfate. The diethyl ether was removed *in vacuo* and the product analysis was carried out using ¹H NMR, GC and GC-MS. If any dihydroanthracene was detected HA^- had most likely been present during the course of the reaction and the results were simply dis-carded. The amount of coupling products isolated consti-tuted about 80% of the theoretical yield.

The identification of coupling products for the reaction between the radical anion of anthracene and the methyl halides was carried out in the previous study by compar-ing with authentic samples.[11] In the present study the characterization of the different isomers was in general obtained simply by recording GC chromatograms and ¹H NMR and GC-MS spectra of the crude reaction mixtures. However, in the case of the 2-butyl halides the spectra were more complicated and the isomers were separated using HPLC. The ratios in Table 5 were calcu-lated from the integrated areas of the characteristic peaks in ¹H NMR, the exceptions being in the case of 1- and 2-ethyl-1,2-dihydroanthracene and 1- and 2-butyl-1,2-dihydroanthracene owing to an overlap of spectra. Instead, the relevant data were obtained by GC assuming equal response factors for each of the two pairs of constitutional isomers. The retention time for the three alkylated dihydroanthracene derivatives in the 9, 1 and 2 position followed the order of compounds listed. In most of the experiments a fourth monoalkylated isomer could be detected by GC-MS. We did not make any attempt to isolate this minor isomer, but presumably it is to be ascribed to 2-alkyl-3,4-dihydroanthracene that has been observed previously in the reaction between anthracene radical anion and *exo*-norbornyl bromide.[6] The 9,10-dialkyl-9,10-dihydroanthracene originating from an S_N2 reaction between RA^- and RX could be observed in varying amounts in the reactions involving the ethyl, butyl and 2-butyl bromides and iodides.

The characteristic peaks used in the yield determina-tion of the substitution products in ¹H NMR are sum-marised in the following.

Anthracene and ethyl halides/triethylsulfonium iodide/ ethyldimethylsulfonium iodide/ethyl methanesulfonate. 9-Ethyl-9,10-dihydroanthracene: δ 3.82 (t, H_9, $J = 7.1$ Hz), 3.87 (d, H_{10}, $J = 18.3$ Hz), 4.13 (d, $H_{10'}$, $J = 18.3$ Hz). 2-Ethyl-1,2-dihydroanthracene: δ 6.09 (dd, H_3, $J = 9.7$ Hz, 3.9 Hz), 6.65 (dd, H_4, $J = 9.7$ Hz, 2.1 Hz). 9,10-Diethyl-9,10-dihydroanthracene: δ 3.77 (t, H_9 and H_{10}, $J = 7.5$ Hz). The spectrum of 1-ethyl-1,2-dihydroanthracene being overlaid by the one of 2-ethyl-1,2-dihydro-anthracene could not be resolved. No methyl substituted or ylide derived products could be detected in the reaction with ethyldimethylsulfonium iodide.

Anthracene and butyl halides/butyldimethylsulfonium iodide/butyl methanesulfonate. 9-Butyl-9,10-dihydro-anthracene: δ 3.87 (d, H_{10}, $J = 18.3$ Hz), 3.91 (t, H_9, $J = 7.3$ Hz), 4.15 (d, $H_{10'}$, $J = 18.3$ Hz). 2-Butyl-1,2-dihydro-anthracene: δ 6.06 (dd, H_3, $J = 9.6$ Hz, 3.7 Hz), 6.62 (dd, H_4, $J = 9.6$ Hz, 1.9 Hz). 9,10-Dibutyl-9,10-dihydro-anthracene: δ 3.88 (t, H_9 and H_{10}, $J = 7.5$ Hz). The spectrum of 1-butyl-1,2-dihydroanthracene being over-laid by the one of 2-butyl-1,2-dihydroanthracene could not be resolved. No methyl substituted products could be detected in the reaction with butyldimethylsulfonium iodide.

Anthracene and 2-butyl halides/2-butyldimethylsulfonium iodide/2-butyl methanesulfonate. The different isomers were isolated by HPLC and characterized fully by NOE (nuclear Overhauser effect) difference spectra and COSY experiments. 9-(2-Butyl)-9,10-dihydroanthracene: δ 0.78 (d, 3 H, $J=6.7$ Hz), 0.87 (t, 3 H, $J=7.2$ Hz), 1.10 (m, 1 H), 1.50 (m, 1 H), 1.70 (m, 1 H), 3.77 (d, H_9, $J=6.8$ Hz), 3.83 (d, H_{10}, $J=18.4$ Hz), 4.15 (d, $H_{10'}$, $J=18.4$ Hz), 7.15–7.33 (m, 8 H). 2-(2-Butyl)-1,2-dihydroanthracene: δ 0.91 (t, 3 H, $J=7.3$ Hz), 0.92 (d, 3 H, $J=6.6$ Hz), 1.26 (m, 1 H), 1.54 (m, 2 H), 2.50 (m, H_2), 2.90 (m, H_1 and $H_{1'}$), 6.04 (dd, H_3, $J=9.7$ Hz, 3.7 Hz), 6.65 (dd, H_4, $J=9.7$ Hz, 2.8 Hz), 7.37 (m, 1 H), 7.44 (s, H_{10}), 7.51 (s, H_9), 7.72 (m, 3 H). Additional signals at 6.02 (dd, H_3, $J=9.7$ Hz, 3.7 Hz) and 6.64 (dd, H_4, $J=9.7$ Hz, 2.8 Hz) are attributed to the presence of the other diastereomeric compounds (produced in equal amount) although it should be noted that the absolute assessment of precisely these two peaks to the one and same diastereomer is not certain. In a NOE difference experiment irradiation of the H_9 proton was found to give rise to a NOE at $\delta=2.90$ ppm and a minor effect at 1.54 ppm. A COSY experiment showed cross coupling between H_3 at $\delta \approx 6.03$ ppm and H_2 at $\delta=2.50$ ppm. 1-(2-Butyl)-1,2-dihydroanthracene: δ 0.88 (t, 3 H, $J=7.3$ Hz), 0.90 (d, 3 H, $J=6.4$ Hz), 0.95–1.40 (m, 2 H), 1.82 (m, 1 H), 2.45 (m, H_2 and $H_{2'}$), 2.88 (q, H_1, $J=5.8$ Hz), 6.05 (m, H_3), 6.59 (bd, H_4, $J=9.7$ Hz), 7.38 (m, 2 H), 7.43 (s, H_{10}), 7.52 (s, H_9), 7.74 (m, 2 H). Additional signals at 2.79 (q, H_1, $J=5.8$ Hz) and 7.48 (s, H_9) are attributed to the presence of the other diastereomeric compounds (produced in equal amount) although it should be noted that the absolute assessment of precisely these two peaks to the one and same diastereomer is not certain. In a NOE difference experiment irradiation of the H_9 proton was found to give rise to a NOE at $\delta=2.88$ and 2.79 ppm as well as in the range 0.9–1.8 ppm. A COSY experiment showed cross couplings between H_3 at $\delta=6.05$ ppm and H_2 and $H_{2'}$ at $\delta=2.45$ ppm. 9,10-Di(2-butyl)-9,10-dihydroanthracene: δ 3.95 (d, H_9 and H_{10}, $J=5.1$ Hz). No methyl substituted products could be detected in the reaction with 2-butyldimethylsulfonium iodide.

Anthracene and neopentyl halides. 9-Neopentyl-9,10-dihydroanthracene: δ 3.82 (d, H_{10}, $J=17.5$ Hz), 4.12 (t, H_9, $J=6.5$ Hz), 4.15 (d, $H_{10'}$, $J=17.5$ Hz). 2-Neopentyl-1,2-dihydroanthracene: δ 6.12 (dd, H_3, $J=9.7$ Hz, 4.0 Hz), 6.59 (dd, H_4, $J=9.7$ Hz, 1.7 Hz). 1-Neopentyl-1,2-dihydroanthracene: δ 6.06 (ddd, H_3, $J=9.7$ Hz, 5.7 Hz, 3.3 Hz), 6.69 (dd, H_4, $J=9.7$ Hz, 2.3 Hz).

Anthracene and 1-adamantyl halides. 9-(1-Adamantyl)-9,10-dihydroanthracene: δ 3.51 (s, H_9), 3.74 (d, H_{10}, $J=18.7$ Hz), 4.19 (d, $H_{10'}$, $J=18.7$ Hz). 2-(1-Adamantyl)-1,2-dihydroanthracene: δ 6.15 (dd, H_3, $J=9.9$ Hz, 4.0 Hz), 6.70 (dd, H_4, $J=9.9$ Hz, 2.1 Hz). 1-(1-Adamantyl)-1,2-dihydroanthracene: δ 6.05 (ddd, H_3, $J=9.7$ Hz, 6.0 Hz, 2.5 Hz), 6.53 (dd, H_4, $J=9.7$ Hz, 2.4 Hz).

Examples of MS data are as follows. 9-Ethyl-9,10-dihydroanthracene [m/z (%)]: 208 (3), 180 (15), 179 (100), 178 (44), 177 (5), 176 (7), 152 (4), 151 (3), 89 (4). 2-Ethyl-1,2-dihydroanthracene [m/z (%)]: 209 (4), 208 (24), 189 (3), 180 (15), 179 (100), 178 (47), 177 (5), 176 (7), 165 (5), 152 (5), 151 (3), 89 (4). 1-Ethyl-1,2-dihydroanthracene [m/z (%)]: 209 (3), 208 (18), 193 (3), 180 (14), 179 (100), 178 (48), 177 (5), 176 (8), 165 (3), 152 (4), 151 (4), 89 (4).

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