

Photoinduced Alkylation of Anthracene by Butyltriphenylborate Ion. A Comparison between Products from the Photochemical and Electrochemical Butylation of Anthracene

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Lund, T., 1996. Photoinduced Alkylation of Anthracene by Butyltriphenylborate Ion. A Comparison between Products from the Photochemical and Electrochemical Butylation of Anthracene. – Acta Chem. Scand. 50: 64–67 © Acta Chemica Scandinavica 1996.

The product mixture of the photoinduced butylation of anthracene by the borate salt $C_4H_9B(C_6H_5)_3$ $N(C_4H_9)_4$ in acetonitrile and *N,N*-dimethylformamide was compared with the product mixture of the reaction of electrogenerated anthracene anion radical with 1-bromobutane. The product mixtures were identical indicating that both reactions proceed through the same radical intermediates.

The reaction of aromatic radical anions $A^{\cdot-}$ with alkyl and benzyl halides RX has been studied intensively over the last 25 years.^{1–4} The generally accepted mechanism is shown in eqns. (1)–(4).

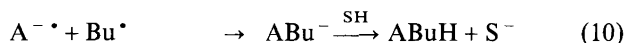
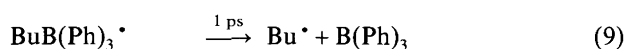
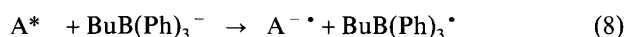


The rate-determining step is an electron transfer (ET) between the radical anion $A^{\cdot-}$ and RX [eqn. (2)]. In the following step the radical R^{\cdot} may either couple with $A^{\cdot-}$ [eqn. (3)] or be reduced [eqn. (4)] depending on the relative reduction potentials of A and R^{\cdot} .⁵ In a series of investigations of the polar vs. ET behaviour of the mechanisms of nucleophilic substitutions^{6–10} and reductive elimination reaction^{10–12} eqn. (2) was assumed to proceed via an outer-sphere ET, defined as an ET in which the electronic overlap in the TS between the donor and the acceptor is less than 1 kcal mol⁻¹.^{13,14} However, based on theoretical calculations,¹⁵ stereochemical,^{16,17} electroanalytical¹⁸ and activation entropy measurements⁸ it has been argued that especially for sterically unhindered alkyl halides there may be an inner-sphere or S_N2 component between $A^{\cdot-}$ and RX in the TS [eqn. (5)].



In this report the question of ET vs. S_N2 of the reaction between anthracene radical anions ($1^{\cdot-}$) and 1-bromobutane is analysed by a new comparative method. The idea is to compare the product mixture of the coupling between photochemically generated freely diffusing $1^{\cdot-}$ and butyl radicals Bu^{\cdot} obtained by the photolysis of solutions of anthracene and butyltriphenylborate ion with the product mixture of the electrochemical generated $1^{\cdot-}$ and radicals from 1-bromobutane. If the product mixtures are identical it may indicate that the reaction between $1^{\cdot-}$ and 1-bromobutane proceeds via an outer-sphere mechanism through the same intermediates as in the photochemical reaction. However, if the S_N2 reaction [eqn. (5)] contributes to the overall coupling reaction, a change in the isomer distribution relative to a pure ET reaction might be expected. Such a change was recently reported in the reactions of $1^{\cdot-}$ with CH_3X ($X = I, Br$ and Cl).¹⁸ In these reactions the ratio between substitution in the 9-position relative to the 2-position in **1** was increased from 1.4:1 ($X = I$) to 50:1 ($X = Cl$) indicating a shift in the mechanism from predominantly ET to predominantly S_N2 .¹⁸

The photoinduced alkylation method of aromatic compounds by alkyltriphenylborates was introduced 10 years ago by Lan and Schuster.^{19,20} They showed that irradiation of acetonitrile solutions of dicyanoarenes with methyl- or benzyl-triphenylborate gave good yields of alkylcyanoarenes. The proposed mechanism is shown in eqns. (7)–(10).



The reaction is initiated by a photoinduced electron transfer (PET) from the alkyltriphenylborate to the excited acceptor A^* followed by a fast cleavage of the alkyltriphenylborane radical. The coupling between the radicals $A^{\cdot-}$ and R^{\cdot} was shown to take place in the solution.²⁰

Anthracene (**1**) may be efficiently alkylated by tetramethylammonium butyltriphenylborate (**2**) in acetonitrile and *N,N*-dimethylformamide (DMF) according to eqns. (7)–(10) with formation of the alkylation products **3**, **4** and **5** in the total yields 26 and 58%, respectively (see Fig. 1). The indirect electrochemical reduction of 1-bromobutane with **1** as a mediator followed the coupling mechanism (1)–(3).⁵ The monoalkylation products **3**–**5** are obtained together with some dialkylation product **6** formed by further alkylation of AR^- by RX . All the photochemical and electrochemical experiments were performed 3–5 times and the average distributions and standard deviations are summarized in Table 1.

It is seen from Table 1 that the photochemical and the electrochemical isomer distributions of **3**–**5** in acetonitrile are identical taking the standard deviation of the distributions into account. The analysis of the electrochemical product mixtures in DMF is more complicated owing to the formation of **6** and minor amounts of other dialkylation products. In order to reduce the formation of dialkylation products H_2O (0.16 mol) was added to the cathodic compartment and the formation of AR_2 products was reduced by a factor of 10. As seen from Table 1 the distribution of **3**:**4**:**5** corrected for the dialkylation product **6** (the amount of **6** is included in **3**) is approximately the same as the distribution in the DMF containing water.

The amount of **4** and **5** relative to **3** obtained by the photochemical method in DMF is somewhat higher than by the electrochemical method and significantly higher than in acetonitrile. However by performing the photolysis in DMF–0.1 M TBABF₄ the amounts of **4** and **5** relative to **3** are decreased compared with the photolysis carried out in pure DMF and the numbers are very close to the composition obtained by the electrochemical method.

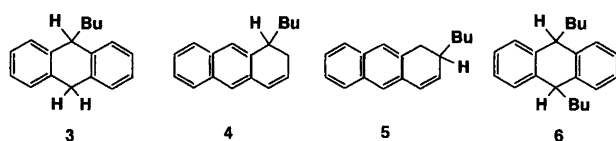


Fig. 1.

The product analysis indicates that the photochemical alkylation of **1** by **2** and the reaction of $1^{\cdot-}$ with 1-bromobutane in both DMF and acetonitrile proceeds via the same intermediates. It is generally accepted that the photochemical alkylation proceeds through the alkyl radical (Bu^{\cdot}) with the acceptor radical anion ($A^{\cdot-}$), so the electrochemically induced coupling is thus indicated to proceed through the same species. The results suggest furthermore that the coupling pattern of the $1^{\cdot-}$ with Bu^{\cdot} is dependent on the solvent and the concentration of supporting electrolyte.

In summary, the above results indicate that the reaction between $1^{\cdot-}$ and 1-bromobutane is initiated by an ET. It is reasonable to assume that the more sterically hindered 2-bromobutane and 2-bromo-2-methylpropane also will react with $1^{\cdot-}$ by an ET mechanism. This conclusion, however, deviates from the interpretation of recent activation entropy measurements⁸ and theoretical calculations²¹ which indicate a certain inner-sphere or $\text{S}_{\text{N}}2$ contribution in the reaction of aromatic anion radicals with BuBr . Finally this report demonstrates that **1** can be alkylated almost quantitatively and efficiently by photolysis of **2** in DMF. Further work in this area with other aromatic compounds and alkyl halides is in progress.

Experimental

Materials. Anthracene and 1-bromobutane were obtained from Aldrich. Tetramethylammonium butyltriphenylborate (**2**),²² 9-butyl-9,10-dihydroanthracene (**3**)²³ and 9,10-dibutyl-9,10-dihydroanthracene (**6**)²³ were prepared according to the references given. The coupling products 1-butyl-1,2-dihydroanthracene (**4**) and 2-butyl-1,2-dihydroanthracene (**5**) were isolated by preparative HPLC from the product mixture of the reduction of anthracene with 1-bromobutane.

Apparatus. Products were identified by GC–MS obtained with a Hewlett Packard 5890 A gas chromatograph equipped with a 5971A MSD. An HP5 25 m, 0.25 mm internal diameter GC-column was used, injection temperature 250°C, helium flow 1.0 ml min⁻¹, temperature programme 100°C in 2 min to 300°C, rate 10°C min⁻¹. Quantitative analysis was performed by GC–FID. The ¹H NMR spectra were recorded with a Bruker 250 MHz spectrometer. Preparative HPLC was performed on an RP-18 column, length 25 cm and 4 mm i.d. with 100% methanol as the eluent, flow 5 ml min⁻¹ and detection wavelength 267 nm.

Photolysis of anthracene and borate. A Pyrex tube containing an argon-saturated solution of anthracene (10 mM) and tetramethylammonium butyltriphenylborate (10 mM) in acetonitrile or DMF was irradiated for 30–60 min with a focused light beam from an Oriel 500 W Hg lamp filtered through a water bath and a Scott

Table 1. Comparison of the product distributions obtained by the photoinduced butylation of anthracene with tetramethylammonium butyltriphenylborate and by the reaction of electrogenerated anthracene radical anions with BuBr.

Method	Solvent	Number of runs	3	4	5	6	Yield ^c 3-6 (%)
Photo	CH ₃ CN	5	100	15.7(1.6)	19.3(3.0)	0	26(4)
Electro	CH ₃ CN	3	100	14.7(0.8)	17.1(3.0)	0-1	44(7)
Photo	DMF	5	100	34.5(1.5)	51.0(3.2)	0	58(10)
Photo	DMF-0.1 M TBABF ₄	5	100	30.9(0.8)	40.0(1.1)	0	36(6)
Electro	DMF ^a	5	100	22.3(1.2)	37.0(1.1)	3-28	97(7)
Electro	DMF ^b	3	100	24.5(1.7)	36.0(1.8)	2.0(0.1)	105(1)

^aThe amount of **6** was added to the amount of **3**. The numbers for **4**, **5** and **6** are calculated relative to ($n_3 + n_6$). ^bH₂O (0.16 M) added to the cathodic compartment. ^cYield = $\{n_3 + n_4 + n_5 + n_6\} / [n_1(\text{start}) - n_1(\text{final})] \times 100\%$.

305 mm cut-off filter. The photolysis mixture was analysed by GC-FID after the addition of naphthalene as an internal standard. The following molar response factors of compounds **1**, **3** and **6** were obtained relative to naphthalene: 1.30 (**1**), 1.72 (**3**), 2.12 (**6**). The response factors of **4** and **5** were assumed to be equal to the response factor of **3**.

Reduction of anthracene and 1-bromobutane. Anthracene (0.56 mmol) and 1-bromobutane (2.40 mmol) was reduced at a platinum electrode at -1.5 V vs. a silver wire reference electrode in an H-cell containing a cathodic volume of 30 ml of argon-deaerated solution of DMF or acetonitrile-0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄). After the consumption of 50-108 C two drops of acetic acid were added together with naphthalene as an internal standard and the reaction mixture analysed by GC-FID.

Identification of compounds: Tetramethylammonium butyltriphenylborate (2). ¹H NMR (CD₃CN): δ 0.82 (t, 3 H, $J = 7.5$ Hz), 0.92 (m, 4 H), 1.22 (quintet, 2 H, $J = 7.06$ Hz), 2.86 (s, 12 H), 6.97 (t, 6 H, $J = 7.25$ Hz), 7.28 (br m, 6 H). ¹³C NMR (CD₃CN): 15.0, 28.8 (q, ²J_{C-B} = 21.75 Hz), 28.8 (q, ¹J_{CB} = 169.0 Hz) 31.7, 56.0 (t, ¹J_{CN} = 4.2 Hz), 122.4, 126.4 (q, ²J_{CB} = 11.0 Hz) 135.7, 166.8 (q, ¹J_{CB} = 192.0 Hz).

9-Butyl-9,10-dihydroanthracene (3). ¹H NMR (CDCl₃): δ 0.83 (t, 3 H, $J = 6.99$ Hz), 1.25 (m, 4 H), 1.61 (m, 2 H), 3.83 (d, H₁₀, ²J = 18.3 Hz), 3.87 (t, H₉, $J = 7.25$ Hz) 4.11 (d, H₁₀, ²J = 18.2 Hz), 7.20 (m, 8 H). MS [m/z (%)]: 236 (1.6), 180 (21), 179 (100), 178 (60), 177 (5), 176 (8), 152 (6), 151 (3), 150 (2), 41 (2).

1-Butyl-1,2-dihydroanthracene (4). ¹H NMR (CDCl₃): δ 0.87 (t, 3 H, $J = 6.96$ Hz), 1.31 (m, 4 H), 1.63 (m, 2 H), 2.30 (H₂, dt, $J = 17.22$, 5.15, 4.51 Hz), 2.59 (H₂', dq, $J = 17.3$, 6.18, 2.95 Hz), 3.92 (H₁, sextet, $J = 7.42$, 5.74, 4.18 Hz), 6.03 (H₃, septet, $J = 9.54$, 5.43, 3.37 Hz), 6.62 (H₄, qt, $J = 9.87$, 2.30 Hz), 7.38 (m, 2 H), 7.45 (s, 1 H), 7.50 (s, 1 H), 7.73 (m, 2 H). MS [m/z (%)]: 237 (7), 236

(33), 180 (30), 179 (100), 178 (85), 177 (8), 176 (11), 165 (8), 152 (9), 151 (5).

2-Butyl-1,2-dihydroanthracene (5). ¹H NMR (CDCl₃): δ 0.89 (t, 3 H, $J = 7.08$ Hz), 1.33 (4 H, m), 1.63 (2 H, m), 2.5 (m, H₂), 4.13 (q, H₁, $J = 11.88$, 4.34 Hz), 4.29 (q, H₁', $J = 11.87$, 4.32 Hz), 6.05 (q, H₃, $J = 9.65$, 3.75 Hz), 6.60 (q, H₄, $J = 9.66$, 1.90 Hz), 7.36 (m, 2 H), 7.43 (s, H), 7.51 (s, H), 7.73 (m, 2 H). MS [m/z (%)]: 237 (7), 236 (37), 193 (7), 180 (31), 179 (100), 178 (89), 177 (9), 176 (11), 165 (11), 152 (9).

9,10-Dibutyl-9,10-dihydroanthracene (6). ¹H NMR (CDCl₃): δ 0.90 (t, 3 H, $J = 7.17$ Hz), 1.3 (m, 2 H), 1.53 (m, 2 H), 1.73 (m, 2 H), 3.85 (t, $J = 7.54$ Hz), 7.21 (m, 8 H). MS [m/z , %] 292 (1.3), 236 (19), 235 (98), 191 (6), 189 (4), 180 (11), 179 (100), 178 (65), 177 (5), 176 (5).

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Received May 12, 1995.