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Reductive Coupling of Anthracene with 1,2- and 1,3-Dihalides

EJNAR HOBOLTH and HENNING LUND

Department of Organic Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

The reductive coupling of electrolytically generated anthracene anion radical with some 1,2- and 1,3-dihalides has been investigated. Coupling of 1,3-dihalides in the 1- or 2-position resulted in ring closure to cyclopentano anthracene derivatives.

Anion radicals, generated chemically [1] or electrochemically, [2,3] are useful reagents for reductive eliminations. Anion radicals may, however, couple with simple [4–6] alkyl halides or dihalides;[7,8] below is described the reaction between electrolytically generated anthracene (*1*) anion radical and the following 1,2- and 1,3-dihalides: 1,2-dichloroethane (*2*), 1,3-dibromopropane (*3*), and 1-bromo-3-chloropropane (*4*).

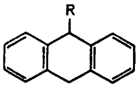
RESULTS

Electrochemical reduction of *1* in *N*,*N*-dimethylformamide (DMF) containing tetrabutylammonium iodide (TBAI) in the presence of *2* gave a mixture of 9-(2′-chloroethyl)-9,10-dihydroanthracene (*5*) and 9,10-dihydro-9,10-ethanoanthracene (*6*). The ratio of *5* to *6* depended on the relative concentrations of *1* and *2*, the higher the *2*/*1* ratio the higher the *5*/*6* ratio. The structure of *5* was proposed on the basis of the ^{1}H NMR and mass spectra (see Experimental). Besides *5* and *6* minor amounts of 9,10-dihydroanthracene were sometimes isolated.

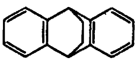
In the presence of *3* the electrochemical reduction of *1* gave a mixture of 2,3,3a,11b-tetrahydrocyclopenta[*a*]-anthracene (*7*) and 9-(3′-bromopropyl)-9,10-dihydroanthracene (*8*). The proposal for the structure of *7* rested on the ^{1}H and ^{13}C NMR spectra, the UV and mass spectra. The UV spectrum excluded a 9,10-dihydroanthracene, the allylic coupling to the ethylenic protons in the ^{1}H NMR spectrum showing the position of the cyclopentano ring.

A reduction of *1* in the presence of *4* gave a mixture of *7* and 9-(3′-chloropropyl)-9,10-dihydroanthracene (*9*).

Table 1 shows the yields of the products, the *n*-values and the differences (ΔE) in the voltammetric peak potentials (E_p) between *1* and the dihalides.



5, $R = CH_2CH_2Cl$
8, $R = CH_2CH_2CH_2Br$
9, $R = CH_2CH_2CH_2Cl$



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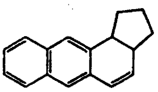

7,

DISCUSSION

Cyclic voltammetry of *1* in the presence of *2*, *3*, or *4* showed that the peak current increased on addition of any one of the dihalides; the increase was largest for *3* and smallest for *2* and thus the larger the smaller ΔE_p (Table 1) was. This may be interpreted [10] as a reduction of the dihalide by electron transfer in solution from $1^{-\cdot}$. The catalytic reduction of the dihalides [2] explains the high *n*-values in the preparative reactions.

The reactions 1 to 5 have previously [2,6] been proposed for the reaction between electrochemically generated anion radicals ($A^{-\cdot}$) and alkyl halides; here the dihalides are represented by YBX.

$$A + e^- \rightleftharpoons A^{\cdot -} \tag{1}$$

$$A^{-\cdot} + YBX \rightleftharpoons A + YBX^{-\cdot} \tag{2}$$

Table 1. Product distribution in the electrochemical reduction in DMF/0.1 M TBAI of anthracene (*1*) in the presence of 1,2-dichloroethane (*2*), 1,3-dibromopropane (*3*), or 1-bromo-3-chloropropane (*4*).

1/mmol	Dihalide (mmol)	n	ΔE_p/V	Yield of products (%)	
10	*2*(50)	8 – 10	> 0.8	*5*(19)	*6*(57)
10	*2*(250)	10 – 12	> 0.8	*5*(38)	*6*(46.5)
10	*2*(375)	10 – 12	> 0.8	*5*(50)	*6*(27)
2.5	*3*(10)	7 – 8	0.33	*7*(55)	*8*(37)
2.5	*4*(10)	5 – 6	0.45	*7*(41)	*9*(34)

$$\mathrm{YBX^{-\cdot} \rightarrow YB^{\cdot} + X^{-}} \qquad (3)$$

$$\mathrm{A^{-\cdot} + YB^{\cdot}} \;\begin{array}{ll} \nearrow\!\rightleftharpoons \mathrm{A + YB^{-} \rightarrow B + Y^{-}} & (4) \\ \searrow\!\rightarrow \mathrm{YBA^{-}} & (5) \end{array}$$

Other mechanisms for the coupling reaction might be possible; the reactions 6 to 10 will also be discussed.

$$\mathrm{A + YB^{\cdot} \rightleftharpoons YBA^{\cdot} \xrightarrow{e^{-}} YBA^{-}} \qquad (6)$$

$$\mathrm{A + YB^{-} \rightleftharpoons YBA^{-}} \qquad (7)$$

$$\mathrm{A^{-\cdot} + YBX \rightleftharpoons YBA^{\cdot} + X^{-} \xrightarrow{e^{-}} YBA^{-}} \qquad (8)$$

$$\mathrm{AH^{-} + YBX \rightleftharpoons YBAH + X^{-}} \qquad (9)$$

$$\mathrm{A^{2-} + YBX \rightleftharpoons YBA^{-} + X^{-}} \qquad (10)$$

A nucleophilic substitution (eqn. 10) of anthracene dianion on YBX is unlikely for two reasons. The concentration of A^{2-}, formed by disproportionation of 2 $A^{-\cdot}$, is very low as $E_{\frac{1}{2}}^{1} - E_{\frac{1}{2}}^{2} = 0.7$ V, where $E_{\frac{1}{2}}^{1}$ and $E_{\frac{1}{2}}^{2}$ are the potentials of the first and second electron transfer, respectively; furthermore, the rate of electron transfer from A^{2-} to YBX would be rapid, and the electron transfer would result in the formation of $A^{-\cdot}$ and $YB^{\cdot}$ after loss of X^{-}, which ought to give a coupling analogous to eqn. 5.

A nucleophilic substitution (eqn. 9) of AH^{-} (dihydroanthracene anion) on YBX is difficult to exclude, but it cannot be the only reaction as it can neither explain the catalytic reduction of YBX indicated by the voltammetric results nor the formation of *6* or *7*. *6* and *7* are believed to be formed by an intramolecular nucleophilic substitution with YBA^{-} [the anion of 9-(2′-chloroethyl)-9,10-dihydroanthracene, respectively 2-(or 1-)-(3′-halopropyl)-1,2-di-dihydroanthracene].

The mechanism shown in eqn. 8 is also considered unlikely, as the S_N-reactivity of an anion radical of an aromatic hydrocarbon is low.[4,5]

A nucleophilic addition of YB^{-} to A (eqn. 7) would require a very fast addition reaction as YB^{-}, if formed at all, would lose Y^{-} with the formation of an alkene or a cyclopropane in a rapid reaction; the formation of such products probably accounts for the high n-value. Furthermore, eqn. 7 could in principle be a reversal of eqn. 4 followed by eqn. 5.

A coupling mechanism according to eqn. 5 and/or eqn. 6 seems thus operating. When ΔE_p is large, and the rate of eqn. 2 thus lower,[10] the colour of $1^{-\cdot}$ is visible in the neighbourhood of the electrode, whereas this is not so when ΔE_p is small. In the latter case the coupling takes place close to the electrode where the concentrations of A and $A^{-\cdot}$ are of comparable magnitude; under these conditions eqn. 6 cannot compete successfully with eqn. 5. At a greater distance from the electrode eqn. 6 might compete better with eqn. 5, but whether a significant part of the coupling proceeds *via* eqn. 6 is not clear. Other investigations[11,12] favour eqn. 5 as the coupling mechanism.

The electron uptake after the coupling required in eqn. 6 might occur *via* the electrode or *via* an anion radical $A^{-\cdot}$; if eqn. 6 occurs only far from the electrode, $A^{-\cdot}$ would be the electron source, but the concentration of $A^{-\cdot}$ would be low. $YBA^{\cdot}$ might abstract a hydrogen atom from solvent rather than accept an electron, but in that case the formation of *6* and *7* is difficult to explain.

Whether the coupling leading to *7* takes place preferentially in the 1- or 2-position is not clear as in both cases ring closure to *7* would result. In a similar coupling between $1^{-\cdot}$ and *t*-butyl bromide the attack in the 2-position predominates, but here steric factors may play a greater role than in the present case.

The preparation of compounds *5* to *9* is a special example of a reaction between electrolytically generated anion radicals and YBX-compounds, where Y represents a functional group. The coupling of anion radicals with YBX-compounds, where Y represents other functional groups than halogen, is being investigated.

EXPERIMENTAL

General procedure for reductions. Anthracene (0.5 – 2 g) was dissolved in dry DMF (150 ml) containing TBAI (7.5 g) and the dihalide (1 – 5 ml) and reduced at a mercury pool electrode (area 25 cm^2) at – 1.95 V *vs.* aq. SCE. After completion of the reduction the catholyte was diluted to 1 l with water and the products extracted with an organic solvent from which DMF and basic impurities were removed by washing with dilute acid and water.

Reduction of anthracene and 1,2-dichloroethane. The products were isolated by extraction with benzene. After evaporation of the washed and dried benzene layer the residue was separated on a column of alumina with 5 % ethyl acetate in light petroleum as eluent; isolated were *5* and *6*, yields are given in Table 1. If the DMF contained traces of proton donors some 9,10-dihydroanthracene was formed and lower yields of *5* and *6* obtained.

9-(2′-Chloroethyl)-9,10-dihydroanthracene, *5*, m.p. 154 – 156 °C. ^{1}H NMR ($CDCl_3$): δ 1.92 (*q*, *J* 6.5 Hz, 2 H, 1′-CH_2), 3.42 (t, *J* 6.5 Hz, 2 H, CH_2-Cl), 3.74 (d, *J* 20 Hz, 1 H, 10-CH), 4.02 (d, *J* 20 Hz, 1 H, 10-CH), 4.18 (t, *J* 7 Hz, 1 H, 9-CH), 7.07 – 7.40 (m, 8 H, arom. H). Mass spectrum, *m/e* (%): 244 (1), 243 (7), 242 (21), 241 (20), 240 (48), 207 (2), 205 (6), 203 (10), 202 (11), 193 (46), 191 (100), 189 (18), 178(20), 165 (25), 63 (22).

9,10-Dihydro-9,10-ethanoanthracene, *6*, m.p. 144 – 145 °C (142 – 143 °C).[13] ^{1}H NMR ($CDCl_3$):[14] δ 1.57 – 1.77 (m, 4 H, $(CH_2)_2$); 4.15 – 4.35 (m, 2 H, 9, 10-CH); 6.85 – 7.40 (m, 8 H, arom. H). The methylene protons in the ethylene bridge and the 9 and 10 protons formed an $A^1A^2A^3A^4B^1B^2$-system, which was analyzed employing LAOCN-3.[9] The best fit was obtained with the following parameters: $\delta A^1 = \delta A^2 = \delta A^3 = \delta A^4 = 1.67_5$, $\delta B^1 = \delta B^2 = 4.25$; $J_{A^2B^1} = J_{A^3B^2} = J_{A^4B^2} = 2.7$ Hz, $J_{A^1A^2} = J_{A^3A^4} = -14.0$ Hz, $J_{A^1A^3} = J_{A^1A^3} = 4.0$ Hz, $J_{A^1A^4} = J_{A^2A^3} = 12.0$ Hz. Other couplings = 0. Mass spetrum, *m/e* (%): 207 (1), 206 (9), 179 (22), 178(100), 176 (10), 165 (3), 152 (14), 151 (13), 88 (22).

Reduction of 1 *plus 1,3-dibromopropane (3).* The products were extracted with ether: the organic solvent was washed, dried and evaporated leaving a residue, which was separated into its components on a column of silica with carbon tetrachloride as eluent. *7* and *8* were isolated, *7* was eluted before *8*.

2,3,3a,11b-Tetrahydrocyclopentano[a]anthracene, *7*, m.p. 77 – 78 °C (light petroleum). ^{1}H NMR ($CDCl_3$): δ 1.35 – 2.25 (m, 6 H, $(CH_2)_3$), 2.75 – 3.33 (m, 2 H, H-3a, H-11b), 5.70 (double d, J_1 10 Hz, J_2 3 Hz, 1 H, H-4), 6.47 (double d, J_1 10 Hz, J_2 2 Hz, 1 H, H-5), 7.07 – 7.82 (m, 6 H, arom. H). ^{13}C NMR ($CDCl_3$): δ 23.78, 33.60, 33.35, 39.19, 42.63, 124.80, 125.19, 125.38, 125.94, 126.15, 127.09, 127.54, 130.66, 132.74, 133.16, 133.72, 137.34. Off-resonance decoupling of *sp*^{3}-carbons showed two methine and three methylene groups. Mass spectrum, *m/e* (%): 220 (100), 192 (76), 191 (90), 179 (69), 178 (78). IR (KBr) cm^{-1}: 2900 (w), 1480 (w), 1435 (w), 945 (w), 880 (s), 742 (s). UV (96 % ethanol) λ_{max}: 299 (log $\varepsilon = 4.04$), 288 (log $\varepsilon = 4.11$), 278 (log $\varepsilon = 4.02$), 263 (log $\varepsilon = 4.32$), 252 (log $\varepsilon = 4.52$), 246 nm (log $\varepsilon = 4.53$). Peak potential E_p (HME, DMF/0.1 M TBAI, $v = 400$ mV/s) = – 2.42 V (aq. SCE).

9-(3′-Bromopropyl)-9,10-dihydroanthracene, *8*, liquid. ^{1}H NMR ($CDCl_3$): δ 1.6 – 1.95 (m, 4 H 1′-CH_2, 2′-CH_2), 3.05 – 3.3 (m, 2 H, –CH_2Br), 3.7 – 4.0 (m, 1 H, 9-CH), 3.79 (d, 19 Hz, 1 H, 10-C), 4.03 (d, 19 Hz, 1 H, 10-C), 6.95 – 7.35 (m, 8 H, arom. H). MS, m/e (%): 302 (0.1), 301 (0.2), 300 (0.4), 299 (0.4), 298 (0.5), 297 (0.3), 221 (0.1), 220 (0.4), 219 (0.5), 192 (1.8), 191 (5), 180 (19), 179 (100), 178 (37). IR (CCl_4) cm^{-1}: 3050 (m); 2910 (s), 1475 (s), 1445 (s), 1250 (m), 1235 (m), 953 (w).

Reduction of 1 *plus 1-bromo-3-chloropropane (4).* The reaction was performed as described above for *1 + 3*. *9* was isolated as well as *7*.

9-(3′-Chloropropyl)-9,10-dihydroanthracene, *9*, m.p. 41 °C (light petroleum). ^{1}H NMR ($CDCl_3$): δ 1.6 – 1.85 (m, 4 H, 1′-CH_2, 2′-CH_2), 3.25 – 3.5 (m, 2 H, 3′-CH_2Cl), 3.75 – 4.1 (m, 1 H, 9-CH), 3.83 (d, *J* 18.5 Hz, 1 H, 10-CH), 4.08 (d, *J* 18.5 Hz, 1 H, 10-CH), 7.10 – 7.30 (m, 8 H, arom. H). MS, *m/e* (%): 258 (0.1), 256 (0.4), 220 (1.1), 219 (1.6), 193 (9), 191 (10), 180 (17), 179 (100), 178 (32), 77 (13), 75 (20).

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