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Electrolysis in Non-nucleophilic Media

Part V.[1] Formation of Mixed Biaryls in the Anodic Oxidation of Naphthalene in the Presence of Alkylbenzenes

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The anodic oxidation of naphthalene in the presence of alkylbenzenes in 0.1 M $Bu_4NBF_4/CH_3CN/CH_3COOH$ at a platinum anode results in the formation of 1-arylnaphthalenes. The products are assumed to be formed in an electrophilic reaction between naphthalene cation radicals and alkylbenzenes. The relative yield of 1-arylnaphthalenes follows the relative nucleophilicity of the alkylbenzenes. Preparative scale electrolysis was carried out with naphthalene/isodurene and naphthalene/pentamethylbenzene mixtures and gave 1-(2,3,4,6-tetramethylphenyl)-naphthalene and 1-(pentamethylphenyl)-naphthalene in 42 % and 56 % yields, respectively.

In Part IV of this series it was shown that anodic oxidation of naphthalene in an acetic acid/acetonitrile mixture and in the presence of mesitylene gave 1,1′-binaphthyl and 1-mesitylnaphthalene as the only products.[1] On the basis of voltammetric data and the products, it was suggested that the mixed biaryl was formed according to eqns. (1)–(3):

$$ArH \rightarrow ArH^{+\cdot} + e \quad (1)$$

$$ArH^{+\cdot} + Ar'H \rightarrow H-\overset{+}{Ar}-\dot{Ar}'-H \quad (2)$$

$$H-\overset{+}{Ar}-\dot{Ar}'-H \rightarrow Ar-Ar' + e + 2H^{+} \quad (3)$$

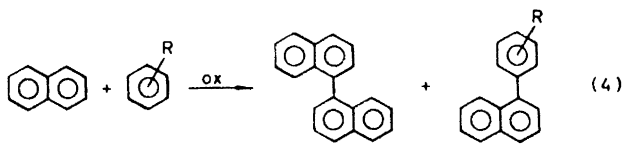
ArH = naphthalene, Ar′H = mesitylene

This type of mechanism has also been suggested for the anodic coupling of polymethylbenzenes.[2]

The preparative and mechanistic aspects of the mixed coupling reaction are further investigated in this paper. Anodic oxidation of naphthalene has been carried out in the presence of a number of alkylbenzenes.

RESULTS

Small scale electrolysis was carried out on 50 ml solutions of CH_3CN/CH_3COOH (volume ratio 9:1) containing 0.1 M Bu_4NBF_4, naphthalene and the appropriate alkylbenzene between two platinum electrodes using the saturated calomel electrode as a reference electrode. In general, only two products were formed, 1,1′-binaphthyl (I) and a mixed biaryl (II). In order



(4)

I II

to reduce further reactions of the products, the current yields of I and II were determined after passage of 0.2 *F*/mol of naphthalene. The results from these experiments are presented in Table 1. The yield of mixed biaryl increases remarkably in going from *m*-xylene to pentamethylbenzene, *i.e.* when the number of methyl groups in the alkylbenzene is increased. An exception is durene, which will be mentioned later.

Table 1. Anodic oxidation of naphthalene (1.0 M) in CH_3CN/CH_3COOH (volume ratio 9:1) containing 0.1 M Bu_4NBF_4 in the presence of alkylbenzenes at a platinum anode. Anode potential 1.4 – 1.5 V.

Alkylbenzene	Conc. (M)	% Yield of 1,1′-binaphthyl	% Yield of mixed biaryl
m-Xylene	3.0	28	0.4
1,2,4-Trimethylbenzene	3.0	24	1.6
Mesitylene [a]	3.0	22	19
Durene	1.0	21	1.1
Isodurene	1.0	10	32
Pentamethylbenzene	1.0	1.6	64
5-Isopropyl-*m*-xylene	3.0	31	8.3
5-*t*-Butyl-*m*-xylene	3.0	36	4.2
1,3,5-Triethylbenzene [b]	1.5	30	6.6

[a] Data from Ref. 1.
[b] Naphthalene conc. 0.5 M.

Durene, isodurene and pentamethylbenzene are oxidized in the same potential region as naphthalene, while the other alkylbenzenes are oxidized at significant higher anode potentials. This means that the latter compounds are not oxidized during the electrolysis, since the working potential was set near the oxidation potential of naphthalene. The mixed biaryl must therefore in these cases be formed from the reaction of oxidized naphthalene, and most

reasonably its cation radical. However, in the case of durene, isodurene, and pentamethylbenzene, one cannot draw the same conclusion by just regarding the difference in oxidation potentials. For this reason anodic oxidation of naphthalene in the presence of isodurene or pentamethylbenzene was carried out at different concentrations of the substrates. The results from these experiments are shown in Tables 2 and 3. Keeping the concentration of naph-

Table 2. Anodic oxidation of naphthalene in CH_3CN/CH_3COOH/0.1 M Bu_4NBF_4 in the presence of isodurene at a Pt anode. Anode potential 1.4 – 1.5 V.

Naphthalene conc. M	Isodurene conc. M	% Yield of binaphthyl	% Yield of mixed biaryl
0.2	1.0	4	29
1.0	0.2	14	8
1.0	1.0	10	32
1.0	2.0	6	36

Table 3. Anodic oxidation of naphthalene in CH_3CN/CH_3COOH/0.1 M Bu_4NBF_4 in the presence of pentamethylbenzene at a Pt anode. Anode potential 1.4 – 1.5 V.

Napthalene conc. M	Pentamethyl-benzene conc. M	% Yield of binaphthyl	% Yield of mixed biaryl
0.2	1.0	–	48
0.5	1.0	1.2	48
1.0	0.2	3.4	21
1.0	0.5	2.7	42
1.0	1.0	1.6	64
1.0	2.0	1.3	62

thalene constant at 1.0 M and increasing the isodurene concentration from 0.2 M to 2.0 M results in a considerable increase in the yield of mixed biaryl. On the other hand there is no significant change in the yield of mixed biaryl when the isodurene concentration is kept constant and that of naphthalene is varied. The same pattern is shown by the results in Table 3, which indicates that only naphthalene is oxidized during the electrolyses.

Two 5-alkylsubstituted *m*-xylenes were also used as substrates. Thus, naphthalene was electrolyzed with 5-isopropyl- and 5-*t*-butyl-*m*-xylene, respectively, but in both experiments only low yields of mixed biaryl were formed, as shown in Table 1. The yields should be compared with that obtained from oxidation of naphthalene in the presence of mesitylene, which is much higher. This behaviour is similar to the one observed from anodic coupling of the same three compounds.[3] Mesitylene affords a biaryl in much higher yield than 5-isopropyl- or 5-*t*-butyl-*m*-xylene.

The preparative use of the mixed coupling reactions was also investigated. The anodic oxidation of naphthalene in the presence of isodurene on a preparative scale produced 1-(2,3,4,6-tetramethylphenyl)-naphthalene (III) in

an isolated current yield of 42 %. Oxidation of naphthalene in the presence of pentamethylbenzene gave 1-(pentamethylphenyl)-naphthalene (IV) in 56 % yield. Although the yields of mixed biaryls from oxidation of naphthalene in the presence of 5-isopropyl-*m*-xylene, 5-*t*-butyl-*m*-xylene, and 1,3,5-triethylbenzene were low, attempts were made to isolate these compounds on a preparative scale. Only in the case of 1,3,5-triethyl-benzene was this practically feasible, the mixed biaryl, 1-(2,4,6-triethylphenyl)-naphthalene, being isolated in a crude state in 2 % current yield.

DISCUSSION

The results presented in this paper clearly support the mechanism proposed for the anodic coupling of aromatic hydrocarbons, *i.e.* eqns. (1) – (3). Mixed biaryls are formed, although only one of the aromatic compounds is electroactive under the conditions used during the electrolysis, which must mean that the cation radical reacts as an electrophile to form the coupled product.

In Part IV of this series,[1] it was demonstrated by current-voltage curves that electrolysis of naphthalene and mesitylene in the system $CH_3CN/CH_3COOH/Bu_4NBF_4$ proceeds by preferential oxidation of naphthalene. If one attempts to apply the same technique to the electrolysis of naphthalene/isodurene or naphthalene/pentamethylbenzene mixtures one does not obtain any useful information, since these three compounds are oxidized at about the same anode potential. Therefore the amount of mixed biaryl and 1,1′-binaphthyl was determined for the electrolysis of the mixtures mentioned under various conditions (Tables 2 and 3). The yields of mixed biaryl increases significantly only when the concentration of the alkylbenzene is increased.

Electrolysis was also carried out in the same medium but in the absence of naphthalene. The products obtained from the anodic oxidation of isodurene or pentamethylbenzene were mainly polymethylbenzyl acetates formed in about 40 % yield, and only small amounts of dehydrodimers, substituted diphenylmethanes, were present.

Further support for an electrophilic reaction is obtained by comparing the relative yields of mixed biaryls with the relative basicity of the alkylbenzenes.[4] The basicity of the alkylbenzenes can also be taken as a measure of their relative nucleophilicity, although some caution should be exercised with the highly substituted benzenes, since steric factors may reduce the nucleophilicity. The data presented in Table 4 show a good correlation between the relative basicity of the alkylbenzenes and the relative yields of mixed biaryls. The latter values were calculated by taking into account the amount of binaphthyl formed at the same concentration level of alkylbenzene. Competitive experiments verified the relation. Electrolysis of naphthalene and durene gave a low yield of mixed biaryl, which certainly is due to the low nucleophilicity of durene. In the presence of the more nucleophilic substrates, mesitylene, isodurene, and pentamethylbenzene, electrolysis of naphthalene gave the highest yields of mixed biaryls.

In connection with the mechanism it is of interest to discuss the observation that naphthalene is the only compound that is oxidized during electrolysis,

Table 4. Relation between the yield of mixed biaryl from anodic oxidation of naphthalene in the presence of alkylbenzenes and the basicity of the alkylbenzenes.

Alkylbenzene	Relative yield of mixed biaryl	Relative basicity
m-Xylene	1	1
1,2,4-Trimethylbenzene	6	3.5
Durene	10	1.4
Mesitylene	61	560
Isodurene	650	5 000
Pentamethylbenzene	7 600	19 000

although the alkylbenzenes are present. If one examines only the oxidation potentials of these compounds, one would expect the alkylbenzenes as well as naphthalene to be oxidized. However, this is obviously not the case. One reason for this behaviour might be a preferential adsorption of naphthalene molecules at the anode surface. This would lead to a blocking of the appropriate alkylbenzene molecules and thereby only oxidation of naphthalene will take place.[5-7]

The synthetic utility of anodic coupling reactions is further demonstrated in this work. Especially the high yield of 1-(pentamethylphenyl)-naphthalene from oxidation of naphthalene in the presence of pentamethylbenzene is remarkable.[8]

However, there are certain limitations in the use of anodic coupling reactions for synthesis of biaryls. Some of these are: firstly, the product should not be oxidizable at a significantly lower anodic potential than the starting materials. Secondly, the substrate should be highly substituted; otherwise further reactions will take place leading to oligomers and polymers. Thirdly, the substrate, or one of the substrates in a mixed coupling, should possess sufficient nucleophilicity to react with the cation radical which is produced. And fourthly, the positive charge density in the cation radical must be large in an unsubstituted position.[2] It is obvious from these restriction that the number of suitable aromatic hydrocarbons, which are available for such coupling, is limited. Experience so far indicates that the anodic coupling of aromatic hydrocarbons will be most useful in the preparation of highly substituted biaryls.

EXPERIMENTAL

The electrolysis cell, potentiostat, and the analytical instruments were the same as previously reported.[1]

Materials. Acetonitrile (Baker, 0.3 %), and acetic acid (*p.a.*) were used as solvents. Bu_4NBF_4 [9] and 1,3,5-triethylbenzene [10] were prepared as previously reported. Isodurene (Aldrich, technical grade) which contains 10 – 15 % durene was purified by treatment with chlorosulphonic acid (an excess of isodurene is necessary in order to avoid the formation of durene sulphonic acid) followed by desulphonation of isodurene sulphonic acid. Thus 1 mol of chlorosulphonic acid dissolved in 100 ml CH_2Cl_2 was added dropwise to a stirred solution of 2 mol of isodurene in 2 l CH_2Cl_2. After the addition, stirring was continued for 30 min and then 2 mol of sodium hydroxide in 1 l water was added drop-

wise. The mixture was filtered and the precipitate was washed with CH_2Cl_2. The precipitate and the water phase were combined and 300 ml concentrated hydrochloric acid was added. This mixture was subjected to steam distillation, the distillate (about 4 l) was extracted with CH_2Cl_2 and the organic phase was dried. After removing the solvent by evaporation *in vacuo*, the residue was distilled at reduced pressure to give isodurene of about 99 % purity (yield 70 – 80 %). All other compounds were of high commercial quality.

Electrolysis. Small scale electrolysis was carried out on 50 ml solutions. All details regarding the amount of materials and the time used for electrolysis are given in the tables. The electrolysis mixtures were worked up by removing the solvents by evaporation *in vacuo*, treating the residue with ether, filtering off the supporting electrolyte and then analyzing the concentrated ether solution by GLC and mass spectrometry. The yields of products were calculated by adding a standard to the ether solutions and then integrating the GLC peak areas. All products except those isolated were identified solely on the basis of their mass spectral fragmentation pattern.

Anodic synthesis of 1-(pentamethylphenyl)-naphthalene. A solution made up of 0.25 mol of naphthalene, 0.25 mol of pentamethylbenzene, 0.025 mol of Bu_4NBF_4, 225 ml acetonitrile and 25 ml acetic acid was electrolyzed between two platinum electrodes at a constant current of 0.5 A until 1 *F*/mol of naphthalene had passed. The solvents were removed by evaporation *in vacuo*, ether was added to the residue and the salt was filtered off (in case the salt does not precipitate, the ether solution was decanted). The ether was distilled off and the residue was distilled up to 115°/12 mm in order to remove naphthalene and pentamethylbenzene. The residue was extracted with 250 ml boiling pentane. The pentane solution was decanted and run through a short alumina column. Another 250 ml pentane was also used as eluent. Pentane was removed from the eluate leaving a white solid, which was recrystallized from a mixture of ethanol (500 ml) and benzene (150 ml) to give 19.3 g of 1-(pentamethylphenyl)-naphthalene, m.p. 119 – 121° (yield 56 %). According to GLC the purity was 98.5 %.

MS: *m/e* 274 (100 % abundance), 259 (51 %), 244 (33 %), 229 (32 %). NMR (CCl_4) δ 1.77 (s, 6, 2,6-CH_3), 2.23 (s, 6, 3,5-CH_3), 2.28 (s, 3, 4-CH_3), 7.03 – 7.87 (m, 7, $C_{10}H_7$).

Anodic synthesis of 1-(2,3,4,6-tetramethylphenyl)-naphthalene. The electrolysis solution consisted of 0.25 mol of naphthalene, 0.50 mol of isodurene, 0,025 mol of Bu_4NBF_4, 225 ml acetonitrile and 25 ml acetic acid. The experiment was performed in the same way as the previous one and work-up procedure was also the same. The white solid obtained after chromatography was recrystallized from 200 ml ethanol to give 13.8 g of 1-(2,3,4,6-tetramethylphenyl)-naphthalene, m.p. 108 – 111° (current yield 42 %). GLC purity 99 %.

MS: *m/e* 260 (100 %), 245 (69 %), 230 (38 %), 229 (42 %), 215 (44 %). NMR (CCl_4) δ 1.78 (s, 6, 2,6-CH_3), 2.20 (s, 3, 3-CH_3), 2.32 (s, 3, 4-CH_3), 6.88 (s, 1, $C_6H(CH_3)_4$), 7.07 – 7.87 (m, 7, $C_{10}H_7$).

Anodic synthesis of 1-(2,4,6-triethylphenyl)-naphthalene. The electrolysis solution consisted of 0.15 mol of naphthalene, 0.45 mol of 1,3,5-triethylbenzene, 0.015 mol of Bu_4NBF_4, 135 ml acetonitrile and 15 ml acetic acid. At a constant current of 0.5 A the electrolysis was continued until 1 *F*/mol of naphthalene had passed. The solvents were removed by evaporation *in vacuo* and ether was added to the residue in order to precipitate the salt. The ether solution was evaporated and the starting materials were then removed by distillation up to 95°/12 mm. Further distillation at 160 – 230°/0.5 mm gave 3.2 g of a liquid. This was dissolved in pentane and chromatographed on an alumina column. After evaporation of pentane 470 mg of a colorless liquid remained which did not solidify. GLC showed one major peak and the peak area corresponded to about 97 % of the total peak areas. This was identified as 1-(2,4,6-triethylphenyl)-naphthalene on the basis of spectral data.

MS: *m/e* 288 (100 %), 273 (28 %), 259 (39 %), 244 (19 %), 229 (17 %) and 215 (41 %). NMR (CCl_4) δ 0.90 (t, 6, 2,6-CH_3CH_2), 1.32 (t, 3, 4-CH_3CH_2), 2.13 (q, 4, 2,6-CH_3CH_2), 2.68 (q, 2, 4-CH_3CH_2), 6.93 (s, 2, $C_6H_2(CH_2CH_3)_3$), 7.17 – 7.83 (m, 7, $C_{10}H_7$).

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