

Electrolysis in Non-nucleophilic Media

Part IV.¹ Anodic Mixed Coupling. Synthesis of 1-Mesitylnaphthalene

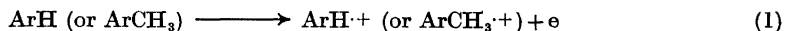
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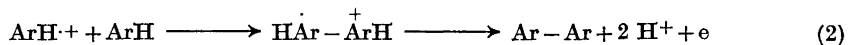
Anodic oxidation of naphthalene in methylene chloride or acetonitrile/acetic acid containing tetrabutylammonium tetrafluoroborate produces 1,1'-binaphthyl at a platinum anode in about 30 % yield at low conversion. At higher conversion the yield decreases considerably because of polymer formation. In the presence of mesitylene, anodic oxidation of naphthalene in acetonitrile/acetic acid produces 1,1'-binaphthyl and 1-mesitylnaphthalene but no bimesityl. Preparative scale electrolysis of naphthalene (1.0 M) and mesitylene (3.0 M) in the same medium until 1 F/mol of naphthalene has passed gives a current yield of 13 % isolated 1-mesitylnaphthalene.

The absence of bimesityl indicates that naphthalene is the only aromatic compound oxidized during electrolysis. It is postulated that the mixed coupling product is formed by attack of naphthalene cation radical on mesitylene.

In previous papers of this series it has been shown that anodic oxidation of alkylbenzenes in media of low nucleophilicity such as methylene chloride,² nitromethane,³ or acetonitrile,^{1,4} containing an electroinactive supporting electrolyte (such as Bu₄NBF₄) produces coupled products, diphenylmethanes and biphenyls, at a platinum anode. It was suggested that the formation of the products was dependent on the positive charge density distribution in the cation radical, the primary anodically generated species (eqn. 1).

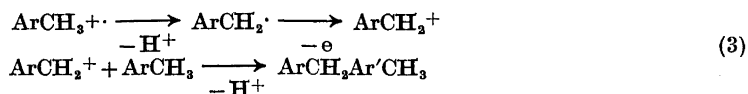


If the positive charge density is high in an *unsubstituted* ring position of the cation radical, the cation radical will react to form a biphenyl derivative by attack on a neutral molecule (eqn. 2).



If the positive charge density is high in an *alkylsubstituted* ring position of the cation radical, formation of a benzylic radical, after loss of a proton, will occur, provided that a benzylic hydrogen is available. The benzylic radical is rapidly

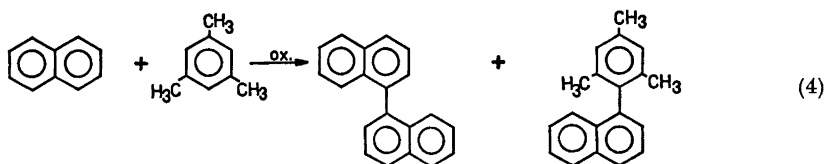
oxidized to a benzyl cation, which reacts with a neutral molecule to form a diphenylmethane derivative (eqn. 3).



The synthesis of biaryls by direct anodic oxidative coupling of aromatic compounds might be a useful alternative to pure chemical methods. This study deals with anodic oxidation of naphthalene and the possibility of obtaining binaphthyl on a preparative scale. The only naphthalene derivative that has been subjected to anodic coupling is 1-methylnaphthalene, the product being 4,4'-dimethyl-1,1'-binaphthyl, obtained in 10 % yield.⁵ Naphthalene, itself, has been shown to undergo anodic oxidation in the system acetic acid/sodium acetate, to yield 1-acetoxynaphthalene as the major product.⁶⁻¹⁰ Anodic oxidation of naphthalene in acetonitrile containing water, KOH and benzoic acid gave 1-naphthol and 4,4'-dihydroxy-1,1'-binaphthyl after saponification of the electrolysis mixture.¹¹

RESULTS

Anodic oxidation of naphthalene was first carried out in methylene chloride containing Bu_4NBF_4 at a platinum anode. The products were 1-chloronaphthalene, 1,1'-binaphthyl and chlorobinaphthyl. Chlorination of starting material and products has been observed earlier during the anodic oxidation of methylbenzenes in methylene chloride and is the result of reduction of methylene chloride at the cathode to form chloride ion followed by its oxidation to chlorine at the anode and subsequent chlorination of the compounds in the solution.² In order to avoid this side-reaction anodic oxidation of naphthalene (1.0 M) was carried out in methylene chloride containing acetic acid (volume ratio 9:1) and Bu_4NBF_4 (0.1 M) at an anode potential of 1.4 V (*vs.* SCE). After passage of 0.2 F/mol of naphthalene a 14 % current yield of 1,1'-binaphthyl was obtained and no chloro products were observed. When the reaction was repeated using a larger amount of acetic acid (50 % by volume), only a slight increase in the yield of 1,1'-binaphthyl was observed. The rather low yield of 1,1'-binaphthyl obtained in these experiments seemed discouraging and it was obvious that another electrolysis medium was necessary to raise the yield.



Acetonitrile is a solvent commonly used for anodic oxidation experiments. It acts as a nucleophile toward carbonium ions generated by anodic oxidation of aliphatic carboxylic acids,¹²⁻¹⁴ and toward benzyl cations from anodic

oxidation of methylbenzenes,^{15,16} but it does not react with aromatic cation radicals.^{1,4} It should therefore be a suitable solvent for anodic coupling of naphthalene. It was found that a mixture of acetonitrile and acetic acid was a useful solvent. In the absence of acetic acid, reduction of naphthalene took place at the cathode. Anodic oxidation of naphthalene (1.0 M) in CH₃CN/HOAc/0.1 M Bu₄NBF₄ was carried out at an anode potential of 1.5 V until 0.2 F/mol of naphthalene had passed. The current yield of 1,1'-binaphthyl was 28 %. Using a higher concentration of naphthalene (2.0 M) gave almost no change in the current yield. When the anodic oxidation of naphthalene was carried out on a preparative scale, it was found that the yield of 1,1'-binaphthyl decreased considerably at higher conversion and large amounts of polymeric material were formed.

The fact that 1,1'-binaphthyl was formed in a fairly good yield at low conversion suggested that the naphthalene cation radical could be trapped by another suitable aromatic compound to produce a mixed biaryl. For this reason anodic oxidation of naphthalene was carried out in the presence of mesitylene, in the system CH₃CN/HOAc/0.1 M Bu₄NBF₄, at a platinum anode under controlled potential conditions. Two products were formed, namely 1,1'-binaphthyl (I) and 1-mesitylnaphthalene (II) (eqn. 4). Bimesityl was not detected. Table 1 shows the current yields of I and II from several experiments.

Table 1. Anodic oxidation of naphthalene in the presence of mesitylene in CH₃CN/HOAc (volume ratio 9:1) containing Bu₄NBF₄ (0.1 M) at a platinum anode. Current yields of I and II calculated after passage of 965 coulombs at 1.5 V vs. SCE.

Naphthalene conc. (M)	Mesitylene conc. (M)	Current yield (%) of	
		I	II
0.2	2.0	6	10
0.2	2.0	15	13
1.0	1.0	27	8
1.0	2.0	25	15
1.0	3.0	22	19

It is interesting to note from the results in the table that the yield of 1-mesitylnaphthalene is not only dependent on the concentration of mesitylene but also on the concentration of naphthalene. The highest yield of II is obtained by electrolyzing a solution containing 1.0 M naphthalene and 3.0 M mesitylene. Using these concentrations of naphthalene and mesitylene, a preparative scale electrolysis was carried out with a 250 ml solution between two platinum electrodes at a constant current of 0.5 A. After passage of 1.5 F/mol of naphthalene, an 8 % isolated yield of 1-mesitylnaphthalene was obtained. When the same electrolysis was carried out until 1 F/mol of naphthalene had passed the yield increased to 13 %. I and II were easily separated by column chromatography.

1-Mesitylnaphthalene has recently been prepared by two different methods, lead tetraacetate oxidation of 1-aminonaphtho(1,8-*de*)triazine in mesitylene and the reaction between 1-naphthylamine and pentyl nitrite in refluxing

mesitylene.¹⁷ The data reported for 1-mesitylnaphthalene (m.p., mass spectrum, NMR) did not correspond properly to the data obtained in this study. The reported melting point was ten degrees lower and some of the mass spectral peaks were absent in the mass spectrum of the electrochemically prepared sample. For this reason 1- and 2-mesitylnaphthalene was prepared in another way, namely by the Ullman reaction between 2-iodomesitylene and 1- and 2-iodonaphthalene, respectively, in the presence of copper bronze at 250°. 1-Mesitylnaphthalene was obtained in a pure state and was found to be identical to the electrochemically synthesized sample. The 2-isomer was obtained in about 90 % purity and was shown to have different GLC retention time as well as different NMR spectrum from the 1-isomer.

The possible presence of 2-mesitylnaphthalene in the anodic oxidation products was checked by GLC by comparison with the authentic sample, but in no case it was shown to be present.

DISCUSSION

The preparative scale oxidation of naphthalene gave mainly polymeric material. This is probably due to further reactions of 1,1'-binaphthyl. The primary product is either further oxidized or is attacked by other oxidized species, and this leads to higher molecular weight aggregates. It has been shown that anodic oxidation of benzene in acetonitrile produces only polymers and biphenyl was not even detected.¹⁸

Anodic oxidation of naphthalene in the presence of mesitylene gave 1,1'-binaphthyl and 1-mesitylnaphthalene. These results are quite interesting both from the mechanistic and the preparative points of view. The fact that bimesityl is not formed in this reaction indicates that the unsymmetrical coupling product is formed by reaction between the naphthalene cation radical and mesitylene. This supports the reaction mechanism proposed for anodic coupling of aromatic hydrocarbons (eqn. 2). Judging from the polarographic half-wave potentials for the anodic oxidation of naphthalene and mesitylene, it is somewhat surprising that mesitylene is not oxidized when naphthalene is present. The polarographic half-wave oxidation potential for naphthalene is lower than that of mesitylene by 0.28 V in HOAc/NaOAc,¹⁰ and by 0.26 V¹⁹ or 0.21 V²⁰ in CH₃CN/NaClO₄. Although this difference may seem large it should be remembered that these values are obtained from very dilute solutions of hydrocarbon. In the experiments described above the concentration of mesitylene was 3 M and that of naphthalene 1 M. Different adsorption behaviour may explain why naphthalene is the only hydrocarbon oxidized even in the constant current experiments.

The current-potential curves for anodic oxidation of naphthalene (1.0 M) and mesitylene (3.0 M) in CH₃CN/HOAc/Bu₄NBF₄ are shown in Fig. 1. Curve A shows the oxidation of mesitylene alone and curve B the oxidation of naphthalene in the presence of mesitylene. In the absence of mesitylene oxidation of naphthalene takes place according to curve B. From the figure it is clear that naphthalene is oxidized at lower potential than mesitylene. When a solution of mesitylene (3.0 M) was oxidized in CH₃CN/HOAc/Bu₄NBF₄ at

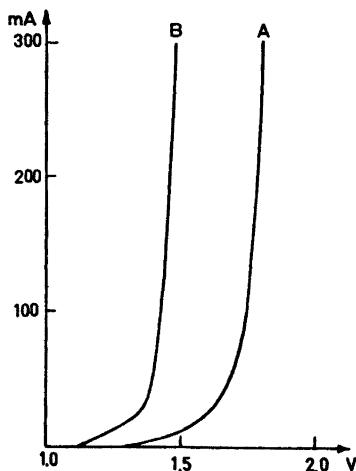


Fig. 1. Current-potential curves for electrolysis of 50 ml $\text{CH}_3\text{CN}/\text{HOAc}$ (volume ratio 9:1)/0.1 M Bu_4NBF_4 at a platinum anode. A, with 3.0 M mesitylene. B, with 3.0 M mesitylene and 1.0 M naphthalene.

an anode potential of about 1.8 V, bimesityl was formed in a 50 % current yield.

The preparative use of anodic coupling of aromatic hydrocarbons has been demonstrated in the oxidation of mesitylene to bimesityl in high yield,⁴ and the oxidation of 4-*t*-butyl-*m*-xylene to 4,4'-di-*t*-butyl-2,6,2',6'-tetramethylbiphenyl.¹ In this study the first successful anodic mixed coupling of aromatic hydrocarbons is presented as a method for the synthesis of 1-mesitylnaphthalene. It is well known that synthesis of unsymmetrical biaryls, where the two aryl units have similar substituents, is often difficult. The most common procedure is photolysis of an iodobenzene in an aromatic solvent.²¹ From a preparative point of view the anodic mixed coupling should not be regarded as a general reaction. In order to obtain the mixed coupling product in a good yield it is necessary to choose the starting compounds carefully. It is desirable that only one of them is oxidized during electrolysis, since this will reduce the primary products to one symmetrical and one unsymmetrical compound. Secondly, the two substrates must be chosen in such a way that the two coupled products have different physical properties (boiling points, solubility, chromatographic properties); otherwise, the separation procedure will be difficult.

EXPERIMENTAL

Controlled potential electrolysis was carried out in a 60 ml water-jacketed cell equipped with a platinum anode (surface area 50 cm²) and a platinum cathode (surface area 12 cm²) using the saturated calomel electrode (SCE) as reference electrode. The anode potential was controlled by means of an Amel Model 557 Potentiostat in connection with an Amel Model 558 Integrator. Constant current experiments were carried out in a 300 ml cell equipped with a platinum anode (surface area 50 cm²) and a platinum cathode (surface area 25 cm²). The current was controlled with a Radiak power supply (2A/60 V). Gas chromatographic analysis was done with a Perkin-Elmer Model 880 instrument, equipped with a Perkin-Elmer D 26 Integrator, on a 2 m × 0.3 cm 5 % SE-30 on Chromosorb W column or a 1.5 m × 0.3 cm 5 % NPGS on Chromosorb W column. Mass spectrometric

analysis was obtained with an LKB Model 9000 instrument, at 70 eV, connected to a gas-liquid chromatograph. NMR spectra were recorded with a Varian A 60 A spectrometer.

Materials. Acetonitrile, acetic acid, methylene chloride (redistilled), naphthalene, and mesitylene were of high commercial quality. The preparation of Bu_4NBF_4 has been described.² 1,1'-Binaphthyl was kindly supplied by Fil. kand. Berit Robertsson.

Electrolysis. Controlled potential oxidation was carried out with 50 ml solutions containing the appropriate concentration of reagents that has already been specified in the text or in Table I. At the end of an electrolysis the solvent was removed by evaporation *in vacuo*, and ether was added to the residue in order to precipitate the salt. After filtration, the ether solution was concentrated and analyzed by GLC. The current yields of the products were calculated against a standard substance. The results of the controlled potential oxidations have already been given.

Anodic synthesis of 1-mesitylnaphthalene. A 250 ml solution containing 0.25 mol naphthalene, 0.75 mol mesitylene and 0.025 mol Bu_4NBF_4 in acetonitrile/acetic acid (volume ratio 9:1) was electrolyzed at a current of 0.5 A until 1 F/mol of naphthalene had passed. The solvents were removed by evaporation *in vacuo* and mesitylene was removed by distillation under reduced pressure. The residue was treated with 400 ml boiling ether and then filtered. The filtrate was concentrated *in vacuo* and unreacted naphthalene was removed by distillation at reduced pressure. From the residue a mixture of 1-mesitylnaphthalene and 1,1'-binaphthyl (8.1 g) was isolated after distillation at 135–200°/0.7 mm. The mixture was treated with boiling pentane. After cooling, the precipitate was filtered off (1,1'-binaphthyl) and the filtrate was subjected to column chromatography on neutral alumina. Elution with a large amount of pentane gave, after removal of the solvent, 1-mesitylnaphthalene (4.0 g; 13 % current yield). M.p. 76.5–77.0° (recrystallized from methanol). (Found: C 92.6; H 7.25. Calc. for $\text{C}_{19}\text{H}_{16}$: C 92.6; H 7.36.) The NMR spectrum (in CCl_4) showed signals at $\delta = 1.82$ ppm (6 H in two *ortho* CH_3 groups), 2.32 ppm (3 H in the *para* CH_3 group), 6.83 ppm (2 H in the mesityl ring), 7.05–7.83 ppm (7 H in the naphthyl ring). The mass spectrum gave the major peaks at $m/e = 246$ (100 % abundance), 231 (50 %), 216 (22 %), 215 (28 %).

Ullman reaction with 2-iodomesitylene and 1-iodonaphthalene. A mixture of 4.9 g (0.02 mol) 2-iodomesitylene, 5.1 g (0.02 mol) 1-iodonaphthalene and 10 g copper bronze were heated at 250°, for 3 h. After cooling, the reaction mixture was extracted several times with ether. The combined ether solutions were evaporated *in vacuo* (GLC analysis of this solution showed three peaks corresponding to bimesityl, 1-mesitylnaphthalene and 1,1'-binaphthyl in the ratio 2:6:2, peak areas). Pentane was added to the residue and the insoluble binaphthyl was filtered off. The filtrate was subjected to column chromatography on neutral alumina. Careful elution with pentane gave a small amount of solid 1-mesitylnaphthalene, that was identical to the sample prepared in the electrolysis experiment.

Ullman reaction with 2-iodomesitylene and 2-iodonaphthalene. This reaction was carried out in the same way as described above for 1-iodonaphthalene. GLC analysis of the reaction product showed bimesityl, 2-mesitylnaphthalene, and 2,2'-binaphthyl in the area ratio 3:6:1 (peak areas). The same isolation technique was used as in the previous experiment, but the fraction containing mostly 2-mesitylnaphthalene was chromatographed once more in order to obtain a sample of 90 % purity. It did not crystallize. The GLC retention time was different from that of the 1-isomer on both GLC columns. The NMR spectrum (in CCl_4) showed signals at $\delta = 1.98$ ppm, 2.29 ppm, 6.83 ppm, and 7.1–7.9 ppm, corresponding to the hydrogens in the two *ortho* methyl groups, the *para* methyl group, the mesityl ring and the naphthyl ring. The signals corresponding to the aromatic naphthyl protons were different from those obtained from the 1-isomer.

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