

Electrolysis in Non-nucleophilic Media

Part III.¹ Anodic Coupling of Some 5-Alkyl-substituted *m*-Xylenes

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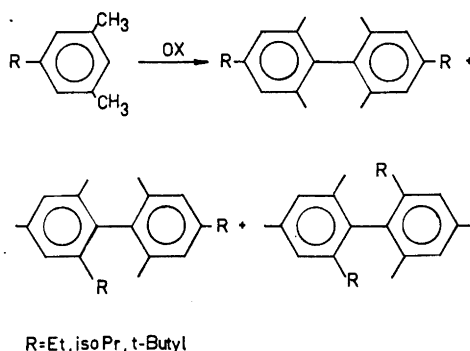
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Anodic oxidation of some 5-alkyl-substituted *m*-xylenes in acetonitrile and nitromethane has been investigated. The results show that the major volatile products are biphenyls and diphenylmethanes although the current yields are low. 5-Ethyl-*m*-xylene produces three isomeric biphenyls formed in 19 % current yield in nitromethane, and almost no diphenylmethanes. 5-Isopropyl-*m*-xylene gave two biphenyls, the ratio of biphenyls to diphenylmethanes being about 2 : 1 and the current yield about 4 %. 5-*t*-Butyl-*m*-xylene gave two isomeric biphenyls, the major one, 4,4'-di-*t*-butyl-2,6,2',6'-tetramethylbiphenyl, being isolated in a preparative electrolysis in a current yield of 15 %. The isolated yield was 25 % on the basis of consumed starting material.

It has recently been shown that anodic oxidation of methylbenzenes results in the formation of dehydrodimeric products (biphenyls, diphenylmethanes) as the major products if the electrolysis medium is made up of solvent and supporting electrolyte of low nucleophilicity. Anodic oxidation of mesitylene in methylene chloride² or nitromethane,¹ containing tetrabutylammonium tetrafluoroborate, produced bimesityl and termesityl as the major products. Anodic oxidation of several methylbenzenes in acetonitrile, containing sodium perchlorate, has been shown to produce *N*-benzylacetamides.^{3,4} The oxidation of mesitylene in the latter medium is, however, an exception in that very little side-chain substitution takes place and instead the major oxidation products are again bimesityl and termesityl.⁵ The oxidation of mesitylene was studied in greater detail with regard to the choice of mesitylene concentration, the choice of supporting electrolyte, the anode material, and the water concentration. The anodic synthesis of bimesityl could be carried out in almost 50 % isolated yield using high mesitylene concentration (2.0 M) in the presence of Bu₄NBF₄ at a platinum anode.

The synthesis of biphenyl derivatives by anodic oxidation of aromatic compounds is an attractive alternative to purely chemical methods and is

presently investigated in this Laboratory. In the present paper the possibility of preparing biphenyl derivatives by anodic oxidation of 5-R-*m*-xylenes (R = Et, iso-Pr, *t*-Bu) is investigated. Three isomeric biphenyl derivatives, previously unreported, can be obtained from each substrate. The reason for choosing these compounds as starting materials is their similarity to mesitylene, *i.e.* the substituents occupy the 1-, 3- and 5-positions in the benzene ring.



RESULTS AND DISCUSSION

Anodic oxidations were carried out in acetonitrile and in nitromethane, containing Bu_4NBF_4 (0.1 M), at a platinum anode at controlled anode potential. Each electrolysis solution was made 2.0 M in aromatic compound and the electrolysis was continued until 0.2 *F*/mol of starting compound has passed. The electrolysis mixture was then analyzed by GLC and mass spectrometry. The results of the electrolyses are summarized in Table 1. Preparative scale

Table 1. Anodic oxidation of 5-R-*m*-xylenes (2.0 M) in acetonitrile and in nitromethane containing 0.1 M Bu_4NBF_4 . Product distribution and current yields are calculated after passage of 0.2 *F*/mol of starting compound. Anode potentials are about 2.0 V (*vs.* SCE) in all experiments.

R	Solvent	Relation I	between II	biphenyls III	Ratio biphenyls to diphenylmethanes	Current yield (%)
Me ^a	CH ₃ CN				100:1	82
Me ^b	CH ₃ NO ₂				100 ^c	23 ^d
Et	CH ₃ CN	21	51	28	97:3	7
Et	CH ₃ NO ₂	30	42	28	100 ^c	19
<i>i</i> -Pr	CH ₃ CN	45	55		66:34	3
<i>i</i> -Pr	CH ₃ NO ₂	60	40		68:32	4
<i>t</i> -Bu	CH ₃ CN	80	20		92:8	4
<i>t</i> -Bu	CH ₃ NO ₂	84	16		85:15	8

^a Data taken from Ref. 5.

^b Data taken from Ref. 1.

^c No diphenylmethane derivative detected.

^d 1.0 M mesitylene solution.

oxidation was only carried out if it seemed possible to obtain a single reaction product.

5-Ethyl-m-xylene. Anodic oxidation of 5-ethyl-*m*-xylene in acetonitrile gave three isomeric biphenyls, in the ratio of 21 : 51 : 28, and at least one diphenylmethane. Oxidation in nitromethane gave the three biphenyls but not the diphenylmethane. The current yield was found to be much higher in nitromethane than in acetonitrile. In acetonitrile the oxidation also produced some compounds as a result of reaction between oxidized species and the solvent (acetamide derivative and oxygen containing products), but the amount of these was much lower than that of the hydrocarbons. The product distribution is similar to that obtained by oxidation of mesitylene, although the current yield is much lower. No diphenylmethane derivative is formed in nitromethane but a small amount in acetonitrile.

5-Isopropyl-m-xylene. Anodic oxidation of this compound produced at least two biphenyl derivatives in the ratios shown in Table 1. One major diphenylmethane derivative was formed, together with at least two minor ones. GLC analysis also indicated that two trimeric hydrocarbons were formed. Whether these are terphenyl derivatives or contain carbon linkage between phenyl rings was not possible to determine from the mass spectra. Although the current yields are low, both in acetonitrile and in nitromethane, the low current efficiency cannot be accounted for by the formation of products resulting from reaction between oxidized hydrocarbon and the solvents. One may note from Table 1 that the amount of diphenylmethane derivatives formed in the oxidation of this compound is considerably higher than in the oxidation of the other hydrocarbons.

5-t-Butyl-m-xylene. Anodic oxidation of this compound produced at least two biphenyl derivatives, the major product being identified as 4,4'-di-*t*-butyl-2,6,2',6'-tetramethylbiphenyl. Two diphenylmethane derivatives were detected by GLC and mass spectrometry. Oxidation in acetonitrile also produced an *N*-benzylacetamide derivative, but in low yield. Since this reaction produced one major biphenyl derivative, preparative scale electrolysis was carried out in order to isolate this product. A 500 ml solution of 5-*t*-butyl-*m*-xylene (2.0 M) in acetonitrile containing Bu_4NBF_4 (0.1 M) was electrolyzed at constant current until 0.6 *F*/mol of the substrate had passed. When unreacted hydrocarbon was removed by distillation it was found that only 60 % of the theoretical amount of starting material had been consumed. The major product of the electrolysis, 4,4'-di-*t*-butyl-2,6,2',6'-tetramethylbiphenyl, was then isolated, after distillation and column chromatography in a 15 % current yield (the yield based on consumed starting material was 25 %). The large-scale oxidation of 5-*t*-butyl-*m*-xylene was also carried out to higher conversion (1 *F*/mol) in order to see if the reaction produced the biphenyl product in comparable yield. However, this did not occur, a lower yield of the product being obtained. In this experiment some starting material was recovered, although 100 % consumption was calculated.

It is somewhat surprising that the yields of the hydrocarbon products from the anodic oxidation of the 5-substituted *m*-xylene are so low compared to the yield of bimesityl in the oxidation of mesitylene. From the similarity between these compounds it would be expected that the anodic oxidation

should give a good yield of biphenyl products. However, the distribution of the positive charge (or the unpaired electron density) in the ring positions of the cation radicals must certainly be altered when one methyl group in mesitylene is replaced by other alkyl groups. It has been suggested that the positive charge density in the cation radicals produced by anodic oxidation of methylbenzenes will determine the outcome of the reaction, *i.e.*, whether biphenyl derivatives or diphenylmethane derivatives are formed.¹ The results obtained in this work show that the tendency to form a benzyl cation is greater in the oxidation of 5-isopropyl-*m*-xylene than with the other compounds, since the amount of diphenylmethane derivatives formed during this oxidation is larger than in any other case studied here. However, since the structure of the major diphenylmethane derivative was not established, it is not possible to determine in which benzylic position a cation was formed.

Although the results show that the ethyl and the *t*-butyl compounds produce predominantly biphenyl derivatives only the latter oxidation seemed worthwhile repeating a preparative scale, since the former produced all three isomeric biphenyl derivatives. The preparative scale oxidation of 5-*t*-butyl-*m*-xylene produced 4,4'-*di-t*-butyl-2,6,2',6'-tetramethylbiphenyl in an acceptable yield, and the isolation of this compound was rather simple. It might seem surprising that the current yield in the preparative scale oxidation is much greater than in the low conversion experiments. However, if a side reaction, *e.g.* oxidation of minor impurities, is occurring during the electrolysis, oxidation of the hydrocarbon will become more efficient as the electrolysis is continued and the impurities are removed. The fact that so much starting material is recovered after the experiment indicates that some side reaction must take place.

The three substrates were also oxidized in methylene chloride but in this case even lower current yields of the biphenyls and the diphenylmethanes were obtained. The major products were found to be chlorinated starting materials.

EXPERIMENTAL

Electrolysis was carried out in a water-jacketed cell (volume 60 ml) equipped with a platinum anode (area 50 cm²) and a platinum cathode (area 15 cm²). Controlled potential experiments were carried out using an Amel Model 557 Potentiostat, Model 558 Integrator, and a saturated calomel reference electrode. Controlled current electrolysis was carried out in a 600 ml cell equipped with a platinum anode (area 50 cm²) and a carbon cathode (area 50 cm²) using a Radiak Power Supply (2 A/60 V). Gas chromatographic analysis was performed, using a Perkin-Elmer Model 880 instrument and a Model D 26 Integrator. The column was a 4 m × 0.3 cm 5% NPGS on Chromosorb W. NMR spectra were obtained with a Varian A 60 A spectrometer. Mass spectrometric analysis, at 70 eV, was carried out with an LKB Model 9000 mass spectrometer, with a gas liquid chromatograph connected to it.

Materials. The following chemicals were used without further purification: acetonitrile (Baker), nitromethane (BDH), 5-*t*-butyl-*m*-xylene (Fluka), 5-iso-propyl-*m*-xylene (Fluka). 5-Ethyl-*m*-xylene was prepared according to the literature procedure in 50 % yield after distillation through a Normag column.⁶ Tetrabutylammonium tetrafluoroborate was prepared from tetrabutylammonium hydrogensulfate (Biotec, Västra Frölunda, Sweden) and sodium tetrafluoroborate.

Electrolysis. Anodic oxidation was carried out using 50 ml solutions of aromatic hydrocarbon (2.0 M) and Bu₄NBF₄ (0.1 M) in acetonitrile or nitromethane until 0.2

F/mol of aromatic hydrocarbon had passed. The electrolysis solution was then concentrated by evaporation of the solvent *in vacuo*. Ether was added to the residue and the insoluble salt was filtered off. The ether solution was then analyzed by GLC and mass spectrometry, and the peaks were identified on basis of their mass spectra. The current yields were calculated by adding a standard substance to the ether solutions. Since most of the compounds formed in the oxidations were not isolated, no calibration could be made against the standard. Therefore bimesityl was chosen as standard since it would be expected to be very similar to the products with regard to detector sensitivity. The results from the electrolysis are given in Table I and the major fragmentation peaks from the mass spectra of the oxidation products are given below.

5-Ethyl-m-xylene. Biphenyl I: $m/e = 267$ (22 % abundance), 266 (100 %), 252 (21 %), 251 (93 %), 237 (25 %), 223 (21 %), 222 (15 %), 221 (11 %), 209 (15 %), 208 (10 %), 207 (19 %), 206 (10 %), 193 (15 %). Biphenyl II: $m/e = 267$ (22 %), 266 (100 %), 252 (17 %), 251 (69 %), 238 (17 %), 237 (48 %), 223 (32 %), 222 (24 %), 221 (13 %), 209 (22 %), 208 (17 %), 207 (29 %), 206 (12 %), 193 (16 %). Biphenyl III: $m/e = 267$ (21 %), 266 (86 %), 251 (27 %), 238 (23 %), 237 (100 %), 223 (27 %), 222 (33 %), 221 (14 %), 209 (27 %), 208 (20 %), 207 (38 %), 206 (11 %), 193 (13 %), 192 (10 %).

The diphenylmethane derivative from the oxidation of 5-ethyl-*m*-xylene gave a mass spectrum that showed a large fragment at $m/e = 146$ which is typical of an unsymmetrical cleavage for similar compounds carrying at least one methyl group *ortho* to the methylene group.⁷ However, there was also a fragment at $m/e = 133$ which could be due to a bibenzyl derivative. The following fragments were recorded: m/e 267 (20 %), 266 (86 %), 252 (23 %), 251 (100 %), 238 (15 %), 237 (60 %), 207 (19 %), 193 (15 %), 147 (17 %), 146 (63 %), 145 (15 %), 133 (55 %), 131 (45 %).

5-Isopropyl-m-xylene. Biphenyl I: $m/e = 295$ (15 %), 294 (60 %), 280 (24 %), 279 (100 %), 209 (11 %), 132 (20 %). Biphenyl II: $m/e = 295$ (25 %), 294 (100 %), 280 (18 %), 279 (79 %), 250 (14 %), 238 (18 %), 237 (89 %), 222 (11 %), 221 (14 %), 209 (36 %), 207 (18 %), 132 (18 %).

The major diphenylmethane derivative from anodic oxidation of 5-isopropyl-*m*-xylene was identified on basis of the following fragments in the mass spectrum: $m/e = 295$ (21 %), 294 (79 %), 280 (34 %), 279 (95 %), 251 (55 %), 209 (21 %), 160 (47 %), 147 (68 %), 145 (28 %), 142 (100 %), 132 (79 %), 100 (40 %), 43 (40 %), 41 (53 %).

5-t-Butyl-m-xylene. Biphenyl I: see below. Biphenyl II: m/e 322 (7 %), 307 (12 %), 193 (7 %), 251 (10 %), 57 (100 %). The two diphenylmethane derivatives were identified on basis of the following mass spectra: (a) $m/e = 322$ (38 %), 307 (40 %), 293 (37 %), 265 (17 %), 251 (15 %), 159 (20 %), 146 (20 %), 145 (30 %), 57 (100 %); (b) 322 (30 %), 308 (28 %), 307 (100 %), 161 (16 %), 146 (21 %).

Preparative scale anodic oxidation of 5-t-butyl-m-xylene. A 600 ml water-jacketed cell equipped with a platinum anode (area 50 cm²) and a carbon cathode (area 50 cm²) was charged with a 500 ml acetonitrile solution containing 1 mol of 5-*t*-butyl-*m*-xylene and 0.05 mol of Bu₄NBF₄. The oxidation was carried out at a current of 1.5 A, at a temperature of about 20°, with stirring, until 0.6 *F*/mol of hydrocarbon had been passed. The electrolysis solution was then distilled in order to remove acetonitrile and unreacted starting compound (104.3 g). Benzene was added to the residue and the solution was removed by decantation. Benzene was then removed from this solution and the residue was distilled at low pressure. The material collected at 145–180°/1.5 mm was dissolved in pentane and eluted through an alumina column using a large amount of pentane. The purified material was recrystallized twice from ethanol to give 4,4'-*di-t*-butyl-2,6,2',6'-tetramethylbiphenyl. M.p. 123–125° (14.2 g; current yield 15 %, yield based on consumed hydrocarbon 25 %). The mass spectrum gave the following peaks: $m/e = 323$ (9 %), 322 (33 %), 308 (28 %), 307 (100 %), 146 (13 %), 132 (7 %), 118 (13 %), 57 (26 %). The NMR spectrum in CDCl₃ gave the following signals at $\delta = 1.30$ ppm (18 CH₃-protons in the *t*-butyl groups), 1.85 ppm (12 CH₃-protons) and 7.05 ppm (4 aromatic protons).

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