

Electrolysis in Non-nucleophilic Media

Part II. ¹ Anodic Oxidation of Polymethylbenzenes in Nitromethane and Methylene Chloride

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Anodic oxidation of several methylbenzenes has been carried out in nitromethane and methylene chloride. Two types of main products are formed. Biphenyls are formed by electrophilic attack of cation radicals on the substrates, while diphenylmethanes are formed by electrophilic reaction between a benzyl cation and the starting compound. Cation radicals carrying a high positive density on the free ring positions react to form biphenyls, and cation radicals having a high positive density on a substituted position are converted to benzyl radicals by loss of a proton, and the benzyl radicals are rapidly oxidized to benzyl cations.

In Part I of this series,¹ it was shown that coupling reactions between aromatic hydrocarbon residues are favoured in media of low nucleophilicity, such as methylene chloride containing tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) as supporting electrolyte, when the aromatic hydrocarbons are subjected to anodic oxidation. Thus *p*-xylene and durene were found to undergo oxidation to yield 2,5,4'-trimethyldiphenylmethane and 2,4,5,2',3',5',6'-heptamethyldiphenylmethane, respectively. On the other hand, oxidation of mesitylene yielded bimesityl and termesityl under the same conditions, and no diphenylmethane derivative was formed. It was suggested that the latter reaction occurred either by coupling of mesitylene cation radicals, or by attack of the cation radicals on mesitylene itself. The coupling of mesitylene to bimesityl was later found to occur in acetonitrile in high yield.² It was also found that some mixed coupling took place when mesitylene was oxidized in the presence of benzene, thus supporting the second reaction mechanism.

In order to further investigate the oxidation paths of aromatic hydrocarbons in media of low nucleophilicity, we have studied the anodic oxidation of 1,2,4-trimethylbenzene, 1,2,3,5-tetramethylbenzene, and pentamethylbenzene in methylene chloride and in nitromethane. Structurally, these compounds combine features of both mesitylene and durene, so that mixtures of

biphenyls and diphenylmethanes might be expected from each of the compounds.

In Part I, it was found that chlorination of the starting material occurred simultaneously with oxidation, due to reduction of methylene chloride and subsequent oxidation of chloride ions. However, the use of nitromethane in this study has avoided this problem. The only disadvantage compared to methylene chloride is the lower solubility of substrates.

RESULTS

Anodic oxidation of 1,2,4-trimethylbenzene was carried out at controlled potential between two platinum electrodes, using the saturated calomel electrode as a reference electrode in either nitromethane or methylene chloride containing 0.1 M Bu_4NBF_4 as supporting electrolyte. By use of GLC and mass spectrometry, seven hydrocarbon products were detected from the electrolysis mixture, after 0.2 *F*/mol of substrate had passed. These included two hexamethylbiphenyls (A and B), two pentamethyldiphenylmethanes (C and D), one hexamethyldiphenylmethane (E), and traces of a pentamethyldiphenylmethane and a nonamethylterphenyl. Attempts to isolate the various products by preparative GLC were unsuccessful. In methylene chloride, side-products were formed by chlorination of the starting material, and in nitromethane, oxygen containing products were formed due to reaction between the oxidized species and residual water. The oxidations were carried out, using three different concentrations of 1,2,4-trimethylbenzene. The relative distribution of the products as well as the current yields are given in Table 1. A different product distribution is observed in nitromethane and methylene chloride, in that a larger percentage of biphenyls are formed in nitromethane. In Part I, it was shown that increasing the mesitylene concentration gave an increase of bimesityl upon anodic oxidation of mesitylene. Similarly, the yield of the product from durene was also found to be concentration dependent. From Table 1 is seen that the current yield is increased by increasing the concentration of 1,2,4-trimethylbenzene, and the percentage of biphenyls is increased by increasing the concentration.

Table 1. Anodic oxidation of 1,2,4-trimethylbenzene in 0.1 M $\text{Bu}_4\text{NBF}_4/\text{CH}_3\text{NO}_2$ or CH_2Cl_2 . Current yields and relative distribution of products calculated after 0.2 *F*/mol of the starting compound has passed.

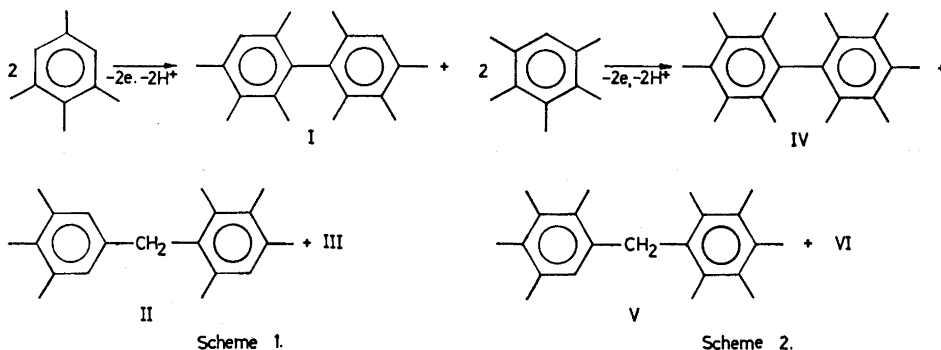
Solvent	Conc. (M)	Anode potential (V)	A	B	C	D	E	Current yield (%)
CH_3NO_2	0.2	2.0	7	28	58	7	—	5
	1.0	2.0	6	41	34	12	7	15
	2.0	2.0	4	54	31	9	2	36
CH_2Cl_2	0.2	1.5	4	25	54	8	9	7
	1.0	1.2	6	27	49	13	5	25
	2.0	1.1	6	40	38	11	5	38

Anodic oxidation of 1,2,3,5-tetramethylbenzene was carried out in 0.1 M $\text{Bu}_4\text{NBF}_4/\text{CH}_3\text{NO}_2$ or CH_2Cl_2 , until 0.2 F/mol of substrate had passed. Three major products were identified by GLC and mass spectrometry. These were 2,3,4,6,2',3',4',6'-octamethylbiphenyl (I), 3,4,5,2',3',4',6'-heptamethyldiphenylmethane (II), and another heptamethyldiphenylmethane (III) (Scheme 1). Mass spectrometric analysis of the GLC peak corresponding to III could not distinguish between the possible isomers (2,4,6,2',3',4',6',- or 2,3,5,2',3',4',6'-

Table 2. Anodic oxidation of 1,2,3,5-tetramethylbenzene in 0.1 M $\text{Bu}_4\text{NBF}_4/\text{CH}_3\text{NO}_2$ or CH_2Cl_2 . Current yields and relative distribution of products calculated after 0.2 F/mol of the starting compound has passed.

Solvent	Conc. (M)	Anode potential (V)	I	II + III	Current yield (%)
CH_3NO_2	0.2	1.8	64	36	13
	1.0	1.8	63	37	42
CH_2Cl_2	0.2	1.1	43	57	11
	1.0	1.0	45	55	21

heptamethyldiphenylmethane). Traces of a hexamethyldiphenylmethane was also observed in the electrolysis mixtures. The results of the electrolyses are given in Table 2. Again we see that the percentage of biphenyls is larger in nitromethane than in methylene chloride, and that the current yields are concentration dependent. On the other hand, the ratio biphenyls to diphenylmethanes is not changed by changing the concentration of 1,2,3,5-tetramethylbenzene. Also here, side-products, similar to those from 1,2,4-trimethylbenzene, were formed.



Anodic oxidation of pentamethylbenzene was carried out in 0.1 M $\text{Bu}_4\text{NBF}_4/\text{CH}_3\text{NO}_2$ or CH_2Cl_2 , until 0.2 F/mol of substrate had passed. Three products were detected by GLC, and the first, according to mass spectrometric

Table 3. Anodic oxidation of pentamethylbenzene in 0.1 M $\text{Bu}_4\text{NBF}_4/\text{CH}_3\text{NO}_2$ or CH_2Cl_2 . Current yields and relative distribution of products calculated after 0.2 *F*/mol of the starting compound has passed.

Solvent	Conc. (M)	Anode potential (V)	IV	V	VI	Current yield (%)
CH_3NO_2	0.2	1.2	14	86	Trace	20
	1.0	1.5	13	87	Trace	27
CH_2Cl_2	0.2	1.2	3	97	Trace	8
	1.0	1.3	6	89	5	34

analysis, corresponded to decamethylbiphenyl (IV). The second product was isolated in a crude state from an exhaustive electrolysis and was identified as 2,3,4,5,2',3',4',5',6'-nonamethyldiphenylmethane (V). The third product was formed in traces in most experiments, and according to mass spectrometric analysis corresponded to an octamethyldiphenylmethane (VI) (Scheme 2). The results of the experiments are given in Table 3. The same effects as in the oxidations of 1,2,3,5-tetramethylbenzene are observed. The ratio of IV to V + VI is larger in nitromethane than in methylene chloride, and the current yields are concentration dependent. Also, in these oxidations, side-products were formed, similar to those in the oxidation of 1,2,4-trimethylbenzene.

In order to make a complete comparison between the different methylbenzenes in methylene chloride and in nitromethane, oxidations of mesitylene and durenene were also carried out in nitromethane. Anodic oxidation of a 1.0 M solution of mesitylene gave the same products as in methylene chloride (bimesityl and termesityl) in a current yield of 23 %. Similarly, oxidation of durenene (0.2 M) in nitromethane gave 2,4,5,2',3',5',6'-heptamethyldiphenylmethane in a 12 % current yield.

DISCUSSION

Many authors have shown that anodic oxidation of aromatic compounds produces cation radicals.³⁻⁶ This suggestion has been based primarily on results obtained by anodic oxidation of polynuclear hydrocarbons. These compounds give rise to cation radicals that can be observed by ESR and that can be distinguished from the dication on cyclic voltammograms. It is therefore reasonable to assume that anodic oxidation of methylbenzenes also produces cation radicals, although these are too shortlived to be observed by electroanalytical techniques.⁷ The reaction of these species in methylene chloride or nitromethane are, however, interesting, giving rise to either biphenyls or diphenylmethanes, or a mixture of these as the final products. One might assume that the formation of biphenyls is the result of coupling between cation radicals. However, as was pointed out earlier, the biphenyls might also be formed by attack of the cation radicals on the neutral molecules.

If we assume that anodic oxidation of methylbenzenes produce cation radicals, then the unpaired electron density in the ring positions will be an

important factor to consider, when we want to describe the reactions following their formation. Calculations have been made on the distribution of the unpaired electron density in the cation radicals of alkylbenzenes,⁷ and polymethoxybenzenes,⁸ and these have been found to agree well with the values obtained from the hyperfine splitting constants in the ESR spectra of the cation radicals. It is therefore of interest to correlate the unpaired electron density in the ring positions of the cation radicals with the type of products that is obtained by anodic oxidation of the parent hydrocarbon. The densities and the percentage of biphenyls formed are given in Table 4. We see that a large value of the unpaired electron density in the free ring positions corresponds to an observation of a large percentage of biphenyls, and that a low value corresponds to a small amount of biphenyls. Thus it is no doubt important to take this correlation into account for a description of the reaction mechanism. However, the fact that the unpaired electron density in the free ring positions correlates with the formation of biphenyls does not necessarily mean that the cation radicals react in a coupling mode. Another important factor is the distribution of the positive charge in the cation radicals. In simple HMO calculations of the cation radicals, the same distribution of the positive charge will be obtained as for the unpaired electron density, which means that the values shown in Table 4 also correspond to the positive charge distribution. Taking this into account, we suggest that the formation of biphenyls

Table 4. Unpaired electron densities in the ring positions of cation radicals of polymethylbenzenes and the percent of biphenyl derivatives formed in anodic oxidation in methylene chloride and in nitromethane of the polymethylbenzenes (1.0 M).

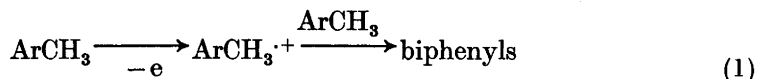
Compound	Position	Unpaired electron density ^a	% Biphenyls ^b	
			CH ₃ NO ₂	CH ₂ Cl ₂
1,2,4-Trimethylbenzene	1	0.262	47	33
	2	0.143		
	3	0.009		
	4	0.191		
	5	0.154		
	6	0.035		
1,3,5-Trimethylbenzene	1,3,5	0.107	100	100 ^c
	2,4,6	0.180		
1,2,3,5-Tetramethylbenzene	1,3	0.087	63	45
	2	0.303		
	4,6	0.055		
	5	0.192		
1,2,4,5-Tetramethylbenzene	1,2,4,5	0.191	0	0 ^c
	3,6	0		
Pentamethylbenzene	1,2,4,5	0.191	13	6
	3,6	0		

^a Values taken from Ref. 8.

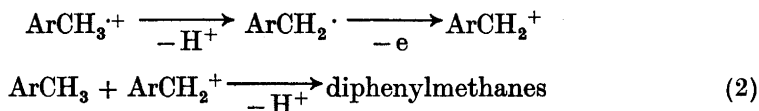
^b Percentage of the total sum of biphenyls and diphenylmethanes.

^c Values taken from Ref. 1.

occurs by an electrophilic attack of the cation radicals on the starting compound (eqn. 1).



From Table 4 it is also clear that if the cation radical carries a large unpaired electron density (and likewise a large positive charge) at a substituted position, the formation of the diphenylmethanes increases at the expense of biphenyls. This is due to the fact that loss of a proton in the benzylic position will be facilitated. The formation of diphenylmethanes will therefore occur by the reaction outlined in eqn. 2.



After loss of a proton from the cation radical, the benzyl radical is rapidly oxidized to a benzyl cation, since the oxidation potentials for benzyl radicals are much lower than for the parent compound, and the benzyl cation will then attack the starting compound in an electrophilic reaction, and subsequent loss of a proton leads to a diphenylmethane.

In some oxidations, we detected diphenylmethanes that carried one methyl group less than the normal oxidation product, such as the octamethyldiphenylmethane from pentamethylbenzene. These diphenylmethanes are probably formed by attack of a benzyl cation on a substituted ring position in the starting compound and subsequent demethylation.

The formation of a hexamethyldiphenylmethane from anodic oxidation of 1,2,4-trimethylbenzene (compound E) can be accounted for by assuming that demethylation occurs and methyl carbonium ion attacks the starting material, to form a tetramethylbenzene that is directly oxidized to a benzyl cation, which reacts in a normal way to form a hexamethyldiphenylmethane.

EXPERIMENTAL

The electrolyses were carried out using the cell, electrodes, and potentiostat described earlier.¹ Gas chromatographic analysis was carried out with a Perkin-Elmer Model 880 instrument, equipped with a Perkin-Elmer Model D 26 integrator and a 2 m x 0.3 cm 5 % NPGS on Chromosorb W column. Mass spectrometric analysis was carried out with an LKB 9000 mass spectrometer in combination with GLC at 70 eV. NMR spectra were recorded with a Varian A 60 A NMR spectrometer.

Materials. 1,2,4-Trimethylbenzene, methylene chloride, and nitromethane were of commercial reagent grade qualities; nitromethane was further purified by drying over anhydrous sodium sulphate. 1,2,3,5-Tetramethylbenzene and pentamethylbenzene were prepared by chloromethylation of mesitylene and durene, respectively, followed by catalytic hydrogenation of the benzyl chlorides. The preparation of tetrabutylammonium tetrafluoroborate has been reported.¹

Electrolysis. The concentration of the aromatic compound, the anode potential employed, and the amount of charge passed have already been described in the Results section. After each electrolysis (50 ml solution were electrolyzed at about 20°), the solvent was removed by evaporation *in vacuo*, ether was added to the residue, and the insoluble Bu₄NBF₄ was filtered off. The ether solution was then analyzed by GLC and mass spectrometry. The identification of the electrolysis products are given below.

1,2,4-Trimethylbenzene. The five main products detected by GLC were assigned the following structures based on mass spectral data. The assignment of a specific structure was based on the fact that methylbiphenyls are stable towards cleavage at the pivot bond, and methylphenylmethanes having at least one methyl group situated *ortho* to the methylene linkage can be cleaved in two ways.^{1,9}

A: hexamethylbiphenyl, *m/e* 239 (21 % abundance), 238 (83 %), 224 (21 %), 223 (100 %), 209 (10 %), 208 (37 %), 193 (25 %), 192 (10 %).

B: hexamethylbiphenyl, *m/e* 239 (20 %), 238 (87 %), 224 (20 %), 223 (100 %), 209 (11 %), 208 (41 %), 207 (13 %), 193 (26 %), 192 (11 %), 178 (10 %).

C: pentamethyldiphenylmethane, *m/e* 239 (16 %), 238 (81 %), 224 (19 %), 223 (87 %), 208 (19 %), 193 (19 %), 133 (16 %), 132 (95 %), 119 (27 %), 118 (100 %), 117 (19 %), and 91 (16 %).

D: pentamethyldiphenylmethane, *m/e* 239 (12 %), 238 (56 %), 224 (20 %), 223 (100 %), 208 (14 %), 193 (16 %), 133 (10 %), 132 (46 %), 119 (14 %), 117 (10 %), and 91 (11 %).

E: hexamethyldiphenylmethane, *m/e* 252 (30 %), 238 (13 %), 237 (40 %), 133 (20 %), 132 (100 %), 117 (10 %).

1,2,3,5-Tetramethylbenzene. The three electrolysis products were identified on basis of their mass spectra. The mass spectrum of 2,3,4,6,2',3',4',6'-octamethylbiphenyl (I) gave the following peaks: *m/e* 267 (23 %), 266 (100 %), 252 (17 %), 251 (89 %), 237 (14 %), 236 (43 %), 235 (13 %), 221 (31 %). The second GLC peak was identified as either 2,4,6,2',3',4',6'-heptamethyldiphenylmethane or 2,3,5,2',3',4',6'-heptamethyldiphenylmethane, or a mixture of both compounds, since the mass spectrum of each would give rise to fragments at *m/e* 146 and *m/e* 132. The following peaks were recorded: *m/e* 266 (33 %), 251 (25 %), 147 (15 %), 146 (81 %), 133 (23 %), 132 (100 %), and 117 (12 %). The third GLC peak was identified as 3,4,5,2',3',4',6'-heptamethyldiphenylmethane (II), since the mass spectrum showed the fragment at *m/e* 146, but no fragment at *m/e* 132. The following peaks were recorded: *m/e* 267 (16 %), 266 (70 %), 252 (20 %), 251 (92 %), 221 (12 %), 147 (17 %), 146 (100 %), 133 (22 %), 131 (11 %), and 92 (12 %).

Pentamethylbenzene. Three products were detected from the electrolysis mixture, and the first was identified as decamethylbiphenyl (IV), on the basis of the mass spectrum that showed peaks at *m/e* 295 (25 %), 294 (100 %), 279 (27 %), and 264 (14 %). The second and major product was isolated in a crude state from an exhaustive electrolysis of pentamethylbenzene in methylene chloride. After the usual work-up procedure, the residue was dissolved in pentane and subjected to column chromatography on alumina. Elution with a large amount of pentane gave after removal of the solvent a white solid. Distillation at low pressure removed unreacted pentamethylbenzene, and the residue was then recrystallized from benzene. The white solid residue (about 90 % pure) was identified as 2,3,4,5,2',3',4',5',6'-nonamethyldiphenylmethane (V). The NMR spectrum (in CDCl₃) gave rise to signals at $\delta = 6.23$ ppm (one aromatic proton), 3.92 ppm (CH₂-protons), 2.32 ppm, 2.25 ppm, 2.15 ppm, and 2.08 ppm (the protons in the nine methyl groups). The aromatic proton is shifted upfield to a large extent, which is due to the shielding effect caused by the steric arrangement of the molecule (compare the NMR spectrum of 2,4,5,2',3',5',6'-heptamethyldiphenylmethane, reported in Ref. 1). This type of shielding would not be expected in the two other isomeric nonamethyldiphenylmethanes. The mass spectrum showed peaks at *m/e* 295 (24 %), 294 (100 %), 279 (34 %), 161 (12 %), 160 (70 %), 147 (12 %), 146 (57 %). The third product was identified as an octamethyldiphenylmethane on the basis of the mass spectrum, that gave the following peaks at *m/e* 281 (19 %), 280 (73 %), 265 (29 %), 147 (16 %), 146 (100 %).

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