

Electrolysis in Non-nucleophilic Media

Part VI.¹ Anodic Coupling of Aromatic Hydrocarbons in Methylene Chloride in the Presence of Strong Acids

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The use of strong acids, such as trifluoroacetic acid, methanesulphonic acid, and trifluoromethanesulphonic acid, in methylene chloride prevents the reductive formation of chloride ion during electrolysis. Anodic coupling of aromatic hydrocarbons in methylene chloride containing any of these acids is, however, affected. In general, the yield of biaryl products is decreased and the yield of diphenylmethanes is increased.

Anodic coupling of aromatic hydrocarbons in methylene chloride is affected adversely by the reductive formation of chloride ion at the cathode.² Chloride ion is oxidized at the anode simultaneously with the aromatic hydrocarbon, producing chlorine that reacts with the hydrocarbon in a homogeneous chlorination process. This side-reaction not only decreases the current yield of the desired product (dehydrodimer) but also makes its isolation difficult. Since methylene chloride is an excellent solvent for anodic reactions in other respects, we have investigated anodic coupling in methylene chloride containing strong acids, in the hope that proton reduction at the cathode would prevent reduction of methylene chloride. Strong acids have been used earlier for the anodic oxidation of alkanes in fluorosulphonic acid³ and for voltammetric experiments in trifluoroacetic acid.⁴

RESULTS AND DISCUSSION

It is obvious that the number of suitable acids is rather limited. The acid should be soluble in methylene chloride and should not react with the aromatic hydrocarbon, except possibly for protonation to form a σ -complex. Therefore, trifluoroacetic acid, methanesulphonic acid, and trifluoromethanesulphonic acid were chosen as potentially useful acids. The first two are of comparable acidity while the last one is one of the strongest organic acids known. Tri-

fluoroacetic acid was used as a 10 % solution, methanesulphonic acid as a 0.4 M solution, and trifluoromethanesulphonic acid as a 0.2 M solution unless otherwise stated. Chlorosulphonic and fluorosulphonic acids were also tried, but could not be used since they rapidly sulphonate the aromatic hydrocarbons.

All anodic oxidations were carried out between two platinum electrodes on solutions containing hydrocarbon, tetrabutylammonium tetrafluoroborate (0.1 M), acid, and methylene chloride, using the saturated calomel electrode as a reference electrode. Analysis of the products was made by GLC, after 0.2 *F* per mol of hydrocarbon had been passed through the electrolyte.

Anodic oxidation of naphthalene in methylene chloride containing trifluoroacetic acid gave 1,1'-binaphthyl in an 8 % current yield. No chlorinated products were formed. However, the yield of binaphthyl is lower than that obtained in methylene chloride containing acetic acid or in acetonitrile containing acetic acid (14 and 28 %, respectively).⁵

Similar results were obtained from the anodic oxidation of mesitylene, as shown in Table 1. The yields of dimeric products are generally lower in the

Table 1. Products from the anodic oxidation of mesitylene (1.0 M).

Acid	Current yields			Anode potential (V)
	I ^a	II	III	
—	5 ^b	30	16	1.8
CF ₃ COOH	—	18	5	1.4
CH ₃ SO ₃ H (0.2 M)	7	6	2	1.4
(0.6 M)	1	11	3	1.4
CF ₃ SO ₃ H	—	37	7 ^c	1.2

^a 2-Chloromesitylene. ^b Data from Ref. 2. ^c 3 % of a tetramer was also formed.

presence of acids than in their absence, with the exception of trifluoromethanesulphonic acid. In all experiments, bimesityl (II) and termesityl (III) were formed, whereas in the presence of trifluoromethanesulphonic acid, a tetrameric product was also observed. Chloride ion formation can be successfully blocked in these experiments as seen from Table 1. It is also worth mentioning that the anode potential is significantly lower when acids are present in the electrolyte (approximately the same current density is used in all experiments).

Anodic coupling of naphthalene or mesitylene represent cases where only biaryls are produced. The yields are generally lower in the presence of acids than in their absence.

Anodic coupling of *p*-xylene (IV) gives 2,5,4'-trimethyldiphenylmethane (V) and 2,5,2',5',4''-pentamethyltriphenylmethane (VI), depending on the reaction conditions (Table 2). In the presence of acids, strong effects on the product distribution as well as the anode potential are again observed. The total yields of V and VI are considerably higher in the presence of acids than in their absence. This is opposite to the effect observed in the oxidation of

Table 2. Products from the anodic oxidation of *p*-xylene (2.0 M).

Acid	Current yields			Anode potential (V)
	IV	V	VI	
—	—	10	—	2.0
CF ₃ COOH ^b	5 ^a	22	4	1.4
CH ₃ SO ₃ H	—	17	4	1.5
CF ₃ SO ₃ H	—	6	18	1.3

^a Data from Ref. 2. ^b 5–10 % yield of *p*-methylbenzyl trifluoroacetate was also obtained.

naphthalene or mesitylene. Oxidation of *p*-xylene in the presence of trifluoroacetic acid produced yet another compound, *p*-methylbenzyl trifluoroacetate.

The highest yields of dehydrodimers were obtained in the oxidation of durene in the presence of acids (Table 3). 3-Chlorodurene (VII) was almost absent in these experiments. The highest yield of 2,3,5,6,2',4',5'-heptamethyldi-

Table 3. Products from the anodic oxidation of durene.

Durene conc. (M)	Acid	Current yields		Anode potential (V)
		VII	VIII	
0.2 ^a	—	14	14	1.4
1.0 ^a	—	12	29	1.4
0.2	CF ₃ COOH	—	65	1.3
1.0	»	—	77	1.3
0.2	CH ₃ SO ₃ H	1	29	1.1
1.0	»	2	54	1.1
1.0	CF ₃ SO ₃ H	—	85	1.2

^a Data from Ref. 2.

phenylmethane (VIII) is remarkably high. Besides VIII, a trimeric product, accounting for 5–10 % of the product mixture, was formed in most reactions. In contrast to the case of *p*-xylene there was no indication of the formation of a side-chain trifluoroacetate.

Anodic oxidation of pentamethylbenzene in methylene chloride produces chloropentamethylbenzene, a small amount of decamethylbiphenyl and a nonamethyldiphenylmethane.⁶ In the presence of acids, oxidation of pentamethylbenzene gave the same hydrocarbons, no significant difference in the yields being observed. In some experiments, two isomeric nonamethyldiphenylmethanes were observed. In the presence of trifluoromethanesulphonic acid, hexamethylbenzene and tetramethylbenzenes were formed in about 20 % yield. The same compounds were observed in a control experiment when no current was passed through the electrolysis mixture.

We also investigated the anodic oxidation of toluene in methylene chloride containing trifluoroacetic acid. No volatile products were formed, the anode being rapidly coated with polymers. The anode potential was also in this case significantly lower than in the absence of the acid.

In all experiments reported, the presence of acids has the effect of decreasing the amount of chlorinated products thus fulfilling our expectations. On the other hand, it influenced the yield of products and the product distribution in a way that is difficult to explain. Biaryl products were generally formed in lower yields in the presence of acid, while diphenylmethane products were formed in higher yields.

From a synthetic point of view the results show that it should be an advantage to use acids in preparing diphenylmethanes. Therefore, some large-scale oxidations were carried out using a newly developed cell construction permitting high currents.⁷ Oxidation of *p*-xylene in the presence of trifluoroacetic acid produced V in a current yield of 16 % together with 10 % of *p*-methylbenzyl trifluoroacetate. Oxidation of durene in the presence of trifluoroacetic acid and methanesulphonic acid gave VIII in 39 and 23 % current yield, respectively.

EXPERIMENTAL

The apparatus and procedure for small-scale electrolysis was the same as previously described.⁵ GLC analysis was carried out on a 2 m × 0.3 cm 3 % OV-17 on Chromosorb W column using an internal standard (Perkin-Elmer 880 gas chromatograph). The following hydrocarbon products were identified on the basis of their mass spectral fragmentation pattern: VI, the tetrameric compound from oxidation of mesitylene, and the trimeric compound from oxidation of durene. All other products have been characterized or isolated in earlier work. Large-scale oxidations were carried out between a carbon anode (surface area 580 cm²) and a steel cathode in the cell described previously.⁷

Oxidation of p-xylene. A solution containing *p*-xylene (4.0 mol), tetrabutylammonium tetrafluoroborate (0.04 mol), trifluoroacetic acid (200 ml), and methylene chloride (1800 ml) was electrolyzed at a constant current of 15 A, an applied voltage of 48 V, and a temperature of 32° until 0.5 *F* per mol of *p*-xylene had passed. Solvent and *p*-xylene were removed by distillation at atmospheric pressure. Further distillation gave a fraction, b.p. 83–85°/12 mm, identified as *p*-methylbenzyl trifluoroacetate by NMR (in CDCl₃, TMS internal standard, δ = 2.33 ppm, 5.28 ppm, 7.23 ppm, integrated area ratio 3:2:4) and MS (*m/e* 218). The yield was 21.3 g (current yield 10 %) and the purity by GLC about 98 %. The residue was treated with pentane and the pentane soluble material run through an alumina column to remove polymeric material. After removing the solvent, further distillation afforded 2,5,4'-trimethyldiphenylmethane, b.p. 130–135°/1.5 mm (34.6 g, current yield 16 %). The purity was 95 %.

Oxidation of durene. A solution containing durene (1.0 mol), tetrabutylammonium tetrafluoroborate (0.01 mol), trifluoroacetic acid (50 ml), and methylene chloride (450 ml) was electrolyzed at a constant current of 10 A, an applied voltage of 31 V, and a temperature of 25° until 0.5 *F* per mol of durene had passed. The solvent was removed by distillation and durene removed from the residue by steam distillation. The residual organic material was extracted into methylene chloride. After removing the solvent, the residue was treated twice with 250 ml boiling pentane. The combined pentane solutions were run through an alumina column. From the eluate, VIII was obtained (26 g, current yield 39 %), contaminated with 7 % of the trimeric hydrocarbon.

The oxidation of durene was repeated using 0.2 mol of methanesulphonic acid instead of trifluoroacetic acid under identical conditions. The yield of VIII was 23 %.

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