ELECTROLYSIS IN NON-NUCLEOPHILIC MEDIA: BENZYLATION WITH ANODICALLY GENERATED PENTAMETHYLBENZYL CATION

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Anodic oxidation of hexamethylbenzene in dichloromethane containing trifluoroacetic acid or methanesulphonic acid has been investigated. In the presence of benzene, toluene, *p*-xylene or mesitylene diphenylmethanes are formed, resulting from reaction of the anodically generated pentamethylbenzyl cation with the added hydrocarbon. The reaction is complicated due to the acidity of the electrolysis medium, giving rise to acid-catalyzed transformation of the initially formed diphenylmethanes. Furthermore, hexamethylbenzene is formed by hydride ion abstraction from the electrolysis medium to the pentamethylbenzyl cation.

In previous parts of this series we have investigated the anodic oxidation of alkylbenzenes in media, such as dichloromethane[1,2] and nitromethane[2,3], where the alkylbenzene itself acts as a nucleophile towards the positive species (aromatic cation radicals or benzyl cations) generated at the anode. Although dichloromethane was found to have better solubilizing properties than nitromethane, it suffered reduction at the cathode with the formation of chloride ions. These were found to be oxidized at the anode simultaneously with the aromatic hydrocarbons resulting in chlorination of the latter or the products. However, this side-reaction could be avoided by the addition of a strong acid, such as trifluoroacetic acid or methanesulphonic acid, to the electrolyte[4]. Under these conditions protons instead of dichloromethane were reduced at the cathode.

In the present work we have investigated the anodic oxidation of hexamethylbenzene in dichloromethane containing trifluoroacetic acid or methanesulphonic acid in the presence of benzene, toluene, *p*-xylene or mesitylene. Anodic oxidation of hexamethylbenzene in the presence of acetic acid or acetonitrile yields pentamethylbenzylacetate[5,6] and N-pentamethylbenzylacetamide[7,8], respectively, by solvolysis of the pentamethylbenzyl cation. Although the hexamethylbenzene cation radical undoubtedly is an intermediate, it is extremely shortlived even at low temperature[9] and is transformed by proton loss into the pentamethylbenzyl radical, the latter undergoing further oxidation to the cation. We therefore expected that the oxidation of hexamethylbenzene in the presence of alkylbenzenes would yield diphenylmethane derivatives from the reaction between the pentamethylbenzyl cation and the alkylben-

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zenes. The oxidation potentials of benzene, toluene, *p*-xylene and mesitylene are considerably higher than that of hexamethylbenzene[10]. In a recent communication it has been shown that controlled potential oxidation of hexamethylbenzene in dichloromethane containing trifluoroacetic acid gives pentamethylbenzyl trifluoroacetate in high yield[11]. The latter was found to be oxidized at a higher potential to a relatively stable species. However, the product at this potential was not identified.

EXPERIMENTAL

Apparatus and compounds. The electrolytic experiments were carried out in a water-jacketed cell between two platinum electrodes. In the controlled potential experiments an Amel Model 557 Potentiostat in connection with an Amel Model 558 Integrator was used. In the constant current experiments a Radiak 2 A/60 V power supply was used. GLC analysis was done with a Perkin-Elmer 880 Gas Chromatograph in connection with a Perkin-Elmer D 24 Integrator using either a 2 m × 0·3 cm 3% OV-17 on Chromosorb Q column or a 2 m × 0·3 cm 5% NPGS on Chromosorb W column. NMR spectra were recorded with a Varian A-60 A instrument. Mass spectrometric analysis was done with a LKB 9000 mass spectrometer.

The starting materials, the solvents and the acids were of high commercial quality. Bu_4NBF_4 was prepared from Bu_4NHSO_4 according to the literature[1]. The following diphenylmethanes were available from earlier work[12]: 2,3,4,5,6-pentamethyldiphenylmethane, 2,3,4,5,6,2',4',6'-octamethyldiphenylmethane, 2,4,6,2',4',6'-hexamethyldiphenylmethane. 2,3,4,5,6,2'-, 2,3,4,5,6,3'-, and 2,3,4,5,6,4'-hexamethyldiphenylmethane were prepared by reduction of the corresponding benzophenones, these being obtained in Friedel–Crafts reactions between pentamethylbenzene and the appropriate methylbenzoyl chloride. The products *II* and *III* from oxidation of hexathylbenzene in the presence of *p*-xylene were identified on the basis of mass spectrometry, a method suitable for *ortho*-substituted diphenylmethanes[13]. 2,3,4,5,6,2',5'-Heptamethyldiphenylmethane gave *m/e* 266 (40% abundance), 251 (26%), 160 (18%), 118 (100%). 2,5,2',5'-tetramethyldiphenylmethane gave *m/e* 244 (34%), 209 (25%), 118 (100%).

Electrolysis. The oxidations were carried out on 50 ml solutions containing the reagents already specified in the Tables under stirring at room temperature. At the end of electrolysis the solvent was removed by evaporation *in vacuo*. Ether was added to the residue and the insoluble Bu_4NBF_4 was filtered off. The filtrate was washed with saturated sodium bicarbonate solution, with water and finally dried over anhydrous sodium sulphate. The ether solution was then analyzed by GLC and the yields were calculated using an internal standard.

The oxidation of hexamethylbenzene in dichloromethane–trifluoroacetic acid in the absence of added hydrocarbon at an anode potential of 1·20 V until 2 *F*/mol had been passed gave after the usual work-up procedure a solid residue, that melted at 103−105°C after recrystallization from hexane. It was identified as pentamethylbenzyltrifluoroacetate on the basis of spectral data: NMR, $\delta = 2 \cdot 23$ p.p.m., 2·30 p.p.m. and 5·52 p.p.m. (integrated area ratio 9 : 6 : 2); MS, *m/e* 274 (28%), 162 (16%), 161 (96%), 160 (100%), 146 (21%), 145 (26%). When the oxidation was carried out until 4 *F*/mol had passed at potentials between 1·40 and 1·70 V, the solid residue contained mainly two components according to GLC. These were identified as 1,2-bis(trifluoroacetoxymethyl)-3,4,5,6-tetramethylbenzene [*m/e* 386 (42%), 273 (88%), 272 (100%), 203 (33%), 176 (35%), 175 (51%), 161 (28%), 160 (32%), 159 (47%), 158 (44%), 148 (63%), 147 (63%)] and 1,4-bis(trifluoroacetoxymethyl)-2,3,5,6-tetramethylbenzene [*m/e* 386 (26%), 273 (72%), 272 (100%), 175 (22%), 160 (22%), 159 (100%), 158 (64%)]. Treating the solid residue with sodium

acetate in boiling acetic acid gave the corresponding diacetates, identified by comparison with authentic samples.

RESULTS

Anodic oxidation of hexamethylbenzene ($0.25M$) was first carried out without any added hydrocarbon in dichloromethane/trifluoroacetic acid ($9 : 1$) containing Bu_4NBF_4 ($0.2M$) between two platinum electrodes. Controlled potential oxidation at 1.20 V (vs S.C.E.) was run until $2\,F$/mol of hexamethylbenzene had passed, resulting in the formation of pentamethylbenzyl trifluoroacetate, I, (93% yield by GLC). If the oxidation was carried out further at potentials between 1.40 V and 1.70 V until another $2\,F$/mol had passed, I was almost completely converted into a mixture of 1,2-bis-(trifluoroacetoxymethyl)-3,4,5,6-tetramethylbenzene and 1,4-bis(trifluoroacetoxy-methyl)-2,3,5,6-tetramethylbenzene. The oxidation of hexamethylbenzene was also carried out at constant current (6 mA/cm^2) until $2\,F$/mol of hexamethylbenzene had passed with a yield of pentamethylbenzyl trifluoroacetate comparable to the controlled potential experiment.
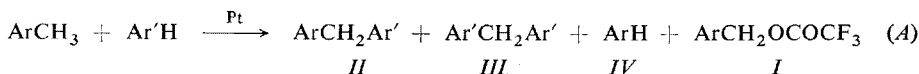
TABLE I

Product Yields from the Anodic Oxidation of Hexamethylbenzene ($0.25M$) in the Presence of Alkylbenzenes ($2.5M$) in CH_2Cl_2/CF_3COOH ($9 : 1$) Containing Bu_4NBF_4 ($0.2M$)

Alkylbenzene	Current yield, %					Total yield, $\%^b$
	$ArCH_3{}^a$	II	III	IV	I	
Benzene	20	8	—	1	48	77
Toluene	14	16^c	4	4	6	40
p-Xylene	42	11	9	15	—	68
Mesitylene	16	66	6	4	—	88

^{a} Unreacted hexamethylbenzene; ^{b} including $ArCH_3$, II and the largest value of III or IV; ^{c} a 6 : 1 ratio of *para* : *ortho* substituted products.

Anodic oxidation of hexamethylbenzene was then carried out in the presence of benzene, toluene, p-xylene or mesitylene ($2.5M$) at a constant current (6 mA/cm^2) until $2\,F$/mol of hexamethylbenzene had passed using the same solvent-supporting electrolyte system as in the absence of added hydrocarbon. The major products (Eq.(A)) were a diphenylmethane (II), formed by reaction of pentamethylbenzyl cation and the added hydrocarbon, a diphenylmethane (III), derived from the added hydrocarbon, pentamethylbenzene (IV) and pentamethylbenzyl trifluoroacetate (I). The results are shown in Table I.

$$ArCH_3 + Ar'H \xrightarrow{\text{Pt}} ArCH_2Ar' + Ar'CH_2Ar' + ArH + ArCH_2OCOCF_3 \quad (A)$$
$$\qquad\qquad\qquad\qquad\quad II \qquad\quad III \qquad\quad IV \qquad\qquad I$$

$ArCH_3$: hexamethylbenzene; $Ar'H$: benzene, toluene, p-xylene, mesitylene.

Next, the reactions were carried out using methanesulphonic acid $(1 \cdot 0\text{M})$ instead of trifluoroacetic acid in dichloromethane as solvent. In the absence of hydrocarbon the controlled potential oxidation of hexamethylbenzene at $0 \cdot 9$ V $(vs$ S.C.E.$)$ until $2\,F/\text{mol}$ of hexamethylbenzene had passed gave 70% unreacted hexamethylbenzene. We were unable to isolate or identify any products by means of GLC. When the oxidation of hexamethylbenzene was carried out in the presence of hydrocarbons at constant current (6 mA/cm^2), the compounds $II-IV$ were formed. The results are presented in Table II.

TABLE II

Product Yields from the Anodic Oxidation of Hexamethylbenzene $(0 \cdot 25\text{M})$ in the Presence of Alkylbenzenes $(2 \cdot 5\text{M})$ in CH_2Cl_2 Containing CH_3SO_3H $(1 \cdot 0\text{M})$ and Bu_4NBF_4 $(0 \cdot 2\text{M})$

Alkylbenzene	Current yield, %				Total yield, %[b]
	$ArCH_3$[a]	II	III	IV	
Benzene	21	15	—	—	36
Toluene	11	81[c]	—	—	92
p-Xylene	58	13	3	6	77
Mesitylene	25	25	37	33	87

[a] Unreacted hexamethylbenzene; [b] including $ArCH_3$, II and the largest value of III or IV; [c] a $6 : 1$ ratio of *para* : *ortho* substituted products.
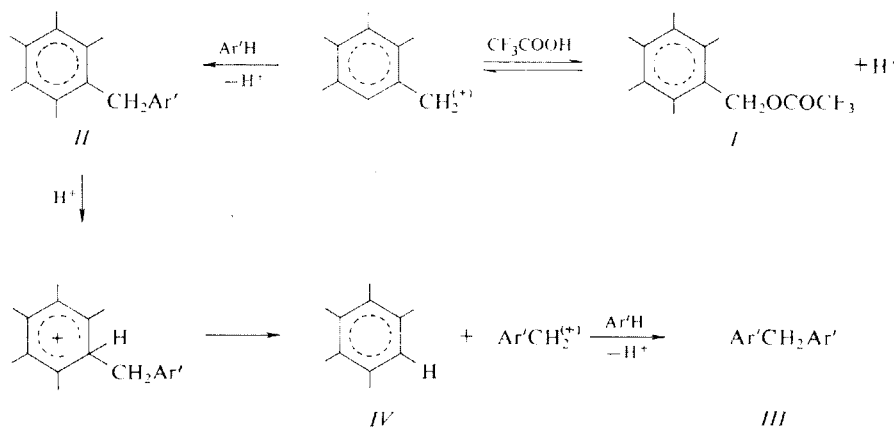
DISCUSSION

The products that are formed from the anodic oxidation of hexamethylbenzene in the presence of benzene, toluene, p-xylene or mesitylene no doubt has the pentamethylbenzyl cation as an intermediate. The oxidation potential of hexamethylbenzene is considerably lower than that of the hydrocarbons. Therefore the primary reaction is electron transfer from hexamethylbenzene to the anode followed by proton loss and a further electron transfer, yielding the pentamethylbenzyl cation $(\text{Eq. } (B))$. Solvolysis of this species gives pentamethylbenzyl trifluoroacetate. We have also shown that oxidation of the latter occurs efficiently at a potential higher than that

$$ArCH_3 \xrightarrow[-e]{} ArCH_3^{+\cdot} \xrightarrow[-H^+]{} ArCH_2\cdot \xrightarrow[-e]{} ArCH_2^+ \qquad (B)$$
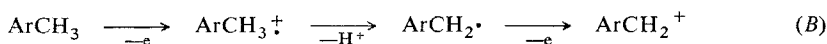
required to oxidize hexamethylbenzene, giving disubstituted products. The formation of the primary diphenylmethanes, *II*, takes place in an electrophilic reaction between the pentamethylbenzyl cation and the aromatic hydrocarbons (Scheme 1). The electrophilic nature of this reaction is evident from the isomer distribution obtained in the oxidation of hexamethylbenzene in the presence of toluene. Negligible amounts of the *meta* isomer could be detected.

The formation of the other diphenylmethane derivative, *III*, and pentamethylbenzene is due to the acidity of the electrolysis medium. Protonation of the primary product, *II*, may result in the formation of pentamethylbenzene and a benzyl cation (Scheme 1). The latter cation can then react with the added aromatic hydrocarbon

Ar'H, $-H^+$, CH_2Ar', *II*, $CH_2^{(+)}$, CF_3COOH, CH_2OCOCF_3, *I*, $+H^+$

H^+

$+$, H, CH_2Ar', H, *IV*, $+$, $Ar'CH_2^{(+)}$, Ar'H, $-H^+$, $Ar'CH_2Ar'$, *III*

SCHEME 1

to produce the diphenylmethane *III*. The success of this reaction is dependent on the stability of the benzyl cation $Ar'CH_2^+$ since all the reactions leading from the pentamethylbenzyl cation to *IV* and *III* are reversible. Similar acid-catalyzed transformation of polymethyldiphenylmethanes has been observed[12,14]. Furthermore, in control experiments we have found that the diphenylmethane formed as the primary product from oxidation of hexamethylbenzene in the presence of mesitylene undergoes acid--catalyzed transformation into pentamethylbenzene and *III* $(Ar' = mesityl)$ when treated with either dichloromethane–trifluoroacetic acid or dichloromethane–methanesulphonic acid mixtures in the presence of mesitylene. In the latter medium the transformation was found to be faster than in the former. This also explains the results in Tables I and II for the oxidation of hexamethylbenzene in the presence of mesitylene. In the presence of methanesulphonic acid more secondary products are formed than in the presence of trifluoroacetic acid.

We have also considered another possibility for the formation of *II* in the medium containing trifluoroacetic acid. The pentamethylbenzyl trifluoroacetate could be converted into the pentamethylbenzyl cation by the acid present, then further reaction would give *II*. This would be similar to the acid-catalyzed Friedel–Crafts benzylation that has been demonstrated for substituted benzyl acetates[12]. In control experiments it was found that pentamethylbenzyl trifluoroacetate was converted into the products *II, III* and *IV* on treatment with a dichloromethane–trifluoroacetic acid mixture containing an aromatic hydrocarbon. However, the rate of formation of the products was at least in the presence of benzene much slower than the rate of formation of the products in the electrolysis experiment. In the presence of mesitylene the rates were comparable.

In all electrolysis experiments shown in the Tables unreacted hexamethylbenzene corresponds to a significant part of the total yield. This could be due to further oxidation of the products. However, the potentials that are necessary to reach in order to have a significant rate of oxidation are much higher than those employed in the experiments. This is especially true for the products formed in the reactions employing *p*-xylene or mesitylene. Therefore we consider it possible that hexamethylbenzene can be formed by hydride ion abstraction from the medium to the pentamethylbenzyl cation $(Eq.(C))$. This type of reaction is well documented in carbonium ion chemistry[15]. It has also been shown that the pentamethylbenzyl cation reacts in acidic media

$$ArCH_2^+ \xrightarrow[H^- \text{ abstr.}]{} ArCH_3 \qquad (C)$$
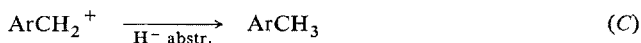
with alkanes or aromatic compounds yielding hexamethylbenzene by hydride ion abstraction[16-18]. Furthermore, hexamethylbenzene is formed upon treating pentamethylbenzyl derivatives with string acids[12,14].

In conclusion, the reactions shown in Eqs (B) and (C) and the Scheme 1 represents the different paths leading to the products formed on anodic oxidation of hexamethylbenzene in acidic media in the presence of alkylbenzenes.

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