

5,4'-dimethyl-2-methoxydiphenylether: a new product from the anodic oxidation of 4-methylanisole

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Anodic oxidation of *p*-methylanisole (1a) in a solution of aqueous 0.05 M H₂SO₄/acetone cosolvent (1 : 1, v/v) on platinum gives 5,4'-dimethyl-2-methoxydiphenylether (3), a compound hitherto unexplored, in 50% yield at a temperature below 15°C. Polymer products are formed in significant amounts (up to 60%) besides the diphenylether derivative (3) when the electrolytic oxidation proceeds in a solution containing AcOH as cosolvent at room temperature. The reaction mechanism includes both side chain anodic oxidation and ring 6e oxidation leading to a reactive intermediate, probably 3-methyl-5-methoxy-1,2-benzoquinone (5), whose polymeric products were also isolated.

1. Introduction

The electrolytic oxidation of *p*-methylanisole (MA, 1a) was investigated by Fichter and Ris [1], who found that only a small amount of anisaldehyde (1b) was formed when an emulsion of MA in aqueous sulphuric acid (or Na₂CO₃ or Na₂SO₄) was oxidized electrolytically at a platinum or lead dioxide anode in an undivided cell. They also isolated a small quantity of anisic acid (1d) and coupled isomeric dicresols and a compound of the elemental formula C₁₅H₁₄O₄ whose structure was not determined.

Degner [2] patented a direct selective anodic oxidation of MA (1a) in a methanolic KF solution on graphite yielding anisaldehyde dimethylacetal at a current yield of 57%. Nishiguchi [3] and coworkers studied the direct oxidation of MA (1a) on graphite in methanolic acetic acid solutions using the quaternary salt Et₄NOTs or KF as supporting electrolytes. Addition of AcOH caused the formation of anisic acid (1d) when KF was used. Torii and coworkers [4] used the electrolytically recovered coordinated compound (NH₄)₂Ce(NO₃)₆ for the oxidation of MA and obtained quinole in addition to anisaldehyde (1b) (Fig. 1).

This paper describes a study of the electrolytic oxidation of MA in aqueous sulphuric acid using glacial AcOH or acetone as cosolvent. The results submitted indicate simultaneous formation of both the new diphenylether derivative and polymer material.

2. Experimental details

p-Methylanisole (MA, 1a) was pure grade (Merck), distilled before use. The compounds corresponding to the products expected, such as anisaldehyde (1b), anisalcohol (1c) and anisic acid (1d) were chemically pure and were redistilled before use. H₂SO₄, glacial AcOH and acetone, used in the preparation of electrolyte solutions, were of reagent grade from Merck.

Preparative electrolyses were carried out galvanostatically in quasidivided, as well as divided magnetically stirred, cells [5]. These contained an axially placed platinum working anode (5 cm × 5 cm in size) and two symmetrically placed auxiliary cathodes made of stainless V2A steel wires. Cellophane served as a diaphragm in the divided cells. A stainless steel wire auxiliary electrode was immersed in the studied solution without MA (1a). The charge passed was measured with a coulometer Amel 558/RM.

The procedure was as follows. The glass cell was filled with 200 ml electrolyte containing 100 mmol (12.2 g) of MA (1a). Glacial AcOH as cosolvent containing MA was mixed with an equal volume of aqueous 0.1 M H₂SO₄. This electrolyte was heterogeneous, but solutions containing 50 mmol of the starting substance were homogeneous. The current density in electrolysis was 50 mA cm⁻². The initial cell voltage was 35 V. The electrolysis was finished as soon as the charge consumption reached 5.5 faraday mol⁻¹. The electrolyte, originally colourless, turned red–orange. The current density decreased during electrolysis as a result of coverage of the working electrode with an orange–red, greasy layer. After interrupting the electrolysis this could be easily removed by rinsing with acetone and the electrolysis continued at the original current density.

The electrolyte was treated in two ways, the first of which was as follows. When orange flakes precipitated from the solution, they were separated. The electrolyte was partly neutralized to pH 2 with a 40% NaOH solution. A 50 ml aliquot was extracted with CH₂Cl₂ and the extract subjected to GC analysis. The main part of the electrolyte, neutralized as mentioned, was, after the extraction with CH₂Cl₂, completely neutralized (40% NaOH) and re-extracted with CH₂Cl₂. The combined extracts were dried over anhydrous Na₂SO₄ and the solvent was evaporated in vacuum. The oily product was dried under a vacuum of 2–2.5 torr at 30–40°C. The obtained brown solid,

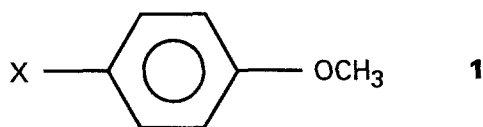


Fig. 1. X = CH₃ (1a); CHO (1b); CH₂OH (1c) or CH₂OH (1d).

foamy substance (4.8 g) melted at 60–70°C under decomposition.

It was further processed by column chromatography using silica gel in toluene. After elution with toluene–AcOEt–Et₂O (6:3:1 by volume) the fractions obtained were analysed by TLC.

Another method of electrolyte treatment was as follows. The orange electrolyte containing acetone and aqueous H₂SO₄ was mixed with an excess of powdered calcium carbonate under stirring, filtered, and the filtrate was diluted with distilled water. A 200 ml portion of this solution was used for isolation of the product and the remainder was, after pretreatment described in the preceding method, used for GC analysis. To isolate the product, acetone was evaporated and the remaining oil was separated on a silica gel column in toluene, similarly to the preceding method.

5,4'-Dimethyl-2-methoxy-diphenylether (3), a pale yellow oil, was isolated from the chromatographic fractions when the solvent was stripped off. Vacuum distillation of this substance yielded a nearly colourless liquid boiling at 115–117°C/1.5 torr.

Corresponding elemental analysis gives the following:

Found: C, 78.80; H, 7.04%. (Calc. for C₁₅H₁₆O₂: C, 78.94; H, 7.01%). H¹NMR: (200 MHz, CDCl₃, Me₄Si) δ 1.67 (s, 3H, CH₃), 2.33 (s, 3H, CH₃), 3.72 (s, 3H, OCH₃), 6.26 (d, 2H, *J* = 10.26, CH_{ar.}), 6.78 (d, 1H, *J* = 8.05, CH_{ar.}), 7.05 (d, 2H, *J* = 5.86, CH_{ar.}), 7.08 (d, 2H, *J* = 8.06, CH_{ar.}).

Mass spectrum: *m/z* (relative intensity in %) M⁺ 228 (100), 213(28), 197(21), 185(33), 141(22), 128(16), 121(20), 115(29).

The mentioned compound had the longest retention time in GC (8.95 min.).

Toluquinol (4): further chromatographic fractions gave a product melting at 74°C after recrystallization from petroleum ether ([8], 74–75°C).

IR (KBr): 3240(s), 1670(s), 1620(s), 1450(w), 1390(s), 1350(m), 1260(m) cm⁻¹.

H¹NMR: (200 MHz, CDCl₃, Me₄Si) δ 1.45 (s, 3H, CH₃), 4.02 (s, 1H, OH), 6.07 (d, 2H_{olef.}), 6.9 (d, 2H_{olef.}).

MS: *m/z* (relative intensity in %) M⁺ 124(26), 109(100), 96(60), 95(26), 81(80). These spectral data are in good agreement with the reference data for toluquinol.

The remaining chromatographic fractions contained polymeric substances of oily or greasy character. They were separated by additional column chromatography on silica gel in CH₂Cl₂. The elution system was CH₂Cl₂–ethanol (9:1 v/v). The fractions were analysed by TLC and the homogeneous polymers were combined. Their elemental analysis and spectral data are summarized in Table 2. The GC analysis was performed by means of an HP 5880 A apparatus with a phase OV–225 and FID detector. Mass spectra were recorded on a Jeol MS-100 and IR spectra on a Nicolet 205. A Varian Unity-200 NMR spectrometer served to obtain H¹NMR spectra.

2-Methoxy-5-methyl-1,4-benzoquinone was prepared as a model substance by the method of Ashley [6].

3. Results and discussion

Table 1 summarizes the results of the anodic oxidation of MA (1a) in aqueous sulphuric acid solutions containing AcOH as a cosolvent on a platinum anode. The material yields (MY) correspond to the diphenylether derivative (3). Anisaldehyde, anisalcohol and anisic acid occurred only in traces.

Polymeric resins also appeared during the processing of electrolyte; the last column of Table 1 gives their total amount in the particular run. Chromatographic separation of these products yielded several fractions exhibiting different solubility. Their elemental analysis and melting points are given in Table 2. The results of the electro-oxidation of the MA (1a) in aqueous sulphuric acid containing acetone cosolvent are given in Table 3. The electrolysis in this case was performed in both divided and quasi-divided cells. Toluquinol (4) was isolated in addition

Table 1. Anodic oxidation of *p*-methylanisole (1a) in 200 ml glacial AcOH/H₂SO₄ 1:1 (v/v) in a quasidivided cell on platinum

T /° C	j /mA cm ⁻²	Q _{passed} /U Faraday mol ⁻¹ /V	Conc. of aq. H ₂ SO ₄ M	Educt/Product ^g			
				MA /mmol	DPE /mmol	MY /%	Polymer resins/g
15	24	4.7/35	0.05	3.75	22.0	88	0.2
6	29	4.2/35	0.1	10.0	17.0	68	0.8
17 ^u	50	5.5/35	0.1	2.5	26.0	52	6.7
10	50	5.1/13	0.5	15.0	12.0	48	1.0
6	50	5.5/10	1.0	15.0	9.0	36	2.2

^u 0.5 mol MA/l, otherwise 0.25 mol MA/l

MY = material yield of DPE

^g Yields determined by the GC

DPE = 5,4'-dimethyl-2-methoxydiphenylether

Table 2. Polymer products isolated after the anodic oxidation of MA (1a) in aq. H₂SO₄ on platinum

Analyte	Composition	Soluble in	m.p. /°C	Elemental analysis found		Groups present*
				C/%	H/%	
AcOH glac/H ₂ SO ₄	(1:1)	acetone	nonmelt.	59.67	5.27	
		CH ₂ Cl ₂	nonmelt.	56.12	4.81	
Acetone H ₂ SO ₄	(1:1)	CH ₂ Cl ₂	195–205	60.95	5.45	CH ₃ /OCH ₃
		CH ₂ Cl ₂	145–150	60.92	5.82	CH ₃ /OCH ₃

Theoretical elemental analysis for C₈H₆O₃ (mol. wt. 150): 64.00% C, 4.02% H
Based on H¹ NMR records

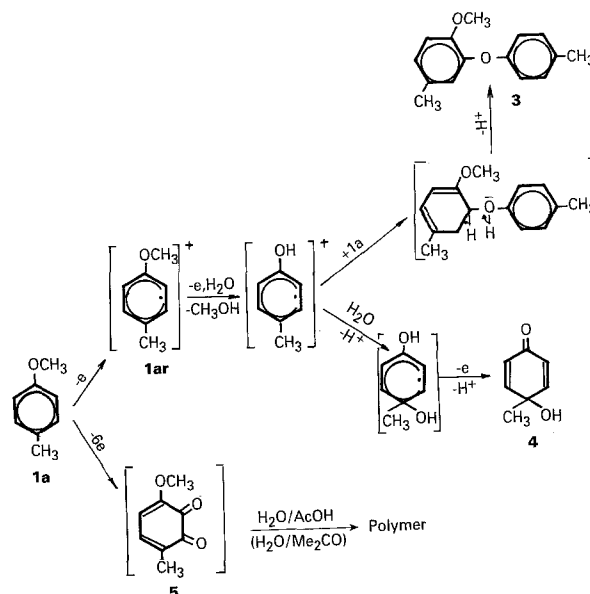
to diphenylether product (3). The orange flaky product filtered off after completion of some electro-preparative runs (AcOH cosolvent, 50 mmol MA) melted at 191–205°C under decomposition.

Elemental analysis:

Found: C, 63.25; H, 5.21%. (Calc. for C₈H₈O₃: C, 63.13; H, 5.29%)

This elemental formula corresponds to the assumed quinone structure (5). Unfortunately, this material was not available in a sufficient quantity for spectral records.

The occurrence of diphenylether product (3) in significant amount suggests the course of electro-oxidative fission of the etheral bond in MA (1a). This proceeds through the loss of the next electron from the intermediate species formed by water addition to the primary radical cation (1ar) (Scheme 1). Another mechanism of etheral bond fission proceeding by 2 electron oxidation of the starting substance 1a via unstable formaldehyde monoacetal intermediate giving *p*-cresol after the formaldehyde elimination can also be assumed. The coupling reaction of *p*-cresol intermediate to the parent compound (1a) or its radical cation forms therefore the final diphenylether product (3). This mechanism is supported by the findings of Chen and coworkers [7], who studied chemical oxidation of *p*-cresol. They also found a diphenylether structure among the reaction products. We also observed the presence of *p*-cresol in the course of the anodic oxidation of substance 1a in methanolic H₂SO₄. The diphenylether substance (3), not specified in the literature, is formed



Scheme 1.

at a high yield (70%) when sulphuric acid is kept at 0.05 M concentration and the temperature during the electrolysis is below 15°C. The charge consumed during electrolysis indicates that a predominant quantity of MA is converted into diphenylether (3). The remainder of the MA (1a) is subjected to the following electrooxidative step yielding the reactive intermediate (5) (only elemental analysis evidenced), that spontaneously gives polymer products (Scheme 1).

When the electrolytic oxidation was carried out

Table 3. Anodic oxidation of 0.2 M *p*-methylanisole in 200 ml acetone/aq. H₂SO₄ 1:1 (v/v) on platinum

MA /mol dm ⁻³	T /°C	j /mA cm ⁻²	Q _{passed} /U	Conc. H ₂ SO ₄ /M	Educt Product ^y				
			Faraday/mol ⁻¹ /V		MA /mmol	DPE /mmol	MY /%	TQ /mmol	Polym. /g
0.5 ^{n,h}	16	27	6.15/15	0.5	—	24	48	—	70
0.5 ^{d,h}	12	20	6.75/15	0.1	—	25	50	15	4.1
0.25 ^d	12	10	3.40/15	0.1	2.3	6	24	3	1.6

^d divided cell; ⁿ quasidivided cell;

TQ = toluquinol

DPE = 5,4'-dimethyl-2-methoxydiphenylether

MY = material yields of DPE

^y yields determined by GC

^h heterogeneous otherwise homogeneous

in a divided cell, toluquinol (4) was also isolated from the product mixture. In the formation of polymeric products, two intermediates can be considered, namely *p*-toluquinol and an unstable quinone structure (5). The only evidence for the latter is its elemental analysis leading to the empirical formula $C_8H_8O_3$ (mol. wt. 152, see above), based on samples isolated at random during some experiments. On the other hand, the results of elemental analyses and spectral records of isolated polymer fractions suggest the nature of the polymer precursor (Scheme 1). The comparison with structurally elucidated and described stable *para*-quinone (5) (2-methoxy-5-methyl-1,4-benzoquinone) points rather to an unstable *ortho*-quinone structure (5). This consideration of the polymers and their precursors is at present, speculative, due to the lack of exact spectral evidence. Nevertheless the above interpretation illustrates the real reaction path.

4. Conclusions

p-Methylanisole is anodically oxidized in an aqueous solution of H_2SO_4 both at the side chain, giving 5,4'-dimethyl-2-methoxydiphenylether (3) in 50% yield (a hitherto unknown substance), and in the

ring (consuming 6e), resulting in an unstable quinone intermediate whose polymer products were isolated. Toluquinol was also isolated after the electrolytic oxidation of *p*-methylanisole in solutions containing acetone cosolvent in aqueous H_2SO_4 . Exact elucidation of the reaction mechanism with respect to polymer products and their quinone precursor (5) has not been achieved.

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