

## Anodic Syntheses. Part XVI.<sup>1</sup> Oxidation of Phenylenediacetic Acids and Benzylic Ethers<sup>1,2</sup>

By Robert F. Garwood, Naser-ud-Din, and Basil C. L. Weedon,\* Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

Electrolysis of *o*-, *m*-, and *p*-phenylenediacetic acids gives the diethers  $C_6H_4(CH_2OMe)_2$  and the aldehydes  $CHO \cdot C_6H_4 \cdot CH_2 \cdot OMe$ , the latter resulting from anodic oxidation of the diethers. The *ortho*-diacid also affords a lactone. The anodic oxidation of ethers of this type to the corresponding aldehydes has been shown to be a general reaction of benzylic ethers having an electron-releasing substituent attached to the ring.

THE half-esters of dibasic acids readily undergo the Kolbe electrolytic coupling reaction. The dicarboxylic acids themselves do not undergo cyclic coupling to give the corresponding cycloalkanes though a few reactions

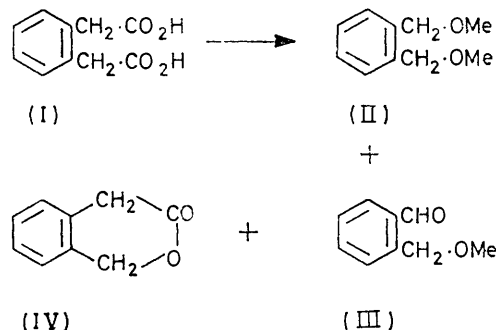
<sup>1</sup> Part XV, R. F. Garwood, C. J. Scott, and B. C. L. Weedon, *J.C.S. Perkin I*, 1973, 2714.

which are formally of this type are known, *e.g.* the formation of benzene from *trans*-1,2-dihydrophthalic acid<sup>3</sup>

<sup>2</sup> Preliminary communication, R. F. Garwood, Naser-ud-Din, and B. C. L. Weedon, *Chem. Comm.*, 1968, 923.

<sup>3</sup> E. A. Pasquinelli, *Anales Asoc. quim. argentina*, 1943, **31**, 181.

and the conversion of *trans,trans,trans*-2,4-bismethoxycarbonylcyclobutane-1,3-dicarboxylic acid into a dimethyl bicyclo[1.1.0]butane-2,4-dicarboxylate.<sup>4</sup> We have examined the electrolysis of *o*-phenylenediacetic acid (I) since the CH<sub>2</sub> groups of the intermediate diradical, if this is formed, would be held close to each other and might be expected to interact. However, when the acid was submitted to Kolbe electrolysis in methanol (Dinh-Nguyen cell), no 1,2-dihydrobenzocyclobutene was detected amongst the products; instead a mixture of *o*-xylylene dimethyl ether (II),  $\alpha$ -methoxy-*o*-tolualdehyde (III), and the  $\delta$ -lactone (IV) was obtained. This result prompted us to examine also



the electrolysis of *m*- and *p*-phenylenediacetic acids; in both cases the products were the corresponding diether C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>·OMe)<sub>2</sub> and the aldehyde CHO·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·OMe.<sup>2</sup>

The formation of ethers from carboxylic acids, and analogous alkoxylation reactions,<sup>5</sup> are believed to involve transfer of a further electron to the anode from the alkyl radical initially formed, followed by reaction of the resulting carbocation with the solvent;<sup>6</sup> the formation of the  $\delta$ -lactone (IV) from *o*-phenylenediacetic acid is consistent with such a mechanism. The formation of the aldehydes of type (III) presumably involves further oxidation of the ether first formed, and we have therefore

Anodic oxidation of benzyl methyl ethers  
(RC<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·OMe)

R	Aldehyde (%) *	R	Aldehyde (%) *
H	32	<i>m</i> -CH <sub>2</sub> ·OMe	48
<i>o</i> -Me	62	<i>p</i> -CH <sub>2</sub> ·OMe	51
<i>m</i> -Me	70	<i>o</i> -CO <sub>2</sub> Me	
<i>p</i> -Me	61	<i>m</i> -CO <sub>2</sub> Me	
<i>o</i> -OMe	52	<i>p</i> -CO <sub>2</sub> Me	
<i>p</i> -OMe	72	<i>p</i> -CN	
<i>o</i> -CH <sub>2</sub> ·OMe	56	<i>p</i> -COMe	

\* Based on ether consumed; recovered ether varied from 20 to 45%.

examined the anodic oxidation of a series of benzyl ethers, RC<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·OMe. The ethers listed (Table) were electrolysed between a platinum anode and a

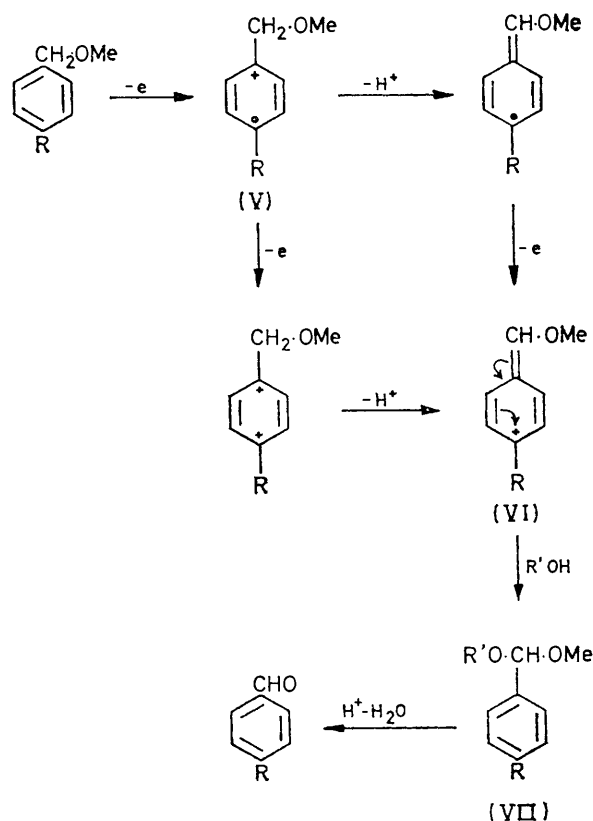
<sup>4</sup> A. E. Velturo and G. W. Griffin, *J. Amer. Chem. Soc.*, 1965, **87**, 3021.

<sup>5</sup> R. P. Linstead, B. R. Shepherd, and B. C. L. Weedon, *J. Chem. Soc.*, 1951, 2854; 1952, 3624.

<sup>6</sup> Cf. E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanova, and E. T. Kaiser, *J. Amer. Chem. Soc.*, 1960, **82**, 2645; cf. 'Organic Electrochemistry,' ed. M. M. Baizer, Dekker, New York, 1973.

mercury cathode in methanol containing sodium acetate as supporting electrolyte.

Benzyl methyl ether and its derivatives having an electron-releasing group attached to the ring readily underwent side-chain oxidation to the corresponding aldehyde. We envisage this type of reaction as occurring by a mechanism similar to that proposed by Lund for the anodic oxidation of 4-methoxybenzyl alcohol.<sup>7</sup> Loss of an electron would give the radical cation (V), which can then lose either a proton followed by a second electron, or *vice versa*, giving the carbocation (VI). This can then react with an acetate ion or the solvent giving a hemiacetal acetate or an acetal (VII; R' = Ac or OMe) which is hydrolysed on acidification during work-up to give the aldehyde. The formation of 4-methoxybenzaldehyde dimethyl acetal as a by-product in the electrolysis of 4-methoxyphenylacetic acid in methanol has been noted previously,<sup>8</sup> and the side-chain anodic acetoxylation of 2,5-dimethylfuran in acetic acid<sup>9</sup> is a related reaction. We detected no nuclear substitution



products although both nuclear and side-chain attack occur in electrolysis of other aromatic compounds.<sup>10</sup>

We found that benzyl methyl ethers in which the ring carries an electron-attracting substituent do not undergo

<sup>7</sup> H. Lund, *Acta Chem. Scand.*, 1957, **11**, 491.

<sup>8</sup> B. Wladislaw and H. Viertler, *Chem. and Ind.*, 1965, 39; *J. Chem. Soc., (B)* 1968, 576.

<sup>9</sup> A. J. Baggaley and R. Brettell, *Chem. Comm.*, 1966, 103.

<sup>10</sup> L. Ebersson and K. Nyberg, *J. Amer. Chem. Soc.*, 1966, **88**, 1686.

anodic oxidation of the type discussed above; instead they undergo reductive cleavage at the cathode to the corresponding toluene.<sup>2</sup> A detailed account of such reductions has been given elsewhere.<sup>11</sup>

Since our preliminary publication,<sup>2</sup> Mayeda *et al.* have described the anodic oxidation of benzylic ethers (including benzyl methyl ether and *p*-methoxybenzyl methyl ether) in acetonitrile; their results are in keeping with ours.<sup>12</sup>

#### EXPERIMENTAL

Electrolyses were carried out in the Dinh-Nguyen cell.<sup>1</sup> N.m.r. spectra were determined for dilute solutions in carbon tetrachloride. Most i.r. spectra were run for liquid films. Starting materials were prepared by standard literature methods. *o*-Xylylene dimethyl ether had  $\delta$  3.26 (6 H, s), 4.37 (4 H, s), and 7.0–7.4 (4 H, m). The *m*-isomer had  $\delta$  3.25 (6 H, s), 4.33 (4 H, s), and 6.9–7.2 (4 H, m), and the *p*-isomer  $\delta$  3.25 (6 H, s), 4.33 (4 H, s) and 7.16 (4 H, s).

*Electrolysis of Phenylenediacetic Acids.*—(a) *o*-Phenylenediacetic acid (5.0 g) was added to sodium methoxide [from sodium (1.1 g) in methanol (100 ml)] and the solution electrolysed (0.5 A; 7.5 h; 5.4 Faraday mol<sup>-1</sup>). The cell contents were acidified with dilute sulphuric acid, and extracted with ether (3 × 150 ml) and the combined extracts were washed with aqueous 5% sodium hydroxide (2 × 50 ml), then with water (50 ml), dried (MgSO<sub>4</sub>), and evaporated. The semi-solid residue (2.8 g) was extracted with light petroleum (b.p. 60–80°) and the solid (1.1 g) filtered off. Recrystallisation from water gave 1,4-dihydro-2-benzopyran-3-one (IV), m.p. 80–82°,  $\nu_{\max}$  1 740 cm<sup>-1</sup> (C=O);  $\delta$  3.53 (2 H, s), 5.16 (2 H, s), and 7.2 (4 H, s) (Found: C, 72.95; H, 5.4. C<sub>9</sub>H<sub>8</sub>O<sub>2</sub> requires C, 72.95; H, 5.45%). The light petroleum extract on evaporation gave a liquid (1.2 g), b.p. 130–140° at 23 mmHg, shown by mixed g.l.c. analysis (20% Carbowax M20; 200 °C) to contain *o*-xylylene dimethyl ether (96.1%) and  $\alpha$ -methoxy-*o*-tolualdehyde (3.9%). These were separated by preparative g.l.c. and their identity was confirmed by comparison (i.r. and n.m.r.) with authentic samples.

(b) *m*-Phenylenediacetic acid (5.0 g) was electrolysed as above and the product worked up as before; the ethereal extract on distillation gave a liquid (0.8 g), b.p. 100–180° at 20 mmHg, shown by mixed g.l.c. analysis (20% Uconpolar; 200 °C) to contain *m*-xylylene dimethyl ether (91.4%) and  $\alpha$ -methoxy-*m*-tolualdehyde (8.5%).

(c) *p*-Phenylenediacetic acid (2.5 g) similarly afforded a liquid (0.6 g) shown by g.l.c. analysis to contain *p*-xylylene dimethyl ether (22.8%) and  $\alpha$ -methoxy-*p*-tolualdehyde

(77.1%); these were separated by preparative g.l.c. and their identity was confirmed by comparison (i.r. and n.m.r.) with authentic samples.

*Anodic Oxidation of Benzyl Methyl Ethers.*—*o*-Xylylene dimethyl ether (5.0 g, 0.03 mol) in methanol (100 ml) containing sodium acetate (24.6 g, 0.3 mol) was electrolysed (0.8 A; 22 h; 21.8 Faraday mol<sup>-1</sup>). The cell contents were acidified (dilute H<sub>2</sub>SO<sub>4</sub>), diluted with water (1.5 l), and extracted with ether (3 × 150 ml), and the combined extracts were washed with sodium hydroxide (2 × 50 ml), dried (MgSO<sub>4</sub>), and evaporated. The liquid residue (3.8 g), b.p. 120–140° at 20 mmHg, was shown by mixed g.l.c. analysis (20% Carbowax M20; 190 °C) to contain *o*-xylylene dimethyl ether (51.4%) and  $\alpha$ -methoxy-*o*-tolualdehyde (48.5%). These were separated by preparative g.l.c. and their identity confirmed by spectroscopic analysis (i.r. and n.m.r.), and by aerial oxidation of the  $\alpha$ -methoxy-*o*-tolualdehyde to  $\alpha$ -methoxy-*o*-toluic acid, m.p. and mixed m.p. 90–92° (lit.,<sup>13</sup> 92–93°). The remaining ethers were oxidised by the same procedure, and the results are given in the Table. The characterisation of the aldehydic products is summarised below.

$\alpha$ -Methoxy-*m*-tolualdehyde had  $\nu_{\max}$  1 695 cm<sup>-1</sup>;  $\delta$  3.35 (3 H, s), 4.45 (2 H, s), 7.3–7.85 (4 H, m), and 9.91 (1 H, s) (Found: C, 71.7; H, 7.0. Calc. for C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>: C, 72.0; H, 6.7%).  $\alpha$ -Methoxy-*p*-tolualdehyde had  $\nu_{\max}$  1 690 cm<sup>-1</sup>;  $\delta$  3.32 (3 H, s), 4.45 (2 H, s), 7.35 (2 H, m), 7.72 (2 H, m), and 9.93 (1 H, s); the 2,4-dinitrophenylhydrazone had m.p. 196° (lit.,<sup>15</sup> 196°). *o*-Methylbenzaldehyde had  $\nu_{\max}$  1 680 cm<sup>-1</sup>;  $\delta$  2.65 (3 H, s), 7–7.8 (4 H, m), and 10.15 (1 H, s); the 2,4-dinitrophenylhydrazone had m.p. and mixed m.p. 190–192° (lit.,<sup>15</sup> 193–194°). *m*-Methylbenzaldehyde had  $\nu_{\max}$  1 700 cm<sup>-1</sup>;  $\delta$  2.38 (3 H, s), 7.1–7.6 (4 H, m), 9.76 (1 H, s); the 2,4-dinitrophenylhydrazone had m.p. and mixed m.p. 209–210° (lit.,<sup>16</sup> 211.5–212.5°). The *p*-isomer gave a 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 234–235° (lit.,<sup>17</sup> 232.5–234.5°). *o*-Methoxybenzaldehyde had  $\nu_{\max}$  1 685 cm<sup>-1</sup>;  $\delta$  3.91 (3 H, s), 6.7–7.9 (4 H, m), and 10.37 (1 H, s); the 2,4-dinitrophenylhydrazone had m.p. and mixed m.p. 246–248° (lit.,<sup>18</sup> 249–250°). The *p*-isomer had  $\delta$  3.86 (3 H, s), 6.91 (2 H, m), 7.73 (2 H, m), and 9.78 (1 H, s); the 2,4-dinitrophenylhydrazone had m.p. and mixed m.p. 245–247° (lit.,<sup>19</sup> 249°). The 2,4-dinitrophenylhydrazone of benzaldehyde had m.p. and mixed m.p. 237–238°.

We thank the Association of Commonwealth Universities for a research studentship (to N.-ud-D.).

[5/601 Received, 2nd April, 1975]

<sup>11</sup> F. E. King, P. L'Ecuyer, and H. T. Openshaw, *J. Chem. Soc.*, 1936, 352.

<sup>12</sup> J. B. Bowen and E. M. Wilkinson, *J. Chem. Soc.*, 1950, 750.

<sup>13</sup> H. H. Strain, *J. Amer. Chem. Soc.*, 1935, **57**, 758.

<sup>14</sup> E. K. Harvill and R. M. Herbst, *J. Org. Chem.*, 1944, **9**, 21.

<sup>15</sup> H. J. Rodda and P. E. Rogasch, *J. Chem. Soc.*, 1956, 3927.

<sup>11</sup> J. P. Coleman, Naser-ud-Din, H. G. Gilde, J. H. P. Utley, B. C. L. Weedon, and L. Ebersson, *J.C.S. Perkin II*, 1973, 1903.

<sup>12</sup> E. A. Mayeda, L. L. Miller, and J. F. Wolf, *J. Amer. Chem. Soc.*, 1972, **94**, 6812.

<sup>13</sup> F. G. Mann and F. H. C. Stewart, *J. Chem. Soc.*, 1954, 2819.

<sup>14</sup> G. Arditti and L. Palfray, *Compt. rend.*, 1946, **223**, 547.