An efficient C-C bond cleavage of 1,2-diols using tetraethylammonium superoxide

Krishna Nand Singh*, Rajesh Kumar & Ajay Kumar Shukla
Department of Applied Chemistry, Institute of Technology, Banaras Hindu University, Varanasi 221 005, India
E-mail: knsinghbbu@yahoo.co.in

Received 7 November 2006, accepted (revised) 2 April 2007

Tetraethylammonium superoxide, generated in situ by the phase-transfer reaction of potassium superoxide and tetraethylammonium bromide in DMF, brings about an easy cleavage of vicinal diols and related dihydroxy arenes under mild reaction conditions, at room temperature.

Keywords: Tetraethylammonium super oxide, 1,2-diols, dihydroxy arenes, phase-transfer catalyst, cleavage reaction

The carbon-carbon bond fission of vicinal diols and related functional groups has attracted a great deal of recent interest in organic synthesis. The common and current reagents employed to effect this transformation are periodate, permanganate, osmium tetroxide, ruthenium tetroxide, H2O2/methyltrioxirhenum, N-bromosuccinimide, chiral LTA, Mitsunobu conditions, Cu-based catalyst, gold catalyst and O2/Co-N-hydroxyphthalimide. Superoxide ion is an oxidising agent and potassium superoxide (KO2) in the presence of 18-crown-6 has been used for the oxidation of hydroxyl- and ketopolyaromatics including internal quinines. Oxidation of dihydroxynaphthalenes by KO2 in heterogeneous aprotic media has also been carried out to afford mono- or dihydroxynaphthoquinones. The use of 18-crown-6 is, however, limited due to its high cost and carcinogenic character. In continuation to our research on superoxide ion and with a view to extending the applicability of tetraethylammonium bromide (Et4NBr) as an inexpensive alternative to 18-crown-6, we report herein the use of in situ generated tetraethylammonium superoxide (Et4NO2) for a facile and mild cleavage of some vicinal diols and dihydroxyarenes (Scheme I).

Note

A number of 1,2-diols viz., 9,10-dihydroxyphenanthrene 1a, 1,2-naphthalenediol 1b, cis-7,8,9,10-tetrahydrobenzo[a]pyrene-7,8-diol 1c, cis-4,5-dihydro-4,5-dihydroxy pyrene 1d, 3,5-di-tert-butylcatechol 1e and some pinacols viz., benzopinacol 1f, 4,4′-dimethylbenzopinacol 1g, 4,4′-dichlorobenzopinacol 1h, 4,4′,4″,4‴-octamethyl-tetraaminobenzopinacol 1i and fluorenopinacol 1j were made to react with KO2 in the presence of Et4NBr in dry DMF at room temperature. As an outcome, under the mild reactions conditions of Et4NO2, the diols 1a-d are oxidised to their corresponding dicarboxylic acids viz., diphenic acid 2a, phthalic acid 2b, pyrene-1,2-dicarboxylic acid 2c and 4,5-phenanthrene dicarboxylic acid 2d respectively, whereas the pinacols 1f-j undergo C-C bond fission providing benzophenone 2f, 4-methylbenzophenone 2g, 4-chlorobenzophenone 2h, 4,4′-bis(dimethylamino)-benzophenone 2i and fluorenophenol 2j respectively in reasonably good yields. Under the same set of conditions, it is interesting to note that 3,5-di-tert-butyl catechol 1e affords a mixture of lactones 3,5-di-tert-butyl-5-(carboxymethyl)-2-furanone 2e and 3,5-di-tert-butyl-5-(carboxyhydroxymethyl)-2-furanone 2e′. The results of the investigation are summarised in Table I.

The reaction of catechol with in situ generated Et4NO2 has also been undertaken, although it led to intractable products, possibly due to oxidative coupling. Subsequently, 3,5-di-tert-butylcatechol 1e was used where most of reactive ring sites were blocked by bulky groups, leading to lactones 2e and 2e′ probably through the dicarboxylic acids, which undergo lactonisation following the oxidative cleavage at 1,2-positions. The above studies were carried out employing a 4.0 fold excess of KO2 and 2.0 fold excess of Et4NBr over the substrate 1 in dry DMF. When the reaction was complete, as checked by TLC, saturated aqueous sodium chloride solution was added to destroy the unreacted KO2. The reaction mixture was then worked up to afford the products. The cleavage of diols is assumed to proceed via the intermediaries of diketones and in order to ascertain it, the reaction was carried out employing an equimolar ratio of a few diols 1a,b,e and KO2. The results are given in Table II. It is worthwhile to mention that the dike-
tones, 9,10-phenanthroquinone 3a, 2-hydroxy-1,4-naphthoquinone 3b and 3,5-di-tert-butyl-o-quinone 3e are isolated although in low yield during these investigations. All the products exhibited physical and spectral data consistent to their structures.

In conclusion, an oxidative cleavage of glycols and related dihydroxyarenes has been accomplished using tetraethylammonium superoxide at room temperature under significantly mild reaction conditions.

Experimental Section

Melting points were measured in open capillaries and are uncorrected. IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer. NMR spectra were run on a JEOL FT-NMR spectrometer FX-90Q and the chemical shifts are expressed as δ/ppm, using TMS as internal reference. Potassium superoxide and tetraethylammonium bromide were procured from E. Merck, and were used as received. Dry DMF of Aldrich, was stored over molecular sieves (4 Å) prior to use. 9,10-Dihydroxyphenanthrene 1a was obtained by the reduction of 9,10-phenanthrenequinone with zinc dust in hot acetic acid. cis-7,8,9,10-Tetrahydrobenzo[a]pyrene-7,8-diol 1e and cis-4,5-dihydro-4,5-dihydroxyphenyrene 1d were prepared following known methods. The pinacols 1f-1j were obtained by the reduction of corresponding ketones using a mixture of magnesium iodide and magnesium according to a reported method.

Reaction of in situ generated tetraethylammonium superoxide with diols 1a-j: General procedure. Potassium superoxide (1.42 g; 0.02 mole) was weighed in a dry capped specimen tube under a nitrogen atmosphere and transferred into a two-necked round bottom flask (100 mL) equipped with a gas inlet and double surface condenser guarded with a CaCl₂ drying tube. The flask was flushed with dry nitrogen and to it were admitted anhydrous DMF (40 mL) and Et₄NBr (2.1 g; 0.01 mole). The mixture was stirred magnetically for about 15 min to facilitate the dissolution of the solids. The diol 1 (0.005 mole) was finally introduced and the stirring was continued at room temperature for 15-20 hr in the presence of N₂ until TLC indicated the complete loss of starting material. The mixture was then successively treated with cold brine (10 mL), NaHCO₃ solution (20 mL) and then extracted with diethyl ether (3 × 20 mL) to give the product 2f-j. The aqueous phase was acidified with hydrochloric acid and extracted with diethyl ether (3 × 25 mL). The ethereal layer was washed with water (3 × 20 mL), dried over anhydrous sodium sulfate, filtered, evaporated and recrystallised to furnish the pure acid 2a-e'. All the products exhibited physical and spectral data consistent with their structures.

Physical and spectral data of the products: 2a: m.p. 230°C (ref.30, 228-29°C); Anal. Caled for C₁₄H₁₀O₄: C, 69.4; H, 4.1. Found: C, 69.2; H, 4.2%. IR (KBr): 3100-2500, 1685, 1595, 1578, 1405, 1300, 1270, 915, 762, 715 cm⁻¹; 1H NMR (DMSO-d₆, δ): 7.4 (m, 2H, ArH), 7.7 (m, 4H, ArH), 8.1 (m, 2H, ArH), 11.0 (s, 2H, COOH).

2b: m.p. 225°C (ref.30, 230°C); Anal. Caled for C₈H₆O₄: C, 57.8; H, 3.6. Found: C, 57.7; H, 3.4%. IR (KBr): 3200-2400, 1682, 1585, 1402, 1280, 1207, 907, 798, 740 cm⁻¹; 1H NMR (DMSO-d₆ + CDCl₃, δ):
Table I — Reaction of *in situ* generated Et₄NO₂ with substrate 1a-j

<table>
<thead>
<tr>
<th>Substrate 1</th>
<th>Product 2</th>
<th>Yield* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>2a</td>
<td>81</td>
</tr>
<tr>
<td>1b</td>
<td>2b</td>
<td>66</td>
</tr>
<tr>
<td>1c</td>
<td>2c</td>
<td>72</td>
</tr>
<tr>
<td>1d</td>
<td>2d</td>
<td>76</td>
</tr>
<tr>
<td>1e</td>
<td>2e</td>
<td>26</td>
</tr>
<tr>
<td>1f</td>
<td>2f</td>
<td>18</td>
</tr>
<tr>
<td>1g</td>
<td>2g</td>
<td>73</td>
</tr>
<tr>
<td>1h</td>
<td>2h</td>
<td>65</td>
</tr>
<tr>
<td>1i</td>
<td>2i</td>
<td>70</td>
</tr>
<tr>
<td>1j</td>
<td>2j</td>
<td>56</td>
</tr>
</tbody>
</table>

*Isolated mass yields based on substrate 1.*
Table II — Reaction of KO₂ and Et₄NBr with diols 1a,b,e (equimolar ratio)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>Yield* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="image" /></td>
<td><img src="image2.png" alt="image" /></td>
<td>65</td>
</tr>
<tr>
<td><img src="image3.png" alt="image" /></td>
<td><img src="image4.png" alt="image" /></td>
<td>56</td>
</tr>
<tr>
<td><img src="image5.png" alt="image" /></td>
<td><img src="image6.png" alt="image" /></td>
<td>51</td>
</tr>
</tbody>
</table>

*Isolated yields are based on substrate 1

7.8 (m, 2H, ArH), 8.35 (m, 2H, ArH), 11.0 (s, 2H, COOH).

2c: m.p. >250°C (ref.20, > 300°C), Anal. Caled for C₁₈H₁₀O₄: C, 74.5; H, 3.4. Found: C, 74.3; H, 3.7%. IR (KBr): 3100-2500, 1675, 1590, 1445, 1250, 1165, 955, 748, 713 cm⁻¹;¹H NMR (DMSO-d₆, δ): 7.7 (m, 4H, ArH), 7.9-8.1 (m, 3H, ArH), 8.2 (s, 1H, ArH), 11.1 (s, 2H, COOH).

2d: m.p. 256°C (ref.30, 260°C), Anal. Caled for C₁₆H₁₀O₄: C, 7.2; H, 3.7. Found: C, 72.0; H, 3.6. IR (KBr): 3200-2450, 1681, 1580, 1445, 1243, 1140, 925, 731, 714 cm⁻¹;¹H NMR (CDCl₃, δ): 7.6 (m, 2H, ArH), 8.1-8.5 (m, 2H, ArH), 8.8 (m, 2H, ArH), 11.0 (s, 2H, COOH).

2e: m.p. >250°C (ref.20, > 300°C), Anal. Caled for C₁₆H₁₀O₄: C, 7.2; H, 3.7. Found: C, 72.0; H, 3.6. IR (KBr): 3200-2450, 1681, 1580, 1445, 1243, 1140, 925, 731, 714 cm⁻¹;¹H NMR (DMSO-d₆, δ): 7.7 (m, 4H, ArH), 7.9-8.1 (m, 3H, ArH), 8.2 (s, 1H, ArH), 11.1 (s, 2H, COOH).

2f: m.p. 48°C (ref.30, 49°C), Anal. Caled for C₁₆H₁₁O₄: C, 85.7; H, 5.5. Found: C, 85.6; H, 5.4%. IR (KBr): 1655, 1595, 1450, 1320, 1280, 765, 705, 695, 640 cm⁻¹;¹H NMR (CDCl₃, δ): 7.35-7.45 (m, 6H, ArH), 7.8 (m, 4H, ArH).

2g: m.p. 58°C (ref.30, 59-60°C), Anal. Caled for C₁₆H₁₂O: C, 85.7; H, 6.1. Found: C, 85.65; H, 6.11%. IR (KBr): 1683, 1607, 1358, 1268, 1182, 958, 816 cm⁻¹,¹H NMR (CDCl₃, δ): 2.3 (s, 3H, CH₃), 7.2 (m, 2H, ArH), 7.4-7.7 (m, 7H, ArH).

2h: m.p. 76°C (ref.30, 77-78°C), Anal. Caled for C₁₃H₁₀OCl: C, 72.0; H, 4.1. Found: C, 71.9; H, 4.0%. IR (KBr): 1650, 1584, 1301, 1285, 1090, 845, 728, 695, 664 cm⁻¹;¹H NMR (CDCl₃, δ): 7.35-7.45 (m, 5H, ArH), 7.6-7.8 (m, 4H, ArH).

2i: m.p. 171°C (ref.30, 172-72.5°C), Anal. Caled for C₁₇H₂₀N₂O: C, 76.1; H, 7.4; N, 10.4. Found: C, 76.0; H, 7.41; N, 10.36%. IR (KBr): 1595, 1530, 1370, 1325, 1288, 1175, 1150, 920, 765 cm⁻¹;¹H
NMR (CDCl₃, δ): 2.85 (s, 12H, CH₃), 6.8 (dd, 4H, ArH), 7.6 (dd, 4H, ArH).

2j: m.p. 81°C (ref.30, 83-83.5°C), Anal. Caled for C₁₅H₂₀O₂: C, 86.6; H, 4.4%. IR (KBr): 1715, 1610, 1595, 1450, 1297, 920, 745, 736, 671 cm⁻¹; ¹H NMR (CDCl₃, δ): 7.3-7.8 (m, 8H, ArH).

3a: m.p. 205°C (ref.33, 208.5°C), Anal. Caled for C₁₀H₆O₃: C, 68.9; H, 3.4%. IR (KBr): 3400-2900, 1661, 1605, 1588, 1367, 1275, 1246, 891 cm⁻¹, ¹H NMR (CDCl₃, δ): 6.3 (s, 1H, ArH), 7.7-8.1 (m, 4H, ArH), 11.6 (s, 1H, OH).

3b: m.p. 190°C (ref.33, 192°C), Anal. Caled for C₁₀H₈O: C, 86.6; H, 4.4%. IR (KBr): 1675, 1590, 1450, 1290, 1280, 1230, 923, 762, 718 cm⁻¹, ¹H NMR (CDCl₃, δ): 7.1-8.3 (m, 8H, ArH).

Acknowledgement

The authors are thankful to CSIR, New Delhi for financial support.

References