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Note

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

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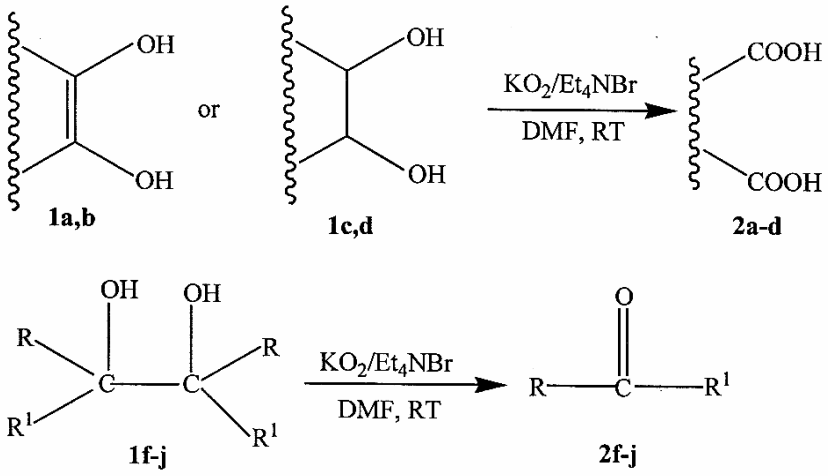
Tetraethylammonium superoxide, generated *in situ* by the phase-transfer reaction of potassium superoxide and tetraethylammonium bromide in DMF, brings about an easy cleavage of vicinal diols and related dihydroxy arenes under mild reaction conditions, at room temperature.

Keywords: Tetraethylammonium superoxide, 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[1-5]. The common and current reagents employed to effect this transformation are periodate[6], permanganate[7], osmium tetroxide[7], ruthenium tetroxide[8,9], H_2O_2 /methyltrioxyrhenium[10], *N*-bromosuccinimide[11], chiral LTA[12], Mitsunobu conditions[13], Cu-based catalyst[14], gold catalyst[15] and O_2/Co-*N*-hydroxyphthalimide[16]. Superoxide ion is an oxidising agent[17,18] and potassium superoxide (KO_2) in the presence of 18-crown-6 has been used for the oxidation of hydroxyl- and ketopolyaromatics including internal quinines[19-21]. Oxidation of dihydroxynaphthalenes by KO_2 in heterogeneous aprotic media has also been carried out to afford mono- or dihydroxynaphthoquinones[22,23]. The use of 18-crown-6 is, however, limited due to its high cost and carcinogenic character. In continuation to our research[24-27] on superoxide ion and with a view to extending the applicability of tetraethylammonium bromide (Et_4NBr) as an inexpensive alternative to 18-crown-6, we report herein the use of *in situ* generated tetraethylammonium superoxide (Et_4NO_2) for a facile and mild cleavage of some vicinal diols and dihydroxyarenes (**Scheme I**).

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-dihydroxypyrene **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 KO_2 in the presence of Et_4NBr in dry DMF at room temperature. As an outcome, under the mild reactions conditions of Et_4NO_2, 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 fluorenone **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 Et_4NO_2 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 KO_2 and 2.0 fold excess of Et_4NBr 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 KO_2. The reaction mixture was then worked up to afford the products. The cleavage of diols is assumed to proceed via the intermediary 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 KO_2. The results are given in **Table II**. It is worthwhile to mention that the dike-



Scheme I

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 tetraethylammoniun superoxide at room temperature under significantly mild reaction conditions.

Experimental Section

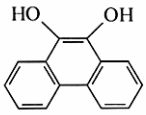
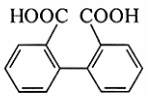
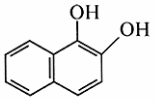
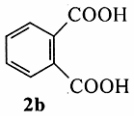
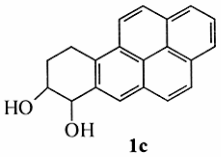
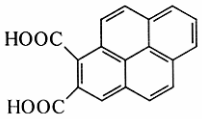
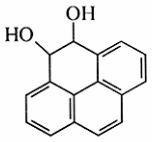
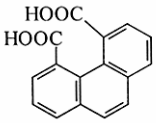
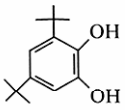
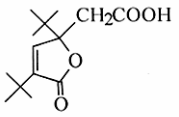
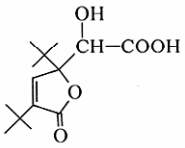
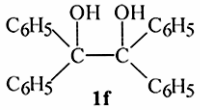
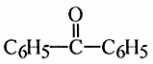
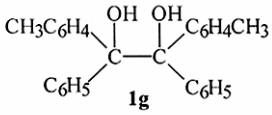
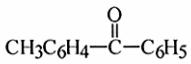
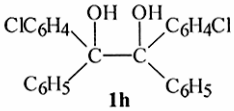
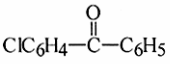
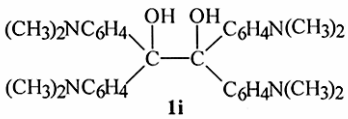
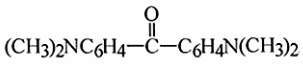
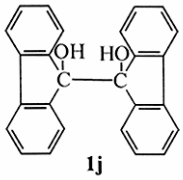
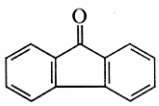
Melting points were measured in open capillaries and are uncorrected. IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer. NMR spectra were run on a JEOL FT-NMR spectrometer FX-90Q and the chemical shifts are expressed as δ/ppm, using TMS as internal reference. Potassium superoxide and tetraethylammonium bromide were procured from E. Merck, and were used as received. Dry DMF of Aldrich, was stored over molecular sieves (4°A) prior to use. 9,10-Dihydroxyphenanthrene **1a** was obtained by the reduction of 9,10-phenanthrenequinone with zinc dust in hot acetic acid[28]. 1,2-Naphthalenediol **1b** and 3,5-di-*tert*-butylcatechol **1e** were commercial products. *cis*-7,8,9,10-Tetrahydrobenzo[*a*]pyrene-7,8-diol **1c** and c*is*-4,5-dihydro-4,5-dihydroxypyrene **1d** were prepared following known methods[20,21]. 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[29].

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 $CaCl_2$ drying tube. The flask was flushed with dry nitrogen and to it were admitted anhydrous DMF (40 mL) and Et_4NBr (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 N_2 until TLC indicated the complete loss of starting material. The mixture was then successively treated with cold brine (10 mL), $NaHCO_3$ 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. Calcd for $C_{14}H_{10}O_4$: 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-d_6, δ): 7.4 (m, 2H, ArH), 7.7 (m, 4H, ArH), 8.1 (m, 2H, ArH), 11.0 (s, 2H, COOH).

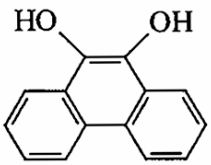
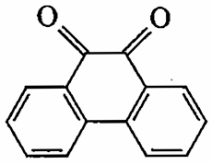
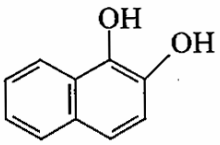
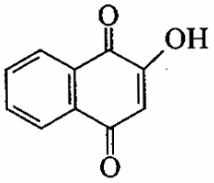
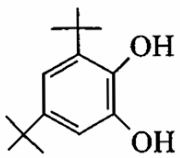
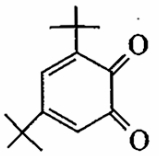
2b: m.p**.** 225°C (ref.30, 230°C); Anal. Calcd for $C_8H_6O_4$: C, 57.8; H, 3.6. Found: C, 57.7; H, 3.4%. IR (KBr): 3200-2400, 1682, 1585, 1402, 1280, 1070, 907, 798, 740 cm^{-1}; ^1H NMR (DMSO-d_6 + $CDCl_3$, δ):

Table I — Reaction of *in situ* generated Et_4NO_2 with substrate **1a-j**

Substrate **1**	Product **2**	Yield* (%)
 **1a**	 **2a**	81
 **1b**	 **2b**	66
 **1c**	 **2c**	72
 **1d**	 **2d**	76
 **1e**	 **2e**	26
	 **2e'**	18
 **1f**	 **2f**	73
 **1g**	 **2g**	65
 **1h**	 **2h**	70
 **1i**	 **2i**	56
 **1j**	 **2j**	62

*Isolated mass yields based on substrate **1**.

Table II — Reaction of KO_2 and Et_4NBr with diols **1a**,**b**,**e** (equimolar ratio)

Substrate 1	Product 2	Yield* (%)
 **1a**	 **3a**	65
 **1b**	 **3b**	56
 **1e**	 **3e**	51

*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. Calcd for $C_{18}H_{10}O_4$: 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-d_6, 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. Calcd for $C_{16}H_{10}O_4$: 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 ($CDCl_3$, 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. 132°C (ref.31, 133-34°C), Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.1; H, 8.6. Found: C, 65.9; H%, 8.6. IR (KBr): 3300-2700, 1745, 1715, 1635 cm^{-1}; ^1H NMR ($CDCl_3$, δ): 1.0-1.2 (s, 18H, CH_3), 2.7 (s, 2H, CH_2), 6.9 (s, 1H, = CH), 8.1-8.5 (m, 2H, ArH).

2e′: m.p. 140°C (ref.32, 139-40°C), Anal. Calcd for $C_{14}H_{22}O_5$: C, 62.2; H, 8.1. Found: C, 62.1; H, 8.0%. IR (KBr): 3550-3350, 3250-2750, 1720, 1705, 1630 cm^{-1}; ^1H NMR (DMSO-d_6, δ): 1.1-1.8 (s, 18H, CH_3), 2.5 (s, 1H, OH), 4.7 (s, 1H, CH), 6.7 (s, 1H, = CH), 10.6 (s, 1H, COOH).

2f: m.p. 48°C (ref.30, 49°C), Anal. Calcd for $C_{13}H_{10}O$: 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 ($CDCl_3$, δ): 7.35-7.45 (m, 6H, ArH), 7.8 (m, 4H, ArH).

2g: m.p. 58°C (ref.30, 59-60°C), Anal. Calcd for $C_{14}H_{12}O$: 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 ($CDCl_3$, δ): 2.3 (s, 3H, CH_3), 7.2 (m, 2H, ArH), 7.4-7.7 (m, 7H, ArH).

2h: m.p. 76°C (ref.30, 77-78°C), Anal. Calcd for $C_{13}H_9OCl$: 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 ($CDCl_3$, 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. Calcd for $C_{17}H_{20}N_2O$: 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 ($CDCl_3$, δ): 2.85 (s, 12H, CH_3), 6.8 (dd, 4H, ArH), 7.6 (dd, 4H, ArH).

2j: m.p. 81°C (ref.30, 83-83.5°C), Anal. Calcd for $C_{13}H_8O$: C, 86.6; H, 4.4. Found: C, 86.6; H, 4.4%. IR (KBr): 1715, 1610, 1595, 1450, 1297, 920, 745, 736, 671 cm^{-1}; ^1H NMR ($CDCl_3$, δ): 7.3-7.8 (m, 8H, ArH).

3a: m.p. 205°C (ref.30, 208.5–10°C), Anal. Calcd for $C_{14}H_8O_2$: C 80.7; H, 3.8. Found: C, 80.6; H, 3.7%. IR (KBr): 1675, 1590, 1450, 1290, 1280, 1230, 923, 762, 718 cm^{-1}, ^1H NMR ($CDCl_3$, δ): 7.1–8.3 (m, 8H, ArH).

3b: m.p. 190°C (ref.33, 192°C), Anal. Calcd for $C_{10}H_6O_3$: C, 68.9; H, 3.4. Found: C, 68.9; H, 3.3%. IR (KBr): 3400-2900, 1661, 1605, 1588, 1331, 1302, 1147, 1117, 863, 771 cm^{-1}, ^1H NMR ($CDCl_3$, δ): 6.3 (s, 1H, ArH), 7.7-8.1 (m, 4H, ArH), 11.6 (s, 1H, OH).

3e: m.p. 111°C (ref.34, 111-13°C), Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.3; H, 9.0. Found: C, 76.2; H, 9.0% IR (KBr): 2964, 1662, 1623, 1568, 1480, 1367, 1275, 1246, 891 cm^{-1}, ^1H NMR ($CDCl_3$, δ): 1.3 (s, 18 H, CH_3), 6.5-6.8 (m, 2H, ArH).

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