Note

Facile transformation of aromatic aldehydes to acids mediated by tetraethylammonium superoxide

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Applicability of *in situ* generated tetraethylammonium super-oxide, as superoxidant, for an efficient conversion of aromatic aldehydes to acids, is demonstrated. The reaction conditions are significantly mild and the yields are exceedingly good.

Oxygen plays a key role in the "breath of life", yet, ironically, reduced oxygen species pose a serious threat to all aerobic organisms[1]. Superoxide anion radical, O_2^-; is an important species ubiquitously generated in living beings by several dark biological processes[2]. The past two decades of research regarding the biological action[2,3] and organic chemistry[4] of O_2^- has revealed that, in aprotic media, this anion radical reacts via several basic modes such as a relatively strong base, a supernucleophile, moderate reducing agent, and only rarely if ever, as a radical.

For current reactivity purposes, superoxide is made available to chemists either by electrochemical reduction of molecular oxygen or by solubilization of potassium superoxide (KO_2) utilizing crown ethers. Prompted by a recent report[5] using KO_2 and tetraethylammonium bromide (Et_4NBr) for efficient production of tetraethylammonium superoxide (Et_4NO_2), our studies are directed to examine and broaden the knowledge of elementary reactivity patterns of this multipotent reagent from a purely chemical viewpoint.

Superoxide chemistry of aldehydes is reported to be complex and interesting[4,6]. Benzaldehyde undergoes no net reaction with electrogenerated O_2^-. The alternative chemical method employing KO_2 and 18-crown-6 ether has also been examined in a number of solvents such as dimethylsulfoxide (DMSO),

pyridine and acetonitrile. While DMSO gave rather intractable products, the major acetonitrile reaction products were identified as cinnamonitrile and ben-zoylacetonitrile. In pyridine, however, work-up of the reaction mixture yields benzoic acid in varying amounts. In view of the above, the chemistry along the way warrants more attention in this direction. As a part of our continued interest on superoxide chemistry[7], we describe herein our results on the reactivity pattern of Et_4NO_2 with a range of aromatic aldehydes **1a-j** (Scheme I).

$$\text{Ar-CHO} \xrightarrow[\text{DMF, RT}]{KO_2/Et_4NBr} \text{Ar-COOH}$$
$$\mathbf{1} \mathbf{2}$$
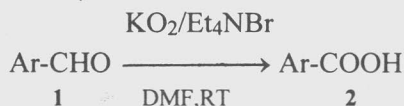
Scheme I

As an outcome, benzaldehyde **1a**, 2-nitrobenzaldehyde **1b**, 4- nitrobenzaldehyde **1c**, *p*-tolualdehyde **1d**, *p*-anisaldehyde **1e**, 3,4,5-trimethoxybenzaldehyde **1f**, 2-furaldehyde **1g**, 2- thiophenecarboxaldehyde **1h**, 1-naphthaldehyde **1i** and 2- naphthaldehyde **1j** are easily oxidized to their corresponding carboxylic acids **2a-j** in fairly good to excellent (71-88%) yields (cf. Table I).

The results were achieved by using a 3.2 fold molar excess of KO_2 and 1.6 fold molar excess of Et_4NBr over the substrate **1** in DMF (anhyd). The molar proportion of KO_2, Et_4NBr and **1** has not been optimized under the present set of reaction conditions. However, an earlier report[5] has shown excess KO_2 and Et_4NBr for an efficient conversion of the substrate. Typically, 0.005 mole of each aldehyde was allowed to react for 2.5-4 hr, at room temperature under dry air. The reaction mixture was then quenched with cold saturated aq. NaCl and worked-up to afford the product **2**. Every reaction was monitored on TLC to check the complete disappearance of starting substrate. All the compounds exhibited physical and spectral data consistent with their structures.

Oxidation of aldehydes is one of the most common reactions in organic chemistry and has been carried out with many oxidizing agents[8]. Even with so many

Table I—Physical data of compounds **2a-j**

Product	Ar	Yield* (%)	m.p. (°C) Found (Reported)[9]
2a	phenyl	79	121 (122)
2b	2-nitrophenyl	84	145 (147-48)
2c	4-nitrophenyl	88	194 (197)
2d	p-tolyl	76	180(182)
2e	p-methoxyphenyl	80	110(110)
2f	3,4,5-trimethoxyphenyl	85	172 (171-72)
2g	furyl	72	132 (133-34)
2h	thienyl	68	127 (129-30)
2i	1-naphthyl	74	158 (161)
2j	2-naphthyl	71	184 (185)

*Isolated mass yield based on **1** as weight %.

available methods for aldehyde oxidation, there is still a demand in terms of use of harsh conditions. In the present investigation, aromatic aldehydes are readily convertible to acids under mild reaction conditions and thus the process seems to be an useful alternative to the existing methods.

Based on the fact that O_2^- and H_2O_2 generated *in situ* are the true oxidants, the initial step of the reaction may be assumed to be nucleophilic attack of O_2^- at the carbonyl carbon of **1** providing an anion radical I. The intermediate I possibly undergoes exchange of hydrogen atom with H_2O_2 via intermediate **II** to anion radical **III** which is ultimately cleaved to yield an acid **2** (Scheme II).

Experimental Section

KO$_2$ and Et$_4$NBr were procured from E Merck, Germany and were used as such. The aldehydes **1a-j** were of AR grade and used only after fresh distillation or recrystallization. DMF (HPLC grade) was stored over 40 nm molecular sieves prior to use. Silica gel G was used for TLC and N$_2$ gas was dried by passing through an alkaline solution of pyrogallol. Melting points were measured in open capillary tubes using Buchii apparatus and are uncorrected. IR (KBr) spectra were recorded on a JASCO FT/IR-5300 infrared spectrophotometer (ν_{max} in cm^{-1}). The experiments were performed at room temperature.

Reaction of tetraethylammonium superoxide with aldehydes 1a-j: General procedure. KO$_2$ (1.17g, 0.016 mole) was placed under nitrogen at-

Scheme II
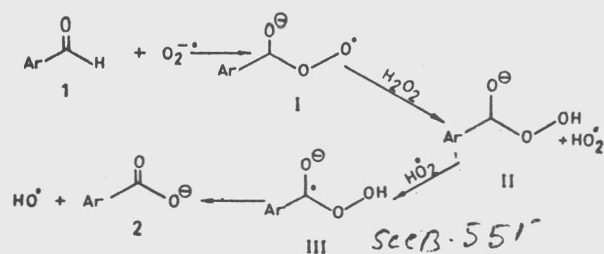
mosphere in a 100 mL three necked flask fitted with a double surface condenser and a N$_2$ inlet dipping into the reaction mixture. The flask was degassed with dry N$_2$ and to it were admitted anhyd. DMF (25mL) and Et$_4$NBR (1.68g, 0.008 mole). The mixture was stirred magnetically for 10 min. to fascilitate the major dissolution of the solids. The aldehydes **1a-j** (0.005 mole) were finally introduced and stirred under dry air for 2.5-4.0 hr at room temperature. After the reaction was over (as checked by TLC), cold saturated aq. NaCl (50 mL) was gradually added to destroy the excess KO$_2$. The mixture was then basified with saturated aq. NaHCO$_3$ and extracted with ether (2×20mL) to remove unreacted aldehyde. Aqueous phase was acidified with conc. HCl and extracted with large volume of ether (4×50 mL). The combined ethereal phase was washed several times with water (4×50 mL), dried over anhyd. Na$_2$SO$_4$, filtered and evaporated to furnish the products **2a-j**. Their melting points and yields are given in Table I.

Acknowledgement

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