

Note

Oxidative cleavage of α -diketones using tetraethylammonium bromide as phase transfer catalyst

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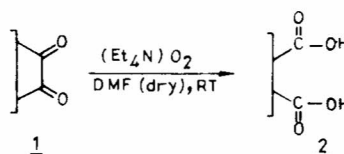
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The efficient use of tetraethylammonium bromide as phase transfer catalyst has led to explore synthetically useful reactions of tetraethylammonium superoxide with a variety of α -diketones. The substrates, furil **1a**, 4,4'-dimethylbenzil **1b**, 4,4'-dimethoxybenzil **1c**, 4,4'-dibromobenzil **1d**, 9,10-phenanthroquinone **1e**, 1,2-naphthoquinone **1f**, (\pm) camphorquinone **1g** and 2,2'-pyridil **1h** are oxidatively cleaved to furnish 2-furancarboxylic acid **2a**, *p*-methylbenzoic acid **2b**, *p*-methoxybenzoic acid **2c**, *p*-bromobenzoic acid **2d**, 2,2'-biphenyldicarboxylic acid **2e**, phthalic acid **2f**, (\pm) camphoric acid **2g** and 2-pyridinecarboxylic acid **2h** respectively, in reasonably good yields under the present set of mild reaction conditions.

Superoxide, O_2^- , is an active oxygen species and is produced ubiquitously in all aerobic organisms¹. The intervention and its key role have recently been made explicit in a vast spectrum of metabolic processes^{2,3}. During the past two decades, considerable attention has been paid to the chemistry and biology of superoxide^{3,4}. From the standpoint of synthetic considerations, O_2^- has diverse reactivities, viz. it acts as Bronsted base, nucleophile, one electron reductant and one electron oxidant depending upon the nature of substrates.

For convenient generation of O_2^- in aprotic media, two basic approaches are in use. The first one involves electrolytic reduction of molecular oxygen⁵ whereas the second one utilizes potassium superoxide (KO_2) through the agency of crown

ethers⁶. Preparation of tetramethylammonium superoxide has also been achieved albeit employing a cumbersome procedure⁷. However, since KO_2 /crown ether combination is expensive, the use of tetraethylammonium superoxide (Et_4NO_2) obtained by the reaction⁸ of KO_2 and tetraethylammonium bromide (Et_4NBr) has recently been recognized as a promising alternative. In view of the significance of O_2^- in natural and synthetic chemistry, we have had an opportunity to explore the reactions of electrogenerated O_2^- with organic compounds from a functional group perspective⁹. Fascinated by the availability of a new approach in hand, we report herein our findings on the reactivity pattern of *in situ* generated Et_4NO_2 with a variety of α -diketones (Scheme I).

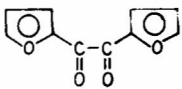
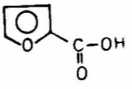
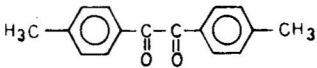
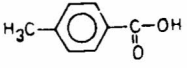
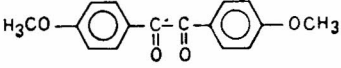
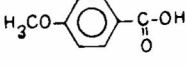
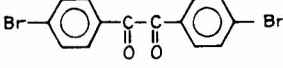
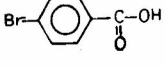
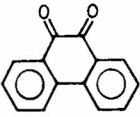
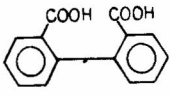
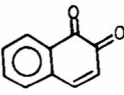
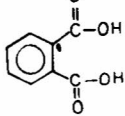
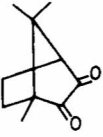
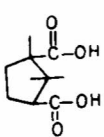
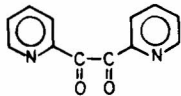
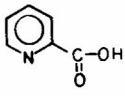


Scheme I

The electrochemical reduction of α -diketones in the presence of oxygen in aprotic solvents is reported to be oxidative with a cleavage of the CO-CO bond affording esters¹⁰. In this connection, it is worthwhile to mention that some diketones have redox potential very close to that of oxygen, thereby delimiting the interpretation of results. Giese *et al.*¹¹ have made use of 18-crown-6 ether for a similar oxidation of hydroxy and keto polyaromatics including internal quinones. With an objective to extend the applicability of Et_4NBr as an inexpensive alternative to crown ethers, the reaction of α -diketones, viz. furil **1a**, 4,4'-dimethylbenzil **1b**, 4,4'-dimethoxybenzil **1c**, 4,4'-dibromobenzil **1d**, 9,10-phenanthroquinone **1e**, 1,2-naphthoquinone **1f**, (\pm) camphorquinone **1g** and 2,2'-pyridil **1h** has been carried out under the mild reaction conditions of Et_4NO_2 to afford 2-furancarboxylic acid **2a**, *p*-methylbenzoic acid **2b**, *p*-methoxybenzoic acid **2c**, *p*-bromobenzoic acid **2d**, 2,2'-biphenyldicarboxylic acid **2e**, phthalic

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

	Substrate 1	Product 2	Yield* (%)	m.p. (°C) Found (Reported)
a			65	130 (133-34) ¹³
b			84	178 (181) ¹³
c			86	183 (184) ¹³
d			69	252 (251-53) ¹³
e			75	230 (228-29) ¹³
f			62	206 (210-11) ¹⁴
g			78	185 (187) ¹³
h			59	137 (136-37) ¹³

*Isolated yield based on diketones **1a-h** as weight %.

acid **2f**, (\pm) camphoric acid **2g**, and 2-pyridinecarboxylic acid **2h**, respectively (cf. Table I).

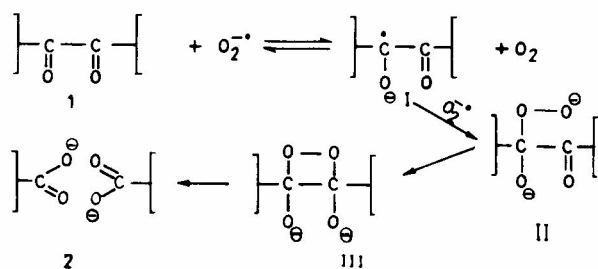
The products **2a-h** were achieved by using a 5.0 fold molar excess of potassium superoxide and a 2.5 fold molar excess of Et_4NBr over the substrates **1a-h** in anhyd. DMF. Generally, the substrates **1a-h** were allowed to react for 3-4 hr at room temperature under dry air (see Experimental Section). The reaction was then quenched with cold saturated aq. NaCl and worked up to afford the carboxylic acids **2a-h** in fairly good yields. Each reaction was monitored on TLC and showed in almost all cases the total disappearance of the starting materials. The structures of the products were elucidated from their melting points and IR spec-

tral data.

Based on product isolation and existing literature, a plausible mechanism is hypothesized (cf. Scheme II). Probably the reaction proceeds by a preliminary electron transfer from O_2^- to the diketone system **1** providing an anion radical **I** which possibly via radical coupling with another molecule of O_2^- gives rise to dianion **II**. The intermediate **II** after necessary internal nucleophilic attack via **III**, may undergo fission to produce the carboxylic acid **2**.

Experimental Section

Melting points were measured on a Buchii apparatus and are uncorrected. IR (KBr) spectra were recorded on a JASCO FT/IR- 5300 infrared spec-



trophotometer. The substrates **1a-c** and **1e** were prepared adopting literature procedure¹². Other materials such as **1d**, **1f-h** (Aldrich, USA) along with KO₂ and Et₄NBr (E Merck, Germany) were used as such. All experiments were conducted at room temperature.

Reaction of tetraethylammonium superoxide with substrates 1a-h: General procedure. KO₂ (1.42 g, 0.02 mole) was weighed under nitrogen atmosphere and transferred into a two necked round bottom flask equipped with N₂ inlet and Liebig condenser guarded with calcium chloride tube. The flask was degassed with dry nitrogen¹² and to it were introduced dry DMF (40 mL) and Et₄NBr (2.10g, 0.01mole). The reaction mixture was stirred magnetically for 15 min to facilitate major dissolution of the solids. The substrate **1a-h** (0.004 mole) was finally admitted to the system and the mixture was stirred vigorously for 3-4 hr at room temperature (30°C). After completion of the reaction, cold saturated aq. NaCl (120 mL) and NaHCO₃ (25 mL) were successively added dropwise over a period of nearly 15 min. The mixture was extracted with diethyl ether (2×25 mL) to remove the unreacted substrate, usually present in negligible amount. Aqueous phase was acidified with conc. HCl and the solid precipitated if any, was filtered. The supernatant was extracted again with large volume of diethyl ether (3×60 mL). The organic phase was thoroughly washed with water (4×60 mL), dried over anhyd. Na₂SO₄, filtered and evaporated to afford the products **2a-h**, which were recrystallised from hot H₂O. Their physical data are given in Table I.

Acknowledgement

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