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Ultrasound Assisted Oxidative Cleavage of α -Keto, α -Hydroxy and α -Halo Ketones by Superoxide

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Potassium superoxide, an oxygen supplier and carbon dioxide scrubber, provided convenient synthetic access to oxidatively cleave α -keto, α -hydroxy, and α -halo ketones to carboxylic acids (Filippo, Jr., *J. Org. Chem.*, 41:1077, 1976). The yields are excellent but the principal disadvantage of this method is the long reaction time required.

We now report that significant improvement in reaction times may be realized by conducting these reactions in the presence of ultrasound (Lindley, *Chem. Soc. Rev.*, 16:275, 1987). Thus, the sonication of camphorquinone with potassium superoxide affords camphoric acid in 85% versus 87% for the same reaction without ultrasound and requires only 1.5 h instead of 24 h. Some other examples are shown in Table 1. In all cases, substantial decreases in reaction times were realized.

In a typical experiment, a dry nitrogen filled 100 mL, three-necked, round-bottomed flask was charged with 18-crown-ether (105 mg, 0.4 mmol), potassium superoxide (284 mg, 4 mmol), d,l-camphorquinone (166 mg, 1 mmol), and dry benzene (25 mL). The flask was submerged in a cold water-bath and the mixture was agitated with ultrasound (Virsonic 300, 400 watt, 20 KHz) for 1.5 hours.

Product isolation was straightforward. The crude product was poured into ice-water (30 mL). The aqueous layer was separated and acidified with 6N hydrochloric acid. The resulting solids were collected and recrystallized from ethanol-water to give 170 mg (85%) of pure camphoric acid. Each product was characterized by m.p., IR, and NMR. These spectra were identical to those of authentic samples.

Table 1.

Substrate	Product	Ultrasound		Thermal (Lit.)	
		Time (h)	Yield %	Time (h)	Yield %
Camphorquinone	Camphoric acid	1.5	85	24	87
Phenanthrenequinone	Diphenic acid	4	63	none	none
2-Chlorocyclohexanone	Adipic acid	2	76	24	60
3-Bromocamphor	Camphoric acid	3	53	24	54
Benzoil	Benzoic acid	1	83	24	98
2-Hydroxycyclohexanone	Adipic acid	3	80	24	69
Ethyl mandelate	Benzoic acid	2.5	85	24	93

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