Microwave-assisted Syntheses of 1,2-Diketones†

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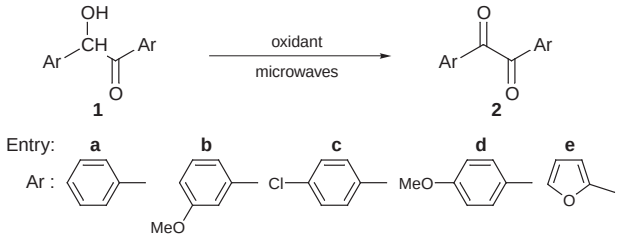
A comparative study of the conversion of a number of α-hydroxyketones into 1,2-diketones by three oxidants under microwave irradiation is reported.

1,2-Diketones are important compounds in organic chemistry and can be utilized for the preparation of a variety of organic compounds.[1] 1,2-Diketones can be converted in alkynes,[2] α-ketohomoallyl alcohols,[3] cyclopentadienones[4] *etc.* In view of a study in salen[5] chemistry, we needed to prepare a number of 1,2-diketones, from which 1,2-diaryl-1,2-diaminoethane[6] can be prepared.

1,2-Diketones can be prepared either by cross coupling of acyltins with acyl halides or by the coupling of acyl chlorides using hexabutylditin in the presence of palladium catalysts.[7] 1-Naphthyllithium and 2,6-dimethylphenyllithium on carbonylation afford the corresponding 1,2-diketone.[8] 1,2-Diketones can also be prepared easily by oxidizing α-hydroxyketones in the presence of iodine,[9] copper(II), [10] nitric acid,[11] dimethyl sulfide ditriflate,[12] ammonium chlorochromate.[13]

There has been a growing interest in the application of microwave irradiation in chemical reaction enhancement,[14] the salient features being improved reaction rates and the formation of cleaner products. A variety of reactions in MORE[15] chemistry have been reported. A rapid synthesis of a number of 1,2-diketones by oxidizing α-hydroxyketones in the presence of a copper(II) catalyst (method A), pyridinium chlorochromate[16] (method B) and concentrated nitric acid (method C) under microwave irradiation have been carried out by us (Scheme 1). We report herein a comparative study of methods A, B and C for the conversion of a number of α-hydroxyketones into 1,2-diketones (Table 1). The results depicted in Table 1 show that these are the most convenient, rapid and high-yielding methods for the conversion of α-hydroxyketones into 1,2-diketones. In the conventional heating method, utilizing copper(II), concentrated nitric acid as oxidants, reactions generally require 1.5 h. To the best of our knowledge this is the first report of a comparative study of the oxidation of α-hydroxyketones to 1,2-diketones by various oxidants under microwave irradiation.



Scheme 1

Experimental

Melting points were determined in open capillaries on an electrically heated metal block. The reactions were carried out in a domestic microwave oven (BPL BMO 700T, 1200 W) at medium power level (power level 5). Reactions were carried out in an Erlenmeyer flask (25 ml) fitted with a funnel (i.d. 5 cm) as a loose top, upon which a round-bottomed flask (10 ml) containing ice (7 g) was placed as a condenser. General procedures for the syntheses of 1,2-diketones 2a–e by methods A, B and C are described below. All the products were characterized by comparing the melting points of the authentic samples.[13,17]

Method A.—A mixture of α-hydroxyketone (1.0 mmol), copper(II) acetate (2.0 mg), ammonium nitrate (1.25 mmol) and 80% (v/v) aqueous acetic acid (0.7 ml) was irradiated in a microwave oven for 1–5 min. It was then cooled, the precipitate was filtered off and washed with cold water. Then it was dried and recrystallized from ethanol.

Method B.—A mixture of α-hydroxyketone (1.0 mmol) and pyridinium chlorochromate (1.5 mmol) in chloroform (2.0 ml) was irradiated in a microwave oven for 1–1.5 min. It was then cooled and extracted with chloroform (3 × 5 ml); removal of the solvent afforded the 1,2-diketone, which was recrystallized from ethanol.

Method C.—A mixture of α-hydroxyketone (1.0 mmol) and concentrated nitric acid (1.06 ml) was irradiated m a microwave oven for 42–60 s. It was then cooled and poured into ice-cold water with stirring. The solid products were filtered off, dried and recrystallized from ethanol.

Table 1 The oxidation of α-hydroxyketones to 1,2-diketones under microwave irradiation

	Method A		Method B		Method C	
1,2-Diketone	Time/min	Yield(%)	Time/min	Yield(%)	Time/s	Yield(%)
2a	1	96	1	94	42	95
2b	3	91	1	90	48	89
2c	1	95	1	90	44	90
2d	5	78	1.5	80	60	79
2e	3	88	1	87	–	–

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