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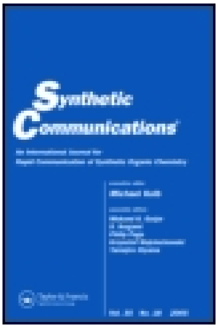

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Oxidation by DMSO II. An Efficient Synthesis of α, β-Diketones from α, β-Dibromides

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SYNTHETIC COMMUNICATIONS, 25(20), 3145-3148 (1995)

OXIDATION BY DMSO II. AN EFFICIENT SYNTHESIS OF α, β-DIKETONES FROM α, β-DIBROMIDES

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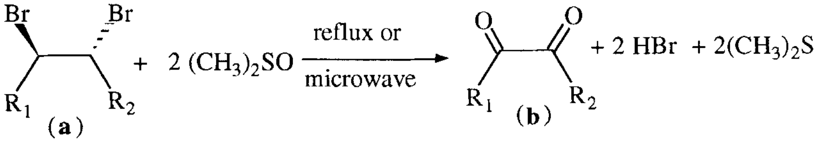
Abstract: α, β–Dibromides refluxed in DMSO are oxidised into α, β–diketones. The reaction take place rapidly under microwave irradiation.

In continuation of our work on DMSO oxidation under microwave irradiation [1], we have studied oxidation of some α, β–dibromides. Although the smooth oxidation of alkyl halides by DMSO known as Kornblum oxidation is widelyused in synthetic organic chemistry [2], the oxidation of α, β–dihalides was poorly studied. During their study of oxidation of stilbenes into benzils, Yusubov et al [3] have reported the oxidation of dibromostilbene into benzil with DMSO-hydrobromic mixture.

We reported herein that α, β–dibromides refluxed in DMSO gave α, β-diketones in good yield. Hydrobromide gas and dimethylsulfide are identified as volatile products. The reaction takes place according to the **Scheme 1**.



The results of there oxidations are compiled in table 1.

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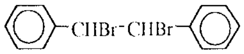
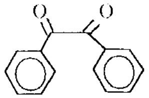
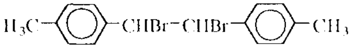
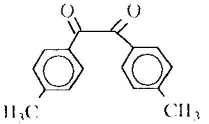
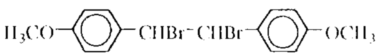
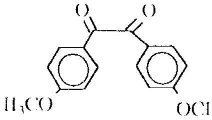
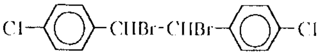
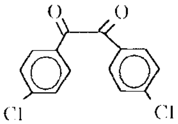
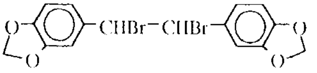
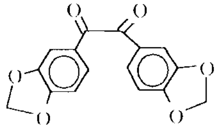
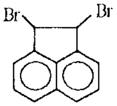
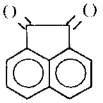
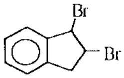
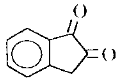
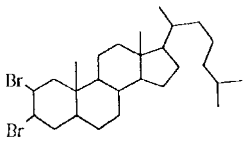
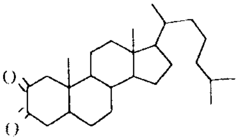
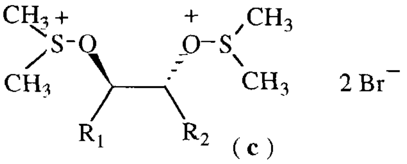
Table 1: Oxidation of dibromides into α,β-diketones in DMSO.

Entry	Dibromide	Products	(Yield%)
1a.			(75)
2a.			(60)
3a.			(65)
4a.			(51)
5a.			(74)
6a			(68)
7a.			(58)
8a.			(52)

The reaction also takes place rapidly under microwave irradiation in an open flask. A possible mechanism is the formation of a bis alkoxysulfonium salt (**c**) and it decomposition according to the literature [4].



(**c**)

In conclusion bromination of olefin and oxidation of crude dibromide by DMSO is a useful route to α,β-diketones from olefins. Microwave irradiation allows a quick and convenient oxidation reaction.

Experimental

Dibromides (**a**) were prepared by bromination of olefins in dichloromethane with one equivalent of bromine at room temperature in dichloromethane in absence of light. The crude bromides obtained by removing solvent under vacuum were used without purification. Olefins used for the preparation of 2a-5a were obtained by Mc Murray coupling [5] ($TiCl_3$-Zn/Cu) of the corresponding aldehydes.

General Procedure

A) Crude dibromides (2 mmol) were refluxed in DMSO (10 ml). The mixture was diluted with ether (150 ml) and washed with water (20X4 ml). After drying on magnesium sulfate, the solvent was removed in vacuo. Pure diketone was obtained by preparative thin layer chromatography on silica.

B) Crude dibromide (1.4 mmol) in DMSO (7 ml) was irradiated in an open flask with a commercial microwave oven (350 W) for 3 mn under a hood.

A similar workup of A was used.

All products were identified by comparison with authentic samples (Mp, TLC) and by their spectroscopic data (IR,PMR, MS).

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