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DIMERIZATION OF ALKYL VINYL KETONES WITH SODIUM NITRITE-ACETIC ACID IN DIMETHYL SULFOXIDE

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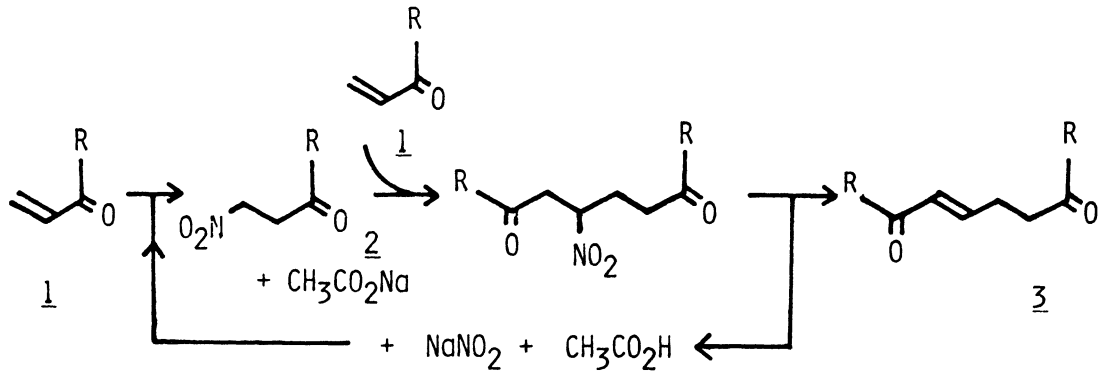
Dimerization of alkyl vinyl ketones in the presence of a catalytic amount of sodium nitrite-acetic acid in DMSO gave the corresponding 1,6-diketones in 58-86% yield.

Dimerization of 3-butene-2-one 1a in the presence of triphenylphoshine[1] or its metal complexes[2] afforded 3-methylene-2,6-heptanedione, a branched dimer. In this reaction, preparation of linear dimer was very difficult.

Recently, we reported[3] a facile synthesis of 4-nitrobutane-2-one 2 from 3-butene-2-one 1a with sodium nitrite-acetic acid in THF. However, when THF was displaced by DMSO, 3-octene-2,7-dione 3, a head to head dimer of 3-butene-2-one 1a was formed together with 4-nitrobutane-2-one 2. We wish to report on the selective dimerization of 3-butene-2-one 1a using sodium nitrite-acetic acid in DMSO according to Scheme 1.

A typical reaction is as follows: acetic acid (0.6 g, 0.01 mol) was added at 20-25 °C to a stirred mixture of sodium nitrite (0.69 g, 0.01 mol), 3-butene-2-one 1a (3.5 g, 0.05 mol) and 10 ml of DMSO, and stirring was continued for 16 h at the same temperature. The reaction mixture was acidified with dil. HCl and extracted with ethyl acetate. The extract was washed with water, dried (Na_2SO_4), and evaporated. The residue was purified by chromatography on a silica gel column using benzene as eluent to yield 3.0 g (86% yield) of *trans*-3-octene-2,7-dione 3a, bp 94-96 °C/3 mmHg.



Scheme 1

Table 1 Dimerization of alkyl vinyl ketones catalyzed by sodium nitrite-acetic acid in DMSO

Dimer 3	R	Ratio[1]	Temp.	Time (h)	Yield[2] of Dimer[3] (%)
a	CH_3	5:1:1	r.t.	16	86
a	CH_3	10:1:1	r.t.	12	79
a	CH_3	20:1:1[4]	r.t.	12	79
b	CH_3CH_2	10:1:1	r.t.	12	70
c	$CH_3(CH_2)_2$	10:1:1	r.t.	12	68
d	$(CH_3)_2CH$	10:1:1	r.t.	12	63
e	$CH_3(CH_2)_5$	10:1:1	r.t.	8	58

1) Molar ratio of 1 / $NaNO_2$ / CH_3CO_2H.
2) Based on alkyl vinyl ketones 1.
3) These dimers 3 are characterized by all-*trans* configuration on the double bond.
4) KNO_2 was used instead of $NaNO_2$.

From Table 1, it is clear that 3-butene-2-one 1a can be dimerized in DMSO in fairly high yield in the presence of a small amount of sodium nitrite-acetic acid, and it seems that potassium nitrite is much more effective than sodium nitrite in catalytic action.

This procedure was extended to the dimerization of alkyl vinyl ketones 1b-e which were reacted with sodium nitrite-acetic acid in DMSO as in the case of 3-butene-2-one 1a, yielding the corresponding head to head dimers in 58-70%.

On the other hand, 4-nitrobutane-2-one 2 was reacted with 3-butene-2-one 1a and sodium acetate in DMSO, giving 3-octene-2,7-dione 3 in 72% yield.

The mechanism of dimerization of 3-butene-2-one 1a is likely to be shown as follows; (1) addition of nitrite anion to 3-butene-2-one 1a, (2) Michael type addition of 4-nitrobutane-2-one 2 to 3-butene-2-one 1a, and (3) elimination of nitrite anion from the formed adduct in the presence of sodium acetate.

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References

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3) T.Miyakoshi, S.Saito, and J.Kumanotani, *Chem. Lett.* 1981 in press.

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