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A NEW SYNTHESIS OF β-NITRO CARBONYL COMPOUNDS FROM ALKYL VINYL KETONES WITH SODIUM NITRITE-ACETIC ACID IN TETRAHYDROFURAN

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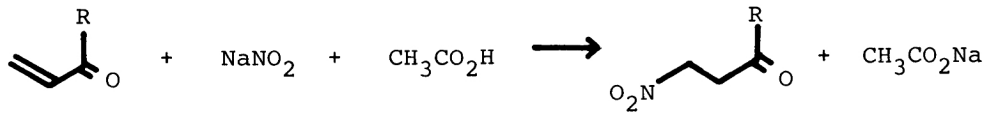
The reaction of alkyl vinyl ketones with sodium nitrite-acetic acid in THF gave the corresponding β-nitro carbonyl compounds in 42-82% yield.

Recently β-nitro carbonyl compounds are increasingly becoming significant intermediates for synthesis of natural products.[1),2)] β-Nitro ketones and esters have been prepared from β-halo carbonyl compounds and silver nitrite in benzene,[3)] sodium nitrite in DMSO[1)] or DMF[4)], and NO_2^--form ion-exchange resins in benzene.[5)]

In the present paper, a new and versatile synthetic procedure of β-nitro carbonyl compounds from alkyl vinyl ketones 1a-f is described. Compounds 1a-f are allowed to react *in situ* with sodium nitrite-acetic acid in THF according to Scheme 1.



1a-f 2a-f

Scheme 1

A typical procedure; acetic acid (6.0g, 0.1 mol) was added at 20-25 °C for 10 min to a stirred mixture of sodium nitrite (6.9g, 0.1 mol), 3-butene-2-one 1a (3.5g, 0.05 mol) and 20 ml of THF, and stirring was continued for 18 h at the same temperature. The reaction mixture was diluted with water and extracted with ethyl acetate. By removal of the ethyl acetate from the extract previously dried over sodium sulfate, a product was obtained as residue, and chromatographed on a silica gel column using benzene as eluent; 4-nitrobutane-2-one 2a was given in a yield of 4.8g (82%); 2a ($R=CH_3$), bp 86 °C/2 mmHg, IR(liquid film); 1715(C=O) and 1540(NO_2)cm^{-1}; NMR(δ,$CDCl_3$); 2.20(s,3H,CH_3CO), 3.07(t,J=6 Hz,2H,CH_2CO) and 4.57(t,J=6 Hz,2H,CH_2NO_2).

When THF is displaced with DMSO in the above reaction, 3-octene-2,7-dione 3 (bp 94-96 °C/3 mmHg) is formed in a 56% yield together with a 30% yield of 4-nitrobutane-2-one 2a.

Furthermore, the use of potassium nitrite instead of sodium nitrite resulted in the yields of 35% of dimer 3 and 18% of 4-nitrobutane-2-one 2a. The combination of sodium nitrite and THF is most favorable to prepare 2a selectively.

This preparative procedure is extended to the synthesis of β-nitro ketones 2b-f ; each of 1b-f was treated with sodium nitrite-acetic acid in THF as in the case of 3-butene-2-one 1a, yielding 42-68% of the aimed β-nitro ketones. The results are shown in Table 1.

Table 1. Reaction of alkyl vinyl ketones 1 with sodium nitrite-acetic acid

Substrate, CH_2=CHCOR		Solvent*)	β-Nitro Ketone	Yield of 2**)
1	R		2	(%)
a	CH_3	THF	$CH_3COCH_2CH_2NO_2$	82
b	CH_3CH_2	THF	$CH_3CH_2COCH_2CH_2NO_2$	46
c	$(CH_3)_2CH$	THF	$(CH_3)_2CHCOCH_2CH_2NO_2$	42
d	$CH_3(CH_2)_2$	H_2O	$CH_3(CH_2)_2COCH_2CH_2NO_2$	57
e	$CH_3(CH_2)_3$	THF	$CH_3(CH_2)_3COCH_2CH_2NO_2$	65
f	$CH_3(CH_2)_5$	THF	$CH_3(CH_2)_5COCH_2CH_2NO_2$	68

*) Molar ratio of 1 / $NaNO_2$ / CH_3CO_2H = 1 / 2 / 2.

**) Based on alkyl vinyl ketone 1.

On the other hand, methyl β-nitropropionate was obtained in a 30% yield, on treatment of methyl acrylate with potassium nitrite-acetic acid in DMSO at 15-18 °C for 24 h.

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