

DIRECT NITROMETHYLATION OF NITRONAPHTHALENE AND ITS HETEROANALOGUES

A NEW METHOD FOR FUNCTIONALIZATION OF NITROARENES¹

W. Danikiewicz and M. Makosza*

Institute of Organic Chemistry Polish Academy of Sciences, 01-224 Warszawa
 Poland

Summary: Some nitroarenes react with nitromethane anion to form nitromethyl derivatives which are easily converted into corresponding nitroaromatic aldehydes.

Carbanions react with aromatic nitrocompounds to form σ -complexes² which can stabilize in a variety of ways: intramolecular redox stoichiometry,^{3,4} oxidation by an external agent,^{5,6} via process known as the vicarious nucleophilic substitution⁷ etc. Here we wish to report a new method for direct nitromethylation of strongly electrophilic nitroarenes with anion of nitromethane. The synthetic utility of nitronate anions is well recognized,⁸ but there are only few reports concerning reactions of these anions with electrophilic arenes.^{4,9}

We have found that 1-nitronaphthalene (1a) and 5-, 6- and 8-nitroquinolines (1b, 1c, and 1d) react easily with nitromethane anion to form corresponding nitromethyl derivatives in which CH_2NO_2 substituent is always ortho to the nitro group (scheme and table 1). Monocyclic nitroarenes do not enter this reaction.

SCHEME AND TABLE 1

		position of $-\text{NO}_2$ (<u>1,2,3</u>)	position of $-\text{CH}_2\text{NO}_2$ (<u>2</u>) and CHO (<u>3</u>)	Yield ^{a)} (%)	m.p. ^{b)} (°C)	δ ^{c)} CH_2NO_2	Yield ^{a)} (%)	m.p. ^{b)} (°C)	δ ^{c)} CHO
<u>a</u>	CH	1	2	35	156-8	6.01	82	100-1 ^{d)}	10.20
<u>b</u>	N	5	6	30	106-7	6.07	92	156-8	10.25
<u>c</u>	N	6	5	44	111-3	6.50	88	152-4	10.57
<u>d</u>	N	8	7	55	136-8	5.99	85	172-4	10.23

a) yields of isolated and purified products; all compounds gave satisfactory elemental analyses

b) all compounds melt with decomposition

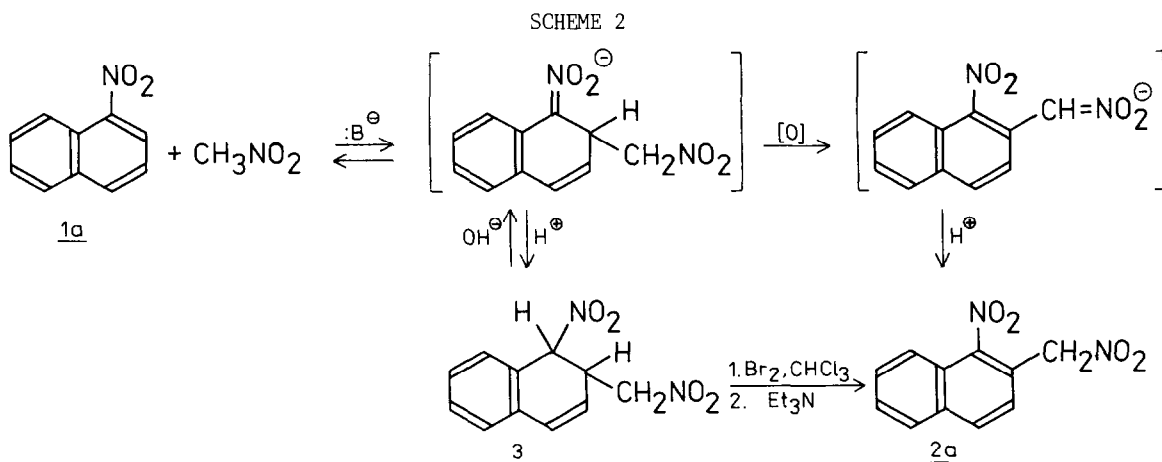
c) ¹H NMR chemical shifts in ppm measured in $(\text{CD}_3)_2\text{CO}$ relative to TMS

d) reported m.p. 99°C¹⁰

For example addition of 1a (1.73 g, 10 mmol) and nitromethane (1.22 g, 20 mmol) in 5 ml of DMSO to a stirred suspension of powdered NaOH (2 g, 50 mmol) in DMSO (15 ml) results in an exothermic reaction which was carried out at 18°C for 30 min. Acidification with aqueous AcOH and chromatographic isolation gave 1-nitro-2-nitromethylnaphthalene (0.81 g, 35%).

Nitromethyl derivatives 2 can be easily transformed into corresponding aldehydes 3 via oxidative Nef reaction, using KMnO_4 in a borate buffer (scheme and table 1). Thus, the overall process can be considered as a nucleophilic formylation of the reactive nitroarenes, in which nitromethyl anion serves as a formyl anion equivalent ($\text{C}\bar{\text{H}}_2\text{NO}_2 = \bar{\text{C}}\text{HO}$).

When the reaction of 1a with nitromethane is carried out under mild conditions (MeONa, DMSO 15°C, 3 min.) the intermediate adduct 3 can be isolated upon acidification (as a mixture of two diastereoisomers). It can be subsequently converted into the final product 2a via bromination-dehydrobromination procedure⁶ or when treated with NaOH/DMSO system (scheme 2).



It is not clear how the oxidation of the intermediate σ -adducts proceeds, nevertheless there are some hints that an electron transfer process is involved (e.g. the reactions carried out under oxygen and under nitrogen gave similar results, but the former are much slower). Moderate yields of the nitromethyl derivatives and the formation of substantial quantities of tars suggest that the σ -complexes are oxidized by the nitroarenes. Results of detailed studies on this new reaction will be published upon completion.

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