Nucleophilic addition of secondary nitro compounds to acetylene

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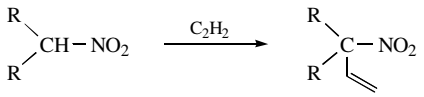
The products of C-vinylation were prepared in 52–65% yield by the reaction of secondary nitroalkanes with acetylene in DMSO–KOH.

Mono- and polynitroalkanes can add to an activated triple carbon–carbon bond under conditions of basic catalysis, for example, to the esters of propiolic acid.[1]

It is well known that nucleophilic addition to acetylene is facilitated in a 'super-base' DMSO–KOH medium.[2]

We found that 2-nitropropane **1a** and nitrocyclohexane **1b** added to acetylene in DMSO–KOH to give corresponding C-vinylation products **2a**,**b**. The process proceeded at an initial acetylene pressure of 14 atm and at 100 °C. The full conversion of compounds **1a**,**b** was reached in 4 h.†

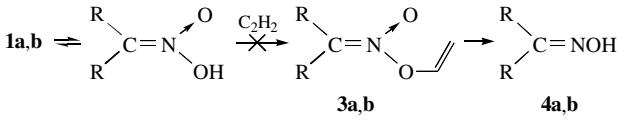


1a,**b** **2a**,**b**

a R = Me
b R + R = $(CH_2)_5$

Scheme 1

The ^{1}H NMR spectra of the reaction mixtures exhibited no signals that could be assigned to the vinylation products of either the *acy*-forms of nitro compounds **3a**,**b** or oxymes **4a**,**b**. The formation of the above compounds results from the splitting of nitro esters. Thus, under the given conditions, the process of O-vinylation did not proceed.



3a,**b** **4a**,**b**

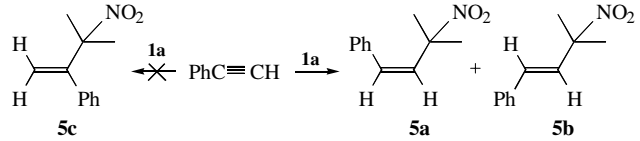
Scheme 2

Our attempts to carry out the C-vinylation of nitro compounds **1a**,**b** using benzene as a solvent were unsuccessful.

In the reactions of acetylene with nitromethane, nitroethane and 1-nitropropane in DMSO–KOH, only resin-like products were isolated. Probably, this was due to the ability of primary nitroalkanes to cause autocondensation under alkaline conditions, for example, to methazonic acid and isooxazole derivatives.[1(*b*),3]

Terminal acetylenes, as well as acetylene, can successfully react with secondary nitroalkane derivatives in DMSO–KOH. Thus, the *E*- and *Z*-isomers of 1-(3-methyl-3-nitro-1-butenyl)-benzene **5a**,**b** were obtained by the reaction of 2-nitropropane and phenylacetylene.‡

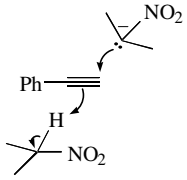
According to ^{1}H NMR data, the amount of the *E*-isomer was higher than that of the *Z*-isomer by a factor of 4.2. Moreover, the ^{1}H NMR spectra of the reaction products exhibited no signals due to 1-[1-(1-methyl-1-nitroethyl)vinyl]benzene **5c**, which is the product of the addition of 2-nitropropane to α-phenylacetylene.



5c **5a** **5b**

Scheme 3

The predominant formation of isomer **5a** and the absence of isomer **5c** in the reaction mixture suggest that the reaction proceeds by a coordinated *trans*-nucleophilic addition mechanism.[4] The nitronate ion[3] [Me_2C^-–N^+(=O)O^- ⇔ Me_2C=$N^+O_2^{2-}$] served as a nucleophile; it was formed by the alkaline deprotonation of the nitroalkane.



Scheme 4

References

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† A mixture of compound **1a** or **1b** (10 g), powdered potassium hydroxide (5 g) and DMSO (100 ml) was placed in a stainless steel 250 ml rotary autoclave. The mixture was saturated with acetylene at 14 atm and heated at 100 °C for 4 h. After cooling, the mixture was poured into 1 dm^3 of cold water and extracted with diethyl ether (3×100 ml). The combined extracts were dried with anhydrous potassium carbonate, and the ether was distilled in a vacuum to give nitroalkenes **2a**,**b**.

2a: yield 52%, bp 71–72 °C (61 torr), n_D^{20} 1.4335, d_4^{20} 0.9576. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.68 (s, 6H, Me), 5.31 (d, 1H, *cis*-CH=C, $^3J_{cis}$ 10.7 Hz), 5.35 (d, 1H, *trans*-CH=C, $^3J_{trans}$ 17.3 Hz), 6.18 (dd, 1H, C–CH=C, $^3J_{cis}$ 10.7 Hz, $^3J_{trans}$ 17.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.37 (Me), 87.78 (NC), 116.56 (=CH_2), 138.12 (=CH). IR (neat, ν/cm^{-1}): 1530 (NO_2), 1630 (C=C), 3085 (=CH_2). Found (%): C, 52.24; H, 7.98; N, 12.02. Calc. for $C_5H_9NO_2$ (%): C, 52.16; H, 7.88; N, 12.17.

2b: yield 65%, bp 77–78 °C (4 torr), n_D^{20} 1.4818, d_4^{20} 1.0336. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.36–1.60 (m, 6H, C_6H_{10}), 1.84 (m, 2H, C_6H_{10}), 2.44 (m, 2H, C_6H_{10}), 5.32 (d, 1H, *cis*-CH=C, $^3J_{cis}$ 10.7 Hz), 5.36 (d, 1H, *trans*-CH=C, $^3J_{trans}$ 17.4 Hz), 5.93 (dd, 1H, C–CH=C, $^3J_{cis}$ 10.7 Hz, $^3J_{trans}$ 17.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.48 (C-3, C-5), 24.75 (C-4), 34.05 (C-2, C-6), 91.19 (NC), 117.96 (=CH_2), 138.38 (=CH). IR (neat, ν/cm^{-1}): 1530 (NO_2), 1635 (C=C), 3090 (=CH_2). Found (%): C, 61.83; H, 8.56; N, 9.14. Calc. for $C_8H_{13}NO_2$ (%): C, 61.91; H, 8.44; N, 9.03.

‡ A mixture of compound **1a** (18.8 g), phenylacetylene (14 g), melted potassium hydroxide (7.5 g) and 150 ml of DMSO was stirred at 100 °C for 6 h. After cooling, the mixture was treated as described above; a mixture of two nitro compounds **5a**,**b** was isolated.

5a,**b**: yield 41%, bp 106–110 °C (3 torr), n_D^{20} 1.5346, d_4^{20} 1.0578. ^{1}H NMR (400 MHz, $CDCl_3$) δ: **5a** (*Z*-isomer): 1.60 (s, 6H, Me), 5.96 (d, 1H, NCCH=C, ^3J 12.5 Hz), 6.78 (d, 1H, CH=C, ^3J 12.5 Hz), 7.12–7.45 (m, 5H, Ph); **5b** (*E*-isomer): 1.43 (s, 6H, Me), 6.37 (d, 1H, NCCH=C, ^3J 16.1 Hz), 6.60 (d, 1H, NCC=CH, ^3J 16.1 Hz), 7.12–7.45 (m, 5H, Ph). IR (neat, ν/cm^{-1}): 1535 (NO_2), 1595, 1605, 1655 (C=C), 3020, 3055, 3080 (=CH). Found (%): C, 69.21; H, 6.77; N, 7.08. Calc. for $C_{11}H_{13}NO_2$ (%): C, 69.09; H, 6.85; N, 7.32.

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