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SHORT COMMUNICATIONS

Nitromethane Reaction with Acetylene in KOH–DMSO System

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Superbasic systems of KOH-DMSO type demonstrated their high efficiency as catalyst of nucleophilic addition to acetylenes of various NH- [1, 2]. OH- [1], and SH- [1, 3] acids (complete list of publications see [4]). Obviously interesting is an extension of this series to CH-acids that would increase synthetic opportunities of this type reactions. It was shown recently [5] that the system KOH-DMSO was capable of promoting addition of secondary nitroalkanes to acetylene and phenylacetylene affording the corresponding C-vinyl derivatives in 41–65% yield. However attempt to isolate vinylation products obtained from primary nitroalkanes (C_1 - C_3) were unsuccessful.

However this reaction would give interesting results. Firstly, the reaction might proceed either as C-vinylation or O-vinylation of the nitro compound. In the latter case the O-vinylated nitro compound could have suffered [2,3]-sigmatropic rearrangement, the process we are currently looking for [6]. Secondly, the C-vinylation might provide either monoadduct (result of vinylation proper) or the product of addition of the second molecule of the nitro compound. Therefore in the course of our systematic studies on nucleophilic addition to the triple carbon-carbon bond in the superbasic systems we investigated the reaction between nitromethane and acetylene in the system KOH–DMSO.

We found that the reaction occurred very fast (within 5 min) at 80°C, and the main isolated product was 1,3-dinitro-2-methylpropane (**III**). Apparently in

HC=CH + MeNO₂
$$\xrightarrow{\text{KOH}-\text{DMS}}$$
 CH₂=CHCH₂NO₂
I
$$\underbrace{I^{1,2H]}}_{\text{II}}$$
 MeCH=CHNO₂ $\xrightarrow{\text{MeNO}_2}$ MeCH(CH₂NO₂)₂
II III

the arising at the first stage 3-nitro-1-propene (I) occurred [1,3H] prototropic shift resulting in 1-nitro-1-propene (II). Its active double bond quickly takes up the second nitromethane molecule (see references in [7]), providing biadduct III.

The low yield of compound III (~2%) is due to its instability in the presence of superbase. The reaction is rather sensitive to its conditions: At increasing the time of reagents contact to 3 h the yield of dinitro derivative III reduces to 0.5%, and raising temperature only by 10°C results in complete tarring of the reaction mixture. Apparently the biadduct III being a primary nitroalkane further reacts with acetylene providing 2,4-dimethyl-1,3,5-trinitropentane (VIII) and afterwards polynitroalkanes IX.

In the ¹H NMR spectrum of a polymer isolated in the run where the reaction mixture was neutralized with NaHCO₃ appeared signals from a CH₂Me group with nonequivalent protons in the methylene group (δ 3.50 and 3.65 ppm). This fact evidences the presence in the molecule of a chiral center that is found in structures **V** and **VII**. In the spectrum the signals are observed of olefin protons (broadened signals at δ 6.86 and 6.95 ppm) adjacent to NO₂ and Me groups, that might correspond to compounds **V** and **VII** (see the Scheme).

Polynitroalkanes can react with acetylene also by methine fragments directly linked to nitro groups forming unsaturated fragments **X** (the presence in the spectrum of signals from C-vinyl group at δ 5.62, 5.65, and 7.07 ppm).

On acidifying the reaction mixture we obtained a polymer (~50% with respect to the weight of the initial nitromethane) in whose ¹H NMR spectrum appeared a set of signals in the δ 7.00–8.00 ppm and downfield signals at 12.5–12.8 ppm that belonged apparently to the possible products of oligomerization and hydrolysis of metazonic acid.

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1,3-Dinitro-2-methylpropane (III), A mixture of 6.1 g (100 mmol) of nitromethane, 1 g (15 mmol) of KOH (containing ~15% of water), and 50 ml of DMSO was charged into a rotating pressure reactor of 0.5 1 capacity. Acetylene was charged into the reactor to a pressure of 14 at, and within 30 min the reactor was heated to 80°C. On reaching this temperature the heating was stopped at once (the reaction mixture remained at 80°C for ~5-6 min). On cooling to the room temperature (the residual pressure was \sim 9 at) the reaction mixture was discharged, diluted by 2 volumes of water, the reaction products were extracted into ethyl ether (20 ml \times 4), the combined ether solution was washed with water $(10 \text{ ml} \times 4)$, and dried with calcined K₂CO₃. On removing ether we obtained 0.27 g (1.8 mmol, yield 1.8%) of compound **III** (purity by GLC data 95%). ¹H NMR spectrum (400.13 MHz, CDCl₃), δ, ppm: 4.60-4.40 m [4H, 2CH₂, ³*J*(CH₂, CH) 6.3 Hz], 3.10 m (1H, CH), 1.18 d [3H, Me, J(Me, CH) 7.0 Hz]. ¹³C NMR spectrum (100.61 MHz, CDCl₂), δ , ppm: 14.76 (Me), 31.09 (CH), 62.50 (CH₂). IR spectrum (thin film), v, cm⁻¹: 2978-2929 m (CH, CH₂, Me), 1557 v.s (v_{as} NO₂), 1431 s (CH₂), 1402 s (CH₂), 1378 v.s (∨_s NO₂). Mass spectrum, m/z) (I_{rel} , %): 116 [M - 20] (5), 85 [M + H - 4O] (3), 69 (C₄H₅O, 89), 57 (C₄H₉, 13), 55 (C_4H_7 , 45), 46 (NO_2 , 100).

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