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Synthesis and physical properties of the (E)-3,3,3-tribromo-1-nitroprop-1-ene

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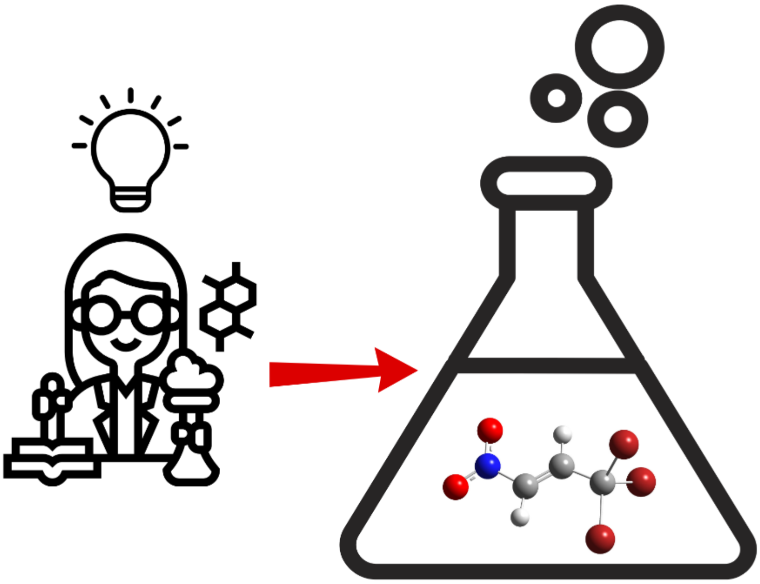

Abstract: The possible protocols for the effective preparation of the individual (E)-3,3,3-tribromo-1-nitroprop-1-ene were examined. It was found that, some strategies dedicated for the preparation of the (E)-3,3,3-trichloro-1-nitroprop-1-ene and (E)-3,3,3-trifluoro-1-nitroprop-1-ene, were not adequate for the obtaining of the title compound. Only diacylation process catalyzed by the inorganic bases, offer the possibility of the preparation of the nitroalkene. Its isolation and purification was also optimized.

Keywords: nitroalkenes, (E)-3,3,3-tribromo-1-nitroprop-1-ene, deacylation,

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Nitroalkenes are very valuable and universal building block in the organic synthesis [1,2]. In this group, the very special role play nitroethene analogs, especially functionalized by perhaloalkyl groups. Using these nitroalkenes, the introduction of the nitro group and the perhaloalkyl group is possible via one stage reaction [3]. For the preparation of 2-CX_3-nitroethenes, different approach can be used. So, (E)-3,3,3-trichloro-1-nitroprop-1-ene **2** can be prepared via dehydratation reaction of the 1,1,1-trichloro-3-nitropropan-2-ol **1** by phosphorous pentoxide (Fig.1.) [4,5].

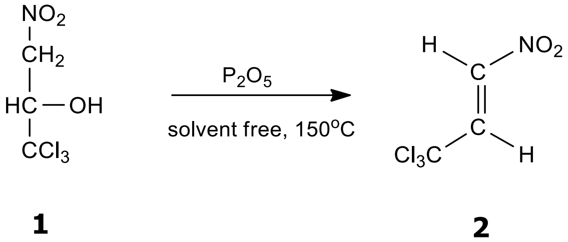

Fig. 1. Dehydration reaction of 1,1,1-trichloro-3-nitropropan-2-ol **1** using phosphorus pentoxide.

Alternatively, the same nitroalkene is synthetized via decomposition of the acetic ester **3** derived from the 1,1,1-trichloro-3-nitropropan-2-ol **1** in the reaction with the acetyl chloride (Fig.2.) [6,7].

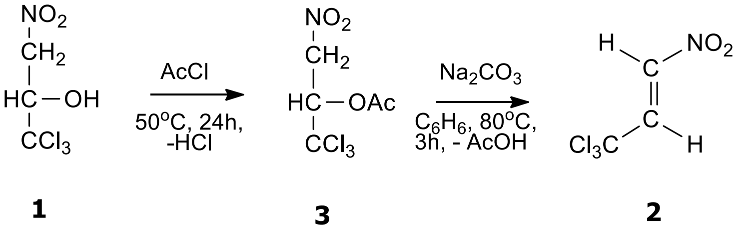

Fig. 2. Reaction of 1,1,1-tribromo-3-nitropropan-2-ol **1** with acetyl chloride and decomposition of acetic ester **3**.

The first of mentioned protocols was applied also for the preparation of the (E)-3,3,3-trifluoro-1-nitroprop-1-ene **6** [8,9]. The same nitroalkene was obtained via decomposition of the phtalic ester **5** of the 1,1,1-trifluoro-3-nitropropan-2-ol **4** (Fig.3.) [10].

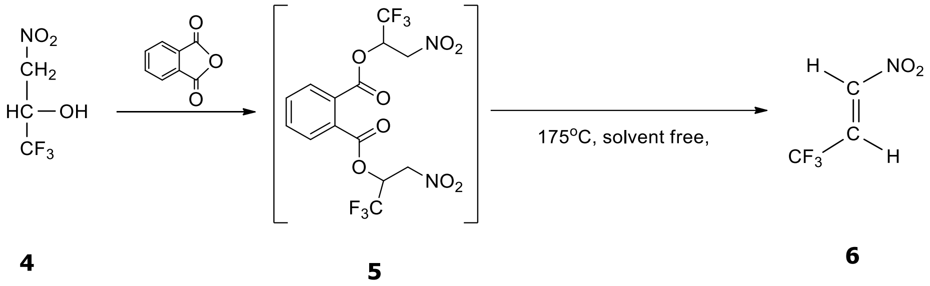

Fig. 3. Decomposition of the phtalic ester **5** of the 1,1,1-trifluoro-3-nitropropan-2-ol **4**.

It was found out, that any from before mentioned strategies are not fully universal as a general method for the preparation of most of conjugated nitroalkenes [11]. It is worth mentioning here, that iodosubstituted analog of the mentioned nitroalkenes is not known yet as the individual substance. However, bromosubstituted analog was only mentioned incidentally in the initial phase of our research. Only some very short notes regarding to its preparation was described some years ago [12]. Unfortunately, these information doesn't offer the possibility of repeating the synthetic process. That is why, detailed and comprehensive studies about the preparation of the title compound was necessary regarding to the possibility of the analysis of the reactivity of vide range of trans-substituted nitroethenes.

In the first part of this research, we synthetized the pure 1,1,1-tribromo-3-nitropropan-2-ol using the procedure described in the literature. Next, we tested synthetic approaches based on the dehydratation of this alcohol using phosphorous pentoxide as well, decomposition of the generated *in situ* phtalic ester.

All these attempts were not successful. Lastly, we adapted the procedure of the decomposition of the acetic ester via modification of the protocol described for the (E)-3,3,3-trichloro-1-nitroprop-1-ene. On this way, we obtained the raw product. Unfortunately, all attempts for the purification via distillation under reduced pressure were failed. In all cases the nitroalkene was decomposed rapidly. Therefore, we decide for use the preparative chromatography for the separation of the target compound. In the available literature, which describes a successful attempt to synthesize the 3,3,3-tribromo-1-nitroprop-1-ene [12], it has been found that in the final step, the mixture of two Z/E isomers were separated via column chromatography eluting with CCl_4. According to the fact that CCl_4 is now on the European list of forbidden to use chemicals, due to its heavy impact on human health, we needed to search for another eluent that might be as good as this one. It was nearly impossible to find only one eluent that could have exactly the same characteristics, which means we had to create a mixture of some solvents to meet this specific value of polarity index of CCl_4 which is equal 1.6. For that we decided to use a rough estimatation via equation (1):

$$P_{CCl4} = (x_1 \cdot P_1) + (x_2 \cdot 2) \tag{1}$$

where x_1,x_2 are the fractions of the solvents, and the $P_{1,2}$ values are polarity indexes of used solvents. We decided to use chloroform which is very similar by chemical structure to carbon tetrachloride, and is also known as a very good organic solvent. Next was to choose second solvent which will balance quite modern polarity of the chloroform 4.1, but the one that won't impact on the product. N-hexane was chosen as the second one with polarity index 0.1. Solution of the equation resulted with needed fractions which were estimated to 0.622 n-hexane : 0.375 chloroform. It turned out that indeed our estimations were correct, obtained mixture worked well in a matter of separation the mixture of nitroalkene isomers. Finally ,we obtained the (E)-3,3,3-tribromo-1-nitroprop-1-ene with the satisfactory, 65% yield. Its individualism and the purity was confirmed by chromatographic techniques. On the IR spectrum of the obtained nitroalkene, we have found the characteristic bands for the nitro group, carbon-carbon double bond and carbon-hydrogene bonds. On the ^{1}H NMR spectrum, only two signals connected with the existence of the vicinal protons were localized, as doublets. The coupling constant confirm, that the isolated nitroalkene exhibit stable E-geometrical configuration.

Experimental

Materials and apparatus

Commercially available chemicals (Sigma–Aldrich, Szelągowska 30, 61-626 Poznań, Poland) and solvents were used. All of used solvents were tested with HPLC methods. Some of the components of the reactions were prepared according to available in literature procedures which have been modified according to trials. Melting points were determined using a BOETIUS PHMK-05 apparatus. The measurements of NMR spectrums were performed with an Agilent 400 MHz NMR spectrometer. The ^{1}H NMR spectra were performed using a working frequency of 400 MHz. Chloroform ($CDCl_3$) was used as the deuterated solvent and tetramethylsilane (TMS) as the standard. The measurements of IR spectrums were performed using a Thermo Scientific Nicolet IS5 spectrometer equipped with an ID7 ATR attachment. The analysis were recorded in the range 500-4000 cm^{-1}.

Preparation of the 1,1,1-tribromo-3-nitropropan-2-ol

Into a three-necked round bottom (RB) flask with a magnetic stirrer, thermometer and reflux condenser, placed in a heating mantle, the solution obtained by mixing 0.084 mole (25 g) of bromal and 40 cm^3 of water was dosed. To this solution 0.125 mole (6.75 cm^3) of nitromethane was added. After dosing all the nitromethane, the reaction mixture was heated up to 45-50^{o}C. In the meantime, 1.05 g K_2CO_3 was dosed in portions to the reaction. When the temperature reached 50°C, the stirring was continuing for another 30 minutes, keeping the temperature constant. Next, the neutralization of the reaction mixture with dilute HCl was carried out. Resulting nitroalcohol was extracted with chloroform (6 x 25 cm^3) and following extract was dried with $CaCl_2$. Next, the chloroform was evaporated in the vacuum. Colourless oil was obtained, which crystallised immediately 21.2 g (yield: 74%) to pale yellow nitroalcohol crystals with a characteristic but pleasant sweetish odour. The melting point is 75-77°C. (m,p. =78°C) [12])

Dehydratation of the 1,1,1-tribromo-3-nitropropan-2-ol over phosphorous pentoxide

A Claisen flask was charged with phosphorus pentoxide (21 g, 0,15 mole). Next, the 1,1,1-tribromo-3-nitropropan-2-ol (26.0 g, 0.08 mole) was added. The flask was heated to 150°C, and the pressure was reduced to 5 mmHg. Any distilled product was not obtained. Experiments were repeated under different pressures and using different temperature impact, however none of them were successful.

Decomposition of the phtalic ester of the 1,1,1-tribromo-3-nitropropan-2-ol

The 1,1,1-tribromo-3-nitropropan-2-ol (26.0 g, 0.08 mole) and phthalic anhydride (18 g, 0.12 mole) were introduced to the Claisen glass and heated at 150°C under 80 mm of Hg until the phthalic anhydride was melted. The temperature was then raised to 180°C, and the pressure was reduced up to 5 mmHg. None of the distilled product was obtained. Experiments were repeated under different pressures and using different temperature, but again were not successful.

Reaction of 1,1,1-tribromo-3-nitropropan-2-ol with acetyl chloride

Into a three-neck RB flask with a magnetic stirrer, thermometer and reflux condenser and placed in a water bath, 0.068 mole (21.2 g) of 1,1,1-tribromo-3-nitropropropan-2-ol was introduced and added 0.124 mole (8.85 cm^3) of acetyl chloride. Next, the reaction mixture was heated up to 77°C until the nitroalcohol crystals dissolved and then incubated for 12 h at room temperature with constant stirring. The excess of acetyl chloride was then distilled off using a vacuum evaporator. Bright yellow crystals 19.72 g (yield: 93%) of 1,1,1-tribromo-3-nitro-2-acetoxypropane were obtained, with a melting point 66-68°C. (Mp.=66-67°C) [12])

Reaction of 1,1,1-tribromo-3-nitro-2-acetoxypropane with sodium carbonate

Into a three-necked RB flask, with a magnetic stirrer, thermometer and reflux condenser, placed in a heating mantle, 19.72 g (0.051 mole) of 1,1,1-tribromo-3-nitro-2-

acetoxypropane and 40 ml of benzene were dosed and then added 6 g (0.057 mole) of sodium carbonate in portions. The whole mixture was heated to boiling point and incubated for 4.5 h. The resulting precipitate was filtered on a fluted filter and the remaining residue was washed with diethyl ether (4 x 25 ml). The resulting extract was dried with CaCl2 and distilled in vacuum to remove the solvent. Obtained dark orange oil, the mixture of isomers, was sequentially separated on a preparative column in an n-hexane:chloroform 0.622:0.375 eluent. Collected fractions were evaporated to remove the solvent. 12.68 g (yield: 65%) of yellowish-orange nitroalkene crystals were obtained, with a characteristic sweetish odour. Key physical constants: brutto formula: $C_3H_2Br_3NO_2$; yellowish-orange crystals, m.p. =48-49°C; IR: υ = 1521 i 1341 (NO_2); 1665 (C=C); 3045-3111 (C-H) cm^{-1}; ^{1}HNMR: 7.74 (d, 1H, J=12.6 Hz) 7.30 (d, 1H, J=12.6 Hz)

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