

SHORT
COMMUNICATIONS

Reaction of 1-Trimethylsilyl-3-chloro-1-propyne with α -Nitroacetophenone

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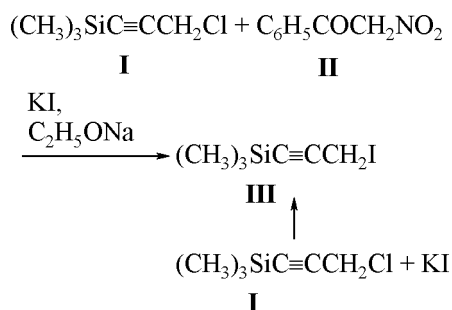
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We studied previously [1] the reactions of 1-trimethylsilyl-3-chloro-1-propyne (**I**) with β -dicarbonyl compounds and cyanoacetamide. Depending on the structure of the CH-acid we obtained products of nucleophilic C-mono- or C,C-dialkylation.

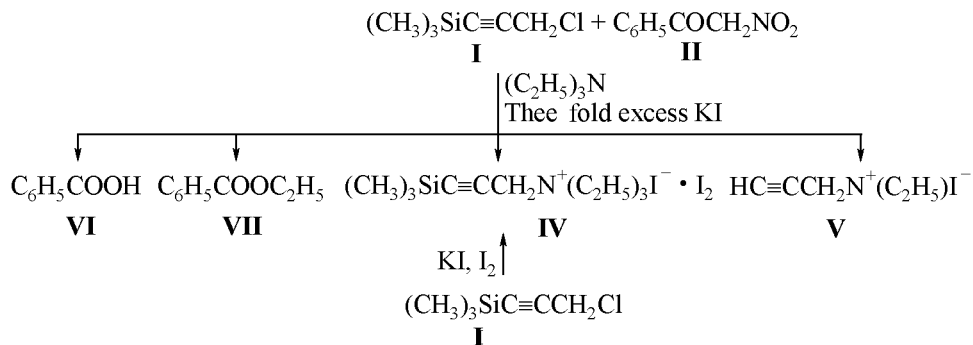
In extension of our studies we report here on results of reaction between 1-trimethylsilyl-3-chloro-1-propyne (**I**) and α -nitroacetophenone (**II**).

Unlike β -diketones the α -nitroacetophenone failed to react with compound **I** under the same conditions. The reaction of 1-trimethylsilyl-3-chloro-1-propyne with α -nitroacetophenone in the presence of equimolar amounts of KI and sodium ethylate afforded only 1-trimethylsilyl-3-iodo-1-propyne (**III**) that as the compound **I** did not enter further into C-alkylation reaction.



Compound **III** we also obtained in the "blank" experiment by reaction of chloride **I** with KI (Finkelstein synthesis). The composition and structure of compound **III** was confirmed by elemental analysis and IR spectroscopy.

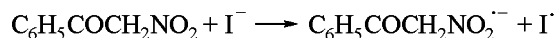
We found that reaction between compound **I** and **II** in the presence of an equimolar amount of triethyl-

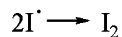


amine and threefold excess of KI takes several concurrent routes yielding compounds **IV-VII** along the above scheme.

The excess KI favors Finkelstein reaction [2]. Simultaneously with this in the system α -nitroaceto-

phenone-KI occurs one-electron transfer. Iodine anion is an active electron donor and easily transmits one electron to nitroacetophenone (acceptor).





The molecular iodine arising from recombination forms with trimethylsilylpropargylammonium iodide a molecular complex **IV** whereas no similar complex was observed with propargyltriethylammonium iodide (**V**). Complexes of allyl and vinylsilanes with molecular iodine were described in the literature [3], and their high stability was noted for compounds with a silicon atom in the α -position to the double bond.

Under the applied conditions were also isolated benzoic acid (**VI**) resulting from fragmentation of nitroacetophenone anion-radical, and ethyl benzoate (**VII**). Complex compound **IV** was also obtained by treating 1-trimethylsilyl-3-chloro-1-propyne with potassium iodide in the presence of triethylamine and iodine. The structure of compounds **III-VII** was proved by IR, ^1H and ^{13}C NMR spectroscopy.

In the IR spectra of compounds **III, IV** are observed the absorption bands from stretching vibrations of the $\text{C}\equiv\text{C}$ bond in the region 2220 cm^{-1} (2193 cm^{-1}) and of Si-C bond at $1240, 840\text{ cm}^{-1}$ ($1250, 864\text{ cm}^{-1}$) respectively.

In the ^1H NMR spectrum (δ , ppm) of compound **IV** the singlet of methyl protons (CH_3)₃Si appears at 0.24 (9H), the triplet of methyl protons and quartet of methylene protons from the $\text{CH}_3\text{-CH}_2$ group in the region respectively 1.48 (9H) and 3.50 (6H). The resonance of methylene protons from the group $(\text{CH}_3)_3\text{SiC}\equiv\text{CCH}_2$ is situated in a weaker field, at 4.12 (2H).

In the ^{13}C NMR spectrum (δ_{C} , ppm) of compound **IV** were identified all the carbon atoms present in the molecule; the carbon signal corresponding to the $(\text{CH}_3)_3\text{Si}$ group was observed at -0.46 , in the region characteristic of trimethylsilyl structures. The chemical shifts of carbons from the ethyl group of triethylammonium are 8.70 ($\text{CH}_3\text{-CH}_2$), 54.66 ($-\text{CH}_2\text{-N}$). The methylene carbon from the group attached to the triple bond appears at 50.09 ($\text{CH}_2\text{-C}\equiv$), acetylene carbons at 89.96 ($\equiv\text{C-Si}$) and 100.49 ($\equiv\text{C-CH}_2$ -).

IR and ^1H NMR spectra of compounds **V** and **VII** were in complete agreement with the assumed structures.

Thus we failed to bring α -nitroacetophenone (**II**) into nucleophilic addition to 1-trimethylsilyl-3-chloro-1-propyne, although compound **II** is usually active in nucleophilic addition reactions.

The synthetic potential of this reaction turned out to be richer than those studied formerly [1].

Reaction of 1-trimethylsilyl-3-chloro-1-propyne (I) with α -nitroacetophenone (II). (a) In the presence of equimolar amounts of potassium iodide and sodium ethylate. To a mixture of 0.58 g (0.025 mol) of sodium and 4.13 g (0.025 mol) of α -nitroacetophenone in 50 ml of anhydrous ethanol was added 4.15 g (0.025 mol) of KI and 3.66 g (0.025 mol) of chloride **I**. The reaction mixture was heated to 76°C for 4 h. From the resinous substance formed was isolated 1.28 g (22%) of 1-trimethylsilyl-3-iodo-1-propyne (**III**), bp 49°C (2 mm Hg), n_{D}^{20} 1.5068. Found, %: C 30.22; H 4.66; I 53.33; Si 11.80. $\text{C}_6\text{H}_{11}\text{ISi}$. Calculated, %: C 30.25; H 4.62; I 53.36; Si 11.76.

(b) In the presence of a three-fold excess of potassium iodide. From 4.13 g (0.025 mol) of α -nitroacetophenone in 70 ml of ethanol, 3.66 g (0.025 mol) of chloride **I**, 12.45 g (0.075 mol) of KI, and 2.53 g (0.025 mol) of triethylamine after heating to 76°C for 4 h by workup of the reaction mixture were separated compounds **IV-VII**: compound **IV**: mp 112°C (from ethanol), yield 1.55 g (11%). Found, %: C 24.07; H 4.54; I 63.78; N 2.16; Si 4.65. $\text{C}_{12}\text{H}_{26}\text{I}_3\text{NSi}$. Calculated, %: C 24.28; H 4.38; I 64.25; N 2.36; Si 4.72. Compound **V**: mp 210°C (from ethanol), yield 2.53 g (38%). ^1H NMR spectrum (δ , ppm): 1.20 t (9H, CH_3), 3.30 q (6H, CH_2), 3.97 t (1H, HC), 4.35 d (2H, CH_2). Found, %: C 39.75; H 6.11; N 4.84. $\text{C}_9\text{H}_{18}\text{IN}$. Calculated, %: C 40.45; H 6.74; N 5.24. Compound **VI**: mp 122°C (from water), yield 0.04 g (1%). Mixed sample with an authentic benzoic acid did not show melting point depression. Compound **VII**: bp 106°C (25 mm Hg), n_{D}^{20} 1.5050, yield 1.28 g (34%). ^1H NMR spectrum (δ , ppm): 1.21 t (3H, CH_3), 4.16 q (2H, CH_2), 7.77 m (5H, C_6H_5). Found, %: C 71.85; H 6.42. $\text{C}_9\text{H}_{10}\text{O}_2$. Calculated, %: C 72.00; H 6.67.

Reaction of 1-trimethylsilyl-3-chloro-1-propyne (I) with I_2 , KI, and triethylamine. From 0.44 g (0.003 mol) of chloride **I**, 0.39 g (0.003 mol) of triethylamine, 1.49 g (0.009 mol) of KI, and 0.76 g (0.003 mol) of I_2 in 20 ml of anhydrous ethanol after

heating to 75–76°C for 6 h and subsequent workup was obtained 0.29 g (16%) of compound **IV**, mp 112°C. Mixed sample with compound **IV** obtained along the preceding method did not show melting point depression. IR spectra were recorded on spectrometer IKS 29 from solutions in chloroform. ¹H NMR spectra were registered on Tesla BS 587 A instrument (operating frequency 80 Hz), solvent CDCl₃, internal reference TMS. ¹³C NMR spectra were measured on Varian T-80A spectrometer at operating frequency 20 MHz, solvent CDCl₃, internal reference TMS.

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