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SHORT COMMUNICATIONS

Dedicated to Academician of the Russian Academy of Sciences N.S.Zefirov on occasion of his70th anniversary

Trimerization of 3-Trimethylsilyl-2-propyn-1-al into 4-Trimethylsilylethynyl-4*H*-pyran-3,5-dicarbaldehyde

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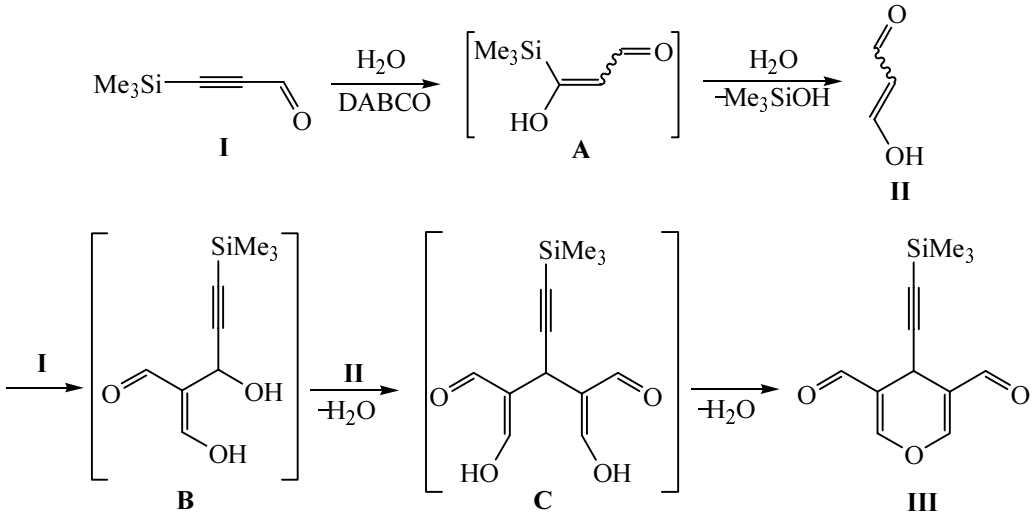
We recently showed the possibility to perform one-pot direct conversion of organoelemental α-acetylene alcohols $R_3MC{\equiv}CCH_2OH$ into 1,3-enynes $R_3MC{\equiv}CCH{=}CR^1R^2$ under the action of pyridinium chlorochromate on Al_2O_3 in the presence of CH-acids $R^1CH_2R^2$ assisted by a microwave irradiation [1]. The reaction occurred as a tandem process involving the alcohol oxidation into the corresponding aldehyde followed by the Knoevenagel condensation with the CH-acid. The 3-trimethylsilyl-2-propyn-1-al is also known to react with nitromethane in the presence of catalytic amount of piperidine to afford a Knoevenagel adduct $Me_3SiC{\equiv}CCH{=}CHNO_2$ in 42% yield [2].

However in reaction of 3-trimethylsilyl-2-propyn-1-al (**I**) with nitromethane in acetonitrile in the presence of 5 mol% of diazabicyclooctane (DABCO) at room temperature instead of the expected nitroenine we isolated 4-trimethylsilylethynyl-4*H*-pyran-3,5-dicarbaldehyde (**III**). The reaction proceeded for 48 h and afforded the product in high yield (98% by ^{1}H NMR data). It was established that the nitromethane was not involved into the formation process of heterocycle **III** since in its absence under the same conditions (25°C, 5 mol% DABCO, MeCN, 48 h) diformylpyran **III** also was the only reaction product. Compound **III** was isolated by column chromatography on SiO_2, its structure was proved by NMR (^{1}H, ^{13}C, HSQC, HMBC), IR spectroscopy, and mass spectrometry, the composition was confirmed by elemental analysis.

We believe that the reaction starts by a nucleophilic addition of water to the triple bond of propynal **I** affording malodianaldehyde **II** which further reacts as a C-nucleophile with the carbonyl group of propynal **I** to furnish aldol **B**. Aldol **B** is able to condense further with the



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second molecule of malondialdehyde **II** to afford intermediate **C**, which via subsequent cyclocondensation results in pyran **III**. According to the suggested scheme the assembling of heterocycle **III** from three molecules of aldehyde **I** involves participation of one water molecule as a reagent. Therewith a molecule of hexamethyldisiloxane forms from the condensation of two trimethylsilanol molecules. At the use of small quantities of the aldehyde the traces of water in the solvent or the atmospheric moisture are sufficient for this process to occur.

The presence of a trimethylsilylethynyl moiety in the molecule of diformylpyran **III** and its high yield suggest that the desilylation occurs not with initial propynal **I** but with intermediate **A**.

Pyran **III** was also obtained in 65% yield (^{1}H NMR data) from propynal **I** in the presence of 20 mol% of 2-aminopyridine and 5 mol% of hydrochloric acid in the aqueous acetonitrile at room temperature in 5 days. Alongside with pyran **III** formed *N*-(2-pyridyl)-2-(trimethylsilylethynyl)-1,2-dihydropyridine-3,5-dicarbaldehyde [3].

Trimerization of an unsubstituted propynal was described [4, 5], but Wille *et al*. did not suggest a scheme of its formation. The presence in the pyran molecule of several reaction sites (a triple bond, Si–C_{sp} bond, aldehyde groups, and a push-pull fragment) provides a possibility to use it as a template in the purposeful synthesis of versatile functionally-substituted heterocyclic compounds.

4-Trimethylsilylethynyl-4*H*-pyran-3,5-dicarbaldehyde (III). A mixture of 0.217 g (1.72 mmol) of propynal **I**, 0.01 g (0.09 mmol) of DABCO, and 5 ml of anhydrous acetonitrile was charged into an ampule and maintained at room temperature for 48 h at intermittent shaking. The solvent was removed in a vacuum, the solid residue (0.13 g, 98%) was analyzed by ^{1}H NMR spectroscopy. After purifying by column chromatography (SiO_2, eluent chloroform) we isolated 0.095 g (72%) of colorless crystalline substance, mp 110–111°C. IR spectrum (KBr), cm^{-1}: 1240, 1530, 1595, 1660, 2175. ^{1}H NMR spectrum, δ, ppm: 0.07 s (9H, Me_3Si), 4.43 s (1H, CH–C≡), 7.32 s (2H, O–CH=), 9.50 s (2H, CH=O). ^{13}C NMR spectrum, δ, ppm: 0.14 (Me_3Si), 19.01 (CH–C≡), 86.05 (≡C–Si), 103.40 (CH–C≡), 120.61 (=C–CH=O), 155.86 (O–CH=), 187.70 (CH=O). Mass spectrum, *m/z* (I_{rel}%): $[M]^+$ 234 (32). Found, %: C 61.10; H 6.15; Si 11.43. $C_{12}H_{14}SiO_3$. Calculated, %: C 61.51; H 6.02; Si 11.99.

IR spectrum was recorded on a spectrometer Specord 75IR. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker DPX-400, internal reference HMDS, solvent $CDCl_3$. GC-MS analysis was carried out on a Hewlett-Packard instrument (electron impact 70 eV, mass-selective detector HP5901A), chromatograph HP5890, column Ultra-2 (5% dimethylsilicone), vaporizer temperatur 250°C, oven temperature 70–280°C, heating rate 20 deg/min, carrier gas helium. Silica gel Merck 60 (70–230 mesh) was used for column chromatography.

REFERENCES

1. Mareev, A.V., Medvedeva, A.S., Khatashkeev, A.V., Afonin, A.V., *Mendeleev Commun.,* 2005 (in press).
2. Borisova, A.I., Medvedeva, A.S., and Vyazankin, N.S., *Zh. Obshch. Khim.,* 1978, vol. 48, p. 2800.
3. Medvedeva, A.S., Mareev, A.V., Afonin, A.V., and Ushakov, I.A., *Zh. Org. Khim*., 2005, vol. 41, p. 478.
4. Wille, F. and Saffer, L., *Lieb. Ann. Chem.,* 1950, vol. 568, p. 34.
5. Wille, F. and Schwab, W., *Chem. Ber*., 1977, vol. 110, no. 3, p. 985.