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SHORT COMMUNICATIONS

Unprecedented Stability of Vinyloxy Group Under Conditions of Acid Hydrolysis: Synthesis of 1-[(2-Vinyloxy)ethyl]-1,5-dihydro-2*H*-pyrrol-2-ones*

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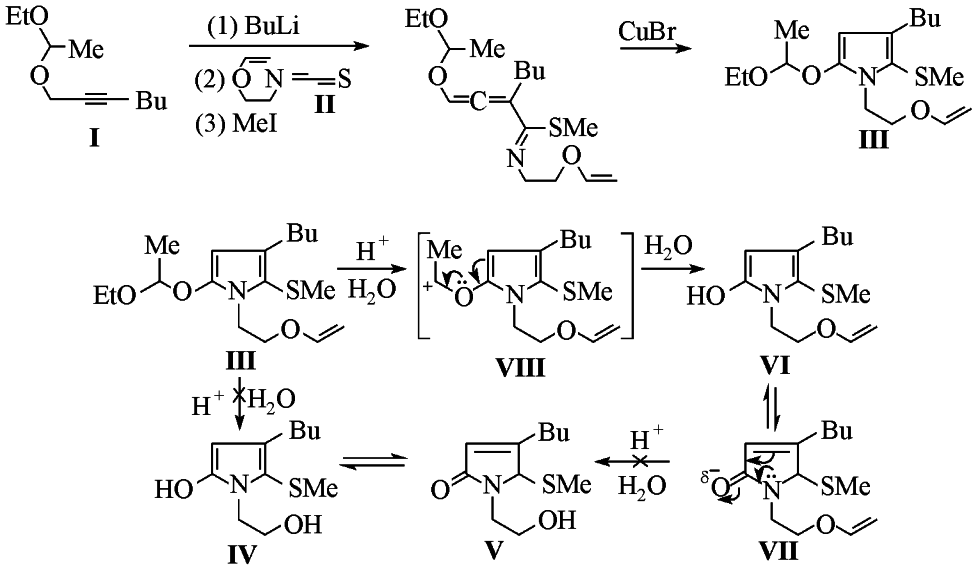
Within the framework of the fundamentally new strategy of pyrrol synthesis that we had developed by reaction of unsaturated carbanions with heterocumulenes [1–3] we introduced a new approach to building up of 2- and 3-hydroxy-substituted pyrrol ring proceeding from available isothiocyanates and 3-(1-ethoxyethoxy)-1-propyne (adduct of ethoxyethene with 2-propyn-1-ol) [4, 5].

At the use in reaction with lithiated (1-ethoxyethoxy)alkynes, e.g. with 1-(1-ethoxyethoxy)-2-heptyne (**I**), of 2-(vinyloxy)ethyl isothiocyanate (**II**) we were able alongside an acetal function to introduce into the pyrrole ring the second reaction site, highly active vinyloxy group. Therefore the synthetic opportunities of the arising 5(1-ethoxyethoxy)-2-(methylsulfanyl)-1-[2-(vinyloxy)ethyl]pyrroles (**III**) are widely extended.

An unprecedented inertness of vinyloxy group under conditions of acid hydrolysis was revealed. Unexpectedly on treating pyrrole **III** with water-dioxane mixture in the presence of HCl aiming at removal of acetal protection instead of obtaining 2-hydroxy-5-(methylsulfanyl)-1[2-(hydroxy)ethyl]-pyrrole (**IV**) or its tautomer **V** that should have formed taking into account the hydrolytic instability of typical vinyl ethers [6] we found a direct way to



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unknown up till now and difficult to prepare 2-hydroxy-5-(methylsulfanyl)-1-[2-(vinyloxy)ethyl]pyrroles (**VI**) which exist as tautomeric 1,5-dihydro-2*H*-pyrrol-2-ones (**VII**).

Obviously the rate of protolytic cleavage of unsymmetrical acetal is considerably higher than the rate of hydrolytic decomposition of vinyl ether. So large difference in reactivity of vinyloxy and acetal functions within the structure of compound **III** under identical hydrolysis conditions is apparently due to essentially dissimilar stability of carbocations arising in the limiting stage of the process. The formation of pyrrol-2-one **VII** as a single hydrolysis product is most likely caused by additional stabilization of carbocation **VIII** by conjugation. In its turn the high hydrolytic stability of the vinyloxy group in pyrrol-2-one **VII** that actually is a cyclic enamide may be due to the binding of the acid catalyst by the amide function, for instance, by the oxygen atom which acquires an excessive negative charge by conjugation effects.

4-Butyl-1-[(2-vinyloxy)ethyl)]-2-(methylsulfanyl)-5-(1-ethoxyethoxy)pyrrole (III). To a solution of 0.03 mol of BuLi in 20 ml of hexane and 30 ml of THF cooled to −100°C was added 4.78 g (0.026 mol) of alkyne **I**. After stirring for 30 min at −50°C the reaction mixture was again cooled to −100°C, and 3.5 g (0.026 mol) of isothiocyanate **II** was added thereto. After stirring for 30 min at −60°C to reaction mixture at −30°C was added 6.18 g (0.044 mol) of MeI and then (at 4°C) 0.7 g of finely dispersed CuBr. After self-heating to 20°C (within ~7 min) and additional stirring for 30 min at 35°C to the reaction mixture was added 100 ml of saturated NH_4Cl containing 2 g of NaCN, the mixture was stirred for 10 min, and the organic layer was then separated. The water fraction was extracted with ethyl ether (5 × 50 ml). The combined organic solution was dried with K_2CO_3, then it was passed through a column charged with the neutral Al_2O_3, and the solvent was removed on rotary evaporator. Yield 8.3 g (98%). By vacuum distillation was separated 5.87 g of pyrrole **III**, bp 145–147°C (0.6 mm Hg). ^{1}H NMR spectrum, δ, ppm: 0.92 t (3H, Me), 1.21 t (3H, Me), 1.34 m (2H, CH_2), 1.44 d (3H, Me), 1.49 m (2H, CH_2), 2.11 s (3H, SMe), 2.51 m (2H, CH_2), 3.50–3.78 m (2H, OCH_2), 3.85 m (2H, NCH_2), 3.95 d.d (1H, *cis*-CH_2=), 4.13 m (2H, OCH_2), 4.18 d.d (1H, *trans*-CH_2=), 5.19 q (1H, C<u>H</u>Me), 5.23 s (1H, H^4), 6.37 q (1H, OCH=). ^{13}C NMR spectrum, δ, ppm: 13.87 (Me), 15.02 (Me), 20.40 (SMe), 22.57 (CHM<u>e</u>), 23.20 (γ-CH_2), 26.75 (β-CH_2), 33.43 (α-CH_2), 40.92 (NCH_2), 63.01 (OCH_2), 86.35 (CH_2=), 88.28 (C^3), 101.77 (<u>C</u>HMe), 110.63 (C^4), 130.02 (C^5), 145.32 (C^2), 151.34 (OCH=). Found, %: C 62.28; H 9.32; N 4.69; S 9.61. $C_{17}H_{29}NO_3S$. Calculated, %: C 62.35; H 8.93; N 4.28; S 9.79.

4-Butyl-1-[(2-vinyloxy)ethyl)]-5-(methylsulfanyl)-1,5-dihydro-2*H*-pyrrol-2-one (VII). To a solution of 1 g (0.003 mol) of pyrrole **III** in 10 ml of dioxane and 3 ml of water cooled to 0°C was added 3 drops of 30% HCl. The mixture was stirred for 5 min and then extracted with ether. The extract was dried with $MgSO_4$, the solvent was removed on rotary evaporator. Yield 0.65 g (85%), n_D^{20} 1.5102. ^{1}H NMR spectrum, δ, ppm: 0.95 t (3H, Me), 1.37 m (2H, CH_2), 1.53 s (3H, SMe), 1.55 m (2H, CH_2), 2.35–2.52 m (2H, CH_2), 3.51–3.93 m (2H, OCH_2), 3.83 m (2H, NCH_2), 3.98 d.d (1H, *cis*-CH_2=), 4.15 d.d (1H, *trans*-CH_2=), 5.01 s (1H, H^3), 5.92 s (1H, H^5), 6.37 q (1H, OCH=). ^{13}C NMR spectrum, δ, ppm: 7.69 (SMe), 13.68 (Me), 22.34 (γ-CH_2), 28.04 (β-CH_2), 29.56 (α-CH_2), 38.15 (NCH_2), 66.57 (OCH_2), 67.75 (C^5), 87.05 (CH_2=), 122.12 (C^3), 151.34 (OCH=), 160.93 (C^4), 170.00 (C^2). Found, %: C 60.43; H 8.68; N 5.46; S 12.59. $C_{13}H_{21}NO_2S$. Calculated, %: C 61.14; H 8.29; N 5.48; S 12.56.

^{1}H and ^{13}C NMR spectra were registered on spectrometer Bruker DPX-400 at operating frequencies 400 and 100 MHz respectively, solvent $CDCl_3$, internal reference TMS. 2-(Vinyloxy)ethyl isothiocyanate (**II**) and 3-(1-ethoxyethoxy)-1-propyne were obtained by procedures from [1]. 1-(1-Ethoxyethoxy)2-heptyne (**I**) was prepared by lithiation of 3-(1-ethoxyethoxy)-1-propyne with lithium amide in liquid ammonia and treating it with BuBr by method [7].

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