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LETTERS TO THE EDITOR

FEATURES OF THE BASE-CATALYZED REACTION OF 1-VINYL-4,5-DIHYDRO-1*H*-BENZO[*g*]INDOLE-2-CARBALDEHYDE WITH PHENYLACETYLENE

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The current chemistry of pyrrolecarbaldehydes is one of the fundamental areas of fine organic synthesis. Pyrrolecarbaldehydes are used as building blocks in the preparation of porphyrins [1, 2], ligands for metal complexes [3, 4], medications [5], and precursors of optoelectronic materials [6-8]. Transformations of pyrrolecarbaldehydes give carbolines [9], cyanopyrroles [10], and divinylpyrroles [11]. The high synthetic potential of a carbonyl group in combination with the biological importance of pyrroles ensures a steady interest in this class of compounds.

There has recently been developed a preparative method for the preparation of 1-vinylpyrrole-2-carbaldehydes by the formylation of 1-vinylpyrroles [12, 13], which are readily obtained from ketones (*via* ketoximes) and acetylene [14, 15].

It is known that aldehydes react with acetylenes in the presence of a base, giving secondary acetylenic alcohols (the Favorsky reaction) [16, 17]. However, examples of pyrrolecarbaldehyde ethynylation using acetylenes have not been reported in the literature. The use of 1-vinylpyrrole-2-carbaldehydes as starting material in the synthesis of acetylenic alcohols could even further broaden their synthetic potential, thanks to the combination of ethynylcarbinol and vinylpyrrole fragments in a single molecule.

Continuing our studies in this area, we have found that 1-vinyl-4,5-dihydro-1*H*-benzo[*g*]indole-2-carbaldehyde (**1**) reacts with phenylacetylene (**2**) in a suspension of KOH–DMSO (20ºC, 1.5 h), forming the *E*-configured α,β-ethylenic ketone **5** in a non-optimized yield of 24%, rather than the expected acetylenic alcohol **3**.

It should be noted that the ketone **5** was obtained exclusively as the *E*-isomer. The analogous *Z*-configured product could not be identified by NMR spectroscopy or by GLC, even in the reaction mixture.

The formation of ketone **5** evidently begins with a nucleophilic addition of phenylacetylene **2** to the carbonyl group of the pyrrolecarbaldehyde **1**, to give the secondary acetylenic alcohol **3**, which prototropically rearranges *via* the allenic alcohol **4** into the α,β-ethylenic ketone **5**.

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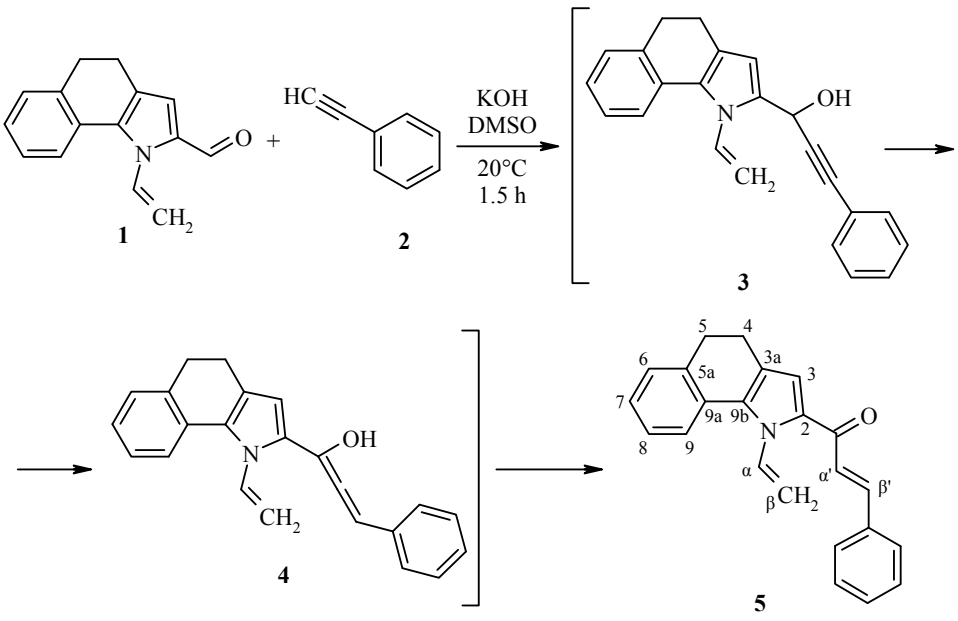

There are examples in the literature of the base-catalyzed isomerization of aromatic series propargyl alcohols (including those formed *in situ* [18-19]), to give α,β-unsaturated ketones [20-24]. However, this reaction has not been previously reported in the chemistry of pyrrole.

The discovered reaction can evidently be used as the basis for developing a preparatively acceptable and stereoselective method for currently unknown 1-vinylpyrrolyl(indolyl)styryl ketones, which are promising building blocks in the design of novel pyrrole and indole derivatives. Such a synthesis broadens preparative possibilities for making available 1-vinylpyrrole-2-carbaldehydes, and also adds to the chemistry of pyrrole and acetylene.

IR spectra were recorded on a Bruker Vertex 70 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer (400 and 100 MHz respectively) using $CDCl_3$ with HMDS as internal standard at δ 0.05 ppm. Assignment of the signals was achieved using the COSY, NOESY, HSQC and HMBC 2D NMR methods. Elemental analysis was performed on a Flash EA 1112 instrument. The melting point was determined on a Micro-Hot-Stage PolyTherm A instrument.

(*E*)-1-(1-Vinyl-4,5-dihydro-1*H*-benzo[*g*]indol-2-yl)-3-phenylprop-2-en-1-one (5). The pyrrolecarbaldehyde **1** (0.22 g, 0.99 mmol), phenylacetylene (**2**) (0.10 g, 0.99 mmol) and $KOH·0.5H_2O$ (0.06 g, 0.92 mmol) were stirred in DMSO (10 ml) for 1.5 h at room temperature. The reaction mixture was diluted with water (20 ml), neutralized with NH_4Cl and extracted with ether (7×5 ml). The ether extract was washed with water (3×5 ml) and dried over $MgSO_4$ (about 12 h). Evaporation of the ether gave a brown, resinous mass (0.30 g) which was chromatographed on a column (basic alumina, pH 8.25, eluent hexane–diethyl ether, 10:1) to yield the pure ketone **5**. Yield 0.08 g (24%). Orange crystals; mp 38-40ºC. IR spectrum, ν, cm^{-1}: 3435, 3105, 3080, 3057, 2929, 2895, 2849, 1646, 1590, 1539, 1495, 1465, 1428, 1356, 1301, 1199, 1172, 1152, 1128, 1109, 1068, 994, 974, 901, 764, 742, 684, 573. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.75-7.77 (1H, m, H-9); 7.74 (1H, dd, ^{3}J = 15.7, ^{3}J = 8.1, α-CH); 7.73 (1H, d, ^{3}J = 15.8, β'-CH); 7.58-7.61 (2H, m, H-2,6 Ph); 7.36-7.39 (2H, m, H-3,5 Ph); 7.37 (1H, d, ^{3}J = 15.8, α'-CH); 7.25-7.26 (1H, m, H-6); 7.16-7.18 (1H, m, H-7); 7.13-7.14 (2H, m, H-4 Ph, H-8); 7.03 (1H, s, H-3); 5.28 (1H, d, ^{3}J = 8.1) and 5.15 (1H, d, ^{3}J = 15.7, β-CH_2); 2.91 (2H, t, ^{3}J = 7.7, 4-CH_2); 2.67 (2H, t, ^{3}J = 7.7, 5-CH_2). ^{13}C NMR spectrum, δ, ppm: 176.8 (C=O); 141.6 (C-β'); 138.3 (C-9a); 136.6 (C-2); 135.4 (C-*i*); 134.6 (C-9b); 134.4 (C-α); 130.0 (C-*p*); 128.9 (C-*m*); 128.6 (C-6); 128.3 (C-*o*); 128.1 (C-5a); 127.2 (C-8); 126.1 (C-7); 124.7 (C-3a); 124.5 (C-9); 123.9 (C-α'); 118.0 (C-3); 113.5 (C-β); 30.7 (C-5); 22.1 (C-4). Found, %: C 85.19; H 6.05; N 4.08. $C_{23}H_{19}NO$. Calculated, %: C 84.89; H 5.89; N 4.30.

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