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LETTERS TO THE EDITOR

UNUSUAL REACTION OF 5-ETHYL-4,5,6,7-TETRAHYDROTHIENO[3,2-*c*]-PYRIDINE WITH ETHYL PROPIOLATE

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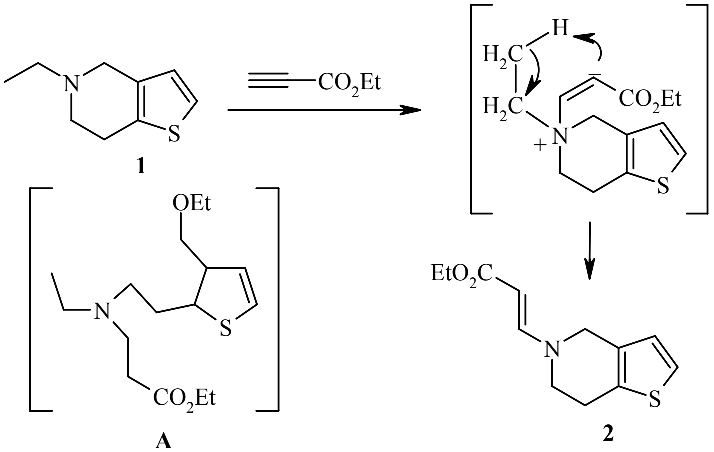
Earlier we carried out tandem transformations of tetrahydropyrrolo[3,2-*c*]pyridines treated with acetylenedicarboxylic ester [1]. We showed that the direction of these transformations is strongly affected by the properties of the solvent. In nonpolar solvents, 2- and 3-vinyl-2(3)-dimethoxycarbonylvinylaminoethyl-(isopropyl)pyrroles are formed [2]; in polar solvents, a mixture of these pyrroles with tetrahydropyrrolo[2,3-*d*]-azocines is formed [3]; and in protic solvents, 3-alkoxy(hydroxy)alkyl-2-dimethoxycarbonylvinylamino-alkylpyrroles are formed [4].



In continuing our study of the synthetic limits for tandem transformation of condensed tetrahydropyridines, we have studied the reaction of 5-ethyl-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridine (**1**) [5] with ethyl propiolate in ethanol. The reaction occurs readily at 20°C. However, instead of the expected ethoxymethylthiophene **A**, we find that the ethyl ester of (*E*)-3-(6,7-dihydro-4H-thieno[3,2-*c*]pyridin-5-yl)-acrylic acid (**2**) is formed in 52% yield, probably due to Hofmann cleavage in the initially formed zwitterion. In

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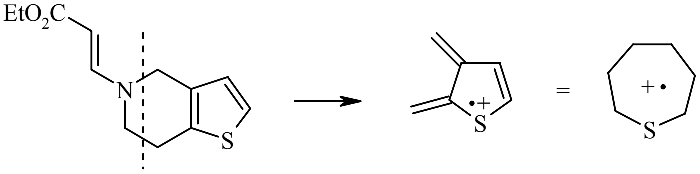
the ^1H NMR spectrum of compound **2**, we observe signals from all the protons in the molecule. The signals from the 4-CH_2 protons have the form of an AB spectrum at 4.90 and 4.50 ppm (^2J = 15.5 Hz). The protons from the N-vinyl group resonate at 6.45 and 6.03 ppm. The spin–spin coupling constant ^3J = 13.5 Hz indicates a *trans* configuration for the enamine moiety. In the mass spectrum, there is a low-intensity molecular ion peak with *m/z* 237 (6%). The maximum peak with *m/z* 110 is due to retrodiene decomposition of the M^+ ion [6], which leads to formation of a thiatropylium cation.



Thus we have established a novel direction for tandem conversions of condensed tetahydropyridines with activated alkynes.

(*E*)-3-(6,7-Dihydro-4H-thieno[3,2-*c*]pyridin-5-yl)acrylic Acid Ethyl Ester (2). A mixture of compound **1** (3 mmol) and ethyl propiolate (3.5 mmol) in absolute ethanol (15 ml) was stirred for 5 h at 20°C. The solvent was evaporated down to 2/3 volume and cooled, and the precipitated crystals were filtered out. Yield 0.37 g (52%); mp 203-204°C. Mass spectrum, *m/z* (I_{rel}, %): 237 $[M]^+$ (6), 192 (18), 167 (25), 152 (20), 111 (20), 110 (100), 44 (35). ^1H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 7.51 (1H, d, *J* = 5.4, 2-H); 6.91 (1H, d, *J* = 5.4, 3-H); 6.44 (1H, d, *J* = 13.5, =CH–N); 6.00 (1H, d, *J* = 13.5, =CH–CO_2Et); 4.93 (1H, d, *J* = 15.5, 4-H); 4.52 (1H, d, *J* = 15.5, 4-H); 4.04 (1H, m, 6-H); 3.79 (1H, m, 6-H); 3.63 (2H, q, *J* = 7.3, $\underline{CH_2}$–CH_3); 3.17 (1H, m, 7-H); 2.90 (1H, m, 7-H); 1.23 (3H, t, *J* = 7.3, CH_2–$\underline{CH_3}$). Found, %: C 60.43; H 6.12; N 5.92. $C_{12}H_{15}NO_2S$. Calculated, %: C 60.76; H 6.33; N 5.90.

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