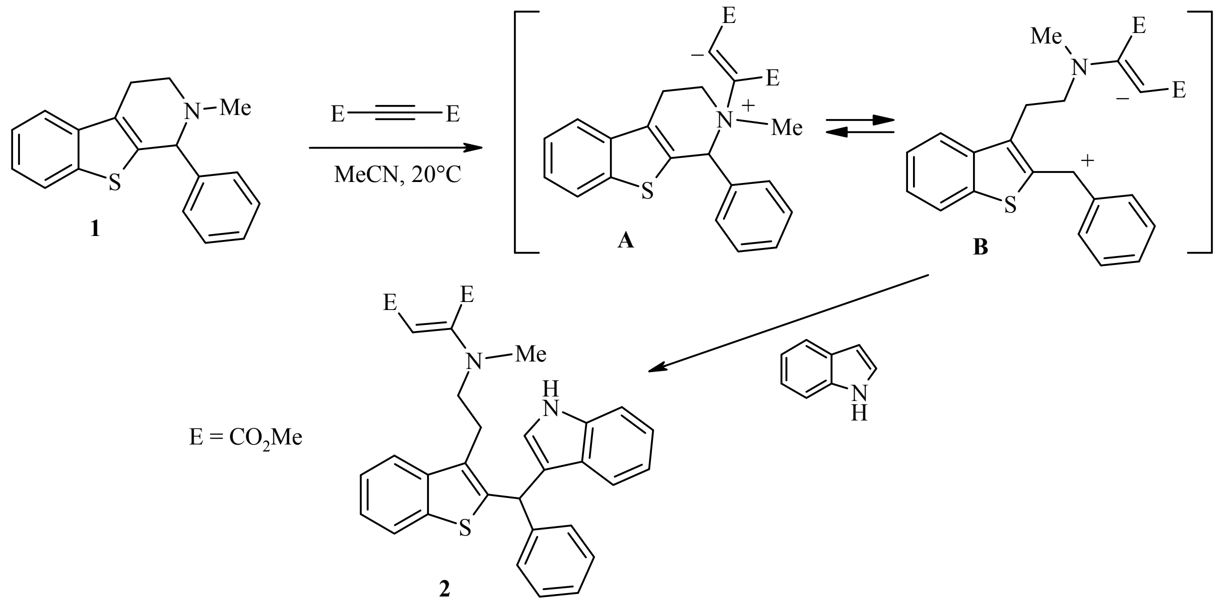
Chemistry of Heterocyclic Compounds, Vol. 46, No. 3, 2010

THE CHEMISTRY OF THE TANDEM REACTION OF 1-ARYLTETRAHYDROBENZOTHIENO[2,3-*c*]PYRIDINES WITH ACTIVATED ALKYNES

L. G. Voskressensky[1]*, T. N. Borisova[1], S. A. Kovaleva[1], L. N. Kulikova[1], A. V. Listratova[1], S. V. Tolkunov[2], and A. V. Varlamov[1]

Keywords: benzothienopyridines, tandem reaction.

Complex reactions of 1,2,3-trisubstituted benzothieno[2,3-*c*]pyridines with activated alkynes occur in methanol to form multicomponent mixtures from which products of cleavage of the tetrahydropyridine ring have been identified [1]. We propose that this feature of the transformation is due to the formation of carbocations (stabilized by methyl groups) *via* cleavage of the C(1)–N bond in the intermediate ammonium



---

* To whom correspondence should be addressed, e-mail: lvoskressensky@sci.pfu.edu.ru.

[1]Peoples' Friendship University of Russia, Moscow 117198, Russia.
[2]L. M. Litvinenko Institute of Physical Organic Chemistry and Coal Chemistry, National Academy of Sciences of Ukraine, Donetsk 83114, Ukraine; e-mail: stolkunov@yahoo.com.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 447-449, March, 2010. Original article submitted January 27, 2010.

zwitterion [1]. In order to confirm this proposal we have carried out the reaction of the 1-phenyltetrahydrothieno-[2,3-*c*]pyridine **1** with acetylene dicarboxylic ester (ADCE) in the presence of indole as an acceptor of the potential carbocation.

The main reaction product was the benzothiophene **2** obtained in 76% yield. Its formation confirms our proposal. The zwitterion **A** is converted to the stable diaryl type carbocation **B** which is captured by the indole.

IR spectra (KBr) were recorded on an Infralum FT-801 Fourier spectrometer. ^{1}H and ^{13}C NMR spectra were taken on a Bruker WP-400 instrument (400 and 100 MHz respectively) using $CDCl_3$ and with TMS as internal standard. Chromato-mass spectra were obtained on a system including an Agilent 1100 series liquid chromatograph and an Agilent Technologies LC/MSD VL mass spectrometer using electrospray ionization (APCI, Sedex 75 ELSD).

Dimethyl (*E*)-2-[(2-{2-[1H-indol-3-yl(phenyl)methyl]-1-benzothien-3-yl}ethyl)(methyl)amino)but-2-ene Dicarboxylate (2). Indole (0.15 g, 2 mmol) and ADCE (0.47 g, 3.3 mmol) were added to a solution of the benzothienopyridine **1** (0.3 g, 1.1 mmol) in acetonitrile (25 ml). The reaction was carried out at room temperature for 30 days and was monitored using TLC. Solvent was evaporated and the residue was chromatographed on aluminium oxide (neutral Brockmann 1) using ethyl acetate–hexane (1:5). Yield 76% as a colorless oil with R_f 0.32 (Sorbfil, ethyl acetate–hexane, 1:2). IR spectrum, ν, cm^{-1}: 1736 (CO), 1684 (CO). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.54 (3H, s, NCH_3); 3.02-3.06 (1H, m, CH_2); 3.14-3.19 (3H, m, CH_2); 3.65 (3H, s, CO_2CH_3); 3.80 (3H, s, CO_2CH_3); 4.54 (1H, s, $=C\underline{H}CO_2CH_3$); 6.05 (1H, s, $CHAr_3$); 6.76 (1H, d, *J* = 1.6, $C\underline{H}NH$); 7.01-7.04 (1H, m, H Ar); 7.19 (1H, td, *J* = 1.1 and *J* = 7.7, H Ar); 7.27-7.40 (9H, m, H Ar); 7.70 (2H, t, *J* = 7.7, H Ar); 8.09 (1H, br. s, $CHN\underline{H}$). ^{13}C NMR spectrum, δ, ppm: 25.7, 37.4, 42.3, 50.8, 52.5, 52.9, 84.6, 111.3, 118.8, 119.3, 119.7, 121.1, 122.4, 122.5, 123.9, 124.0, 124.1, 126.7, 127.0, 127.3, 128.6 (4C), 136.5, 139.0, 140.0, 143.0, 145.8, 154.4, 166.1, 168.0. LC-MS spectrum: $[M+H]^+$ 539. Found, %: C 71.29; H 5.67; N 5.29. $C_{32}H_{30}N_2O_4S$. Calculated, %: C 71.35; H 5.61; N 5.20. M 538.

This work was carried out with the financial support of the Russian Fund for Basic Research and the Ukrainian National Academy of Sciences (grant 08-03-90451 Ukraine).

REFERENCES

1. L. G. Voskressensky, T. N. Borisova, A. V. Listratova, E. A. Sorokina, S. V. Tolkunov, and A. V. Varlamov, *Izv. Akad. Nauk, Ser. Khim.*, 1003 (2007).