Letters to the Editor

Regio- and stereoselective ring opening in the reactions of ethyl 2-aryl-4-azidopyrimidine-5-carboxylates with ethyl cyanoacetate: formation of highly polarized bis(en)amines

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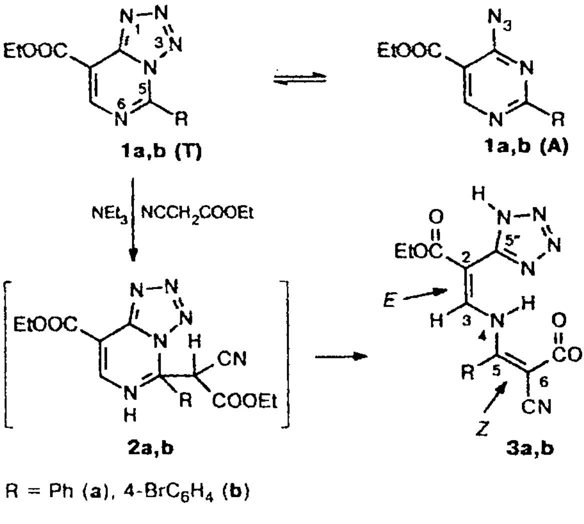
Condensation of (hetero)aromatic azides with ethyl cyanoacetate in the presence of bases is a method for the reduction of the azido group to amine and the synthesis of ethyl 5-amino-1-(het)aryl-1*H*-1,2,3-triazole-4-carboxylates (see Ref 1 and literature cited therein). In the case of (het)arylazides with *o*-$CO_2R(CN)$-substituents, the intramolecular condensation of primarily formed 5-aminotriazoles, resulting in a tricyclic system, occurs under the reaction conditions (see Refs. 2 and 3 and literature cited therein). The reactions of 4-azidopyrimidines (**1A**) with ethyl cyanoacetate in the presence of Et_3N in ethanol at −20 °C (Scheme 1) occurs unexpectedly with regio- and stereoselective ring opening and formation of *E,Z*-bis(en)amines (**3a,b**) (according to the analytical and spectral data).

Enamines **3** are evidently obtained by the addition of ethyl cyanoacetate to tautomer **T** (for compounds **1a,b**, the content of the **A** form is 91 and 100% in $CDCl_3$ and 42 and 53% in DMSO-d_6) followed by pyrimidine ring opening in intermediates **2**.

Scheme 1



Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 7, pp. 1453—1454, July, 1998.

1066-5285/98/4707-1413 $20.00

The E-configuration relative to the C=C bond of compounds **3** was confirmed by the values of vicinal SSC constants in the ^{13}C NMR spectra, for example, for **3a** $^3J^{cis}_{C(1)O,H(3)}$ = 3.7 Hz < $^3J^{trans}_{C(5''),H(3)}$ = 10.3 Hz (*cf.* to E-enamine similar in structure[4]). The downfield shifts of the NH signals in the ^{1}H NMR spectra prove the presence of a strong intramolecular hydrogen bond. These data and the same set of signals in $CDCl_3$ and DMSO-d_6 indicate the Z-configuration of another C=C bond in compounds **3**.

Diethyl (2*E*,5*Z*)-6-cyano-5-phenyl-2-(1*H*-tetrazol-5-yl)-4-azahepta-2,5-dienoate (3a), yield 75%, m.p. 195—198 °C (decomp.). IR (KBr), ν/cm^{-1}: 2210 (CN), 1710, 1690 (C=O). ^{1}H NMR (400 MHz, DMSO-d_6), δ: 1.09 (t, 3 H, Me); 1.33 (t, 3 H, Me); 4.15 (q, 2 H, CH_2); 4.39 (q, 2 H, CH_2); 7.52 (d, 1 H, 3-H, $^3J_{H(3),NH}$ = 12.4 Hz); 7.70—7.60 (m, 5 H, Ph); 13.35 (d, 1 H, NH, $^3J_{NH,H(3)}$ = 12.4 Hz). ^{13}C NMR (100 MHz, DMSO-d_6), δ: 13.75 (Me); 14.09 (Me); 61.12 (CH_2); 61.71 (CH_2); 84.73 (C(6)); 95.94 (C(2)); 116.15 (CN); 128.84, 129.25, 130.36, 131.42 (Ph); 141.91 (C(3)); 148.5 (C(5″)); 163.66 (C(5)); 163.84 (C(7)); 164.80 (C(1)). High-resolution MS, *m/z*: M^+ 382.1395, calculated M 382.1389.

Diethyl (2*E*,5*Z*)-5-(4-bromophenyl)-6-cyano-2-(1*H*-tetrazol-5-yl)-2-azahepta-2,5-dienoate (3b), yield 77%, m.p. 201—205 °C (decomp.). IR (KBr), ν/cm^{-1}: 2210 (CN), 1690 br. (C=O). ^{1}H NMR (200 MHz), δ: in DMSO-d_6: 1.13 (t, 3 H, Me); 1.33 (t, 3 H, Me); 4.20 (q, 2 H, CH_2); 4.40 (q, 2 H, CH_2); 7.48 (d, 1 H, 3-H, $^3J_{H(3),NH}$ = 12.4 Hz); 7.62 (d, 2 H, Ph, J = 8.5 Hz); 7.91 (d, 2 H, Ph, J = 8.5 Hz); 13.35 (d, 1 H, NH, $^3J_{NH,H(3)}$ = 12.4 Hz); 16.08 (br.s, 1H, $NH_{tetr.}$); in $CDCl_3$: 1.19 (t, 3 H, Me); 1.39 (t, 3 H, Me); 4.23 (q, 2 H, CH_2); 4.47 (q, 2 H, CH_2); 7.34 (d, 2 H, Ph, J = 8.5 Hz); 7.67 (d, 1 H, 3-H, $^3J_{H(3),NH}$ = 12.0 Hz); 7.75 (d, 2 H, Ph, J = 8.5 Hz); 13.28 (br.s, 1 H, $NH_{tetr.}$); 13.68 (d, 1 H, NH, $^3J_{NH,H(3)}$ = 12.0 Hz). High-resolution MS, *m/z*: M^+ 460.0494, calculated M 460.0495 for $C_{18}H_{17}BrN_6O_4$.

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Received January 5, 1998;
in revised form March 17, 1998

Chemiluminescence in the reaction of dimethyldioxirane with quaternary ammonium salts

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The reaction of methyl(trifluoromethyl)dioxirane with Bu_4NI (**1**) has been studied previously.[1] It was shown that salt **1** catalyzes the decomposition of dioxirane to give 1,1,1-trifluoroacetone and oxygen. Superoxide-ion is the intermediate of this reaction.

In this work, we have shown for the first time that the reaction of dimethyldioxirane (**2**)[2] with quaternary ammonium salts $Et_3(PhCH_2)NCl$ (**3**), $Et_3(PhCH_2)NBr$ (**4**), and **1** was accompanied by intense chemiluminescence (CL) in the visible and IR spectral regions. Salts **1**, **3**, and **4** were purified by recrystallization. The reaction was carried out in a temperature-controlled 2 mL-reactor at 0—33 °C. A 0.02—0.2 *M* solution of a quaternary ammonium salt (0.01—0.1 mmol) in MeCN was placed in the reactor, and a 0.012—0.05 *M* temperature-controlled solution of salt **2** (0.012—0.05 mmol) in an acetone—acetonitrile mixture (1 : 1, v/v). The changes in intensity of chemiluminescence in the visible and IR regions was measured as reported earlier.[3] The kinetics of consumption of salt was studied by spectrophotometry.[4]

In the case of salt **3**, the visible CL was of unusual character. Several maxima were observed on the curves of the changes in the CL intensity. The number of

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 7, pp. 1455—1456, July, 1998.
1066-5285/98/4707-1414 $20.00 © 1998 Plenum Publishing Corporation