Chemistry of Heterocyclic Compounds, Vol. 38, No. 9, 2002

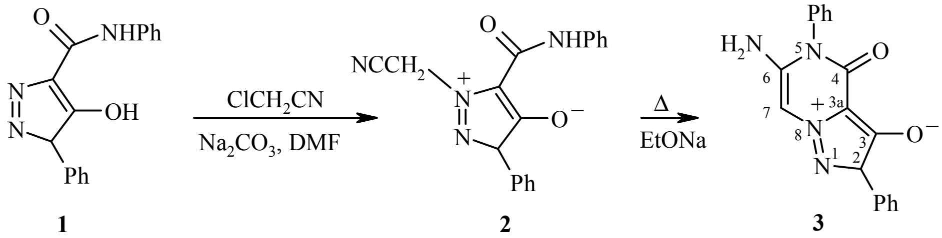
SYNTHESIS OF [1,2,3]TRIAZOLO-[1,5-*a*]PYRAZINIUM-3-OLATE

Yu. I. Nein, Yu. Yu. Morzherin, Yu. A. Rozin, and V. A. Bakulev

Keywords: 1,2,3-triazolo[1,5-*a*]pyrazinium-3-olates, triazoles, alkylation reactions, zwitter-ion.

In previous work [1], we showed that the alkylation of sodium salts of 1-aryl- and 1-arylmethyleneamino-1,2,3-triazol-5-olates by alkyl halides leads to a zwitter-ion, namely, 3-alkyl-1,2,3-triazol-3-ylium-5-olate. We have attempted to use this reaction for the synthesis of new zwitter-ions of condensed heterocyclic systems.

We found that the reaction of 1-phenyl-1,2,3-triazole-4-N-phenylcarboxamide (**1**) with chloroacetonitrile leads to the analogous alkylation product **2**, which, upon heating at reflux, reacts with sodium ethylate to give [1,2,3]triazolo[1,5-*a*]pyrazinium-5-olate **3**. The ^{13}C NMR spectrum of **3** shows $^3J_{H(6)-C(3a)}$ = 3.2 Hz, while the signal for $C_{(3)}$ is a singlet.



1-Cyanomethyl-3-phenyl-5-phenylcarbamoyl-3H-1,2,3-triazolinium-4-olate (2). Chloroacetonitrile (0.20 ml, 3 mmol) was added to a suspension of triazole **1** (0.28 g, 1 mmol) and Na_2CO_3 (0.11 g, 1 mmol) in DMF (1 ml) and heated for 3 h at 100°C. After cooling to room temperature, **2** was precipitated out by adding water (50 ml), filtered off, and crystallized from ethanol. Yield of **2** 0.21 g (66%); mp 144°C. Mass spectrum, *m/z* (I_{rel}, %): 319 [M$^+$] (55), 227 (16), 187 (11), 116 (5), 105 (15), 92 (5), 77 (100). ^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm, *J* (Hz): 10.22 (1H, s, NH); 8.00 (2H, d, *J* = 7.3, ArH); 7.50-7.77 (5H, m, ArH); 7.35 (2H, dd, *J* = 7.6, *J* = 8.2, ArH); 7.11 (1H, dd, *J* = 7.5, *J* = 8.1, ArH); 6.11 (2H, s, CH_2). Found, %: N 22.30. $C_{17}H_{13}N_5O_2$. Calculated, %: N 21.94.

6-Amino-4-oxo-2,5-diphenyl-4,5-dihydro-2H-1,2,3-triazolo[1,5-*a*]pyrazinium-5-olate (3). A solution of **2** (0.20 g, 0.6 mmol) and sodium ethylate prepared from sodium (0.014 g, 0.6 mmol) in absolute ethanol (25 ml) was heated at reflux for 5 h and cooled. The precipitate formed was filtered off and crystallized from ethanol to give 0.16 g (80%) of **3**; mp 280°C. Mass spectrum, *m/z* (I_{rel}, %): 319 [M$^+$] (39), 278 (5), 227 (15), 187 (11), 130 (14), 119 (10), 116 (6), 105 (5), 93 (27), 92 (8), 91 (8), 77 (100). ^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm, *J* (Hz): 8.29 (1H, s, NH); 8.03 (2H, d, *J* = 7.9, ArH); 7.36-7.50 (4H, m, ArH); 7.40 (1H, br. s, NH);

Urals State Technical University, 620002 Yekaterinburg, Russia; e-mail: morzherin@htf.ustu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1302-1303, September, 2002. Original article submitted May 29, 2002.

7.15-7.22 (3H, m, ArH); 6.98 (1H, s, $C_{(7)}H$); 6.82 (1H, dd, *J* = 7.2, *J* = 7.3, ArH), ^{13}C NMR spectrum (DMSO-d_6), δ, ppm, *J* (Hz): 164.32 (s, $C_{(4)}$); 153.77 (s, $C_{(3)}$); 152.72 (d, *J* = 3.4, $C_{(6)}$); 141.87 (dd, *J* = 8.0, *J* = 9.3, $C_{(Ph)}$); 136.53 (dd, *J* = 9.4, *J* = 8.8, $C_{(Ph)}$); 128.84 (dd, *J* = 157.3, *J* = 8.2, $C_{(Ph)}$); 128.50 (dd, *J* = 158.4, *J* = 7.4, $C_{(Ph)}$); 125.48 (ddd, *J* = 162.7, *J* = 7.6, *J* = 7.3, $C_{(Ph)}$); 120.23 (ddd, *J* = 159.8, *J* = 7.3, *J* = 7.9, $C_{(Ph)}$); 119.16 (dm, *J* = 165.0, $C_{(Ph)}$); 118.77 (dm, *J* = 161.8, $C_{(Ph)}$); 106.72 (d, *J* = 3.2, $C_{(3a)}$); 85.41 (d, *J* = 189.4, $C_{(7)}$). Found, %: N 21.59. $C_{17}H_{13}N_5O_2$. Calculated, %: N 21.94.

This work was carried out with the financial support of CRDF (Project RC1-2393-EK-02) and the Russian Basic Research Fund RFFI (Grant 02-03-96421 Ural).

REFERENCES

1. Yu. A. Rozin, E. A. Savel'eva, Yu. Yu. Morzherin, W. Dehaen, S. Toppet, L. Van Meervelt, and V. A. Bakulev, *J. Chem. Soc., Perkin Trans. 1*, 211 (2002).