SYNTHESIS OF 2,2'-(2-OXOIMIDAZOLIDINE-4,5-DIYLIDENE)DIACETATES

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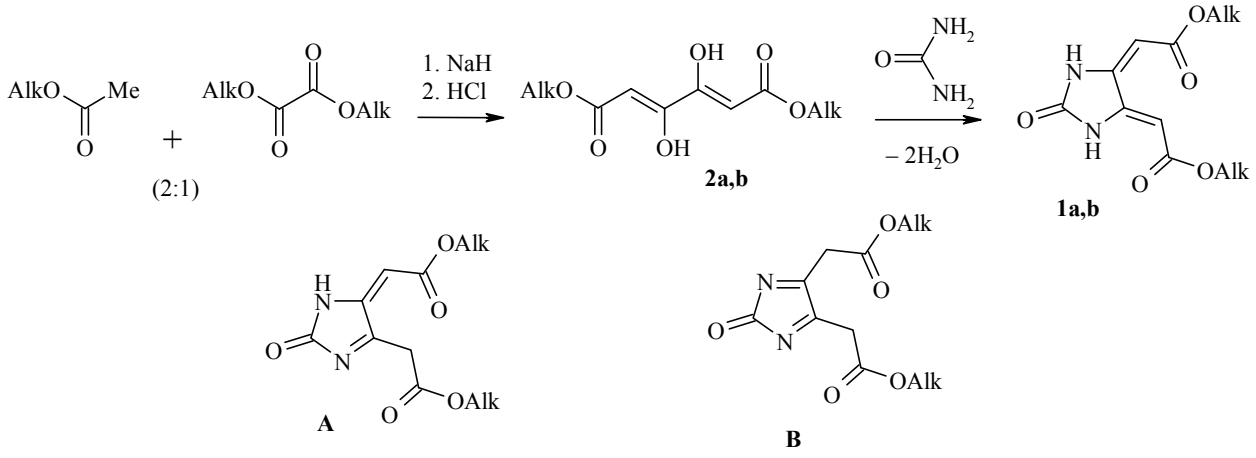
Ylidene derivatives of nitrogen oxoheterocycles have been used in the synthesis of biologically active compounds [1-3]. Bisoxoylidene-substituted azoles and, in particular, diylidene acetates derived from imidazolidine had not been available prior to our investigation.

We have developed a simple method for the preparation of previously unreported 2,2'-(2-oxoimidazolidine-4,5-diylidene)diacetates **1a**,**b** by the reaction of esters of 3,4-dihydroxy-2,4-hexadiene-1,6-dioic acid (the dienol form of dialkyl ketipinates) **2a**,**b** with urea.



1, 2 a Alk = Me, **b** Alk = Et

Starting dialkyl ketipinates **2a**,**b** were obtained by the condensation of alkyl acetates with dialkyl oxalates in the presence of sodium hydride [4].

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The ^{1}H NMR spectra of **1a**,**b** show singlets for magnetically-equivalent protons of two methine groups at 5.55 and 5.57 ppm as well as two heterocyclic ring NH groups at 9.23 and 9.25 ppm. The finding of these protons at relatively high field suggests (2*E*,2'*E*) configuration for ylideneazoles **1a**,**b**. There are no signals for methylene group protons. This absence permits us to exclude possible tautomeric forms, namely, the imidazoline form (**A**) and imidazole form (**B**), in solutions of compounds **1a**,**b**.

The IR spectra of imidazolidines **1a**,**b** were taken on an FT-02 Infralyum FT-02 spectrometer in vaseline mulls. The ^{1}H NMR spectra were taken on a Bruker DRX-500 spectrometer at 500 MHz in $CDCl_3$ with TMS as the internal standard.

Dimethyl Ester of 2,2'-(2-Oxoimidazolidine-4,5-diylidene)diacetic Acid (1a). A mixture of dimethyl ketipinate **2a** (1.0 g, 5 mmol) and urea (0.3 g, 5 mmol) was heated for 5 min at 110°C. The residue was triturated with ether and recrystallized from ethanol to give 0.18 g (16%) compound **1a**; mp 225-226°C. IR spectrum, ν, cm^{-1}: 3397 (NHCO), 3022 (CH), 2954 (OCH_3 ν_{as}), 2846 (OCH_3 ν_s), 1770 ($COOCH_3$), 1697 (CONH), 1649 (C=C), 1445 (CH_3 δ_{as}), 1379 (CH_3 δ_s), 1287 (C–O–C $\nu_{as\ ester}$), 1092 (C–O–C $\nu_{s\ ester}$), 1034, 988, 929, 882, 848, 799 (C–C ν_{skel}), 518 (C–C δ_{skel}). ^{1}H NMR spectrum, δ, ppm: 3.77 (6H, s, $2OCH_3$); 5.57 (2H, s, 2CH); 9.23 (2H, s, 2NH). Found, %: C 47.98; H 4.21; N 12.17. $C_9H_{10}N_2O_5$. Calculated, %: C 47.79; H 4.46; N 12.39.

Diethyl Ester of 2,2'-(2-Oxoimidazolidine-4,5-diylidene)diacetic Acid (1b) was obtained analogously from diethyl ketipinate **2b** (1.15 g, 5 mmol) and urea (0.3 g, 5 mmol). The yield of compound **1b** was 0.28 g (22%); mp 170°C (ethanol). IR spectrum, ν, cm^{-1}: 3395 (NHCO), 3034 (CH), 2983 (CH_3 ν_{as}), 2940 (CH_2 ν_{as}), 2873 (CH_2 ν_s), 1759 ($COOC_2H_5$), 1685 (CONH), 1650 (C=C), 1465 (CH_2 δ_{scis}), 1423 (CH_3 δ_{as}), 1365 (CH_3 δ_s), 1324 (CH_2 δ_{wag}), 1280 (C–O–C $\nu_{as\ ester}$), 1088 (C–O–C $\nu_{s\ ester}$), 1033, 975, 929, 816 (C–C ν_{skel}), 743 (CH_2 δ_{rock}), 480 (C–C δ_{skel}). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.30 (6H, t, $J = 7.1$, $2OCH_2CH_3$): 4.23 (4H, q, $J = 7.1$, $2OCH_2CH_3$); 5.55 (2H, s, 2CH); 9.25 (2H, s, 2NH). Found, %: C 52.25; H 5.32; N 10.92. $C_{11}H_{14}N_2O_5$. Calculated, %: C 51.97; H 5.55; N 11.02.

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REFERENCES

1. S. G. Perevalov, Ya. V. Burgart, V. I. Saloutin, and O. N. Chupakhin, *Usp. Khim.*, **70**, 1039 (2001).
2. V. O. Kozminykh and E. N. Kozminykh, in: *Selected Methods for the Synthesis and Modification of Heterocycles* [in Russian], vol. 1, IBS Press, Moscow (2003), p. 255.
3. P. P. Mukovoz, V. O. Kozminykh, E. A. Kirillova, A. S. Ivanov, and A. A. Fadeev, in: *Abstracts of the International Conference on New Trends in Heterocyclic Chemistry* [in Russian], Stavropol State University, Kislovodsk (2009), p. 392.
4. V. O. Kozminykh, P. P. Mukovoz, and E. A. Kirillova, *Vestn. Orenburgsk. Gos. Univ.*, No. 5, 155 (2009); http://vestnik.osu.ru/2009_5/28.pdf