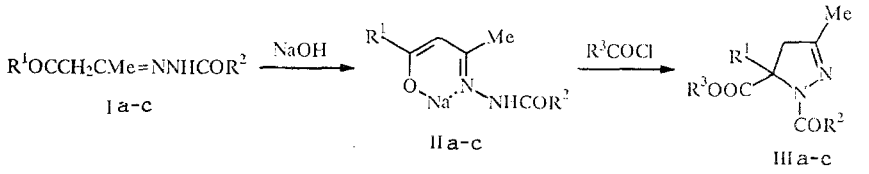
1-ACYL-5-ACYLOXY-2-PYRAZOLINES

A. K. Zelenin, B. A. Ershov, I. P. Bezhan, and K. N. Zelenin

Salts of nitrogen derivatives (imines, oximes, hydrazones) of 1,3-dioxo compounds with alkali metals are known. We found that upon the action of base on the monoacylhydrazones of acetylacetone and benzoylacetones Ia-c [1, 2] in methanol, the corresponding sodium salts IIa-c were formed in quantitative yield. Upon treatment of a suspension of the salts in acetonitrile with acyl chlorides, the previously unknown 1-acyl-5-acyloxy-2-pyrazolines IIIa-c were formed in yields of 40-50%.



Ia-c IIa-c IIIa-c

I, IIa) R^1 = Me, R^2 = Ph; b) R^1 = Ph, R^2 = Me; c) R^1 = R^2 = Ph; IIIa) R^1 = R^3 = Me, R^2 = Ph; b) R^2 = R^3 = Ph, R^2 = Me; c) R^1 = R^2 = Ph, R^3 = Me

Salt IIa* ($C_{12}H_{13}N_2NaO_2$). ^{1}H NMR spectrum (DMSO-d_6): 1.84 (3H, s, CH_3), 2.06 (3H, s, CH_3), 4.70 (1H, s, CH), 7.10-8.00 (5H, m, H_{arom}), 12.50 ppm (1H, s, NH).

Salt IIb ($C_{12}H_{13}N_2NaO_2$). ^{1}H NMR spectrum (DMSO-d_6, two forms): 1.98 (3H, s, CH_3), 2.30 (3H, s, CH_3), 5.64 (1H, s, CH), 7.30-8.00 (5H, m, H_{arom}), 14.60 (1H, s, NH); 2.05 (3H, s, CH_3), 2.10 (3H, s, CH_3), 5.18 (1H, s, CH), 7.30-8.10 (5H, m, H_{arom}), 14.60 ppm (1H, s, NH). The doubled signals probably are produced by the (Z, E)-isomers, characteristic of derivatives of acetylhydrazines [3].

Salt IIc ($C_{17}H_{15}N_2NaO_2$). ^{1}H NMR spectrum (DMSO-d_6): 2.38 (3H, s, CH_3), 5.72 (1H, s, CH), 7.40-8.30 (10H, m, H_{arom}), 10.68 ppm (1H, s, NH).

5-Acetyloxy-1-benzoyl-3,5-dimethyl-2-pyrazoline (IIIa, $C_{14}H_{16}N_2O_3$). Oil, R_f 0.6 (CCl_4–benzene–acetone, 2:1:1). ^{1}H NMR spectrum ($CDCl_3$): 1.76 (3H, s, CH_3), 2.04 (3H, s, CH_3), 2.22 (3H, s, CH_3), 3.18, 3.56 (2H, AB system, J = 18 Hz, CH_2), 7.20-7.80 ppm (5H, m, H_{arom}).

1-Acetyl-5-benzoyloxy-3-methyl-5-phenyl-2-pyrazoline (IIIb, $C_{19}H_{18}N_2O_3$). Oil, R_f 0.4 (ether–hexane, 1:1). ^{1}H NMR spectrum ($CDCl_3$): 1.77 (3H, s, CH_3), 1.87 (3H, s, CH_3), 3.63, 4.27 (2H, AB system, J = 18 Hz, CH_2), 7.33-8.33 ppm (10H, m, H_{arom}).

5-Acetyloxy-1-benzoyl-3-methyl-5-phenyl-2-pyrazoline (IIIc, $C_{19}H_{18}N_2O_3$). mp 105-106°C (hexane–benzene). ^{1}H NMR spectrum ($CDCl_3$): 1.91 (3H, s, CH_3), 2.20 (3H, s, CH_3), 3.69, 4.12 (2H, AB system, J = 18 Hz, CH_2), 7.20-7.94 ppm (10H, m, H_{arom}).

Elemental analysis data for C, H. and N corresponded with the calculated values.

The mechanism of formation of the 1-acyl-5-acyloxy-2-pyrazolines is being studied at the present time because of interest in their role as polyfunctional derivatives of pyrazole.

*The salts II melted above 250°C with decomposition.

St. Petersburg State University, St. Petersburg 199004. S. M. Kurova Academy of Military Medicine, St. Petersburg 194175. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 564-565, April, 1993. Original article submitted May 6, 1993.

0009-3122/93/2904-0485$12.50

REFERENCES

1. V. G. Yusupov, S. I. Yakimovich, S. D. Nasirdinov, and N. A. Parpiev, Zh. Org. Khim., **16**, 415 (1980).
2. S. I. Yakimovich, V. N. Nikolaev, and V. Yu. Kutsenko, Zh. Org. Khim., **18**, 762 (1982).
3. K. N. Zelenin, I. P. Bezhan, V. A. Khrustalev, and V. P. Nikolaev, Zh. Org. Khim., **14**, 574 (1977).