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CYCLIZATION OF 6-CHLORO-2,3-DIAZAHEXA-1,3,5-TRIENE TO 1-CHLOROMETHYLPYRAZOLE WITH [1,3] MIGRATION OF THE CHLORINE ATOM

N. A. Konyukhova, O. P. Krasnykh, Z. G. Aliev, and A. N. Maslivets

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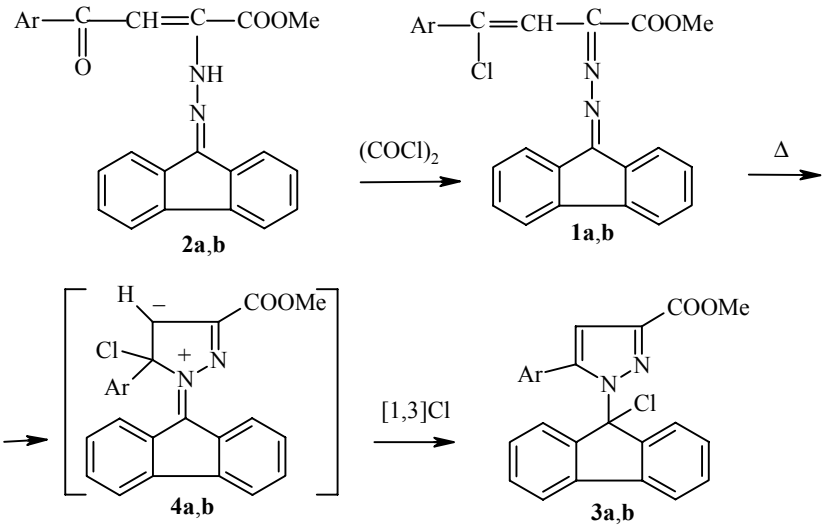
When solutions of methyl esters of 4-aryl-2-(9-fluorenylidene)hydrazono-4-chloro-3-butenoic acids **1a,b** [1], synthesized from the methyl esters of 4-aryl-4-oxo-2-(9-fluorenylidene)hydrazino-2-butenoic acids **2a,b** and oxalyl chloride, are held in *p*-xylene at 138-140°C for 20 min, they undergo ring closure to methyl 5-aryl-1-(9-chloro-9-fluorenyl)-1H-3-pyrazolecarboxylates **3a,b**, identified by X-ray diffraction.



1–4 a Ar = Ph, **b** Ar = *p*-$EtOC_6H_4$

Cyclization of compounds **1a,b** probably occurs through the corresponding zwitterions **4a,b** with subsequent stabilization due to [1,3] sigmatropic migration of the chlorine atom.

Analogs of compounds **3a,b** containing an OH group instead of a chlorine atom are probably intermediates in cyclization of esters of 4-aryl-2-diarylmethylenehydrazino-4-oxo-2-butenoic acids to methyl 5(3)-aryl-3(5)-pyrazolecarboxylates.

Perm State University, Perm 614000, Russia; e-mail: info@psu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 843-845, June, 2001. Original article submitted March 19, 2001.

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Methyl Ester of 4-Chloro-2-(9-fluorenylidene)hydrazono-4-phenyl-3-butenoic Acid (1a). Oxalyl chloride (0.27 ml, 0.0031 mol) was added to a solution of ester **2a** (1.00 g, 0.0026 mol) in absolute benzene (7 ml), boiled for 100 min, and cooled. The precipitate was filtered off. Yield 0.62 g (60%); mp 223-225°C (benzene). IR spectrum (vaseline oil), ν, cm^{-1}: 1740 (COO), 1590 w (C=C, C=N). ^1H NMR spectrum (60 MHz, DMSO-d_6, δ, ppm): 3.80 (3H, s, MeO); 6.80 (1H, s, $C_{(3)}H$); 7.57 (13H, group of s, ArH). Found, %: C 72.08; H 4.34; Cl 8.91; N 6.94. $C_{24}H_{17}ClN_2O_2$. Calculated, %: C 71.91; H 4.27; Cl 8.84; N 6.99.

Methyl Ester of 4-Chloro-4-*p*-ethoxyphenyl-2-(9-fluorenylidene)hydrazono-3-butenoic Acid (1b). Yield 0.40 g (52%); mp 162-163°C (benzene). IR spectrum (vaseline oil), ν, cm^{-1}: 1720 (COO), 1620 w (C=C, C=N). Found, %: C 69.95; H 4.72; Cl 7.90; N 6.48. $C_{26}H_{21}ClN_2O_3$. Calculated, %: C 70.19; H 4.76; Cl 7.97; N 6.30.

Methyl 1-(9-Chloro-9-fluorenyl)-5-phenyl-1H-3-pyrazolecarboxylate (3a). A solution of ester **1a** (0.25 g, 0.0007 mol) in absolute *p*-xylene (3 ml) was held for 20 min at 138-140°C and then cooled. The precipitate was filtered off. Yield 0.19 g (76%); mp 204-205°C (benzene). IR spectrum (vaseline oil), ν, cm^{-1}: 1740 (COO), 1615 w (C=C, C=N). ^1H NMR spectrum (400 MHz, DMSO-d_6, δ, ppm, *J* (Hz)): 3.90 (3H, s, MeO); 6.32 (2H, d, *J* = 8.0, 2 *o*-CH in C_6H_5); 6.73 (1H, s, $C_{(4)}H$); 6.83-7.63 (11H, group of s, ArH). Found, %: C 71.98; H 4.39; Cl 8.83; N 6.92. $C_{24}H_{17}ClN_2O_2$. Calculated, %: C 71.91; H 4.27; Cl 8.84; N 6.99.

Methyl 1-(9-Chloro-9-fluorenyl)-5-(*p*-ethoxyphenyl)-1H-3-pyrazolecarboxylate (3b). Yield 0.18 g (90%); mp 175-177°C (benzene). IR spectrum (vaseline oil), ν, cm^{-1}: 1710 (COO), 1610 w (C=C, C=N). ^1H NMR spectrum (400 MHz, DMSO-d_6, δ, ppm, *J* (Hz)): 1.26 (3H, t, *J* = 7.0, Me); 3.89 (3H, s, MeO); 3.90 (2H, q, *J* = 7.0, CH_2O); 6.21, 6.36 (4H, dd, *J* = 8.7, AB system, *p*-$EtOC_6H_4$); 6.68 (1H, s, $C_{(4)}H$); 7.24-7.63 (8H, group of s, ArH). Found, %: C 70.26; H 4.60; Cl 7.87; N 6.27. $C_{26}H_{21}ClN_2O_3$. Calculated, %: C 70.19; H 4.76; Cl 7.97; N 6.30.

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