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THERMAL RECYCLIZATION OF 1-AMINO-2,3-DIHYDRO-2,3-PYRROLEDIONES TO 2,3-DIHYDRO-1H-PYRAZOL-3-ONES

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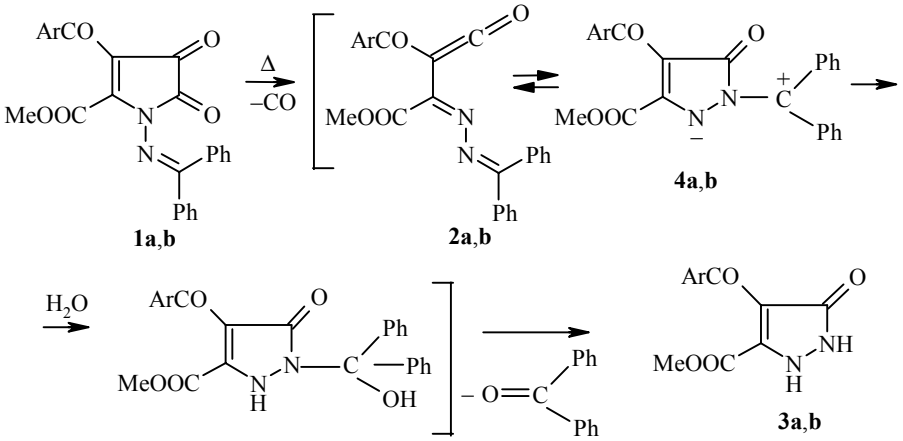
Thermal decarbonylation of substituted 4-acyl-2,3-dihydro-2,3-pyrrolediones leads to generation of unstable acyl(imidoyl) ketenes. In the absence of potential reaction partners, acyl(imidoyl) ketenes are stabilized either by intramolecular cyclization to substituted furanones [1], furoisoquinolinones [2], or quinolones [3] or by participation in intermolecular [4+2]-cycloaddition reactions with formation of substituted pyridobenzoxazinediones [4] or pyridoquinoxalinetriones [5].

We have studied the thermolysis of 4-aroyl-1-diphenylmethyleneamino-5-methoxycarbonyl-2,3-dihydro-2,3-pyrrolediones (**1a,b**), obtained by the method in [6], in which we might expect formation of the first representatives of the class of aroyl(hydrazonoyl) ketenes: the ketenes **2a,b**. When the pyrrolediones **1a,b** are held in *p*-xylene at 138-140°C for 50-60 min, we obtain 4-aroyl-5-methoxycarbonyl-2,3-dihydro-1H-pyrazol-3-ones **3a,b**.



1–**4 a** Ar = *p*-MeC_6H_4, **b** Ar = *p*-FC_6H_4

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Ketenes **2a,b**, formed upon thermal decarbonylation of the pyrrolediones **1a,b**, probably can undergo intramolecular cyclization to substituted 2,3-dihydro-3-oxo-2-methyliopyrazolides **4a,b** (analogs of the known stable substituted 2,3,4,5-tetrahydro-3-oxo-2-methyliopyrazolides [7,8]), which are hydrolyzed on exposure to traces of water in the solvent with cleavage of benzophenone to the pyrazolones **3a,b**. The alternative route to formation of pyrazolones **3a,b**, hydrolysis of the ketenes **2a,b** themselves, is unlikely.

5-Methoxycarbonyl-4-*p*-toluene-2,3-dihydro-1H-pyrazol-3-one (3a). A solution of pyrroledione **1a** (1.19 g, 0.026 mol) in of *p*-xylene (7 ml) was held at 138°C for 60 min and then cooled. The precipitate was filtered out. Yield 0.08 g (12%); mp 210-212°C (toluene). IR spectrum (vaseline oil), ν, cm^{-1}: 3230 (NH), 1745 (COO), 1645 ($C_{(3)}$=O, *p*-MeC_6H_4CO). ^{1}H NMR spectrum (300 MHz, DMSO-d_6, δ, ppm, *J* (Hz)); 2.40 (3H, s, Me); 3.60 (3H, s, MeO); 7.26 (2H, d, *J* = 8.0, 2CH(*m*)); 7.61 (2H, d, *J* = 8.0, 2CH(*o*)); 10.35 (1H, br. s, NH); 13.20 (1H, br. s, NH). Found, %: C 60.10; H 4.71; N 10.93. $C_{13}H_{12}N_2O_4$. Calculated, %: C 60.00; H 4.65; N 10.76.

4-*p*-Fluorobenzoyl-5-methoxycarbonyl-2,3-dihydro-1H-pyrazol-3-one (1b). Yield 0.09 g (15%); mp 184-186°C (toluene). IR spectrum (vaseline oil), ν, cm^{-1}: 3280 (NH), 1745 (COO), 1695 ($C_{(3)}$=O), 1635 (*p*-FC_6H_4CO). ^{1}H NMR spectrum (300 MHz, DMSO-d_6, δ, ppm, *J* (Hz)): 3.53 (3H, s, MeO); 7.25 (2H, d, *J* = 7.5, 2CH(*m*)); 7.80 (2H, d, *J* = 7.5, 2CH(*o*)); 10.48 (1H, br. s, NH); 13.10 (1H, br. s, NH). Found, %: C 54.76; H 3.48; N 10.93. $C_{12}H_9FN_2O_4$. Calculated, %: C 54.55; H 3.43; N 10.60.

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REFERENCES

1. Z. G. Aliev, O. P. Krasnykh, A. N. Maslivets, O. S. Stepanov, Yu. S. Andreichikov, and L. O. Atovmyan, *Izv. Akad. Nauk, Ser. Khim.*, 2150 (1999).
2. Z. G. Aliev, O. P. Krasnykh, A. N. Maslivets, Yu. S. Andreichikov, and L. O. Atovmyan, *Izv. Akad. Nauk, Ser. Khim.*, 563 (1997).
3. A. N. Maslivets, O. P. Krasnykh, L. I. Smirnova, and Yu. S. Andreichikov, *Zh. Org. Khim.*, **25**, 1045 (1989).
4. Z. G. Aliev, O. P. Krasnykh, A. N. Maslivets, Yu. S. Andreichikov, and L. O. Atovmyan, *Izv. Akad. Nauk, Ser. Khim.*, 2154 (1999).
5. A. N. Maslivets, O. V. Golovnina, O. P. Krasnykh, and Z. G. Aliev, *Khim. Geterotsikl. Soedin.*, 699 (2000).
6. N. A. Konyukhova, O. P. Krasnykh, and A. N. Maslivets, *Khim. Geterotsikl. Soedin.*, 700 (2001).
7. H. Dorn and T. Kreher, *Tetrah. Lett.*, **29**, 2939 (1988).
8. H. Dorn, in: *Transactions of the Academy of Sciences of the DDR [East Germany]* [in German], Akademie-Verlag, Berlin (1988); 1N, 21.