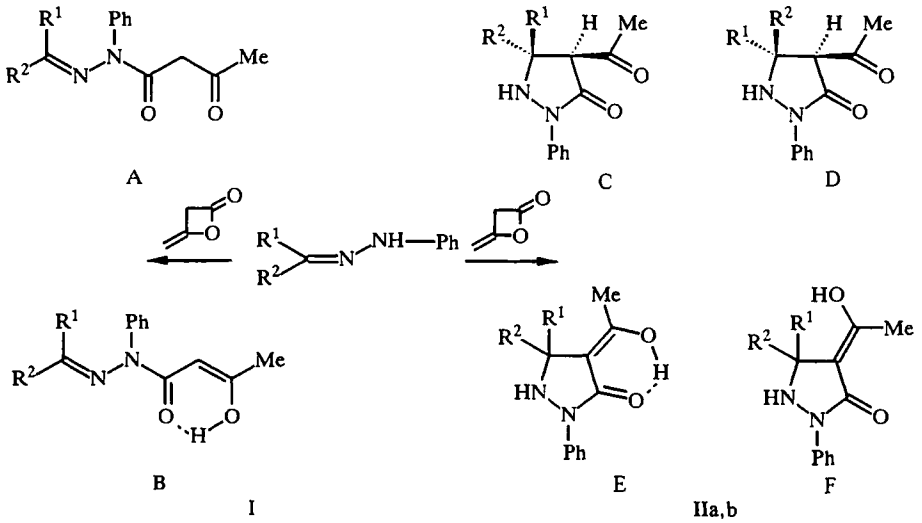
Chemistry of Heterocyclic Compounds, Vol.35, No. 6, 1999

TAUTOMERISM OF 4-ACYL-2-PHENYL-2-PYRAZOLIDIN-3-ONES

S. V. Oleinik, K. N. Zelenin, V. V. Alekseev, and A. A. Potekhin

The reaction of diketene with hydrazones was only studied for some phenylhydrazones [1]. It was confirmed that aldophenylhydrazones form the corresponding N-acetoacetylhydrazones, and the reactions of phenylhydrazones of ketones lead to 4-acyl-2-phenyl-2-pyrazolidin-3-ones. The structure of these substances was not studied in detail. According to PMR spectroscopic data, we found that they correspond with the proposed structure at the initial moment of solution, however the composition of the solutions changes significantly after several hours.

Compound I in the solution of DMSO is the mixture of the linear tautomers – the hydrazone A (89%) and the enhydrazine B. Its ^{1}H and ^{13}C NMR spectra contain signals of the HC=N, CH_2 and OH, HC=C groups correspondingly, with the absence of signals of the quaternary carbon atoms of the cyclic forms at 60-80 ppm. The low-field signal of the OH group at 13.84 ppm indicates the existence of the intramolecular H-bond in the tautomer B.



I R^1 = H, R^2 = C_6H_4OMe-*p*; IIa R^1 = R^2 = Me;
IIb R^1 = Me, R^2 = Ph

Another result is observed in the case of acetone derivative IIa, which occurs as the mixture of the cyclic forms C (95%) and E. Its ^{13}C NMR spectrum has signals of the $C_{(5)}$ and $C_{(4)}$ carbon atoms at 56.6 and 59.3 ppm, and 67.1 and 110.5 ppm correspondingly. The intramolecular H-bond, with the signal of the OH group at 12.25 ppm exists in the enol isomer E.

Military-Medical Academy, St. Petersburg 194044, Russia. St. Petersburg State University, St. Petersburg 198904, Russia. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 837-838, June, 1999. Original article submitted February 23, 1999.

 0009-3122/99/3506-0748$22.00

The change of the methyl group by the phenyl (compound IIb) gives rise to four cyclic tautomers, which can be seen from the spectral set of signals of the quaternary $C_{(4)}$ and $C_{(5)}$ carbon atoms in the region of 61.7-68.2 ppm. Two of these tautomers are the diastereomers C and D (68% and 14% correspondingly). The two others are enhydrazine forms E and F (6% and 12% correspondingly). Their structure is confirmed by the signals of the "olefinic" carbon atoms in the ^{13}C NMR spectrum at 110.3, 111.6, 168.7, and 170.3 ppm.

N-Acetoacetyl-N'-*p*-methoxybenzylidene-N-phenylhydrazine (I). $C_{18}H_{18}N_2O_3$. This compound was obtained by the method [1]. Yield 53%; mp 109-111°C (ethyl acetate–heptane). PMR spectrum ($CDCl_3$) (form A): 2.35 (3H, s, CH_3); 3.78 (3H, s, CH_3O); 4.07 (2H, s, CH_2); 6.24 (1H, br. s, CH=C); 6.8-7.6 ppm ($9H_{arom}$). PMR spectrum (form B): 2.08 (3H, s, CH_3); 3.78 (3H, s, CH_3O); 6.59 (1H, br. s, CH=C); 6.8-7.6 ($9H_{arom}$); 13.84 ppm (1H, br. s, OH). ^{13}C NMR spectrum ($CDCl_3$) (form A): 29.6 (CH_3); 50.6 (CH_2); 55.0 (CH_3O); 113.4-135.5; 168.6 (C_{Ar}); 142.2 (HC=N); 160.9 [N-C(O)]; 201.5 ppm ($CH_3\underline{C}O$). ^{13}C NMR spectrum (form B): 21.8 (CH_3); 55.0 (CH_3O); 88.4 ($\underline{C}H$=C); 113.4-135.5; 168.6 (C_{Ar}); 142.2 (HC=N); 172.0 [N-C(O)]; 175.6 ppm [$CH_3\underline{C}$(OH)].

4-Acetyl-5,5-dimethyl-2-phenylpyrazolidin-3-one (IIa). $C_{13}H_{16}N_2O_2$. This compound was synthesized analogously. Yield 51%; mp 110-112°C (chloroform–heptane). Lit. mp 111-113°C [1]. PMR spectrum ($CDCl_3$) (forms C, D): 1.22 (3H, s, CH_3); 1.30 (3H, s, CH_3); 2.27 (3H, s, CH_3CO); 3.46 (1H, s, 4-H); 4.97 (1H, s, NH); 7.0-7.9 ppm ($5H_{arom}$). PMR spectrum (form E): 1.22 (3H, s, CH_3); 1.30 (3H, s, CH_3); 1.95 [3H, s, $\underline{CH_3}$C(OH)]; 4.43 (1H, br. s, NH); 7.0-7.9 ($5H_{arom}$); 12.25 ppm (1H, br. s, OH). ^{13}C NMR spectrum ($CDCl_3$) (forms C, D): 20.5 (CH_3); 26.5 (CH_3); 32.2 (CH_3CO); 59.3 ($C_{(5)}$); 67.1 ($C_{(4)}$); 117.6-138.7 (C_{Ar}); 168.8 ($C_{(3)}$); 203.9 ppm (CH_3CO). ^{13}C NMR spectrum (form E): 18.0 ($2CH_3$); 25.6 [$\underline{CH_3}$C(OH)]; 56.6 ($C_{(5)}$); 110.5 ($C_{(4)}$); 117.6-138.7 (C_{arom}); 164.0 [$CH_3\underline{C}$(OH)]; 170.3 ppm ($C_{(3)}$).

4-Acetyl-5-methyl-2,5-diphenylpyrazolidin-3-one (IIb). $C_{18}H_{18}N_2O_2$. Yield 63%; mp 114-115°C (chloroform–heptane). Lit. mp 114-115°C [1]. PMR spectrum (DMSO-d_6) (form C): 1.50 (3H, s, CH_3); 2.51 (3H, s, CH_3CO); 4.23 (1H, s, 4-H); 6.69 (1H, s, NH); 7.0-8.0 ppm ($10H_{arom}$). PMR spectrum (form D): 1.63 (3H, s, CH_3); 2.44 (3H, s, CH_3CO); 4.31 (1H, s, 4-H); 6.77 (1H, s, NH); 7.0-8.0 ppm ($10H_{arom}$). PMR spectrum (form E): 1.75 (3H, s, CH_3); 1.89 (3H, s, CH_3CO); 6.45 (1H, br. s, NH); 7.0-8.0 ($10H_{arom}$); 12.35 ppm (1H, s, OH). PMR spectrum (form F): 1.80 (3H, s, CH_3); 1.93 (3H, s, CH_3CO); 6.10 (1H, br. s, NH); 7.0-8.0 ($10H_{arom}$); 10.24 ppm (1H, s, OH). ^{13}C NMR spectrum (DMSO-d_6) (form C): 23.1 (CH_3); 32.4 ($\underline{C}H_3CO$); 64.4 ($C_{(5)}$); 68.1 ($C_{(4)}$); 116-148 (C_{Ar}); 168.8 ($C_{(3)}$); 204.4 ppm ($CH_3\underline{C}O$). ^{13}C NMR spectrum (form D): 25.6 (CH_3); 31.5 ($\underline{C}H_3CO$); 64.5 ($C_{(5)}$); 68.2 ($C_{(4)}$); 116-148 (C_{Ar}); 168.6 ($C_{(3)}$); 203.9 ppm ($CH_3\underline{C}O$). ^{13}C NMR spectrum (form E): 18.9 (CH_3); 61.7 ($C_{(5)}$); 110.3 ($C_{(4)}$); 116-148 (C_{Ar}); 165.1 ($C_{(3)}$); 170.3 ppm [C=$\underline{C}$(OH)CH_3]. ^{13}C NMR spectrum (form F): 17.5 (CH_3); 28.0 ($\underline{C}H_3CO$); 63.8 ($C_{(5)}$); 111.6 ($C_{(4)}$); 116-148 (C_{Ar}); 160.7 ($C_{(3)}$); 168.7 ppm [C=$\underline{C}$(OH)CH_3].

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