STRUCTURE OF BIS(ACYLHYDRAZONES) OF 1,3-DIOXO COMPOUNDS

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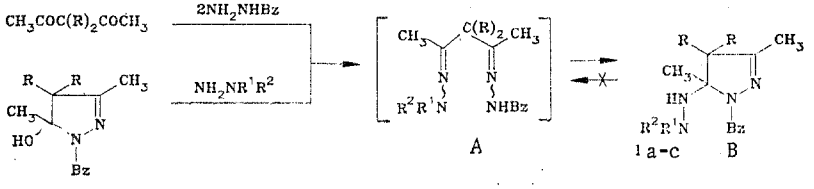
Contrary to the data of [1, 2], we have found that the products of the condensation of β-diketones and hydrazines in 1:2 ration are not the linear hydrazones (A), but have a cyclic (B) structure.



a R=R¹=H, R²=Bz; b R=CH₃, R¹=H, R²=Bz; c R=H, R¹=R²=CH₃

1-Benzoyl-5-benzoylhydrazino-3,5-dimethylpyrazoline-2 (Ia) [1]. PMR spectrum ($CDCl_3$): 1.78 (s, 3H), and 1.88 (t, 3H, J = 1.0 Hz, 2-CH_3), 2.80 and 3.18 (2H, J_{AB} = 19.0, J = 1.0 Hz, 4-H), 5.40 (d, 1H, J = 2.5 Hz, NH), 8.59 (d, 1H, J = 2.5 Hz, NHCO), 7.2-7.8 ppm (m, 10H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$): 15.9 and 22.4 (J_{CH} = 129.0 Hz, CH_3), 48.1 (J_{CH} = 133.0 Hz, $C_{(4)}$), 84.8 ($C_{(5)}$), 155.2 (J_{CCH} = 7.5 Hz, $C_{(3)}$), 166.9 and 168.8 (C=O), 126-135 ppm (C_{arom}).

1-Benzoyl-5-benzoylhydrazino-3,4,4,5-tetramethylpyrazoline-2 (Ib) [2]. PMR spectrum ($CDCl_3$): 1.33, 1.38, 1.62, and 2.04 (s, 12H, CH_3), 4.83 (d, 1H, J = 2.5 Hz, NH), 9.43 (d, 1H, J = 2.5 Hz, NHCO), 7.2-7.9 ppm (m, 10H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$): 12.2, 15.8 18.0, and 18.6 (CH_3), 52.0 ($C_{(4)}$), 87.4 ($C_{(5)}$), 163.5 ($C_{(3)}$), 165.6 and 168.9 (C=O), 126-135 ppm (C_{arom}).

Compound I can also be obtained by the action of the corresponding hydrazine on 1-acyl-5-hydroxypyrazolines-2, as illustrated by the synthesis of Ic; this forms in quantitative yield after 1-benzoyl-5-hydroxy-3,5-dimethylpyrazoline-2 [3] stands with excess dimethylhydrazine for 1 day at room temperature.

1-Benzoyl-5-dimethylhydrazino-3,5-dimethylpyrazoline-2 (Ic). Mp 67-69° (from ether). PMR spectrum (DMFA-D_7): 1.58 (s, 3H) and 1.85 (t, 3H, J = 1.0 Hz, 2-CH_3), 2.29 (s, 6H, CH_3N), 2.63 and 3.25 (2H, J_{AB} = 18.0; J = 1.0 Hz, 4-H), 4.05 (br. s, 1H, NH), 7.2-7.8 ppm (m, 5H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$): 16.0 (J_{CH} = 129.0 Hz) and 24.6 (J_{CH} = 129.0, J_{CCCH} = 4.0 Hz, 2-CH_3), 46.8 (J_{CH} = 133.0, J_{CCCH} = 4.0 Hz, $C_{(4)}$), 48.8 (J_{CH} = 133.0, J_{CNCH} = 5.0 Hz, CH_3N), 83.1 ($C_{(5)}$), 155.4 ($C_{(3)}$), 166.8 (CO), 127-135 ppm (C_{arom}).

At the same time the reaction product of phenylhydrazine and 3,3-dimethylpentanedione-2,4 [4] is a bis(hydrazone), like the 4- and 2,4-nitrophenylhydrazones of β-diketones described in [5, 6]. PMR spectrum (DMSO-D_6): 1.45 (s, 6H, α-CH_3), 1.87 (s, 6H, CH_3CN), 8.79 (br. s, 2H, NH), 6.8-7.5 ppm (m, 10H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$): 10.9 (α-CH_3), 23.3 (CH_3CN), 49.9 (α-C), 148.4 (CN), 112.7, 119.4, 128.9, 145.7 ppm (C_{arom}).

Thus the bis(hydrazones) of 1,3-dioxo compounds having even only one hydrazine residue are the corresponding 1-acyl-5-hydrazinopyrazolines-2.

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5-HYDRAZINO-2-ISOXAZOLINES

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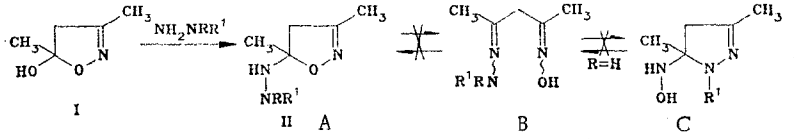
In view of the high and varied biological activity of many isoxazole derivatives [1], to find new methods for their synthesis is becoming timeyl. We have established that a simple method of obtaining some 5-hydrazino-2-isoxazolines IIa-c is the reaction of the readily available 5-hydroxy-3,5-dimethyl-2-isoxazolines I [2] with the respectivey hydrazines.



II a R=H, R¹=COC_6H_5; b R=H, R¹=$COC_6H_4NO_2$-*p*; c R=R¹=CH_3

According to ^1H and ^{13}C NMR data, the compounds IIa-c have the cyclic structure A, and show no tendency to go over in various solvents to the linear form B. Incidentally the hydrazinooximes of 1,3-dioxo compounds are unknown.

With IIa,b the theoretical possibility of formation of a pyrazoline ring C must also be considered. But this variant must be excluded because in the ^{13}C NMR spectra, the $C_{(5)}$ atom of tautomer C ought to be located in the 80-90 ppm range [3]. In the case of IIc, however, which is incapable of such a transition, the $C_{(5)}$ signal appears at a weaker field (98.9 ppm). The value for the $C_{(5)}$ signal in IIa, viz., 100.2 ppm, is also evidence that it is located in a N,O-, and not a N,N environment. An attempt to synthesize a type C compound by another route, by the reaction of hydroxylamine and 1-benzoyl-5-hydroxy-3,5-dimethyl-2-pyrazoline [4] yielded benzhydrazide and a mixture of I with acetylacetone dioxime.

II was synthesized by boiling equimolar amounts of the reagents in benzene solution in the presence of KU-2 carion exchanger in the H^+ form. The elemental compositions of IIa-c agree with those calculated.

IIa: yield 72%, mp 107-108° (from hexane–ethyl acetate mixture). PMR spectrum (DMFA-D_7): 1.69 (s, 3H), and 2.01 (t, 3H, J = 1.0 Hz) — 2 CH_3 groups; 2.99 and 3.21 (2H, J_{AB} = 18.0, J = 1.0 Hz, 4-H); 5.85 (d, 1H, J = 6.0 Hz, NH); 7.53-8.0 (m, 5H, H_{arom}); 9.85 ppm (d, 1H, J = 6.0 Hz, NHCO). ^{13}C NMR spectrum ($CDCl_3$): 13.6 J_{CH} = 129.0 Hz) and 23.6 (J_{CH} = 129.0, J_{CCCH} = 4.0 Hz) — 2 CH_3 groups; 47.0 (J_{CH} = 136.0, J_{CCCH} = 4.0 Hz, $C_{(4)}$); 100.2 ($C_{(5)}$); 158.3 (J_{CCH} = 4.5 Hz, $C_{(3)}$); 170.2 (J_{CCH} = 6.8 Hz, C=O); 128.7-134.6 ppm (C_{arom}).

IIb: yield 62%, mp 153-155° (from toluene). PMR spectrum (DMFA-D_7): 1.50 (s, 3H) and 1.83 (t, 3H, J = 1.0 Hz) — 2 CH_3 groups; 2.92 and 3.10 (2H, J_{AB} = 18.0, J = 1.0 Hz, 4-H); 5.93 (d, 1H, J = 5.0 Hz, NH); 8.07 (d, 2H, J = 9.0 Hz) and 8.31 (d, 2H, J = 9.0 Hz, H_{arom}) 10.13 ppm (d, 1H, J = 5.0 Hz, NHCO).

IIc: yield 85%, mp 48-49° (from hexane–ethyl acetate mixture). PMR spectrum (DMFA-D_7): 1.44 (s, 3H), and 1.92 (t, 3H, J = 1.0 Hz) — 2 CH_3 groups; 2.46 (s, $(CH_3)_2N$); 2.72 and 3.00 (2H, J_{AB} = 16.0, J = 1.0 Hz, 4-H); 3.94 ppm (br. s, 1H, NH). ^{13}C NMR spectrum (CD_3OD): 13.1 (J_{CH} = 129.0 Hz) and 24.1 (J_{CH} = 129.0, J_{CCCH} = 4.5 Hz) — 2 CH_3 groups; 45.3 (J_{CH} = 135.0, J_{CCCH} = 3.0 Hz, $C_{(4)}$); 49.5 (J_{CH} = 132.0, J_{CCCH} = 4.5 Hz, $(CH_3)_2N$); 98.9 (J_{CCH} = 3.0 Hz, $C_{(5)}$, 154.9 ppm (J_{CCH} = 6.5 Hz, $C_{(3)}$).

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