SPECTRAL FEATURES OF SUBSTITUTED 2-(NITROMETHYL)PENTANONES CONTAINING AN ASYMMETRIC CARBON ATOM

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3-Nitropropenoates and -propenones react with carbo- and heterocyclic CH acids to form Michael adducts [1, 2], and the presence of a chiral atom in their structure results in diastereotopic effects in their ^{1}H NMR spectra [3]. The aim of this study was to investigate the structure adducts of 3-nitropropenoates and -propenones with the aliphatic CH acid pentane-2,4-dione obtained for the first time. Analysis of the ^{1}H NMR spectra revealed that in the case of methyl 3-acetyl-2-(nitromethyl)-4-oxopentanoate **1**, the CH_2NO_2 group protons and the methine protons H^C and H^M form an ABCM-type spin system. Thus, the signals of the methylene protons appear as two doublets of doublets at 4.71 ppm (^{2}J 15.0, ^{3}J 6.9 Hz) and 4.58 ppm (^{2}J 15.0, ^{3}J 4.0 Hz), the methine proton H^C – a doublet of doublets of doublets at 3.89 ppm (^{3}J 6.9, ^{3}J 4.0, ^{3}J 6.9 Hz), and the methine proton H^M forms a doublet at 4.39 ppm (^{3}J 6.9 Hz). In turn, differences are observed in the ^{1}H NMR spectrum of 3-acetyl-1-(4-methoxyphenyl)-2-(nitromethyl)pentane-1,4-dione **2**. Geminal coupling in methylene group is not manifested and the signal of this protons form a doublet at 4.70 ppm (^{3}J 5.8 Hz), the signal of the methine proton H^C appears as a doublet of triplets at 4.81 ppm (^{3}J 8.4, 5.8 Hz), and the methine proton H^M forms a doublet at 4.51 ppm (^{3}J 8.4 Hz). Probably, this change in the spectral picture is associated with the additional influence of the aromatic ring. The assignment of signals is confirmed by the results of ^{1}H-^{1}H dqf-COSY experiments obtained for compounds **1, 2**. The ^{13}C-{^{1}H} NMR spectra of adducts **1, 2** are similar and contain signals of all structural fragments of the molecule. Thus, it was shown that structurally similar 2-(nitromethyl)pentanones containing an asymmetric carbon atom, but differing in the presence of an alkoxycarbonyl or aroyl substituent, exhibit differences in the signal shapes in the ^{1}H NMR spectra.

[1] V.V. Pelipko, S.V. Makarenko, R.I. Baichurin, V.M. Berestovitskaya, K.S. Kovalenko, Rus. J. Org. Chem. 53 (2017) 1799-1808
[2] V.V. Pelipko, M.A. Kuritsyna, R.I. Baichurin, S.V. Makarenko, Rus. J. Gen. Chem. 90 (2020) 1398-1402
[3] V.V. Pelipko, R.I. Baichurin, E.M. Leontyeva, M.A. Kuritcyna, S.V. Makarenko, Magnetic resonance and its applications. Spinus - 2018. 223-226 (2018)