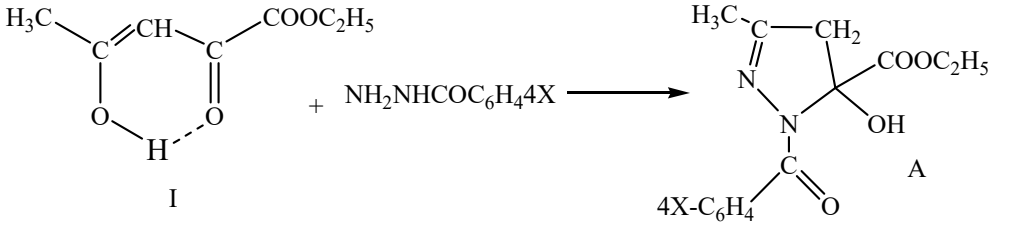
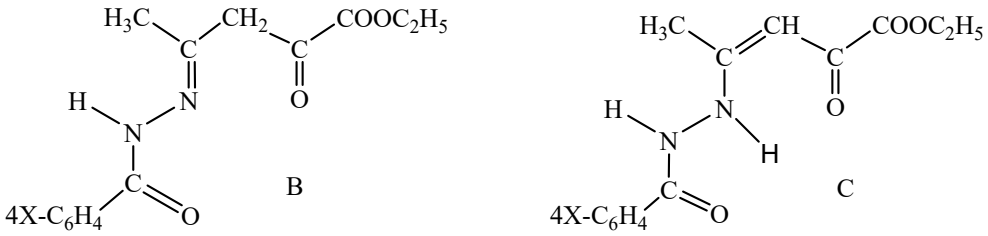
SYNTHESIS AND STRUCTURE OF PARA-SUBSTITUTED ARYLHYDRAZONES OF ETHYL 2,4-DIOXOPENTANOATE

Tursunov Murod Amonovich
Bukhara State University
Research Institute of Natural Sciences and Agroinnovations
Professor of the Department of Chemistry and Oil and Gas Technologies
Shukurov Hidoyat O'ktam o'g'li
Bukhara State Medical Institute
Assistant at the Department of Medical and Biological Chemistry
E-mail: tursunovma@mail.ru
https://doi.org/10.5281/zenodo.23044540

Acyl- and thioacylhydrazones of 1,3-diketones constitute a class of compounds of considerable interest in terms of their tautomeric possibilities and continue to attract increasing attention. Interest in the detailed structure of acylhydrazones stems primarily from their ability to exist in different tautomeric forms. Depending on the structural features of the dicarbonyl component, a three-way ring–chain equilibrium may be expected among the linear (hydrazone and enehydrazine) and cyclic 5-hydroxy-2-pyrazoline tautomeric forms of acylhydrazones of 1,3-diketones. It should be noted that a two-form prototropic equilibrium has been observed for acylhydrazones of both 1,3-ketoesters and 1,3-ketoaldehyde derivatives.

We studied the structure of the condensation products of ethyl 2,4-dioxopentanoate with hydrazides of para-substituted aromatic acids. According to proton NMR spectroscopy data, the free 1,3-ketoester, namely ethyl 2,4-dioxopentanoate, exists in a ring–chain tautomeric form (Table). The composition and structure of the resulting acylhydrazones were established by elemental analysis, IR and proton NMR spectroscopy:





X=H(II), NO_2(III), $(CH_3)_2N$(IV) II-IV

The stretching vibration band of the C=O bond of the ethoxy group in compounds II-IV is observed at 1750-1765 cm^{-1}. The IR spectra of these compounds are characterized by a broad stretching

© Ushbu material Creative Commons Attribution 4.0 International (CC BY 4.0) litsenziyasi asosida tarqatiladi.

vibration band around ~3400 cm^{-1} $\nu_{(O-H)}$, while the absorption band of the amide fragment is recorded at approximately 1660-1680 cm^{-1} $\nu_{(C=O)}$. In the multiple-bond stretching region, the IR spectra of the compounds show intense absorption bands at 1633, 1595, 1574, 1558 and 1490 cm^{-1}. The absorption band at 1633 cm^{-1} indicates the presence of a C=N bond; the remaining absorption bands correspond to vibrations of the aromatic ring bonds of order 1.5 and bending vibrations of the N–H bond. Analysis of the IR spectra indicates that the synthesized compounds II-IV in the solid state predominantly exist in the cyclic 5-hydroxy-2-pyrazoline tautomeric form (A). However, IR spectroscopy does not establish the regioselectivity of the condensation reaction at the carbonyl group adjacent to the $–CH_3$ or $–COOC_2H_5$ moiety, and the results are contradictory.

To provide unambiguous support for the conclusions concerning the structure of compounds II-IV, we recorded their proton NMR spectra in $CDCl_3$ solution. The proton NMR spectra indicate retention of the cyclic tautomeric form (A). As an example, consider the proton NMR spectrum of compound II, recorded immediately after preparing the solution. Particularly informative are the signals of the methylene protons of the pyrazoline ring, which appear as asymmetric doublets at δ 3.00 and 3.26 ppm, forming a typical AB system with a spin–spin coupling constant J_{AB} = 21 Hz. This is due to the presence of a chiral center in the molecule, namely the carbon atom at position 5 of the 5-hydroxy-2-pyrazoline ring. The ethoxy protons form a characteristic pattern of triplet and quartet signals with an integral intensity ratio of 3:2 at δ 1.31 and 4.34 ppm. The phenyl-ring protons of the benzhydrazide moiety (5 H) resonate as a somewhat broadened multiplet signal with centers at δ 7.44 and 7.92 ppm. The signal of the single hydroxyl proton attached to the fifth carbon atom of the 5-hydroxy-2-pyrazoline ring is observed at δ 7.28 ppm (Table).

Table

Proton NMR spectral parameters of I–IV in $CDCl_3$ (δ, ppm)

	C**H**$_3$-CO	C**H**$_3$-CN	C**H**$_3$-CH_2O	CH_3-C**H**$_2$O	C**H**$_2$	O**H**	C_6**H**$_4$-X	(C**H**$_3$)$_2$N
	2,26	-	1,37	4,35	-	6,37	-	-
I	-	2,13	1,31	4,34	3,00; 3,26	7,28	7,44; 7,92	-
II	-	2,12	1,27	4,37	3,03; 3,28	7,28	8,06; 8,29	-
V	-	2,12	1,27	4,32	2,98; 3,17	7,28	6,68; 8,00	3,04

Substituents at the para-position of the benzene ring in the amide portion of the molecule, through their electron-donating or electron-withdrawing nature, strongly affect the chemical shifts of the proton signals of all terminal substituents and functional groups in the molecule.

Использованная литература

1. Умаров Б.Б., Турсунов М.А., Минин В.В. Комплексы с производными кетоальдегидов и кетоэфиров.- Ташкент.- Нишон-ношир.- 2016.- 350 с.

© Ushbu material Creative Commons Attribution 4.0 International (CC BY 4.0) litsenziyasi asosida tarqatiladi.

2. Tursunov M.A., Avezov K.G. and Umarov B.B. Nickel(II) and Zinc(II) Complexes with Benzoylacetaldehyde Derivatives. Russian Journal of Coordination Chemistry. 2019, V. 45, N. 7, P. 484-488.
3. Турсунов М.А., Умаров Б.Б., Эргашов М.Я., Авезов К.Г. Синтез и кристаллическая структура комплекса никеля(II) с ароилгидразоном этиловогоэфира 5,5-диметил-2,4-диоксогексановой кислоты // ЖСХ.-2020.-Т.61.-№1.-С. 78-90.
4. Турсунов М.А. Комплексы некоторых 3d-металлов на основе производных кетоальдегидов и кетоэфиров; их строение и свойства : Дис. … канд.хим.наук.- Т.: БГУ.- 2019.- 120 с.
5. Умаров Б.Б., Ларин Г.М., Якимович С.И., Минин В.В., Парпиев Н.А. Синтез и спектры комплексов меди(II) на основе ароилгидразонв формилпинаколина и метилового эфира 5,5-диметил-2,4-диоксогексановой кислоты // Узб. хим. журн.- 1993.- № 3.- С. 12-14.
6. Ramazonov S.H., Tursunov M.A., Xudoyberganov O.I. Degidroasetik kislotasi atsetil gidrazonining sintezi, tuzilishi va xossalari. Development of science 2025 / 10 issue 10. volume 5. p 170-175.
7. Турсунов М.А., Умаров Б.Б., Якимович С.И., Севинчов Н.Г., Зерова И.В., Абдурахмонов С.Ф., Парпиев Н.А. Синтез и исследование пара-замещенных бензоилгидразонов этилового эфира 2,4-диоксопентановой кислоты // Современные технологии и инновации горно–металлургической отрасли.- НавГГИ, Навои. 14-15 июня. 2012.- С. 349-350.
8. Турсунов М.А., Умаров Б.Б., Авезов К.Г., Якимович С.И., Абдурахманов С.Ф., Севинчов Н.Г., Парпиев Н.А. Синтез и стереоизомерия ацилгидразонов кетоэфиров // Наука и технологии. Т.1. Тр. Международного симпозиума по фундаментальным и прикладным проблемам науки". Глава 8.- М.: РАН.- 2012.- С. 158-178.
9. Турсунов М.А., Умаров Б.Б. Синтез и кристаллическая структура комплекса никеля(II) на основе бензоилгидразона метилового эфира 4-фенил-2,4-диоксобутановой кислоты // Universum: химия и биология: электрон. научн. журн.- 2018.- №12(54).- С. 50-53.
10. Турсунов М.А., Умаров Б.Б., Бахронова Д.А. Темплатный синтез комплекса никеля(II) на основе бензоилгидразона метилового эфира 4-фенил-2,4-диоксобутановой кислоты // Международная конференция "Современные инновации: Химия и химическая технология ацетиленовых соединений. Нефтехимия. Катализ" Посвящается 100-летию Национального университета Узбекистана и 80-летию со дня рождения профессора Т.С. Сирлибаева.- 14-17 ноября. 2018.- Ташкент.- С. 305-306.
11. Nigina Qahramon Qizi Savriyeva, Murod Amonovich Tursunov, Bakhtiyor Shukrulloyevich Ganiev. Novel [5-Hdroxy-3-phenyl-5-(trifluoromethyl)-4,5-dihydro-1H-pyrazol-1-yl](phenyl)methanone: Synthesis, Characterization and Computational Analysis. Advanced Journal of Chemistry, Section A, 2026, 9(2), 192-207.
12. Ramazonov S.H., Tursunov M.A., Xudoyberganov O.I. Degidroasetik kislotasi atsetil gidrazonining sintezi, tuzilishi va xossalari. Development of science 2025 / 10 issue 10. volume 5. p 170-175.
13. Husenov Q.Sh., Tursunov M.A., Xudoyarova E.A., Ilhomov A.A. 4-fenil-2,4-dioksobutan kislota metil efiri aroilgidrazoni asosida Ni(II) va Cu(II) ionlarining kompleks birikmalar sintezi, tuzilishi va xossalari. International Journal of Advanced Technology and Natural Sciences Vol.3(6), 2025, IF=4.372, ICV 59.69. P. 31-39.
14. Tursunov M.A., Umarov B.B,. Tulisova N.Z. 2,4-dioksopentan kislota etil efirining aroilgidrazonlarining Cu(II) ioni bilan kompleks birikmalari. Development of science 2025 / oktyabr/10. volume 3. p 95-102

© Ushbu material Creative Commons Attribution 4.0 International (CC BY 4.0) litsenziyasi asosida tarqatiladi.