

REACTION OF 1,1,1-TRIFLUOROMETHYL-4-PHENYLBUTANEDIONE-2,4 WITH BENZOIC ACID HYDRAZIDE

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Annotation

Study of the composition and structure of newly synthesized compounds by modern methods of physicochemical research and the direction of the condensation reaction of aroyltrifluoroacetylmethanes with acid hydrazides, depending on the reaction conditions.

Keywords: aroyltrifluoroacetylmethanes, hydrazide, benzoylhydrazide, trifluoromethyl group, ligand, TLC. , PMR spectra, asymmetric doublets, β -dicarbonyl part, X-ray structural analysis.

A). Synthesis of 1-benzoyl-3-phenyl-5-hydroxy-5-trifluoromethyl-2-

pyrazoline. Alcoholic solutions of 1.08 g (0.005 mol) of 1,1,1-trifluoro-4-phenylbutanedione-2,4 and 0.68 g (0.005 mol) of benzoic acid hydrazide were stirred in a round-bottomed container of 100 cm³. The reaction mixture was left at room temperature. The reaction progress was monitored by TLC. After distilling off the solvent, the precipitated crystals were washed with

ethanol. Product yield H2L1 -1.39 g (83%), T_m = 490C.

The reactions for the preparation of 1-acyl-3-aryl-5-hydroxy-5-trifluoromethyl-2-pyrazolines H2L2-H2L6 with the structure by the interaction of alcohol solutions of aroyltrifluoroacetylmethanes with hydrazides at room temperature were carried out in a similar way. The yields and results of the synthesis are shown in Table 1.

Table 1.
Yields, Melting Points, and Elemental Analysis Results for 1-benzoyl-3-phenyl-5-hydroxy-5-trifluoromethyl-2-pyrazolines

No.	Output, %	Temp, °C	Found %		Gross formula	Calculated, %	
			W	H		W	H
H2L1	83	49	60.93	3.98	C ₁₇ H ₁₃ N ₂ O ₂ F ₃	61.08	3.92
H2L2	80	93	61.96	4.00	C ₁₈ H ₁₅ N ₂ O ₂ F ₃	62.07	4.04
H2L3	82	77	59.09	4.21	C ₁₈ H ₁₅ N ₂ O ₂ F ₃	59.34	4.15
H2L4	79	76	55.33	3.24	C ₁₇ H ₁₂ N ₂ O ₂ CF ₃	55.37	3.28
H2L5	87	99-100	49.08	2.70	C ₁₇ H ₁₂ N ₂ O ₂ BrF ₃	49.42	2.73
H2L6	78	148	53.60	3.21	C ₁₇ H ₁₂ N ₂ O ₄ F ₃	53.83	3.19

B) Synthesis of 1-benzoyl-3-trifluoromethyl-5-phenyl-5-hydroxy-2-pyrazoline 1.08 g (0.005 mol) of 1,1,1-trifluoromethyl-4-phenylbutanedione-2,4 and 0,68 g (0.005 mol) of benzoic acid hydrazide in 50 ml of isopropyl alcohol. A flask equipped with a reflux condenser was refluxed for several days, monitoring the progress of the reaction by TLC. After the completion of the reaction, the solvent was removed. The mixture of the reaction products for both carbonyl groups was recrystallized from ethyl alcohol, thus isolating 1-benzoyl-3-trifluoromethyl-5-phenyl-5-hydroxy-2-pyrazoline in pure form. The yield of the H2L7 product was 0.78 g (49%), mp = 47°C.

The reaction of the remaining aroyltrifluoroacetylmethanes with benzoylhydrazide in boiling isopropyl alcohol was carried out in a similar manner. It should be noted that in the case of donor substituents in the aromatic ring of 1,3-diketones, after removal of the solvent, only condensation products at the trifluoromethyl group were obtained. The results of the synthesis of other products H2L8 -H2L10 are summarized in Table 2.

table 2
Yields, Melting Points, and Elemental Analysis Results for 1-benzoyl-3-trifluoromethyl-5-aryl-5-hydroxy-2-pyrazolines

No.	E xi t, n o.	T m elt . 0C	Found ,%		Grossfo rmula	Calcul ated,%	
			W IT H	H		W IT H	H
H2 L7	4 9	47	61 .0 3	4. 0 6	C17H13 N2O2F 3	61 .0 8	3. 9 2
H2 L8	5 8	17 2	61 .9 5	4. 2 8	C18H15 N2O2F 3	62 .0 7	4. 3 4
H2 L9	6 2	15 4	59 .2 0	4. 0 5	C18H15 N2O2F 3	59 .3 4	4. 1 5
H2 L1 0	6 4	58	55 .4 8	3. 2 2	C17H12 N2O2CI F3	55 .3 7	3. 2 8
H2 L1 1	8 7	87 - 88	49 .1 4	2. 6 6	C17H12 N2O2CI F3	49 .4 2	2. 9 3

In order to unambiguously prove the conclusions about the structure of the obtained ligands in the solid state and in solutions, we recorded the PMR spectra of these compounds immediately after the preparation of solutions and after some time. For example, in the PMR spectrum of a solution of the compound H2L3 in CDCl₃, taken immediately after preparation (Fig. 1) and reflecting the structure of the substance in the solid state, a set of signals corresponding to the 5-hydroxypyrosoline structure is observed. Two asymmetric doublets with a total intensity of two protons, at δ 3.57 and 3.73 ppm and with a spin-spin coupling constant (SSCC) of 20 Hz, belonging to the methylene group of the cycle, a singlet signal at δ 3.87 ppm. intensity of three protons, corresponding to the CH₃-group of the aromatic ring of the β -dicarbonyl part of the molecule, the signal at δ 6.82 ppm. intensity in one proton-OH-group,

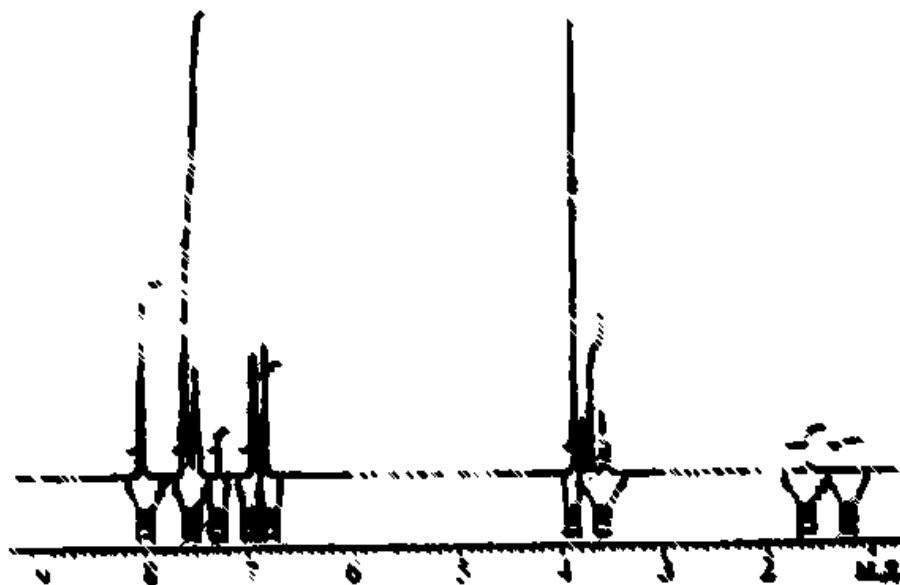


Fig. 1: NMR spectrum of 1-benzoyl-3- (4-methoxyphenyl) -5-hydroxy-5-trifluoromethyl-2-pyrazoline (H2L) of structure XLII in CDCl₃ solution.

The spectrum does not change over time, indicating the absence of possible tautomeric transitions to the hydrazone A1 or enhydrazine B1 forms. These data, of course, do not allow us to conclude that we are dealing with a condensation product specifically for aroyl carbonyl. Such a conclusion follows from consideration of the ¹³C NMR spectrum. [2]

The most characteristic of it is the presence of a quartet signal at δ 93.58 ppm. (CSCR 32 Hz). It belongs to the carbon atom in position 5 of the ring, the cleavage is due to the interaction with the adjacent trifluoromethyl group. The carbon signal of the methoxy group of the aromatic ring is fixed at δ 153.36 ppm, the C \equiv N bond at δ 162.33 ppm, and the C = O bond at δ 171.36 ppm, [1] ...

Table 3.

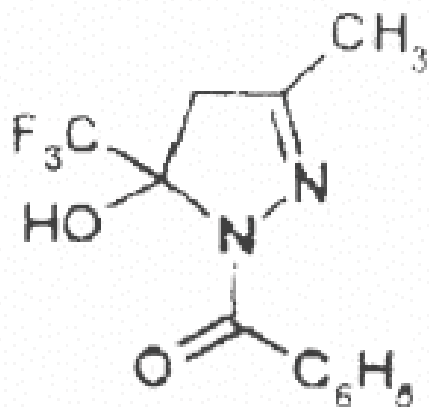
Parameters of the PMR spectra of 1-benzoyl-3-aryl-5-hydroxy-5-trifluoromethyl-2-pyrazolines in a CDCl₃ solution (δ , ppm)

Compound	NS	CH 2 *	H E	C ₆ H ₅	N S
H2L1	H	3.5 9; 3.7 3	6. 72	7.45m; 7.75m; 7.96m	-
H2L2	CH 3	3.5 7; 3.7 5	6. 77	7.25m; 7.56m; 8.02m	2. 44
H2L3	OC H3	3.5 7; 3.7 3	6. 82	6.91m; 8.03m	3. 87
H2L4	Cl	3.5 8; 3.7	6. 72	7.45m8. 01m	-

		6			
H2L5	Br	3.5 6; 3.7 5	6. 74	7.50m; 7.95m	-
H2L6	NO 2	3.6 1.; 3.8 0	6. 60	7.84m; 7.63m; 8.05m	-

* Note: JAB = 20-22Hz

For an unambiguous verification of our conclusions, we point out that the product of the interaction of trifluoroacetylacetone with benzoylhydrazine was subjected to X-ray structural analysis in (1, 3).



This method, which directly determines the structure, showed that the specified compound is a condensation product with respect to acetyl carbonyl and has a 5-hydroxypyrazoline structure [5]. The PMR spectrum of this condensation product is in full agreement with this conclusion (the signal of the methyl group at δ 2.06 ppm., two asymmetric doublets - protons of the methylene group - at δ 3.09 and 3.25 ppm with a

coupling constant of 19 Hz, the signal at 6.79 ppm, is the proton of the hydroxyl group in position 5 of the oxypyrazoline ring), and in the ^{13}C NMR spectrum the carbon signal in position 5 of the cycle is at δ 94.80 ppm, has the form of a quartet with a SSCR of 32 Hz [3,4] Comparison of spectral data relating to the compound H2L3 and the condensation product of trifluoroacetylacetone with benzoylhydrazine, the structure of which was determined by the method of X-ray structural analysis [3] allows us to say with complete confidence that the compound H2L3 is a condensation product at the acetyl carbonyl and has a cyclic 5-hydroxypyrazoline structure B1.

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