



## PREPARATION OF ALIPHATIC AND AROMATIC 1,3-DIKETONES WITH POLYFLUOROALKYL SUBSTITUTES

KuchkorovaRanoRasulovna Candidate of Chemical Sciences, Associate Professor  
Tashkent State Pedagogical University named after Nizami.

B.B. Umarov Doctor of Chemistry, Prof. BukhGU,

Sh.Z.Kadirova is a 5th year student of TashFarmi.

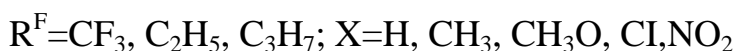
Phone +998995275009

E-mail: early. [qochqorova@bk.ru](mailto:qochqorova@bk.ru)

Keywords: Aroyltrifluoroacetylmethanes, polyfluoroalkyl substituents, polyfluorinated unsymmetrical 1,3-diketones, NMR,  $\beta$ -diketones, CCl<sub>4</sub>, CDCl<sub>3</sub> and DMF-d<sub>7</sub>, tautomerism.

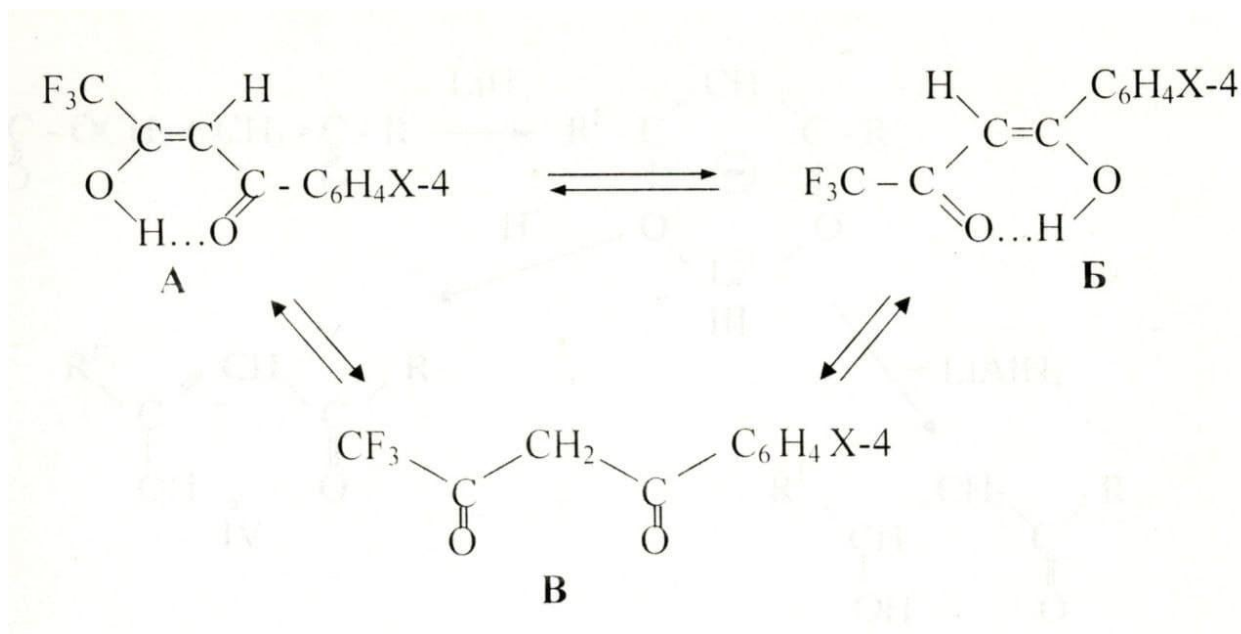
**Abstract:** The article is devoted to the preparation of aromatic and aliphatic 1,3-diketones with polyfluoroalkyl substituents.

Polyfluorinated unsymmetrical 1,3-diketones as objects of study seem to be unique [1.] and no systematic study of their properties has been undertaken before. As examples, the following compounds were synthesized according to the reaction:

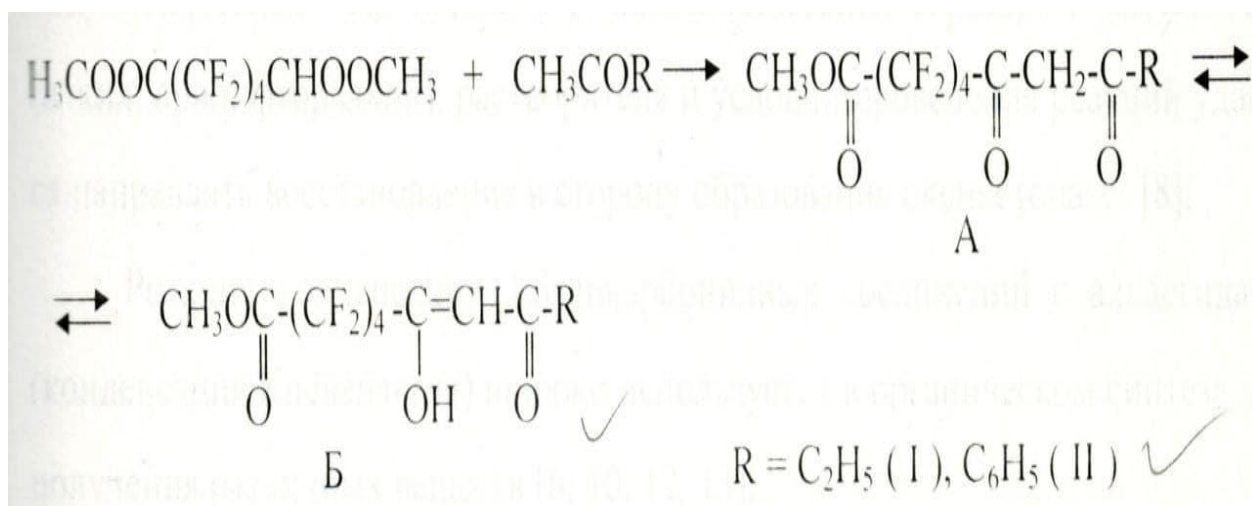


Aroyltrifluoroacetylmethanes exist in solutions as conjugated enols, which are clearly detected by NMR. In the specially taken PMR spectra of these compounds, there are no signals corresponding to the diketone form [2.3]. Previously performed spectroscopic studies of these  $\beta$ -diketones also indicate the presence of an equilibrium between two cis-enol structures A and B, and these tautomeric forms

are present in comparable amounts [2]:



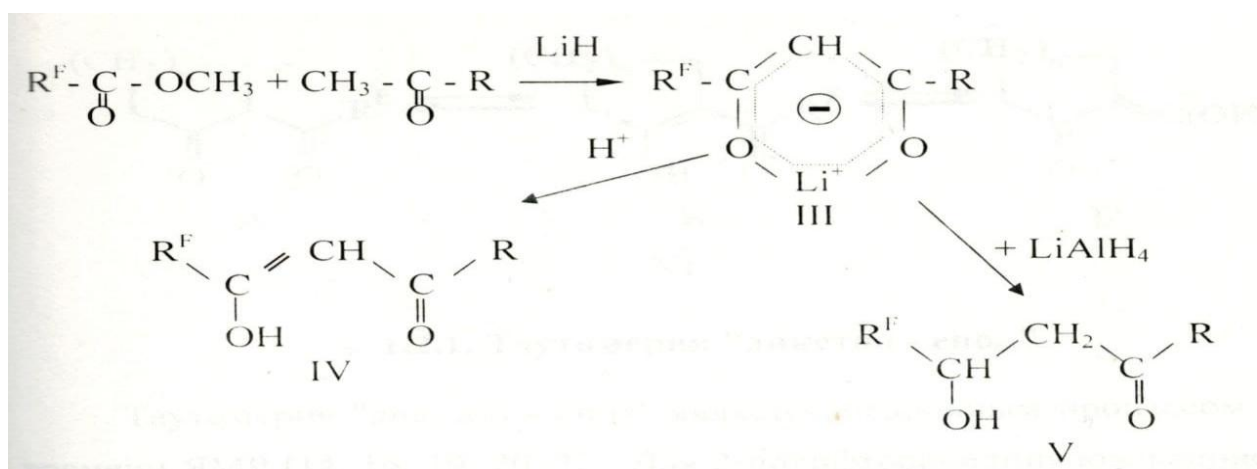
The interest in the synthesis of such compounds is explained by the fact that they are the starting materials for the preparation of fluorinated polyketones [7], where the authors studied the interaction of perfluoroadipic acid dimethyl ester with acetone, methyl ethyl ketone, and acetophenone:



PMR spectroscopy showed that the content of the enol form for compound I is 90%, and for II - 84%.

The authors[8,11] propose original methods for the preparation of fluoroalkyl-containing compounds. In contrast to conventional Claisen condensation reactions [1–3], the authors use lithium hydride instead of sodium alcoholate as a catalyst. The obtained lithium salts of diketones in the form of colorless powders (III) in high

yields are easily converted into  $\beta$ -diketones (IV) by the action of acids, and when the reaction mass is treated with lithium tetrahydridoaluminate, they are reduced to  $\beta$ -hydroxyketones (V):



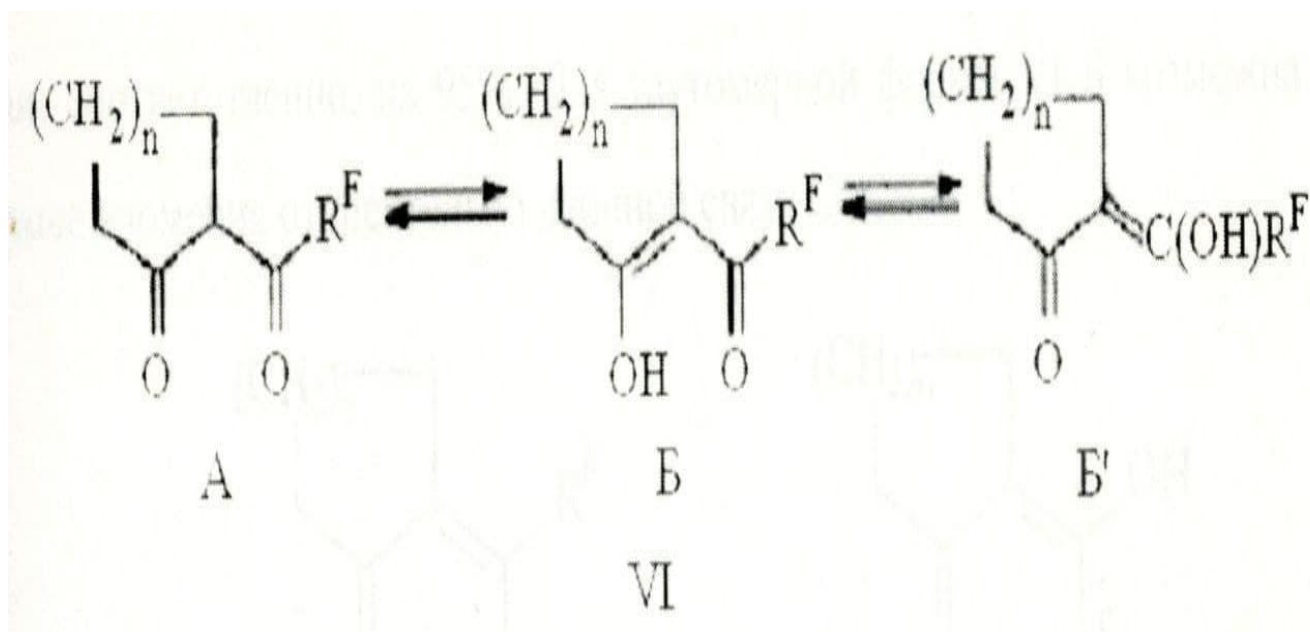
Compounds (V) can be synthesized in high yields when  $R=C_6H_5$ . At  $R = Alk$ , a large number of side products of the reaction are observed [8,11], in particular, regioisomeric  $\beta$ -hydroxy ketones,  $\alpha$ ,  $\beta$ -enones,  $\beta$ -aminovinyl ketones are formed. By choosing a substitute (alkyl, aryl, fluoroalkyl), solvent, and reaction conditions, it is possible to direct the reduction towards the formation of oxyketone V [8].

The condensation reaction of 1,3-dicarbonyl compounds with aldehydes (Knoevenagel condensation) is widely used in organic synthesis to obtain various substances [6].

The structure of 2-polyfluoroalkylcycloalkanones

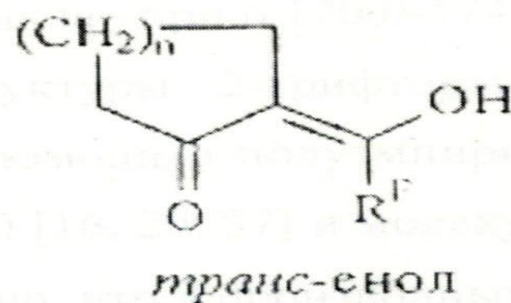
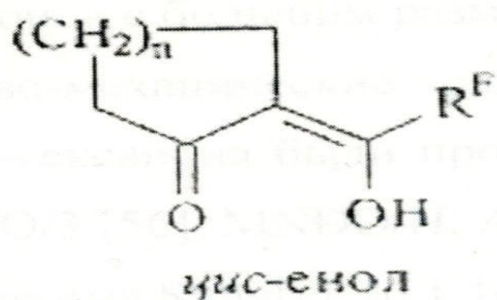
2-Polyfluoroalkylcycloalkanones are a prototropic system and can exist as diketo- and keto-enol tautomers (A, B, and B1). The structure of such 1,3-diketones was studied by  $^1H$  [1] NMR,  $^{13}C$  [2],  $^{19}F$  [1] and two-dimensional NMR [6], as well

as by UV [7], IR spectroscopy [1] and mass spectrometry [2]:



The diketone-enol tautomerism is a slow process on the NMR time scale [8]. For 2-polyfluoroalkylcycloalkanones, as well as for linear polyfluorinated 1,3-diketones [9], the diketone-enol tautomeric equilibrium is strongly shifted towards the enol form, both for pure compounds and for solutions in  $\text{CCl}_4$ ,  $\text{CDCl}_3$ , and  $\text{DMF-d}_7$ . This is confirmed by the presence in the  $^1\text{H}$  NMR spectra of the proton signal of the enol hydroxy group in the region of  $\delta$  11.4-16.3 ppm, while the signal of the methine proton of the diketo form is fixed in the region of  $\delta$  3.7-4.8 ppm. either cannot be detected at all [1], or its intensity is low [5]. It is known [6] that the introduction of an alkyl substituent into the second position of a linear 1,3-dicarbonyl system shifts the equilibrium towards the diketo-tautomer. approach. At the same time, 2-perfluorohexanoylcyclododecanone exists, according to  $^1\text{H}$  NMR data, in  $\text{CDCl}_3$  by 90% as a diketo form [11]. Apparently, in this case, the conformational features of the macrocycle no longer have a noticeable effect on the state of tautomeric equilibrium. Non-fluorinated 2-alkanoylcycloalkanones also exist predominantly in the enol form [12]. Thus, the content of enol in 2-acetylcyclopentanone and hexanone is 95-100%. 2-acetylcyclopentanone and -octanone are enolized by 70% or, respectively, by 95%. For the tautomeric form VI B, cis-trans isomerism is

possible with respect to the C=C double bond



The most probable, as well as for linear polyfluorinated 1,3-diketones, is the cis-enol form (28,32), since it can be stabilized simultaneously with two O–H...F HMWBs. Such an IMHB should shift the signal of the enol OH proton in the NMR spectrum downfield, which is observed in practice [1].

The results of IR spectroscopic studies confirm the coexistence of diketone and enol forms in 2-polyfluorinated cycloalkanones [2]. In the spectra recorded for pure compounds, solutions in  $\text{CHCl}_3$ , and KBr tablets, a broad absorption band was found in the region of 2300–3500  $\text{cm}^{-1}$ , corresponding to the vibrations of the hydroxy group bound by HMWC. In addition, in the region of 1560-1700  $\text{cm}^{-1}$ , bands were found attributed to vibrations of the  $\text{V}(\text{C}=\text{C}-\text{C}=\text{O})$  system, and in the region of 1670-1780  $\text{cm}^{-1}$ , bands of low intensity of isolated carbonyl groups of the diketo form were found.

Tautomerism "enol-enol".

It is now generally accepted [1–3] that the enol tautomer of diketones is not an averaged "pseudoaromatic" structure with an enol OH proton located symmetrically between two oxygen atoms [6], but an equilibrium mixture of two enol forms A and B. the type of electronic environment of the  $\text{CF}_3$  group in this case is also indicated by the chemical shift of the carbon nucleus of the carbonyl group of polyfluoroacyl. If for the cyclopentanone derivative the above signal was detected at  $\delta$  161.0 ppm, then for 1,3-diketones with a large alicycle size, at  $\delta$  170.0-174.3 ppm.

Quantum-mechanical calculations of the structure of 2-trifluoroacetylcyclopentanone and hexanone were carried out using semiempirical methods (MINDO/3 [6], MNDO/H, AMI, and PM3) [8] and molecular mechanics (Sybyl program [12]). It was found that in For cyclopentanone derivatives, the exo-enol form is the most stable, while for 2-acyl-substituted cyclohexanones, both enol forms are comparable in stability.

The greater stability of the exo-enol form for acylcyclopentanones (two exocyclic double bonds) and the endo-enol form for acylcyclohexanones (no exocyclic double bond) can be explained by conformational effects associated with different voltages of five-six-membered alicycles [2].

#### **LIST OF USED LITERATURE**

1. Кучкарова Р.Р. Комплексные соединения никеля, меди и цинка с производными фторированных  $\beta$ -дикетонатов. Дис. ... канд. хим. наук. - Ташкент: ИУ АН РУз, 2007 г. - 11-18 с.
2. REACTION OF 1, 1, 1-TRIFLUOROMETHYL-4-PHENYLBUTANEDIONE-2, 4 WITH BENZOIC ACID HYDRAZIDE  
KR Rasulovna INFORMATION TECHNOLOGY IN INDUSTRY 9 (3), 2021. 939-944
2. Methodology of the organization of the professional circle "Classroom teacher" in pedagogical higher educational institutions  
KR Rasulovna Journal of aeronautical materials 5 (42), 2022. 185-189
3. COMPLEX COMPOUNDS OF FLUORINATED B-DIKETONE DERIVATIVES WITH TRANSITION METALS  
KR Rasulovna International journal of Early Childhood Special Education (INT-JECSE), 2022. 7948-7951
4. Комплексные соединения производных фторированных  $\beta$ -дикетонатов с переходными металлами КР Rasulovna "INTERNATIONAL CONFERENCE ON EDUCATIONAL INNOVATIONS AND APPLIED SCIENCES 2022."

5. Кучкарова Р.Р., Умаров Б.Б., Якимович С.И., Зерова И.В., Абдурахмонов С.Ф., Эргашева Н.М., Мардонов У.М., Парпиев Н.А. Региоспецифичность реакции конденсации фторированных  $\beta$ -дикетонов с бензоилгидразидом / Академик С.Ю. Юнусов хотирасигабагишланган ёш олимлар илмий анжуманининг дастури ва маърузаларининг қисқача маъмуни. - УзРФАУМКИ. - 2004 йил 18-19 март. - Тошкент. 2004. - 17-бет.
6. Аvezов К.Г., Кучкарова Р.Р., Умаров Б.Б., Якимович С.И., Зерова И.В., Кузиева З.Э., Камолова З.К., Парпиев Н.А. Конденсация бензоилгидразонов фторированного  $\beta$ -дикетона пентачленным гетероциклом / Академик С.Ю. Юнусов хотирасигабагишланган ёш олимлар илмий анжуманининг дастури ва маърузаларининг қисқача маъмуни. - УзРФАУМКИ. - 2004 йил 18-19 март. - Тошкент. 2004. - 18-бет.
7. Умаров Б.Б., Кучкарова Р.Р., Мардонов У.М., Алимов Ё., Адинов Н. Синтез комплексов меди (II) с бензоилгидразонами 1-(2-теноил)-3,3,3-трифторацетона / Сборник тезисов докладов Международной научной технической конференции «Истиклол» «Современная техника и технология горнометаллургической отрасли и пути и их развития». - НавГГИ. - 23-25 сентября 2004 года. - Навоий, С. 134-135.
8. Умаров Б.Б., Кучкарова Р.Р., Абдурахмонов С.Ф., Якимович С.И., Зерова И.В., Парпиев Н.А. Конденсация 1-(2-теноил)-3,3,3-трифторацетона с гидразидом изоникотиновой кислоты // Доклады академии наук РУз. Ташкент. - 2004. - № 4. - С. 49-52.
9. Якимович С.И., Николаев В.Н., Блохтина С.А., Таутомерия в ряду бензоилгидразонов алифатических  $\beta$ -дикарбонильных соединений // Журн. Орг. химии. - Санкт-Петербург, 1984. - Т. 20. - № 7. - С. 1371-1378.

10. Якимович С.И., Зерова И.В., Пумпор К.Б. 1-Ацил-5-гидрокси-4,5-дигидрокси-пиразолы на основе фторированных 1,3-дикетонов: Материалы I Международной конференции «Химия и биологическая активность азотистых гетероциклов и алкалоидов»-М., 2001.-Т.2.-356.

11. Зеленин К.Н., Алексеев В.В., Якимович С.И., Зерова И.И. региоселективность реакции фторированных 1,3-дикетонов с гидразидами и таутомерия её продуктов: Тезисы докладов XVII Менделеевского съезда по общей и прикладной химии.-21-26 сентября 2003.-Казань, Т.2.-С.338.

12. Салоутин В.И., Бургарт Я.В., Чупахин О.Н., Фторсодержащие 2,4-диоксокислоты в синтезе гетероциклических соединений.-Успехи химии. -Москва, 199.-Т.68.-№3.-С.227-239