Synthesis of asymmetric perfluoro-substituted β-diketones according to Meerwein method

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Usually, to create nitrogen-containing cycle,reactions of intramolecular dehydro-, dehydra- and deaminocyclization and also reactions of intermolecular condensation of amino-, imino- and oxygen-containing compounds (aldehydes, ketones, alcohols) are used. In particular, one of widely used methods to synthesize derivatives of 1,3-diazine is condensation of 1,3-diketones (or their analogues) with different derivatives of guanidine and urea; a range of compounds produced in a similar way is extremely wide [1]. Since β-diketones in this method are used as C-C-C fragments, it is expedient to consider main methods to synthesize such compounds. It is known, a catalyzed by bases reaction of ethers of carbonic acids with ketones containing active hydrogen in α-position (Claisen condensation) is mostly used [2].

R-COOEt + R'-CH_2-COR'' -> R-CO-CHR'-CO-R'' + EtOH

The reaction takes place in the presence of metal sodium (potassium), *alcoholates* of alkali metals in suspension or in alcohol solutions. Stronger condensating agents such as sodium hydride or amide, mesitylmagnesium bromide, triphenylmethyl sodium [2a] are also used. Numerous symmetric and asymmetric β-diketones of linear structure containing different substituents have been synthesized using Claisen method [2b].

Meerwein condensation also gives β-diketones in a good yield by acylation of ketones with acid halides in the presence of Lewis acids as catalysts [3]:

R-C(=O)X + Me-C(=O)R ' -> RC(=O)CH_2 C(=O)R',

where R,R'=alkyl, aryl, hetaryl; X= halogen, RC(O)O-.

But the Meerwein condensation is used rather seldom in applied organic chemistry.

Systematic investigation of fluorinated β-diketones containing different numbers of fluorine atoms in the molecule was begun in the early 60-s.

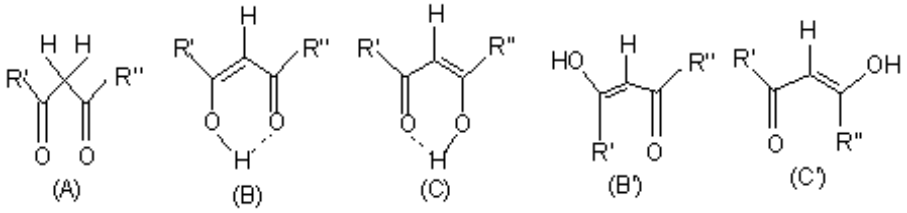
An impressive series of polyfluorinated β-diketones containing one fluorinated substituent has been produced by the Claisen method: R_F = CH_2F, CCl_2F, CHF_2, $CClF_2$, CF_2OCF_3, CF_3, C_2F_4H, $CF_2(CF_2)_4O$, C_2F_5, C_3F_7, C_4F_8H, C_4F_9, C_5F_{11}, C_7F_{15}, C_8F_{17}, C_6H_5XF (X = CH_3, Cl, OH, CF_3), $C_6H_4CF_3$, C_6F_5 (in this case the second substituent R= alkyl, aryl, or hetaryl). Yields vary from 11 to 80% in dependence on solvent, condensing agent and the nature of carbonyl and methylene component [4].

Other methods to produce polyfluorinated β-diketones are also known. I.L.Knunants et al. [5] synthesized 1,3-diketones containing trifluoromethyl group by difluoronitromethane detachment from oxyketones obtained by nitropentafluoroacetone condensation with methylketones (100^{O}C,20h, 33.5-38%).

A perspective method to synthesize β-diketones difficult to access was proposed. It consists in interaction of fluoroolefins with fluoroanhydrides of acids under pressure in the presence of antimony pentafluoride at 20^{O}C (ratio of F-acyl/SbF5 = 6/1, 40% yield). The authors of method [6] assume that in the reaction ketone is formed first, then it reacts with fluoroanhydride according to the scheme of the Claisen condensation catalyzed by acid.

For the purpose of separation and purification β-diketones are fractionated or converted to copper chelates, which further are recrystallized from organic solvents and decomposed with sulfuric acid or hydrogen sulfide [2b]. Chelates of high purity are produced by means of vacuum sublimation [4].

b-Diketones are known to be a prototropic system existing as three tautomeric forms (A)-(C), for two of them [(B) and (C)] *cis-trans*-isomerism [(B') and (C')] is possible. A number of investigations has shown that acyclic b-diketones exist only in tautomeric forms (A) – (C) [7]:



Introduction of electron-deficient fluorine-containing groups changes considerably electron density distribution in the β-diketone molecule affecting keto-enol equilibrium. It has been found that polyfluorinated b-diketones are distinguished by a higher degree of enolization in comparison with nonfluorinated ones. On the basis of IR, UV, NMR spectroscopy data, existence of β-diketones in *cis*-form (B)- (C) with intermolecular hydrogen bond has been proved [7,8]. Analysis of NMR spectra of liquid 1,2-diketones (R_F = C_3F_7, C_5F_{11},C_7F_{15}) demonstrates that an increase in fluorine content leads to a shift of keto-enol equilibrium to enol side; and in the presence of four and more fluorine atoms in the molecule enolization becomes complete [8], mainly regarding oxygen bound to more electron-deficient substituent. It is in good agreement with data on enolization of ethers of fluorine-containing β-keto-acids and connected with high electron-deficiency of fluoroalkyl groups [7]. More over, it is necessary to note substantial influence of the solvent nature on keto-enol equilibrium [9,10].

A scheme of synthesis of 1,3-diketones, given in this investigation, is most convenient because it is based on commercial perfluoroacylfluorides $C_6F_{13}COF$, $C_8F_{17}COF$, $C_3F_7[OCF(CF_3)CF_2]_nCOF$ (n =1,2,3,9). The process was carried out in one stage according to the Meerwein method [3], this is a difference from the Claisen condensation and is more attractive from technological point of view. The reaction was carried out at boiling by treatment of perfluoroacylfluorides with 3-5- fold excess of acetone in the presence of hydrogen fluoride

acceptor (NaF) for 10-15 hours. As a result, asymmetric perfluorosubstituted β-diketones were produced (1-6):

R_F-C(=O)F + CH_3C(=O)CH_3 -> R_F-C(=O)CH_2C(=O)-CH_3

R_F = C_6F_{13} (1), C_8F_{17} (2), CF(CF_3)OC_3F_7 (3), CF(CF_3)$OCF_2CF(CF_3)OC_3F_7$ (4), CF(CF_3)[$OCF_2CF(CF_3)$]$_2OC_3F_7$ (5), CF(CF_3)[$OCF_2CF(CF_3)$]$_n$$OC_3F_7$ (n = 9) (6).

The structure of synthesized β-diketones (1-6) was proved by data of IR spectra, which show characteristic bands of valence vibrations of the methyl group in a range of 3450-2985cm^{-1} and valence vibrations of the carbonyl group at 1770 cm^{-1}, which is in accordance with reference values [11]. The analytical and spectral data are given in the Table.

Table. *Yields, boiling points, refraction coefficients and data of IR spectra of asymmetric perfluoro-substituted β-diketones (1-6)*

Compound	Yield	b.p., ^oC	n^d_{20}	IR spectrum, cm^{-1}
1	21	176-177	1.3160	3500, 2950, 1780, 1660, 1600, 1450, 1350-1000
2	15	139-141/ 25Torr	1.3095	2985,2940,1770,1650, 1590,1455,1350-980
3	18	78-80	1.3048	3450, 3000,2500, 1770, 1650, 1430,1350-980
4	22	115-117	1.2980	3410, 2990,2450,1770, 1590,1440,1350-950
5	23	156-160	1.2950	3480,2960,1770, 1670, 1620,1450,1350-980
6	23	180/ 0.1 Torr	1.3070	3300,2910, 2300, 1770, 1720,1430,1350-950

Experimental

IR spectra were recorded on a Shimadzu IR-470 (Japan) instrument (film).

1,1,1,3,3-Pentahydroperfluorodecane-2,4-dione (1). 200g (0.55 mole) of acylfluoride of tridecafluoroheptanic acid was added dropwise to a mixture of 23.5g (0.56 mole) of NaF and 210 mL of acetone. The reaction mass was kept at 70^{o}C, washed with water to pH =6-7, extracted with R-113 (1,1,2-trifluorotrichloroethane), filtered and the solvent was distilled. The yield was 46.7g (21%), yellow oily liquid, b.p.=176-177^{o}C, n^d_{20} 1.3160.

1,1,1,3,3-Pentahydroperfluorododecane-2,4-dione (2), 1,1,1,3,3-pentahydroperfluoro(5-methyl-6-oxanonane)-2,4-dione (3), 1,1,1,3,3-pentahydroperfluoro (5,8-dimethyl-6,9-dioxadodecane)-2,4-dione (4), 1,1,1,3,3-pentahydroper-fluoro (5,8,11-trimethyl-6,9,12-trioxapentadecane)-2,4-dione (5) and 1,1,1,3,3-pentahydroperfluoro (5,8,11,14,17,20,23,26,29,32-decamethyl-6,9,12,15,18, 21,24,27,30,33-decaoxahexatriacontane)-2,4-dione (6) were produced similarly to compound (1) from the appropriate acylfluorides of perfluorocarbonic acids. The physical and chemical characteristics are given in the Table.

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