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Fluorine-containing β-Diketones

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The methods of synthesis, the keto-enol tautomerism, the chemical reactions (including the formation of heterocycles), and the applications of fluorine-containing β-diketones are examined. The influence of the introduction of fluorine-containing substituents on the properties of β-diketones is discussed.
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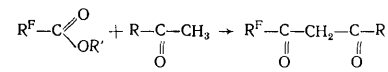
I. INTRODUCTION

β-Diketones and their metal chelates are widely used in industry and in laboratory practice as extractants and analytical reagents for the lanthanides, as shift reagents, as biologically active substances, and as catalysts of various reactions. By virtue of the presence of two carbonyl groups and their tendency towards enolisation, they lead to the possibility of investigating the keto–enol tautomerism, dual reactivity, the nature of the intramolecular hydrogen bond, and the synthesis of various heterocyclic compounds. Fluorine-containing β-diketones are in many instances superior as regards their useful properties to their non-fluorinated analogues [extraction, gas-liquid chromatography (GLC) of chelates, and biological activity] and have a number of characteristic features due to the presence of fluorine atoms in the molecule.

Extremely extensive data concerning the synthesis, chemistry, and possible applications of polyfluorinated β-diketones and heterocycles based on them have now accumulated in the literature, but the problem has not been surveyed, with the exception of a review[1] covering the literature up to 1968 and devoted to a large extent to the metal chelates of fluorine-containing β-diketones. Data on the metal chelates of fluorinated β-diketones are also contained in another review[2] and those on the applications of non-fluorinated metal β-diketonates are given in two other publications[3,4]. This review provides a survey of the literature data on the synthesis, keto–enol tautomerism, and the most characteristic synthetic reactions and practically useful properties (including biological activity) of polyfluorinated β-diketones. The literature up to 1979 inclusive is covered.

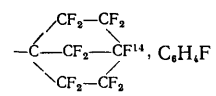
II. METHODS OF SYNTHESIS

The most common and universal method of synthesising polyfluorinated β-diketones is the Claisen condensation[5,6] using the esters of carboxylic polyfluoroacids and methyl ketones as the starting materials and sodium alkoxides[7,8], sodium amide[9,10], sodium hydride[11], and boron trifluoride[12] as the condensing agents. The condensation is usually carried out in anhydrous diethyl ether[5,6], but benzene[13], dimethoxyethane[14], dimethyl sulphoxide (DMSO),[11] and acetic acid[12] are used sometimes. Depending on the solvent, the condensing agent, and the nature of the carbonyl and methylene components, the yields vary from 20 to 80%:

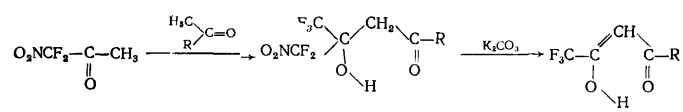


(I)

β-Diketones with a single fluorinated substituent have been obtained by this method: $R^F = CH_2F$,[12,15] CCl_2F,[16] CHF_2,[17] $CClF_2$,[18] CF_2OCF_3,[19,20] $CF_2\overline{CFCF_2CF_2CF_2}O$,[19,20] CF_3,[7,8] C_2F_4H,[21] C_2F_5,[18] C_3F_7,[22] C_4F_8H,[17] C_4F_9,[23] C_5F_{11},[24] C_7F_{15},[24,26] C_8F_{17},[27] C_6H_3XF (X = CH_3, Cl, OH, or CF_3),[9,10,28] $C_6H_4CF_3$,[29] or C_6F_5[11] (the second substituent is R = alkyl, aryl, or heteroaryl). Diketones with two fluorinated substituents have also been synthesised: $R^F = R = CF_3$,[7,15,30] HCF_2,[31] HC_2F_4,[31] C_7F_{15},[24,25] or C_6F_5;[11] $R^F = CH_3$, R = HCF_2,[31] C_2F_5,[32] C_3F_7,[32] C_7F_{15},[25] or

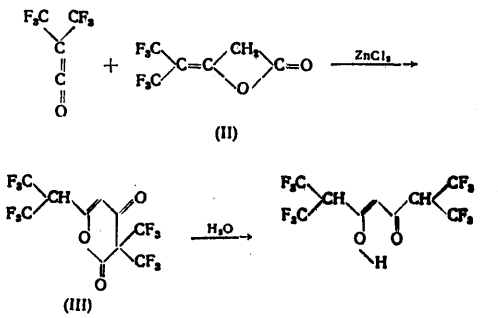


A number of other methods of synthesising polyfluorinated β-diketones are known. Knunyants and coworkers[34] described a synthesis of β-diketones containing the trifluoromethyl group; it is carried out by eliminating difluoronitromethane from β-hydroxyketones obtained by the condensation of pentafluoronitroacetone with methyl ketones:

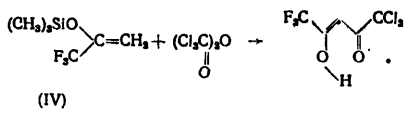


A novel method of synthesising 1,1,1,7,7,7-hexafluoro-2,6-bis(trifluoromethyl)heptane-3,5-dione in 70% yield has been patented; it consists in condensing bis(trifluoromethyl)keten with the β-lactone of 3-hydroxy-4,4-bis(trifluoromethyl)but-3-enoic acid (II) [acetyl chloride can be used instead of compound (II)] in the presence of zinc chloride and subsequent hydrolysis of the resulting δ-lactone of 5-hydroxy-2,2,6,6-tetrakis(trifluoromethyl)-3-oxohex-4-enoic acid

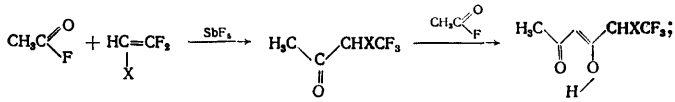
(III):[35]



Fokin and Uzun[36] showed that, when β-nitrotetrafluoroethyl nitrite reacts with acetone or acetophenone, up to 40% of the corresponding β-diketones (I, $R^F = CF_2NO_2$; R = CH_3 or C_6H_5) is formed. It has been established[37] that *O*-silyl-substituted enols (IV) are acetylated by the anhydrides of carboxylic halogenoacids at the terminal sp^2-hybridised carbon atom with formation of up to 43% of the corresponding β-diketone:

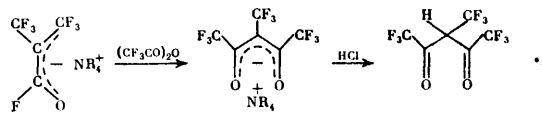


An interesting and promising method has been proposed[38] for the synthesis of β-diketones which are difficult to obtain, consisting in the interaction of fluoro-olefins with acid fluorides under pressure in the presence of antimony pentafluoride. The authors[38] suggest that a ketone is formed initially in the reaction and then reacts with the acid fluoride via a mechanism involving an acid-catalysed Claisen condensation:

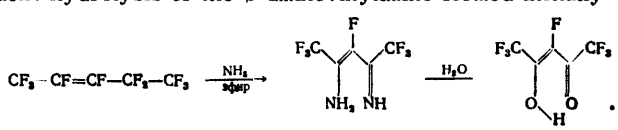


X = F or H.

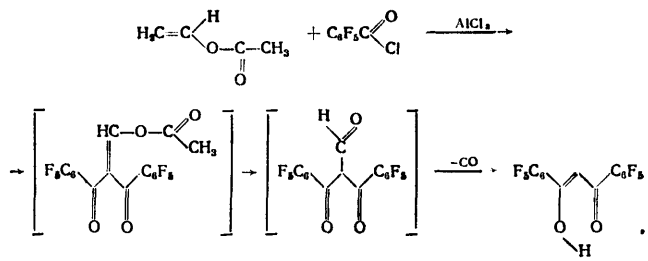
Knunyants and coworkers[39] succeeding in synthesising β-diketones with a fluorinated substituent in the α-position by treating mesomeric fluorocarbanions with the anhydrides of carboxylic perfluoroacids:



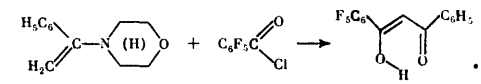
Heptafluoroacetylacetone has been synthesised recently by treating *trans*-perfluoropent-2-ene with ammonia and subsequent hydrolysis of the β-aminovinylimine formed initially[40]:



The use of the Claisen condensation[11,33] for the synthesis of β-diketones with pentafluorophenyl substituents frequently leads to the formation of chromones and flavones[41,42] owing to to ease of displacement of the *ortho*-fluorine atom from the pentafluorobenzoyl group by nucleophiles. A number of specific methods are therefore used for the synthesis of such diketones[11,42]. Thus Osadchii and Barkhash[42] synthesised decafluorodibenzoylmethane (DFBM), pentafluorodibenzoylmethane (PFDM), and 1,4-bis(pentafluorophenyl)butane-1,3-dione by acylating pentafluorobenzoylacetic ester with the chlorides of pentafluorobenzoic, benzoic, and pentafluorophenylacetic acids respectively and subsequent hydrolysis and decarboxylation under the influence of concentrated sulphuric acid. They were also the first to obtain perfluorodibenzoylmethane by fluorinating the sodium salt of DFBM with perchloryl fluoride[43]. Although DFBM is formed also when the dichloride of malonic acid is acted upon by pentafluorophenylcopper in absolute ether (yield 20%),[11] the difficulty of obtaining pentafluorophenylcopper and the low yield of DFBM limit the employment of this method. The same compound was synthesised by condensing pentafluorobenzoyl chloride with vinyl acetate in the presence of aluminium chloride (yield 34%):[11]



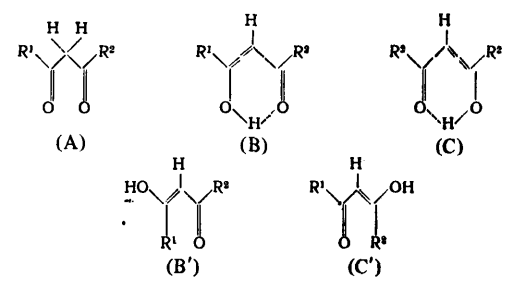
PFBM is obtained in 25% yield by the reaction of α-morpholinostyrene with pentafluorobenzoyl chloride in anhydrous dioxan[11]. The attempt to extend the method to the synthesis of DFBM proved unsuccessful.



In order to isolate and purify them, β-diketones are distilled[8,19,20] or converted into copper chelates, which are then recrystallised from organic solvents and decomposed with sulphuric acid[22] or hydrogen sulphide[7]. Vacuum sublimation is used to prepare high-purity chelates[25].

III. STRUCTURE AND ENOLISATION

β-Diketones constitute a prototropic system, which can exist in three tautomeric forms (A)–(C), for two of which [(B) and (C)] there is a possibility of geometrical *cis–trans* isomerism [(B') and (C')]. However, a number of studies have shown[44] that non-cyclic β-diketones exist only in the tautomeric forms (A)–(C).



The introduction of electron-accepting fluorine-containing groups greatly alters the distribution of electron density in the β-diketone molecule, which influences the keto–enol equilibrium. Indeed, a higher degree of enolisation of polyfluoro-β-diketones compared with the non-fluorinated compounds

was established as early as 1953 (with the aid of bromination) and infrared spectra have led to the hypothesis that they exist in the *cis*-forms (B)–(C) with an intramolecular hydrogen bond (IAHB).[23] Subsequently this hypothesis was confirmed by infrared spectroscopic[33,45–49], ultraviolet spectroscopic[33,45,50,51], and ^{1}H NMR [44,52,53] data.

The study of the ^{1}H NMR spectra of liquid β-diketones showed that the increase of the fluorine content shifts the keto–enol equilibrium towards the enol (Table 1) and that in the presence of four or more fluorine atoms in the molecule the enolisation is complete[12,17,20,54]. This agrees well with data for the enolisation of esters of fluorine-containing β-ketoacids[55] and is associated with the pronounced electron-accepting properties of the fluoroalkyl groups[46,56]. It is of interest that 1,1,1,5,5,5-hexafluoro-3-trifluoromethylpentane-2,4-dione, containing three CF_3 groups, is not enolised and exists fully in the diketo-form[39], although its non-fluorinated analogue is 30% enolised[57]. The influence of the solvent on the keto–enol equilibrium and on the chemical shifts of the protons of trifluoroacetylacetone (TFAA) and hexafluoroacetylacetone (HFAA) has been investigated[58].

Table 1. The contents of the enolic form in polyfluoro-β-diketones R^1–CO–CH_2–CO–R^2 according to ^{1}H NMR data for the pure liquids at 33–35 °C.

R^1	R^2	Content of enol, %	δ_{OH}, p.p.m.	Refs.
CH_3	CH_3	81	15.6	52
H_2CF	CH_3	87*	14.7	12
HCF_2	CH_3	95–97	15.6	17
CF_3	CH_3	97	14.1	54
HCF_2CF_2	CH_3	100	14.86	13
HCF_2	HCF_2	100	12.98	31
CF_3	CF_3	100	13.0	54

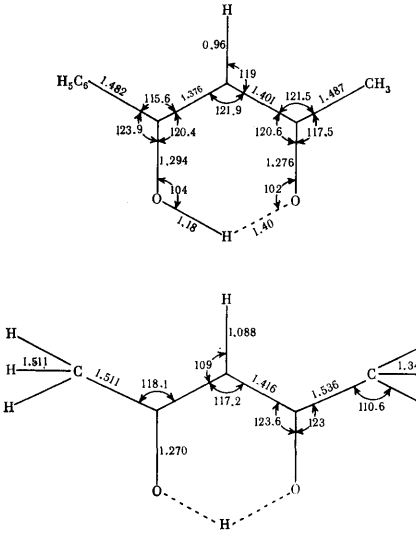
*At 26 °C.

The pronounced electron-accepting properties of fluoroalkyl substituents are also manifested by the weakening of the IAHB in fluorine-containing β-diketones compared with the non-fluorinated compounds. Thus it has been established[59] that the signal of the O–H proton is displaced upfield on passing from acetylacetone (AA) to TFAA and HFAA and also from benzoylacetone (BA) to trifluorobenzoylacetone (TFBA); according to the authors[59], this demonstrates a weakening of the IAHB. An analogous relation has been found[60] for β-diketones of the selenophen series. On the basis of HFAA as an example, Gunnarsson et al.[61] suggest that the strength of the IAHB be estimated from the correlation between the proton chemical shifts and the isotope effect on replacement of the OH proton by deuterium for the same hydrogen-bonded systems; however, studies of this kind have not been carried on fluorine-containing β-diketones.

Asymmetric polyfluoro-β-diketones with a fluoroalkyl substituent at only one carbonyl group are convenient objects for the investigation of the position of the proton in the *cis*-enol form with an IAHB (a study of the enol–enol equilibrium), but here too the studies which have been carried out are restricted mainly to the non-fluorinated dicarbonyl compounds. Thus, analysis of the chemical shifts of the enol protons in the ^{1}H NMR spectra of *para*-substituted BA led to the conclusion[62] that the fraction of the enolic form with the proton at the oxygen atom linked to the benzene ring increases as the electron-accepting properties of the *para*-substituent in the ring are enhanced. This is also confirmed by data[63] where an analogous conclusion concerning the preferred mode of enolisation of β-diketones involving the oxygen atom linked to the more electron-accepting substituents was reached on the basis of a study of ^{17}O NMR. This mode of enolisation was confirmed elegantly for asymmetrical polyfluoro-β-diketones by the results of a study[64] in which the influence of the solvent on the chemical shifts of the carbon nuclei of both carbonyl groups in AA, dibenzoylmethane (DBM), TFAA, and salicylaldehyde was investigated by ^{13}C NMR; it was established that in TFAA the carbonyl group linked to the trifluoromethyl group is enolised.

On the basis of the study of the ^{13}C NMR spectra of the enolic forms of fluorine-containing and hydrocarbon β-diketones, it was concluded that they do not undergo the enol–enol tautomerism and the observed changes in the chemical shifts of the carbon nuclei were explained by a redistribution of the electron density in the chelate ring with an IAHB.[65] Nevertheless the same investigators[66] proposed a method for determining the position of the proton in the chelate with an IAHB from the ^{13}C NMR spectra of metal chelates; the presence of two equivalent potential wells for the bridging hydrogen atom in HFAA was pointed out in an earlier study[67].

The recently observed simultaneous presence of the enolic and enthiol forms in solutions of fluorine-containing monothio-β-diketones cooled to −70 °C constitutes a convincing confirmation of the occurrence of intrachelate tautomerism in β-diketones[68].



The bond lengths (in Å) and angles (in degrees) in BA [71] and TFAA [69] molecules.

Molecular Structure

The determination of the molecular geometries of the enolic forms of TFAA [69] and HFAA [70] by electron diffraction in the gas phase and X-ray diffraction study of the crystal and

molecular structures of BA,[71] *p*-nitrobenzoylacetone[72], and DBM [73] also failed to provide an unambiguous answer to the question of the position of the proton in the enolic tautomers (see Figure). According to Andreassen and coworkers[69,70], the experimental distances between the two oxygen atoms are in best agreement with the symmetrical form (an analogous conclusion was reached by Jones[72]); on the other hand, an asymmetric structure of BA and DBM molecules was indicated in other investigations[71,73].

Two O(1) ionisation bands, differing by 1.5 eV, were recently found by photoelectron X-ray spectroscopy and it was established that AA and HFAA exist in two tautomeric forms (B) and (C), the barrier to their interconversion via the enolic form with a symmetrical location of the proton being low.[74] For HFAA, this conclusion was confirmed[61] by a study of the ^1H NMR and ^2H NMR spectra.

Distribution of Electron Density

The distribution of electron density in the enolic forms of polyfluoro-β-diketones has been calculated by the CNDO method[75-77]. An increased electron density at the carbon atom linked to the fluorinated substituents has been observed for TFAA.[75,76] The study of the influence of the structure of the fluoroalkyl substituent on the distribution of electron density showed[77] that the distribution depends little on the position of the proton in the enolic forms of β-diketones.

Table 2. The ionisation constants of polyfluoro-β-diketones $R^1-CO-CH_2-CO-R^2$.

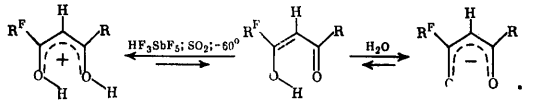
R^1	R^2	pK_a	Solvent	Temp., °C	Refs.
CH_3	CH_3	9.05±0.04	5% aqueous ethanol	20	31
CH_3	CF_2H	7.07±0.09	ditto	20	31
CH_3	CF_3	6.56±0.09	»	20	31
CH_3	CF_2CF_2H	5.51±0.09	»	20	31
CH_3	CF_2CF_3	5.17±0.02	»	20	31
CH_3	$(CF_2)_4H$	4.7±0.10	»	20	31
CF_2H	CF_2H	5.37±0.06	»	20	31
CF_3	CF_3	4.6	water	25	84
CF_3	CF_3	5.3	»	25	85
CF_3	CF_3	6.0	75% aq. dioxan	25	79
CF_2CF_2H	CF_2CF_2H	2.43±0.07	5% aq. ethanol	20	31
	CF_3	6.35±0.03	80% aq. methanol	25	20
ditto	CF_2OCF_3	6.22±0.03	ditto	25	20
»		4.95±0.70	»	25	20

IV. ACID–BASE PROPERTIES

Depending on the acidity of the medium, β-diketones exhibit the properties of acids or bases, splitting off or combining with a proton. In aqueous media polyfluoroalkyl-β-diketones are stronger acids by 2–3 orders of magnitude than the corresponding non-fluorinated analogues. This was demonstrated by the determination of their ionisation constants in a series of aqueous organic systems (50% dioxan–water[78], 75% dioxan–water,[79,80] 46% acetone–water,[81] 80% methanol–water,[20] 5% ethanol–water,[31] and dimethylformamide [82]) and in water[83-85] and are clearly illustrated by measurements[85] of the pK_a of *m*- and *p*-substituted benzoyltrifluoroacetones.

The influence of the structure of the fluorinated substituent on the acid dissociation constants of polyfluoro-β-diketones in solutions are illustrated in Table 2. However, even the lowest of the available literature values of pK_a for HFAA, which is 4.6,[84] is in poor agreement with the pK_a of other β-diketones and in all probability characterises the acidity of the dihydrate of hexafluoroacetyl-1,1,1,5,5,5-hexafluoropentane-2,2,4,4-tetraol which is formed extremely readily when HFAA comes into contact with water (see Section V).[31] A linear relation has been found between pK_a and the Taft σ* constants of the substituents R for constant R^F, which is not observed when R^F is varied and R is kept constant; it was established that the acidity of polyfluoro-β-diketones increases with the chain length of R^F from CF_3 to $(CF_2)_4H$.

In weakly acid solutions non-fluorinated β-diketones form both monocations (96% H_2SO_4) and dications ($HFSbF_5$ in SO_2);[86,87] polyfluoroalkyl-β-diketones undergo monoprotonation under the same conditions[87,88]:



The basicity constant pK_b of thenoyltrifluoroacetone (TTFA) in sulphuric acid proved to be −5.2 in a spectrophotometric determination and −5.3 in a potentiometric determination[89].

V. CHEMICAL REACTIONS

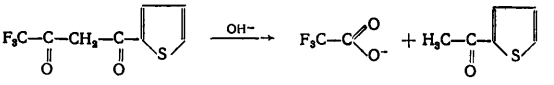
1. Reactions of Carbonyl Groups

Most of the synthetic studies on polyfluoro-β-diketones are associated with the investigation of the reactions of carbonyl groups with nucleophiles, since these reactions in fact open the way to different β-diketone derivatives and make it possible to obtain a wide range of compounds, including aza-heterocycles, with fluorine-containing substituents in the heteroring, many of which exhibit a high biological activity.

(a) Interaction with hydroxy-compounds.

The interaction of polyfluoro-β-diketones with hydroxyl-containing nucleophiles (water and alcohols) has been little studied, although it is of interest, because β-diketones are used fairly widely as extractants of metal cations from aqueous media[90].

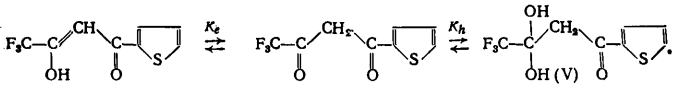
In an alkaline medium polyfluoro-β-diketones are cleaved like their hydrocarbon analogues[91] and diketones with a single polyfluoroalkyl substituent form a salt of a carboxylic polyfluoroacid and a methyl ketone[92]:



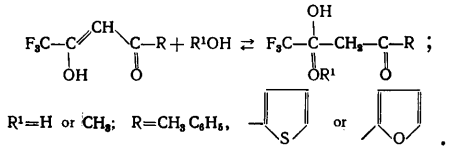
This shows that the nucleophilic attack is directed to the carbonyl linked to the fluorinated substituent. The replacement of one of the fluorine atoms of the trifluoromethyl group by the nitro-group facilitates hydrolytic cleavage still further and 1,1-difluoro-1-nitropentanedione is cleaved on being simply boiled with water[36].

Nevertheless asymmetric polyfluoro-β-diketones without NO_2 groups in the molecule are not hydrolysed under the usual condition in an acid or neutral medium and, like other halogen-containing carbonyl compounds[94], form geminal

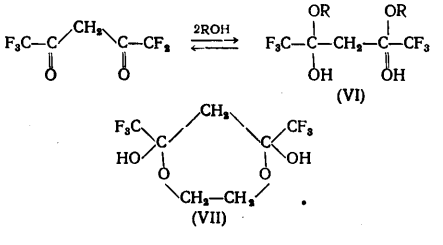
adducts. Thus, when TTFA was dissolved in the benzene–water two-phase system, it was observed[95] that the diketone in benzene solution is hydrated to a large extent (12%). These data are confirmed by the anomalously low (2%) content of the enolic form of TTFA in aqueous solution, which has been attributed[96] to the formation of the hydrate (V), which shifts the diketone–enol equilibrium towards the diketo-form and further towards the hydrate:



In a series of studies[97–99] investigation of the NMR ^{19} and ^{1}H NMR spectra of a series of trifluoromethyl-β-diketones showed that water or an alcohol adds reversibly to one of the carbonyl groups. The equilibrium constants and the heats of formation of the adducts have been determined. From the study of the equilibrium between the initial forms of the trifluoroacetoacetic ester (the keto- and enolic forms), on the one hand, and the corresponding hydrates and hemiketals, on the other, it was concluded that water interacts exclusively with the keto-form[100]. The rate of this interaction exceeds the rate of the keto–enol transformation. It has been shown[101] that the tendency of fluorine-containing β-diketones to form geminal adducts diminishes when one CF_3 group in HFAA is replaced by the α-thienyl (TTFA), phenyl (BTFA), or methyl (TFAA) groups:



In the case of HFAA, which contains two trifluoromethyl groups, water or alcohol adds to both carbonyl groups and the resulting geminal adducts (IV) (tetraols and bishemiketals) are so stable that they can be isolated in a free form[30,102,103]. The reaction of HFAA with ethylene glycol leads to 5,7-dihydroxy-5,7-bis(trifluoromethyl)dioxepan (VII):[104]

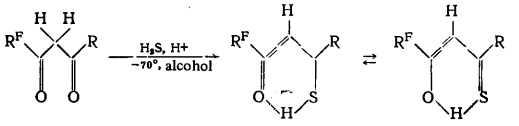


The equilibrium in the reaction of HFAA with water is strongly displaced towards the adduct, while in ethereal solution only an insignificant amount of the enolic form is present[30] and the abstraction of both water molecules requires prolonged refluxing over P_2O_5.

It is of interest that an increase in the length of even one of the two fluoroalkyl substituents in β-diketones (analogues of HFAA) reduces sharply the stability of the dihydrates. For example, the crystalline adducts of water with a diketone incorporating CF_3 and C_3F_7 groups, namely 1,1,1,5,5,6,6,7,7-decafluoroheptane-2,4-dione is stable only at −25 °C, decomposing on heating to room temperature with elimination of water[32], although the similar adduct of a β-diketone containing the CF_3 and C_2F_5 groups is entirely stable. On the other hand, a stable dihydrate is formed when one trifluoromethyl group is retained in the molecule, while the other is replaced by the difluoromethyl-containing group $-HCF_2-C(OH)_2-CH_2-C(OH)_2-CF_3$.[31]

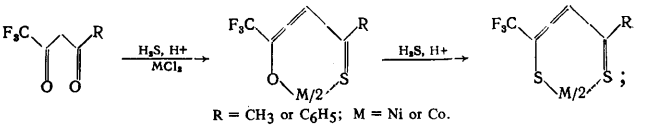
(b) Interaction with hydrogen sulphide.

The interaction of β-diketones with hydrogen sulphide in the presence of basic[105,106] or acid[107,108] catalysts leads to the replacement of one or both oxygen atoms in the carbonyl groups by sulphur. The study of this reaction in relation to polyfluoro-β-diketones demonstrated the necessity to increase the concentration of the catalyst (anhydrous hydrogen chloride) as the electron-accepting properties of the substituents at the carbonyl groups are enhanced, which can be accounted for[108] by the necessity to displace the keto–enol equilibrium towards the reactive diketo-form. A series of monothio-β-diketones with different fluoroalkyl (CF_3,[108–113] HCF_2CF_2,[114] C_2F_5,[110,113] and C_3F_7 [113,115]) and hydrocarbon groups have now been obtained by this method:



It has been shown by mass spectrometry that the condensation involves the carbonyl group linked to the least electron-accepting substituent[108,116]. On this basis, it is suggested[117] that the attacking species in the reaction of β-diketones with hydrogen sulphide is H_3S^+ and the reaction is electrophilic. The mechanism involving the protonation of the carbonyl group and nucleophilic attack by hydrogen sulphide is more probable[118].

The replacement of the oxygen of the second carbonyl group by sulphur with formation of dithio-β-diketones is possible, but these compounds are relatively unstable and readily dimerise[119,120]. The attempts to synthesise dithiohexafluoroacetylacetone and its chelates proved unsuccessful[121,122]. Only the synthesis and spectroscopic study of the nickel and cobalt chelates of dithiotrifluoroacetylacetone and dithiodifluorobenzoylacetone when hydrogen sulphide is passed into concentrated solutions of β-diketones and salts of the corresponding metals in absolute alcohol saturated with hydrogen chloride has been reported; the yields amount to 15–30%. The reaction mechanism proposed by Barraclough et al.[122] involves the formation of a monothio-β-diketone, which is then coordinated to the metal, so that the subsequent introduction of sulphur takes place, as it were, on a matrix. In all probability this reaction is possible by virtue of the presence of hydrogen chloride, which prevents the formation of the metal sulphide and the reversible decomposition of the metal chelate by hydrogen sulphide:



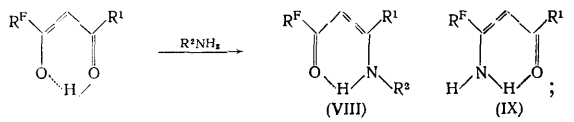
R = CH_3 or C_6H_5; M = Ni or Co.

(c) Reactions with amino-compounds

The interaction of polyfluoro-β-diketones with an amine can involve one or both carbonyl groups of the β-diketone molecule (and sometimes also the α-carbon atom), depending on the nature of the amine, the reaction conditions, and the

structure of the substituents at the carbonyl groups, with formation of β-aminovinyl ketones (β-AVK), as well as various saturated or aromatic heterocycles.

Reactions with ammonia and primary amines. When solutions of polyfluoro-β-diketones are refluxed with ammonia or primary amines under the conditions of acid catalysis or in the absence of a catalyst, β-AVK (VIII) are formed[29,123–127] and, in the case of asymmetric β-diketones with a single fluoroalkyl substituent, the carbonyl group linked to the non-fluorinated substituent is involved in condensation. This has been established by the synthesis of isomeric β-AVK (IX) with the amino-group at the fluoroalkyl substituent[128] and has been confirmed mass-spectrometrically[127]:



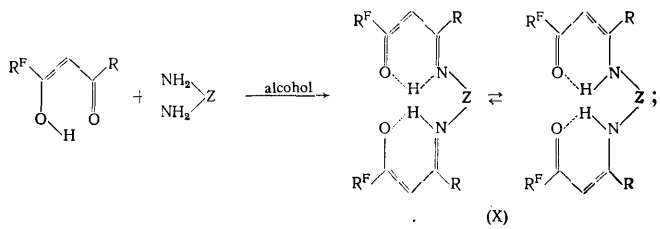
(VIII) (IX)

R^F=CF_3[123], HCF_2[127], H $(CF_2)_2$[126,127], H $(CF_2)_4$[127], $CF_3C_6H_4$[29]; R^1 — alkyl, fluoroalkyl, or aryl; R^2—H, alkyl, aryl, or $N{=}C(CF_3)_2$

The analogous reactions of the esters of fluorine-containing β-ketoacids involve the ketone carbonyl group linked to the fluorinated substituent[129,130].

The condensation of both carbonyl groups in polyfluoro-β-diketones with free monoamines, leading to the formation of fluorine-containing β-di-imines, is unknown, but treatment of an alkaline solution of TFAA with platinum hexammine gave a β-di-imineplatinum complex in 40% yield[131,132]. According to the authors[131,132], the reaction constitutes a promising method for the synthesis of β-aminovinylketimines, but they did not describe the isolation of the ligand in a free form. In our view the interaction of perfluoro-olefins with ammonia may serve as a simpler and more reliable method of synthesising fluorine-containing β-aminovinylketimines[40].

In the interaction of polyfluoro-β-diketones with polyalkylenepolyamines one carbonyl group from each two diketone molecules and both terminal amino-groups of the polyalkylenepolyamine are as a rule involved in condensation; this leads to high yields of the corresponding bis(β-dioxo)-alkylenedi-imines (X):[133–140]



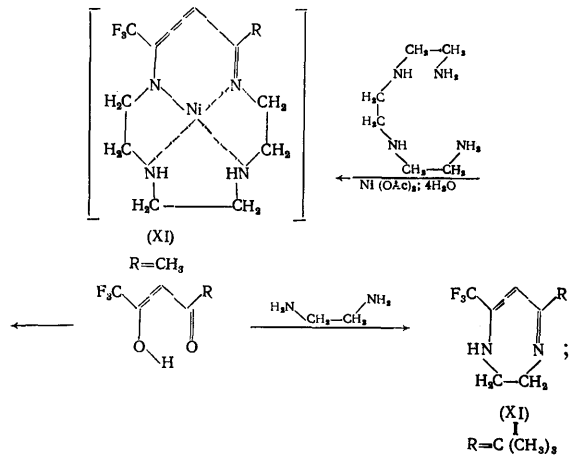
(X)

Z=CH_2CH_2[133,134,136,138], $CH_2CH(CH_3)$[134], $CH_2CH_2CH_2$[135,136,138], $CH_3CHCHCH_3$[137], $(CH_2)_2NH(CH_2)_2NH(CH_2)_2$[139], or $(CH_2)_2NH(CH_2)$—$_2$[140].

Recently there has been a growth of interest in these compounds in view of the discovery of their properties satisfying many of the requirements of the metal chelate gas chromatography[136–138]. The monomeric structure of bis(β-dioxo)alkylenedi-imines has been confirmed by the determination of their molecular weights[139] and by the formation of individual metal chelates[134,137,138]. The direction of nucleophilic attack in the case of asymmetric β-diketones on the carbonyl linked to the non-fluorinated substituent has been established by determining the dipole moments[134,135] and by the mass-spectrometry[93,141] of the compounds themselves, as well as the X-ray diffraction analysis of their nickel(II) chelates[142]. On the basis of this direction of attack, it is suggested that the electron-accepting CF_3 group induces a larger δ+ charge on the remote carbonyl than on the carbonyl linked to this group[142].

The question of the tautomeric structure of the compounds remains controversial: some workers[134,135] are inclined towards the iminoenol structure, while in other investigations[93,139] preference is given to the enaminoketone form on the basis of the ^1H NMR spectra and dipole moments, which appears to be more correct.

Only isolated instances of the formation of cyclic compounds in this reaction have been described. Thus the reaction of TFAA with triethylenetetramine in the presence of nickel ions yielded compound (XI),[143] and the synthesis of dihydrodiazepine (XII) has been reported[144]:



(XI)

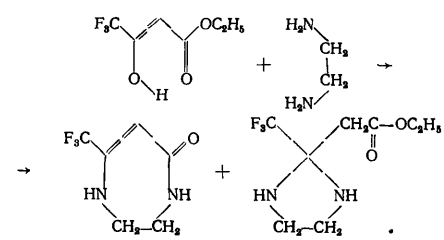
R=CH_3

(XI)

I

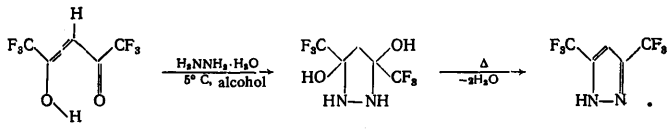
R=$C(CH_3)_3$.

Depending on the conditions, the condensation of the esters of fluorine-containing β-ketoacids with ethylenediamine leads either to a mixture of a substituted 2,3-dihydro-1,4-diazepin-5-one and imidazolidine in various proportions or to the imidazolidine alone[129,145]:



Reactions with hydrazines and hydroxylamine. Like their hydrocarbon analogues[146], polyfluoro-β-diketones react with hydrazines at room temperature[147] or on heating to form pyrazoles[93,148–153], among which compounds with anti-inflammatory and analgesic activities[147,148], highly active herbicides[150], preparations for the treatment of hyperglycemia[152], heat resistant heat exchanger, and surfactants[153] have been patented. Interaction of bis-β-diketones with hydrazines proceeds similarly and leads to bispyrazoles[93].

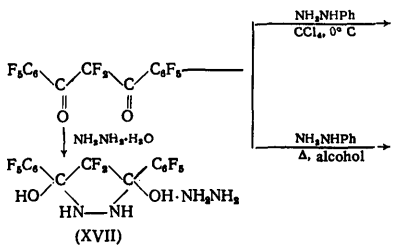
In contrast to this, the interaction of HFAA with hydrazine hydrate in alcohol (5 °C) gives rise to 3,5-dihydroxy-3,5-bis(trifluoromethyl)pyrazolidine (XIII),[154] which splits off two water molecules only on heating and is converted into pyrazole:



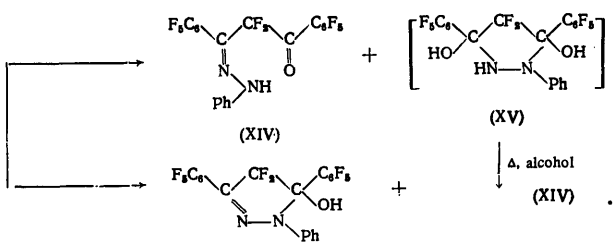
(XIII)

For symmetrical polyfluoro-β-diketones with large aliphatic fluorosubstituents [153] and with fluorinated substituents containing an ω-hydrogen atom[93], the formation of pyrazolidines was not observed at all in this reaction; this is consistent with the reactivity of symmetrical polyfluoro-β-diketones in relation to hydroxylated nucleophiles.

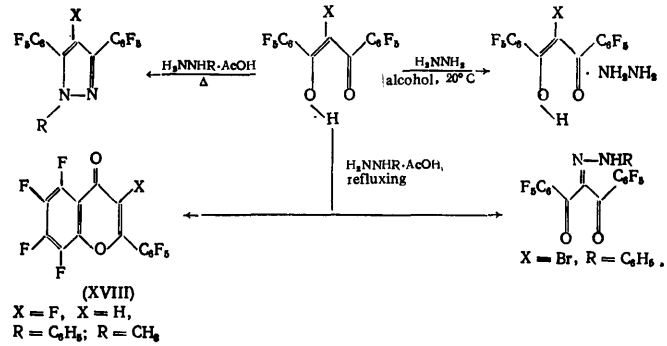
The behaviour of β-diketones with perfluorophenyl substituents in reactions with hydrazines is unusual; perfluorodibenzoylmethane, which has no α-hydrogen atom, reacts with phenylhydrazine at 0 °C to give a mixture of the β-ketohydrazone (XIV) and the unstable pyrazolidine (XV), the refluxing of which in alcohol results in the elimination of one water molecule and the formation of the pyrazoline (XVI), together with the partial opening of the ring and conversion into compound (XIV).[155] The reaction with hydrazine hydrate yields the pyrazolidine (XVII) as an adduct with a hydrazine molecule:



(XVII)

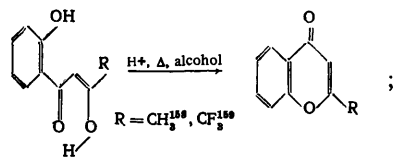


The enolising aromatic polyfluoro-β-diketones react with hydrazine at room temperature to form salts, pyrazoles being produced only on boiling. However, depending on the nature of the α-substituent in the β-diketone and the structure of the hydrazine, on heating with hydrazine acetates they form either pyrazoles or the flavones (XVIII) via the intramolecular elimination of an *ortho*-fluorine atom from the pentafluorophenyl ring[156]:



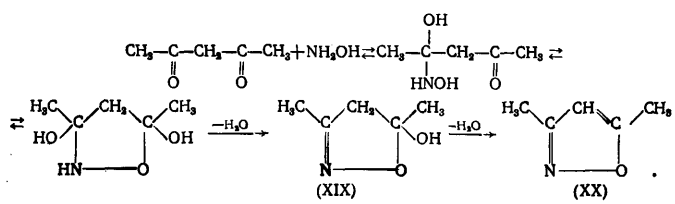
(XVIII)
X = F, X = H,
R = C_6H_5; R = CH_3

A similar reaction, leading to the formation of flavones by the intramolecular cyclisation of β-diketones with a non-fluorinated phenyl substituent, occurs only on heating in the presence of an inorganic acid and requires the obligatory presence of a hydroxy-group in the *ortho*-position in the benzene ring[157,158]:



Recent studies of the reaction mechanism by NMR in relation to AA have shown that the interaction of β-diketones with hydroxylamine involves several stages and ultimately leads to isoxazoles (XX).[159,160]

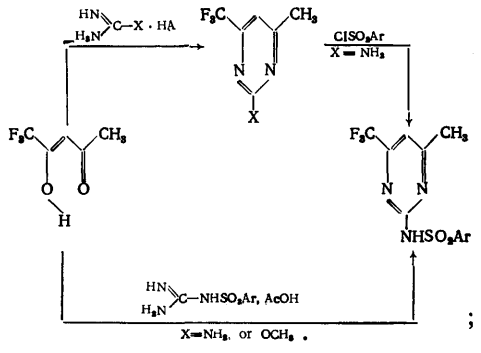
In the case of polyfluoro-β-diketones the intermediate 5-hydroxy-Δ^2-isoazoline of type (XIX) is so stable that it can be isolated in a free form and its conversion into isoxazole requires heating with polyphosphoric acid[161,162]. This demonstrates yet again the stabilisation of the intermediates of the nucleophilic addition reaction by fluoroalkyl residues:



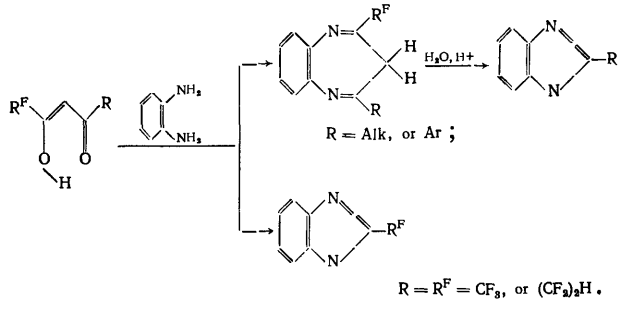
Fluoroalkylisoxazoles have been patented as high-temperature heat exchangers and surfactants[161] and also as substances reducing the sugar content in blood[163].

Reactions with urea derivatives and o-phenylenediamine. When TFAA is fused together with guanidine carbonate[149] and on heating alcoholic solutions of TFAA with guanidine carbonate[164] or *O*-methylisourea hydrochloride[175], 2-amino- or 2-hydroxy-pyrimidines with the trifluoromethyl group in the heteroring are formed, among which trifluoromethylsulphonamides—the analogues of the familiar non-fluorinated preparation sulphamethazine and sulphisoamidine—have been obtained[164]. The synthesis of these compounds in a single

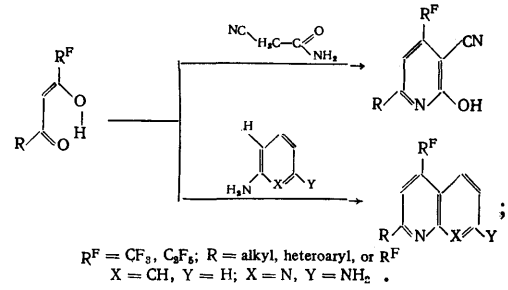
stage by refluxing TFAA with arenesulphonylguanidines has been patented[166]. The same patent reports their higher biological activity compared with the hydrocarbon analogues. It has been shown[167] that in an acid medium the reaction mechanism involves the acid-catalysed attack by urea on the keto–enol with subsequent cyclisation:



Although the formation of substituted 1,5-benzodiazepines from o-phenylenediamine (OPD) and β-diketones without fluorine was described as early as 1907,[168] the study of the interaction of fluorine-containing β-diketones with OPD was begun only in recent years. It has been established[169] that the condensation of fluoroalkyl-β-diketones with OPD results in the formation of between 3 and 25% of the open-chain β-aminovinyl ketone, depending on the substituents in the β-diketone, together with 1,5-benzodiazepines. It is recommended that the 1,5-benzodiazepines with a fluoroalkyl substituent in the heteroring obtained in this reaction be used as surfactants and heat exchangers[170]. It has been observed[93] that benzodiazepines can be obtained successfully only from β-diketones containing a single fluoroalkyl substituent, while β-diketones with two fluoroalkyl substituents give rise to salts under the usual conditions of condensation with OPD,[168] refluxing in alcohol in the presence of acetic acid producing 2-fluoroalkylbenzimidazoles[93]. This course of the reaction is associated in all probability with the enhanced reactivity of the C=N bond adjoining the fluoroalkyl substituent, which leads to attack by the free amino-group on this bond and not on the carbonyl group:



Reactions with amino-compounds containing mobile α-hydrogen atoms. Under the influence of basic reagents[171,172], sulphur[173], polyphosphoric acid[174,175] phosphoric acid[176–178], and also on heating[179], polyfluoro-β-diketones readily condense with amino-compounds containing a mobile hydrogen atom in the β-position with formation of a pyridine ring:

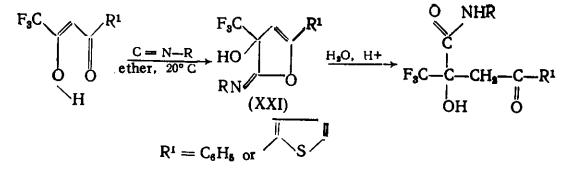


The reaction is of interest from the standpoint of the introduction of fluorine-containing substituents into the pyridine ring and the synthesis of potential biologically active compounds. Thus the substituted 4-trifluoromethylpyridone, synthesised from cyanoacetamide and TFAA, has been used to prepare trifluoromethyl analogues of vitamin B_6,[171] pyrazolopyridines with a 4-fluorophenyl substituent have been patented as anti-inflammatory preparations[174], and the naphthyridines obtained from fluorine-containing β-diketones and 2,6-diaminopyridine have been patented as compounds with hypotensive and bronchodilating activities[175,177,178]. The analogous cyclisation with esters of fluorine-containing β-ketoacids leads to γ-pyridones[180], from which trifluoromethyl analogues of quinine and quinidine have been obtained. The formation of trifluoromethylpyrazolo[1,5-d]pyrimidines by the condensation of TFAA with 2-aminopyrimidine has been described[181]. The compounds obtained are depressants of the central nervous system.

(d) Reactions with other nucleophiles

Selenothenoyltrifluoroacetone has been obtained by the reaction of an alcoholic solution of TTFA with hydrogen selenide in a stream of nitrogen in the presence of anhydrous hydrogen chloride[182]. The site of nucleophilic attack has not been established, but, by analogy with hydrogen sulphide[108], it has been suggested[182] that the oxygen of the carbonyl group linked to the non-fluorinated substituent is substituted (see also Section V).

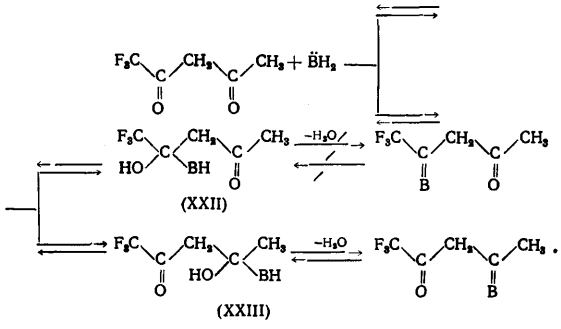
In contrast to their non-fluorinated analogues[183], fluoroalkyl-β-diketones readily give rise to cyclicadducts with isonitriles in the absence of catalysts[184], which is attributed to their virtually complete enolisation. The structure of the reaction product (XXI) and hence the direction of nucleophilic attack† on the carbonyl linked to the fluoroalkyl substituent have been established by ^{19}F NMR and the acid hydrolysis of the cyclicadduct:



† The authors[184] do not rule out the possibility of 1,4-cycloaddition.

The interaction of fluorine-containing β-diketones with the hydride ion leads to the reduction of both the carbonyl group and of the C=C double bond of the enol with formation of diols[185].

Thus polyfluoro-β-diketones readily react with nucleophiles, forming geminal adducts or condensation products. The unusual direction of nucleophilic attack on the carbonyl carbon atom linked to the less electron-accepting substituent can be accounted for either by the initial protonation of the carbonyl group linked to the non-fluorinated substituent or by treating the reaction as a series of reversible stages involving intermediate and final products[127]:



(XXII)

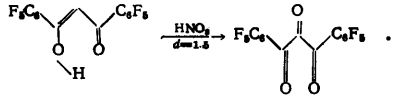
(XXIII)

The formation of the adduct (XXII) is more likely than that of the adduct (XXIII), but the former does not tend to eliminate a group and the reaction virtually stops at the stage involving its formation. The adduct (XXIII) readily eliminates either the added nucleophile molecule, being reconverted into the initial β-diketone, or a water molecule, forming a condensation product; in the presence of a large excess of the reagent, the equilibrium is displaced towards the condensation product. In an alkaline medium, the β-diketone molecule is cleaved irreversibly at the C–C bond.

2. Other Reactions

(a) Electrophilic reactions

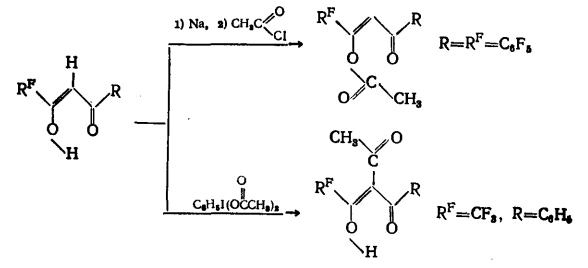
The interaction of fluorine-containing β-diketones with electrophiles has been studied less thoroughly than the interaction with nucleophiles, probably owing to the smaller practical and synthetic importance of the compounds formed. However, the available data emphasise certain features due to the presence of fluorine-containing substituents. For example, under conditions characteristic of the introduction of the nitro-group in the α-position of DBM, the fluorinated analogue of the latter is not nitrated and treatment with more concentrated HNO_3 results in the formation of a triketone, which is entirely stable in air[42]:



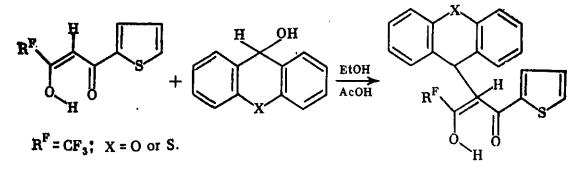
An analogous reaction has been observed for pentafluorobenzoylacetic ester on treatment with selenium dioxide[186].

Fluorine-containing substituents also hinder the bromination and nitration of chromium and copper β-diketonates. This is associated both with the reduction of the nucleophilicity of the α-position and with the decrease of the stability of the metal chelates themselves[187,188].

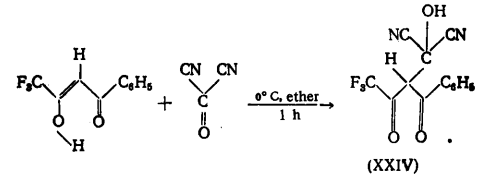
The dual reactivity of fluorine-containing β-diketones and their enolate ions has been very little investigated. It has been established that treatment of the sodium salt of DFBM with acetyl chloride results in the exclusive formation of the *O*-acetyl derivative[43]. The interaction of BTFA with diacetoxyiodobenzene leads to C-acylation[189]:



Alkylation of TTFA with xanthydrol and thioxanthydrol in acetic acid takes place at the α-carbon atom[190] and does not differ from the similar reaction of the non-fluorinated analogues:

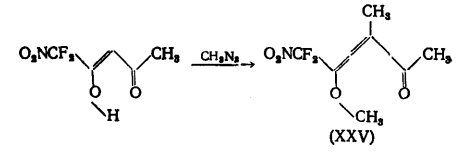


O-Alkylation also does not occur on interaction of TFBA with carbonyl cyanide, the relatively unstable *C*-alkylation product (XXIV) being formed in quantitative yields[191]:



(XXIV)

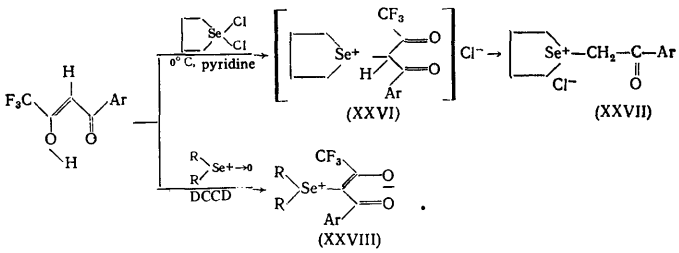
On the other hand, 1,1-difluoro-1-nitropentane-2,4-dione is methylated by diazomethane at the oxygen and α-carbon atoms, being converted into 5,5-difluoro-4-methoxy-3-methyl-5-nitropent-3-en-2-one (XXV);[36] this is yet another example of the dual reactivity of fluorine-containing β-diketones:



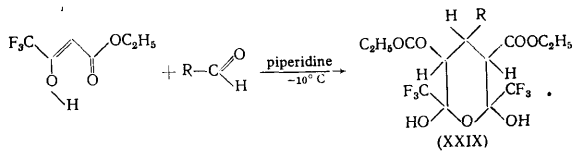
(XXV)

The attempt to extend to fluorine-containing β-diketones the reaction leading to the formation of selenonium ylids by treatment with selenolane dichlorides, which is usual for the non-fluorinated analogues, led to the selenonium salts (XXVII).[192] According to the authors, this is associated with the cleavage of the selenonium derivative of the diketone (XXVI) formed initially. The instability of the latter is

caused by the high positive charge on the carbonyl carbon atom linked to the trifluoromethyl group due to the inductive effect of the CF_3 and $>Se^+$ groups. The selenonium ylids (XXVIII) have been obtained only from selenoxides and the benzoyl- and thenoyl-trifluoroacetone in the presence of dicyclohexylcarbodi-imide (DCCD):[192]



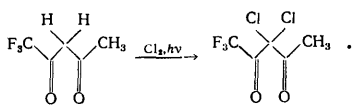
The condensation of the α-methylene group of fluorinated β-diketones with polymethine compounds containing a terminal aldehyde group has been described; the products have been patented as filtering dyes for photographic and textile materials[193]. The condensation of the trifluoroacetoacetic ester with aqueous solutions of aldehydes leads to the tetrahydropyrans (XXIX) containing fluoroalkyl substituents in the heteroring[194]:



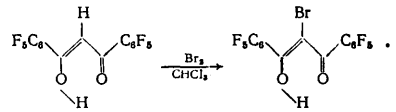
Heating of TFAA with thionyl chloride leads to the substitution of the hydroxy-group by chlorine with formation of 2-chloro-1,1,1,5,5,5-hexafluoropentan-1-one.[195,196]

(b) Radical reactions

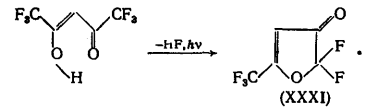
There have been several examples of radical reactions of fluorine-containing β-diketones. Chlorination of TFAA in the light leads to 3,3-dichloro-1,1,1-trifluoropentane-2,4-dione (XXX):[23]



The bromination of DFBM with bromine results in the formation of only the monobromo-derivative, although under the same conditions the non-fluorinated analogue can give rise to both mono- and di-bromo-derivatives[42]:



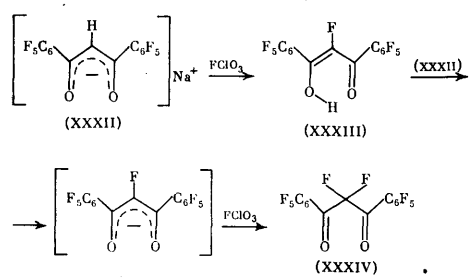
It has been shown by EPR that trifluoronitrosomethane adds to TFAA and HFAA in the α-position with formation of nitroxy- and iminoxy-radicals[197]. Irradiation of HFAA with ultraviolet light leads to the elimination of HF and to cyclisation to 2,2-difluoro-5-trifluoromethyl-2,3-dihydro-3-furanone (XXXI):[198]



в) Фторирование

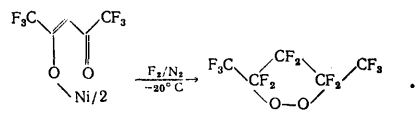
(c) Fluorination

It has been shown[43] that the sodium salt of DFBM (XXXII) is fluorinated by perchloryl fluoride at the α-carbon atom with formation of perfluorodibenzoylmethane (XXXIV), which is consistent with data[199–201] for the interaction of non-fluorinated β-diketones with perchloryl fluoride and can be accounted for[43,199] by the higher acidity of the diketone (XXXIII) compared with DFBM, leading to its metallation by the sodium salt (XXXII) and further exhaustive fluorination:



The introduction of only one fluorine atom at the α-carbon atom has been achieved[43] by fluorinating α-bromodecafluorodibenzoylmethane with subsequent debromination and also by fluorinating the sodium salt of bis(pentafluorobenzyl)acetic ester, and the acid cleavage of the resulting product with 100% sulphuric acid. The possible mechanism of the fluorination of CH-active compounds by perchloryl fluoride has been discussed in a book[202].

Fluorination with elemental fluorine has been described only for the copper and nickel chelates of hexafluoroacetylacetone; the authors were able to isolate perfluoro-3,5-dimethyl-1,2-dioxolan in 5% yield:[203]



VI. APPLICATIONS

1. Extraction and Extraction-Photometric Determination of Metals

The presence of fluorine-containing groups is reflected also in the applications of β-diketones, giving rise to new fields of application of these compounds or improving the properties for employment in familiar fields.

Thus the acidity of polyfluoro-β-diketones exceeds by 2–3 orders of magnitude the acidity of their non-fluorinated analogues[204,205], which permits the extraction of readily hydrolysable metal β-diketonates from much more acid solutions[90]. The studies on the extraction properties of TTFA and furoyltrifluoroacetone, which have been investigated in greatest detail in this sense, have been reviewed in a monograph[90] and the synergism of TTFA in combination with various compounds has been discussed in a review[206].

In publications of recent years much attention is devoted to the study of the extraction of metals with TTFA in the presence of tertiary amines[207–214] and phosphorus compounds[215–217] and also to the application of TTFA in the extraction-photometric determination of the elements[218–222]. Other polyfluoro-β-diketones are more rarely used in the extraction and spectrophotometric determination of metal ions[223–225], although perfluoroalkylvinylphenylpropanediones have been patented as monomers for the synthesis of polymers capable of extracting metals ions from highly acid media[226], while β-diketones containing the pentafluorophenyl substituent together with a perfluoroalkyl substituent have been patented as extractants of vanadium from highly acid media[26,227].

2. The GLC Separation and Determination of Metal Cations

Fluorine-containing substituents increase the volatility of metal β-diketonates, which permits their gas-chromatographic separation and determination at much lower temperatures[228] and with the aid of electron-capture detectors; the sensitivity and selectivity of the analysis are thus improved[229]. The problems of the application of polyfluoro-β-diketones in the GLC of metal cations have been considered in a monograph[228] and the advances in recent years are described in reviews[229–234].

3. The Biological Activity of Fluorine-containing β-Diketones

Several forms of the biological activity of non-fluorinated β-diketones are known. The antiviral activity of α-substituted β-diketones and its relation to their structure[235–239], the antiallergic activity of α-cyano-derivatives[240], and the inhibition of the central nervous system by and the weakening effect of α-amino-β-dicarbonyl compounds on muscles[241] have been reported. A weak antitumour activity of β-diketones has been observed[242]. Derivatives of β-diketones have been patented as insecticides[243] and herbicides[244]. Few data are available on the biological activity of polyfluoro-β-diketones. The insecticidal activity of BTFA derivatives[245] as well as the fungicidal activity of TTFA and benzofuroyltrifluoroacetone[246] have been reported.

TFFA is also known to have an effect on enzymes. It has been shown that TTFA inhibits the oxidation of succinates[247, 248] and lowers the activity of cytochrome reductase[249–262] and malate dehydrogenase[263]. The mechanism of the action of TTFA on enzymes has not been elucidated, but it has been suggested that TTFA interacts with the components of the respiratory chain and not with the enzymes themselves, the inhibiting effect being attributed to the ability of TTFA to form complexes with iron[251]. The differences in the effects of TTFA on various enzymes are most probably associated with the differences in the structures of the membranes and not with the differences in the structures of the enzymes[262], the inhibition in plant mitochondria being weaker than in animal mitochondria[264]. As regards other β-diketones, it is only known that AA and BA prevent the thermal inactivation of enzymes[265] and that furoyltrifluoroacetone inhibits the electron transfer in the oxidation of hexacyanoferrate in mitochondria[266].

4. Other Applications

Apart from their wide-scale employment for the separation and determination of metal cations, polyfluoro-β-diketones have also other less familiar applications. It has been established, for example, that TTFA retards the corrosion of engine cylinders[267]; HFAA has been recommended as an additive preventing gel formation in polymer solutions for spinning[268].

A number of fluorine-containing β-diketones have been patented as compounds imparting water repellant properties to paper[35]. 4,4,4-Trifluoro-1-(2-naphthyl)butane-1,3-dione has been patented as an additive increasing the light sensitivity of mixtures polymerisable by light[269], and TTFA is used in the membranes of ion-specific electrodes, particularly for Ca^{2+} ions[270,271], and for impregnating electrode membranes designed for the determination of 'onium ions[272].

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Analysis of the present state of research into the chemistry, properties, and applications of fluorine-containing β-diketones permits the conclusion that, while the methods of their synthesis have been thoroughly developed and a number of their properties of applied and theoretical importance are known, many questions have still been little investigated. The study of the interaction of fluorine-containing β-diketones with eletrophiles (alkylation, acylation, reactions with fluoro-olefins, oxirans, and thi-irans), the expansion of studies on nucleophilic reactions, determination of quantitative data concerning the influence of the introduction of fluorine atoms on the properties and reactivity of β-diketones, as well as the study of reaction mechanisms are of interest. Studies and comparative estimates of the biological activity of fluorine-containing β-diketones and heterocycles based on them are promising.

During the preparation of the manuscript for the press, the synthesis of pentafluorobenzoylacetone (I, $R_F = C_6H_5$, $R = CH_3$) by the condensation of pentafluoroacetophenone with its enolate anion was reported. In view of the splitting of the signal due to the vinyl proton by the *ortho*-fluorine atoms, the authors postulate the enolisation of the resulting compound at the carbonyl group linked to the non-fluorinated substituent[273]. The existence of the enols of symmetrical β-diketones in the *cis*-form with an asymmetric hydrogen bond has been confirmed by photoelectron spectroscopy and it has been established that the upper limit to the barrier in the interconversion of the C_S-forms via the C_{2v}-form is 6 kcal mol^{-1}.[274] The ionisation potentials and the electronic spectra of TFAA and HFAA have been calculated[275]. It has been established by ^1H, ^{19}F, and ^{13}C NMR that the interaction of asymmetric fluorine-containing β-diketones with alcohols results in the preferential formation of adducts via the carbonyl group linked to the fluorinated substituent[276]; this confirms the mechanism of the interaction of β-diketones with nucleophiles described above. Pyrazolo-β-diketones have been obtained for the first time from fluorine-containing bis-β-diketones[277] and their high catalytic activity in the formation of polyurethanes has been established. A number of studies published during this period have been devoted to the interaction of polyfluoro-β-dicarbonyl compounds with urea[278] and its derivatives[279–281] and also to their condensation with amino-compounds containing a mobile hydrogen atom in the α-position: aminopyrazolone[282], aminocyclohexane[283], aminopyrazole[284], and substituted aminodihydroindole[285]. 1,2,3,3,8-Pentamethyl-7-oxo-5-trifluoromethyl-2,3,7,8-tetrahydro-1*H*-pyrrolo[3,2-*d*]quinoline has been patented as a source of blue-green laser radiation[285]. The formation of a γ-trifluoromethylpyridone in the condensation of TFAA with malonodinitrile has been demonstrated[286]. The polarographic reduction of polyfluoro-β-diketones has been investigated[287]. Numerous studies have been devoted to the

applications of polyfluoro-β-diketones in the extraction of metal cations[288–292].

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