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Synthesis of novel 2-perfluoroacylcyclohexane-1,3-diones

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Abstract

A one-pot synthesis of 2-perfluoroalkanoylcyclohexane-1,3-diones via C-acylation of cyclohexane-1,3-diones with *N*-perfluoroacylimidazole as an acylating agent is reported. A reaction was examined with isolated *N*-trifluoroacetylimidazole and with *N*-perfluoroacylimidazoles generated *in situ* from perfluorocarboxylic acid anhydrides or perfluorocarboxylic acids.

Keywords: 2-Perfluoroacylcyclohexane-1,3-diones; Cyclohexane-1,3-diones; *N*-Trifluoroacetylimidazole; *N*-Perfluoroacylimidazole; C-acylation

1. Introduction

Cyclic β,β′-triketones are widespread in nature and possess interesting biological properties. A structural fragment of cyclic triacylmethanes is found as a part of many biologically active compounds produced by various plants, insects and microorganisms [1]. They have a high synthetic potential due to their polyfunctional tricarbonyl system. Depending on the structure of the cyclic part and side chain of a molecule, 2-acylcycloalkane-1,3-diones are used as universal building block-synthones in a total synthesis of steroids, prostanoids, some antibiotics and other biomolecules [2].

Application of fluorine-containing compounds in organic synthesis has received an intensive development, especially for preparing medicines and pesticides [3]. It is connected with specific features of fluorine and its compounds, for example, in the case of medicines, for reinforcing their efficiency and selectivity [4]. The incorporation of fluorine atoms or fluorinated substituents into biologically active molecules allows simultaneous modulation of their parameters, such as electronic, lipophilic and steric, and can considerably change their properties including biological activity [5]. Acyclic and cyclic fluorine-containing β-dicarbonyl and acyclic β,β′-tricarbonyl compounds, their properties, tautomerism and reactivity are widely investigated [6]. Yet, there were no reports of synthesis, structure and chemical transformations of fluorine-containing cyclic β,β′-triketones.

In this paper, we wish to report a synthesis of 2-acylcyclohexane-1,3-diones containing an perfluoroalkanoyl group as a side chain.

2. Results and discussion

A number of methods of synthesis of 2-acylcycloalkane-1,3-diones have been proposed, that allow preparation of β,β′-triketones with different side chains and substituents [7]. However, our attempts to synthesize the 2-perfluoroacylcyclohexane-1,3-diones by well-known methods such as O-C-isomerization of fluorinated enolacylates of cyclohexane-1,3-diones in the presence of *N*,*N*-dimethylaminopyridine, $ZnCl_2$, and other Lewis acids, C-acylation of cyclohexane-1,3-diones by fluorinated carboxylic acids in the presence of dicyclohexylcarbodiimide and triethylamine, C-acylation of cyclohexane-1,3-diones by fluorinated carboxylic acid anhydrides in the presence of sodium salts of carboxylic acids were unsuccessful. The failure was likely due to the lability of the polyfluorinated 2-acylcyclohexane-1,3-diones.

To overcome the problem we employed the imidazolide method for the preparation of 2-perfluoroalkanoylcyclohexane-1,3-diones (**2**). *N*-Trifluoroacetylimidazole is an effective acylating agent, which has been used for the acylation of amines, alcohols, enamines, Meldrum's acid in sufficient mild conditions [8]. Enolyzing cyclic β-diketones, as with other

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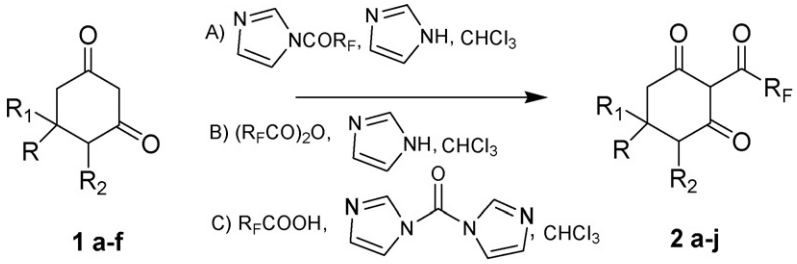


1: R= R_1=CH_3, R_2=H(a); R= R_1=R_2=H(b);
R=R_2=H, R_1=CH_3(c); R=R_1=CH_3, R_2=CO_2CH_3(d);
R=H, R_1=C_6H_5, R_2=H(e); R=H, R_1=4-$CH_3OC_6H_4$, R_2=H(f)

Scheme 1.

β-dicarbonyl compounds, exhibit a dual reactivity and can give both O- and C-derivatives during their alkylation and acylation [9]. We have found that an acylation of cyclohexane-1,3-diones (**1**) by *N*-perfluoroacylimidazoles results in regioselective C-acylation of β-diketones (**1**) and gives the 2-perfluoroalkanoylcyclohexane-1,3-diones (**2**) in high yields. A reaction was carried out with both isolated *N*-trifluoroacetylimidazole and fluorinated acyl imidazolides generated *in situ* (Scheme 1).

2-Trifluoroacetylcyclohexane-1,3-diones (**2a–d**) were synthesized in 71–78% yields by treatment of an equimolar mixture of cyclohexane-1,3-diones (**1a–d**) and imidazole with 10% excess of *N*-trifluoroacetylimidazole in dry chloroform at room temperature (method A, Table 1). *N*-Trifluoroacetylimidazole was prepared from imidazole and trifluoroacetic anhydride [10]. We have also prepared a number of 2-perfluoroalkanoylcyclohexane-1,3-diones (**2a–j**) via C-acylation of cyclohexane-1,3-diones (**1a–f**) with *N*-acylimidazole generated *in situ* from perfluorocarboxylic acid anhydrides and imidazole or perfluorocarboxylic acids and 1,1′-carbonyldiimidazole. The treatment of perfluorocarboxylic acid anhydrides with imidazole (method B) or perfluorocarboxylic acids (method C) with 1,1′-carbonyldiimidazole followed by the reaction of *N*-acylimidazole obtained *in situ* with β-diketones (**1**) in the presence of imidazole gave the desired compounds in 69–98% yields (Table 1).

Table 1
2-Perfluoroalkanoylcyclohexane-1,3-diones (**2a–j**)

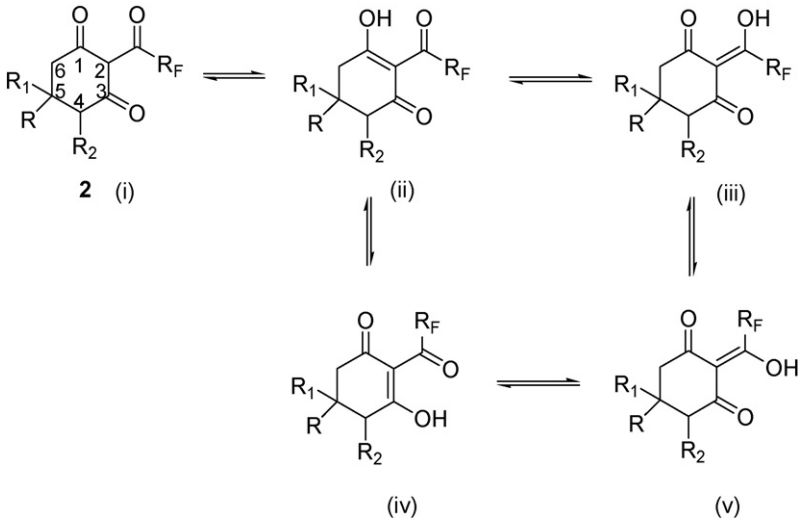
N compound	R	R_1	R_2	R_F	Isolated yield, % (method)
2a	CH_3	CH_3	H	CF_3	78 (A), 83 (B), 88 (C)
2b	H	H	H	CF_3	76 (A), 95 (B), 95 (C)
2c	H	CH_3	H	CF_3	71 (A), 89 (B)
2d	CH_3	CH_3	CO_2CH_3	CF_3	71 (A), 69 (B)
2e	H	Ph	H	CF_3	89 (B)
2f	H	*p*-CH_3OPh	H	CF_3	98 (B)
2g	CH_3	CH_3	H	C_2F_5	94 (B), 88 (C)
2h	H	H	H	C_2F_5	97 (B), 83 (C)
2i	CH_3	CH_3	H	C_3F_7	92 (B), 80 (C)
2j	H	H	H	C_3F_7	98 (B)

The structures of all compounds obtained were confirmed by their IR spectra, ^{1}H, ^{13}C and ^{19}F NMR and GC–MS spectra. From the spectral data, 2-perfluoroacylcyclohexane-1,3-diones (**2a–j**) are completely enolized in solution similarly to non-fluorinated 2-acylcyclohexane-1,3-diones [11]. The single set of signals observed in their ^{1}H, ^{13}C and ^{19}F NMR spectra indicates the predominance of one tautomeric enolic form. ^{1}H NMR spectra of the triacylmethanes (**2a–j**) show a single enol proton signal in the range of δ 14.8–15.3 ppm even for the unsymmetric example (**2d**), where two signals might be expected from two enols in equilibrium. Due to an influence of electronegative perfluoroalkyl group, the strength of an intramolecular hydrogen bonding is obviously weakened and resonance of enolic protons occurs at higher field than its usual position for 2-acylcyclohexane-1,3-diones (δ 17–18 ppm) [12]. In ^{13}C NMR spectra of β,β′-triketones (**2a–j**) a signal of the carbon atom of a carbonyl group of a perfluoroacyl side chain is observed at δ 183.7–187.9 ppm, signals of carbon atoms of cyclic carbonyl groups at δ 187.3–191.8 ppm and at δ 196.4–197.6 ppm. In the ^{19}F NMR spectrum of compounds **2a–f** an singlet at approximately δ −74 ppm was assigned to the fluorine atoms of an trifluoroacetyl group. In the ^{19}F NMR spectrum of compounds **2g**, **h** signals at δ −80.2 (CF_3) and −118.3 (CF_2) and compounds **2i**, **j** at δ −80.7 (CF_3), −113.7 (CF_2), −122.8 (CF_2) were observed. In IR spectra **2a–j** the characteristic frequencies in the range of 1560–1705 cm^{-1} corresponding to conjugated non-chelated (1685–1705 cm^{-1}), chelated (1640–1650 cm^{-1}) carbonyl groups and double bond (1555–1565 cm^{-1}) were found. An absorbance of ester carbonyl group (compound **2d**) occured at 1740 cm^{-1}.

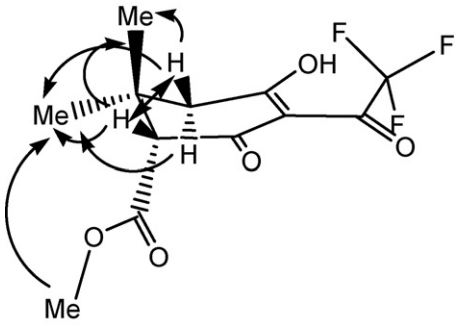
Earlier works have demonstrated that cyclic β,β′-tricarbonyl compounds exist as endo- and/or exo-enol tautomers with a strong intramolecular bond (Scheme 2) [13].

For elucidating a structure of the compound **2d** bearing the carboxymethyl substituent was analyzed by means of 2D NMR spectroscopy in order to make the complete assignment of all atoms of molecule including spatial relationships between protons.

The assignment of protonated carbons is straightforward and follows from HSQC and COSY correlations. Relative



Scheme 2.

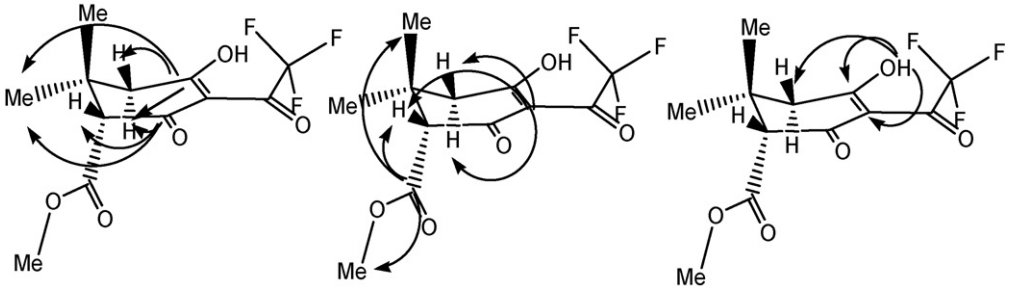


Scheme 3. NOE correlation of **2d**.

stereochemistry of ring protons and methyl groups was established by analysis of the NOESY spectrum (Scheme 3). We assume that the proton at C-4 is over the plane of ring and state its position as 4β, therefore, other groups over the plane will have the β-configuration. The proton at C-4 has cross-peaks with the proton at δ 2.54 ppm (6β) and methyl group at δ 1.16 ppm (5βMe). Presumably, in solution and conditions of NMR experiments, 4β and 6β protons occupy pseudo-equatorial position. These follow from observation of rather weak cross-peak between 4β and 6β protons and interaction of these protons with both methyl groups. Having protons in axial conformation, with the carboxymethyl group in equatorial position, one can expect intensive cross-peaks with the β-methyl group and a full absence of interaction with the α-methyl group. The α-methyl group shows a weak correlation with the ester methyl group.

Quaternary carbons atoms were deducted via their long-range couplings in the HMBC spectrum (Scheme 4). The carbon atoms of the trifluoroacyl group have no cross-peaks but can be found easily due to coupling with fluorine nuclei. The carbon of the trifluoromethyl group was found as quartet at δ 116.19 ppm with the coupling constant in 286 Hz and the carbon of exocyclic carbonyl group did as quartet at δ 183.96 ppm with the coupling constant in 39 Hz. Similarly, the quaternary carbons C-2, C-5 and of the ester group can be assigned without difficulties. The carbon of the ester group (δ 168.66 ppm) shows strong interaction with the protons of the methoxy group, the 4β proton and less intensive cross-peak with the protons of the 5β-methyl group. The carbon C-5, in own turn, correlates with methyl groups and protons at C-4 and C-6 having chemical shift at δ 33.33 ppm. The nucleus of C-2 resonates at δ 109.54 ppm as expected and shows cross-peaks with protons at C-4 and C-6.

The nuclei of the endocyclic carbonyls resonate in rather close fields and one of them exists in pure enolic form judging by data of 1D ^{1}H and ^{13}C NMR spectra. Based on the HMBC spectrum data and chemical shifts, we failed to assign these carbons unambiguously. We suggest that the low temperature experiment with deuterium exchange [14] could resolve the



Scheme 4. HMBC correlation of **2d**.

position of the enolized carbonyl. Two ^{13}C spectra of compound **2d** were acquired at −40 °C in $CDCl_3$ with and without addition of D_2O and the area of carbonyls was analysed. It was found, that the biggest isotopic shift (0.8 ppm upfield) was shown by the carbon nucleus resonated at δ 196.46 ppm. Therefore, it can be concluded that the carbonyl at δ 196.46 ppm is enolized and position of its carbon was assigned at C-1 due to its coupling with both protons at C-6 and 5α-methyl group in the HMBC spectrum. The second carbonyl (δ 187.36 ppm) is placed at C-3 position. It has intensive cross-peaks with 4β and 5α-methyl group protons and a weaker peak with the 6α-proton. Additionally, the HMBC spectrum of **2d** was recorded at −40 °C and, in contrast to one obtained at ambient temperature, it revealed clear intensive cross-peaks of enolic proton with C-1, C-2, and C-6 and this is in agreement with the above considerations.

Being successful in low temperature experiment with β,β′-triketone (**2d**), we applied this procedure for symmetric compound **2a** in order to specify the chemical shift of the enolized endocyclic carbonyl. It was found, that low field carbonyl (196.40 ppm) gave upfield shift approximately 0.8 ppm at −40 °C after addition D_2O. These data correspond to those obtained with compound **2d** and also were confirmed by low temperature HMBC experiment. Thus, the enolic proton gave cross-peaks with C-1, C-2 and C-6 (δ 45.46 ppm). Furthermore, it allowed assignment of proton positions in the ring because C-1 carbon has interaction with protons at δ 2.67 ppm (C-6), but C-3 has cross-peak with protons at δ 2.42 ppm (C-4), respectively.

3. Conclusion

2-Perfluoroalkanoylcyclohexane-1,3-diones containing different substituents were prepared in a one-pot synthesis by an acylation of cyclohexane-1,3-diones using *N*-perfluoroacylimidazoles as an acylating agents. The use of isolated *N*-trifluoroacetylimidazole or acyl imidazolides generated *in situ* gives the 2-perfluoroalkanoylcyclohexane-1,3-diones (**2**) in high yields. The triacylmethanes obtained can act as important fluorinated building blocks for synthesis a great number of fluorinated compounds of biological interest.

4. Experimental

Melting points were measured on Boetius apparatus and are uncorrected. The NMR spectra were recorded in 5 mm tubes in $CDCl_3$ solutions on Bruker AVANCE 500 spectrometer. Tetramethylsilane (TMS) for ^1H (500 MHz) and ^{13}C NMR (125 MHz) spectra was used as an internal standard. α,α,α-Trifluorotoluene for ^{19}F NMR (470 MHz) spectra was used as an external standard. The chemical shifts were converted from α,α,α-trifluorotoluene to CCl_3F. IR spectra were measured with UR-20 spectrophotometer in KBr pellets. GC–MS spectra (EI, 70 eV) were measured using Hewlett-Packard 5890 gas chromatograph with mass selective detector HP 5972. Cyclohexane-1,3-diones, trifluoroacetic anhydride, imidazole and 1,1′-carbonyldiimidazole are commercially available and were used as purchased. Chloroform was distilled over P_2O_5 prior to use.

4.1. General procedure for the preparation of 2-trifluoroacetylcyclohexane-1,3-diones (2a–d) with isolated N-trifluoroacetylimidazole (method A)

To a stirred solution of 10 mmol of 1,3-cyclohexanedione (**1**) and 10 mmol of imidazole in 30 ml dry chloroform 12 mmol of *N*-trifluoroacetylimidazole in 40 ml dry chloroform at room temperature was added dropwise. After 1 h the reaction mixture was washed three times with 10 ml dilute HCl (1:10), twice with a small amount of water and dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure at temperature ≤20 °C gave pure 2-trifluoroacetylcyclohexane-1,3-dione (**2a–d**) as colorless solid compound in 71–78% yield (Table 1).

4.2. General procedure for the preparation of 2-perfluoroalkanoylcyclohexane-1,3-diones (2a–j) with N-perfluoroalkanoylimidazole generated in situ from perfluorocarboxylic acid anhydrides (method B)

To a pre-cooled (0 °C) stirred solution of 4 mmol of imidazole in 10 ml dry chloroform a solution of 2 mmol of perfluorocarboxylic acid anhydride in 15 ml dry chloroform was added dropwise. Then at room temperature to a suspension resulted a solution of 1 mmol of cyclohexane-1,3-dione (**1**) and 1 mmol of imidazole in 10 ml dry chloroform was added dropwise and stirring was continued for further 45 min. After that the reaction mixture was washed three times with 10 ml dilute HCl (1:10), twice with a small amount of water and dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure gave pure 2-perfluoroalkanoylcyclohexane-1,3-dione (**2a–j**) as colorless solid compound in 69–98% yield (Table 1).

4.3. General procedure for the preparation of 2-perfluoroalkanoylcyclohexane-1,3-diones (2a, b, g, h, i) by acylation with N-perfluoroalkanoylimidazole generated in situ from perfluorocarboxylic acids (method C)

To a stirred solution of 2 mmol of 1,1′-carbonyldiimidazole in 10 ml dry chloroform a solution of 4 mmol of perfluorocarboxylic acid in 15 ml dry chloroform was added dropwise. Then at room temperature to a suspension resulted a solution of a mixture of 1 mmol of cyclohexane-1,3-dione (**1**) and 1 mmol of imidazole in 10 ml dry chloroform was added dropwise and stirring was continued for further 45 min. After that the reaction mixture was washed three times with 10 ml dilute HCl (1:10), twice with a small amount of water and dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure gave pure 2-perfluoroalkanoylcyclohexane-1,3-dione (**2a**, **b**, **g**, **h**, **i**) as colorless solid compound in 80–95% yield (Table 1).

2-Trifluoroacetyl-5,5-dimethylcyclohexane-1,3-dione (**2a**). This compound was obtained as colorless crystals, mp 48–49 °C. IR (KBr): ν 1705, 1650, 1565 cm^{-1}. NMR: ^1H δ 1.13 (6H, s, $2CH_3$), 2.42 (2H, s, CH_2-4), 2.67 (2H, s, CH_2-6), 15.29 (1H, bs, OH). ^{13}C: δ 28.12 ($2CH_3$ at C-5), 31.01 (C-5), 45.46 (C-6), 51.79 (C-4), 110.37 (C-2), 116.32 (q, $^1J_{C-F}$ = 286 Hz, CF_3), 183.90 (q, $^2J_{C-F}$ = 39 Hz, *C*OCF_3), 191.63 (C-3), 196.40 (C-1). ^{19}F: δ

−74.13 (c, CF_3). GC–MS (EI 70 eV), *m/z* (rel. int.): 236 $[M]^+$ (20), 180 $[M - CH_2CH_2CO]^+$ (49), 167 $[M - CF_3]^+$ (80), 152 $[M - CH_2COCH_2CO]^+$ (35), 139 $[M - CF_3CO]^+$ (7), 124 $[M - CF_3CO–CH_3]^+$ (100), 111 $[M - CF_3CO–CO]^+$ (29), 97 $[CF_3CO]^+$ (11), 83 $[CHCOCH_2CO]^+$ (93), 69 $[CF_3]^+$ (73), 55 $[CHCH_2CO]^+$ (34), 42 $[CH_2CO]^+$ (20). Anal. Calcd for $C_{10}H_{11}O_3F_3$: C, 50.85; H, 4.69. Found: C, 50.69; H, 4.61.

2-Trifluoroacetylcyclohexane-1,3-dione (**2b**). This compound was obtained as colorless crystals, mp 31–32 °C. IR (KBr): ν 1700, 1650, 1565 cm^{-1}. NMR: ^1H δ 2.10 (2H, qui, *J* = 6.5 Hz, C-5), 2.57 (2H, t, *J* = 6.5 Hz, C-4), 2.82 (2H, t, *J* = 6.5 Hz, C-6), 15.29 (1H, s, OH). ^{13}C: δ 18.91 (C-5), 31.95 (C-6), 37.86 (C-4), 111.35 (C-2), 116.32 (q, $^1J_{C–F}$ = 286 Hz, CF_3), 184.34 (q, $^2J_{C–F}$ = 39 Hz, $COCF_3$), 191.75 (C-3), 197.45 (C-1). ^{19}F: −74.17 (c, CF_3). GC–MS (EI 70 eV), *m/z* (rel. int.): 208 $[M]^+$ (17), 152 $[M - CH_2CH_2CO]^+$ (20), 139 $[M - CF_3]^+$ (73), 124 $[M - CH_2COCH_2CO]^+$ (100), 111 $[M - CF_3CO]^+$ (29), 97 $[CF_3CO]^+$ (8), 69 $[CF_3]^+$ (86), 55 $[CHCH_2CO]^+$ (27), 42 $[CH_2CO]^+$ (22). Anal. Calcd for $C_8H_7O_3F_3$: C, 46.17; H, 3.39. Found: C, 46.25; H, 3.42.

2-Trifluoroacetyl-5-methylcyclohexane-1,3-dione (**2c**). This compound was obtained as colorless crystals, mp 63–65 °C. IR (KBr): ν 1685, 1640, 1555 cm^{-1}. NMR: ^1H δ 1.14 (3H, d, *J* = 6.4 Hz, CH_3 at C-5), 2.23 (1H, dd, ^1J = 12.3 Hz, ^2J = 15.8 Hz, H_a, C-4), 2.31 (1H, m, C-5), 2.51 (1H, dd, ^1J = 10.3 Hz, ^2J = 18.3 Hz, H_a, C-6), 2.64 (1H, bd, *J* = 15.8 Hz, H_e, C-4), 2.83 (1H, bd, *J* = 18.3 Hz, H_e, C-6), 15.2 (1H, bs, OH). ^{13}C: δ 20.65 (CH_3 at C-5), 26.52 (C-5), 39.70 (C-6), 46.04 (C-4), 110.85 (C-2), 116.27 (q, $^1J_{C–F}$ = 286 Hz, CF_3), 184.10 (q, $^2J_{C–F}$ = 39 Hz), 191.67 (C-3), 196.86 (C-1). ^{19}F: δ −74.17 (c, CF_3). GC–MS (EI 70 eV), *m/z* (rel. int.): 222 $[M]^+$ (14), 180 $[M - CH_2CO]^+$ (29), 153 $[M - CF_3]^+$ (66), 124 $[M - H–CF_3CO]^+$ (73), 69 $[CF_3]^+$ (100), 55 $[CHCH_2CO]^+$ (18), 42 $[M - 180]^+$ (22), 41 $[CH_2CO]^+$ (29). Anal. Calcd for $C_9H_9O_3F_3$: C, 48.66; H, 4.08. Found: C 48.58; H, 3.99.

2-Trifluoroacetyl-4-carbomethoxy-5,5-dimethylcyclohexane-1,3-dione (**2d**). This compound was obtained as colorless crystals, mp 75–78 °C. IR (KBr): ν 1740, 1700, 1650, 1560 cm^{-1}. NMR: ^1H δ 1.16 (3H, s, 5βCH_3), 1.18 (3H, s, 5αCH_3), 2.54 (1H, d, *J* = 18.9 Hz, H_β, C-6), 3.13 (1H, d, *J* = 18.9 Hz, H_α, C-6), 3.34 (1H, s, H, C-4), 3.74 (3H, s, CH_3COO), 15.30 (1H, s, OH). ^{13}C: δ 25.85 (5αCH_3), 28.16 (5βCH_3), 33.33 (C-5), 43.15 (C-6), 52.4 ($COOCH_3$), 64.37 (C-4), 109.54 (C-2), 116.19 (q, $^1J_{C–F}$ = 286 Hz, CF_3), 168.66 ($COOCH_3$), 183.96 (q, $^2J_{C–F}$ = 39 Hz, $COCF_3$), 187.36 (C-3), 196.46 (C-1). ^{19}F: δ −74.26 (c, CF_3). GC–MS (EI 70 eV), *m/z* (rel. int.): 294 $[M]^+$ (5), 152 $[M - 142]^+$ (10), 124 $[M - 170]^+$ (20), 97 $[CF_3CO]^+$ (14), 83 $[CHCOCH_2CO]^+$ (100), 69 $[CF_3]^+$, 59 $[CO_2Me]^+$ (13), 55 $[CHCH_2CO]^+$ (22), 42 $[CH_2CO]^+$ (10), 41 $[CHCO]^+$ (22). Anal. Calcd for $C_{12}H_{13}O_5F_3$: C, 48.99; H, 4.45. Found: C, 48.87; H, 4.37.

2-Trifluoroacetyl-5-phenylcyclohexane-1,3-dione (**2e**). This compound was obtained as colorless crystals, mp 85–87 °C. IR (KBr): ν 1695, 1635, 1560 cm^{-1}. NMR: ^1H δ 2.86 (4H, m, C-4, C-6), 3.44 (1H, m, C-5), 7.24 (2H, m, H_{ar}), 7.31 (1H, m, H_{ar}), 7.38 (2H, m, H_{ar}), 15.27 (1H, bs, OH). ^{13}C: δ 36.82 (C-5), 39.21 (C-6), 45.04 (C-4), 110.98 (C-2), 116.30 (q, $^1J_{C–F}$ = 286 Hz, CF_3), 126.46 (C_{ar}), 127.72 (C_{ar}), 129.36 (C_{ar}), 140.92 (C_{ar}-1′), 184.24 (q, $^2J_{C–F}$ = 39 Hz, $COCF_3$), 191.00 (C-3), 196.35 (C-1). ^{19}F: δ −74.18 (c, CF_3). GC–MS (EI 70 eV), *m/z* (rel. int.): 284 $[M]^+$ (17), 215 $[M - CF_3]^+$ (10), 131 $[M - CH_2COCH_2CO]^+$ (9), 104 $[M - 180]^+$ (100), 69 $[CF_3]^+$ (21). Anal. Calcd for $C_{14}H_{11}O_3F_3$: C, 59.16; H, 3.90. Found: C, 59.25; H, 3.95.

2-Trifluoroacetyl-5-(4-methoxyphenyl)cyclohexane-1,3-dione (**2f**). This compound was obtained as colorless crystals, mp 104–107 °C. IR (KBr): ν 1695, 1635, 1565 cm^{-1}. NMR: ^1H δ 2.86 (4H, m, C-4, C-6), 3.39 (1H, m, C-5), 3.81 (3H, s, CH_3O), 6.91 (2H, d, *J* = 8.7 Hz, H_{ar} at C-3′, C-5′), 7.15 (2H, d, *J* = 8.7 Hz, H_{ar} at C-2′, C-6′), 15.27 (1H, bs, OH). ^{13}C: δ 36.07 (C-5), 39.47 (C-6), 45.34 (C-4), 55.35 (CH_3O), 110.98 (C-2), 114.48 (C-3′, C-5′), 116.32 (q, $^1J_{C–F}$ = 286 Hz, CF_3), 127.47 (C-2′, C-6′), 159.01 (C-4′), 184.22 (q, $^2J_{C–F}$ = 39 Hz, $COCF_3$), 191.17 (C-3), 196.45 (C-1). ^{19}F: δ −74.17 (c, CF_3). GC–MS (EI 70 eV), *m/z* (rel. int.): 314 $[M]^+$ (17), 134 $[M - 180]^+$ (100), 121 $[M - 193]^+$ (40), 69 $[CF_3]^+$ (13). Anal. Calcd for $C_{15}H_{13}O_4F_3$: C, 57.33; H, 4.17. Found: C, 57.45; H, 4.21.

2-Pentafluoropropionyl-5,5-dimethylcyclohexane-1,3-dione (**2g**). This compound was obtained as colorless crystals, mp 87–89 °C. IR (KBr): ν 1700, 1625, 1575 cm^{-1}. NMR: ^1H δ 1.13 (6H, s, 2CH_3), 2.43 (2H, s, CH_2-4), 2.76 (2H, s, CH_2-6), 15.08 (1H, bs, OH). ^{13}C: δ 28.12 (2CH_3 at C-5), 31.13 (C-5), 45.53 (C-6), 51.86 (C-4), 108.21 (tq, $^1J_{C–F}$ = 270 Hz, $^2J_{C–F}$ = 36 Hz, CF_2), 111.64 (C-2), 118.45 (qt, $^1J_{C–F}$ = 288 Hz, $^2J_{C–F}$ = 34 Hz, CF_3), 187.11 (t, $^2J_{C–F}$ = 30 Hz, COC_2F_5), 191.57 (C-3), 196.17 (C-1). ^{19}F: δ −80.29 (CF_3), −118.31 (CF_2). GC–MS (EI 70 eV), *m/z* (rel. int.): 286 $[M]^+$ (5), 230 $[M - CH_2CH_2CO]^+$ (14), 202 $[M - CH_2COCH_2CO]^+$ (14), 174 $[M - CF_3–CH_3–CO]^+$ (50), 167 $[M - C_2F_5]^+$ (100), 111 $[M - C_2F_5CO–2CH_3 + 2H]^+$ (21), 83 $[CHCOCH_2CO]^+$ (54), 69 $[CF_3]^+$ (47), 55 $[CHCH_2CO]^+$ (25), 41 $[CHCO]^+$ (22). Anal. Calcd for $C_{11}H_{11}O_3F_5$: C, 46.16; H, 3.87. Found: C, 46.07; H, 3.81.

2-Pentafluoropropionylcyclohexane-1,3-dione (**2h**). This compound was obtained as colorless crystals, mp 37–38 °C. IR (KBr): ν 1700, 1620, 1560 cm^{-1}. NMR: ^1H δ (2H, qui, *J* = 6.5 Hz, C-5), 2.56 (2H, bt, C-4), 2.79 (2H, bt, C-6), 15.02 (1H, s, OH). ^{13}C: δ 18.92 (C-5), 31.99 (C-6), 37.84 (C-4), 108.17 (tq, $^1J_{C–F}$ = 270 Hz, $^2J_{C–F}$ = 36 Hz, CF_2), 112.61 (C-2), 118.44 (qt, $^1J_{C–F}$ = 288 Hz, $^2J_{C–F}$ = 35 Hz, CF_3), 187.61 (t, $^2J_{C–F}$ = 30 Hz, COC_2F_5), 191.70 (C-3), 197.12 (C-1). ^{19}F: δ −80.21 (CF_3), −118.29 (CF_2). GC–MS (EI 70 eV), *m/z* (rel. int.): 258 $[M]^+$ (8), 230 $[M - CO]^+$ (10), 202 $[M - CH_2CH_2CO]^+$ (16), 174 $[M - CH_2COCH_2CO]^+$ (53), 139 $[M - C_2F_5]^+$ (100), 119 $[C_2F_5]^+$ (10), 111 $[M - C_2F_5CO]^+$ (18), 69 $[CF_3]^+$ (81), 55 $[CHCH_2CO]^+$ (32), 42 $[CH_2CO]^+$ (31). Anal. Calcd for $C_9H_7O_3F_5$: C, 41.88; H, 2.73. Found: C, 41.78; H, 2.67.

2-Heptafluorobutyryl-5,5-dimethylcyclohexane-1,3-dione (**2i**). This compound was obtained as colorless crystals, mp 69–72 °C. IR (KBr): ν 1695, 1635, 1575 cm^{-1}. NMR: ^1H δ 1.13 (6H, s, 2CH_3), 2.43 (2H, s, CH_2-4), 2.67 (2H, s, CH_2-6), 14.98 (1H, bs, OH). ^{13}C: δ 28.12 (2CH_3 at C-5), 31.15 (C-5), 45.45 (C-6), 51.79 (C-4), 109.65 (m, CF_2), 110.06 (tt, $^1J_{C–F}$ = 269 Hz, $^2J_{C–F}$ = 31 Hz, CF_2), 111.93 (C-2), 117.76 (qt, $^1J_{C–F}$ = 288 Hz, $^2J_{C–F}$ = 34 Hz, CF_3), 187.34 (t, $^2J_{C–F}$ = 29 Hz, COC_3F_7), 191.65 (C-3), 195.59 (C-1). ^{19}F: δ −80.73 (3F, CF_3), −113.73 (2F, CF_2),

−123 (2F, CF_2). GC–MS (EI 70 eV), *m/z* (rel. int.): 336 $[M]^+$ (3), 280 $[M - CH_2CH_2CO]^+$ (10), 224 $[M - CF_3–CH_3–CO]^+$ (27), 167 $[M - C_3F_7]^+$ (100), 111 $[M - C_3F_7CO–2CH_3 + 2H]^+$ (17), 83 $[CHCOCH_2CO]^+$ (38), 69 $[CF_3]^+$ (38), 55 $[CHCH_2CO]^+$ (15), 41 $[CHCO]^+$ (12). Anal. Calcd for $C_{12}H_{11}O_3F_7$: C, 42.85; H, 3.30. Found: C, 43.74; H, 3.33.

2-Heptafluorobutyrylcyclohexane-1,3-dione (**2j**). This compound was obtained as colorless crystals, mp 29–30 °C. IR (KBr): ν 1695, 1635, 1570 cm^{-1}. NMR: ^1H δ 2.05 (2H, qui, J = 6.5 Hz, CH_2-5), 2.56 (2H, bt, CH_2-4), 2.74 (2H, bt, CH_2-6), 14.86 (1H, bs, OH). ^{13}C: δ 18.96 (C-5), 31.98 (C-6), 37.76 (C-4), 109.37 (m, CF_2), 110.04 (tt, $^1J_{C–F}$ = 269 Hz, $^2J_{C–F}$ = 31 Hz, CF_2), 112.90 (C-2), 117.67 (qt, $^1J_{C–F}$ = 288 Hz, $^2J_{C–F}$ = 34 Hz, CF_3), 187.94 (t, $^2J_{C–F}$ = 29 Hz, C-1′), 191.83 (C-3), 196.59 (C-1). ^{19}F: δ −80.77 (3F, CF_3), −113.75 (2F, CF_2), −122.82 (2F, CF_2). GC–MS (EI 70 eV), *m/z* (rel. int.): 308 $[M]^+$ (10), 239 $[M - CF_3]^+$ (28), 139 $[M - C_3F_7]^+$ (38), 111 $[M - C_3F_7CO]^+$ (37), 69 $[CF_3]^+$ (100), 55 $[CHCH_2CO]^+$ (67), 41 $[CHCO]^+$ (20). Anal. Calcd for $C_{10}H_7O_3F_7$: C, 38.98; H, 2.29. Found: C, 39.15; H, 3.31.

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