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Synthesis and Properties of Fluorinated 2-Benzoylcyclohexane-1,3-diones

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Abstract — Fluorinated 2-benzoylcyclohexane-1,3-diones were obtained by the O–C isomerization of the corresponding 3-benzoyloxycyclohex-2-en-1-ones under the action of acetone cyanohydrin in the presence of triethylamine in the medium of absolute acetonitrile. The structure of the target compounds was investigated by the means of IR and NMR spectroscopy, and X-ray diffraction analysis.
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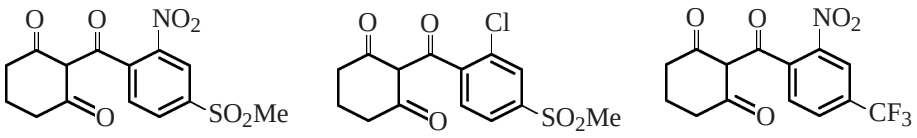
Widespread natural cyclic β,β'-triketones of various structures, possessing various types of biological activity, constitute an interesting class of polyfunctional compounds [1, 2]. 2-Acylcycloalkane-1,3-diones both of the cyclohexane and cyclopentane series are widely used in the synthesis of biologically active compounds due to the rich synthetic potential of the polyfunctional β,β'-tricarbonyl system [3–7]. Presently various 2-benzoylcyclohexane-1,3-diones and other cyclic β,β'-triketones are used in agriculture as effective herbicides, such as mesotrione and salcotrione, and others [8–10]. 2-[2-Nitro-4-(trifluoromethyl)benzoyl]cyclohexane-1,3-dione (NTBC) is successfully applied in the therapy of tyrosinemia type I [11]. One of the possible mechanisms of action of these compounds, both as herbicides and medicines, is inhibition of 4-hydroxyphenylpyruvate dioxygenase by chelating the iron(II) ion of this enzyme with the enol form of β,β'-triketones [12, 13].

Scheme 1.



Mesotrione Salcotrione NTBC

Recently, based on the nitrile oxide synthetic approach to 2-benzoylcyclohexane-1,3-diones [14, 15], Akhrem et al. [16] performed effective synthesis of coleophomones isolated from two species of fungi, whose biological profile includes fungicide and antibiotic activity and myocardial chimase inhibition.

The goal of the present work was to obtain new fluorinated 2-benzolcyclohexane-1,3-diones and investigate their structure.

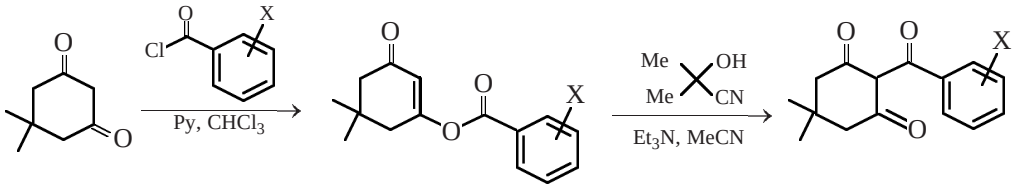
It is important to note that fluorinated compounds have gained extensive application in organic synthesis, primarily in the production of medicines and pesticides [17, 18]. This is connected with the fact that fluorine and its compounds can, for example, enhance efficiency and selectivity of medicines [19]. It is known that introduction of fluorine and fluorinated substituents in the molecule of a biologically active compound can alter the physicochemical and biological properties of the latter.

There are a number of synthetic approaches to cyclic β,β'-triketones [20]. Among the most effective methods of synthesis of 2-acylcyclohexane-1,3-diones

is O–C isomerization of cyclohexane-1,3-dione enol acylates under the action of some catalysts, such as aluminum chloride, *N*,*N*-dimethylaminopyridine, zinc chloride, and others. Attempted synthesis of fluorinated 2-benzoylcyclohexane-1,3-diones **Ia**–**Ie** by isomerization of 3-benzoyloxycyclohex-2-en-1-ones **IIa**–**IIe** in boiling absolute toluene in the presence of dimethylaminopyridine or zinc chloride under the conditions described in [21] were unsuccessful. Thus, acylation of 5,5-dimethylcyclohexane-1,3-dione with fluorobenzoic acids in the presence of 1,3-dicyclohexylcarbodiimide, triethylamine, and dimethylaminopyridine in chloroform by the procedure described in [22] resulted in isolation of enol acylates **IIa**–**IIe** only. It was reported [23, 24] that isomerization of 3-benzoylcyclohex-2-en-1-ones containing fluorine in the *ortho* position of the benzene ring, in the presence of aluminum chloride in dichloroethane or in the presence of KCN and triethylamine in methylene chloride led to intramolecular nucleophilic heterocyclization of the β,β'-triketones formed with HF liberation and formation of 2,3,4,9,-tetrahydro-1*H*-xanten-1,9-diones.

We found that the O–C isomerization of fluorinated enol acylates **IIa**–**IIe** into the corresponding 2-benzoylcyclohexane-1,3-diones **Ia**–**Ie** proceeds under the action of catalytic amounts of acetone cyanohydrin in the presence of triethylamine in absolute acetonitrile [25, 26]. The yields of the target products were 72–93%. Under these conditions, no intramolecular heterocyclization of 2-(2-fluorobenzoyl)-5,5-dimethylcyclohexane-1,3-dione (**Ia**) and 2-(2,3,4,5,6-pentafluorobenzoyl)-5,5-dimethylcyclohexane-1,3-dione (**Ie**) was observed.

Scheme 2.



IIa–**IIe** **Ia**–**Ie**

I, II, X = 2-F (**a**), 3-F (**b**), 4-F (**c**), 4-CF_3 (**d**), 2,3,4,5,6-F (**e**).

Enol derivatives **IIa**–**IIe** were prepared by a routine procedure via O-acylation of 5,5-dimethylcyclohexane-1,3-dione with fluorobenzoyl chlorides in the presence of an equivalent amount of pyridine in absolute chloroform in 73–95% yields [27].

The structure of compounds **Ia**–**Ie** and **IIa**–**IIe** was confirmed by IR, ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy and elemental analysis. Parameters of known compounds were compared with published data. Thus, the IR spectra of enol acylates **IIa**–**IIe** show characteristic absorption bands of the ester carbonyl group (1740–1770 cm^{-1}), conjugated carbonyl group (1670–1680 cm^{-1}), and double bond (1600–1620 cm^{-1}). The ^{1}H NMR spectra of these compounds contain, along with methyl, methylene, and aromatic proton signals, a vinyl proton signal as a broad triplet at δ 6 ppm (*J* 1 Hz) and a methylene proton signal as a broadened doublet (*J* 1 Hz) at δ 2.6 ppm. For complete assignment of signals of enol acylates **Ia**–**Ie** in the ^{1}H and ^{13}C NMR spectra, we measured the HMBC spectrum of 3-(2-fluorobenzoyloxy)-5,5-dimethylcyclohex-2-en-1-one (**IIa**).

The presence of the β-tricarbonyl group in compounds **Ia**–**Ie** suggests keto–enol equilibrium and formation of *exo*/*endo*-enol tautomers differing from each other by the positions of the conjugated carbonyl group and conjugated chelate system with a strong intramolecular bond [28].

According to the spectral data, fluorinated 2-benzoylcyclohexane-1,3-diones **Ia**–**Ie** are completely enolized, like other cyclic β,β'-triketones [29, 30]. The IR spectra of compounds **Ia**–**Ie** contain an absorption band of the conjugated carbonyl group (1675–1700 cm^{-1}) and a broad absorption band in the range

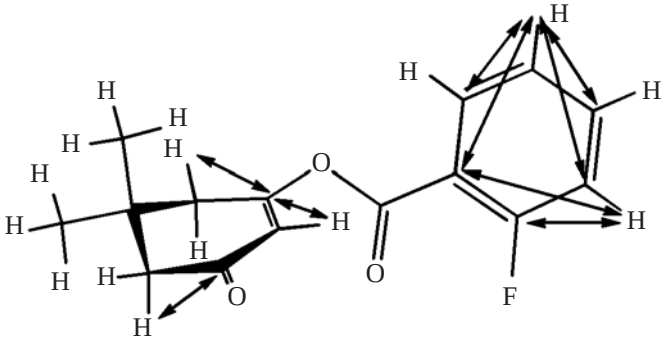


Fig. 1. Principal correlations in the HMBC spectrum of enol acylate **IIa**.

Table 1. ^{13}C NMR parameters of compounds **Ia**–**Ie**, δ, ppm (J_{C-F}, Hz)[a]

Atom	Ia	Ib	Ic	Id	Ie
Ph*C*O	194.86	197.34	197.06	197.54	187.07
C^1	193.95	194.01	194.21	193.89	194.13
C^2	113.82	112.39	112.26	112.25	113.19
C^3	194.75	195.62	195.60	196.05	196.00
C^4	45.88	46.09	46.19	46.06	44.96
C^5	31.00	31.20	31.13	31.09	31.21
C^6	51.71	52.24	52.36	51.10	51.07
CH_3	28.24	28.43	28.42	28.30	28.08
$C^{1'}$	127.55 d (^2J 14)	140.35 d (^3J 7)	134.22 d (^4J 3)	141.62	114.80 t.d (^2J 38, ^3J 4)
$C^{2'}$	159.33 d (^1J 250)	115.26 d (^2J 23)	131.22 d (^3J 10)	128.21	142.22 d.m (^1J 256)
$C^{3'}$	115.32 d (^2J 22)	162.15 d (^1J 246)	114.99 d (^2J 22)	124.80	137.41 d.t.d (^1J 254, ^2J 14, ^3J 5)
$C^{4'}$	132.77 d (^3J 9)	118.69 d (^2J 22)	165.11 d (^1J 253)	132.89 q (^2J 33)	143.24 d.m (^1J 250)
$C^{5'}$	124.15 d (^4J 3)	129.48 d (^3J 8)	114.99 d (^2J 22)	124.80	137.41 d.t.d (^1J 254, ^2J 14, ^3J 5)
$C^{6'}$	128.94 d (^5J 2)	123.97 d (^4J 3)	131.22 d (^3J 10)	128.21	142.22 d.m (^1J 256)
Ph*C*F_3	–	–	–	123.75 q (^1J 273)	–

[a] The spectra of compounds **Ia** and **Ie** were recorded at –40°C, and the other, at room temperature.

of 1555–1585 cm^{-1} due to the carbonyl group intramolecularly hydrogen-bonded with the enol hydroxyl). The ^1H NMR spectra of compounds **Ia**–**Ie** display a downfield enol proton signal at δ 16.8–16.9 ppm. The presence of fluorine atoms bonded to the aromatic ring in compounds **Ia**–**Ie** is confirmed by the observation in the ^{13}C NMR spectra (Table 1) of a doublet signal at 160–165 ppm (*J* 246–253 Hz). In the ^{13}C NMR spectrum of compound **IId** containing the CF_3 group, a quartet carbon signal is observed at δ_C 123.75 ppm (*J* 273 Hz). The ^{13}C NMR spectrum of compound **IIe** displays three doublets of multiplets due to carbon atoms of the pentafluorinated benzene ring at δ_C, ppm: 137.41 d.d ($C^{3'}$, $C^{5'}$, *J* 254; 15 Hz), 142.22 d.m ($C^{2'}$, $C^{6'}$, *J* 257 Hz), and 143.22 d.m ($C^{4'}$, *J* 250 Hz). Further evidence for the presence of fluorine atoms bonded to the aromatic ring in compounds **Ia**–**Ie** is provided by the occurrence of corresponding signals in the ^{19}F NMR spectra. The ^{13}C NMR spectra of compounds **Ia**–**Ie** contain three signals from the exo- and endocyclic carbonyl groups in the region of δ_C 186–197 ppm.

To reveal the enolization direction and assign signals in the ^1H and ^{13}C NMR spectra, we measured the HMBC spectra of fluorinated 2-benzoylcyclohexane-1,3-diones **Ia**–**Ie**.

In the all the cases, a similar coupling pattern was observed: The protons at C^6 and C^4 had cross-peaks with C^1 and C^3, respectively. The enol proton gave

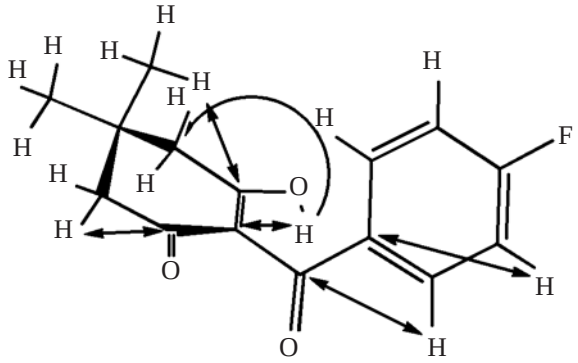
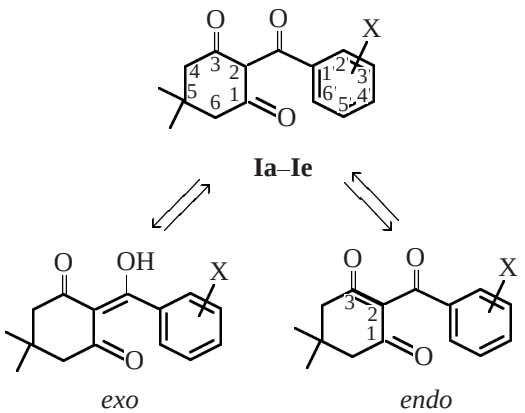


Fig. 2. Principal correlations in the HMBC spectrum of β,β'-triketone **Ic**.

Scheme 3.



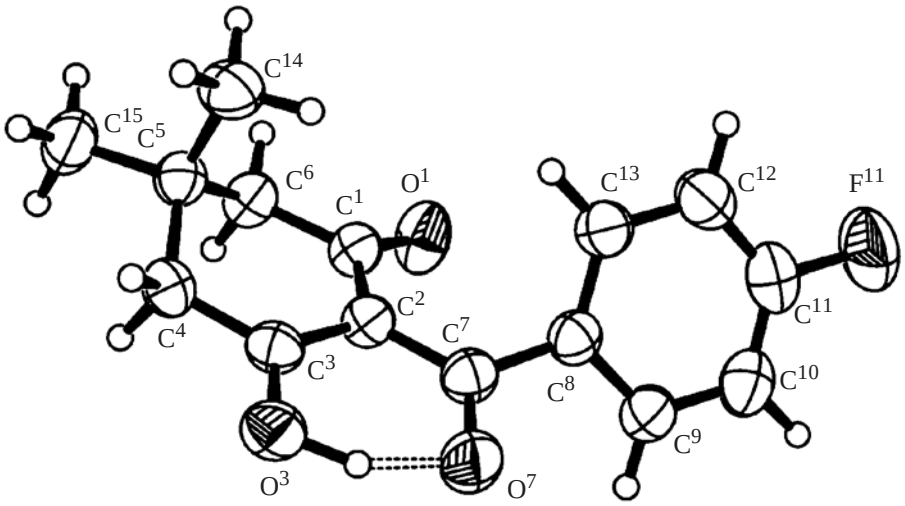


Fig. 3. Structure of molecule **Ic**. The dashed line shows the intramolecular hydrogen bond.

cross-peaks with C^2, C^3, and C^4. Coupling of the exocyclic carbonyl carbon with the *ortho* proton of the aromatic ring was observed in the spectra of all the compounds, except for compound Ie which has no *ortho* proton. The above evidence led us to conclude that the enolized endocyclic carbonyl in compounds **Ia**–**Ie** resonates downfield from nonenolized. The same picture was observed with other our synthesized fluorinated β,β'-triketones [31]. To obtain further evidence for our assignments, we recorded low-temperature ^{13}C NMR spectra with deuterium exchange for compounds **Ia**, **Id**, and **Ie**. In all the cases, the largest upfield shift upon addition of heavy water was detected for C^3, in complete agreement with the HMBC results. The deuterium-induced shifts of signals in the ^{13}C NMR spectra are listed in Table 2 (a negative sign means an upfield shift and a positive, a downfield shift).

The structure of fluorinated 2-benzoylcyclohexane-1,3-diones **Ia**–**Ie** was single-crystal X-ray diffraction data for compound **Ic**. Figure 3 shows the molecular structure of **Ic** which is evidently the *endo*-enol tautomer.

The bonds length and angles in this molecule are normal values [32]. The hydroxyl hydrogen atom is involved into a strong intramolecular hydrogen bond O^3–H^3···O^7 (Table 3) which can be referred to as a resonance-assisted hydrogen bond [33].

The structure also includes C–H···O intermolecular hydrogen bonds which cause dimer formation (Fig. 4).

It should be noted that compound **Ic** belongs to the same structural type as 2-benzoyldimedone we studied earlier [34]. The crystallographic data and parameters of the least-squares refinement (MLS) for structure **Ic** are presented in Table 4, and the atomic coordinates and equivalent thermal parameters are given in Table 5.

Table 2. Isotopic chemical shifts of signals (ppm) in the ^{13}C NMR spectra of compounds **Ia, Ic**, and **Ie**

Atom	**Ia**	**Ic**	**Ie**
C^1	0.3	0.11	0.05
C^2	0.10	0.16	0.04
C^3	–1.8	–1.9	–1.3
C^4	–0.5	–0.5	–0.33
C^6	–0.08	–0.12	–0.05
*C*OPh	0.13	0.16	0.22
$C^{1'}$	0.4	0.4	–

Table 3. Parameters of hydrogen bonds in the crystal of compound **Ic** (Å, deg)

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(D–H···A)
O^3–H^3···O^7	1.07(2)	1.45(2)	2.4572(15)	153.7(17)
C^{12}–H^{12}···O^1#1 [a]	0.976(19)	2.586(19)	3.558(2)	174.0(15)

[a] Symmetry code: (#1) –*x*, 1 – *y*, –*z*.

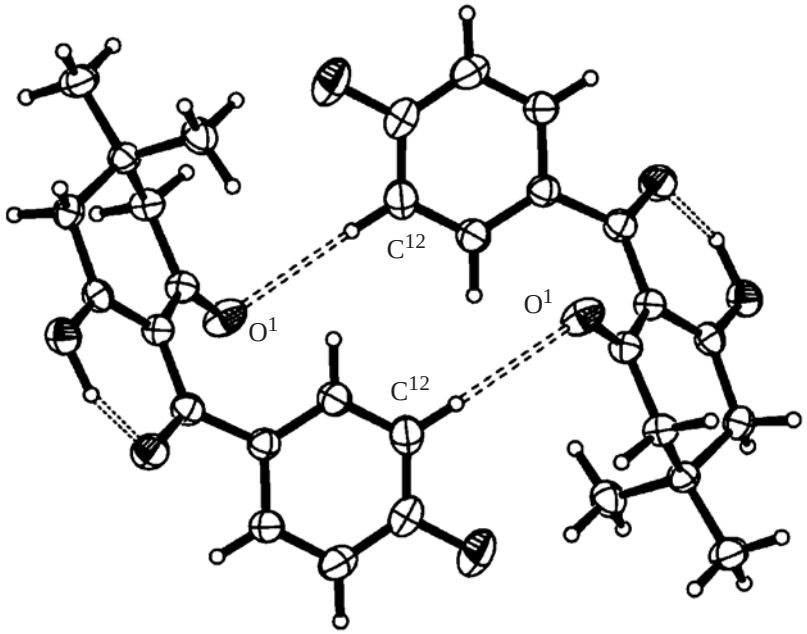


Fig. 4. Dimer in the crystal structure of compound **Ic**. The dashed line shows hydrogen bonds.

Table 4. Crystallographic data and MLS refinement parameters for structure **Ic**

Formula	$C_{15}H_{15}FO_3$
Molecular weight	262.27
λ, Å	0.71073
Syngony	Monoclinic
Space group	$P2_1/n$
Unit cell parameters	
a, Å	7.3360 (13)
b, Å	15.139 (3)
c, Å	11.932 (3)
β, deg	101.526 (16)
V, Å^3	1298.4 (5)
Z	4
d_{calc}, g cm^{-3}	1.342
Absorption coefficient, μ, cm^{-1}	1.02
Crystal dimensions, mm	0.54 × 0.36 × 0.32
Reflections measured/independent	3230/3004 [R_{int} 0.0138]
Fullness of data collection to θ 27.55%	100
Method of refinement	full-matrix MLS on F^2
Data/restrictions/ parameters	3004/0/232
Quality of refinement on F^2	1.047
R [$I > 2\sigma(I)$]	R^1 0.0382, wR^2 0.1029
R^1 (all data)	R^1 0.0499, wR^2 0.1124
Max and min residual peaks, e Å^{-3}	0.125 and –0.182

EXPERIMENTAL

The NMR spectra were recorded on a Bruker Avance-500 spectrometer operating at 500 MHz (^{1}H) and 125 MHz (^{13}C) in $CDCl_3$ against internal TMS. The ^{19}F NMR spectra were measured at 470 MHz against CCl_3F. The IR spectra were obtained on a UR-20 spectrometer from KBr pellets. The melting points were measured on a Boetius hot stage. The reaction progress and purity of compounds were monitored by TLC on Silufol UV-254 plates, eluent ether. The ^{13}C NMR spectra of compounds **Ia**–**Ie** are presented in Table 1.

The 3D set of X-ray diffraction data for structure **Ic** was obtained on an autonomic fourcircle Nicolet R3 diffractometer (MoK_α radiation, graphite monochromator, θ/2θ scanning, $2\theta_{max}$ 55°). The structure was solved by the direct method (SIR2004 [35]) and refined by full-matrix least squares anisotropically for non-hydrogen atoms (SHELXL 97 [36]). Hydrogen atoms were located by the difference Fourier synthesis and refined isotropically. The drawings were performed by the ORTEP-3 program [37].

Synthesis of fluorinated 2-benzoylcyclohexane-1,3-diones Ia–**Ie**. To a solution of 13.5 mmol of cyclohexane-1,3-dione enol acylate **IIa**–**IIe** in 10 ml of acetonitrile, 27.0 mmol of triethylamine and 0.5 ml of acetone cyanohydrin were added. The reaction mixture was stirred at room temperature for 3 h (**IIa**–**IId**) or 0.5 h (**IId**), and 50 ml of chloroform was added to the mixture. The chloroform solution was washed

Table 5. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) in structure **Ic**

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
C^1	3275(2)	3934(1)	2418(1)	45(1)
O^1	1665(1)	4179(1)	2272(1)	67(1)
C^2	3813(2)	3083(1)	1984(1)	43(1)
C^3	5636(2)	2791(1)	2358(1)	45(1)
O^3	6133(1)	1983(1)	2178(1)	58(1)
C^4	7154(2)	3360(1)	2980(1)	51(1)
C^5	6731(2)	4348(1)	2886(1)	47(1)
C^6	4786(2)	4481(1)	3135(1)	49(1)
C^7	2507(2)	2498(1)	1278(1)	48(1)
O^7	2917(2)	1695(1)	1187(1)	66(1)
C^8	705(2)	2788(1)	576(1)	47(1)
C^9	–813(2)	2223(1)	478(1)	56(1)
C^{10}	–2477(2)	2428(1)	–240(1)	64(1)
C^{11}	–2575(2)	3188(1)	–870(1)	62(1)
F^{11}	–4200(1)	3377(1)	–1596(1)	93(1)
C^{12}	–1112(2)	3759(1)	–812(1)	62(1)
C^{13}	539(2)	3558(1)	–71(1)	55(1)
C^{14}	6827(2)	4686(1)	1690(1)	61(1)
C^{15}	8161(2)	4838(1)	3778(2)	64(1)
H^3	4860(30)	1681(12)	1747(17)	96(6)
H^{4A}	8290(20)	3227(11)	2696(13)	71(5)
H^{4B}	7380(20)	3180(10)	3813(14)	71(5)
H^{6A}	4420(20)	5121(11)	3039(13)	70(4)
H^{6B}	4800(20)	4303(10)	3949(14)	63(4)
H^9	–690(20)	1700(10)	946(13)	63(4)
H^{10}	–3580(30)	2037(13)	–309(16)	93(6)
H^{12}	–1240(30)	4302(12)	–1262(16)	85(5)
H^{13}	1610(20)	3977(10)	–3(13)	65(4)
H^{14A}	8100(30)	4583(11)	1512(14)	77(5)
H^{14B}	5860(20)	4378(11)	1062(14)	71(5)
H^{14C}	6540(30)	5339(14)	1634(15)	86(5)
H^{15A}	9410(30)	4744(12)	3627(14)	79(5)
H^{15B}	7890(20)	5481(13)	3757(14)	80(5)
H^{15C}	8140(30)	4570(12)	4577(16)	87(5)

with 10% HCl (3×20 ml) and water (2×20 ml) and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was recrystallized from ether. Compounds **Ia**–**Ie** were isolated as colorless crystals in 72–93% yields.

2-(2-Fluorobenzoyl)-5,5-dimethylcyclohexane-1,3-dione (Ia). Yield 93%, mp 105–107°C. IR spectrum, ν, cm^{-1}: 1680 ($C=O_{conjug}$), 1575 (C=O chelat.). ^1H NMR spectrum, δ, ppm: 1.13 s (6H, $2CH_3$), 2.36 s (2H, CH_2, C^6), 2.63 s (2H, CH_2, C^4), 7.04 d.d.d (1H, H_{arom}, $C^{3'}$, *J* 10.3, 8.3, 1 Hz), 7.22 t.d (1H, H_{arom}, $C^{5'}$, *J* 7.7, 1 Hz), 7.43 m (1H, H_{arom}, $C^{6'}$), 7.46 m (1H, H_{arom}, $C^{4'}$), 16.90 br.s (1H, OH). ^{19}F NMR spectrum, δ_F, ppm: –112.6 m. Found, %: C 68.57; H 5.71. $C_{15}H_{15}FO_3$. Calculated, %: C 68.69; H 5.76.

2-(3-Fluorobenzoyl)-5,5-dimethylcyclohexane-1,3-dione (Ib). Yield 87%, mp 88–90°C.IR spectrum, ν, cm^{-1}: 1675 ($C=O_{conjug}$), 1585 ($C=O_{chelat}$). ^1H NMR spectrum, δ, ppm: 1.16 s (6H, $2CH_3$), 2.40 s (2H, CH_2, C6), 2.66 s (2H, CH_2, C^4), 7.19 d.d (1H, H_{arom}, $C^{2'}$, *J* 9.0, 1.3 Hz), 7.20 m (1H, H_{arom}, $C^{4'}$), 7.26 d.t (1H, H_{arom}, $C^{6'}$, *J* 7.9, 1.3 Hz), 7.37 m (1H, H_{arom}., $C^{5'}$), 16.83 br.s (1H, OH). ^{19}F NMR spectrum, δ_F, ppm: –113.3 m. Found, %: C 68.35; H 5.81. $C_{15}H_{15}FO_3$. Calculated, %: C 68.69; H 5.76.

2-(4-Fluorobenzoyl)-5,5-dimethylcyclohexane-1,3-dione (Ic). Yield 79%, mp 135–137°C. IR spectrum, ν, cm^{-1}: 1670 ($C=O_{conjug}$), 1565 ($C=O_{chelat}$). ^1H NMR spectrum, δ, ppm: 1.16 s (6H, $2CH_3$), 2.40 s (2H, CH_2, C^6), 2.65 s (2H, CH_2, C^4), 7.08 m (2H, H_{arom}, $C^{3'}$, $C^{5'}$), 7.55 m (2H, H_{arom}, $C^{2'}$, $C^{6'}$), 16.99 br.s (1H, OH). ^{19}F NMR spectrum, δ_F, ppm: –106.9 m. Found, %: C 68.41, H 5.82. $C_{15}H_{15}FO_3$. Calculated, %: C 68.69, H 5.76.

5,5-Dimethyl-2-[4-(trifluromethyl)benzoyl]cyclohexane-1,3-dione (Id). Yield 73%, mp 102–105°C. IR spectrum, ν, cm^{-1}: 1680 ($C=O_{conjug}$), 1555 ($C=O_{chelat}$). ^1H NMR spectrum, δ, ppm: 1.16 s (6H, $2CH_3$), 2.39 s (2H, CH_2, C^6), 2.67 s (2H, CH_2, C^4), 7.57 d (2H, H_{arom}, $C^{3'}$, $C^{5'}$, *J* 8.3 Hz), 7.65 d (2H, H_{arom}, $C^{2'}$, $C^{6'}$, *J* 8.3 Hz), 16.92 br.s (1H, OH). Found, %: C 61.43, H 4.79. $C_{16}H_{15}F_3O_3$. Calculated, %: C 61.54, H 4.84.

2-(2,3,4,5,6-Pentafluorobenzoyl)-5,5-dimethylcyclohexane-1,3-dione (Ie). Yield 72%, mp 53–55°C. IR spectrum, ν, cm^{-1}: 1700 ($C=O_{conjug}$), 1585 ($C=O_{chelat}$). ^1H NMR spectrum, δ, ppm: 1.14 s (6H, $2CH_3$), 2.35 s (2H, CH_2, C^6), 2.69 s (2H, CH_2, C^4), 16.35 br.s (1H, OH). ^{19}F NMR spectrum, δ_F, ppm: –142.78 m (2F, $C^{2'}$,$C^{6'}$), –152.27 t (1F, $C^{4'}$, *J* 20 Hz), –161.70 m (2F, $C^{3'}$, $C^{5'}$). Found, %: C 46.18, H 2.89. $C_{15}H_{11}F_8O_3$. Calculated, %: C 46.05, H 2.83.

3-Benzoyloxycyclohex-2-en-1-ones IIa–**IIe** were prepared by a known method from 5,5-dimethylcyclohexane-1,3-dione and corresponding fluorobenzoyl chlorides in the presence of pyridine in anhydrous chloroform [22] and isolated by recrystallization from ether–hexane (2 : 1) as colorless crystals in 73–95% yields.

3-(2-Fluorobenzoyloxy)-5,5-dimethylcyclohex-2-en-1-one (IIa). Yield 95%, mp 40–42°C (40–43°C [18]). IR spectrum, ν, cm^{-1}: 1745 (C=O ester), 1680 ($C=O_{conjug}$), 1620 (C=C). ^1H NMR spectrum, δ, ppm: 1.16 s (6H, $2CH_3$), 2.33 s (2H, CH_2, C^6), 2.56 d (2H,

CH_2, C^4, ^4J 1 Hz), 6.06 t (1H, H_{vinyl}, C^2, ^4J 1 Hz), 7.20 d.d (1H, H_{arom}, $C^{3'}$, J 10.5, 8.8 Hz.), 7.27 m (1H, H_{arom}, $C^{5'}$), 7.62 m (1H, H_{arom}, $C^{4'}$), 7.99 t.d (1H, H_{arom}, $C^{6'}$, J 7.6, 1.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.22 (CH_3), 33.31 (C^5), 42.25 (C^4), 50.93 (C^6), 117.03 (C^2), 117.15 d ($C^{1'}$, J_{C-F} 22 Hz), 117.35 d ($C^{3'}$, J_{C-F} 22 Hz), 124.29 d ($C^{5'}$, J_{C-F} 4 Hz), 132.50 ($C^{6'}$), 135.82 d ($C^{4'}$, J_{C-F} 9 Hz), 160.85 d (COO, J_{C-F} 4 Hz), 162.36 d ($C^{2'}$, J_{C-F} 262 Hz), 168.12 (C^3), 199.33 (C^1).

3-(3-Fluorobenzoyloxy)-5,5-dimethylcyclohex-2-en-1-one (IIb). Yield 92%, mp 27–29°C. IR spectrum, ν, cm^{-1}: 1750 (C=O ester), 1680 ($C=O_{conjug}$), 1600 (C=C). ^1H NMR spectrum, δ, ppm: 1.16 s (6H, $2CH_3$), 2.34 s (2H, CH_2, C^6), 2.56 br.d (2H, CH_2, C^4), 6.06 br.t (1H, H_{vinyl}, C^2), 7.35 m (1H, H_{arom}.), 7.50 m (1H, H_{arom}), 7.76 m (1H, H_{arom}), 7.89 d (1H, H_{arom}, J 7.9 Hz).

3-(4-Fluorobenzoyloxy)-5,5-dimethylcyclohex-2-en-1-one (IIc). Yield 73%, mp 40–42°C. IR spectrum, ν, cm^{-1}: 1740 (C=O ester), 1680 ($C=O_{conjug}$), 1610 (C=C). ^1H NMR spectrum, δ, ppm: 1.16 s (6H, $2CH_3$), 2.34 s (2H, CH_2, C^6), 2.56 br.d (2H, CH_2, C^4), 6.05 br.t (1H, H_{vinyl}, C^2), 7.18 m (2H, H_{arom}), 8.11 m (2H, H_{arom}).

5,5-Dimethyl-3-[4-(trifluoromethyl)benzoyloxy]-cyclohex-2-en-1-one (IId). Yield 79%, mp 54–56°C. IR spectrum, ν, cm^{-1}: 1760 (C=O ester), 1670 ($C=O_{conjug}$), 1625 (C=C). ^1H NMR spectrum, δ, ppm: 1.17 s (6H, $2CH_3$), 2.35 s (2H, CH_2, C^6), 2.58 br.d (2H, CH_2, C^4), 6.07 br.t (1H, H_{vinyl}, C^2), 7.77 d (2H, H_{arom}, J 8.3 Hz.), 8.21 d (2H, H_{arom}, J 8.3 Hz).

3-(2,3,4,5,6-Pentafluorobenzoyloxy)-5,5-dimethylcyclohex-2-en-1-one (Ie). Yield 87%, mp 72–74°C. IR spectrum, ν, cm^{-1}: 1760 (C=O ester), 1680 ($C=O_{conjug}$), 1510 (C=C). ^1H NMR spectrum, δ, ppm: 1.16 s (6H, $2CH_3$), 2.34 s (2H, CH_2, C^6), 2.55 br.d (2H, CH_2, C^4), 6.09 br.t (1H, H_{vinyl}, C^2). ^{13}C NMR spectrum, δ_C, ppm: 28.18 (CH_3), 33.34 (C^5), 41.96 (C^4), 50.85 (C^6), 117.41 (C^2), 137.90 d.m ($C^{3'}$,$C^{5'}$, J_{C-F} 257 Hz), 144.13 d.m ($C^{2'}$, $C^{6'}$, J_{C-F} 256 Hz), 145.94 ($C^{4'}$, J_{C-F} 258 Hz), 166.96 (C^3), 198.82 (C^1). ^{19}F NMR spectrum, δ_F, ppm: –136.98 m (2F, $C^{2'}$, $C^{6'}$), –145.95 t.t (1F, $C^{4'}$, J 21, 6 Hz), –159.65 m (2F, $C^{3'}$, $C^{5'}$).

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