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2-Perfluoroalkanoylcyclopentane-1,3-diones. Synthesis and Some Transformations

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Abstract—2-Perfluoroalkanoylcyclopentane-1,3-diones were synthesized for the first time by acylation of cyclopentane-1,3-dione with perfluorocarboxylic acids in the presence of 1,1′-carbonyldiimidazole or with perfluorocarboxylic anhydrides in the presence of imidazole. 2-Perfluoroalkanoylcyclopentane-1,3-diones were selectively reduced to 2-(1-hydroxyperfluoroalkyl)cyclopentane-1,3-diones by the action of triethylsilane in trifluoroacetic acid in the presence of a catalytic amount of lithium perchlorate. Treatment of the title compounds with oxalyl chloride and subsequent reaction with 2 equiv of primary amine (4-fluoroaniline, 4-fluorobenzylamine, 3,4-difluoroaniline, 3-trifluoromethylbenzylamine) gave the corresponding 3-arylamino-2-perfluoroalkanoylcyclopent-2-en-1-ones.

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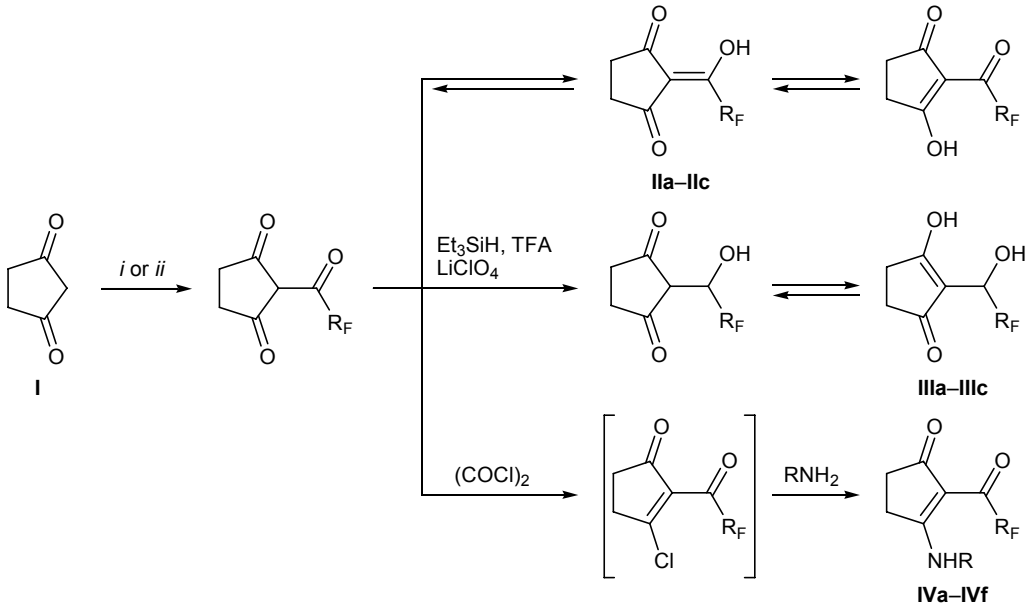
Fluorinated derivatives of β-di- and β-triketones constitute an interesting class of compounds; in many cases these compounds are superior to non-fluorinated analogs in useful properties. They are used as ligands for catalysts in various reactions, metal extractants, analytical reagents, etc. [1], and the presence of reactive carbonyl groups in their molecules makes them effective reagents in the synthesis of biologically active compounds. Introduction of fluorine atoms into organic molecules produces considerable variation of their chemical and physical properties [2]. Replacement of hydrogen by fluorine often enhances biological activity of organic compounds as a result of increase of their lipophilicity and change of steric and electronic properties [3]. Polyfunctional 2-perfluoroalkanoylcyclocyclopentane-1,3-diones are promising as building blocks for the synthesis of various polyfluoroalkyl-containing compounds. Non-fluorinated β-triketones of the cyclopentane series are widespread in nature, as well as among synthetic biologically active compounds [4]; they are also used as intermediates in the synthesis of other natural compounds and related physiologically active substances [5]. However, unlike non-fluorinated analogs, neither methods of synthesis of perfluoroalkanoyl-substituted β-diketones of the cyclopentane series nor their reactions have been reported so far.

The goal of the present work was to develop a procedure for the synthesis of 2-perfluoroalkanoylcyclopentane-1,3-diones and examine their chemical transformations. Our attempts to obtain 2-perfluoroalkanoylcyclopentane-1,3-diones according to the procedure commonest for their fluorine-free analogs, i.e., by O–C-isomerization of 3-oxocyclopent-1-enyl carboxylates in the presence of different catalysts ($AlCl_3$, acetone cyanohydrin), were unsuccessful. The most efficient method for the synthesis of cyclopentane β-triketones having a perfluorinated aliphatic acyl side chain is based on acylation of cyclopentane-1,3-dione (**I**) with perfluorocarboxylic acids in the presence of 1,1′-carbonyldiimidazole or with perfluorocarboxylic anhydrides in the presence of imidazole in chloroform.

Presumably, the reaction of perfluorocarboxylic acids with 1,1′-carbonyldiimidazole or of their anhydrides with imidazole gives *N*-perfluoroacylimidazoles that are efficient acylating agents [6, 7]; the latter react with cyclopentane-1,3-dione (**I**) in the presence of imidazole, yielding 2-perfluoroalkanoylcyclopentane-1,3-diones with high yield and regioselectivity. By reactions of perfluoropropionic and perfluorobutyric acids with 1,1′-carbonyldiimidazole in chloroform, followed by treatment of *N*-perfluoroacylimidazole thus obtained with a solution of cyclopentane-1,3-dione (**I**) and imidazole in chloroform (4 h, room temperature),

Scheme 1.



i: R_FCOOH, 1,1′-carbonyldiimidazole; *ii*: $(R_FCO)_2O$, imidazole; **II**, **III**, $R_F = CF_3$ (**a**), C_2F_5 (**b**), C_3F_7 (**c**); **IV**, $R_F = CF_3$, R = 4-FC_6H_4 (**a**); $R_F = C_2F_5$, R = 4-FC_6H_4 (**b**); $R_F = C_3F_7$, R = 4-FC_6H_4 (**c**), 3,4-$F_2C_6H_3$ (**d**), 4-$FC_6H_4CH_2$ (**e**), 3-$CF_3C_6H_4CH_2$ (**f**).

we obtained β-triketones **IIb** and **IIc** in 91 and 90% yield, respectively. Alternatively, trifluoroacetic and perfluoropropionic anhydrides reacted with imidazole in chloroform at 0°C, and the subsequent treatment of intermediate *N*-perfluoroacylimidazole with a solution of cyclopentane-1,3-dione (**I**) and imidazole in chloroform (3 h, room temperature) afforded β-triketones **IIa** and **IIb** in 90 and 92% yield, respectively (Scheme 1).

The presence of a β-tricarbonyl fragment in molecules **IIa**–**IIc** implies the possibility for keto–enol tautomerism with formation of structures differing by the position of the enol fragment (endo- or exocyclic) with strong intramolecular hydrogen bond. Analysis of the spectral data (IR, NMR) showed that triketones **IIa**–**IIc**, as well as their nonfluorinated analogs, are completely enolized [5]. The IR spectra of **IIa**–**IIc** lacked absorption in the region 1720–1740 cm^{-1}, which is typical of free carbonyl group, but a band at 1705 cm^{-1} was present due to conjugated carbonyl group; in addition, absorption bands at 1640–1655 (carbonyl group involved in H-chelate ring) and 1570–1565 cm^{-1} (C=C) were observed. Compounds **IIa**–**IIc** displayed in the ^1H NMR spectra a broadened singlet at δ ~13 ppm due to enolic hydroxy proton; the corresponding proton in cyclohexane analogs resonated in a weaker field [7].

We examined transformations of 2-perfluoroalkanoylcyclopentane-1,3-diones **IIa**–**IIc** under conditions of ionic hydrogenation [8]. It is known that ionic hydrogenation of non-fluorinated 2-acylcyclopentane-1,3-diones is regioselective; it results in reduction of the side-chain carbonyl group to methylene with formation of 2-alkylcyclopentane-1,3-diones [9]. This transformation was successfully used in syntheses of prostaglandins [10] and phytoprostanes [11]. Treatment of compounds **IIa**–**IIc** with triethylsilane in trifluoroacetic acid in the presence of lithium perchlorate at room temperature (reaction time 5 h) led to selective formation of 2-(1-hydroxyperfluoroalkyl)cyclopentane-1,3-diones **IIIa**–**IIIc** in 82–89% yield. According to spectral data, diketo alcohols **IIIa**–**IIIc**, like their cyclohexane analogs [12], exist in the enol form. Their IR spectra contained absorption bands at 1615 and 1555 cm^{-1} due to vibrations of conjugated carbonyl group and double bond, respectively, whereas no absorption bands were present in the region 1720–1740 cm^{-1}. In the ^{13}C NMR spectrum of trifluoroethyl derivative **IIa**, the COH carbon atom resonated as a quartet at δ_C 67.1 ppm ($^2J_{CF}$ = 34 Hz), and the corresponding signals in the spectra of pentafluoropropyl and hexafluorobutyl analogs **IIb** and **IIc** appeared, respectively, as a doublet of doublets at δ_C 66.6 (J_{CF} = 29, 24 Hz) and a triplet at δ_C 67.1 ppm ($^2J_{CF}$ = 27 Hz). The fluorine signal in the ^{19}F NMR spectrum of **IIa** was a doublet at δ_F –79.62 ppm ($^3J_{FH}$ = 6.4 Hz). The ^{19}F NMR spectra of **IIb** and **IIc** were complicated due to magnetic nonequivalence of CF_2 fluorine atoms.

Molecules of 2-perfluoroalkanoylcyclopentane-1,3-diones **II** possess three electrophilic centers capable of undergoing attack by nucleophiles. With a view to obtain new fluoroalkyl derivatives, we examined the reactivity of compounds **IIa**–**IIc** toward nitrogen-centered nucleophiles (4-fluoroaniline, 4-fluorobenzylamine, 3,4-difluoroaniline, and 3-trifluoromethylbenzylamine). Non-fluorinated 2-acylcyclopentane-1,3-diones existing in the enol form are fairly strong vinylogous acids which readily react with *N*-nucleophiles at the exocyclic carbonyl group [5] to produce the corresponding enamino derivatives. However, treatment of 2-perfluoroalkanoylcyclopentane-1,3-diones **IIa**–**IIc** with the above primary amines resulted in the formation of complex mixtures of products; reactions of their cyclohexane analogs with primary amines were accompanied by loss of the perfluoroacyl group, and the products were the corresponding 3-aminocyclohex-2-en-1-ones [13].

Enamino derivatives of compounds **IIa**–**IIc** at the endocyclic carbonyl group were obtained by nucleophilic substitution in their enol derivatives (chlorovinyl diketones). For this purpose, triketones **IIa**–**IIc** were treated with oxalyl chloride (4 h, room temperature), and 3-chloro-2-perfluoroacylcyclopent-2-en-1-ones obtained after removal of the chlorinating agent under reduced pressure were brought into reaction with 2 equiv of primary amine (4-fluoroaniline, 4-fluorobenzylamine, 3,4-difluoroaniline, and 3-trifluoromethylbenzylamine; reaction time 1 h). The target enamino derivatives **IVa**–**IVf** were isolated in 68–90% yield (Scheme 1).

The IR spectra of **IVa**–**IVf** contained absorption bands at 1695–1705 and 1640–1645 cm^{-1} due to stretching vibrations of the conjugated endo- and exocyclic carbonyl groups, respectively. In the ^1H NMR spectra of **IVa**–**IVf** we observed signals from methylene protons and signals at δ 10.47–11.67 ppm from the NH proton involved in strong intramolecular hydrogen bond with the carbonyl group. Compounds **IVa**–**IVf** displayed in the ^{13}C NMR spectra signals from the endocyclic carbonyl carbon atom (δ_C 195.3–196.2) and carbon atom linked to the NH group (δ_C 183.6–184.4 ppm). The exocyclic carbonyl carbon atom in the ^{13}C NMR spectrum of trifluoroacetyl derivative **IVa** resonated as a quartet at δ 176.8 ppm ($^2J_{CF}$ = 39 Hz), and the corresponding signal in the spectra of pentafluoropropionyl and heptafluorobutanoyl derivatives was a triplet at δ_C 179.7 ($^2J_{CF}$ = 30 Hz; **IVb**) or 179.2–180.1 ppm (J_{CF} 29–30 Hz; **IVc**–**IVe**). The singlet at δ_F –76.1 ppm in the ^{19}F NMR spectrum of **IVa** was typical of trifluoroacetyl group. Signals from side-chain fluorine atoms in the spectra of the other enamines were observed at δ_F, ppm: –81.4 s (CF_3), –120.8 s (CF_2) (**IVb**); –80.4 to −80.5 s (CF_3), –117.2 s (CF_2), –125.1 to −125.2 s (CF_2) (**IVc**–**IVf**).

EXPERIMENTAL

The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded at 293 K on a Bruker-Biospin Avance 500 spectrometer operating at 500.13, 125.77, and 470 MHz, respectively, using a 5-mm QNP probe (*z*-gradient) from solutions in $CDCl_3$ (unless otherwise stated); the chemical shifts were determined relative to the residual proton or carbon signal of the solvent (δ 7.26 ppm, δ_C 77.16 ppm) or trifluoromethylbenzene (external reference; δ_F −63 ppm). The melting points were measured on a Boetius melting point apparatus. The elemental compositions were determined on a Eurovector EA3000 CHNS-O analyzer. The progress of reactions was monitored, and the purity of products was checked, by TLC on Silufol UV-254 plates using ethyl acetate–hexane as eluent.

Acylation of cyclopentane-1,3-dione (*general procedures***).** *a*. *With perfluorocarboxylic acids*. A solution of 40 mmol of pentafluoropropionic or heptafluorobutyric acid in 30 ml of anhydrous chloroform was added dropwise at room temperature to a solution of 20 mmol (3.24 g) of 1,1′-carbonyldiimidazole in 50 ml of anhydrous chloroform. A solution of 10 mmol (0.98 g) of cyclopentane-1,3-dione and 10 mmol (0.68 g) of imidazole in 100 ml of anhydrous chloroform was added dropwise to the resulting suspension, and the mixture was stirred for 4 h at room temperature and washed with a dilute (1:10) solution of hydrochloric acid (3×50 ml) and a saturated solution of sodium chloride (50 ml). The organic phase was dried over $MgSO_4$, the aqueous phase was extracted with ethyl acetate (3×50 ml), the extracts were combined with the organic phase, washed with a saturated solution of sodium chloride NaCl (40 ml), and dried over $MgSO_4$, the solvent was removed under reduced pressure, and the residue was dried in a vacuum to obtain compound **IIb** or **IIc** as colorless crystals.

b. *With perfluorocarboxylic anhydrides*. A solution of 20 mmol (1.36 g) of imidazole in 50 ml of anhydrous chloroform was cooled to 0°C, a solution of 10 mmol of trifluoroacetic or pentafluoropropionic anhydride in 30 ml of anhydrous chloroform was added dropwise, and a solution of 5 mmol (0.49 g) of

cyclopentane-1,3-dione and 5 mmol (0.34 g) of imidazole in 70 ml of anhydrous chloroform was added dropwise. The mixture was stirred for 3 h at room temperature and washed with a solution of HCl (1 : 10; 3×50 ml) and a saturated solution of sodium chloride (50 ml). The organic phase was dried over $MgSO_4$, the aqueous phases were extracted with ethyl acetate (3×50 ml), the extracts were combined, washed with a saturated solution of sodium chloride (40 ml), and dried over $MgSO_4$, the solvent was removed under reduced pressure, and the residue was dried in a vacuum. Compounds **IIa** and **IIb** were isolated as colorless crystals.

2-Trifluoroacetylcyclopentane-1,3-dione (IIa). Yield 92% (*b*), mp 83–86°C. IR spectrum, ν, cm^{-1}: 1705, 1655, 1605. ^1H NMR spectrum, δ, ppm: 2.78 s (4H, CH_2). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 32.5, 113.1, 117.7 q ($^1J_{CF}$ = 287 Hz), 179.7 q ($^2J_{CF}$ = 40 Hz), 201.9, 202.0. ^{19}F NMR spectrum: δ_F –77.4 ppm, s (CF_3). Found, %: C 43.30; H 2.58. $C_7H_5F_3O_3$. Calculated, %: C 43.31; H 2.60.

2-Pentafluoropropanoylcyclopentane-1,3-dione (IIb). Yield 91 (*a*), 90% (*b*), mp 117–119°C. IR spectrum, ν, cm^{-1}: 1705, 1640, 1570. ^1H NMR spectrum, δ, ppm: 2.77 s (4H, CH_2), 13.04 br.s (1H, OH). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 32.6, 109.1 t.q ($^1J_{CF}$ = 268, $^2J_{CF}$ = 36 Hz), 114.3, 120.2 q.t ($^1J_{CF}$ = 287, $^2J_{CF}$ = 34 Hz), 182.8 t ($^2J_{CF}$ = 30 Hz), 201.7 br.s. ^{19}F NMR spectrum, δ_F, ppm: –82.4 s (CF_3), –122.5 s (CF_2). Found, %: C 39.33; H 2.06. $C_8H_5F_5O_3$. Calculated, %: C 39.36; H 2.06.

2-Heptafluorobutanoylcyclopentane-1,3-dione (IIc). Yield 90% (*a*), mp 76–78°C. IR spectrum, ν, cm^{-1}: 1705, 1640, 1565. ^1H NMR spectrum, δ, ppm: 2.77 s (4H, CH_2), 13.45 br.s (1H, OH). ^{13}C NMR spectrum (acetone-d_6), δ_F, ppm: 32.6, 110.7 t.t ($^1J_{CF}$ = 268, $^2J_{CF}$ = 32 Hz), 111.3 t.m ($^1J_{CF}$ = 268 Hz), 114.8, 119.6 q.t ($^1J_{CF}$ = 287, $^2J_{CF}$ = 33 Hz), 183.1 t ($^2J_{CF}$ = 27 Hz), 201.5, 201.6. ^{19}F NMR spectrum, δ_F, ppm: –80.6 s (CF_3), –118.9 s (CF_2), –125.7 s (CF_2). Found, %: C 36.78; H 1.74. $C_9H_5F_7O_3$. Calculated, %: C 36.75; H 1.71.

Reduction of 2-perfluoroalkanoylcyclopentane-1,3-diones IIa–IIc (*general procedure*). Triketone **IIa–IIc**, 1 mmol, was dissolved in 2 ml of trifluoroacetic acid, 2 ml of a 1% solution of lithium perchlorate in trifluoroacetic acid and 4 mmol of triethylsilane were added, and the mixture was stirred for 5 h at room temperature. The solvent was removed under reduced pressure, the residue was ground with hexane (4×4 ml) and dissolved in diethyl ether, and the solution was filtered. The solvent was removed under reduced pressure, and the residue (compound **IIIa–IIIc**) was recrystallized from diethyl ether–hexane.

2-(2,2,2-Trifluoro-1-hydroxyethyl)cyclopentane-1,3-dione (IIIa). Yield 82%, mp 113–116°C. IR spectrum, ν, cm^{-1}: 1615, 1555. ^1H NMR spectrum (acetone-d_6), δ, ppm: 2.59 s (4H, CH_2), 4.87 m (1H, C**H**OH). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 32.0, 67.1 q ($^2J_{CF}$ = 34 Hz), 111.1, 126.7 q ($^1J_{CF}$ = 283 Hz), 199.7 br.s. ^{19}F NMR spectrum (acetone-d_6): δ_F –79.62 ppm, d ($^3J_{FH}$ = 6.4 Hz). Found, %: C 42.88; H 3.62. $C_7H_7F_3O_3$. Calculated, %: C 42.87; H 3.60.

2-(2,2,3,3,3-Pentafluoro-1-hydroxypropyl)cyclopentane-1,3-dione (IIIb). Yield 85%, mp 109–112°C. IR spectrum, ν, cm^{-1}: 1615, 1555. ^1H NMR spectrum (acetone-d_6), δ, ppm: 2.61 s (4H, CH_2), 5.03 d.d (1H, C**H**OH, J = 20.6, 6.0 Hz). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 32.1, 66.6 d.d (J_{CF} = 29, 24 Hz), 110.8, 115.8 t.q ($^1J_{CF}$ = 255, $^2J_{CF}$ = 35 Hz), 121.2 q.t ($^1J_{CF}$ = 286, $^2J_{CF}$ = 36 Hz), 199.8 br.s. ^{19}F NMR spectrum (aceton-d_6), δ_F, ppm: –82.7 s (CF_3), –123.1 d.d (1F, $^2J_{FF}$ = 272, $^3J_{FH}$ = 6 Hz), –130.6 d.d (1F, $^2J_{FF}$ = 273, $^3J_{FH}$ = 20 Hz). Found, %: C 39.09; H 2.91. $C_8H_7F_5O_3$. Calculated, %: C 39.04; H 2.87.

2-(2,2,3,3,4,4,4-Heptafluoro-1-hydroxybutyl)cyclopentane-1,3-dione (IIIc). Yield 89%, mp 93–96°C. IR spectrum, ν, cm^{-1}: 1615, 1555. ^1H NMR spectrum (acetone-d_6), δ, ppm: 2.60 s (4H, CH_2), 5.10 d.d (1H, C**H**OH, J = 22.6, 2.7 Hz). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 32.1, 67.1 t ($^2J_{CF}$ = 27 Hz), 110.6, 111.5 t.m ($^1J_{CF}$ = 265 Hz), 117.4 t.m ($^1J_{CF}$ = 256 Hz), 119.9 q.t ($^1J_{CF}$ = 287, $^2J_{CF}$ = 34 Hz), 198.7 br.s. ^{19}F NMR spectrum (acetone-d_6), δ_F, ppm: –82.0 t (3F, CF_3, ^2J = 194 Hz), –120.1 d (1F, ^2J = 279 Hz), –126.0 d (1F, ^2J = 282 Hz), –128.1 d (1F, ^2J = 280 Hz), –128.2 d (1F, ^2J = 282 Hz). Found, %: C 36.48; H 2.36. $C_9H_7F_7O_3$. Calculated, %: C 36.50; H 2.38.

Enamino diketones IVa–IVf (*general procedure*). Oxalyl chloride, 5 ml, was added to 2 mmol of triketone **IIa–IIc**, and the mixture was stirred for 4 h. Excess oxalyl chloride was removed under reduced pressure, the residue was dissolved in 25 ml of chloroform, 4 mmol of the corresponding amine was added, and the mixture was stirred for 1 h, washed with water (8 ml), and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was subjected to chromatography to isolate compound **IVa–IVf** as colorless crystals.

3-(4-Fluorophenylamino)-2-(trifluoroacetyl)cyclopent-2-en-1-one (IVa). Yield 88%, mp 146–149°C. IR spectrum, ν, cm^{-1}: 1705, 1640. ^1H NMR spectrum, δ, ppm: 2.52 m (2H, CH_2), 2.80 m (2H, CH_2), 7.20 m (2H, H_{arom}), 7.30 m (2H, H_{arom}), 11.52 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 25.9, 33.5, 107.4, 116.3 q ($^1J_{CF}$ = 287 Hz), 117.1 d ($^2J_{CF}$ = 23 Hz), 126.9 d ($^3J_{CF}$ = 9 Hz), 131.9 d ($^3J_{CF}$ = 2 Hz), 162.1 d ($^1J_{CF}$ = 250 Hz), 176.8 q ($^2J_{CF}$ = 39 Hz), 183.9, 196.2. ^{19}F NMR spectrum, δ_F, ppm: –76.1 s (3F, CF_3), –111.9 s (1F). Found, %: C 54.40; H 3.19; N 4.84. $C_{13}H_9F_4NO_2$. Calculated, %: C 54.36; H 3.16; N 4.88.

3-(4-Fluorophenylamino)-2-(pentafluoropropanoyl)cyclopent-2-en-1-one (IVb). Yield 90%, mp 130–133°C. IR spectrum, ν, cm^{-1}: 1705, 1640. ^1H NMR spectrum, δ, ppm: 2.51 m (2H, CH_2), 2.80 m (2H, CH_2), 7.20 m (2H, H_{arom}), 7.30 m (2H, H_{arom}), 11.61 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 26.0, 33.5, 107.9 t.q ($^1J_{CF}$ = 268, $^2J_{CF}$ = 36 Hz), 108.6, 117.1 d (^2J = 23 Hz), 118.5 q.t ($^1J_{CF}$ = 287, $^2J_{CF}$ = 34 Hz), 126.9 d ($^3J_{CF}$ = 9 Hz), 131.9 d ($^3J_{CF}$ = 2 Hz), 162.2 d ($^1J_{CF}$ = 250 Hz), 179.7 t ($^2J_{CF}$ = 30 Hz), 184.1, 195.8. ^{19}F NMR spectrum, δ_F, ppm: –81.4 s (3F, CF_3), –112.0 s (1F), –120.8 s (2F, CF_2). Found, %: C 49.90; H 2.71; N 4.12. $C_{14}H_9F_6NO_2$. Calculated, %: C 49.86; H 2.69; N 4.15.

3-(4-Fluorophenylamino)-2-(heptafluorobutanoyl)cyclopent-2-en-1-one (IVc). Yield 80%, mp 97–99°C. IR spectrum, ν, cm^{-1}: 1705, 1640. ^1H NMR spectrum, δ, ppm: 2.51 m (2H, CH_2), 2.79 m (2H, CH_2), 7.19 m (2H, H_{arom}), 7.28 m (2H, H_{arom}), 11.66 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 25.9, 33.4, 109.1, 109.6 t.m ($^1J_{CF}$ = 268 Hz), 109.7 t.t ($^1J_{CF}$ = 268, ^2J = 32 Hz), 117.1 d ($^2J_{CF}$ = 23 Hz), 118.9 q.t ($^1J_{CF}$ = 288 Hz), 126.9 d ($^3J_{CF}$ = 9 Hz), 131.9, 162.2 d ($^1J_{CF}$ = 250 Hz), 179.9 t ($^2J_{CF}$ = 30 Hz), 183.8, 195.5. ^{19}F NMR spectrum, δ_F, ppm: –80.4 s (CF_3), –111.8 s (1F), –117.2 s (CF_2), –125.1 s (CF_2). Found, %: C 46.56; H 2.36; N 3.60. $C_{15}H_9F_8NO_2$. Calculated, %: C 46.53; H 2.34; N 3.62.

3-(3,4-Difluorophenylamino)-2-(heptafluorobutanoyl)cyclopent-2-en-1-one (IVd). Yield 71%, mp 131–133°C. IR spectrum, ν, cm^{-1}: 1705, 1640. ^1H NMR spectrum, δ, ppm: 2.53 m (2H, CH_2), 2.82 m (2H, CH_2), 7.06 m (1H, H_{arom}), 7.18 m (1H, H_{arom}), 7.30 (1H, H_{arom}), 11.67 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 25.9, 33.4, 109.4, 109.6 t.m ($^1J_{CF}$ = 268 Hz), 109.7 t.t ($^1J_{CF}$ = 268, $^2J_{CF}$ = 32 Hz), 114.8 d ($^2J_{CF}$ = 19 Hz), 118.7 d ($^2J_{CF}$ = 19 Hz), 118.9 q.t ($^1J_{CF}$ = 288, $^2J_{CF}$ = 33 Hz), 121.5 m, 132.2 m, 150.1 d.d ($^1J_{CF}$ = 253, $^2J_{CF}$ = 13 Hz), 150.6 d.d ($^1J_{CF}$ = 253, $^2J_{CF}$ = 13 Hz), 180.1 t ($^2J_{CF}$ = 30 Hz), 183.6, 195.3. ^{19}F NMR spectrum, δ_F, ppm: –80.5 s (CF_3), –117.2 s (CF_2), –125.1 s (CF_2), –132.8 s (1F), –135.8 s (1F). Found, %: C 44.39; H 1.95; N 3.40. $C_{15}H_8F_9NO_2$. Calculated, %: C 44.46; H 1.99; N 3.46.

3-(4-Fluorobenzylamino)-2-(heptafluorobutanoyl)cyclopent-2-en-1-one (IVe). Yield 68%, mp 66–69°C. IR spectrum, ν, cm^{-1}: 1705, 1640. ^1H NMR spectrum, δ, ppm: 2.52 m (2H, CH_2), 2.84 m (2H, CH_2), 4.61 d (2H, CH_2, J = 6 Hz), 7.11 m (2H, H_{arom}), 7.28 m (2H, H_{arom}), 10.47 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 25.0, 33.3, 47.8, 108.5, 109.6 t ($^1J_{CF}$ = 268, $^2J_{CF}$ = 32 Hz), 109.7 t.m ($^1J_{CF}$ = 268 Hz), 116.4 d ($^2J_{CF}$ = 21 Hz), 117.9 q.t ($^1J_{CF}$ = 288, $^2J_{CF}$ = 33 Hz), 129.2 d ($^3J_{CF}$ = 8 Hz), 130.4, 162.9 d ($^1J_{CF}$ = 248 Hz), 179.2 t ($^2J_{CF}$ = 29 Hz), 184.1, 195.3. ^{19}F NMR spectrum, δ_F, ppm: –80.5 s (CF_3), –112.8 s (1F), –117.1 s (CF_2), –125.1 s (CF_2). Found, %: C 47.92; H 2.74; N 3.48. $C_{16}H_{11}F_8NO_2$. Calculated, %: C 47.89; H 2.76; N 3.49.

2-(Heptafluorobutanoyl)-3-[(3-trifluoromethyl)-benzylamino]cyclopent-2-en-1-one (IVf). Yield 88%, mp 79–82°C. IR spectrum, ν, cm^{-1}: 1695, 1645. ^1H NMR spectrum, δ, ppm: 2.54 m (2H, CH_2), 2.85 m (2H, CH_2), 4.71 d (2H, CH_2, J = 6 Hz), 7.51 m (1H, H_{arom}), 7.58 m (1H, H_{arom}), 7.66 m (2H, H_{arom}), 10.55 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 25.0, 33.3, 47.9, 108.7, 109.0 t.m ($^1J_{CF}$ = 267 Hz), 109.6 t.t ($^1J_{CF}$ = 267, $^2J_{CF}$ = 31 Hz), 117.8 q.t ($^1J_{CF}$ = 288, $^2J_{CF}$ = 34 Hz), 123.7 q ($^1J_{CF}$ = 272 Hz), 124.3 d ($^3J_{CF}$ = 3 Hz), 125.7 d ($^3J_{CF}$ = 3 Hz), 130.1, 130.6, 131.5 q ($^2J_{CF}$ = 33 Hz), 135.7, 179.3 t ($^2J_{CF}$ = 29 Hz), 184.4, 195.4. ^{19}F NMR spectrum, δ_F, ppm: –63.1 s (CF_3), –80.5 s (CF_3), –117.2 s (CF_2), –125.2 s (CF_2). Found, %: C 45.28; H 2.48; N 3.07. $C_{17}H_{11}F_{10}NO_2$. Calculated, %: C 45.25; H 2.46; N 3.10.

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