

# Reactions of polyfluorinated cyclohexadienones with diazoalkanes.

## Part 1. Formation of cyclopropanes from polyfluorinated cyclohexa-2,4-dienones with diazomethane and phenyldiazomethane

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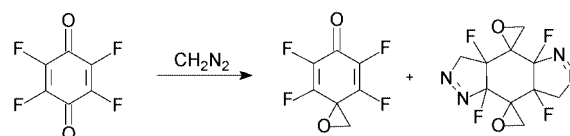
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The reaction of 6-chloro-2,3,4,5,6-pentafluorocyclohexa-2,4-dienone (**1**) with diazomethane gives a mixture of two diastereoisomers of 6-chloro-3a,4,5,6,7a-pentafluoro-3,3a,6,7a-tetrahydrospiro[indazole-7,2'-oxirane] **2a** and **2b**. In contrast phenyldiazomethane reacts with polyfluorinated cyclohexa-2,4-dienones **1**, **9**, and **10** in acetonitrile to form the fluorinated 7-phenylbicyclo[4.1.0]hept-4-en-2-ones **4a,b**, **11a,b**, and **12a,b** as the main products. This reaction shows a remarkable dependence on the polarity of the solvent. While a complex mixture of products was formed in pentane, the reaction in acetonitrile proceeds with high stereoselectivity giving only the two *endo*-isomers.

### Introduction

It is known, that alkyl substituted cyclohexa-2,4-dienones react with diazomethane and alkyl- or phenyldiazomethanes only at the carbon-carbon double bonds.<sup>1</sup> Acetoxyalkylcyclohexadienone cycloadducts, formed in these reactions, can be easily transformed into 7-hydroxyindazoles<sup>1a</sup> or to methyl substituted cyclohexa-2,4-dienones.<sup>1c,2</sup> The influence of the substituent's position on the regioselectivity of cycloaddition has been intensively studied. Usually the cycloaddition occurs on the C<sup>2</sup>=C<sup>3</sup> bond.<sup>1a,c,d</sup> Alkyl groups (except the *tert*-butyl group) in position 2 do not hinder the cycloaddition on the C<sup>2</sup>=C<sup>3</sup> double bond.<sup>1a,c</sup> In contrast an alkyl group in position 3 steers the reaction to the C<sup>4</sup>=C<sup>5</sup> double bond.<sup>1a</sup> If the geminal substituents in position 6 of cyclohexa-2,4-dienones are relatively small (e.g. methyl groups or one hydroxy and one methyl group) bis-adducts can be formed with both double bonds.<sup>1b,d,3</sup> A few more inter- and intramolecular cycloadditions of cyclohexa-2,4-dienones with specific diazo compounds giving polycyclic pyrazoles and cyclopropanes in subsequent steps have been described.<sup>4</sup> To the best of our knowledge cycloaddition reactions of fluorinated cyclohexa-2,4-dienones and diazomethane or its derivatives are not known.

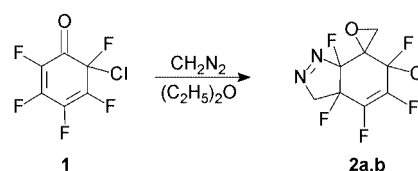
Fluorine-containing, especially polyfluorinated, cyclohexadienones, are of great interest due to their high and diverse reactivity. The nucleophilic substitution of fluorine in polyfluorinated cyclohexadienones and subsequent reduction of the products to form phenols are well known.<sup>5</sup> We also investigated nucleophilic reactions of the carbonyl group of polyfluorinated cyclohexa-2,5-dienones.<sup>6</sup> Recently it has been found that polyfluorinated cyclohexa-2,4-dienones undergo cycloadditions with substituted acetylenes, alkenes and vinyl fluorides to give the [2 + 4] cycloadducts with high regio- and stereoselectivity.<sup>7</sup> Earlier we have shown, that diazomethane reacts with both the carbonyl groups and the double bonds of tetrafluorobenzoquinone giving a spirocyclohexadienone as the main product and a small amount of a pentacycle (Scheme 1).<sup>8</sup> Here we present our results of the reactions of several fluorinated cyclohexa-2,4-dienones with diazomethane or phenyldiazomethane, respectively.



Scheme 1

### Results and discussion

The reaction of 6-chloro-2,3,4,5,6-pentafluorocyclohexa-2,4-dienone (**1**)<sup>9</sup> with diazomethane in ether at 0 °C results in the formation of a 58:42 mixture of two isomers of 6-chloro-3a,4,5,6,7a-pentafluoro-3,3a,6,7a-tetrahydrospiro[indazole-7,2'-oxirane] (**2a,b**) in 52% overall yield (Scheme 2). The struc-



Scheme 2

ture of compounds **2a** and **2b** was attributed on the basis of the analysis of <sup>1</sup>H and <sup>19</sup>F NMR spectra of a mixture of isomers (Table 1). One of the isomers, **2a**, shows three signals in the <sup>19</sup>F NMR spectrum, at -173.4 (F<sup>3a</sup>), -100.6 (F<sup>6</sup>) and -155.1 (F<sup>7a</sup>) ppm with corresponding hyperfine splitting constants of J<sub>F<sup>3a</sup>F<sup>6</sup></sub> = J<sub>F<sup>6</sup>F<sup>3a</sup></sub> = 7 and J<sub>F<sup>6</sup>F<sup>7a</sup></sub> = J<sub>F<sup>7a</sup>F<sup>6</sup></sub> = 12.5 Hz. For the other isomer, **2b**, these constants are <2 Hz. These data allowed us to assume that the isomers **2a** and **2b** differ in spatial orientation of the geminal fluorine and chlorine atoms.

The reaction of 6-chloro-2,3,4,5,6-pentafluorocyclohexa-2,4-dienone (**1**)<sup>9</sup> with phenyldiazomethane in acetonitrile (addition of the solution of diazoalkane to the solution of **1**) also gave a mixture of the isomeric 6-chloro-3a,4,5,6,7a-pentafluoro-3,3'-diphenyl-3,3a,6,7a-tetrahydrospiro[indazole-7,2'-oxirane] (**3a** and **3b**, 67:33) but in low yield (5%). The main products of this reaction are the isomeric 3-chloro-1,3,4,5,6-pentafluoro-7-

Table 1 <sup>1</sup>H and <sup>19</sup>F NMR spectra of 6-chloro-3a,4,5,6,7a-pentafluoro-3,3a,6,7a-tetrahydrospiro[indazole-7,2'-oxirane]s

Chemical shift (δ from CFCl <sub>3</sub> or TMS)	J/Hz									
	J <sub>H3E3a</sub>	J <sub>F3aF4</sub>	J <sub>F3aF5</sub>	J <sub>F3aF6</sub>	J <sub>F3aF7a</sub>	J <sub>F4F5</sub>	J <sub>F4F6</sub>	J <sub>F4F7a</sub>	J <sub>F5F6</sub>	J <sub>F6F7a</sub>
2a, R = H	28.5	28.0	—	7.0	≤5	6.0	7.0	≤2	24.0	12.5
2b, R = H	18.5	28.0	—	—	≤5	6.0	10.0	≤2	21.5	—
3a, R = Ph <sup>a</sup>	18.5	27.9	1.8	6.7	7.3	7.3	7.6	2.4	25.0	10.7
3b, R = Ph <sup>a</sup>	22.5	27.4	≈3	3.1	4.9	7.3	10.4	2.4	23.2	1.8

Chemical shift (δ from CFCl <sub>3</sub> or TMS)	H <sup>3'</sup>		
	F <sup>7a</sup>	F <sup>3a</sup>	F <sup>6</sup>
2a, R = H	-155.8	-173.4	-142.3
2b, R = H	-152.3	-172.8	-144.5
3a, R = Ph <sup>a</sup>	-152.3	-142.7	-142.8
3b, R = Ph <sup>a</sup>	-149.3	-143.3	-144.7

Chemical shift (δ from CFCl <sub>3</sub> or TMS)	H <sup>3</sup>		
	F <sup>5</sup>	F <sup>6</sup>	F <sup>3</sup>
2a, R = H	-140.4	-100.6	4.41; 5.31 ( <i>J</i> <sub>HH</sub> = 18.0 Hz)
2b, R = H	-149.8	-134.4	4.44; 5.33 ( <i>J</i> <sub>HH</sub> = 18.0 Hz)
3a, R = Ph <sup>a</sup>	-141.4	-96.8	4.91
3b, R = Ph <sup>a</sup>	-150.5	-132.1	4.69

<sup>a</sup> The <sup>1</sup>H NMR spectrum of the mixture of **3a,b** also contains signals of C<sub>6</sub>H<sub>5</sub> groups in the region of δ = 7.08–7.38 ppm.

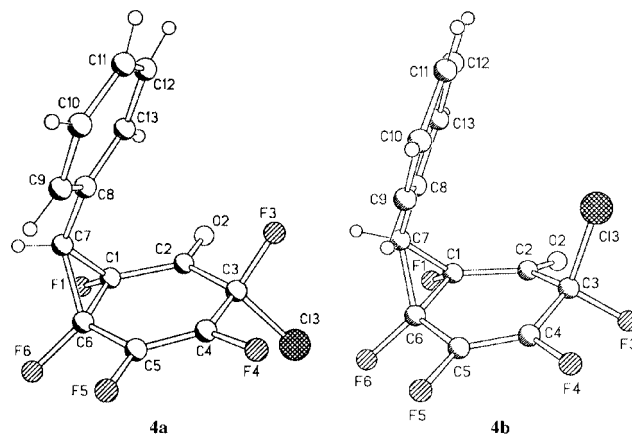
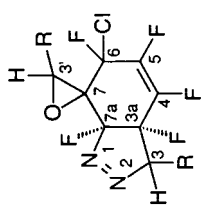
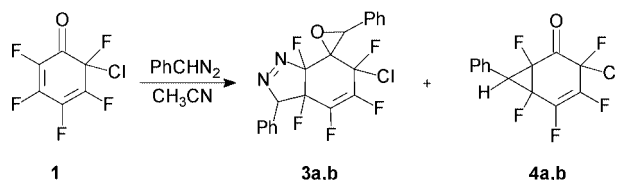


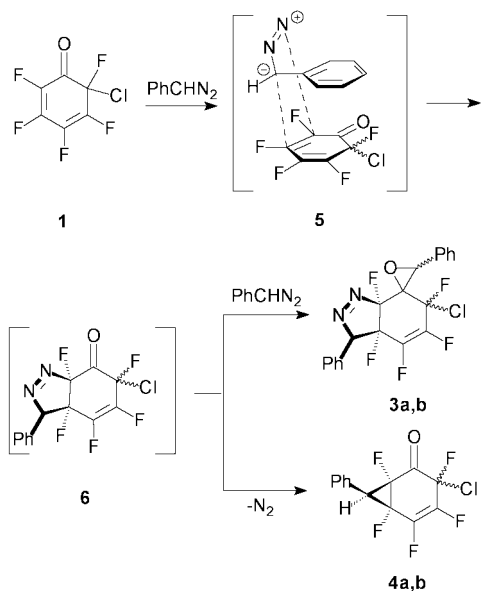
Fig. 1 X-Ray crystal structure of the diastereomeric 3-chloro-1,3,4,5,6-pentafluoro-7-phenylbicyclo[4.1.0]hept-4-en-2-ones (**4a** and **4b**).



Scheme 3

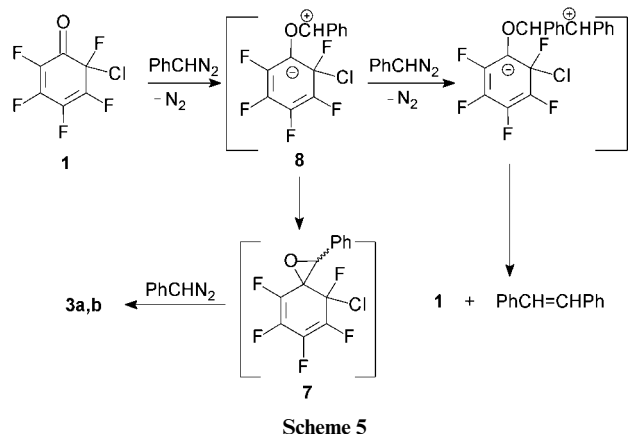
phenylbicyclo[4.1.0]hept-4-en-2-ones (**4a** and **4b**, 62:38) (Scheme 3). These compounds can be viewed as masked  $\sigma$ -homobenzo-1,2-quinones<sup>10</sup> and could give access to fluorinated tropolones. The <sup>1</sup>H and <sup>19</sup>F NMR spectra of the isomeric compounds **3a** and **3b** (Table 1) are similar to those for compounds **2a** and **2b**, however the signals of fluorine atoms<sup>3a</sup> next to the phenyl group in the pyrazoline ring of compounds **3a** and **3b** exhibit a down field shift of about 10 ppm.

The bicycloheptenones **4a** and **4b** were isolated in pure form and their structure was determined by X-ray structural analysis (Fig. 1). The X-ray structures show that the cycloaddition of 6-chloro-2,3,4,5,6-pentafluorocyclohexa-2,4-dienone (**1**) with phenyldiazomethane proceeds with high selectivity; both isomers **4a** and **4b** have the *endo*-configuration. It is possible to consider two routes for the formation of these compounds. One possible way might be the reaction of phenylcarbene with a double bond of cyclohexadienone **1**. However, it is known, for example, that the reaction of cyclohexene with phenylcarbene proceeds without stereoselectivity.<sup>11</sup> That is why a second route, the 1,3-dipolar cycloaddition of phenyldiazomethane to 6-chloro-2,3,4,5,6-pentafluorocyclohexa-2,4-dienone (**1**), is more probable in our opinion. The selectivity of this reaction may be a result of the transition state **5** in which the aromatic ring of phenyldiazomethane is coordinated to the cyclohexadienone ring of 6-chloro-2,3,4,5,6-pentafluorocyclohexa-2,4-dienone (**1**) as a charge transfer complex (Scheme 4). The cycloadduct **6** formed, evidently from **5**, quite possibly reacts with a second molecule of phenyldiazomethane to give products **3a** and **3b** or eliminates nitrogen to form the cyclopropane derivatives **4a** and **4b**. As for the formation of **4a** and **4b** it is known that pyrazoline-type products are quite stable and usually require heating for transformation to cyclopropanes.<sup>12</sup> However, in the diazoalkane reactions with alkenes containing electron-withdrawing substituents, the cyclopropane derivatives have been obtained without heating and the formation of pyrazolines as intermediates was only supposed.<sup>13</sup> In certain cases, particularly in polar solvents, the pyrazolines are easily transformed to cyclopropanes with retention of configuration<sup>14</sup> which is in agreement with the formation of **4a** and **4b** in our case.



Scheme 4

If **3a** and **3b** are formed according to this mechanism, an excess of phenyldiazomethane or mixing of the reactants in reverse order (addition of **1** to a solution of the diazo compound) should change the ratio of **3**:**4**. This was not the case. Therefore we explain the formation of **3a** and **3b** as a result of the following sequence. At first phenyldiazomethane attacks the carbonyl group of dienone **1** giving the zwitterion **8** which cyclizes to the oxirane **7**. The reaction of **7** with a second molecule of the diazo compound leads to **3a** and **3b** (Scheme 5).

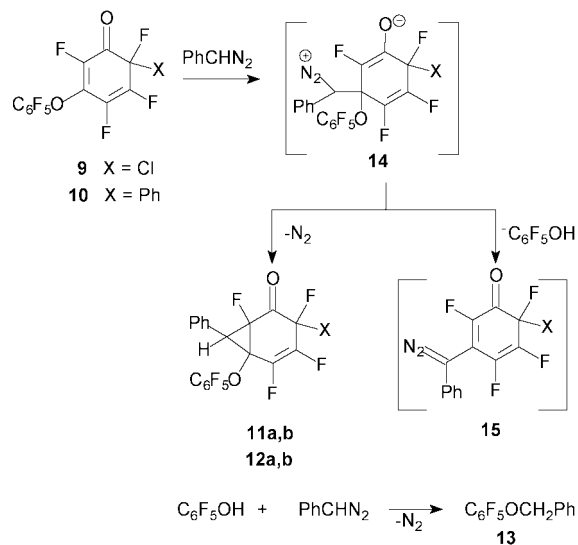


Scheme 5

This mechanism agrees with the observed influence of solvent polarity on the course of reaction of 6-chloro-2,3,4,5,6-pentafluorocyclohexa-2,4-dienone (**1**) with phenyldiazomethane. The reaction in pentane results in the expected change of the ratio of **3** and **4**. According to the  $^{19}\text{F}$  NMR spectra of the reaction mixtures, the ratio of **3a,b** and **4a,b** is approximately 1:3 in acetonitrile and 1:1 in pentane, while the ratio of **a**:**b** did not change. Moreover, the reaction in pentane gives a complex mixture of more than ten compounds. The main pathway of reaction is the catalytic decomposition of phenyldiazomethane to form almost equal amounts of (*Z*)- and (*E*)-stilbene. This is similar to the well known decomposition of phenyldiazomethane induced by oxidizing agents such as tetrahalobenzoquinones.<sup>15</sup> Note that a more than three-fold excess of the diazo compound was necessary to complete the conversion of **1** in pentane, while the reaction in acetonitrile needed only one equivalent.

Moreover, reactions of 6-chloro-3-(pentafluorophenoxy)-tetrafluorocyclohexa-2,4-dienone (**9**) and 3-(pentafluoro-

phenoxy)tetrafluoro-6-phenylcyclohexa-2,4-dienone (**10**) with phenyldiazomethane in acetonitrile gave mixtures of isomeric cyclopropane derivatives **11a** and **11b** (67:33) or **12a** and **12b** (83:17), respectively, as main products and pentafluorophenyl benzyl ether (**13**). Furthermore, (*Z*)- and (*E*)-stilbenes are produced as competitive products. In these reactions no bicyclic tetrahydroindazoles have been detected. We suggest the following mechanism of formation of compounds **11a,11b** or **12a,12b**, respectively, and **13** (Scheme 6).



Scheme 6

The zwitterion **14** formed from **9** or **10** at the first stage perhaps *via* a transition state like **5** can be transformed by two routes: (i) the elimination of nitrogen followed by cyclization forming the cyclopropane derivatives **11a** and **11b** or **12a** and **12b**, respectively, or (ii) elimination of pentafluorophenol and formation of dienone **15** which is apparently unstable and decomposed during isolation. Pentafluorophenol reacts further with phenyldiazomethane to give pentafluorophenyl benzyl ether (**13**) as a by-product. The probability of the last reaction was checked by an independent experiment. The following literature data also support the proposed mechanism. It is well known that diazoketones can be synthesized by reaction of acyl halides with diazomethane.<sup>16</sup> It is also known that polyfluorinated cyclohexadienones, which are the vinylogues of acyl fluorides, have a very nucleophilic mobile fluorine atom at position 3<sup>5</sup> and its orientation in the reaction of diazomethane with polyfluorinated alkenes is the same as in nucleophilic reactions.<sup>17</sup> Furthermore, it is known that the pentafluorophenoxy group at position 3 of polyfluorinated cyclohexadienones can be easily substituted by different nucleophilic reagents.<sup>18</sup>

## Conclusion

Thus, we have found that polyfluorinated cyclohexa-2,4-dienones, in contrast to non-fluorinated cyclohexadienones, react with diazoalkanes not only at C=C double bonds but also at the carbonyl group. Treatment of 6-chloro-2,3,4,5,6-pentafluorocyclohexa-2,4-dienone (**1**) with diazomethane gave mainly a mixture of two diastereomeric tetrahydrospiro[indazole-7,2'-oxirane]s **2a** and **2b**. The reactions of phenyldiazomethane with polyfluorinated cyclohexa-2,4-dienones depended on the polarity of the solvent and gave two diastereomeric fluorinated 7-phenylbicyclo[4.1.0]hept-4-en-2-ones **4a,b**, **11a,b**, or **12a,b** with *endo*-orientation of the phenyl group as the main products in acetonitrile, while in pentane the diazo compounds interact mainly with the carbonyl group which led to complex product mixtures and partial decomposition of the diazo compound.

## Experimental

### General

Thin layer chromatography was performed with TLC plates 60 F<sub>254</sub> by Merck. Column chromatography was performed using silica gel (Merck, particle size 22–63 μm). Gas chromatographic analysis was done using a Hewlett Packard 5890 II apparatus, temperature programme 40 to 280 °C, heating rate 10 °C min<sup>-1</sup>. Mass spectra were measured on a Finnigan MAT-8200 instrument operating at 70 eV. NMR spectra were recorded on a Bruker WP-200SY (200.00 MHz for <sup>1</sup>H and 188.28 MHz for <sup>19</sup>F) or Bruker WN-300 (300.13 MHz for <sup>1</sup>H and 282.40 MHz for <sup>19</sup>F) with TMS or CFCl<sub>3</sub> as internal standards, respectively, in CDCl<sub>3</sub> or CCl<sub>4</sub> solution. 6-Chloropentafluorocyclohexa-2,4-dienone (**1**) was prepared according to ref. 9. All other starting materials and reagents were obtained from Fluka or Acros. Solvents were dried by storage over molecular sieves 0.4 nm.

### 6-Chloro-3a,4,5,6,7a-pentafluoro-3,3a,6,7a-tetrahydrospiro[indazole-7,2'-oxirane] (**2a,b**)

A solution of CH<sub>2</sub>N<sub>2</sub> obtained from *N*-nitroso-*N*-methylurea (0.5 g, 5 mmol) in diethyl ether (10 cm<sup>3</sup>) was added at 0 °C to a solution of cyclohexadienone **1** (0.53 g, 2.4 mmol) in diethyl ether (10 cm<sup>3</sup>). After 2 hours the solvent was evaporated and the residue was purified by column chromatography on silica gel using CCl<sub>4</sub> as eluent to give a mixture of compounds **2a,b** (0.35 g, 52%, 58:42). <sup>1</sup>H and <sup>19</sup>F NMR spectra of compounds **2a,b** are given in Table 1. In the mass spectra of both isomers **2a** and **2b** the molecular ion was found at *m/z* = 274.

### General procedure for reactions of fluorinated cyclohexadienones with phenyldiazomethane

**In acetonitrile.** To a solution of phenyldiazomethane in pentane (250 cm<sup>3</sup>) prepared from benzaldehyde tosylhydrazone (*cf.* Table 3) according to the protocol given in ref. 19, acetonitrile (10–20 cm<sup>3</sup>) was added, the pentane was removed under reduced pressure and the remaining solution was added at an appropriate temperature to the solution of the cyclohexadienone in acetonitrile (10 cm<sup>3</sup>) and stirred for 2–24 h. After evaporation of the solvent, the residue was purified by column chromatography on silica gel using cyclohexane–dichloromethane (gradient, 20:1 to 1:2) as eluent to afford the corresponding cycloadducts. The <sup>1</sup>H and <sup>19</sup>F NMR data for all products are listed in Tables 1 and 2. More details on the reaction conditions and analytical data for all products are given in Table 3.

**In pentane.** A solution of cyclohexadienone **1** (0.6 g, 2.7 mmol) in pentane (5 cm<sup>3</sup>) was added at 0 °C to a pentane solution (20 cm<sup>3</sup>) of phenyldiazomethane, obtained from benzaldehyde tosylhydrazone<sup>19</sup> (3.2 g, 1.2 mmol), and stirred for 20 h. Evaporation of pentane gave a mixture of more than 10 compounds (1.8 g) in an approximately equimolar ratio (GC, <sup>1</sup>H and <sup>19</sup>F NMR). In the reaction mixture the following compounds have been identified: (*E*)- and (*Z*)-stilbene, benzyl pentafluorophenyl ether (**13**), compounds **3a,b** and **4a,b** (**3**:**4** ≈ 1:1). This mixture was partially separated by column chromatography on silica gel using cyclohexane as eluent to give a mixture (0.32 g) of (*Z*)- (28%), (*E*)-stilbenes (30%), **13** (4%) and unidentified products, a mixture (0.12 g) containing ≈60% of compounds **4a** and ≈10% of **13**, a mixture (0.08 g) containing ≈9% of compound **4a**, ≈46% of compound **4b** and traces of compounds **3a,b**.

### Benzyl pentafluorophenyl ether

Pentafluorophenol (0.92 g, 5 mmol) was added with stirring to a solution of phenyldiazomethane obtained from benzaldehyde tosylhydrazone (2.0 g, 7 mmol) in acetonitrile (10 cm<sup>3</sup>). The

Table 2 <sup>1</sup>H and <sup>19</sup>F NMR spectra of polyfluorinated 7-phenylbicyclo[4.1.0]hept-4-en-2-ones

	Chemical shift (δ from CFCl <sub>3</sub> or TMS)										J/Hz				
	F <sup>1</sup>	F <sup>3</sup>	F <sup>4</sup>	F <sup>5</sup>	F <sup>6</sup>	H <sup>7a</sup>	J <sub>HFF1</sub>	J <sub>F1F3</sub>	J <sub>F1F5</sub>	J <sub>F1F6</sub>	J <sub>F3F4</sub>	J <sub>F3F5</sub>	J <sub>F4F5</sub>	J <sub>F5F6</sub>	J <sub>F6H7</sub>
<b>4a</b> X = Cl, Y = F	-198.0	-124.6	-151.9	-140.1	-208.6	4.09	26.5	3.5	2.6	7.0	20.9	10.5	9.2	21.3	18.6
<b>4b</b> X = Cl, Y = F	-198.8	-110.4	-149.0	-137.5	-204.9	4.16	25.8	—	2.2	6.1	27.0	6.5	10.0	21.8	19.3
<b>11a</b> X = Cl, Y = OC <sub>6</sub> F <sub>5</sub>	-194.7	-121.9	-150.6	-138.4	<sup>b</sup>	4.06	26.5	3.5	≈2	<sup>b</sup>	22.0	10.5	9.0	<sup>b</sup>	<sup>b</sup>
<b>11b</b> X = Cl, Y = OC <sub>6</sub> F <sub>5</sub>	-195.1	-110.2	-146.6	-135.9	<sup>c</sup>	4.07	25.5	—	≈2	<sup>c</sup>	27.5	6.0	9.7	<sup>c</sup>	<sup>c</sup>
<b>12a</b> X = Ph, Y = OC <sub>6</sub> F <sub>5</sub>	-192.2	-153.8	-145.8	-137.8	<sup>d</sup>	4.09	26.7	3.8	—	<sup>d</sup>	24.8	3.8	10.9	<sup>d</sup>	<sup>d</sup>
<b>12b</b> X = Ph, Y = OC <sub>6</sub> F <sub>5</sub>	-197.0	-130.8	-139.8	-135.3	<sup>e</sup>	4.04	24.8	—	—	<sup>e</sup>	30.5	3.8	11.4	<sup>e</sup>	<sup>e</sup>

<sup>a</sup> The <sup>1</sup>H NMR spectra of compounds **4a,b**, **11a,b** and **12a** also have signals due to C<sub>6</sub>H<sub>5</sub> groups in the region of δ = 7.08–7.38 ppm, compound **12b** has signals due to C<sub>6</sub>H<sub>5</sub> groups in the region of δ = 6.4–7.5 ppm.  
<sup>b</sup> OC<sub>6</sub>F<sub>5</sub>: δ = -162.2 (2F<sub>meta</sub>), -159.9 (1F<sub>para</sub>), -155.7 (2F<sub>ortho</sub>); J<sub>F1Fortho</sub> = 11.5 Hz, J<sub>F5Fortho</sub> = 5.0 Hz, J<sub>F5Fortho</sub> = 5.0 Hz, J<sub>F1Fortho</sub> = 161.8 (2F<sub>meta</sub>), -160.4 (1F<sub>para</sub>), -156.8 (2F<sub>ortho</sub>); J<sub>F1Fortho</sub> = 9.7 Hz, J<sub>F5Fortho</sub> = 4.5 Hz, J<sub>F5Fortho</sub> = 4.5 Hz, J<sub>F1Fortho</sub> = 161.8 (2F<sub>meta</sub>), -158.9 (1F<sub>para</sub>), -154.0 (2F<sub>ortho</sub>); J<sub>F1Fortho</sub> = 13.3 Hz, J<sub>F5Fortho</sub> = 9.5 Hz, J<sub>F5Fortho</sub> = 9.5 Hz, J<sub>F1Fortho</sub> = 161.6 (2F<sub>meta</sub>), -160.0 (1F<sub>para</sub>), -155.0 (2F<sub>ortho</sub>); J<sub>F1Fortho</sub> = 11.4 Hz, J<sub>F5Fortho</sub> = 5.8 Hz, J<sub>F5Fortho</sub> = 5.8 Hz.

**Table 3** Analytical data for products of the reaction of polyfluorinated cyclohexadienones with phenyldiazomethane

Entry	Cyclohexadienone/ (solvent) g (mmol)	TsNHN=CHPh/ g (mmol)	<i>T</i> /°C	Time/h	Products, yield g (%)	Mp/°C (solvent)	Analytical data found (calculated)																
							C (%)	H (%)	<i>M</i>														
1	<b>1</b> (Acetonitrile) 1.7 (8)	3.2 (12)	−20→rt	2.5	<b>3a,b</b> 0.15 (5)	Viscous oil			426.05490 (426.05582)														
										<b>4a</b> 0.91 (38)	79–81 (Pentane)		308.00022 (308.00273)										
														<b>4b</b> 0.42 (18)	92–94 (Pentane)		308.00205 (308.00273)						
																		<b>13 + stilbenes</b> 0.27 <sup>a</sup>					
																						<b>11a</b> 0.57	81–84 (Pentane)
<b>11b</b> 0.25	115–117 (Pentane)	48.39 (48.25)	1.40 (1.27)	471.99262 (471.99127)																			
2	<b>9</b> (Acetonitrile) 1.35 (4)	2.0 (7)	0→rt	4.5	<b>13 + stilbenes</b> 0.27 <sup>a</sup>				471.99302 (471.99127)														
										<b>11a</b> 0.57	81–84 (Pentane)	48.26 (48.25)	1.35 (1.27)	471.99302 (471.99127)									
															<b>11b</b> 0.25	115–117 (Pentane)	48.39 (48.25)	1.40 (1.27)	471.99262 (471.99127)				
																				<b>13 + stilbenes</b> 0.47 <sup>b</sup>			
<b>12b</b> 0.05	Viscous oil			514.06209 (514.06152)																			
3	<b>10</b> (Acetonitrile) 0.8 (1.9)	3.7 (13.5)	rt	24	<b>13 + stilbenes</b> 0.47 <sup>b</sup>				514.06261 (514.06152)														
										<b>12a</b> 0.27	90–93 (CH <sub>3</sub> OH + H <sub>2</sub> O)	58.46 (58.37)	2.40 (2.14)	514.06261 (514.06152)									
															<b>12b</b> 0.05	Viscous oil			514.06209 (514.06152)				
																				<b>13 + stilbenes</b> 0.47 <sup>b</sup>			
<b>12b</b> 0.05	Viscous oil			514.06209 (514.06152)																			

<sup>a</sup> The mixture contains 48% benzyl pentafluorophenyl ether (**13**), 14% (*E*)-stilbene and 38% (*Z*)-stilbene (<sup>1</sup>H NMR). <sup>b</sup> The mixture contains 14% benzyl pentafluorophenyl ether (**13**), 33% (*E*)-stilbene and 53% (*Z*)-stilbene (<sup>1</sup>H NMR).

reaction mixture was stirred for 1 h and evaporated. The residue was purified by column chromatography on silica gel using pentane as eluent to give a mixture (0.71 g) containing 69% of benzyl pentafluorophenyl ether (**13**), 13% of (*E*)-stilbene and 18% of (*Z*)-stilbene (<sup>1</sup>H NMR). Benzyl pentafluorophenyl ether (**13**) was identified by comparison of its spectral data with those published in ref. 20.

#### X-Ray crystal data

**3-Chloro-1,3,4,5,6-pentafluoro-7-phenylbicyclo[4.1.0]hept-4-en-2-one (4a).** Formula C<sub>13</sub>H<sub>6</sub>ClF<sub>5</sub>O, *M<sub>r</sub>* = 308.63; monoclinic *P*2<sub>1</sub>/*c*; *a* = 8.889(2), *b* = 10.377(2), *c* = 13.610(3) Å; *a* = 90, *β* = 95.57(3), *γ* = 90°, *V* = 1249.5(5) Å<sup>3</sup>, *Z* = 4. Data were measured in a 2θ range from 5.00 to 70.37°. A total of 2312 reflections were collected. Among them, 2056 were considered to be observed (*I* > 2.0σ(*I*)). Final agreement indices are *R*(*F*) = 0.0609, *wR*(*F*<sup>2</sup>) = 0.1413, *GoF* = 1.015, based on anisotropic refinement of all non-hydrogen atoms. H atom positional parameters were calculated and refined as riding on their parent atom.

**3-Chloro-1,3,4,5,6-pentafluoro-7-phenylbicyclo[4.1.0]hept-4-en-2-one (4b).** Formula C<sub>13</sub>H<sub>6</sub>ClF<sub>5</sub>O, *M<sub>r</sub>* = 308.63; monoclinic *P*2<sub>1</sub>/*c*; *a* = 11.205(1), *b* = 13.755(1), *c* = 7.725(1) Å; *a* = 90.0, *β* = 91.28(1), *γ* = 90.0°, *V* = 1190.3(2) Å<sup>3</sup>, *Z* = 4. Data were measured in the 2θ range from 2.96 to 30.48°. A total of 9988 reflections were collected. Among them, 3517 were considered to be independent and 2683 were observed (*I* > 2.0σ(*I*)). Final agreement indices are *R*(*F*) = 0.041, *wR*(*F*<sup>2</sup>) = 0.094, *GoF* = 1.037, based on anisotropic refinement of all non-hydrogen atoms. H atom positional parameters were calculated and refined as riding on their parent atom.

CCDC reference number 207/426. See <http://www.rsc.org/suppdata/p1/b0/b001618g/> for crystallographic files in .cif format.

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