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Sodium dithionite initiated addition of CF_2Br_2 to β-pinene and reactions of the adduct Synthesis and the reactivity of new 1,1-difluorodienes

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Abstract

Sodium dithionite effectively promotes the addition of dibromodifluoromethane to the exocyclic double bond of β-pinene. The reaction proceeded in a MeCN/H_2O system to give almost quantitatively an adduct, 1-(2-bromo-2,2-difluoroethyl)-4-(2-bromoisopropyl)-cyclohexene, as the sole product. On treatment of the adduct with 2,2,6,6-tetramethylpiperidine elimination of HBr only from the $(CH_3)_2CHBr$ group occurred to give a mixture of regioisomeric dienes, while treatment with 50% KOH under phase transfer catalysis conditions or with K_2CO_3 in DMF resulted in total dehydrobromination to give trienes possessing an exocyclic CH=CF_2 group. Surprisingly, the main course of the reactions of the adduct with DBU (1,8-diazabicyclo[5.4.0]undece-7-ene) and also with *t*-BuOK in THF was elimination of HBr only from the CH_2CF_2Br group to afford 1-(2,2-difluorovinyl)-4-(2-bromoisopropyl)cyclohexene as the main product. Catalytic hydrogenation of the adduct followed by treatment with DBU afforded a conjugated diene, 1-(2,2-difluorovinyl)-4-isopropylcyclohexene. Compounds bearing the CH=CF_2 group are new 1,1-difluorodienes which readily reacted with 4-phenyl-3*H*-1,2,4-triazoline-3,5-dione to give cycloadducts, derivatives of triazolo[1,2-α]cinnoline.

Keywords: Dibromodifluoromethane; Sodium dithionite; Pinene; Radical addition; Difluoromethyl terpenoids; 1,1-Difluorodienes; Cycloaddition

1. Introduction

The reaction of perfluoroalkyl halides (R_FI, R_FBr) with sodium dithionite in aqueous medium, known as ''sulfinatodehalogenation'', provides an easy way of generating perfluoroalkyl radicals [1,2]. The addition of perfluoroalkyl iodides, $Cl(CF_2)_4I$ and $Cl(CF_2)_6I$, to α-pinene under such conditions was reported to proceed with ring opening to give unstable (not isolated) adducts, 4-(2-iodoisopropyl)-1-methyl-6-perfluoroalkylcyclohexenes, which after *in situ* hydrodeiodination afforded 4-(isopropyl)-1-methyl-6-perfluoroalkylcyclohexenes in reasonable yields [3,4]. A stable adduct was obtained in a similar reaction of β-pinene with 1,1,1-tribromo-2,2,2-trifluoroethane [5] and more recently, in our laboratory, with 1-bromo-1-chloro-2,2,2-trifluoroethane [6]. The latter compound was transformed, with 50% overall yield, to a conjugated diene, 4-isopropyl-1-(*trans*-3,3,3-trifluoropropenyl)-cyclohexene, which has shown no activity in the Diels–Alder type cycloadditions.

In the present paper we report the sodium dithionite initiated addition of dibromodifluoromethane to (1*S*,5*S*)-(−)-β-pinene and transformations of the adduct **1** to various terpenoids substituted with the –CH_2CF_2Br and –CH=CF_2 moieties. The main goal of this work was, however, the synthesis of new conjugated 1,1-difluorodienes **4–6** and **10** and investigation of their behaviour in the Diels–Alder cycloaddition reactions. The only 1,1-difluorodienes synthesized so far were 1-alkoxy-4,4-difluoro-2-(trimethylsiloxy)-buta-1,3-dienes [7], 1,1-difluoro-4-phenyl-1,3-butadiene [8–13] and its analogues substituted in the aromatic ring [14]. The latter compounds, albeit in unsatisfactory yields, were obtained in our laboratory by addition of CF_2Br_2 to allylbenzenes and dehydrohalogenation of the adducts [14]. All 1,1-difluorodienes were found to be unstable and reactive towards strong dienophiles like benzylidene-phenylamine [7] and 4-phenyl-3*H*-1,2,4-triazoline-3,5-dione [13,14].

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2. Results and discussion

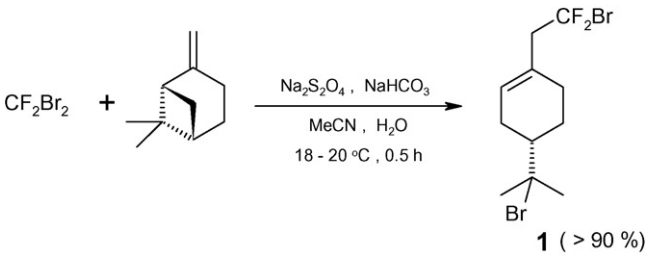
Addition of CF_2Br_2 to β-pinene was carried out under typical sulfinatodehalogenation conditions ($Na_2S_2O_4$/$NaHCO_3$/MeCN/H_2O) by following, in general, the procedure described earlier for the reaction of β-pinene with $CF_3CHClBr$ [6]. Because of the volatility of CF_2Br_2 (bp ca. 22 °C), it was added to the mixture of other reagents and solvents which was pre-cooled to 15 °C and the reaction was controlled to maintain the temperature within the range of 18–20 °C. The reaction was completed within 30 min to give the adduct, 1-(2-bromo-2,2-difluoroethyl)-4-(2-bromoisopropyl)cyclohexene (**1**) (Scheme 1), initially as yellow oil which after 1 h in a refrigerator crystallized to form large colourless crystals. Elemental analysis of this crude product gave almost theoretical values for all the elements indicating its high purity. ^{1}H NMR and ^{19}F NMR spectra have shown no impurities. In numerous experiments yields of adduct **1** repeatedly exceeded 90%.

Similarly to the reaction of β-pinene with $CF_3CHClBr$, as little as 0.2 equiv. of $Na_2S_2O_4$ was satisfactory for the reaction with CF_2Br_2 to proceed with high rates and to give almost quantitative yields. This suggests an effective free radical chain mechanism as depicted previously [6].

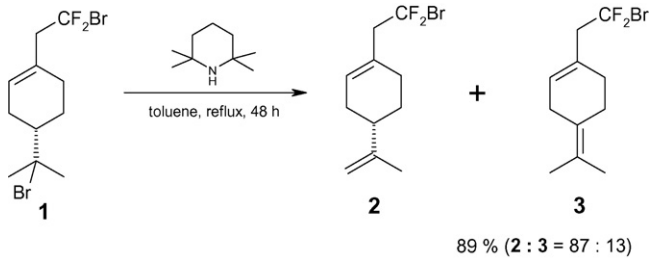
The structure of compound **1** was unequivocally assigned by spectral data. High magnetic non-equivalence of fluorine atoms ($^2J_{FF}$ = 155 Hz), appearance of two signals for the CH_3 groups and AB systems for all the CH_2 groups reflects the asymmetric structure of this molecule. High optical activity of adduct **1** and the same sign of its optical rotation coefficient as of the starting β-pinene gave evidence for the retention of absolute configuration *S* at the carbon atom C-4.

Compound **1** is stable enough to be stored in an refrigerator (4–6 °C) for long time but slowly decomposes at ambient temperature with evolution of HBr and formation of brown tar. Attempted distillation resulted in rapid decomposition. A reason for the thermal instability of **1** is, most probably, the presence of a bromine atom in the highly crowded isopropyl group. Therefore, with the aim to obtain a more stable compound, we carried out a number of attempts to remove this bromine, either by controlled elimination of HBr or by reductive debromination.

In spite of the thermal instability of **1**, this compound was found to be reasonably stable against weak bases; no dehydrobromination occurred by prolonged refluxing in triethylamine/Et_2O and only partial dehydrobromination took place with pyridine in boiling toluene. However, treatment of **1** with 2,2,6,6-tetramethylpiperidine resulted in total elimination of HBr from the 2-bromoisopropyl group to give a mixture of regioisomeric dienes, 1-(2-bromo-2,2-difluoroethyl)-4-isopropenylcyclohexene (**2**) and 1-(2-bromo-2,2-difluoroethyl)-4-isopropenylidenecyclohexene (**3**), in a 87:13 ratio and in a 89% total yield (Scheme 2). No elimination of HBr from the CH_2CF_2Br group was observed.



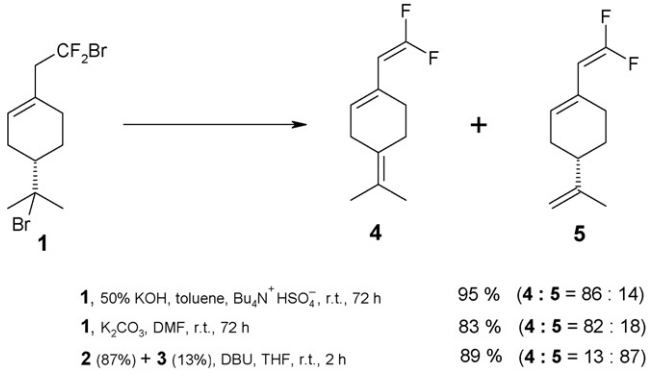
Scheme 1.



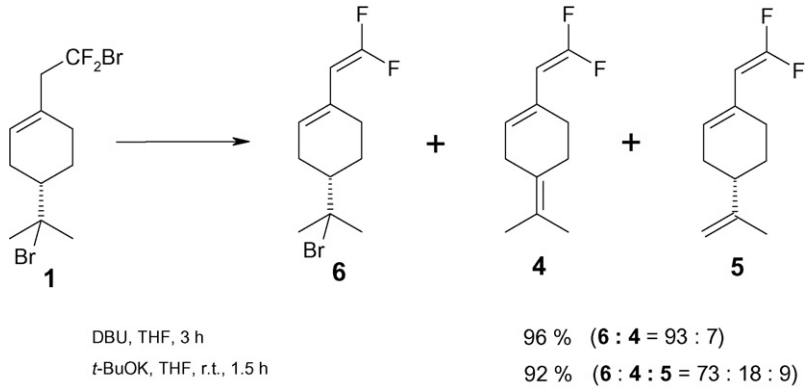
Scheme 2.

Compounds **2** and **3** are stable at ambient temperature but their attempted separation by distillation resulted in total decomposition and therefore they were identified in their mixtures. These mixtures gave correct elemental analyses, identical mass spectra for both components, structures of which were unambiguously differentiated by the ^{1}H NMR spectra. The spectrum of **2** exhibited only one signal of the CH_3 group and two signals of vinylic protons of the isopropenyl group while two CH_3 group signals appeared in the spectrum of **3**. Additionally, the lack of asymmetry at carbon atom C-4 in compound **3** resulted in simplification of both ^{1}H NMR and ^{19}F NMR spectra of the CH_2CF_2Br group; only one signal appeared for the CH_2 group protons and the CF_2Br group fluorine atoms. As compound **2** was the main component, the mixture of **2** and **3**, similarly to **1**, exhibited high optical activity.

Treatment of compound **1** with 50% KOH under phase transfer catalysis conditions or with K_2CO_3 in DMF at ambient temperature resulted in elimination of both HBr molecules to give a mixture of trienes, 1-(2,2-difluorovinyl)-4-isopropylidenecyclohexene (**4**) and 1-(2,2-difluorovinyl)-4-isopropenylcyclohexene (**5**), respectively, in a 95% and 83% total yields. The same compounds were obtained from the reaction of the mixture of **2** and **3** with DBU (1,8-diazabicyclo[5.4.0]undece-7-ene) in THF but in opposite proportion, similar to the **2**:**3** ratio (Scheme 3).



Scheme 3.



Scheme 4.

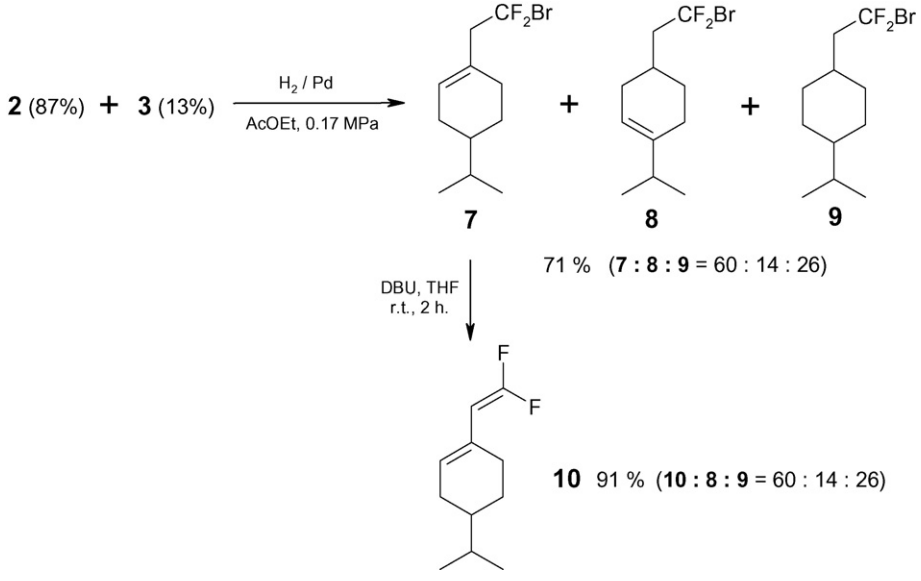
Surprisingly, the main course of the reactions of **1** with DBU and also with *t*-BuOK in THF, even when an excess of the base was used, was elimination of HBr from the CH_2CF_2Br group to afford 1-(2,2-difluorovinyl)-4-(2-bromoisopropyl)cyclohexene (**6**) as the main product; compounds **4** and **5** formed by the elimination of two HBr molecules were only minor components of the reaction mixtures (Scheme 4).

Compounds **4**–**6** possessing structures of 1,1-difluorodienes were not isolated because they are very unstable and may be stored only in solutions for a rather short time; on removal of a solvent they polymerise to form brown tar. Nevertheless, structures of these compounds were unambiguously determined from the NMR spectra. The existence of the $CH{=}CF_2$ group was confirmed by appearance of two signals of fluorine atoms with typical geminal coupling constants ($^2J_{FF}$ = ca. 41 Hz) and *trans* and *cis* coupling of fluorines to single hydrogen atom ($^3J_{HF}$ = 27 and 4 Hz, respectively).

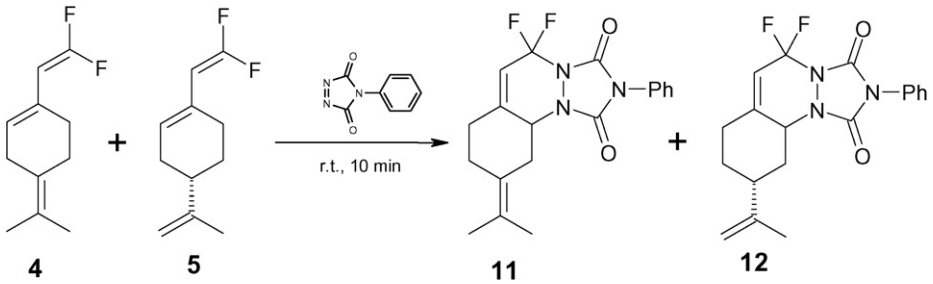
The attempted reductive debromination of 2-bromoisopropyl group in adduct **1** by typical methods failed. Treatment with Bu_3SnH in the presence of AIBN resulted mainly in dehydrobromination to give **2** and **3**. No reaction occurred with zinc in refluxing THF and in ethanol complex mixture of unidentified products was obtained. The most successful way to derivatives bearing the $(CH_3)_2CH$ group in position 4 of the cyclohexenyl ring was catalytic hydrogenation of the mixture of compounds **2** and **3**. The best results were obtained when hydrogenation was carried out in ethyl acetate under 0.17 MPa pressure of hydrogen using 10% palladium on charcoal as a catalyst; a mixture containing 60% of the required 1-(2-bromo-2,2-difluoroethyl)-4-isopropylcyclohexene (**7**) together with 14% of isomeric compound **8** and 26% of fully hydrogenated compound **9** was obtained in a 71% total yield (Scheme 5). Higher pressure of hydrogen resulted in increased contents of saturated compound **9**.

The mixture of compounds **7**–**9** exhibited only small optical activity. This suggests that compounds **7** and **8** exist in both enantiomeric forms, that the hydrogenation proceeded not stereoselectively and may involve a number of hydrogenation–dehydrogenation processes. Surprisingly, only one diastereoisomer of **9** was detected by the NMR spectroscopy.

Treatment of the mixture of compounds **7**–**9** with DBU resulted in dehydrobromination of alkene **7** to give



Scheme 5.



Scheme 6.

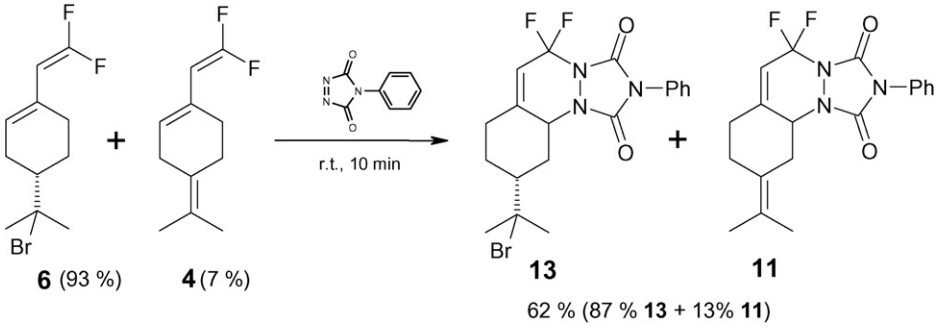
diene, 1-(2,2-difluorovinyl)-4-isopropylcycloxene (**10**), while compounds **8** and **9** remain unchanged (Scheme 5).

Because of the instability of compounds **4**–**6** and **10**, their attempted cycloadditions with common dienophiles, which require elevated temperature or long reaction time, failed; only polymeric products were formed. However, all these compounds reacted immediately with 4-phenyl-3*H*-1,2,4-triazoline-3,5-dione, the most reactive dienophile known, to give in good yields crystalline cycloadducts, derivatives of cinnoline. Thus, addition of 4-phenyl-3*H*-1,2,4-triazoline-3,5-dione to a solution containing compounds **4** and **5** (86 and 14%, respectively) gave a product containing mainly cycloadduct **11** and small amount of cycloadduct **12**. The later was obtained as the main product from the analogous reaction with a solution containing largely **5** (Scheme 6).

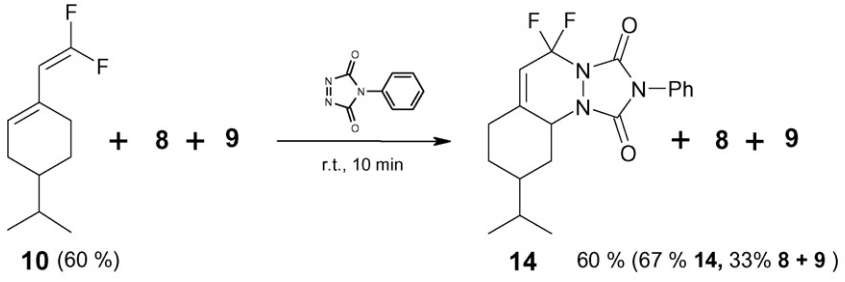
Similarly, treatment of the mixture containing mainly compound **6** (Scheme 4) with 4-phenyl-3*H*-1,2,4-triazoline-3,5-dione gave as the major product cycloadduct **13** substituted with 2-bromoisopropyl group (Scheme 7).

From among the compounds obtained by hydrogenation of a mixture of **2** and **3** followed by treatment with DBU (Scheme 5) only diene **10** is able to react with 4-phenyl-3*H*-1,2,4-triazoline-3,5-dione, therefore, after column chromatography, pure cycloadduct **14** was obtained (Scheme 8).

Cycloadducts **12**, **13** and **14** possessing two asymmetric carbon atoms, as found by the NMR spectrometry, were mixtures of diastereoisomers in ratios of 1.8:1, 1.2:1 and 1.3: 1, respectively. The NMR spectra of these compounds exhibited double set of signals for the =CH–CF_2 group and for the CH group neighbouring to nitrogen. Separation of the diastereoisomers was very difficult but a combination of crystallisation and column chromatography allowed to obtained the major diastereoisomer **12a** in pure state. Careful analysis of the ^{1}H NMR spectra, including COSY and ^{1}H{^{1}H}NOE experiments



Scheme 7.



Scheme 8.

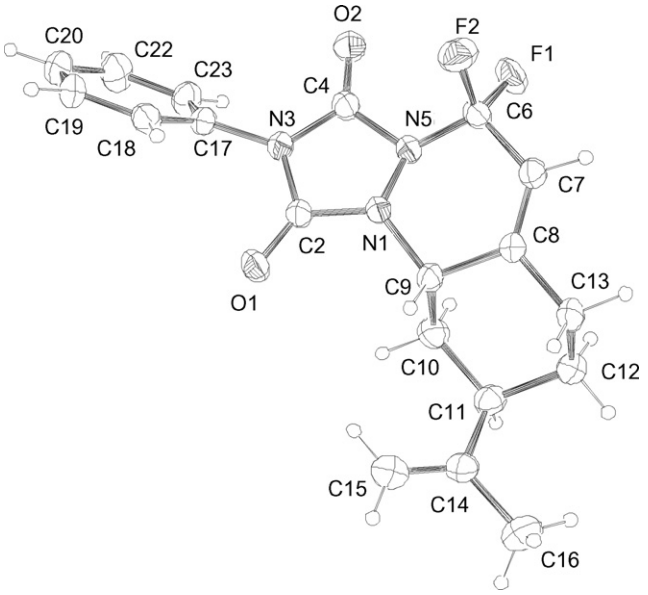


Fig. 1. X-ray crystal structure of **12a**. Thermal ellipsoids shown in 30% probability.

suggested that this diastereoisomer exists in a configuration in which the proton of the methine group neighbouring to nitrogen (C-10a) and that on the carbon atom bearing the isopropenyl group (C-9) are mutually *trans* one to another. Since all chemical transformations leading from β-pinene to **12** proceeded with retention of the (*S*)-conformation at the carbon atom bearing the isopropenyl group, the conformation of the new asymmetric centre in compound **12a** (C-10a) should also be assigned as (*S*). This was fully confirmed by the X-ray analysis as shown in Fig. 1.

In conclusion, sodium dithionite initiated addition of dibromodifluoromethane to β-pinene provides a way to a number of terpenic dienes with exocyclic CH=CF_2 group. These compounds are new examples of conjugated 1,1-difluorodienes and were found to be highly reactive towards strong dienophiles like 4-phenyl-3*H*-1,2,4-triazoline-3,5-dione.

3. Experimental

Melting points were determined in capillaries and are uncorrected. ^{1}H NMR, and ^{19}F NMR spectra were recorded with a Varian 400 spectrometer in $CDCl_3$ solutions (or as indicated otherwise). Chemical shifts are quoted in ppm from internal TMS for ^{1}H and from internal $CFCl_3$ for ^{19}F nuclei. Coupling constants (*J*) values are in Hz. NOE and COSY experiments were obtained with a Brucker AM-500 instrument. Mass spectra were obtained with an AMD-604 spectrometer. IR spectra were obtained with Perkin-Elmer 2000 spectrometer (frequencies in cm^{-1}) and optical rotation coefficients were measured with a JASCO-1020 polarimeter equipped with a sodium lamp.

Dibromodifluoromethane and (1*S*,5*S*)-(−)-β-pinene [purity ≥99%, $[\alpha]_D^{20} = -21 \pm 1$ (neat)] were commercial reagents. 4-Phenyl-3*H*-1,2,4-triazoline-3,5-dione was prepared according to the literature procedure [15].

3.1. (4S)-1-(2-Bromo-2,2-difluoroethyl)-4-(2-bromoisopropyl)-cyclohexene (*1*)

Sodium dithionite (0.4 g [85%], 2 mmol) and sodium hydrogen carbonate (0.17 g, 2 mmol) were suspended in an acetonitrile–water solution (1:1, 40 ml). The reaction mixture was vigorously stirred and cooled to 15 °C, then β-pinene (1.36 g, 10 mmol) and CF_2Br_2 (3.0 g, 14.3 mmol) were added one by one. After few minutes gas evolution (CO_2) began and a noticeable exothermic effect occurred. The temperature was kept at 18–20 °C (by cooling with an external water bath) for about half an hour after which time the reaction ceased (no more gas evolution) and most of inorganic salts dissolved. Addition of water (50 ml) and removal of acetonitrile on a rotary evaporator resulted in formation of an oily layer which after 1 h in a refrigerator (ca. 4 °C) solidified to form colourless crystals. The crystals were filtered off, washed few times with cold water and dried over P_4O_{10} under reduced pressure. Yield: 3.15 g (90%). mp 30–32 °C. $[\alpha]_D^{22} = -46.6$ (1% in EtOH). ^{1}H NMR: 1.44 (ddd, J_{HH} = 12.3, 11.8 and 5.6, 1H); 1.65 (tdd, J_{HH} = ca. 11.5, 5.0 and 2.3, 1H); 1.75 (s, CH_3); 1.80 (s, CH_3); 2.00–2.35 (complex m, 5H); 3.04 (narrow AB system, J_{AB} = ca. 3, $^3J_{HH}$ = 15.5 and 12.8, 2H, –CH_2CF_2Br); 5.70 (narrow m, 1H, –CH=). ^{19}F NMR: −42.8 (ddd, $^2J_{FF}$ = 155.0, $^3J_{HF}$ = 15.5 and 12.8, 1F); −43.6 (dt, $^2J_{FF}$ = 155.0, $^3J_{HF}$ = 15.5, 1F). MS (EI): *m*/*z* (rel. int., ion): 348, 346, 344 (5, 10, 5, M^+); 267, 265 [75, 77, (M − Br)$^+$]; 266, 244 [72, 64 (M − HBr)$^+$]; 251, 249 [16, 17, (M − HBr–CH_3)$^+$]; 225, 223 [11, 14, (M − C_3H_6Br)$^+$]; 211, 209 (98, 100, $C_7H_8F_2Br^+$); 185 [9, (M − 2Br)$^+$]; 141 (57, $C_8H_7F_2^+$); 129 (28, $C_7H_7F_2^+$); 121 (20, $C_9H_{13}^+$); 91 (18, $C_7H_7^+$); 79 (21, $C_6H_7^+$); 69 (19, $C_5H_9^+$); 43 (19, $C_3H_7^+$); 41 (23, $C_3H_5^+$). Analysis—found: C, 38.2; H, 4.5; Br, 46.3; F, 11.0%. Calculated for $C_{11}H_{16}Br_2F_2$ (346.05): C, 38.2; H, 4.7; Br, 46.2; F, 11.0%.

3.2. Dehydrohalogenation of *1*

3.2.1. With 2,2,6,6-tetramethylpiperidine

Compound **1** (10 g, 28.9 mmol) and 2,2,6,6-tetramethylpiperidine (14.6 ml, 86.7 mmol) were refluxed in dry toluene (100 ml) for 48 h. The precipitate of piperidine hydrobromide was filtered off, the solution was washed with 5% hydrochloric acid (3× 20 ml), followed with brine until neutral, and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave an oily liquid which was subjected to column chromatography (silica gel, hexanes). Evaporation of the solvent afforded 6.8 g (25.7 mmol, yield: 89%) of colourless liquid composed of diene **2** (87%) and diene **3** (13%) (estimated from the integrated NMR spectra). Analysis—found: C, 49.2; H, 5.9; Br, 29.8; F, 15.0%. Calculated for $C_{11}H_{15}BrF_2$ (265.14): C, 49.8; H, 5.7; Br, 30.1; F, 14.3%. $[\alpha]_D^{20} = -45.7$ (1% in EtOH).

(4*S*)-1-(2-Bromo-2,2-difluoroethyl)-4-isopropenylcyclohexene (**2**): ^{1}H NMR: 1.43–1.55 (complex m, 1H); 1.74 (dm, J = ca. 1.0, CH_3); 1.82 (dm, $^2J_{HH}$ = 13.5, 1H); 2.00 (dm, $^2J_{HH}$ = 13.5, 1H); 2.25–2.10 (complex m, 4H); 3.02 (t, $^3J_{HF}$ = 14.8, 2H, –CH_2CF_2Br); 4.72 (sext, J = 0.9,

1H, CH_2=); 4.74 (qn, J = 1.5, 1H, CH_2=); 5.69 (narrow m, 1H, –CH=). ^{19}F NMR: −42.8 (dt, $^2J_{FF}$ = 155, $^3J_{HF}$ = 14.8, 1F); −43.4 (dt, $^2J_{FF}$ = 155, $^3J_{HF}$ = 14.8, 1F).

(4*S*)-1-(2-Bromo-2,2-difluoroethyl)-4-isopropenylidenecyclohexene (**3**): ^{1}H NMR: 1.66 (s, CH_3); 1.69 (s, CH_3); 2.13 (m, 2H); 2.33 (t, $^3J_{HH}$ = 6.2, 2H); 2.82 (broad s, 2H); 3.04 (t, $^3J_{HF}$ = 14.8, 2H, –CH_2CF_2Br); 5.72 (narrow m, 1H, –CH=). ^{19}F NMR: −43.30 (t, $^3J_{HF}$ = 14.8, 2F).

3.2.2. With KOH

Compound **1** (0.5 g, 1.45 mmol), 50% aqueous KOH (0.42 ml, 8.7 mmol) and Bu_4NHSO_4 (0.49 g, 1.45 mmol) were vigorously stirred at ambient temperature for 72 h. The reaction was quenched with 5% aq. HCl (10 ml), extracted with ether (3× 30 ml), the combined extracts were washed with water until neutral and dried over $MgSO_4$. Evaporation of the solvent afforded 0.26 g (1.38 mmol, yield: 95%) of oily liquid composed of triene **4** (86%) and triene **5** (14%) (estimated from the integrated NMR spectra).

1-(2,2-Difluorovinyl)-4-isopropylidenecyclohexene (**4**): ^{1}H NMR: 1.69 (s, CH_3), 1.73 (s, CH_3); 2.31 (m, 2H); 2.37 (d, J_{HH} = 6.4, 2H); 2.87 (broad s, 2H); 4.86 (dd, $^3J_{HF}$ = 27.3, $^3J_{HF}$ = 4.6 H, 1H, –*CH*=CF_2); 5.66 (narrow m, 1H, –CH=). ^{19}F NMR: −85.4 (ddm, $^2J_{FF}$ = 41.0, $^3J_{HF}$ = 27.3, 1F), −88.7 (dm, $^2J_{FF}$ = 41.0, 1F).

1-(2,2-Difluorovinyl)-4-isopropenylcyclohexene (**5**): ^{1}H NMR and ^{19}F NMR signals in agreement with given in Section 3.2.4.

3.2.3. With K_2CO_3

Compound **1** (0.5 g, 1.45 mmol) and K_2CO_3 (0.8 g, 5.8 mmol) in DMF (5 ml) were vigorously stirred at ambient temperature for 72 h. The reaction mixture was diluted with water (5 ml), extracted with ether (3× 10 ml) and the combined extracts were washed with water and dried over $MgSO_4$. Evaporation of the solvent afforded 0.22 g (1.2 mmol, yield: 83%) of oily liquid composed of triene **4** (77%), triene **5** (17%) and compound **3** (6%) (estimated from the integrated NMR spectra).

3.2.4. With DBU

Compound **1** (0.5 g, 1.45 mmol) and DBU (0.87 ml, 5.8 mmol) in dry THF (5 ml) were vigorously stirred at ambient temperature for 3 h. Precipitate of DBU hydrobromide was filtered off, the eluent was washed with 5% aq. HCl (3× 10 ml) followed with brine until neutral and dried over $MgSO_4$. Evaporation of the solvent afforded 0.37 g (1.4 mmol, yield: 96%) of oily liquid containing 93% of compound **6** and 7% of compound **4** (estimated from the integrated NMR spectra).

1-(2,2-Difluorovinyl)-4-(2-bromoisopropyl)cyclohexene (**6**): ^{1}H NMR: 1.42 (ddd, $^2J_{HH}$ = 24.6, $^3J_{HH}$ = 12.0 and 5.3, 1H); 1.64 (tdd, $^3J_{HH}$ = 11.4, 4.9 and 2.4, 1H); 1.75 (s, CH_3); 1.80 (s, CH_3); 2.00–2.15 (m, 2H); 2.20–2.44 (complex m, 3H); 4.83 (dd, $^3J_{HF}$ = 27.3, 4.4, 1H, –*CH*=CF_2); 5.63 (narrow m, 1H, –CH=). ^{19}F NMR: −84.9 (dd, $^2J_{FF}$ = 40.2, $^3J_{HF}$ = 27.3, 1F); −88.2 (dm, $^2J_{FF}$ = 40.2, 1F).

^{1}H NMR and ^{19}F NMR signals of compound **4** in agreement with given in Section 3.2.2.

Similar treatment of the mixture of compounds **2** and **3** gave a mixture of **5** (87%) and **4** (13%) in 89% total yield.

1-(2,2-Difluorovinyl)-4-isopropenylcyclohexene (**5**)—^{1}H NMR: 1.43–1.55 (m, 1H); 1.74 (s, CH_3); 1.82 (m, 1H); 2.00 (m, 1H); 2.10–2.35 (complex m, 4H); 4.71 (narrow m, 1H, CH_2=); 4.73 (narrow m, 1H, CH_2=); 4.83 (dd, $^3J_{HF}$ = 27.4, 4.7, 1H, –*CH*=CF_2); 5.66 (narrow m, 1H, –CH=). ^{19}F NMR: −85.1 (dd, $^2J_{FF}$ = 41.0, $^3J_{HF}$ = 27.4, 1F); −88.5 (dm, $^2J_{FF}$ = 41.0 Hz, 1F).

3.2.5. With t-BuOK

Compound **1** (0.5 g, 1.45 mmol) and *t*-BuOK (0.32 g, 2.9 mmol) in dry THF (5 ml) were vigorously stirred at ambient temperature for 1.5 h. The reaction mixture was acidified with 5% aq. HCl (15 ml), extracted with ether (3× 20 ml) and the combined extracts were washed with water and dried over $MgSO_4$. Evaporation of the solvent afforded 0.33 g (1.33 mmol, yield: 92%) of oily liquid which by the integrated NMR spectra was found to be composed of compounds **6** (72%), **4** (19%) and **5** (9%).

3.3. Hydrogenation of the mixture of 2 and 3 and dehydrobromination of products

Mixture of compounds **2** and **3** (87 and 13%, respectively, Section 3.2.1) was dissolved in ethyl acetate (150 ml) and hydrogenated in the presence of 10% Pd/C catalyst (0.1 g) in a Parr apparatus for 4 h at ambient temperature under 0.17 MPa pressure of hydrogen. The catalyst was filtered off through a layer of Celite then the eluent was evaporated and the oily residue which was purified by column chromatography (silica gel, hexanes) to give colourless liquid (0.71 g, yield 71%) composed of compounds **7**, **8** and **9** (60, 14 and 26%, respectively; estimated from the integrated NMR spectra). Analysis—found: C, 50.0; H, 7.0; Br, 29.5; F, 13.5%. Calculated for $C_{11}H_{17}Br\ F_2$ (267.16): C, 49.5; H, 6.4; Br, 29.9; F, 14.2%. $[\alpha]_D^{23}$ = −8.9 (1% in ethanol).

1-(2-Bromo-2,2-difluoroethyl)-4-isopropylcyclohexene (**7**): ^{1}H NMR: 0.88 (d, $^3J_{HH}$ = 4.4, CH_3); 0.90 (d, $^3J_{HH}$ = 4.4, CH_3); 1.16–1.34 (complex m, 2H); 1.46 (q, $^3J_{HH}$ = 6.6, 2H); 1.78 (m, 2H); 2.10 (m, 2H); 3.00 (t, $^3J_{HF}$ = 14.4, 2H, –CH_2CF_2Br); 5.68 (narrow m, 1H, –CH=). ^{19}F NMR: −42.6 (dt, $^2J_{FF}$ = 154, $^3J_{HF}$ = 14.4, 1F); −43.4 (dt, $^2J_{FF}$ = 154, $^3J_{HF}$ = 14.4, 1F).

^{1}H NMR and ^{19}F NMR signals of compounds **8** and **9** in agreement with given in Section 3.4.3.

The above mixture of compounds **7–9** was treated with DBU and worked up as in Section 3.2.4 to give a mixture containing 60% of diene **10** (91% yield in relation to **7**) and unchanged compounds **8** and **9**.

1-(2,2-Difluorovinyl)-4-isopropylcyclohexene (**10**): ^{1}H NMR: 0.82 (complex m, 6H, 2xCH_3); 1.10–1.25 (complex AB system, 2H); 1.42 (q, $^3J_{HH}$ = 6.5, 2H); 1.74 (m, 2H); 2.02 (m, 2H); 4.74 (dd, $^3J_{HF}$ = 27.5 and 4.7, 1H, *CH*=CF_2); 5.56 (narrow m, 1H, CH=). ^{19}F NMR: −85.40 (dd, $^2J_{FF}$ = 41.3, $^3J_{HF}$ = 27.5, 1F); −88.92 (dm, $^2J_{FF}$ = 41.3, 1F).

3.4. Reactions of dienes **4–6** and **10** with 4-phenyl-3H-1,2,4-triazoline-3,5-dione

Mixtures of compounds obtained as described in Sections 3.2.2 and 3.2.4 (4.0 mmol) were dissolved in CH_2Cl_2 (7 ml) then 4-phenyl-3*H*-1,2,4-triazoline-3,5-dione (ca. 4.5 mmol) was added portionwise. Immediate colour change, from red to pale-yellow, occurred after addition of each portion of the dienophile. After addition of the last portion, colour did not changed during 10 min. Solid material obtained after evaporation of the solvent was purified by column chromatography (silica gel, hexanes/ethyl acetate 1:1).

3.4.1. Reaction of the mixture of **4** and **5**

Mixture containing 86% of **4** and 14% of **5** (Section 3.2.2) gave crystalline product (1.1 g, 3.07 mmol, total yield 77%) composed of 95% of cycloadduct **11** and 5% of cycloadduct **12** (integrated NMR estimate). mp 189–190 °C. Analysis—found: C, 63.7; H, 5.2; F, 10.8; N, 11.7%. Calculated for $C_{19}H_{19}F_2N_3O_2$ (359.38): C, 63.5; H, 5.3; F, 10.6; N, 11.7%. MS (EI): *m/z* (rel. int., ion): 359 (11, M^+); 316 [3, $(M - C_3H_7)^+$]; 220 (1, $C_{12}H_{13}FN_2O^+$); 197 (3, $C_9H_7F_2N_2O^+$); 183 (100, $C_9H_7F_2NO^+$); 178 (11, $C_9H_7FN_2O^+$); 159 (4, $C_9H_7N_2O^+$); 119 [4, $(PhNCO)^+$]; 91 [3, PhN^+]; 77 (2, $C_6H_5^+$); 41 [3, $(C_3H_5)^+$]. $[\alpha]_D^{24} = -8.7$ (1% in CH_2Cl_2). 5,5-Difluoro-8,9,10,10a-tetrahydro-9-isopropylideno-2-phenyl-2*H*-[1.2,4]-triazolo-[1,2-α]cinnoline-1,3(5*H*,7*H*)-dione (**11**)—^{1}H NMR: 1.74 (s, CH_3); 1.76 (s, CH_3); 1.85 (t, J_{HH} = 12.4, 1H); 2.01 (t, J_{HH} = 12.4, 1H); 2.17 (sept., J_{HH} = ca. 6.2, 1H); 2.55 (ddd, J_{HH} = 13.1, 4.5 and 2.5, 1H); 2.93 (dm, J_{HH} = 13.6, 1H); 3.54 (ddd, J_{HH} = 12.5, 4.7 and 2.2, 1H); 4.63 (dm, J_{HH} = ca. 12, 1H, N–CH–); 5.75 (dd, $^3J_{HF}$ = 6.6, $^4J_{HH}$ = 1.5, 1H, =CH–CF_2); 7.38–7.55 (m, 5H, Ph). ^{19}F NMR: −77.8 (dm, $^2J_{FF}$ = 216.6 Hz, 1F); −84.8 (dd, $^2J_{FF}$ = 216.6 Hz, $^3J_{HF}$ = 6.6 Hz, 1F). IR (in KBr): ν(C=O) = 1722 (vs) and 1787 (vs), ν(C=C) = ca. 1670 (overlapped). $[\alpha]_D^{24} = -91.8$ (1% in CH_2Cl_2).

From the mixture containing 87% of **5** and 13% of **4** (Section 3.2.4 bottom) gave a product (0.54 g, 3.1 mmol, total yield 62%) composed of 89% of **12** and 11% of **11** (integrated NMR estimate). mp 135–137 °C. Cycloadduct **12** was found to be a mixture of two diastereoisomers in a 1.8: 1 ratio. The major diastereoisomer **12a** was isolated by repeated crystallisation from hexenes/ethylacetate (2:1). The minor isomer **12b** was identified in the mixture of diastereoisomers by ^{1}H NMR and ^{19}F NMR spectroscopy.

5,5-Difluoro-8,9,10,10a-tetrahydro-9-isopropenylo-2-phenylo-2*H*-[1.2,4]triazolo[1,2-α]cinnoline-1,3(5*H*,7*H*)-dione: major diastereoisomer (**12a**): Analysis—found: C, 63.7; H, 5.2; F, 10.8; N, 11.7%. Calculated for $C_{19}H_{19}F_2N_3O_2$ (359.38): C, 63.5; H, 5.3; F, 10.6; N, 11.7%. MS (EI): *m/z* (rel. int., ion): 359 (43, M^+); 344 [3, $(M - CH_3)^+$]; 339 [4, $(M - HF)^+$]; 331 [2, $(M - CO)^+$]; 316 [100, $(M - C_3H_7)^+$]; 303 [5, $(M - 2CO)^+$]; 290 (10, $C_{15}H_{12}F_2N_2O_2^+$); 197 [73, $(M - PhNCO–C_3H_7)^+$]; 183 (31, $C_9H_7F_2NO^+$); 171 (16, $C_8H_6F_2NO^+$); 159 (6, $C_9H_7N_2O^+$); 141 (6, $C_8H_7F_2^+$); 128 (6, $C_9H_6N^+$); 119 (4, $PhNCO^+$); 91 (3, $C_7H_7^+$, PhN^+); 77 (2, $C_6H_5^+$); 41 (3, $C_3H_5^+$). ^{1}H NMR: 1.70 (tt, J_{HH} = 13.30, and 5, 1H); 1.80 (td, J_{HH} = 13.89 and 5, 1H); 1.84 (s, CH_3); 2.28–2.46 (complex m, 3H); 2.63 (narrow m, 1H); 2.85 (dm, J_{HH} = 12.5, 1H); 4.64 (dm, J_{HH} = ca. 12, 1H, N–CH–); 5.08 (narrow m, 2H, CH_2=); 5.70 (d, $^3J_{HF}$ = 6.6, 1H, =*CH*–CF_2); 7.37–7.54 (m, 5H, Ph). ^{19}F NMR: −77.44 (dm, $^2J_{FF}$ = 216.3, 1F); −85.3 (dd, $^2J_{FF}$ = 216.3, $^3J_{HF}$ = 6.6, 1F). IR (in KBr): ν(C=O) = 1794 (s) and (vs), ν(C=C) = 1684 (m). $[\alpha]_D^{24} = -91.8$ (1% in CH_2Cl_2). Minor diastereoisomer (**12b**): ^{1}H NMR: 1.43 (ddd, $^2J_{HH}$ = 25.7, $^3J_{HH}$ = 13.2 and 4.01, 1H); ca. 1.60 (overlapped m, 1H); 1.74 (s, CH_3); ca. 2.35 (overlapped m, 3H); 2.58 (m, 2H); 4.53 (dm, J_{HH} = ca. 12, 1H, N–CH–); 4.75 (d, J_{HH} = ca. 0.7, 1H, CH_2=); 4.78 (qn, J_{HH} = 1.5, 1H, CH_2=); 5.75 (d, $^3J_{HF}$ = 6.7, J = 1.51, 1H, =CH–CF_2); 7.37–7.54 (m, 5H, Ph). ^{19}F NMR: −77.3 (ddd, $^2J_{FF}$ = 216.6, $^3J_{HF}$ = 6.7, 4.3, 1F); −85.8 (dd, $^2J_{FF}$ = 216.6, $^3J_{HF}$ = 6.7, 1F).

X-ray crystallographic studies of compound. **12a**: $C_{19}H_{19}F_2N_3O_2$, F_w = 359.37. Suitable crystal of dimensions 0.63 mm × 0.38 mm × 0.27 mm was mounted on a glass fiber. Data collection was performed at 295 on a Nonius BV MACH diffractometer with graphite monochromated Cu Kα (λ = 1.54178 Å). Unit cell dimensions: a = 7.1650 (6), b = 15.6390 (10), c = 8.1820 (7) Å, β = 105.550 (7)°, V = 883.3 (1) Å^3, Z = 2, d_x = 1.351 Mg m^{-3}, F(000) = 376, μ (Cu Kα) = 0.870 mm^{-1}, monoclinic system, space group $P2_1$. Thousand nine hundred and sixty one reflections were collected in the θ-range 5.61–74.05°, 1823 unique [R(int) = 0.0339] were used for structure elucidation.

Structure was solved with direct methods using the SHELXS97 [16] and refined with SHELXL97 [17] software. Refinement was performed anisotropically for all non-hydrogen atoms using the full-matrix least-squares method. In general, hydrogen atoms were assigned to idealized positions and were allowed to ride with thermal parameters fixed at $1.2U_{eq}$ of the parent atom. The residual electron densities were of no chemical significance. Final R indices [1823 reflections with $I > 2\sigma(I)$]: R_1 = 0.0453, wR_2 = 0.1191, and for all data R_1 = 0.0984, wR_2 = 0.1483. CCDC-644964 contains the supplementary crystallographic data for this paper [18].

3.4.2. Reaction of the mixture of **6** and **4**

Mixture containing 93% of **6** and 7% of **4** (§ *3.2.4*) gave crystalline product (1.16 g, 2.64 mmol, total yield 66%) composed of 87% of cycloadduct **13** and 13% of cycloadduct **11** (integrated NMR estimate). Mp 110–111 °C. Analysis – found: C, 52.0; H, 5.0; Br, 18.1; F, 8.6; N, 9.7%. Calculated for $C_{19}H_{20}BrF_2N_3O_2$ (440.29): C, 51.8; H, 4.9; Br, 18.2; F, 8.6; N, 9.5%. MS (EI): m/z (rel. int., ion): 441, 439 (7, 8, M^+); 359 [34, $(M - HBr)^+$]; 339 [9, $(M - HBr–HF)^+$]; 316 [79, $(M - HBr–C_3H_7)^+$]; 290 (6, $C_{15}H_{12}F_2N_2O_2^+$); 197 [42, $(M - PhNCO–C_3H_7)^+$]; 183 (100, $C_9H_7F_2NO^+$); 159 (7, $C_9H_7N_2O^+$); 141 (6, $C_8H_7F_2^+$); 119 (24, $PhNCO^+$); 91 (21, PhN^+); 77 (10, $C_6H_5^+$); 41 (28, $C_3H_5^+$). IR (in KBr): ν(C=O) = 1795 (s) and 1733 (vs), ν(C=C) = 1684 (m). $[\alpha]_D^{24} = -157.1$ (1% w CH_2Cl_2). $[\alpha]_D^{24} = -157.1$ (1% in CH_2Cl_2). Cycloadduct **13** was found to be a mixture of two diastereoisomers, **13a** and **13b**, in a 1.2: 1 ratio (not separated).

9-(2-Bromoisopropyl)-5,5-difluoro-8,9,10,10a-tetrahydro-2-phenyl-2*H*-[1.2,4]-triazolo-[1,2-α]cinnoline-1,3-(5*H*,7*H*)-dione (**13**): major diastereoisomer (**13a**): ^{1}H NMR: 1.68–1.92 (complex m, 2H); 1.76 (s, CH_3); 1.79 (s, CH_3); 1.99 (m, 2H); 2.52 (dt, J_{HH} = 13.3 Hz, 3.8, 2H); 2.74 (m, 1H), 4.82 (m, 1H, N–CH–); 5.78 (d, $^3J_{HF}$ = 6.0, 1H, =CH–CF_2); 7.37–7.54 (m, 5H, Ph). ^{19}F NMR: −77.87 (dm, $^2J_{FF}$ = 217,1F); −85.82 (dm, $^2J_{FF}$ = 217, 1F). Minor diastereoisomer (**13b**): ^{1}H NMR: 1.22–1.36 (complex AB system, 2H); 1.48 (m, 1H), 1.61 (q, $^3J_{HH}$ = 12, 1H); 1.78 (s, CH_3); 1.80 (s, CH_3); 2.28 (m, 2H); 2.60 (dm, $^3J_{HH}$ = ca. 11, 1H); 4.53 (dm, J_{HH} = ca. 12, 1H, N–CH–); 5.75 (d, $^3J_{HF}$ = 6.7, 1H, =*CH*–CF_2); 7.37–7.54 (m, 5H, Ph). ^{19}F NMR: −77.6 (dm, $^2J_{FF}$ = 217, 1F); −85.8 (dd, $^2J_{FF}$ = 217, $^3J_{HF}$ = 6.7, 1F).

3.4.3. Reaction of the mixture of *10*, *8* and *9*

Mixture containing 60% of **10**, 14% of **8** and 26% **9** (Section 3.3) gave an oil which was separated by column chromatography in two fractions. The first fraction (oil, 0.19 g, 0.73 mmol) consisted of 34% compound **8** and 66% of compound **9** (^{19}F NMR estimate). $[\alpha]_D^{23} = -1.75$ (1% in ethanol). The second, crystalline fraction (0.57 g, 1.47 mmol) was found by integrated ^{19}F NMR to be a mixture of diastereoisomers **14a** and **14b** in a 1.3:1 ratio. Yield: 61% relative to **10**. mp 119–121 °C. Repeated column chromatography (silica gel, hexanes/ethyl acetate 4:1) allowed to obtain a fraction containing 81% of **14a**. $[\alpha]_D^{24} = -8.38$ (1% in ethanol).

4-(2-Bromo-2,2-difluoroetylo)-1-isopropylcyclohexene (**8**)—^{1}H NMR: 0.98 (s, CH_3); 0.99 (s, CH_3); 1.50 (complex m, 2H); 1.67(complex m, 1H); 1.83–1.94 (complex m, 2H); 2.01 (m, 2H); 2.13–2.46 (complex m, 3H, 1H-*CH*$(CH_3)_2$, 2H – *CH*$_2$$CF_2$); 5.34 (narrow m, 1H, *CH*=). ^{19}F NMR: −40.90 (ddd, $^2J_{FF}$ = 154, $^3J_{HF}$ = 16.1 and 14.0, 1F); −41.50 (dm, $^2J_{FF}$ = 154, 1F).

4-(2-Bromo-2,2-difluoroetylo)-1-isopropylcyclohexane (**9**)—^{1}H NMR: 0.86 (d, $^3J_{HH}$ = 6.8, 6H, 2xCH_3); 1.01 (narrow m, 3H); 1.26 (narrow m, 3H); 1.42 (complex m, 1H); 1.54 (m, 1H); 1.63–1.76 (complex m, 2H); 1.83–1.94 (complex m, 1H); 3.00 (dt, $^3J_{HF}$ = 15.5 Hz, $^3J_{HH}$ = 6.2 Hz, 2H, *CH*$_2$$CF_2$). ^{19}F NMR: −40.95 (t, $^3J_{HF}$ = 15.5 Hz, 2F).

5,5-Difluoro-8,9,10,10a-tetrahydro-9-isopropyl-2-phenyl-2*H*-[1.2,4]triazolo[1,2-α]cinnoline-1,3(5*H*,7*H*)-dione (**14**): Analysis—found: C, 63.2; H, 5.9; F, 10.5%, N, 11.6%. Calculated for $C_{19}H_{21}F_2N_3O_2$ (361.39): C, 63.2; H, 5.9; F, 10.5; N, 11.6%. MS (EI)—*m*/*z* (rel. int., ion): 361 (100, M^+); 341 [3, $(M - HF)^+$]; 318 [100, $(M - C_3H_7)^+$]; 291 (3, $C_{14}H_{11}F_2N_3O_2^+$); 278 (4, $C_{13}H_8F_2N_3O_2^+$); 277(5, $C_{13}H_7F_2N_3O_2^+$); 214 (7, $C_{11}H_{16}F_2N_2^+$); 199 [5, $(M - PhNCO–C_3H_7)^+$]; 184 (14, $C_{11}H_{14}F_2^+$); 178 (18, $C_9H_7FN_2O^+$); 159 (6, $C_9H_7N_2O^+$); 143 (17, $C_8H_9F_2^+$); 129 (17, $C_9H_7N^+$); 119 (20, $PhNCO^+$); 91 (12, $C_7H_7^+$, PhN^+); 77 (8, $C_6H_5^+$); 43 (8, $C_3H_7^+$); 41 (12, $C_3H_5^+$). IR (in KBr): ν(C=O) = 1792 (s) and 1728 (vs), ν(C=C) = 1680 (m). Major diastereoisomer (**14a**)—^{1}H NMR: 0.98 (d, $^3J_{HH}$ = 6.6 Hz, CH_3); 1.07 (d, $^3J_{HH}$ = 6.6, CH_3); 1.55 (m, 2H); 1.68 (td, J_{HH} = 12.4 and 4.4, 1H); 1.86 (dq, J_{HH} = 10.5 and 6.6, 1H); 2.10 (dm, J_{HH} = 14.7, 1H); 2.38 (narrow m, 2H); 2.68 (dm, J_{HH} = 12.7, 1H); 4.75 (dm, J_{HH} = 12.4, 1H, N–*CH*–); 5.70 (d, $^3J_{HF}$ = 6.6, 1H, =CH–CF_2); 7.36–7.55 (m, 5H, Ph). ^{19}F NMR: −77.75 (dm, $^2J_{FF}$ = 216, 1F); −85.04 (dd, $^2J_{FF}$ = 216, $^3J_{HF}$ = 6.6 Hz, 1F). Minor diastereoisomer (**14b**)—^{1}H NMR: 0.89 (s, CH_3); 0.91 (s, CH_3); 1.23 (ddd, $^2J_{HH}$ = 25, $^3J_{HH}$ = 13 and 4.0, 1H); 1.38 (q, $^3J_{HH}$ = 11.5 Hz, 1H); 1.55 (overlapped m, 1H); 1.96 (dm, J_{HH} = ca. 13, 1H); 2.23 (m, 1H); 2.52 (tdd, $^3J_{HH}$ = 13, 4.03 and 2.8, 1H); 4.75 (dm, J_{HH} = 11.7 1H, N–*CH*–); 5.72 (d, $^3J_{HF}$ = 6.9, 1H, =*CH*–CF_2); 7.36–7.55 (m, 5H, Ph). ^{19}F NMR: −77.14 (ddd, $^2J_{FF}$ = 216, $^3J_{FH}$ = 6.0 and 4.3 Hz, 1F); −85.52 (dd, $^2J_{FF}$ = 216, $^3J_{HF}$ = 6.9, 1F).

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[18] These data can be obtained free of charge at "http://www.ccdc.cam.ac.uk/conts/retrieving.html" [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; CCDC-644964. E-mail: deposit@ccdc.cam.sc.uk.