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Extremely facile ring inversion and rearrangement in fluorobicyclo[2.1.0]pentanes

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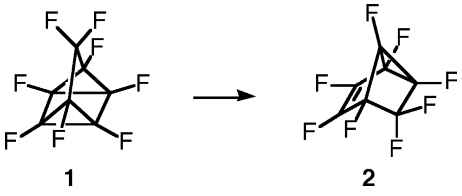
Abstract

cis-1,2,3,4,5,5-Hexafluorobicyclo[2.1.0]pentane and 1,4,5,5-tetrafluorobicyclo[2.1.0]pentane have been synthesized from hexafluorobenzene. The former hydrofluorocarbon, which exists entirely in the endo configuration, rearranges to *cis*-1,2,3,3,4,5-hexafluorocyclopentene below room temperature (E_a = 21.9 kcal/mol, log A = 13.4). The latter undergoes degenerate ring inversion with extraordinary ease ($\Delta G^{\ddagger}$ = 6.8 ± 0.2 kcal/mol at −55 °C). Density functional calculations indicate that significant bonding between the bridgehead carbons is retained in the ring inversion transition state. Analogous calculations predict for hexafluorobicyclo[1.1.0]butane a considerably lower barrier for ring inversion and more 1,3-bonding in the transition state.

Keywords: Bicyclo[2.1.0]pentane; Bicyclo[1.1.0]butane; Ring inversion; Rearrangement; Weak bonds; Effect of fluorine

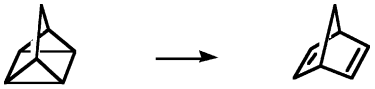
1. Introduction

The remarkable facility with which certain polycyclic fluorocarbons rearrange reveals the presence of very weak C–C bonds. A case in point is the transformation of perfluoroquadricyclane (**1**) into perfluorotricyclo[3.2.0.0^{2,7}]hept-3-ene (**2**), which occurs readily and spontaneously at temperatures above 0 °C (Eq. (1)) [1].



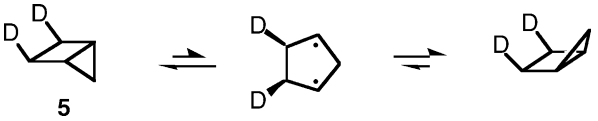
1 **2** (1)

A likely pathway for the rearrangement in shown in Scheme 1. The ease with which **1** isomerizes is the more striking when compared with the behavior of the very stable parent hydrocarbon (**3**), which reverts to norbornadiene (**4**) with $t_{1/2}$ = 3.9 h at 154 °C (Eq. (2)) [2]. In Scheme 1, the first bond to cleave is the central bond of a bicyclo[2.1.0]pentane ring system, outlined in bold. We set out to investigate the strength of that bond in fluorobicyclopentanes unadorned by fusion with additional rings.



3 **4** (2)

By determining the barrier for ring inversion in a deuterium-labelled bicyclopentane (**5**, E_a = 37.8 kcal/mol, log A = 3.9), Baldwin established an upper limit for the strength of the central bond (Eq. (3)) [3]. His value lies about 45 kcal/mol below that of a typical C–C single bond because of the great relief of strain that accompanies the opening of two small rings.



5 (3)

Though substitution by fluorine on cyclobutane rings has a modest stabilizing effect [4], fluoro substituents strongly destabilize cyclopropane rings [5]. To learn how weak the central bond of a fluorobicyclopentane can be, we therefore chose as

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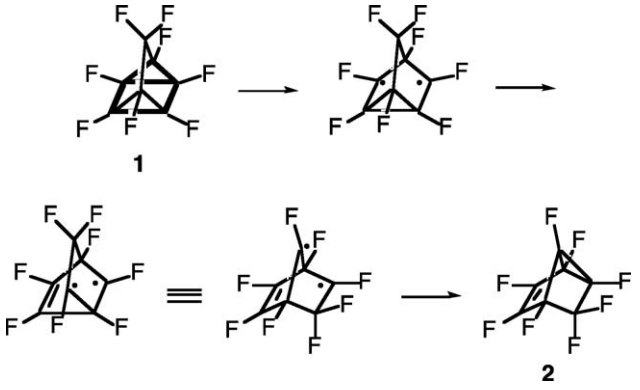
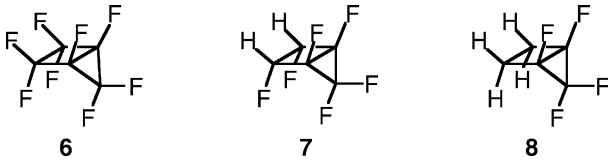


Scheme 1.

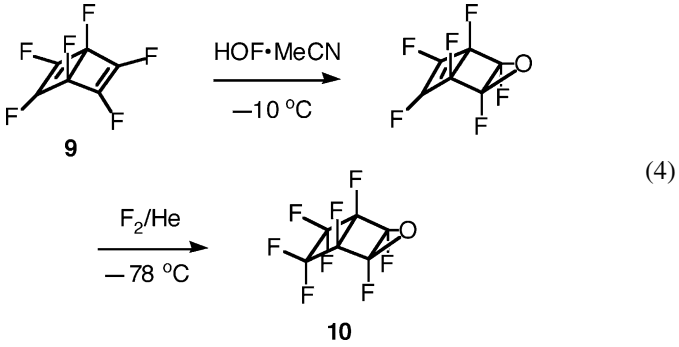
target molecules bicyclopentanes fully fluorinated on the three-membered rings; namely, **6**–**8**.



2. Results and discussion

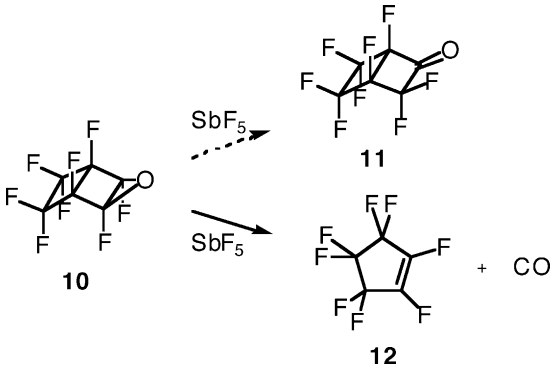
2.1. Approaches to octafluorobicyclo[2.1.0]pentane (6)

In light of the anticipated lability of 6–8, it was essential that the final step in their synthesis be performed at low temperature. The photochemical extrusion reactions in Scheme 2 met this criterion. In the hope of using the decarbonylation approach to obtain octafluorobicyclopentane **6**, epoxide **10** was prepared from hexafluoro Dewar benzene (**9**) [6] with Rozen's acetonitrile complex of hypofluorous acid (Eq. (4)) [7]. Rearrangement of **10** with a strong Lewis acid was



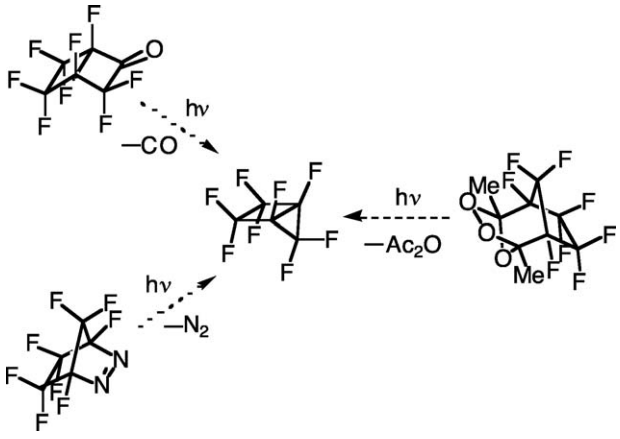
(4)

expected to yield ketone **11**, a well precedented transformation of fluoroepoxides [8], but gave instead octafluorocyclopentene (**12**) with extrusion of carbon monoxide (Eq. (5)). Apparently the desired process was subverted by strain in the ring system, which caused a C–C bond shift to preclude fluorine migration. A likely pathway is depicted in Scheme 3.

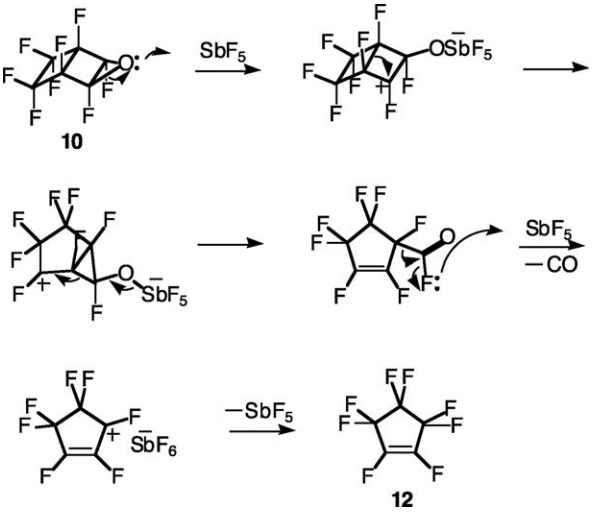


(5)

Our efforts became focused on the nitrogen extrusion approach to fluorocarbon **6**, which required synthesis of hexafluorocyclopentadiene (**13**). The most frequently used route to this diene entails high temperature cobaltic fluoride fluorination of hexachlorocyclopentadiene, distillation to obtain a mixture of $C_5Cl_4F_6$ isomers, and zinc dechlorination [9]. Because the fluorination requires specialized apparatus, a stirred bed reactor, we prepared diene **15** by fluorination of pentafluorophenol (**13**) with bromine trifluoride to give a

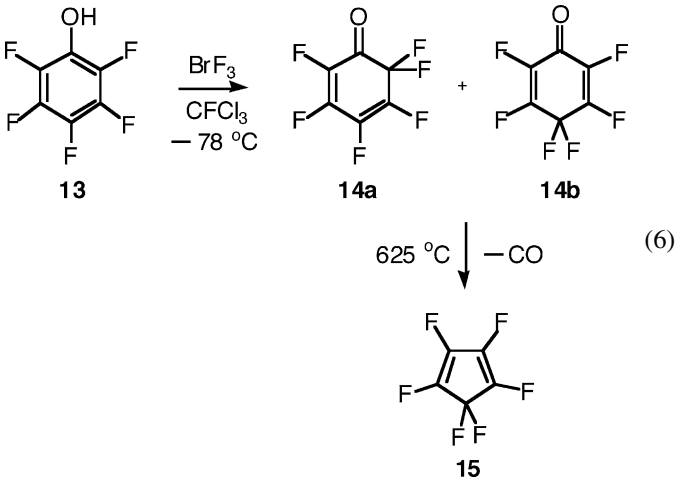


Scheme 2.



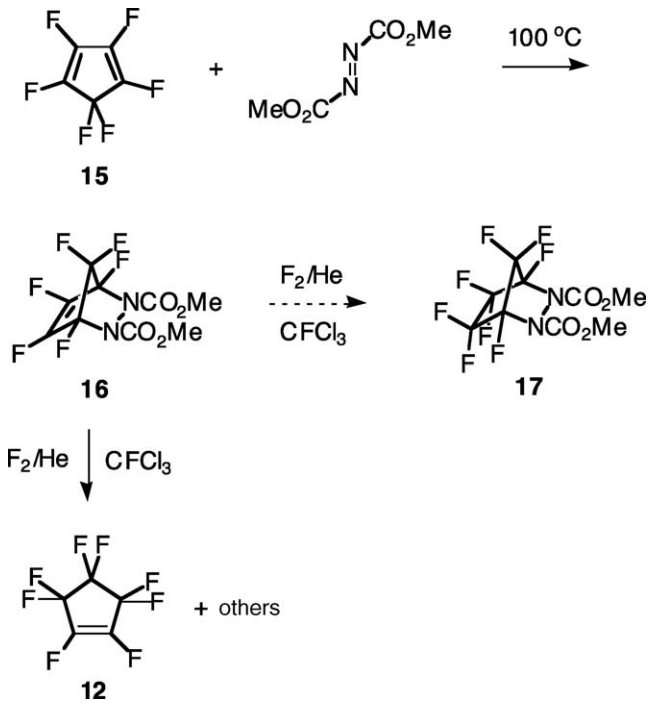
Scheme 3.

mixture of cyclohexadienones (**14**), followed by flash vacuum pyrolysis to extrude carbon monoxide (Eq. (6)) [10]. The diene reacted with dimethyl azodicarboxylate at 100 °C with long-wavelength UV irradiation [11] to afford the Diels–Alder adduct **16** (Scheme 4).

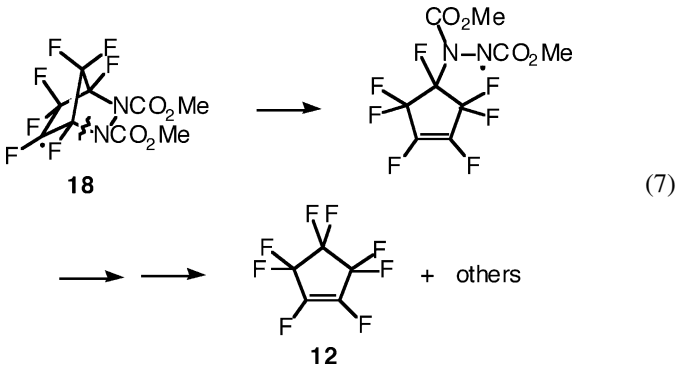


(6)

In the ^{19}F spectrum of **16** at RT, the vinyl, and to a lesser extent the bridgehead signals are broadened as a consequence of stereoisomer interconversion. Our synthetic plan called for saturation of the alkene double bond with fluorine to give **17**, followed by hydrolysis and oxidation to obtain an azo photoprecursor for bicyclopentane **6**. Attempts to prepare **17** were unsuccessful, however, and the only product identified was (again) octafluorocyclopentene (**12**). Probably the radical intermediate **18** formed in the course of fluorination suffered cleavage of the neighboring C–N bond, thereby relieving strain in the bicyclic system (Eq. (7)).



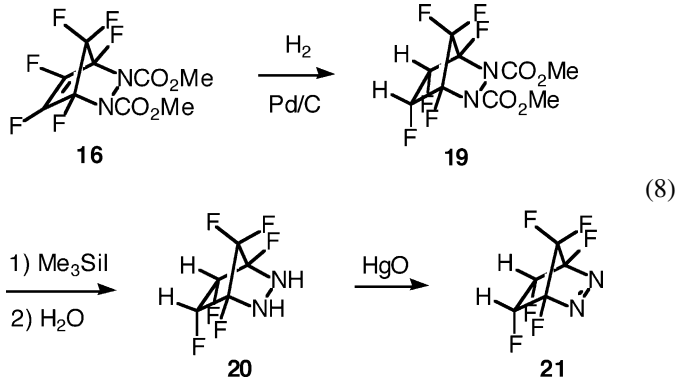
Scheme 4.



(7)

2.2. Synthesis and rearrangement of cis-1,2,3,4,5,5-hexafluorobicyclo[2.1.0]pentane (7)

Given the difficulties encountered en route to **6**, we turned our attention to synthesis of hydrofluorocarbon **7**. Hydrogenation of the adduct **16** proceeded smoothly, yielding **19** (Eq. (8)). Presumably because of the increased steric hindrance relative to **16** on the endo face of the molecule, the ^{19}F spectrum of **19** at RT reveals the presence of two distinct stereoisomers with very similar chemical shifts in the ratio 6:1. Since both the vinyl and the bridgehead fluorines are inequivalent in each isomer, both N-inversion and C–N bond rotation must be slow on the NMR time scale.



(8)

As the temperature is raised, ^{19}F NMR reveals that the two forms interconvert, and that the compound ultimately approaches C_s symmetry on the NMR time scale. The fact that the resonance of one of the geminal fluorines is broad even at 150 °C seems to require that C–N rotation has not become fast on that time scale, but we are unable to determine with confidence whether N-inversion or C–N bond rotation is the faster process. Calculations at the semiempirical AM1 level of theory [12] indicate that all cisoid invertomer conformations lie significantly above the transoid minima, all four rotamers of which are close in energy (Fig. 1). Both of the observed stereoisomers presumably belong to this set. Interconversion

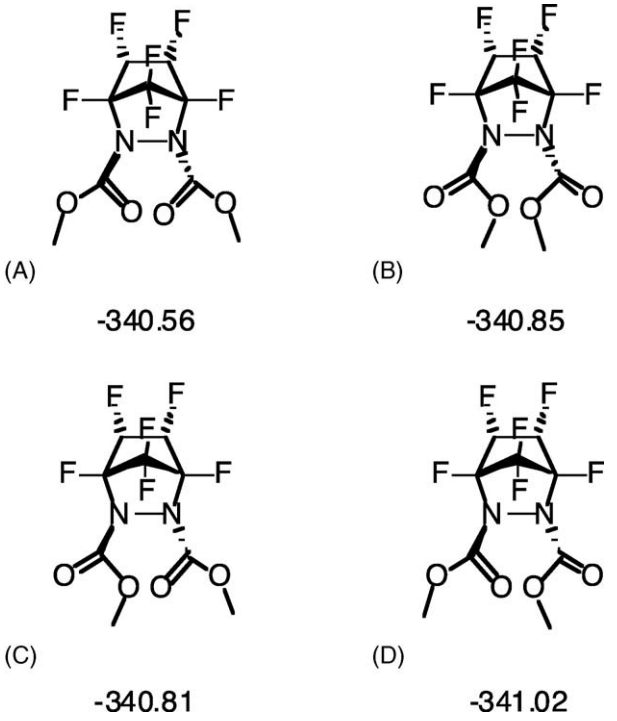


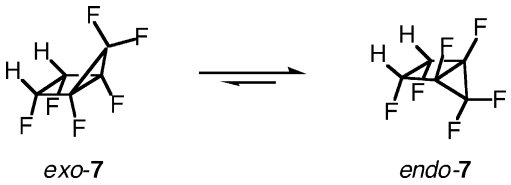
Fig. 1. Conformations and AM1 heats of formation (kcal/mol) of the transoid minima of **19**.

of A and B would be expected to cause both bridgeheads to shift in the same direction, but they actually shift the same amount in opposite directions as the temperature is raised. Also, interconversion of either A or B with C or D should shift one bridgehead fluorine selectively. For these reasons, we believe the interconverting forms are C and D.

The ester linkages in **19** were cleaved with iodotrimethylsilane [13], and the resulting trimethylsilyl esters underwent hydrolysis even in moist air, affording the hydrazine **20**. Interestingly, when the hydrazine is fully dry, the NMR signal for the bridgehead fluorines is broadened into the baseline, but in the presence of moist air it becomes a sharp singlet. Apparently water catalyzes N-inversion in this molecule. Mercuric oxide transformed **20** into the azo precursor (**21**) of bicyclopentane **7** [14].

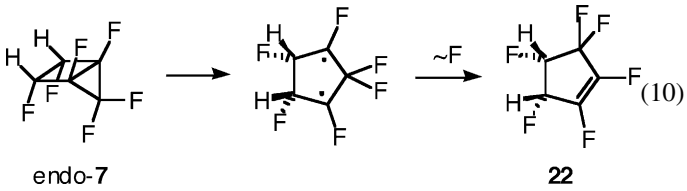
Ring inversion in **7**, unlike that in **6** and **8**, is not degenerate. We hoped that, whatever its isomeric composition, the initial product of photolysis of **21** would be significantly different from the equilibrium mixture of endo–exo isomers. Study of the relaxation to equilibrium would then reveal (an upper limit to) the strength of the central bond. Compound **21** turned out to belong to a class of azo compounds called ''reluctant'' [15], as its photolysis was extremely slow, allowing ample time for equilibration of the bicyclopentane product.

Photolysis of **21** in trichlorofluoromethane at temperatures down to −45 °C gave only the endo isomer, and calculations at the B3LYP/6–31G* level of theory [16] indicated that this isomer lies 4.8 kcal/mol below exo-**7** (Eq. (9)). The endo configuration was confirmed by an nOe experiment.



(9)

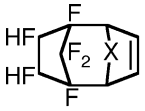
Although it was not possible to observe ring inversion in **7**, information about the strength of the central bond was obtained by studying another kind of isomerization, rearrangement to *cis*-1,2,3,3,4,5-hexafluorocyclopentene (**22**) [17] (Eq. (10)).



(10)

The rate of this process was measured with ^{19}F NMR in 1,2-dichlorotetrafluoroethane over the temperature range 0–30 °C. From the Arrhenius plot of the data (Fig. 2), these activation parameter values were obtained: E_a = 21.9 kcal/mol, log A = 13.4. For rearrangement of the parent bicyclopentane to cyclopentene, E_a = 45.6 kcal/mol and log A = 14.1 [18,19], so the effect of fluorine substitution on the barrier height is dramatic. Since the barrier for rearrangement in the parent hydrocarbon is about 8 kcal/mol higher than that for ring inversion (E_a = 37.8 kcal/mol, log A = 13.9) [3], the ring inversion barrier for **7** must be considerably smaller than 21 kcal/mol, even in the endo → exo direction.

Bicyclopentane endo-**7** reacted in [4 + 2] fashion at room temperature with furan and cyclopentadiene, yielding adducts **23** and **24**.[1] No adducts of dienes with the parent



23 X=O
24 X=CH_2

bicyclo[2.1.0]pentane have been reported. Furan adduct **23** decomposed upon gentle warming, presumably as a consequence of ring opening initiated by the oxygen lone pair. There is reason to believe that the Diels–Alder-like cycloadditions leading to **23** and **24** occur concertedly, because stepwise

[1] For **23**: ^{1}H NMR ($CDCl_3$): 6.66 (s, vinyl H, 2H), 5.31 (subsplit d, J = 56, CFH, 2H), 5.02 (br s, bridgehead H, 2H). ^{19}F NMR ($CDCl_3$): δ −112.0 (d, J = 244 Hz, CF_2, 1F), −124.9 (d, J = 244 Hz, CF_2, IF), −198.3 (s, bridgehead F, 2F), −222.8 (d, J = 56 Hz, CHF, 2F). GC–MS (EI): m/z 244 (M^+), 176, 157, 149, 131 (base), 113, 99, 83, 68, 51.

For **24**: ^{19}F NMR ($CDCl_3$): δ −112.1 (d, J = 240 Hz, CF_2, 1F), −123.3 (d, J = 240 Hz, CF_2, 1F), −186.0 (s, bridgehead F, 2F), −219.5 (d, J = 56 Hz, CHF, 2F). GC–MS (EI): m/z 242 (M^+), 209, 183, 177, 159, 145, 130, 127, 109 (base), 96, 77, 66, 51.

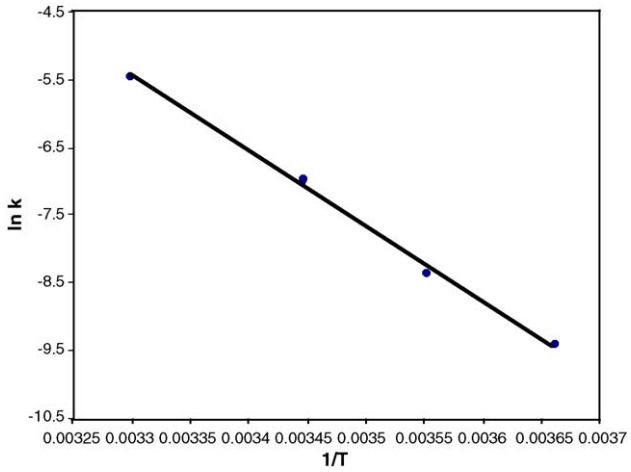


Fig. 2. Arrhenius plot for the rearrangement of bicyclopentane **7** to cyclopentene **22**.

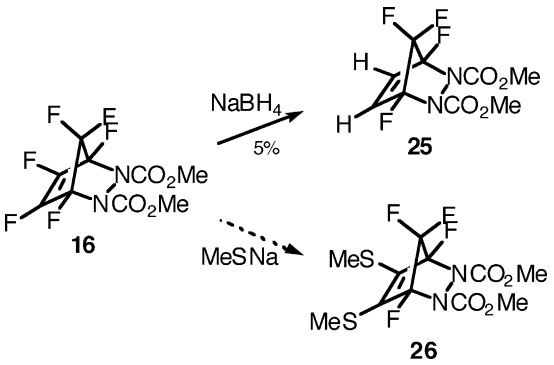
reaction probably would produce at least some [2 + 2] adduct, as happens in the reactions of fluoroalkenes with dienes [20].

Formation of **23** and **24** took place slowly enough that extensive rearrangement to the cyclopentene would have been expected to accompany cycloaddition, yet none was observed. The implication that complexation of the dienes with **7** stabilizes them against rearrangement gains credibility from the finding that **7** remains unchanged in benzene for more than a day at 10 °C!

*2.3. Synthesis and ring inversion of 1,4,5,5-tetrafluorobicyclo[2.1.0]pentane (**8**)*

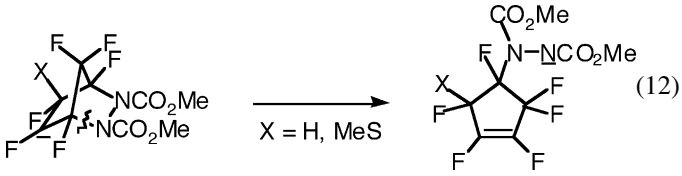
With **6** unavailable and **7** a single isomer, it was necessary to achieve the synthesis of **8** if we were to measure the ring inversion barrier for a bicyclopentane fully fluorinated on the three-membered ring. Of these three molecules, **8** should have the weakest central bond, as fluorination on the four-membered ring is minimal [4].

Diels–Alder adduct **16** was again the starting point, and the synthetic plan began with replacement of the vinyl fluorines with hydrogens via addition–elimination chemistry. Reaction of **16** with sodium borohydride gave the desired product **25**, but in only 5% yield (Eq. (11)). Addition–elimination was also attempted with methanethiolate ion to obtain **26**, with the expectation that Raney nickel would then replace the sulfurs with hydrogens.



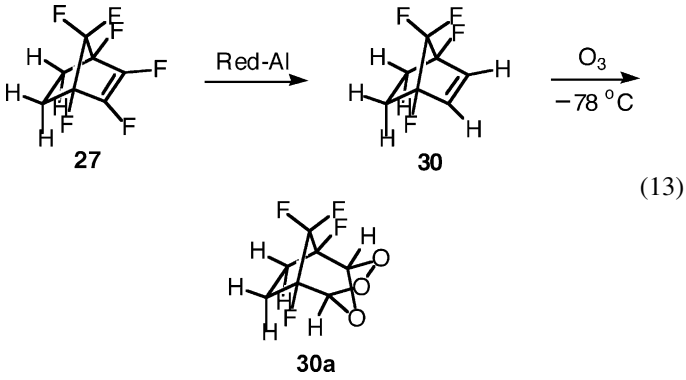
(11)

No **26** was found, however, and it was clear from the ^{19}F NMR spectrum that the ring system was being destroyed in these reactions. Just as the bicyclic system was ring opened via radical intermediates during fluorination to obtain **17**, it was apparently cleaved similarly via anionic intermediates in the reactions with nucleophiles (Eq. (12)).



(12)

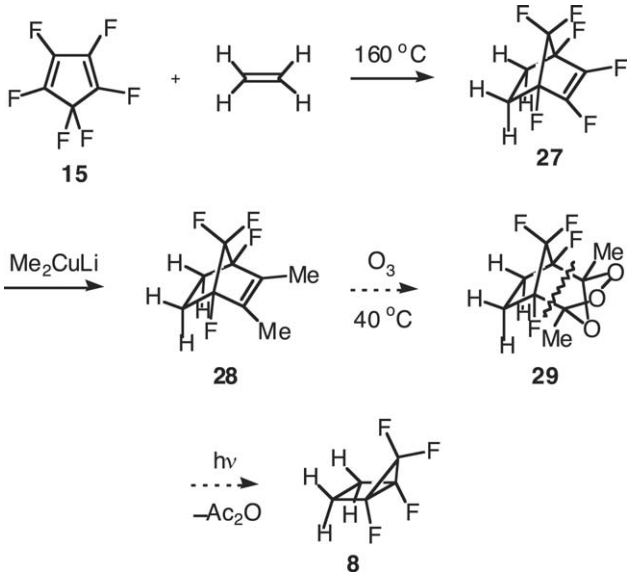
A new strategy was adopted whereby the ethylene bridge of bicyclopentane **8** was to be installed at the outset, with the culminating step ozonide photolysis [21] (Scheme 5). Diels–Alder addition of ethylene to hexafluorocyclopentadiene (**15**) at 160 °C afforded adduct **27** in 95% yield [22]. In order to obtain a normal ozonide, the vinyl fluorines of **27** were replaced by methyls to give **28** using lithium dimethylcuprate [23]. Again ring opening was a competing process, and the yield of **28** was just 30%. To our surprise, this alkene resisted attack by ozone to give **29** even at 40 °C, and was recovered unchanged. Surmising that the problem was steric in part, we substituted hydrogens for the vinyl fluorines of **27** with sodium bis(methoxyethoxy)aluminohydride (Red-Al^{TM}), obtaining **30** in 89% yield (Eq. (13)). The choice of this hydride was critical, as more powerful reagents such as lithium aluminum hydride decomposed the starting material, and gentler reagents such as sodium borohydride were insufficiently reactive except at elevated temperatures where decomposition was again the result. In contrast to **28**, alkene **30** underwent rapid ozonation to **30a** even at −78 °C. A single stereoisomer was obtained, but the configuration shown was not established.



(13)

Unfortunately, this ozonide proved to be extremely labile, decomposing rapidly even at −50 °C. This synthetic scheme was therefore discontinued. Incidentally, 2,3-dimethylnorbornene (the hydrocarbon analogue of **28**) forms a stable, crystalline ozonide [24], but norbornene (the analogue of **30**) yields an ozonide that decomposes at room temperature [25].

Attention turned to synthesis of the unknown diene 1,4,5,5-tetrafluorocyclopentadiene (**31**), with the expectation that its

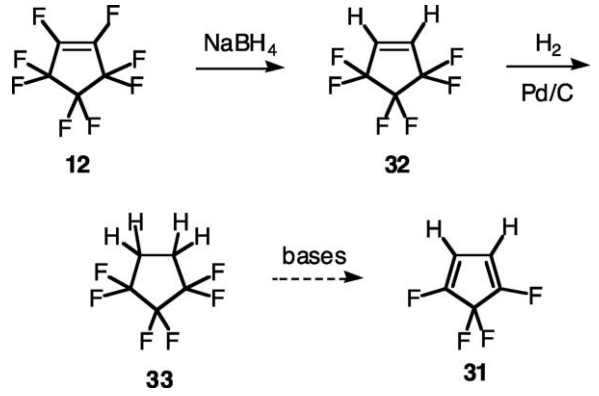


Scheme 5.

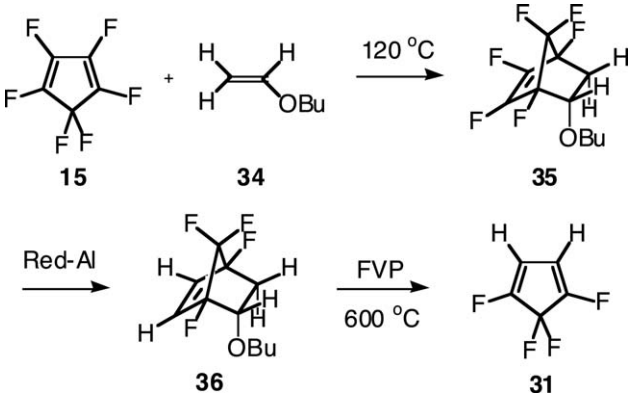
Diels–Alder reaction with dimethyl azodicarboxylate would afford the adduct **25**, obtained earlier in unacceptably low yield by borohydride reduction of **16**. Diene **31** was approached initially via the three-step route shown in Scheme 6.

Borohydride reduction of octafluorocyclopentene (**12**) proceeded in quantitative yield, giving **32**, and catalytic hydrogenation of this alkene smoothly afforded hydrofluorocarbon **33**. However, treatment of **33** with a variety of bases under several sets of conditions failed to produce a detectable amount of the desired diene. In some experiments **33** was passed over hot alumina in the vapor phase, while in others it was bubbled in a stream of nitrogen through molten potassium hydroxide or a hexane solution of LDA or lithium tetramethylpiperidide.

Consequently, the decision was made to generate diene **31** via a retro-Diels–Alder reaction. In a first attempt, tetrafluoronorbornene **30** was subjected to flash vacuum pyrolysis at 630 °C, but the reaction was messy and conversion low. An electron-donor substituent on the dienophilic fragment should facilitate the retro reaction, in light of the electron-deficiency of the diene fragment.[2] Accordingly, *n*-butyl vinyl ether (**34**) was allowed to react with hexafluorocyclopentadiene (**15**) at 120 °C to obtain adduct **35** (Scheme 7). The product was exclusively the endo isomer, as revealed by a $^{1}H–^{19}F$ NOESY experiment. The key interaction in establishing the stereochemistry was a strong one between the proton geminal to oxygen and one of the geminal fluorines. Red-Al replaced the vinyl fluorines in the adduct with hydrogens, giving **36**. Flash vacuum pyrolysis of **36** at 600 °C afforded the diene **31**, which was trapped at liquid nitrogen temperature.

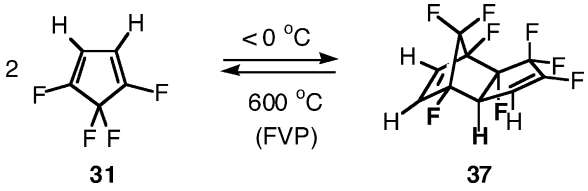


Scheme 6.



Scheme 7.

This compound dimerized to **37** extremely readily, even in the upper portion of the U-trap during the pyrolysis (Eq. (14)). It is far more labile than hexafluorocyclopentadiene (**15**) [9b], a property it shares with other partially fluorinated cyclopentadienes such as **38** and **39** [26].

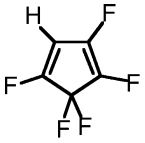


(14)

Whereas the dimer of **15** has the endo configuration [9b], we were surprised to find that the configuration of **37** is exo,[3] as demonstrated by a $^{1}H–^{19}F$ NOESY experiment. The proton shown in bold connected with the two bolded fluorines, but not with a geminal fluorine, as would have been the case were the configuration endo.

[2] Lowering the barrier to adduct formation means lowering the barrier to the retro reaction, with the reasonable assumption that the product energy is not lowered significantly by the donor–acceptor interactions that stabilize the transition state.

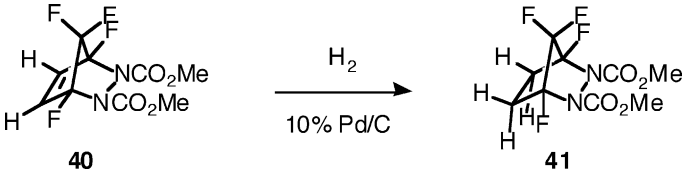
[3] Interestingly, the dimer of tetrafluorocyclopentadienone also has the exo configuration [27].



38

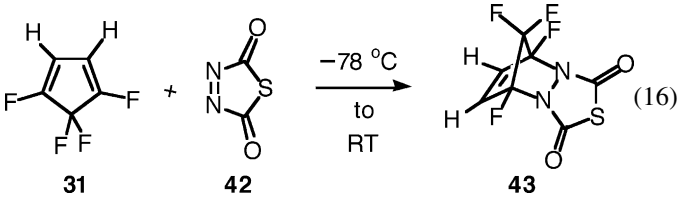
39

Reaction of diene **31** with a 10-fold excess of dimethyl azodicarboxylate afforded less than 5% of the desired Diels–Alder adduct **40**, and a 90% yield of the dimer **37**. Catalytic hydrogenation of **40** gave the saturated adduct **41**, the ^{19}F spectrum of which lacked a signal for the bridgehead fluorines (Eq. (15)). Broadening of that signal into the baseline reveals that conformational interconversion in **41** is faster than in the similar structure **19**, consistent with the greater size of the endo fluorines in **19** relative to the hydrogens in **41**. Given the extremely low yield of adduct **40**, an alternative approach to the bicyclopentane was necessary.



40 41 (15)

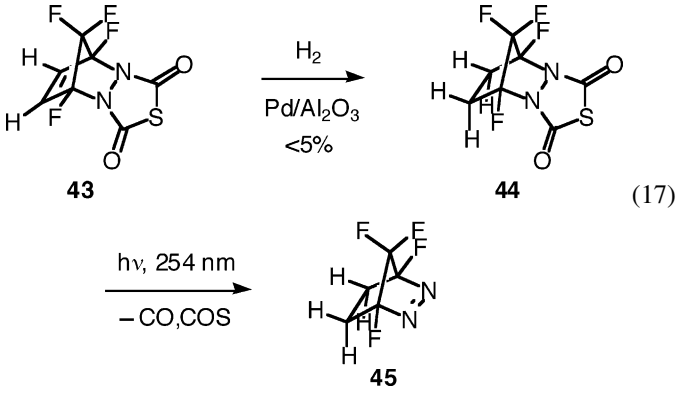
Because 1,2,4-triazolinediones are far more reactive than azoesters, formation of a Diels–Alder adduct with **31** should succeed, but subsequent removal of the heterocyclic ring would require conditions too vigorous for our sensitive ring system [28]. The problem was solved with 1-thia-3,4-diazoline-2,5-dione (**42**) [29]. Diene **31** was introduced into a purple solution of **42** in acetone at −78 °C, and the solution was allowed to warm to room temperature. Diels–Alder adduct **43** formed cleanly, and excess **42** fragmented into nitrogen, carbon monoxide and carbonyl sulfide when the temperature rose above −35 °C (Eq. (16)). In cases like this where cycloaddition occurs at very low temperatures, self-destruction



31 42 43 (16)

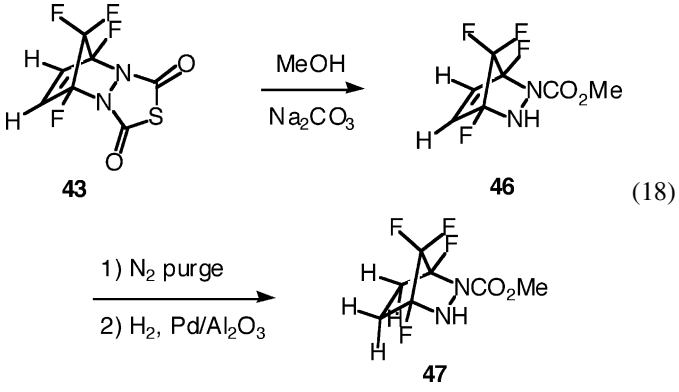
of the thiadiazolinedione is convenient, but with less reactive addends it is a serious limitation. For example, we had not been able to obtain an adduct of this reagent with hexafluorocyclopentadiene (**15**).

Saturation of the C=C double bond of **43** proved to be problematic. Whereas catalytic hydrogenation of the Diels–Alder adduct **40** proceeded smoothly, hydrogenation of **43** failed with several catalysts under a variety of conditions. Diimide and borane either did not react or gave unwanted products, depending upon conditions. Catalytic hydrogenation over a large amount of palladium-on-alumina afforded a tiny (<5%) yield of the reduced adduct **44**. Irradiation of **44** in a quartz vessel with 254 nm light brought about efficient fragmentation into carbon monoxide, carbon oxysulfide and the desired azo compound **45** (Eq. (17)) [30], but it was necessary to find a better route to this key compound.



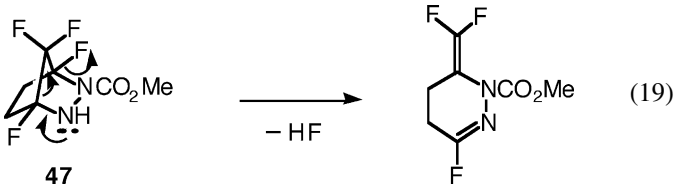
43 44 45 (17)

It was clear that the problem with catalytic hydrogenation was catalyst poisoning by the sulfur in the adduct **43**. Thus, the sulfur had to be excised, but without making the unsaturated azo compound, which would instantly fragment [31]. Corey and Snider found that 1-thia-3,4-diazolidine-2,5-dione rings open at ambient temperature in methanol containing sodium carbonate with loss of carbonyl sulfide, yielding methyl hydrazinecarboxylates [32]. Their procedure worked well on adduct **43**, giving **46** (Eq. (18)).



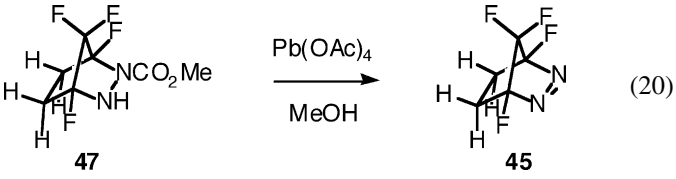
43 46 47 (18)

This compound was extremely labile, decomposing even upon removal of the solvent at −15 °C. The reaction mixture was therefore immediately purged with nitrogen to expel dissolved carbonyl sulfide, then hydrogenated over palladium-on-carbon in the methanol solvent, affording **47**. Somewhat more stable than **46**, compound **47** was nonetheless very sensitive. Degradation of the heterocyclic ring had considerably increased the nucleophilicity of the NH nitrogen in these molecules, probably resulting in fragmentation as shown for **47** in Eq. (19), a first step in decomposition.



(19)

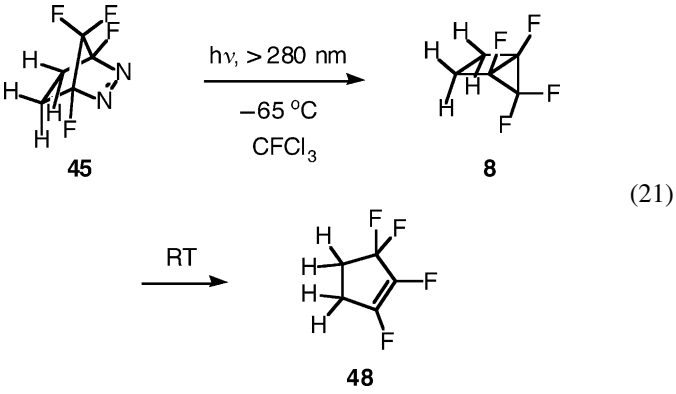
An attempt to cleave the *O*-methyl bond in **47** with iodotrimethylsilane destroyed the molecule. Using lead tetraacetate, Dreiding had accomplished oxidative scission of a methoxycarbonyl group from a triazane nitrogen, generating a N=N double bond [33]. That method worked smoothly at room temperature with **47** to give azo compound **45** (Eq. (20)).



(20)

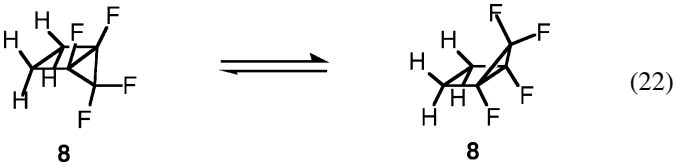
A likely pathway for this transformation is shown in Scheme 8.

Photolysis of azo compound **45** was carried out at −65 °C in a pyrex vessel. Unlike azo compound **21**, **45** photolyzed readily to give bicyclopentane **8**, albeit in low yield (Eq. (21)).



(21)

Upon warming to RT, **8** isomerized slowly to tetrafluorocyclopentene **48**. The ^{19}F NMR spectrum of **8** at −65 °C comprised a sharp singlet at δ −163.8 representing the bridgehead fluorines and a very broad singlet at δ −128.1 corresponding to the geminal fluorines, indicating that ring inversion was occurring at an intermediate exchange rate on the NMR time scale at this temperature (Eq. (22)). As the temperature was lowered, the latter signal further broadened and disappeared into the baseline, not to reappear even at −110 °C, the melting point of the solvent.



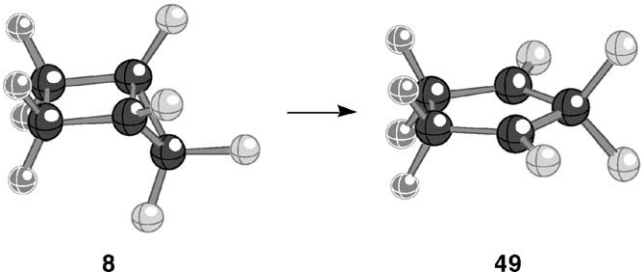
(22)

When the experiment was repeated in dichlorodifluoromethane (mp −158 °C), broad signals corresponding to the individual geminal fluorines emerged by −150 °C at δ −119.8 and −136.1.

From simulation of the spectra as a function of temperature [34], the free energy of activation for ring inversion was determined to be $\Delta G^{\ddagger} = 6.8 \pm 0.2$ kcal/mol (−55 °C). We initially assumed that this value represents an upper limit for the free energy of cleavage of the central bond of bicyclopentane **8**, as is the case for the inversion barrier of the parent bicyclopentane (**5**). However, theoretical calculations point to a different conclusion.

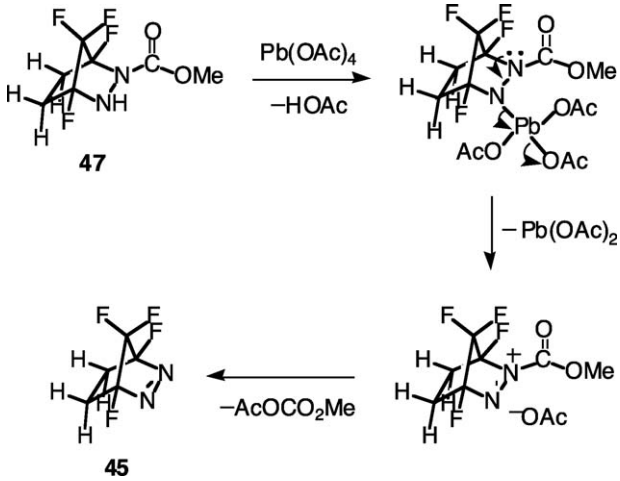
2.4. Theoretical considerations

We examined the ring opening of bicyclopentane **8** at the B3LYP/G-311 + G** level of density functional theory [16]. The calculated activation parameters are: $\Delta G^{\ddagger} = 8.92$ kcal/mol (25 °C), $\Delta G^{\ddagger} = 8.47$ kcal/mol, and $\Delta S^{\ddagger} = -1.53$ cal/mol K. Agreement of theory with experiment is quite good, with the experimental free energy of activation lower by 2 kcal/mol.



(23)

Bicyclopentane **8** is strongly bent, with a flap angle of 62.8° and a central C–C bond distance of 1.59 Å (Eq. (22)). The transition state for inversion (**49**) has C_{2v} symmetry, but the planar carbon skeleton is strongly distorted from regular pentagonal geometry (Fig. 3). Indeed, the distance between C_1 and C_4 is only 2.15 Å (cf. cyclopentane, 2.48 Å).



Scheme 8.

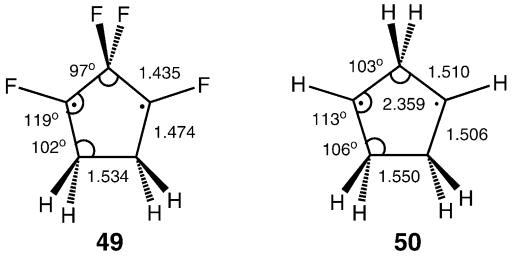
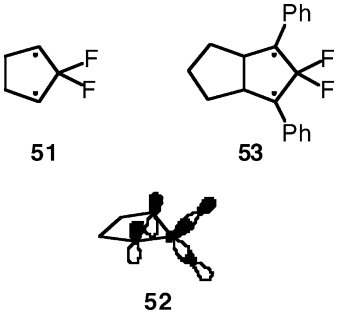


Fig. 3. Calculated bond distances (Å) and angles in two C_{2v} structures, transition state **49** and biradical **50** [35].

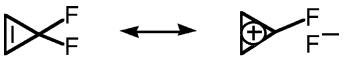
High level ab initio calculations by Schaefer et al. indicate that the potential energy surface for the parent bicyclopentane near the top of the inversion barrier is very complex, having several stationary points [35]. The transition state (C_s) is reached before the molecule has flattened completely, but the planar C_{2v} structure **50** (Fig. 3) that leads directly to the invertomer lies only 0.7 kcal/mol below it. The distance between the formerly bonded carbons in **50** is 2.36 Å, much longer than in transition state **49**.

Understanding this contrast requires consideration of through-space and through-bond interactions between those carbons in both species. Modeling through-space interaction in **50**, Goldberg and Dougherty [36] calculated that for two π-oriented methyl radicals separated by 2.37 Å, the singlet state lies 7.2 kcal/mol below the triplet. Thus, even at that long distance, π overlap lowers the symmetric (S) formally nonbonding orbital and raises the antisymmetric (A) one considerably. The triplet state corresponding to **50** is actually the ground state of the biradical ($\Delta S_{ST} = \sim 1$ kcal/mol), however, because there is a countervailing through-bond interaction [35–40]. The S, but not the A orbital is raised by mixing with the intervening CH_2 σ orbital of π symmetry, narrowing the S–A separation and thus inverting the singlet–triplet gap.

In **49** the through-bond interaction is very different because of fluorine's electronegativity: the dominant interaction of the S orbital is with the CF_2 σ^*, not the σ orbital, with π symmetry. Borden predicted that this interaction in 2,2-difluoro-1,3-cyclopentanediyl (**51**), depicted in **52**, would lower the S orbital sufficiently to make the ground state of this biradical singlet [41]. Adam et al. have confirmed that prediction for the phenyl-substituted derivative **53** [42].



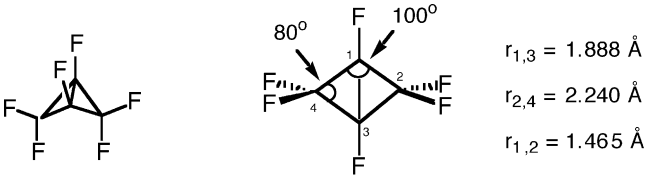
In the transition state **49** we have calculated for inversion of **8**, the stabilizing influence recognized by Borden is enhanced by the relatively large through-space interaction, as the resulting cyclic 3-center, 2-electron interaction formally resembles the aromatic cyclopropenium ion. A closer analogue is 3,3-difluorocyclopropene (**54**), in which this kind of aromatic interaction was recognized long ago by Greenberg et al. [43]. In a forthcoming theoretical paper, Borden et al. offer further insight into the inversion of **8** and other bicyclopentanes [44].



54

The difference in ring inversion barriers between **8** and the parent system (**5**) of ca. 31 kcal/mol testifies to the potency of the fluorine substituent effect, but it is now clear that this effect is a composite one, not solely the consequence of enhanced ring strain in the bicyclopentane. For the bicyclopentane–cyclopetene rearrangement, the difference in barrier heights for endo-**7** versus the parent molecule is ca. 24 kcal/mol. A part of the roughly 7 kcal/mol difference between these differences may reflect greater strength of the central bond in endo-**7** as compared with **8**, but the larger share is presumably attributable to the retention of some C_1–C_4 bonding in the ring inversion transition state and perhaps also greater reluctance of fluorine to migrate in a 1,3-biradical as compared with hydrogen.

Finally, it is interesting to compare the ring inversion of bicyclo[2.1.0]pentane **8** with that predicted for the unknown hexafluorobicyclo[1.1.0]butane (**55**). The parent bicyclobutane does not undergo ring inversion, but opens instead to butadiene at high temperatures ($E_a = 40.58$ kcal/mol, $\log A = 14.02$) [45]. At the level of density functional theory employed with **8** above, ring inversion of **55** is characterized by these activation parameter values: $\Delta G^{\ddagger} = 4.15$ kcal/mol (25 °C), $\Delta H^{\ddagger} = 3.05$ kcal/mol, and $\Delta S^{\ddagger} = -3.70$ cal/mol K. If theory slightly exaggerates the barrier height here as it does for bicyclopentane **8**, the barrier for **55** will be almost nonexistent!

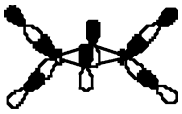


55 **56**

The geometry calculated for the transition state **56** is quite revealing, as the distance between C_1 and C_3 in this planar species is only 1.89 Å, just 0.2 Å longer than their bond in **55** (1.69 Å). Clearly, considerably more bonding is retained in transition state **56** than in **49**. In **56**, the electrons of the C_1–C_3 bond enjoy delocalization into a C–F σ^* orbital encompassing both C_2 and C_4, as shown in **57**.[4] Thus, we predict that extreme strain in the bicyclobutane and special stabilization of the

[4] This kind of interaction is very strong in 2,2,4,4-tetrafluorocyclobutane-1,3-diyl [46].

transition state will conspire to make the bicyclobutane flap its wings with astonishing ease.



57

3. Conclusions

endo, *cis*-1,2,3,4,5,5-Hexafluorobicyclo[2.1.0]pentane (**7**) has been synthesized in eight steps from hexafluorobenzene. It rearranges to *cis*-1,2,3,3,4,5-hexafluorocyclopentene (**22**) with $E_a = 21.9$ kcal/mol, $\log A = 13.4$. Compound **7** readily cycloadds in [4 + 2] fashion to furan and cyclopentadiene. Owing to the lability of various synthetic intermediates, several different synthetic approaches were explored before success was achieved in synthesizing 1,4,5,5-tetrafluorobicyclo[2.1.0]pentane (**8**) in 11 steps from hexafluorobenzene. This molecule undergoes degenerate ring inversion with $\Delta G^{\ddagger} = 6.8 \pm 0.2$ kcal/mol (−55 °C). Both the rearrangement barrier for **7** and the ring inversion barrier for **8** are far lower than the corresponding barriers for the parent hydrocarbon, signifying dramatic weakening of the central bond in these molecules by fluorine substitution. Density functional calculations indicate that some 1,4-bonding is retained in the ring inversion transition state for **8**, and they predict for the unknown hexafluorobicyclo[1.1.0]butane both a lower ring inversion barrier and greater bonding between the bridgehead carbons in the transition state.

4. Experimental

NMR spectra were recorded on a Varian Unity Plus 300 or 500 FT NMR spectrometer. ^{1}H and ^{13}C NMR chemical shifts are based on internal tetramethylsilane, and ^{19}F NMR chemical shifts on internal trichlorofluoromethane as reference. GC/MS measurements were made on a Hewlett-Packard 5890 Series II instrument. Infrared spectra were taken on a Perkin-Elmer 1600 Series FTIR spectrometer, and ultraviolet spectra on a Hewlett-Packard 8451A Diode Array spectrometer. Preparative GLC was done with a Hewlett-Packard 5750 chromatograph using a thermal conductivity detector and a $1/4'' \times 10'$ column packed with 10% OV–101 Chromosorb AW DMCS. Vacuum transfers were carried out from room temperature to −196 °C unless noted otherwise. Melting points were determined in open capillary tubes on a Thomas–Hoover capillary melting point apparatus and are uncorrected.

Pyrolysis apparatus was constructed from three concentric pyrex, vycor or quartz tubes, depending upon temperature requirements. The innermost tube carried the vapor to be pyrolyzed, the middle tube was wrapped with a coil of chromel wire (22 gauge, 1 Ω/ft.) heated with a variac, and the outer tube was wrapped with insulation. Furnace cement at the ends held the outer tubes in place, and glass or quartz wool plugs inhibited air flow around the removable inner tube. A J thermocouple mounted between the inner and middle tubes in the center of the heated zone was monitored with a 1000 °C temperature readout (Omega Engineering).

Elemental analyses were done by Atlantic Microlab, Inc., Atlanta, GA. High resolution mass spectra were obtained from the Mass Spectrometry Center, University of Massachusetts, Amherst, MA. Compounds were prepared under nitrogen, unless otherwise indicated, and all solvents and reagents were reagent grade.

4.1. 1,2,4,5,6,7-Hexafluoro-3-oxatricyclo[3.2.0.0^{2,4}]hept-6-ene

Into a 2-L three-necked round-bottom flask equipped with mechanical stirrer, gas inlet and gas outlet, was added 800 mL acetonitrile and 80 mL water. The mechanical stirring was started and the solution was cooled to −13 °C by an ethylene glycol/dry ice bath. The solution was flushed with nitrogen for 10 min, and then a fluorine (30% in helium) stream was bubbled through. Excess fluorine was destroyed by passage through an aqueous potassium hydroxide bath. After 1.5 h, a small sample of the solution (0.50 mL) was allowed to react with excess potassium iodide (more than 0.50 g). About 20 mL water was added followed by several drops of starch solution. The solution was titrated with sodium thiosulfate (0.10 M), and the end point was indicated by the disappearance of blue color. From the amount of sodium thiosulfate consumed (6 mL), the concentration of hypofluorous acid acetonitrile complex was calculated as 0.60 M. An acetonitrile solution of perfluorodewarbenzene (37.0 g, 199 mmol, with 12.4 g perfluorobenzene in about 100 mL acetonitrile) was added quickly and the solution was stirred at 0 °C. After 1 h, the reaction reached completion as revealed ^{19}F NMR spectra. The reaction mixture was poured into 1100 mL water, extracted with 1,2,4-trichlorobenzene (4× 100 mL), washed with water (4× 500 mL), dried with anhydrous sodium sulfate and vacuum transferred (40 mTorr) to give 44.8 g colorless liquid containing the epoxide, perfluorobenzene and a small amount of diepoxide. By ^{19}F NMR, the epoxide comprised 61% of the mixture, corresponding to a yield of 68%. ^{19}F NMR ($CDCl_3$): δ −117.7 (s, vinyl F, 2F), −163.0 (s, perfluorobenzene, 6F), −171.8 (s, CFO, 2F), −194.0 (s, bridgehead-F, 2F). MS *m/e*: 202 (M^+), 174 ($C_5F_6^+$), 155 ($C_5F_5^+$), 124 ($C_4F_4^+$), 93 ($C_3F_3^+$).

4.2. 1,2,4,5,6,6,7,7-Octafluoro-3-oxatricyclo[3.2.0.0^{2,4}]heptane (**10**)

The unsaturated epoxide (2.0 g, 10 mmol, containing 2.0 g perfluorobenzene) was placed in a 250 mL three-neck round-bottom flask equipped with a dry ice condenser, a mechanical stirrer and a gas inlet. After about 60 mL dichlorodifluoromethane was condensed in the flask cooled at −78 °C, the gas inlet was replaced with a jet that extended below the surface of the liquid. The reaction mixture was flushed with nitrogen for 10 min, then fluorine (30% in helium) was bubbled through the solution slowly with good stirring. After 4 h, ^{19}F NMR showed that all starting material had been consumed and the target

compound was the main component. The solvent was removed by evaporation through a 30-cm low temperature fractionating column and condensed in a steel cylinder cooled in a dry ice/acetone bath. A stream of nitrogen was passed through a copper coil cooled by liquid nitrogen, a temperature-controlled heater and the jacket surrounding the column. The nitrogen temperature was maintained at about −30 °C. After evaporation of the dichlorodifluoromethane, the remaining liquid was washed out with 1,2,4-trichlorobenzene (2× 5 mL) and vacuum transferred. Compound **10** was isolated together with perfluorobenzene and a small amount of the Freon **12** as a pale yellow liquid (2.7 g, purity 48%, yield 54%). Separation of **10** from the benzene was attempted by preparative GC, but it decomposed on the column. ^{19}F NMR ($CDCl_3$): δ −6.60 (s, Freon 12, 2F), −115.3, −129.4 (AB q, J = 231 Hz, CF_2,4F), −162.1 (s, perfluorobenzene, 6F), −178.4 (s, CFO, 2F), −196.6 (s, bridgehead-F, 2F).

4.3. Decarbonylation of epoxide *10*

A small amount of **10** in perfluorobenzene (1:1) and antimony pentafluoride were combined in an autoclave, which was shaken at 90 °C for 7 h. The volatiles were vacuum transferred into a NMR tube containing $CDCl_3$. ^{19}F NMR showed mainly perfluorocyclopentene (**12**) and perfluorobenzene (1:2.1). Yield 67%. ^{19}F NMR ($CDCl_3$): δ −117.5 (s, 3,5-F, 4F), −129.6 (s, 4-F, 2F), −148.8 (s, vinyl-F, 2F), −162.3 (s, C_6F_6, $_6$F).

4.4. Hexafluoro-2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (*16*)

In a 20 mL pressure tube with a threaded Teflon stopper was placed a solution of 3.00 g (20.4 mmol) of dimethyl azodicarboxylate in 5 mL of benzene. The solution was exposed to filtered UV irradiation (filter plate Corning C.S. no. 0–53) from a 450 W Hanovia medium pressure mercury lamp for 2 h. Then 1.44 g (8.3 mmol, 0.9 mL) of perfluorocyclopentadiene was added. The tube was totally immersed in an oil bath heated to 100 °C and irradiation was continued for another 1.5 days. After the solvent was roto-evaporated, the yellow product was treated with 6 g activated basic alumina to decompose excess dimethyl azodicarboxylate. The alumina–product mixture was placed on a silica gel (30 g) column and eluted with ether, yielding an oil (0.89 g, 2.7 mmol, 33%). The low yield of this reaction was due to the dimerization of perfluorocyclopentadiene. ^{1}H NMR ($CDCl_3$): δ 3.92. ^{19}F NMR ($CDCl_3$): δ −135.2 (d, J = 167 Hz, geminal F), −148.7 (d, J = 167 Hz, geminal F), −144.7 (br m, vinyl F), −181.1(s, bridgehead F). ^{13}C NMR ($CDCl_3$, CF_2 ^{19}F decoupled): δ 156.1 (CO), 135.1 (vinyl, $^1J_{CF}$ = 281 Hz), 117.6 (methylene), 97.9 (bridgehead, $^1J_{CH}$ = 269 Hz), 55.3 (CH_3, $^1J_{CH}$ = 149 Hz). IR (neat, cm^{-1}): 2964 (CH), 1755 (br s C=O and CF=CF). GC–MS (EI): m/z 320 (M^+), 289 ($C_8F_6H_3N_2O_3^+$), 276 ($C_8F_6H_6N_2O_2^+$), 174 (C_5F_6 +), 124 ($C_4F_4^+$), 93 ($C_3F_3^+$), 59 ($C_2H_3O_2^+$, base). HRMS (EI): calcd for $C_9H_6F_6N_2O_4$ (M^+) 320.0232, found 320.0236.

4.5. cis-1,4,5,6,7,7-Hexafluoro-2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylic acid dimethyl ester (*19*)

To a heavy-walled hydrogenation bottle were added 0.85 g (2.6 mmol) of **16** in 10 mL of methanol and 0.08 g of 10% Pd on carbon. The bottle was fixed on a Parr hydrogenation apparatus, and evacuated and flushed with H_2 three times. The solution was agitated under 4 atm of H_2 for 3 days. After filtration and roto-evaporation, the residual solid was recrystallized with ether, yielding 0.78 g of white crystals (91%, mp 132.5–133.5 °C). ^{1}H NMR ($CDCl_3$): δ 3.89 (s, CH_3, 3H), 3.87 (s, CH_3, 3H), 5.28 (br t, J = 60 Hz, CFH, 2H). ^{19}F NMR ($CDCl_3$) major conformer: δ −139.4 (d, J = 217 Hz, CF_2, area 6), 147.6 (d, J = 217 Hz, CF_2, area 6), −172.0 (s, bridgehead F, area 6), −179.4 (s, bridgehead F, area 6), −222.9 (d, J = 50 Hz, CHF, area 6), −223.8 (d, J = 50 Hz, CHF, area 6); minor conformer: −140.8 (d, J = 217 Hz, CF_2, area 1), −147.2 (d, J = 217 Hz, CF_2, area 1), −172.3 (s, bridgehead F, area 1), −178.5 (s, bridgehead F, area 1), −222.9 (d, J = 50 Hz, CHF, area 1), −223.0 (d, J = 50 Hz, CHF, area 1). ^{13}C NMR ($CDCl_3$, ^{19}F decoupled): δ 155.03 (s, CO), 154.99 (s, CO), 113.4 (s, methylene), 113.3 (s, methylene), 99.1 (s, bridgehead), 98.7 (s, bridgehead), 84.0 (t, J_{CH} = 181 Hz, CHF), 83.6 (t, J_{CH} = 181 Hz, CHF), 55.2 (q, J_{CH} = 148 Hz, CH_3), 54.6 (q, J_{CH} = 148 Hz, CH_3). IR (neat, cm^{-1}): 2962 (CH_3), 1727 (vs, CO), 1518, 1445, 1360, 1228 (vs). GC–MS (EI): m/z 322 (M^+), 278, 258, 219, 214, 169, 155 (base), 59. Anal. Calcd for $C_9H_8F_6N_2O_4$: C, 33.50; H, 2.50; F, 35.38; N, 8.70. Found: C, 33.63; H, 2.57; F, 35.39; N, 8.78.

4.6. cis-1,4,5,6,7,7-Hexafluoro-2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylic acid trimethylsilyl ester

In a 20 mL pressure tube were quickly placed 0.50 g (1.6 mmol) of **19** in 3 mL of CH_2Cl_2, 0.62 g (3.1 mmol) of iodotrimethylsilane and a stir bar. The tube was then sealed and fully immersed in an oil bath. The reaction mixture was stirred and heated at 80 °C for 2 days. After transfer to a round-bottomed flask, the resulting solution was freed of CH_2Cl_2 and CH_3I at reduced pressure. Silyl ester (0.61 g, 1.4 mmol, 92%) was obtained as a moisture-sensitive oil comprising a mixture of stereoisomers. ^{19}F NMR ($CDCl_3$): δ −139.7 (m, geminal F, 1F), −146.8 (m, geminal F, 1F), −172.0 to −180.7 (ms, bridgehead F, 2F), −220.3 (m, CHF, 1F), −222.9 (m, CHF, 1F).

4.7. cis-1,4,5,6,7,7-Hexafluoro-2,3-diazabicyclo[2.2.1]heptane (*20*)

In a round-bottomed flask connected to a N_2 bubbler and equipped with a magnetic stir bar were added 0.61 g (1.4 mmol) of the trimethylsilyl ester and 52 mg (2.9 mmol) of water. The reaction was spontaneous. Then a quick vacuum transfer (2 Torr) removed the hexamethyldisiloxane byproduct. A second vacuum transfer (40 mTorr) yielded 0.23 g (1.1 mmol, 79%) of the solid hydrazine **20**. ^{1}H NMR ($CDCl_3$):

δ 5.21 (dq, J = 55 Hz, 3.3 Hz, 2H, CFH), 4.83 (br s, 2H, NH). ^{19}F NMR ($CDCl_3$): δ −145.1 (d, J = 229 Hz, 2F, CF_2), −148.8 (d, J = 229 Hz, 2F, CF_2), −177 (br s, 2F, bridgehead F), −225.4 (d, J = 55 Hz, 2F, CHF). When the hydrazine is thoroughly dry, the bridgehead F peak is too broad to observe, but it becomes sharp when the hydrazine is wet. GC–MS (EI): *m/z* 206 (M^+, base), 186, 157, 142, 113, 97, 79, 69, 51, 46.

4.8. *cis-1,4,5,6,7,7-Hexafluoro-2,3-diazabicyclo[2.2.1]hept-2-ene (**21**)*

To a round-bottomed flask equipped with a stir bar were added 0.23 g (1.1 mmol) of **20** dissolved in 1.5 mL of CH_2Cl_2 and 0.98 g (4.5 mmol) of yellow HgO. After the mixture was stirred for 6 h, it was vacuum-transferred (40 mTorr) to obtain the azo compound (**21**) in CH_2Cl_2. The azo compound was purified by preparative gas chromatography (inj. 110 °C, col. 40 °C, det. 110 °C) to give white needles (0.17 g, 0.83 mmol 74%, mp 27.5–28.0 °C). ^{1}H NMR ($CDCl_3$): δ 5.34 (subsplit d, J = 50 Hz, 2H, CFH). ^{1}H NMR (C_6D_6): δ 3.89 (subsplit d, J = 50 Hz, 2 H, CFH). ^{19}F NMR ($CDCl_3$): δ −134.1 (d, J = 214 Hz, 1F, CF_2), −147.8 (d, J = 214 Hz, 1F, CF_2), −177.2 (s, 2F, bridgehead F), −223.2 (d, J = 50 Hz, 2F, CFH). ^{13}C NMR (CD_2Cl_2, geminal and bridgehead ^{19}F-decoupled): δ 124.1 (CF_2), 113.5 (bridgeheads), 83.3 (CHF, J_{CF} = 224 Hz, J_{CH} = 160 Hz). UV λ_{max} (nm): 352.6 (384), 336.2 (128), 321.4 (29). IR (neat, cm^{-1}): 2998 (CH), 1484 (N=N), 1380, 1335, 1260, 1043, 968, 859. MS (EI): *m/z* 204 (M^+), 176, 157, 147, 137, 126 (base), 113, 107, 93, 75, 69, 57, 46. HRMS (EI): calcd for $C_5H_2F_6N_2$ (M^+) 204.0122, found 204.0128.

4.9. *endo,cis-1,2,3,4,5,5-Hexafluorobicyclo[2.1.0]pentane (endo-**7**)*

In an annular reactor (height 100 mm, internal diameter 75 mm, chamber width 5mm) was placed 56 mg (0.27 mmol) of azo compound **21** in 50 mL of $CFCl_3$. The annular reactor was immersed in a Dewar flask containing methanol cooled to −20 °C by cold isopropanol (−36 °C) circulating from a refrigerated bath through a copper coil surrounding the reactor. An assembly comprising a 450 W medium pressure Hanovia mercury lamp in a quartz immersion well contained in a cylindrical pyrex vessel was mounted in the Dewar so that the annular reactor was aligned with the center of the lamp arc. Irradiation was continued until all the azo compound had reacted (3d), giving endo-**7**. ^{1}H NMR ($CFCl_3$): δ 5.69 (subsplit d, J = 55 Hz, 2H, CFH). ^{19}F NMR ($CFCl_3$): δ −127.9 (d, J = 181 Hz, 1F, CF_2), −144.9 (d, J = 181 Hz, 1F, CF_2), −195.2 (d, J = 55 Hz, 2F, CHF) −196.5 (d, J_{HF} = 33 Hz, 2F, bridgehead Fs).

4.10. *cis-1,2,3,3,4,5-Hexafluorocyclopentene (**22**)*

When endo-**7** was allowed to warm up, it isomerized to *cis*-1,2,3,3,4,5-hexafluorocyclopentene (**22**) [17]. ^{1}H NMR (C_6D_6): δ 4.11 (subsplit d, J = 57 Hz, 1H, H_5), 3.78 (subsplit d, J = 49 Hz, 1H, H_4). ^{19}F NMR (C_6D_6): δ −108.5, −110.0 (AB q, J = 252 Hz, 2F, CF_2), −137.9 (s, 1F, vinyl F_2), −153.9 (s, 1F, vinyl F_1), −197.6 (d, J = 57 Hz, 1F, F_5), −214.7 (d, J = 49 Hz, 1F, F_4).

4.11. *3,3,4,4,5,5-Hexafluorocyclopentene (**32**) [47]*

In a 50 mL round-bottomed flask cooled in an ice/water bath and equipped with a magnetic stir bar were placed 3.0 g (14 mmol) of octafluorocyclopentene (**12**) [48], 20 mL of dry diglyme (distilled from lithium aluminum hydride) and 0.82 g (22 mmol) of $NaBH_4$. The solution was stirred for 30 min and then vacuum transferred at 6 Torr to obtain 2.4 g (14 mmol, 99%) of colorless liquid 3,3,4,4,5,5-hexafluoropentene. ^{19}F NMR ($CDCl_3$): δ −110.4 (s, F3, F5, 4F), −133.2 (s, F4, 2F).

4.12. *1,1,2,2,3,3-Hexafluorocyclopentane (**33**) [49]*

To a heavy-walled hydrogenation bottle were added 2.00 g (11.3 mmol) of 3,3,4,4,5,5-hexafluoropentene (**32**) in 15 mL of dry diglyme (distilled from lithium aluminum hydride) and 0.10 g of 10% Pd on carbon. The bottle was mounted on a Parr hydrogenation apparatus and flushed with H_2. The solution was agitated under 4 atm of H_2 for 1 day and then vacuum transferred at 6 Torr to obtain 2.01 g (11.3 mmol, 99%) of colorless liquid 1,1,2,2,3,3-hexafluoropentane. ^{1}H NMR ($CDCl_3$): δ 1.93 (s, CH_2, 4H). ^{19}F NMR ($CDCl_3$): δ −115.3 (s, F1, F3, 4F), −136.9 (s, F2, 2F).

4.13. *1,2,3,4,7,7-Hexafluorobicyclo[2.2.1]hept-2-ene (**27**) [22]*

In a 50 mL monel bomb equipped with a valve was placed 3.5 g (20 mmol) of freshly made perfluorocyclopentadiene (**15**). The bomb was sealed, cooled in liquid nitrogen, and ethylene (3.5 g, 125 mmol) was condensed into it. After warming to room temperature, the bomb was immersed in an oil bath heated to 160 °C. After 2.5 days, 3.7 g (18 mmol, 90% yield) of liquid 1,2,3,4,7,7-hexafluorobicyclo[2.2.1]hept-2-ene was obtained. bp 107–108 °C. ^{1}H NMR ($CDCl_3$): δ 2.43 (m, CH_2, 2H), 2.14 (m, CH_2, 2H). ^{19}F NMR ($CDCl_3$): δ −144.3 (s, geminal F, 2F), −158.4 (s, vinyl F, 2F), −206.9 (s, bridgehead F, 2F). GC–MS (EI): *m/z* 202 (M^+), 181, 163, 152, 133 (base), 124, 113, 101, 93, 83, 69, 57.

4.14. *1,4,7,7-Tetrafluoro-2,3-dimethylbicyclo[2.2.1]hept-2-ene (**28**)*

In a 50 mL three-necked round-bottomed flask equipped with a reflux condenser connected to a nitrogen bubbler, a septum, a dropping funnel and a magnetic stir bar was placed 2.5 g (13 mmol) of CuI and 5 mL of anhydrous ether. Methyllithium in ethyl ether (18 mL, 1.5 M, 27 mmol) was introduced into the flask through the septum via a syringe at RT. The slurry was stirred for 0.5 h, then cooled in an ice/water bath. 1,2,3,4,7,7-Hexafluorobicyclo[2.2.1]hept-2-ene

(0.50 g, 2.5 mmol) in 5 mL of anhydrous ether was added dropwise from the dropping funnel with stirring. The initial reaction was exothermic. The slurry was stirred for another 50 h at room temperature, then cooled in an ice/water bath and acidified with 10 mL of 6 M HCl. The ether layer was separated, washed with saturated NaCl aqueous solution twice, and dried over sodium sulfate. After removal of sodium sulfate, the ether was distilled through a Vigreux distilling column. The product was vacuum transferred at 4 Torr and further purified by GC separation (column temperature 30 °C). The product was obtained as a colorless liquid (112 mg, 23%). ^{1}H NMR ($CDCl_3$): δ 1.75 (br s, CH_2, 4H), 1.58 (s, CH_3, 6H). ^{19}F NMR ($CDCl_3$): δ −137.1 (d, J = 168 Hz, CF_2, 1F), −155.2 (d, J = 168 Hz, CF_2, 1F), −202.1 (s, bridgehead Fs, 2F). GC–MS (EI): m/z 194 (M^+), 179, 166, 151, 143 (base), 129, 116, 109, 97, 77, 69, 51. HRMS (EI): calcd for $C_9H_{10}F_4$ (M^+) 194.0719, found 194.0737.

4.15. 1,4,7,7-Tetrafluorobicyclo[2.2.1]hept-2-ene (30)

Red-Al (2.00 g of 65% toluene solution, 6.4 mmol) was placed in a round-bottomed flask with 5 mL of dry triglyme (distilled over lithium aluminum hydride). The toluene was then removed by vacuum transfer to obtain a Red-Al/triglyme solution, which was placed in a dropping funnel. A three-necked round-bottomed flask containing 0.50 g (2.5 mmol) of **27** in 3 mL of dry triglyme was equipped with the dropping funnel, a stir bar and connection to a nitrogen bubbler. It was cooled in an ice/water bath. The Red-Al/triglyme solution was added dropwise with stirring during 20 min and the stirring was continued at RT for another 2 h. 1,4,7,7-Tetrafluorobicyclo[2.2.1]hept-2-ene (**30**) (0.37 g, 89%) was obtained as a colorless liquid after vacuum transfer. ^{1}H NMR ($CDCl_3$): δ 6.34 (m, vinyl H, 2H), 1.76 (m, CH_2, 2H), 1.53 (m, CH_2, 2H). ^{19}F NMR ($CDCl_3$): δ −136.6 (d, J = 170 Hz, CF_2, 1F), −155.2 (d, J = 170 Hz, CF_2, 1F), −196.7 (s, bridgehead Fs, 2F). GC–MS (EI): m/z 166 (M^+), 165, 151, 145, 138, 127, 116, 115, 97 (base), 88, 69, 65, 57, 51. HRMS (EI): calcd for $C_7H_6F_4$ (M^+) 166.0406, found 166.0411.

4.16. Ozonolysis of 1,4,7,7-tetrafluorobicyclo[2.2.1]hept-2-ene (30)

Alkene **30** (33 mg, 0.20 mmol) in 0.6 mL of CD_2Cl_2 was placed in an NMR tube capped with a septum and cooled in an isopropanol/dry ice bath. A long needle that reached the bottom of the NMR tube and a short needle that was connected to a nitrogen bubbler were introduced through the septum. An O_3/O_2 stream was passed through the solution for 2 min via the long needle at a rate of ca. 1 bubble/s, and unreacted gas was released via the short needle. The ^{19}F NMR spectrum of the reaction solution, measured immediately at −50 °C, revealed a new compound, presumably the ozonide **31**. ^{19}F NMR (CD_2Cl_2): δ −134.6, −135.9 (AB q, J = 206 Hz, geminal Fs, 2F), −204.6 (s, bridgehead Fs, 2F). The ozonide decomposed within 5 min at −50 °C.

4.17. endo-5-Butoxy-1,2,3,4,7,7-hexafluorobicyclo[2.2.1]hept-2-ene (35)

Freshly made perfluorocyclopentadiene (**15**, 3.0 g, 18 mmol), *n*-butyl vinyl ether (**34**, 7.2 g, 72 mmol) and basic alumina (0.30 g) were placed in a 50 mL monel bomb equipped with a stir bar. The bomb was sealed and immersed in an oil bath heated to 120 °C with stirring. After 1.5 days the reaction product was dissolved in 8 mL of tetraglyme and vacuum transferred to give **35** as a colorless liquid (3.9 g, 14 mmol, 83%). ^{1}H NMR (CD_2Cl_2): δ 4.40 (m, CHOBu, 1H), 3.53 (m, OCH_2, 2H), 2.70 (m, CH_2, 1H), 2.00 (m, CH_2, 1H), 1.52 (quintet, J = 8Hz, CH_2, 2H), 1.34 (sextet, J = 8 Hz, CH_2, 2H), 0.92 (t, J = 8 Hz, CH_3, 3H). ^{19}F NMR (CD_2Cl_2): δ −133.6 (d, J = 182 Hz, CF_2, 1F), −146.8 (d, J = 182 Hz, CF_2, 1F), −153.0 (s, vinyl F, 1F), −157.8 (s, vinyl F, 1F), −204.9 (s, bridgehead F, 1F), −209.3 (s, bridgehead F, 1F). ^{13}C NMR (CD_2Cl_2, ^{19}F-decoupled): δ 132.9 (s, vinyl C, 1C), 131.4 (s, vinyl C, 1C), 123.4 (s, C7, 1C), 95.9 (s, bridgehead C, 1C), 89.9 (s, bridgehead C, 1C), 78.3 (d, $^1J_{CH}$ = 156 Hz, C5, 1C), 38.4 (t, $^1J_{CH}$ = 140 Hz, C6). ^{13}C NMR (CD_2Cl_2, ^{1}H-decoupled): δ 78.3 (d, $^2J_{CF}$ = 21 Hz, C5, 1C), 71.0 (s, OCH_2, 1C), 38.4 (d, $^2J_{CF}$ = 20 Hz, C6), 31.8 (s, CH_2, 1C), 19.2 (s, CH_2, 1C), 13.7 (s, CH_3, 1C). IR (neat, cm^{-1}): 2963 (s), 2938 (s), 2877 (s), 1751 (s, CF=CF), 1452, 1371 (s), 1341, 1312, 1296 (s), 1223, 1166 (s), 1124, 1103 (s), 1081, 1002 (s), 956 (s), 922, 906. GC–MS (EI): m/z 274 (M^+), 255, 225, 198, 169, 150, 119, 101, 69, 57 (base). HRMS (EI): calcd for $C_{11}H_{11}F_6O$ $(M-1)^+$ 273.0714, found 273.0717.

4.18. endo-5-Butoxy-1,4,7,7-tetrafluorobicyclo[2.2.1]hept-2-ene (36)

In a 25 mL three-necked round-bottomed flask equipped with a stir bar, a septum and an adaptor connected to a nitrogen bubbler was placed 1.5 g (5.5 mmol) of **35** in 6 mL of benzene. The flask was cooled in an ice/water bath to ca. 5 °C. Red-Al toluene solution (3.5 g of 65% toluene solution, 11 mmol) was introduced into the flask slowly via a syringe through the septum. The stirring was continued at RT for another 14 h. Water (5 mL) was added to the flask dropwise to destroy remaining Red-Al and the solution was acidified with 6N HCl to pH 1. Remaining solid was removed by filtration through Celite and the filtrate was extracted with 20 mL of CH_2Cl_2 twice. The CH_2Cl_2 solution was washed with 10 mL of saturated NaCl solution and dried over sodium sulfate. After removal of sodium sulfate, the solvent was distilled through a Vigreux column. Vacuum transfer gave **36** as a colorless liquid (1.2 g, 5.0 mmol, 92%). ^{1}H NMR (CD_2Cl_2): δ 6.43 (m, vinyl H, 1H), 6.25 (m, vinyl H, 1H), 4.30 (m, CHOBu, 1H), 3.51 (m, OCH_2, 2H), 2.62 (m, CH_2, 1H), 1.76 (m, CH_2,1H), 1.54 (quintet, J = 8 Hz, CH_2, 2H), 1.37 (sextet, J = 8 Hz, CH_2, 2H), 0.94 (t, J = 8 Hz, CH_3, 3H). ^{19}F NMR (CD_2Cl_2): δ −134.0 (d, J = 180 Hz, CF_2, 1F), −148.5 (d, J = 180 Hz, CF_2, 1F), −194.4 (s, bridgehead F, 1F), −199.0 (s, bridgehead F, 1F). ^{13}C NMR (CD_2Cl_2, ^{1}H decoupled): δ 131.2 (ddd, J = 25.6, 6.0, 3.8 Hz, vinyl C, 1C), 128.4 (ddd, J = 25.6, 6.0, 3.8 Hz, vinyl C, 1C),

127.7 (tt, $J = 272$, 16.1 Hz, CF_2, 1C), 100.3 (dt, $J = 231$, 17.9 Hz, bridgehead C, 1C), 95.2 (dtd, $J = 229$, 17.4, 3.1 Hz, bridgehead C, 1C), 76.6 (ddd, $J = 13.2$, 5.5, 1.8 Hz, C5, 1C), 70.2 (s, OCH_2, 1C), 38.3 (dd, $J = 20.6$, 4.6 Hz, C6, 1C), 31.9 (s, CH_2, 1C), 19.4 (s, CH_2, 1C), 13.8 (s, CH_3, 1C). IR (neat, cm^{-1}): 2961 (s), 2936 (s), 2875 (s), 1662(w), 1580 (w), 1448 (w), 1366 (s), 1334 (s), 1271, 1156 (s), 1121 (s), 1082, 1043, 995, 952 (s), 891. GC–MS (EI): *m/z* 238 (M^+), 195, 182, 162, 145, 133, 114, 95, 57 (base). HRMS (EI): calcd for $C_{11}H_{13}F_4O$ $(M-1)^+$ 237.0903, found 237.0897.

4.19. 1,4,5,5-Tetrafluorocyclopentadiene (*31*)

Flash vacuum pyrolysis (60 mTorr, 8 mm × 1000 mm quartz tube) at 600 °C of 0.45 g (1.9 mmol) of endo-5-butoxy-1,4,7,7-tetrafluorobicyclo[2.2.1]hept-2-ene (**36**), evaporated from a 0 °C reservoir, gave 1,4,5,5-tetrafluorocyclopentadiene (**31**) in a U-trap cooled to −196 °C. Acetone (3 mL) was frozen at the incoming mouth of the U-trap before the pyrolysis to prevent the dimerization of **31** upon thawing. A complete conversion of **36** to **31** was obtained. 1,4,5,5-Tetrafluorocyclopentadiene was allowed to react with dienophiles right after it was made. ^{1}H NMR ($CDCl_3$): δ 5.51 (br s, vinyl H, 2H). ^{19}F NMR ($CDCl_3$): δ −141.2 (t, $J = 10.8$ Hz, 2F), −141.6 (t, $J = 10.8$ Hz, 2F).

4.20. 1,1,2,4,7,7a,8,8-Octafluoro-3a,4,7,7a-tetrahydro-1H-4,7-methanoindene (*37*)

This experiment was intended to yield the Diels–Alder adduct **40** of **31** with dimethyl azodicarboxylate, but gave predominantly instead the cyclopentadiene dimer **37**. To a 20 mL pressure tube with a threaded Teflon stopper was added a solution of 2.00 g (13.6 mmol) of dimethyl azodicarboxylate in 5 mL of benzene. The solution was exposed for 2 h to filtered UV irradiation (filter plate Corning C.S. no. 0–53) from a 450 W Hanovia medium pressure mercury lamp. Then a 1,4,5,5-tetrafluorocyclopentadiene benzene solution which was obtained from the complete pyrolysis of 0.15 g (0.62 mmol) of endo-5-butoxy-1,4,7,7-tetrafluorobicyclo[2.2.1]hept-2-ene was added. The tube was totally immersed in an oil bath heated to 100 °C and irradiation was continued for another 12 h. ^{19}F NMR showed that the cyclopentadiene dimer **37** and the Diels–Alder adduct **40** were obtained in a ratio of 19:1. After the solvent was roto-evaporated, the yellow product was treated with 4 g activated basic alumina to decompose excess dimethyl azodicarboxylate. The alumina/product mixture was placed on a silica gel (30 g) column and eluted first with hexanes, yielding 1,4,5,5-tetrafluorocyclopentadiene dimer (**37**, 78 mg, 0.28 mmol, 90%), and then with hexanes/CH_2Cl_2 (1:1), yielding a small amount of adduct **40**. ^{1}H NMR of **37** ($CDCl_3$): δ 6.40 (m, vinyl H, 1H), 6.22 (m, vinyl H, 1H), 5.65 (m, vinyl H, 1H), 3.69 (m, bridgehead H, 1H). ^{19}F NMR ($CDCl_3$): δ −108.5 (d, $J = 277$ Hz, CF_2, 1F), −117.9 (d, $J = 277$ Hz, CF_2, 1F), −129.1 (dd, $J = 169$, 24 Hz, CF_2, 1F), −131.4 (s, vinyl F, 1F), −142.7 (d, $J = 169$ Hz, CF_2, 1F), −191.1 (s, bridgehead F, 1F), −100.1 (s, bridgehead F, 1F), −207.9 (s, bridgehead F, 1F). IR (neat, cm^{-1}): 2962 (s), 1688 (w), 1446 (w), 1412 (w), 1371 (w), 1335 (w), 1260 (s), 1094 (vs), 1024 (vs), 802 (vs), 701. GC–MS (EI): *m/z* 276 (M^+), 257, 238, 226, 207, 187, 176, 157, 138 (base, $C_5F_4H_2$), 119, 88, 75, 59. HRMS (EI): calcd for $C_{10}H_4F_8$ (M^+) 276.0185, found 276.0182. ^{19}F NMR of 1,4,7,7-tetrafluoro-2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (**40**) ($CDCl_3$): δ −137.7 (d, $J = 172$ Hz, CF_2, 1F), −148.7 (d, $J = 172$ Hz, CF_2, 1F), −163.1 (s, bridgehead Fs, 2F).

4.21. 1,4,7,7-Tetrafluoro-2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylic acid dimethyl ester (*41*)

In a heavy-walled hydrogenation bottle were placed about 6 mg (0.02 mmol) of **40** in 4 mL of THF and 20 mg of 10% Pd on carbon. The bottle was mounted on a Parr hydrogenation apparatus, evacuated and flushed with H_2 three times. The suspension was agitated under 5 atm of H_2 for 1d, resulting in complete conversion to **41**. ^{19}F NMR ($CDCl_3$): δ −145.4 (d, $J = 196$ Hz, CF_2, 1F), −151.9 (d, $J = 196$, CF_2, 1F). Bridgehead Fs were not observed at RT because of conformational interconversion. GC–MS (EI): *m/z* 286 (M^+), 242, 222, 183, 161, 155, 130, 116, 88, 75, 59 (base).

4.22. 1,7,10,10-Tetrafluoro-4-thia-2,6-diazatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-3,5-dione (*43*)

A 1,3,4-thiadiazole-2,5-dione (**42**) acetone solution was prepared as follows. 1,3,4-Thiadiazolidine-2,5-dione [29] (0.62 g, 5.2 mmol) was stirred with 0.62 mL (5.2 mmol) of *tert*-butyl hypochlorite in 10 mL of acetone for 3 h at −78 °C in a three-necked round-bottomed flask equipped with stir bar, dropping funnel and connection to a nitrogen bubbler. 1,4,5,5-Tetrafluorocyclopentadiene (**31**, 0.55 g, 4.0 mmol) in 4 mL of acetone was added to the flask via the dropping funnel. After the addition was complete, the reaction solution was allowed to warm up slowly to RT. The solvent was removed by roto-evaporation, and 0.98 g (3.9 mmol, 97%) of **43** was obtained as an oil. ^{1}H NMR ($CDCl_3$): δ 6.87 (dt, $J = 4.0$, 2.5 Hz, vinyl H, 2H). ^{1}H NMR (CD_3OD): δ 7.12 (dt, $J = 4.0$, 2.5 Hz, vinyl H, 2H). ^{19}F NMR ($CDCl_3$): δ −133.5 (d, $J = 173$ Hz, CF_2, 1F), −144.2 (d, $J = 173$ Hz, CF_2, 1F), −174.1 (s, bridgehead F, 2F). ^{13}C NMR (CD_3OD, ^{19}F decoupled): δ 171.1 (s, CO, 2C), 131.2 (d, $^1J_{CH} = 191$ Hz, vinyl C, 2C), 120.4 (s, CF_2, 1C), 104.8 (t, $J = 6.4$ Hz, bridgehead C, 2C). IR (neat, cm^{-1}): 2963, 1756, 1714 (s), 1361, 1234, 1187, 1118, 1087, 1027, 945, 786, 685, 677. GC–MS (EI): *m/z* 254 (M^+), 194, 175, 152, 138 (base), 88, 60. HRMS (EI): calcd for $C_7H_2F_4N_2O_2S$ (M^+) 253.9773, found 254.0004.

4.23. 1,7,10,10-Tetrafluoro-4-thia-2,6-diazatricyclo[5.2.1.$0^{2,6}$]decane-3,5-dione (*44*)

In a heavy-walled hydrogenation bottle were placed 0.45 g (1.8 mmol) of **43** in 10 mL of THF and 0.90 g of 5% Pd-on-alumina. The bottle was mounted on a Parr hydrogenation apparatus, evacuated and flushed with H_2 three times. The

suspension was agitated under 5 atm of H_2 for 20 h. After removal of the catalyst by filtration through Celite and roto-evaporation of the methanol, just a few milligrams of the hydrogenated product **44** was obtained, based on the strength of its NMR signals. ^{19}F NMR ($CDCl_3$): δ −140.7 (d, J = 195 Hz, CF_2, 1F), −149.3 (d, J = 195 Hz, CF_2, 1F), −170.7 (s, bridgehead Fs, 2F).

4.24. 1,4,7,7-Tetrafluoro-2,3-diazabicyclo[2.2.1]hept-5-ene-2-carboxylic acid methyl ester (46)

To a solution of 50 mg of anhydrous potassium carbonate in 1 mL of methanol was added 12 mg (0.047 mmol) of **43**. After being stirred at RT for 2 h, the solution was neutralized with acetic acid. The partially hydrolyzed product **46** was obtained, but it was too labile to be isolated. The yield was 88%, based on trifluorotoluene as internal standard. ^{1}H NMR (CD_3OD): δ 6.92 (m, vinyl H, 1H), 6.76 (m, vinyl H, 1H), 4.88 (br s, NH, 1H), 3.47 (s, CH_3, 3H). ^{19}F NMR (CD_3OD): δ −139.0 (d, J = 187 Hz, CF_2, 1F), −150.6 (d, J = 187 Hz, CF_2, 1F), −174.9 (s, bridgehead F, 1F), −184.9 (br s, bridgehead F, 1F). GC–MS (EI): m/z 226 (M^+), 211, 207, 194, 175, 162, 148, 138, 119, 116, 103, 88, 69, 59 (base).

4.25. 1,4,7,7-Tetrafluoro-2,3-diazabicyclo[2.2.1]heptane-2-carboxylic acid methyl ester (47)

Nitrogen was bubbled for 30 min through 3 mL of a methanol solution of 1,4,7,7-tetrafluoro-2,3-diazabicyclo[2.2.1]hept-5-ene-2-carboxylic acid methyl ester (**46**, 140 mg, 0.61 mmol), obtained from the reaction above, to get rid of COS. The solution was then treated with $ZnCl_2$. After removal of the solid by filtration, the solution was placed in a heavy-walled hydrogenation bottle with 70 mg of 5% Pd-on-alumina. The bottle was mounted on a Parr hydrogenation apparatus and flushed with H_2. The suspension was agitated under 60 psi of H_2 for 20 h. After removal of the catalyst by filtration through Celite, **47** was obtained in methanol in a 98% yield, based on trifluorotoluene as internal standard. ^{1}H NMR ($CDCl_3$): δ 4.69 (br s, NH, 1H), 3.66 (m, CH_2, 2H), 3.58 (m, CH_2, 2H), 3.50 (s, CH_3, 3H). ^{19}F NMR (CD_3OD): δ −147.6 (br d, J = 190 Hz, CF_2, 1F), −154.5 (d, J = 190 Hz, CF_2, 1F), −170.7 (s, bridgehead F, 1F), −182.5 (br s, bridgehead F, 1F). GC–MS (EI): m/z 228 (M^+), 169, 150, 141, 120, 119, 95, 89, 69, 59.

4.26. 1,4,7,7-Tetrafluoro-2,3-diazabicyclo[2.2.1]hept-2-ene (45)

(1) From 1,7,10,10-tetrafluoro-4-thia-2,6-diazatricyclo-[5.2.1.0^{2,6}]decane-3,5-dione (**43**). A 5-mm quartz NMR tube containing about 5 mg (0.02 mmol) of 1,7,10,10-tetrafluoro-4-thia-2,6-diazatricyclo[5.2.1.0^{2,6}]decane-3,5-dione in 0.6 mL of dry acetonitrile was capped with a septum pierced with a long and a short needle. The solution was deoxygenated by bubbling nitrogen gas through for 5 min, then irradiated at 254 nm in a cylindrical cavity photoreactor containing ten 25 W low pressure mercury lamps. Progress of the reaction was monitored by ^{19}F NMR. When the photolysis was complete, the reaction solution was taken up in 2 mL of water and extracted twice with 1.5 mL of $CFCl_3$. The organic extracts were washed three times with saturated sodium chloride solution and dried over sodium sulfate. Evaporation of the solvent gave a few mg of **45**, as judged from the strength of NMR signals. ^{19}F NMR ($CDCl_3$): δ −140.3 (d, J = 191 Hz, CF_2, 1F), −155.1 (dt, J = 191, 4.2 Hz, CF_2, 1F), −173.1 (s, bridgehead F, 2F). GC–MS (EI): m/z 140 ($C_5H_4F_4^+$), 139, 121, 119, 113, 101, 95, 90 (base, $C_4H_4F_2^+$), 75, 69.

(2) From 1,4,7,7-tetrafluoro-2,3-diazabicyclo[2.2.1]heptane-2-carboxylic acid methyl ester (**46**). In a round-bottomed flask equipped with a magnetic stir bar and connected to a nitrogen bubbler were placed 100 mg (0.22 mmol) of 95% lead tetraacetate and 40 mg (0.18 mmol) of **46** in 1.5 mL of methanol. The solution was stirred vigorously for 30 min, then vacuum transferred. GC separation of the distillate (inj. 110 °C, col. 40 °C, det. 110 °C) gave 1,4,7,7-tetrafluoro-2,3-diazabicyclo[2.2.1]hept-2-ene (**45**) as a colorless liquid (about 25 mg, 0.15 mmol, 81%). ^{1}H NMR ($CDCl_3$): δ 3.66 (m, CH_2, 2H), 3.58 (m, CH_2, 2H). ^{19}F NMR (CD_3OD): δ −141.2 (d, J = 191 Hz, CF_2, 1F), −156.4 (d, J = 191 Hz, CF_2, 1F), −174.6 (s, bridgehead F, 2F). ^{13}C NMR (CD_2Cl_2, ^{19}F and ^{1}H decoupled): δ 119.8 (CF_2), 110.0 (bridgehead Cs), 50.7 (CH_2). UV λ_{max} (nm): 348.5 (373), 335.0 (259). GC–MS (EI): m/z 140 ($C_5H_4F_4^+$), 139, 121, 119, 113, 101, 95, 90 (base, $C_4H_4F_2^+$), 75, 69. HRMS (CI): calcd for $C_5H_8F_4N_3$ $(M + NH_4)^+$ 186.0654, found 186.0650.

4.27. 1,4,5,5-Tetrafluorobicyclo[2.1.0]pentane (8)

In a pyrex NMR tube was placed 8 mg (0.05 mmol) of 1,4,7,7-tetrafluoro-2,3-diazabicyclo[2.2.1]hept-2-ene (**45**) in 0.5 mL of $CFCl_3$. Argon was bubbled through the solution for 10 min to eliminate oxygen. Through a rubber plug the NMR tube was then inserted into a quartz Dewar flask with a transparent tailpiece. A thermocouple and a nitrogen inlet were also inserted into the Dewar through the rubber plug. Cold nitrogen gas from a liquid nitrogen boiler was bled into the Dewar. The rate of nitrogen flow was tuned to give −65 °C inside the Dewar. The azo compound was then irradiated for 3 h with a 450 W medium pressure Hanovia mercury lamp mounted close to the Dewar. 1,4,5,5-Tetrafluorobicyclo[2.1.0]-pentane (**8**) was obtained in 17% yield, based on an internal standard. ^{19}F NMR ($CFCl_3$, −55 °C): δ −128.1 (v br s, CF_2, 2F), −163.8 (s, bridgehead F, 2F).

4.28. 1,2,3,3-Tetrafluorocyclopentene (48)

When 1,4,5,5-tetrafluorobicyclo[2.1.0]pentane was warmed up to RT, it slowly isomerized to 1,2,3,3-tetrafluorocyclopentene (**48**). ^{19}F NMR ($CFCl_3$): −127.8 (s, CF_2, 2F), −157.1 (s, vinyl F, 1F), −163.2 (s, vinyl F, 1F). GC–MS (EI): m/z 140 (M^+), 121 ($C_5H_4F_3^+$), 90 ($C_4H_4F_2^+$), 69 (CF_3^+), 58 (base, $C_3H_3F^+$).

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