159. The Reaction of Dihalocarbenes with Quadricyclane

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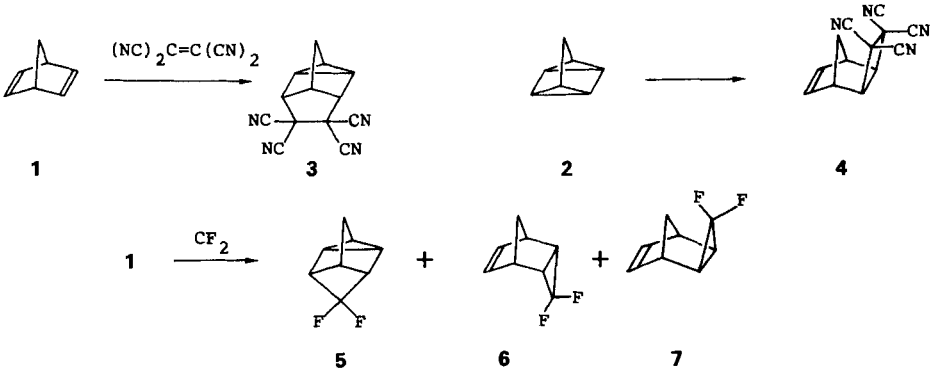
The reactions of difluoro-, dichloro- and dibromocarbene with quadricyclane (**2**) were examined. In all cases, conversions were low (4–15%), but three distinct reaction courses were observed: cleavage, 1,2-addition, and 1,4-addition. Difluorocarbene gave mainly 6-*endo*-(2,2-difluorovinyl)-*cis*-bicyclo[3.1.0]hex-2-ene (**8**; 52–89% relative yield), together with minor amounts of *exo*-3,3-difluorotricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**7**; 13–17%), and 4,4-difluorotetracyclo[3.3.0.$0^{2,8}$.$0^{3,6}$]octane (**5**; 2–4%). Dichlorocarbene gave analogous products, but in relative yields of 35 (**17**), 51 (**11**), and 12% (**16**). The product **11** of 1,2-*exo* addition underwent further rearrangement to its allylic derivative **12**. A small amount of 1,2-*endo* addition also occurred (2% of **14**/**15**). Dibromocarbene gave predominantly products derived from rearrangement of the 1,2-*exo* (61% of **20**/**21**) and 1,2-*endo* adducts (10% of **23**/**24**). In addition, a significant amount of 4,4-dibromotetracyclo[3.3.0.$0^{2,8}$.$0^{3,6}$]octane (**25**; 21%) was formed. The cleavage product, 6-*endo*-(2,2-dibromovinyl)-*cis*-bicyclo[3.1.0]hex-2-ene (**26**) was also observed (7%). The yields and product compositions were compared to those obtained from norbornadiene (**1**) and found to be entirely different *(Table 1)*, for example no cleavage occurred with difluorocarbene.

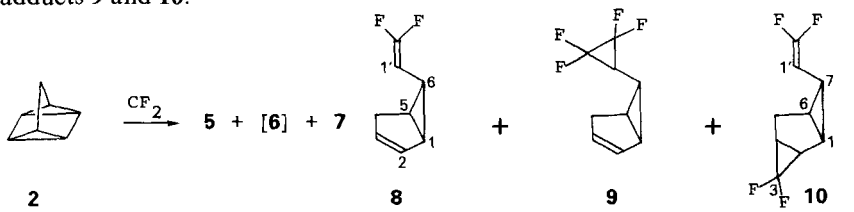
Introduction. – Norbornadiene (**1**) and quadricyclane (**2**) constitute an oddly matched mechanistic couple. They possess essentially the same skeleton, therefore, presenting a similar steric profile to an attacking reagent, but they differ in having sets of frontier orbitals of inverse symmetry [1]. This difference is revealed to good advantage by ethylenetetracarbonitrile. Its reaction with norbornadiene (**1**) leads solely to the [2 + 2 + 2] adduct **3**, whereas quadricyclane (**2**) only undergoes *exo* addition to form the cyclobutane adduct **4** [2] [3]. Another potentially revealing reagent is difluorocarbene. It invariably adds to olefins, including conjugated dienes, to afford geminal difluorocyclopropanes [4]. A rare exception is provided by norbornadiene which gives the homo-1,4 adduct **5** as well as the conventional 1,2 adducts **6** and **7** [5]. This



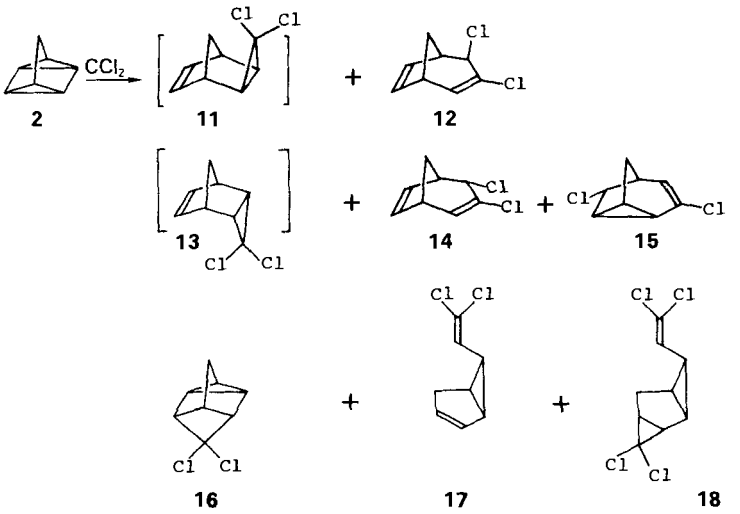
unusual occurrence of normal and homo-conjugate addition prompts the question of how quadricyclane (**2**) will behave. Will both addition modes operate as they do with **1**, and if so, will the product compositions be similar or radically different? On the other hand, viewed as a cyclopropane, **2** could well be inert.

Consequently, difluoro-, dichloro-, and dibromocarbenes were allowed to react with quadricyclane. The products were separated, identified, and compared with those obtained from norbornadiene.

Results. – The generation of a stoichiometric amount of difluorocarbene in the presence of pure quadricyclane (**2**) at 20° for 120 h gave a mixture of five products in an overall yield of 3–4.5%. Two of these were the expected, known 1:1 adducts **5** and **7**. The 1,2-*endo* adduct **6** was not detected[1]). The *exo* adduct **7** and the homo-1,4 adduct **5** constituted the minor components. The bulk of product (52–89% relative yield) consisted of 6-*endo*-(2,2-difluorovinyl)-*cis*-bicyclo[3.1.0]hex-2-ene[2]) (**8**) and its difluorocarbene adducts **9** and **10**.



The action of dichlorocarbene, generated in excess by phase-transfer catalysis at 20°, on quadricyclane **2** resulted in a 7% conversion to at least seven products. The major component (51% relative yield) was 3,4-*exo*-dichlorobicyclo[3.2.1]octa-2,6-diene (**12**).

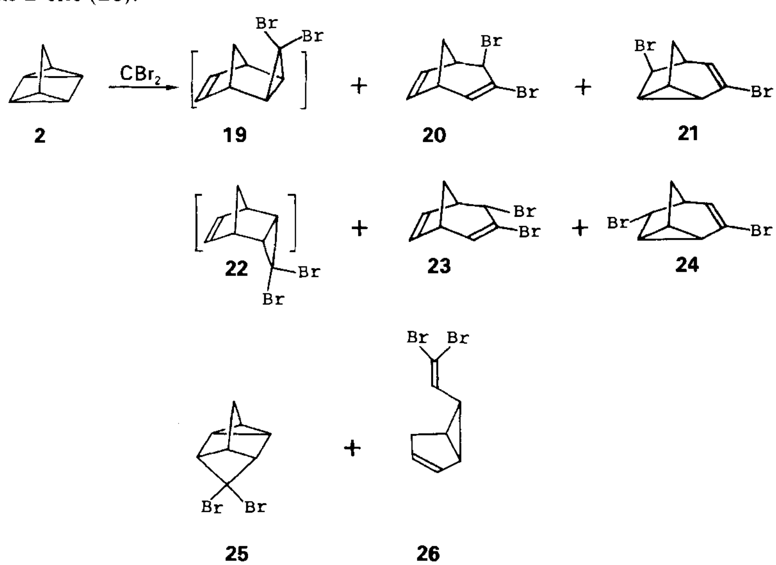


[1]) The terms 1,2 and homo-1,4 adduct are only correct for norbornadiene. However, for the sake of convenience, they are also used to designate the same products obtained from quadricyclane, although the 'additions' are really insertions into C,C bonds.

[2]) The descriptors *endo*/*exo* in *cis*-bicyclo[3.1.0]hex-2-ene derivatives refer to the position of the substituent at C(6).

Its presumed precursor, the 1,2-*exo*-adduct **11** was not seen at 20°, but was detected spectroscopically at −10°. The presumed 1,2-*endo*-adduct **13** was not observed either, but its related allylic *endo* isomer **14** together with its further rearranged homoallylic *endo* isomer **15** were detected in minute amounts (2% relative yield). Further minor products were identified as the homo-1,4 adduct **16** together with 6-*endo*-(2,2-chlorovinyl)-*cis*-bicyclo[3.1.0]hex-2-ene (**17**) and its dichlorocarbene adduct **18**.

Similarly, dibromocarbene was produced in excess by phase-transfer catalysis and allowed to react with **2**. The preponderant products were 3,4-*exo*-dibromobicyclo[3.2.1]octa-2,6-diene (**20**) and 3,6-*exo*-dibromotricyclo[3.2.1.$0^{2,7}$]oct-3-ene (**21**). Their presumed precursor, the 1,2-*exo* adduct **19** was not isolated. In a complementary manner, the rearranged *endo* analogues **23** and **24** were also formed, but only in minor amounts. No trace of their presumed precursive 1,2-*endo* adduct **22** was found. The other minor products were the homo-1,4 adduct **25** and 6-*endo*-(2,2-dibromovinyl)-*cis*-bicyclo-[3.1.0]hex-2-ene (**26**).



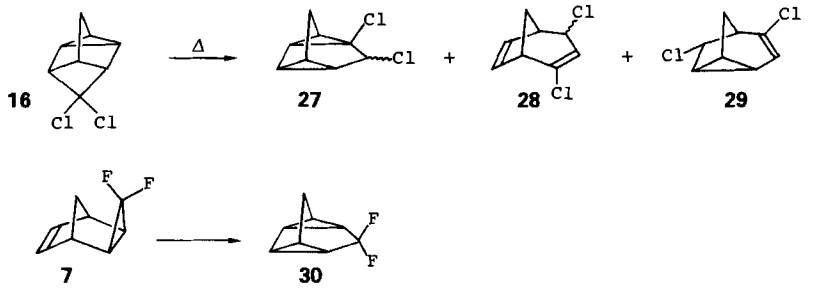
To ensure that all the foregoing products really derived from quadricyclane and not from traces of norbornadiene arising from its isomerization, a number of tests were performed. Quadricyclane was unaffected when subjected to the phase-transfer conditions. Moreover, unreacted quadricyclane, when isolated from the carbene addition reaction remained as such. Reexamination of the addition of the dihalocarbenes to norbornadiene showed that essentially the same products were formed as with quadricyclane, but that the yields and compositions were substantially different (*Table 1*).

The thermal behavior of most of the 1:1 adducts has already been described [5] [6]. However, in order to get useful information on the properties of the remaining products, preliminary tests of thermal stability were undertaken. The allylic *endo* chloride **14** was heated in diglyme at 200°. Rearrangement occurred to the corresponding allylic *exo* isomer **12** and to 3,6-*endo*-dichlorotricyclo[3.2.1.$0^{2,7}$]oct-3-ene (**15**). Further heating of **12** at 210° for 42 h was without effect [7].

Table 1. *Product Composition Obtained by the Action of Dihalocarbenes on Norbornadiene* (**1**) *and Quadricyclane* (**2**)

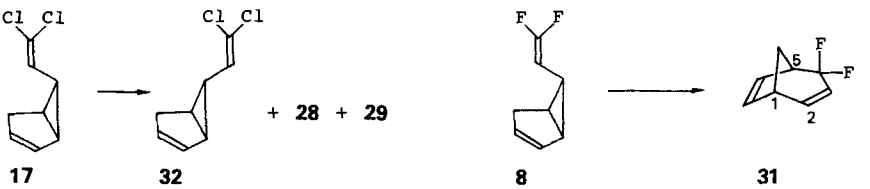
Substrate	Carbene	Overall conversion [%]	1,2-*exo*[a]) Adducts [%]	1,2-*endo*[a]) Adducts [%]	1,4-homo Adducts [%]	Cleavage[b]) products [%]	Non-identified compounds [%][c])
1	CF_2	54–62	**7**, 60	**6**, 4	**5**, 35	**8**, 0.5	0.5
2		3–4.5	**7**, 13–17	**6**, 0	**5**, 2–4	**8**, 52–89	0–4
1	CCl_2	51	**12**, 70	**14/15**, 11	**16**, 10	**17**, 9	8
2		7	**12**, 51	**14/15**, 2	**16**, 12	**17**, 35	6
1	CBr_2	60	**20/21**, 77	**23/24**, 6	**25**, 9	**26**, 8	31
2		15	**20/21**, 61	**23/24**, 10	**25**, 21	**26**, 7	7

[a]) Included are the corresponding products of rearrangement.
[b]) Included are the corresponding secondary cyclopropane adducts where appropriate.
[c]) Relative yields normalized to 100% excluding non-identified compounds.



The dichloro 1,4-homo adduct **16** proved relatively stable. Nevertheless, at 190° in dimethoxyethane, it rearranged to give the dichloro derivatives **27**–**29** of homoquadricyclane, bicyclo[3.2.1]octa-2,6-diene and tricyclo[3.2.1.$0^{2,7}$]oct-3-ene, respectively [8]. In contrast, the analogous difluoro homo-1,4 adduct **5** survived unchanged even on heating to 300°.

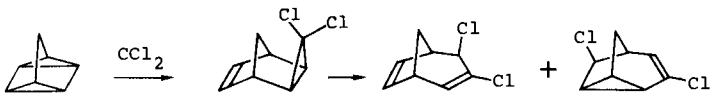
As the difluoro 1,2-*exo* adduct **7** is a possible precursor to the vinylbicyclo[3.1.0]hex-2-ene **8** *via* a $[2\pi_s + 2\sigma_a + 2\sigma_a]$ sigmatropic rearrangement [9], its thermal behavior was reexamined. Heating of **7** at temperatures between 180 and 210° in triglyme gave only the difluorohomoquadricyclane **30** [5].



The thermal stabilities of the cleavage products **8** und **17** were also studied. As previously reported [10], strong heating was needed to bring about rearrangement of the dichloro derivative **17** to its bridged bicyclic octene isomers **28** and **29**. Although the thermolysis of the dibromo derivative **26** was not tried, a similar fate is likely. The difluoro product **8**, on heating in deuteriobenzene at 90–120°, gave solely 4,4-difluorobicyclo[3.2.1]octa-2,6-diene (**31**).

Discussion. – The most striking property of quadricyclane in its reaction with dihalocarbenes is its inertness. In general, quadricyclane gives high yields of 1,2 adducts with *bona fide* electrophiles such as ketenes and olefins bearing electron-withdrawing substituents [3] [11]. In contrast, the yields of products with dihalocarbenes are uniformly poor. Difluorocarbene reacts only with some 5% of **2**, whereas the more electrophilic dibromocarbene brings about a conversion of 15% at best *(Table 1)*. Paradoxically norbornadiene, which should be less reactive towards electrophiles on account of its lower lying HOMO compared to that of quadricyclane [1], gives consistently high yields of adducts with all the dihalocarbenes.

A consequence of this lack of reactivity has been the difficulty of determining the product composition with precision. Even the purest obtainable quadricyclane (**2**) is contaminated with some 0.5% of its more reactive isomer **1**. Depending on time, place, and methods of carbene generation, as well as conditions of workup, the products detected or at least described have varied widely. Initially, we briefly reported [12] that only 1,2 and homo-1,4 adducts were obtained together with their rearrangement products. Difluorocarbene gave a larger proportion of cyclopropanes and their derivatives, while dichlorocarbene favored the cyclobutane adduct. In a subsequent study, *Jones et al.* [13] stated that dichlorocarbene generated in no less than four different ways furnished



2 **11** **12** **33**

Ref. [13]

almost exclusively just two products, 3,4-*exo*-dichlorobicyclo[3.2.1]octa-2,6-diene (**12**) and the purported *exo* isomer **33** of 3,6-dichlorotricyclo[3.2.1.$0^{2,7}$]oct-3-ene. The near absence of the 1,4-homo adduct **16** and other *endo* products was regarded as significant and characteristic of **2**. Whence it was construed that the underlying cause was the favorable interaction between the complementary frontier orbitals of the two partners, provided they collided on the *exo* face of quadricyclane. By the same token, norbornadiene having frontier orbitals of inverse symmetry, was thought to favour products derived from *endo* addition. Unfortunately, inspection of *Table 1* shows that this simple qualitative picture is not corroborated by experiment. Although it is true that difluorocarbene displays little propensity to attack the *endo* side of **2** (4%) compared to **1** (39%), dichlorocarbene gives roughly equivalent amounts of *endo* adducts with both **2** and **1** (14 and 21%, resp.). Moreover, a complete reversal is seen with dibromocarbene. It attacks the *endo* face of **1** to some 15% and gives even more *endo* product with **2** (31%).

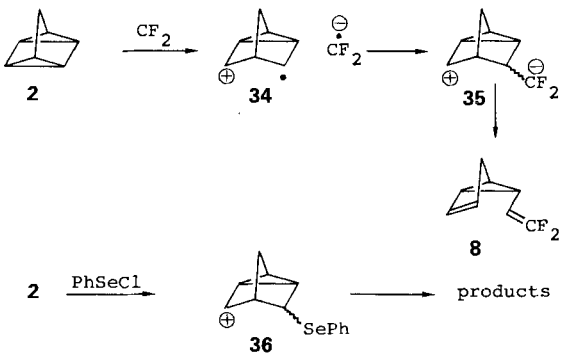
Further examination of the product compositions shows that systematic differences characterize the different carbenes. Difluorocarbene gives with **2** predominantly (52–89%) **8** in which the carbene has severed two C,C bonds of quadricyclane. The 1,2-*exo* adduct **7** is certainly formed, albeit in small amount, as is the homo-1,4 adduct **5** in even smaller yield. 1,2-*endo* Addition may have occurred, but was not observed, owing perhaps to easy stereomutation of the presumed precursive 1,2-*endo* adduct **6** to its more stable 1,2-*exo* adduct **7**. In stark contrast, norbornadiene gives practically no cleavage

product with difluorocarbene, but undergoes instead overwhelming 1,2-*exo* addition (→**7**; 60%). Homo-1,4 addition (→**5**) is also a major occurrence (35%).

Dichlorocarbene presents a similar reaction course, but modified in two important respects. Firstly, the amount of cleaved product (**17**) obtained with **2** is diminished, while the 1,2-*exo* adduct **11** or rather the product of its rearrangement (**12**) now constitute the bulk of material. The 1,2-*endo* adduct **13** and its derivatives **14** and **15** were formed, but to a negligible degree. Significantly, the dichloro homo-1,4 adduct **16** was formed in minor yield. Norbornadiene (**1**) gave a similar product pattern, however more 1,2-*exo* adduct **11** was formed at the expense of cleavage product **17**. The dichloropropane adducts **11** and **13**, unlike their difluoro analogues, are thermally unstable and readily rearrange to their allylically related derivatives **12**, **14**, and **15** thanks to the good nucleofugacity of the Cl-substituent. The rearranged products are those expected and have been characterized in our earlier studies [7] [14].

The chemo- and regioselective trend displayed by difluoro- and dichlorocarbene is confirmed by dibromocarbene which gives with **2** greater amounts of products arising from 1,2-*exo* and 1,2-*endo* addition (**20**, **21**, **23**, and **24**), but with commensurately less of the cleavage product **26**. The dibromo homo-1,4 adduct **25** is well in evidence. The product composition arising from **1** is remarkably similar, except that a greater bulk of reaction mixture defied separation and identification owing to extensive rearrangement. In fact, rearrangement, common for the chloro and bromo adducts, constitutes a complication not encountered with the fluoro adducts. Moreover, the latter on account of their NMR visibility, are easier to identify (see *Exper. Part*).

We have shown elsewhere that dihalocarbenes behave as typical electrophiles in both their 1,2 and homo-1,4 addition modes [15–17]. Consequently, the variation in product composition arising from these two modes may reflect steric discrimination by the quadricyclane skeleton as a response to the increasing volume of the incoming carbene partner. On the other hand, the increasing extent of cleavage on passing from dibromo- to difluorocarbene could be due to the decrease of electrophilicity along the series. It could be argued that frontier-orbital control becomes more relaxed and that charge control assumes greater importance, especially so for the case of difluorocarbene and quadricyclane. Electron transfer would initially give the radical ion pair **34**. Combination would form the zwitterionic entity **35** in which both charges are stabilized as a cyclopropylmethyl cation and a difluoromethide ion, respectively. In principle, combination of the



first-formed radicals **34** or even direct union of the reagents, could occur to give both *exo* and *endo* products. Ring closure could subsequently occur and account just as well as the usual concerted one-step processes for the 1,2 and homo-1,4 adducts. An alternative to closure is charge cancellation by cleavage which produces the 6-(difluorovinyl)-bicyclo[3.1.0]hex-2-ene **8** of the *endo,cis* configuration, regardless of the *exo* or *endo* nature of the precursor. This proposed mechanism finds a cationic counterpart in the reaction of benzeneselenenyl chloride with quadricyclane [18]. The adducts arise by 1,3 and conjugative 1,6 addition. Their composition indicates that the electrophile favors *endo* over *exo* attack in a 2:1 ratio to initially create the nortricyclyl cation **36**.

What determines the subtle balance between the concerted pathway and the stepwise one is difficult to ascertain. It could be inferred that as quadricyclane (**2**) is less reactive than norbornadiene (**1**), its transition state would be later and more product-like, thereby favoring an intermediate like **35** [19].

Such non-concerted reactions of singlet carbenes are rare [10] [20]. Although difluorocarbene provides the best example in that it strongly differentiates the behavior of quadricyclane from norbornadiene, the other two carbenes also react stepwise with both substrates, but to a lesser degree. It is also worth noting that apart from the formation of conventional cyclopropane adducts, quadricyclane just like norbornadiene undergoes substantial electrophilic addition of dihalocarbene to the basal C,C bond to give homo-1,4 adducts.

On reviewing our past experiments with quadricyclane [12] and those of *Jones* [13], we now find that there are discrepancies in the reported product compositions, in particular for the reaction with dichlorocarbene. Clearly, there were problems of separation and of assignment of structure to the individual components of these complex mixtures in which rearrangement is rife. The missing products arising from cleavage and homo-1,4 addition were undoubtedly formed, but may have been counted in with the cyclopropane adducts. Our results also indicate that the same two products were also previously missed with norbornadiene on reaction with dichloro- and dibromocarbene, respectively [21].

The present findings permit the conclusion that quadricyclane (**2**) and norbornadiene (**1**), although giving varying amounts of the same products, do in fact exhibit a net chemical difference. For the most electrophilic carbene of the series, dibromocarbene, the product compositions are almost identical, however, the reactivity of quadricyclane is decidely lower than that of norbornadiene. Similar sluggishness is observed with the other carbenes, but when difluorocarbene is employed, a dramatic change in reaction course is elicited; quadricyclane reacts to give mostly the cleavage product; norbornadiene, in contrast, behaves normally. This result is doubly novel in that it constitutes a rare example of a *stepwise*, formal reaction of a singlet carbene with two C,C *single* bonds. Furthermore, the concomitant formation of homo-1,4 adducts from **2** is an instance, perhaps the first, of the insertion of a singlet carbene into a C,C *single* bond.

Experimental Part

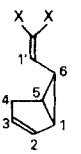
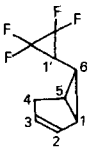
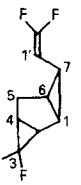
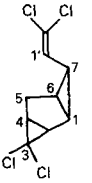
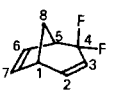
1. *General.* Column chromatography: silica gel *60*, 230–400 mesh ASTM. Gas liquid chromatography (GLC): *Hewlett-Packard-5880A* chromatograph (anal., F.I.D., carrier gas N_2) and *Perkin-Elmer-990* chromatograph (semi-prep., H.W. detector, carrier gas He); columns: A (1.8 m × 2 mm, glass, 5% *Carbowax 20M* on *Chromosorb*

W-HP (80–100 mesh)), B (25 m × 0.2 mm, capillary fused silica, cross-linked 5% phenylmethyl silicone), C (3.2 mm × 6 mm, stainless steel, 10% *FFAP* on *Chromosorb W-HP* (80–100 mesh)), D (3.2 m × 6 mm, stainless steel, 15% *FFAP* on *Chromosorb W-HP* (80–100 mesh)), and E (3.2 m × 6 mm, stainless steel, 15% *SE30* on *Chromosorb W-HP* (80–100 mesh)). M.p. on *Büchi SMP20* apparatus (uncorrected). B.p. are uncorrected. IR: *Perkin-Elmer-681* spectrophotometer. Mass spectra: *Varian-SM-1-B* mass spectrometer and *Finnigan GC/MS 4023* instrument. ^{1}H- and ^{13}C-NMR (δ's in ppm relative to internal TMS (= 0 ppm), J's in Hz): *Bruker-WH 360* and *Varian-XL-100* spectrometers. ^{19}F-NMR (δ's in ppm relative to internal $CFCl_3$ (= 0 ppm), J's in Hz): *Varian-XL-100* spectrometer. Elemental analyses were carried out by Dr. *H. Eder*, Service de Microchimie, Institut de Chimie Pharmaceutique, University of Geneva, and by Dr. *A. Steiner*, Mikrolabor 170/008, *Ciba-Geigy AG*, Marly (for the fluorinated compounds).

2. *Starting Materials.* Commercial norbornadiene (= *bicyclo[2.2.1]hepta-2,5-diene;* (**1**) was purified by distillation from Na prior to use. Quadricyclane (= *tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane;* **2**) was prepared from **1** according to *Smith*'s procedure [22] and was shown to be 99.5% pure by capill. GLC. Commercial Ph_3P was recrystallized from EtOH. Commercial KF (anal. grade) was dried in a solid-addition funnel by heating over a naked flame under a stream of dry N_2 and then allowed to cool in a dessicator over P_2O_5 prior to use. Commercial CBr_2F_2 and hexadecyltrimethylammonium bromide (CTAB) were used without further purification. All solvents were distilled prior to use from the appropriate drying reagent and stored under N_2.

3. *Procedure for Difluorocarbene Additions* [23]. To a soln. of Ph_3P (2.85 g, 10.9 mmol) in triglyme (20 ml) was added CBr_2F_2 (2.50 g, 11.9 mmol). After the initial formation of (bromodifluoromethyl)triphenylphosphonium bromide, stirring was continued for 30 min. Next was added **2** (1 g, 10.9 mmol) and KF (2.53 g, 43.6 mmol). Stirring

Table 2. *^{1}H-NMR Chemical Shifts δ [ppm] in $CDCl_3$ at 360 MHz Relative to Internal Me_4Si*

Numbering Systems					
	8, 17	**9**	**10**	**18**	**31**

	8	**17**	**9**		**10**	**18**		**31**
H–C(1')	3.88	5.50	*ca.* 1.82	H–C(1')	4.06	5.70	H–C(1)	2.92
H–C(3)	5.59	5.67	5.66	H–C(2)	1.96	2.09	H–C(2)	6.64
H–C(2)	5.65	5.72	5.73	H–C(4)	*ca.* 1.61	1.75	H–C(3)	5.35
H_{exo}–C(4)	2.59	2.61	2.68	H_{exo}C(5)	2.31	2.27	H–C(5)	3.23
H_{endo}–C(4)	2.15	2.18	*ca.* 2.19	H_{endo}–C(5)	1.96	2.09	H–C(6)	6.00
H–C(1)	2.22	2.34	*ca.* 2.19	H–C(1)	1.72	1.90	H–C(7)	6.64
H–C(5)	1.84	2.00	*ca.* 1.82	H–C(6)	*ca.* 1.45	1.50	H–C(8)	2.27
H–C(6)	1.65	1.85	1.14	H–C(7)	*ca.* 1.52	1.75		

Table 3. *^{19}F-NMR Chemical Shifts δ [ppm] in $CDCl_3$ at 94.1 MHz Relative to Internal $CFCl_3$*[a])

8		**9**		**10**		**31**	
F_{trans}	−86.5	F[b])	−142.1	F_{exo}	−129.1	F_{exo}	− 88.9
F_{cis}	−90.8		−154.9	F_{endo}	−153.1	F_{endo}	−104.8
				F_{trans}	− 85.9		
				F_{cis}	− 90.2		

[a]) Tentative assignments.
[b]) Not individually assigned.

Table 4. *Characteristic Homo- and Heteronuclear Coupling Constants [Hz]*

	8	**17**	**9**	**10**	**18**	**31**
^3J(H,H)	$J(1',6) = 8.5$ $J(1,5) \approx J(5,6)$ $\approx J(4exo,5)$ $\approx J(1,6) \approx 7.5$	$J = (1',6) = 8.5$ $J(1,5) \approx J(5,6)$ $\approx J(4exo,5)$ $\approx J(1,6) \approx 7.5$	$J(1',6) \approx 7.5$ $J(1,5) \approx J(5,6)$ $\approx J(4exo,5)$ $\approx J(1,6) \approx 7.5$	$J(1',7) = 8$ $J(4,5endo)$ $\approx J(5exo,6)$ $= 6$ $J(2,4) = 8$	$J(1',7) = 8$ $\approx J(4,5)endo)$ $\approx J(5exo,6)$ $= 6$ $J(2,4) = 7$	$J(2,3) = 9.5$ $J(6,7) = 5.5$
^2J(H,H)	$J(4exo,4endo)$ $= 19$	$J(4exo,4endo)$ $= 19$	$J(4exo,4endo)$ $= 19$	$J(5exo,5endo)$ $= 14$	$J(5exo,5endo)$ $= 14$	
^3J(H,H)	$J(2,3) = 5.5$	$J(2,3) = 5$	$J(2,3) = 6$			
^2J(H,F)	$J(1',F_{cis}) = 26$ $J(1',F_{trans}) = 2.5$			$J(1',F_{cis}) = 26$ $J(1',F_{trans}) = 2$ $J(2,F_{exo}) =$ $J(4,F_{exo}) = 14$		$J(5,F_{exo}) = 12$
^2J(F,F)		–	176	$J(F_{cis},F_{trans})$ $= 44$ $J(F_{exo},F_{endo})$ $= 156$	–	^2J(F,F) = 273

was continued at r.t. for 120 h, whereupon a dark brown suspension resulted. The crude mixture was flash-distilled under high vacuum at r.t. to give a colorless soln. which was subsequently analyzed by GLC (column **B**), thereby giving typical overall and rel. yields (average of 5 runs). In the case of additions to **1**, abs. and rel. yields were also estimated from the ^{19}F-NMR integrals relative to hexafluorobenzene as internal integral standard. Products were isolated by prep. GLC (column D or E, 90°), and their structures were unambiguously characterized by the ^{1}H- and ^{19}F-NMR parameters (new adducts, *Tables 2–4*).

6-endo-*(2,2-Difluorovinyl)*-cis-*bicyclo[3.1.0]hex-2-ene* (**8**). Colorless liquid. IR (neat): 3060*m*, 2915*m*, 2845*w*, 1745*vs*, 1405*w*, 1357*m*, 1335*w*, 1297*vs*, 1205*m*, 1185*s*, 1160*m*, 1070*w*, 1040*w*, 985*s*, 960*s*, 910*s*, 760*m*, 730*s*. ^{13}C-NMR (90.6 MHz, $CDCl_3$): 157.9 (*'q'*), 131.1 (*d*), 129.2 (*d*), 73.0 (*'q'*), 32.4 (*t*), 29.3 (*d*), 21.0 (*d*), 21.0 (*d*), 14.7 (*'dd'*). MS: 142 (62, M^+), 127 (28), 121 (8), 114 (9), 109 (8), 101 (21), 96 (12), 91 (65), 77 (100), 65 (24), 51 (55). Anal. calc. for $C_8H_8F_2$ (142.15): C 67.60, H 5.67, F 26.73; found: C 67.43, H 5.66, F 25.4.

6-endo-*(2,2,3,3-Tetrafluorocyclopropyl)*-cis-*bicyclo[3.1.0]hex-2-ene* (**9**). Colorless liquid. IR (CCl_4): 3060*m*, 3050*m*, 3010*w*, 2910*m*, 2840*w*, 1505*s*, 1435*w*, 1355*m*, 1287*m*, 1273*m*, 1258*s*, 1180*vs*, 1098*m*, 1035*m*. ^{13}C-NMR (90.6 MHz, $CDCl_3$): 131.5 (*d*), 129.6 (*d*), 107.5 (*tm*), 106.8 (*tm*), 32.6 (*t*), 28.0 (*d*), 27.9 (*d*), 19.0 (*d*), 12.0 (*d*). MS: 192 (2, M^+), 191 (3), 177 (9), 142 (26), 141 (47), 128 (17), 127 (42), 123 (17), 115 (35), 109 (15), 101 (21), 96 (13), 91 (90), 77 (100), 65 (28), 51 (41). Anal. calc. for $C_9H_8F_4$ (192.16): C 56.25, H 4.20, F 39.55; found: C 56.68, H 4.17, F 38.94.

3,3-Difluoro-7-(2,2-difluorovinyl)tricyclo[4.1.0.0.^{2,4}]heptane (**10**). Colorless liquid. MS: 192 (4, M^+), 141 (12), 127 (21), 123 (15), 115 (36), 101 (21), 95 (26), 91 (19), 77 (100), 66 (28), 57 (18), 51 (66).

4. *Procedure for Dichlorocarbene Additions* [24]. To a mixture of **2** (0.9 g, 10 mmol), CTAB (0.035 g, 10 mmol), and 50% NaOH (21.3 ml), $CHCl_3$ (10 ml, 130 mmol) was added during 4 h. The mixture was stirred mechanically for 24 h at r.t. Ice (50 ml) was then added. The soln. was extracted with Et_2O (4 × 30 ml). The org. extracts were dried (Na_2SO_4) and evaporated without heating. The crude product was analyzed immediately by GLC (column A). Products were isolated either by prep. GLC (column C, 100–140°) or by distillation under vacuum on a *Fischer-Spaltrohr-HMS-500* column. For dichlorocarbene additions to **1**, the reaction mixture was acidified (10% H_2SO_4, pH 6.5) prior to extraction. The org. extracts were washed with H_2O (3 × 100 ml), brine (100 ml), dried (Na_2SO_4), and analyzed as indicated above.

3,6-endo-*Dichlorotricyclo[3.2.1.0^{2,7}]oct-3-ene* (**15**). Colorless liquid. IR (CCl_4): 3030*w*, 2965*m*, 2930*m*, 2910*m*, 2845*m*, 1625*s*, 1385*m*, 1315*vs*, 1200*m*, 1045*s*, 1035*s*, 880*m*, 870*m*, 670*vs*, 650*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.75 (*dd*, J = 8, 3, 1H); 4.20 (*dd*, J = 4.5, 2.5, 1H); 2.88 (*m*, 1H); 2.07 (*td*, J = 7, 3, 1H); 1.86 (*m*, 1H); 1.81 (*ddd*, J = 12, 4.5, 2.5, 1H); 1.70 (*m*, 1H); 1.05 (*d*, J = 12, 1H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): 127.2 (*s*), 119.2 (*d*), 57.3 (*d*), 37.7 (*d*), 26.9 (*t*), 23.1 (*d*), 22.5 (*d*), 17.3 (*d*). MS: 174 (M^+), 176 ($M^+ + 2$), 178 ($M^+ + 4$), 141, 139 (100), 112, 103, 77, 52. Anal. calc. for $C_8H_8Cl_2$ (175.06): C 54.89, H 4.61, Cl 40.50; found: C 54.79, H 4.74, Cl 40.36.

6-endo-*(2,2-Dichlorovinyl)*-cis-*bicyclo[3.1.0]hex-2-ene*[1] (**17**). Colorless liquid, b.p. 90°/12 Torr. IR (CCl_4): 3040*m*, 3030*m*, 2890*m*, 2820*w*, 1610*m*, 1595*w*, 1350*m*, 1285*m*, 1245*m*, 1075*m*, 1030*w*, 970*m*, 920*s*, 885*vs*, 625*vs*. ^{13}C-NMR (90.6 MHz, $CDCl_3$): 131.5 (*d*), 129.4 (*d*), 125.5 (*d*), 119.8 (*s*), 32.9 (*t*), 31.4 (*d*), 23.1 (*d*), 21.9 (*d*). MS: 174 (M^+), 176 ($M^+ + 2$), 178 ($M^+ 4$), 161, 159, 141, 139, 111, 109, 103 (100), 78, 77, 51.

3,3-Dichloro-7-(2,2-dichlorovinyl)tricyclo[4.1.0.0^{2,4}]heptane (**18**). Colorless solid, m.p. 49.7–51.3°, b.p. 85°/12 Torr. IR (CCl_4): 3050*m*, 3030*m*, 2930*m*, 2870*m*, 1615*m*, 1515*m*, 1330*m*, 1270*m*, 1185*m*, 1105*m*, 1030*s*, 940*s*, 895*vs*, 660*s*, 650*m*. ^{13}C-NMR (90.6 MHz, $CDCl_2$): 125.0 (*d*), 121.9 (*s*), 67.7 (*s*), 38.5 (*d*), 34.2 (*d*), 287 (*d*), 27.6 (*t*), 23.8 (*d*), 22.0 (*d*). MS: 256 (M^+), 258 ($M^+ + 2$), 260 ($M^+ + 4$), 262 ($M^+ + 6$), 225, 223, 221, 189, 187, 185, 149, 147, 111, 109 (100), 75, 59. Anal. calc. for $C_9H_8Cl_4$ (257.97): C 41.90, H 3.13, Cl 54.97; found: C 42.01, H 3.20, Cl 55.12.

The 1,2-*exo* and 1,2-*endo* adducts **11** and **13**, resp., were not isolated. However, they were observed when both **1** and **2** were allowed to react at −10° with dichlorocarbene generated in excess by phase-transfer catalysis. The procedure was strictly the same as above, except that **1** and **2** were used as 1.8M solns. in Et_2O. The crude mixture was examined by ^{1}H-NMR permitting the assignment of the following resonances. exo-*3,3-Dichlorotricyclo[3.2.1.0^{2,4}]oct-6-ene* (**11**): ^{1}H-NMR (100 MHz, $CDCl_3$): 6.60 (*t*, *J* = 1.5, 2H); 3.20 (*m*, 2H); 2.30 (*d*, *J* = 10, 1H); 1.85 (*m*, 2H); 1.02 (*dm*, *J* = 10, 1H). endo-*3,3-Dichlorotricyclo[3.2.1.0^{2,4}]oct-6-ene* (**13**): ^{1}H-NMR (100 MHz, $CDCl_3$): only the signal at 6.04 (*t*, *J* = 1.5, 2H) could be assigned with confidence, the other signals being masked.

5. *Procedure for Dibromocarbene Additions* [24]. The procedure followed was that described in *Exper. 4*. Immediate GLC (column A) of the crude mixture gave the overall and rel. yields shown in *Table 1*. The known adducts **20**, **21**, **23**, and **24** were separated by column chromatography using hexane. They had physical and spectral data as described [7]. The 1,4-homo adduct **25** was isolated by careful distillation of the crude mixture. The fraction obtained at 40°/0.01 Torr was recrystallized from pentane at −78° to give colorless *4,4-dibromotetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane* (**25**), m.p. 50–51°. IR (CS_2): 3060*w*, 3030*w*, 3010*w*, 2980*m*, 2910*m*, 2840*m*, 1320*m*, 1260*vs*, 1190*m*, 1030*m*, 945*s*, 830*vs*, 810*s*, 795*vs*, 770*vs*, 700*s*, 670*s*. MS: 264 (M^+), 266 ($M^+ + 2$), 262 ($M^+ - 2$), 185, 183, 104 (100), 103, 78, 77, 63, 51. Anal. calc. for $C_8H_8Br_2$ (263.97): C 36.40, H 3.05, Br 60.54; found: C 36.34, H 3.30, Br 60.18.

Adducts **19** and **26** were not isolated. They were observed from the reaction of **1** and **2** at −18° with excess dibromocarbene generated by phase-transfer catalysis. ^{1}H-NMR examination of the crude mixture so obtained permitted the assignment of the following resonances. exo-*3,3-Dibromotricyclo[3.2.1.0^{2,4}]oct-6-ene* (**19**): ^{1}H-NMR (100 MHz, $CDCl_3$): 6.60 (*t*, *J* = 1, 2H); 3.16 (*m*, 2H); 2.41 (*d*, *J* = 10, 1H); 1.96 (*m*, 2H); 0.87 (*d*, *J* = 10, 1H).

6-endo-*(2',2'-Dibromovinyl)*-cis-*bicyclo[3.1.0]hex-2-ene*[1] (**26**). ^{1}H-NMR (100 MHz, $CDCl_3$): only the signals at 6.05 (*d*, *J* = 8.5, 1H) and 5.70 (*m*, 2H) could be assigned with confidence, the others being masked.

6. *Thermal Rearrangements*. 6.1. *Thermolysis of 3,4*-endo-*Dichlorobicyclo[3.2.1]octa-2,6-diene* (**14**). A soln. of **14** (500 mg) in anh. diglyme (3 ml) was sealed under N_2 in a *Pyrex* ampoule. After heating for 16 h at 200°, the mixture was cooled to r.t. and filtered through *Celite*. GLC (column A): 54% overall conversion. The *exo* isomer **12** (43% rel. yield) and **15** (33% rel. yield) were identified by GLC double injection with authentic samples isolated from dichlorocarbene additions. The remaining material (24% overall percentage) contained 5 unidentified compounds.

6.2. *Thermolysis of 4,4-Dichlorotetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane* (**16**). A soln. of **16** (500 mg) in anh. monoglyme (3 ml) under N_2 in a sealed *Pyrex* ampoule was heated for 24 h at 190°. The mixture was cooled to r.t. and filtered through *Celite*. GLC (column A): 33% overall conversion; mixture of *2,3*-exo-*dichloro-* (65%) and *2,3*-endo-*dichlorotetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane* (20%; **27**), *2,4*-exo-*dichloro-* (5%) and *2,4*-endo-*dichlorobicyclo[3.2.1]octa-2,6-diene* (6%; **28**), and *4,6*-endo-*dichlorotricyclo[3.2.1.0^{2,7}]octane* (4%; **29**). The identity of **28** and **29** was established by GLC double injection with authentic samples isolated from the thermolysis of **17** *(vide infra)*.

Synthesis of **27**. To a soln. of **16** (1.6 g, 9.1 mmol) in aq. dioxane (ml), a soln. of $AgNO_3$ (1.6 g, 9.4 mmol) in aq. dioxane (80 ml) was added slowly [8]. After standing for 1 h at 25°, the soln. was heated for 30 min at 40°, 1 h at 60°, cooled to r.t. and then neutralized with a sat. $NaHCO_3$ soln. The aq. phase was extracted with Et_2O and the combined org. layers were washed with brine. Drying ($MgSO_4$) and subsequent solvent evaporation (40°/12 Torr) left a residue which was distilled (54°/0.01 Torr) to give an epimeric mixture (1.4 g, 98%) as colorless oil. The two epimers were separated by prep. GLC (column D, 165°). *2-Chloro-3*-exo-*hydroxytetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane:* colorless solid, m.p. 42–44°, b.p. 54°/0.01 Torr. IR (CCl_4): 3600*s*, 3450*m* (br.), 3080*m*, 3050*m*, 2940*s*, 2870*s*, 1325*s*, 1285*s*, 1210*s*, 1085*vs*, 1075*vs*, 1040*vs*, 1030*vs*, 930*m*, 910*m*, 710*w*, 695*w*, 645*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 3.87 (*s*, 1H); 2.22 (*dd*, *J* = 7, 4, 1H); 2.07–1.95 (*m*, 3H); 1.88–1.76 (*m*, 2H); 1.63 (*dd*, *J* = 8, 1H); 1.54 (*m*, 1H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): 71.2 (*d*), 55.2 (*s*), 34.3 (*d*), 30.6 (*d*), 28.5 (*d*), 25.6 (*t*), 24.8 (*d*), 22.6 (*d*). MS: 158 ($M^+ + 2$), 156 (M^+), 141, 138, 121, 103, 91 (100), 77. *2-Chloro-3*-endo-*hydroxytetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane:* colorless

liquid, b.p. 54°/0.01 Torr. IR (CCl_4): 3610*m*, 3490*w* (br.), 3070*w*, 3050*m*, 2950*w*, 2930*m*, 2890*w*, 2870*m*, 1330*m*, 1280*m*, 1230*m*, 1210*m* (br.), 1090*vs*, 1055*vs*, 1030*m*, 920*m*, 890*w*, 685*w*, 675*w*, 645*w*. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.81 (*d*, *J* = 5, 1H); 2.28 (*d*, *J* = 13, 1H); 2.17 (*dd*, *J* = 7, 4, 1H); 1.97–1.84 (*m*, 4H); 1.56 (*m*, 1H); 1.49 (*m*, 1H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): 79.2 (*d*), 51.9 (*s*), 36.2 (*d*), 31.8 (*d*), 26.7 (*t*), 25.2 (*d*), 24.9 (*d*), 22.3 (*d*). MS: 158 (M^+ + 2), 156 (M^+), 138, 121, 103, 91 (100), 77.

A soln. of the epimers (1.4 g, 8.9 mmol) and Ph_3P (3 g, 11.4 mmol) in CCl_4 (10 ml) was refluxed for 16 h [25]. The mixture was cooled to r.t., filtered, washed with Et_2O, and concentrated. Distillation (45°/0.01 Torr) gave 1.1 g (70%) of a mixture of the epimeric chlorides which were isolated by prep. GLC (column C, 160°). *2,3*-exo-*Dichlorotetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane* (exo-**27**): colorless liquid. IR (CCl_4): 3080*m*, 3050*m*, 2960*m*, 2940*s*, 2870*s*, 1365*m*, 1315*s*, 1290*m*, 1280*m*, 1270*m*, 1230*s*, 1210*m*, 1080*vs*, 1035*m*, 980*s*, 915*s*, 830*s*, 700*m*, 680*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.22 (*s*, 1H); 2.33 (*dd*, *J* = 7, 4, 1H); 2.18 (*dd*, *J* = 10, 6, 1H); 2.15 (*m*, 1H); 1.95–1.88 (*m*, 2H); 1.85 (*dd*, *J* = 9, 7, 1H); 1.61 (*m*, 1H). MS: 174 (M^+), 176 (M^+ + 2), 178 (M^+ + 4), 141, 139 (100), 114, 112, 103, 91, 77. *2,3*-endo-*Dichlorotetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane* (endo-**27**): colorless liquid. IR (CCl_4): 3070*w*, 3050*m*, 2960*m*, 2940*m*, 2880*m*, 1370*m*, 1325*m*, 1305*m*, 1280*m*, 1240*s*, 1080*s*, 1070*m*, 955*m*, 940*m*, 920*m*, 660*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 4.70 (*d*, *J* = 5, 1H); 2.42 (*d*, *J* = 13, 1H); 2.29 (*dd*, *J* = 7, 4, 1H); 2.03 (*m*, 2H); 1.86 (*m*, 1H); 1.73–1.60 (*m*, 2H). MS: 174 (M^+), 176 (M^+ + 2), 178 (M^+ + 4), 141, 139, 114, 112, 103, 100, 91, 77.

6.3. *Thermolysis of* exo-*3,3-Difluorotricyclo[3.2.1.0^{2,4}]oct-6-ene* (**7**). Samples (2 ml) of a 1M soln. of **7** in anh. triglyme were sealed under Ar in a *Pyrex* ampoule which had been previously treated with NH_3 gas. The ampoules were opened at intervals and the rearrangement followed by GLC (column B) of 0.05-ml aliquots after filtration through *Celite*. Heating for 2 h at 180° resulted in almost quantitative conversion to *3,3-difluorotetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane* (**30**).

Thermolysis of **8**. Samples (0.4 ml) of a 1M soln. of **8** in C_6D_6 were sealed under N_2 in NMR tubes and heated in a thermostated oil bath at 90 to 120°. GLC (column B): only **31**, which was characterized after GLC purification (column E, 90°) and by independent synthesis [26]. *4,4-Difluorobicyclo[3.2.1]octa-2,6-diene* (**31**): colorless liquid. IR (neat): 3070*w*, 3045*w*, 2955*m*, 2880*w*, 1740*w*, 1635*w*, 1450*w*, 1380*s*, 1310*m*, 1260*m*, 1105*s*, 1090*s*, 1040*s*, 1020*s*, 750*s*, 710*s*. ^{13}C-NMR (90.6 MHz, $CDCl_3$): 145.5 (*d*), 143.6 (*dt*), 130.2 (*d*), 121.2 (*dt*), 118.4 (*t*), 48.6 (*dt*), 45.6 (*t*), 39.7 (*d*). MS: 142 (100, M^+), 127 (47), 122 (11), 96 (17), 91 (89), 78 (90), 77 (80), 65 (26), 51 (42). Anal. calc. for $C_8H_8F_2$ (142.15): C 67.60, H 5.67, F 26.73; found: C 67.49, H 5.66, F 26.56.

6.4. *Thermolysis of* **17**. Compound **17** could only be isolated as a mixture with its *exo* isomer[1]) **32** in minor amounts owing to epimerization at 120°. A mixture of the two epimers (83 mg) was dissolved in $CDCl_3$ (0.4 ml) and sealed under N_2 in an NMR tube. After 25 h at 170°, GLC (column A) showed an almost quant. conversion (4% **17**/**32** unchanged) to a mixture of *endo*- and *exo*-**28** (30 and 46%, resp.) and of **29** (20%). Compounds **32**, **28**, and **29** were isolated by prep. GLC (column D, 140–220°). *6*-exo-*(2',2'-Dichlorovinyl)*-cis-*bicyclo[3.1.0]hex-2-ene*[1]) (**32**): colorless liquid. IR (CCl_4): 3050*m*, 3020*m*, 2990*w*, 1615*w*, 1590*w*, 1350*m*, 1280*m*, 1265*m*, 1135*m*, 1040*m*, 1010*m*, 965*w*, 920*vs*, 910*s*, 880*s*, 865*s*, 715*s*, 680*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.96 (*m*, *J* = 5.5, 1H); 5.51 (*m*, *J* = 5.5, 1H); 5.32 (*d*, *J* = 10, 1H); 2.67 (*dd*, *J* = 18, 7.5, 1H); 2.46 (*dd*, *J* = 18, 3, 1H); 2.03 (*m*, *J* = 7.5, 2, 1H); 1.75 (*m*, *J* = 7.5, 3, 1H); 1.11 (*dt*, *J* = 10, 2–3, 1H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): 132.7 (*d*), 131.4 (*s*), 131.3 (*d*), 129.5 (*d*), 36.1 (*t*), 38.8 (*d*), 30.3 (*d*), 24.5 (*d*). MS: 174 (M^+), 176 (M^+ + 2), 178 (M^+ + 4), 161, 159, 141, 139, 111, 109, 103 (100), 78, 77, 51.

exo-**28**: Colorless liquid. ^{1}H-NMR (100.1 MHz, $CDCl_3$): 6.77 (*dd*, *J* = 5, 3, 1H); 5.93 (*dd*, *J* = 5.5, 3.0, 1H); 5.41 (*dt*, *J* = 4, 1–2, 1H); 4.38 (*dd*, *J* = 4, 1–2, 1H); 2.91 (*m*, 2H); 2.37 (*d*, *J* = 10, 1H); 2.21–2.00 (*m*, 1H).

endo-**28**: Colorless liquid. ^{1}H-NMR (360 MHz, $CDCl_3$): 6.60 (*dd*, *J* = 5.5, 3, 1H); 6.02 (*dd*, *J* = 5.5, 3, 1H); 5.34 (*m*, 1H); 3.26 (*m*, 1H); 2.86 (*m*, 1H); 2.25–2.18 (*m*, 1H); 2.09 (*d*, *J* = 10, 1H).

29: Colorless liquid. ^{1}H-NMR (100.1 MHz, $CDCl_3$): 6.13 (*dd*, *J* = 6, 2, 1H); 4.31 (*ddd*, *J* = 5, 2.5, 1, 1H); 2.90 (*m*, 1H); 2.00–1.50 (*m*, 4H); 1.16 (*d*, *J* = 12, 1H).

7. *Remarks on the NMR Data.* The structure of **18** has been secured by X-ray analysis [27], consequently, its NMR properties serve as valid references for structures **8**–**10** and **17**. The dichlorovinyl group in **18** in both solid and liquid states is disposed *endo*[2]) and adopts a *transoid* conformation with respect to the cyclopropane ring. ^3J (H–C(1'), H–C(7)) in **18** is 8.0 Hz and corresponds to a calculated dihedral angle of 160° [28]. ^3J = 7.5–8.0 Hz are found for **8**, **17**, **9**, and **10**, hence they contain the same *transoid*-disposed dihalovinyl group *(Table 4)*.

The (dichlorovinyl)cyclopropane unit in **18** is *cis*-fused; the *cis*-disposed protons attached thereto give a characteristic ^3J of 6 Hz. Similar values are found for the same coupling in **8**, **17**, **9**, and **10**, hence their (dihalovinyl)cyclopropane (or (tetrafluorocyclopropyl)cyclopropane) units are also *cis* fused. That the difluoro- and dichlorocyclopropane moieties of **10** and **18** are *cis*-fused too is confirmed by the similar value for ^3J(2,4) *(Table 4)*.

The close similarity of the δ_H's (H–C(1), H–C(2), H–C(3), H–C(4), and H–C(5)), together with the constancy of the shift difference between H_{exo}–C(4) and H_{endo}–C(4) for **8**, **17**, and **9** is consistent with their common structural element, the cyclopentene moiety *(Table 2)*.

The δ of the cyclopropane proton (H–C(6) or H–C(7)) is an accurate reflection of its immediate environment. The difluorovinyl compounds **8** and **10** give similar values as do the dichlorovinyl compounds **17** and **18**. The tetrafluorocyclopropane **9** is an exception, H–C(6) appearing at high field owing to shielding by the cyclopropane ring.

The spectral data of **31** are fully consistent with the bicyclo[3.2.1]octadiene structure. $^2J(F,F) = 273$ Hz is in accord with geminally disposed F-substituents in a six-membered ring [29].

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