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CAPTODATIVE SUBSTITUENT EFFECTS - PART XXXI[1]

OLEFINS WITH CAPTODATIVE SUBSTITUTION IN [2+2] CYCLOADDITIONS

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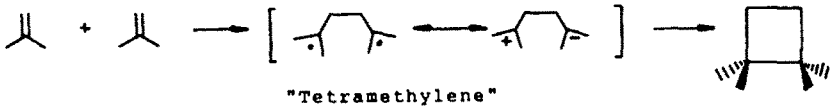
Summary : *Olefins with captodative substitution are excellent partners in [2+2] cycloadditions leading to cyclobutane derivatives. The reaction rates increase with the radical stabilising power of the substituents. Thio- and selenoalkyl(aryl) substituted gem-difluoroolefins allow the synthesis of new cyclobutane derivatives.*

INTRODUCTION

Since cyclobutane was discussed by Baeyer exactly 100 years ago in his theory of angle strain[2], the thermal [2+2] cycloaddition and dimerisation of olefines to cyclobutane derivatives and their cycloreversion have found great synthetic and theoretic interest [3-6].

According to the Woodward-Hoffmann rules the thermal [π^2s + π^2a] cycloaddition is allowed but it is sterically disfavoured. In practice most thermal [2+2] cycloadditions appear as two step reactions via tetramethylene with varying degree of diradical or zwitterionic nature depending on the substituents[4,6].



"Tetramethylene"

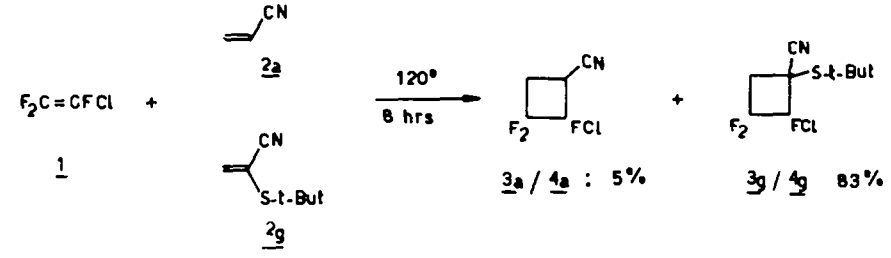
As a part of our research concerning the extent of captodative (**cd**) radical stabilisation[7] we have examined [2+2] cycloaddition reactions of olefins bearing **cd** substitution.

It is established now, that these **cd** olefins add readily radicals giving radical adducts which are stabilised due to the synergic effect of electron-acceptor (capto-) with donor (dative) substituents either on the same carbon or in vinylogous position [7,8]. Furthermore, **cd**-olefins show in addition reactions higher reactivity toward isobutyronitrile radical than expected from polar factors[9]. This behaviour can be anticipated since **cd** substitution on ethylene reduces the HOMO-LUMO gap while it increases the coefficients of both orbitals on the β-carbon[7,9]. In agreement with this interpretation, some of the **cd** olefins dimerise already at room temperature to head-to-head cyclobutane derivatives via

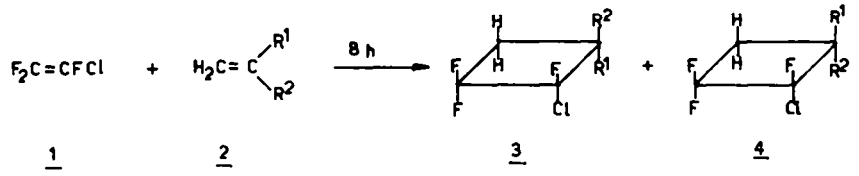
1,4 diradical type tetramethylene intermediates [10]. It could thus be expected that **cd** olefins would be efficient partners in [2+2] thermal cycloadditions to ethylene derivatives having pronounced tendency for this reaction : allenes, methylene cyclopropanes and gem-difluoroethylene derivatives.

RESULTS

In this report four series of cycloaddition reactions leading to cyclobutanes are described. First we studied the reaction of chlorotrifluoroethylene **1**, as a well recognized partner in [2+2] cycloadditions with the captodative (**cd**) olefins **2**. An overnight reaction in a sealed tube without solvent gives satisfactory yields and requires temperatures of 80, 120 or 160°C depending on reactivity. The results (Table 1) show that the reactions occur the easiest with **cd** olefines, which have the best radical stabilising substituents. Competition reactions confirm this interpretation. Thus, when an equimolar mixture of acrylonitrile **2a**, α-tert.butyl thioacrylonitrile **2g** and chlorotrifluoroethylene **1** is heated for 8 hours at 120°C, only 5% of cyclobutane derivatives **3a** and **4a** are formed while the yield of **3g** and **4g** amounts to 83 %.



The most significant NMR data of the new cyclobutanes **3** and **4** are collected in Table 5.

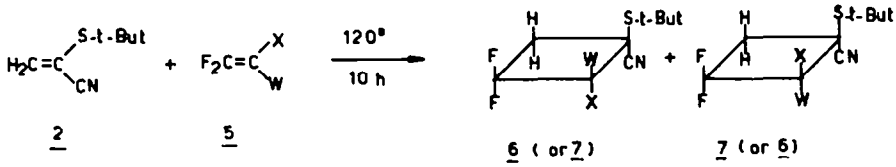


Olefins	R^1	R^2	Temp.°C	Yield[a]	Cyclobutanes
2 **a**	CN	H	160	65	**3a,4a**
b	St-But	COOMe	120	68	**3b,4b**
c	Cl	CN	120	72	**3c,4c**
d	SePh	CN	120	70	**3d,4d**
e	SEt	CN	120	83	**3e,4e**
f	SPh	CN	120(80)	85(52)	**3f,4f**
g	St-But	CN	120	90	**3g,4g**
h	OMe	COOMe	80	20	**3h,4h**

a) Pure phase, molar ratio of **1** to **2** = 1.5/1, yield calculated on **2**

Table 1. [2+2] cycloadditions of **cd**-olefins to chlortrifluoroethylene.

Various other gem-difluoroethylene derivatives **5** have been studied in the reaction with the acrylonitrile α-thioether **2g** as a unique partner and producing cyclobutanes in good yields (Table 2). The known thio- or selenoethers **5e-f** were never used until now in cycloaddition reactions and the new difluorochloroethylene thio- and seleno ethers **5h,i,j**[11] invite for further exploration. Again these gem-difluoroethylenes appear to react best when their β substituents are good radical stabilising groups.



2 **5** **6** (or **7**) **7** (or **6**)

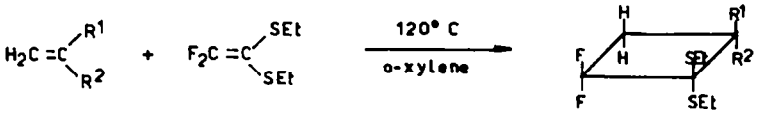
Olefins	X	W	Yield[a]	Cyclobutanes
5 a	H	Ph	39	**6a,7a**
b	H	OPh	35	**6b,7b**
c	H	SPh	47	**6c,7c**
d	H	SePh	46(65)[b]	**6d,7d**
1	F	Cl	90[c]	**3g,4g**
5 e	F	SPh	57	**6e,7e**
f	F	SePh	67	**6f,7f**
g	Cl	Cl	75	**6g**
h	Cl	SPh	88	**6h,7h**
i	Cl	SePh	92	**6i,7i**
j	SEt	SEt	71	**6j**

a) for stoichiometric amounts in pure phase
b) at 140°C
c) **1/2g** = 1.5/1

Table 2 [2+2] cycloadditions with α-tert.butylthioacrylonitrile **2g**.

1,1-Bis-(ethylthio)-difluoroethylene **5j** has been used in kinetic competition measurements in order to determine relative rates of cycloaddition to different **cd** olefins (Table 3). Equimolar quantities of two **cd** olefins **2** were heated to 120°C in o-xylene solution with 2.2 equivalents of **5j** in the NMR spectrometer and the olefin signal decay was monitored by 1H-NMR. Final spectra of fluorine-19 NMR did not show other products than the cycloadducts. The rate acceleration due to the variation of substituents does not exceed a factor of 10 and follows in general the order of the radical stabilising effect of the substituents. Heating for 24 hours of pure cycloadducts under the same conditions remained without effect and thus exclude reverse reaction at 120°C.

Thermal [2+2] cyclodimerisation of some **cd** olefins or gem-difluoroethylenes is well known[10,12]. 1,1-Alkyl or arylthio and nitrile substitution favours this process in the temperature range around 20°C. Selenium analogues[13] **2m** and **2d** dimerize around 60°C. The resulting cyclobutanes reverse to olefins at about 200°C. If the captor substituent is -CHO(**2n**) or -COMe (**2o**) the final products are not cyclobutanes, but as for the thioalkyl analogues [10a] the corresponding dihydropyrane isomers **12a,b** as formal [4+2] dimers. **2n** dimerises even at 0°C, this olefin has been characterized at -40°C by NMR only [13]. The difluoroethylene derivative **5j** cyclodimerise at 140-160°C (Table 4).



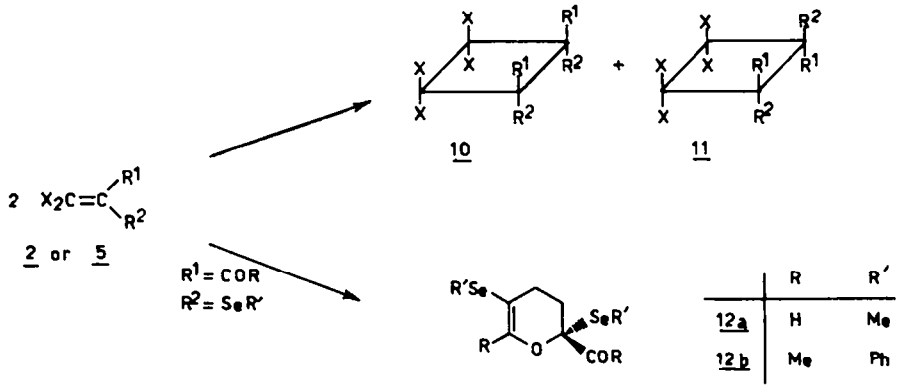
2 5j 8 (6j)

Olefins	R^1	R^2	Yield[a]	Cyclobutanes	Relative rate
2 i	OMe	CN	-	8 a	1
j	SePh	COOMe	-	b	4.17
b	St-But	COOMe	-	c	5.62
g	St-But	CN	71	6 j	7.04
k	SPh	COOMe	-	8 d	7.75
l		CN	75	e	8.29
d	SePh	CN	85	f	8.71
f	SPh	CN	b)	g	9.33

a) at 120° in 10^{-4} molar solution in benzene, yields relative to 5j

b) 100% conversion at 65°C with a molar ratio of 2f to 5j = 1/20

Table 3. [2+2] cycloadditions with 1,1-diethylthio-2,2-difluoroethylene 5j.



10 11

2 or 5

R^1 = COR
R^2 = SeR'

	R	R'
12a	H	Me
12b	Me	Ph

Olefin	X	R^1	R^2	Product	Temp.(time) °C (hours)	Yield %
2 m	H	SeMe	CN	10a/11a	65(48)	56
2 d	H	SePh	CN	10b/11b	65(88)	57
					140(8)	45
5 j	F	SEt	SEt	10c	120(8)	30
					140(8)	70
2 n	H	SeMe	CHO	12a	20(20)	100
2 o	H	SePh	COMe	12b	60(20)	79

Table 4 : Cyclodimerisation of olefins.

DISCUSSION

The reactions described above can best be interpreted as [2+2] cycloadditions via tetramethylene diradical type intermediates. The rates of these reactions are substituent dependent. Since in this series always the same type of olefinic partners are implied, namely the β-unsubstituted olefins (2) and the β,β-difluoro-derivatives (5) one probably may neglect in a first approach activation entropy variations ; furthermore it can be assumed that the rate determining transition state is close to the intermediate diradicals. The enthalpy of activation can be lowered by two factors : destabilisation of the olefin and stabilisation of the intermediate tetramethylene diradical structure. Fluorine substitution most probably destabilises the π-bond[4]. Such destabilisation may also result from strain such as in cumulated systems[14] and methylene cyclopropane[15]. Stabilisation of olefins by 1,2 push-pull substitution is substantial whereas the thermodynamic effect of 1,1 captodative substitution on the olefin π-bond has not yet been determined. Until recently, no significant radical stabilisation has been imputed to fluorine substitution[4] but recent calculations indicate 3.7 Kcal/mole stabilisation energy for difluoromethyl radicals[16].In contrast, **cd**-radical stabilisation is now demonstrated by different methods. ESR evidence clearly illustrates the synergic effect of **cd**-substitution on spin delocalisation [17]. Different kinetic measurements show the same order of rate acceleration resulting from **cd** substitution provided that radical intermediates are involved. The examples include the cis-trans isomerisation of **cd**-substituted cyclopropanes[18], tetraarylethylenes[19], as well as meso-dl isomerisation of **cd**-benzylic dimers[20]. Analogous substituent effects on rotation barriers in allylic radicals[21] and on the dissociation energies of the corresponding allylic dimers can be observed[22].

The results listed in this paper concerning [2+2] cycloadditions also show the same trend on rate acceleration thereby reflecting the varying degree of radical stabilisation by the substituents. The effect is demonstrated by low reaction temperatures, increased yields (Table 1 and 2) and relative rate measurements (Table 3) which indicate the following order :

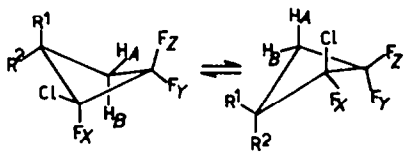
$CN/OR < COOR/SeR < COOR/SR < CN/SR \approx CN/SeR \approx CN/NR_2$

The biradical character of the intermediate leads to head-to-head cycloadditions without exception. Whereas the stereoselectivity remains to be studied for **cd** olefins carrying β-substituents, the cis and trans stereoisomers are generally formed in nearly 1:1 ratio. Kinetics are under investigation in order to measure cis-trans equilibration rates and to determine the activation parameters of the cycloaddition process.

Seleno gem-difluoroolefins **5d,f,i** and their thio analogues **5c,e,h,j** merit particular interest in cycloaddition reactions because of their reactivity and their potential for further functionalisation. These compounds can be considered as difluoroketene equivalents. Furthermore these reagents have the practical advantage of their relatively high boiling point permitting reaction without autoclave or sealed tubes. As reaction partners of **cd**-olefins [23] for cycloadditions allenes[24], methylene cyclopropanes[25], and ynediamines[26] are under investigation in our laboratory.

It should be stressed furthermore, that **cd**-olefins are also excellent dienophiles [27].

^{19}F and ^{1}H NMR was extensively used for structure and isomer ratio determination of the cyclobutanes. These bear generally two or three bulky



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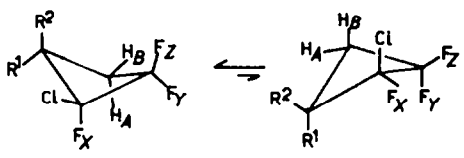

4

Comp.	Substitution		^1H δ(ppm)		^{19}F -δ(CCl_3F,ppm)			F-F coupl.const.(Hz)		
	R^1	R^2	A	B	X	Y	Z	$^2J_{YZ}$	$^3J_{XY}$	$^3J_{XZ}$
3a[28]	CN	H	3.1	2.8	112.5	116.9	97.0	197.8	-6.8	6.5
b	St-But	COOMe	2.89	3.47	122.6	113.0	99.5	194.8	10.6	5.4
c	Cl	CN	3.21	3.49	119.2	109.1	98.5	200.4	9.5	5.5
d	SePh	CN	2.82	3.12	115.4	109.5	99.8	197.0	14.1	5.2
e	SEt	CN	2.69	3.33	120.4	112.0	97.7	198.5	12.5	4.0
f	SPh	CN	2.8	3.15	112.3	111.2	98.1	198.8	7.5	3.9
g	St-But	CN	2.53	3.18	110.4	114.3	95.8	197.4	7.7	5.8
h[a)]	OMe	COOMe	2.67	3.22	133.6	111.0	100.2	197.4	6.8	4.3
4a	CN	H	3.1	2.9	124.1	108.0	104.3	199.6	-6.5	0.8
b	St-But	COOMe	2.96	3.74	122.1	111.4	103.8	198.8	9.1	<0.5
c	Cl	CN	3.12	3.56	115.7	111.0	99.7	202.3	8.4	2.7
d	SePh	CN	2.83	3.17	115.1	112.1	100.4	198.2	7.1	2.6
e	SEt	CN	2.78	3.27	112.1	107.2	98.3	199.2	7.0	3.8
f	SPh	CN	2.9	3.25	120.1	107.4	98.8	198.9	12.6	3.8
g	St-But	CN	2.77	3.32	120.5	105.8	100.1	200.4	12.8	1.7
h[a)]	OMe	COOMe	2.75	3.39	127.0	110.8	101.8	200.4	9.7	<0.5

a) assignement of configuration remains arbitrary.

Table 5. NMR data of cyclobutanes 3 and 4.

substituents (such as Cl, SR, SeR) which have the tendency to occupy equatorial positions. Vicinal cis disubstitution in isomers **3** (Table 1 and 5) should lead to a near to 1:1 conformer equilibrium whereas two bulky trans substituents cause an excess of population of the diequatorial forms (isomer **4**). This equilibrium influences several NMR parameters and in particular the fluorine-19 chemical shifts and F-F coupling constants [28] which permitted to attribute the configuration of the cyclobutanes **3** and **4** (Table 5).

In agreement with chemical shift calculations[29] chlorine in cis position to fluorine causes a high frequency shift in fluorine-19 NMR (electric field effect or Van der Waals shift)[28-30]. A comparable effect is calculated for the respective C-H bond[29].

The chemical shift difference between signals of geminal fluorine atoms (F_X-F_Y) in the spectra of **4** is always smaller than in **3** (Table 5)[28]. Assuming the same puckering angle for all conformations the cis interactions do not change from **3** to **4**, but the trans interactions are different. In the favoured conformation of **4**, the equatorial-equatorial position of F_Y-Cl and of F_Y-H_B (in contrast to the axial-axial F_Z-H_A) induces opposite shifts for F_Y and F_Z. For the same substitution pattern the geminal F-F coupling constants are generally smaller in **3** than in **4**. The vicinal $^3J_{XZ}$ couplings for **4** are near to zero (max. 3-4 Hz) indicating the axial-axial arrangement for F_Z and F_X in accordance with the dihedral angle dependence of these coupling constants[28]. The distinction between the isomers **6** and **7** (Table 3) is much less obvious. A thorough analysis of NMR spectra which takes into account F-H interactions is under way.

EXPERIMENTAL

^1H and ^{19}F NMR spectra were taken on a Varian XL-200 spectrometer using TMS or $CFCl_3$ as reference in $CDCl_3$ solution ; unless otherwise indicated, NMR signals represent one single proton or fluorine and are multipletts. The majority of the NMR data of **3** and **4** are collected in Table 5. Mass spectra were registered on Varian MAT 44S spectrometer. Chlorotrifluoroethylene (CTFE) **1** was purchased from Matheson Gas Products and was redistilled before use (B.p.- 36.5°C). Yields are generally not optimized.

General procedure for the cycloadditions with CTFE :
The corresponding olefin (0.01 mole) is introduced into a glass tube (its volume should not be less than 15-20 ml) together with a few crystals of hydroquinone. The tube is then connected to a vessel containing CTFE (1.7 g, 0.015 mole) which is distilled into it by cooling to -78°C. The tube is then sealed in vacuum inserted into a metal tube and the whole is heated into an oil bath during 8 hours behind a safety shield (Temp.: see Table 1). **Caution : the ampoule may explode if not properly sealed.**
The tube is cooled in liquid nitrogen and opened. Excess CTFE is left to evaporate under hood and the residue is either distilled or chromatographed. The yields refer to olefins **2**.

2-chloro-2,3,3-trifluoro-1-cyanocyclobutane 3a, 4a is already known in the literature [26].

2-chloro-2,3,3-trifluoro-1-tert-butylthio-1-methoxycarbonylcyclobutane 3b, 4b : unreacted acrylate is removed at 20°C/1 Torr and the residue is chromatographed on silicagel/Pet.ether : ethyl acetate = 95:5. M.p.: 58-60°. Yield 68 %. IR (CCl_4): ν = 2965, 2950, 2930, 2905, 2870, 1790, 1635, 1370, 1310, 1270, 1230, 1170, 1120, 1110 and 1085 cm^{-1}. MS EI M$^+$ = **290**; 234, 201, 175, 107, 89. ^1H NMR **3b(4b)** δ = 1.37 (1.35,s,9H), 2.89(2.96), 3.47(3.74), 3.87(s,3H).

1,2-dichloro-2,3,3-trifluoro-1-cyanocyclobutane 3c, 4c : B.p.: 88-89°C/17 Torr. Yield 72 %. IR(CCl_4): ν = 3040, 2980, 2245, 1415, 1320, 1245 cm^{-1}. NMR see Table 5. MS(CI, isobutene) M+1 = **204**.

2-chloro-2,3,3-trifluoro-1-phenylseleno-1-cyanocyclobutane 3d, 4d : the residue is chromatographed as with **3b** and distilled in a Kugelrohr. B.p.: 120-125°C/0.001 Torr. Yield 78 %. ^1H NMR **3d(4d)** δ = 2.82(2.83), 3.12(3.17), 7.3-7.4(m,3H), 7.7 (m,2H).

2-chloro-2,3,3-trifluoro-1-ethylthio-1-cyanocyclobutane 3e, 4e: the residue is distilled to give a colorless liquid. B.p.: 94-96°C/0.05 Torr. Yield 83 %. IR

(CCl_4) : ν = 2980, 2940, 2880, 2245, 1425, 1315, 1245, 1110 and 675 cm^{-1}. ^1H NMR **3e(4e)** δ = 1.36(t,3H), 2.69(2.78), 2.95(q,2H), 3.33(3.27).

2-chloro-2,3,3-trifluoro-1-phenylthio-1-cyanocyclobutane 3f, 4f : B.p. 106-110°C/0.05 Torr. Yield 85 %. IR (CCl_4) : ν = 3065, 3030, 2970, 2240, 1580, 1570, 1480, 1445, 1420, 1325, 1240, 1175, 1110, 1005 and 675 cm^{-1}. MS (EI) M^+ = **277**; 242, 197, 161, 134, 109, 91, 65. ^1H NMR **3f(4f)** : δ = 2.8(2.9), 3.15(3.25), 7.4-7.5(m,3H), 7.7(m,2H)ppm.

2-chloro-2,3,3-trifluoro-1-tert-butylthio-1-cyanocyclobutane 3g, 4g : the residue is purified by distillation. B.p.: 98-102°C/0.05 Torr. Yield 90 % and by chromatography on silicagel/Pet. ether. IR (CCl_4) : ν = 2970, 2950, 2930, 2885, 2245, 1475, 1460, 1420, 1370, 1315, 1240, 1180, 1110, 1005 and 670 cm^{-1}. MS (EI) M^+ = **257**; 242, 215, 201, 141, 116, 85. ^1H NMR **3g(4g)** δ = 1.52(s,9H), 2.53(2.77), 3.18(3.32)ppm.

2-chloro-2,3,3-trifluoro-1-methoxy-1-carbomethoxycyclobutane 3h, 4h : the residue is distilled at 65-67°C/17 Torr. Yield 20 %. IR (CCl_4) : ν = 3010, 2960, 2840, 1740, 1475, 1440, 1300, 1230, 1160, 1140, 1110, 1090, 1005 and 670 cm^{-1}. MS (EI) M^+ = **232**; 217, 173, 116, 87. ^1H NMR **3h(4h)** δ = 2.67(2.75), 3.22(3.39), 3.35(3.27,s,3H), 3.89(3.90,s,3H) ppm.

General procedure for the cycloadditions of α-tert-butylthioacrylonitrile 2g with gem-difluoroolefins : 2 mmoles of **2g** and 2 mmoles of fluoroolefine are heated without any solvent in a small (10 ml) sealed ampoule at 120° for 10 hours.

3,3-difluoro-2-phenyl-1-tert-butylthio-1-cyanocyclobutane 6a,7a : starting olefin is removed at 20°C/0.01 Torr and the residue is chromatographed on silicagel/Pet. ether. B.p. (Kugelrohr) 60-62°C/0.01 Torr. Yield 39 %. IR (CCl_4) : ν = 3095, 3070, 2960, 2230, 1610, 1500, 1460, 1370, 1285 cm^{-1} MS (EI) M^+ = **281**; 225, 190, 161, 140, 57, 41. NMR **6a(7a)** ^1H : δ = 1.40(1.26,s,9H), 3.08(3.17), 3.43(3.48), 4.15(4.67), 7.3-7.4(m,5H)ppm ^{19}F : -δ = 108.9(101.7), 79.8(81.4)ppm J = 196.8(198.4)Hz.

3,3-difluoro-2-phenoxy-1-tert-butylthio-1-cyanocyclobutane 6b, 7b : same work-up as for **6a**, the eluent is pet. ether/ethyl acetate = 95:5. B.p.: 82-84°C/0.01 Torr. Yield 35 %. IR (CCl_4) : ν = 3070, 2970, 2240, 1595, 1495, 1420, 1370, 1305, 1235, 1170 cm^{-1}. MS(EI) M^+ = **297**; 241, 156, 147, 127, 94, 77, 57, 41. NMR **6b(7b)** ^1H : δ = 1.53(1.55), 2.77(3.16), 3.31(3.28), 4.87(5.27), 7.07(m,2H), 7.13(m,1H), 7.36(m,2H)ppm ; ^{19}F : -δ = 116.2(110.8), 86.1(87.2)ppm J = 204.7(205.5)Hz.

3,3-difluoro-2-phenylthio-1-tert-butylthio-1-cyanocyclobutane 6c, 7c : B.p.:100-105°C/0.02 Torr. Yield 47 % a yellow liquid. IR (CCl_4) : ν = 3080, 3065, 2970, 2235, 1585, 1485, 1440, 1370, 1300 cm^{-1} MS (EI) M^+ = **313**; 257, 226, 192, 172, 141, 110, 77, 57, 41. NMR **6c(7c)** ^1H : δ = 1.41(1.48,s,9H), 2.87(3.11), 3.32(3.29), 4.07(4.66), 7.2-7.3(m,3H), 7.44(m,2H), ^{19}F : -δ = 105.2(99.6), 82.4(84.5)ppm J = 199.4 (199.2)Hz.

3,3-difluoro-2-phenylseleno-1-tert-butylthio-1-cyanocyclobutane 6d, 7d : the heating was done at 140° for 28 hours. The crude product is chromatographed (SiO_2/CH_2Cl_2) and distilled. B.p.: 108-111°C/0.001 Torr, pale yellow oil. Yield 65 %. IR (film) : ν = 3070, 2980, 2250, 1580, 1480, 1465, 1445, 1305, 1260, 1175 cm^{-1}. MS (EI) M^+ = **361**; 305, 220, 157, 141, 77, 51. NMR **6d(7d)** ^1H : δ = 1.46(1.55,s,9H), 3.21(2.98), 3.42(3.29), 4.81(4.21), 7.25-7.35(m,3H), 7.7(m,2H)ppm; ^{19}F : -δ = 102.7(93.7), 82.3(85.3)ppm J = 197.8(197.9)Hz.

2,3,3-trifluoro-2-phenylthio-1-tert-butylthio-1-cyanocyclobutane 6e, 7e : the residue is chromatographed (SiO_2/Pet.ether) and distilled B.p. 90-92°C/0.02 Torr. Yield 57 %. IR (CCl_4) : ν = 3095, 3070, 2970, 2240, 1575, 1475, 1445, 1370, 1305, 1230, 1165, 1095 cm^{-1}. MS (EI) M^+ = **331**; 275, 242, 190, 166, 141, 127, 109, 77, 57, 41. NMR **6e(7e)** ^1H : δ = 1.48(1.60,s,9H), 2.79(2.82), 3.01(3.35), 7.3-7.4(m,3H), 7.62(7.68,m,2H)ppm ; ^{19}F : -δ = 124.3(131.9,X), 110.4(102.6,Y), 93.1,Z)ppm J = 195.8(199.6), J_{XY} = 15.1(18.0), J_{XZ} = 8.5(4.0)Hz.

2,3,3-trifluoro-2-phenylseleno-1-tert-butylthio-1-cyanocyclobutane 6f, 7f : chromatography (SiO_2/CH_2Cl_2) and distillation afford 67 % of 6f as a pale yellow oil. B.p.: 110-115°C/0.001 Torr. IR (film) : ν = 3080, 2990, 2880, 2250, 1580, 1480, 1465, 1445, 1420, 1310 cm^{-1}. MS(EI) M^+ = **379**; 323, 238, 157, 77, 51. NMR **6f(7f)** ^1H = 1.54(1.32,m,9H), 2.71(2.69), 3.01(3.31), 7.2-7.3(m,3H), 7.7(m,2H), ^{19}F: -δ = 128.0(132.7,X), 112.7(104.9,Y), 89.7(90.5,Z)ppm, J = 195.6(200.5), J_{XY}= 13.4(14.6); J_{XZ} = 6.4(2.6)Hz.

2,2-dichloro-3,3-difluoro-1-tert-butylthio-1-cyanocyclobutane 6g : the solid redisue is chromatographed (SiO_2/Pet.ether) to give 75 % of **6g**, M.p. 39-40°. IR (CCl_4) : ν = 2970, 2240, 1470, 1460, 1430, 1370, 1305, 1235, 1195, 1160 cm^{-1}. MS (EI) M^+ = 273; 258, 217, 182, 154, 132, 82, 57, 41. NMR ^1H : δ = 1.47(s,9H), 2.72, 3.23ppm; ^{19}F : -δ = 101.3, 93.9ppm; J = 186.4 Hz.

2-chloro-3,3-difluoro-2-phenylthio-1-tert-butylthio-1-cyanocyclobutane 6h, 7h : the residue is chromatographed (SiO_2/Pet.ether : CH_2Cl_2 = 95:5) and distilled. B.p. 122-124°C/0.01 Torr. Yield 88 %. IR (CCl_4) : ν = 3080, 2970, 2235, 1585, 1475,

1440, 1370, 1295, 1190 cm^{-1}. MS (EI) M^+ = **347**; 291, 256, 224, 206, 181, 159, 141, 127, 109, 77, 57. NMR **6h(7h)** ^1H : δ = 1.62(1.55,s,9H), 2.96(3.08), 3.32(3.23), 7.3-7.4(m,3H), 7.66(m,2H)ppm ; ^{19}F : -δ = 97.1(96.5), 89.6(90.6)ppm ; J = 186.2(186.1)Hz.

2-chloro-3,3-difluoro-2-phenylseleno-1-tert-butylthio-1-cyanocyclobutane 6i, 7i : chromatography (SiO_2, benzene) and distillation 118-125°C/0.005 Torr give 92% yield. **6i** crystallises spontaneously, M.p.: 127-128°C. IR(film) : ν = 3070, 2970, 2900, 2880, 2240, 1580, 1480, 1460, 1440, 1370 cm^{-1}. MS(EI) M^+ = **395**, 338, 306, 254, 157, 77, 51. NMR **6i(7i)** ^1H : δ = 1.63(1.52,s,9H), 2.96(3.00), 3.32(3.46), 7.3-7.4(m,3H), 7.75(7.8,m,2H)ppm ; ^{19}F : -δ = 97.1(90.8), 89.6(90.8)ppm J = 186.2 Hz.

3,3-difluoro-2,2-bis-(ethylthio)-1-tert-butylthio-1-cyanocyclobutane 6j : chromatography (SiO_2/Pet.ether : CH_2Cl_2 = 9:1) and distillation (B.p.92-95°C/0.001 Torr.) give 72% of **6j**. IR (CCl_4) : ν = 2970, 2880, 2235, 1475, 1460, 1430, 1370, 1030 cm^{-1}. MS (EI) M^+ = **325**; 269, 240, 208, 156, 128, 83, 57, 41. NMR ^1H: δ = 1.29 (t,3H), 1.34(t,3H), 1.52(s,9H), 2.77(m,2H), 2.83(m,2H), 3.30, 3.45ppm; ^{19}F : -δ = 96.5, 91.7 J = 191.2 Hz.

Relative rate measurements (cf Table 3): 0.1 mmole each of the two cd-olefins **2** 0.22 mmole of 1,1-bis-(thioethyl)-2,2 difluoroethylene **5j** and 0.05 mmole of pyrazine are dissolved in 0.5 ml of o-xylene-d-10 and heated overnight in the NMR probe at 120°C. 18 spectra are registered at programmed time intervals. The logarithms of peak heights, which are calibrated with pyrazine as internal standard are plotted for each compound against time to verify the first order kinetics relative to each olefin, and relative rates are calculated from the two plots.

2,2-bis(ethylthio)-3,3-difluoro-1-morpholino-1-cyanocyclobutane 8e: Chromatography (SiO_2/Pet.ether : ethyl acetate = 7:3). White crystals, yield 75%, M.p.:89-90°. I.R.(CCl_4): ν = 2970,2860,2225,1455,1295,1270,1215,1110,1130,1120,1045 cm^{-1}. M.S.(EI)M^+ is absent : 302, 293, 262, 235, 206, 184, 155, 138, 105, 82, 69, 42. NMR ^1H : δ = 1.20(t,3H), 1.26(t,3H), 2.48(m,4H), 2.6(m,1H), 2.66(q,2H), 2.7 (m,1H), 2.93, 3.01, 3.7(m,4H)ppm; ^{19}F : -δ = 101.9; 94.3ppm J = 194.8Hz.

2,2-bis(ethylthio)-3,3-difluoro-1-phenylseleno-1-cyanocyclobutane 8f : Chromatography (SiO_2/Pet.ether :ethyl acetate = 95:5) and distillation furnish 85% of **8f**, B.p.: 135-137°C/0.001 Torr. I.R.(film) : ν = 3080, 2870, 2230, 1580, 1475, 1440, 1290, 1200, 1140, 1025 cm^{-1}. M.S.(EI) M^+ = **393**; 364, 314, 184, 157, 77, 51. NMR ^1H : δ = 1.27(t,3H), 1.36(t,3H), 2.7(m,2H), 2.8(m,2H), 3.02, 3.39ppm ; ^{19}F: -δ= 94.7, 91.2ppm J = 194.8 Hz.

Cyclodimerisation of 2i,f,j,h and of 5j

1,2-dicyano-1,2-bis-(selenomethyl)-cyclobutane 10a, 11a. α-methylselenoacrylonitrile 1.47 g (10 mmoles) is heated in refluxing chloroforme (10 ml) for 48 hours. The crude product is recrystallised from pentane ; ether = 1:9 at -20°C. Yield 56% of a mixture cis : trans = 5:1. M.p.: 91-92°C. ^1H NMR ($CDCl_3$) : cis-isomer δ = 2.33(s,6H), 2.55(m,2H), 2.95(m,2H); trans-isomer δ = 2.22(m,2H), 2.45(s,6H), 3.12(m,2H). IR (CH_2Cl_2): ν = 2990, 2880, 2250, 1110, 810 cm^{-1}. MS (EI) M^+ = **294**; 147, 95. For $C_8H_{10}N_2Se_2$ (292.10) found : C : 32.12, H : 3.07, N : 9.72; requires : C : 32.89, H : 3.45, N : 9.59.

1,2-dicyano-1,2-bis(selenophenyl)-cyclobutane 10b, 11b: α-phennylselenoacrylonitrile **2d**, 2.08 g (10 mmoles) is refluxed in 10 ml $CHCl_3$ for 88 hours. Evaporation of the solvent gives 57% of cis and trans-cyclobutane (45:55). They can be separated by chromatography (SiO_2/Pet.ether : ethyl acetate = 9:1) and are recrystallized from CH_2Cl_2/hexane at -20°C. M.p. of the cis isomers 104-5°C, trans-isomer 117-118°C. ^1H NMR ($CDCl_3$): cis-isomer δ = 2.64(m,2H), 2.77(m,2H), 7.4-7.5(m,6H), 7.80(m,4H); trans-isomer δ = 2.40(m,2H), 2.93(m,2H), 7.3-7.8(m,6H), 7.75(m,4H). IR(CH_2Cl_2): ν = 3060, 2980, 2880, 2125, 1580, 1480, 1440, 1200, 995 cm^{-1}. MS (CI/IB): 475 $(M+57)^+$, 419. $(M+1)^+$, 315, 266, 210, 105. For $C_{18}H_{14}N_2Se_2$ (416.24) found: C : 51.92, H : 3.48, N : 6.67; requires: C : 51.94, H : 3.39, N : 6.73.

2-formyl-2,5-bis-selenomethyl)-2,3-dihydropyrane 12a: the mixture of regioisomers from the addition of methane selenenyl bromide to acroleine is treated by triethylamine in ether at -40°C and allowed to stir one hour at 20°C. The precipitate is removed and the crude product is chromatographed (SiO_2/Pet.ether : ethyl acetate = 9:1). Yield 40% of a pale yellow oil which is rather unstable. ^1H NMR ($CDCl_3$): δ = 1.9(s,3H), 2.12(s,3H), 2.1-2.2(m,2H), 2.35(m,1H), 2.61(m,1H), 6.70 (t,1H ^4J = 1.7Hz), 9.1 (s,1H). M.S. (EI) M^+ = **300**; 285, 262, 205, 150, 95.

2-acetyl-2,5-bis(phenylseleno)-5-methyl-2,3-dihydropyrane 12b : the freshly distilled 3-phenylseleno-3-butene-2-one **2o**, 1.6 g (7.1 mmoles) is heated in refluxing chloroform (10 ml) for 20 hours. The crude product is chromatographed (Al_2O_3/Pet.ether : ethyl acetate = 9:1). Yield 79% of a pale yellow oil which decomposes slowly to give diphenyldiselenide. ^1H NMR ($CDCl_3$) : δ = 1.96(m,1H), 2.17(s,3H), 2.43 (s,3H), 2.14-2.46(m,2H), 2.68(m,1H), 7.3-7.6(m,10H). ^{13}C NMR δ = 19.7 and 24.2(Q,s), 27.2 and 28.3(T,m), 88.8, 99.0, 124.0 and 126.0(S,m), 128.9, 129.2, 129.4, 129.6, 136.5 and 137.2(D,m), 152.5 and 201.0(S,m). IR (film) : ν =

3070, 3050, 2920, 2840, 1710, 1645, 1580, 1480, 1440, 1355, 1220, 1110, 800, 740, 695 cm^{-1}. MS (EI) M^+ = **452**; 427, 409, 295, 157, 77, 51.

1,1,2,2-tetrakis(ethylthio)-3,3,4,4-tetrafluorocyclobutane 10c : olefin **5j**, 2.54 g (0.013 mole) is heated in pure phase in a sealed tube at 140°C during 10 hours. The product is purified (SiO_2/Pet.ether) : a white solid of M.p. : 91-92°C. Yield 92%. ^1H NMR ($CDCl_3$) : δ = 1.2 (3H,t), 2.6(2H,q); ^{19}F : -δ = 111.9. IR (CCl_4) : ν = 1345, 1165, 1110 cm^{-1}. MS (EI) M^+ = **368**; 339, 279, 246, 221, 184, 155, 136, 111, 89, 61.

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