1,2-Bis(trifluoromethyl)ethene-1,2-dicarbonitrile and Vinyl Ethers: Cyclic Ketene Imines on the Pathway to 1:2 Cycloadducts

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Dedicated to *Wolfgang Beck* on the occasion of his 80th birthday

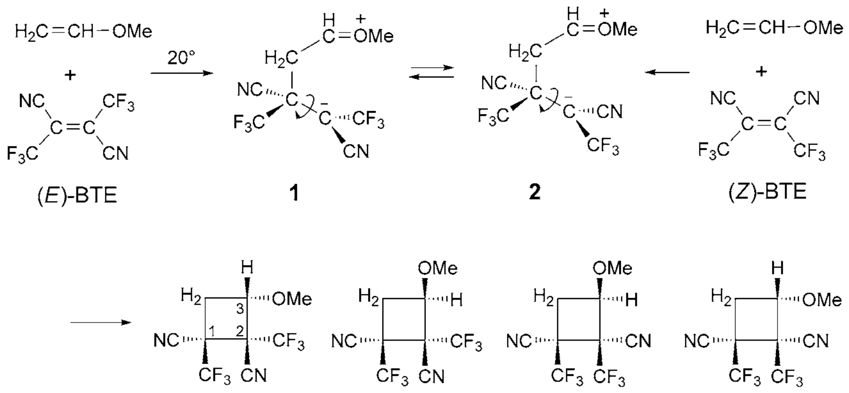
(*E*)- and (*Z*)-1,2-bis(trifluoromethyl)ethene-1,2-dicarbonitrile (BTE; (= *E*)- and (*Z*)-1,2-bis(trifluoromethyl)but-2-enedinitrile) were reacted with an excess of methyl vinyl ether, used as solvent, and furnished 1:2 adducts **6** (54%) and cyclobutanes **3** as 1:1 adducts (41%). The four diastereoisomeric bis-adducts **6** (different ratios from (*E*)- and (*Z*)-BTE) are derivatives of 1-azabicyclo[4.2.0]oct-5-ene; X-ray analyses and ^{19}F-NMR spectra revealed their structures. Since the cyclobutanes **3** are resistant to vinyl ether, the pathways leading to mono- and bis-adducts must compete on the level of the intermediate 1,4-zwitterions **1** and **2**. The latter either cyclize to the cyclobutanes **3** or to six-membered cyclic ketene imines **8** which accept a second molecule of vinyl ether to yield the bis-adducts **6**. The occurrence of the highly strained ketene imines **8** gains credibility by comparison to stable seven-membered cyclic ketene imines recently reported.

1. Introduction. – 1,2-Bis(trifluoromethyl)ethene-1,2-dicarbonitrile (= 1,2-bis(trifluoromethyl)but-2-enedinitrile) occurs in geometrical isomers; the symbols (*E*)-BTE and (*Z*)-BTE will be used in this paper. In 1966, the pioneers, *Cairns* and co-workers [1], described the (2 + 2) cycloadditions of both isomers to vinyl ethers and to *tert*-butyl vinyl sulfide as highly stereospecific. Using superior ^{19}F-NMR technique, we showed recently that the reactions of (*E*)- and (*Z*)-BTE with methyl vinyl ether in CH_2Cl_2 proceeded with only moderate stereospecificity [2]. The violation of the retention principle coincidentally amounted to 27% in both reactions of (*E*)- and (*Z*)-BTE *(Scheme 1)*.

This interaction of the donor-substituted ethene with BTE as a tetra-acceptor-substituted ethene starts with the formation of 1,4-zwitterions **1** and **2**, which can either cyclize directly or after rotation about the former acceptor bond. Four racemic diastereoisomers of cyclobutane **3** were isolated, crystallized, and structurally established. The highly different product ratios obtained in experiments with (*E*)- and (*Z*)-BTE revealed that the *gauche*-zwitterions **1** and **2** are far from reaching equilibrium [2]. The assumption of zwitterionic intermediates goes back to careful mechanistic studies on the cycloadditions of ethenetetracarbonitrile with electron-rich C=C bonds (for a review, see [3]).

In addition to cyclobutanes **3** as 1:1 adducts, minor side-products of BTE with two molecules of methyl vinyl ether were observed. The structures of these 1:2 adducts and the pathway of their formation will be described here.

Scheme 1

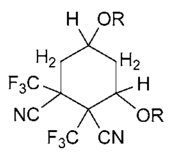


% rel. with	3(*trans*-1)	3(*trans*-2)	3(*cis*-1)	3(*cis*-2)
(*E*)-BTE	52	21	1	26
(*Z*)-BTE	2	25	66	7

2. Results and Discussion. – 2.1. *First Structural Evidence.* In the reactions of (*E*)- and (*Z*)-BTE with vinyl ethers in CH_2Cl_2, the share of the 1:2 products increased with rising concentration of the unsaturated ethers. When *ca.* 100 equiv. of methyl vinyl ether were used as solvent at room temperature, (*E*)-BTE furnished 53% of 1:2 adducts and 41% of cyclobutanes **3** (^{19}F-NMR spectrum); the corresponding results of the reaction with (*Z*)-BTE were 32% bis-adducts and 64% mono-adducts. The ^{19}F-NMR signals of the bis-adducts indicated four diastereoisomers; they were formed in different ratios from (*E*)-BTE and (*Z*)-BTE, respectively.

Mono- and bis-adducts were separated by high-vacuum distillation; the spectra of the bis-adducts showed no change before and after the distillation at 135°. The mixture was a colorless oil furnishing correct elemental analyses. Due to the high solubility of the low-melting bis-adducts, only modest amounts of crystalline material were isolated: two diastereoisomers from methyl vinyl ether, **6**(*trans-a*) and **6**(*cis-b*) (see below), and one from ethyl vinyl ether, **7**(*trans-a*).

A guiding observation: the mono-adducts, *i.e.*, the cyclobutanes **3**, did not react with vinyl ethers. Mono- and bis-adducts emerge from parallel reactions and not in consecutive order. It was not a far-fetched assumption that the mentioned 1,4-zwitterions **1** and **2** are among the common intermediates.



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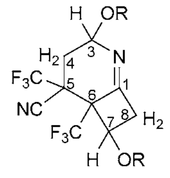

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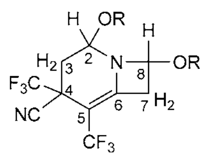
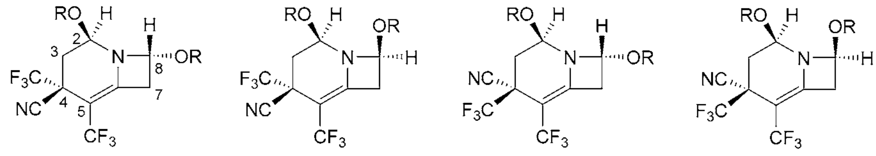


6

The cyclohexane structure **4** was not compatible with the ^{1}H-NMR spectra of the pure bis-adducts that clearly exhibited two separate *ABX* systems; a more complex coupling pattern would be expected for **4**. Furthermore, strong IR absorptions at 1682 and 1690 cm^{-1} for the two crystalline compounds, respectively, suggested a C=N bond in a bicyclic structure **5**. However, X-ray analyses of '*trans-a*' and '*cis-b*' indicated structure **6** which is likewise consistent with the IR bands.

The similarity of the ^{19}F-NMR spectra hinted at four diastereoisomers of one and the same 1-azabicyclo[4.2.0]oct-5-ene system. Two bis-adducts possess *trans*-located 2-MeO and 4-CF$_3$ groups, and two bear these substituents in *cis*-positions. The configurations of 8-MeO are symbolized by *a* and *b*. The formulae shown in *Scheme 2* correspond to the (2*R*)-enantiomers.

Scheme 2



6 R = Me *trans-a* *trans-b* *cis-a* *cis-b*
7 R = Et (2*R*,4*R*,8*R*) (2*R*,4*R*,8*S*) (2*R*,4*S*,8*R*) (2*R*,4*S*,8*S*)

2.2. *X-Ray Analyses of Two Bis-Adducts.* Compounds **6**(*trans-a*) and **6**(*cis-b*) are the major bis-adducts obtained from the reaction of methyl vinyl ether with (*E*)-BTE and (*Z*)-BTE, respectively. Their X-ray diffraction patterns are reproduced in the *Figure* as ZORTEP plots [4]. The two structures differ in the configuration of the 2-MeO group; thus, one belongs to the *trans*- and the other to the *cis*-series. The azacyclohexene ring of **6**(*trans-a*) appeared as a half-chair, whereas that of **6**(*cis-b*) could be better

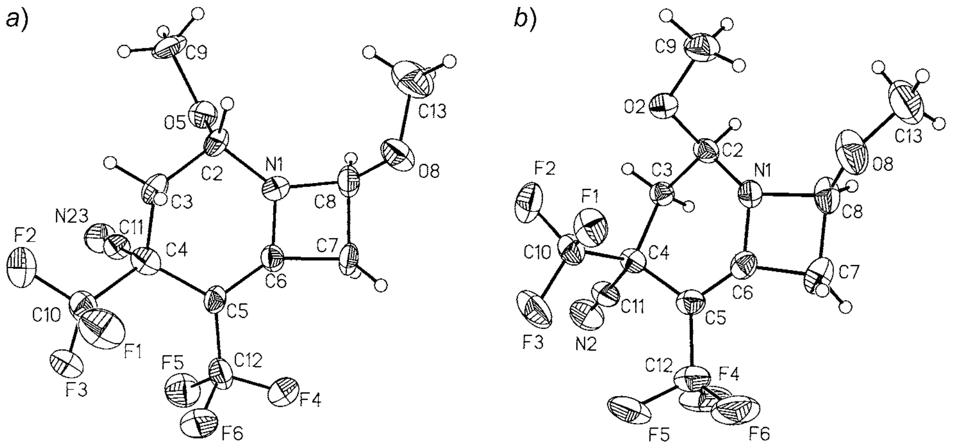


Figure. *X-Ray structures* (ORTEP; ellipsoids with 30% probability) *of* a) *(2RS,4RS,8RS)-2,8-dimethoxy-4,5-bis(trifluoromethyl)-1-azabicyclo[4.2.0]oct-5-ene-4-carbonitrile* (**6**(*trans-a*)) *and* b) *(2RS,4SR,8SR)-diastereoisomer* **6**(cis-b) described as a deformed half-boat. The involvement of a sp^2 C-atom keeps the puckering of the four-membered ring at a low value: 6.6° for **6**(*trans-a*) and 12.9° for **6**(*cis-b*).

The pyramidal shape of the N-bonds in *tert*-amines is not completely leveled out in enamines, as the zwitterionic resonance structure might suggest. In **6**(*trans-a*), the N(1)-atom is located at the top of a flat pyramid, by $\Delta = 0.117$ Å above the plane of C(2), C(6), and C(8); a larger distance, $\Delta = 0.230$ Å, in **6**(*cis-b*) points to a higher pyramidalization. *Dunitz* and co-workers [5] carefully compared the X-ray structures of seven crystalline enamines and observed an astonishing range of Δ from 0.402 to 0.013 Å. Another indication of the pyramidal shape is the shrinking sum of the three bond angles at the N-atom: 358.3° was found for **6**(*trans-a*) and 351.8° for **6**(*cis-b*).

The short C(5)=C(6) bond (1.338 Å in **6**(*cis-b*; *Table 1*) had a rather expected length for an olefinic bond, but the length of the single bond C(6)–N(1) with 1.365 Å appeared strongly shortened when compared with C(8)–N(1), 1.484 Å. The bond of CF_3 to the sp^2-hybridized C(5)-atom, 1.475 Å, was noticeably shorter than 1.547 Å for C(4)–CF_3. Considering the close relation of **6**(*trans-a*) and **6**(*cis-b*), the bond lengths and angles are compiled in *Table 1* for only one of the diastereoisomers.

Table 1. *Selected Bond Lengths and Angles* (standard deviations in parentheses) *of X-Ray Structure of (2*SR*,4*RS*,8*RS*)-2,8-Dimethoxy-4,5-bis(trifluoromethyl)-1-azabicyclo[4.2.0]oct-5-ene-4-carbonitrile* (**6**(*cis-b*))

Bond lengths [Å]			
N(1)–C(2)	1.446(2)	C(7)–C(8)	1.536(3)
C(2)–C(3)	1.518(2)	C(8)–N(1)	1.484(2)
C(3)–C(4)	1.568(2)	C(2)–O(2)	1.407(2)
C(4)–C(5)	1.520(3)	C(8)–O(8)	1.386(3)
C(5)–C(6)	1.338(3)	C(4)–CF_3	1.547(3)
C(6)–N(1)	1.365(2)	C(5)–CF_3	1.475(3)
C(6)–C(7)	1.505(3)	C(4)–CN	1.483(3)
Bond angles [°]			
C(2)–N(1)–C(6)	124.1(2)	N(1)–C(6)–C(7)	92.4(2)
N(1)–C(2)–C(3)	109.3(2)	C(6)–C(7)–C(8)	86.0(2)
C(2)–C(3)–C(4)	116.3(2)	C(7)–C(8)–N(1)	86.8(2)
C(3)–C(4)–C(5)	109.8(2)	C(8)–N(1)–C(6)	93.3(2)
C(4)–C(5)–C(6)	115.9(2)	C(2)–N(1)–C(8)	134.4(2)
C(5)–C(6)–N(1)	126.9(2)	C(6)–C(5)–C(12)	120.9(2)

2.3. *Contributions of ^{19}F-NMR Spectroscopy to Structure Analyses.* Two further bis-adducts were not isolated in pure state, but their signals were observed in the ^{19}F-NMR spectrum of the mixture. In the X-ray structure of **6**(*trans-a*), the shortest distance of the F-atoms between the two CF_3 groups amounts to 2.66 Å; for **6**(*cis-b*), it is somewhat longer (2.78 Å). Since F,F coupling takes place through space [6], it is not surprising that ^5J(F,F) = 8.5 Hz for **6**(*trans-a*) exceeds the corresponding value for **6**(*cis-b*) (6.5 Hz). *Table 2* contains the data of the not-isolated diastereoisomers, **6**(*trans-b*) and **6**(*cis-a*), which fit in with their coupling constants, ^5J(F,F) = 8.5 and 6.6 Hz, respectively.

Table 2. *The ^{19}F-NMR Chemical Shifts* (δ in ppm) *and Coupling Constants* (J in Hz) *of 1-Azabicyclo[4.2.0]octenes* **6** *and* **7** *in CH_2Cl_2* (in brackets: partial overlapping in diastereoisomer mixtures)

	(*trans-a*)	(*trans-b*)	(*cis-a*)	(*cis-b*)
6 (R = Me)				
4-CF_3	– 72.7	– 72.0	– 70.5	– 71.4
5-CF_3	– 57.1	(– 56.1)	(– 56.2)	(– 56.3)
^5J(F,F)	8.5	8.5	6.6	6.5
7 (R = Et)				
4-CF_3	– 72.7	– 72.1	– 70.4	– 71.3
5-CF_3	– 57.0	(– 56.0)	(– 56.0)	(– 56.1)
^5J(F,F)	8.5	8.5	6.9	6.7

The ratios of the four diastereoisomers of **6** (*Table 3*) indicate that the reaction of (*E*)-BTE with methyl vinyl ether gave rise to 96% of **6**(*trans-a* + *trans-b*), whereas that of (*Z*)-BTE furnished 90% of **6**(*cis-a* + *cis-b*). Thus, rotation in the initially formed 1,4-zwitterions, **1** and **2**, is only a modest side reaction.

Table 3. *1-Azabicyclo[4.2.0]octenes* **6** *and* **7** *Obtained from (*E*)- and (*Z*)-BTE with Alkyl Vinyl Ethers in CH_2Cl_2 at 20°; ^{19}F-NMR Analysis of Diastereoisomer Ratios* (rel. %)

BTE	Compound	(*trans-a*)	(*trans-b*)	(*cis-a*)	(*cis-b*)
(*E*)	**6** (R = Me)	69	27	1	3
(*Z*)	**6** (R = Me)	4	6	32	58
(*E*)	**7** (R = Et)	66	27	2	5

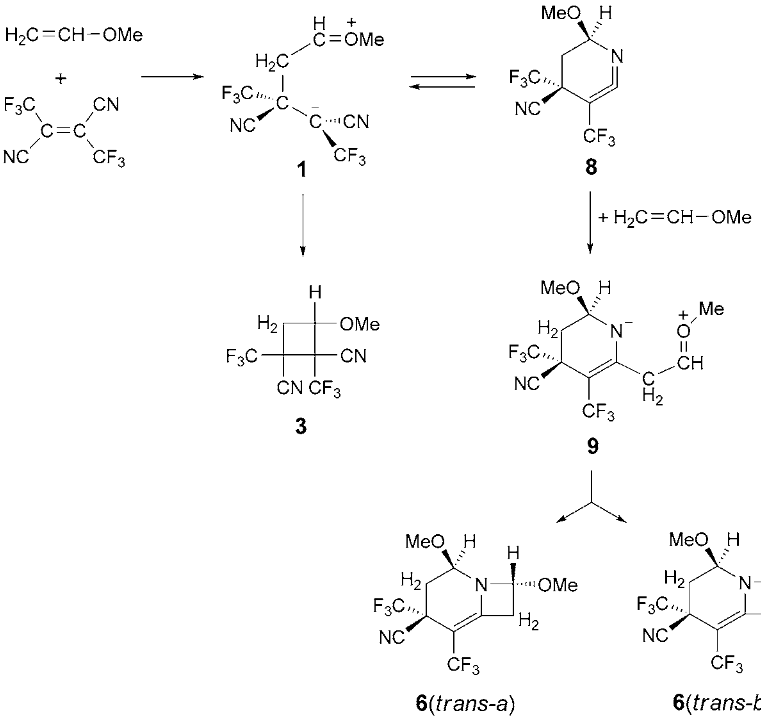
Analogously, ethyl vinyl ether, used in excess as solvent, was reacted with (*E*)-BTE and yielded bis-adducts **7** as well as mono-adducts **3**, R = Et instead of Me, in the ratio of 42 : 58. The virtually identical ^{19}F-NMR spectra of **6** and **7** (*Table 2*) corroborated the diastereoisomer assignments of **7**. Even their ratios observed for **6** and **7** were nearly the same (*Table 3*).

2.4. *Mechanistic Considerations.* Since the cyclobutanes **3** do not react with methyl vinyl ether, the somewhat daring formula **8** of a six-membered cyclic ketene imine may be proposed as a second intermediate on the way to the bis-adducts. The zwitterions **1** and **2** (*Scheme 3* illustrates the events for the *gauche*-zwitterion **1**) undergo intramolecular methoxyalkylations rendering the cyclobutanes **3**. There is a competing reversible alkylation at the N-atom of the CN group which closes the six-membered ring of **8**. The concentration of this highly strained species **8** is probably small, and the equilibrium with **1** might never be fully established.

X-Ray analyses of open-chain ketene imines showed a linear cumulated bond system C=C=N [7], and its incorporation into a six-membered ring should generate strain. The N-free analog, cyclohexa-1,2-diene, is known as a short-lived intermediate, which was intercepted *in situ* [8][9]. *Wentrup et al.* prepared cyclohexa-1,2-diene by flash pyrolysis and recorded its IR spectrum at < 170 K [10].

The addition of the second molecule of methyl vinyl ether to the C=N bond of **8** required a substantial concentration of the intercepting reagent. Even in methyl vinyl

Scheme 3

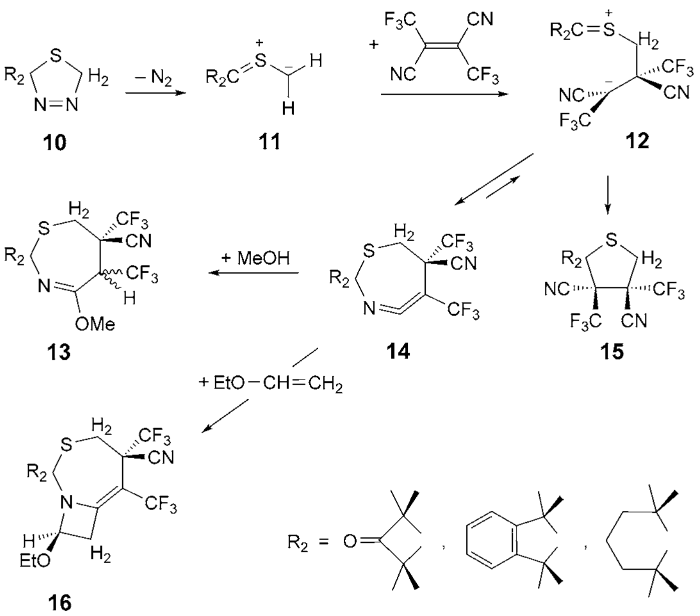


ether as solvent, only 53% of the material were captured *via* **8** to provide the bis-adducts; still, 41% of the cyclobutanes **3** were formed. The *trans*-ketene imine **8** afforded **6**(*trans-a*) and **6**(*trans-b*). Similarly, rotamer **2** of the zwitterion equilibrated with a *cis*-isomer of ketene imine **8** and was converted by vinyl ether to the bis-adducts **6**(*cis-a*) and **6**(*cis-b*).

The addition of the second molecule of vinyl ether is depicted in *Scheme 3* as a *two-step* process; no experimental evidence is available. A concerted pathway would be a ${}_{\pi}2_s + {}_{\pi}2_s$ process, forbidden by orbital symmetry. Whereas ketenes accept vinyl ethers in (2+2) cycloadditions, open-chain ketene imines no longer do. We assume that the strain relief makes the cycloaddition of vinyl ether to the cyclic ketene imine **8** feasible.

Doubts about the fleeting occurrence of the six-membered cyclic ketene imine **8** may be hushed by considering the relatively stable seven-membered cyclic ketene imines **14**, which were previously isolated in our laboratory [11–13] and structurally established by X-ray diffraction (*Scheme 4*). Thioketones add CH_2N_2, and the dihydrothiadiazoles **10** lose N_2 at *ca.* 60°. The thiocarbonyl *S*-methylides **11** were *in situ* intercepted by (*E*)-BTE and yielded the still strained ketene imines **14**. They isomerized in hot solution to the thiolanes **15** and smoothly added MeOH to afford the imidate **13**.

Scheme 4



The ketene imines **14** with various R substituents accepted, at room temperature, ethyl vinyl ether at the C=N bond and gave diastereoisomeric adducts of type **16** [10], as confirmed by an X-ray analysis [14].

Thus, the pathway to the bis-adducts **6** appears to be well established. Ring-strain promoting reactivity is not a new experience.

Experimental Part

1. *General.* See [2][15]. NMR Spectra: Solvent was $CDCl_3$, if not stated otherwise; ^{19}F chemical shifts are based on $CFCl_3$ as standard, and the CF_3 chemical shifts have negative signs.

2. *Bis-Adducts* **6** *from BTE and Methyl Vinyl Ether.* 2.1. *(*E*)-BTE.* MeO–CH=CH_2 (11.9 g, 205 mmol) was condensed into a flask at − 78° under Ar. Through a septum, (*E*)-BTE [1][2] (470 mg, 2.20 mmol) in CH_2Cl_2 (0.5 ml) was injected at + 10°. The yellow soln. (EDA complex) in the pressure-proof flask lost its color within *ca.* 20 h at 25°. After evaporation of the vinyl ether, the partially crystalline, colorless oil was submitted to ^{19}F-NMR analysis with fluorobenzene (δ − 113.7) as weight standard in CH_2Cl_2: 43% of cyclobutanes **3** and 53% of bisadducts **6**. The latter contained 69% **6**(*trans-a*), 27% **6**(*trans-b*), 1% **6**(*cis-a*), and 3% **6**(*cis-b*) (rel. to the sum of integrals). Bulb-to-bulb distillation at 0.01 Torr gave at 60° the cyclobutanes **3** (216 mg, 36%), at 90° a mixture of **3** and **6** (33 mg), and at 115–130° bis-adducts **6** (359 mg, 49%). In a new ^{19}F-NMR analysis of **6**, the ratio of diastereoisomers was virtually unchanged. Elemental analysis of diasteroisomer mixture: calc. for $C_{12}H_{12}F_6N_2O_2$ (330.23): C 43.64, H 3.66, N 8.48; found: C 43.81, H 3.63, N 8.62.

2.2. *(*Z*)-BTE.* Analogously, methyl vinyl ether (14.1 g, 243 mmol) was reacted with (*Z*)-BTE (434 mg, 2.03 mmol, purity 99.3%); the yellow color faded within 11 h. Bulb-to-bulb distillation at 0.01 Torr afforded cyclobutanes **3** (64%) and bisadducts **6** (32%). The ^{19}F-NMR integrals indicated 4% **6**(*trans-a*), 6% **6**(*trans-b*), 32% **6**(*cis-a*), and 58% **6**(*cis-b*) (rel. to the sum of integrals). Anal. calc. for $C_{12}H_{12}F_6N_2O_2$ (330.24): C 43.64, H 3.66, N 8.48; found: C 43.66, H 3.65, N. 8.65.

2.3. *(2*RS*,4*RS*,8*RS*)-2,8-Dimethoxy-4,5-bis(trifluoromethyl)-1-azabicyclo[4.2.0]oct-5-ene-4-carbonitrile* (**6**(*trans-a*)). The distilled oily bis-adduct fraction (*Sect. 2.1*) became partially crystalline at 0° and was twice recrystallized from pentane: colorless prisms (8 mg, 1%), m.p. 55–56°. The ^{19}F- and ^{1}H-NMR spectra were identical to those of the main product in the diastereoisomer mixture. IR (KBr): 1072*s*, 1103*s*, 1130*m*, 1145*m*, 1189*s*, 1208*s* (incompletely separated, C–O, C–F); 1343*s*; 1682*s* (C=C of enamine). ^{1}H-NMR (100 MHz, F-decoupled): 3.41, 3.51 (2 *s*, 2 Me); first *ABX* system calc. by the method of effective *Larmor* frequencies [16]: 2.32, 2.64 (*AB*, ^{2}J(3a,3b) = 14.3, H$_a$–C(3), H$_b$–C(3)); 4.57 (*X*, ^{3}J(2,3a) = 2.9, ^{3}J(2,3b) = 3.8, H–C(2)); second *ABX* system: 3.10, 3.21 (*AB*, ^{2}J(7a,7b) = 15.5, H$_a$–C(7), H$_b$–C(7)); 5.37 (*X*, ^{3}J(7a,8) = 2.9, ^{3}J(7b,8) = 4.5, H–C(8)). ^{19}F-NMR (CH$_2$Cl$_2$, 94 MHz, H-decoupled): –72.7 (*q*, ^{5}J(F,F) = 8.5, 4-CF$_3$); –57.1 (*q*, ^{5}J(F,F) = 8.5, 5-CF$_3$); (H-coupled): –57.1 (*ddq*, partially resolved, ^{5}J(5-CF$_3$,H$_a$–(7)) = 2.1, ^{5}J(5-CF$_3$,H$_b$–(7)) = 1.7). ^{13}C-NMR (22.5 MHz, H-decoupled): 31.6 (*q*, ^{3}J(C,F) = 1.8, C(3)); 36.4 (*s*, C(7)); 39.4 (*q*, ^{2}J(C,F) = 32, C(4)); 54.1, 56.5 (2*s*, 2 Me); 80.0 (*s*, C(2)); 86.0 (*s*, C(8)); 115.2 (*s*, broadened, C≡N); 123.5 (*q*, ^{1}J(C,F) = 285, CF$_3$); 124.2 (*q*, ^{1}J(C,F) = 269, CF$_3$); 152.8 (*q*, ^{3}J(C,F) = 4.8, C(6)). MS (70 eV, 40°): 330 (45, M^+), 311 (8, $[M-\mathrm{F}]^+$), 299 (55, $[M-\mathrm{MeO}]^+$), 261 (45, $[M-\mathrm{CF_3}]^+$), 202 (23), 75 (100), 69 (13, CF$_3^+$).

2.4. *(2*RS*,4*RS*,8*SR*)-***6***(*trans-b*): ^{19}F-NMR (CH$_2$Cl$_2$, 94 MHz): –72.0 (*q*, ^{5}J(F,F) = 8.5, 4-CF$_3$); –56.1 (*q*, broadened, ^{5}J(F,F) = 8.5, 5-CF$_3$).

2.5. *(2*RS*,4*SR*,8*SR*)-2,8-Dimethoxy-4,5-bis(trifluoromethyl)-1-azabicyclo[4.2.0]oct-5-ene-4-carbonitrile* (**6**(*cis-b*)). The distilled bis-adduct fraction, obtained from methyl vinyl ether and (*Z*)-BTE (*Sect. 2.2*), slowly crystallized at 0° in several weeks. After separating from oily products, two recrystallizations from pentane gave colorless prisms (7 mg, 1%), m.p. 77–78°, which were also used for the X-ray analysis. IR (KBr): broad absorption with peaks at 1073, 1104, 1154, 1204 (C–O, C–F str.); 1349*s* (br.); 1690*s* (br.; C=C of enamine), no C≡N str. ^{1}H-NMR (100 MHz, ^{19}F-decoupled): 3.40, 3.44 (2*s*, 2 Me); *ABX* calc. [16]: 2.31, 2.65 (*AB*, ^{2}J(3a,3b) = 14.2, H$_a$–C(3), H$_b$–C(3)); 4.52 (*X*, ^{3}J(2,3a) = ^{3}J(2,3b) = 4.7, H–C(2)); 3.21 (*d*, ^{3}J(7,8) = 3.6, CH$_2$(7)); 5.12 (*t*, ^{3}J(7,8) = 3.6, H–C(8)) ^{1}H-NMR: (100 MHz, F-coupled, partially resolved *q* splitting): 2.2–2.8 (*m*, ^{4}J(H$_a$,CF$_3$) = 0.9, CH$_2$(3)); 3.21 (*dq*, ^{5}J(CH$_2$(7),5-CF$_3$) = 1.7, ^{3}J(7,8) = 3.5, CH$_2$(7)). ^{19}F-NMR (CH$_2$Cl$_2$, 94 MHz): –71.4 (*dq*, ^{5}J(F,F) = 6.5, ^{4}J(H$_a$–C(3),CF$_3$) = 0.9, 4-CF$_3$); –56.3 (*tq*, ^{5}J(F,F) = 6.5, ^{5}J(CH$_2$(7),CF$_3$) = 1.7, 5-CF$_3$).

2.6. *(2*RS*,4*SR*,8*RS*)-Diastereoisomer* (**6**(*cis-a*)). ^{19}F-NMR (CH$_2$Cl$_2$, 94 MHz, in mixture with **6**(*cis-b*): –70.5 (*dq*, ^{5}J(F,F) = 6.6, ^{4}J(3-H$_a$,CF$_3$) = 1.1, 4-CF$_3$); –56.2 (*q*, partial overlap, 5-CF$_3$).

3. *Bis-Adducts* **7** *from (*E*)-BTE and Ethyl Vinyl Ether.* (*E*)-BTE (465 mg, 2.17 mmol) was reacted with freshly distilled ethyl vinyl ether (9.79 g, 136 mmol) at r.t.; the yellow soln. became colorless after 3.5 h. Evaporation of the vinyl ether left a colorless oil (634 mg). The bulb-to-bulb distillation yielded cyclobutanes (395 mg, 64%) at 85°/0.1 Torr, and bis-adducts **7** (152 mg, 20%) at 130°/0.05 Torr. The ^{19}F-NMR spectrum (CH$_2$Cl$_2$) exhibited isolated 4-CF$_3$ *q*s at –72.7 (**7**(*trans-a*); 66%), –72.1 (**7**(*trans-b*); 27%), –71.3 (**7**(*cis-b*); 5%), and at –70.4 (**7**(*cis-a*); 2%). Anal. calc. for $C_{14}H_{16}F_6N_2O_2$ (358.28): C 46.93, H 4.50, N 7.82; found: C 46.91, H 4.61, N 7.94.

In another experiment with (*E*)-BTE (1.11 g, 5.19 mmol) and ethyl vinyl ether (132g, 1.83 mol), high-vacuum distillation provided cyclobutanes and 1:2 adducts in the ratio of 58:42. The oily bis-adduct mixture partially crystallized at –30°; from pentane separated colorless rhombs of **7**(*trans-a*).

3.1. *(2*RS*,4*RS*,8*RS*)-2,8-Diethoxy-4,5-bis(trifluoromethyl)-1-azabicyclo[4.2.0]oct-5-ene-4-carbonitrile* (**7**(*trans-a*)). M.p. 60–60.5°. IR (KBr): 1026*m*, 1044*s*, 1053*s*, 1075*s*, 1092*s*, 1132*s* (C–O str.); 1164*s*, 1203*s*, 1254*s*, 1278*m*, 1345*s* (C–F str.); 1375*m*; 1694v*s* (C=C of enamine); 2240v*w* (C≡N str.). ^{1}H-NMR (100 MHz, ^{19}F-decoupled): 1.25, 1.29 (2*t*, *J* = 7.0, 2 Me of 2 Et); 3.4–3.9 (*m*, 2 diastereotopic CH$_2$ of 2 Et); first *ABX* [16]: 2.31, 2.62 (*AB*, ^{2}J(3a,3b) = 14.2, H$_a$–C(3), H$_b$–C(3); irradiation at 4.66 converts *ABC to AB*); 4.66 (*X*, ^{3}J(2,3a) = 2.8, ^{3}J(2,3b) = 3.7, H–C(2)); second *ABX:* 3.08, 3.26 (*AB*, ^{2}J(7a,7b) = 15.4, H$_a$–C(7), H$_b$–C(7)); 5.37 (*X*, ^{3}J(7a,8) = 2.6, ^{3}J(7b,8) = 4.5, H–C(8); irradiation at 5.37 made visible ^{5}J(7a,CF$_3$) = 1.4 and ^{5}J(7b,CF$_3$) = 2.2). ^{19}F-NMR (CH$_2$Cl$_2$, 84 MHz, ^{1}H-decoupled): –72.0 (*q*, ^{5}J(F,F) = 8.5, 4-CF$_3$); –57.0 (*q*, ^{5}J(F,F) = 8.5, 5-CF$_3$) ^{19}F-NMR (CDCl$_3$, ^{1}H-coupled): –72.7 (*q*, ^{5}J(F,F) = 8.5, 4-CF$_3$); –57.4 (*dq*, ^{5}J (F,F) = 8.5, ^{5}J(F,H–C(7)) = 2.3, 5-CF$_3$). ^{13}C-NMR (50.3 MHz, ^{1}H-decoupled): 15.1, 15.6 (2*s*, 2 Me of 2 Et); 32.2 (br. *s*, C(3)); 37.3 (*q*, ^{4}J(C,F) = 1.0, C(7)); 39.4 (*q*, ^{2}J(C,F) = 32, C(4)); 63.2, 64.8 (2*s*, 2 CH$_2$ of 2 Et); 78.5 (*s*, C(2)); 84.9 (*s*, C(8)); 115.1 (*s*, broadened, C≡N); 123.5 (*q*, ^{1}J(C,F) = 285, CF$_3$); 124.2 (*q*, ^{1}J(C,F) = 269, CF$_3$); 152.9 (*q*, ^{5}J(C,F) = 5.0, C(6)). MS

(70 eV, 40°): 358 (58, M^+), 313 (45, $[M - OEt]^+$), 289 (35, $[M - CF_3]^+$), 285 (31, $[313 - C_2H_4]^+$), 269 (23, $[313 - MeCHO]^+$), 230 (19), 215 (20), 187 (45), 103 (85), 69 (11, CF_3^+), 29 (100, $C_2H_5^+$).

4. X-Ray Diffraction Analyses (see also *Tables 1* and *4*, and *Fig.*). The crystals of **6**(*trans-a*) and **6**(*cis-b*) were sealed in glass capillaries and mounted on the goniometer head of a *Syntex R3* four-circle diffractometer operating with MoK_α radiation at 193 K and graphite monochromator. The cell constants were determined from 25 centered reflections; further data are given in *Table 4*. Structure solution and refinement: SHELXS-86 and SHELXL-93 [17]. Non-H-atoms were refined anisotropically, H-atoms isotropically with fixed U_i of 0.05, blocked matrix refinement. The molecules were drawn in the *Figure* using ZORTEP [4] on the basis of 30% probability ellipsoids. Crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 IEZ, UK, with deposition Nos. CCDC-856014 for **6**(*trans-a*) and CCDC-856015 for **6**(*cis-b*).

Table 4. *X-Ray Crystallographic Data of Two Bisadducts*

Compound	**6**(*trans-a*)	**6**(*cis-b*)
CCDC Deposition No.	856014	856015
Molecular formula	$C_{12}H_{12}F_6O_2N_2$	$C_{12}H_{12}F_6O_2N_2$
Molecular mass	330.23	330.23
Crystal system	monoclinic	monoclinic
Crystal size [mm]	0.36 × 0.45 × 0.05	0.19 × 0.205 × 0.30
Space group, *Z*	*P*2(1), 4	$P2_1/c$, 4
Unit cell dimensions:		
a [Å]	14.475(3)	8.202(4)
b [Å]	10.790(2)	8.000(5)
c [Å]	9.295(2)	22.169(9)
β [°]	102.73(3)	98.672(3)
Volume [Å^3]	1416.1(5)	1438.0(13)
Density calc. [g/cm^3]	1.549	1.525
F(000)	672	672
Index range	$-15 \leq h \leq 15$	$0 \leq h \leq 9$
	$-11 \leq k \leq 11$	$0 \leq k \leq 9$
	$-0 \leq l \leq 10$	$-26 \leq l \leq 26$
2*θ* Range [°]	45.22	50.00
Temp. (K)	193	193
Reflections, collected	3993	2725
Reflections, unique	3724	2534
Reflections, observed (4*σ*)	2651	1945
R(int)	0.0150	0.0135
Goodness-of-fit	1.029	1.062
Final *R*(4*σ*)	0.0384	0.0394
Final wR^2	0.0962	0.0927
Residual electron density [e/Å^3]	0.135	0.138

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