1,2-Bis(trifluoromethyl)ethene-1,2-dicarbonitrile: Enol Ethers and Ketene Acetals as Cycloaddition Partners

by **Rolf Huisgen***[a]) and **Gonzalo Urrutia Desmaison**[b])

[a]) Department Chemie der Ludwig-Maximilians-Universität, Butenandt-Strasse 5–13, D-81377 München

[b]) Institut für Chemie und Biochemie der Freien Universität, Takustrasse 3, D-14195 Berlin

Dedicated to the memory of *Emanuel Vogel*

(*E*)- and (*Z*)-1,2-bis(trifluoromethyl)ethene-1,2-dicarbonitrile ((*E*)- and (*Z*)-BTE, resp., =(*E*)- and (*Z*)-2,3-bis(trifluoromethyl)but-2-enedinitrile) were used as a stereochemical probe in studying (2 + 2) cycloadditions of acceptor with donor alkenes. The additions to methyl (*E*)- and (*Z*)-propenyl ether gave rise to the eight conceivable cyclobutanes **8**, although in different ratios in reactions of (*E*)- and (*Z*)-BTE. The ^{19}F-NMR data served the structural assignment and the quantitative analysis. The mechanistic discussion is based on rotations and ring closures of the assumed 1,4-zwitterionic intermediates. Dimethylketene dimethyl acetal, methylketene dimethyl acetal, and ketene diethyl acetal show an increasing rate in their reactions with BTE as well as in the equilibration of the cycloadducts.

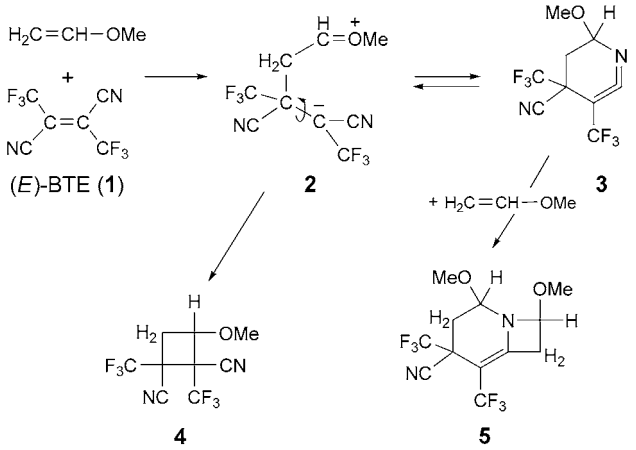
1. Introduction. – A classic paper by *Cairns* and co-workers of 1966 [1] described not only the first preparation of (*E*)-1,2-bis(trifluoromethyl)ethene-1,2-dicarbonitrile (=(*E*)-2,3-bis(trifluoromethyl)but-2-enedinitrile; **1**; (*E*)-BTE) and the corresponding (*Z*)-isomer, but also dealt with their (2 + 2) cycloadditions to several donor-substituted ethenes. The claim that the cyclobutane formation from (*E*)- and (*Z*)-BTE with ethyl vinyl ether proceeds with full retention of the BTE configuration turned out to be incorrect. It was shown in our preceding publication that all four *rac*-diastereoisomeric cycloadducts **4** are formed, although in different ratios, from (*E*)- and (*Z*)-BTE [2]. The *gauche*-zwitterions **2**, assumed intermediates, can cyclize directly to **4** or do so after rotation about the former acceptor bond.

The cyclobutanes **4** did not react with an excess of vinyl ether. The isolated bis-adducts **5** (again four diastereoisomers) are derivatives of 1-azabicyclo[4.2.0]oct-5-ene; the strained cyclic ketene imine **3** is a plausible second intermediate on the pathway to **5** [3], as shown in *Scheme 1* for methyl vinyl ether.

Described here are the reactions of (*E*)- and (*Z*)-BTE with further donor-substituted ethenes: enol ethers, and ketene acetals. Mixtures of diastereoisomeric adducts were usually obtained. In the structure elucidation and quantitative analysis, ^{19}F-NMR spectroscopy played a dominant role. With Cl_3CF as zero standard, the ^{19}F-NMR shifts of CF_3 groups have negative signs, and screening effects by substituents reduce the (negative) numerical values.

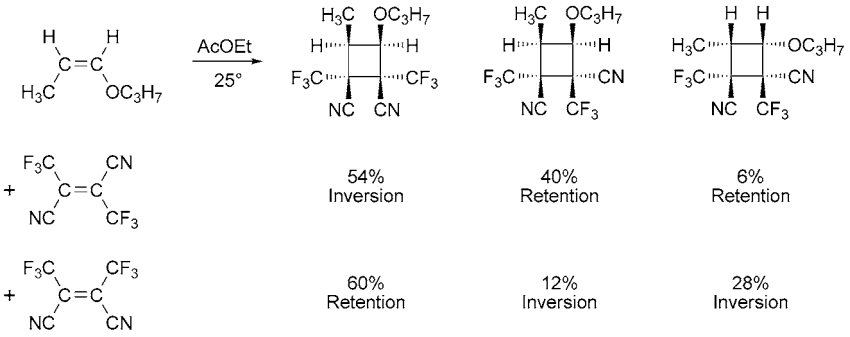
2. Results and Discussion. – 2.1. *Previous Observations.* In the reactions of (*E*)- and (*Z*)-BTE with (*Z*)-prop-1-enyl propyl ether, *Cairns* and co-workers [1] discovered a

Scheme 1



violation of the retention principle, as outlined in *Scheme 2*. Substantial amounts of inversion products were found, whereas the cycloadditions of (*E*)- and (*Z*)-BTE with the (*E*)-propenyl propyl ether allegedly were stereospecific. Out of respect for the pioneering work of the American authors, we begin with supplements and corrections concerning the propenyl ether system.

Scheme 2



2.2. *Methyl Prop-1-enyl Ether* (**6**) *as Donor Alkene.* 2.2.1. *Ratios of Products.* The reactions of (*E*)- and (*Z*)-BTE with methyl prop-1-enyl ether ((*E*)-**6** and (*Z*)-**6**; *cf. Scheme 3*) are slower than those with methyl vinyl ether. The homopolymerization of **6** as a side reaction reduced the adduct yields. The disappearance of the orange-red color of the charge-transfer (CT) complex allowed a visual control of BTE consumption.

When equimolar amounts of (*E*)-BTE and (*E*)-**6** were reacted in CH_2Cl_2 at room temperature, the ^{19}F-NMR spectrum indicated 58% of cyclobutanes **8** (53% after distillation; *cf. Scheme 4*, below) and 15% of 1:2-adducts. In *Table 1*, the results for all four (*E*,*Z*)-isomer combinations are compiled. After short reaction times, differences of rate showed up. Whereas the reaction (*E*)-BTE + (*E*)-**6** reached only few percent

Table 1. *Reactions of* (E)*- and* (Z)*-BTE with Methyl* (E)*- and* (Z)*-Prop-1-enyl Ether* (**6**) *at Room Temperature for 25 d*. Analysis by ^{19}F-NMR spectroscopy.

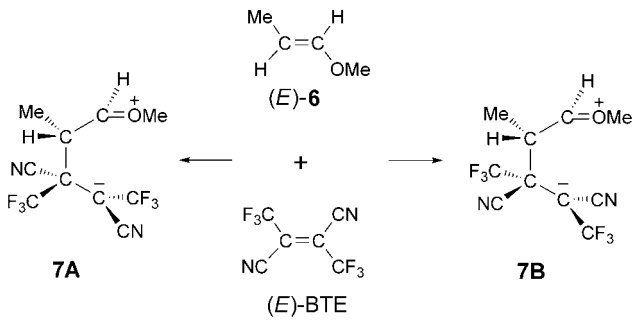
Reaction	Solvent	Cyclobutanes **8** [%]	1 : 2 Adducts [%]
(*E*)-BTE + (*E*)-**6**	CH_2Cl_2	53	15
(*Z*)-BTE + (*E*)-**6**	CH_2Cl_2	61	10
(*E*)-BTE + (*Z*)-**6**	neat	91	~1
(*Z*)-BTE + (*Z*)-**6**	neat	71	~1

cyclobutanes **8** after 3 h, the combination (*Z*)-BTE + (*Z*)-**6** produced 10% of **8** after 10 min.

According to kinetic measurements (CH_2Cl_2, 25°) carried out by *Oshima* and co-workers [4], (*Z*)-BTE reacts 3.0 times faster than (*E*)-BTE with butyl vinyl ether. The rate constants of (*E*)-BTE with the geometrical isomers of methyl prop-1-enyl ether (**6**) showed a 6.2-fold superiority of (*Z*)-**6**. Thus, the four combinations in *Table 1* cover a factor of 18 in rate constants.

In the formation of the intermediate zwitterion, two centers of tetrahedral asymmetry are generated, as shown in *Scheme 3* for the interaction of (*E*)-BTE with (*E*)-**6**. Two diastereoisomeric *gauche*-zwitterions, **7A** and **7B**, are generated. Ring closure without or with preceding rotation in the upper cationic or the lower anionic part of the zwitterion furnishes cyclobutanes which possess four stereogenic centers, corresponding to eight *racemic* diastereoisomers.

Scheme 3

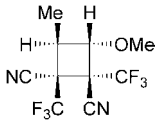
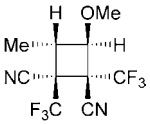
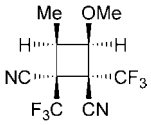
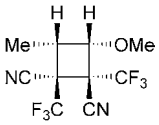
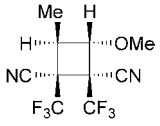
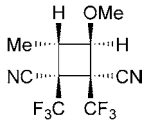
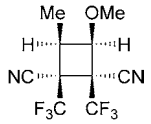
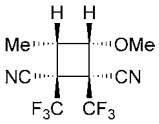


Each of the zwitterions **7A** and **7B**, can give rise to four diastereoisomeric cyclobutanes **8**. The four reactant combinations listed in *Table 1* produced grossly different ratios of diastereoisomeric cyclobutenes, as revealed by *Table 2*. Rotation in the zwitterion and ring closure are in keen competition. The data of *Table 2* are relative percentages of the distilled cycloadduct fraction, and the (1*S*)-enantiomer was chosen as illustration.

The 1,4-ring closure of the zwitterion is irreversible under the reaction conditions. The ratio of diastereoisomer mixtures of cyclobutanes **8** neither changed on distillation nor on month-long storage.

Of the stereochemical descriptors used for the formulae in *Table 2*, the first suffix, *trans* or *cis*, refers to the relative positions of the CF_3 groups, and the second to those of

Table 2. *Cycloadditions of* (E)*- and* (Z)*-BTE with Methyl* (E)*- and* (Z)*-Prop-1-enyl Ether* ((*E*)-**6** and (*Z*)-**6**, resp.) *in* CH_2Cl_2 *at Room Temperature.* ^{19}F-NMR Analysis of cycloadducts **8** (rel. %).

BTE + **6**	 *trans,trans*-1	 *trans,trans*-2	 *trans,cis*-1	 *trans,cis*-2
(*E*)+(*E*)	39	34	1	5
(*E*)+(*Z*)	–	–	4	47
(*Z*)+(*E*)	2	3	1	1
(*Z*)+(*Z*)	–	–	49	3
	 *cis,trans*-1	 *cis,trans*-2	 *cis,cis*-1	 *cis,cis*-2
(*E*)+(*E*)	14	–	2	5
(*E*)+(*Z*)	–	–	–	49
(*Z*)+(*E*)	3	88	–	2
(*Z*)+(*Z*)	–	2	15	31

MeO and Me groups at C(3) and C(4). The third suffix, *1* or *2*, designates the pathways of initial bonding illustrated by **7A** and **7B**, respectively, in *Scheme 3*. Their ring closures with retention lead to the cyclobutanes **8**(*trans,trans*-1) and **8**(*trans,trans*-2). According to (*R*,*S*) convention, **8**(*trans,trans*-2) would be (1*SR*,2*SR*,3*RS*,4*SR*)-**8**.

A complicating phenomenon: (*Z*)-BTE was isomerized to (*E*)-BTE during the reaction with olefin **6**. This catalytic isomerization (CH_2Cl_2, room temperature) amounted to 1% after 4 h, 26% after 3 d, and 93% after 25 d. The equilibrium (*E*)-BTE $\rightleftharpoons$ (*Z*)-BTE, 93 : 7, was determined in C_6D_6 at 40° with weak nucleophilic catalysis [5]. This conversion of (*Z*)- to (*E*)-BTE will change the ratio of diastereoisomeric cyclobutanes **8** during the reaction course. The determination of the undisturbed initial product ratio would require short reaction time. The cycloadditions of (*E*)-BTE are not free of this disadvantage; up to 7% (*Z*)-BTE could be formed, but (*Z*)-BTE reacts faster with the enol ether **6**.

The catalytic isomerization of BTE which accompanies the cycloaddition is a new phenomenon. It was checked that, in the faster reaction of (*E*)- and (*Z*)-BTE with methyl vinyl ether, no isomerization of the unconsumed BTE was detectable [2]. In solutions of cyclobutanes **8**, BTE did not isomerize. Formation and dissociation of the rotameric zwitterions such as **7** would be a possible pathway, but why is it missing in the reactions with vinyl ethers? Steric hindrance is conceivable; furthermore, the catalytic isomerization may be entangled in the homopolymerization of the enol ether **6**, which was mentioned above, as a steady side reaction.

The majority of our cycloadditions is faster than this puzzling isomerization of BTE. Otherwise, the ratios of diastereoisomeric cyclobutanes listed in *Table 2* could not be so

very different for the four reactant pairs. Nevertheless, the isomerization of BTE could be a source of some systematic error.

Cairns and co-workers [1] analyzed the cycloadducts from (*Z*)-prop-1-enyl *propyl* ether with (*E*)- and (*Z*)-BTE (*Scheme 2*). The agreement with our data, of methyl prop-1-enyl ether, is only moderate. The claim that the (*E*)-form of the enol ether combined stereospecifically with (*E*)- and (*Z*)-BTE [1] is hardly defendable. The higher resolution of modern ^{19}F-NMR spectrometers, compared with those of 1963, might well be the cause of divergences.

2.2.2. *Structural Assignments of Cyclobutanes* **8**. Among the eight cyclobutanes **8**, obtained from BTE and enol ether **6**, only **8**(*trans*,*trans*-2) and **8**(*cis*,*cis*-2) were obtained in pure and crystalline form. All the structural information comes from the ^{19}F-NMR spectra of diastereoisomer mixtures which were produced for the four reactant pairs (*Table 2*). Apart from ill-defined side-products, we are dealing with eleven-component spectra: eight cycloadducts, (*E*)- and (*Z*)-BTE, and the frequency standard. The coupling of *cis*-located CF_3 groups led to *quadruplet*s with $^5J(F,F) \approx$ 11 Hz, whereas CF_3 groups in *trans*-position couple with $^5J(F,F) \approx 1-2$ Hz; often the *quadruplet* structure of *trans*-coupling was not resolved.

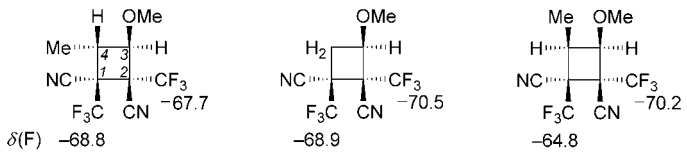
The four diasteroisomeric cyclobutanes **4**, available from BTE and methyl vinyl ether, were separated and crystallized [2]. Their structures were secured by X-ray analyses and ^{19}F-NMR spectra.

The ^{19}F-NMR chemical shifts of cyclobutanes **8** are the outcome of an intricate net of mutual deshielding effects for the six substituents. This net was unveiled for the five substituents in the four diastereoisomeric cycloadducts **4** of methyl vinyl ethers [2] and is extended here to the six-substituent system **8** in the preferred conformations. The *cis*-substitutents deshield more strongly than *trans*-located ones; *trans*-effects are often neglectable. Substituents can be ordered by the strength of the deshielding in $\delta(CF_3)$:

$$\textit{cis}\text{-vic-Me} > \textit{cis}\text{-vic-MeO} > \textit{cis}\text{-vic-CF}_3 > \textit{cis}\text{-1,3-MeO}$$

A statistical analysis could provide numerical contributions. *Scheme 4* exemplifies how the deshielding by Me is established. A 4-Me group is introduced in **4**(*trans*-2). In **8**(*trans*,*cis*-1), the decrease of δ(1-CF_3) from -68.9 to -64.8 evidences the strong deshielding by *cis*-vic-Me, whereas 2-CF_3 remains untouched. In **8**(*trans*,*trans*-2), we face *cis*-1,3-interactions of Me and MeO at the two $\delta(CF_3)$; δ(1-CF_3) shows no influence of the *trans*-vic-Me. Analogously, the formal introduction of 4-Me into the other three diastereoisomers of **4** enabled assignment of the structures of three further pairs of **8**. This structural assignment cannot claim certainty as in the **4**-series.

Scheme 4



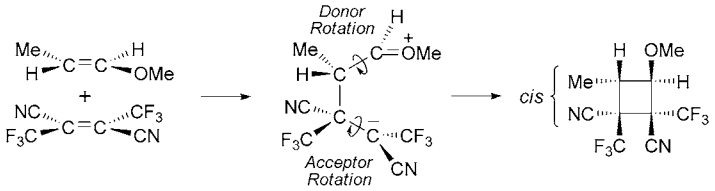
8(*trans*,*trans*-2) **4**(*trans*-2) **8**(*trans*,*cis*-1)

How are the δ(F) values extracted from the ^{19}F-NMR spectra of the mixtures resulting from the addition of (*E*)- and (*Z*)-BTE? Signal pairs of equal intensity for 1-CF_3 and 2-CF_3, *i.e.*, *quadruplet*s for *cis*- and *singlet*s for *trans*-CF_3 groups, are collected. Their assignments to the diastereoisomers of **8** are optimal when they fit the expectation for deshielding effects. The assignments are no longer definitive, when the two δ(F) values become similar as illustrated by **8**(*trans*,*trans*-2) in *Scheme 4*.

2.2.3. *Mechanistic Considerations.* The rate-determining step of the (2 + 2) cycloaddition is the formation of the zwitterion [2]. The former C=C bonds of the acceptor- and donor-substituted alkene are involved in the conformational rotation about the C–C bonds. The variety of adducts was broken down in *Table 3* into processes in the zwitterion. 'Acceptor rotation' as defined in the formula, exceeded 'donor rotations' by far. The reason is not *a priori* clear; the stronger solvation of the positive point charge of the carboxonium ion may play a role. The column 'retention' – 46–91% in the four reactant pairs – marks not only ring closure without rotation; even-numbered 180° rotations likewise show up in the figure.

Newman projections of zwitterions were helpful in interpreting the pathways to the

Table 3. *Cycloadditions of BTE and Methyl Propenyl Ether* (CH_2Cl_2, at room temperature): *Ordering of Diastereoisomers* **8** *by Steric Course* (rel. %)



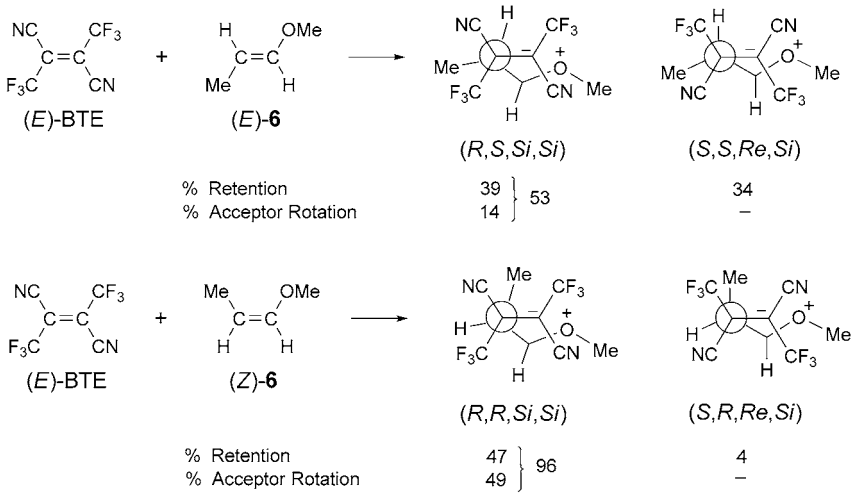
BTE + **6**	Retention at acceptor and donor	Inversion only at acceptor	Inversion only at donor	Inversion at acceptor and donor
(*E*) + (*E*)	73	14	6	7
(*E*) + (*Z*)	51	49	–	–
(*Z*) + (*E*)	91	5	2	2
(*Z*) + (*Z*)	46	52	2	–

diastereoisomers of **4** [2]. For two reactant pairs, *Scheme 5* presents the pairs of *gauche*-zwitterions resulting from the two modes of establishing the first σ-bond (**7A** and **7B** in *Scheme 3*). Conformational energy and *Coulombic* attraction of the charge-bearing termini settle the energy level of the zwitterion.

The different stabilization of the anionic charge, CN > CF_3, enters the *Coulombic* term and allows a greater dihedral angle for (*R*,*S*,*Si*,*Si*) than for (*S*,*S*,*Re*,*Si*). This energetic advantage is counteracted by the repulsive interaction CF_3/CH_3 in (*R*,*S*,*Si*,*Si*); both zwitterions participate to a comparable extent. For the reactants (*E*)-BTE + (*Z*)-**6**, the two retarding effects accumulate in (*S*,*R*,*Re*,*Si*), and the reaction *via* (*R*,*R*,*Si*,*Si*) is strongly preferred.

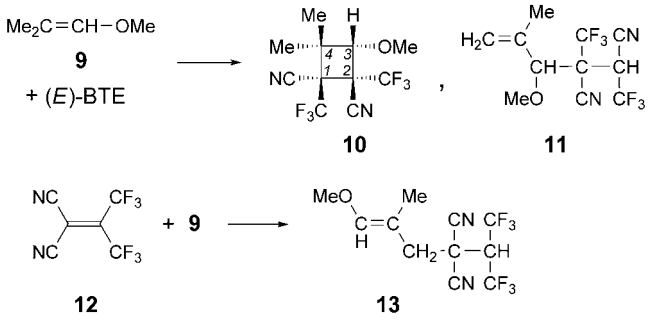
2.3. *Methyl 2-Methylprop-1-enyl Ether* (**9**). The slow reaction of (*E*)-BTE with **9** (1:1) in MeCN (*Scheme 6*) provided after 42 d 35% (^{19}F-NMR) of a single cyclobutane, a small amount of which was obtained in crystalline form. The lack of F,F coupling

Scheme 5



indicated a *trans*-cyclobutane, and δ(F) values of -63.4 and -64.5 ppm signalled deshielding by *cis*-vic-substituents in harmony with structure **10**. The 1-CF_3 couples with 4-Me, and $^5J(F,H) = 2.0$ was observed in ^{19}F- and ^{1}H-NMR spectrum.

Scheme 6

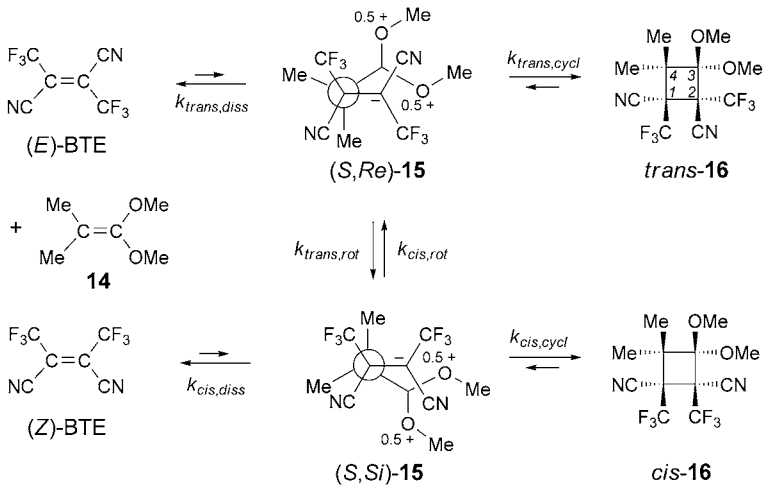


The reaction without solvent furnished the ene product **11** (44%; twice recrystallized) besides some **10**. The CF_3 groups couple with a $^5J(F,F)$ value of 9.2 Hz, and the coupling constant between the terminal CF_3 with H–C(2), *i.e.*, $^3J(F,H)$, amounts to 7.2 Hz. In the ^{1}H-NMR spectrum, a 2H *multiplet* at 5.4 – 5.6 is attributed to two vinylic H-atoms. Two low-field ^{13}C-resonances at δ 124.9 and 136.5 are ascribed to two olefinic C-atoms.

Ene reactions of the isomeric 2,2-bis(trifluoromethyl)ethene-1,1-dicarbonitrile (**12**) have been thoroughly studied [6]; representatives with terminal $(CF_3)_2CH$ as well as $(CN)_2CH$ groups were observed and suggested differences in mechanism. Notably, the reaction of **12** with alkene **9** gave rise to the ene product **13**, which bears the MeO group in a conjugated position [7] (*Scheme 6*).

2.4. *Dimethylketene Dimethyl Acetal* (**14**). In the reaction of **14** with (*E*)-BTE in CH_2Cl_2, the orange-red color of the CT complex disappeared in *ca.* 60 min, and in the experiment with (*Z*)-BTE after 45 min. The quantitative formation of *trans*-**16** with (*E*)-BTE testified to a high stereospecificity. An amount of 0.4% *cis*-**16** would still be indicated in the ^{19}F-NMR spectrum, but was not detected in the crude product. That suggested $k_{cycl}/k_{rot} > 250$ for the intermediate zwitterion (*S*,*Re*)-**15** (*Scheme 7*). In contrast, (*Z*)-BTE and **14** in CH_2Cl_2 generated a 91:9 mixture *cis*-**16**/*trans*-**16**; the ratio was unchanged after 45 d indicating kinetic control. Two *gauche*-zwitterions, (*S*,*Re*)-**15** and (*S*,*Si*)-**15**, were involved; (*S*,*Si*)-**15** underwent ring closure and rotation in a ratio 10:1.

Scheme 7



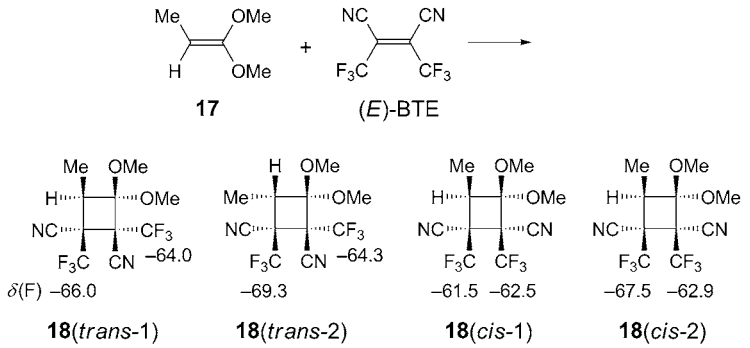
One more finding: during the reaction of (*Z*)-BTE with **14**, the ^{19}F-NMR spectrum indicated the occurrence of (*E*)-BTE. After 14 min and 90% reaction, the unconsumed BTE contained 18% of (*E*)-isomer. Thus, part of the zwitterion (*S*,*Re*)-**15**, formed from (*S*,*Si*)-**15** by rotation, dissociated to (*E*)-BTE and **14**.

The zwitterion **2** from BTE and methyl vinyl ether (*Scheme 1*) shows a higher propensity for conformational rotation than zwitterion **15**. A conceivable reason: the charge of the oxonium ion in **2** spreads in **15** over two O-functions. That diminishes solvation and increases the contact area of positive and negative charge, thus retarding rotation. We have previously compared the *gauche*-zwitterions with 'contact ion pairs' [8].

The penta-substituted cyclobutanes **4** from vinyl ether and BTE are stable in MeCN. The octa-substituted *trans*-**16** and *cis*-**16** slowly equilibrate in MeCN to a 93:7 ratio; *e.g.*, a 59:41 *trans*/*cis* mixture of **16** reached the ratio 88:12 in 145 d at room temperature, and the equilibrium (93:7) was established after 395 d. Steric hindrance in the octa-substituted **16** and increased stabilization of the zwitterion diminish the ionization energy.

2.5. *Methylketene Dimethyl Acetal* (**17**). The reaction with BTE in CH_2Cl_2 was so fast that the red color of the CT complex could hardly be noticed. The ^{19}F-NMR analysis with standard indicated quantitative formation of the cyclobutanes **18** (*Scheme 8*). Three stereogenic centers in **18** allow four *rac*-diastereoisomers.

Scheme 8



When (*E*)-BTE was reacted with acetal **17** at room temperature, the ^{19}F-NMR spectrum displayed signals of **18**(*trans*-1) and **18**(*trans*-2) in a ratio of 74 : 26, *i.e.*, the *gauche*-zwitterions involved underwent the ring closure without acceptor rotation. The reaction of (*Z*)-BTE with **17** furnished 88% *cis*-adducts and 12% *trans*-cyclobutanes **18** (*Table 4*); the molar ratio of the reactants had no influence on the composition of diastereoisomers **18**. The partially crystalline adduct mixtures were isolated in high yield. In view of the easy isomerization, the separation and purification was not attempted.

Table 4. *Reactions of BTE with Methylketene Dimethyl Acetal* (**17**) *in Various Solvents at Room Temperature* (rel. % of the cycloadducts **18**)

Solvent	BTE [mol-equiv.]	*trans*-1	*trans*-2	*cis*-1	*cis*-2
Reactions with (*E*)-BTE					
CH_2Cl_2	0.66	74	26	< 1	< 1
CH_2Cl_2	1.33	73.5	26.5	< 1	< 1
Reactions with (*Z*)-BTE					
Cyclohexane	0.46	8	4	73	15
Cyclohexane	1.6	6	5	75	14
CH_2Cl_2	0.68	9	3	72	16
CH_2Cl_2	5.0	9	3	72	16
Equilibrium after 41 d					
CH_2Cl_2		30	50	< 1	20

The disturbing isomerization of cyclobutanes **18** required repeated ^{19}F-NMR analyses in intervals of 2 – 3 min. Back-extrapolation to the time of mixing provided the diastereoisomer ratios compiled in *Table 4*. In the sequence cyclohexane, CH_2Cl_2, and MeCN as solvent, increasing rate of isomerization was observed. The *Figure* confirms

the rapid changes in the shares of **18**(*cis*-1) and **18**(*trans*-1) in the first 12 min (CH_2Cl_2, room temperature); we are dealing with acceptor rotation in the zwitterion. The concentration of **18**(*trans*-1) increased further, reached a maximum of 78% after 7 h, and plummeted to 30% after 41 d. The portion of **18**(*trans*-2) remains in the short time span of the *Figure* at *ca.* 3%, but rises to 50% in 41 d. Obviously, the cyclobutanes **18** considerably vary in the rate of dissociation to the reactants. A trace of free BTE occurred in the solution of the diastereoisomer mixture in CH_2Cl_2.

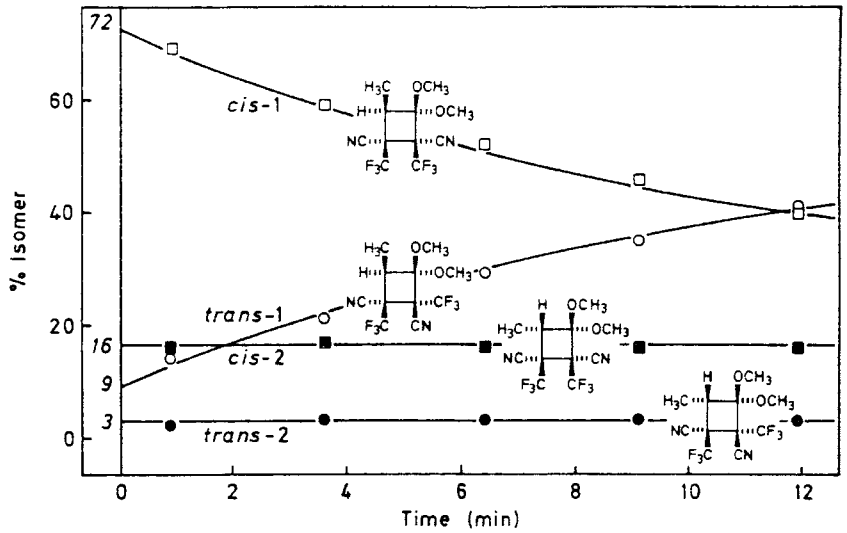
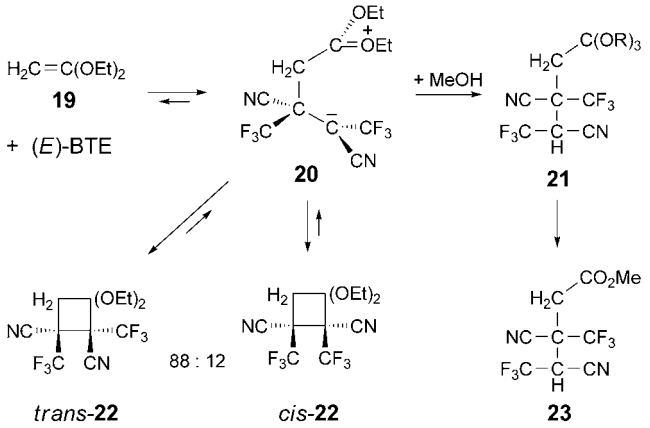


Figure. *Methylketene dimethyl acetal and (Z)-BTE in CH_2Cl_2: Isomerization of Cyclobutanes* **18**

The concentrations in the equilibrium mixture of **18** is included in *Table 4*. Cyclobutane **18**(*cis*-1) accounted for more than 70% of the total product from (*Z*)-BTE and acetal **17** under conditions of kinetic control, but the equilibrium contained only a trace of it. Compound **18**(*cis*-1) is the diastereoisomer which bears the four voluminous substituents on the same side of the ring. In the equilibrium, **18**(*trans*-2) exceeds with 50% even the 30% share of **18**(*trans*-1); the two differ in the configuration of the 4-Me group. The top position of CF_3 in steric demand finds a numerical basis in the 'conformational energy' (*a*/*e* in cyclohexane) [9].

2.6. *Ketene Diethyl Acetal* (**19**). The rate of cycloaddition with (*E*)-BTE is so high that the red color of the CT complex was briefly observable only when the reaction was run at $-30°$. The resulting 88:12 mixture of cyclobutanes *trans*-**22** and *cis*-**22** (*Scheme 9*) was the same when (*Z*)-BTE served as reactant. Thus, the equilibration of the cyclobutanes **22** is also faster than in the examples so far discussed. At room temperature, **22** can only be handled as equilibrium mixture. The *trans*/*cis* assignment and the ratio rest on ^{19}F-NMR evidence, and the ^{13}C-NMR signals clearly confirm the cyclobutane structure.

Scheme 9



Several minutes after dissolving **22** in MeOH, the ^{1}H-NMR spectrum revealed the formation of a methyl ester group, and the ^{19}F-NMR signals disclosed the presence of two diastereoisomers (63 : 37). The data point to the derivative **23** of methyl valerate, and the orthoester **21** is a conceivable intermediate.

Why does the methyl-free cyclobutane **22** isomerize much faster than the 4-methylcyclobutanes **18** and the 4,4-dimethylcyclobutanes **16**? Steric crowding in the highly substituted cyclobutanes should favor the opposite sequence. Supposedly, the Me groups hinder the solvation of the carboxonium part of the zwitterion.

The application of BTE as a stereochemical probe discloses new phenomena and may provide deeper understanding.

Experimental Part

1. *General.* See [5]. ^{19}F-NMR Spectra were recorded on *Varian XL 100* (94.1 MHz) or *Jeol FX 90* (84.3 MHz), and $FCCl_3$ served as internal standard; then $\delta(CF_3)$ has a negative sign.

2. *Materials.* 2.1. *Methyl prop-1-enyl ether* (**6**) was prepared by elimination of MeOH from propionaldehyde dimethyl acetal [10], catalyzed by H_3PO_4 [11]; b.p. 42–46°. The separation of (*E*)-**6** and (*Z*)-**6** was achieved by vapor-phase chromatography (VPC) on a column (4 m × 2 cm) with 20% of *Dow Corning 705* (1,3,5-trimethyl-1,1,3,5,5-pentaphenyltrisiloxane) on acid-treated *Kieselgur* (*Anakrom A* 0.15–0.18 mm of *Antechnika*); followed by a column (2 m × 2 cm) with *XF 1150* (2-cyanoethyl)(methyl)silicon). Inlet 50°, column 34°, detector 55°, 0.7 at of N_2. t_R 65.3 min for (*Z*)-**6** and 76.3 min for (*E*)-**6**.

2.2. *Dimethylketene Dimethyl Acetal* (=*1,1-Dimethoxy-2-methylprop-1-ene*; **14**). Compound **14**, b.p. 106–109°, was synthesized by elimination of MeOH from trimethyl orthoisobutyrate [12]. Products of the facile hydrolysis induce isomerization of (*Z*)-BTE. VPC on the column with *Dow Corning 705*, as described, above furnished pure **14**. Inlet block, 45°; column, 34°; detector, 70°; 0.4 atm N_2; t_R 126 min. The material was handled under Ar for immediate use.

2.3. *Methylketene Dimethyl Acetal* (=*1,1-Dimethoxyprop-1-ene*; **17**). Compound **17**, b.p. 98–100°, was obtained from acrolein dimethyl acetal by KNH_2-catalyzed isomerization [13]; it was stored over molecular sieves at −30° and distilled under Ar before use.

2.4. *Ketene Diethyl Acetal* (=*1,1-Diethoxyethene*; **19**). Compound **19** was prepared from bromoacetaldehyde diethyl acetal by elimination of HBr [14]. Before use, **19** was distilled over solid NaH.

2.5. *(*E*)- and (*Z*)-BTE* (**1**). See [1][2].

3. *(2+2) Cycloadditions with Methyl Prop-1-enyl Ether.* 3.1. *(*E*)-BTE and (*E*)-***6***. Methyl (*E*)-prop-1-enyl ether* ((*E*)-**6**; 161 mg, 2.23 mmol; 99% isomer purity) and (*E*)-BTE (499 mg, 2.33 mmol) in CH_2Cl_2 (0.5 ml) were reacted in a NMR tube at r.t.; the orange-red soln. turned to light-orange after 3 d. After 25 d, (1,1-dichloro-2,2,2-trifluoroethyl)benzene ($\delta(F) = -78.2$) was added as weight standard, and the ^{19}F-NMR spectrum was recorded. The soln. was evaporated and distilled from a microflask; at 85°/0.01 Torr, **8** was obtained as a colorless oil (339 mg, 53%). A new ^{19}F-NMR spectrum (CH_2Cl_2) indicated an unchanged mixture of diastereoisomers, except for the disappearence of a trace of BTE. The ^{19}F-NMR analysis (*Table 5*) was based on free-standing signals for **8**(*trans*,*trans*-1), **8**(*trans*,*cis*-1), **8**(*trans*,*cis*-2), and **8**(*cis*,*trans*-1). The signal pairs of **8**(*trans*,*trans*-2) and **8**(*cis*,*cis*-2) partially overlap, and the ratio may be burdened with ±3% error. Anal. of distilled mixture, calc. for $C_{10}H_8F_6N_2O$ (286.18): C 41.97, H 2.82, N 9.79; found: C 42.14, H 3.00, N 9.49.

Table 5. *^{19}F-NMR Signals of the Cyclobutanes* **8** *in CH_2Cl_2* (in brackets: exchange possible)

Diastereoisomer	δ(1-CF_3) [ppm]	δ(2-CF_3) [ppm]	^5J(F,F) [Hz]
trans,*trans*-1	(– 65.3) (*s*)	(– 65.8) (*s*)	broadened *s*
trans,*trans*-2	(– 68.8) (*q*)	(– 67.7) (*q*)	1.8, partly resolved
trans,*cis*-1	– 64.8 (*s*)	– 70.2 (*s*)	broadened
trans,*cis*-2	– 71.5 (*s*)	– 64.5 (*s*)	
cis,*trans*-1	– 62.2 (*q*)	– 67.0 (*q*)	11.8
cis,*trans*-2	– 67.7 (*q*)	– 62.3 (*q*)	11.0
cis,*cis*-1	– 62.5 (m_c)		*multiplet*
cis,*cis*-2	(– 67.5) (*q*)	(– 68.6) (*q*)	11.9

The ratios of diastereoisomers collected in *Table 2* were based on this experiment and a second one which was run for 13 d and gave 32% of **8** after distillation. The 1:2 adduct was recognized in the crude product before distillation by the signals at – 54.6 and – 68.4 (2*q*, $J = 6.0$, 2 CF_3).

3.2. *(1*RS*,2*RS*,3*SR*,4*RS*)-3-Methoxy-4-methyl-1,2-bis(trifluoromethyl)cyclobutane-1,2-dicarbonitrile* (**8**(*trans*,*trans*-2)). From the distilled diastereoisomer mixture in little $CDCl_3$ at – 30°, prisms (6 mg, *ca.* 1%) were obtained, which after recrystallization had a m.p. of 80–81° (closed tube); 34% of the distilled **8** consisted of **8**(*trans*,*trans*-2) (*Table 2*). IR (KBr): 983*s*, 1024*s*; fused v*s* signals 1175, 1200, 1260 (C–O, C–F, str.); 1398*m*, 1461*m*; 2255v*w* (C≡N). ^{1}H-NMR ($CDCl_3$, 100 MHz; F-decoupled): 1.47 (*d*, ^3J(H,Me) = 6.8, Me–C(4)); 3.12 (*dq*, ^3J(3,4) = 8.7, ^3J(4,Me) = 6.8, H–C(4)); 3.53 (*s*, MeO); 4.01 (*d*, ^3J(3,4) = 8.7, H–C(3)). ^{19}F-NMR (CH_2Cl_2, 94.1 MHz): – 67.7, – 68.8 (2*q*, partially resolved, ^5J(F,F) = 1.8, 2 CF_3).

3.3. *(*E*)-BTE and (*Z*)-***6***.* The reaction of (*Z*)-**6** (151 mg, 2.09 mmol, isomer purity 99.4%) and (*E*)-BTE (497 mg, 2.32 mmol) in CH_2Cl_2 (0.5 ml) took place at r.t. in a NMR tube. Workup, as described in *Sect. 3.1*, gave a colorless distillate (324 mg, 54%), which was resistant to refluxing 2,3-dimethylbuta-1,3-diene, *i.e.*, no BTE, an active dienophile, occurred as dissociation product. Anal. of diastereoisomer mixture, calc. for $C_{10}H_8F_6N_2O$ (286.18): C 41.97, H 2.82, N 9.79; found: C 42.29, H 2.95, N 9.55.

3.4. *(1*RS*,2*SR*,3*SR*,4*RS*)-3-Methoxy-4-methyl-1,2-bis(trifluoromethyl)cyclobutane-1,2-dicarbonitrile* (**8**(*cis*,*trans*-2)). (*Z*)-BTE (453 mg, 2.12 mmol) was mixed with (*E*)-**6** (133 mg, 1.84 mmol); after 3 d at r.t., the unconsumed BTE showed 26% (*E*)-content, and 93% after 25 d. Distillation at 85°/0.1 Torr gave a colorless oil (412 mg, 78%), which partially crystallized at 0°. The oily part was adsorbed by filter paper; two recrystallizations from pentane afforded leaflets (87 mg, 17%). M.p. 54.5–55.5°. The ^{19}F-NMR spectrum after distillation indicated 88% of the same diastereoisomer. IR (KBr): 731*m*, 755*w*; 1008*s*, br. fused signals at 1175, 1204, 1230, 1257, 1288 (C–O, C–F, str.); 2246v*w* (C≡N). ^{1}H-NMR ($CDCl_3$, 100 MHz, ^{19}F-decoupled): 1.47 (*d*, ^3J (H,Me) = 6.6, Me–C(4)); 3.1–3.4 (*m*, H–C(4)); 3.60 (*s*, MeO); 4.16 (*dq*, ^3J(3,4) = 9.7, ^4J(4-H,2-CF_3) = 1.7, H–C(3)). ^{19}F-NMR (CH_2Cl_2, 80 MHz; ^{1}H-decoupled): – 62.3 (*q*, broadened) and – 67.7 (*q*, $^5J = 11.0$). Anal. calc. for $C_{10}H_8F_6N_2O$ (286.18): C 41.97, H 2.82, N 9.79; found: C 42.00, H 2.86, N 9.59.

4. *Reactions with Isobutenyl Methyl Ether* (= *Methyl 2-Methylprop-1-en-1-yl Ether*; **9**). 4.1. *(1*RS,*2*RS,*4*RS*)-4-Methoxy-3,3-dimethyl-1,2-bis(trifluoromethyl)cyclobutane-1,2-dicarbonitrile* (**10**). The orange-red soln. of of **9** (172 mg, 2.00 mmol) and (*E*)-BTE (428 mg, 2.00 mmol) in MeCN (10 ml) turned yellow after 42 d at r.t.; the ^{19}F-NMR spectrum revealed *ca.* 35% of **10**, some **11**, and further products. Pure **10** crystallized from pentane. M.p. 74–75° (closed tube). ^{1}H-NMR (C_6D_6, 100 MHz, atom numbering as indicated in *Scheme 6*): 0.73 (*q*, ^{5}J(Me,1-CF_3) = 2.0, Me–C(4)); 1.08 (*s*, Me–C(4)); 2.68 (*s*, MeO); 3.54 (br. *s*, H–C(3)). ^{19}F-NMR (CH_2Cl_2, 94.1 MHz): −63.4 (*s*, 2-CF_3); −64.5 (*q*, partially resolved, ^{5}J(F,H) = 2.0; conversion to *s* on ^{1}H-decoupling, 1-CF_3). Anal. calc. for $C_{11}H_{10}F_6N_2O$ (300.21): C 44.01, H 3.36; found: C 43,95, H 3.43.

4.2. *1,1,1-Trifluoro-4-methoxy-5-methyl-3-(trifluoromethyl)hex-5-ene-2,3-dicarbonitrile* (= *2-(1-Methoxy-2-methyl-2-propen-1-yl)-2,3-bis(trifluoromethyl)butanedinitrile*; **11**). Compound **9** (150 mg, 1.74 mmol) and (*E*)-BTE (171 mg, 0.80 mmol) were reacted without solvent for 35 d at r.t.; excess of reactants was evaporated, and oily crystals (211 mg; m.p. 42–51°) remained. Recrystallization (2×) from pentane afforded **11** as colorless needles (105 mg, 44%). M.p. 59.5–61.0°. The mother liquor contained some **10** and unidentified products. IR (KBr): 1062*m*; 1101*s*, 1142*s* (C–O), v*s* fused bands at 1183, 1204, 1215, 1242 (C–O, C–F, str.); 1355v*s*; 1637v*s* (C=CH_2); C≡N uncertain. ^{1}H-NMR ($CDCl_3$, 100 MHz): 1.94 (m_c, Me–C(5)); 3.35 (*s*, MeO); 3.76 (*q*, ^{3}J(H,F) = 7.2, H–C(2)); 4.15 (*s*, H–C(4)); 5.4–5.6 (*m*, CH_2(6)). ^{13}C-NMR ($CDCl_3$, 50.3 MHz, ^{1}H-decoupled): 16.6 (*s*, Me); 40.1 (*q*, ^{2}J(C,F) = 35, C(2)); 49.1 (*q*, ^{2}J(C,F) = 29, C(3)); 57.3 (*s*, MeO); 83.9 (*s*, C(4)); 109.1, 110.7 (2*s*, 2 CN); 120.9 (*q*, ^{1}J(C,F) = 284, CF_3); 122.0 (*q*, ^{1}J(C,F) = 288, CF_3); 124.9 (*s*, C(6)); 136.5 (*s*, C(5)). ^{19}F-NMR ($CDCl_3$, 84.3 MHz): −61.9 (*dq*, ^{5}J(F,F) = 9.2, ^{3}J(F,H) = 7.3, CF_3–C(2)); −65.0 (*q*, ^{5}J(F,F) = 9.2, CF_3–C(3)). Anal. calc. for $C_{11}H_{10}F_6N_2O$ (300.21): C 44.01, H 3.36, N 9.33; found: C 44.42, H 3.40, N 9.27.

5. *Reactions with Dimethylketene Dimethyl Acetal* (**14**). 5.1. *(1*RS,*2*RS*)-3,3-Dimethoxy-4,4-dimethyl-1,2-bis(trifluoromethyl)cyclobutane-1,2-dicarbonitrile* (*trans*-**16**). Acetal **14** (100 mg, 0.86 mmol) was injected to (*E*)-BTE (170 mg, 0.79 mmol) in CH_2Cl_2 (0.5 ml) under Ar; the orange-red color disappeared within 1 h. Evaporation, finally at 0.1 Torr, left a crystalline solid (260 mg, 99%) with a m.p. of 150–152°. Recrystallization (2×) from $CHCl_3$/pentane furnished small crystals (63 mg) with m.p. 153–153.5° (closed tube). ^{1}H-NMR ($CDCl_3$, 100 MHz): 1.56 (*q*, ^{5}J(H,F) ~ 2, Me–C(4)); 1.57 (*s*, Me–C(4)); 3.45, 3.56 (2*s*, 2 MeO). ^{13}C-NMR ($CDCl_3$, 50.3 MHz, ^{1}H-decoupled): 20.4 (*q*, ^{4}J(C,F) = 3.0, Me–C(4)); 23.5 (*s*, Me–C(4)); 48.6 (*q*, ^{2}J(C,F) = 30, C(1)); 52.4, 53.2 (2*s*, 2 MeO); 54.7 (*s*, C(4)); 55.2 (*q*, *J*(C,F) = 31, C(2)); 103.7 (*s*, C(3)); 110.6 (*q*, ^{3}J(C,F) = 1.9, CN); 111.0 (*q*, ^{3}J = 2.0, CN); 120.8 (*q*, ^{1}J(C,F) = 284, CF_3); 122.3 (*q*, ^{1}J(C,F) = 285, CF_3). ^{19}F-NMR (CH_2Cl_2, 34.1 MHz): −63.5 (m_c, CF_3); −63.7 (*q*, partially resolved, *J* = 1.6, CF_3). Anal. calc. for $C_{12}H_{12}F_6N_2O_2$ (330.23): C 43.64, H 3.66, N 8.48; found: C 43.72, H 3.83, N 8.71.

Further experiments were performed, and ^{19}F-NMR spectra were analyzed after shorter times (CH_2Cl_2 and C_6H_6): no isomerization of unconsumed (*E*)-BTE was observed.

5.2. *Diastereoisomer* cis-**16**. (*Z*)-BTE (342 mg, 1.60 mmol) was injected with a septum into **14** (208 mg, 1.79 mmol) in CH_2Cl_2 (1.0 ml); the orange color faded within 25 min. Removal of solvent led to a colorless solid (528 mg, 100%) with a m.p. of 153–154°. The ^{19}F-NMR spectrum indicated a 91:9 mixture *cis*-**16**/*trans*-**16**. Attempts to obtain pure *cis*-**16** by fractional crystallization failed.

Data of cis-**16**. ^{1}H-NMR (C_6D_6, 100 MHz): 0.93 (*q*, ^{5}J(H,F) = 1.8, Me–C(4)); 1.37 (*s*, Me–C(4)); 2.68, 2.98 (2*s*, 2 MeO); ($CDCl_3$): 1.46 (*q*, *J*(H,F) = 1.7, Me); 1.68 (*s*, Me); 3.45, 3.56 (2*s*, 2 MeO); most signals coincided with those of *trans*-**16**, except for the *q* of Me–C(4) of *trans*-**16**, which appeared in the gap between the Me signals of *cis*-**16**. ^{19}F-NMR (CH_2Cl_2, 94.1 MHz): −60.6 to −61.7 (*m*, 2 CF_3). Anal. calc. for $C_{12}H_{12}F_6N_2O_2$ (330.23): C 43.64, H 3.66, N 8.48; found: C 43.84, H 3.72, N 8.26.

5.3. *Steric Course of Cycloaddition for (*Z*)-BTE + **14***. The reaction in CH_2Cl_2 provided *cis*-**16**/*trans*-**16** 91:9 (^{19}F-NMR analysis). Analogous experiment in benzene led to ratio 92:8 and that in cyclohexane to 94:6. When the reaction in CH_2Cl_2 was run with increasing excess concentration of (*Z*)-BTE, the (*E*)-BTE as dissociation product has a reduced chance of cycloaddition. Equivalents of (*Z*)-BTE and the *cis*-**16**/*trans*-**16** ratios were 1.1 and 91:9, 3.0 and 94:6, 4.7 and 97:3, as well as 5.1 and 96:4.

6. *Reactions with Methylketene Dimethyl Acetal* (**17**). 6.1. *3,3-Dimethoxy-4-methyl-1,2-bis(trifluoromethyl)cyclobutane-1,2-dicarbonitrile* (**18**(*trans*-1) + **18**(*trans*-2)). Freshly distilled methylketene dimethyl acetal (107 mg, 1.05 mmol) was injected into the soln. of (*E*)-BTE (300 mg, 1.40 mmol) in CH_2Cl_2 (4 ml); the red CT color instantly disappeared. (1,1-Dichloro-2,2,2-trifluoroethyl)benzene (δ(F) −78.2)

served as weight standard for the ^{19}F-NMR analysis (*ca.* 100%). Distillation at 0.1 Torr gave **18** which consisted of 69% **18**(*trans*-1), 25% of **18**(*trans*-2), and 6% **18**(*cis*-2), Isomerization became noticeable after storage for several days. ^{1}H-NMR (C_6D_6, 80 MHz) of **18**(*trans*-1): 0.92 (*dq*, ^3J(Me,H) = 7.1, ^5J(Me,F) = 1.9, Me–C(4)); 2.62, 3.16 (2*s*, 2 MeO); 2.8–3.3 (*m*, H–C(4), overlap); of **18**(*trans*-2): 0.98 (*d*, ^3J = 7.2, Me–C(4); 2.83, 2.92 (2*s*, 2 MeO). ^{19}F-NMR (CH_2Cl_2, 84.3 MHz; ^{1}H-decoupled) of **18**(*trans*-1): −66.0 (*s*, CF_3–C(1)); −64.0 (*s*, CF_3–C(2)); of **18**(*trans*-2): −69.3 (*s*, CF_3–C(1)); −64.3 (*s*, CF_3–C(2)). Anal. calc. for $C_{11}H_{10}F_6N_2O_2$ (316.21): C 41.78, H 3.19, N 8.86; found: C 41.90, H 3.17, N 8.81.

6.2. *Reaction with (Z)-BTE.* Acetal **17** (21.8 mg, 0.214 mmol) and (*Z*)-BTE (30.8 mg, 0.144 mmol) were reacted in a NMR tube under Ar. After adding the weight standard, the ^{19}F-NMR spectrum indicated *ca.* 94% yield and the following rel. %: **18**(*cis*-1) 68, **18**(*cis*-2) 16, **18**(*trans*-1) 13, and **18**(*trans*-2) 3. ^{1}H-NMR (additional experiment in C_6D_6, 80 MHz) of **18**(*cis*-1): 0.8–1.2 (*m*, Me–C(4)); 2.90, 2.93 (2*s*, 2 MeO); of **18**(*cis*-2): 2.69, 3.21 (2*s*, 2 MeO). ^{19}F-NMR (CH_2Cl_2, 84.3 MHz): see *Scheme 8*.

6.3. *Dissociation of Cyclobutanes* **18**. Diastereoisomer mixture (87 mg, 0.275 mmol) and 2,3-dimethylbuta-1,3-diene (160 mg, 1.90 mmol) reacted in CH_2Cl_2 (0.5 ml) in the NMR tube for 11 d at r.t.; the ^{19}F-NMR analysis with standard indicated formation of 4,5-dimethyl-1,2-bis(trifluoromethyl)cyclohex-4-ene-1,2-dicarbonitrile (25%; *Diels–Alder* adduct of BTE) besides 75% of **18**.

6.4. *Diastereoisomerization of* **18**. The mixture of **18** was prepared from (*Z*)-BTE (0.149 mmol) and **17** (0.257 mmol) in CH_2Cl_2 (0.5 ml) in a NMR tube, which remained in the ^{19}F-NMR spectrometer for the first hour. In the *Figure* and *Sect. 2.5*, the changes in diastereoisomer ratio were described; **18**(*cis*-1) had disappeared after 7 h. After 41 d, decomposition products and free BTE increased. The analysis after 116 d at r.t. was disturbed by secondary products; rel. yields [%] of **18**: **18**(*trans*-1) 7, **18**(*trans*-2) 66, and **18**(*cis*-2) 27%.

7.1. *3,3-Diethoxy-1,2-bis(trifluoromethyl)cyclobutane-1,2-dicarbonitrile* (**22**). Ketene diethyl acetal (**19**; 143 mg, 1.23 mmol) was introduced into (*E*)-BTE (239 mg, 1.12 mmol) in CH_2Cl_2 (1.0 ml). A slight warming, but no color was noticeable; a short-term red color was observed, when the reaction was run at −30°. Bulb-to-bulb distillation at 50°/0.001 Torr furnished **22** as a colorless oil (313 mg, 85%), which contained *trans*-**22** and *cis*-**22** in a 88 : 12 ratio (^{19}F-NMR-analysis); reddish color appeared on exposure to air. The analogous reaction of (*Z*)-BTE with **19** gave the same isomer mixture of **22**. ^{1}H-NMR ($CDCl_3$, 100 MHz) of *trans*-**22**: 1.30 (br. *t*, *J* = 7.0, 2 *Me*CH_2); 3.04 (br. *s*, CH_2(4)); 3.4–4.0 (*m*, 2 Me*C*H_2). ^{13}C-NMR ($CDCl_3$, 20.2 MHz; ^{1}H-decoupled) of *trans*-**22**: 14.4 (*s*, 2 *Me*CH_2); 39.2 (*s*, C(4)); 59.7 (*s*, 2 Me*C*H_2); 98.8 (*s*, C(3)); 109.6 (*d*, *J*(C,F) = 1.8, 2 CN); 120.6 (*q*, ^1J(C,F) = 284, CF_3); 121.8 (*q*, ^1J(C,F) = 289, CF_3); an off-resonance spectrum confirmed the multiplicities of the H-coupled species. ^{19}F-NMR (CH_2Cl_2, 94.1 MHz) of *trans*-**22**: −65.1, −70.2 (2 br. *s*, 2 CF_3); of *cis*-**22**: −63.3, −68.6 (2*q*, *J* = 12.5, 2 CF_3). Anal. calc. for $C_{12}H_{12}F_6N_2O_2$ (330.23): C 43.64, H 3.66, N 8.48; found: C 43.68, H 3.65, N 8.43.

7.2. *Spontaneous Dissociation of* **22**. Ethyl vinyl ether (180 mg, 2.50 mmol) was added to freshly distilled **22** (298 mg, 0.90 mmol) in CH_2Cl_2 (1 ml). After 11 d at r.t., double distillation at 80°/0.02 Torr gave a colorless oil (192 mg); the ^{19}F-NMR analysis indicated the BTE adduct of ethyl vinyl ether [2] and non-identified products.

7.3. *Methyl 3,4-Dicyano-5,5,5-trifluoro-3-(trifluoromethyl)pentanoate* (**23**). The soln. of **22** (497 mg, 1.50 mmol) in MeOH (4 ml) was evaporated after 3 min; distillation at 60°/0.15 Tor furnished **23** as a partially crystalline and intensely smelling oil (250 mg, 58%), which contained two diastereoisomers in a ratio of 63 : 37 (^{19}F-NMR). IR (Film): 1107*m* (C–O); 1145*s*, 1195v*s*, 1255v*s* (C–F, C–O, str.); 1740*s* (C=O); 2255v*w* (C≡N). ^{1}H-NMR ($CDCl_3$, 80 MHz), major isomer: 3.28 (*s*, CH_2(2)); 3.82 (*s*, MeO); 5.16 (*q*, ^3J(H,F) = 7.9, H–C(4)); minor isomer: 3.22 (*s*, CH_2(2)); 3.80 (*s*, MeO); 5.09 (*q*, ^3J(H,F) = 7.4, H–C(4)). ^{19}F-NMR ($CDCl_3$, 84.3 MHz), major isomer: −69.6 (*q*, ^5J = 8.1, CF_3–C(3)); −63.4 (*quint.*, *J*(F,F,H) = 7.6, F_3C(5)); minor isomer: −69.2 (*q*, ^5J = 7.7, F_3C–C(3)); −62.7 (*quint.*, *J*(F,F,H) = 7.6, F_3C(5)). Anal. calc. for $C_9H_6F_6N_2O_2$ (288.15): C 37.51, H 2.10, N 9.72; found: C 37.72, H 2.27, N 9.70.

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