Reactions of Di(*tert*-butyl)diazomethane with Acceptor-Substituted Ethylenes[1])

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Dedicated to *Herbert Mayr* on the occasion of his 60th birthday

Di(*tert*-butyl)diazomethane (**4**) is a nucleophilic 1,3-dipole with strong steric hindrance at one terminus. In its reaction with 2,3-bis(trifluoromethyl)fumaronitrile ((*E*)-**BTE**), a highly electrophilic tetra-acceptor-substituted ethene, an imino-substituted cyclopentene **9** is formed as a 1:2 product. The open-chain zwitterion **10**, assumed as intermediate, adds the second molecule of (*E*)-**BTE**. The ^{19}F- and ^{13}C-NMR spectra allow the structural assignment of two diastereoisomers, **9A** and **9B**. The zwitterion **10** can also be intercepted by dimethyl 2,3-dicyanofumarate (**11**) and furnishes diastereoisomeric cyclopentenes **12A** and **12B**; an X-ray-analysis of **12B** confirms the 'mixed' 1:1:1 product. Competing is an (*E*)-**BTE**-catalyzed decomposition of **4** to give 2,3,4,4-tetramethylpent-1-ene (**7**) + N_2; the reaction of (*E*)-**BTE** with a trace of water appears to be responsible for the chain initiation. The H_2SO_4-catalyzed decomposition of diazoalkane **4**, indeed, produced the alkene **7** in high yield. The attack on the hindered diazoalkane **4** by **11** is slower than that by (*E*)-**BTE**; the zwitterionic intermediate **21** undergoes cyclization and furnishes the tetrasubstituted furan **22**. In fumaronitrile, electrophilicity and steric demand are diminished, and a 1,3-cycloaddition produces the 4,5-dihydro-1*H*-pyrazole derivative **25**. The reaction of **4** with dimethyl acetylenedicarboxylate leads to pyrazole **29** + isobutene.

1. Introduction. – 1,3-Dipoles are ambiphilic by definition [2a]. The predominant reactivity allows their classification into nucleophilic, nucleophilic–electrophilic, and electrophilic 1,3-dipoles. In the framework of the MO-perturbation theory (PMO), the three classes correspond to different contributions of the HO–LU interactions between the cycloaddition partners to the energy of the transition structure (TS) [2b][3] (for reviews, see [4][5]).

Methyl diazoacetate (**1**) is a 1,3-dipole with well-balanced nucleophilicity and electrophilicity; *i.e.*, **1** undergoes cycloadditions with electrophilic (α,β-unsaturated carbonyl compounds and nitriles) and nucleophilic dipolarophiles (enamines, ynamines) [1][6]. Whereas dimethyl diazomalonate (**2**) and methyl diazo(phenylsulfonyl)acetate (**3**) move towards electrophilic 1,3-dipoles on the continuous scale [6], diazomethane, higher diazoalkanes, and phenylated diazomethanes are nucleophilic

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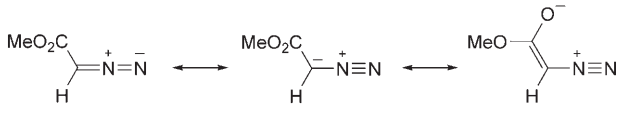
1,3-dipoles. Diazomethane no longer reacts with enamines, but the increase of the cycloaddition rate by electron-attracting substituents in the ethylenic dipolarophile is dramatic: ethyl acrylate reacts 10^7 times faster than butyl vinyl ether (DMF, 25°), and the cycloadditions with dimethyl fumarate or dimethyl acetylenedicarboxylate are beyond the range of conventional rate measurements [7][8].



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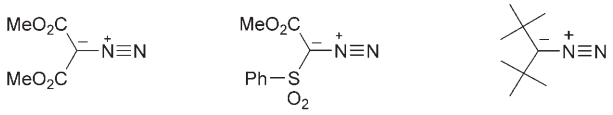
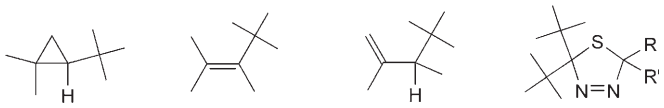


2 **3** **4**

A switch from concerted cycloaddition to a two-step pathway was observed when two conditions were fulfilled: a great difference in nucleophilicity and electrophilicity between the reactants, and steric hindrance at least at one terminus of the 1,3-dipole. Such a change of mechanism has been studied for cycloadditions of thiocarbonyl ylides [9] (for a review, see [10]) and sulfonyl azides [11][12]. A similar cooperation of steric and electronic effects is described here for cycloadditions of di(*tert*-butyl)diazomethane (**4**).

The chemistry of 3-diazo-2,2,4,4-tetramethylpentane (**4**) is not nearly as developed as the reaction profile of diazomethane. The bulky **4** was first prepared by *Barton et al.* and served as a building block in the synthesis of overcrowded ethylenes [13][14]. Thermolysis of **4** at 135° furnished the cyclopropane derivative **5** (84%) [14], a CH-insertion product, that suggests the intermediacy of di(*tert*-butyl)carbene. Under varied conditions (presence of Se and Bu_3N), the branched alkene **6** was the major product (32%) [14].

Bock et al. studied the conversions of **4** in a flow system above 600 K at 10^{-2} mbar on the surface of metal catalysts [15]. The ratio of the produced hydrocarbons **5**–**7** varied with the nature of the catalyst, and 'chemisorbed di(*tert*-butyl)carbene' was assumed responsible. Both radical cation and radical anion of **4** appear to lose N_2 rapidly [15]. We are not aware that reactions of **4** with *Brønsted* acids have been studied. Cycloadditions of **4** with thiones gave rise to 2,5-dihydro-1,3,4-thiadiazoles **8** [13][16].



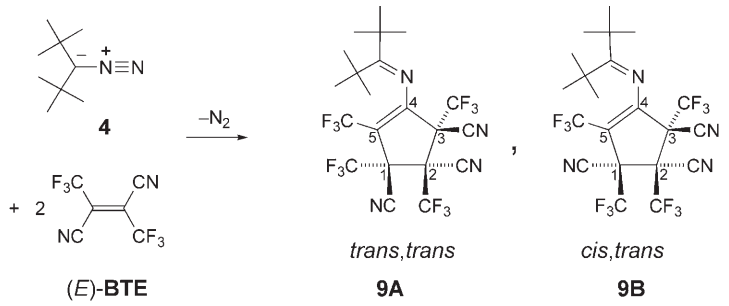
5 **6** **7** **8**

2. Results and Discussion. – 2.1. *Formation and Structure of 1:2 Products with* (*E*)-**BTE**. Like ethenetetracarbonitrile, (*E*)- and (*Z*)-1,2-bis(trifluoromethyl)ethene-1,2-

dicarbonitrile (=(*E*)- and (*Z*)-2,3-bis(trifluoromethyl)but-2-enedinitrile), abbreviated as (*E*)-**BTE** and (*Z*)-**BTE**, are highly reactive tetra-acceptor-substituted ethylenes [17]. They beautifully serve as stereochemical probes in mechanistic investigations. It has recently been demonstrated that the 1,3-dipolar cycloadditions of methyl diazoacetate (**1**) to (*E*)- and (*Z*)-**BTE** proceed with retention of dipolarophile configuration (> 99.93% and > 99.8%, resp.) [1]. Retention is a necessary, though not sufficient, criterion of concertedness.

When di(*tert*-butyl)diazomethane (**4**) was reacted with (*E*)-**BTE** (CH_2Cl_2; $-5°$ to room temperature), not the usual dihydropyrazole was formed, but rather the diastereoisomeric 1:2 products **9A** and **9B** (54%, **A**/**B** *ca.* 60:40) were isolated (*Scheme 1*); the elemental analyses and an *m*/*z* value of 554 left no doubt about the molecular formula. The diastereoisomeric cyclopentenes **9A** and **9B** were separated by preparative layer chromatography (PLC) and obtained crystalline.

Scheme 1



In the ^{19}F-NMR spectrum of the diastereoisomer mixture (*Fig. 1*), the integrals disclose the ratio **9A**/**9B**, and the chemical shifts underline the structural relation, whereas the splitting pattern of the signals allows the configurational assignment. The F,F-coupling constants and the multiplicities enable the allocation of the four CF_3 groups.

The downfield *quadruplet*s, δ −56.65 for **9A** and −56.50 for **9B**, belong to CF_3–C(5) which are located at a sp^2-hybridized C-atom. The coupling partner, CF_3–C(1), resonates at −67.23 (**A**) and −66.72 (**B**), and these signals appear in *Fig. 2* as a *nonadecet* for **A** and a *decet* for **B**, both with equidistant lines.

When rotation about the bond CF_3–C is fast on the NMR time scale, the three F-atoms are isochronous, and the coupling with a second CF_3 group leads to two *quadruplet*s with equidistant lines; the heights (1:3:3:1) are determined by the binomial coefficients. Not at all surprisingly, sets of binomial coefficients in the presence of several coupling partners can cooperate to afford simple patterns with equidistant lines, provided the *J* values are multiples of the lowest one, and the spectra are of first-order. The CF_3–C(1) in **9A** couples with the other three CF_3 groups with *J* = 3.0, 6.0, and 8.9 Hz; the small deviation of the last value from 9.0 leads to a tiny increase of line width. Coincidence of lines reduces a formal system of 64 lines (*qqq*) to nineteen lines (*Fig. 2*, left). The two ^5J parameters of CF_3–C(1) in **9B**, 6.4 and 12.8 Hz, are multiples, too, and the *quadruplet* of *quadruplet*s is simplified to ten equidistant

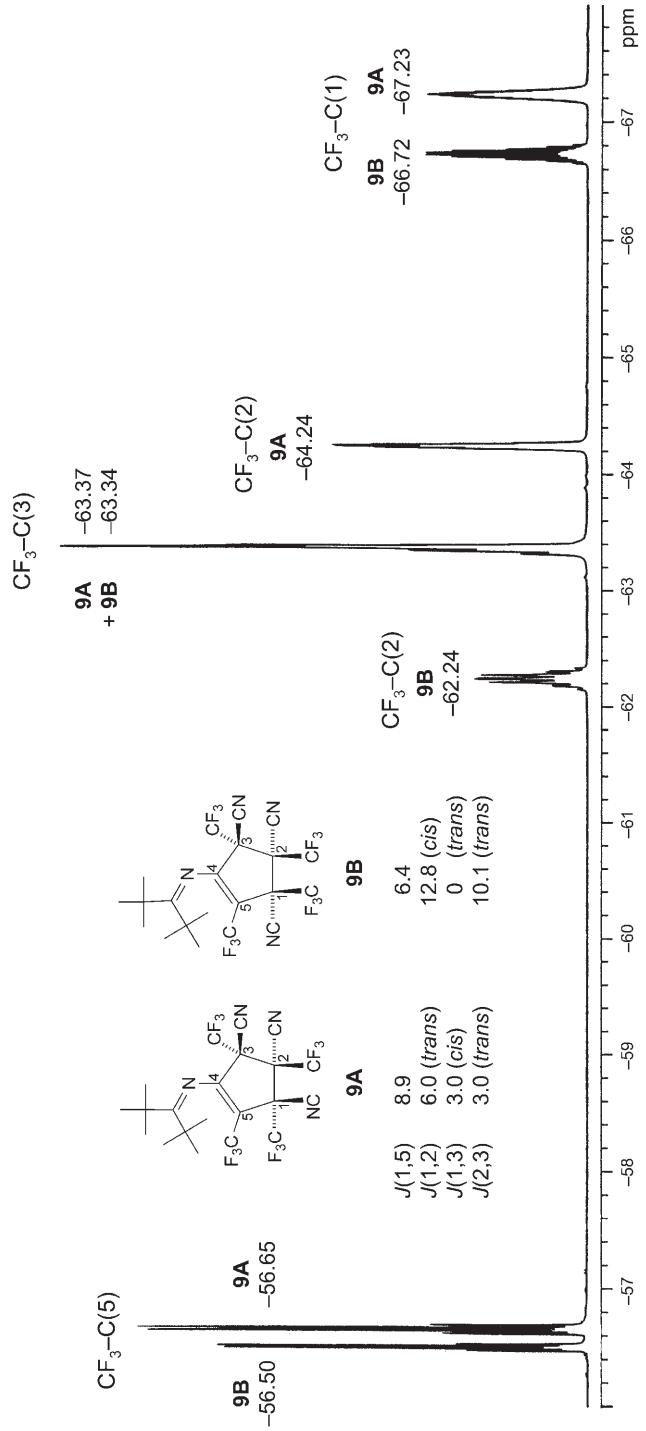


Fig. 1. *^{19}F-NMR Spectrum* (376.3 MHz) *of cyclopentene derivatives* **9A** *and* **9B** (**A**/**B** 57:43) *in* $CDCl_3$

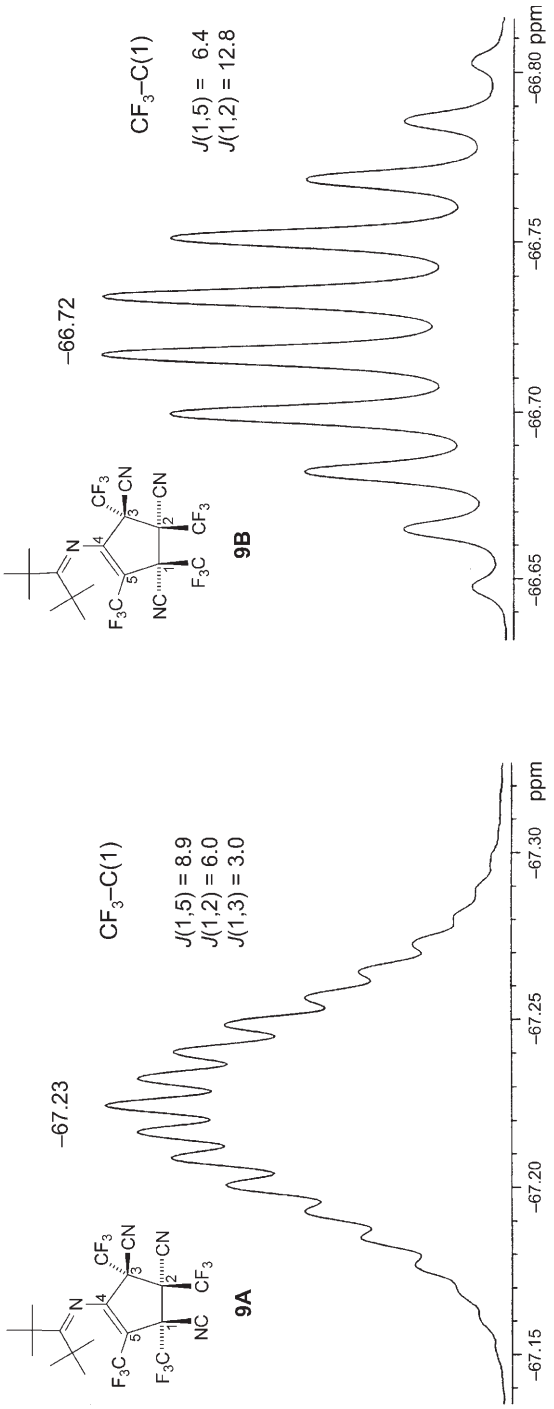


Fig. 2. *Expanded ^{19}F-NMR signals* (376.3 MHz) *of CF_3–C(1) in* **9A** *and* **9B**

lines (*Fig. 2*, right). The heights of the lines are virtually identical with those calculated by the binomial superposition of types 1:3:3:1. Of course, the appropriate coupling constants emerge again in the signals of CF_3–C(2) and CF_3–C(3).

F,F Coupling is predominantly transmitted through space, and $J_{cis,\mathrm{vic}} > J_{trans,\mathrm{vic}}$ is expected for CF_3 groups in five-membered rings. In the dihydro-1*H*-pyrazole from methyl diazoacetate and (*E*)-**BTE**, $J_{trans,\mathrm{vic}} = 0$ was found [1]. *Van der Waals* strain in the persubstituted cyclopentenes **9** probably distorts the regular half-chair conformation, *i.e.*, substantial values of $J_{trans,\mathrm{vic}}$ were observed (*Fig. 1*). Sterically hindered 3,4-bis(trifluoromethyl)spirothiolanes showed $J_{trans,\mathrm{vic}} = 4.1 - 11.6$ Hz, but $J_{cis,\mathrm{vic}}$ was always somewhat larger [18].

It is only in **9A** that CF_3–C(1) couples with CF_3–C(3), *i.e.*, across the ring; $^6J(1,3) = 3.0$ Hz establishes a *cis*-relation of these CF_3 groups and allows the structural assignment of **9A** and **9B**. The atom C(2) is another stereogenic center; could a formal (*Z*)-**BTE** unit be built into the five-membered ring? The coupling network finds in **9A** and **9B** the best solution by far; it is buttressed by the largest constant ($^5J(1,2) = 12.8$ Hz in **9B**) for the sole *cis*,vic-coupling. One more argument: the CF_3–C(2) groups in **9A** and **9B** exhibit the greatest difference in chemical shifts (2.0 ppm). Previous experience reveals that *cis*,vic-CF_3 generates a greater downfield shift than *cis*,vic-CN. The CF_3–C(2) has a *cis*,vic-CF_3 group in **9B**, but not in **9A**.

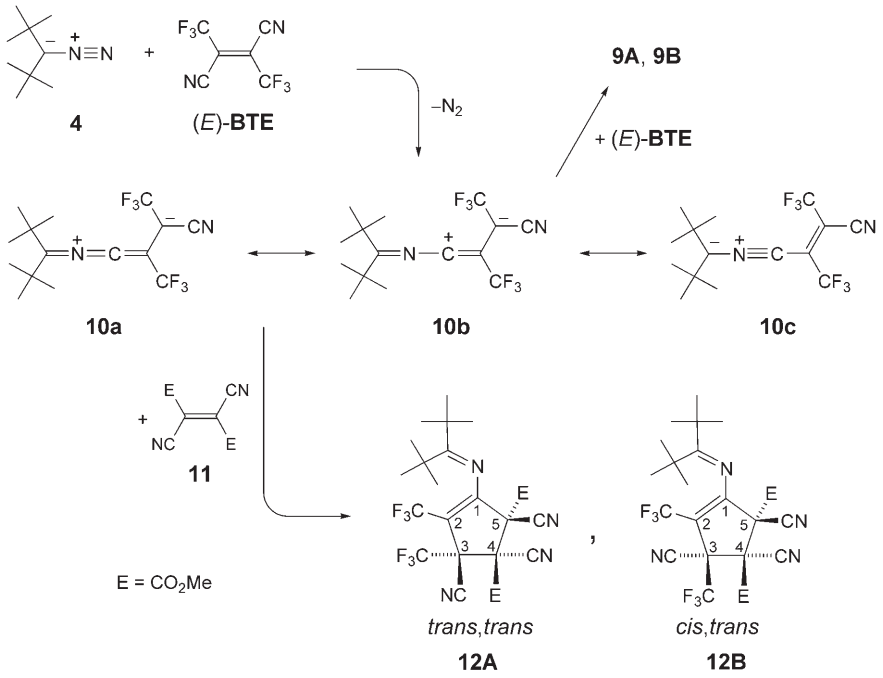
The ^{13}C-NMR spectra are in accordance with **9A** and **9B**, and the C,F couplings, $^2J = 29 - 37$, are helpful in the assignments. Thus, the *quadruplet*s at δ 84.8 (**9A**) and 82.1 (**9B**) must belong to C(5), *i.e.*, the enamine β-position, whereas the *singlet*s of C(4) are found at 142.1 and 139.7. The imino C-atoms resonate at δ 192.8 (**A**) and 191.8 (**B**). Furthermore, the X-ray-analysis of **12B** (see below) indirectly confirms the structure **9**.

2.2. *Interception of Intermediate* **10**. The formation of the 1:2 product **9** passes at least one intermediate by necessity. Structure **9** suggests that it is the CN group of (*E*)-**BTE** and not the electrophilic C-atom which attacks the highly hindered C-atom of diazoalkane **4**. The assumed zwitterionic intermediate **10** is illustrated in *Scheme 2* by three resonance structures. Formula **10c** reveals a nitrile ylide, a 1,3-dipole; the cycloaddition of the second molecule of (*E*)-**BTE** to yield a dihydro-3*H*-pyrazole is prevented by the voluminous *t*-Bu groups. The charge distribution in **10b** does not fit an 'classical' 1,3-dipole, but symbolizes the pathway by which the stepwise addition of the second (*E*)-**BTE** could furnish the persubstituted cyclopentenes **9**.

Our attempts of trapping intermediate **10** by a third reagent were successful with dimethyl 2,3-dicyanofumarate (= dimethyl (*E*)-2,3-dicyanobut-2-enedioate; **11**). It turned out that (*E*)-**BTE** is faster than **11** in the initial reaction with diazo compound **4**, whereas **11** exceeds (*E*)-**BTE** in its readiness to combine with intermediate **10**. When (*E*)-**BTE** (0.7 mmol) was slowly introduced into the deep-blue mixture (CT complex) of **4** and **11** (1.0 mmol each) in CH_2Cl_2 at room temperature, ^{19}F-NMR analysis indicated the 1:1:1 product **12** (45%) in two diastereoisomers, **A**/**B** 57:43, and little **9A** + **9B**. Remarkably, half of (*E*)-**BTE** – applied in less than the stoichiometric amount – remained unreacted. The liberation of 1.0 mmol of N_2 suggests a catalytic decomposition of **4** which competes with the adduct formation (see *Sect. 2.3*).

Layer chromatography allowed a partial separation of the diastereoisomer mixture. The minor component **12B** was obtained pure and crystalline; the spectra of **12A** were determined by the difference method. The ^{19}F-NMR *quadruplet*s of **12B** at -57.88 and

Scheme 2



– 65.12 ppm with $^5J(F,F) = 7.7$ Hz are separated from those of **12A** which couple with 8.2 Hz. The ^{13}C-NMR spectrum of **12B** exhibits a similarly polarized C=C bond as **9B**: δ 81.6 for C(4) and 146.0 for C(3) of **12B** *vs.* 82.1 for C(5) and 139.7 for C(4) of **9B**.

The X-ray diffraction analysis (*Fig. 3* and *Table*) reveals a *cis,trans*-structure for **12B** (and by exclusion, *trans,trans* for **12A**). As expected, the cyclopentene ring appears in an envelope conformation with C(4) (crystallographic atom numbering as shown in *Fig. 3*) as the flap; C(4) is located 0.41 Å below the plane of the other four C-atoms. Due to a twist angle of 89.4° at the central bond, the system C(13)=N(1)–C(1)=C(2) lacks π-conjugation, probably as a consequence of steric constraints. *Van der Waals* strain is likewise responsible for the stretching of the C–C bonds: 1.601 Å for C(3)–C(4) and 1.581 Å for C(4)–C(5).

2.3. *Competing Reactions and Mechanistic Considerations.* In the reaction of di(*tert*-butyl)diazomethane (**4**) with (*E*)-**BTE**, part of the latter remained unconsumed, even when applied much below the 1:2 stoichiometry required for the formation of **9** (*Scheme 1*). The N_2 volume liberated and the ^{1}H-NMR spectrum showed that **4** was always completely consumed. Thus, the formation of **9** competed with a decomposition of **4**, which afforded **7** + N_2 and was catalyzed by (*E*)-**BTE**.

The rate ratio for the formation of **9** and the (*E*)-**BTE**-catalyzed dediazoniation of **4** determines the yield of **9**; the yield fluctuated. When, two years after the original study, another experimentalist repeated the reaction with newly prepared reagents, the yield of **9A** + **9B** (64:36) dropped to 2.5%, and 89% of 2,3,4,4-tetramethylpent-1-ene (**7**) was obtained. The blue-violet CT color now disappeared even at –45° within

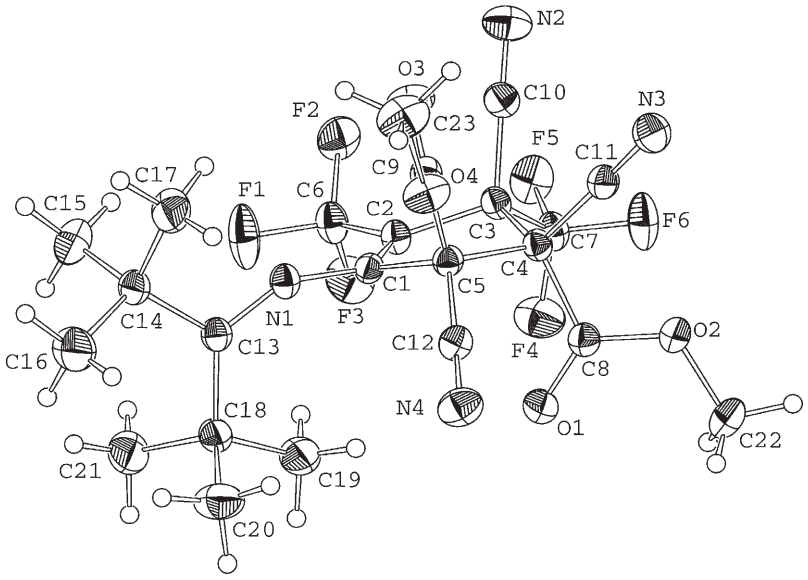


Fig. 3. *X-Ray crystal structure of the 1:1:1 product* **12B** (ZORTEP plot; thermal ellipsoids represent 30% probability)

Table. *X-Ray Structure of Cyclopentene Derivative* **12B**: *Selected Bond Lengths and Angles* (position numbering from *Fig. 3*; standard deviations in parentheses)

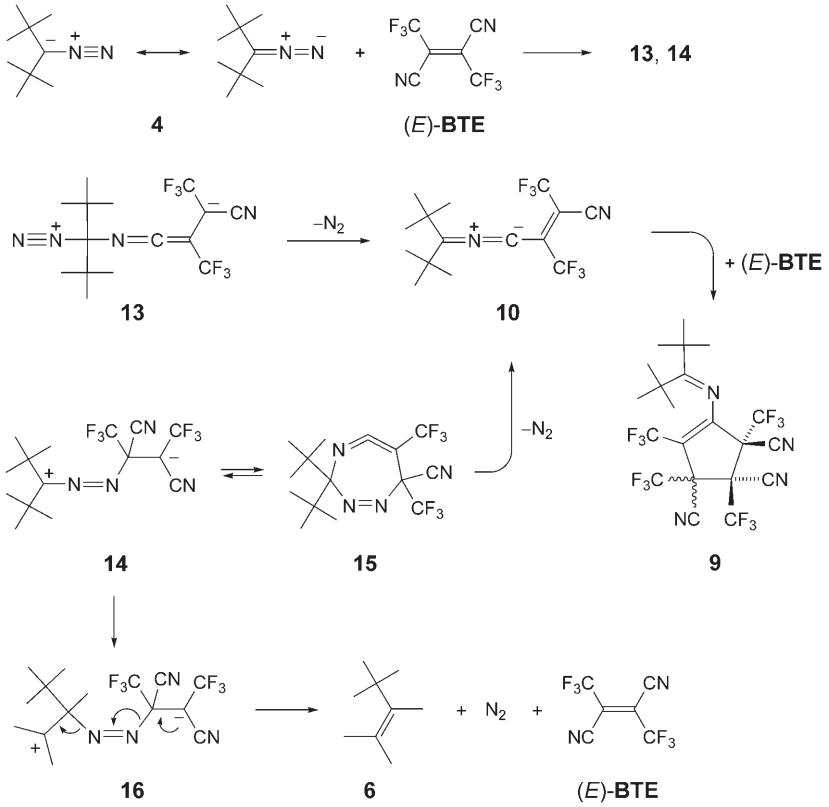
	Bond length [Å]		Angle [°]
C(1)=C(2)	1.347(3)	C(5)–C(1)–C(2)	111.2(2)
C(2)–C(3)	1.517(3)	C(1)–C(2)–C(3)	113.1(2)
C(3)–C(4)	1.601(3)	C(2)–C(3)–C(4)	102.6(2)
C(4)–C(5)	1.581(3)	C(3)–C(4)–C(5)	103.4(2)
C(5)–C(1)	1.531(3)	C(4)–C(5)–C(1)	103.5(1)
C(1)–N(1)	1.332(2)	C(1)–N(1)–C(13)	147.8(2)
N(1)=C(13)	1.266(2)		
F_3C(6)–C(2)	1.482(3)		
F_3C(7)–C(3)	1.551(3)		

minutes, and N_2 was evolved; in the absence of (*E*)-**BTE**, **4** is stable at room temperature and distillable. Not reproducible yields are an embarassment for the experimentalist and reveal that not all parameters are under control. In search of an unknown co-catalyst, our first guess was an electron-transfer process induced by a trace of metal; it did not find experimental confirmation.

According to *McGarrity* and *Cox*, diazomethane is protonated by superacid at C- and N-atom in the ratio 71:29 (FSO_3H/SbF_5, $-127°$, kinetic control) [19]. Two of the four initial interactions of (*E*)-**BTE** with **4** are worth consideration. In di(*tert*-butyl)diazomethane (**4**), C-attack by electrophilic reagents should be retarded, but the

CN N-atom of (*E*)-**BTE** may still be capable of piercing through the di(*tert*-butyl) shield and give rise to the diazonium zwitterion **13** (*Scheme 3*). Loss of N_2 affords intermediate **10**, suggested above as the precursor of products **9** and **12**.

Scheme 3



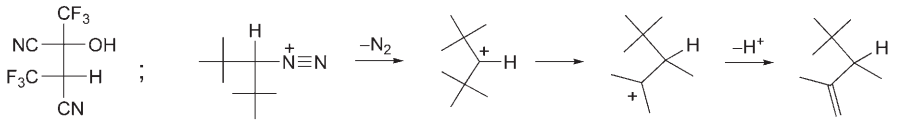
Attack by the C-atom of (*E*)-**BTE** on the terminal N-atom of **4** would furnish zwitterion **14**. Conceivably, a cyclization of **14** affords the seven-membered cyclic ketene imine **15**, and subsequent elimination of N_2 would offer a second pathway to zwitterion **10**. An analogy to the 1,7-cyclization: the zwitterions, which are formed from thiocarbonyl ylides and (*E*)-**BTE**, furnish isolable cyclic seven-membered ketene imines [18][20].

The loss of N_2 may also occur on the level of **14**, after a Me shift generated the *tertiary* carbocation **16**. The recovery of (*E*)-**BTE** in the ensuing fragmentation warrants the catalytic character of this decomposition mode of **4**. However, this pathway should lead to 2,3,4,4-tetramethylpent-2-ene (**6**), whereas the isolated hydrocarbon is the pent-1-ene derivative **7** (purity $>95\%$).

Pentene **7** is expected, when the catalytic role is ascribed to the proton (*Scheme 4*). Interestingly, (*E*)-**BTE** is more sensitive to H_2O and alcohol than ethenetetracarbonitrile (TCNE); the latter can be recrystallized from MeOH at low temperature.

Conceivably, a trace of H_2O converts **BTE** to **17**, which might be sufficiently acidic for the protonation of **4**. The diazonium ion **18** loses N_2, and the carbocationic rearrangement follows known principles (review: [21]). When the Me shift occurs in concert with the cleavage of the C–N bond, the *secondary* carbocation **19** would not be required as an intermediate. In the deprotonation of the *tertiary* carbocation **20** by the diazoalkane **4**, the methyl H-atom is strongly preferred to the H-atom at the *tertiary* center – for obvious steric reasons –, thus paving the way to the thermodynamically less stable olefin **7**.

Scheme 4



17 **18** **19** **20** **7**

Are adventitious traces of H_2O in the reaction of **4** with (*E*)-**BTE** responsible for the catalytic decomposition of **4**? The assumption was nurtured by the observation that the addition of 1 equiv. of H_2O to the reaction system at low temperature induced rapid fading of the deep CT color and evolution of N_2. The original experiments were carried out with a sample of **4**, which was prepared by thermolysis (80–100°) of the dry lithium salt of di(*tert*-butyl) ketone tosylhydrazone. For the later rework, **4** was obtained from the oxidation of di(*tert*-butyl) ketone hydrazone with nickel peroxide, described by *Mloston et al.* [16], and some humidity may have escaped removal.

A test experiment revealed that a sample of di(*tert*-butyl)diazomethane (**4**), prepared by the nickel peroxide method and distilled, still showed a small IR absorption of H_2O. When its solution in $CDCl_3$ was treated with a small amount of H_2SO_4 at room temperature, N_2 was evolved, and the ^{1}H-NMR analysis indicated 91% of pentene **7**, free of isomer **6**.

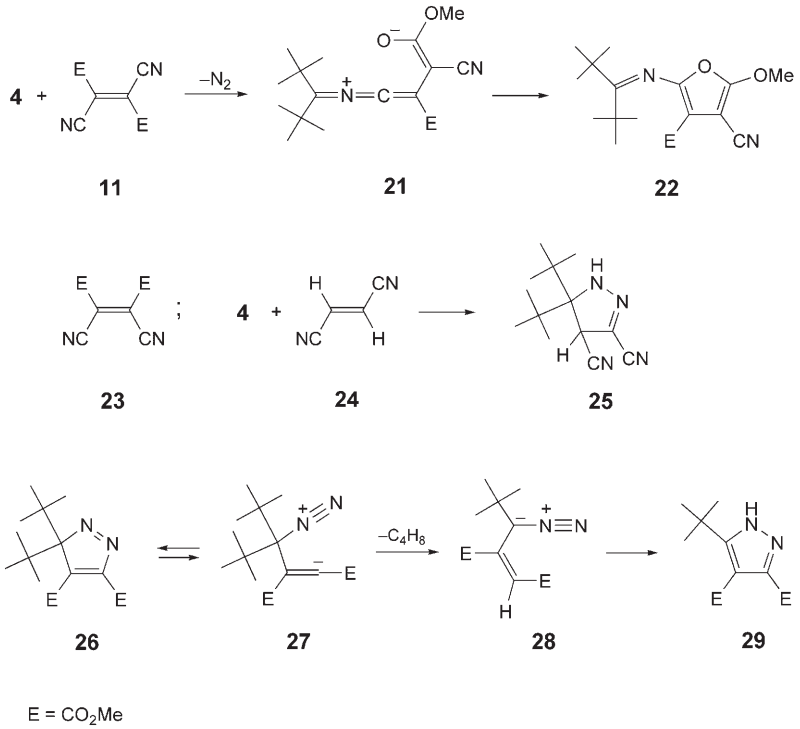
2.4. *Reactions with Further Electrophilic Multiple Bonds.* Diazoalkane **4** and dimethyl 2,3-dicyanofumarate (**11**) gave a deep-blue CT complex, and the reaction with N_2 evolution took place at 0–20°. The product $C_{17}H_{24}N_2O_4$ was obtained pure by distillation and corresponded to **4** + **11** – N_2. The intermediate **21** (*Scheme 5*), an analogue of **10**, attained stabilization by intramolecular nucleophilic addition and furnished the tetrasubstituted furan **22**. Among several structures discussed, **22** fits the ^{13}C-NMR spectrum best.

The yield of isolated pure **22** amounted to 40%, but the elimination of N_2 from **4** was complete. Again, the highly electrophilic **11** catalyzed the conversion **4** → **7** + N_2 in the presence of some H_2O, as shown above for (*E*)-**BTE**; the ratio of furan **22** and alkene **7** was likewise fluctuating.

In a preliminary experiment, **4** was reacted with (*E*)-**BTE** and dimethyl 2,3-dicyanomaleate (**23**); two new products, with two CF_3 groups each, require further study.

Fumaronitrile (**24**) is less electrophilic than **11** and has lower steric demands. 1,3-Dipolar cycloaddition with **4** afforded the 4,5-dihydro-1*H*-pyrazole derivative **25**

Scheme 5



(83%). The IR NH absorption and the ^{13}C-NMR parameters are in accordance with the structure **25**.

Dimethyl acetylenedicarboxylate is strongly electrophilic, but of low steric demand, in the cycloaddition process. Its reaction with **4** at $-20°$ furnished dimethyl 5-(*tert*-butyl)pyrazole-3,4-dicarboxylate (**29**; 58%) and an equivalent amount of isobutene. ^{1}H-NMR Monitoring ($-20°$, $CDCl_3$) revealed an intermediate which could be – but need not be – the 3*H*-pyrazole **26**. An initially formed zwitterion **27** could either undergo ring closure to give **26**, or induce the elimination of isobutene by its carbanionic terminus and provide **28** as an open-chain intermediate. The pyrazole **29** would emerge from a pentadienyl-anion type electrocyclization of **28**. Pyrazole **29** was independently synthesized by the reaction of 1-diazo-2,2-dimethylpropane ('diazoneopentane') with dimethyl acetylenedicarboxylate.

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Experimental Part

1. *General.* For instruments and procedures, see [1].

2. *Starting Materials.* 2.1. *3-Diazo-2,2,4,4-tetramethylpentane* (**4**): [13]. Instead of the sodium salt of 2,2,4,4-tetramethylpentan-3-one tosylhydrazone, the dry lithium salt was thermolyzed at 80–100°/0.1 Torr, and **4** was condensed in a cold trap at −78°; orangered liquid, 46% crude product, 39% after redistillation at 50–51°/12 Torr.

2.2. *(*E*)- and (*Z*)-1,2-Bis(trifluoromethyl)ethene-1,2-dicarbonitrile* ((*E*)- and (*Z*)-**BTE**): [17][22].

2.3. *Dimethyl 2,3-Dicyanofumarate* (**11**): [23]; *2,3-Dimethyl Dicyanomaleate* (**23**): [24].

3. *Reactions of* **1** *with* (E)-**BTE**. 3.1. *Isolation of* **9A** + **9B**. The soln. of **4** (159 mg, 1.03 mmol) in abs. CH_2Cl_2 (0.5 ml) was dropwise added to (*E*)-**BTE** (216 mg, 1.01 mmol) in CH_2Cl_2 (1 ml), and the mixture was magnetically stirred at −4°. The blue-violet color (CT complex) changed on slow warming to r.t. *via* red-violet to light-yellow, while N_2 was evolved. After evaporation of the solvent, the residue was subjected to column chromatography (CC) on silica gel with CH_2Cl_2/pentane 1:1. The fraction with R_f 0.75–0.89 was eluted with CH_2Cl_2 and furnished, after concentration and recrystallization from pentane at −18°, the anal. pure 1:2 adducts **9** (150 mg, 54%; **9A**/**9B** *ca.* 60:40). ^{19}F-NMR: *Fig. 1*. MS (40°): 554 (1, M^+), 535 (1, $[M-F]^+$), 497 (6, $[M-t\text{-Bu}]^+$), 471 (1, $[497-CN]^+$), 429 (0.3, $[497-CF_3+H]^+$), 327 (0.5), 284 (0.5), 214 (0.5, **BTE**$^+$), 69 (0.4, CF_3^+), 57 (100, t-Bu$^+$), 41 (16, [allyl]$^+$). Anal. calc. for $C_{21}H_{18}F_{12}N_4$ (554.39): C 45.49, H 3.27, N 10.11; found: C 45.75, H 3.23, N 10.06.

The separation of the diastereoisomers succeeded by PLC with Et_2O/light petroleum 1:20, 8× development. Elution with CH_2Cl_2 and crystallization from pentane afforded **9B**/**9A** 95:5 from the first fraction and pure **9A** from the second fraction.

3.2. trans,trans-*4-{[1-(1,1-Dimethylethyl)-2,2-dimethylpropylidene]amino}-1,2,3,5-tetrakis(trifluoromethyl)cyclopent-4-ene-1,2,3-tricarbonitrile* (**9A**). M.p. 57°. UV ($CHCl_3$): 260 (4.22), 306 (3.12). IR (KBr): 670*m*, 727*m*, 729*m*, 825*m*, 968*m*; 1134*s*, 1203v*s*, 1223v*s*, 1237v*s*, 1264*s* (C–F stretch.); 1355*s*; 1563*s* (C=N); 1775*s* (br.) (C=C?); 2255v*w* (C≡N). ^{1}H-NMR (80 MHz): 1.3, 1.4 (2*s*, 2 × 3 Me). ^{13}C-NMR (50.3 MHz, H-decoupled, J(C,F) couplings, ^3J(C,F) unresolved): 29.8 (*s*, 3 Me); 30.4 (*s*, 3 Me); 46.2, 47.2 (2*s*, 2 Me_3C); 3*q* of C(1), C(2), C(3): 55.0 (^2J = 29.8), 57.5 (^2J = 33.5), 59.8 (^2J = 30.5); 84.8 (*q*, ^2J = 34.1, C(5)); 107.7, 109.4, 109.8 (3*s*, 3 CN); 4*q* of 4 CF_3: 121.08 (^1J = 289.8), 121.22 (^1J = 287.4), 121.32 (^1J = 282.8), 121.46 (^1J = 282.1); 142.1 (*s*, C(4)); 192.8 (*s*, C(2′)). ^{19}F-NMR (376.3 MHz, δ based on CF_3OPh as secondary standard (−58.38)): *Figs. 1* and *2*.

3.3. trans,cis-*Isomer* **9B**. M.p. 79–81. UV ($CHCl_3$): 254 (4.17), 305 (3.23). IR (KBr): 667*m*, 717*m*, 824*m*, 1046*m*; 1140*s*, 1183v*s*, 1215v*s* (br.), 1269*m*, 1345*s* (C–F stretch.); 1583*s* (C=N); 1751, 1762*s* (br.) (C=C?); 2255v*w* (C≡N). ^{1}H-NMR (80 MHz): 1.3, 1.4 (2*s*, 2 × 3 Me). ^{13}C-NMR (50.3 MHz, H-decoupled, coupling constants J(C,F); ^3J(C,F) unresolved): 29.47, 29.63 (2*s*, 2 × 3 Me); 45.60, 46.70 (2*s*, 2 Me_3C); 3*q* of C(1), C(2), C(3): 56.7 (^2J = 31.7), 57.8 (^2J = 34.7), 58.7 (^2J = 33.2); 82.1 (*q*, ^2J = 36.2, C(5)); 108.1, 108.7, 109.9 (3*s*, 3 CN); 4 *q* of 4 CF_3: 119.73 (^1J = 288.4), 120.66 (^1J = 289.9), 121.02 (^1J = 272.2), 121.46 (^1J = 288.9); 139.7 (*s*, C(4)); 191.8 (*s*, C(2′)). ^{19}F-NMR (376.3 MHz, δ based on CF_3OPh): *Figs. 1* and *2*.

3.4. *^{19}F-NMR Monitoring.* The deep-blue-violet soln. of (*E*)-**BTE** (58.3 mg, 0.27 mmol) and **4** (34 mg, 0.22 mmol) in CD_2Cl_2 (0.55 ml) in the NMR tube at −10° required 4 h for complete reaction. The analysis showed (**9A** + **9B**)/(*E*)-**BTE** 71:29, a trace of (*Z*)-**BTE**, and some small unidentified signals. Thus, part of **BTE** remained unconsumed despite an insufficient concentration for bisadduct formation. According to the ^{1}H-NMR spectrum, no **4** was left.

3.5. *Competing Reactions of* **4** *with (*E*)-***BTE***.* The fluctuations in the yield of the 1:2 products **9** were mentioned in *Sect. 2.3*. One of the experiments with moist **4** [16] and isolation of pentene **7** is described. (*E*)-**BTE** (2.20 mmol) in $CDCl_3$ (0.7 ml) was introduced into the soln. of **4** (1.10 mmol) in $CDCl_3$ (0.5 ml) at −5°. The blue color was visible only for seconds, and N_2 (24 ml) evolved without delay. Part of the unreacted (*E*)-**BTE** crystallized from the pale-yellow soln. At r.t., $PhOCF_3$ (0.564 mmol) and 1,1,2,2-tetrachloroethane (0.586 mmol) were added as weight standards for ^{19}F- and ^{1}H-NMR analysis: 17.2 μmol (1.6%) of **9A** and 10.1 μmol (0.9%) of **9B** (**A**/**B** 64:36), and 0.98 mmol (89%) of the C_9-alkene **7**. The solvent was removed by distillation over a small *Vigreux* column, and *2,3,4,4-tetramethylpent-1-ene* (**7**; 98 mg, 78%) was distilled from a microflask at 120–123°. The ^{1}H- and ^{13}C-NMR spectra are in full

agreement with those described by *Rüchardt* and co-workers [25] for a specimen of **7** which was obtained from 2,2,4,4-tetramethylpentan-3-ol with HMPT (3 h, 220°) [26]. The parameters of the ^{1}H-coupled ^{13}C-NMR spectrum (100.6 MHz; J(C,H) are given here): 15.02 (*dq*, $^2J = 4.6$, $^1J = 125.5$, Me–C(3)); 22.61 (*ddq*, $^3J = 3.6$, 4.8, $^1J = 125.5$, Me–C(2)); 28.17 (*qm*, 10 lines resolved, $^1J = 124.8$, diastereotopic Me of *t*-Bu); 33.1 (*d*, $^2J = 3.8$, C(4)); 50.68 (*d*, $^1J = 123.9$, C(3)); 111.86 (*t* of *quint.*, $^1J = 154.2$, $^3J = 6.0$, C(1)); 149.25 (*s* with fine splitting, C(2)). The ^{1}H-NMR spectrum showed unidentified signals at 0.9–1.9 ppm, less than 5%; the only ^{13}C-NMR signals of olefinic C-atoms were those of **7**.

A corresponding experiment with (*Z*)-**BTE** gave similar results; the unreacted **BTE** had reached equilibrium, (*E*)/(*Z*) 94:6.

3.6. *Variation of Conditions.* Freshly distilled **4** (1.0 mmol) [16] and freshly sublimed (*E*)-**BTE** (0.5 mmol) in CH_2Cl_2 (1.0 ml) afforded a blue-violet soln. at −40°; the CT color disappeared in some min, and N_2 was liberated (23 ml). The ^{19}F-NMR analysis showed 8.9 μmol (3.6%) of **9A** + **9B**. Another experiment was carried out in the presence of benzophenone (20 mol-%); the violet color was stable at −45° for 40 min, but, below 0°, the N_2 evolution set in, and the color changed to yellow; NMR analysis: 8.3% of **9**, **A**/**B** 64:36. Experiments in the presence of 1,4-dinitrobenzene or di(*tert*-butyl)nitroxyl furnished 3–4% of **9**. In a further experiment, H_2O (1.0 mmol) was added to the blue-violet soln. of **4** + (*E*)-**BTE** at −40°; the deep color rapidly turned to light-yellow, and no **9** was found.

3.7. *Acid-Catalyzed Decomposition of* **4**. Di(*tert*-butyl) ketone hydrazone was oxidized with nickel peroxide [16][27][28]. After distillation of **4** from a microflask at 40°/8–10 Torr, the IR absorption at 3330 cm^{-1} was attributed to a trace of H_2O. When $CDCl_3$ is shaken with some drops of 98% H_2SO_4 and allowed to settle for 3 h, the clear supernatant phase was carefully pipetted and is 5–7 mM in H_2SO_4 [29][30]. A weighed amount of **4** was reacted with the mentioned $CDCl_3$ soln. (0.5 ml) in an NMR tube; the N_2 evolution at r.t. terminated after 15 min. The ^{1}H-NMR analysis with *sym*-$C_2H_2Cl_4$ as weight standard indicated 90% of **7** (= CH_2 at 4.60–4.83 ppm).

4. *Reaction of* **4** *with* (*E*)-**BTE** *and Dimethyl 2,3-Dicyanofumarate* (= *Dimethyl* (E)*-2,3-Dicyanobut-2-enedioate*; **11**). 4.1. *Isolation of 1:1:1 Adducts.* Diazo compound **4** (162 mg, 1.05 mmol) and (*E*)-**BTE** (169 mg, 0.79 mmol) were combined in CH_2Cl_2 (3 ml) at −35° and slowly introduced into the stirred suspension of **11** (204 mg, 1.05 mmol) in CH_2Cl_2 (4 ml) at 0°; **11** dissolved within several min. The N_2 evolution started, and the deep color faded, when the cooling bath was removed, and r.t. was reached. After adding $PhCCl_2CF_3$ (δ(F) −78.27) as weight standard, the ^{19}F-NMR analysis (in % of applied **BTE**) indicated unconsumed (*E*)-**BTE** (439 μmol, 56%, δ −62.26), a trace of (*Z*)-**BTE** (−59.2), the mixed cycloadducts **12** (266 μmol, 34%, two diastereoisomers **A**/**B** 57:43), and **9A**/**9B** (41 μmol, 10%). PLC (silica gel; light petroleum/Et_2O 3:1) gave five fractions. The third fraction (R_f 0.67–0.73) furnished the pure minor adduct **12B**. Isomer **12A** was in the second fraction (R_f 0.3–0.4), but was not obtained pure (^{19}F-NMR in $CDCl_3$: −57.23, −66.19 (2*q*, J(F,F) = 8.2)). The fourth fraction contained **9A** + **9B**.

4.2. *Improved Procedure.* In a second experiment, **4** (1.0 mmol) and **11** (1.0 mmol) in CH_2Cl_2 (8 ml) were stirred in a bath at r.t.; when (*E*)-**BTE** (0.75 mmol) in CH_2Cl_2 (1 ml) was added in some min, decolorization of the blue-violet soln. was observed, and N_2 (22 ml) was liberated. The ^{19}F-NMR analysis (as above) showed 50% unconsumed (*E*)-**BTE** and 45% of **12**.

4.3. *Dimethyl (1*RS,*2*RS,*5*RS*)-1,2,5-Tricyano-3-{[1-(1,1-dimethylethyl)-2,2-dimethylpropylidene]-amino}-4,5-bis(trifluoromethyl)cyclopent-3-ene-1,2-dicarboxylate* (**12B**). Colorless crystals from CH_2Cl_2/pentane; m.p. 140° after sintering (modification change) at 115°. IR (KBr): 974*m*; 1123*m* (br.), 1178*s*, 1223*s*, 1247v*s* (br., C–F); 1352*m*; 1583*m* (br., C=N); 1772v*s*, 1755 (sh), 1730 (C=O, C=C). ^{1}H-NMR: 1.22 (*s*, 3 Me); 1.33 (*s*, 3 Me); 3.95, 4.03 (2*s*, 2 MeO). ^{13}C-NMR (20.2 MHz, ^{1}H-decoupled): 29.9 (*s*, 3 Me); 30.9 (*s*, 3 Me); 44.8, 46.9 (2*s*, 2 Me_3C); 53.5, 62.9 (2*s*, C(1), C(2)); 55.68, 56.11 (2*s*, 2 MeO); 60.2 (*q*, $^2J = 33$, C(5)); 81.6 (*q*, $^2J = 36$, C(4)); 111.0, 111.6 (2*s*, 3 CN); 120.72 (*q*, $^1J = 287$, CF_3); 120.94 (*q*, $^1J = 277$, CF_3); 146.0 (*s*, C(3)); 159.8, 160.8 (2*s*, 2 C=O); 189.8 (*s*, C(2′)). ^{19}F-NMR (94.2 MHz): −57.88, −65.12 (2*q*, ^5J(F,F) = 7.7, 2 CF_3). MS (70°): 534 (3, M^+), 519 (1, $[M-Me]^+$), 515 (1, $[M-F]^+$), 502 (0.7, $[M-MeOH]^+$), 477 (41, $[M-C_4H_9]^+$), 452 (0.7), 419 (1.2, $[M-CO_2Me-C_4H_8]^+$), 392 (1), 292 (1), 69 (1, $[CF_3]^+$), 57 (100, $[C_4H_9]^+$), 56 (4, $[C_4H_8]^+$), 41 (17, [allyl]$^+$). Anal. calc. for $C_{13}H_{24}F_6N_4O_4$ (534.45): C 51.68, H 4.53, N 10.48; found: C 52.15, H 4.58, N 10.29.

4.4. *X-Ray Diffraction Analysis of* **12B** (*Fig. 3* and *Table*). The crystal was sealed in a glass capillary and mounted on the goniometer head of a *CAD4* diffractometer operating with MoK_α radiation

($\lambda = 0.71069$ Å) and graphite monochromator. Unit cell dimensions: $a = 29.438(6)$ Å, $b = 18.467(4)$ Å, $c = 9.205(2)$ Å, $\alpha = \beta = \gamma = 90°$; $V = 5004.5$ Å^3, $Z = 4$, $D_{calc.}$ 1.419 mg/mm^3, $F(000) = 2160$, $T = 293$ K, $\mu = 0.127$ mm^{-1}. The unit cell dimensions resulted from a least-squares fit of 25 centered reflections, $\omega - 2\theta$ scan; θ range 2.21–24.97° for all $\pm h$, $\pm k$, $\pm l$ reflections, 3581 reflections collected, 2706 with $I > 2\sigma(I)$. The structure was solved by the SHELXS-86 program and refined with SHELXL-93 [31] with goodness-of-fit = 1.060. Final $R_1 = 0.0320$ and $wR2 = 0.0985$ for reflections with $I > 2\sigma(I)$; $R_1 = 1.0597$ and $wR2 = 0.1047$ for all data. Maximum and minimum of the final difference *Fourier* synthesis were 0.197 and -0.137 eÅ^3. Non-H-atoms were refined anisotropically, H-atoms isotropically. The final difference map was featureless with 345 refined variables; ZORTEP plot was generated according to [32]. The deposition No. CCDC-297357 contains supplementary data which can be obtained from the *Cambridge Crystallographic Data Centre* (*CCDC*), 12 Union Road, Cambridge CB21EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

4.5. *Reaction of* **4** *with* (E)-**BTE** *and Dimethyl 2,3-Dicyanomaleate* (= *Dimethyl* (Z)*-2,3-Dicyanobut-2-enedioate*; **23**). The violet soln. of **4** (72 mg, 0.47 mmol) and (*E*)-**BTE** (92 mg, 0.43 mmol) in $CDCl_3$ (2 ml) was dropwise added to **23** (97 mg, 0.50 mmol) in CH_2Cl_2 (2 ml) at r.t.; the color disappeared, and N_2 evolved. With $PhCCl_2CF_3$ as weight standard, the ^{19}F-NMR analysis (94.2 MHz) indicated unchanged (*E*)-**BTE** (0.281 mmol, 65%), new products in diastereoisomers **D** and **E** (0.135 mmol, 31%; **D**/**E** 73:27), and **9** (0.006 mmol, 1.3%). Product **D**: δ(F) -57.80, -65.53 (2*q*, $^5J = 8.1$); product **E**: -57.48, -67.86 (2*q*, $^5J = 8.5$). The separation of **D** and **E** by PLC was not achieved.

5. *Reaction of* **4** *with Dimethyl 2,3-Dicyanofumarate* (**11**). 5.1. *Methyl 4-Cyano-5-methoxy-2-{[1-(1,1-dimethylethyl)-2,2-dimethylpropylidene]amino}furan-3-carboxylate* (**22**). When **4** (156 mg, 1.0 mmol) in CH_2Cl_2 (0.5 ml) was added to the magnetically stirred suspension of **11** (194 mg, 1.0 mmol) in CH_2Cl_2 (5 ml) at 0°, the deep-blue color of the CT complex was stable. The N_2 evolution started after removal of the cooling bath and was complete (25 ml) after 5 h at 20°. The solvent was distilled *i.v.*, and the brown residue was digested with little $CDCl_3$; the undissolved excess of **11** was filtered. Bulb-to-bulb distillation at 140°/0.1 Torr gave anal. pure **22** (127 mg, 40%). Viscous yellow oil. IR (film): 980*m*; 1087*s*, 1123*m*, 1226*s*, 1284*m*, 1338*s* (C–O of ester and ether); 1555*m* (C=N); 1624*s*, 1636*s*, 1685v*s* (arom. ring vibr.), 1718*s* (C=O); 2229*m* (C≡N). ^{1}H-NMR (400 MHz): 1.31 (*s*, 6 Me); 3.77 (*s*, MeO, ether); 4.15 (*s*, MeO, ester. ^{13}C-NMR (100.6 MHz, ^{1}H-decoupled): 30.1 (6 Me); 44.8 (2 Me_3C); 51.1, 59.7 (2 MeO); 70.8 (C(4)); 91.4 (C(3)); 113.0 (C≡N); 150.9 (C(2)); 160.4, 161.8 (C(5), C=O); 195.5 (C=N). MS: 320 (10, M^+), 305 (3, $[M - Me]^+$), 263 (22, $[M - C_4H_9]^+$; ^{13}C calc. 3.18, found 3.19), 249 (6), 207 (19, $[M - C_4H_9 - C_4H_8]^+$; ^{13}C 1.85/1.78), 111 (11), 69 (14), 57 (100, *t*-Bu^+), 41 (24, $[allyl]^+$). Anal. calc. for $C_{17}H_{24}N_2O_4$ (320.38): C 63.73, H 7.55, N 8.74; found: C 63.75, H 7.58, N 8.61.

5.2. *Competition with Olefin Formation.* The recovery of unconsumed **11** and the evolution of 100% N_2 suggest that a decomposition of **4**, catalyzed by **11**, competes with the formation of **22**, as described in *Sect. 3.5* for (*E*)-**BTE**. In an experiment with moist **4** [16], the ^{1}H-NMR analysis (*sym*-$C_2H_2Cl_4$ as standard) indicated 23% of **22** (2*s* at 3.77, 4.15) and 63% of **7** (2*s* at 4.65, 4.72). *Dimethyl 2,3-dicyanomaleate* (**23**) is easily soluble in CH_2Cl_2 and produced the blue CT color with **4** at $-45°$; soon the less soluble **11** precipitated. The reaction at 0–20° afforded **22** (17%) and alkene **7** (58%).

6. *Diazo Compound* **4** *and Fumaronitrile* (= (E)*-But-2-enedinitrile*; **24**). In the reaction of **4** (1.0 mmol) with **24** (2.0 mmol) in $CDCl_3$ (2 ml) at r.t., the red color of **4** disappeared within 1 h, and N_2 (4.0 ml, 16%) was liberated. The ^{1}H-NMR analysis disclosed *5,5-di*(tert*-butyl)-4,5-dihydro-1*H*-pyrazole-3,4-dicarbonitrile* (**25**; 83%) and alkene **7** (16%). PLC on silica gel with CH_2Cl_2 provided **25** (174 mg, 75%). Colorless prisms. M.p. 252–254° (dec.) after recrystallization from CH_2Cl_2/pentane. IR (KBr): 1179*s*, 1292*m*, 1376*s*, 1431*s*, 1475*s*; 1535*s* (C=N); 2210*s*, 2248*s* (C≡N), 3347v*s* (N–H). ^{1}H-NMR (400 MHz): 1.15 (sharp *s*, 3 Me); 1.28 (br. *s*, 3 Me); 4.37 (*s*, H–C(4)); 6.94 (br. *s*, NH; disappears on shaking with D_2O). ^{13}C-NMR (100.6 MHz, ^{1}H-coupled): 29.04 (br. *q*, ^1J(C,H) = 126.3, Me); 29.13 (*q*, $^1J = 126.4$, 3 Me); 29.20 (*q*, $^1J = 126.3$, 2 Me); 41.39 (*dd*, $^1J = 136.9$, $^4J = 4.6$ (possibly homoallyl coupling with NH), C(4)); 41.53, 42.37 (2*m*, $^2J \approx 4$, 2 Me*C*); 84.78 (*m*, *J* small, C(5)); 112.59 (*d*, $^2J = 12.2$, C(3) or *C*N–C(4)); 112.71 (*s*, *C*N–C(3)); 115.46 (*d*, $^2J = 12.6$, *C*N–C(4) or C(3)). Anal. calc. for $C_{13}H_{20}N_4$ (232.32): C 67.20, H 8.68, N 24.12; found: C 67.21, H 8.62, N 23.93.

7. *Diazoalkane* **4** *and Dimethyl Acetylenedicarboxylate* (DMAD). 7.1. *^{1}H-NMR Monitoring.* DMAD (70 µl, 80.9 mg, 0.57 mmol) was injected (*Hamilton* syringe) into the soln. of **4** (98.4 mg, 0.48 mmol) in

$CDCl_3$ (0.6 ml) at $-60°$. Signals: δ 1.19 (**4**); 1.17 (**26** or **28**); 1.28 (**29**); 1.69, 4.58 (isobutene); 0.86, 4.70 (**7**); due to overlap, the MeO region is not useful. After 30 min at $-20°$, **4** and the nearby *s* of **26** (or **28**) had equal heights, corresponding to 43% of the total integral for the sat. CH region; isobutene (22%) and **29** (20%) indicated the secondary products, and the *s* at 0.86 could belong to **7** (7%). After further 30 min at $-20°$, the *s* of **26** (or **28**) was only a shoulder of the *s* of **4** (15%). The signals of **4** and the intermediate disappeared after 1 h at 20°; **29** (58%) and isobutene (54%) showed the expected equivalence; the integral of the olefinic CH of isobutene was nearly a third of the Me_2 signal.

7.2. *Isolation of* **29**. The red soln. of **4** (2.7 mmol) and DMAD (2.0 mmol) in $CDCl_3$ (3 ml) slowly decolorized at $-20°$. Work-up of the light-yellow soln. afforded *dimethyl 5-(*tert*-butyl)pyrazole-3,4-dicarboxylate* (**29**). Colorless crystals. M.p. 146°. A sample prepared from 'diazoneopentane' and DMAD was identical in m.p. and spectra. IR (KBr): 1090*m*, 1165*m*, 1247*m* (br.), 1286*m* (C–O); 1472*m*, 1506*m*, 1653*w* (pyrazole vibr.), 1734v*s* (C=O); 3176*w* (br., N–H assoc.), 3422*m* (br., N–H free). ^{1}H-NMR (80 MHz): 1.26 (*s*, *t*-Bu); 3.77, 3.81 (2*s*, 2 MeO). ^{13}C-NMR (25.15 MHz, H-decoupled): 29.1 (*s*, 3 Me); 32.4 (*s*, Me_3C); 52.13, 52.40 (2*s*, 2 MeO); 112.8 (*s*, C(4)); 141.4, 153.3 (2*s*, C(3), C(5)); 161.9, 165.8 (2*s*, 2 C=O). MS (60°): 240 (20, M^+), 225 (18, $[M-Me]^+$), 209 (17, $[M-MeO]^+$), 193 (100), 57 (2, $[C_4H_9]^+$). Anal. calc. for $C_{11}H_{16}N_2O_4$ (240.25): C 54.99, H 6.71, N 11.66; found: C 55.28, H 6.73, N 11.36.

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