trans-1-(Dimethylamino)-1,3-butadiene – Concerted and Stepwise (4 + 2) Cycloadditions

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trans-1-(Dimethylamino)-1,3-butadiene is allowed to react with methyl acrylate, acrylonitrile, maleo- and fumaronitrile, dimethyl maleate and fumarate, as well as with dimethyl dicyanomaleate and dicyanofumarate. In all cases except the two last ones where only a single isomer is obtained mixtures (*endo*/*exo*) of cycloadducts are formed. Structures are determined by a combination of one- and two-dimensional NMR spectroscopy. The *E*/*Z* isomeric maleo- and fumaronitrile add stereospecifically to the diene. Cycloaddition of dimethyl maleate and fumarate leads to the same mixture of isomers in almost the same ratio. The reaction of dimethyl dicyanomaleate and dimethyl dicyanofumarate yields a cycloadduct which seems to be the thermodynamically most stable one. The results are interpreted in such a manner that a concerted cycloaddition takes place with maleo- and fumaronitrile, while stepwise reactions, presumably proceeding via zwitterions, are observed with dimethyl maleate, fumarate, the strongly electrophilic dimethyl dicyanomaleate and dicyanofumarate. With increasing capability of the dienophile to stabilize a negative charge the mechanism changes from a concerted to a stepwise reaction.

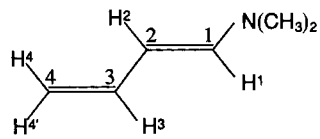
(4 + 2) Cycloadditions of *trans*-1-(dimethylamino)-1,3-butadiene are, at a first glance, not expected to show special features. As a donor-substituted diene it should display enhanced reactivity towards electron-accepting olefins. A few cycloadditions of 1-(dialkylamino)-1,3-butadienes have been reported. Langenbeck et al.[1,2] described reactions with acrolein and crotonaldehyde and derived the cyclic structure from the compounds which were formed after elimination of dimethylamine. Hünig and Kahanek[3] carried out a careful study on cycloadditions of *trans*-1-(dimethylamino)-1,3-butadiene to methyl acrylate, methyl vinyl ketone, acrolein, and acrylonitrile. Both investigations concluded that "*ortho*"-substituted cyclohexenes are produced. A thorough analysis of the configuration of the adducts was not possible at the time due to the lack of modern spectroscopic techniques. Thus, the question whether *endo* or *exo* addition occurs, or whether a mixture of both isomers is encountered could not be answered. Some time after this early work a few more cycloadditions of 1-(dialkylamino)-1,3-butadienes were described by Satzinger[4].

It may be asked what kind of new information one may obtain from further studies on this diene system. Presently, we investigate the influence of one and several dialkylamino substituents in different positions of a diene on the reactivity, the regioselectivity, the stereochemistry, and the mechanism of cycloaddition. Preliminary results on reactions of *cis,trans*- and *trans,trans*-1,4-bis(dimethylamino)-1,3-butadiene have already been reported[5]. A full account on the behavior of 1,1-bis(dimethylamino)-1,3-butadiene of which a part has been described earlier[6] is given in an accompanying publication[7]. The aspects being studied in this work are whether a common mechanism is followed in all cases and whether a polar reaction path can be induced by suitable substitution.

Preparation and properties of trans-(1-dimethylamino)-1,3-butadiene (1)

Dieneamine **1** can be easily prepared by condensation of crotonaldehyde with dimethylamine. The NMR spectral data, the photoelectron (PE) spectrum, and electrochemical measurements support the nucleophilic character of the π-system.

The 200-MHz ^{1}H-NMR spectrum in trichlorodeuteriomethane displays five chemically non-equivalent olefinic protons. An analysis reveals that the proton-proton coupling constants (see Experimental) are very similar to those of 1,3-butadiene[8], thus showing that **1** exists, as expected, in a preferred antiperiplanar conformation. Similar chemical shifts are reported for *trans*-1-(dimethylamino)-2-methyl-1,3-butadiene[9]. The ^{13}C-NMR chemical shifts can be assigned unambiguously on the basis of calculated values[10] and the multiplicity of the signals.



1

The He(I) photoelectron spectrum of **1** is shown in Figure 1. Three distinct bands are recognized in the region from 7–11 eV. They describe ionizations from the three π-MOs of the 6π-electron 5-atom skeleton. A pentadienyl structure of the HOMO is clearly indicated by MNDO and AM1 calculations (reported in Table 1) in which the geometries were optimized with respect to an antiperiplanar conformation of the diene. The MOs π_2 and π_3 are bonding and antibonding combinations of the lowest π-MO of butadiene

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with a nitrogen lone pair. A first vertical ionization potential of 7.24 eV classifies **1** as an electron-rich diene. Compared to butadiene itself (1st IP = 9.03 eV[11]) the HOMO has been raised by 1.7 eV. A half-wave oxidation potential of 0.23 V vs. SCE demonstrates the easy removal of an electron from a π-molecular orbital.

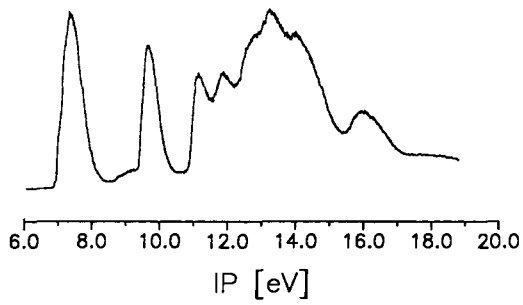
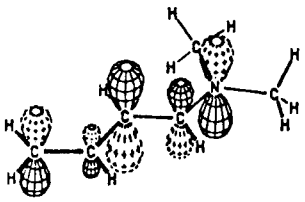
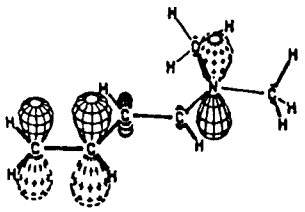
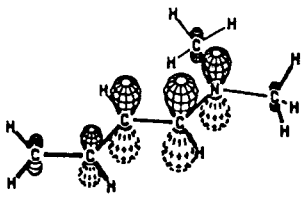


Figure 1. He(I) photoelectron spectrum of *trans*-1-(dimethylamino)-1,3-butadiene

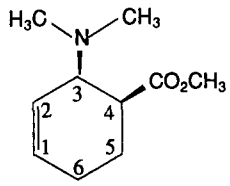
Table 1. Comparison of calculated (MNDO and AM1) orbital energies with IP_v from PE spectra

Molecular orbital of **1**	Orbital energy [eV] MNDO	AM1	Vertical IP [eV]
	-8.08	-7.76	7.24
	-10.28	-10.29	9.52
	-11.74	-11.35	11.00

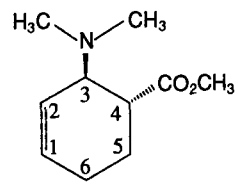
Cycloadditions

Methyl acrylate: The reaction of *trans*-1-(diethylamino)-1,3-butadiene with methyl acrylate was reported by Hünig and Kahanek[3]. It was established that an "*ortho*"-substituted cyclohexene had been formed, an analysis regarding possible *endo/exo* isomerism could not be carried out conclusively.

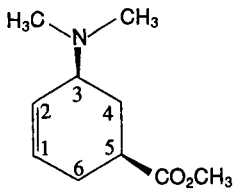
Methyl acrylate and **1** reacted to give a mixture of stereoisomers in a ratio of 61:39 (GC). Their separation turned out to be impossible. Identification of the compounds was performed by spectroscopic studies on the mixture. Four isomeric cycloadducts have to be considered because both the "*ortho*" (**2a** and **2b**) and the "*meta*" (**3a** and **3b**) adducts might have been produced in an *endo* or *exo* fashion.



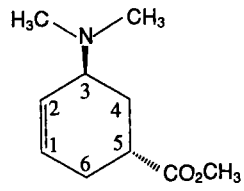
2a



2b



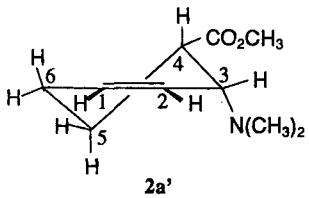
3a



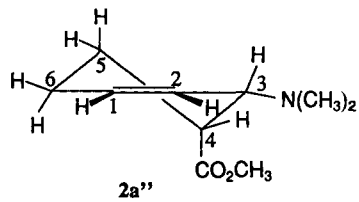
3b

A discrimination between **2** and **3** should be possible by ^{1}H-NMR spectroscopy if the signals of the methine protons at C-3 and C-4 or at C-3 and C-5 can be identified in the ^{1}H-NMR spectrum and if their coupling pattern can be established. The analysis is complicated by the fact that the signals of the two isomers overlap considerably. By a combination of a broad-band decoupled ^{13}C-NMR, a DEPT-90 (shows methine carbon signals), and a DEPT-135 spectrum (allows a differentiation of quaternary and secondary from primary carbon atoms) the number of hydrogen atoms directly attached to individual carbon atoms was ascertained. Thus, the aliphatic methine carbon atoms could be identified. A (^{1}H,^{13}C)-COSY spectrum gave the exact location of the methine protons in the ^{1}H-NMR spectrum for both isomers. Their chemical shift difference in deuterioacetone is sufficient for individual identification.

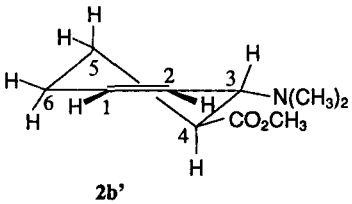
The regiochemistry of the cycloaddition can be derived immediately from the coupling pattern of the methine proton signal of the methoxycarbonyl-substituted carbon atom and from cross peaks in the (^{1}H,^{1}H)-COSY spectrum. Both isomers show a ddd pattern for this proton which is only compatible with "*ortho*" substitution. The presence of a cross peak in the (^{1}H,^{1}H)-COSY spectrum for the two methine protons in each isomer is an additional hint to their direct neighborhood. Thus, the product mixture consists of **2a** and **2b**.



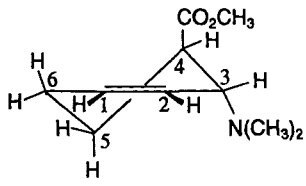
2a'



2a''



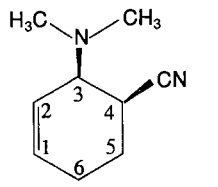
2b'



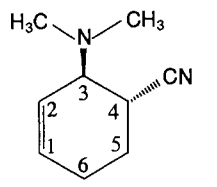
2b''

In a next step it was investigated whether the slight selectivity (61:39) is in favor of *endo* or *exo* addition. The magnitude of the $^1H,^1H$-coupling constants $J_{3\text{-}H,4\text{-}H}$ and $J_{4\text{-}H,5\text{-}H}$ (*cis* and *trans*) is the basis for this distinction. **2a** and **2b** will assume half-chair conformations, each compound can be envisaged to exist in two such conformations, **2a′** and **2a″**, and **2b′** and **2b″**, respectively. Experimentally, an averaged coupling constant will be seen because rapid interconversion of the conformations has to be assumed. The magnitude of the coupling constants will depend on the ratio of the conformers.

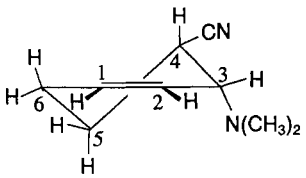
In **2a′** and **2a″** the protons at C-3 and C-4 are in an e′,a- and an a′,e-relationship, in **2b′** and **2b″** it is a′,a and e′,e. Model studies on *trans*-3,4-disubstituted cyclohexenes have been interpreted in terms of a strong preference for an e′,e-position of the substituents[12,13]. The equilibrium in **2b** should, therefore, be on the side of **2b′**, displaying an a′,a-arrangement of 3-H and 4-H. For one isomer this coupling constant is 9.5 Hz. It indicates the a′,a-arrangement of 3-H and 4-H. The coupling constants of 12.0 Hz and 2.0 Hz between 4-H and the two hydrogen atoms at C-5 in the same isomer are derived from axial-axial and axial-equatorial positions. This means that 4-H assumes in this isomer an axial position. We assign this coupling pattern to isomer **2b** in conformation **2b′**. This is in line with the above-mentioned results on *trans*-3,4-disubstituted cyclohexenes. As a consequence of this interpretation we expect a smaller coupling constant $J_{3\text{-}H,4\text{-}H}$ for the other isomer. Values of 6.5 Hz or 4.0 Hz have to be considered. Due to the unresolvable multiplet structure of 3-H and 5-H, in contrast to the multiplet structure of 4-H, it cannot be decided which of the two coupling constants (6.5 Hz or 4.0 Hz) is due to interaction of 4-H with 3-H or 5-H. One coupling constant of 12.0 Hz of 4-H with a hydrogen at C-5 is assigned to an axial-axial coupling. 4-H must therefore be in an axial position. Tentatively we attribute the smaller value (4.0 Hz) to the 4-H,5-H axial-equatorial interaction. The other coupling constant (6.5 Hz) then corresponds to $J_{3\text{-}H,4\text{-}H}$. The magnitude is in agreement with other (3-H_e, 4-H_a) coupling constants which can be determined unambiguously in some of the other examples. This assignment, however, does not influence the conclusion regarding the stereochemistry of the adduct.



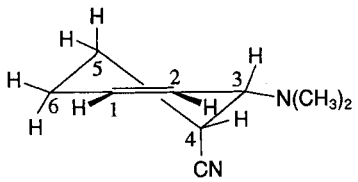
4a



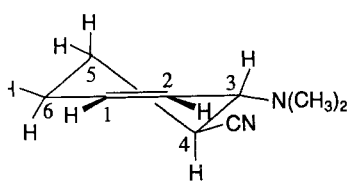
4b



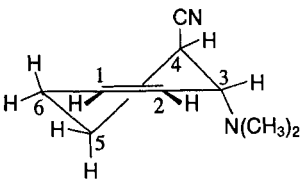
4a′



4a″



4b′



4b″

The isomer with the coupling constant $J_{3\text{-}H,4\text{-}H}$ of 6.5 Hz is assigned structure **2a′** which is the product of *endo* addition and the main component (61%). Thus, a slight preference for the *endo* addition is observed in this cycloaddition.

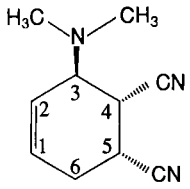
Acrylonitrile: The dienophile and **1** reacted to give 81% of a 63:37 mixture of cycloadducts **4a** and **4b**. A reaction time of six days at room temperature is comparable to that for methyl acrylate under the same conditions. By analogy with the results for methyl acrylate it was assumed that an "*ortho*"-substituted cyclohexene derivative had been formed as a mixture of *endo* and *exo* isomers which could, also in this case, not be separated. This interpretation is confirmed by the NMR spectroscopic results.

The structure determination followed the same line of arguments as in the case of methylacrylate. ^{13}C-NMR measurements (broadband decoupled, DEPT-90, Dept-135) led to the identification of the signals for the methine C-atoms. Correlation peaks in the ($^1H,^{13}C$)-COSY spectrum gave the position of the signals of the corresponding protons. These protons have a cross peak in the ($^1H,^1H$)-COSY spectrum. The multiplicity of the signal for the hydrogen atom at C-4 (ddd for both isomers) and the magnitude of the $^1H,^1H$ coupling constants $J_{3\text{-}H,4\text{-}H}$ (8.5 and 6.0 Hz) demonstrate that dimethylamino group and cyano group are attached to neighboring carbon atoms, thus supporting the above assumption that the product is a mixture of **4a** and **4b**.

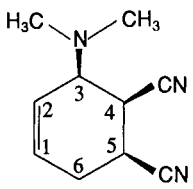
Both **4a** and **4b** may exist in two conformations each (**4a′**, **4a″** and **4b′**, **4b″**). As in the case of the corresponding methoxycarbonyl-substituted cyclohexenes **2a** and **2b** a preference for **4a′** and **4b′** might be anticipated. The values of the ^3J coupling constants between the hydrogen atoms at C-3 and C-4 in **4a** and **4b** can be determined although the corresponding protons show a complicated splitting pattern due to several long-range couplings. The coupling constant is 8.5 Hz for one isomer and 6.0 Hz for the other. The value of 8.5 Hz is attributed to **4b′** (axial-pseudoaxial relationship of the protons). The axial position of 4-H in this isomer follows also from the coupling constants of 12.0 and 2.8 Hz with the hydrogen atoms at C-5. The main conformation of the other isomer seems to be **4a″**. Although both conformations (**4a′** and **4a″**) have an e,a-relationship of the protons at C-3 and C-4, a distinction should be possible on the basis of the proton coupling constants between the hydrogen atoms at C-4 and C-5. Values of 3.5 and 6.0 Hz are more in line with an e,e- and e,a-relationship of the hydrogen atoms than with an a,a- and e,a-arrangement. This, however, suggests that conformation **4a″** is more populated than **4a′**, in contrast to the corresponding methyl acrylate cycloadduct. The major isomer **4b** derives from *exo* addition.

Maleo- and fumaronitrile: The reactions of the two dienophiles with **1** provided each mixtures of two isomers. The isomeric product pairs are not identical, as can be shown by recording NMR spectra of artifical mixtures of the products. Within the limit of detection by ^1H-NMR spectroscopy (ca. 1%) the cycloadditions take place stereospecifically.

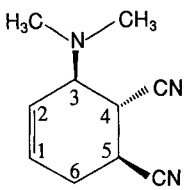
For the maleonitrile adducts where a ratio of 63:37 of the isomers had been obtained in the raw product (yield 98%) a separation of the mixture was impossible. In the case of fumaronitrile, extraction of the mixture (99% yield) with diethyl ether gave the main isomer in pure form. The isomer ratio is temperature-dependent being 76:24 at room temperature and 85:15 at −20°C. On the basis that the reaction occurs with retention of stereochemistry of the dienophiles and that endo/exo isomerism is the cause for the formation of mixtures the products should have structures **5a**/**5b** and **6a**/**6b**. Each of these molecules can exist in two different half-chair conformations which are shown in formulas **5a′**/**5a″**, **5b′**/**5b″**, **6a′**/**6a″**, and **6b′**/**6b″**.



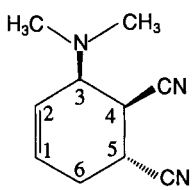
5a



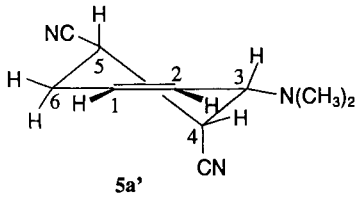
5b



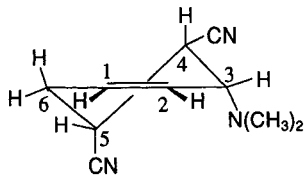
6a



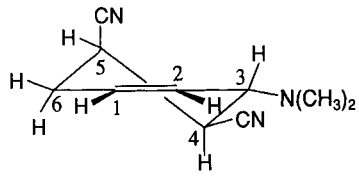
6b



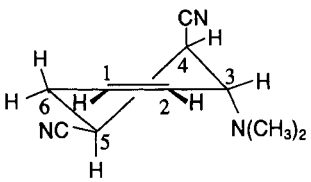
5a′



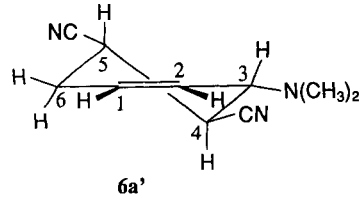
5a″



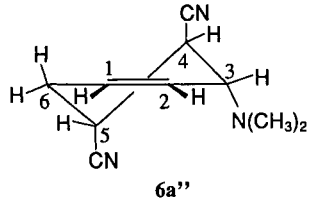
5b′



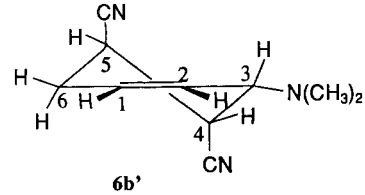
5b″



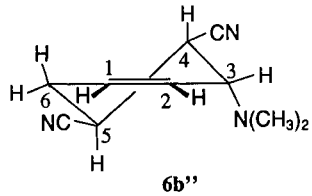
6a′



6a″



6b′



6b″

Structures were determined by a combination of 1D- and 2D-NMR spectra [(^{1}H,^{1}H)-COSY and (^{1}H,^{13}C)-COSY]. This leads to the assignment of chemical shifts and coupling constants and supports the assumption of concerted cycloadditions. The main product of the Diels-Alder reaction of maleonitrile with *trans*-1-(dimethylamino)-1,3-butadiene has structure **5a**. It follows from an "*ortho*" *endo* addition of the dienophile. The minor component has structure **5b**.

Although not all coupling constants in the ^{1}H-NMR spectrum of **5a** could be determined some values which are important for the structural and conformational analysis are known. These coupling constants are $J_{4\text{-H},5\text{-H}}$ = 2.8 Hz, $J_{5\text{-H},6\text{-H}}$ = 11.2 Hz, and $J_{5\text{-H},6\text{-H}'}$ = 5.7 Hz. The small value for $J_{4\text{-H},5\text{-H}}$ shows the e,a relationship of these protons. The magnitude of the coupling constants between 5-H and 6-H supports conformation 5a′ where one a,a′- and one a,e′-relationship exists. In **5a″** this would be e,a′ and e,e′ where both coupling constants should be significantly smaller than 10 Hz.

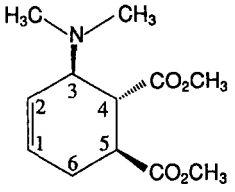
The following coupling constants could be obtained for the minor isomer **5b**: $J_{3\text{-H},4\text{-H}}$ = 8.0 Hz, $J_{4\text{-H},5\text{-H}}$ = 3.5 Hz, $J_{5\text{-H},6\text{-H}}$ = $J_{5\text{-H},6\text{-H}'}$ = 5.3 Hz. A value of 8.0 Hz for $J_{3\text{-H},4\text{-H}}$ shows an a′,a(**5b′**) rather than the e′,e(**5b″**)-relationship. The 5-H,6-H coupling constants are also in accord with **5b′**.

The main isomer of the cycloaddition reaction of fumaronitrile with **1** was obtained in pure form. It is assigned structure **6a**, mainly in conformation **6a′**. This follows from $J_{3\text{-H},4\text{-H}}$ = 10.1 Hz (a′,a-arrangement) and $J_{4\text{-H},5\text{-H}}$ = 11.7 Hz (a,a-arrangement). These values would neither be in agreement with **6a″** nor with **6b′** and **6b″**. In the latter case a smaller $J_{3\text{-H},4\text{-H}}$ would be expected. The ^{1}H-NMR spectrum of **6b** is so complicated that exact coupling constants cannot be given. Fortunately, however, its structure automatically follows by exclusion. The cycloadduct is not identical with **5a**, **5b**, or **6a**. This leads to **6b** as the only possible structure, the preferred conformation (**6b′** or **6b″**) of which cannot be deduced.

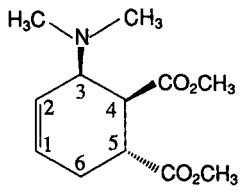
Dimethyl maleate and dimethyl fumarate: The same product mixture was obtained in high yield after one day when equimolar amounts of dimethyl maleate and dimethyl fumarate reacted with *trans*-1-(dimethylamino)-1,3-butadiene (**1**). The ratio of isomers was 61:39 and 66:34, respectively. In the reaction with dimethyl maleate the yield was 83%. Remaining dimethyl maleate had completely isomerized to dimethyl fumarate as was shown by GC. Unreacted **1** was no longer present in the solution, presumably, it had polymerized. The reaction of dimethyl fumarate led to 99% of the identical product mixture. The main component could be obtained in pure form by crystallization.

The interpretation of the results for the cycloaddition of dimethyl maleate and fumarate is not straightforward. If the reactions had taken place by a concerted pathway different adducts would have been expected for the isomeric olefins as in the case of maleo- and fumaronitrile. Up to four distinguishible compounds might have been formed. The higher

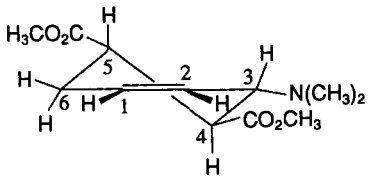
order character of the 300-MHz ^{1}H-NMR spectra do not allow an unambiguous identification of the relative configurations of the substituents in both cases. The agreement of the ^{1}H chemical shifts and the olefinic coupling constants of 10.1 and 10.0 Hz with those of the other cycloadducts leaves no doubt as to the cyclohexene structure. The relative configuration of the substituents in the minor component could be established. The hydrogen atom at C-4 shows two coupling constants: J = 10.2 Hz and J = 11.5 Hz. The value of 10.2 Hz corresponds to the 3-H,4-H coupling. As both are greater than 10 Hz (3-H, 4-H) and (4-H, 5-H) must exhibit a,a-arrangements. This is further substantiated by the coupling constants of 5-H: J = 11.5 Hz (2H) and J = 5.5 Hz (1H). The couplings of 11.5 Hz and 5.5 Hz are derived from the interaction with the hydrogen atoms at C-6, showing one a,a- and one a,e-arrangement. From this analysis it follows that this compound exists in the conformation **7a'** which is the product of *exo* addition of dimethyl fumarate.



7a



7b



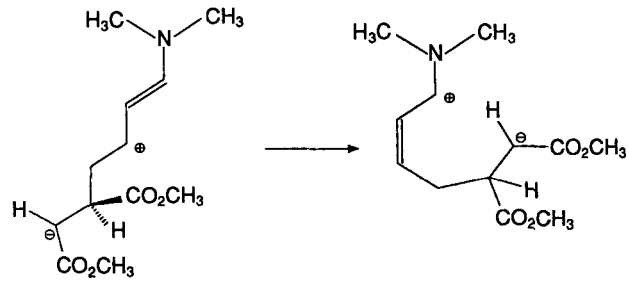
7a'

In the second isomer, the signals of 4-H and 5-H have almost identical chemical shifts leading to a complex signal pattern from which no coupling constants can be deduced directly. Thus, it is not possible to decide what the relative configuration of the two methoxycarbonyl groups is. The second isomer might have a *trans* arrangement of the substituents, corresponding to the product of *endo* addition of dimethyl fumarate, or a *cis* arrangement, corresponding to one of the possible products of concerted cycloaddition of dimethyl maleate.

The situation is further complicated by the fact that the remaining dimethyl maleate had isomerized completely to dimethyl fumarate. The configurational stability of dimethyl maleate under the reaction conditions was investigated in order to check its isomerization. A thermal isomerization at 35°C in solution needs three months to be complete. As the cycloaddition is much faster, this possibility can be excluded as being responsible for the observed results. It has, however, been known for some time that the olefin isomerizes to dimethyl fumarate under the influence of ammonia, primary and secondary amines[14]. Tertiary amines like triethylamine or diethylaniline are not capable of effecting the isomerization.

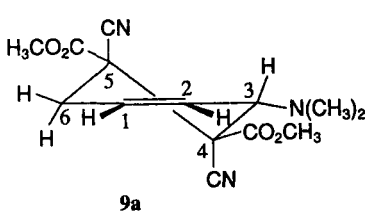
Does dimethyl maleate isomerize in the presence of **1**? As a tertiary amine it should not be capable of isomerizing the dienophile, as a tertiary dieneamine the situation might, however, be different. Dimethyl maleate and **1** were mixed in THF in a ratio of 10:1. Within one day at room temperature, 63% of the olefin had isomerized. After four days the diene had reacted quantitatively to the cycloadduct and could no longer be detected. The concentration ratio of 80:20 of the excess dienophile in favor of dimethyl fumarate now remained unchanged. This observation means that isomerization occurs as long as free **1** is still present. The product being a tertiary amine should not isomerize dimethyl maleate. A cross check, addition of isolated product to a solution of the olefin, confirmed the presumption.

If tertiary amines do not isomerize dimethyl maleate, the most plausible explanation of the observations is a reversible formation of zwitterions **8a** and **8b**. This would also explain why unreacted olefin had isomerized to dimethyl fumarate in the cycloaddition of dimethyl maleate. The complete isomerization in the preparative experiment as compared to the experiment where excess dienophile was used results from the higher concentration of the reactants.

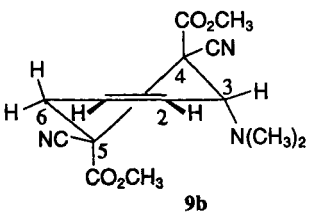


8a **8b**

Dimethyl dicyanofumarate and dimethyl dicyanomaleate: The reaction of both dienophiles with **1** resulted in one and the same cycloadduct. Solutions of the reagents were mixed at −60°C and allowed to warm to room temperature. Immediately after mixing a yellow color appeared which faded away during the reaction. The products were isolated in 86% and 91% for dimethyl dicyanomaleate and dimethyl dicyanofumarate, respectively.



9a



9b

The combination of different NMR spectroscopic techniques leads to **9** as the structure of the cycloadduct. The magnitude of the ^{1}H,^{1}H- and ^{13}C,^{1}H-coupling constants suggests that **9a** dominates in the conformational equilibrium of **9a** and **9b**.

^{1}H-NMR spectra were first recorded in dichloromethane and trichloromethane. The analysis of the 300- as well as the 400-MHz

proton NMR spectra in these solvents proved to be impossible due to the almost identical chemical shift of the protons at the CC double bond. It did not permit the determination of coupling constants which is necessary for an unequivocal structural assignment. In [D_6]benzene as solvent the olefinic protons showed a sufficient chemical shift difference to carry out an analysis of the 300-MHz proton NMR spectrum. The chemical shift data and the $^1H,^1H$-coupling constants are collected in Table 2. Besides a one-dimensional ^1H-NMR spectrum we recorded a double-quantum filtered (DQF) phase-sensitive ($^1H,^1H$)-COSY spectrum[15]. While the one-dimensional spectrum provided the multiplicity of the individual signals and the coupling constants we were able to assign exactly the active coupling constant between two hydrogen atoms from the two-dimensional spectrum. If the magnitude of the coupling constants of the two olefinic hydrogen atoms with the methylene hydrogens is taken as a criterion for their assignment then it is suggested that the hydrogen atom with $\delta = 5.25$ is 1-H (as given in Table 2). This is confirmed by a NOE difference spectrum where irradiation on 3-H led to an enhancement of the signal at $\delta = 5.48$ and to no effect on the signal at $\delta = 5.25$. The decision for the axial or equatorial hydrogen atom at C-6 is based on the magnitude of the pair of coupling constants with one of the olefinic protons. It is assumed that the proton having a coupling constant of 5.2 Hz is in the equatorial position. A further argument in this direction can be derived from the homoallylic coupling constants of 3-H with 6-H and 6-H′.

Table 2. ^1H-NMR data for **9** for 300-MHz spectra in [D_6]benzene at room temperature

Hydrogen atom	δ	Multiplicity	J [Hz]
1-H	5.25	dddd	$J_{1\text{-H,2-H}} = 10.4$
2-H	5.48	dddd	$J_{1\text{-H,3-H}} = 2.7$
3-H	4.38	dddd	$J_{1\text{-H,6-Ha}} = 2.1$
6-H_e	2.80	dddd	$J_{1\text{-H,6-He}} = 5.2$
6-H_a	2.37	dddd	$J_{2\text{-H,3-H}} = 1.9$
$N(CH_3)_2$	2.21	s (6H)	$J_{2\text{-H,6-Ha}} = 2.8$
CO_2CH_3	3.01	s (3H)	$J_{2\text{-H,6-He}} = 1.5$
CO_2CH_3	3.37	s (3H)	$J_{3\text{-H,6-Ha}} = 4.0$
			$J_{3\text{-H,6-He}} = 2.0$
			$J_{6\text{-Ha,6-He}} = 18.4$

The ($^1H,^{13}C$)-COSY spectrum shows which carbon atom is bound to the individual protons by using the ^1H-chemical shifts as reference. These data are displayed in Table 3 together with $^{13}C,^1H$-coupling constants which were obtained from a carbon hydrogen heteronuclear multiple-quantum coherence (HMQC) experiment with decoupling of ^{13}C during acquisition[16]. Important information concerning the configurations at C-3 to C-5 can be obtained from the $^{13}C,^1H$-coupling constants of the nitrile carbon atoms. One displays a doublet splitting, the other signal is a doublet of a doublet. Thus, it is possible to assign the signal at $\delta = 115.39$ to the cyano group at C-4 and that at $\delta = 115.70$ to the cyano group at C-5. Moreover, the magnitude of the coupling constants permits the determination of the relative configuration at C-3 to C-5.

It is assumed that the dimethylamino group prefers a pseudoequatorial position and, therefore, the proton at C-3 is pseudoaxial. This preference for the equatorial arrangement of a substituent at C-3 in cyclohexene derivatives is well documented[13]. The $^{13}C,^1H$-coupling constant of 3-H with the carbon atom of the cyano group is 8.8 Hz. The $^{13}C,^1H$-coupling constants of the methylene protons at C-6 with the other cyano carbon atom are 9.8 and 4.0 Hz. The magnitude of the latter values indicates that one coupling constant describes an a′,a- and the other an e′,a-relationship. This means that the cyano group at C-5 assumes an axial position. If it were in an equatorial arrangement we would expect comparable coupling constants with both protons. Correspondingly, the value of 8.8 Hz for the coupling constant of the proton at C-3 with the cyano group at C-4 is interpreted as an axial-pseudoaxial coupling constant. This places the cyano groups in **9** in a *trans* arrangement in axial positions.

In conclusion, it can be stated that the $^1H,^1H$- and $^{13}C,^1H$-coupling patterns confirm the cyclohexene structure of the adduct and furthermore support the relative arrangement of substituents and conformation **9**.

Table 3. ^{13}C-NMR chemical shifts and $^{13}C,^1H$ coupling constants for **9** in [D_6]benzene

Carbon atom	δ	Multiplicity	$^1J_{CH}$ [Hz]
C-1	124.59	"dq"	164.2
C-2	125.70	"dq"	165.8
C-3	66.83	d	139.7
C-4	49.18, 52.38		
C-5			
C-6	33.45	t	135.9
$N(CH_3)_2$	42.52	"qquint"	134.1
OCH_3	53.62, 53.83	q	148.6, 149.3
OCH_3			
COOR	167.18, 165.12		
COOR			
CN (C-4)	115.39	d	8.8 ($^3J_{CH}$)
CN (C-5)	115.70	dd	9.8, 4.0 ($^3J_{CH}$)

Discussion

trans-1-(Dimethylamino)-1,3-butadiene undergoes cycloadditions with electron-deficient olefins in high yield. With methyl acrylate, acrylonitrile, and the isomeric fumaro- and maleonitrile mixtures of *endo* and *exo* isomers are formed with low selectivity. Methyl acrylate shows a low *endo* preference, acrylonitrile in contrast a low *exo* selectivity. The *E*/*Z* isomeric dicyanoethylenes add stereospecifically to **1**. In each case two diastereomers are formed. The reaction of dimethyl maleate and dimethyl fumarate leads for both dienophiles to the same mixture of two isomers. One of the isomers can be identified unequivocally by NMR spectroscopy as the product of exo addition of dimethyl fumarate, the relative configuration of the substituents in the other compound is presumably that which results from formal *endo* addition of dimethyl fumarate. The assignment seems to be well supported by the comparison with the other examples.

The formation of the same products from dimethyl maleate and dimethyl fumarate can be interpreted in two ways:

A) The non-stereospecific cycloaddition is due to a two-step process with a zwitterion as an intermediate and two isomers out of the four possible ones are formed.

B) *trans*-1-(Dimethylamino)-1,3-butadiene isomerizes dimethyl maleate to dimethyl fumarate and the latter olefin

adds stereospecifically to **1**. This requires that the major isomer the stereochemistry of which could not be clarified because of the complex ^{1}H-NMR spectrum would be the *endo* cycloadduct of dimethyl fumarate. The stereochemical lability of dimethyl maleate is known. In the presence of primary and secondary amines rapid isomerization takes place, while tertiary amines do not act in this respect (see above). *trans*-1-(Dimethylamino)-1,3-butadiene constitutes a tertiary amine besides being a diene. As such it should not isomerize the dienophile. A possible isomerization pathway would be reversible zwitterion formation (**8a**) by reaction of C-4 of the diene. The isomerization of dimethyl maleate in the presence of **1** is observed experimentally (see above). It is, however, also found that the isomerization stops as soon as all of the diene has formed the cycloadduct and that the isolated cycloadduct does not isomerize dimethyl maleate. This supports the result that simple tertiary amines do not isomerize the olefin.

The hypothesis that concerted cycloaddition of dimethyl fumarate after isomerization of dimethyl maleate takes place requires reversible zwitterion formation (**8a**). There is, however, no reason that such a zwitterion should not undergo ring closure to the cycloadduct instead of only isomerizing the olefin. If further a zwitterion is formed from dimethyl maleate there is no reason to assume that it should not be formed also from dimethyl fumarate. The discussion, thus, leads to the conclusion that the zwitterionic pathway for cycloadduct formation should be followed instead of a concerted cycloaddition of dimethyl fumarate.

The reaction of dimethyl dicyanofumarate and dimethyl dicyanomaleate leads to only one cycloadduct out of the four possibilities which could result from stereospecific and simultaneous exo/endo addition. The structure of the adduct **9a** which has been established by a thorough NMR analysis can be interpreted as the thermodynamically most stable arrangement of the substituents in the cyclohexene ring. The behavior of dimethyl dicyanomaleate is similar to that of dimethyl maleate. Besides cycloaddition an isomerization is observed. In this case a two-step cycloaddition via a zwitterionic intermediate is strongly supported by kinetic studies[17].

In conclusion, it can be said that the mechanism of normal Diels-Alder cycloadditions is a function of substituents in diene and dienophile. In terms of the frontier-molecular orbital (FMO) description of the reaction it follows that dienes and dienophiles which have strongly opposite electronic character, i.e. where one is a strong donor and the other a potent acceptor, will prefer to undergo a two-step cycloaddition via zwitterions. In the case of a reduced acceptor character of the dienophile (maleo- and fumaronitrile) the concerted pathway seems to be energetically more favorable.

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Experimental

^{1}H and ^{13}C NMR: Varian XL 200 and Bruker AMX 300. The often complex splitting patterns in the ^{1}H-NMR spectra were analyzed as far as possible. Generally, not all coupling parameters of the spin systems could be obtained. The chemical shifts are referenced to the signal of the undeuterated solvent and given relative to TMS, if not otherwise stated. – MS: Finnigan MAT 312/188. – IR: Pye Unicam SP3-100 and Perkin-Elmer 1600 FT-IR. – PE: Leybold-Heraeus UPG 200. – Polarography: Bruker E 310, with Metrom-modified equipment. – GLC: Varian 3700 with columns A) 1.9-m glas column, inner diameter 2 mm, filled with chromosorb WHP, impregnated with 10% SE 30; B) 35-m glas capillary column SE 30; C) 50-m glas capillary column OV 101. – Solvents: All solvents were dried and distilled according to the literature.

trans-1-(Dimethylamino)-1,3-butadiene (**1**): The compound was synthesized in 46% yield according to a procedure used in the reaction of the diethylamino compound[18], b.p. 26°C (1 kPa). – ^{1}H NMR ($CDCl_3$): δ = 6.27 ("dt", 3-H, $^3J_{2,3}$ = $^3J_{3,4cis}$ = 10.4 Hz, $^3J_{3,4trans}$ = 17.0 Hz), 6.23 (d, 1-H, $^3J_{1,2}$ = 13.6 Hz), 5.02 (dd, 2-H, $^3J_{2,1}$ = 13.6 Hz, $^3J_{2,3}$ = 10.4 Hz), 4.77 (dd, 4-H, $^2J_{4,4'}$ = 2.1 Hz, $^3J_{4trans,3}$ = 17.0 Hz), 4.51 (dd, 4-H', $^2J_{4,4'}$ = 2.1 Hz, $^3J_{4cis,3}$ = 10.6 Hz), 2.68 [s, 6H, $N(CH_3)_2$]. Similar chemical shifts are reported for *trans*-1-(dimethylamino)-2-methyl-1,3-butadiene[9]. – ^{13}C NMR ($CDCl_3$): δ = 143.4 (d), 136.6 (d), 104.7 (t), 99.9 (d), 40.0 (q).

Methyl acrylate and acrylonitrile were dried over calcium hydride stabilized with hydroquinone monomethyl ether and freshly distilled under argon prior to use. Commerical *dimethyl maleate* was distilled and kept under argon at −20°C in the dark. – *Dimethyl fumarate* was sublimed twice and kept under argon. – *Maleonitrile* was prepared from commercial fumaronitrile by a literature procedure[19]. – *Fumaronitrile* was recrystallized from diethyl ether and further purified by sublimation. – *Dimethyl dicyanofumarate* was prepared by oxidative dimerization of methyl cyanoacetate[20]. – *Dimethyl dicyanomaleate* was generated by photochemical isomerization of dimethyl dicyanofumarate[21] and directly used after purification. The experiments were carried out in the dark.

Cycloadditions of 1

With Methyl Acrylate: Separately prepared solutions of **1** (0.486 g, 5.0 mmol) in benzene (5.0 ml each) were combined at room temperature and the reaction was monitored by GLC (column B). After completion of the reaction (8 d) the solvent was removed in vacuo (100 Pa). The crude reaction product (0.83 g, 91%) consisted of two compounds in a ratio of 61:39 (GC). The viscous oily product mixture was purified by condensation at 35°C in vacuo (100 Pa) without affecting the isomer ratio. Separation of the products on a preparative scale by GLC or LC on silica could not be achieved. Reactions in THF or methyl acrylate as solvent gave identical results.

Isomer **2a** (major component): ^{1}H NMR ([D$_6$]acetone): δ = 5.98 (m, 1-H), 5.78 (dddd, 2-H, $^3J_{1,2}$ = 10.0 Hz, J = 4.6, 2.5, and 1.75 Hz), 3.63 (s, 3H, CO_2CH_3), 3.42 (m, 3-H), 2.67 (ddd, 4-H, $^3J_{4,5}$ = 12.5 Hz, $^3J_{4,3}$ = 6.5 Hz, $^3J_{4,5e}$ = 4.0 Hz), 2.26 [s, 6H, $N(CH_3)_2$], 1.6–2.5 (m, 4H, 5-H and 6-H). – (^{1}H,^{1}H)-COSY: cross peaks for (3-H,4-H), (3-H,2-H), and (1-H,6-H). Complex overlap of signals of the two isomers in the region from δ = 1.6–2.5 prohibited a detailed analysis of the signals of 5-H and 6-H. – ^{13}C NMR ([D$_6$]acetone, DEPT-90, DEPT-135): δ = 174.56 (C=O), 131.50 (CH, C-1), 124.21 (CH, C-2), 58.98 (CH, C-3), 51.14 (CH_3, OCH_3), 45.95 (CH, C-4), 43.82 [CH_3, $N(CH_3)_2$], 25.02 and 21.24 (CH_2, C-5/C-6). – (^{1}H,^{13}C)-COSY: correlation peaks for (1-H,C-1), (2-H,C-2), (3-H,C-3), and (4-H,C-4). – GC-MS (70 eV): *m/z* (%): 184 (7) [M + 1], 183 (44) [M$^+$], 152 (18), 97 (100), 82 (100), 79 (37), 72 (53).

Isomer **2b** (minor component): ^{1}H NMR ([D$_6$]acetone): δ = 5.84 (m, 1-H, $^3J_{1,2}$ = 10.0 Hz), 5.69 ("dq", 2-H, $^3J_{2,1}$ = 10.0 Hz, J = 2.0 Hz), 3.63 (s, 3H, CO_2CH_3), 3.49 ("dquint", 3-H, $^3J_{3,4}$ = 9.5 Hz, J = 2.0 Hz), 2.57 (ddd, 4-H, $^3J_{4,3}$ = 9.5 Hz, $^3J_{4,5}$ = 12.0 Hz, $^3J_{4,5'}$ =

2.0 Hz), 2.21 [s, 6H, $N(CH_3)_2$], 1.6–2.5 (m, 4H, 5-H and 6-H). Complex overlap of signals prohibited an analysis of 5-H and 6-H. – 1-H and 2-H were assigned in analogy to **2a**. – (^{1}H,^{1}H)-COSY: cross peak for (3-H,4-H). – ^{13}C NMR ([D$_6$]acetone, combination of Dept-90 and Dept-135): δ = 176.21 (C=O), 129.99 (CH, C-1), 126.67 (CH, C-2), 62.89 (CH, C-3), 51.62 (CH_3, OCH_3), 40.81 [CH_3, $N(CH_3)_2$], 43.54 (CH, C-4), 26.81, and 25.27 (CH_2, C-5/C-6). C-1 and C-2 were assigned in analogy to **2a**. – (^{1}H,^{13}C)-COSY: correlation peaks for (C-3,3-H), (C-4,4-H), (C-1,1-H), and (C-2,2-H). – GC-MS (70 eV): *m/z* (%) = 184 (3) [M + 1], 183 (100) [M$^+$], 152 (7), 97 (80), 82 (86), 79 (17), 72 (22). – IR (film, mixture): $\tilde{\nu}$ = 3040 cm^{-1} (CH_2), 2880 [$N(CH_3)_2$], 1740 (C=O), 1650 (C=C).

$C_{10}H_{17}NO_2$ (183.2)
Calcd. C 65.54 H 9.35 N 7.64
Found C 65.72 H 9.63 N 7.79

With Acrylonitrile: 0.976 g (7.0 mmol) of **1** in 10.4 g of acrylonitrile needed 3 d at room temperature for complete reaction (GLC). Excess acrylonitrile was removed in vacuo (100 Pa), leaving 0.61 g (81%) of a 58:42 oily mixture of **4a** and **4b** which could not be separated. Purification was performed by condensation in vacuo (100 Pa) at 45°C.

Isomer **4a** (minor component): ^{1}H NMR ([D$_6$]acetone): δ = 5.86 (m, 1-H, $^3J_{1,2}$ = 10.4 Hz), 5.72 (m, 2-H, $^3J_{1,2}$ = 10.4 Hz, *J* = 1.0, 2.0, and 2.5 Hz), 3.21 (m, 3-H, *J* = 2.5 Hz, *J* = 3.5 Hz, $J_{3,4}$ = 6.0 Hz), 3.30 (m, 4-H, *J* = 3.5 Hz, 1H, $J_{3,4}$ = $J_{4,5}$ = 6.0 Hz), 2.40 [s, 6H, $N(CH_3)_2$], 1.8–2.6 (m, 4H, 5-H and 6-H). Complex overlap of signals prohibited an analysis of the signals of 5-H and 6-H. – (^{1}H,^{1}H)-COSY: cross peak for (3-H,4-H), (1-H,2-H), (1-H,6-H), and (2-H,3-H). – ^{13}C NMR ([D$_6$]acetone, Dept-90, Dept-135): δ = 129.40 (CH, C-1), 126.88 (CH, C-2), 121.46 (CN), 61.60 (CH, C-3), 42.46 [CH_3, $N(CH_3)_2$], 29.07 (CH, C-4), 25.21 (CH_2, C-5), 22.90 (CH_2, C-6). A (^{13}C,^{1}H)-COSY spectrum established the connection of ^{13}C and ^{1}H chemical shifts and allowed the exact location of the methine protons.

Isomer **4b** (major component): ^{1}H NMR ([D$_6$]acetone): δ = 5.90 (m, 1-H, $^3J_{1,2}$ = 10.4 Hz), 5.67 ("ddt", 2-H, $^3J_{1,2}$ = 10.4 Hz, *J* = 2.5 Hz, *J* = 1.7 Hz), 3.35 ("dquint", 3-H, $^3J_{3,4}$ = 8.5 Hz, *J* = 2.2 Hz), 2.91 (ddd, 4-H, $^3J_{3,4}$ = 8.5 Hz, $^3J_{4,5}$ = 12.0 Hz, $^3J_{4,5'}$ = 2.8 Hz), 2.28 [s, 6H, $N(CH_3)_2$], 1.8–2.6 (m, 4H, 5-H and 6-H). Due to the complex overlap the signals of 5-H and 6-H could not be analyzed. – (^{1}H,^{1}H)-COSY: cross peak for (3-H,4-H), (1-H,2-H), (1-H,6-H), and (2-H,3-H). – ^{13}C NMR ([D$_6$]acetone, Dept-90, Dept-135): δ = 130.55 (CH, C-1), 125.71 (CH, C-2), 122.74 (CN), 63.04 (CH, C-3), 41.08 [CH_3, $N(CH_3)_2$], 28.99 (CH, C-4), 26.17 (CH_2, C-5), 24.26 (CH_2, C-6). A (^{13}C,^{1}H)-COSY spectrum established the connection of ^{13}C- and ^{1}H-chemical shifts and enabled the exact location of the methine protons. – GC-MS (70 eV, **4a** and **4b**): *m/z* (%) = 150 (19) [M$^+$], 97 (97), 82 (100). – IR (film, mixture of **4a** and **4b**): $\tilde{\nu}$ = 3040 (CH_2), 2800 (CH_3), 2250 (CN), 1660 (C=C), 1060 (CN).

$C_9H_{14}N_2$ (150.2)
Calcd. C 71.96 H 9.39 N 18.65
Found C 71.51 H 9.65 N 18.30

With Maleonitrile: Diene **1** (0.991 g, 10.2 mmol) and 0.784 g (10.0 mmol) of maleonitrile were each dissolved in 12.5 ml of THF, cooled to –50°C, combined and kept in the dark. An orange color developed immediately which changed to yellow in the reaction course. After warming to room temperature the reaction needed 1 d for completion (GLC). Two products had formed in a ratio of 63:77 (GLC, column C). Removal of the solvent in vacuo (10 Pa) gave 1.46 g (98%) of crystals (m.p. 95–100°C). Recrystallization from diethyl ether gave 1.38 g (93%) of a mixture of **5a** and **5b** with m.p. 101°C in a ratio of 64:36.

Isomer **5a** (major component): ^{1}H NMR ([D$_6$]benzene): δ = 5.45 [m, 2H, 1-H and 2-H, ^3J = 10.7 Hz (from a spectrum in $CDCl_3$ where the chemical shifts of the olefinic protons are slightly different)], 3.26 (m, 4-H), 2.88 (m, 3-H), 2.65 (ddd, 5-H, $J_{5,6}$ = 11.2 Hz, $J_{5,6'}$ = 5.7 Hz, $J_{4,5}$ = 2.8 Hz), 2.16 [s, 6H, $N(CH_3)_2$], 1.9–2.3 (m, 2H, 6-H and 6-H'). – ^{13}C NMR ([D$_6$]benzene): δ = 126.68 (CH, C-2), 125.73 (CH, C-1), 119.45 (CN), 117.89 (CN), 60.45 (CH, C-3), 40.94 [CH_3, $N(CH_3)_2$], 30.45 (CH, C-4), 26.52 (CH, C-5), 24.96 (CH_2, C-6). Assignment of C-4 and C-5 is based on a comparison with computed values[22]. – GC-MS (70 eV): *m/z* (%) = 175 (5) [M$^+$], 97 (100), 82 (100), 77 (6).

Isomer **5b** (minor component): ^{1}H NMR ([D$_6$]benzene): δ = 5.45 (m, 2H, 1-H and 2-H), 3.21 (m, 3-H), 3.03 ("dt", 5-H, $^3J_{4,5}$ = 3.5 Hz, $^3J_{5,6}$ = $^3J_{5,6'}$ = 5.3 Hz), 2.74 (dd, 4-H, $^3J_{4,5}$ = 3.5 Hz, $^3J_{3,4}$ = 8.0 Hz), 1.99 [s, 6H, $N(CH_3)_2$], 1.91–2.33 (m, 2H, 6-H, 6-H'). – ^{13}C NMR ([D$_6$]benzene): δ = 126.68 (CH, C-2), 125.83 (CH, C-1), 119.56 (CN), 118.14 (CN), 59.75 (CH, C-3), 40.38 [CH_3, $N(CH_3)_2$], 30.14 (CH, C-4), 26.31 (CH, C-5), 25.89 (CH_2, C-6). Assignment of C-4 and C-5 as in the case of isomer **5a**. – GC-MS (70 eV): *m/z* (%) = 175 (4) [M$^+$], 97 (98), 82 (100), 77 (7). – IR (KBr, **5a** + **5b**): $\tilde{\nu}$ = 2960 cm^{-1} (CH_2), 2800 (CH_3), 2250 (CN), 1650 (C=C).

$C_{10}H_{13}N_3$ (175.2)
Calcd. C 68.54 H 7.48 N 23.98
Found C 68.30 H 7.67 N 24.31

With Fumaronitrile: Solutions of 0.486 g (5.0 mmol) of **1** in 5.0 ml of THF and 0.391 g (5.0 mmol) of fumaronitrile in 5.0 ml of THF were combined at –50°C, warmed to room temperature, and kept under these conditions for 1 d. Removal of the solvent in vacuo (10 Pa) gave 0.846 g (96%) of solid of m.p. 96°C which was recrystallized from diethyl ether to give 0.690 g (79%) of colorless rhombic crystals with m.p. 104–105°C. The crude mixture consisted of a 76:34 mixture of **6a** and **6b**. A similar experiment carried out at –20°C needed 5 d for completion and led to **6a** and **6b** in a ratio of 85:15. The recrystallized product consisted of pure **6a**, **6b** could not be isolated in pure form. Structure elucidation was done on **6a** and the mixture **6a**/**6b**.

Isomer **6a** (major component): ^{1}H NMR ([D$_6$]benzene): δ = 5.06 (m, 2H, 1-H and 2-H), 2.96 (m, 3-H, $^3J_{3,4}$ = 10.1 Hz), 2.30 ("ddt", 4-H, $^3J_{3,4}$ = 10.1 Hz, $^3J_{4,5}$ = 11.7 Hz, *J* = 0.4 Hz), 2.14 (m, 5-H), 1.95 [s, 6H, $N(CH_3)_2$], 1.62 (m, 2H, 6-H and 6'-H). – (^{1}H,^{1}H)-COSY: cross peaks for (6-H,5-H), (6-H,3-H), (5-H,4-H), (5-H,6-H), (1-H,3-H), (1-H,6-H), (2-H,3-H), and (2-H,6-H). – ^{13}C NMR ([D$_6$]benzene, Dept-135, (^{1}H,^{13}C)-COSY): δ = 126.07 (CH, C-1 or C-2), 125.44 (CH, C-2 or C-1), 119.13 (CN), 118.96 (CN), 62.20 (CH, C-3), 40.32 [CH_3, $N(CH_3)_2$], 32.00 (CH, C-4), 28.82 (CH, C-5), 27.79 (CH_2, C-6). – (^{1}H,^{13}C)-COSY: correlation peaks for (6-H,C-6), (5-H,C-5), (3-H,C-3). – GC-MS (70 eV): *m/z* (%) = 175 (5) [M$^+$], 97 (98), 82 (100), 77 (6).

Isomer **6b** (minor component): ^{1}H NMR ([D$_6$]benzene): δ = 5.35 ("dq", 1-H or 2-H, $^3J_{1,2}$ = 10.8 Hz, *J* = 2.8 Hz), 5.23 ("dm", 1-H or 2-H, $^3J_{1,2}$ = 10.8 Hz), 3.09 (m, 3-H, *J* = 2.6), 2.52 (m, 4-H and 5-H), 2.12 [s, 6H, $N(CH_3)_2$], 1.62 (m, 2H, 6-H and 6'-H). – A (^{1}H,^{1}H)-COSY spectrum confirmed the assignment. – ^{13}C NMR ([D$_6$]benzene, DEPT-135): δ = 125.34 and 125.76 (C-1/C-2), 119.30 (CN), 118.12 (CN), 58.18 (C-3), 42.51 [$N(CH_3)_2$], 31.94 and 26.63 (C-4/C-5), 26.19 (CH_2, C-6). – IR (KBr, **6a** + **6b**): $\tilde{\nu}$ = 2990 cm^{-1} (CH_2), 2880 (CH_3), 2280 (CN), 1660 (C=C).

$C_{10}H_{13}N_3$ (175.2)
Calcd. C 68.54 H 7.48 N 23.98
Found (**6a**) C 68.31 H 7.47 N 23.76
Found (**6a** + **6b**) C 68.43 H 7.88 N 23.65

With Dimethyl Maleate: Solutions of 0.486 g (5.0 mmol) of **1** in 5.0 ml THF and 0.740 g (5.1 mmol) of dienophile in 5.0 ml of THF were cooled to −50°C and combined. The mixture was allowed to warm to room temperature and kept in the dark under these conditions for 1 d. It was shown by GLC (column C) that all of the diene had disappeared and two products had formed in a ratio 61:39. Unreacted dienophile had isomerized to dimethyl fumarate. Removal of solvent in vacuo (10 Pa) left an oil (1.18 g). 83% of this oil consisted of cycloadducts, 17% was dimethyl fumarate (GLC). As shown by NMR spectroscopy the products were identical to those of the cycloadditon of **1** to dimethyl fumarate (characterization below).

With Dimethyl Fumarate: Diene **1** (0.486 g, 5.0 mmol) and 0.721 g (5.0 mmol) of dimethyl fumarate in 5.0 ml of THF each were combined at −50°C. After 1 d at room temperature, needed for complete reaction, the solvent was removed in vacuo (10 Pa) and 1.20 g (99%) of a product mixture (66:34) was obtained as an oil which was contaminated by a small amount of dimethyl fumarate. 2.0 ml of pentane was carefully added on top of the oil and the sample kept at −20°C for two months. The pentane phase was then separated, the solvent removed in vacuo (10 Pa) at room temperature. 0.82 g (34%) of a crystalline compound with m.p. 53°C (major isomer) was isolated and recrystallized from diethyl ether and pentane (m.p. 56–57°C). The other isomer could not be obtained in pure form. Identification of cycloadducts was carried out on the isolated isomer and the mixture.

Major isomer: ^{1}H NMR ($CDCl_3$): The hydrogen atoms form a 7-spin system and give rise to a higher order spectrum. Only three coupling contants ($^2J_{6\text{-H},6'\text{-H}}$, $^3J_{1\text{-H},2\text{-H}}$ and $^2J_{5\text{-H},6'\text{-H}}$) can be identified unambiguously. The assignment of individual chemical shifts is derived from the (^{1}H,^{1}H)-COSY spectrum and the major cross peaks therein. δ = 5.93 (m, 1-H, $^3J_{1,2}$ = 10.1 Hz), 5.78 (m, 2-H, $^3J_{2,1}$ = 10.1 Hz), 3.67 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.54 (m, 3-H), 3.03 (m, 4-H and 5-H), 2.44 (m, 6-H_e, ^2J = 17.5 Hz), 2.25 [s, 6H, $N(CH_3)_2$], 1.97 (m, 6-H_a, ^2J = 17.5 Hz). The assignment is supported by a *J*-resolved ^{1}H-NMR spectrum. – ^{13}C NMR ($CDCl_3$): The chemical shifts were ascribed to individual carbon atoms on the basis of the assignment of the ^{1}H chemical shifts and a (^{1}H,^{13}C)-COSY spectrum. δ = 175.95 (C=O), 173.51 (C=O), 128.19 (CH, C-1), 123.33 (CH, C-2), 58.14 (CH, C-3), 43.35 [$N(CH_3)_2$], 47.36 and 37.45 (CH, C-4/C-5), 28.51 (CH_2, C-6), 51.92 and 51.49 (2 × OCH_3). – (^{1}H,^{1}H)-COSY: Intense cross peaks were found for: 1-H with 2-H and 6-H; 2-H with 1-H, 3-H, and 6-H; 3-H with 4-H or 5-H; 4-H and 5-H with 6-H, 6-H′ and 3-H; 6-H with 6-H′, 4-H and 5-H; 6-H′ with 6-H, 4-H, and 5-H.

Isomer **7a** (minor component): ^{1}H NMR ($CDCl_3$): The data were extracted from the NMR spectra of a mixture of the two isomers. The spectrum is of higher order and only a few coupling constants can be determined. The assignments of chemical shifts follows the same procedure as for the major isomer: δ = 5.80 (m, 1-H or 2-H), 5.73 (m, 2-H or 1-H, $^3J_{1,2}$ = 10.0 Hz), 3.57 (m, 3-H), 2.80 (dd, 4-H, $^3J_{3,4}$ = 10.2 Hz, $^3J_{4,5}$ = 11.5 Hz), 2.96 ("dt", 5-H, $^3J_{5,6}$ = 5.5 Hz, $^3J_{4,5}$ = $^3J_{5,6'}$ = 11.5 Hz), 2.17–2.55 (m, 2H, 6-H and 6-H′), 3.71 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 2.28 [s, 6H, $N(CH_3)_2$]. – ^{13}C NMR (75.47 and 50.31 MHz, $CDCl_3$, APT): Assignment on the basis of the hydrogen chemical shifts and a ^{1}H-detected (^{1}H,^{13}C)-COSY spectrum. δ = 175.20 (C=O), 174.00 (C=O), 127.29 (CH, C-1), 125.90 (CH, C-2), 63.29 (CH, C-3), 52.01 (OCH_3), 45.16 (CH, C-4), 42.83 (C-5), 40.45 ($N(CH_3)_2$), 28.24 (CH_2, C-6). – (^{1}H,^{1}H)-COSY: Cross peaks were found for: 1-H with 6-H; 2-H with 3-H, 6-H; 3-H with 4-H, 2-H; 4-H with 3-H, 5-H; 5-H with 4-H, 6-H, 6-H′; 6-H with 1-H, 5-H. – GC-MS (70 eV): Major isomer *m/z* (%): 242 (5) [M + 1], 241 (27) [M^+], 210 (8), 182 (16), 98 (12), 97 (100), 82 (79), 72 (17), 59 (12). Minor isomer, *m/z* (%): 242 (2) [M + 1], 241 (19) [M^+], 210 (6), 182 (10), 98 (7), 97 (100), 82 (63), 72 (12), 59 (8). – IR (film, mixture): $\tilde{\nu}$ = 3030 cm^{-1} (CH_2), 2820 [$N(CH_3)_2$], 1780 (C=O), 1740 (C=O), 1640 (C=C), 1340 (O–CH_3).

$C_{12}H_{19}NO_4$ (241.3)			
Calcd.	C 59.73	H 7.94	N 5.81
Found (**7a** + **7b**)	C 59.72	H 8.15	N 5.69
Found (**7a′**)	C 59.74	H 8.26	N 5.87

With Dimethyl Dicyanomaleate: Freshly prepared dienophile (194.2 mg, 1.0 mmol), dissolved in 10.0 ml of dichloromethane, cooled to −50°C, and kept in the dark under argon was combined with 5.0 ml of a −50°C solution of **1** (97.2 mg, 1.0 mmol) in dichloromethane. 4 h after warming up to room temperature (reactants could no longer be detected by GLC) the solvent was removed in vacuo (10 Pa); yield 250 mg (86%) of a solid (dec. 86°C) was isolated after washing twice with ice-cold diethyl ether. The compound was identical to that obtained from **1** and dimethyl dicyanofumarate as shown by NMR, IR, and mass spectroscopy. No other stereoisomeric cycloadducts could be detected.

With Dimethyl Dicyanofumarate: 0.486 g (5.0 mmol) of dienophile was added to 0.971 g (5.0 mmol) of **1**, each separately dissolved in a total of 45 ml of dichloromethane and cooled to −50°C. A yellow color which formed immediately faded away after warming to room temperature (3.5 h). No reagents remained, so the solvent was evaporated in vacuo (10 Pa). The solid residue was washed twice with ice-cold diethyl ether; yield 1.28 g (88%, dec. 86°C). At room temperature the product decomposed even under argon within a few days. The compound was identical to that obtained from the reaction of **1** with dimethyl dicyanomaleate and was only a single isomer. – ^{1}H NMR (300 MHz, [D_6]benzene): See above. – ^{13}C NMR (75.47 MHz, [D_6]benzene): See above. – MS (70 eV): *m/z* (%) = 291 (2) [M^+], 163 (14), 97 (100), 86 (14), 84 (19), 82 (52), 68 (10), 59 (37), 44 (52), 42 (34). – IR (KBr): $\tilde{\nu}$ = 2860 cm^{-1} (CH_3), 2260 (CN), 1760 (CO), 1740 (CO), 1630 (C=C).

$C_{14}H_{17}N_3O_4$ (291.3)			
Calcd.	C 57.72	H 5.88	N 14.42
Found	C 57.41	H 5.92	N 14.50

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