a(*E*)-1-Methoxy-1,3-butadiene and 1,1-Dimethoxy-1,3-butadiene in (4 + 2) Cycloadditions. A Mechanistic Comparison

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Abstract: The reactions of (*E*)-1-methoxy-1,3-butadiene (**1**) and 1,1-dimethoxy-1,3-butadiene (**2**) with a series of dienophiles of increasing electrophilicity are described. Stereochemical studies reveal that the cycloadditions of **1** are concerted processes, even for the most electron-deficient olefins dimethyl dicyanofumarate and dimethyl dicyanomaleate. 1,1-Dimethoxy-1,3-butadiene reacts under our conditions (dilute solutions and temperatures ≤60 °C) only with those dienophiles which can give zwitterions out of the antiperiplanar conformation of the diene. Zwitterionic intermediates can be trapped by methanol. In the case of tetracyanoethene the kinetics of decay of an intermediate, interpreted as the zwitterion, can be followed by stopped flow techniques: $E_a = 14.8 \pm 0.2$ kcal mol^{-1}, log $A = 11.9 \pm 0.1$, $\Delta H^{\ddagger} = 10.8 \pm 0.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = -6.2 \pm 0.1$ cal mol^{-1} K^{-1}, and $\Delta G^{\ddagger} = 11.40 \pm 0.03$ kcal mol^{-1}.

Systematic studies on the influence of substituents in different positions of a diene in Diels−Alder reactions have shown that the mechanism of these (4 + 2) cycloadditions depends critically on the number and kind of substituents.[1] A similar influence on the mechanism derives from the nature of the dienophile. Thus it was found that (*E*)-1-(dimethylamino)-1,3-butadiene changes from a concerted to a stepwise mechanism when the dienophile can stabilize a negative charge effectively, e.g. dimethyl dicyanofumarate.[2,3] It could also be shown that electron transfer may be involved in cycloadditions of 1,4-bis-(dimethylamino)-1,3-butadiene.[4,5] 1,1-Bis(dimethylamino)-1,3-butadiene is still another case as it is locked in the antiperiplanar conformation and forms stable zwitterions with dienophiles of strong electrophilicity, e.g. dimethyl dicyanofumarate and tetracyanoethylene.[6] These, however, do not cyclize to (4 + 2) cycloadducts. Here we report on cycloadditions of (*E*)-1-methoxy-1,3-butadiene and 1,1-dimethoxy-1,3-butadiene to a series of dienophiles of increasing electrophilicity. Kinetic measurements on cycloadditions of **1** were reported some time ago.[7] The same diene was also included in mechanistic studies on cycloadditions of electron-rich conjugated dienes to β-cyanostyrenes by Scheeren et al.[8] (4 + 2) cycloadditions of **2** have not been described so far.

The choice of **1** and **2** as dienes in Diels−Alder reactions was made in order to probe the borderline between concerted and two-step Diels−Alder reactions via zwitterions. For these dienes the mechanistic alternative to a concerted cycloaddition

Scheme 1

D = Donorsubstituent
A = Acceptorsubstituent
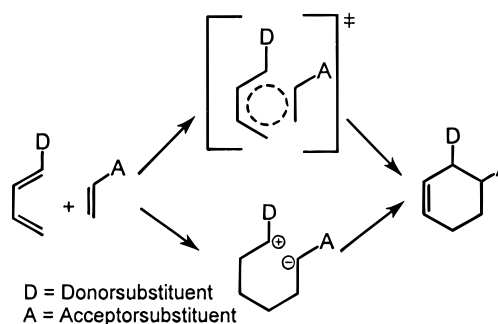
should be the zwitterionic pathway as indicated for a donor-substituted diene and an acceptor-substituted dienophile in Scheme 1.

Electronic Structure and Conformation of 1 and 2

The first vertical ionization potentials, obtained by photoelectron spectroscopy and interpreted as the π-HOMO energies of **1** and **2**, are 8.21[9] and 7.04 eV. Cyclovoltammographically a first irreversible oxidation is observed at +1.29 V vs SCE for **1** and at +0.75 V vs SCE for **2**. Compared with 1,3-butadiene (1. Ip$_v$ = 9.08 eV[10]) both **1** and **2** are significantly more nucleophilic. The data from PE spectroscopy and from the electrochemical measurements indicate high-lying π-HOMOs and, therefore, high reactivity toward electrophilic dienophiles. Diene **2** should exceed **1** in reactivity.

Concerted (4 + 2) cycloadditions require a synperiplanar or at least synclinal conformation of the diene. While this conformation should be easily accessible for **1**, diene **2** housing one *Z*-substituted double bond should strongly prefer the antiperiplanar conformation. As a consequence its reactivity in concerted cycloadditions should be influenced by this steric effect. A reduced reactivity of dienes where one or two double bonds are *Z* substituted is a known phenomenon.[7] Besides orbital energy considerations the structures of the FMOs

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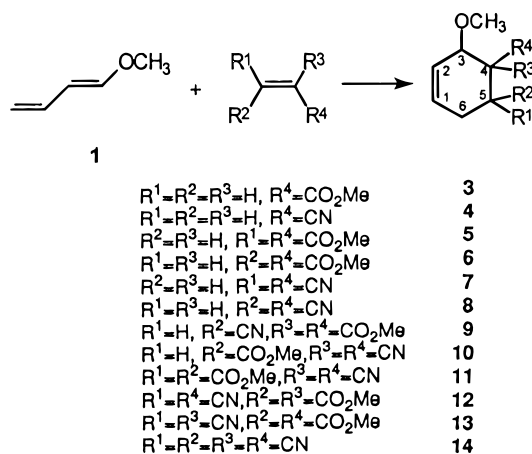
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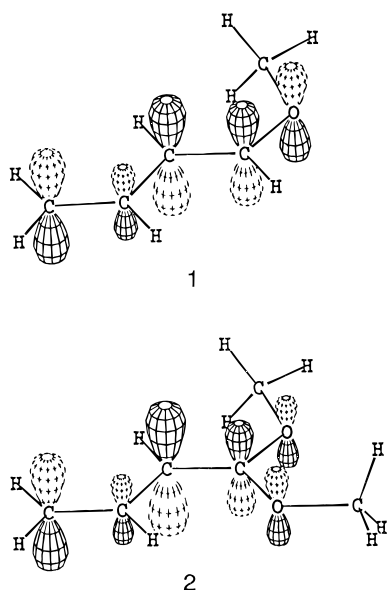
Table 1. (4 + 2) Cycloadditions of (*E*)-1-Methoxy-1,3-butadiene

dienophile	reaction time[a] (d)	yield,[b] %	endo/exo	NMR coupling constants (Hz)
$H_2C=CH-CO_2Me$	46 (t)	79–85	64/36	$^3J_{1-H,2-H} = 10.3$, $^3J_{3-H, 4-H} = 4.0$ (endo), 8.5 (exo)
$H_2C=CH-CN$	38 (t)	70	73/27[c]	$^3J_{3-H,4-H} = 6.0$ and 4.5
(*E*)-$MeO_2C-HC=CH-CO_2Me$		78–88	68/32	$^3J_{3-H,4-H} = 5.0$ (endo), 9.0 (exo); $^3J_{4-H,5-H} = 12.0$ (endo), 11.0 (exo)
(*Z*)-$MeO_2C-HC=CH-CO_2Me$	24 (t)[e]	81	62/25/9/4[d]	$^3J_{3-H,4-H} = 3.5, 6.0$; $^3J_{4-H,5-H} = 3.5$ (major components)
(*E*)-$NC-HC=CH-CN$	28 (a)	60	27/73	$^3J_{3-H,4-H} = 7.6$ (exo), 3.8 (endo); $^3J_{4-H,5-H} = 10.4$ (exo), 9.5 (endo)
(*Z*)-$NC-HC=CH-CN$	7 (t)[e]	85	83/17[c]	$^3J_{3-H,4-H} = 3.0, 3.2$; $^3J_{4-H,5-H} = 5.6, 3.2$
$NC-HC=C(CO_2Me)_2$	5 (t)[f]	82	69/31[g]	$^3J_{5-H,6a-H} = 12.0$; $^3J_{5-H,6e-H} = 5.5$ (major component)
$(NC)_2C=CH-CO_2Me$	3 (t)[f]	92	71/29[g]	$^3J_{5-H,6-H} = 10.9, 6.2$ (major); 10.7, 5.9 (minor)
$(NC)_2C=C(CO_2Me)_2$	2 (t)[f]	96		$^3J_{C(CN),H} = 6.1 (\delta = 113.6)$ and $2.2 (\delta = 116.5)$
(*E*)-$MeO_2C(NC)C=C(CN)CO_2Me$	1 (a)[f]	85	55/45	$^3J_{CN,3-H} = 3.5$ (major), 8.0 (minor); $^3J_{CN,6-H} = 3.6, 9.7$ (major), 4.3, 9.4 (minor)
(*Z*)-$MeO_2C(NC)C=C(CN)CO_2Me$	2 (t)[f]	78	84/16	$^3J_{CN,3-H} = 4.4$ (major), 11.5 (minor); $^3J_{CN,6-H} = 4.7, 9.9$ (major), 3.5, 7.8 (minor)
$(NC)_2C=C(CN)_2$	0.5[f]	90		

[a] Refers to the time necessary for complete reaction (GLC); reactions were carried out under standard conditions: equimolar (ca. 0.25 M) solutions of reactants in toluene (t) or acetonitrile (a) at room temperature. [b] Isolated yields. [c] Assignment of endo/exo not possible. [d] Minor components = endo/exo **5**. [e] 60 °C. [f] Reaction time in h. [g] Refers to relative position of substituent at C-5.

Scheme 2

R¹=R²=R³=H, R⁴=CO₂Me **3**
R¹=R²=R³=H, R⁴=CN **4**
R²=R³=H, R¹=R⁴=CO₂Me **5**
R¹=R³=H, R²=R⁴=CO₂Me **6**
R²=R³=H, R¹=R⁴=CN **7**
R¹=R³=H, R²=R⁴=CN **8**
R⁴=H, R²=CN, R³=R⁴=CO₂Me **9**
R¹=H, R²=CO₂Me, R³=R⁴=CN **10**
R¹=R²=CO₂Me, R³=R⁴=CN **11**
R¹=R⁴=CN, R²=R³=CO₂Me **12**
R¹=R³=CN, R²=R⁴=CO₂Me **13**
R¹=R²=R³=R⁴=CN **14**

determine the reactivity. The HOMOs of **1** and **2**, shown as obtained from MNDO-PM3 calculations on RHF/3-21G* optimized structures, indicate a polarization toward C-4 of the dienes with smaller contributions of C-1. Further, **2** shows a significant contribution of C-2 which is even greater than that of C-4.

1

2

Cycloadditions of (*E*)-1-Methoxy-1,3-butadiene

The reactions of **1** with dienophiles (Scheme 2) were performed in dilute solutions (ca. 0.25 M) and in argon atmosphere in order to avoid polymerization of the diene which had been observed at higher concentration (3 M).[11] Photochemical *E/Z* isomerization of *Z*-substituted dienophiles was excluded by carrying out these cycloadditions in the dark. Reaction times were determined by GLC, and the corresponding values in Table 1 can, therefore, be considered as a qualitative reactivity scale of the dienophiles. The reactions provide the (4 + 2) cycloadducts in all cases. Pertinent data are given in Table 1. The ratio of isomers was determined in the crude reaction mixture and the yields refer to isolated product. The cycloaddition of methyl acrylate[12] and dimethyl cyanomethylidenemalonate[11] to **1** had been described earlier but were repeated here under our standard condition for comparison.

The reactivity sequence as deduced from the reaction times corresponds to expectation, i.e. the most electrophilic dienophiles react fastest. Endo/exo selectivity refers where applicable to the substituents at C-3 and C-4. Generally the preference in favor of one isomer is not very pronounced. Some cycloadditions need special attention, in particular with respect to the mechanistic interpretation. Mono- and 1,1,2-trisubstituted dienophiles add regiospecifically to **1** (**3**, **4**, **9**, **10**). On the basis of the structures of the important FMO pair it is no surprise that methyl acrylate and acrylonitrile form the "ortho" adducts exclusively.[13] Similarly dimethyl cyanomethylidenemalonate and methyl β,β-dicyanoacrylate should give cycloadducts **9** and **10**. The proof of structure **9** and **10** follows from the observation that the hydrogen atom at the formerly monosubstituted side of the olefin shows ^3J couplings to two neighboring hydrogen atoms (see Table 1). An interesting regiochemical question results from the cycloaddition of dimethyl β,β-dicyanomethylidenemalonate. Which type of substituent, cyano or methoxycarbonyl, is dominant? The presence of a $^3J_{CH}$ coupling constant for each cyano carbon atom to one hydrogen atom proves that the two cyano groups are on C-4, next to the C atom with the methoxy group (**11**).
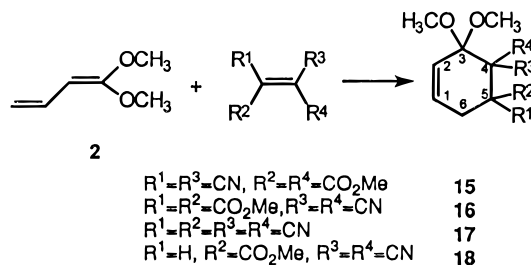
Stereospecificity of a cycloaddition is generally considered to be a strong indication for a concerted mechanism. Dimethyl fumarate yielded a mixture of two cycloadducts in which the methoxycarbonyl groups at C-4 and C-5 are in a trans arrangement according to the $^3J_{4-H,5-H}$ coupling constants. Dimethyl maleate, however, provided a mixture of four cycloadducts. The two minor components were identical with the cycloadducts of dimethyl fumarate to **1**. The $^3J_{4-H,5-H}$ coupling constants for

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Scheme 3

$R^1=R^3=CN, R^2=R^4=CO_2Me$　　**15**
$R^1=R^2=CO_2Me, R^3=R^4=CN$　　**16**
$R^1=R^2=R^3=R^4=CN$　　**17**
$R^1=H, R^2=CO_2Me, R^3=R^4=CN$　　**18**

Table 2. (4 + 2) Cycloadditions of 1,1-Dimethoxy-1,3-butadiene

dienophile	product	isolated yield (%)	NMR coupling constants (Hz)
(E)-MeO$_2$C(NC)C=C-(CN)CO$_2$Me	**15a,15b**	87	$^3J_{1-H,2-H} = 10.7$ (**15a** and **15b**)
(Z)-MeO$_2$C(NC)C=C-(CN)CO$_2$Me	**15a,15b**	92	$^3J_{1-H,2-H} = 10.7$ (**15a** and **15b**)
(NC)$_2$C=C(CO$_2$Me)$_2$	**16**	91	$^3J_{1-H,2-H} = 10.7$
(NC)$_2$C=C(CN)$_2$	**17**	84	$^3J_{1-H,2-H} = 10.9$
(NC)$_2$C=CHCO$_2$Me	**18**	83	$^3J_{1-H,2-H} = 10.6,$ $^3J_{5-H,6-H} = 11.4, 6.0$

the two other compounds prove their cis arrangement. The result might be explained either by a non-stereospecific cycloaddition of dimethyl maleate to **1** or by an isomerization of the *Z* to the *E* dienophile prior to the cycloaddition. To distinguish between this alternative a toluene solution of dimethyl maleate was kept for 24 h at 60 °C in the dark, the temperature at which the cycloaddition was carried out, and then analyzed by GLC. It contained 85.3% of the original dienophile and 14.7% of dimethyl fumarate, thus suggesting that the minor components in the reaction mixture were due to the cycloaddition of isomerized dimethyl maleate. The cycloaddition, therefore, should have taken place stereospecifically. The *E/Z* isomeric dienophiles maleonitrile/fumaronitrile and dimethyl dicyanomaleate/dimethyl dicyanofumarate lead each to mixtures of two cycloadducts. As they are different for each pair of dienophiles stereospecific reactions must have taken place. The magnitudes of the $^3J_{4-H,5-H}$ coupling constants in **7** and **8** prove the retention of the relative position of the cyano groups as in the dienophiles. For **12** and **13** we determined the $^3J_{CN,4-H}$ and the $^3J_{CN,6-H}$ coupling constants (Table 1). The four sets of coupling constants are consistent with the picture of a concerted cycloaddition with retention of the dienophile stereochemistry in the products.

Cycloadditions of 1,1-Dimethoxy-1,3-butadiene

Cycloadditions of **2** were attempted with a series of acceptor substituted alkenes. Reactions with methyl acrylate, acrylonitrile, fumaro- and maleonitrile, dimethyl fumarate, and dimethyl maleate were carried out under standard conditions, i.e. an equimolar solution of diene and dienophile (ca. 0.1 M) was kept at 60 °C and the disappearance of the diene was monitored by GLC. After several days, up to two weeks, the diene had reacted and in most cases a white precipitate had been formed. This, however, turned out to be polymeric material. No cycloadduct could be identified or isolated. In order to suppress polymerization the reaction was also run in the presence of hydroquinone, but also under these conditions no adduct could be detected. Polymerization competes successfully with cycloaddition, an observation which we correlate with the inaccessiblity of a synperiplanar conformation. Thus **2** seems to be a poor diene in (4 + 2) cycloadditions under our conditions.

The situation changes when more electrophilic dienophiles are employed in these reactions. Successful cycloadditions (Scheme 3) could be carried out with dimethyl dicyanofumarate, dimethyl dicyanomaleate, dimethyl dicyanomethylidenemalonate, tatracyanoethylene, and methyl β,β-dicyanoacrylate. Due to the high reactivity of the dienophiles the reactions were usually run at −60 to −70 °C. Isolated yields and pertinent ^{1}H-NMR coupling constants of the cycloadducts are given in Table 2. In particular, the $^3J_{1-H,2-H}$ coupling constant demonstrates the cyclohexene structure of the cycloadducts. As we wanted to probe the mechniasm of these cycloadditions we analyzed each of them separately very carefully.

Immediately after mixing precooled solutions of dimethyl dicyanofumararte and **2** starting material could no longer be detected, either by GLC or by NMR spectroscopy. Removal of the solvent under reduced pressure yielded almost quantitatively (>95%) a crystalline mixture of two 1:1 adducts in a ratio which was slightly solvent dependent and varied between 32:68 (toluene) and 42:58 (acetone). From the combined ^{1}H- and ^{13}C-NMR data, including (^{1}H,^{1}H)- and (^{1}H,^{13}C)-COSY spectra, we conclude that **15** is formed in a non-stereospecific cycloaddition as a mixture of two isomeric products. The data exclude (2 + 2) adducts as alternatives.

The very fast reaction, even at −70 °C, excludes the detection of possible intermediates by NMR spectroscopy. We recurred, therefore, to trapping experiments in order to check on the multistep nature of these reactions. Zwitterionic intermediates which are the obvious candidates in these experiments have been trapped in several cases.[6,14−16] Dimethyl dicyanofumarate was dissolved in a mixture of methanol and acetonitrile (1:2 v/v) whereas diene **2** was applied in acetonitrile only due to its instability in methanol. The solutions were mixed at −50 °C. Immediately afterwards the solvents were removed at −20 °C under vacuum. According to GC-MS and ^{1}H NMR the residue, a colorless solid (97%), consisted of a mixture of three compounds in the ratio of 60:31:9. The minor component (9%) turned out to be a mixture itself of the isomers of **15**, the two major components were two diastereomers resulting from trapping of a zwitterionic intermediate (**19**) by methanol (**20a** and **20b**). Diastereomers are formed because zwitterion **19** generates a second chiral center on protonation of the carbanionic C-atom.

19　　　　　**20a/20b**
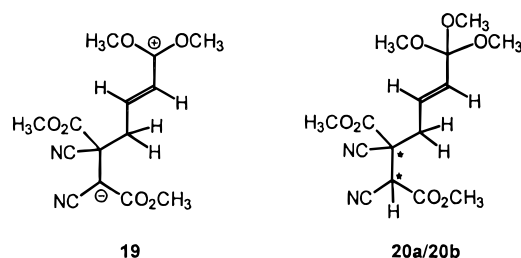
The structure of **20a** and **20b** follows from the NMR spectroscopical data. Two protons at the CC double bond show $^3J = 15.6$ Hz for **20a** and **20b**, thereby proving the *E* configuration. The pattern is very similar to that observed for the zwitterions and their trapping products from the reaction of 1,1-bis(dimethylamino)-1,3-butadiene with dimethyl dicyanofumarate or tetracyanoethylene.[6] A (^{1}H,^{13}C)-COSY spectrum established the relationship of H-atoms and the corresponding

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carbon atoms. For further details on the spectroscopic data see the Experimental Section.

In order to exclude that the cycloadduct is formed first and a zwitterion is generated by ring opening which is then trapped by methanol we dissolved the isolated cycloadducts **15** in methanol. Even after several weeks at room temperature no trapping product **20** could be found. The cycloadduct is stable under these conditions.

The reaction of dimethyl dicyanomaleate with 1,1-dimethoxy-1,3-butadiene was carried out at -70 °C in toluene with freshly prepared and isomerically pure dimethyl dicyanomaleate. A mixture (98%) of the same diastereomers (**20a/20b**) as for dimethyl dicyanofumarate was obtained in a 52:48 ratio. Thus, also this cycloaddition seems to be two-step in nature. As dimethyl dicyanomaleate isomerizes easily to the *E*-isomer the possibility exists that isomerization takes place prior to the cycloaddition. This possibility was checked by carrying out the reaction in the presence of an excess of dienophile. After completion the remaining dienophile consisted *solely* of dimethyl dicyanomaleate. The loss of the dienophile stereochemistry thus must have occurred during the cycloaddition process. It is not surprising that the postulated zwitterion could also be trapped in the reaction of 1,1-dimethoxy-1,3-butadiene with dimethyl dicyanomaleate. The product mixture (>90%) was composed of **15**, **20a**, and **20b** in a 6:49:44 ratio. The slight difference in composition compared with dimethyl dicyanofumarate can be explained by the assumption that the initial zwitterion has a different conformation at the former dienophile double bond, and that thermodynamic equilibration competes with addition of methanol.

The electrophilicity of the double bond of dimethyl dicyanomethylidenemalonate should be similar to that of the former two alkenes. It, therefore, can be expected that it is able to react with 1,1-dimethoxy-1,3-butadiene in its antiperiplanar conformation. Regardless of the solvent (toluene, acetonitrile, or dichloromethane) a single cycloadduct (**16**) was obtained in 94–98% at temperatures of -40 to -70 °C. An interesting problem arises as to the regiochemistry. On the basis of a two-dimensional $^3J_{C,H}$ experiment at -50 °C in CDCl$_3$ we were able to show that one hydrogen atom of the methylene group correlates with the carbon atoms of the carbonyl C-atom of the ester groups and not with those of the cyano groups. Thus, **16** is the correct structure of the cycloadduct. When temperature dependent ^{1}H-NMR spectra of **16** were recorded in deuteriotrichloromethane in the range of -70 to $+50$ °C the broad signal of the methylene protons at room temperature sharpened at >30 °C and split into two multiplets, doublet and doublet of a doublet at <-30 °C. The difference in chemical shifts of the two protons (172.0 Hz) and the coalescence temperature of the multiplet (ca. -5 °C) allowed the calculation of the free energy of activation for this dynamic process: $\Delta G^{\ddagger}(268) = 12.3$ kcal mol^{-1}. We interpret this in terms of the interconversion of the two possible half-chair conformations of **16** which interchange the hydrogen atoms of the methylene group on ring inversion.

The cycloaddition of dimethyl dicyanomethylidenemalonate is also a two step process as was found by trapping experiments at low temperature. If a solution of the alkene in acetonitrile/methanol (7:1 v/v) is added slowly to a solution of the diene in acetonitrile at -45 °C a mixture of two products was isolated in a ratio of 64:36 which could be separated by neither distillation nor chromatography. The minor component is cycloadduct **16** which was proved by admixture of authentic **16** and comparison of the ^{1}H-NMR spectra. The structure of **21**, the major component, rests on the following spectroscopic

observations: Two olefinic protons at 5.91 and 5.56 ppm show $^3J = 15.6$ Hz, i.e. *E* configuration of the double bond. The allylic coupling of one olefinic H-atom with two methylene protons is 7.6 Hz. The singlet at 4.37 ppm is assigned to the proton at the C-atom substituted by the two cyano groups. Support for this assignment comes from a $^2J_{CH}$-coupling experiment in which the signals of the C-atoms of the cyano groups appeared as a doublet due to the neighborhood of the single proton. Furthermore, the ratio of the methoxy to the methoxycarbonyl ^{1}H-NMR signals (3:2) strengthens structure **21**. If the trapping experiment is carried out with methanol containing 10% of water a third compound is found in the reaction mixture which we identify as **22**.
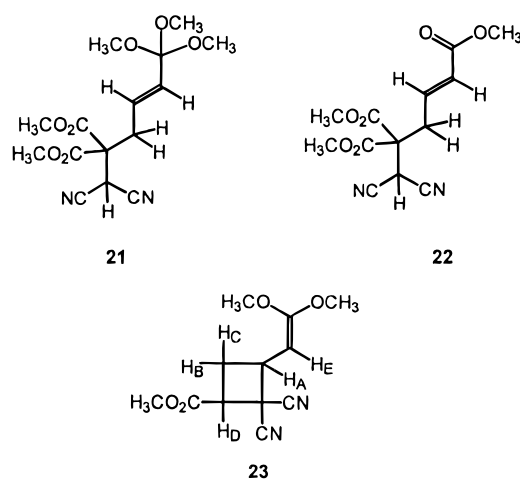
A single product (≥ 93%) is obtained when equimolar solutions of tetracyanoethene and **2** are mixed at low temperature (-40 to -60 °C) in acetonitrile or dichloromethane. Due to its spectroscopic data, in particular the coupling constant of 10.9 Hz for two olefinic protons at 5.96 and 6.07 ppm we assign structure **17** to the product. Although it was not possible to trap a zwitterionic intermediate in this reaction, even if a 15 M excess of methanol was applied we are convinced of the stepwise formation of **17** by our stopped-flow experiments (see below).

Methyl β,β-dicyanoacrylate is a trisubstituted dienophile which could be reacted successfully with 1,1-dimethoxy-1,3-butadiene. Equimolar solutions of diene and dienophile led to the formation of a single product (89–96%) within 1 h at -40 to -60 °C in acetonitrile, toluene, or dichloromethane. Structure **18** can be assigned on the basis of the spectroscopic data. A doublet of a doublet at 3.42 ppm with $^3J = 11.4$ and 6.0 Hz is in agreement with the regiochemistry shown in **18**. The reaction of this dienophile requires approximately 1 h under our standard conditions, indicating a reduced reactivity compared with the other alkenes. An attempt was made to identify intermediates by low temperature NMR experiments. Solutions of diene and dienophile in [D$_8$]toluene were mixed at -80 °C and transferred immediately to the precooled NMR probehead (-70 °C). The first spectrum (ca. 2 min after mixing) showed the presence of two major components in a 3:2 ratio. The major compound corresponds to the cycloadduct **18** whereas the second was assigned vinylcyclobutane structure **23** (see Experimental Section). If the temperature of the NMR probe is raised to -30 °C the signals of **23** disappear in favor of **18**. The structural assignment of **23** rests mainly on the following argument: The intermediate displays a proton connectivity pattern of five protons as derived from a (^{1}H,^{1}H)-COSY spectrum. Their chemical shift is consistent with the vinylcyclobutane structure.

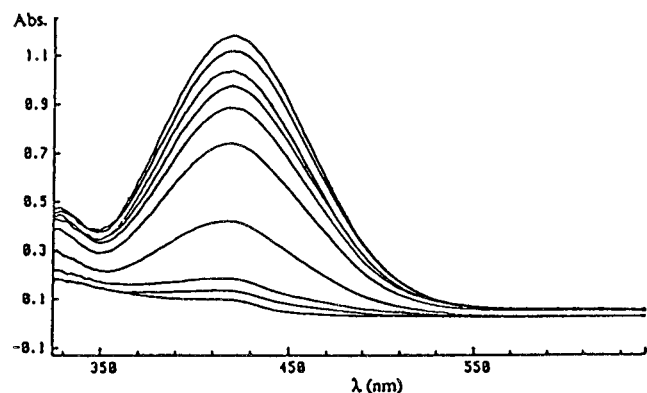**Figure 1.** Stopped-flow UV/vis spectra of an intermediate in the cycloaddition of 1,1-dimethoxy-1,3-butadiene at −35 °C in acetonitrile. The curve with the highest absorption was recorded after 0.003 s, and the others were taken after the following time intervals: 0.006, 0.008, 0.012, 0.017, 0.025, 0.052, 0.102, 0.121, and 0.264 s.

Stopped-Flow Measurements

The cycloaddition of 1,1-dimethoxy-1,3-butadiene to tetra-cyanoethylene was studied in acetonitrile and dichloromethane at low temperature by stopped-flow techniques in order to identify possible intermediates. This study was devised in analogy to that for the reaction of (*E*)-1-(dimethylamino)-1,3-butadiene with dimethyl dicyanofumarate where a transient absorption had been detected which was assigned to the zwitterionic intermediate in this cycloaddition.[3]

When equimolar solutions of diene **2** and TCNE in acetonitrile were mixed in the stopped-flow cell at −35 °C a new absorption was identified after 3 ms with $\lambda_{max} = 420$ nm (Figure 1). The new band had disappeared after 250 ms. Figure 1 shows only a weak absorption below 350 nm. As the concentrations of the reactants were 3.0×10^{-2} mol L^{-1} a strong absorption should have been present at this wavelength if the reactants were still present in solution. Thus we conclude that diene and dienophile already have reacted completely after 3 ms, the shortest time after which a UV/vis spectrum can be recorded. At −35 °C the absorption decayed with a first order rate constant of $k = 24.5$ s^{-1} ($\tau = 0.041$ s). Temperature dependent measurements were carried out to determine the activation parameters for the decay process. The Arrhenius activation energy was determined to 14.8 ± 0.2 kcal mol^{-1}, and the log of the preexponential factor is 11.9 ± 0.1. The corresponding Eyring parameters are $\Delta H^{\ddagger} = 10.8$ kcal mol^{-1}, $\Delta S^{\ddagger} = -6.2$ cal mol^{-1} K^{-1}, and $\Delta G^{\ddagger} = 11.4$ kcal mol^{-1}.

Discussion

(*E*)-1-Methoxy-1,3-butadiene forms (4 + 2) cycloadducts with electrophilic dienophiles. The reactivity trend is in accordance with the expectation from the FMO model.[13] The FMO approach rationalizes also the observed regiochemistry although other explanations invoking the stability of possible intermediates[17] or electrostatic potentials[18] will lead to the same result. The cycloadditions of *E/Z* isomeric olefins take place with retention of the dienophile stereochemistry. The deviation observed in the case of dimethyl maleate can be attributed to the isomerization of dimethyl maleate to dimethyl fumarate prior to the cycloaddition. Using the stereochemical argument it is concluded that a concerted mechanism is the best description of the reaction course. Obviously, the restriction to be made is that the same stereochemical result would have been obtained in a two-step reaction if ring closure of an intermediate occurred faster than isomerization at the stage of the intermediate. As

no evidence for this can be presented we will not follow this line any further.

The study of the cycloaddition behavior of 1,1-dimethoxy-1,3-butadiene has revealed a significant difference between dienophiles of weak and of strong electrophilicity. The former, ranging from monosubstituted olefins, e.g. acrylonitrile, to 1,2-disubstituted olefins, e.g. fumaronitrile, did not provide cycloadducts under our conditions. The strong acceptor-substituted olefins, bearing three or four carbomethoxy or cyano groups, however, reacted even at very low temperatures (−70 °C) very fast and provided the cycloadducts in high yield. 1,1-Dimethoxy-1,3-butadiene classifies as a strongly nucleophilic and polarized diene and should, therefore, be very well suited for cycloadditions, even with dienophiles like acrylonitrile. The diene, however, assumes in its ground state an antiperiplanar conformation. For a concerted cycloaddtion it has to assume the synperiplanar or at least a synclinal conformation. This should be difficult energetically as one methoxy group will point inwards to the hydrogen atom at C-4. A reduced reactivity of such a substitution pattern is generally observed.[7]

In our reactions a competition, namely polymerization of 1,1-dimethoxy-1,3-butadiene, prohibits the cycloaddition with weaker electrophilic dienophiles which can only cycloadd by a concerted reaction. The situation is different with the highly electrophilic substituted olefins. The presumption is that 1,1-dimethoxy-1,3-butadiene, locked in the antiperiplanar conformation, forms (4 + 2) cycloadducts with these dienophiles because of the possibility of zwitterion formation. These zwitterions may be formed directly from the antiperplanar conformation. This is supported by the configuration at the double bond of the trapped zwitterions. In a stepwise reaction, further experimental evidence is the non-stereospecific cycloaddition of dimethyl dicyanofumarate and dimethyl dicyanomaleate, where the (4 + 2) adduct is formed from the zwitterion. In this sequence it is possible that the zwitterion reacts directly to the (4 + 2) cycloadduct or that it forms reversibly a vinyl cyclobutane structure from which the (4 + 2) adduct results by rearrangement, i.e. ring opening after change to a conformation which leads to a favorable arrangement for 6-membered ring formation. The latter pathway had been discussed in the reaction of (*E*)-1-(dimethylamino)-1,3-butadiene with dimethyl dicyanofumarate.[3] The reason for this presumption was that a zwitterion formed from an antiperiplanar conformation of a diene houses an allyl cation subunit. In order to achieve closure to a six-membered ring, rotation about a partial double bond has to occur. It is questionable whether this is possible under our low temperature conditions. Therefore the alternative of ring closure to a vinylcyclobutane, rotation about a single bond and subsequent ring opening to a conformation favorable for six-membered ring closure, was suggested. The reaction of β,β-dicyanomethylacrylate with 1,1-dimethoxy-1,3-butadiene where a vinylcyclobutane structure could be made probable is an experimental support for this hypothesis. It can be taken as a hint for this reaction sequence also in the other cases, where it has to be postulated that rearrangement is faster, as no intermediates could be detected by low temperature ^{1}H-NMR experiments.

By stopped-flow measurements we identified an intermediate in the cycloaddition of 1,1-dimethoxy-1,3-butadiene to tetracyanoethene in acetonitrile. It is interesting to compare the activation parameters for the disappearance of the intermediate ($E_a = 14.8 \pm 0.2$ kcal mol^{-1}, log $A = 11.9 \pm 0.1$, $\Delta H^{\ddagger} = 10.8$ kcal mol^{-1}, $\Delta S^{\ddagger} = -6.2$ cal mol^{-1} K^{-1}, and $\Delta G^{\ddagger} = 11.4$ kcal mol^{-1}) with those found in the cycloaddition of (*E*)-1-(dimethylamino)-1,3-butadiene to dimethyl dicyanofumarate in aceto-

nitrile: $E_a = 14.5 \pm 0.1$ kcal mol^{-1}, log $A = 14.71 \pm 0.01$, $\Delta H^{\ddagger} = 14.1 \pm 0.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = 7.2 \pm 0.2$ cal mol^{-1} K^{-1}, $\Delta G^{\ddagger} = 11.95$ kcal mol^{-1}.[3] There is a close resemblance, indicating that a similar process is observed in both cases. In the former case we interpreted the new absorption as due to a zwitterionic intermediate which disappears by cyclizing to a cycloadduct, either to a (2 + 2) adduct which further rearranges to the (4 + 2) adduct or directly to the (4 + 2) product. The small positive value of the activation entropy was taken as evidence that a solvated zwitterion has to lose its solvation shell which is accompanied by a positive entropy contribution. In the reaction of 1,1-dimethoxy-1,3-butadiene with TCNE we find a small negative value of $\Delta S^{\ddagger}$ which is, however, far from the highly negative values which are observed in concerted cycloadditions. Thus we suggest that we have found additional spectroscopic evidence for a zwitterionic intermediate and its cyclization. The close relationship between the two cases is borne out also in their behavior in dichloromethane. For both reactions it was not possible to detect the UV/vis absorption at $\lambda_{max} = 420$ nm in this solvent. The explanation proposed in the first example was that the zwitterion which is also formed in dichloromethane is not stabilized by solvation, with the consequence that the rate-determining step is zwitterion formation and not cyclization, as suggested for the observations in acetonitrile.

Experimental Section

Analytical Instruments. ^{1}H and ^{13}C NMR spectra (internal standard TMS): Bruker AMX-300, Varian Gemini 200. MS(EI 70 eV): Finnigan MAT 312/188. GC/MS (EI 70 eV): Hewlett Packard HP5971 A and HP 5890 Series II chromatograph. GC: Varian 3700, 50 m. UV/vis: Cary 219. PE: Leybold-Heraeus UPG 200. Pölarography: Bruker E 310, Metrohm Polarographiestand. Elemental analyses: Heraeus EA 301. Melting points (uncorrected): Büchi 510.

Methyl acrylate, acrylonitrile, dimethyl fumarate, dimethyl maleate, fumaronitrile, and tetracyanoethylene (Aldrich) were purified by fractional distillation over a 20 cm Vigreux column, by recrystallization or sublimation. Maleonitrile,[19] dimethyl cyanomethylidenemalonate,[20,21] methyl β,β-dicyanoacrylate,[19,22] dimethyl dicyanomethylidenemalonate,[20] dimethyl cyanomaleate,[23] dimethyl dicyanofumarate,[24] and (E)-1-methoxy-1,3-butadiene[25] (purity >97%) were synthesized as described in the literature. A description of the experimental procedures is given for the cycloaddition of **1** to methyl acrylate and for the cycloadditions and trapping experiments of **2** to dimethyl dicyanofumarate and methyl β,β-dicyanoacrylate. Experimental details for the other reactions are given in the Supporting Information.

Cycloaddition of 1 to Methyl Acrylate. (E)-1-Methoxy-1,3-butadiene (**1**) (0.501 g, 6.0 mmol) in toluene (11 mL) was mixed with methyl acrylate (0.518 g, 6.0 mmol) in toluene (11 mL) at room temperature. After 46 d, monitored by GLC, **1** had reacted. The solvent was removed under reduced pressure (10 Pa) and the product was purified by "Kugelrohr" distillation at 10 Pa, 85 °C. Yield: 0.86 g (85%) of a 64:36 mixture of **3a** and **3b** as a colorless oil. The same reaction at 60 °C needed 18 d for completion. Yield: 0.90 g (89%). ^{1}H NMR (300 MHz, C$_6$D$_6$) of **3a**: δ 5.81 (dddd, $^3J_{1-H,2-H} = 10.3$ Hz, $^3J_{2-H,3-H} = 4.0$ Hz, $^4J_{2-H,6-H} = 2.5$ Hz, $^4J_{2-H,6-H'} = 1.5$ Hz, 1 H, 2-H), 5.69 (dddd, $^3J_{1-H,2-H} = 10.3$ Hz, J= 5.4 Hz, J= 2.0 Hz, J = 1.3 Hz, 1 H, 1-H), 3.97 (dd, "t", $^3J_{2-H,3-H} = 4.0$ Hz, $^3J_{3-H,4-H} = 4.0$ Hz, 1 H,

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3-H), 3.46 (s, 3 H, H-9), 3.18 (s, 3 H, H-7), 2.33 (ddd, $^3J_{4-H,5a-H} = 13.0$ Hz, $^3J_{3-H,4-H} = 4.0$ Hz, $^3J_{4-H,5e-H} = 2.8$ Hz, 1 H, 4-H), 2.14 (dddd, 12 lines, $^3J_{4-H,5a-H} = 13.0$ Hz, $^2J_{5a-H,5e-H} = 17.5$ Hz, $^3J_{5a-H,6a-H} = 5.9$ Hz, $^3J_{5a-H,6e-H} = 5.5$ Hz, 1 H, H-5a), 1.95−1.56 (m, 3 H, 5-He and 6-H). ^{13}C NMR (75 MHz, CDCl$_3$, DEPT) of **3a**: δ 173.60 (s, C-8), 132.22 (d, C-2, could also be C-1), 124.53 (d, C-1, could also be C-2), 72.66 (d, C-3), 57.01 (q, C-7), 51.53 (q, C-9), 44.79 (d, C-4), 25.08 (t, C-6), 18.67 (t, C-5). ^{1}H NMR (300 MHz, C$_6$D$_6$) of **3b**: $\delta = 5.77$ ("dm", $^3J_{1-H,2-H} = 10.3$ Hz, 1 H, 2-H), 5.55 ("dm", $^3J_{1-H,2-H} = 10.3$ Hz, 1 H, 1-H), 4.30 ("dt", $^3J_{3-H,4-H} = 8.5$ Hz, 1 H, 3-H), 3.39 (s, 3 H, 9-H), 2.73 (ddd, $^3J_{3-H,4-H} = 8.5$ Hz, $^3J_{4-H,5a-H} = 11.0$ Hz, $^3J_{4-H,5e-H} = 3.8$ Hz, 1 H, 4-H), 1.95−1.56 (m, 4 H, 5-H and 6-H). ^{13}C NMR (CDCl$_3$, DEPT): δ 175.21 (s, C-8), 129.29 (d, C-2, could also be C-1), 126.16 (d, C-1, could also be C-2), 76.20 (d, C-3), 56.20 (q, C-7), 51.79 (q, C-9), 45.33 (t, C-4), 24.26 (t, C-6), C-5 (not found, perhaps hidden under signal at 18.67 of **3a**). IR (CH$_2$Cl$_2$, cm^{-1}) 1730 (s, $\nu_{C=O}$). MS m/z (%) **3a**: 170 (M$^+$, 1), 155 (10), 138 (23), 123 (9), 110 (22), 84 (100), 79 (75), 69 (32), 55 (11). **3b**: 170 (M$^+$, 2), 155 (26), 138 (19), 123 (28), 110 (65), 95 (18), 84 (100), 79 (82), 69 (32), 59 (12), 55(25). Anal. Calcd for C$_9$H$_{14}$O$_3$ (170.04): C, 63.53; H, 8.24. Found: C, 63.25; H, 8.60.

Reactions of 1,1-Dimethoxy-1,3-butadiene with Methyl Acrylate, Acrylonitrile, Dimethyl Fumarate, Dimethyl Maleate, Fumaronitrile, and Maleonitrile. Equimolar amounts of the reactants (2.6 mmol) in 14 mL of toluene were kept at 60 °C in the dark. Progress of the reactions was monitored by following the decrease in diene by GLC. After variable time from 15 d (methyl acrylate) to 5 d for fumaronitrile no more diene could be detected. During these times a white solid precipitate had been deposited which turned out not to be the expected cycloadducts but rather polymeric material. Under these conditions which were modeled after those of the reaction of 1-methoxy-1,3-butadiene with these dienophiles polymerization is faster than cycloaddition.

Cycloaddition of 2 to Dimethyl Dicyanofumarate. 1,1-Dimethoxy-1,3-butadiene (0.312 g, 2.7 mmol) and dimethyl dicyanofumarate (0.530 g, 2.7 mmol) were each dissolved in 18 mL of toluene The solutions were cooled to −70 °C and combined at this temperature. Immediately afterwards the solvent was removed at room temperature under vacuo (10 Pa). The residue consisted of 0.82 g (97%) of colorless solid which consisted of two isomers (NMR) and was recrystallized from petrolether at low temperature. Crystals (0.73 g, 87%) with mp 134−136 °C were isolated. The ratio of cycloadducts is 31:69 in the raw material and 35:65 in the recrystallized solid according to ^{1}H NMR. **15a**: ^{1}H NMR (CDCl$_3$): δ 6.09 (ddd, $^3J_{1-H,2-H} = 10.7$ Hz, $^3J_{1-H,6a-H} = 4.6$ Hz, $^3J_{1-H,6e-H} = 2.7$ Hz, 1 H, 1-H), 5.76 ("dt", $^3J_{1-H,2-H} = 10.7$ Hz, $^4J_{2-H,6e-H} = 2.4$ Hz, $^4J_{2-H,6a-H} = 2.0$ Hz, 1 H, 2-H), 3.93 (s, 3 H, CO$_2$CH$_3$), 3.88 (s, 3 H, CO$_2$CH$_3$), 3.60 (s, 3 H, OCH$_3$), 3.46 (s, 3 H, OCH$_3$), 3.25 ("dt", $^2J_{6a-H,6e-H} = 18.4$ Hz, $^3J_{1-H,6e-H} = 2.7$ Hz, $^4J_{2-H,6e-H} = 2.4$ Hz, 1 H, 6-He), 2.94 (ddd, $^2J_{6a-H,6e-H} = 18.4$ Hz, $^3J_{1-H,6a-H} = 4.6$ Hz, $^4J_{2-H,6a-H} = 2.0$ Hz, 1 H, 6-Ha). ^{13}C NMR (CDCl$_3$, DEPT): δ 166.07 (s, CO$_2$CH$_3$, C-10 or C-13), 163.12 (s, CO$_2$CH$_3$, C-10 or C-13), 128.15 (d, C-2), 125.09 (d, C-1), 115.99 (s, CN, C-9 or C-12), 115.73 (s, CN, C-9 or C-12), 96.79 (s, C-3), 54.93 (q, CO$_2$CH$_3$, C-11 or C-14), 54.01 (q, CO$_2$CH$_3$, C-11 or C-14), 51.05 (q, OCH$_3$, C-7 or C-8), 50.54 (q, OCH$_3$, C-7 or C-8), 55.14* (s, C-4 or C-5), 49.23 (s, C-4 or C-5), 33.20 (t, C-6). (An asterisk indicates this could also be C-4 or C-5 of the minor product.) **15b**: ^{1}H NMR (CDCl$_3$): δ 6.16 (ddd, $^3J_{1-H,2-H} = 10.7$ Hz, $^3J_{1-H,6-H} = 4.9$ Hz, $^3J_{1-H,6'-H} = 2.4$ Hz, 1 H, 1-H), 5.99 ("dt", $^3J_{1-H,2-H} = 10.7$ Hz, $^4J_{2-H,6-H} = 2.4$ Hz, $^4J_{2-H,6'-H} = 1.8$ Hz, 1 H, 2-H), 3.93 (s, 3 H, CO$_2$CH$_3$), 3.92 (s, 3 H, CO$_2$CH$_3$), 3.51 (s, 3 H, OCH$_3$), 3.46 (s, 3 H, OCH$_3$), 3.05 ("dt", $^2J_{6-H,6'-H} = 18.4$ Hz, $^3J_{1-H,6-H} = 2.4$ Hz, $^4J_{2-H,6'-H} = 2.4$ Hz, 1 H, 6-H), 2.95 ("dt", $^2J_{6-H,6'-H} = 18.4$ Hz, J = 2.4 Hz, 1 H, 6-H). ^{13}C NMR (CDCl$_3$, DEPT): δ 166.03 (s, CO$_2$CH$_3$, C-10 or C-13), 164.16 (s, CO$_2$CH$_3$, C-10 or C-13), 127.73 (d, C-2), 125.91 (d, C-1), 115.35 (s, CN, C-9 or C-12), 113.94 (s, CN, C-9 or C-12), 99.13 (s, C-3), 54.70 (q, CO$_2$CH$_3$, C-11 or C-14), 54.37 (q, CO$_2$CH$_3$, C-11 or C-14), 52.26 (q, OCH$_3$, C-7 or C-8), 51.47 (q, OCH$_3$, C-7 or C-8), 57.03* (s, C-4 or C-5), 47.39 (s, C-4 or C-5), 33.94 (t, C-6). (An asterisk indicates this could also be C-4 or C-5 of the major product.) Two-dimensional CH- and CC-COSY spectra were also recorded. IR (KBr, cm^{-1}) 2984 (ν_{CH_2}), 2230 (ν_{CN}), 1722 (ν_{CO}), 1650 ($\nu_{C=C}$). MS m/z (%): **15a**, 308 (M$^+$,2), 276 (2), 268 (8), 252

(71), 220 (22), 192 (30), 181 (26), 160 (28), 148 (43), 132 (39), 114 (100), 99 (27), 69 (20), 59 (41): **15b**, 308 (M$^+$, 2), 276 (2), 268 (4), 252 (60), 220 (15), 192 (14), 181 (13), 160 (14), 148 (21), 132 (19), 114 (100), 99 (17), 59 (24). Anal. Calcd for C$_{14}$H$_{16}$N$_2$O$_6$ (308.34): C, 54.55; H, 5.20; N, 9.09. Found: C, 54.41; H, 4.92; N, 9.12.

Low-Temperature ^{1}H NMR Experiments. Solutions of equimolar amounts of the reactants, precooled to −80 °C, were mixed and 2 min afterwards the ^{1}H NMR spectrum was recorded at −70 °C. Only signals of the (4 + 2) cycloadduct could be detected.

Trapping Experiment. 1,1-Dimethoxy-1,3-butadiene (0.30 g, 2.6 mmol), dissolved in 10 mL of acetonitrile and cooled to −50 °C, was added to a −50 °C solution of dimethyl dicyanofumarate (0.46 g, 2.6 mmol) in a mixture of 9 mL of acetonitrile and 10 mL of methanol within 5 min. Immediately afterwards the solvents were removed at −20 °C and 0.7 kPa. The solid raw material (0.81 g, 97%) consisted of three products: two diastereomeric trapping products and the cycloadduct. The material was dissolved in 38 mL of *n*-hexane and cooled to −78 °C and 0.73 g (88%) of slightly yellow crystals with mp of 75 °C dec were isolated, the cycloadduct remained in solution. The ratio of the two diastereomeric 1,1,1-trimethoxy-5,6-bis(methoxycarbonyl)-5,6-dicyano-(*E*)-hex-2-enes **20a** and **20b** is 67:33. ^{1}H NMR (300 MHz, CDCl$_3$) of **20a**: δ 5.88 (ddd, $^3J_{5-H,6-H}$ = 15.6 Hz, $^3J_{4-H,5-H}$ = 7.1 Hz, $^3J_{4'-H,5-H}$ = 8.0 Hz, 1 H, 5-H), 5.51 ("dt", $^3J_{5-H,6-H}$ = 15.6 Hz, $^4J_{4-H,6-H}$ = 1.0 Hz, $^4J_{4'-H,6-H}$ = 1.0 Hz, 1 H, 6-H), 4.31 (s, 1 H, 2-H), 3.85 (s, 6 H, CO$_2$CH$_3$), 3.14 (s, 9 H, OCH$_3$), 3.25 (ddd, $^2J_{4-H,4'-H}$ = 14.0 Hz, $^3J_{4-H,5-H}$ = 7.1 Hz, $^4J_{4-H,6-H}$ = 1.0 Hz, 1 H, 4-H), 2.94 (ddd, $^2J_{4-H,4'-H}$ = 14.0 Hz, $^3J_{4'-H,5-H}$ = 8.0 Hz, $^4J_{4'-H,6-H}$ = 1.0 Hz, 1 H, 4'-H). ^{13}C NMR (75 MHz, CDCl$_3$, DEPT) of **20a**: δ 165.96 (s, *C*O$_2$CH$_3$), 162.75 (s, *C*O$_2$CH$_3$), 133.47 (d, C-6), 126.18 (d, C-5), 115.01 (s, CN), 112.33* (s, C-7), 54.63 (q, CO$_2$*C*H$_3$), 54.51 (q, CO$_2$*C*H$_3$), 49.51 (q, OCH$_3$), 48.42 (s, C-3), 42.79 (d, C-2), 38.67 (t, C-4). (An asterisk indicates this may also be C-7 of the minor product.) Further spectroscopic characterization was done by H,H- and C,H-COSY in CDCl$_3$. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.00 (ddd, $^3J_{5-H,6-H}$ = 15.6 Hz, $^3J_{4-H,5-H}$ = 7.3 Hz, $^3J_{4'-H,5-H}$ = 8.1 Hz, 1 H, 5-H), 5.60 (d, $^3J_{5-H,6-H}$ = 15.6 Hz, 1 H, 6-H), 4.14 (s, 1 H, 2-H), 3.83 (s, 6 H, CO$_2$CH$_3$), 3.15 (s, 9 H, OCH$_3$), 2.88 (m, 2 H, 4-H). ^{13}C NMR (75 MHz, CDCl$_3$, DEPT): δ 165.72 (s, *C*O$_2$CH$_3$), 162.87 (s, *C*O$_2$CH$_3$), 133.95 (d, C-6), 126.49 (d, C-5), 115.39 (s, CN), 111.89* (s, C-7), 54.81 (q, CO$_2$*C*H$_3$), 53.88 (q, CO$_2$*C*H$_3$), 49.55 (q, OCH$_3$), 47.83 (s, C-3), 41.73 (d, C-2), 37.81 (t, C-4). (An asterisk indicates this could also be C-7 of the major product.) Further spectroscopic characterization was done by H,H- und C,H-COSY in CDCl$_3$. IR (KBr, cm^{-1}) 2240 (ν_{CN}), 1762 (ν_{CO}), 1634 ($\nu_{C=C}$). MS *m/z* (%): **20a**, 340 (M$^+$, 2), 254 (3), 238 (44), 210 (78), 206 (34), 178 (38), 170 (91), 153 (12), 146 (26), 138 (53), 100 (100), 68 (28), 59 (55); **20b**, 340 (M$^+$, 2), 254 (5), 238 (32), 210 (100); 206 (29), 178 (50), 170 (55), 153 (16), 146 (30), 138 (41), 100 (43), 68 (18), 59 (54). Anal. Calcd for C$_{15}$H$_{20}$N$_2$O$_7$ (340.12): C, 52.94; H, 5.88; N, 8.24. Found: C, 53.22; H, 6.02; N, 8.11.

Cycloaddition of 2 to Methyl 2,2-Dicyanoacrylate. Cooled solutions (−60 °C) of diene **2** (0.300 g, 2.6 mmol) and the dienophile (0.326 g, 2.6 mmol) each in 12 mL of toluene were mixed. After 1 h the solvent was removed under vacuum (10 Pa) and 0.600 g (96%) of a colorless solid was isolated. Recrystallization from diethyl ether gave 0.52 g (83%) of product with mp 109−111 °C. ^{1}H NMR (200 MHz, CDCl$_3$) of **18**: δ 6.08 (ddd, $^3J_{1-H,2-H}$ = 10.6 Hz, $^3J_{1-H,6-H}$ = 4.5 Hz, $^3J_{1-H,6'-H}$ = 2.7 Hz, 1-H), 5.76 (dt, $^3J_{1-H,2-H}$) = 10.6 Hz, $^4J_{2-H,6-H}$ = 2.2 Hz, 2-H), 3.85, 3.66, 3.39 (s, OCH$_3$), 3.42 (dd, $^3J_{5-H,6-H}$ = 11.4 Hz, $^3J_{5-H,6-H'}$ = 6.0 Hz, 5-H), 2.62 (dm, $^2J_{6-H,6-H'}$ = 19.0 Hz, 6-H, 6-H′). ^{13}C NMR (50 MHz, CDCl$_3$): δ 169.46 (*C*O$_2$CH$_3$), 130.06, 125.25 (C-1,C-2), 113.48, 111.42 (CN), 98.26 (C-3), 53.10, 51.17, 51.06 (OCH$_3$), 45.15 (C-5), 42.70 (C-4), 26.57 (C-6). IR (KBr, cm^{-1}) 2270 (ν_{CN}), 1752 (ν_{CO}), 1635 ($\nu_{C=C}$). MS *m/z* (%): 238 (M$^+$, 1), 219 (19), 191 (10), 159 (16), 148 (9), 134 (19), 114 (100), 99 (20), 69 (10). Anal. Calcd for C$_{12}$H$_{14}$N$_2$O$_4$ (238.16): C, 60.5; H, 5.88; N, 11.76. Found: C, 60.43; H, 5.91; N, 12.02.

Low Temperature ^{1}H-NMR Experiment. Diene **2** (22.5 mg) was dissoved in 0.6 mL of [D$_8$]toluene, cooled to −80 °C, and added to a solution of 24.6 mg of dienophile in 0.6 mL of toluene, cooled to −80 °C. After 1 min the first ^{1}H-NMR spectrum was recorded at −70 °C. Besides the signals of the (4 + 2) cycloadduct and those of residual diene other signals were observed in a 65:35 ratio with respect to the (4 + 2) cycloadduct. The latter ones and those of the residual diene disappeared slowly above −30 °C in favor of the (4 + 2) cycloadduct. A ^{1}H,^{1}H-COSY spectrum allowed the establishment of a proton connectivity pattern. ^{1}H NMR (300 MHz, [D$_8$]toluene) of **23**: δ 3.26, 3.25 (s, 2OCH$_3$), 3.51 (m, 1-H, H$_A$), 3.23 (m, 1-H, H$_E$), 2.42 (m, 1-H, H$_D$), 2.24 (m, 1-H, H$_B$), 1.80 (m, 1-H, H$_C$), Thus the proton at 2.42 ppm is correlated with two protons at δ 2.24 and 1.80. The two latter ones are correlated further with a proton at δ 3.51. This proton in turn correlates with one at δ 3.23. The chemical shift of δ 3.23 compares favorably with that of 3.09 for the olefinic protons of diethyl ketene acetal[24] and is associated with the olefinic proton at the exocyclic double bond.

Supporting Information Available: Experimental details and spectroscopic and analytical characterization of the cycloadducts and trapped zwitterions (12 pages). See any current masthead page for ordering and Internet access instructions.

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