Influence of Lewis Acids on the Cycloaddition Reactions of Cyano- and Carbomethoxy-Substituted Olefins

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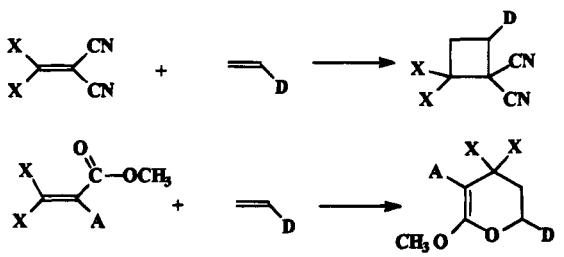
The reactions of electrophilic olefins substituted with cyano and/or carbomethoxy groups with donor olefins are investigated. The donor olefins include, in order of decreasing donor character, phenyl vinyl sulfide, isobutyl vinyl ether, *tert*-butyldimethylsilyl vinyl ether, *p*-methoxy- and *p*-methylstyrene, and styrene. The reactions vary from [2 + 2] cycloadditions to Diels–Alder reactions to spontaneous free radical copolymerizations. The course of the reaction is determined by both the electron disparity between the two reacting olefins and by the substitution pattern on the electrophilic olefin. Lewis acids ($ZnCl_2$ or ethereal $LiClO_4$) are added to form complexes with the acceptor olefins, resulting in a larger electron disparity between the reactants. With the highly electrophilic olefins with *gem*-dicyano groups, such as tetracyanoethylene, dimethyl 1,1-dicyanoethylene-2,2-dicarboxylate, and methyl β,β-dicyanoacrylate, [2 + 2] cycloadditions occur at room temperature, except for the reaction of TCNE with styrene which has to be carried out in 5 M ethereal $LiClO_4$. With olefins containing one cyano and one carbomethoxy group on the same carbon, dimethyl dicyanofumarate and dimethyl cyanofumarate, inverse electron demand Diels–Alder cycloaddition involving the ester substituent dominates in reactions with the most nucleophilic olefins. The [2 + 2] cycloadducts can be obtained in the presence of Lewis acid. With olefins with two carbomethoxy-substituents on the same carbon, dimethyl 2-cyanoethene-1,1-dicarboxylate and trimethyl ethylenetricarboxylate, the reactions are much slower, and [2 + 4] cycloaddition dominates with the most reactive donor olefins, while the [2 + 2] cycloadduct can be obtained in the presence of Lewis acid. With several acceptor olefins, free radical copolymerizations compete with the cycloadditions when reacted with the least reactive donor olefins. The reaction tendencies are discussed in light of the electron disparity between the olefins. The influence of the Lewis acid on the conformational equilibria and on the reaction course is also addressed.

Introduction

The reactions of electron-rich olefins with electron-poor olefins lead to both cycloadducts and polymers. As outlined in a recent review article, the nature of the reaction products and the rate of the reaction are greatly dependent on the electron disparity which exists between the two reaction partners.[1] The reaction products also depend on the specific substituents on the olefinic double bond. In this study we will concentrate on the reactions of electron-rich olefins (high HOMO) with electrophilic olefins (low LUMO) in which the substituents are exclusively cyano and carbomethoxy groups.

From earlier studies of the reactions of these electrophilic olefins, it is known that the product of the cycloaddition is largely determined by the nature of the substituents on the most electrophilic terminus of the electrophilic olefin.[2] For olefins with two cyano groups on one carbon (lowest LUMO), cyclobutane adducts with the electron-rich olefin are the most common outcome. For olefins with one ester and one cyano group on the most electrophilic terminus, inverse electron-demand Diels–Alder reaction involving the ester carbonyl is the dominant cycloaddition reaction.[3] The olefins with two ester functionalities on one carbon (highest LUMO) have rather low reactivity, but again the inverse electron-demand cycloaddition is usually observed.



X = H, CN or COOMe; A = CN or COOMe
D = donor substituent such as OR, SR or aryl

Spontaneous polymerizations often accompany cycloadditions when electron-rich olefins react with electron-poor olefins.[4,5] The electron disparity between the reaction partners (HOMO–LUMO gap) has a great influence on the nature of the spontaneous polymerizations. Great electron disparity, such as between *N*-vinylcarbazole and dimethyl 1,1-(dicyanoethylene)-2,2-dicarboxylate, leads to the homopolymer of the electron-rich olefin formed via cationic propagation.[6] With less extreme olefins, such as *p*-methoxystyrene and dimethyl cyanofumarate, free radical copolymerization is the main outcome of the reaction.[7] We have previously postulated that the true initiators in these systems are the tetramethylene inter-

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(5) The values obtained for the LUMO levels of all electrophilic olefins by AM1 calculations are submitted as supplementary material. A detailed discussion of these data is not possible at this time as we cannot calculate the LUMO levels of these electrophilic olefins in the presence of a Lewis acid or of lithium perchlorate.
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mediates, which are zwitterionic or diradical in nature depending on the reaction partners.[2,4]

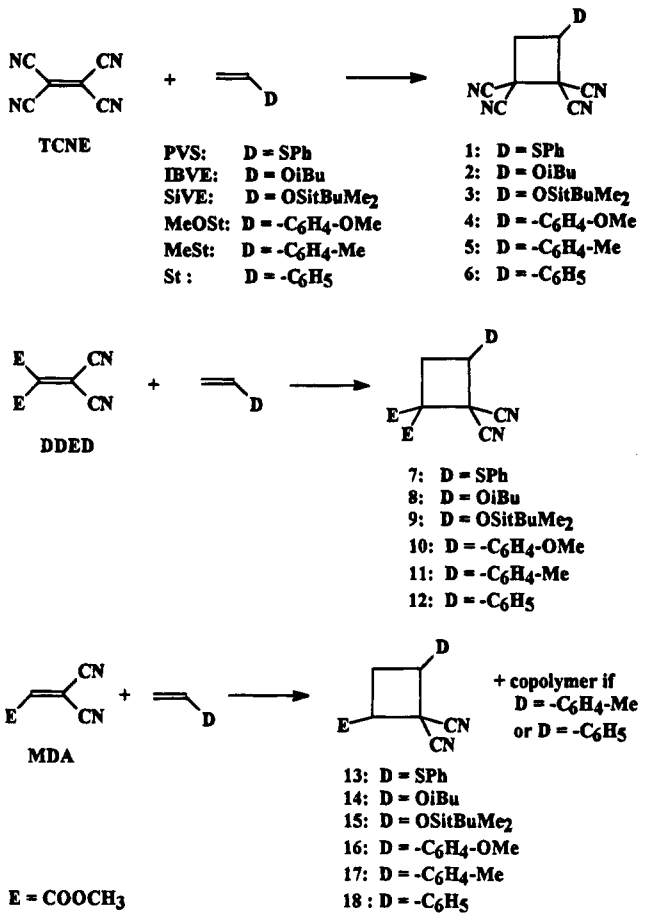
This paper describes a systematic study of the influence of the electrophilicity and substitution pattern of the acceptor olefins on their reactions with electron-rich olefins going from the largest electron disparity between the reaction partners to the least. To achieve a clear overview of the reactions, the results from previous papers will be included in the description of the results. The electron-rich olefins used in this study are moderately electron-rich and range from vinyl sulfides and vinyl ethers to *p*-methoxystyrene and styrene.[8] The acceptor olefins have cyano and carbomethoxy substituents. The electrophilicity of these acceptor olefins decreases as the substitution decreases and as cyano groups are gradually replaced by carbomethoxy groups.[9]

On the other hand, the electrophilicity of these olefins can be increased by the addition of Lewis acids which form complexes with the cyano and/or carbomethoxy substituents, thereby lowering the LUMO level and reducing the HOMO–LUMO gap. Lewis acids are often used to enhance the Diels–Alder reactions of diene/dienophile combinations.[10] However, there are only sporadic reports in the literature of Lewis acid-catalyzed [2 + 2]-cycloadditions.[11] Several of these reactions were found to be stereoselective which was ascribed to steric effects[12] or to the asymmetric nature of the Lewis acid used.[8]

The effect of 5 M lithium perchlorate in ether on Diels–Alder reactions has generated a lot of interest recently.[13] Dramatic accelerations of the DA reactions were observed, and the usefulness of the reactions was explored.[14] Originally, the effect of ethereal $LiClO_4$ was ascribed to the large "internal pressure" of the solvent. However, more recently several reports have surfaced describing the lithium cation as a Lewis acid.[15] In a recent paper we have described the effect of ethereal $LiClO_4$ on a few selected olefin–olefin reactions.[16] Some previously unsuccessful [2 + 2] cycloadditions were found to proceed in ethereal $LiClO_4$. Interestingly, this electrophilic catalysis was also able to divert previously reported [2 + 4] cycloadditions into a [2 + 2] cycloaddition pathway. These results are also included in this paper.

Lewis acids also influence copolymerizations of electron-rich hydrocarbon olefins with electron-poor olefins, such as acrylonitrile, by favoring spontaneous reactions and alternation in the polymer backbone.[17]

Scheme 1. Reactions of 1,1-Dicyano Olefins



Results

We will discuss the reactions in order of decreasing electrophilicity of the acceptor olefin. These olefins are categorized according to the two substituents on the most electrophilic carbon of the double bond, as these substituents have a major impact on the reaction outcome. The olefins are arranged from geminal dicyano, to cyano ester, to diester termini. The electron-rich olefins range in nucleophilicity from phenyl vinyl sulfide (PVS),[8] to isobutyl vinyl ether (IBVE), to *tert*-butyldimethylsilyl vinyl ether (SiVE), to *p*-methoxystyrene (MeOSt), to *p*-methylstyrene (MeSt), to styrene (St).

The reactions were first investigated in standard room temperature conditions. The reactions were followed by the disappearance of the color of the charge transfer complex or by NMR analysis of aliquots. In the cases where no cyclobutanes were formed, Lewis acidic catalysts were added. First the use of 5 M ethereal $LiClO_4$ was checked, but in some cases the reactants were not soluble in this medium. The reactions were then run in the presence of $ZnCl_2$ as the Lewis acid. When Lewis acids were added, some complications in the workup did arise. Moreover, the Lewis acid can initiate cationic polymerization of the donor olefin as will be discussed below.

1,1-Dicyano Olefins (Scheme 1). Tetracyanoethylene (TCNE). TCNE is a widely used electrophilic olefin in [2 + 2] cycloadditions with nucleophilic olefins,

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and its reactions with vinyl ethers and vinyl sulfides have been extensively studied by Huisgen.[18] The [2 + 2]-cycloadditions take place at room temperature in acetonitrile through zwitterionic tetramethylene intermediates. The same holds true for the reaction of TCNE with MeOSt.[19] The reactivity of the electron-rich olefins decreases in the order of decreasing nucleophilicity: PVS, IBVE, and MeOSt.[6]

St does not react with TCNE in standard reaction conditions. This reaction has only been described at high pressure leading to a Diels–Alder adduct in reversible fashion.[20] However, when we used 5 M ethereal $LiClO_4$ as solvent, the [2 + 2]-cycloaddition of TCNE and styrene occurred at room temperature through the bright yellow charge transfer complex. This charge transfer complex gradually faded, and the reaction was finished in 2 days, giving the new crystalline cyclobutane adduct **6** as a solid in 67% yield after purification. The same behavior was observed in the reaction of TCNE with MeSt in ethereal $LiClO_4$, leading to the cyclobutane adduct **5**.

Dimethyl 2,2-Dicyanoethylene-1,1-dicarboxylate (DDED). The spontaneous [2 + 2]-cycloadditions and copolymerizations of the tetrasubstituted electrophilic olefin DDED and various nucleophilic olefins were studied previously.[21] The initially formed charge-transfer complex, witnessed by the intense color, leads to a tetramethylene intermediate which then collapses to a cyclobutane. We have postulated that this same tetramethylene initiates the copolymerization, depending on the reaction conditions. Cycloaddition of DDED with IBVE at room temperature led exclusively to cyclobutane **8**. With MeOSt, [2 + 2]-cycloadduct **10** and a small amount of the homopoly(MeOSt) were obtained in bulk. With the least nucleophilic olefins, St and MeSt, spontaneous copolymerizations with DDED took place at room temperature in bulk, while [2 + 2]-cycloadditions occurred in acetonitrile.

To complete the series, the reactions of DDED with the electron-rich olefins PVS and SiVE were investigated and the expected [2 + 2]-cycloadducts **7** and **9** were obtained. The time required for the reaction corresponded well with the reactivity of the electron-rich olefin: St required the longest time (4 days) and PVS required the least, 20 h. The cyclobutane of PVS and DDED **7** was obtained in 89% yield after purification by column chromatography, while the cyclobutane adduct with SiVE **9** was obtained in 85% yield by NMR. The latter material was so sensitive that no purification could be done without decomposition of the cyclobutane to unidentified products.

Methyl β,β-Dicyanoacrylate (MDA). We have previously reported that the reaction of MDA with MeOSt leads to a variety of products depending on the solvent used.[22] Alternating copolymerization dominated in nonpolar solvents, while cycloaddition to cyclobutane **16** was favored in protic polar solvents.

In this study, [2 + 2]-cycloadditions of MDA with the three most nucleophilic olefins, PVS, IBVE, and SiVE, proceeded at room temperature giving the corresponding cyclobutanes **13**, **14**, and **15**. Again, the time required for the reaction corresponded well with the reactivity of the nucleophilic olefin: the more nucleophilic the olefin used, the less time was required for complete reaction. For PVS and IBVE, the disappearance of the charge transfer complex color indicated the end of the reaction, 1 and 2 days, respectively. Since for SiVE no charge transfer is observed, the reaction was followed by ^1H NMR spectroscopy and was complete within 2 days.

Two isomers of cyclobutane products were obtained, yielding oily products in every case. For PVS, two isomeric cyclobutanes, *cis*- and *trans*-**13**, were obtained in 80% yield. The ratio of cis-/trans-isomer was 86:14. The isomer structures were assigned by comparison of their ^1H NMR spectra with the spectra of the known isomers of the [2 + 2]-cycloadduct of MeOSt and MDA **16**.[22] A characteristic of the ^1H NMR spectra of the *cis*-cyclobutanes is that the protons H_1 (on ester-substituted C) and H_3 (on thiophenyl C) give peaks with similar splitting patterns, usually doublets of doublets with coupling constants in the range 10–11 Hz and 8–9 Hz, because they have similar relationships to the two vicinal protons at C_4. Also the peaks for H_3 of the trans-isomer are further downfield than those of the cis-isomer. In this case, the *cis*-cyclobutane was easily identified by the peaks of H_3 at δ 4.2 ppm, while those of the trans-isomer were further downfield at δ 4.4 ppm. These cis- and trans-isomers of **13** could be separated by column chromatography. The cis-isomer was crystalline, while the trans-isomer was an oil.

For IBVE, the crude cyclobutane oils could be purified by quickly passing through a silica gel column using 1% triethylamine to decrease the acidity of silica gel. The ratio of cis-/trans-isomer **14** was 40:60 as determined from the ^1H NMR spectra. The peaks for H_3 of the trans-isomer were at δ 4.6 ppm, while those of the cis-isomer were at δ 4.3 ppm. The cyclobutanes derived from the silyl ether **15** (cis/trans ratio 67:33) were so unstable that no further purification could be done without decomposition.

For the less nucleophilic olefin MeSt, the [2 + 2]-cycloaddition did not take place at room temperature in 1,2-dichloroethane, but it did occur in 5 M ethereal $LiClO_4$ as solvent. A bright yellow charge-transfer complex was observed. As part of a general trend observed for less reactive partners, spontaneous free radical alternating copolymerization accompanied this [2 + 2]-cycloaddition. The polymerization could be inhibited by addition of a free radical inhibitor and/or by using dilute conditions. The ratio of *cis*-/*trans*-cyclobutanes **17**, based on the integration of ^1H NMR spectra, was equal to 85:15. The cis-isomer could be recrystallized at −50 °C, while the trans-isomer was an oil.

The reaction mixture of MDA and St in 5 M ethereal $LiClO_4$ also turned bright yellow due to the charge transfer complex, but the copolymerization totally dominated. However, in the presence of a free radical inhibitor, 2,2,6,6-tetramethylpiperidinoxyl radical (TEMPO), the desired cyclobutane **18** was obtained in 40% yield.

Cyano Ester Olefins. As mentioned in the Introduction, inverse electron-demand [2 + 4]-cycloaddition is the favored cycloaddition pathway in the reactions of electrophilic olefins with one cyano and one carbomethoxy group at the most electrophilic terminus. The question arises if we can control the reaction conditions to obtain the cyclobutane adducts.

Dimethyl Dicyanofumarate (DCF). We have previously reported the reactions of DCF with nucleophilic olefins such as IBVE, MeOSt, MeSt, and St at 70 °C leading to the corresponding 3,4-dihydro-2*H*-pyran ad-

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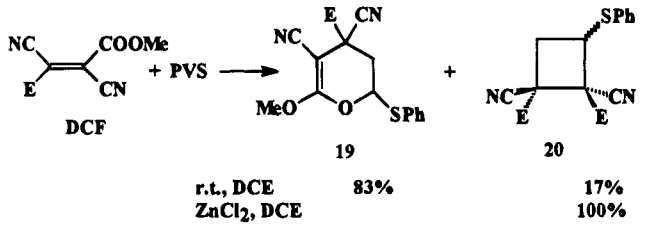
ducts **21**, **22**, **24**, and **25**, respectively.[16,23] Alternating copolymerizations also took place when DCF was mixed with MeOSt or St.[24]

In this study, when PVS was used as the nucleophilic olefin with DCF, two competing cycloadditions occurred at room temperature in 1,2-dichloroethane. The major product was the 3,4-dihydro-2*H*-pyran derivative **19** (83%) from the inverse electron-demand Diels–Alder reaction and the [2 + 2]-cycloadduct **20** was present as a minor product (17%), as determined by ^{1}H-NMR. When 1 molar equiv of zinc chloride was added to the reaction mixture, the [2 + 2]-cycloaddition occurred at room temperature giving cyclobutane as the only product. Again, two isomeric cyclobutanes were obtained which were separated by column chromatography, giving the cyclobutanes in 62% yield in a cis/trans ratio 25/75. An effort to promote the [2 + 2]-cycloaddition using 5 M ethereal $LiClO_4$ did not succeed due to the poor solubility of the electrophilic olefin in this medium.



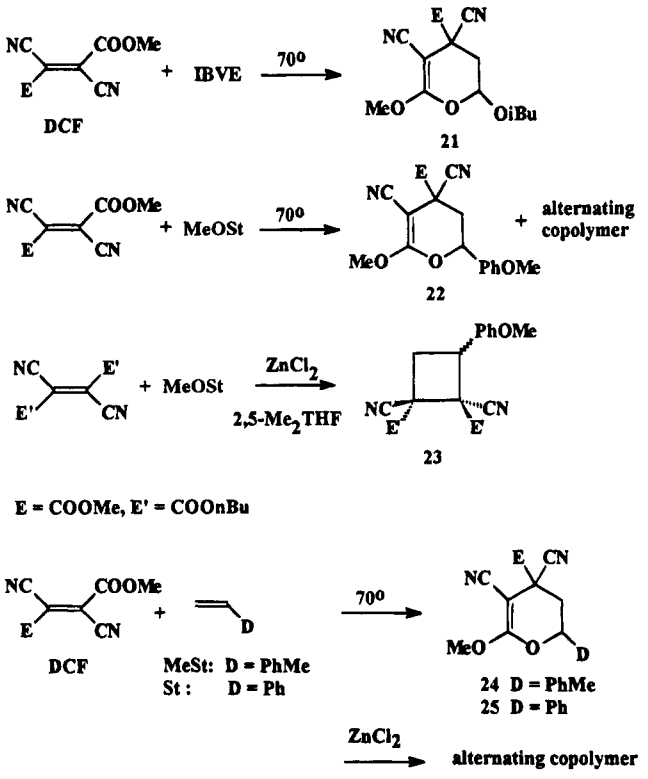
Because the dimethyl ester is so extremely insoluble, dibutyl dicyanofumarate was used in the following experiments. Using 1 molar equiv of zinc chloride in 1,2-dichloroethane in the reactions of dibutyl dicyanofumarate with IBVE and MeOSt as electron-rich olefins resulted in cationic homopolymerization of the latter. This result is reasonable since MeOSt and IBVE easily undergo cationic homopolymerization in the presence of acid. Attempts were made to inhibit these cationic homopolymerizations by the addition of a hindered base such as ethyldiisopropylamine to the system, but this led only to side reactions.

We then resorted to the use of 2,5-dimethyltetrahydrofuran as solvent. Its basicity was expected to inhibit the cationic homopolymerization, while it cannot homopolymerize like its parent tetrahydrofuran. For MeOSt as the electron-rich olefin and 1 molar equiv of zinc chloride as Lewis acid in 2,5-dimethyltetrahydrofuran at room temperature, cyclobutane **23** was obtained in 75% yield.

When IBVE and SiVE were tried under these optimum conditions, unidentified products were always obtained, which may be due to the instability of the cyclobutanes in the acidic reaction medium.

When MeSt or St was used as nucleophilic olefin in the presence of $ZnCl_2$, copolymerization was always obtained exclusively, even when free radical inhibitor was added.

Dimethyl Cyanofumarate (CNF) (Scheme 2). Using dimethyl cyanofumarate CNF as the electrophilic olefin leads generally to the same reaction products as with DCF. Inverse electron-demand Diels–Alder reaction takes place with electron-rich olefins giving the corresponding 3,4-dihydro-2*H*-pyran at low concentrations, as was previously reported for IBVE and MeO-



St.[16,23] In the case of MeOSt efficient free radical copolymerization occurred at higher concentration and this polymerization has been studied in great detail.[5,7] The reaction of CNF with MeSt similarly led to spontaneous copolymerization.[25]

In this study, PVS underwent spontaneous cycloaddition with CNF giving mainly the [2 + 4]-cycloadduct **26** and a small amount of cyclobutane **27**. This was confirmed by following the reaction by ^{1}H NMR spectroscopy. Three different methods were used to obtain the cyclobutane **27** as the only product, namely using 1 molar equiv of zinc chloride in benzene, using 5 M ethereal $LiClO_4$ as solvent, or running the reaction at higher temperature (refluxing acetonitrile) in the presence of a trace of free radical inhibitor, 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide, for at least 2 days. The thermal and Lewis acid promoted reactions led to comparable yields of **27**, in the range of 70–80%. Two isomers were obtained with a cis/trans ratio of 80:20 for the Lewis acid promoted reaction and 43:57 for the thermal [2 + 2]-cycloaddition. These two isomers were separated by column chromatography. Again, the cis-isomer was crystalline, while the trans-isomer was an oil.

In refluxing acetonitrile the reaction of either IBVE or MeOSt with CNF led to mixtures of the dihydropyran derivative, **28** and **32**, respectively, with trace amounts of the corresponding cyclobutane **29** or **33**. Using 5 M ethereal $LiClO_4$ as solvent or using 1 molar equiv of $ZnCl_2$ afforded instead the homopolymers of IBVE and MeOSt. Attempts to use base (ethyldiisopropylamine or 2,6-lutidine) to inhibit cationic homopolymerization did not succeed due to reaction between CNF and the base. In contrast, when 1 M $ZnCl_2$ in 2,5-dimethyltetrahydrofuran was used, the [2 + 2]-cycloadducts **29** and **33** were obtained exclusively. The cyclobutane adduct **33** of MeOSt and CNF was obtained in 72% yield after aqueous workup (cis/trans ratio 50:50). In the case of IBVE as the electron-rich olefin, cyclobutane **29** was isolated along

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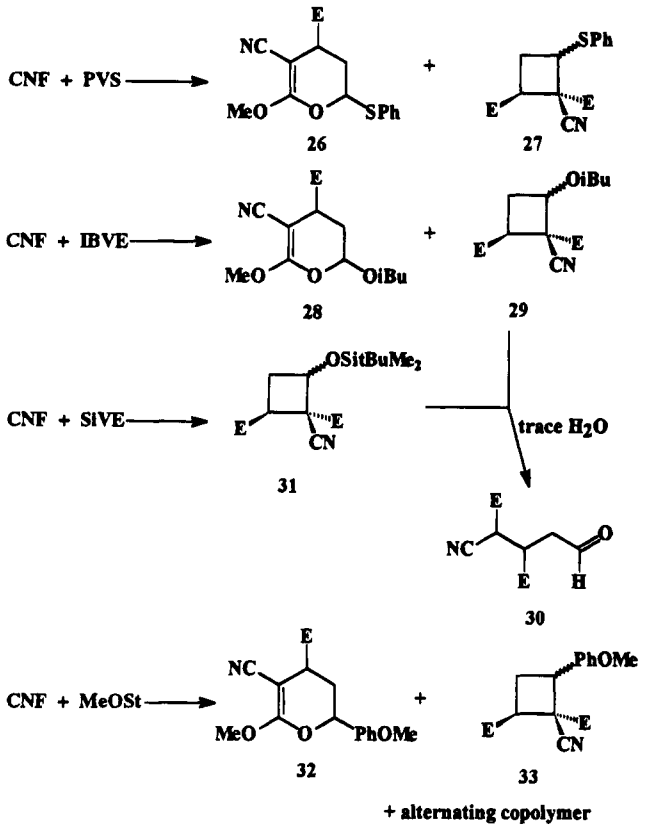
(25) Hall, H. K., Jr.; Daly, R. C. *Macromolecules* **1975**, *8*, 22.

Scheme 2. Reactions of Dimethyl Cyanofumarate CNF



with the ring-opened aldehyde derivative, 4-cyano-3,4-dicarbomethoxybutanal (**30**), which is believed to be formed through acid hydrolysis of the isobutyl ether group. This ring-opening process occurred during the aqueous workup procedure and could be avoided by removing the $ZnCl_2$ with anhydrous Me_4NCl. The crude cyclobutane **29** was obtained in 72% yield with a cis/trans ratio of 58:42, as determined by the integration of ^1H NMR spectra. No further purification could be performed without partial hydrolysis of this cyclobutane.

When SiVE was used as the electron-rich olefin under the optimum conditions, 1 M $ZnCl_2$ in 2,5-dimethyltetrahydrofuran at room temperature, a small amount of [2 + 2]-cycloadduct **31** was obtained along with the ring-opened aldehyde **30** as the major product. This was do to the extreme hydrolytic instability of the siloxy substituent.

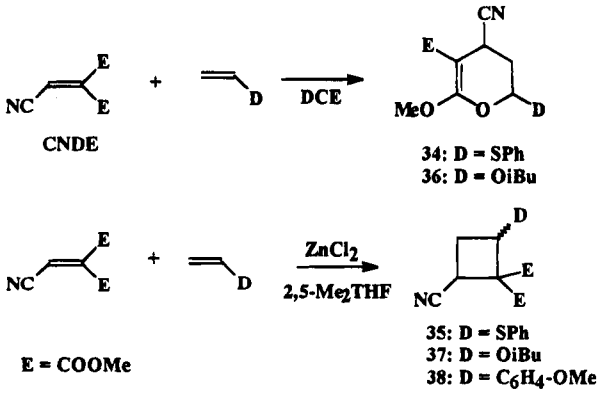
Spontaneous copolymerizations took place when the less nucleophilic olefins MeSt and St were mixed with CNF in the presence of $ZnCl_2$. In the case of MeSt, a trace of cyclobutane adduct was observed in the NMR spectrum if 3 equiv of $ZnCl_2$ was used.

The different reaction pathways were investigated in more detail for the reaction of IBVE with CNF. The cycloaddition was run in deuterated acetonitrile at room temperature and followed by ^1H-NMR spectroscopy. The 3,4-dihydro-2*H*-pyran **28** formed in essentially quantitative yield after 7 days, along with a trace amount of copolymer. The pyran derivative **28** was purified and redissolved in 2,5-dimethyltetrahydrofuran in the presence of 1 mol equiv of $ZnCl_2$. An aliquot was taken at different time intervals and treated with Me_4NCl to remove the Lewis acid. The isomerization of pyran **28** to cyclobutane **29** was followed by NMR. The peaks at δ 5–6 ppm are characteristic for the acetal proton, while the peaks at δ 4–5 ppm are due to H_3 adjacent to the isobutoxy group in the cyclobutane **29**. This isomerization took 2 weeks, while the $ZnCl_2$-catalyzed [2 + 2]-cycloaddition of IBVE and CNF was complete in 3 days. This experiment showed that the [2 + 4]-cycloadduct was not an intermediate in the [2 + 2]-cycloaddition. In addition, it showed that the cyclobutane adduct is the thermodynamically favored product in the presence of Lewis acid.

Diester olefins. Dimethyl 2-Cyanoethylene-1,1-dicarboxylate (CNED). This olefin is less reactive than dimethyl cyanofumarate. Only with the highly nucleophilic olefin IBVE has the inverse electron-demand Diels–Alder reaction to give **36** been reported.[16,23] With MeOSt a mixture of the copolymer and the double Diels–Alder adduct was obtained.[26]

In this work when PVS was used as the nucleophilic olefin, only inverse electron-demand Diels–Alder reaction to give **34** occurred at room temperature as determined by ^1H NMR spectroscopy. However, when the reaction was done in the presence of 1 mol equiv of $ZnCl_2$ or using 5 M ethereal $LiClO_4$, the cyclobutane **35** is retained exclusively in 70–85% yield (cis/trans ratio ~80:20). The two isomers were separated by column chromatography, giving oily *trans*-cyclobutane and crystalline *cis*-cyclobutane.

When IBVE and MeOSt were used as nucleophilic olefins, the [2 + 2]-cycloaddition again succeeded using 1 M $ZnCl_2$ in 2,5-dimethyltetrahydrofuran as solvent. For IBVE, a small amount of the ring-opening aldehyde product was obtained along with the cycloadduct **37**. Again ring-opening was avoided by workup of the reaction mixture with anhydrous Me_4NCl. For MeOSt the two isomeric cyclobutanes **38** were obtained in 82% yield with a cis/trans ratio of 80:20. Recrystallization in ether at −50 °C afforded the crystalline *cis*-cyclobutane and the oily *trans*-cyclobutane. Neither pyran nor copolymer was formed in this case.

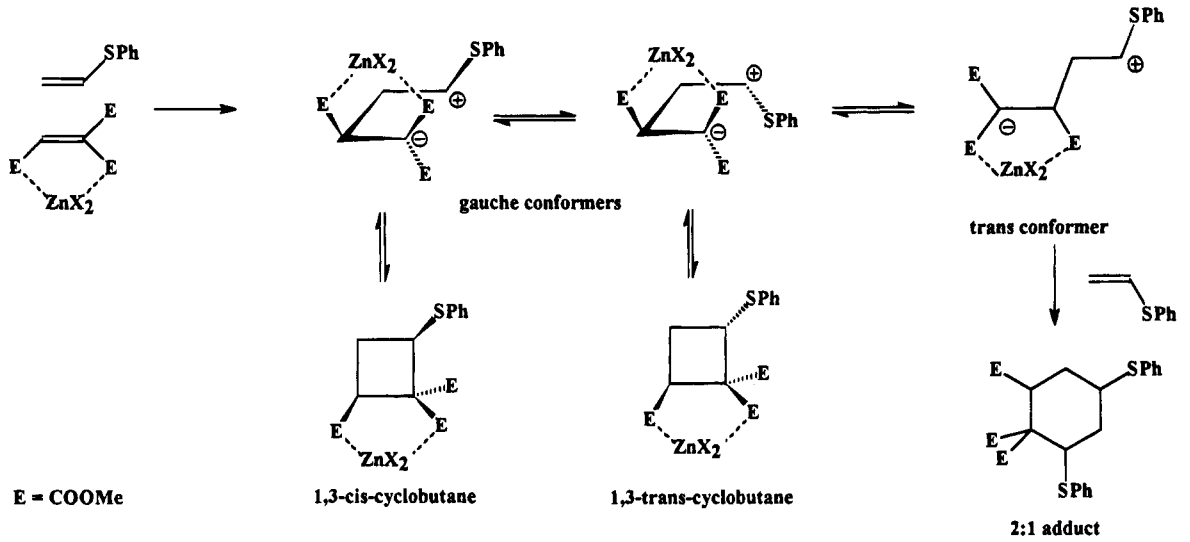


No reaction occurred upon mixing CNDE with MeSt or St, while in the presence of $ZnCl_2$ only alternating copolymers were observed.

Trimethyl Ethylenetricarboxylate (TrE). The inverse electron-demand Diels–Alder reaction of this electron-poor olefin with IBVE and MeOSt at 70 °C to give **41** and **42**, respectively, has been reported, accompanied

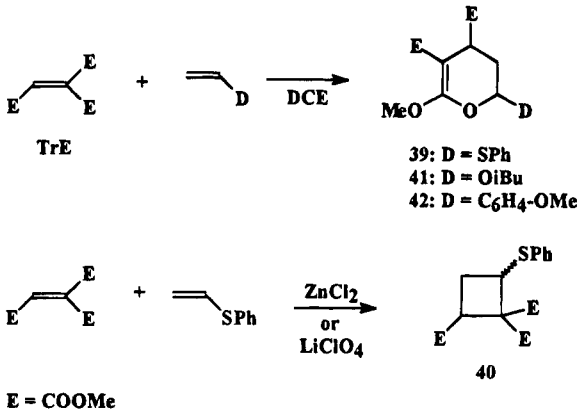
(26) Gillard, M.; Hall, H. K., Jr. Unpublished results.

Scheme 3. Influence of Lewis Acid



by spontaneous free radical copolymerization which can be inhibited.[16,23]

In this study, [2 + 4]-cycloaddition to give **39** occurred exclusively when PVS was used. The [2 + 2]-cycloaddition of PVS and TrE took place when 1 M $ZnCl_2$ was used or if the reaction was carried out in 5 M ethereal $LiClO_4$. Two isomeric cyclobutanes **40** were obtained with a cis/trans ratio of 38:62 for $ZnCl_2$ as Lewis acid and 57:43 for lithium perchlorate, as determined by integration of the ^1H NMR spectra. The triplets for H_3 (on thiophenyl C) at δ 4.2 and for H_1 at δ 3.4 are diagnostic for the cis-isomer. The triplet for H_3 at δ 4.8 is diagnostic for the *trans*-cyclobutane. These two isomers were separated by column chromatography. The *cis*-cyclobutane was again crystalline, whereas the *trans*-cyclobutane was an oil.[41]



Reaction of MeOSt and IBVE with TrE in the presence of Lewis acid led to alternating copolymers and inverse electron-demand Diels–Alder reaction. Even with 3 equiv of Lewis acid, no [2 + 2] cycloadducts were obtained. The reactions of TrE with St and MeSt were not investigated in the presence of Lewis acid due to their extremely low reactivity.

Different Lewis Acids. For a more in-depth study of the catalysis of [2 + 2]-cycloadditions by a variety of Lewis acids, we chose the reaction between PVS and TrE forming cyclobutane **40** as the standard reaction. The main advantage of this olefin pair was that PVS is not susceptible to cationic homopolymerization in the presence of Lewis acids, in contrast to all the other nucleophilic olefins. The [2 + 2]-cycloaddition did not take place spontaneously, and $ZnCl_2$ promoted this reaction under mild conditions at room temperature. The ^1H NMR spectrum of each cycloadduct isomer was well established. This [2 + 2]-cycloaddition was followed by ^1H NMR in the presence of various Lewis acids in deuterated benzene.

Of the alkylaluminum halide Lewis acids, only Et_2AlCl led to the desired [2 + 2]-cycloaddition. The stronger Lewis acids $EtAlCl_2$ and $Et_{1.5}AlCl_{1.5}$ gave unidentified products, due to the instability of the cyclobutanes in the presence of strong Lewis acids.

Of the boron halide Lewis acids, the weaker Lewis acid BF_3 in ether afforded the [2 + 2]-cycloadduct, while the stronger BCl_3 yielded unidentified products. Again the cyclobutane was unstable in the presence of a strong Lewis acid. Therefore the reaction with BCl_3 was tried at lower temperature, but an unidentified product mixture was still observed by ^1H NMR.

When zinc halide Lewis acids were used, the [2 + 2]-cycloadduct **40** was obtained as the only product with $ZnCl_2$. As described above, the two isomeric [2 + 2]-cycloadducts were obtained in a cis/trans ratio 38:62. Using zinc bromide afforded the [2 + 2]-cycloadducts along with the 2:1 cycloadduct, trimethyl 4,6-bis-(phenylthio)-1,1,2-cyclohexanetricarboxylate, as identified by ^1H NMR. Surprisingly, this cyclohexane derivative was not stable enough for chromatography, and no purification could be done without decomposition. Following the reaction by ^1H NMR, we observed that in the first stages of this [2 + 2]-cycloaddition the *cis*-cyclobutane was formed almost exclusively. When the reaction was finished, the *cis*-cyclobutane, *trans*-cyclobutane, and 2:1 cycloadduct were observed in approximately a 1:1:1 ratio. Using zinc iodide as Lewis acid, the 2:1 cycloadduct was found to be the only product.

As a general trend the weaker Lewis acids, such as $BF_3{\cdot}Et_2O$, Et_2AlCl, $ZnCl_2$, and $LiClO_4$, were the most effective because the cyclobutane products tend to undergo further reactions in the presence of strong Lewis acids.

As shown in Scheme 3, the zwitterionic tetramethylene intermediate, complexed with the Lewis acid, can exist as either the gauche- or trans-conformer. The [2 + 2]-cycloaddition occurs through the gauche conformer, which can be either 1,3-cis or 1,3-trans. The reaction was carried out in a nonpolar solvent, benzene, in which the gauche-conformer was favored due to coulombic interaction between the ionic ends so that it easily underwent

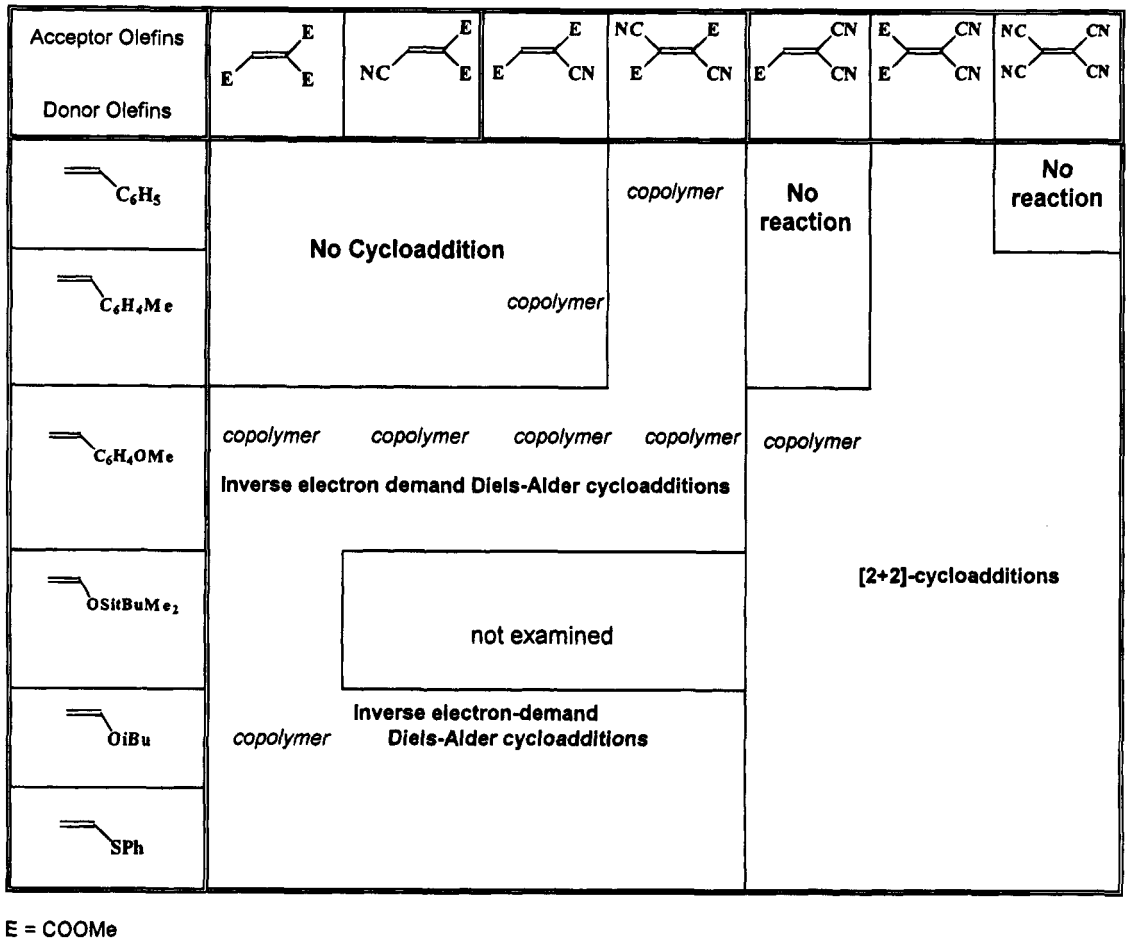


Figure 1. Cycloaddition reactions of acceptor olefins with donor olefins without Lewis Acid.

ring-closure. The cyclobutane formation was reversible, which allowed for equilibration between *cis*- and *trans*-cyclobutanes. The intermediate zwitterion could also add to another electron-rich olefin giving the 2:1 cycloadduct.

With $ZnCl_2$, an equilibrium between *cis*- and *trans*-cyclobutanes was established. With zinc bromide as Lewis acid, *cis*-cyclobutane was the kinetic product. The equilibrium between the two zwitterionic conformers with $ZnBr_2$ was shifted more toward the trans-conformer than with $ZnCl_2$ due to the increased bulkiness and the increased Lewis acidity of $ZnBr_2$. The addition of another electron-rich olefin could then take place. Therefore, a mixture of *cis*- and *trans*-cyclobutanes and 2:1 cycloadduct was observed. Zinc iodide is an even bulkier acid and a somewhat stronger Lewis acid, the zwitterion–Lewis acid complex was further stabilized and sterically hindered, and the 2:1 cycloadduct was formed.

These results using zinc halides as Lewis acids show that when milder and smaller Lewis acids are used, the gauche-zwitterionic tetramethylene intermediate will be favored, giving cyclobutanes. When stronger Lewis acids are used, the product mixture is controlled more by the steric requirements in the intermediate zwitterion than in the cyclobutane product. The more stabilized zwitterion also allows formation of the thermodynamically favored cyclohexane product. A 2:1 cycloaddition between electron-rich and electron-poor olefins had already been reported for the reaction between ketene acetal and maleic anhydride[27] and between *N*-vinylcarbazole and dimethyl 1,1-dicyanoethene-2,2-dicarboxylate.[28]

Discussion

Our results can be presented most easily by using a periodic table format.[28,29] The acceptor olefins are listed in order of increasing electrophicity from left to right, while the donor olefins are arranged vertically in order of increasing donor character. For the reactions investigated in this paper, this table is presented both with and without Lewis acid (Figures 1 and 2). As cycloadditions are the most common reaction, the table is divided according to the cycloadduct type. In cases where copolymers are spontaneously formed by olefin–olefin combinations, this is indicated.

For the reactions without Lewis acid (Figure 1), the product for the olefin pairs with the greatest olefin disparity (strong donor olefin with strong acceptor olefin) is the [2 + 2] cycloadduct. This is true for the olefins with two vicinal cyano groups. The reactions of acceptor olefins with at least one ester group on the most electrophilic carbon invariably lead to an inverse electron-demand Diels–Alder reaction. Reactions of moderately donating olefins with moderately accepting olefins also lead to competing free radical copolymerization. Olefin pairs with rather small electron disparity do not react under these conditions.

The reaction pattern changes when Lewis acids are added, as shown in Figure 2. Most olefin–olefin combinations now result in [2 + 2]-cycloaddition, either in the presence or absence of Lewis acid. The reaction of rather weak olefin pairs leads to the [2 + 4]-cycloadduct at enhanced rates (MeSt with DCF or CNF, MeOSt or IBVE

(27) McElvain, S. M.; Cohen, H. *J. Am. Chem. Soc.* **1942**, *64*, 260.
(28) Hall, H. K., Jr.; Ykman, P. *J. Am. Chem. Soc.* **1975**, *97*, 800.
(29) Hall, H. K., Jr. *J. Chem. Educ.* **1980**, *57*, 49.

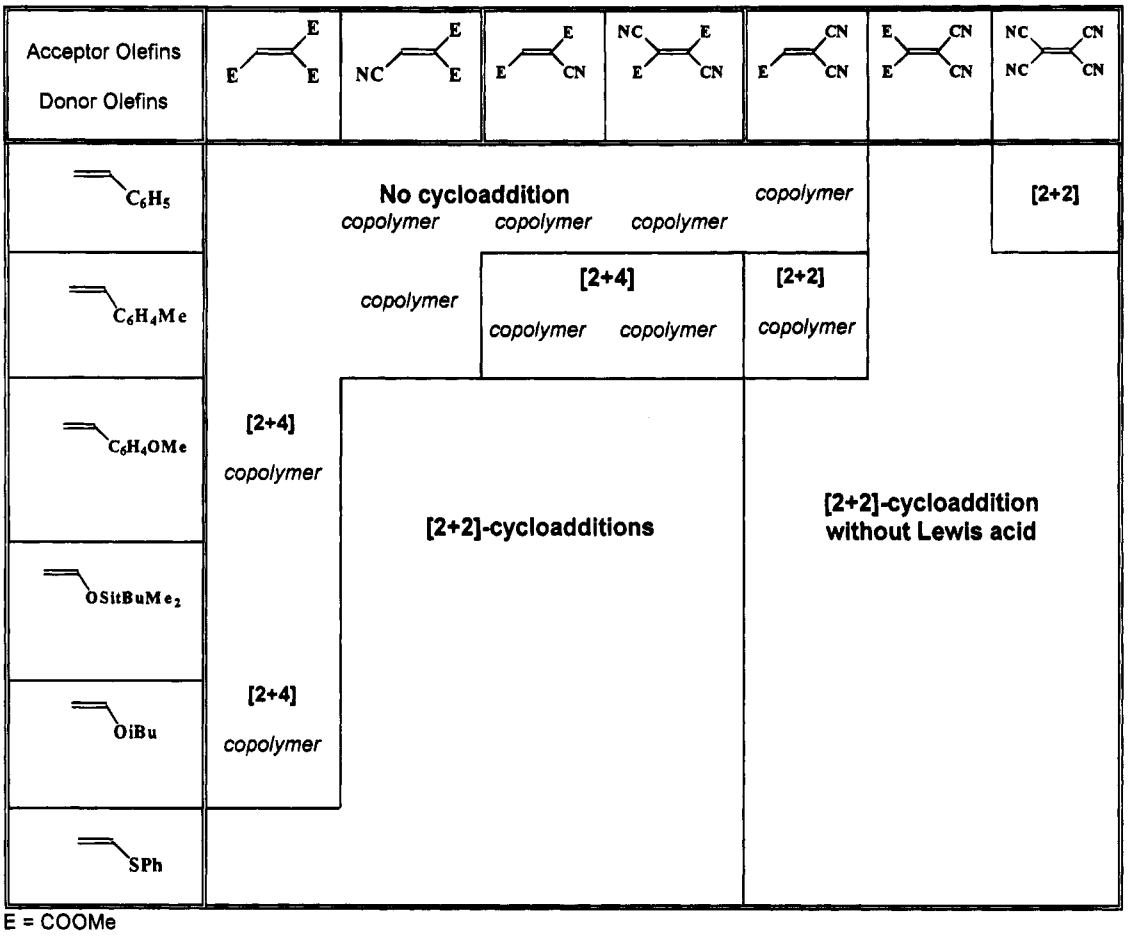


Figure 2. Cycloaddition reactions of acceptor olefins with donor olefins in the presence of Lewis acid.

with TrE). The occurrence of the free radical copolymerizations has also shifted to the less reactive olefin pairs in the presence of the Lewis acid (more toward the upper left hand corner of the table, Figure 2).

For olefin pairs with a small HOMO–LUMO gap, [2 + 2]-cycloadditions take place spontaneously at room temperature. When weaker electrophilic olefins with a carbomethoxy substituent are used, the HOMO–LUMO gap is larger and the concerted [2 + 4]-cycloadditions dominate. $ZnCl_2$ or ethereal lithium perchlorate are capable of facilitating the [2 + 2]-cycloadditions by lowering the LUMO energy level of the electrophilic olefin. Finally, when very weak nucleophilic and electrophilic olefins are used, only spontaneous free radical copolymerizations occur. Here the large HOMO–LUMO gap prevents the concerted cycloaddition, but bond formation between the two reacting partners can still give a diradical tetramethylene. A small amount of initiating radicals will lead to isolable amounts of copolymer formed by the chain polymerization reaction. These spontaneous free radical copolymerizations still occur with weak donor–acceptor pairs such as styrene and acrylonitrile, even without the addition of Lewis acid, but only at elevated temperatures.[30]

A change in the nature of the intermediate in the [2 + 2]-cycloadditions can be observed in the diagonal direction. The [2 + 2]-cycloadditions with TCNE and other highly electrophilic olefins are clearly zwitterionic.[18] Moving to less reactive olefin pairs, the nature of the formed tetramethylene intermediate will switch to one of predominantly diradical character. The point at which this change occurs is difficult to pinpoint, as these diradicals are still highly dipolar. However, when copolymerizations are observed, the tetramethylene intermediates, which are the postulated initiators of the polymerization, are predominantly free radical in character.

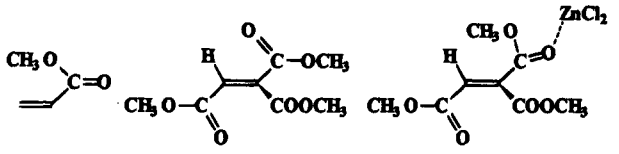
The observed inverse electron-demand [2 + 4]-cycloaddition is assumed to be concerted in nature since no evidence for an intermediate has been found. The HOMO–LUMO gap necessary for this concerted reaction overlaps with the transition from zwitterionic to diradical intermediates. The [2 + 4]-cycloadduct is the kinetically controlled product in the reactions of nucleophilic olefins with ester-substituted olefins, while in the presence of a Lewis acid the [2 + 2]-cycloadduct is the thermodynamically controlled product. This rather surprising fact suggests that the steric crowding in the 3,4-dihydropyran derivatives is so great that the cyclobutane with its additional ~20 kcal/mol ring strain is more stable. In a cyclobutane the substituents interfere less with each other due to the 90° angles between adjacent substituents. Electrophile-catalyzed diversion of a [2 + 4] cycloaddition into a [2 + 2] pathway has been reported in the literature.[31]

The rates of the reactions also correlate well with the electron disparity of the reacting olefins, i.e., with the HOMO–LUMO gap. For example, with MDA the reaction rates increase as we move down in the table.

(30) Kirchner, K.; Schlapkohl, H. *Makromol. Chem.* **1979**, *180*, 2649. Hall, H. K., Jr.; Liu, D. Unpublished results. Wang, H.; Chu, G.; Srisiri, W.; Padias, A. B.; Hall, H. K., Jr. *Acta Polymer* **1994**, *45*, 26.

(31) Magnus, P.; Schultz, J. *Tetrahedron Lett.* **1986**, *27*, 655. Magnus, P.; Rigollier, P.; Lacour, J.; Tobler, H. *J. Am. Chem. Soc.* **1993**, *115*, 12629.

In methyl acrylate, the heterodiene C=CC=O is predominantly in the s-trans conformation.[32] However, in the multisubstituted electrophilic olefins used in this study, this heterodiene moiety probably exists mostly in the s-cis conformation to minimize the dipole moment of the molecule. An X-ray crystal structure analysis of TrE shows that the two trans ester groups have the carbonyl group in the s-cis conformation to the C=C bond, while the third ester group is twisted ~75° out of the plane.[33] Moreover, an X-ray structure analysis of a complex between DCF and tetrathiafulvalene shows the two carbonyl groups s-cis to the C=C bond.[34] The s-cis conformation of the heterodiene is very favorable for the inverse electron-demand Diels–Alder reaction and might be a reason why this reaction is so predominant when a carbomethoxy substituent is available on the most electrophilic carbon.



However, in the presence of Lewis acids, the [2 + 2]-cycloaddition overshadows the concerted reaction. Lewis acids preferentially complex to the carbonyl oxygen of an ester group.[10] In the olefins under study, the Lewis acids have two effects: lowering the LUMO level while sterically blocking the C=O bond. Both effects would lead to enhanced [2 + 2] cycloaddition over [2 + 4], as observed. With weak olefin pairs such as MeSt with DCF or CNF, the Lewis acid accelerates the [2 + 4]-cycloaddition. To our knowledge this is the first case of a Lewis acid-catalyzed inverse electron-demand Diels–Alder reaction. With even weaker olefin pairs, no cycloaddition occurs and spontaneous free radical copolymerization takes place.

Complexation of cyano groups is also known.[35] Clear evidence for the complexation of the cyano group by a Lewis acid is found in the [2 + 2]-cycloaddition of St and TCNE. In the other cases cyano complexation presumably also plays a role, but is probably less important than the corresponding ester complexation.

Experimental Section

Instrumentation. ^{1}H and ^{13}C NMR spectra(s) were recorded with a Bruker WM-250 magnetic resonance spectrometer. Infrared spectra were obtained on a Perkin-Elmer 983 spectrometer. Melting points were measured using a Thomas-Hoover capillary melting point apparatus and are corrected. Elemental analyses were performed by Desert Analytics, Tucson AZ.

Chemicals. *p*-Methoxystyrene (MeOSt) and *p*-methylstyrene (MeSt) were dried with CaH_2 and then distilled under vacuum. Isobutyl vinyl ether (IBVE) was washed with water, dried over potassium hydroxide, and then distilled from sodium metal under nitrogen. Tetracyanoethylene (TCNE) was purified by sublimation (120–130 °C/0.5 mmHg) through an activated carbon layer (mp 198–200 °C). Poly(methyl glyoxylate) was obtained from E.I. Du Pont de Nemours. Malononitrile was distilled before use and stored at −50 °C. Methyl cyanoacetate and dimethyl malonate were distilled before use. All solvents were refluxed over CaH_2, distilled under argon, and then stored over 5 Å molecular sieves.

Dimethyl 2,2-dicyanoethylene-1,1-dicarboxylate (DDED),[21] diethyl dicyanofumarate (DCF),[36] dialkyl 2-cyanoethylene-1,1-dicarboxylate (CNDE),[37] and **trimethyl ethylenetricarboxylate (TrE)[38]** were synthesized following literature procedures.

Methyl 3,3-Dicyanoacrylate (MDA). By modification of the method of Sentman and Hall,[21] 8.8 g (0.1 mol) of poly(methyl glyoxylate), 3.3 g (0.05 mol) of malononitrile, 70 mL of acetonitrile, and 2 drops of acetic anhydride were mixed and heated at reflux with a Soxhlet extractor containing molecular sieves for 3 h. The solvent and unreacted starting material were removed under aspirator vacuum, and the remaining liquid was distilled under vacuum twice (65% yield). Bp: 87 °C at 1.4 mmHg. ^{1}H NMR ($CDCl_3$): 7.2 (s, 1H); 3.9 (s, 3H) ppm. IR (NaCl, neat): 2225; 1740; 1600 cm^{-1}.

Dimethyl Cyanofumarate (CNF).[5,7,23] CNF was synthesized by modification of the synthesis procedure used for MDA. Poly(methyl glyoxylate) (15.48 g, 0.18 mol) and methyl cyanoacetate (9.0 g, 0.090 mol) were dissolved in acetonitrile (75 mL) and refluxed for 8 h. The reflux apparatus was outfitted with a soxhlet extractor fillwed with freshly activated 4 Å molecular sieves. Acetonitrile and unreacted methyl glyoxylate were removed using a rotary evaporator. The resulting reddish brown liquid was distilled at 0.5 mmHg and then recrystallized from ether giving the pure product in 63% yield. Mp: 60–61 °C. ^{1}H NMR ($CDCl_3$): 7.43 (s, 1H); 3.95 (s, 3H); 3.91 (s, 3H) ppm. IR (NaCl, neat): 2226; 1730; 1630 cm^{-1}.

***tert*-Butyldimethylsilyl Vinyl Ether (SiVE).** *tert*-Butyldimethylsilyl vinyl ether was synthesized by modifying the synthesis of trimethylsilyl vinyl ether.[39] Dry tetrahydrofuran (THF, 50 mL, 0.61 mol) was placed in a flame-dried round-bottomed flask under dry nitrogen. *n*-Butyllithium (2.5 M in *n*-hexane, 32.4 mL, 0.08 mol) was added via a syringe. After 3 h stirring at room temperature under nitrogen, *tert*-butyldimethylsilyl chloride (11.16 g, 0.074 mol) was added dropwise at 0 °C over 20 min. After a further 2 h stirring at room temperature, the THF was evaporated. The residue was extracted with ether–water, and the ether layer was dried with anhydrous magnesium sulfate. Upon evaporation of the ether and distillation of the crude product, SiVE was obtained in 72% yield. Bp: 137 °C. ^{1}H-NMR ($CDCl_3$): 6.45–6.36 (dd, J = 13.7, 5.8 Hz, 1H); 4.44–4.38 (dd, J = 13.7, 0.8 Hz, 1H); 4.10–4.07 (dd, J = 5.8, 0.7 Hz, 1H); 0.90 (s, 9H); 0.13 (s, 6H) ppm. ^{13}C-NMR ($CDCl_3$): 146.44; 94.32; 25.63; 22.69; 14.08 ppm. IR (NaCl): 2956; 2930; 2885; 2858; 1630; 1257; 1018 cm^{-1}.

Typical Procedure for Spontaneous [2 + 2]-Cycloaddition. One molar equiv of electron rich olefin and 1 molar equiv of electron poor olefin were mixed in acetonitrile at room temperature and stirred until the reaction was finished. The end of the reaction was indicated by disappearance of the color due to the charge-transfer complex, or the reaction was monitored by ^{1}H-NMR spectroscopy. The solvent was evaporated, and the crude product was purified as described for each reaction.

Typical Procedure for $ZnCl_2$-Promoted [2 + 2]-Cycloaddition. One molar equiv of $ZnCl_2$ was placed in a reaction flask and dried under vacuum at 300 °C. Under dry nitrogen 1 molar equiv of electron poor olefin and solvent were added and stirred vigorously for at least 20 min. One molar equiv of electron rich olefin was added. The reaction was followed by ^{1}H-NMR spectroscopy. When the reaction was finished, the mixture was extracted with chloroform and 6 N hydrochloric acid. The chloroform layer was washed with water and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the crude product was purified as described for each reaction.

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(33) Ashby, M. T. Internal University of Arizona Chemistry Report submitted as supplementary material.
(34) Mulvaney, J. E.; Pang, L.; Cramer, R. J.; Hall, H. K., Jr. *J. Crystallogr. Spectrosc. Res.* **1982**, *12*, 331.
(35) Wang, H.; Chu, G.; Srisiri, W.; Padias, A. B.; Hall, H. K., Jr. *Acta Polymer* **1994**, *45*, 26 and references cited therein.
(36) Ireland, C. J.; Jones, K.; Pizey, J. S. *Synth. Chem.* **1976**, *6*, 185.
(37) Hall, H. K., Jr.; Ykman, P. *Macromolecules* **1977**, *10*, 1977.
(38) Evans, S. B.; Abdelkader, M.; Padias, A. B.; Hall, H. K., Jr. *J. Org. Chem.* **1989**, *54*, 2848.
(39) Lee, J. Y.; Hall, H. K., Jr. *J. Heterocycl. Chem.* **1990**, *27*, 1653.

Typical Procedure for 5 M Ethereal $LiClO_4$-Promoted [2 + 2]-Cycloaddition. One molar equiv of electron poor olefin was dissolved in 5 M ethereal $LiClO_4$, and then 1 molar equiv of electron rich olefin was added. The reaction was followed by ^{1}H-NMR spectroscopy. When the reaction was finished, the mixture was extracted with chloroform and saturated potassium chloride solution. The chloroform layer was dried over anhydrous magnesium sulfate. Upon evaporation of the solvent, the crude cyclobutane was obtained and purified as described for each reaction.

1,1,2,2-Tetracyano-3-(phenylthio)cyclobutane (1).[40] The [2 + 2]-cycloaddition between TCNE and PVS occurred spontaneously at room temperature in acetonitrile. The crude cyclobutane was recrystallized from cyclohexane–1,2-dichloroethane (3:1) (82% yield). Mp: 111–112.5 °C. ^{1}H-NMR ($CDCl_3$): 7.50 (m, 5H); 4.90 (dd, J = 8.7, 7.0 Hz, 1H); 3.30 (dd, J = 12.7, 7.0 Hz, 1H); 3.09 (dd, J = 12.7, 8.7 Hz, 1H) ppm. IR (KBr): 2963; 2252; 1287; 1016 cm^{-1}.

1,1,2,2-Tetracyano-3-isobutoxycyclobutane (2).[18] The [2 + 2]-cycloaddition between TCNE and IBVE occurred spontaneously at room temperature in acetonitrile. The crude cyclobutane was purified by recrystallization from dichloromethane/hexane. ^{1}H-NMR ($CDCl_3$): 4.7 (m, 1H); 3.7–2.9 (m, 4H); 2.1–1.6 (m, 1H); 0.93 (s, 6H) ppm. IR (KBr): 2963; 2252; 1287; 1016 cm^{-1}.

1,1,2,2-Tetracyano-3-(*tert*-butyldimethylsiloxy)cyclobutane (3). The [2 + 2]-cycloaddition between TCNE and SiVE occurred spontaneously at room temperature in acetonitrile and was finished in 1 day. The crude cyclobutane was purified by recrystallization from pentane (89% yield). Mp: 97–99 °C. ^{1}H-NMR ($CDCl_3$): 4.90 (dd, J = 8.7, 7.0 Hz, 1H); 3.31 (dd, J = 12.7, 7.0 Hz, 1H); 3.08 (dd, J = 12.7, 8.7 Hz, 1H); 0.93 (s, 9H); 0.18 (s, 3H); 0.13 (s, 3H) ppm. IR (KBr): 2961; 2249 cm^{-1}.

1,1,2,2-Tetracyano-3-(*p*-methoxyphenyl)cyclobutane (4).[19] The [2 + 2]-cycloaddition between TCNE and MeOSt occurred spontaneously at room temperature in acetonitrile and was finished in 1 day. Mp: 180–181 °C. ^{1}H-NMR (acetone-d_6): 7.57 (d, J = 8.8 Hz, 2H); 7.08 (d, J = 8.8 Hz, 2H); 5.00 (dd, J = 12.2, 9.0 Hz, 1H); 3.86 (dd, J = 12.2, 13.0 Hz, 1H); 3.62 (dd, J = 13.0, 9.0 Hz, 1H) ppm. IR (KBr): 2984; 2251; 1555; 1453; 1257; 1030 cm^{-1}.

1,1,2,2-Tetracyano-3-(*p*-methylphenyl)cyclobutane (5). The [2 + 2]-cycloaddition between TCNE and MeSt occurred spontaneously at room temperature in 5 M ethereal $LiClO_4$ and finished in 4 days. The crude solid cyclobutane was purified by washing with ether several times. Mp: 169–170 °C. ^{1}H-NMR ($CDCl_3$): 7.32 (d, J = 8.1 Hz, 2H); 7.23 (d, J = 8.1 Hz, 2H); 4.60 (dd, J = 12.3, 8.6 Hz, 1H); 3.40 (dd, J = 12.5, 12.3 Hz, 1H); 3.30 (dd, J = 12.5, 8.6 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$): 130.41; 130.05; 128.92; 127.10; 110.23; 109.07; 109.53; 108.27; 91.18; 97.93; 47.68; 35.69; 21.30 ppm. IR (KBr): 2986; 2250; 1555; 1453; 1248 cm^{-1}. Elem. Anal. Calcd: C, 73.17; H, 4.07; N, 22.76. Found: C, 72.81; H, 3.96; N, 22.62.

1,1,2,2-Tetracyano-3-phenylcyclobutane (6).[16] The [2 + 2]-cycloaddition between TCNE and St was conducted at room temperature in 5 M ethereal $LiClO_4$ and was finished in 5 days. The crude cyclobutane solid was purified by washing with ether several times. The cyclobutane was obtained in 67% yield. Mp: 162 °C. ^{1}H-NMR ($CDCl_3$): 7.45 (m, 5H); 4.58 (dd, J = 12.3, 8.7 Hz, 1H); 3.37 (dd, J = 12.5, 12.8 Hz, 1H); 3.22 (dd, J = 12.5, 8.7 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$): 130.94; 130.73; 129.76; 127.12; 109.79; 91.01; 82.23; 47.63; 35.53 ppm. IR (KBr): 3010; 2253; 1536; 1496; 775; 720 cm^{-1}.

1,1-Dicarbomethoxy-2,2-dicyano-3-(phenylthio)-cyclobutane (7). The [2 + 2]-cycloaddition between DDED and PVS occurred spontaneously at room temperature in acetonitrile. After solvent was removed, the crude cyclobutane was purified by column chromatography (8:2 pentane/ethyl acetate) (89% yield). Mp: 114–116 °C. ^{1}H-NMR ($CDCl_3$): 7.55–7.37 (m, 5H); 4.59–4.28 (m, 5H); 2.97–2.73 (m, 2H); 1.42–1.28 (m, 6H) ppm. ^{13}C-NMR ($CDCl_3$): 165.48; 164.68; 132.48; 129.41; 128.85; 130.81; 111.53; 110.87; 63.80; 63.09; 55.73; 42.34; 48.18; 32.92; 13.56 ppm. IR (KBr): 2983; 2204; 1737; 1581; 1474; 1439 cm^{-1}. Elem. Anal. Calcd: C, 60.34; H, 5.03; N, 7.82. Found: C, 60.31; H, 5.03; N. 7.52.

1,1-Dicarbomethoxy-2,2-dicyano-3-isobutoxycyclobutane (8).[21] The [2 + 2]-cycloaddition between DDED and IBVE occurred spontaneously at room temperature in acetonitrile. After solvent was removed, the cyclobutane was recrystallized from ether (95% yield). Mp: 38–39 °C. ^{1}H-NMR ($CDCl_3$): 4.70 (dd, J = 8.4, 8.3 Hz, 1H); 3.91 (s, 3H); 3.89 (s, 3H); 3.73–3.14 (m, 3H); 2.23–1.54 (m, 1H); 0.90 (d, J = 6.4 Hz, 6H) ppm.

1,1-Dicarbomethoxy-2,2-dicyano-3-(*tert*-butyldimethylsiloxy)cyclobutane (9). The [2 + 2]-cycloaddition between DDED and SiVE occurred spontaneously at room temperature in acetonitrile. After solvent was removed the cyclobutane was dried under vacuum overnight (85% yield). ^{1}H-NMR ($CDCl_3$): 4.87 (dd, J = 8.7, 7.5 Hz, 1H); 4.35 (m, 5H); 2.8 (m, 2H); 1.40 (t, J = 7.1 Hz, 6H); 0.94 (s, 9H); 0.21 (s, 3H); 0.17 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$): 166.38; 165.20; 111.98; 110.62; 268.62; 63.82; 63.09; 52.56; 43.72; 38.29; 25.33; 17.69; 13.74 ppm. IR (KBr): 2932; 2859; 2249; 1742; 1267; 1062 cm^{-1}. Elem. Anal. Calcd: C, 56.84; H, 7.37; N, 7.37; O, 21.05; Si, 7.37. Found: C, 56.54; H, 7.48; N, 7.50.

1,1-Dicarbomethoxy-2,2-dicyano-3-(*p*-methoxyphenyl)cyclobutane (10).[21] The [2 + 2]-cycloaddition between DDED and MeOSt occurred spontaneously at room temperature in acetonitrile. After solvent and p-methoxystyrene were removed under vacuum, the cyclobutane was recrystallized from ether–pentane (40% yield). Mp: 56–58 °C. ^{1}H-NMR ($CDCl_3$): 7.42–6.84 (m, 4H); 4.50 (dd, J = 8.5, 11.0 Hz, 1H); 3.91 (s, 3H); 3.85 (s, 3H); 3.80 (s, 3H); 3.43–2.59 (m, 2H) ppm.

1,1-Dicarbomethoxy-2,2-dicyano-3-(*p*-methylphenyl)-cyclobutane (11).[21] The [2 + 2]-cycloaddition between DDED and MeSt occurred spontaneously at room temperature in acetonitrile. After solvent and *p*-methylstyrene were removed under vacuum, an orange oil was obtained. This oil was dissolved in ether and kept at −60 °C, whereupon the mixture separated into two layers. The ether layer was decanted and the oil was placed under vacuum again (52% yield). ^{1}H-NMR ($CDCl_3$): 7.24–6.93 (m, 4H); 4.83–4.47 (m, 1H); 3.89 (s, 3H); 3.81 (s, 3H); 3.62–3.01 (m, 2H); 2.41 (s, 3H) ppm.

1,1-Dicarbomethoxy-2,2-dicyano-3-phenylcyclobutane (12).[21] The [2 + 2]-cycloaddition between DDED and St occurred spontaneously at room temperature in acetonitrile. After the solvent and styrene were removed under vacuum, the cyclobutane was recrystallized from ether–pentane (33% yield). Mp: 41–43 °C. ^{1}H-NMR ($CDCl_3$): 7.24–7.15 (m, 5H); 4.72–4.67 (m, 1H); 3.82 (s, 3H); 3.79 (s, 3H); 3.52–3.28 (m, 2H) ppm.

1-Carbomethoxy-2,2-dicyano-3-(phenylthio)cyclobutane (13). The reaction between MDA and PVS occurred spontaneously at room temperature in acetonitrile and finished in 1 day. The crude cyclobutane was purified by column chromatography (3:1 heptane–ethyl acetate). Two stereoisomeric cyclobutanes were obtained in 80% yield. The trans: cis ratio was 14:86. ^{1}H-NMR ($CDCl_3$): trans isomer (14%) 7.50 (m, 5H); 4.44 (dd, J = 11.2, 8.6 Hz, 1H); 3.80 (s, 3H); 3.70 (dd, J = 11.2, 8.7 Hz, 1H); 2.91 (ddd, J = 11.1, 12.0, 8.7 Hz, 1H); 2.45 (ddd, J = 12.0, 11.2, 8.7 Hz, 1H); cis isomer (86%) 7.48–7.39 (m, 5H); 4.22 (dd, J = 11.2, 8.6 Hz, 1H); 3.79 (s, 3H); 3.62 (dd, J = 11.2, 8.7 Hz, 1H); 2.68 (ddd, J = 11.1, 12.0, 8.7 Hz, 1H); 2.51 (ddd, J = 12.0, 11.2, 8.7 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$): isomer 1 (14%) 168.5; 132.4; 132.2; 129.6; 128.2; 118.2; 112.2; 53.5; 49.6; 44.2; 38.0; 27.4; isomer 2 (86%) 167.9; 131.2; 132.2; 129.6; 128.2; 113.9; 111.1; 52.8; 48.2; 43.6; 39.1; 28.3 ppm. IR (KBr): 2249, 1741, 1512, 1438 cm^{-1}. Elem. Anal. Calcd: C, 61.76; H, 4.41; N, 10.29; O, 11.77, S, 11.77. Found: C, 61.78; H, 4.43; N, 10.35.

1-Carbomethoxy-2,2-dicyano-3-isobutoxycyclobutane (14). The reaction between MDA and IBVE occurred spontaneously at room temperature in acetonitrile and was finished in 2 days. After solvent was evaporated, the cyclobutane was purified by column chromatography (1% triethylamine in pentane/ethyl acetate). Two stereoisomeric cyclo-

(40) Okuyama, T.; Nakada, M.; Toyoshima, K.; Fueno, T. *J. Org. Chem.* **1978**, *43*, 4546.

(41) The author has deposited atomic coordinates for TrE with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

butanes were obtained in 75% yield. The ratio of trans:cis was 40:60. ^{1}H-NMR ($CDCl_3$): 4.63 (60%, t, J = 8.1 Hz, 1H), 4.34 (40%, t, J = 8.3 Hz, 1H); 3.93 (60%, s, 3H), 3.85 (40%, s, 3H); 3.60–3.44 (m, 2H); 3.30 (m, 1H); 2.8 (m, 2H); 1.9 (m, 1H); 0.9 (m, 6H) ppm. ^{13}C-NMR ($CDCl_3$): cis isomer (60%) 170.10; 112.01; 111.70; 100.87; 74.76; 69.35; 52.41; 41.11; 32.58; 28.31; 24.13; 19.06; trans isomer (40%) 164.80; 112.80; 112.59; 100.87; 74.76; 69.35; 53.42; 42.22; 34.27; 28.31; 24.13; 19.06 ppm. IR (KBr): 2958; 2249; 1740; 1233; 1023 cm^{-1}. Elem. Anal. Calcd: C, 60.02; H, 6.78; N, 11.86. Found: C, 60.16; H, 6.54; N, 12.24.

1-Carbomethoxy-2,2-dicyano-3-(*tert*-butyldimethylsiloxy)cyclobutane (15). The reaction between MDA and SiVE occurred spontaneously at room temperature in acetonitrile and was finished in 2 days. After solvent was evaporated, two stereoisomeric cyclobutanes were obtained in the ratio of 30:70 trans/cis (78% yield). ^{1}H-NMR ($CDCl_3$): isomer 1 (30%) 4.54 (t, J = 7.8 Hz, 1H); 3.85 (s, 3H); 3.18 (t, J = 10.3 Hz, 1H); 2.6 (m, 2H); 0.92 (s, 9H); 0.18 (s, 3H); 0.13 (s, 3H) ppm; isomer 2 (70%) 4.83 (t, J = 7.5 Hz, 1H); 3.83 (s, 3H); 3.55 (dd, J = 10.0, 3.5 Hz, 1H); 2.6 (m, 2H); 0.92 (s, 9H); 0.18 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$): isomer 1 (30%) 167.62; 113.90; 110.77; 69.75; 53.13; 40.60; 38.05; 33.83; 25.42; 17.78; 4.46; isomer 2 (70%) 169.24; 112.52; 112.38; 71.65; 53.32; 40.20; 39.33; 33.83; 25.42; 17.78; 4.46 ppm. IR (KBr): 2858, 2247; 1744 cm^{-1}.

1-Carbomethoxy-2,2-dicyano-3-(*p*-methoxyphenyl)cyclobutane (16). The reaction between MDA and MeOSt occurred spontaneously in methanol at room temperature. After solvent was evaporated, the cyclobutane was recrystallized from ether–petroleum ether. The two cyclobutane isomers were obtained in the ratio of trans:cis 25:75 (71% yield). Mp: 111–118 °C. ^{1}H-NMR ($CDCl_3$): 7.16 (m, 4H); 4.08 (dd, J = 10.3, 8.0 Hz, 1H); 3.87 (s, 3H); 3.82 (s, 3H); 3.72–3.54 (m, 1H); 3.00 (m, 1H); 2.6 (m, 1H) ppm. IR (KBr): 2960; 2231; 1739; 1612; 1514; 1439; 1203; 1030 cm^{-1}.

1-Carbomethoxy-2,2-dicyano-3-(*p*-methylphenyl)cyclobutane (17). The reaction between MDA and MeSt was conducted in 5 M ethereal $LiClO_4$ solvent and was finished in 3 days. The crude cyclobutane was dissolved in ether and then filtered. The filtrate was concentrated and kept at −50 °C until the cyclobutane precipitated (34% yield). ^{1}H-NMR ($CDCl_3$): 7.2 (m, 4H); 4.06 (dd, J = 11.8, 8.2 Hz, 1H); 3.88 (s, 3H); 3.67 (dd, J = 11.1, 8.6 Hz, 1H); 2.93 (dd, J = 11.1, 11.8 Hz, 1H); 2.55 (dd, J = 12.0, 8.5 Hz, 1H); 2.30 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$): 166.94; 133.04; 127.51; 125.20; 113.44; 112.83; 110.77; 56.51; 55.73; 52.60; 42.88; 42.04; 24.84 ppm. IR (KBr): 3024, 2956, 2250, 1740, 1493, 1437 cm^{-1}. Elem. Anal. Calcd: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.45; H, 5.44; N, 11.37.

1-Carbomethoxy-2,2-dicyano-3-phenylcyclobutane (18). The [2 + 2]-cycloaddition between MDA and St was conducted at room temperature in 5 M ethereal $LiClO_4$ in the presence of 10 mol % TEMPO. The reaction was finished in 2 days. The crude cyclobutane solid was purified by precipitation with ether at −50 °C. The cyclobutane **18** was obtained in 40% yield. ^{1}H-NMR ($CDCl_3$) for cis isomer: 7.47–7.18 (m, 5H); 4.08 (dd, J = 11.8, 8.2 Hz, 1H); 3.78 (s, 3H); 3.70 (dd, J = 11.1, 8.6 Hz, 1H); 2.95 (q, J = 11.7 Hz, 1H); 2.59 (dt, J = 11.8, 8.4 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$): 167.81; 133.88; 129.01; 128.91; 127.08; 114.24; 111.66; 58.07; 52.89; 46.03; 42.79; 25.65 ppm. IR (KBr): 2957; 2250; 1741 cm^{-1}.

1,2-Dicarbomethoxy-1,2-dicyano-3-(phenylthio)cyclobutane (20). The [2 + 2]-cycloaddition between DCF and PVS was conducted in the presence of $ZnCl_2$ and 1,2-dichloroethane and finished in 1 day. The crude cyclobutane was purified by column chromatography (4:1 heptane–ethyl acetate). Two stereoisomeric cyclobutanes (ratio 25:75) were obtained in 62% yield. ^{1}H-NMR ($CDCl_3$): cis isomer (25%) 7.55–7.26 (m, 5H); 4.55 (dd, J = 10.1, 11.1 Hz, 1H); 4.06 (s, 3H); 4.00 (s, 3H); 3.24 (dd, J = 10.1, 11.8 Hz, 1H); 3.07 (dd, J = 11.1, 11.8 Hz, 1H); trans isomer (75%) 7.55–7.26 (m, 5H); 4.63 (dd, J = 9.5, 10.5 Hz, 1H); 4.06 (s, 3H); 3.99 (s, 3H); 3.00 (dd, J = 9.5, 12.9 Hz, 1H); 2.73 (dd, J = 10.6, 12.9 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$): cis isomer (25%) 163.36; 162.92; 133.08; 131.46; 128.46; 126.37; 114.07; 54.73; 47.93; 55.10; 54.87; 43.93; 43.50; trans isomer (75%) 164.87; 162.72; 131.46; 129.40; 128.46; 126.37; 114.07; 55.93; 48.17; 54.33; 50.64; 54.81; 35.79 ppm. IR (NaCl, neat): 3492; 2241; 1750; 1478; 1436 cm^{-1}. Elem. Anal. Calcd: C, 58.18; H, 4.24; N, 8.48; O, 19.40; S, 9.70. Found: C, 57.70; H, 4.40; N, 8.13.

1,2-Dicarbobutoxy-1,2-dicyano-3-(*p*-methoxyphenyl)cyclobutane (23). Di-*n*-butyl dicyanofumarate and MeOSt were mixed in the presence of $ZnCl_2$ and 2,5-dimethyltetrahydrofuran solvent. After the reaction was finished, the crude cyclobutane **23** was purified by column chromatography (ethyl acetate/pentane) (68% yield). ^{1}H-NMR ($CDCl_3$): 7.06 (d, J = 8.7 Hz, 2H); 6.80 (d, J = 8.7 Hz, 2H); 4.44 (dd, J = 11.4, 8.8 Hz, 1H); 4.34 (q, J = 6.6 Hz, 2H); 4.22–3.79 (m, 2H); 3.70 (s, 3H); 3.35 (dd, J = 9.1, 8.8 Hz, 1H); 2.98 (dd, J = 11.4, 9.1 Hz, 1H); 1.7 (m, 4H); 1.4 (m, 4H); 1.10 (t, J = 7.1 Hz, 3H); 0.89 (t, J = 7.3 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$): 165.02; 159.87; 128.84; 114.19; 126.90; 115.07; 113.42; 112.05; 68.13; 67.62; 55.24; 54.56; 43.30; 42.57; 32.62; 30.16; 18.84; 13.54 ppm. IR (KBr): 2960, 2873, 2210, 1745, 1515, 1462, 1258, 1035 cm^{-1}.

1,2-Dicarbomethoxy-2-cyano-3-(phenylthio)cyclobutane (27). The cyclobutane adduct of CNF and PVS was obtained by two methods: (1) Equivalent molar amounts of dimethyl cyanofumarate and phenyl vinyl sulfide were refluxed in acetonitrile with a trace of radical inhibitor for 2 days. (2) The cycloaddition was conducted in the presence of $ZnCl_2$ or using 5 M ethereal $LiClO_4$ as the solvent. The crude cyclobutane was purified by column chromatography (4:1 pentane–ethyl acetate). Cyclobutanes were obtained in 75% yield (cis:trans ratio of 43:57 for the thermal reaction and 80:20 for the Lewis acid-catalyzed reaction). ^{1}H-NMR ($CDCl_3$): isomer 1 (43%) 7.47 (m, 5H); 4.57 (t, J = 9.1 Hz, 1H); 3.8 (s, 6H); 3.86 (ddd, J = 12.5, 9.0, 4.7 Hz, 1H); 2.90 (dt, J = 12.5, 9.0 Hz, 2H); isomer 2 (57%) 7.3 (m, 5H); 4.13 (dd, J = 8.4, 10.4 Hz, 1H); 3.77 (s, 3H); 3.60 (s, 3H); 3.78 (dd, J = 10.2, 8.9 Hz, 1H); 2.6 (m, 2H) ppm. ^{13}C-NMR ($CDCl_3$): 168.5; 166.65; 131.86; 131.66; 130.80; 130.23; 114.24; 53.94; 53.66; 52.50; 50.02; 43.24; 27.56 ppm. IR (NaCl): 3002; 2245; 1752; 1581; 1437 cm^{-1}. Elem. Anal. Calcd: C, 59.02; H, 4.92; N, 4.59; O, 20.98; S, 10.49. Found: C, 59.11; H, 4.96; N, 4.60.

1,2-Dicarbomethoxy-2-cyano-3-isobutoxycyclobutane (29). [2 + 2]-Cycloaddition between CNF and IBVE was accomplished in the presence of $ZnCl_2$ and 2,5-dimethyltetrahydrofuran solvent. When the reaction was finished, anhydrous tetramethylammonium chloride was added and the mixture was stirred for 1 h. After filtration and then evaporation of the filtrate, cyclobutanes were obtained in 72% yield. The cis:trans ratio was 58:42. ^{1}H NMR ($CDCl_3$): 4.54–4.07 (58%, m), 3.86–3.79 (42%, m); 3.71 (s, 3H); 3.68 (s, 3H); 3.38–3.25 (m, 2H); 3.18–3.10 (m, 1H); 2.22–1.75 (m, 3H); 0.85 (d, J = 6.7 Hz, 6H) ppm. ^{13}C NMR ($CDCl_3$): 171.80; 168.29; 115.21; 74.24; 73.60; 55.62; 53.67; 53.58; 52.65; 38.53; 32.54; 28.60; 19.37 ppm. IR (NaCl): 2958; 2253; 1744; 1261 cm^{-1}.

When the reaction mixture was worked up using the usual aqueous workup, the ring-opened aldehyde **30** was obtained. ^{1}H NMR ($CDCl_3$): 9.87 (s, 1H); 4.22 (d, J = 5.86 Hz, 1H); 3.86 (s, 6H); 3.69–3.62 (m, 1H); 3.33–2.84 (m, 2H) ppm.

1,2-Dicarbomethoxy-2-dicyano-3-(*p*-methoxyphenyl)cyclobutane (33). The [2 + 2]-cycloaddition between CNF and MeOSt was conducted in the presence of $ZnCl_2$ and 2,5-dimethyltetrahydrofuran. After the usual workup, the crude cyclobutane was dissolved in cyclohexane and filtered, and the filtrate was concentrated. Two stereoisomeric cyclobutanes were obtained in a cis:trans ratio of 50:50 (72% yield). ^{1}H-NMR ($CDCl_3$): cis isomer (50%) 7.10 (m, 2H); 6.82 (m, 2H); 3.98 (dd, J = 11.6, 8.2 Hz, 1H); 3.83 (s, 3H); 3.76 (m, 1H); 3.73 (s, 3H); 2.85 (t, J = 11.4 Hz, 1H); 2.47 (dt, J = 11.4, 8.2 Hz, 1H); trans isomer (50%) 7.11 (m, 2H); 6.82 (m, 2H); 4.33 (t, J = 9.5 Hz, 1H); 3.79 (s, 3H); 3.76 (m, 1H); 3.72 (s, 3H); 2.74 (m, 2H) ppm. ^{13}C-NMR ($CDCl_3$): 169.13; 165.87; 128.66; 113.54; 128.40; 117.95; 62.18; 61.89; 55.21; 42.92; 26.03; 25.52 ppm. IR (NaCl): 2956; 2241; 1735; 1581; 1513; 1435; 1257; 1030 cm^{-1}.

2,2-Dicarbomethoxy-1-cyano-3-(phenylthio)cyclobutane (35). The [2 + 2]-cycloaddition between CNED and PVS was conducted in 5 M ethereal $LiClO_4$ solvent and was finished in 3 days. The crude cyclobutane was purified by column chromatography (9:1 pentane–ethyl acetate). Cyclobutanes were obtained (trans:cis ratio 20:80) in 85% yield. ^{1}H-

NMR ($CDCl_3$): 7.35–7.17 (m, 5H); 4.73 (t, J = 8.5 Hz, 1H); 4.106 (q, J = 7.2 Hz, 1H); 3.77; 3.65 (s, 6H); 2.76–2.65 (m, 1H); 2.44–2.32 (m, 1H) ppm. ^{13}C-NMR ($CDCl_3$): 168.23; 166.06; 133.96; 131.64; 128.84; 127.63; 117.10; 63.34; 52.97; 46.33; 30.61; 25.43 ppm. IR (NaCl, neat): 2979; 2215; 1742; 1567; 1453; 1429 cm^{-1}.

2,2-Dicarbomethoxy-1-cyano-3-isobutoxycyclobutane (37). The reaction between CNED and IBVE was conducted in the presence of $ZnCl_2$ and 2,5-dimethyltetrahydrofuran. The crude cyclobutane was washed with cyclohexane. ^{1}H-NMR ($CDCl_3$): 4.62 (dd, J = 6.5, 4.4 Hz, 1H); 4.28–4.14 (m, 5H); 3.63 (d, J = 7.4 Hz, 2H); 3.39–3.29 (m, 1H); 3.16 (dd, J = 6.5, 8.9 Hz, 1H); 1.96–1.75 (m, 1H); 1.29–1.14 (m, 1H); 0.90–0.77 (m, 6H) ppm. ^{13}C-NMR ($CDCl_3$): 165.90; 118.76; 100.57; 73.54; 73.35; 62.75; 62.02; 52.59; 33.39; 28.07; 19.07; 13.65 ppm. IR (NaCl): 2958; 2872; 2245; 1729; 1258; 1052 cm^{-1}.

2,2-Dicarboethoxy-1-cyano-3-(*p*-methoxyphenyl)-cyclobutane (38). The [2 + 2]-cycloadduct of diethyl 2-cyanoethylene-1,1-dicarboxylate and MeOSt was obtained in the presence of $ZnCl_2$ and 2,5-dimethyltetrahydrofuran. After workup, the crude cyclobutane was washed with cyclohexane and crystallized from ether at −50 °C. A cis:trans ratio of 80:20 was obtained (82% yield). Mp: 70–71 °C. ^{1}H-NMR ($CDCl_3$): 7.24 (d, J = 9.0 Hz, 1H); 6.84 (d, J = 9.0 Hz, 1H); 4.39–4.23 (m, 2H); 4.13 (dd, J = 11.6, 8.8 Hz, 1H); 3.96–3.81 (m, 2H); 3.79 (s, 3H); 3.40 (dd, J = 11.67, 8.8 Hz, 1H); 3.15–3.02 (q, J = 11.57 Hz, 1H); 2.61–2.50 (dt, J = 11.57, 8.76 Hz, 1H); 1.35–1.29 (t, J = 7.23 Hz, 3H); 0.93–0.87 (t, J = 7.19 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$): 159.05, 157.41 (CO); 128.68 (CH in Ph); 119.36 (C in Ph); 117.95 (C in Ph); 113.58 (CH in Ph); 107.32 (CN); 62.45 ($C(CO)_2$); 62.08, 61.93 (CH_2O); 55.23 (CH_3O); 42.95 (*C*HCN); 39.39 (CH in Ph); 26.86 (CH_2); 13.96, 13.57 (CH_3) ppm. IR (NaCl, neat): 2932, 2836 (CH); 2242 (CN); 1728 (CO); 1581, 1512, 1436 (C=C); 1253, 1109 (COC) cm^{-1}. Elem. Anal. Calcd: C, 65.42; H, 6.39; N, 4.23. Found: C, 65.50; H, 6.45; N, 4.53.

1,2,2-Tricarbomethoxy-3-(phenylthio)cyclobutane (40). The [2 + 2]-cycloaddition between TrE and PVS was conducted in 5 M ethereal $LiClO_4$ solvent and finished in 2 days. The crude product was purified by column chromatography (8:2 pentane/ethyl acetate). Two isomeric cyclobutanes were obtained in 72% yield (ratio of cis:trans is 50:50). ^{1}H-NMR ($CDCl_3$): trans isomer (40%) δ 7.29–7.26 (m, 5H); 4.80–4.72 (dd, J = 9.41, 8.93 Hz, 1H); 3.79 (s, 3H); 3.74 (s, 3H); 3.72 (s, 3H); 3.95–3.89 (ddd, J = 9.93, 4.92, 0.98 Hz, 1H); 2.63–2.57 (m, 2H) ppm; cis isomer (60%) 7.42–7.40 (m, 5H); 4.28–4.20 (t, J = 9.89 Hz, 1H); 3.73 (s, 3H); 3.70 (s, 3H); 3.65 (s, 3H); 3.48–3.39 (t, J = 10.25 Hz, 1H); 2.39–2.27 (m, 2H) ppm. ^{13}C-NMR ($CDCl_3$): 172.53, 170.92, 167.93 (CO); 134.58 (C in Ph); 131.23, 128.93; 127.14 (CH in Ph): 61.99 (*C*CO); 53.20 (*C*HCO); 42.54 (CH-S); 44.75, 41.42, 40.30 (CH_3); 28.60 (CH_2) ppm. IR (NaCl, neat): 2249 (CN); 1741 (CO) cm^{-1}. Elem. Anal. Calcd: C, 56.80; H, 5.36. Found: C, 56.70; H, 5.36.

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Supplementary Material Available: Copies of ^{1}H NMR spectra for compounds lacking elemental analyses, ^{13}C NMR carbon assignments, results of AM1 calculations on the electrophilic olefins, and X-ray details on trimethyl ethylenetricarboxylate (21 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.