J. Org. Chem. 1993, 58, 7049–7058 7049

Evidence for 2-Hexene-1,6-diyl Diradicals Accompanying the Concerted Diels–Alder Cycloaddition of Acrylonitrile with Nonpolar 1,3-Dienes[1]

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Received September 2, 1993[●]

The spontaneous reactions of a series of alkyl 1,3-dienes with acrylonitrile (AN) were investigated. Reproducible spontaneous copolymerizations were shown to compete with the expected concerted [4 + 2] cycloadditions. For dienes which exist in s-cis/s-trans equilibrium, both copolymer and cycloadduct are formed. Kinetic measurements show that the alternating copolymerization and cycloaddition are two independent parallel second order reactions. With 1,3-cyclohexadiene and 1,2-dimethylenecyclohexane, for which s-gauche is in equilibrium with s-cis, copolymerization still competes with cycloaddition. The s-trans-locked verbenene forms only copolymer, while s-cis-locked cyclopentadiene and 1,2-dimethylenecyclopentane form only cycloadduct rapidly. Our explanation involves a 2-hexene-1,6-diradical, formed by combination between the terminal carbons of the s-gauche or s-trans diene and acrylonitrile. This does not cyclize but initiates copolymerization. Competitively s-cis conformer undergoes classical concerted [4 + 2] addition.

Introduction

The Diels–Alder reaction of a diene with a dienophile is a cornerstone of organic chemistry. Countless papers have dealt with this reaction and many reviews discuss the scope of this reaction.[2] The mechanism of the Diels–Alder reaction is generally, if not universally, agreed to be concerted in accordance with the Woodward–Hoffmann rules.[3] Firestone had raised the possibility of a stepwise mechanism involving a 2-hexene-1,6-diradical which could then cyclize,[4] but Huisgen was able to marshal very strong evidence against this point of view and summarized the evidence for the concerted mechanism.[2d] Nevertheless the question remains of interest.

Recently we have extended our study of the spontaneous polymerizations which occur upon mixing an electron-rich olefin with an electron-poor olefin to the reactions of electron-rich dienes with electron-poor olefins.[5,6] In a preliminary communication we have briefly described our early findings that, in the reaction of alkyl-substituted 1,3-dienes with acrylonitrile, spontaneous copolymerizations accompany the expected [4 + 2] cycloadditions.[1] In a related paper the reactions of 1-arylbutadienes with highly electrophilic olefins are described in which cationic homopolymerization of the diene competes with [4 + 2] cycloaddition.[7]

Polymerization is an extremely sensitive method for detecting free radical or ionic reaction intermediates. As we have pointed out in some previous papers, it possesses both amplification and diagnostic features. We have previously used this method to look for intermediates in zwitterionic,[8] diradical[9] and 1,3-dipolar cycloadditions.[10] According to this method, if the diene and dienophile reactants in Diels–Alder reactions are able to copolymerize by deliberately added free radical initiators, spontaneous copolymer formation can be taken as evidence for the presence of (di)radicals in the reaction mixture.

Copolymerizations accompanying Diels–Alder reactions have in fact been previously described. It must be stressed that such results are meaningful only if obtained in the known complete absence of adventitious initiators and/or inhibitors. The fact that copolymer can be formed along with cycloadduct, may have been known to the fathers of the Diels–Alder reaction, who added hydroquinone, a known free radical inhibitor, to their reaction mixtures.[11] In an early systematic investigation, Koningsberger and Salomon found that copolymer accompanied cycloadduct in the reaction of 2,3-dimethylbutadiene with acrylonitrile.[12] Nagai and his co-workers observed spontaneous copolymerizations along with cycloaddition in the reactions of cyclic 1,3-dienes with acrylonitriles and acrylates,[13] while Satake and his co-workers had to use hydroquinone as polymerization inhibitor to obtain the Diels–Alder adduct of cycloocta- and cyclonona-1,3-diene with maleic anhydride.[14] Stepek claimed to observe competitive cycloaddition and spontaneous copolymerization for the reaction of 1-methoxybutadiene with maleic anhydride.[15] Other-

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[●] Abstract published in *Advance ACS Abstracts*, November 1, 1993.

(1) Preliminary Communication: Hall, H. K., Jr.; Padias, A. B.; Li, Y.; Clever, H.A.; Wang, G. *J. Chem. Soc., Chem. Commun.* **1991**, 1279.

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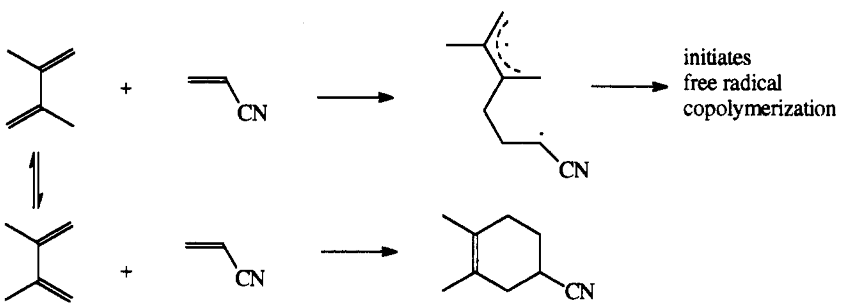
0022-3263/93/1958-7049$04.00/0

Scheme I



wise we found no studies of the thermal reactions of dienes with dienophiles mentioning polymerization in the literature.

In view of continued interest in the mechanism of the Diels–Alder reaction and our interest in the initiation mechanism of spontaneous polymerizations, we have now systematically studied the spontaneous thermal reactions of a variety of 1,3-diene hydrocarbons with acrylonitrile (AN). The dienes in this study are subdivided in three categories: first, dienes which react with AN to form both the Diels–Alder cycloadduct and copolymer, including 2,3-dimethylbutadiene (DMB), isoprene (IP), (*E*)-1,3-pentadiene, 1,3-cyclohexadiene (CHD), and 1,2-dimethylenecyclohexane; second, dienes which only form copolymer with AN, namely (*Z*)-1,3-pentadiene, 2,5-dimethyl-2,4-hexadiene, and verbenene; third, dienes which only lead to cycloadduct, namely cyclopentadiene and 1,2-dimethylenecyclopentane.

The mechanism we propose for the initiation of the observed copolymerizations is similar to the mechanism previously postulated for the spontaneous polymerization of olefin–olefin systems.[5,6] For the latter the bond-forming initiation theory proposes that the true initiator for the polymerizations which accompany the [2 + 2] cycloadditions is the tetramethylene intermediate, which can be zwitterionic or diradical. In analogy to this theory we have proposed in our preceding communication[1] on the reactions of 2,3-dimethyl-1,3-butadiene and similar dienes with acrylonitrile, that the s-trans conformer of the diene can react with the olefin to form a π-allyl hexene-1,6-diyl.[1,7] This diradical can initiate free radical copolymerization (See Scheme I). The current study was undertaken to provide support to this theory by a systematic investigation of the competitive cycloadditions and polymerizations for different dienes.

Results

Control Experiments and Reproducibility of Results. It was important to establish whether reproducible, kinetics-quality results could actually be obtained for the spontaneous reactions of alkyl 1,3-dienes with acrylonitrile. The control experiments were done by heating each monomer alone under the same conditions as the reactions of dienes with AN (see below). AN was stable under the reaction conditions, as we have demonstrated previously.[16] None of the dienes used in this study underwent thermal reaction alone, except isoprene, under the reaction conditions employed. IP was stable at 50 °C for 48 h, although at 80 °C for 38 h and at 100 °C for 24 h, respectively, 1.3 and 1.2% yields of polymer were obtained. However, as will be shown below, this amounts only to about 10% of the amount of polymers obtained in the IP/AN system. Moreover at 50 °C, where IP is completely stable, the copolymerization of IP and AN still proceeds spontaneously and reproducibly (see below).

After spontaneous homopolymerizations of acrylonitrile or of the various alkyl 1,3-dienes under the conditions used were excluded, the reaction of isoprene and acrylonitrile was carried out under various conditions. Gravimetric analysis was used to measure the yields of both copolymers and cycloadducts. High reproducibility of the yields of cycloadduct and copolymer was found and the time-conversion curves were reasonable. Each data point in this study represents an independent experiment. Two independent investigators in this laboratory obtained essentially identical results. Similar reproducibility was observed for other dienes as well.

With these results in hand, systematic variations of concentration, solvent, temperature, and feed ratios in the reactions of a variety of alkyl 1,3 dienes with acrylonitrile could be carried out with confidence.

Dienes Which Give Both Copolymer and Cycloadduct with AN. 2,3-Dimethyl-1,3-butadiene (DMB). The reaction of DMB and AN gives the highest yield of alternating copolymer among the acyclic 1,3-dienes tested. At 80 °C the copolymerization proceeds almost at the same rate as the cycloaddition, while at 100 °C the cycloaddition predominates. This agrees with the results obtained by Koningsberger and Salomon[12] for radical-initiated copolymerization of these monomers. The copolymer composition is 1:1 and alternating throughout the run, which simplifies kinetics calculations. The molecular weight was high (η_{inh} = 1.44 dL/g) indicating a clean polymerization. Therefore this system was chosen for thorough examination.

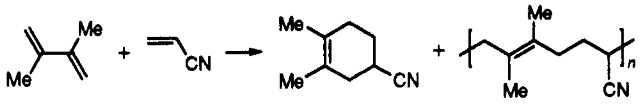


Figure 1 represents typical conversion-time curves for the reactions in DMB/AN system at 80 °C and 100 °C. The yields at different reaction times, but at the same concentration and same temperature, produced reasonably smooth curves, showing our data are reproducible and not due to impurities. No induction periods were observed.

The copolymerization was demonstrated to be free radical in nature by using known inhibitors. The stable free radicals DPPH or TEMPO and the inhibitor 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide completely eliminated copolymer formation.

The azeotropic composition for this copolymerization system is 50.5:49.5 DMB/AN. The kinetics experiments were carried out using equimolar initial concentrations.

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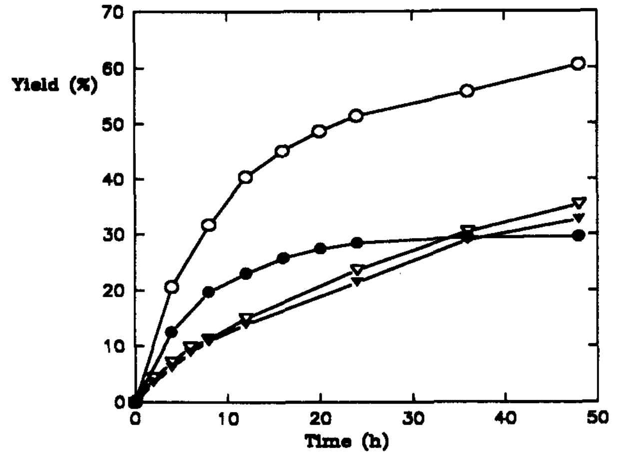

Figure 1. Time-conversion curves for 2,3-dimethylbutadiene with acrylonitrile at 3 M each in benzene: (○) yield cycloadduct 100 °C, (●) yield copolymer 100 °C, (▽) yield cycloadduct 80 °C, (▼) yield copolymer 80 °C.

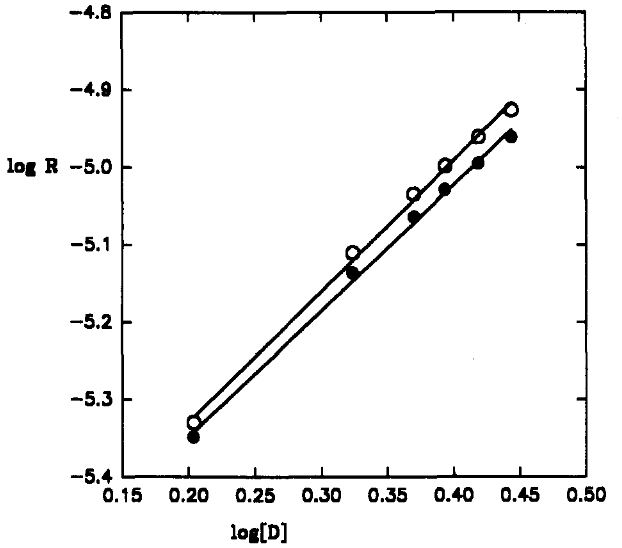

Figure 2. Differential second-order plots for alternating copolymerization and cycloaddition of 2,3-dimethylbutadiene with acrylonitrile at 80 °C and 3 M each in benzene: (○) log R_p versus log [D], (●) log R_C versus log [D].

Table I. Reaction Rates and Reaction Order of Cycloaddition and Copolymerization of Dienes with AN

		cycloaddition		copolymerization	
diene	temp (°C)	k_c (L mol^{-1} s^{-1})	reaction order	k_{pol} (L mol^{-1} s^{-1})	reaction order
DMB	80	1.45×10^{-6}	2.11	1.72×10^{-6}	2.05
	100	10.3×10^{-6}	2.05	7.17×10^{-6}	1.83
	80[a]	1.3×10^{-6}	1.97		
	100[a]	8.8×10^{-6}	2.02		
CHD	70	3.16×10^{-7}	1.91	1.3×10^{-7}	2.06
VB	100			6.09×10^{-7}	2.07

[a] In presence of inhibitor.

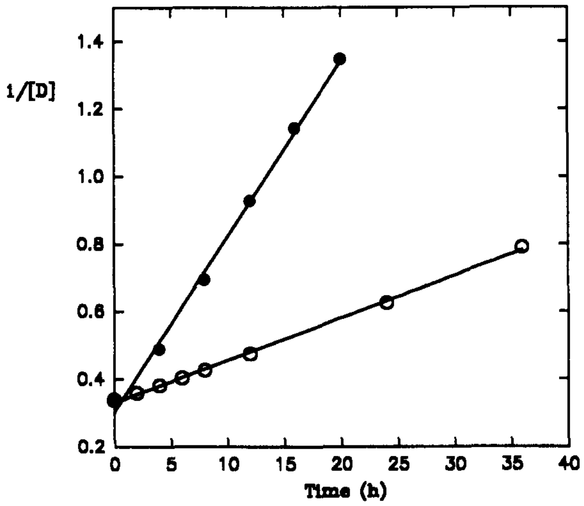

Figure 3. Integrated second-order overall kinetics for the 2,3-dimethylbutadiene with acrylonitrile reaction at 80 °C (○) and at 100 °C (●).

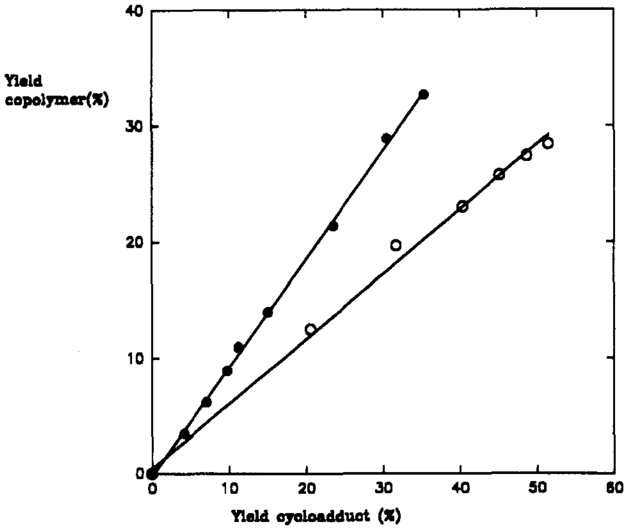

Figure 4. Yield of cycloadduct versus yield of copolymer for DMB/AN at 80 °C (●) and 100 °C (○) and 3 M each in benzene.

Since one molecule of donor and one molecule of acceptor disappear together in both the copolymerization and cycloaddition reactions, the instantaneous donor and acceptor concentrations can be calculated by subtracting the concentration of both formed cycloadduct and copolymer units from the starting concentration. The data were collected for reaction times shorter than 20 h. After about 24 h the solution became more viscous, the stirring became difficult, and the data no longer fit a straight line, which may indicate diffusion control. Plots of copolymer and cycloadduct yield against time were fitted to an empirical equation using a polynomial curve-fitting program. Rates of polymerization, R_{pol}, and of cycloaddition, R_c, were obtained as the slopes of the above curves. Plotting log R_{pol} vs log [D] (diene concentration), as well as plotting log R_c vs log [D], resulted in straight lines as shown in Figure 2 for the runs at 80 °C. The rate constants for cycloaddition k_c and for copolymerization k_{pol}, calculated, from the intercepts, are summarized in Table I for both 80 °C and 100 °C. The slopes indicate that both copolymerization and cycloaddition are second-order reactions. In confirmation of overall second order behavior, plots of 1/[D] vs t are linear at both 80 °C and 100 °C (Figure 3).

Plots of the yield of copolymer versus the yield of cycloadduct at both 80 °C and 100 °C were linear throughout the reaction (Figure 4). The significance of this observation will be discussed below.

The DMB/AN cycloaddition reaction could be studied independently of the copolymerization by adding 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide as inhibitor. The calculated rate constants k_c at 80 °C and 100 °C are included in Table I ($k_c = 8.8 \times 10^{-6}$ L mol^{-1} s^{-1}). The value of the cycloaddition rate constant k_c is the same as the

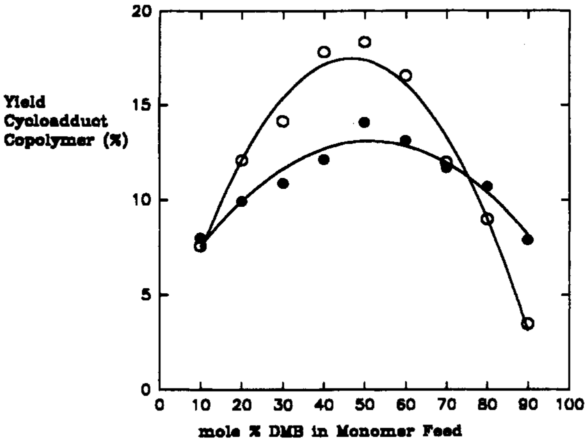

Figure 5. Effect of the monomer feed ratio (DMB/AN) on the yields of cycloadduct and copolymer at 70 °C in benzene after 24 h: (○) yield cycloadduct, (●) yield copolymer.

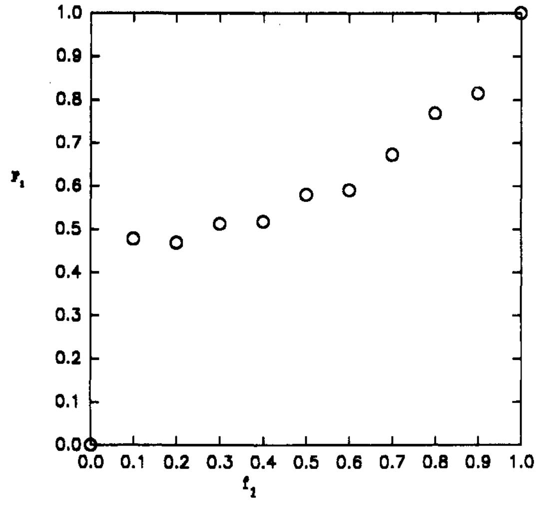

Figure 6. Dependence of copolymer composition (F_1) on the initial monomer feed (f_1) for isoprene (M_1) and acrylonitrile (M_2) at 80 °C in benzene. (r_1 = 0.42, r_2 = 0.07).

value obtained in the uninhibited competitive cycloaddition–copolymerization reaction within the experimental error at both temperatures, demonstrating that the two processes are parallel and independent.

The thermal reaction of DMB and AN is not influenced by solvent polarity, as shown by a series of experiments run in solvents of different polarity: benzene, dichloroethane, toluene, THF, DMSO, acetone and acetonitrile. The reactions were run at 80 °C, 3 M each, and for 48 h. The yield of cycloadduct was 41.9 ± 1.5% and that of copolymer 40.5 ± 1.0%. Therefore solvent polarity has no influence on either the cycloaddition or the copolymerization.

The yields of both copolymer and cycloadduct varied greatly with the DMB/AN ratio (Figure 5). The experiments were run at 70 °C for 24 h at 10.0 M total monomer concentration. The rates of both cycloaddition and copolymerization passed through a maximum at 1:1 feed ratio as would be expected for these second-order reactions.

Isoprene (IP). The IP/AN system is known to differ from the DMB/AN system in that the copolymer is no longer alternating. The dependence of the copolymer composition on the initial monomer composition in the IP(M_1)/AN(M_2) system without initiator is presented in Figure 6. The total initial monomer concentration was 10.0 M (5 M each) and the copolymer yields were kept below 10%. The copolymer compositions were determined by elemental analysis. The reactivity ratios were calculated to be r_1 = 0.42 ± 0.04, r_2 = 0.07 ± 0.02 in terms of the copolymer composition equation, which is in good agreement with the literature values for the initiated free radical copolymerization (r_1 = 0.45 ± 0.04, r_2 = 0.03 ± 0.03).[17]

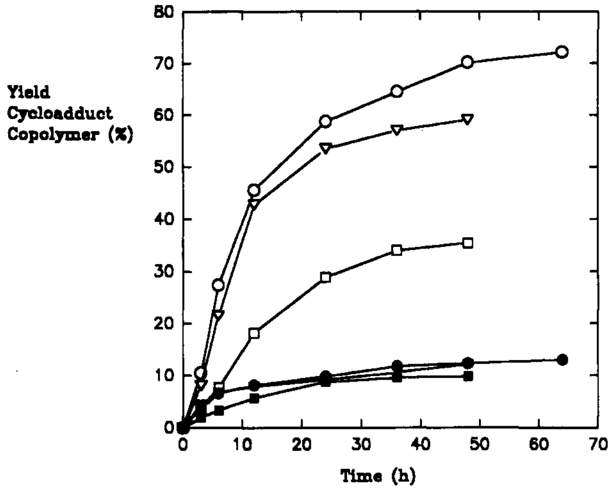

Figure 7. Time conversion curves for isoprene with acrylonitrile in benzene: 100 °C, 5 M each, (○) yield cycloadduct, (●) Yield copolymer; 100 °C, 3 M each, (▽) yield cycloadduct, (▼) yield copolymer; 80 °C, 3 M each, (□) yield cycloadduct, (■) yield copolymer.

Figure 7 illustrates typical time-conversion curves in this system. At 100 °C high yields of cycloadduct are obtained, while the yields are lower at 80 °C. In contrast to the DMB system, the copolymerization is much less competitive in this system. The copolymer yields are all below 15%. Again molecular weight was high (η_{inh} = 2.96 dL/g). Although isoprene spontaneously homopolymerized at 80 °C and 100 °C in our control experiments, the amount of homopolymer in those control experiments was only 5–10% of the copolymer yield described here when isoprene was reacted with acrylonitrile. At 50 °C, where no homopolymer of isoprene formed, copolymer was still produced reproducibly (4.9% after 95 h).

Because of the varying copolymer composition, we did not attempt a complete kinetics analysis for the IP/AN system. However the yields of both cycloadduct and copolymer were determined in benzene at 80 °C with different feed ratios. As in the DMB/AN system, maximum yields are obtained at a 1:1 feed ratio.

Reactions run with 0.5 mol % of various free radical inhibitors (hydroquinone, TEMPO, DPPH, or 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide) showed that the copolymerization was totally inhibited irrespective of the type of the inhibitor. When 0.01 M azobis(isobutyronitrile) (AIBN) was added to the reaction mixture of isoprene and acrylonitrile, copolymer formation at 70 °C predominated after 72 h (71.3% yield), but even under these conditions a small amount of cycloadduct (6.8%) was collected.

The thermal reactions of isoprene and acrylonitrile were run in six solvents with different polarities (benzene, toluene, 1,2-dichloroethane, THF, DMSO, and acetonitrile), all at the same temperature (120 °C), same con-

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[17] *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; J. Wiley & Sons: New York, 1974, p II-134.

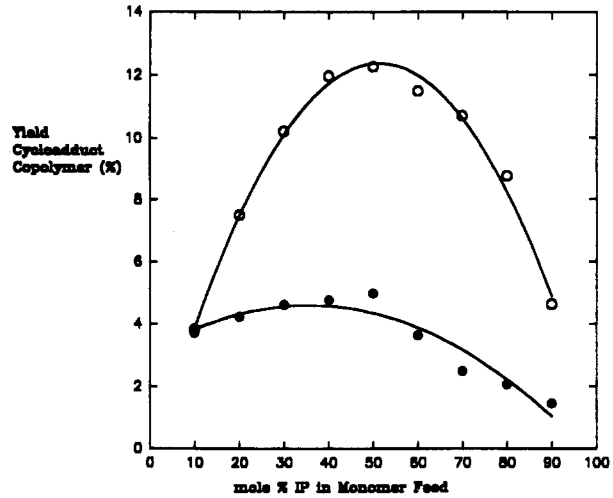


Figure 8. Influence of monomer feed on the yield of cycloadduct and copolymer in the isoprene/acrylonitrile system at 80 °C in benzene after 17 h: (○) yield cycloadduct, (●) yield copolymer.

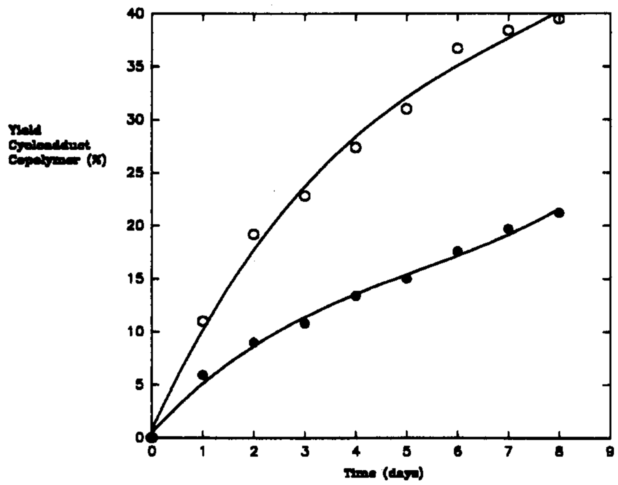


Figure 9. Time-conversion curves for the reaction of 1,3-cyclohexadiene with acrylonitrile at 3 M each at 70 °C in benzene: (○) yield cycloadduct, (●) yield copolymer.

centration (3 M each), and stopped at the same time (106 h). The yield of cycloadduct was 73.0 ± 3.0% and that of copolymer was 18.6 ± 0.6% under the given conditions. Solvent polarity has no significant influence on cycloaddition and copolymerization.

(*E*)-1,3-Pentadiene. The reaction of (*E*)-1,3-pentadiene with AN at 70 °C, 5 M each, for 120 h gave 37.3% cycloadduct and 16.9% alternating copolymer. The cycloadduct was obtained as a mixture of the two expected regioisomers, namely 4-cyano- and 5-cyano-3-methylcyclohexene in a 62:38 ratio. The copolymer has 1:1 composition as confirmed by elemental analysis and had high molecular weight (η_{inh}=2.73dL/g).

1,3-Cyclohexadiene (CHD). 1,3-Cyclohexadiene formed both cycloadduct and alternating copolymer in spontaneous reactions with AN, in agreement with literature data.[13a] The cycloadduct is 5-cyanobicyclo[2.2.2]oct-2-ene and is obtained as a mixture of the endo and exo isomers (60:40). The copolymer has 1:1 composition as shown by elemental analysis and has high molecular weight (η_{inh} = 2.38 dL/g).

The CHD/AN reactions were run with varying reaction times at 5.0 M each in benzene at 70 °C as shown in Figure 9. These data also gave linear second order plots and the rate constants are included in Table I.

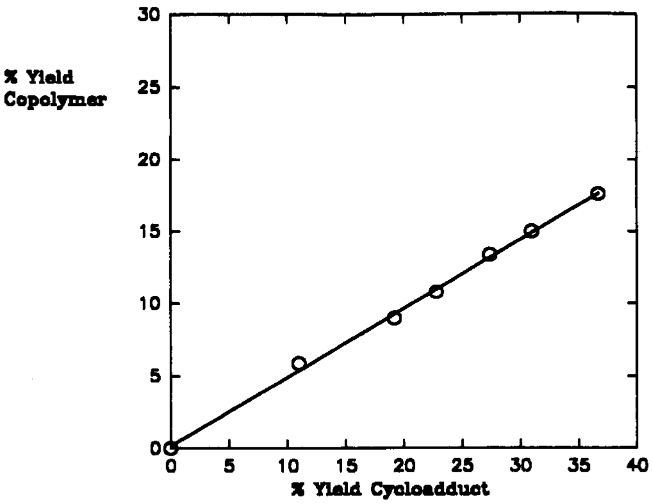


Figure 10. Yield of cycloadduct versus yield of copolymer for the reaction of cyclohexadiene and AN at 3 M each at 70 °C in benzene.

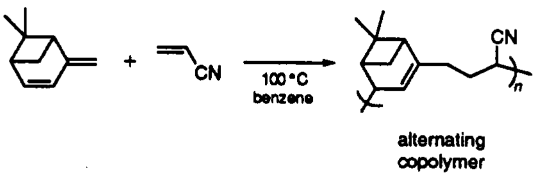
In this case, too, a linear relationship between the yields of cycloadduct and the alternating copolymer was found, as shown in Figure 10. Again the significance will be discussed below.

1,2-Dimethylenecyclohexane. With AN at 80 °C and 3 M each in 1,2-dichloroethane, 1,2-dimethylenecyclohexane gave 68.0% cycloadduct accompanied by 17.9% copolymer after 45 h. The cycloadduct was the expected [4 + 2] cycloadduct, 3-cyanobicyclo[4.4.0]dec-2-ene. The copolymer was not alternating, but contained only 43.4 mol % of the diene, as determined by elemental analysis. The inherent viscosity was reasonably high (η_{inh} = 0.99 dL/g).

Dienes Which Give Only Copolymer. (*Z*)-1,3-Pentadiene. At 70 °C and 5 M each and 120-h reaction time, (*Z*)-1,3-pentadiene with AN gave 19.2% alternating copolymer of very high molecular weight (η_{inh} = 3.08 dL/g). No cycloadduct is formed in agreement with the reported very low reactivity of (*Z*)-1,3-pentadiene in Diels–Alder reactions.[18]

2,5-Dimethyl-2,4-hexadiene. In the reaction of 2,5-dimethyl-2,4-hexadiene with AN, no cycloadduct was formed. Copolymer formed slowly: at 60 °C and 3 M after 96 h, 11.6% yield was obtained, while at 100 °C, 4 M, and 264 h, only 12.8% yield was obtained. This copolymer contained about 40% diene and 60% AN units as determined by elemental analysis. This copolymer too possessed high molecular weight. (η_{inh} = 2.57 dL/g).

Verbenene (VB). Verbenene, a trans-locked bicyclic diene,[19] gave a perfectly alternating, high molecular weight copolymer with AN (η_{inh} = 2.94 dL/g). Due to the diene structure, [4 + 2] cycloaddition is impossible, and no [2 + 2] cycloadduct was found even after long reaction time in the presence of large amounts of free radical inhibitor.



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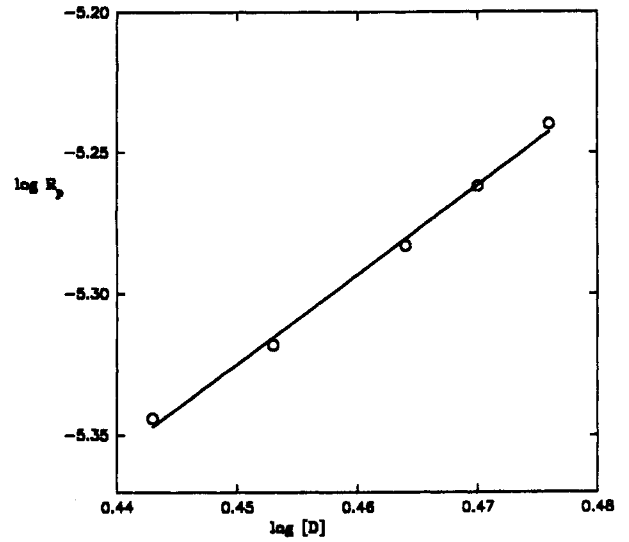


Figure 11. Differential second-order plot for the spontaneous copolymerization of verbenene with AN at 3 M each in benzene at 100 °C.

The kinetics of the spontaneous copolymerization in the verbenene/AN system was studied at 100 °C in benzene using 3 M concentration of each monomer. Plotting log R_{pol} vs log [VB] at different times yields a straight line with a slope of 2.07 indicating a second-order reaction (Figure 11).

The value for k_{pol} at 100 °C is included in Table I and is about 1 order of magnitude smaller than the k_{pol} value for DMB/AN.

Dienes Which Give Only Cycloadducts. Cyclopentadiene. Cyclopentadiene and AN were reacted in bulk in equimolar amounts to give cycloadduct in 80.5% isolated yield after 24 h. The adduct 5-cyanobicyclo[2.2.1]-hept-2-ene was obtained as an endo/exo isomer mixture (64:36 ratio) as expected. No spontaneous copolymer was formed. The cycloaddition reaction is undoubtedly much faster than that, but was not investigated further.

Photoinitiated free radical copolymerizations of cyclopentadiene and AN were attempted at 0 °C using AIBN or benzoyl peroxide as photoinitiators. After 24 h at 3 M in each monomer in 1,2-dichloroethane, the copolymer yield was only 2–4%. Even at this low temperature, the cycloaddition is so predominant as to preclude the polymerization.

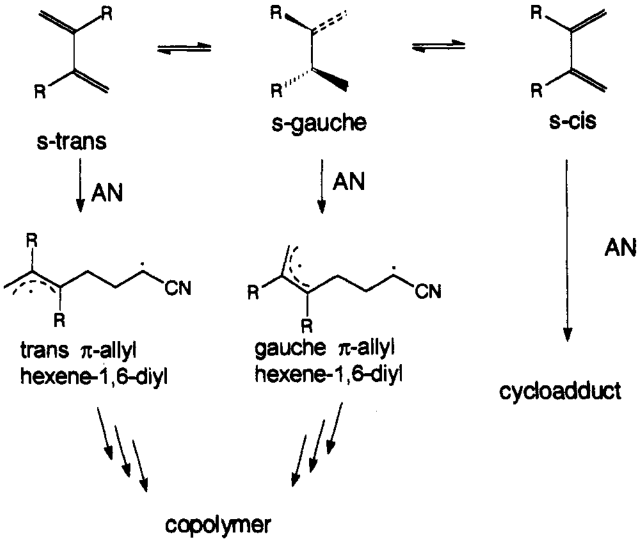
1,2-Dimethylenecyclopentane. Reaction of 1,2-dimethylenecyclopentane with AN at 100 °C in 3 M concentration each in 1,2-dichloroethane led to an isolated yield of 90.3% of the expected [4 + 2] cycloadduct, 3-cyanobicyclo[4.3.0]nonene. No [2 + 2] cycloadduct or copolymer were detected.

Discussion

The present work demonstrates that spontaneous free radical copolymerizations accompany the Diels–Alder reaction of various 1,3-dienes with acrylonitrile. The data are fully reproducible and internally consistent. Neither the dienes nor acrylonitrile undergo thermal homopolymerization at these temperatures; the only exception to this statement is isoprene, which under certain conditions gave traces of homopolymer.

The proposed mechanism is shown in Scheme II and will be discussed both from the polymer and cycloaddition point of view. The conformation of the diene is a very important factor in determining the outcome of these reactions. We suggest that the free radical initiating species is a 2-hexene-1,6-diradical formed by reaction of the s-trans or s-gauche conformation of the diene with acrylonitrile, while the s-cis conformation clearly prefers the concerted cycloaddition.

Scheme II



All the polymerization results support a standard free radical propagation mechanism. The copolymers of AN with all of these dienes are identical with those deliberately prepared by free radical initiation. The copolymerization can be inhibited by a standard free radical inhibitor and no rate change can be observed with changing solvent polarity. Enhancement of copolymer yield can be observed by deliberate addition of free radical initiators. The copolymerization reaction rates are at a maximum for equal initial concentrations of diene and acrylonitrile, as shown for both DMB and IP, so the initiating species must arise from their combination.

The importance of the s-trans/s-cis equilibrium in determining diene reactivity in [4 + 2] cycloaddition has already been stressed by Sustmann.[18] For the acyclic dienes such as IP and DMB with no terminal substituents, the s-gauche and s-cis are nearly indistinguishable in energy, the gauche form being slightly favored in each case as shown by ab initio calculations.[20] The s-trans or anti is always the lowest energy conformation. That the s-trans conformer can react with AN to form a diradical is shown by the copolymerization observed for the s-trans-locked diene verbenene. For 1,3-cyclohexadiene and 1,2-dimethylenecyclohexane, the six-membered cyclic structure may cause a significant energy difference between s-gauche and s-cis forms, and the two forms can react differently. The s-cis will undergo concerted cycloaddition. As shown by the spontaneous polymerization observed for both of these cyclic dienes with AN, the s-gauche form can also react with AN to form a hexene diradical initiator.

Substituents in the 1-position have a large influence on the relative equilibrium preferences for s-trans versus s-gauche/s-cis for acyclic diene. For (*Z*)-1,3-pentadiene and 2,5-dimethyl-2,4-hexadiene, the equilibrium is almost

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(20) (a) Bock, C. W.; Panchenko, Y. N. *J. Mol. Struct.* **1990**, *221*, 159. (b) Bock, C.W.; Panchenko, Y. N. *J. Mol. Struct.* **1989**, *187*, 69. (c) Panchenko, Y. N.; Pupyshev, V. I.; Abramenkov, A. V.; Traettenberg, M.; Cyvin, S. J. *J. Mol. Struct.* **1985**, *130*, 355. (d) Panchenko, Y. N.; Abramenkov, A. V.; Bock, C. W. *J. Mol. Struct.* **1986**, *140*, 87. (e) Mui P. W.; Grunwald, E. *J. Am. Chem. Soc.* **1982**, *104*, 6562. (f) Squillacote, M. E.; Sample, T. C.; Mui, P. W. *J. Am. Chem. Soc.* **1985**, *107*, 6842.

completely toward the s-trans conformation,[18,21] and consequently no cycloadduct is formed with AN as dienophile.

All of the dienes with terminal $CH_2=C$ groups underwent spontaneous copolymerization with AN with fairly comparable yields. This is reasonable, inasmuch as the steric factor, involving the approach of AN to a terminal $CH_2=C$ group in the diene, is almost constant and all these dienes should form comparably stabilized 2-hexene 1,6-diradicals. Such unexpected uniformity of reaction confirms that our results cannot be attributed to adventitious impurities in one or another of the dienes. Support for the bond-formation postulate is given by the fact that 2,5-dimethyl-2,4-hexadiene, with steric hindrance at both terminals, is the slowest diene we have found.

The Diels–Alder cycloaddition reaction is generally agreed to involve a concerted reaction of planar s-cis diene with acrylonitrile, simultaneously if not synchronously forming both bonds. This is supported by the much higher cycloaddition rates for the planar s-cis dienes cyclopentadiene and 1,2-dimethylenecyclopentane, giving only cycloadduct and no copolymer.[2a] Moreover the always-observed preservation of stereochemistry in the Diels–Alder reaction and its insensitivity to solvent polarity speak very strongly for a concerted mechanism. We do not challenge the concerted nature of the cycloaddition.

The kinetics equations for the copolymerization and cycloaddition reactions can be deduced if they are considered as two parallel independent reactions. The cycloaddition rate R_c can be written as follows:

$$R_c = \frac{d[CA]}{dt} = k_c[D][A] = k_c[D]^2$$

where [CA], [D], and [A] are the instantaneous concentration of cycloadduct, diene, and AN, respectively, and k_c is the rate constant for the concerted Diels–Alder cycloaddition, and [D] = [A] at all times in our kinetics experiments.

For copolymer, a conventional steady-state derivation can be done. In this scheme the diradical generation corresponds to the hexene diradical formation, while initiation is the reaction of this diradical with either diene or AN.

diradical generation: $R_{DR} = k_{gen}[D][A] = k_{gen}[D]^2$

initiation:

$$R_i = \frac{d[cop^\bullet]}{dt} = k_i[DR]\big([D] + [A]\big) = 2k_i[DR][D]$$

Therefore,

$$\frac{d[DR]}{dt} = k_{gen}[D]^2 - 2k_i[DR][D]$$

propagation: $R_p = k_p[cop^\bullet][D]$

termination by recombination only:

$$R_t = \frac{-d[cop^\bullet]}{dt} = k_t[cop^\bullet]^2$$

where [DR] and [cop$^\bullet$] are the instantaneous concentration of diradicals and copolymer radicals, respectively, and k_{gen} is the rate constant for generation of diradical species. Initiation and termination rates are equal in steady-state conditions, as are the rates of formation and disappearance of diradical. Steady-state expressions lead respectively to:

$$R_p = k_p\left\{\frac{2k_i}{k_t}[DR][D]\right\}^{0.5}[D]$$

$$R_p = k_p\left\{\frac{k_{gen}}{k_t}\right\}^{0.5}[D]^2$$

Diene and AN disappear at equal rates in both the cycloaddition and propagation reactions.

Therefore,

$$\frac{-d[D]}{dt} = k_c[D]^2 + k_p\left\{\frac{k_{gen}}{2k_t}\right\}^{0.5}[D]^2$$

with the overall polymerization rate constant k_{pol} (see Table I) equal to $k_p\ (k_{gen}/2k_t)^{1/2}$ or $-d[D]/dt = k[D]^2$.

This kinetic derivation for the simplest case, namely two independent reactions, gives second-order kinetics for both cycloaddition and copolymerization. Accordingly the observed overall second-order rate constants are the sum of the two individual second-order k values and can be dissected using the constant fraction of each product. That this fraction remains constant during the runs has been shown in Figures 4 and 10, for DMB and CHD with AN, respectively.

If the diradical competitively cyclized and initiated copolymerization, the two reactions, namely, the cycloaddition and the copolymerization, would not be independent. The fraction of copolymer formed during each run would decline as the monomer concentrations fell because the cyclization reaction of the diradical would be independent of the monomer concentration, while the initation and propagation rates of the polymerization are not. This is not in agreement with our finding that the copolymer/cycloadduct ratio is constant during the reaction.

Because of the enormous amplification provided by polymerization, very few diradicals need be formed to provide comparable quantities of copolymer and cycloadduct. This is nicely confirmed by the careful studies of Doering and Mastrocola, who showed that the transition states for stepwise [2 + 2] cycloaddition of butadiene to acrylonitrile lay 10.2–11.2 kcal mol^{-1} above that for concerted cycloaddition.[22] That unsaturated compounds can cyclodimerize thermally by way of diradical formation is well established.[23] Accordingly diradical formation by reaction of a diene with an olefin is entirely reasonable.

Firestone suggested that 2-hexene 1,6-diradicals formed when diene and dienophile are allowed to react, and that these diradicals can cyclize to Diels–Alder adducts.[4] The observed spontaneous copolymerizations strongly support his first contention. As to the second statement, Huisgen has already analyzed the objections.[2d] The 2-hexene-1,6-diradical formed from s-trans diene has a trans π-allyl structure, which could cyclize only to a vinyl cyclobutane and not to a Diels–Alder adduct. Moreover, the adherence to second order kinetics also refutes this statement.

The gauche-locked dienes 1,3-cyclohexadiene and 1,2-dimethylenecyclohexane give gauche π-allyl diradicals. Although these would be expected to cyclize very readily, each still gives a substantial amount of copolymer and no

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(21) O'Shea, K. E.; Foote, C. S. *Tetrahedron Lett.* **1990**, *31*, 841.

(22) Doering, W. von E.; Mastrocola, A. R. *Tetrahedron* **1981**, *37*, (1), 329–344.

(23) Review: Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, *117*.

evidence is found to substantiate this cyclization hypothesis. For the CHD/AN case we also observed kinetics corresponding to two parallel independent reactions.

Single electron transfer to form initiating ion-radicals can also be excluded as an initiation mechanism for the observed spontaneous copolymerizations. If that were the case, 2,5-dimethyl-2,4-hexadiene, being the most electron-rich diene in the study, would react fastest with AN. Instead it happens to be the slowest to react.

A Mayo-type mechanism,[24] wherein initial [4 + 2] cycloaddition is followed by H-atom transfer to form initiating monoradicals, can also be excluded. This mechanism would require that the rates increase with cycloadduct concentration, also contrary to fact.

We have observed spontaneous copolymerizations competing with cycloadditions in other cases as well. 1-Methoxybutadiene[25] and 4-methyl-1,3-pentadiene[26] also react with electrophilic olefins to give both copolymers and cycloadducts. Accordingly this phenomenon may be of wide generality.

Conclusion

Our investigations of the spontaneous reactions of alkyl-1,3-dienes with AN have shown that spontaneous copolymerization competes with the expected [4 + 2] cycloadditions. We have correlated the structure of the various dienes with their ability to initiate these alternating copolymerizations.

For acyclic dienes, the main factor determining their ability to form a hexene diradical with AN is the presence or absence of an unhindered $CH_2=C$ terminal group. As has been shown by other researchers previously[2,18] the ability of these dienes to undergo concerted [4 + 2] cycloadditions is governed by their s-trans/s-cis (s-gauche) equilibrium. Therefore copolymerization competes rather efficiently with cycloaddition for dienes such as 2,3-dimethylbutadiene and isoprene, which have a $CH_2=C$ terminal and for which the s-cis and s-trans forms both exist. Only copolymer is obtained for (*Z*)-1,3-pentadiene, which exists almost exclusively in the s-trans form. The slowest reaction was observed with the highly substituted 2,5-dimethyl-2,4-hexadiene.

A very similar situation is observed for the cyclic dienes. Cyclopentadiene and 1,2-dimethylenecyclopentane, which exist in s-cis conformation, only yield cycloadduct with AN. In the reactions of s-gauche cyclic 1,3-dienes, such as 1,3-cyclohexadiene and 1,2-dimethylenecyclohexane with AN, competition between the concerted [4 + 2] cycloadditions and the alternating copolymerization is found, indicating that the s-gauche conformation is able to form a hexene diradical initiating species by bond formation with AN. This is further supported by the fact that the Diels–Alder cycloadducts of cycloocta- and cyclonona-1,3-diene with maleic anhydride can only be obtained in the presence of free radical inhibitor.[14] The trans-locked cyclic diene verbenene is also able to form the initiating diradical with AN, and in this case concerted [4 + 2] cycloadditions are naturally impossible.

All data presented in this study are in agreement with the proposed mechanism. The concerted cycloadditions and the alternating copolymerizations compete as two independent parallel, second-order reactions. The polymerizations are proof that a diene can react with AN to form a hexene 1,6-diradical. The amplification feature associated with polymerization permits us to observe this small fraction of diradicals.

Experimental Section

Instrumentation. ^1H NMR and ^{13}C NMR spectra were taken on a Bruker WM-250 and a Bruker AM-500 nuclear magnetic resonance spectrometer. GC/MS spectra were obtained with a Hewlett-Packard GC/MS system. Gas chromatograms were performed using a Varian 3300 GC with an OV-17 and an OV-101 column. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. Melting points were measured from a Thomas-Hoover capillary melting point apparatus and are corrected. Elemental analyses were determined by Desert Analytics, Tucson, AZ. Inherent viscosities were measured with an Ostwald-Fenske viscosimeter at 30 °C.

Solvents. Benzene, toluene, 1,2-dichloroethane, carbon tetrachloride, acetonitrile, and dimethyl sulfoxide (DMSO) were refluxed from CaH_2 overnight and distilled. Tetrahydrofuran (THF) was refluxed over sodium, distilled, and stored over 4-Å molecular sieves under argon.

Reactants. Acrylonitrile (AN), isoprene (IP), 2,3-dimethyl-1,3-butadiene (DMB), 1,3-cyclohexadiene, and (*E*)-1,3-pentadiene were purchased from Aldrich Chemical Co., refluxed over calcium hydride overnight, distilled at atmospheric pressure, and stored over 4-Å molecular sieves under argon. 2,5-Dimethyl-2,4-hexadiene was treated in the same way as above reagents but was distilled under reduced pressure. (*E*)-1,3-Pentadiene (Aldrich) in sealed ampules was used immediately after opening without further purification. Cyclopentadiene was obtained by cracking dicyclopentadiene.

Synthesis of Verbenene (VB). Verbenene was prepared in two steps according to a literature procedure.[27] In the first step (1*S*)-(−)-α-pinene is reacted with *N*-bromosuccinimide (NBS) in carbon tetrachloride. After removal of solvent and remaining starting material, a mixture of verbenyl bromide, myrtenyl bromide, and other bromo derivatives was collected at 57–70 °C (0.5 mmHg). After removing some crystalline material which formed on cooling, redistillation with a spinning band column assembly gave 58% of a mixture of verbenyl bromide and myrtenyl bromide at 60–62 °C (0.7 mmHg). GC showed 98.4% purity in verbenyl bromide and myrtenyl bromide, the two isomers. ^1H NMR showed two new vinyl peaks at 3.93 and 4.65 ppm.

The verbenyl bromide–myrtenyl bromide mixture was treated with 2,4,6-collidine, using a slightly modified procedure from the literature.[27] The mixture was heated at 140 °C for 4 h and cooled to room temperature. Hydrochloric acid was added to pH 3–4 and *n*-pentane was added several times to extract the product. After drying over $MgSO_4$ and evaporation of the solvent, the residue was distilled through a 12-in. Vigreux column in the presence of 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide as inhibitor. Verbenene was obtained at 73–74 °C (8 mmHg) with 98% purity by GC: yield 47%; ^1H NMR ($CDCl_3$) δ 6.32 (1H, t), 6.03 (1H, d), 4.67 (2H, q), 2.65–2.62 (1H, m), 2.55–2.51 (1H, m), 2.31–2.27 (1H, m) 1.50 (1H, d), 1.36 (3H, s), 0.86 (3H, s); ^{13}C NMR ($CDCl_3$) δ 150.3, 138.4, 126.7, 107.2, 51.9, 43.7, 42.9, 36.1, 26.3, 22.3; MS (70 eV) *m/e* (%) 134 (M^+, 42), 119 ($M^+ - CH_3$, 68), 91 ($M^+ - CH_3CHCH_3$, 100), 77 ($M^+ - CH_3CHCH_3 - CH_3$, 38). Anal. Calcd for $C_{10}H_{14}$: C 89.49, H 10.51. Found: C 89.04, H 10.23.

Synthesis of 1,2-Dimethylenecyclohexane. This synthesis was modified from the synthetic route of Bailey and Golden:[28] To a suspension of lithium aluminum hydride (7.59 g, 0.2 mol) in 300 mL of dry ether in a flask equipped with a mechanical stirrer under nitrogen was added *cis*-1,2-cyclohexanedicarboxylic anhydride (15.4 g, 0.1 mol) in 50 mL ether dropwise at 0 °C. The mixture was heated to reflux overnight. The reflux condenser was then exchanged for a distillation setup and 100 mL of acetic anhydride (1.0 mol) was added dropwise while the ether distilled out. After the gray color of LAH turned white, about 6 mL of

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(24) Mayo, F. R. *J. Am. Chem. Soc.* **1968**, *90*, 1289.

(25) Mikhael, M.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1993**, *26*, 4100.

(26) Mikhael, M.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules*, in press.

(27) Zweifel, G.; Whitney, C. C. *J. Org. Chem.* **1966**, *31*, 4178.

(28) Bailey, W. J.; Golden, H. R. *J. Am. Chem. Soc.* **1953**, *75*, 4780.

acetic acid (0.1 mol) was added and the reaction mixture was refluxed for another 12 h. The mixture was poured into ice–water and stirred for 3 h. Since the aluminum salts are not very soluble in water, 6 N HCl was added and the product was extracted several times with ether. The ether layer was washed with 10% NaHCO$_3$ until pH 8.0, washed with water three times, and dried over MgSO$_4$. After evaporating the ether, the residue was vacuum distilled with a Vigreux column and 21.25 g of *cis*-1,2-bis(acetoxymethyl)cyclohexane was ollected at 130–134 °C (5 mmHg): yield 93%; ^{1}H NMR (CDCl$_3$) δ 4.04–3.94 (4H, m), 1.92–1.88 (2H, m), 1.76 (6H, s), 1.37–1.25 (6H, m), 1.20–1.15 (2H, m); ^{13}C NMR (CDCl$_3$) δ 170.58, 64.84, 36.60, 26.53, 23.55, 20.76; IR (KBr, cm^{-1}) 2929, 2860, 1728, 1450, 1421, 1368, 1284, 1248; MS (70 eV), the parent ion can be identified by CI (methane) ionization MS, *m/e* (%) 229 ((M + 1)$^+$, 16), 271 ((M + 43)$^+$, 8), 169 ((M + 1)$^+$ – COOCH$_3$, 60), 109 ((M + 1)$^+$ – 2COOCH$_3$, 100). Anal. Calcd for C$_{12}$H$_{20}$O$_4$: C 63.14, H 8.83. Found: C 63.12, H 8.85.

The diacetate (23.5 g, 0.1 mol) was pyrolyzed at 540–550 °C through a 32-in. quartz column at the rate of 0.5 g/min. Nitrogen gas was used as a carrier, and the pyrolysate was collected at –78 °C. The pyrolysate was washed exhaustively with 10% NaHCO$_3$ to remove the acetic acid formed during pyrolysis, washed with water, and dried over MgSO$_4$. GC showed three peaks (ratio 19.6, 39.2, and 41.2%). The mixture was distilled under reduced pressure in the presence of 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide through a Vigreux column and a typical run gave the following: fraction 1 , 4.02 g (37.2% yield), bp 63–65 °C at 90 mmHg, 100% pure 1,2-dimethylenecyclohexane by GC; fraction 2, 7.33 g (43.6% yield), bp 116–119 °C at 40 mmHg, 1-methylene-2-(acetoxymethyl)cyclohexane; fraction 3, 3.87 g (17% recovery), bp 131–134 °C at 5 mmHg, starting diacetate. Fractions 2 (7.2 g) and 3 (3.8 g) were repyrolyzed and treated with the same workup process, and an additional 2.45 g of 1,2-dimethylenecyclohexane resulted: total yield 59%; ^{1}H NMR (CDCl$_3$) δ 4.91 (2H, t), 4.62 (2H, d), 2.24 (4H, bs), 1.65–1.60 (4H, m); ^{13}C NMR (CDCl$_3$) δ 149.6, 107.8, 35.4, 26.9; MS (70 eV), *m/e* (%) 108 (M$^+$, 46), 93 (M$^+$ – CH$_2$ – H, 38), 79 (M$^+$ – CH$_2$CH$_2$ – H, 24). Anal. Calcd for C$_8$H$_{12}$: C, 88.89; H, 11.11. Found: C, 88.64; H, 10.90.

Synthesis of 1,2-Dimethylenecyclopentane. This synthetic route was modified from a literature procedure.[29] In a 300-mL three-neck flask fitted with a soxhlet was placed 2.88 g of lithium aluminum anhydride in 150 mL of anhydrous ether. *trans*-1,2-Cyclopentanedicarboxylic acid (6 g, 37.1 mmol) was placed in the soxhlet thimble and the LAH solution was heated to reflux to extract the diacid slowly into the reaction flask overnight. The ether was distilled off while 25 mL of acetic anhydride followed by 5 mL of acetic acid were added. The reaction mixture was refluxed for another 12 h and was poured into ice–water and just enough 10% HCl was added to dissolve the aluminum salt. The product was extracted with ether several times, washed with 10% NaHCO$_3$ and with water, and dried over MgSO$_4$, and the ether was evaporated. The product *trans*-1,2-bis(acetoxymethyl)-cyclopentane (7.51 g, 35 mmol, 92.6% yield) was used without further purification (purity 92% by GC): ^{1}H NMR (CDCl$_3$) δ 4.06–3.99 (4H, m), 2.05 (6H, s), 1.98–1.95 (2H, m), 1.84–1.80 (2H, m), 1.64–1.60 (2H, m), 1.41–1.37 (2H, m); ^{13}C NMR (CDCl$_3$) δ 170.8, 67.4, 41.5, 29.6, 24.2, 20.7; MS (70 eV) CI (methane) ionization *m/e* (%) 215 ((M + 1)$^+$, 10), 155 ((M + 1)$^+$ – CH$_3$COOH, 14), 95 ((M + 1)$^+$ – 2CH$_3$COOH, 100).

The pyrolysis furnace and column were the same as the one described above. At 540 °C, 7.5 g (35 mmol) of diacetate was passed through the quartz column in 0.1 g/min. The pyrolysate was collected and dissolved in ether and then washed several times with 10% NaHCO$_3$ followed by water. After K$_2$CO$_3$ drying and evaporation of the ether, the residue was vacuum distilled with a short-path apparatus. Three fractions were collected: fraction 1, bp 55–57 °C (110 mmHg), 0.46 g, 4.9 mmol, 14% yield of 1,2-dimethylenecyclopentane and the purity was only 91.3% from GC analysis contaminated with 7% of monoacetate, fraction 2, bp 114–117 °C (40 mmHg), 0.92 g, 6.0 mmol, 16% yield of 1-methylene-2-(acetoxymethyl)cyclopentane; fraction 3, bp 112–117 °C (2.0 mmHg) 2.97 g, 13.9 mmol, 37.4% recovery of the starting diacetate. The obtained mono- and diacetate were combined (total 19.8 mmol), repyrolyzed at 550 °C, and treated in the same workup procedure, and 0.367 g (3.9 mmol) of product was obtained in 19.6% yield. This time the product was pure (98% by GC): ^{1}H NMR (CDCl$_3$) δ 5.34 (2H, s), 4.87 (2H, s), 2.44–2.40 (4H, m), 1.69–1.64 (2H, m); ^{13}C NMR (CDCl$_3$) δ 148.8, 103.4, 34.1, 24.0; MS (70 eV) *m/e* (%) 94 (M$^+$, 42), 79 (M$^+$ – CH$_2$ – H, 100), 65 (M$^+$ – 2CH$_2$ – H, 14).

Typical Procedure for Spontaneous Reactions of 1,3-Dienes with AN. Calculated amounts of acrylonitrile, the 1,3-diene, and solvent were transferred to a polymerization tube equipped with a vacuum adapter. The mixture was degassed three times using the freeze–thaw method. The reaction mixture was placed in a thermostated bath behind a blast shield. After a certain time the mixture was cooled in ice and some chloroform containing inhibitor (usually 1–2 mL) was quickly added to quench the reaction. The solution was then added to 50–100 mL of methanol dropwise with stirring. The precipitate (generally copolymer) was filtered, dried under vacuum to constant weight, and characterized. For dienes with high boiling points such as 2,5-dimethyl-2,4-hexadiene, 1,2-dimethylenecyclohexane, and verbenene, several reprecipitations in hexane were necessary to remove all traces of diene. The solvent was evaporated and the residue (mostly cycloadduct) was characterized and further purified.

Control Reactions. The 1,3-dienes or acrylonitrile were purified, degassed, heated alone to desired temperature, and then treated in a similar way as described above. If no polymer precipitated in methanol, the solution was checked by GC to see whether new compounds had formed. The residue after evaporation of solvent was analyzed by NMR or GC/MS. Acrylonitrile was heated at 80 °C, 100 °C for 48 h; 2,3-dimethyl-1,3-butadiene was heated at 80 °C and 100 °C for 24 and 48 h, respectively; 2,5-dimethyl-2,4-hexadiene was heated at 100 °C for 264 h; verbenene was heated at 100 °C for 70 h; 1,3-cyclohexadiene was heated at 60 °C for 26 h; 1,2-dimethylenecyclohexane was heated at 60 °C for 48 h. No spontaneous dimerizations or homopolymerizations were detected by gravimetric analysis and NMR analysis, except that a trace amount of polymer of 2,3-dimethyl-1,3-butadiene was observed at 80 °C, which was too small to be accounted for. (*E*)-1,3-Pentadiene was checked at 65 °C for 48 h and no spontaneous homopolymerization was found as well. Isoprene was heated at 50 °C for 48 h and no spontaneous dimerization or homopolymerization was observed. However, at 80 °C polyisoprene was obtained in 1.3% yield after 38 h and no small molecules were found. The homopolymer was also detected in 1.2% yield at 100 °C after 24 h.

2,3-Dimethyl-1,3-butadiene and Acrylonitrile. The [4 + 2] cycloadduct 1,2-dimethyl-4-cyanocyclohexene is liquid: ^{1}H NMR (CDCl$_3$) δ 2.75 (1H, m), 2.24 (2H, bs), 2.17–1.73 (4H, m), 1.62 (6H, s); ^{13}C NMR (CDCl$_3$): δ 125.7, 122.4, 122.3, 34.3, 29.4, 26.2, 25.4, 18.9, 18.7; MS (70 eV) *m/e* (%) 135 (M$^+$, 39), 120 (M$^+$ – CH$_3$, 30), 109 (M$^+$ – CN, 15), 93 (M$^+$ – CN – CH$_3$, 62), 82 (M$^+$ – CH$_2$CHCN, 58), 67 (M$^+$ – CH$_2$CH$_2$CN – CH$_3$, 100), 53 (M$^+$ – CH$_2$CH(CH$_3$)CH(CH$_3$)CH$_2$, 28). Anal. Calcd for C$_9$H$_{13}$N: C, 79.95; H, 9.69; N, 10.36. Found: C, 79.89; H, 9.77; N, 10.11.

Copolymer (1:1 feed ratio): ^{1}H NMR (CDCl$_3$) δ 2.98–2.86 (1H, br m), 2.30–2.04 (6H, br m), 1.88–1.70 (6H, br m), 1.61 (3H, s); inherent viscosity 1.44 dL/g at 30 °C in chloroform. Anal. C, 79.21; H, 9.77; N, 10.46; corresponding to DMB/AN ratio of 50.4:49.6.

Isoprene and Acrylonitrile. The [4 + 2] cycloadduct isomer mixture, 4-cyano-1-methylcyclohexene and 5-cyano-1-methylcyclohexene, is liquid. The cycloadduct is composed of the two regioisomers in which the two functional groups are located either "para" or "meta" and the ratio is 65:35: ^{1}H NMR (CDCl$_3$) of the mixture, δ 5.44 (0.33H, br s), 5.34 (0.67H, br s), 2.77 (1H, m), 2.35–2.20 (2H, m), 2.10–1.88 (4H, m), 1.67 (3H, s); ^{13}C NMR (CDCl$_3$) of the mixture, δ 134.2, 130.4, 122.5, 120.9, 117.4, 32.7, 28.4, 27.7, 25.7, 25.1, 24.4, 23.5, 23.3, 23.0, 22.7; GC-MS (70 eV) para isomer *m/e* (%), 121 (M$^+$, 30), 106 (M$^+$ – CH$_3$, 19), 94 (M$^+$ – HCN, 10), 79 (M$^+$ – CH$_3$CHCH$_2$, 29), 68 (M$^+$ – CH$_2$CHCN, 100), 53 (M$^+$ – CH$_2$CH(CH$_3$)CH$_2$, 30); meta isomer *m/e* (%) 121 (M$^+$, 49), 106 (M$^+$ – CH$_3$, 41), 94 (M$^+$ – HCN, 38), 79 (M$^+$ – CH$_3$CHCH$_2$, 100), 68 (M$^+$ – CH$_2$CHCN, 52), 53 (M$^+$ – CH$_2$CH(CH$_3$)CH$_2$, 39); IR (KBr, cm^{-1}) 2928, 2850, 2236, 1735, 1677, 1438. Anal. Calcd. for C$_8$H$_{11}$N: C, 79.29; H, 9.15; N, 11.55. Found: C, 78.89; H, 9.37; N, 11.21.

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(29) Bailey, W. J.; Sorenson, W. R. *J. Am. Chem. Soc.* **1954**, *76*, 5421.

Copolymer (1:1 feed ratio): ^{1}H NMR ($CDCl_3$) δ 5.30–5.26 (broad d), 5.10–5.08 (broad d), 2.71–2.68 (broad m), 2.28–2.25 (broad m), 2.17 (s), 2.13–2.05 (broad m), 1.68–1.56 (broad m); IR (KBr, film, cm^{-1}) 2928, 2846, 2240, 1729, 1689, 1434, 1368; inherent viscosity 2.96 dL/g at 30 °C in chloroform. Anal. C, 79.61; H, 9.56; N, 9.47; corresponding to IP/AN ratio of 56.5:43.5.

(*E*)-1,3-Pentadiene and Acrylonitrile. The [4 + 2] cycloadduct (4-cyano-3-methyl-1-cyclohexene and 5-cyano-3-methyl-1-cyclohexene) is a liquid consisting of two regioisomers, ortho and meta, as shown by GC with ratio 62:38: ^{1}H NMR ($CDCl_3$) δ 5.74–5.48 (2H, m), 2.96–2.93 (1H, m), 2.50–1.82 (4H, m), 1.20–1.02 (at 250 MHz: four singlets, at 500 MHz: 1.19 dd, 1.17 dd, 1.03 dd, 1.02 dd, the ratio of four stereoisomers is 56:33:8:3 according to intensity of the peaks.); MS (70 eV) meta isomer, *m/e* (%) 121 (M^+, 23), 106 ($M^+ - CH_3$, 18), 94 ($M^+ - HCN$, 20), 79 ($M^+ - HCN - CH_3$, 38), 68 ($M^+ - CH_2CHCN$, 100), 53 ($M^+ - CH_2CHCH(CH_3)$, 26); ortho isomer, *m/e* (%) 121 (M^+, 20), 106 ($M^+ - CH_3$, 15), 94 ($M^+ - HCN$, 18), 79 ($M^+ - HCN\text{-}CH_3$, 36), 68 ($M^+ - CH_2CHCN$, 100), 53 ($M^+ - CH_2CHCH(CH_3)$, 26). Anal. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.55. Found: C, 79.00; H, 9.67; N, 11.36.

Copolymer (1:1 feed ratio): ^{1}H NMR ($CDCl_3$) δ 5.81–5.67 (br d), 5.65–5.44 (br s), 5.43–5.40 (br m), 2.75–2.56 (br s), 2.50–2.27 (br m), 1.79–1.58 (br m), 1.22–1.05 (br m); inherent viscosity 2.73 dL/g at 30 °C in chloroform. Anal. C, 78.34; H, 9.08; N, 11.07; corresponding to a diene AN ratio of 49.6:50.4.

1,3-Cyclohexadiene and Acrylonitrile. The [4 + 2] cycloadduct 5-cyanobicyclo[2.2.2]oct-2-ene is a solid, recrystallized from petroleum ether: mp 55–60 °C, a mixture of two stereoisomers and the ratio of endo isomer to exo isomer by GC or GC/MS was 64:36 (±4) the purity of the mixture of two isomers is 100%; ^{1}H NMR ($CDCl_3$) δ 6.46 (1H, t), 6.34–6.30 (1.7H, m), 6.25–6.22 (0.6H, m), 2.90-2.87 (0.6H, m), 2.79–2.77 (0.3H, m), 2.73–2.70 (0.6H, m), 2.66–2.61 (0.8H, m), 2.07–1.93 (0.8H, m), 1.75–1.68 (0.7H, m), 1.56–1.44 (2H, m), 1.37–1.25 (2H, m); ^{13}C NMR ($CDCl_3$) δ 136.2, 135.3, 132.3, 130.9, 123.3, 123.0, 32.6, 32.0, 31.6, 30.6, 28.7, 28.6, 27.8, 27.2, 24.8, 24.4, 23.7, 20.8; MS (70 eV) exo isomer, *m/e* (%) 133 (M^+, 2.5), 117 ($M^+ - CN$, 1.0), 105 ($M^+ - CH_2CH_2$, 14), 80 ($M^+ - CH_2CHCN$, 100), endo isomer, *m/e* (%) 133 (M^+, 3.0), 117 ($M^+ - CN$, 1.0), 105 ($M^+ - CH_2CH_2$, 8.2), 80 ($M^+ - CH_2CHCN$, 100). Anal. Calcd for $C_9H_{11}N$: C, 81.16; H, 8.32; N, 10.52. Found: C, 80.64; H, 8.20; N, 10.08.

Copolymer (in 1:1 feed ratio): ^{1}H NMR ($CDCl_3$) 5.92–5.57 (2H, broad m), 2.73–2.60 (1H, broad m), 2.39–1.50 (8H, broad m); inherent viscosity 2.38 dL/g at 30 °C in chloroform. Anal. C, 80.24; H, 8.38; N, 10.09; corresponding to unit diene/AN ratio of 49.8:50.2.

1,2-Dimethylenecyclohexane and Acrylonitrile. The [4 + 2] cycloadduct 3-cyano-1-bicyclo[4.4.0]decene is a viscous liquid, 100% pure: ^{1}H NMR ($CDCl_3$) δ 2.81–2.76 (1H, m), 2.19–2.15 (2H, m), 2.07–2.02 (1H, m), 1.97–1.92 (1H, m), 1.87–1.81 (5H, m), 1.64–1.54 (5H, m); ^{13}C NMR ($CDCl_3$) δ 127.9, 124.5, 122.3, 32.9, 29.7, 27.8, 25.7, 25.1, 22.6; MS (70 eV) *m/e* (%) 161 (M^+, 66), 133 ($M^+ - CH_2CH_2$, 58), 119 ($M^+ - CH_2CH_2CH_2$, 42), 105 ($M^+ - CH_2CH_2CH_2CH_2$, 26), 93 ($M^+ - CH_2CHCN$, 100), 79 ($M^+ - CN - CH_2CH_2CH_2CH_2$, 86). Anal. Calcd for $C_{11}H_{15}N$: C, 81.94; H, 8.68; N, 9.38. Found: C, 81.72; H, 8.60; N, 9.28.

Copolymer (at 1:1 feed ratio): ^{1}H NMR ($CDCl_3$) 2.76–2.44 (br m), 2.38–2.15 (br m), 2.07–1.92 (br s), 1.80–1.56 (br m); inherent viscosity 0.99 dL/g at 30 °C in chloroform. Anal. Found: C, 81.08; H, 9.33; N, 10.08; corresponding to a diene/AN ratio of 43.4:56.6.

(*Z*)-1,3-Pentadiene and Acrylonitrile. Only copolymer was formed in this reaction (1:1 feed ratio): ^{1}H NMR ($CDCl_3$) δ 5.50–5.49 (broad s), 5.46–5.40 (broad m), 2.70–2.62 (broad m), 2.29–2.19 (broad m), 1.78–1.61 (broad m); 1.12–1.04 (broad m); inherent viscosity 3.08 dL/g at 30 °C in chloroform. Anal. C, 77.91; H, 9.17; N, 10.24; corresponding to a diene/AN ratio of 49.3:50.7.

2,5-Dimethyl-2,4-hexadiene and Acrylonitrile. This reaction gave the copolymer as the only product (1:1 feed ratio): ^{1}H NMR ($CDCl_3$) δ 5.51–5.28 (2H, br m), 2.77–2.56 (1H, br m), 2.17–1.46 (2H, m), 1.21–1.02 (12H, 4 br s); inherent viscosity 2.24 dL/g at 30 °C in chloroform. Anal. Found: C, 78.22; H, 9.80; N, 10.77; corresponding to a diene/AN ratio of 38.7:61.3.

Verbenene and Acrylonitrile. Copolymer was the only product (1:1 feed ratio): ^{1}H NMR ($CDCl_3$) δ 5.38–5.31 (1H, br d), 2.65–2.52 (1H, m), 2.39–1.56 (8H, m), 1.33 (3H, br s), 0.96 (3H, t); inherent viscosity 2.94 dL/g at 30 °C in chloroform. Anal. C, 82.69; H, 9.23; N, 7.40; corresponding to a VBE/AN ratio of 50:50.

Cyclopentadiene and Acrylonitrile. Only the expected cycloadduct 5-cyanobicyclo[2.2.1]hept-2-ene was formed as an oily liquid. The ratio of endo/exo is 64/37 as determined by GC: ^{1}H NMR ($CDCl_3$) of isomer mixture: δ 6.32 (0.6H, q), 6.19–6.15 (1.2H, m), 6.03 (0.33H, q), 3.22 (1H, m), 3.02 (1H, d), 2.86 (0.55H, m), 2.19–2.11 (1H, m), 1.95 (0.4H, m), 1.57–1.49 (1.7H, m), 1.33–1.29 (0.6H, m), 1.20 (0.6H, d); ^{13}C NMR ($CDCl_3$) δ 138.5, 137.8, 133.8, 132.5, 123.2, 122.6, 48.2, 47.2, 46.9, 45.5, 42.1, 41.6, 32.2, 32.0, 27.0, 26.9; GC-MS (70 eV) exo isomer, *m/e* (%) 119 (M^+, 1.6), 104 ($M^+ - CH_2 - H$, 3.0), 91 ($M^+ - HCN - H$, 4.5), 77 ($M^+ - HCN - CH_2 - H$, 4.2), 66 ($M^+ - CN - CHCH_2$, 100); endo isomer, *m/e* (%) 119 (M^+, 1.6), 104 ($M^+ - CH_2 - H$, 2.4), 91 ($M^+ - HCN - H$, 4.0), 77 ($M^+ - HCN - CH_2 - H$, 3.8), 66 ($M^+ - CN - CHCH_2$, 100). Anal. Calcd for C_8H_9N: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.64; H, 7.34; N, 11.55.

1,2-Dimethylenecyclopentane and Acrylonitrile. This system leads only to the [4 + 2] cycloadduct 3-cyano-1-bicyclo[4.3.0]nonene as an oily liquid. The purity of this compound was 90% with 5% starting diene by GC analysis: ^{1}H NMR ($CDCl_3$) δ 2.84–2.81 (1H, m), 2.33–2.25 (5H, m), 2.18–2.0 (1H, m), 1.98–1.79 (6H, m); ^{13}C NMR ($CDCl_3$) δ 134.3, 130.7, 122.4, 35.6, 35.5, 29.2, 26.1, 25.3, 23.6, 21.6; MS (70 eV) *m/e* (%) 147 (M^+, 44), 119 ($M^+ - HCN - H$, 30), 94 ($M^+ - CH_2CHCN$, 44), 79 ($M^+ - CH_2CH_2CH_2CN$, 100).

Acknowledgment. The authors gratefully acknowledge Professor R. Huisgen, Dr. R. A. Firestone, Prof. K. N. Houk, and Dr. Jacques Penelle for helpful discussions, Dr. Hua Wang for checking cycloaddition rates, and Mr. Scott Lyon for help with calculations. Financial support from the National Science Foundation, Division of Materials Research, is gratefully acknowledged.